HyMARC: LBNL Technical Activities

2019 DoE Hydrogen and Fuel Cells Program Review
May 1, 2019

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Lawrence Berkeley National Laboratory, Berkeley, CA, USA

Project ID #: ST130

Overview

Timeline

Project Start: 10/1/2015
Phase 2 Start: 10/1/2018
End: Project continuation determined by DoE. Currently scheduled through 9/30/22

Budget

Federal Share (Prendergast)
    FY18 (Phase 1): $575k
    FY18 (Phase 2): $735k
    FY19 (through 3/31/19): $200k

Federal Share (Long)
    FY18 (Phase 1): $300k
    FY18 (Phase 2): $983k
    FY19 (through 3/31/19): $400k

Barriers Addressed

General: (A) Cost, (B) Weight and Volume, (C) Efficiency, and (E) Refueling Time
Reversible Solid-State Material: (M) Hydrogen Capacity and Reversibility (N) Understanding of Hydrogen Physi- and Chemisorption, and (O) Test Protocols and Evaluation Facilities

Partners/Collaborators

LBNL – Walter Drisdell
LLNL – Brandon Wood
NIST – Craig Brown, Terry Udovic
NREL – Tom Gennett, Phillip Parilla
PNNL – Tom Autrey, Mark Bowden
SNL – Mark Allendorf, Vitalie Stavila
H_2ST^2 – H_2 Storage Tech Team

Approach: LBNL leads or is Part of Several Focus Area Teams

Focus Areas discussed in this presentation are in red

Task 1: Sorbents
- 1.A Enthalpy/entropy under practical conditions (<u>Lead</u>; NREL, PNNL)
- 1.B Strong-binding sites (theory and synthesis) (<u>Lead</u>)
- 1.C Sorbent packing: MOF monolith synthesis (<u>Lead</u>)
- 1.D Dynamic sorbent materials (<u>Lead</u>)
- 1.E Multiple H_2 binding (<u>Lead</u>)

Task 2: Metal hydrides
- 2.A Non-ideal surfaces and phase nucleation
- 2.C Modulation of B–B and B–H bond strength (<u>Lead</u>)
- 2.D.1 Nanoscale metal hydrides under mechanical stress
- 2.D.2 Non-innocent hosts
- 2.D.3 MgB_2 nanosheets (<u>Lead</u>)
- 2.E Microstructural impacts

Task 3: Hydrogen carriers
- 3.B Aqueous organic carriers
- 3.D.1 Sorbents as hydrogen carriers (<u>Lead</u>)
- 3.D.2 Porous liquids
- 3.F Plasmon interactions for "On-demand" H_2 release

Task 4: Advanced characterization
- 4.C.1 NMR-FTIR-PCT instrument (<u>Lead</u>)
- 4.D.3 XAS/EXAFS
- 4.D.4 Soft X-ray spectroscopies and microscopy (ALS) (<u>Lead</u>)
- 4.D.6 ATR DRIFTS (<u>Lead</u>)

Relevance – FY19 Project Objectives

Sorbents (Task 1)

- Research and development of metal-organic frameworks with high volumetric and gravimetric H_2 storage capacities (Barrier A – C, E).
- Development of metalation procedures for high volumetric and gravimetric H_2 storage capacities (Barrier B)
- *In situ* IR and NMR characterization (Barrier N,O)
- Perform accurate simulations of high-pressure H_2 adsorption in MOFs based upon information from CoRE database

Metal hydrides (Task 2)

- Develop more complete model for metal hydride-graphene interface based upon *in situ* X-ray spectroscopy and theoretical modeling
- Develop synthesis of pure $Mg(BH_4)_2$ NPs wrapped by rGO
- Develop synthesis to enable targeted extrinsic doping using graphene nanoribbon-based systems

Hydrogen carriers (Task 3)

- Set up new flow reactors with GC/MS to probe liquid carrier reactions
- Evaluate sorbents as potential carriers

Advanced characterization (Task 4)

- Develop new methodologies to enable *in-situ* X-ray spectroscopic probing of buried interfaces in metal hydrides under working temperatures

Accomplishment 4.D: Expanded/Enhanced Characterization Capabilities at LBNL. Our Focus is on *in Situ*/Operando Methods

In Situ/Operando Soft X-ray Spectroscopy

- H_2 adsorption, 1 bar, RT, transmission (bulk)

- H_2 release, RT–500 °C TFY (μm), TEY (nm)

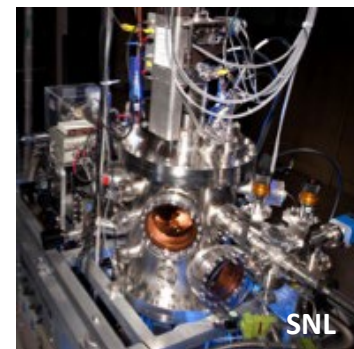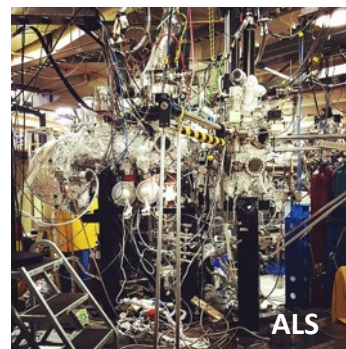- Hydrogenation, 1 bar, RT–250 °C TFY (μm), TEY (nm)
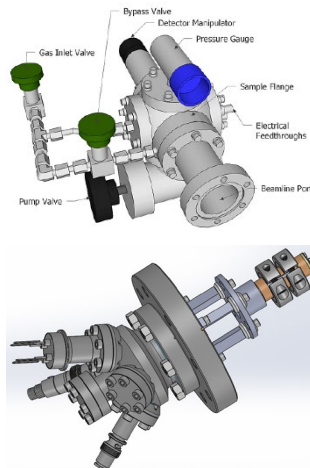
Ex Situ X-ray Spectroscopy

- Multiple ALS BLs for relevant elements (e.g. Mg, B, Li, Na K-edge)

- DFT XANES simulations of "standards" can reveal presence of impurities/ additives
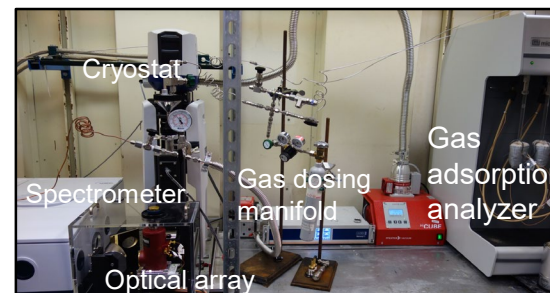
Simulated Spectra ⟷ Data Hub ⟷ Measured Spectra

NREL
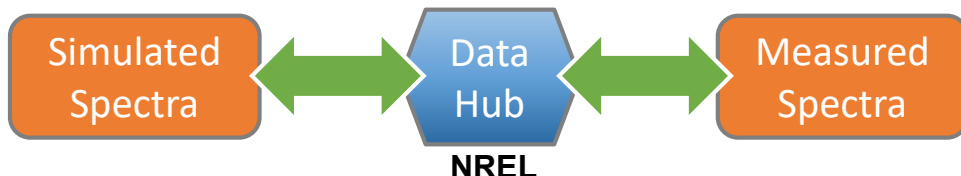
Ambient Pressure XPS (LBNL+SNL)

- Synchrotron AP-XPS, ALS BL 11.0.2

- Lab-based AP-XPS, SNL

In Situ Infrared Spectroscopy

- Diffuse reflectance system coupled to cryostat (15–373 K) and gas adsorption analyzer (0–100 bar)

Approach – Hydride Nanoscaling (2.D): Form Nanocomposites with Ultrathin Carbon Nanomaterials as Hosts or Encapsulants

bulk phase

Technical issues for Task 2 (hydrides):
- Bulk materials typically present thick oxidation layer
- Active region buried underneath this
- X-ray probes perhaps too surface sensitive
- Requires cleaning of surface – non-operando

**Synergies with Task 4 (Advanced Characterization, 4d3, 4d4):**
- Nanocomposites exhibit high interface:bulk ratio
- Active region distributed throughout sample
- X-ray probes (and bulk techniques) suitable
- Samples resistant to contamination
- Encapsulation to minimize weight penalty

LBNL nano-hydride Phase 2 2D. approaches:
- Build on Phase 1 material platforms
- 2.A: Thermodynamics modulation to avoid thermodynamic sinks
- 2.D.1, 2.D.2: Nanoencapsulants as non-innocent hosts
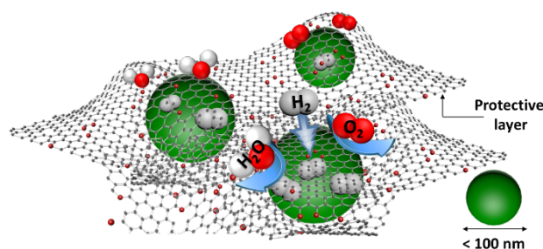
Functionalized nanoribbons
(Felix Fischer)
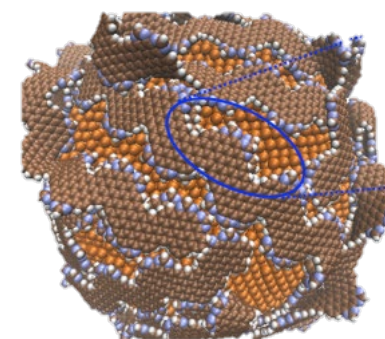
Reduced graphene oxide
(rGO) (Jeff Urban)

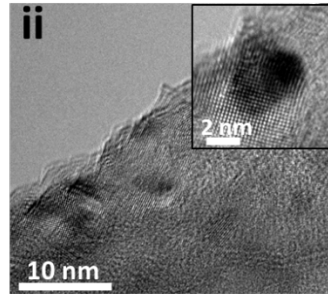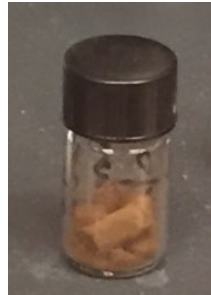# Accomplishment 2.D: rGO Enables Retention of Nanoscale Active Material

LBNL: Urban, Jeong. SNL: White, Stavila

Mg(BH$_4$)$_2$@rGO

$\xrightarrow{}$ 390 ºC
0 bar H$_2$

Dehydrogenated (Mg)
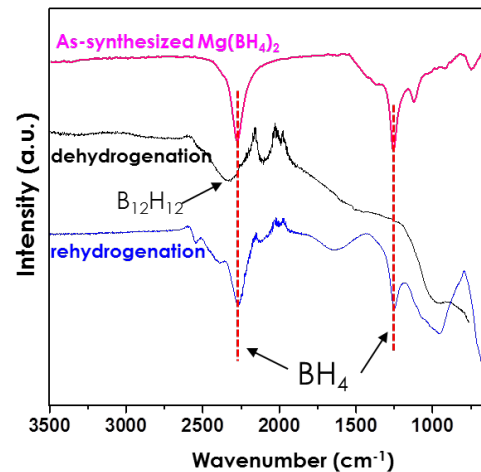

ii

$\xrightarrow{}$ 400 ºC
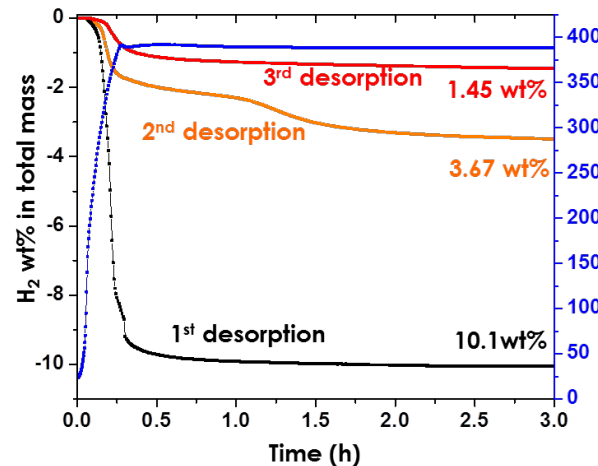700 bar H$_2$

Rehydrogenated (MgH$_2$)

iii
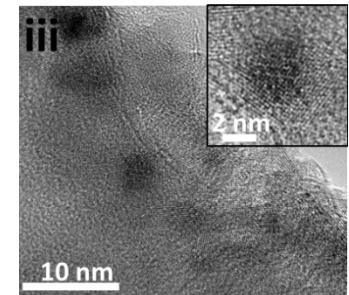
Well-preserved nanostructures after de/rehydrogenation

FT-IR: reduced B$_{12}$H$_{12}$ after rehydrogenation

Higher H$_2$ capacity than bulk γ-MgBH

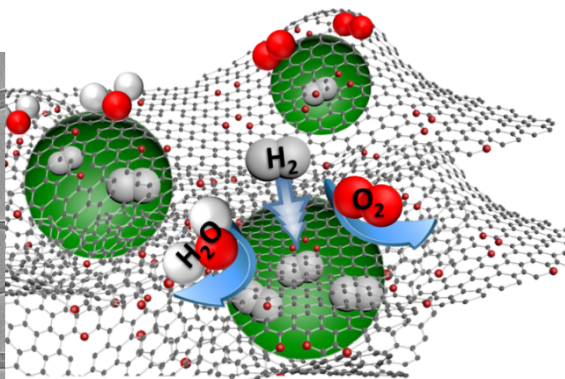**Increased oxidation stability vs. bulk**
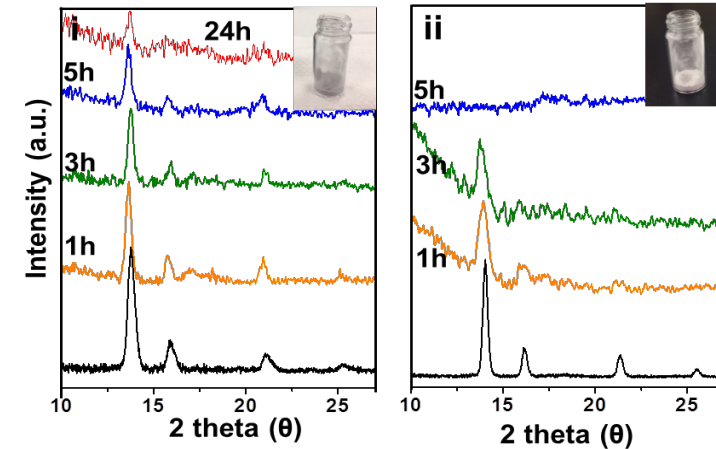
Mg(BH$_4$)$_2$ @rGO exhibits >10 wt% – a record stable capacity for a complex nanohydride

Accomplishment 2.D: Nanoencapsulation Creates Synergy with Task 4 to Enable *in situ* Characterization of Complex Hydrides

Materials synthesized by S. Jeong and J. Urban (MF/LBNL)
SNL: High-P hydrogenations and Sieverts measurements
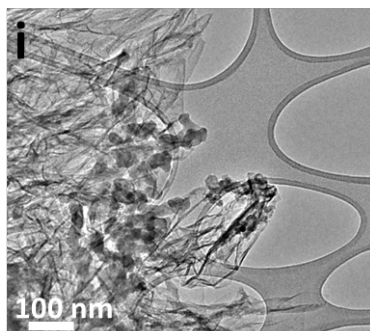
$Mg(BH_4)_2$ nanoparticles (~25 nm) encapsulated in reduced graphene oxide – selective barrier to environmental oxidation
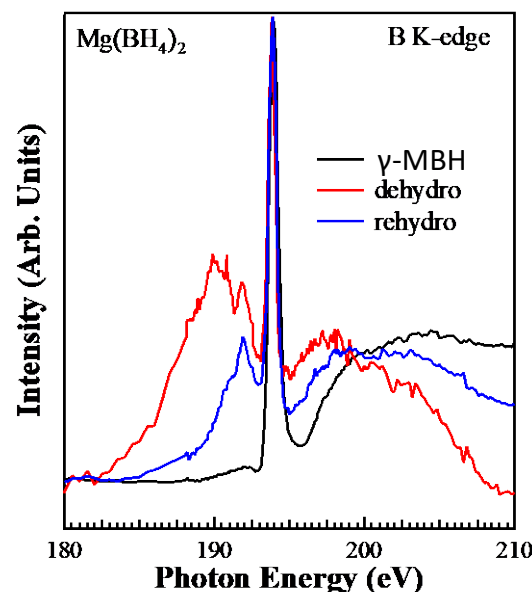
γ-Mg(BH$_4$)$_2$@rGO :

- H_2 release temperature reduced (<400 °C vs. 500 °C bulk)
- New XANES-accessible T-range (250 °C hydrogenation; 500 °C dehydrogenation) enables operando probing of complex hydrides
- Reduced oxidized content observed at nanoparticle surface
    - Borohydride spectral intensity below 193 eV
    - 194 eV peak from oxidized B
- 1 bar sufficient to rehydrogenate

Accomplishment 2.D: Accelerated H₂ Release from Mg(BH₄)₂ Nanoencapsulated in MOF Hosts

Guo, Liu (LBNL); Stavila (SNL)

UiO-67-bpy: $Zr_6O_4(OH)_4(bpydc)_6$
UiO-67: $Zr_6O_4(OH)_4(bpdc)_6$

MBH

MBH@UiO-67-bpy

Mg K-edge

TEY
TFY

MgB₂
Mg(OH)₂
MBH
MBH@UiO-67
MBH@UiO-67-bpy
MBH(Bu)

Intensity (a.u.)

Photon Energy (eV)

B K-edge

TFY

MBH
MBH@UiO-67
MBH@UiO-67-bpy
MBH(Bu)

Intensity (a.u.)

Photon Energy (eV)
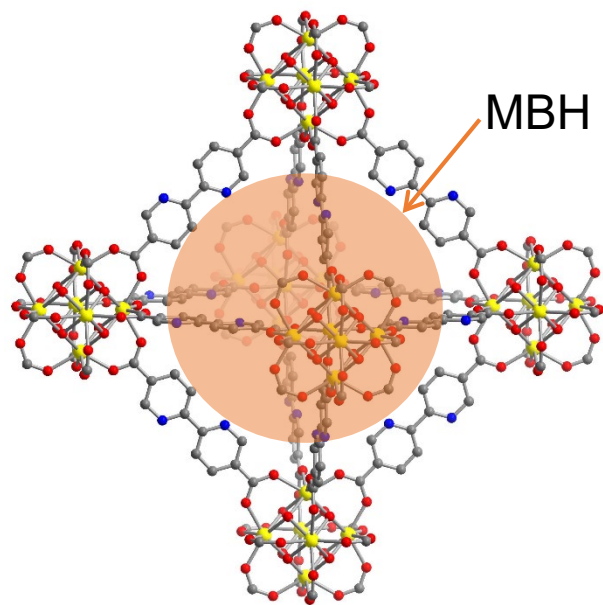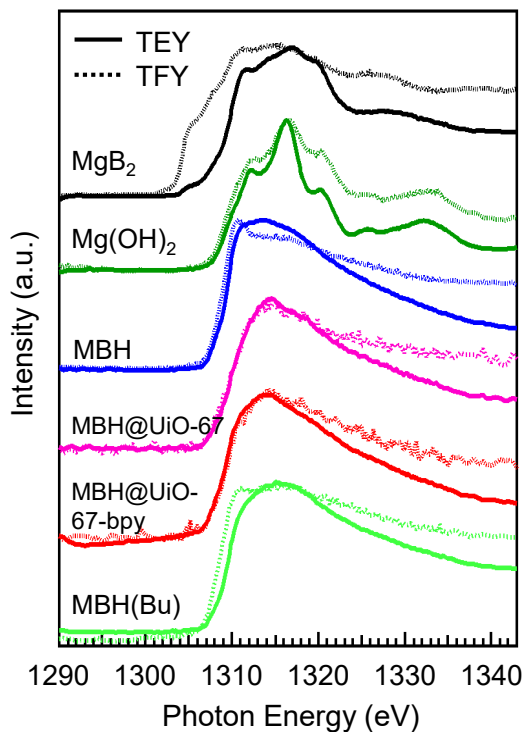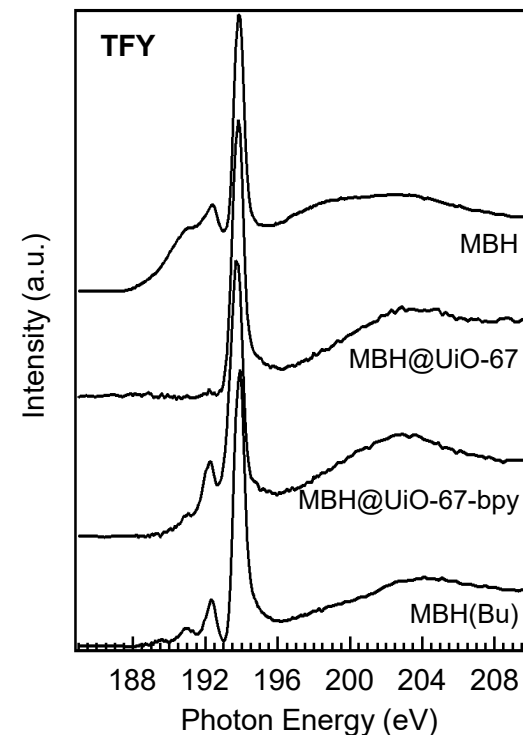
- TGA suggests range 120–260 °C where MBH is losing mass
- RGA indicates mostly H₂ at 120 °C → record low onset T for MgBH dehydrogenation
- XAS confirms MgBH is present within MOF pores

Prof. Gabor Somorjai, Dr. Ji Su

Newly refurbished capabilities in Somorjai lab will be employed to develop catalysts for dehydrogenation/hydrogenation of organic hydrogen carriers. Projects underway:

Methanol Decomposition

900 °C; 300psi; GC;
Liquid- and/or gas-phase reactions

Methane Dehydrogenation
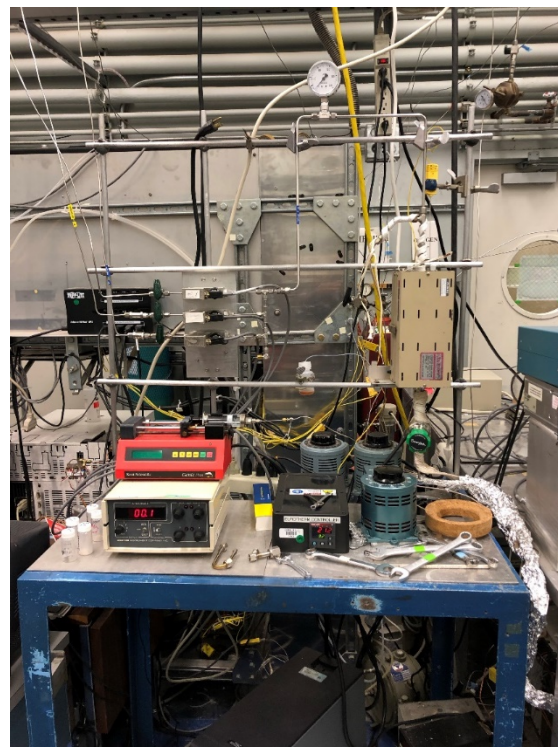
250 °C; GC;
Liquid metal catalyst exploration

Phase-2 Approaches: New Concepts for Boron-based Storage Materials

Urban, Jeong, Zhang (LBNL)
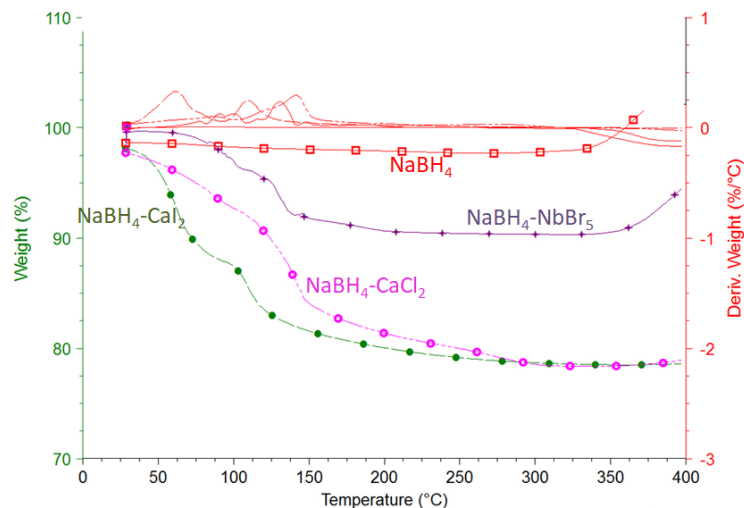
Focus Area 2.C: Borohydrides destabilization by divalent halides

<u>Preliminary data</u>: Thermogravimetric analysis shows that divalent halides enhance decomposition of borohydrides.

Focus Area 1.B.2: porous BN as novel sorbent
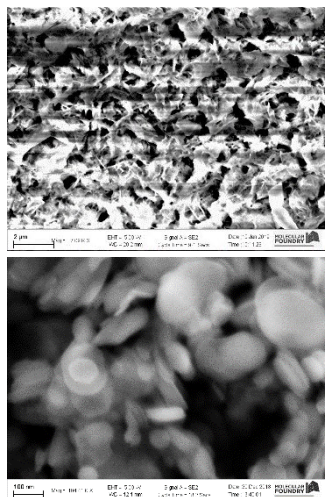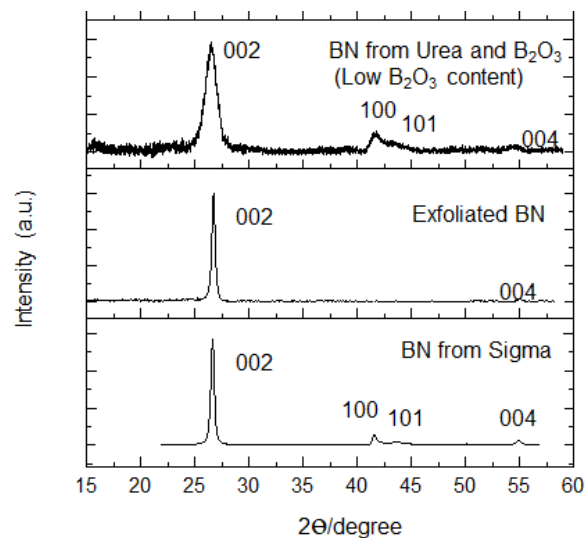
Bottom up method

Top down exfoliation method

Recent theory: 8.65 wt% H_2 at 300 K (Zhang et al. *J. Mater. Chem. A*, **2015**, *3*, 9632)

Synthesis of BN sheet materials and further substitutional doping or defects engineering for hydrogen storage

Approach 1.B (Strong Binding Sites): Validation Effort

Is it possible to create MOFs that adsorb H_2 with an enthalpy in the optimal range of –15 to –25 kJ/mol?

- Values are based upon assumptions about the correlation between adsorption enthalpy and entropy, but these assumptions are not necessarily valid

Bhatia, Myers *Langmuir* **2006**, *22*, 1688
Garrone, Bonelli, Otero Arean *Chem. Phys. Lett.* **2008**, *456*, 68

Open Cu$^+$ Metal Site

H_2

– 2 ZnCl$^+$
+ 2 Cu$^+$

0.83 Å

1.66 Å

MFU-4*l*
Zn$_5$Cl$_4$(btdd)$_3$

DFT-calculated structure
Measured
Q_{st} = –33 kJ/mol
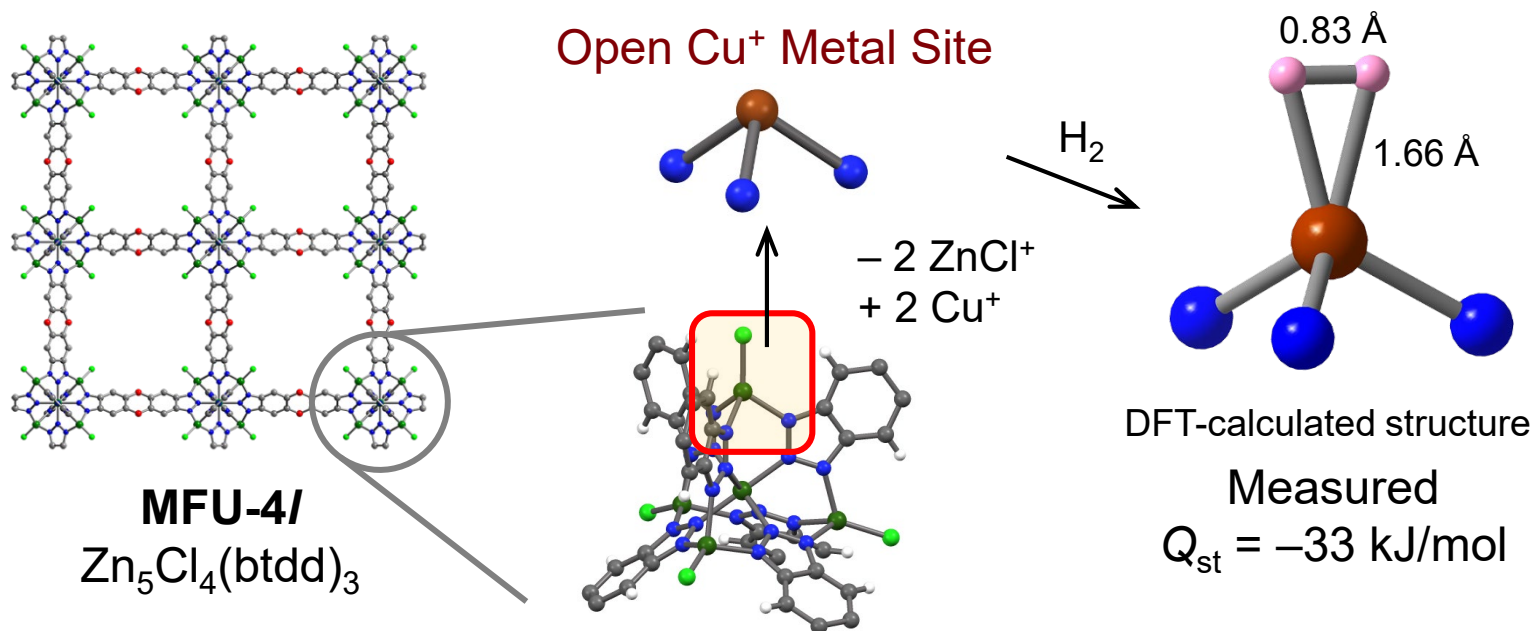
Denysenko, Jelic, Reuter, Volkmer, *Angew. Chem. Int. Ed.* **2014**, *53*, 5832

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In situ Powder Neutron Diffraction Results

D₂ 1.60(3) Å

Cu

1.1 D₂/Cu
dosed at 100 K
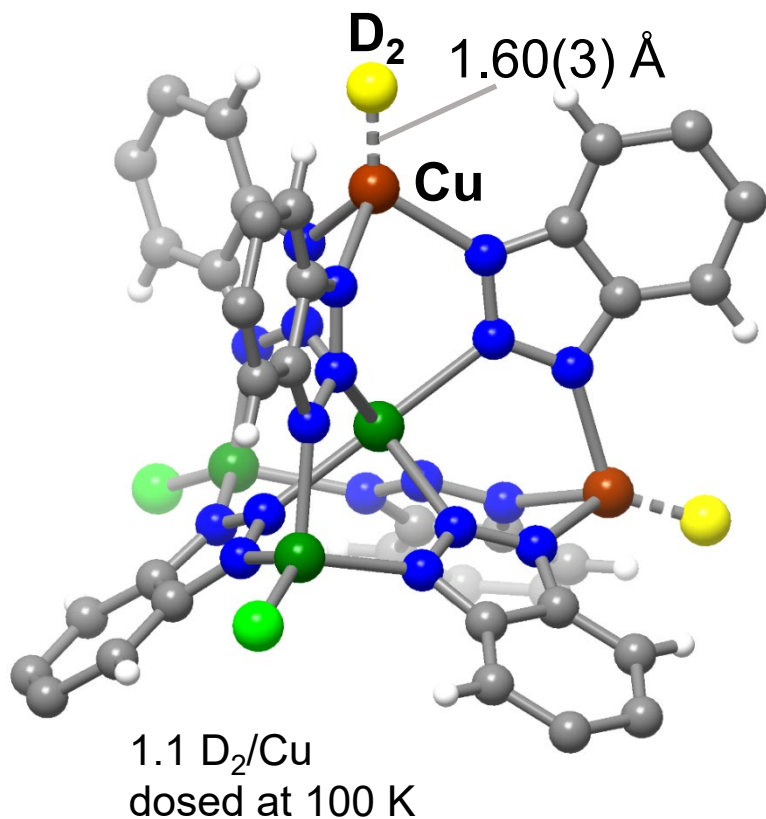
with Craig Brown and Jacob Tarver (NIST)

- Bare Framework
- 0.75 D₂ per Cu, heating
- 0.75 D₂ per Cu, cooling

Lattice Parameter (Å) vs Temperature (K)
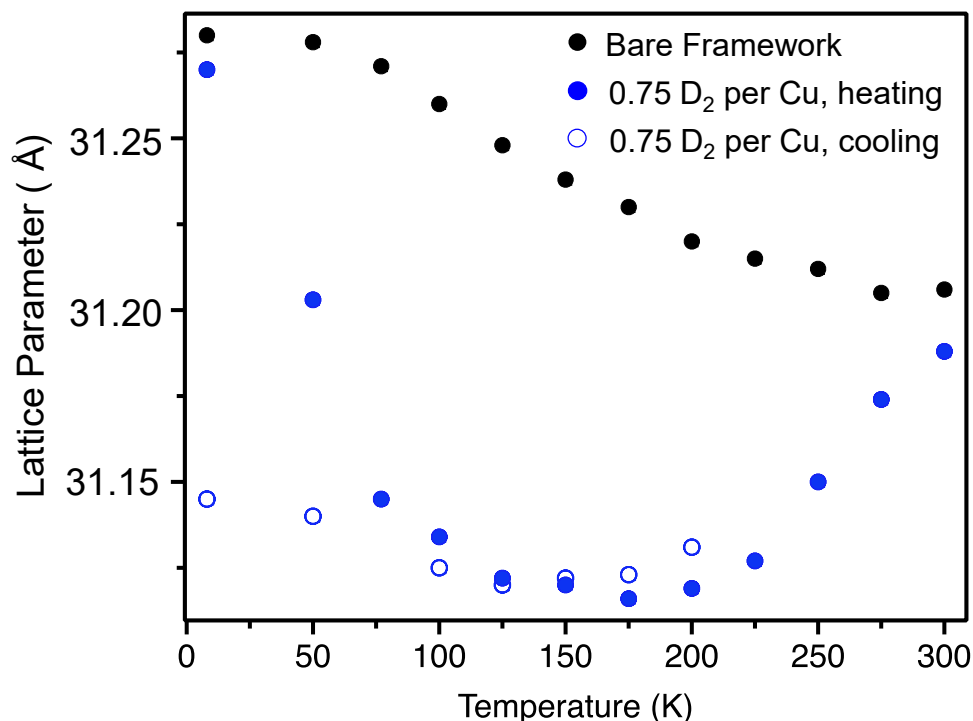
- Cu-bound D_2 can be resolved despite disorder with Zn–Cl at these sites
- Dosing below 80 K leads to a metastable structure with d(Cu–D_2) ~ 1.9 Å
- Significant lattice contraction with strong D_2 binding
- Kinetics data will allow us to measure the activation energy for D_2 binding

In Situ X-ray Absorption Spectra of Cu^I-MFU-4*l*
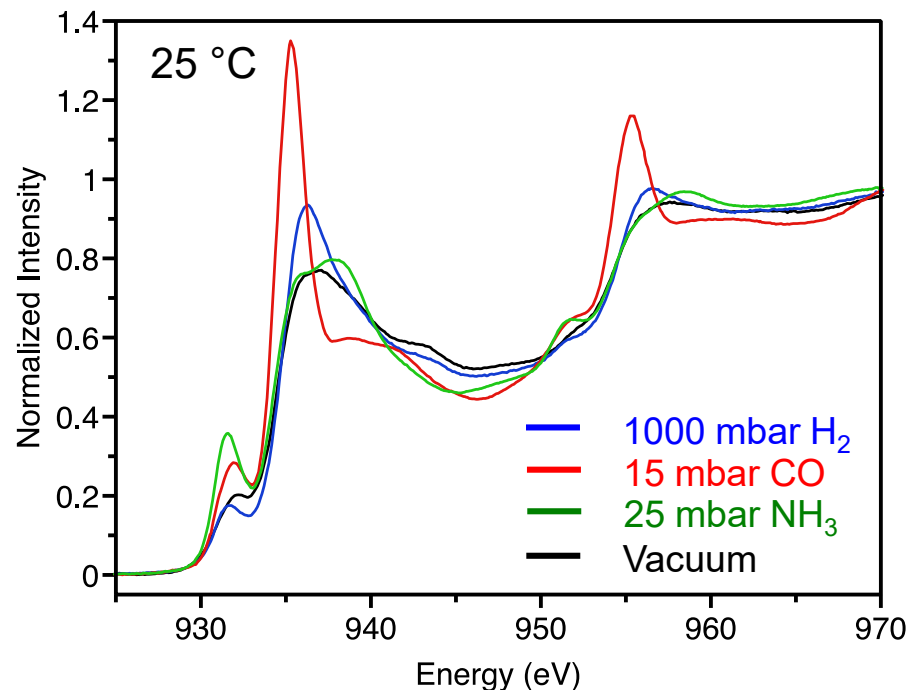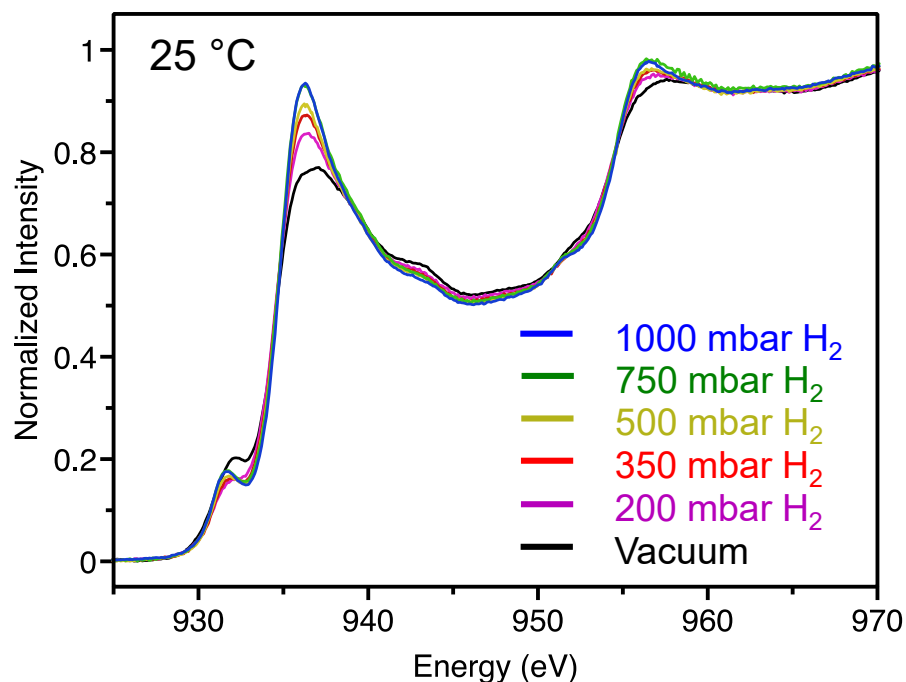
- Cu L-edge data probe how 3*d* manifold is affected by interaction with adsorbate

- Increase in edge intensities indicate increased 3*d* hole character on H$_2$ binding

- CO produces a similar response to H$_2$ while NH$_3$ shifts the edges to higher energy

- Calculations to map spectral changes to adsorbate electronic character in progress

with Greg Su, Walter Drisdell, and David Prendergast (LBNL)

Accomplishment 1.B: Synthesis of MOF with Validated Adsorption Energy in Optimal Range

Hypothesis:
Open V^{2+} coordination sites will place us in this range

- No such MOFs were known, but we've finally made one
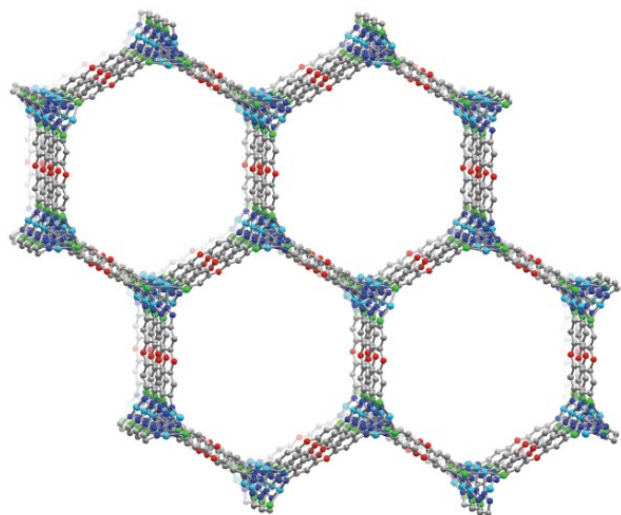
$V_2Cl_{2.8}(btdd)$

- Crystal structure determined from powder X-ray diffraction of activated sample

  (*R*-3*m, a* = 38.943(3) Å, *c* = 8.259(1) Å, *V* = 10842(2) Å^3)

- Langmuir SA = 3290 m^2/g, BET SA = 1930 m^2/g

- ΔH from DRIFTS = –21.0 kJ/mol

IR Spectra for $V_2Cl_{2.8}$(btdd) Dosed with H_2 and D_2

Legend:
- $V_2Cl_{2.8}$(btdd)$_3$, activated
- $V_2Cl_{2.8}$(btdd)$_3$, 84 mbar D_2
- $V_2Cl_{2.8}$(btdd)$_3$, 86 mbar H_2
- Difference

Plot labels: H_2 on secondary sites; H_2 on V^{2+}; D_2 on secondary sites; D_2 on V^{2+}; 97 K

Axes: Pseudo-absorbance / counts (y); Wavenumber (cm^{-1}) (x)
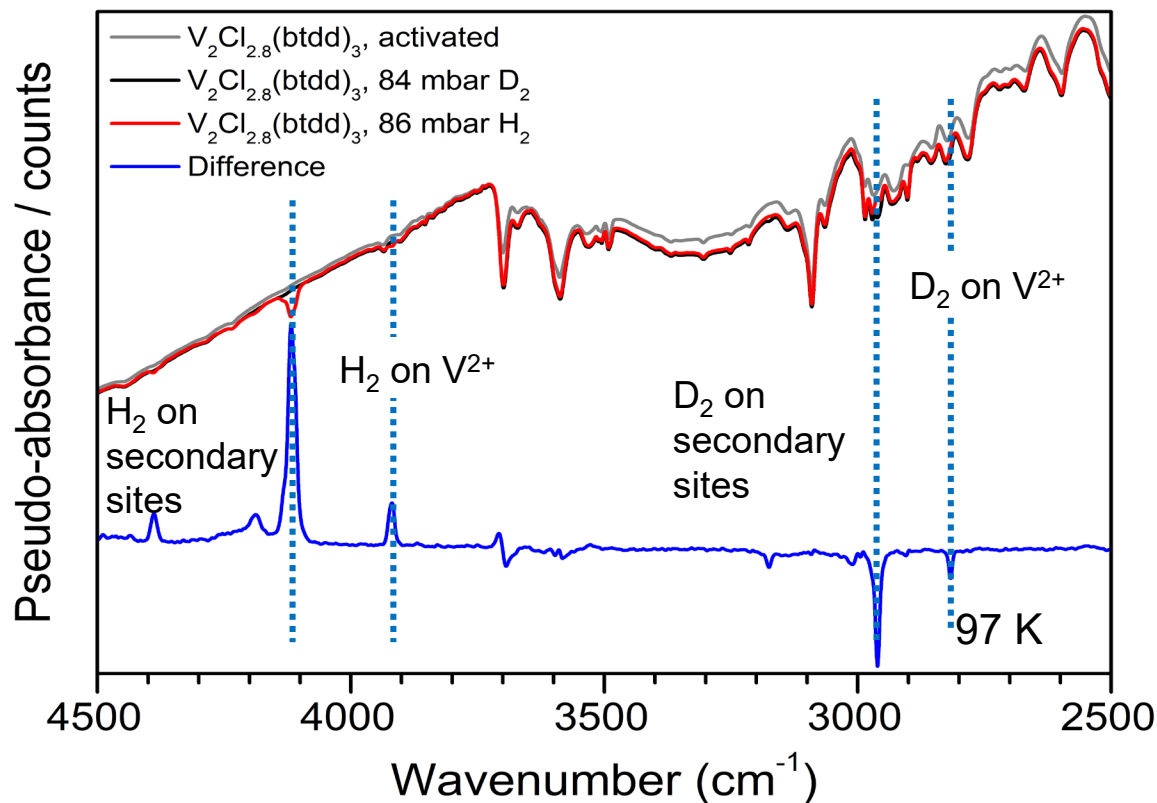
	ν(H–H) (cm^{-1})
free H_2	4161
Ni_2(m-dobdc)	4025
$V_2Cl_{2.8}$(btdd)	3919
Cu^I-MFU-4l	3252

- Subtraction of D_2 spectrum from H_2 spectrum unambiguously resolves peaks
- Largest bathochromic shift yet observed for M^{2+} in a porous material
- Energy decomposition analysis exhibits that V^{2+} has the most favorable energetics in $M^{II}_2Cl_2$(btdd) (M = Ti, V, Mn, Co, and Ni)

Challenges to Address Moving Forward

MOF	Metal ion	ΔH from DRIFTS (kJ/mol)	Q_{st} from isotherms (kJ/mol)	ΔH from theory (kJ/mol)	Total H$_2$ uptake at 298 K, 100 bar (g/L of crystal)
Ni$_2$(m-dobdc)	Ni^{2+}	–13.7	–12.3	–18.6	11.9
Cu^I-MFU-4l	Cu$^+$	–33.6	–32.7	–44.8	11.0
Cu^I-CFA-1*	Cu$^+$	in progress	in progress	in progress	in progress
V$_2$Cl$_{2.8}$(btdd)	V^{2+}	–21.0	–21	–25.4	in progress

*See the reviewer-only slides section for details

- Gain a complete understanding of H$_2$ adsorption in these V^{II} and Cu^I systems:

    High-pressure adsorption isotherms and *in situ* spectroscopy

    Neutron diffraction studies

    Computational studies to understand strong temperature dependence of ΔH

- Increase the density of the available metal binding sites

Approach 1.E: Is it Possible to Create MOFs with Open Metal Sites That Adsorb More Than Two H_2 Molecules?

- This is a long-standing, "holy grail" challenge in MOF chemistry
- Highly complex synthetic challenge

Mn_2(dsbdc) adsorbs two H_2 at a Mn^{2+} site: Runčevski, Kapelewski, Torres-Gavosto, Tarver, Brown, Long
Chem. Commun. **2016**, *52*, 8351

Next-Generation
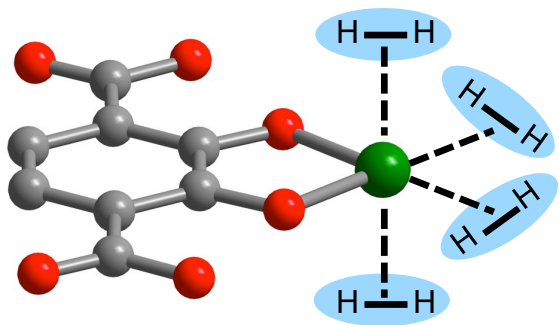
4 or 5 H_2 per metal cation

Gas phase reaction*
- Established ALD materials
- No solvent
- Good pore accessibility
- No counter-ions remain

Cu—N(SiMe$_3$)$_2$
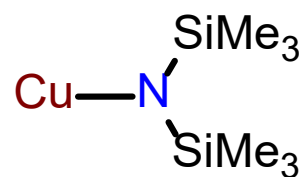
CuHMDS
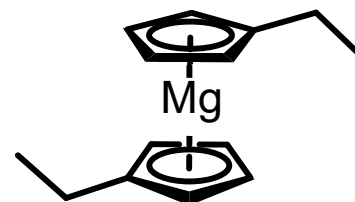
Mg(Cp^{Et})$_2$

* Summary table is in the backup slides section

Future Directions (Sorbents)

- Synthesize smaller pore analogues of Cu^I-MFU-4l and V$_2$Cl$_{2.8}$(btdd) to increase volumetric H$_2$ capacities

- Develop further sampling and data processing methods (e.g. H$_2$/D$_2$ subtraction) to measure accurate ΔH_{ads} and ΔS_{ads} in frameworks with open metal sites

- Continue metalation of frameworks with functionalized linkers to access low-coordinate metal sites

- Pursue flexible MOFs that can maximize H$_2$ usable capacity through step-shaped adsorption isotherms

- Characterize molecular H$_2$ binding free energies across three families of sorbent materials

- Complete and upload the H$_2$ storage benchmark database

Any proposed future work is subject to change based on funding levels

Collaborations

- **LBNL/UC Berkeley (adsorbents) Jeffrey Long:** synthesis & characterization, *in situ* IR-NMR spectroscopy; **Martin Head-Gordon:** computation

- **LBNL/UC Berkeley (hydrides) David Prendergast:** theory, simulated spectroscopy; **Jeffrey Urban:** nanomaterials synthesis; **Jinghua Guo:** soft X-ray characterization; **Felix Fischer:** molecular synthesis; **Gabor Somorjai:** heterogeneous catalysis; **Stephen Whitelam:** theory, kinetics of porous materials

- **LBNL/UC Berkeley (H_2 carriers) Jeffrey Long:** synthesis & characterization; **Hanna Breunig:** techno-economic analysis

- **LBNL (advanced characterization) David Prendergast:** theory, simulated spectroscopy; **Jeffrey Long:** *in situ* IR-NMR spectroscopy

- **LLNL Brandon Wood:** multi-scale modeling and computational spectroscopy

- **NREL Thomas Gennett, Phillip Parilla:** characterization

- **PNNL Thomas Autrey, Mark Bowden:** carriers, NMR

- **SNL Mark Allendorf, Vitalie Stavila:** synthesis & characterization

- **NIST Craig Brown:** neutron diffraction and neutron spectroscopy

- **Additional collaborations Walter Drisdell** (LBNL); **Stephen FitzGerald** (Oberlin College); **Jeffrey Grossman** (MIT); **Agiltron, Inc.**

Summary (FY19 Internal LBNL Milestones)

Task	Milestone	Due	Status
1.B.1	**Electronic structure computations:** Generate a benchmark database tailored towards H_2 with the goal of providing inexpensive predictive analytics.	9/2019	50%
1.B.2	**Synthesis of adsorbents with optimal binding energies:** Determine the enthalpy of H_2 binding in V_2Cl_2(btdd) using both low-P isotherms and variable-temperature DRIFTS.	9/2019	100%
1.C.1	**MOF monolith synthesis:** Demonstrate monolith HKUST-1 takes up 50% greater volumetric H_2 uptake compared to the corresponding powder MOF.	9/2019	50%
1.D.1	**Flexible MOFs:** Synthesize 4 derivatives of Co(bdp) derivatives. Measure isotherms at 77 K to observe how step pressure changes with substitution pattern.	9/2019	20%
1.E	**Multiple H_2s per metal:** Demonstrate metalation of both Mg and Ca in two different frameworks and measure H_2 heat of adsorption.	9/2019	20%
2.C	**B–B bond activation:** Synthesize halide-substituted MgB_2 and/or organic compounds incorporated into the MgB_2 matrix.	6/2019	5%
3.D.1	**Analysis of adsorbents as carriers:** TEA to establish metrics for H_2 delivery.	9/2019	30%
4.C.1	**NMR-FTIR-PCT instrument:** Set up a benchtop NMR magnet with a high-pressure gas adsorption analyzer.	9/2019	20%
4.D	**Advanced synchrotron and ATR DRIFTS characterization techniques:**		

Acknowledgements

Reviewers: Thank you for the constructive feedback.

Technical Backup Slides

Accomplishment 1.B: Benchmarking Density Functionals

- **Objective:** To identify inexpensive density functionals which can predict hydrogen binding energies accurately

- Dataset consists of wide variety of binding motifs commonly encountered in hydrogen adsorption frameworks:
  - Organic linkers, main group and transition metal open binding sites

- 40 density functionals including LDAs, GGAs, metaGGAs and hybrids, with and without empirical dispersion correction (-D3) assessed

Density functional	Rank	Root Mean Square Error*
ωB97M-V	1	1.55 kJ/mol
ωB97X-V	2	1.80 kJ/mol
B97-D3(BJ)	4	1.91 kJ/mol
PBE	18	2.99 kJ/mol
B3LYP-D3	16	2.64 kJ/mol

Best performing functionals { ωB97M-V, ωB97X-V, B97-D3(BJ)

Commonly used functionals { PBE, B3LYP-D3

- **ωB97M-V** is a range-separated, hybrid metaGGA with VV10 non-local correlation offers the best performance

- B97-D3(BJ), a GGA functional with empirical dispersion correction represents the best tradeoff between accuracy and cost

Accomplishment 1.C: HKUST-1 Monolith Synthesis is Reproducible

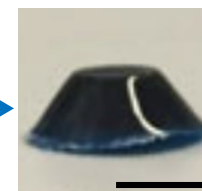|	Density (g/cm^3)	Cu:BTC ratio[1]	Langmuir SA (m^2/g)	Pore volume (cm^3/g)	H$_2$ uptake at 77 K, 1 bar (g/L)
Monolith	1.01[2]	1.43	1750	0.63	22.5
Reported monolith[3]	1.10[2] (1.04)[4]		1470	0.52	
Powder	0.43[5]	1.37	2150	0.77	11.2
.cif data	0.881	1.50	2240[6]	0.80[6]	n.a.
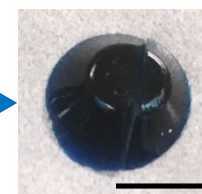
0.5 cm

0.5 cm

[1]Determined from TGA data. [2]Archimedean immersion method. [3]Tian, Zeng, Vulpe, Casco, Divitini, Midgley, Silvestre-Albero, Tan, Moghadam, Fairen-Jimenez *Nat. Mater.* **2018**, *17*, 174. [4]Mercury porosimetry. [5]Hand packing density: Peng, Krungleviciute, Eryazici, Hupp, Farha *J. Am. Chem. Soc.* **2013**, *135*, 11887. [6]Calculated using *Materials Studio*.

- HKUST-1 monolith density is greater than HKUST-1 powder density
- At 77 K and 1 bar, volumetric H$_2$ uptake of the monolith is twice as high as observed for the packed powder
- High-pressure H$_2$ and CH$_4$ isotherms will be collected

Accomplishment 1.E: Summary of Zr-Based MOF Metalations

Metal Site	Metalating Reagent	Metalation yield (%)	Langmuir SA (m^2/g)	H_2 Uptake* (mmol/g)
UiO-67-PhOpydc system				
UiO-67-PhOpydc		n/a	2880	9.2
Cu	$Li[Cu(CH_3)_2]$	86	70	0.78
Cu	$Cu(CH_3CO_2)$	72	2370	8.4
Cu	$Cu(N(SiMe_3)_2$	22	2000	9.4
Cu	$[Cu(Mes)]_n$	9	2640	9.4
$Mn(CO)_x$	$Mn(CO)_5Br$	40	1500**	5.3
$Re(CO)_x$	$Re(CO)_5Cl$	26	1510**	6.2
Li	*n*-BuLi	33	n.d.	5.3
UiO-68-cat system				
UiO-68-cat		n/a	3470	6.7
Ni	$Ni(C_3H_5)_2$	17	1870	3.4
Mg	$Mg(Cp^{Et})_2$	108	3220	7.0

*Excess uptake at 77 K and 1 bar. **Measured before photolysis.

Remaining Challenges and Barriers

- Complete insertion of metal cations into O,O-, N,O- or N,N-chelating groups within MOFs is a key synthetic challenge

- Can we demonstrate adsorption of 3 or more H_2 molecules per metal?

- Establishing a valid correlation between ΔH and ΔS for H_2 adsorption under target operating conditions: 5-100 bar and –40 to 60 °C

- Can we manipulate ΔS with synthetic chemistry?

- While accurate computational tools are available for calculating binding energies, the optimal trade-off point between accuracy and expense is still under investigation

- Achieve size control in synthesis and reversibility of encapsulated $Mg(BH_4)_2$ materials

- Incorporate theoretical insights on graphene-hydride interface into advanced synthesis of these materials

- Performing *in situ* soft X-ray spectroscopies achieving realistic hydrogen storage (i.e. UHV requirement)

- Understanding coordination/reactivity of $Mg(BH_4)_2$ with oxide and graphene interfaces

- The relations between the strength and number of open metal sites, overall pore morphology and the adsorbent performance in H_2 storage are not fully understood

Any proposed future work is subject to change based on funding levels

Responses to Previous Year Reviewers' Comments

FY18 Reviewer Comment	FY19 Response to Comment
ANL (ST-001, Ahluwalia) showed that even in the most optimistic case of 4 H_2 molecules per metal, the theoretical uptake (at 25 °C, 100 bar) is still a factor of two lower than the value needed to reach the system target.	Our current focus is the development of (gas-phase) metalation procedures for the multiple H_2 adsorption per metal site. Once experimental protocols are established, metalation of open metal site MOFs with f-block elements (higher coordination number) and optimization of framework dead space will be considered. In addition, we initiated a new task for the monolith formation, whose volumetric uptake can be twice as large as powder samples.
The theory effort has not supported the experimental work closely. Much of the work on predicting candidates and variations could use a more HT DFT. Also, it remains to be seen whether this functional has such a good performance across the board. More effort needs to be devoted to multiple H_2s and understanding bonding, polarization, and dynamics.	The Density Functional benchmarking effort assesses the performance of dispersion-corrected density functionals (e.g. PBE-D3) across a range of chemically diverse binding motifs, containing one or multiple H_2s bound to a single metal site. Quantifying anharmonic effects and polarization of gas binding are the subject of current research, but slightly outside the scope of this particular database endeavor. We will be reporting progress on both these topics shortly.
A stronger integration of theory in the design of experiments is recommended. This connection needs to be more direct.	HyMARC is structured to leverage capabilities and investments at individual labs. Regarding theory/modeling, these capabilities are largely centered at LLNL (although computational spectroscopy is a strong capability of the Molecular Foundry). Five 2017-18 hydride-related HyMARC publications involve close theory-experimental collaborations. In addition, two review articles were published coauthored by theorist with experimentalists.

Reviewer-Only Slides

Task 1 (Sorbents): Overall Project Objectives

- Determine if adsorbents have a pathway to achieve the binding energies, capacities and kinetics necessary to reach the 2020 DOE targets for H_2 storage by synthesizing and characterizing new porous framework and nanoconfined hydrides (A)

- Double H_2 storage energy density (increase from 25 g/L to 50 g/L) (B)

- Design interfaces with chemical specificity for thermodynamic and kinetic control of hydrogen storage/sorption and selective transport (E)

- Provide accurate computational modeling for H_2 adsorbed in adsorbents (N)

- Advanced characterization – combine with next bullet Refine chemical synthesis strategies based on atomic/molecular scale insight from characterization/theory (N)

- Develop *in situ*/operando soft X-ray characterization capabilities in combination with first-principles simulations to extract atomic/molecular details of functional materials and interfaces (N, O)

- Develop *in situ* NMR-FTIR-PCT as a tool for characterizing emerging H_2 storage materials (N, O)

Critical Assumptions and Issues

Synthesis and characterization of metal-organic frameworks

- Desolvation of the metal centers incorporated into the catechol ligands remains the largest challenge to achieving very high volumetric densities.

- Volumetric capacities are based on single crystal densities to more easily compare materials; in an actual system, the packing density of the material and other engineering concerns would be important in determining the actual volumetric capacity.

First-principles calculations of hydrogen binding enthalpies

- Transferability between the computationally predicted H_2 binding enthalpies and actual systems requires more experimental evidence and fine-tuning of computational protocols.

Summary of New Task Activities Initiated in Phase 2

- **Task 1: Flexible MOFs** that could allow for a greater usable capacity, heat management, and desorption without pressure loss.

- **Task 1: Monolith MOFs** that can minimize the losses in H_2 storage capacity due to loosely packed adsorbent particles inside a tank.

- **Task 2: Boron-containing materials:** Thermogravimetric analysis, the effect of valence state of additives on decomposition of borohydrides. Synthesis of BN sheet materials and further substitutional doping/defects engineering for H_2 storage.

- **Task 2: Theory:** (i) Thermal conductivity of hydrides, (ii) experiment and computation (with Grossman, MIT) – Initial work on phonon band structure and instabilities in Li_3N, (iii) predictive phenomenological modeling of cooperative gas adsorption in MOFs.

- **Task 3: H_2 carriers:** (i) Techno-economic analysis (TEA) toward H_2 transportation by a tube trailer and (ii) development of MOFs exhibiting significantly higher storage capacities at 250 bar and 298 K.

- **Task 4: NMR-FTIR-PCT Instrument** to study H_2–adsorbent interactions (e.g. contribution of back-donation to the system).

- **Task 6: Datahub for XAS:** Developing a workflow for upload of XAS measurements at ALS to NREL to initiate theoretical analysis and validation of materials components.

LBNL Phase 2 Accomplishments to Date (FY19)

- **Cu^I-MFU-4*l*:** Located the D_2 adsorption sites in using *in situ* powder neutron diffraction. Analyzed the H_2 storage capacity at ambient temperatures.

- **$V_2Cl_{2.8}$(btdd):** Determined ΔH_{ads} and ΔS_{ads} using VT DRIFTS.

- **Gas-phase metalation:** Cu^I loading and performance in UiO-67-PhOHpydc improved, Mn, Re, and Li metalation demonstrated.

- Computed binding energy contributions due to orbital interactions and permanent electrostatics for MOFs with open metal site.

- Assessed the performance of different density functionals and *ab initio* methods for H_2 storage and characterized the origin of errors in binding energies.

Publications

- "Record High Hydrogen Storage Capacity in the Metal-Organic Framework Ni$_2$(*m*-dobdc) at Near-Ambient Temperatures" Kapelewski, M. T.; Runcevski, T.; Tarver, J. D.; Jiang, H. Z. H.; Hurst, K. E.; Parilla, P. A.; Ayala, A.; Gennett, T.; FitzGerald, S. A.; Brown, C. M.; Long, J. R. *Chem. Mater.* **2018**, *30*, 8179-8189.

- "An Assessment of Strategies for the Development of Solid-State Adsorbents for Vehicular Hydrogen Storage" Allendorf, M. D.; Hulvey, H.; Gennett, T.; Ahmed, A.; Autrey, T.; Camp, J.; Cho, E. S.; Furukawa, H.; Haranczyk, M.; Head-Gordon, M.; Jeong, S.; Karkamkar, A.; Liu, D.; Long, J. R.; Meihaus, K. R.; Nayyar, I. H.; Nazarov, R.; Siegel, D. J.; Stavila, V.; Urban, J. J.; Veccham, S. P.; Wood, B. C. *Energy Environ. Sci.* **2018**, *11*, 2784-2812.

- "Synthesis and Characterization of Metal−Organic Frameworks", *in Gas Adsorption in Metal-Organic Frameworks: Fundamentals and Applications*. Furukawa, H. *CRC Press* 2018, ISBN: 9780429469770 (ebook).

- "Identifying the Role of Dynamic Surface Hydroxides in the Dehydrogenation of Ti-doped NaAlH$_4$" White, J. L.; Rowberg, A. J. E.; Wan, L.; Kang, S. Y.; Ogitsu, T.; Kolasinski, R. D.; Whaley, J. A.; Baker, A.; Lee, J. R. I.; Liu, Y. S.; Trotochaud, L.; Guo, J.; Stavila, V.; Prendergast, D.; Bluhm, H.; Allendorf, M. D.; Wood, B. C.; Gabaly, F. E. *ACS Appl. Mater. Interfaces* **2019**, *11*, 4930-4941.

- "Nanostructured Metal Hydrides for Hydrogen Storage" Schneemann, A.; White, J. L.; Kang, S. Y.; Jeong, S.; Wan, L. F.; Cho, E. S.; Heo, T. W.; Prendergast, D.; Urban, J. J.; Wood, B. C.; Allendorf, M. D.; Stavila, V. *Chem. Rev.* **2018**, *118*, 10775-10839.

Publications (cont'd)

- "Critical Factors in Computational Characterization of Hydrogen Storage in Metal-Organic Frameworks" Camp, J. S.; Stavila, V.; Allendorf, M. D.; Prendergast, D.; Haranczyk, M. *J. Phys. Chem. C* **2018**, *122*, 18957-18967.

- "In-Situ/Operando X-ray Characterization of Metal Hydrides" Liu, Y. S.; Jeong, S.; White, J. L.; Feng, X.; Cho, E. S.; Stavila, V.; Allendorf, M. D.; Urban, J. J.; Guo, J. *ChemPhysChem* **2019**, *20*, 1-12.

- "Edge-functionalized graphene nanoribbon encapsulation to enhance stability and control kinetics of hydrogen storage materials" Wan, L. F.; Cho, E. S.; Marangoni, T.; Shea, P.; Kang, S. Y.; Rogers, C.; Zaia, E.; Cloke, R. R.; Wood, B. C.; Fischer, F. R.; Urban, J. J.; Prendergast, D. *Chem. Mater.* **2019**, DOI: 10.1021/acs.chemmater.9b00494.

Presentations

- Long, J. R.; Head-Gordon M.; Breunig, H. "HyMARC: LBNL Technical Activities–Hydrogen Storage in Metal–Organic Frameworks", DOE H_2 Tech Team Meeting, Detroit, MI (February 20, 2019).

- Furukawa, "Chemistry of Metal–Organic Frameworks" H. Soongsil University, Korea (November 19, 2018).

- Furukawa, H. "Metal–Organic Frameworks with Exposed Metal Sites" UNIST Chemistry Seminar, Ulsan National Institute of Science and Technology (UNIST), Korea (November 20, 2018).

- Furukawa, H. "Chemistry of Metal–Organic Frameworks" Sookmyung Women's University, Korea (November 21, 2018).

- Barnett, B. R.; Jiang, H. Z. H.; Long, J. R. "Augmenting Hydrogen Sorption Enthalpies via p-Backdonation: Thermodynamic Ramifications for Optimizing Adsorptive Hydrogen Storage", Organometallic Chemistry Gordon Research Conference, Newport, RI (July 10, 2018).

- Chakraborty R., Head-Gordon M. "Multiscale Simulations in Chemistry with the Lattice Boltzmann Method", Voth group at the University of Chicago, IL (February 8, 2018).

- Furukawa, H.; Kapelewski, M. T.; Jiang, H. Z. H.; Runčevski, T.; Lin, Y.-Y. ; Barnett, B. R.; Hou, K.; Thiele, G.; Long, J. R. "Hydrogen Storage in Metal–Organic Frameworks", 255th ACS National Meeting & Exposition, New Orleans, LA (March 21, 2018).

- Jiang H. Z. H.; Long, J. R. "*In Situ* Characterization of Adsorbates in Nanoporous Materials with IR Spectroscopy", 255th ACS National Meeting & Exposition, New Orleans, LA (March 22, 2018).

- Chakraborty R., Head-Gordon M. "Modeling Adsorption with the Lattice Boltzmann Method", West-Coast Theoretical Chemistry Symposium, Stanford University, CA (March 28, 2018).

Optimal ΔG° for a High Usable Capacity at 298 K
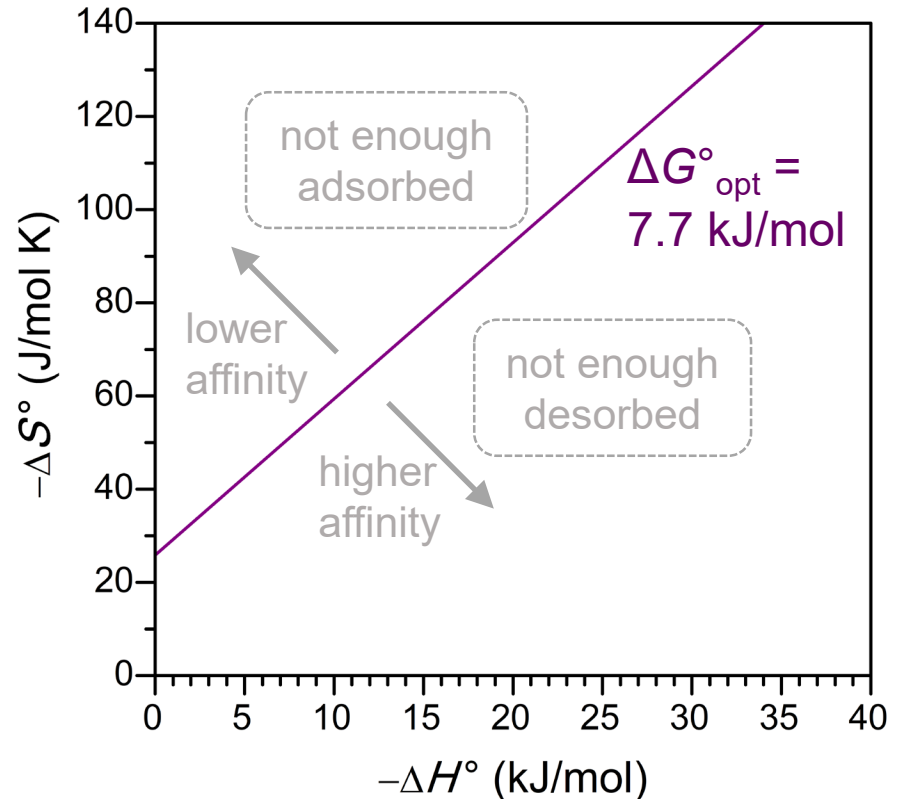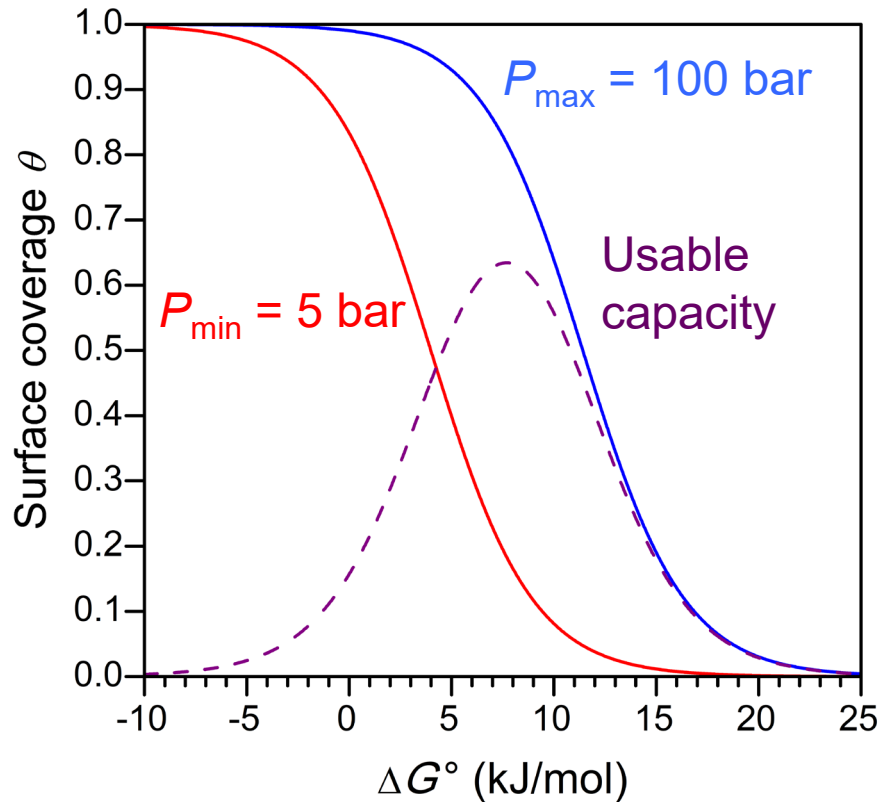
- Usable H_2 storage capacity determined by $\Delta G°$, not $\Delta H°$ alone

- Optimal $\Delta G°$ of 7.7 kJ/mol balances the tradeoff between maximizing capacity during adsorption and minimizing capacity during desorption
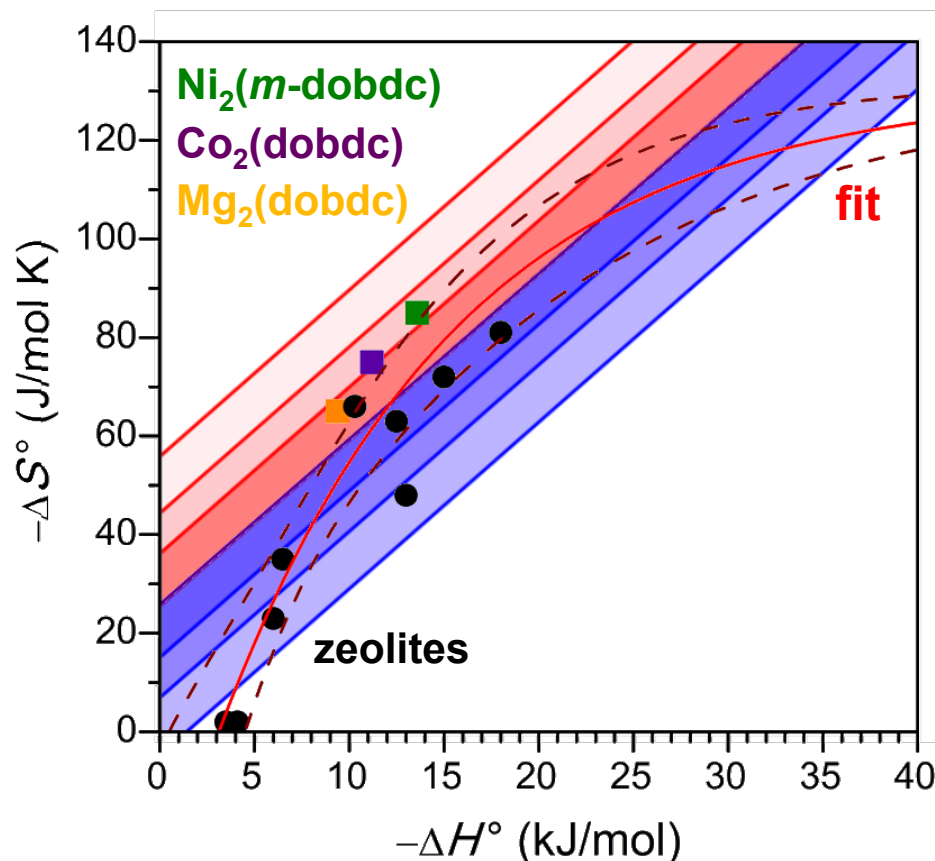
Optimal Δ*G*° of H₂ Adsorption
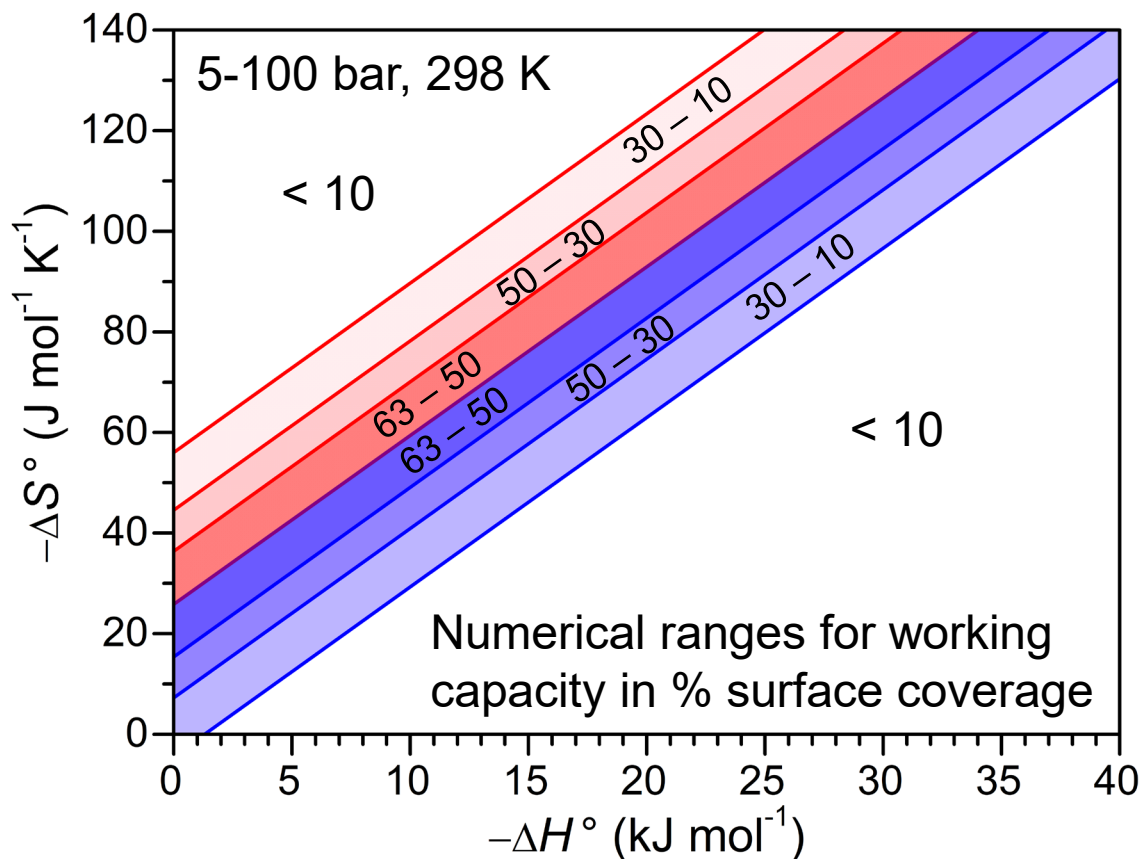
- Δ*G*° determines working capacity of Langmuir site
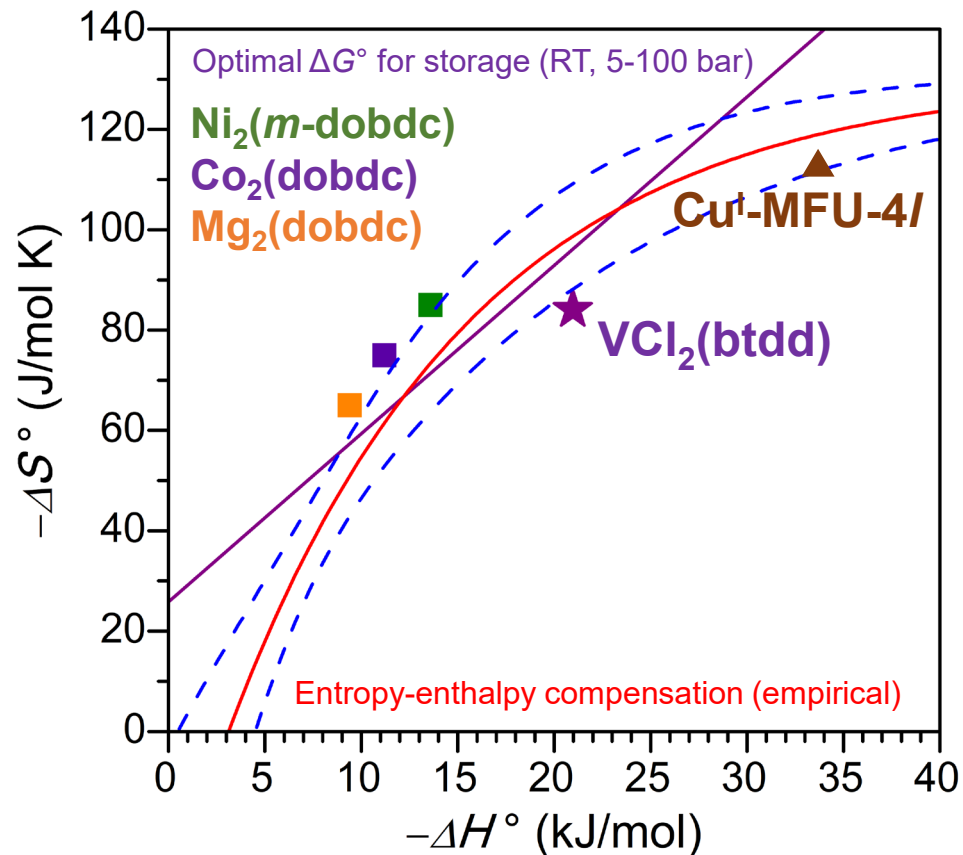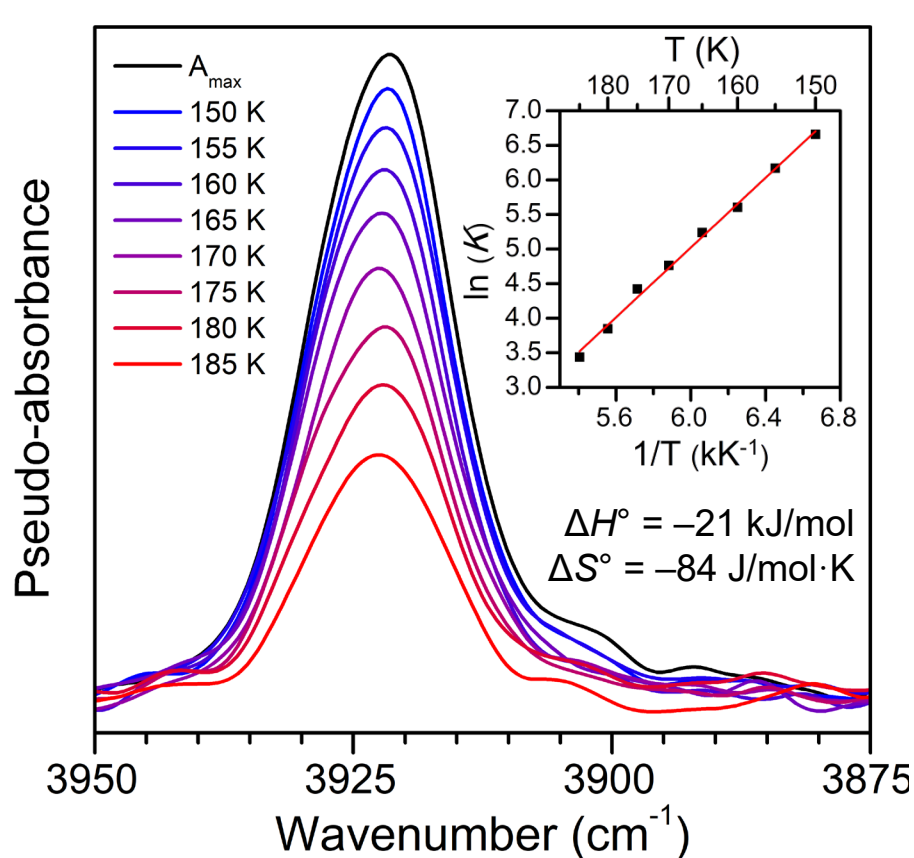- Drastic change in site efficiency with change in Δ*G*°

Enthalpy–Entropy Correlations for H_2 Adsorption

	$-\Delta H°$ (kJ/mol)	$-\Delta S°$ (J/mol K)
(Mg,Na)-Y	18	81
(Ca,Na)-Y	15	72
Ca-X	13	63
Mg-X	13	48
Li-ZSM-5	6.5	35
Na-ZSM	10	66
Li-FER	4.1	2
Na-FER	6	23
K-FER	3.5	2

- Need a good correlation between $\Delta H°$ and $\Delta S°$ to determine $\Delta H°_{opt}$
- Sweet spot is indeed in the optimal range of $\Delta H°_{opt}$ = –15 to –25 kJ/mol

# Variable-Temperature IR Spectra of H$_2$ in V$_2$Cl$_{2.8}$(btdd)

Left panel legend:
- A$_{max}$
- 150 K
- 155 K
- 160 K
- 165 K
- 170 K
- 175 K
- 180 K
- 185 K

Inset: $\ln(K)$ vs $1/T$ (kK^{-1}), upper axis T (K)

$\Delta H° = -21$ kJ/mol
$\Delta S° = -84$ J/mol·K

Y-axis: Pseudo-absorbance
X-axis: Wavenumber (cm^{-1})

Right panel:
- Optimal $\Delta G°$ for storage (RT, 5–100 bar)
- Ni$_2$(*m*-dobdc)
- Co$_2$(dobdc)
- Mg$_2$(dobdc)
- Cu†-MFU-4*l*
- VCl$_2$(btdd)
- Entropy-enthalpy compensation (empirical)

Y-axis: $-\Delta S°$ (J/mol K)
X-axis: $-\Delta H°$ (kJ/mol)

- First example of a MOF with ΔH in the optimal range between -15 and -25 kJ/mol
- Enthalpy-entropy relation distinct from M$_2$(dobdc) family

H₂ Adsorption in Cu^I-MFU-4*l*
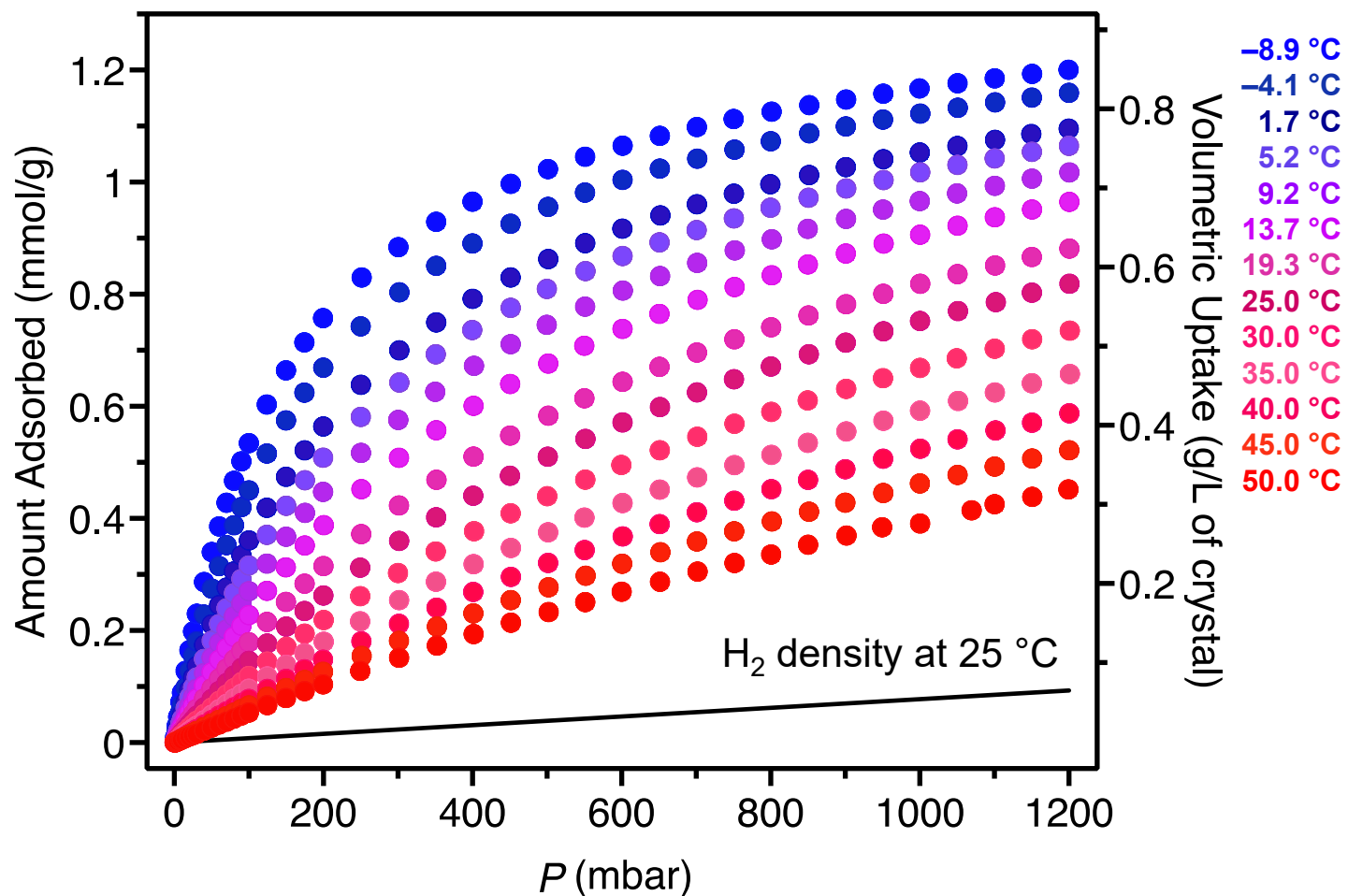
- Loading of 1 H₂ per Cu corresponds to 1.7 mmol/g
- Good performance for low-pressure, high-temperature storage
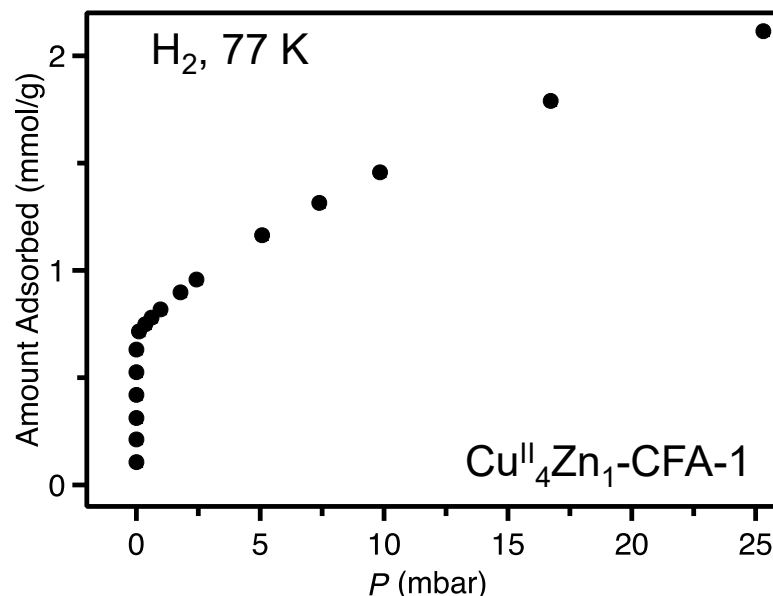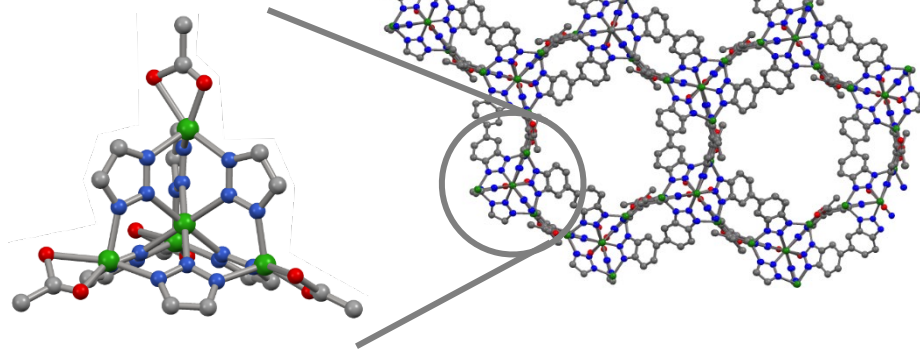
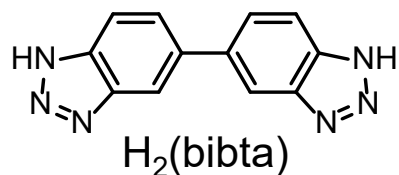# High Pressure H$_2$ Adsorption in Cu^I-MFU-4*l*
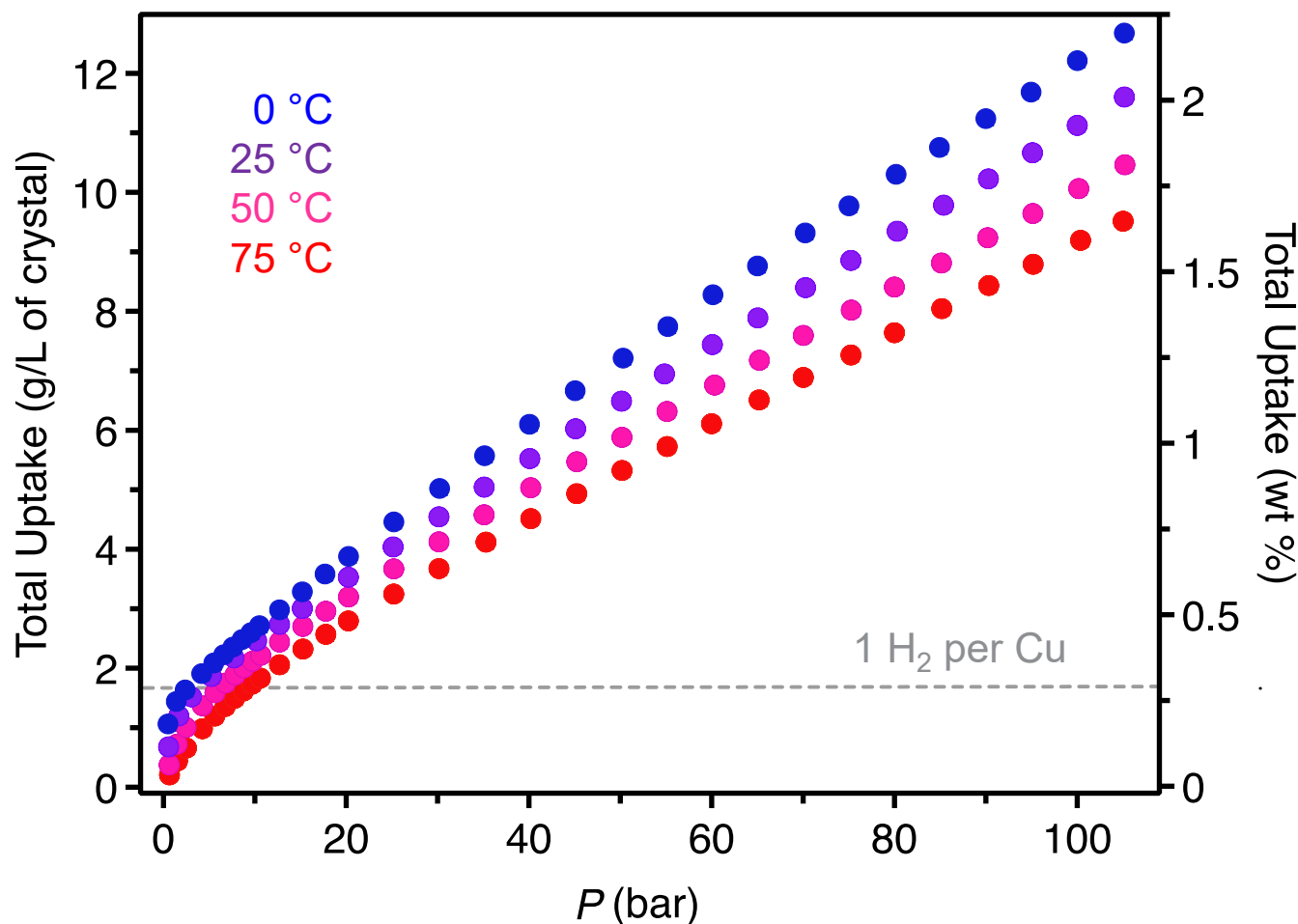
- Open Cu$^+$ sites saturate at relatively low pressures
- At sub-ambient temperatures, Cu$^+$ sites do not contribute to usable capacity

Comparisons of Usable Capacity

Temperature	0 °C	25 °C	50 °C	75 °C
Compressed H_2 (g/L)	7.9	7.3	6.7	6.3
Cu^I-MFU-4*l* (g/L crystal)	10.2	9.3	8.6	8.1
Ni_2(*m*-dobdc) (g/L crystal)	14.1	11.0	9.3	7.9
Cu^I-MFU-4*l* (wt %)	1.8	1.6	1.5	1.4
Ni_2(*m*-dobdc) (wt %)	1.1	0.9	0.8	0.7

- Usable capacities for adsorbent operation between 5 and 100 bar

- Volumetric usable capacity for Cu^I-MFU-4*l* surpasses Ni_2(*m*-dobdc) at 75 °C

- Gravimetric usable capacity for Cu^I-MFU-4*l* is superior at all temperatures

Analogous Zn$_5$ Nodes in CFA-1

H$_2$(bibta)

Amount Adsorbed (mmol/g) vs P (mbar)

H$_2$, 77 K

Cu$^{II}_4$Zn$_1$-CFA-1

CFA-1: Zn$_5$(bibta)$_3$(CH$_3$CO$_2$)$_4$ $\xrightarrow[\text{DMA, }\Delta]{\text{excess CuCl}_2}$ **Cu$^{II}_n$Zn$_{5-n}$-CFA-1**
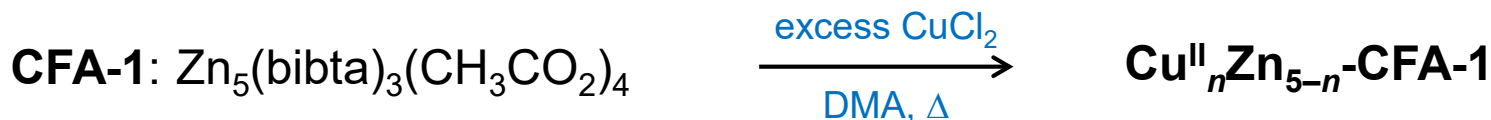
- Volumetric density of Zn$_5$ nodes is 30% higher than in MFU-4*l*

- First demonstration of the replacement of Zn^{2+} in CFA-1 with Cu^{2+}

- Exchange of chloride for formate and heating at 120 °C converts Cu^{II} to Cu^{I}

- Attempts to increase density of open Cu^{I} sites is in progress

IR Spectra and Thermochemistry of Cu^I-MFU-4*l*

(a) 4455 cm^{-1} (b) 3593 cm^{-1} (c) 1094 cm^{-1} (d) 772.9 cm^{-1}
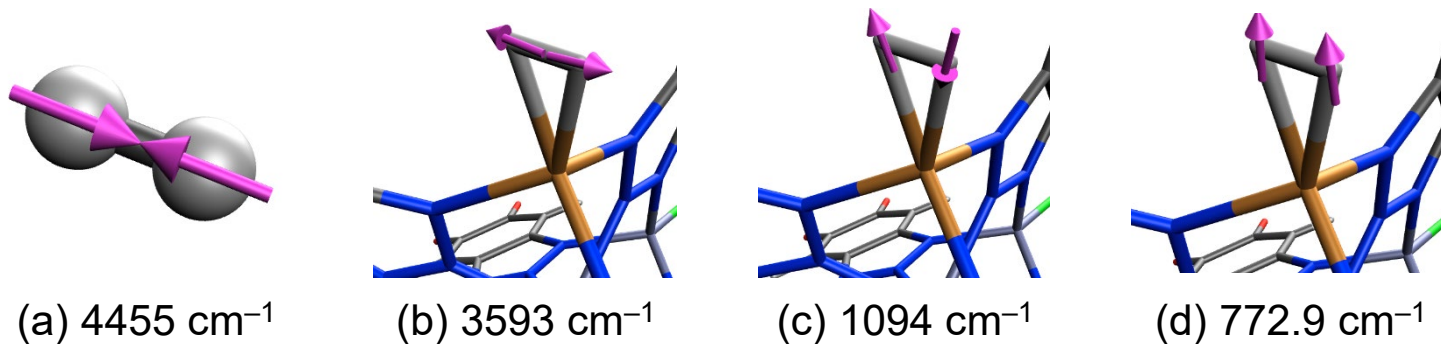
- Harmonic vibrational modes for free and bound H_2
- Predicted red shift of 862 cm^{-1} (919 cm^{-1} observed)

Enthalpy change from normal mode analysis

Effect	Contribution (kJ/mol)
ΔE	–44.8
$\Delta H(0)$	–33.8
ΔH(STP)	–38.1

Anharmonic corrections to ΔH and ΔS
$Cu^+ + H_2 \rightarrow Cu–H_2$

Method	$\Delta H(0)$ (kJ/mol)	$\Delta H(650)$ (kJ/mol)	$\Delta S(650)$ (J/mol K)	$\Delta G(650)$ (kJ/mol)
Experiment*	–15.4	–17.1	–19.7	–4.3
RRHO	–14.7	–15.1	–15.0	–5.4
VCI(4)	–14.6	–15.1	–15.2	–5.3

*Kemper, Weis, Bowers, Maitre *J. Am. Chem. Soc.* **1998**, *120*, 13494

H$_2$ Binding to V^{II} and Cu^I Metal Centers

	V$_2$Cl$_2$(btdd)	Cu^I-MFU-4l
ALMO energy decomposition analysis		
Component	Energy (kJ/mol)	
Frozen	11.6	53.6
Polarization	−12.6	−39.3
Charge transfer	−24.4	−59.0
Total	−25.4	−44.8
Forward and backbonding contributions		
	Energy (kJ/mol)	
H$_2$ → M bonding	−14.7	−26.2
M → H$_2$ backbonding	−3.4	−21.5
IR spectra and thermochemistry		
	Red shift (cm^{-1})	
Red Shift	240	862

0.76 Å

2.19 Å

0.82 Å

1.63 Å
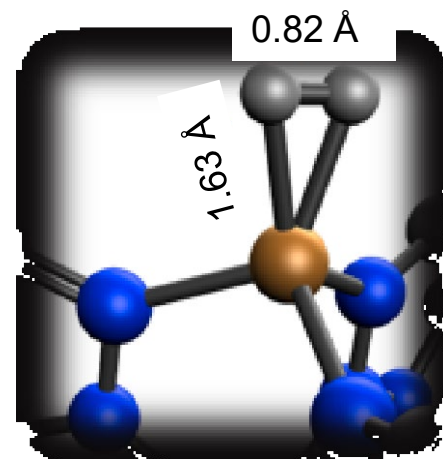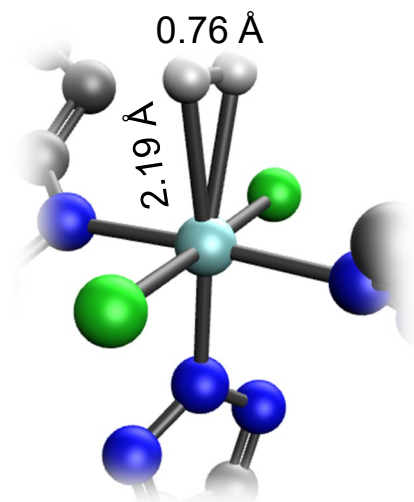
Binding Trends Across First Row Transition Elements

Energy decomposition analysis in $M^{II}_2Cl_2(btdd)$ (M = Ti, V, Mn, Co, and Ni)

	Ti^{2+}	V^{2+}	Mn^{2+}	Co^{2+}	Ni^{2+}
ALMO energy decomposition analysis					
Component	Energy (kJ/mol)				
Frozen	–0.2	1.9	–1.1	0.9	2.4
Polarization	–2.5	–7.4	–5.5	–3.8	–3.8
Charge transfer	–7.0	–21.6	–8.2	–8.6	–5.7
Total	**–9.6**	**–27.1**	**–14.7**	**–11.5**	**–7.0**
Forward and backbonding contributions					
	Energy (kJ/mol)				
$H_2 \rightarrow$ M bonding	–4.1	–12.4	–4.2	–4.5	–1.6
M $\rightarrow H_2$ backbonding	–1.2	–3.3	–1.9	–2.0	–2.9

0.76 Å
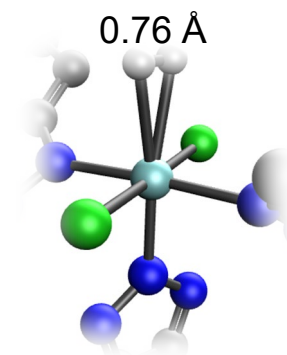
Molecular H_2 binding to $V_2Cl_2(btdd)$

- ▪ V^{2+} has the most favorable binding energy
- ▪ Forward donation dominates for most open metal sites binding molecular H_2

New Approaches in MOF Metalation

UiO-68-cat
$Zr_6O_4(OH)_4(tpdc\text{-}cat)_6$

catechol

UiO-67-PhOpydc
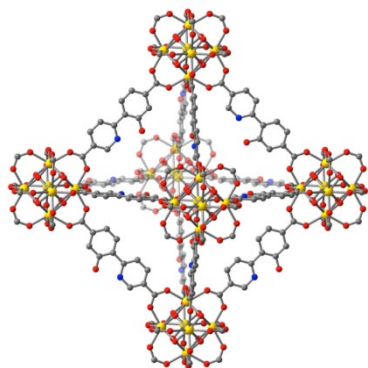$Zr_6O_4(OH)_4(PhOHpydc)_6$
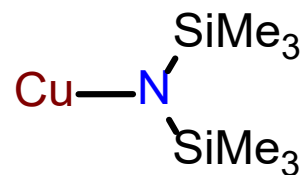
pyridinylphenol
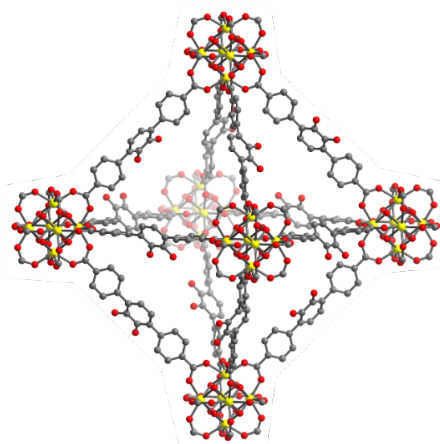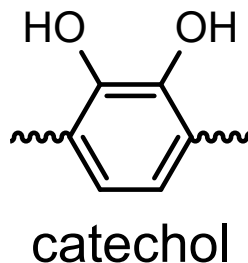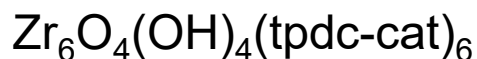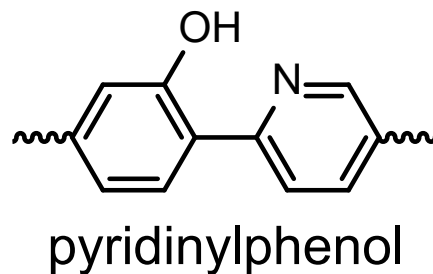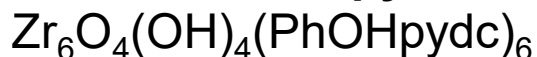
Solution phase reaction
- ✓ Variety of reagents
- ✓ Frequently used
- ✗ Coordinating solvents
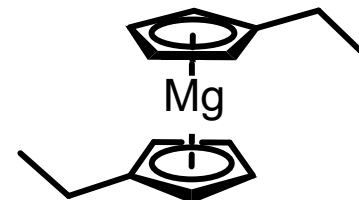- ✗ Residual counter-ions

Gas phase reaction
- ✓ Established ALD materials
- ✓ No solvent
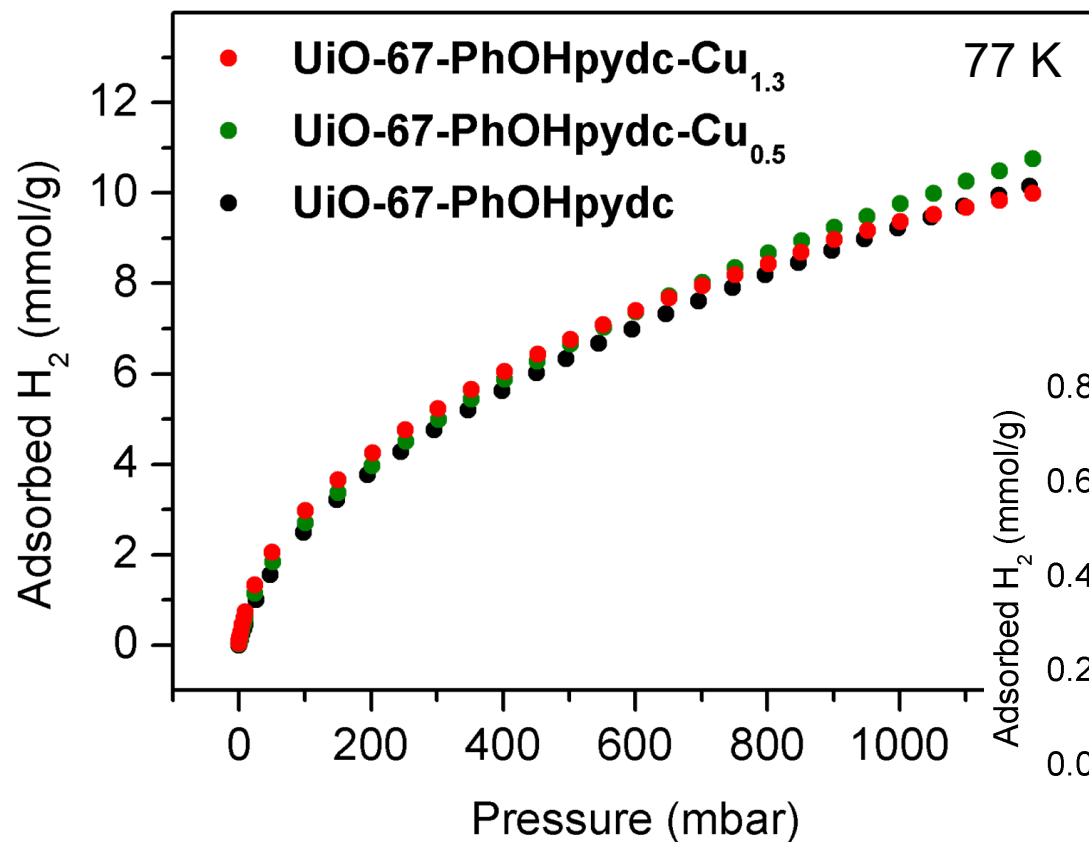- ✓ Good pore accessibility
- ✓ No counter-ions remain

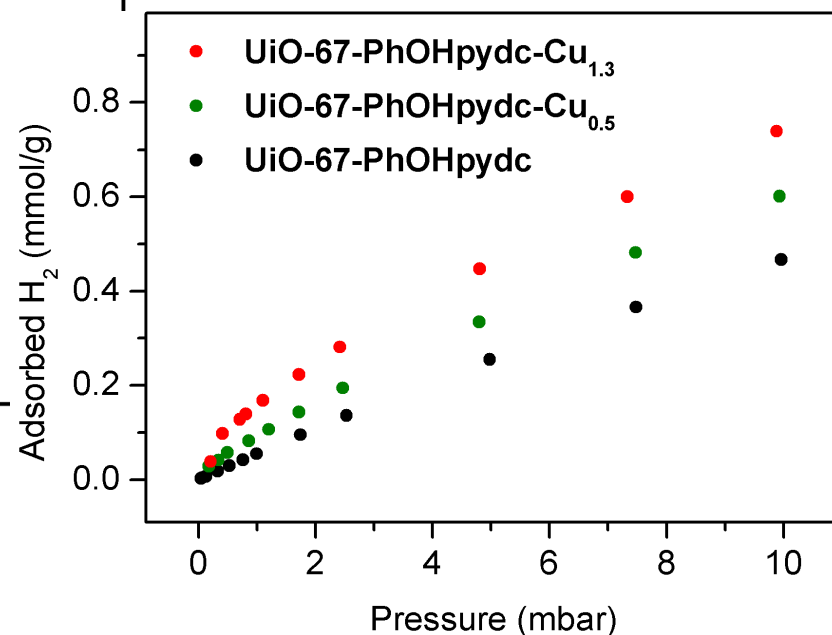$Cu-N$ $SiMe_3$ / $SiMe_3$

CuHMDS

Mg

Mg(Cp^{Et})$_2$
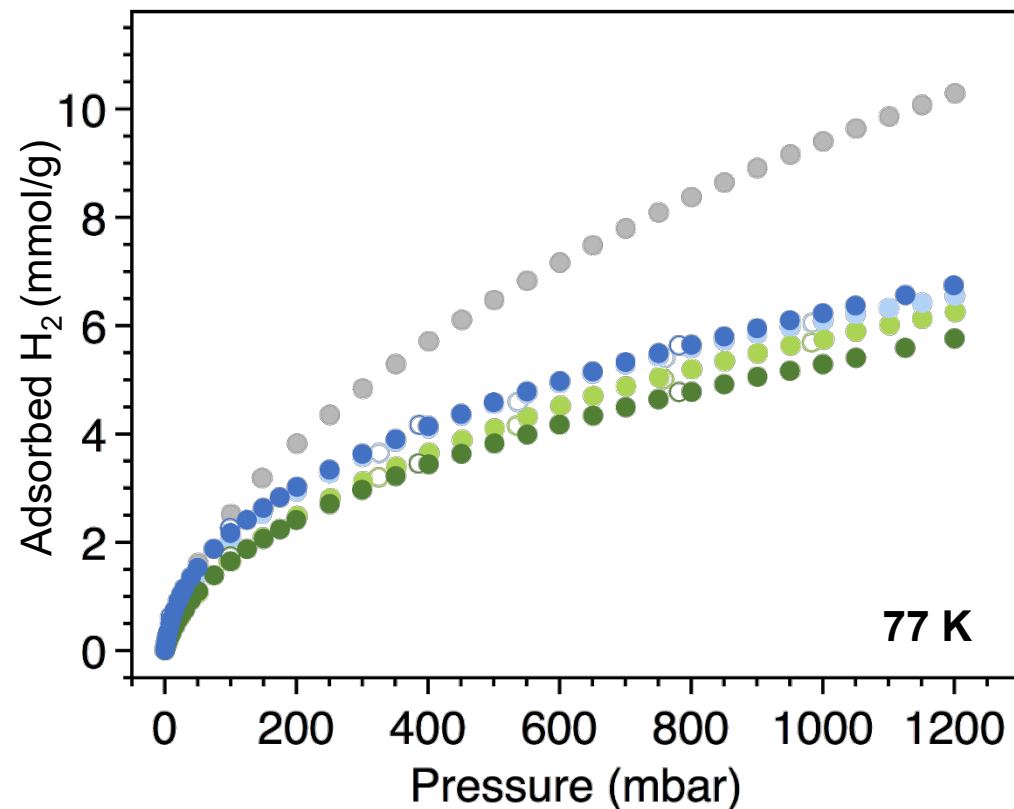
Metalation of UiO-67-PhOHpydc with Cu^I

Metalation conditions:
- 1 eq. CuHMDS per linker
- 140 °C for 3 d, no solvent
- Activated at 140 °C

- Initial H$_2$ uptake increases with higher Cu^I loading
- Gas phase metalation extent is 22% according to ICP-OES
- Attempts to improve metalation and workup procedures are ongoing

Photolysis of Carbonyl Complexes

Metalation conditions:
- 1 eq. $Mn(CO)_5Br$ (or $Re(CO)_5Cl$) and H^+ sponge per linker
- 60 ºC in DMF for 1 day
- Photolyzed with Xe lamp under N_2 (1 atm) for 2 h
- Activated at 150 ºC

- UiO-67-PhOHpydc
- UiO-67-PhOpydc-[Mn(CO)_4]_{2.4}
- UiO-67-PhOpydc-[Re(CO)4]_{1.6}
- UiO-67-PhOpydc-[Mn(CO)_4]_{2.4} after $h\nu$
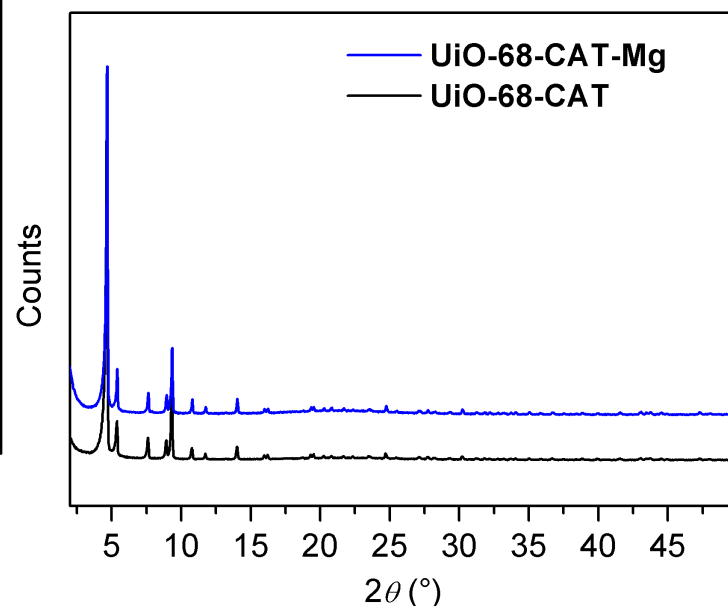- UiO-67-PhOpydc-[Re(CO)4]_{1.6} after $h\nu$

- The initial slope of H_2 isotherm for Re-metalated framework slightly improved
- Photolysis conditions need to be optimized

Mg^{II} in Catechol-Functionalized Framework
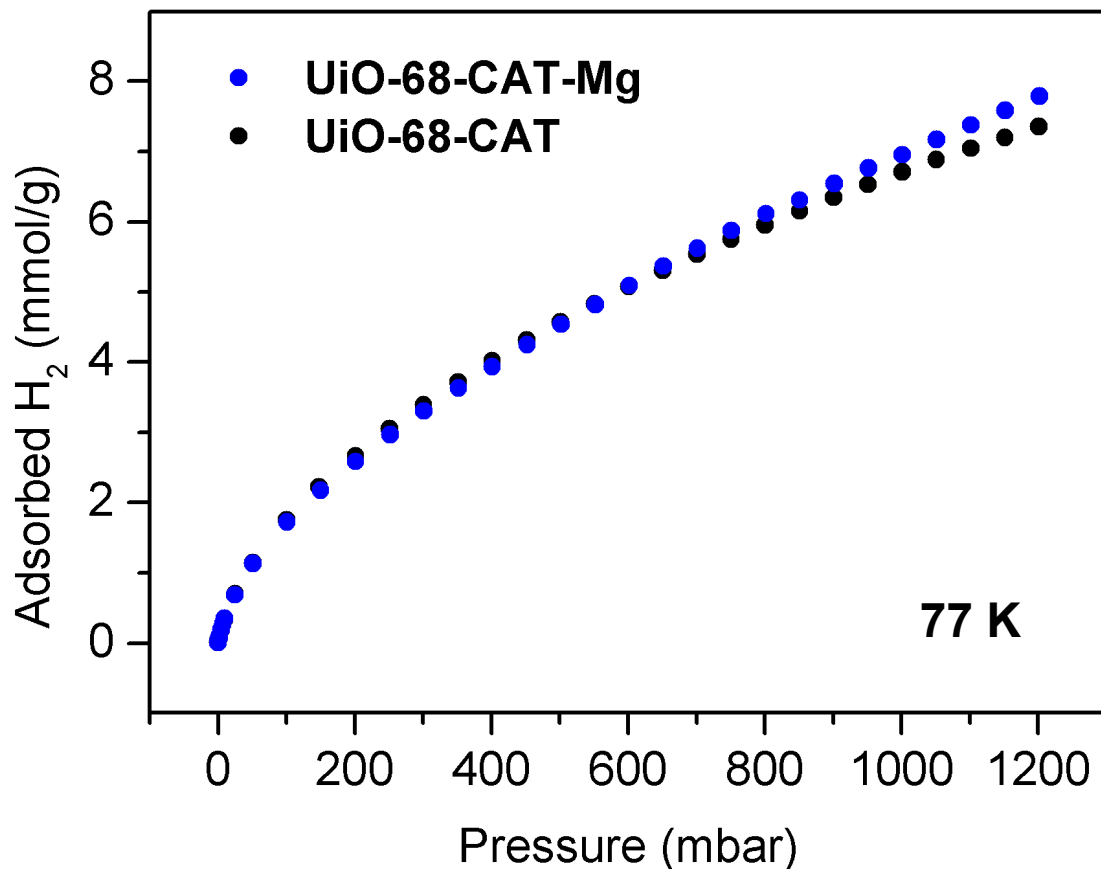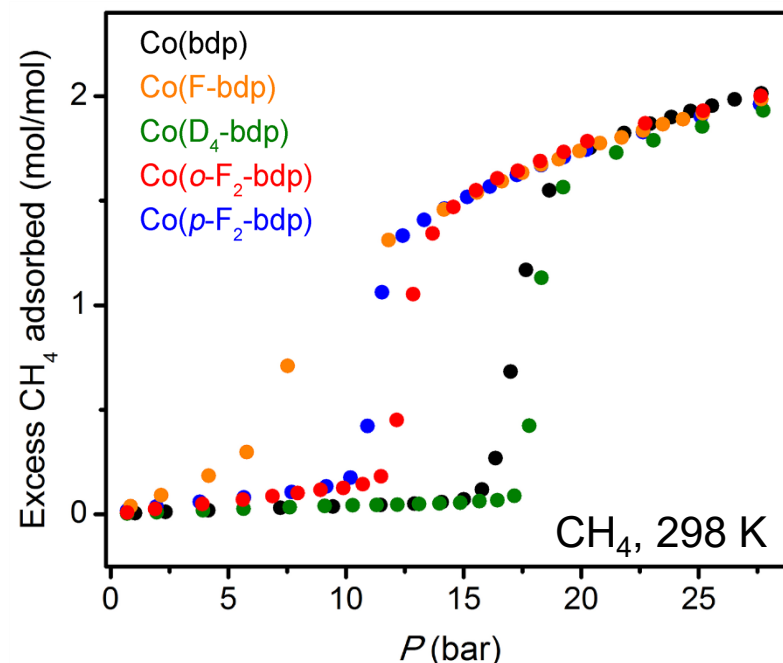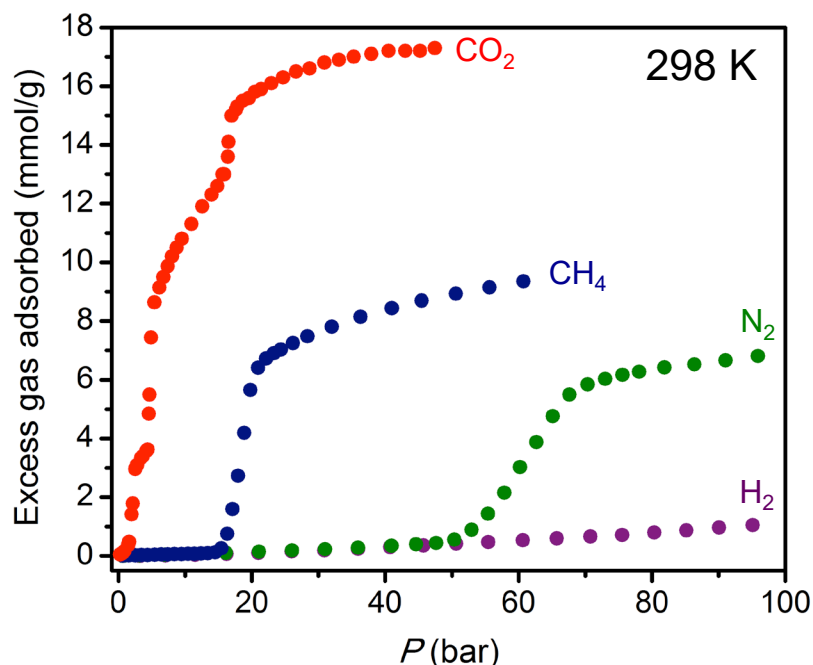

Metalation conditions:
- 1 eq. $Mg(Cp^{Et})_2$ per linker
- 120 °C for 2d, no solvent
- Activated at 120 °C

- Langmuir surface area decreased only slightly from 3470 m^2/g (pristine) to 3250 m^2/g

- Metalation appears to be 100%, but ^{1}H-NMR indicates residual Cp^{Et}H

- Control studies show $Mg(Cp^{Et})_2$ to react also with μ-OH groups of the MOF nodes

Co(bdp) Derivatives for H₂ Storage and Carriers

- Identity of the adsorbate dramatically influences pressure of the adsorption step; H₂ step at very high pressure

- Functionalization can tune phase change pressure (target phase change pressure: storage <100 bar, carriers 200-250 bar)

- Synthesis and high pressure H₂ adsorption measurements are underway

Taylor, Runčevski, Oktawiec, Gonzalez, Siegelman, Mason, Ye, Brown, Long *J. Am. Chem. Soc.* **2016** *138,* 15019

Taylor, Runčevski, Oktawiec, Bachman, Siegelman, Jiang, Mason, Tarver, Long *J. Am. Chem. Soc.* **2018** *140,* 10324

New High-*P*, High-*T In Situ* Spectroscopy Set-Up

DRIFTS (installed)

High-P gas adsorption analyzer

Benchtop NMR spectrometer

Adsorbed H_2
6.5 ppm

Mg_2(dobdc)
0.7 H_2 per Mg^{2+}
298 K

δ ^{1}H / ppm
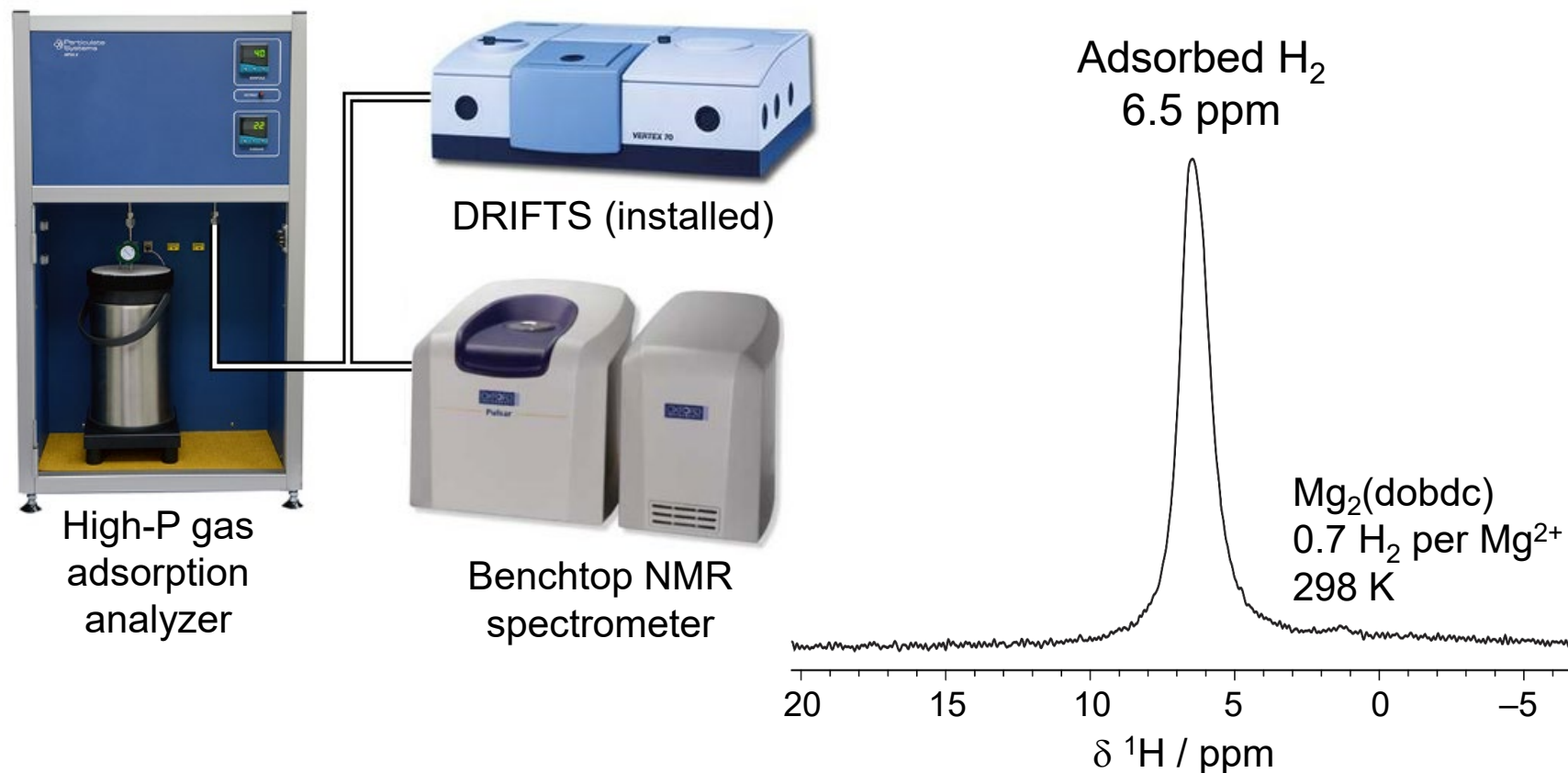
- Chemical shift differs from free H_2 gas (7.4 ppm)
- Variable-pressure studies planned, and studies of other MOFs ongoing
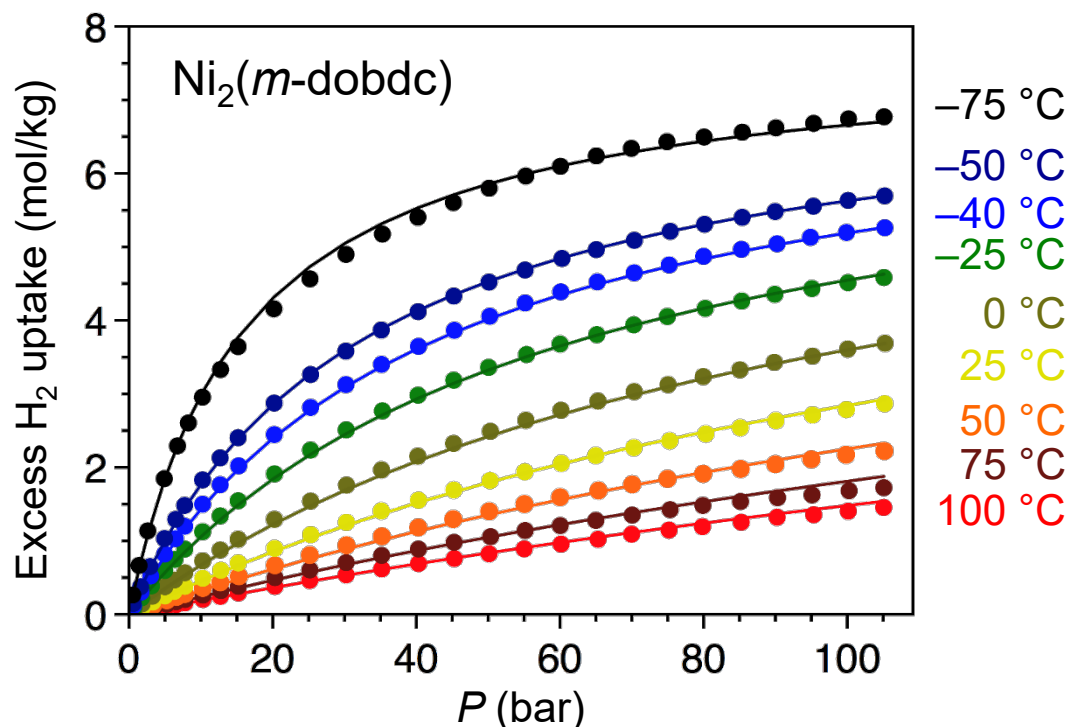- Purchase of benchtop NMR machine in progress

Bulk Transportation Techno-Economic Analysis Effort

What are possible system targets for adsorbent-based bulk transportation of hydrogen?

9 tube trailer compressed H_2

d: 0.56 m
h: 10 m

http://cmwelding.com

Adsorption Transportation

H₂ Storage

Refueling Station

H_2 source

Compressor H_2 storage & fueling

Compressor   High Mid Low

Compressor   High-P buffer system   Cooling system   Filling station

Compression Transportation (Baseline)

Boundary for techno-economic analysis
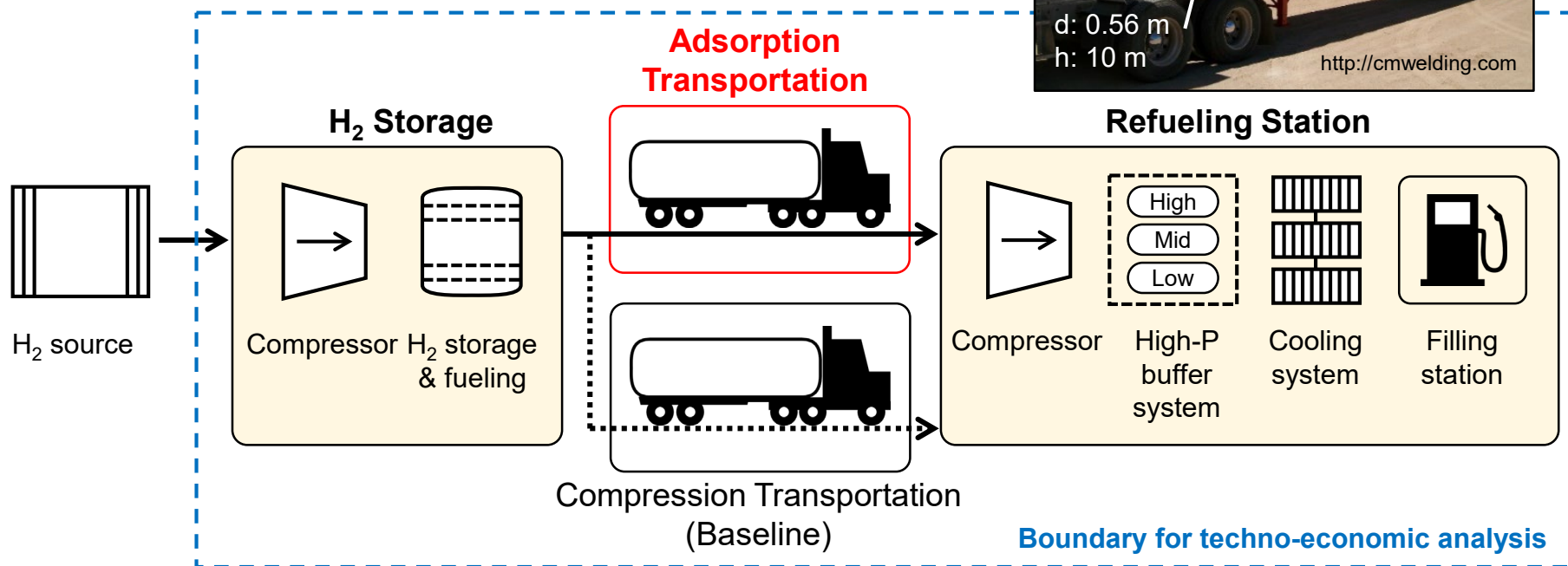
- Theoretical H_2 storage in one Ni_2(*m*-dobdc) packed bed tube at 30 bar ~51 kg-H_2 (compared to 51 kg-H_2 per compressed gas tube of same size at 290 bar)

- Past work has not rigorously evaluated the effects of adsorption column design, thermodynamics, and operating conditions on H_2 storage in MOFs at bulk scale

MOF Packed Bed Column Model

Ni$_2$(*m*-dobdc)

Excess H$_2$ uptake (mol/kg) vs P (bar)

Temperature series: −75 °C, −50 °C, −40 °C, −25 °C, 0 °C, 25 °C, 50 °C, 75 °C, 100 °C

Langmuir model

H$_2$ uptake =

$$\frac{\left[q_{m0} \cdot \exp\left(\frac{q_{m1}}{T}\right)\right] \cdot \left[(K_0 \cdot \exp\left(\frac{K_1}{T}\right)\right] \cdot P}{\left(1 + \left[K_0 \cdot \exp\left(\frac{K_1}{T}\right)\right] \cdot P\right)}$$

***ProSim* parameters to be needed**
Bed void ratio (m^3/m^3)
Particles diameter (mm)
Particles density (g/cm^3)
Specific heat of the solid (J/g K)
Particle surface/volume ratio (m^2/m^3)

- Initial attempts at developing a model in *ProSim* and converging simulations have been successful using isotherm model fits to experimental data* and analog values for adsorbent physical properties and thermodynamics.

- This capability will allow us to fully characterize the affects and interdependencies of parameters and optimize for DoT regulations and potential operating conditions.

* Kapelewski, Runčevski, Tarver, Jiang, Hurst, Parilla, Ayala, Gennett, FitzGerald, Brown, Long, *Chem. Mater.* **2018**, *30*, 8179