

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Soup to nuts: metrics for Production, Transport, and Storage of Fuels

SAND2019-12826C

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Vitalie Stavila, Timothy C. Wang**

**Sandia National Laboratories
Livermore, CA**

Sandia National Laboratories; a multi-program DOE facility with 2 primary sites



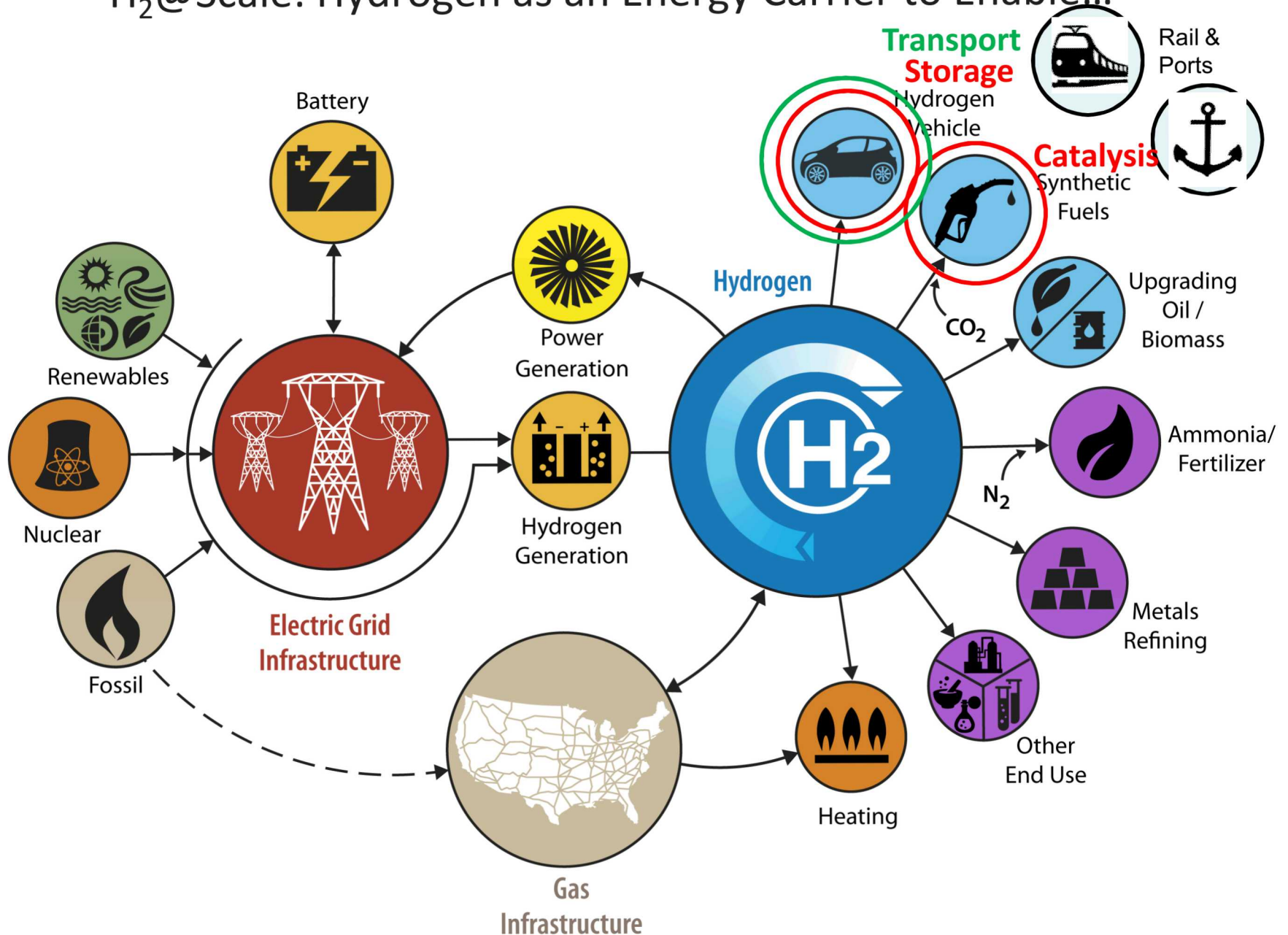
~ 13,000 people total
~ 1200 in California
~ 1650 w/ Ph.D. (lab-wide)
~ \$3.0B budget (total)



Livermore



H₂@Scale: Hydrogen as an Energy Carrier to Enable...



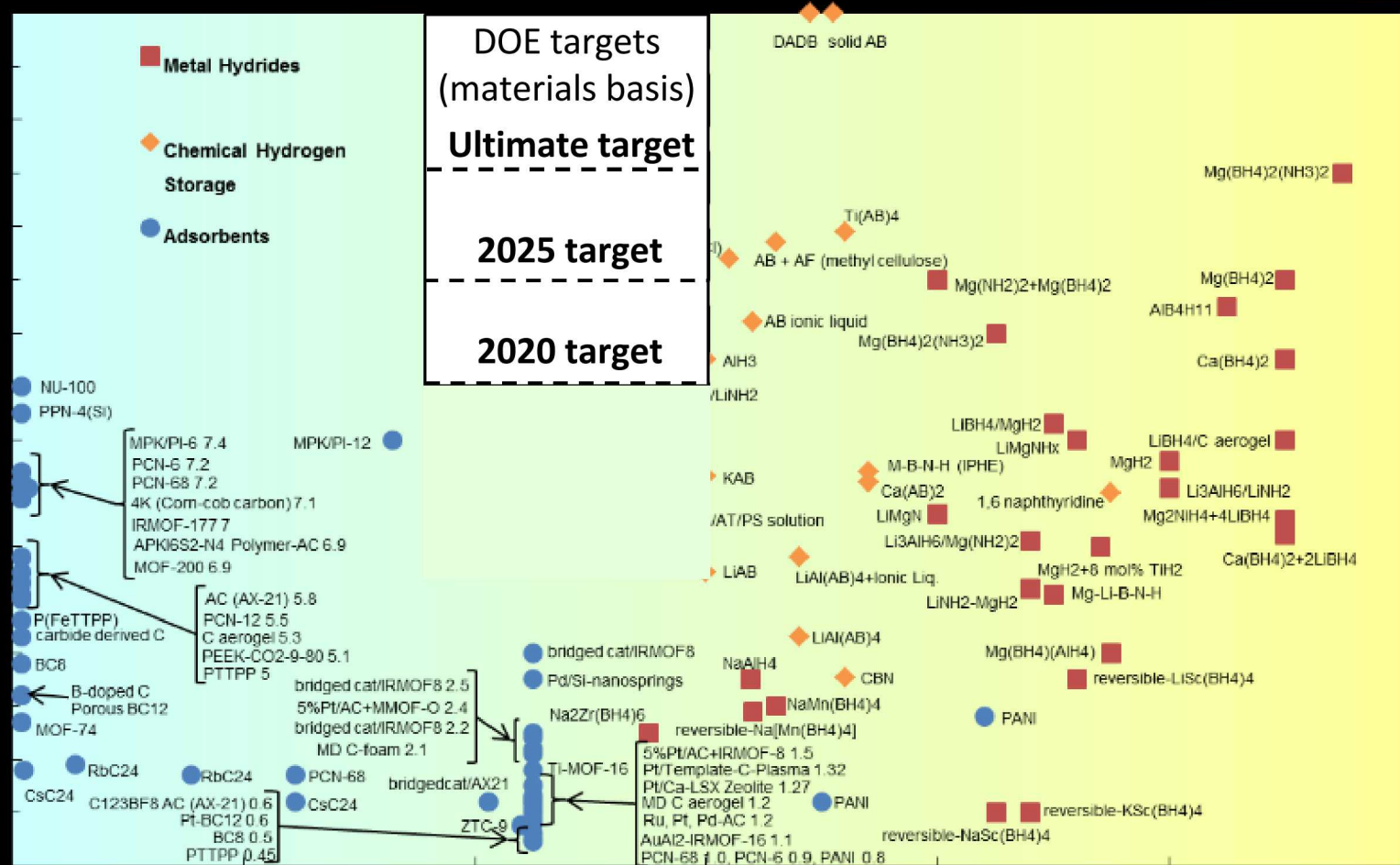
Hydrogen-powered cars are now commercially available



- 700 bar pressurized tanks
- 265 – 312 mile range
- Refueling stations being installed in some areas



**2005-2013: 3 DOE/EERE-funded Centers of Excellence
focused on materials development**



Although many materials were investigated, none were identified that met all DOE technical targets

Hydrogen Materials Advanced Research Consortium (HyMARC): highly coordinated capabilities to accelerate materials discovery

HyMARC Phase 1:

- FY16 – FY 18
- 3 DOE Labs
- Budget \$3M/yr

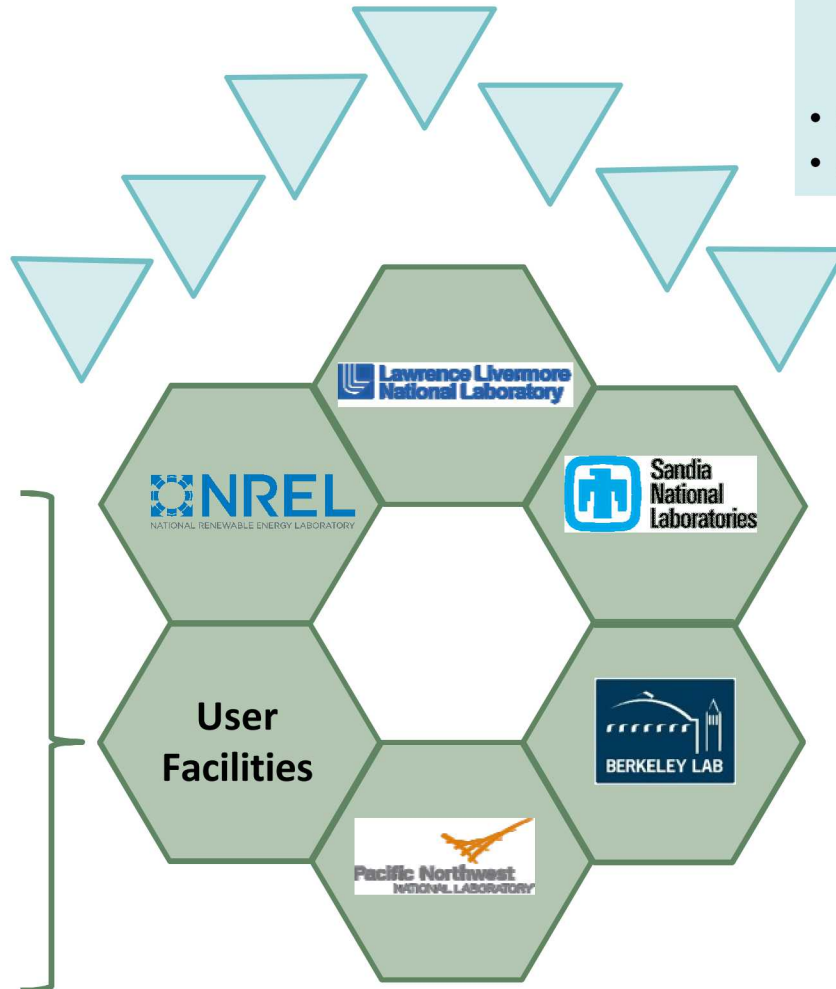
HyMARC Phase 2:

- FY19 – FY22
- 5 DOE Labs
- Budget \$8 M/yr



Seedling Projects

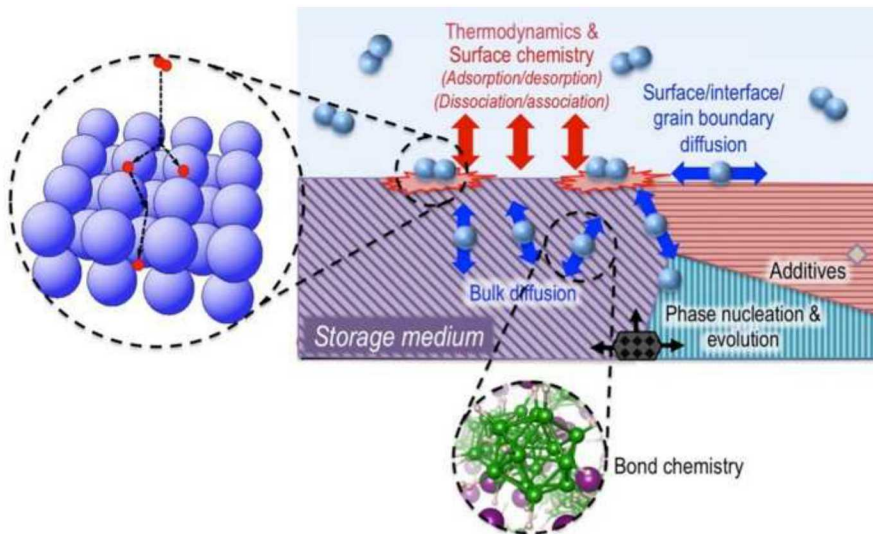
- Applied material development
 - Novel material concepts
 - High-risk, high-reward
- Concept feasibility demonstration
- Advanced development of viable concepts



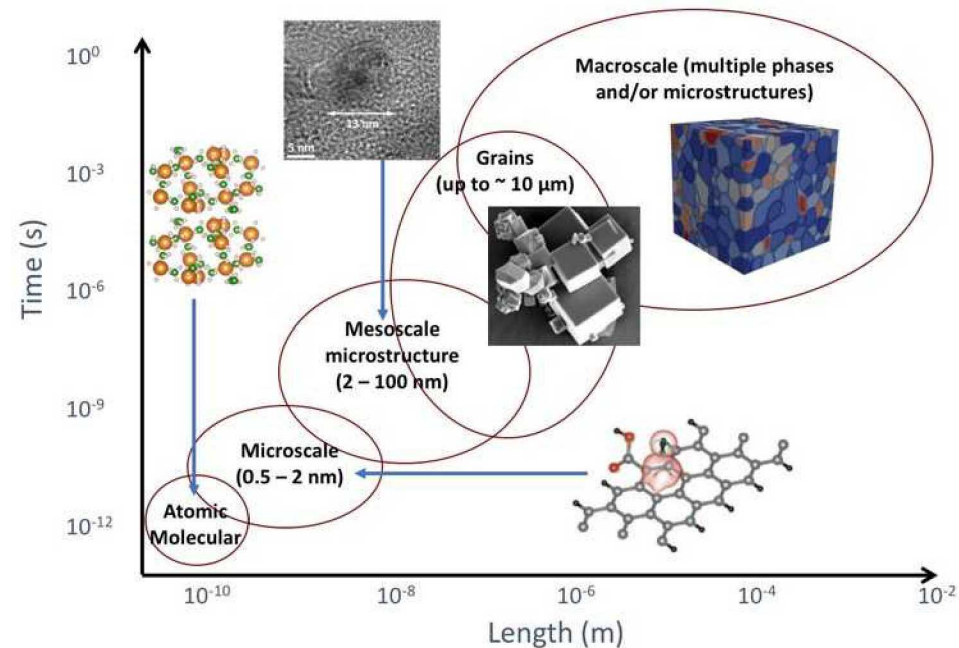
- Foundational R&D
- Computational models
- Synthetic protocols
- Advanced characterization tools
- Validation of material performance
- Guidance to FOA projects
- Database development

Poorly understood phenomena at length scales from < 1 nm to μm govern storage material behavior

Distinct chemical/physical processes affect the bulk properties of storage materials



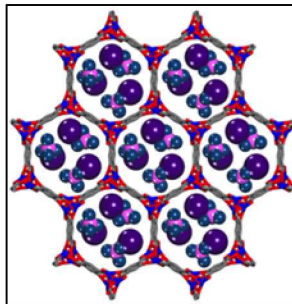
Multiple length scales must be taken into account



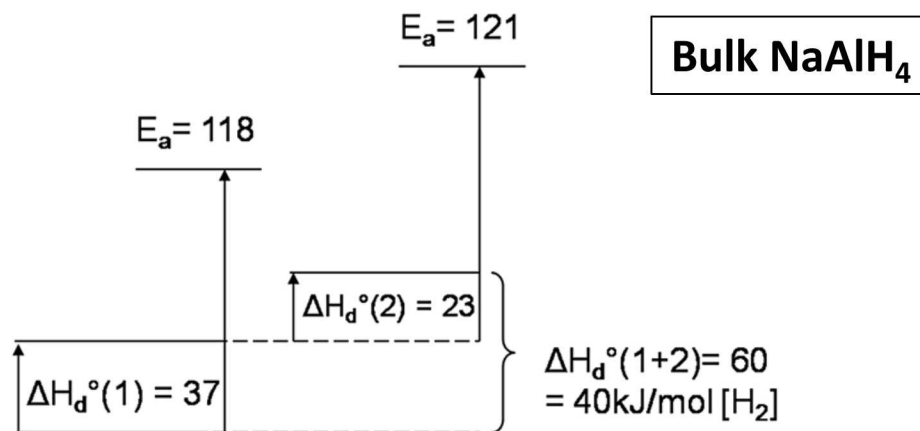
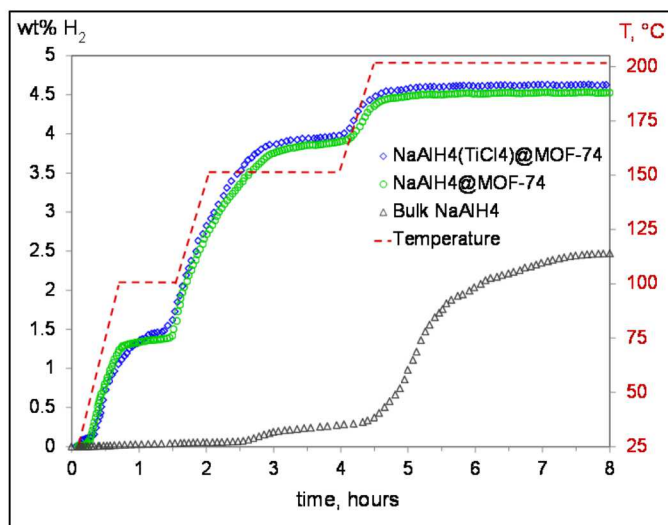
“Design rules” are needed to guide materials discovery

Nanoscaling: both thermodynamics and kinetics can be modified

NaAlH₄@MOF has altered reaction pathway and accelerated desorption kinetics

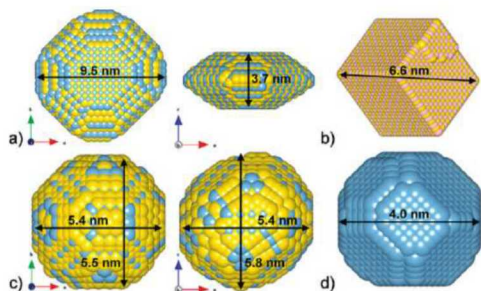


NaAlH₄@Mg-MOF-74



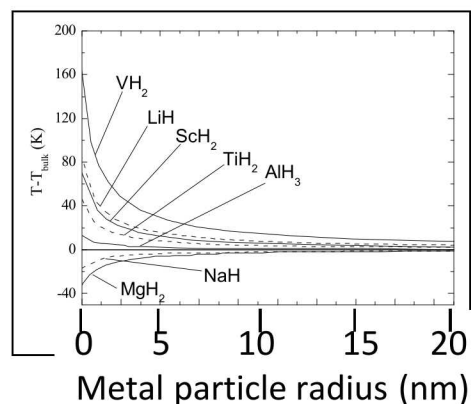
Theory suggests thermodynamics are affected only for extremely small particles

2-10 nm NaAlH_4 Clusters:
1-step reaction, no Na_3AlH_6
intermediate



Mueller and Ceder
ACS Nano, **4**, 5647 (2010)

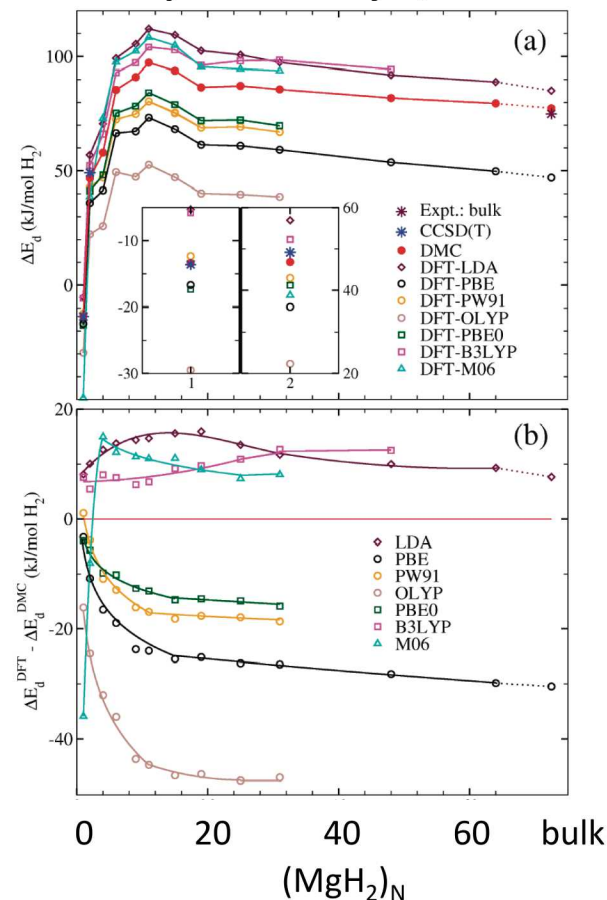
Hydride destabilization as a
function of particle size,
predicted by Wulff construction



Kim, Johnson, Sholl
Nanotech., **20**, 204001 (2009)

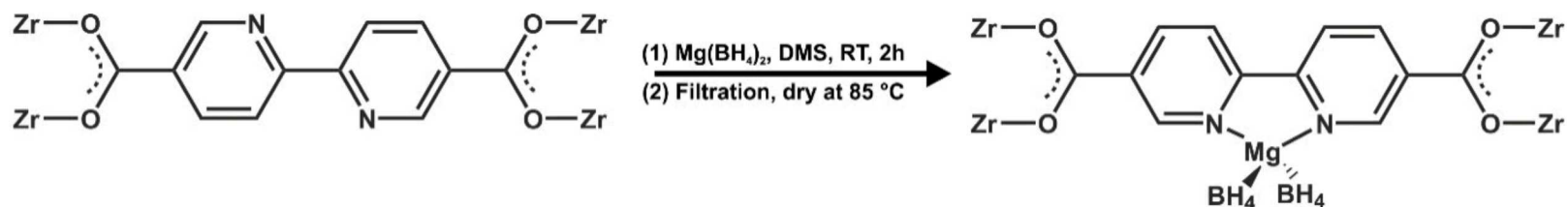
How small can we get?

MgH_2 desorption energy
predicted by QMC

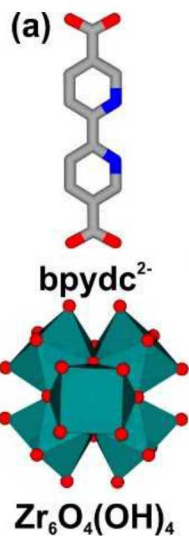


Wu, Allendorf, Grossman
JACS, **131**, 13918 (2009)

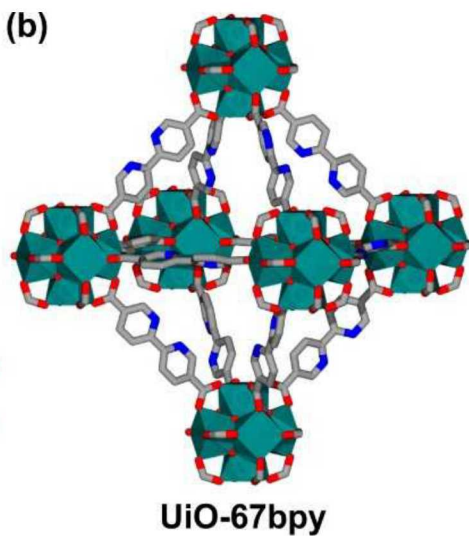
“Molecular” $\text{Mg}(\text{BH}_4)_2$? non-innocent MOF hosts for metal hydrides



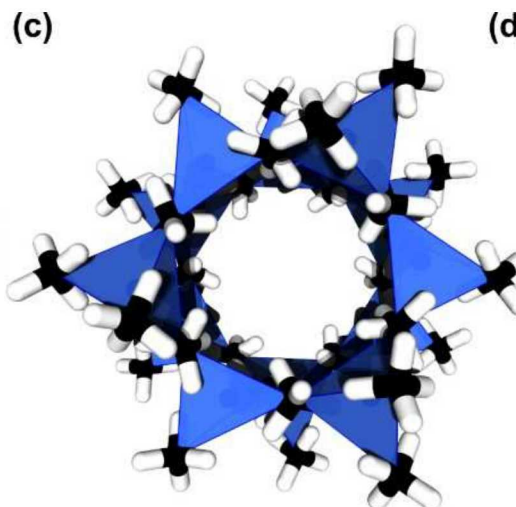
MOF building blocks



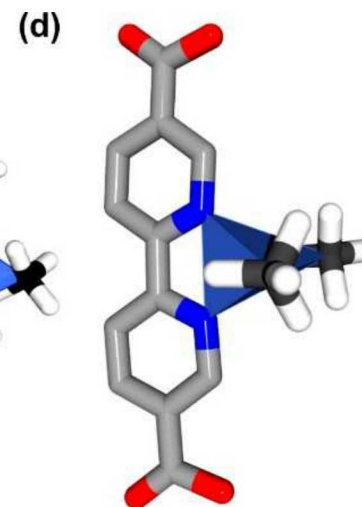
O_h pore



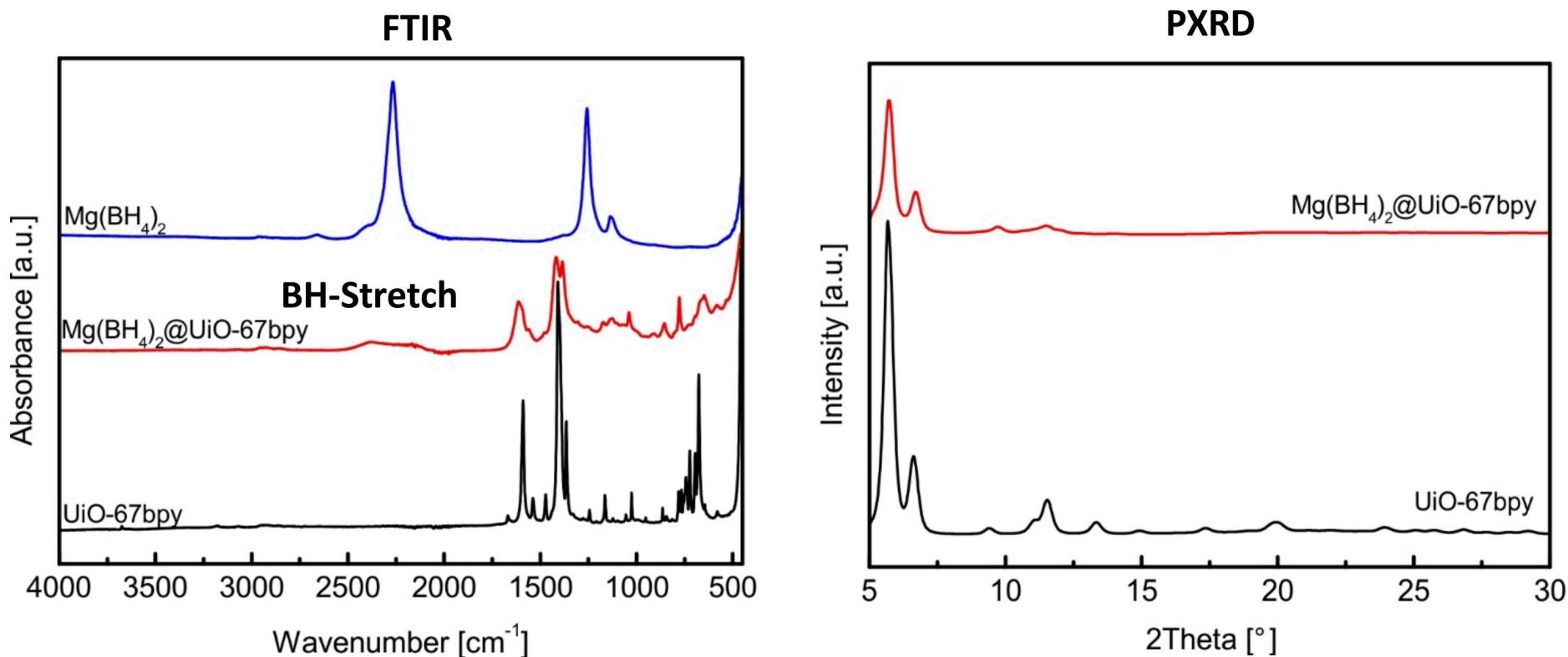
$\gamma\text{-Mg}(\text{BH}_4)_2$ fragment



$\text{Mg}(\text{BH}_4)_2$ coordinated bpydc^{2-} linker

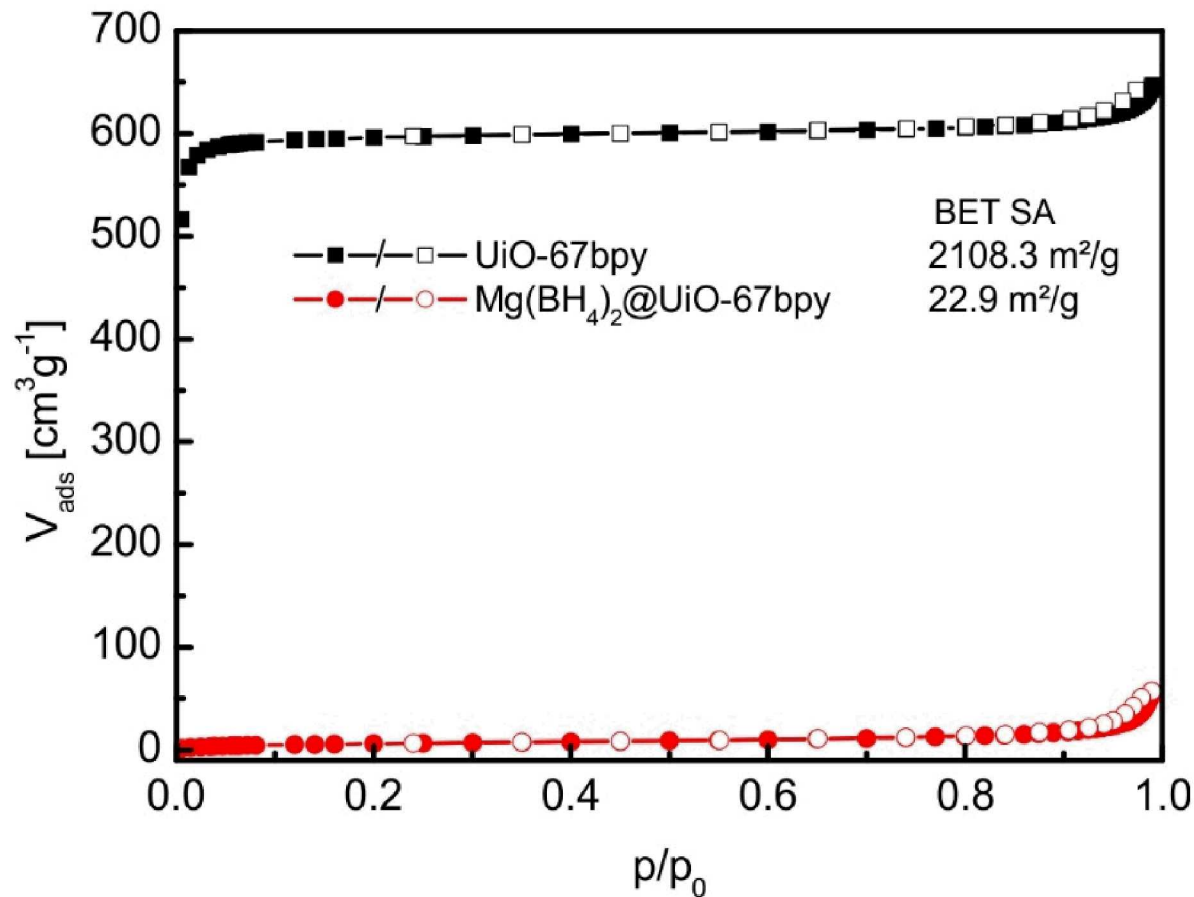


Installation of hydrides on chelating ligands



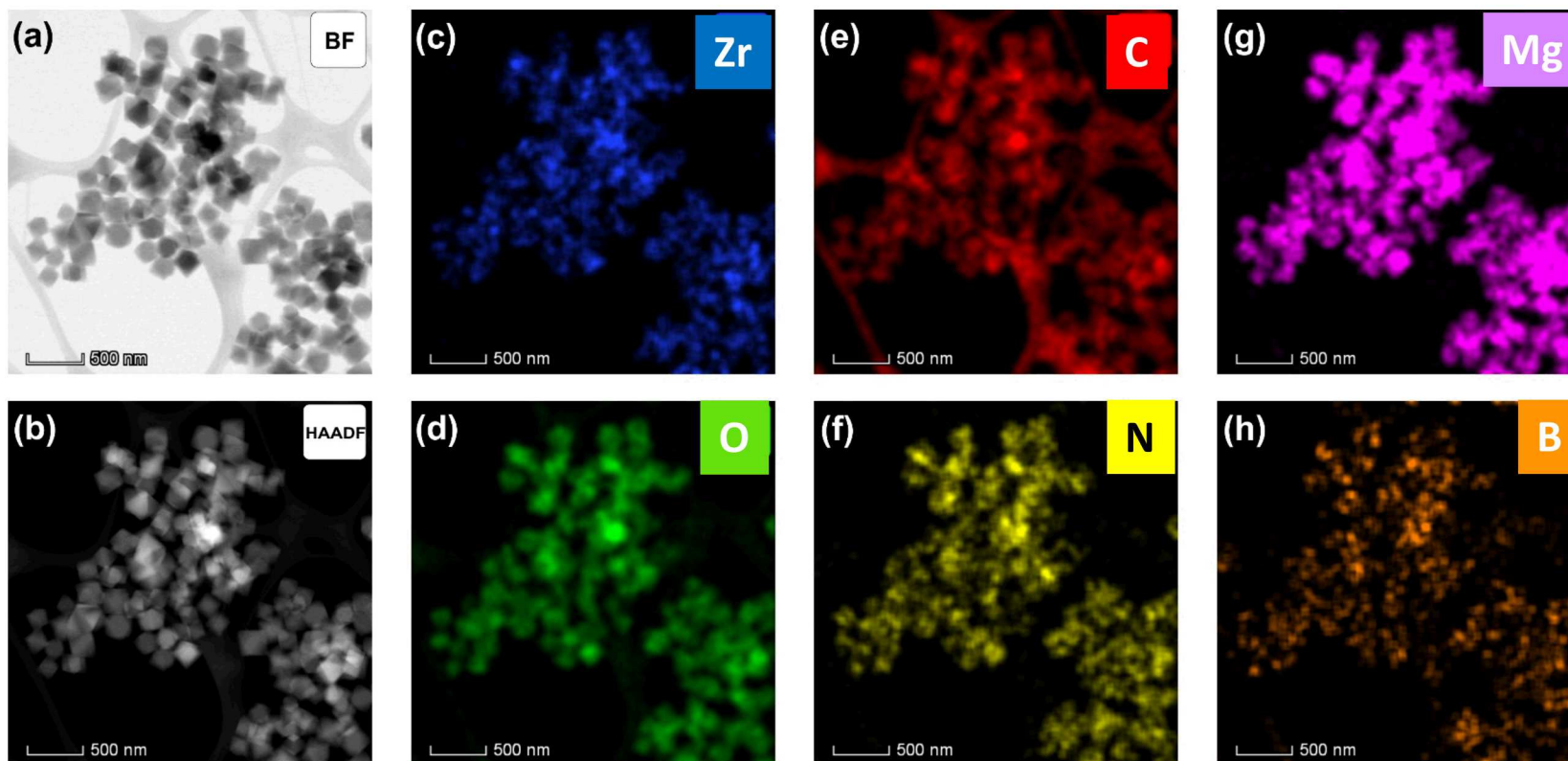
- **BH stretch visible after infiltration**
- **Slight decrease in cristallinity**

Hydride infiltration results in complete pore filling



- $\text{Mg}(\text{BH}_4)_2$ occupy the pores fully
- Elemental Analysis suggests a formula of $[\text{Mg}(\text{BH}_4)_2]_{12}@\text{Zr}_6\text{O}_6(\text{bpydc})_{12}$
→ 1 hydride formula unit/chelating ligand

$\text{Mg}(\text{BH}_4)_2$ uniformly distributed throughout the crystals

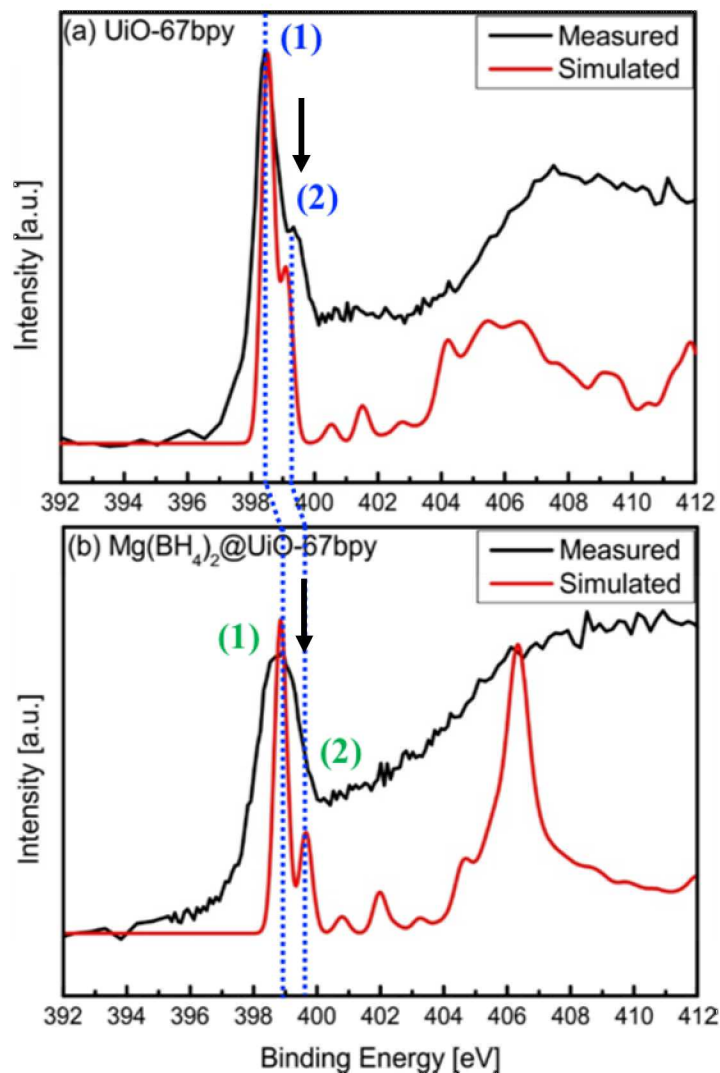


- No evidence of bulk hydride or hydride particles outside the pores
- EDS Spectrum rules out presence of S and Cl from precursors

X-ray Adsorption Spectroscopy confirms Mg-N coordination

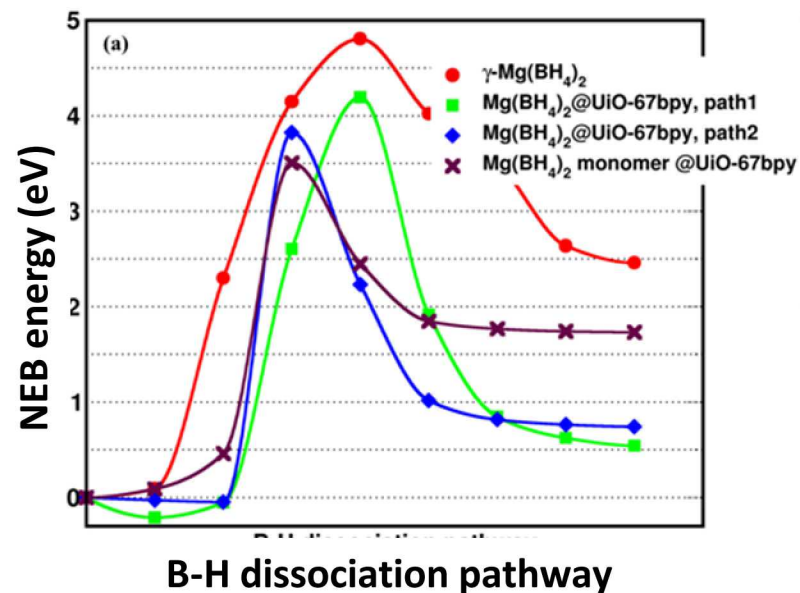
N K-edge spectra fit well with simulated spectra

(1) = trans bpy; (2) = cis $\text{Mg}(\text{BH}_4)_2@\text{bpy}$



- Slight shift of N K-edge to higher energy consistent with Mg^{2+} coordination
- DFT calculations:
 - trans-bpy more stable than cis-bpy
 - $\text{Mg}(\text{BH}_4)_2@\text{bpy} \rightarrow$ cis is more stable
 - Hydride coordination increases bpy excited state delocalization $\rightarrow$ intensity decreases

DFT calculations suggest a lower H_2 release energy



Two binding scenarios:

- Molecular Dispersion
- Molecular Dispersion + formation of small hydride entities inside the pores

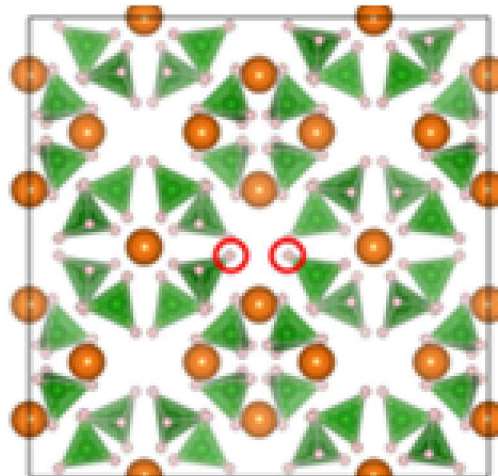
(f) $\text{Mg(BH}_4)_2$ mono

(d) $\text{Mg(BH}_4)_2$

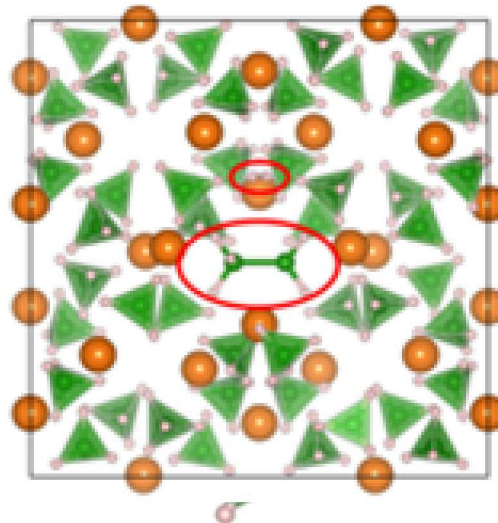


(e)

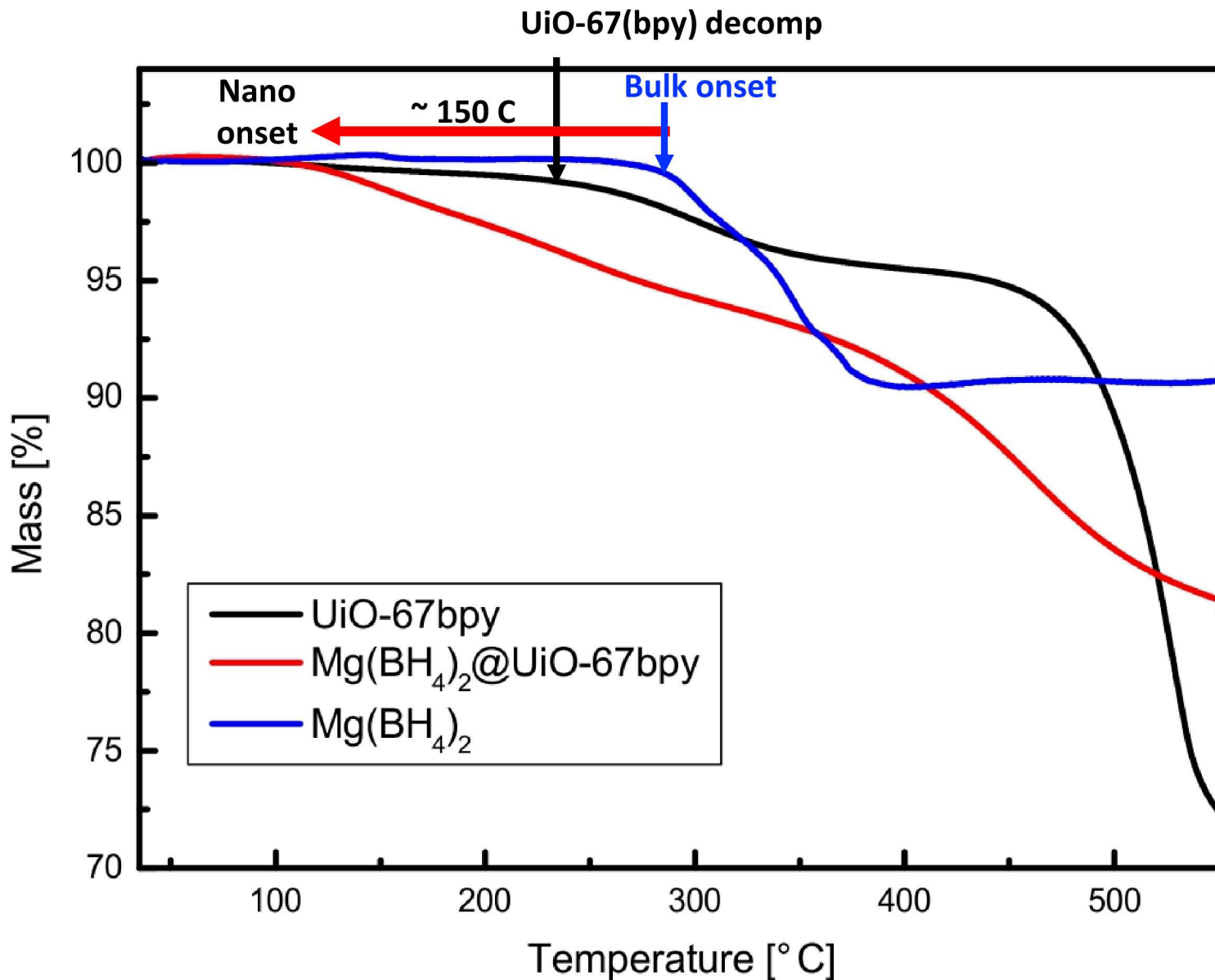
$\gamma\text{-Mg(BH}_4)_2$, initial



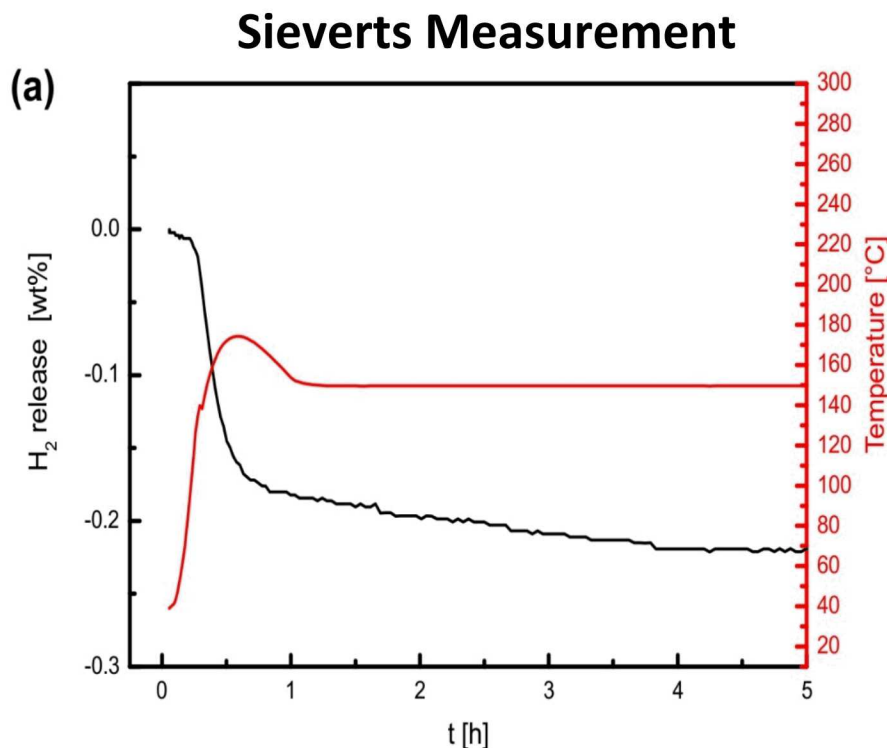
$\gamma\text{-Mg(BH}_4)_2$, final



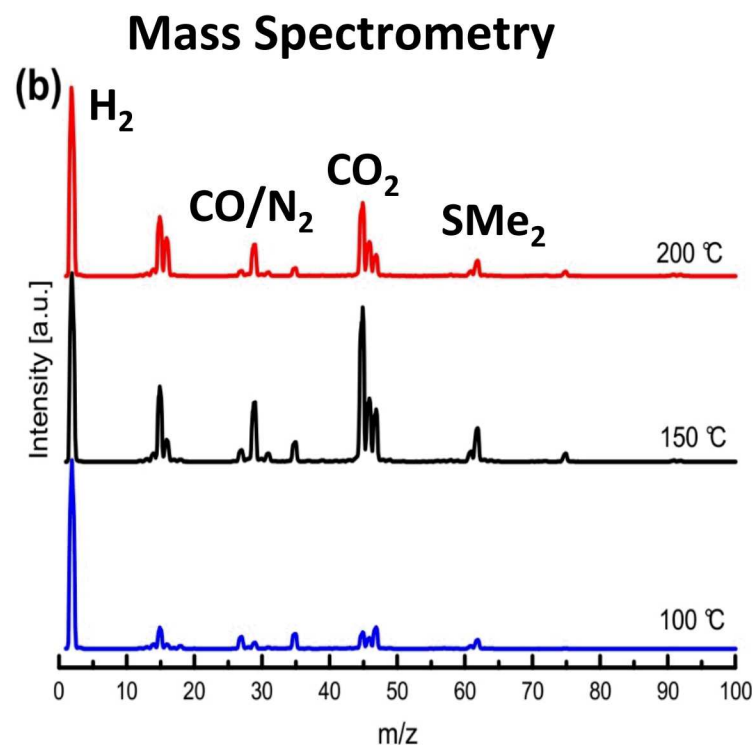
TGA supports DFT predictions, revealing H₂ release at much lower temperature compared to bulk



Material releases clean H_2 at low temperatures: reaction pathway altered (no B_2H_6 as in bulk)



0.2 wt% H_2 released at 150 $^{\circ}\text{C}$

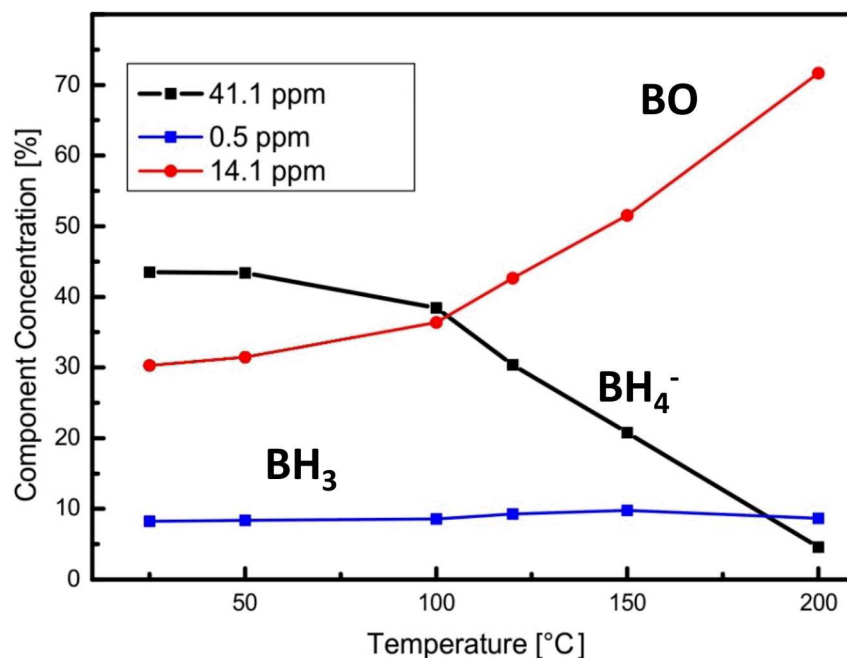
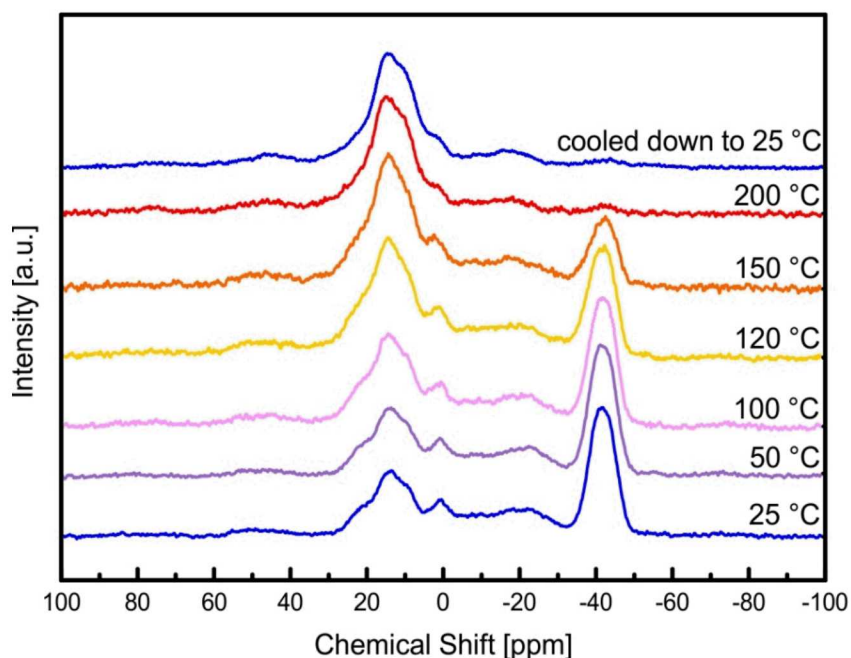


**At low desorption T clean H_2
(Measurement not quantitative)**

Material releases H_2 , but also some decomposition of the framework occurs

MAS NMR shows that during dehydrogenation no $B_{10}H_{10}^{2-}$ or $B_{12}H_{12}^{2-}$ species are formed

^{11}B -MAS NMR



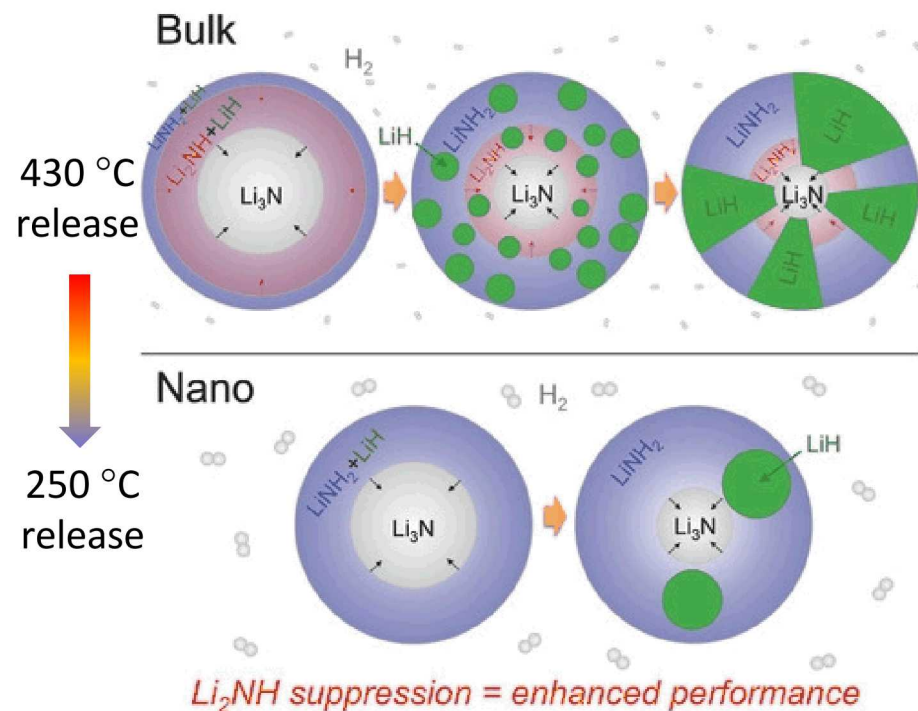
Signal at -41.1 ppm represents BH_4^-

Signal at 14.1 ppm represents BO species – interaction with ZrO cluster

Signal at 0.5 ppm represents BH_3 species

Take home lesson: “molecularizing” a complex hydride has a huge effect on the reactivity

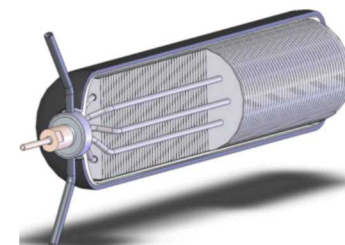
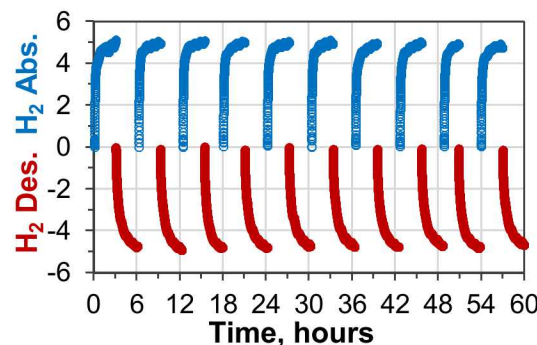
Nanoscale metal hydrides have faster H₂ uptake and release



Metal Hydride Finite Element model reveals non-intuitive tradeoffs and benefits of using nanoscale metal hydrides in an operational H₂ storage tank

Design Parameters	bulk-Li ₃ N	KH-6nm-Li ₃ N
Reversible capacity, wt%	8.2	5.4
Thermal cond., W m ⁻¹ K ⁻¹	1.0	9.6
Density of hydride bed, kg m ⁻³	710	760
Total system mass, kg	312	252
Total hydride mass, kg	112	116
Tank outer diameter, m	0.46	0.45
Tank length, m	2.21	2.19
System volume, m ³	0.256	0.227
% 2025 Gravimetric Target	33	40
% 2025 Volumetric Target	55	62

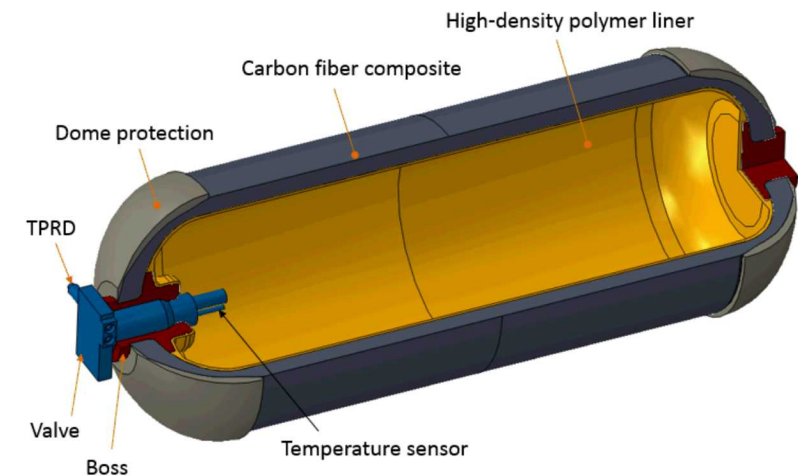
B. C. Wood Adv. Mater. Interfaces (2017)
<https://doi.org/10.1002/admi.201600803>



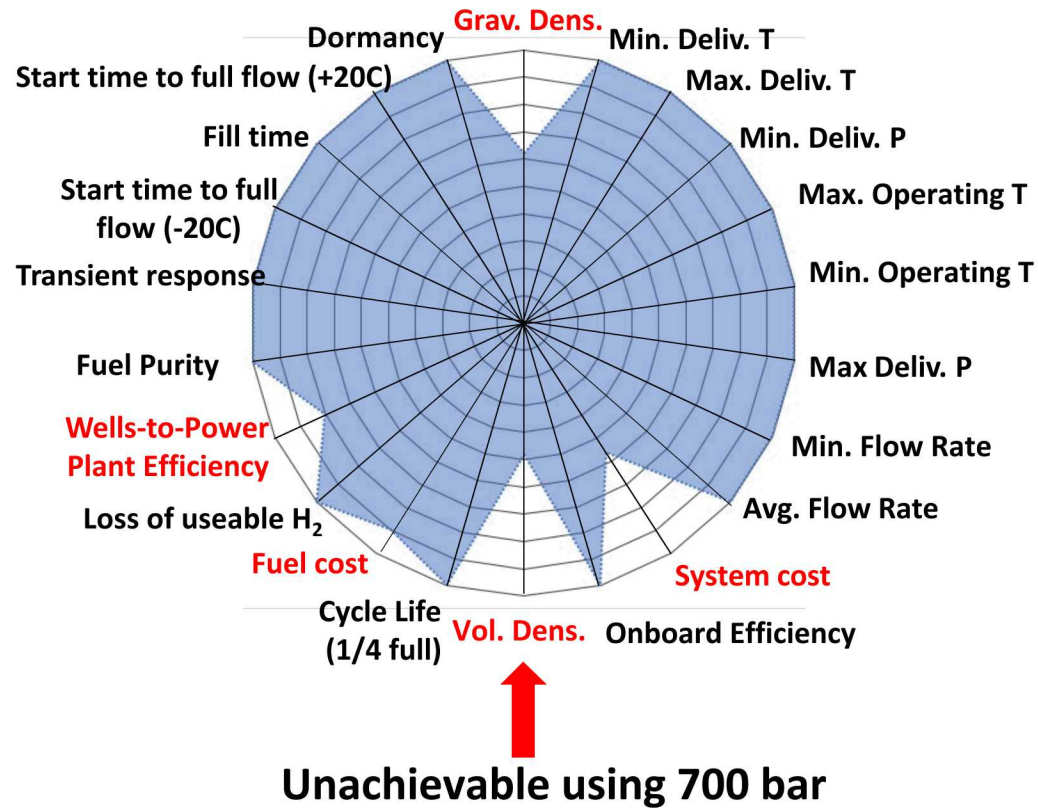
MHFE-SA tank design

Although fuel cell vehicles are now commercially available, compressed H₂ storage falls short of several DOE targets

700 Bar Compressed Gas (2015 record) vs. revised DOE Ultimate Targets



TPRD = Thermally Activated Pressure Relief Device
Credit: Process Modeling Group, Nuclear Engineering Division, Argonne National Laboratory (ANL)



Hydrogen Carriers:

MOF catalysts for releasing H₂ from alcohols and polyols

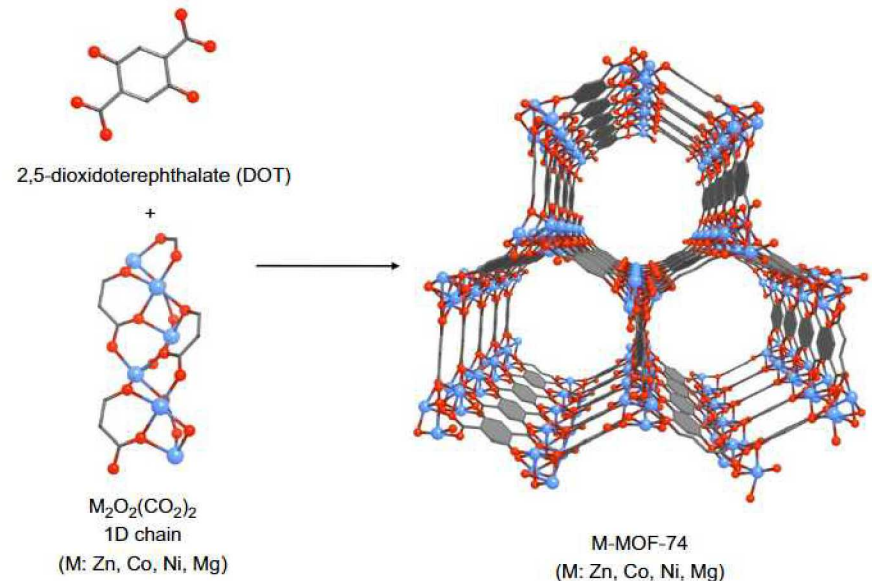
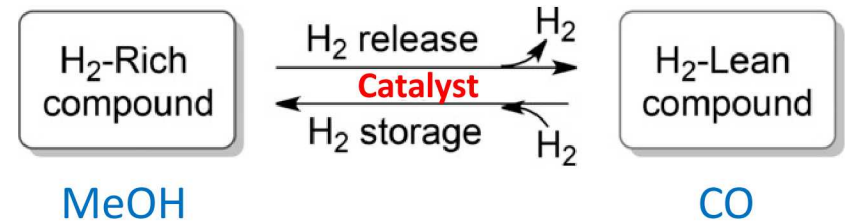
Efficient transport of hydrogen from point of production to fueling station is not possible using compressed gas:

- 1 kg H₂ = 1 gallon of gasoline (~4 L)
- Steel tubes: 280 kg per tanker
- Somewhat better: Composite tanks: 550 kg of hydrogen at 250 bar
- **Typical gas station stores 75,000 – 230,000 L (20,000 – 60,000 gallons)**



MOF Catalysts for Hydrogen Storage in LOHCs

- **Liquid organic hydrogen carriers**
 - Improved storage/transportation over gaseous hydrogen
 - With an appropriate catalyst, hydrogen can be reversibly produced on demand
- **Metal organic frameworks (MOFs)**
 - Open metal sites (OMS) can be catalytically active
 - Homogeneously dispersed reactive centers
 - High porosity and surface area
 - Tunable structure
- **This study is focused on methanol dehydrogenation to explore the potential of MOFs as dehydrogenation catalysts**



Top: Xie, Y., et al. *Angew. Chem. Int. Ed.* 2019, 58, 5105-5109

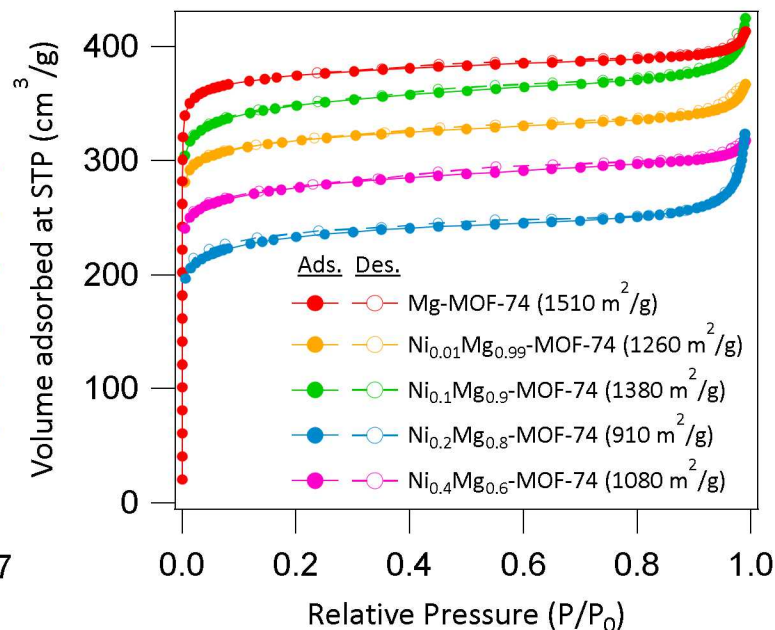
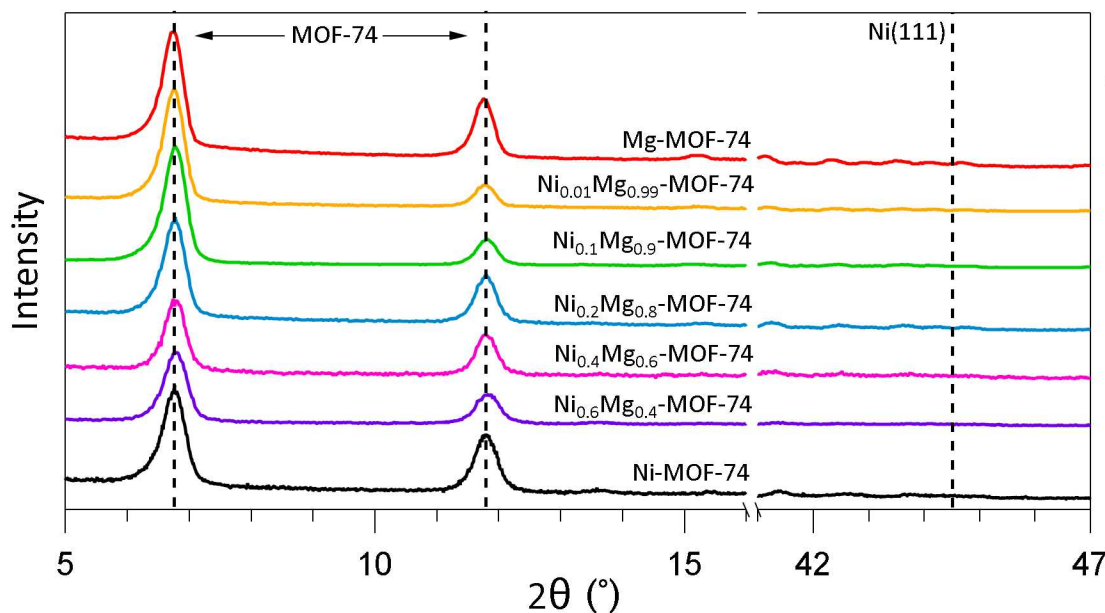
Bottom: Glover, T.G., et al. *Chem. Eng. Sci.* 2011, 66, 163-170

Catalyst series: $\text{Ni}_x\text{Mg}_{1-x}$ -MOF-74

- **MOF-74 is promising for dehydrogenation:**
 - Adsorbs MeOH
 - Catalyzes MeOH-activated H_2O dissociation
 - G. Flores et al. *Appl. Sci.-Basel* **8** (2018), 270
- **Synthesis of $\text{Ni}_x\text{Mg}_{1-x}$ -MOF-74**
 - React solution of MgCl_2 , NiCl_2 , and DHTA in DMF/EtOH/ H_2O at 120°C
 - Wash product then activate at 170°C in vacuo
- **Characterization reveals a similar structure across the samples**
 - MOF-74 crystal structure with high surface area of $910\text{--}1510\text{ m}^2/\text{g}$



1% Ni 10% Ni 20% Ni



MeOH dehydrogenation on $\text{Ni}_x\text{Mg}_{1-x}$ -MOF-74

- **Mg-MOF-74 is inactive for MeOH dehydrogenation**
- **The addition of Ni improves catalyst activity**
 - Above 250 °C, H_2 productivity is maximized by an intermediate Ni content (20-40%)
- **Catalyst performance is stable after a brief activation period**
- **Conversion can be increased up to 100% by lowering the space velocity**

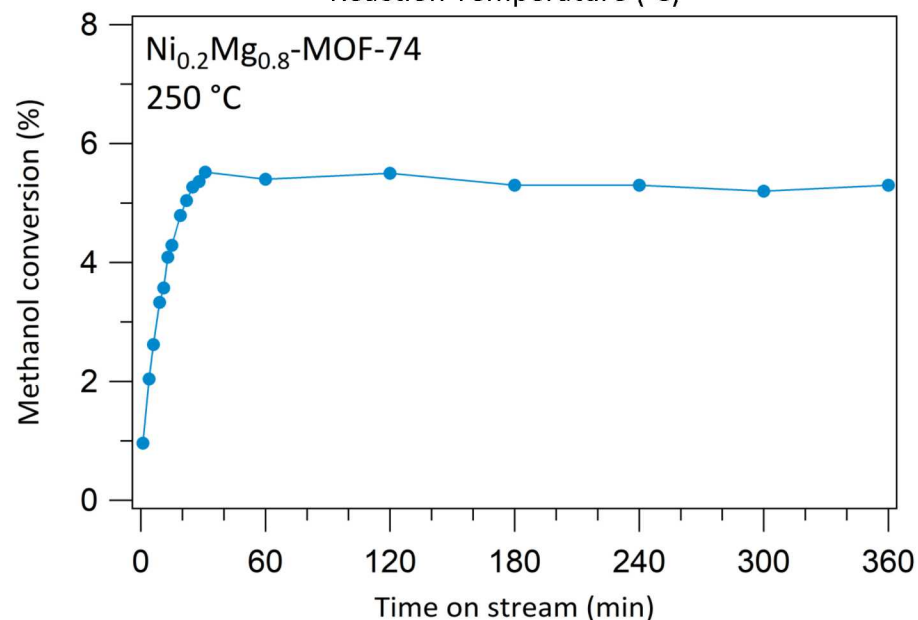
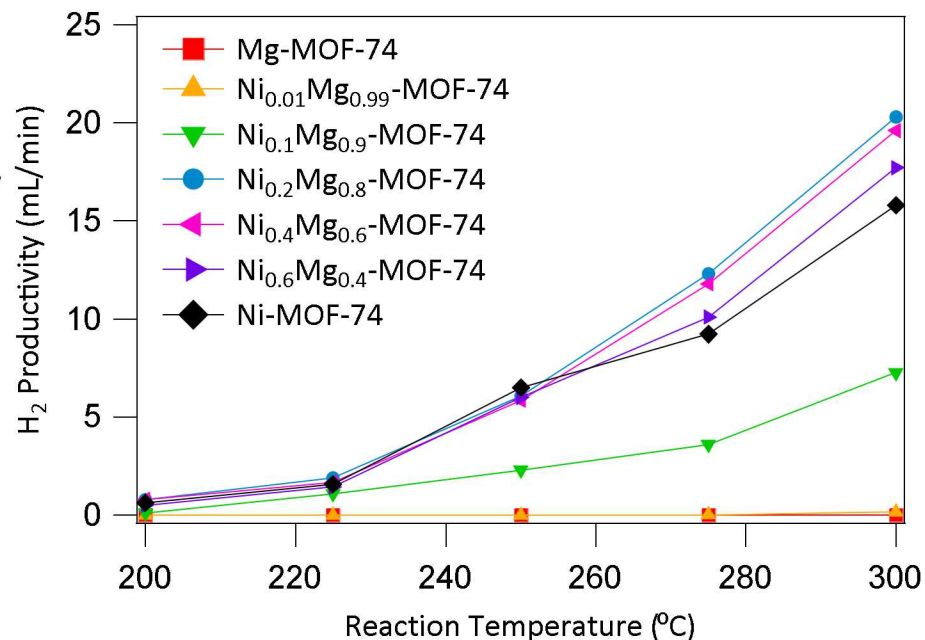
Test conditions:

1 bar

35 sccm N_2 , 55 sccm MeOH vapor

100 mg catalyst, diluted with sand

Products consist solely of H_2 and CO

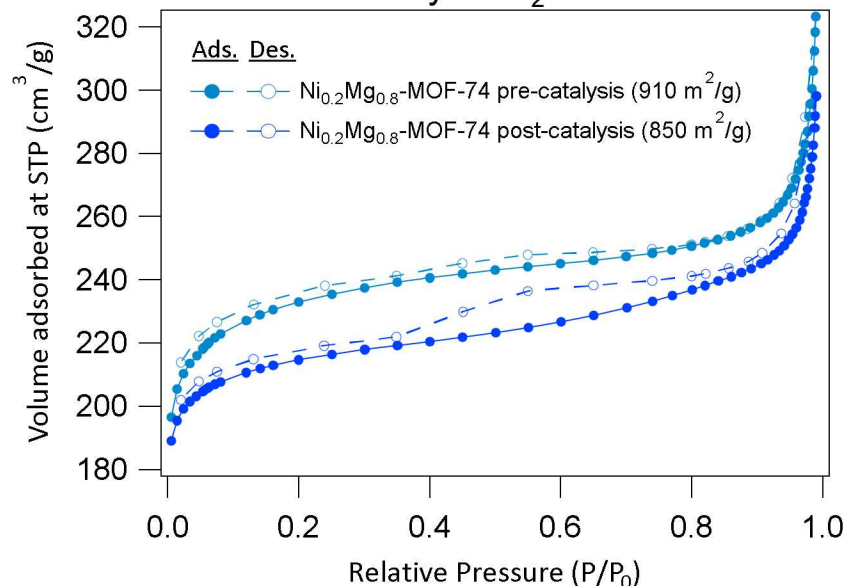


Structural stability of bimetallic MOF-74 after reaction

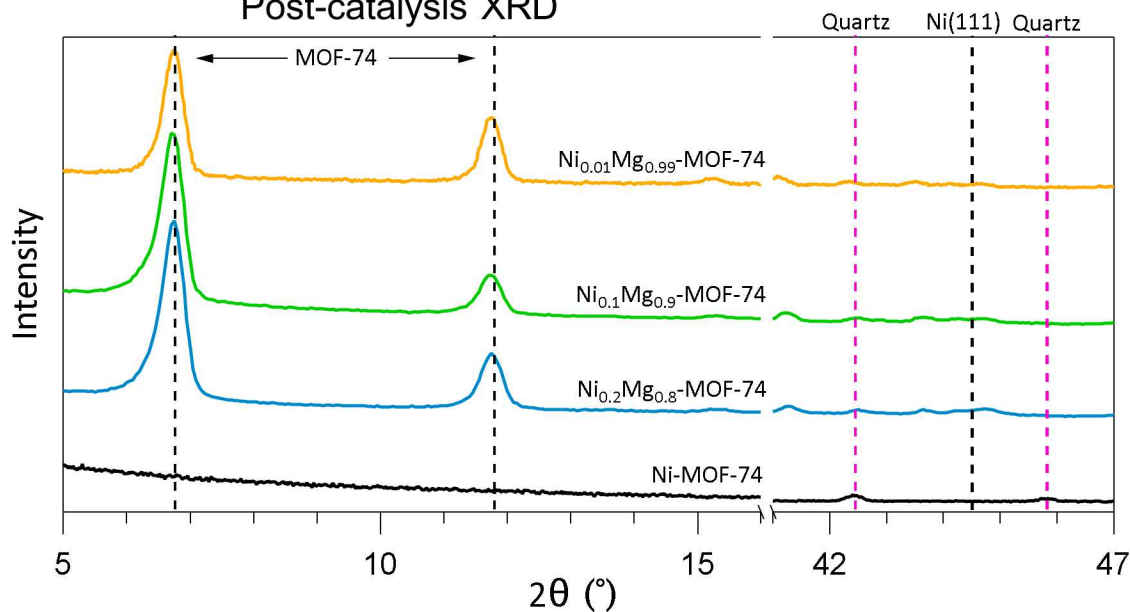
- The high surface area MOF-74 framework is maintained post-catalysis in the bimetallic MOF materials
 - Hysteresis indicates a change in porosity
- Mg helps to stabilize the MOF-74 structure under methanol dehydrogenation conditions
 - Without the addition of Mg, Ni-MOF-74 is unstable under these conditions
 - No peaks for Ni(111) are observed; however, highly dispersed particles are possible
- Future work includes APXPS to probe the active Ni sites

Bimetallic compositions balance the stability of Mg-MOF-74 with the activity of Ni-MOF-74

Post-catalysis N₂ isotherm

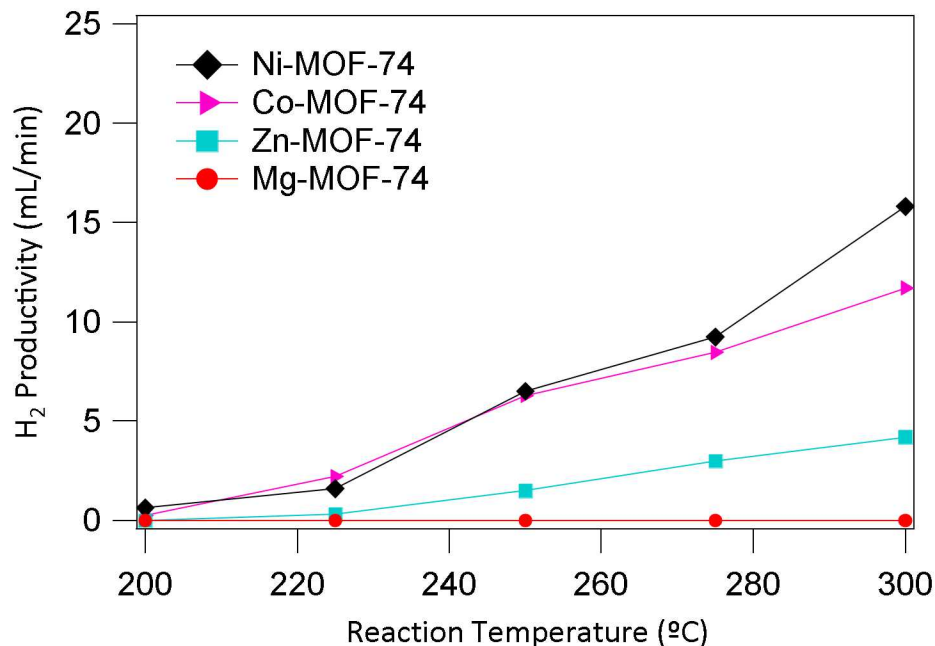
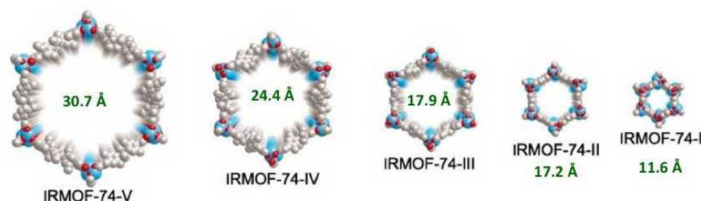


Post-catalysis XRD



Tunable catalyst design with MOF-74

- The MOF-74 framework can incorporate many metals as open metal sites (OMS)
 - Co-MOF-74 shows comparable performance to Ni-MOF-74
 - Other transition metals possible
- Pore size can also be tuned as a parameter by varying organic linkers
 - Deng, Yaghi et al. *Science* 2012



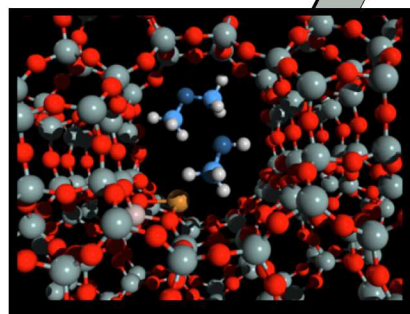
- Our current research is considering MOF catalysts for the reversible dehydrogenation of other LOHCs
 - e.g. ethylene glycol and other polyols

MOF-catalyzed upgrading of biomolecules



Biomass Indirect Liquefaction

Light oxygenate intermediates



Multi-functional catalysts for unique transformations

Balancing acidic, basic, metallic sites

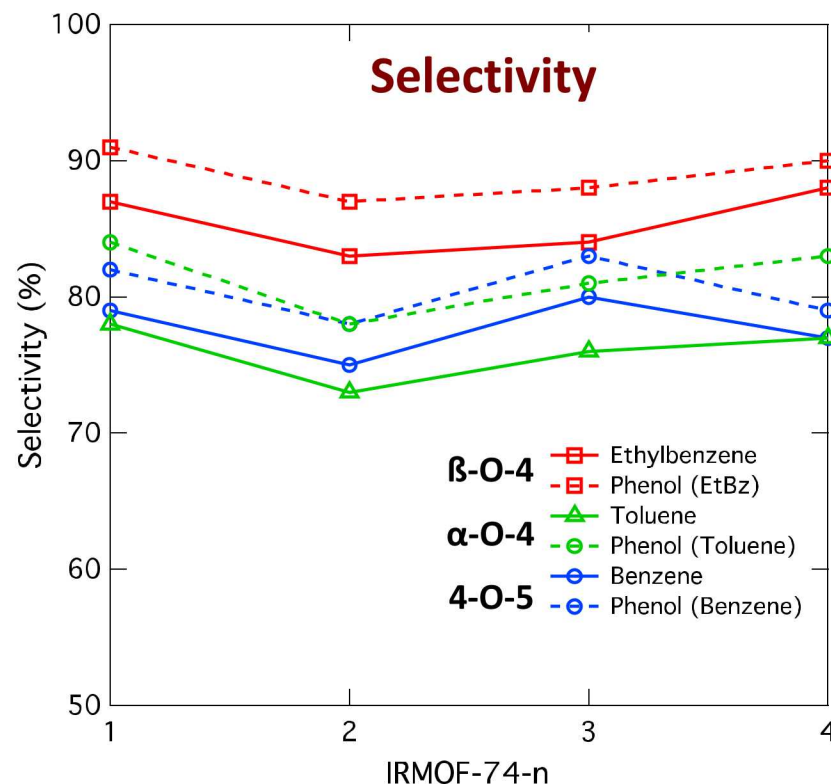
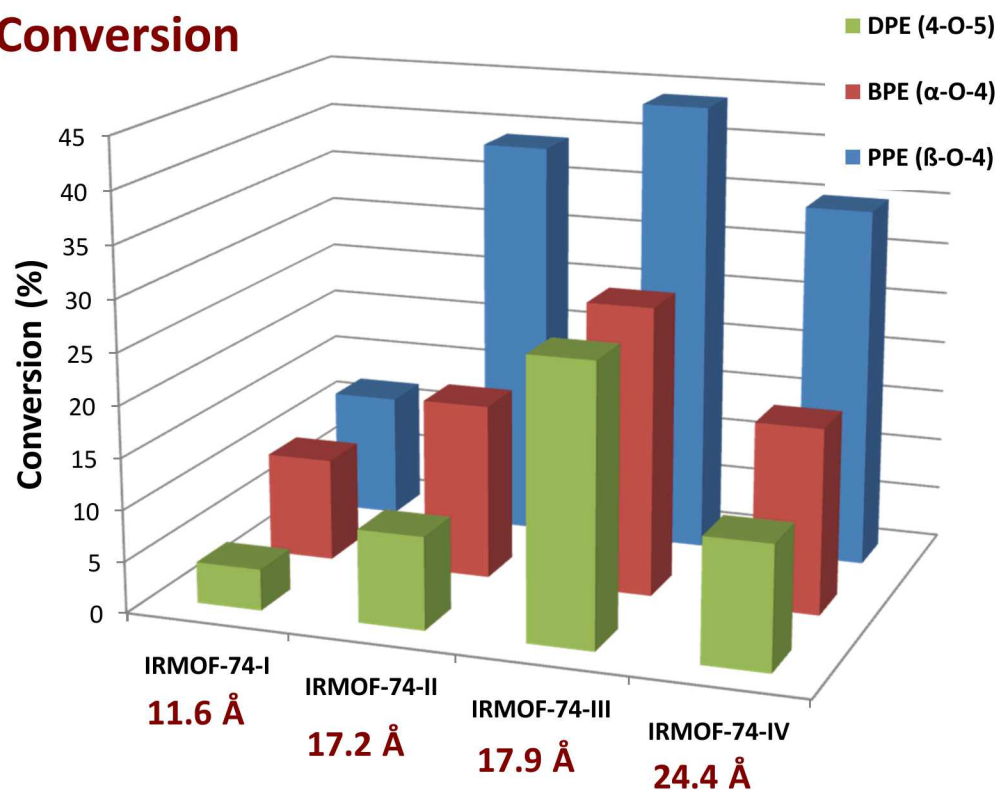


Suite of biofuels and co-products to meet market demand

High-octane gasoline, distillate fuels, and polymer precursors

IRMOF-74-n(Mg) is intrinsically catalytic for hydrogenolysis

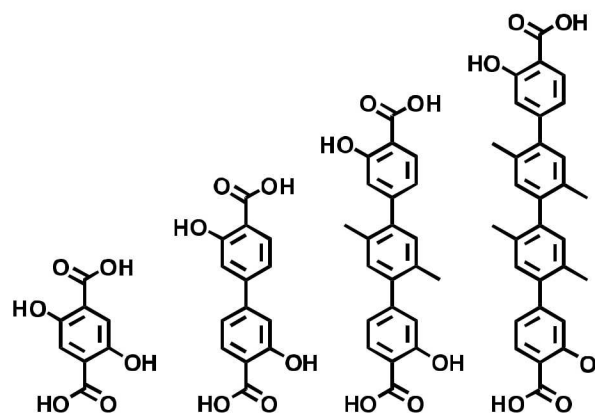
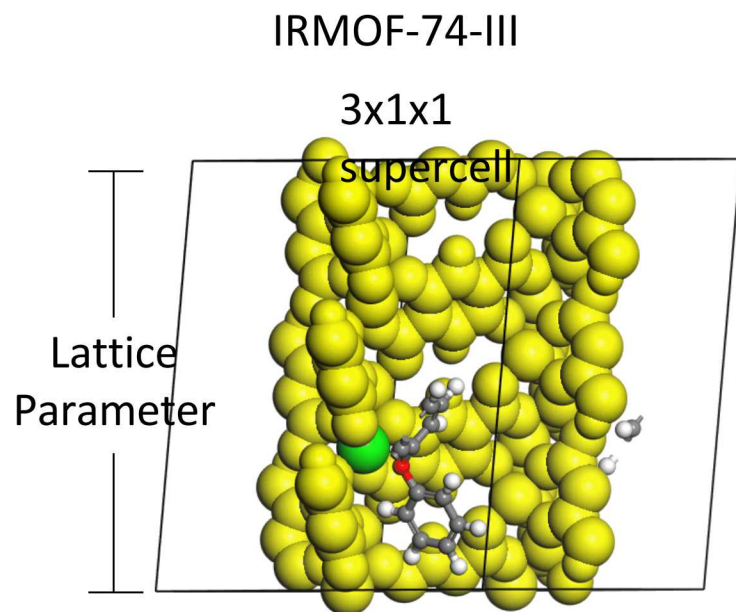
Conversion



- Conversion trend: β -O-4 > α -O-4 > 4-O-5
- Pore size effect: max conversion at IRMOF-74-III
- High selectivity: no ring hydrogenation or ring opening

	Ring opening	PPE % Ring hydrogenation
IRMOF-74-I	0	1
IRMOF-74-II	0	1
IRMOF-74-III	0	1
IRMOF-74-IV	0	2

Aryl ether binding to IRMOF-74-III is significantly stronger than IRMOF-74-(I, II, or IV)

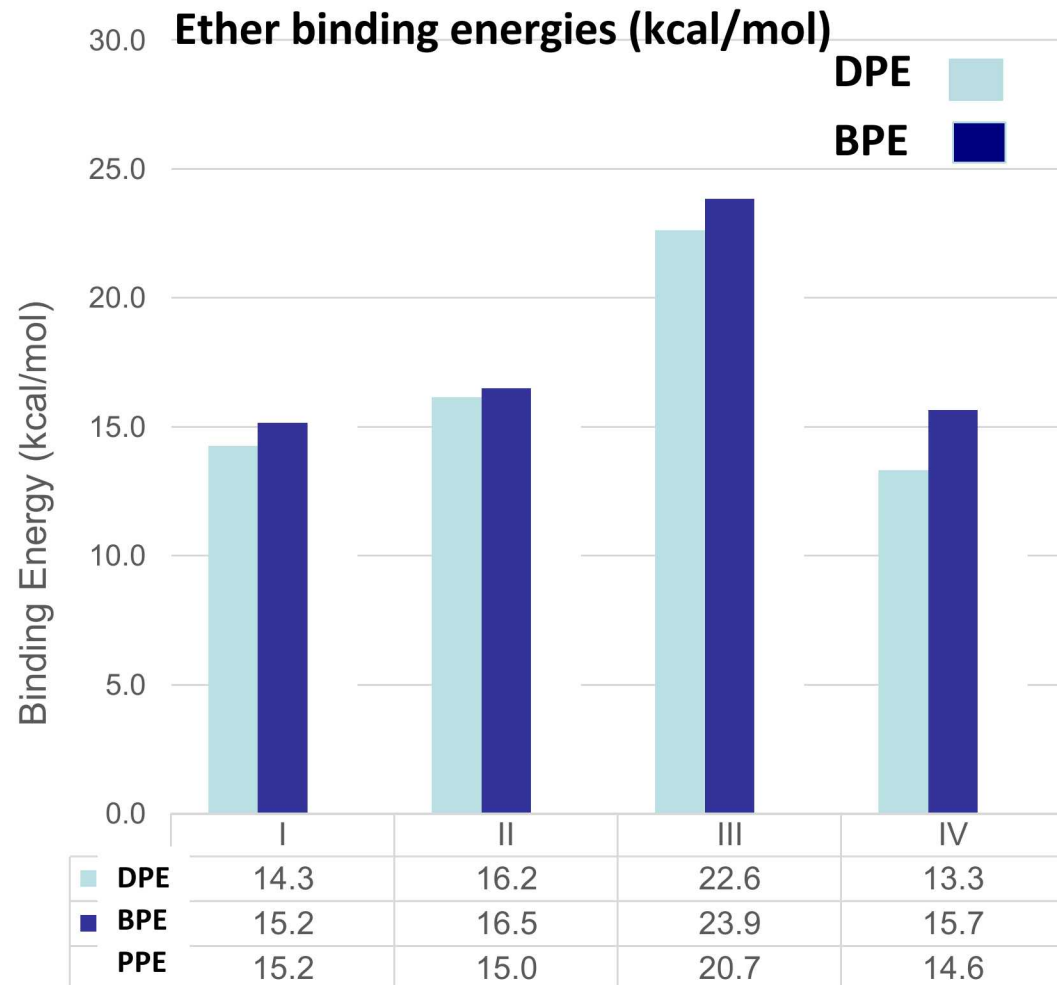


DOT, I

II

III

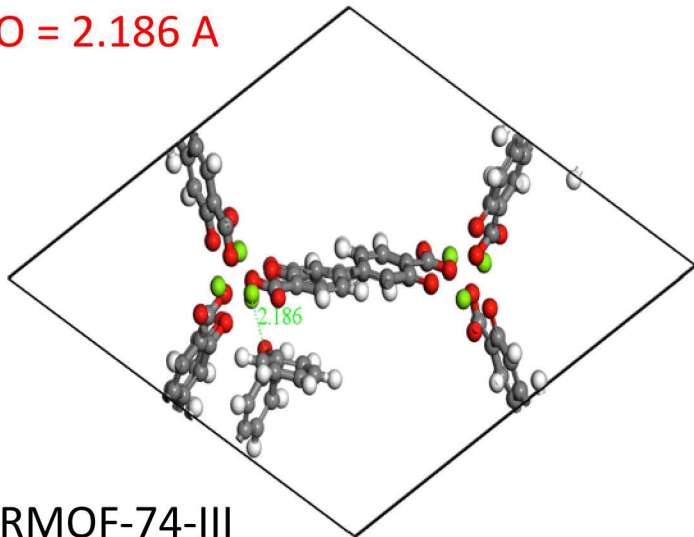
IV



The Mg(II)-O(ether) bond distance is also shorter in IRMOF-74-III, consistent with stronger binding

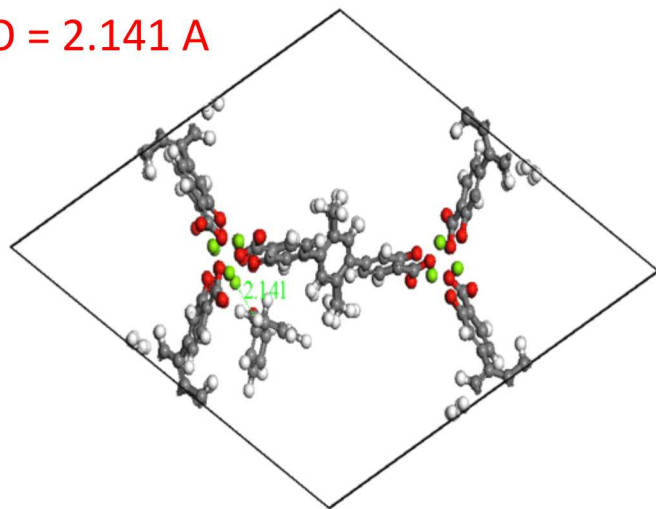
4-O-5@IRMOF-74-II

Mg(II)—O = 2.186 Å

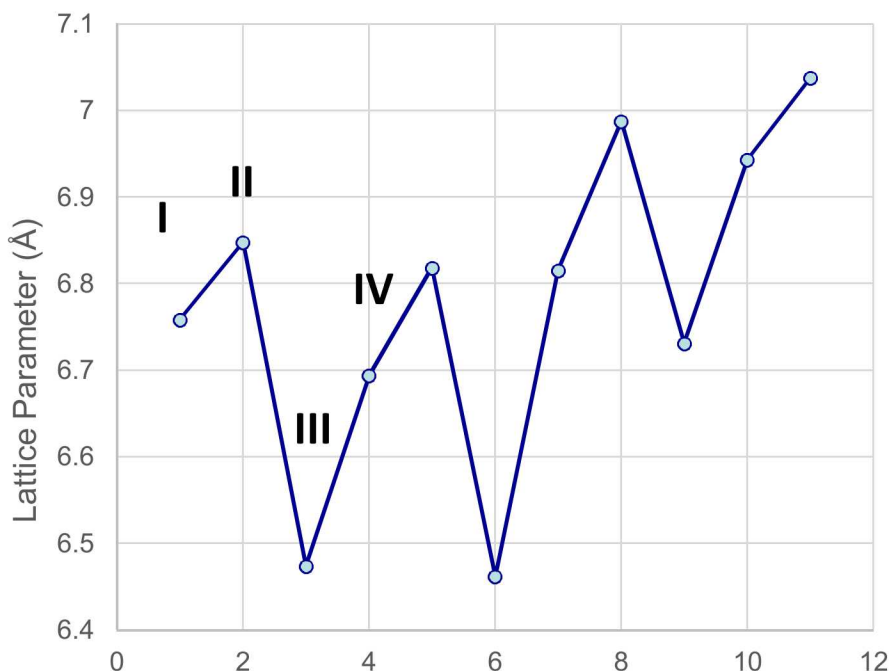


4-O-5@IRMOF-74-III

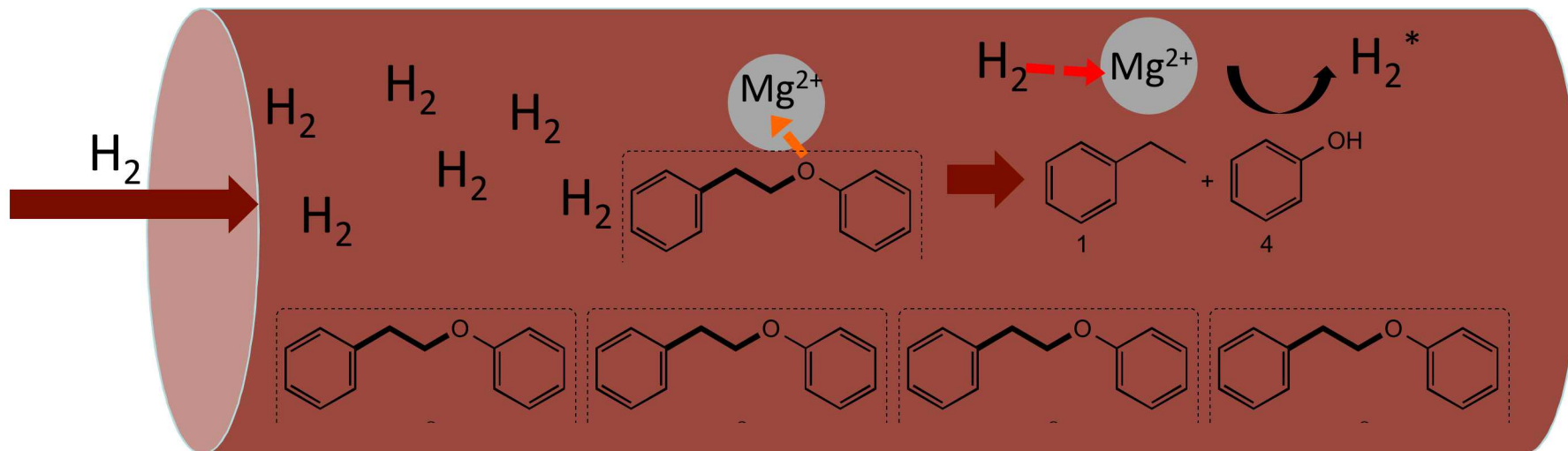
Mg(II)—O = 2.141 Å



Lattice parameter of
4-O-5@IRMOF-74-n



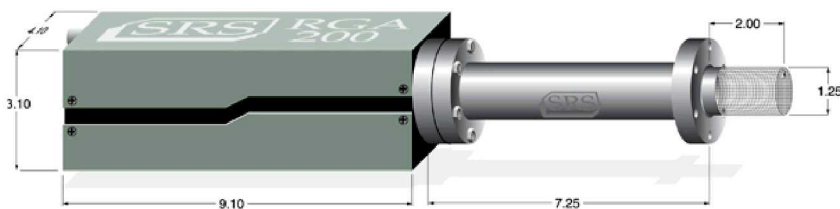
Proposed mechanism of hydrogenolysis and the role of the Mg(II) open metal site



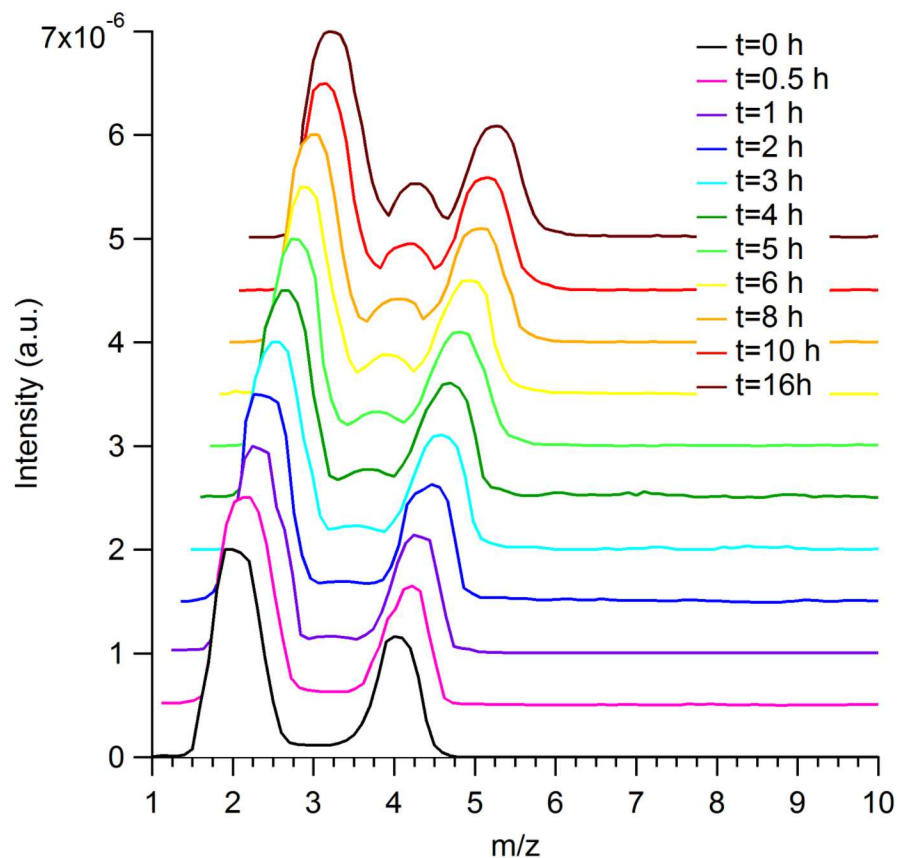
Proposed mechanism:

- OMS in Mg^{2+} in MOF-74 is 5-coordinate Lewis acid
- H_2 Qst (77K) by $Mg_2(dobdc)$: 10.6 kJ/mol
- Computed Q_{st} for PPE: ~ 70 kJ/mol (I, II, IV); ~ 100 kJ/mol (III)

H₂/D₂ Exchange in MOF-catalyzed hydrogenolysis reactions



Residual Gas Analyzer

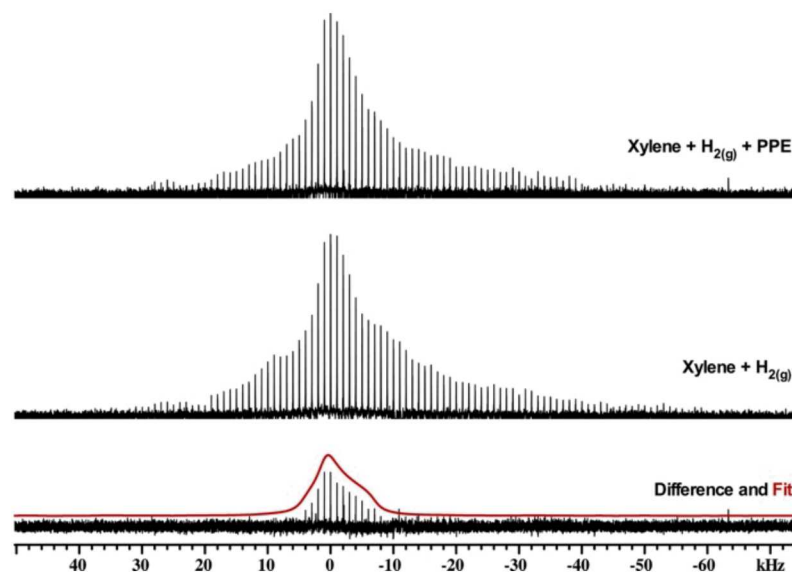
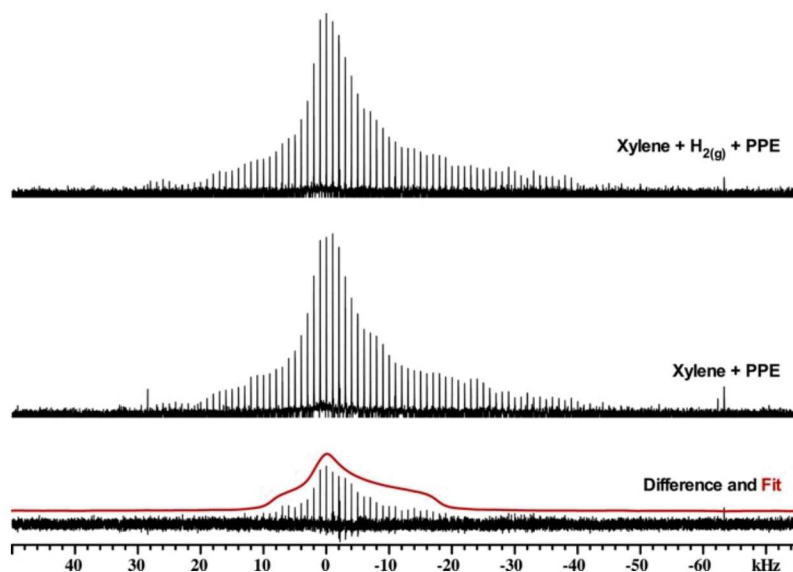


H-D isotope exchange experiment (at 120 ° C) showing the formation of HD (m/z=3) in p-xylene in the presence of Mg-MOF-74



Sandia RGA setup

Solid-state ^{25}Mg NMR indicate that both H_2 and ether molecules interact with the Mg(II) OMS



Take-home messages

- **Compressed gas (700 bar): physically impossible to meet DOE volumetric target**
→ **Solid-state materials, including metal hydrides, have potential to meet DOE targets**
- **Compressed gas is equally inefficient as a carrier for transporting hydrogen**
→ **MOFs can catalyze dehydrogenation of alcohols, which could be low-cost hydrogen carriers**
- **Reactions to upgrade biological intermediates (e.g. aryl ethers from lignin) can be catalyzed by MOFs and exhibit higher selectivity than catalysts both homogeneous catalysts and Rainey nickel**

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Bioenergy Technologies Office



ChemCatBio
Chemical Catalysis for Bioenergy



Enabling twice the energy density for onboard H₂ storage

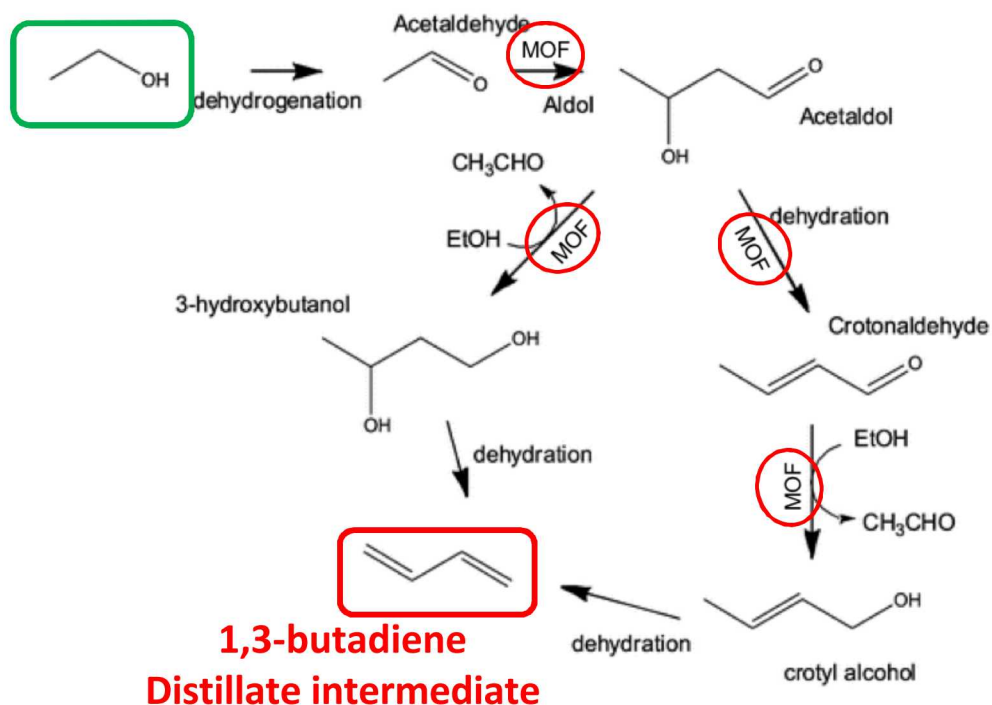


Backup Slides

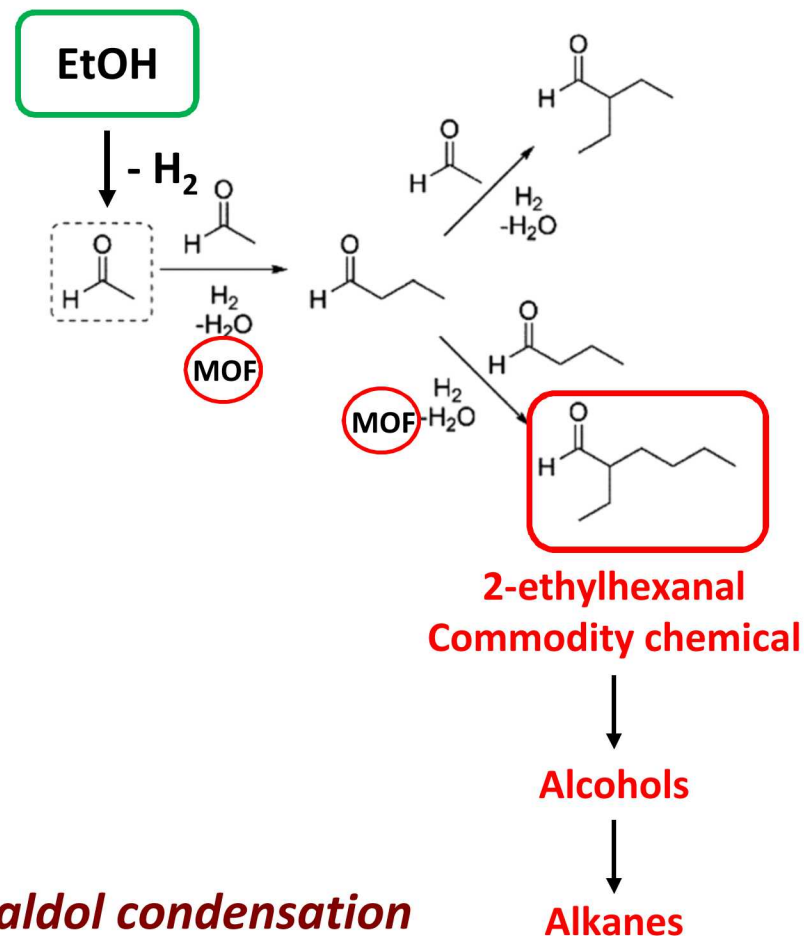
Upgrading ethanol to fuels and valuable chemicals



Butadiene Production (Guerbet Reaction)



2-Ethylhexanal Production (Aldol+hydrogenation)

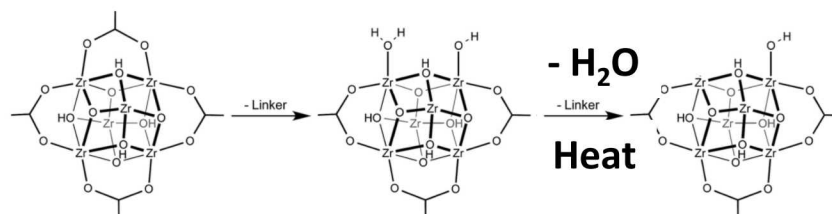
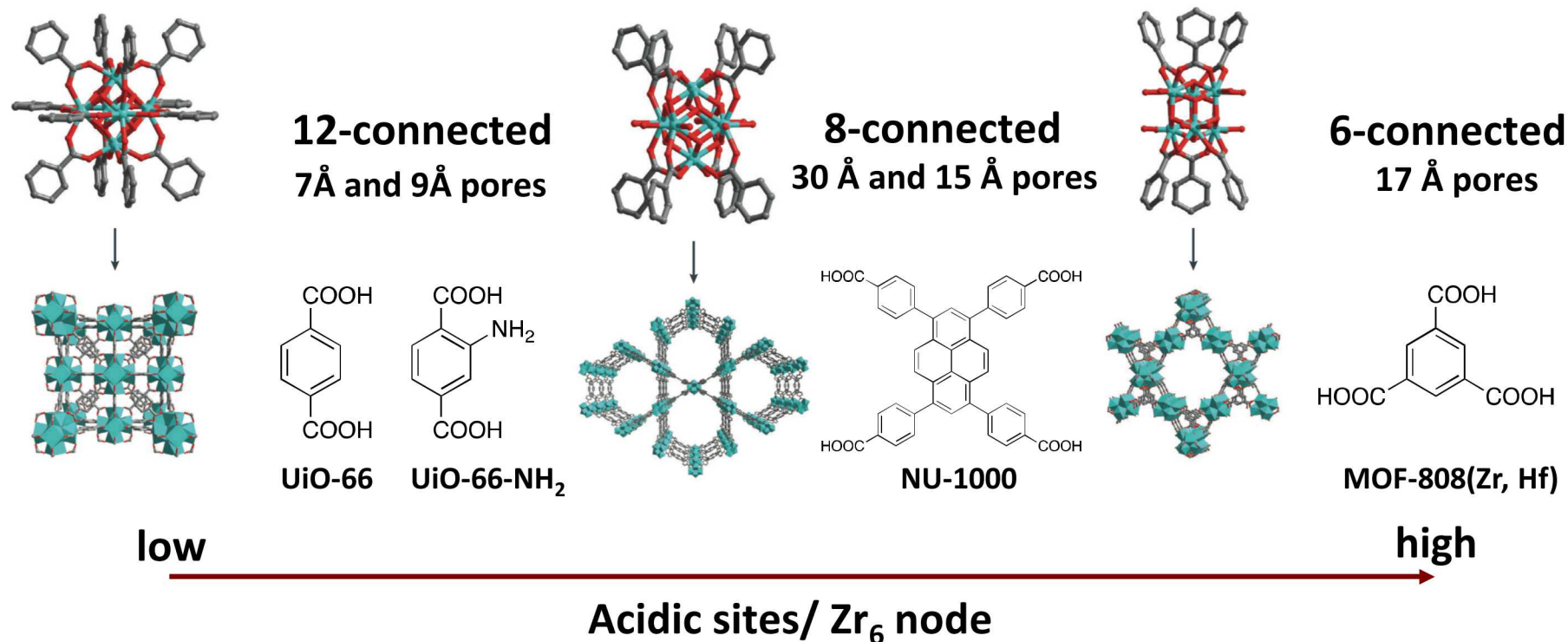


Both targets require C—C bond formation by aldol condensation

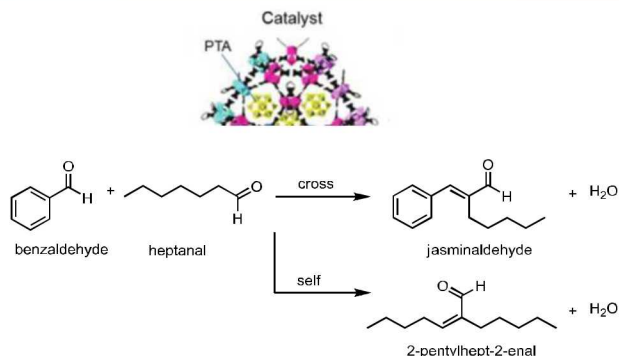
MOFs present a strategy to independently control pore size and density of catalytic sites

Brønsted acidity is required for catalyzing aldol condensation

Zr₆ nodes in Zr-MOFs are Lewis/Bronsted acidic



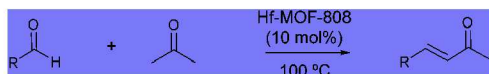
Several MOFs are known to catalyze aldehyde condensation reactions



MIL-101 Bromberg & Hatton *ACS Appl. Mater. Interfaces* 2011, 3, 4756

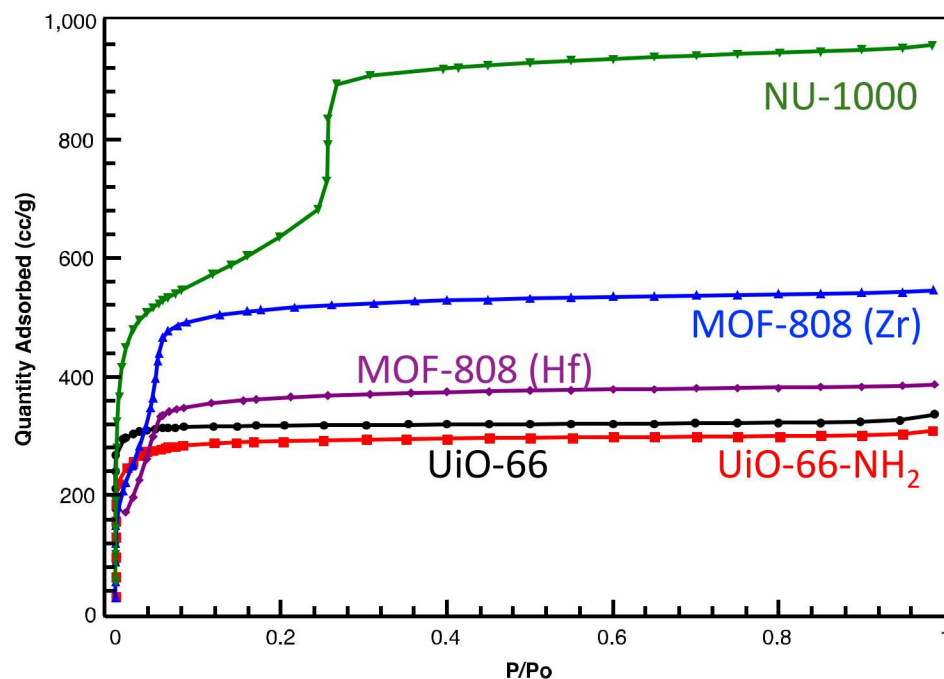
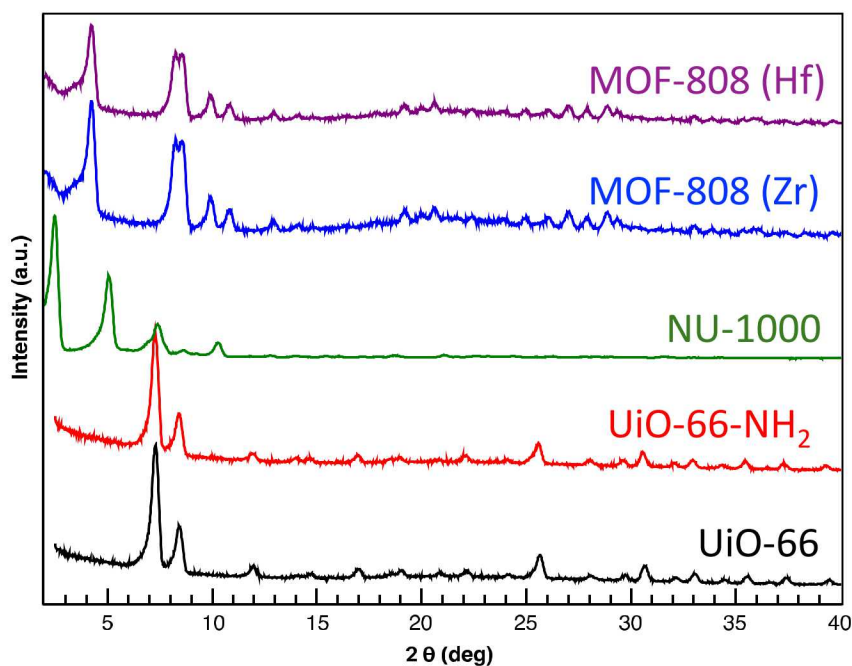
UiO-66(NH₂) Vermoortele et al. *Chem. Comm.* **47** (2011), 1521

UiO-66 and UiO-66(NH₂) Hajek et al. *J. Catal.* **331** (2015), 1



Hf-MOF-808 Rojas-Buzo et al. *Green Chem.* **20** (2018), 3081

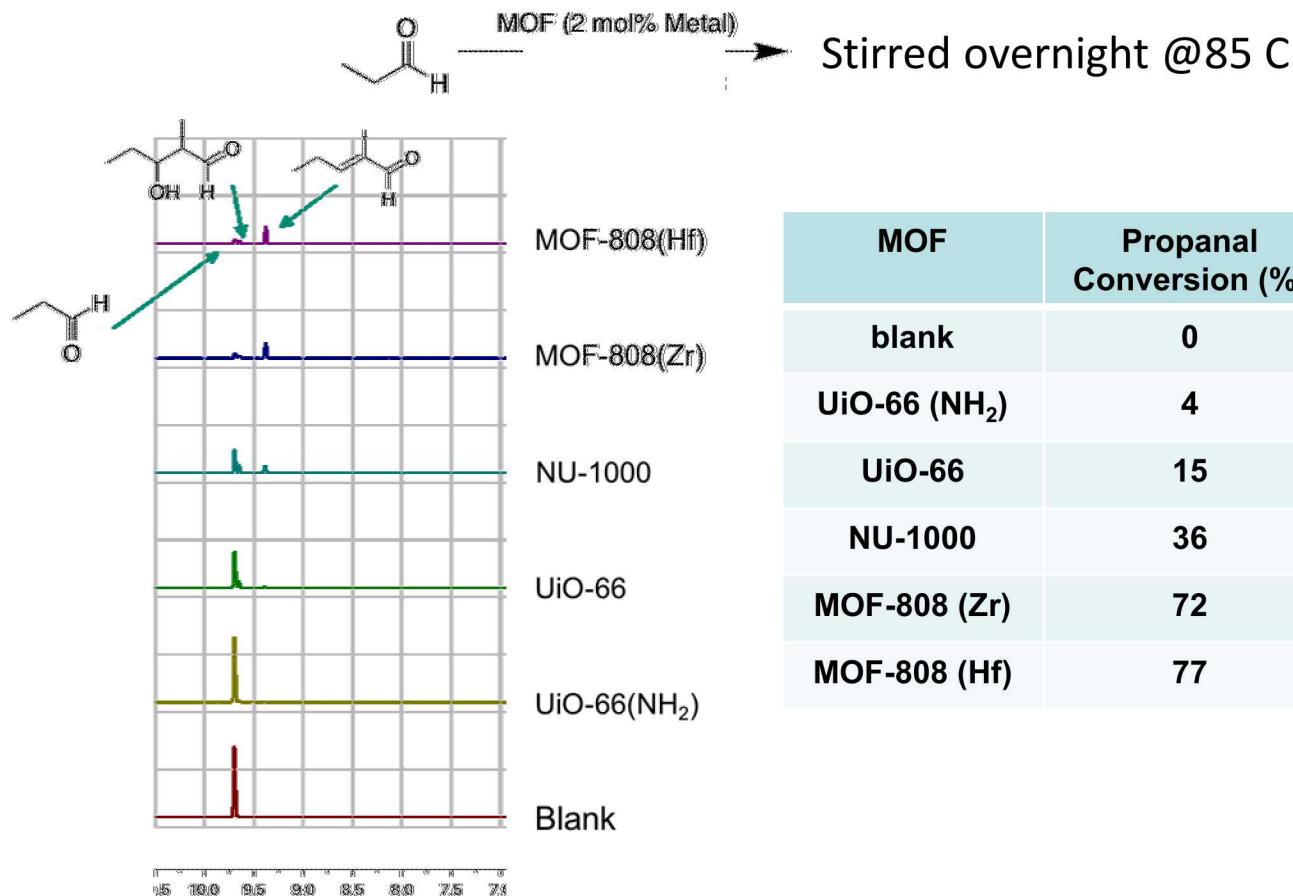
MOFs were synthesized following published literature procedures



Aldol coupling of aldehydes with MOF catalysts

Goal: Demonstrate control of Bronsted/Lewis acidic sites and pore structure in MOFs to tune the selectivity/conversion of C-C coupling reactions.

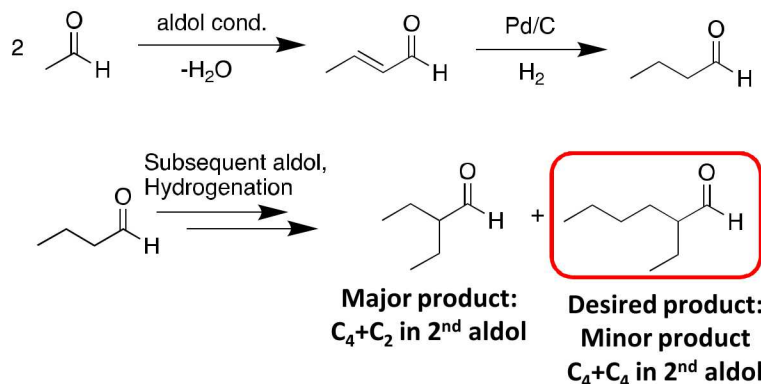
Aldol reaction using propanal as model compound



Result: MOF-808 (Hf, Zr), the MOF with the highest density of (Bronsted+Lewis) acidic sites, shows the highest conversion (77% and 72%) in aldol condensation

Polyaldol condensation reactions under hydrogen to generate high-value C₆ and C₈ products

Goal: increase selectivity for 2-ethylhexanal (2-EH) from < 20% to ≥ 50% in the cascade reaction



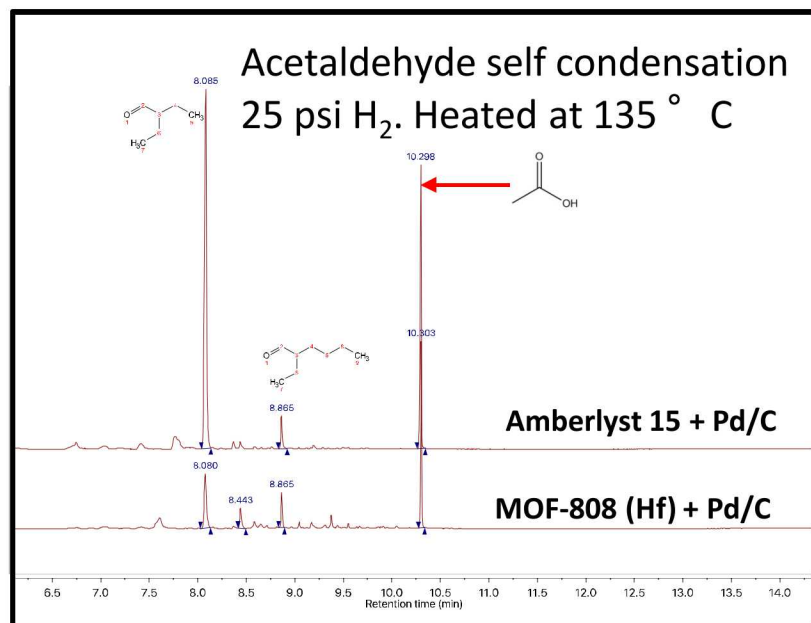
Improved selectivity to 2-EH over commercial catalyst (physical mixture of MOF and Pd/C)

Issues:

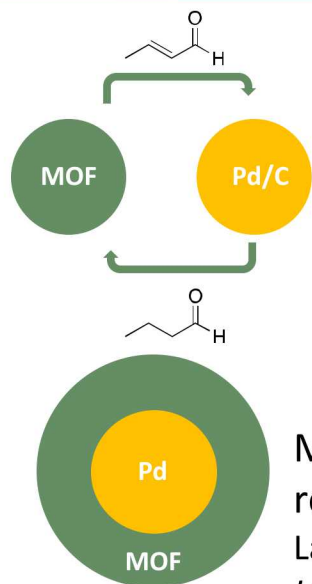
- Selectivity improved but still < 50%
- CH₃COOH impurity

Potential solutions:

- Reduce reaction temperature to decrease rate of side reactions
- increase H₂ to create more reducing conditions



Loading with Pd for MPV reduction improves selectivity



Hypothesis: enol diffusion to Pd/C for hydrogenation reduces selectivity

Solution: infiltrate MOF pores w/ Pd
Pd infiltration by Pd(acac)₂

Meerwein–Ponndorf–Verley reduction
Larson et al.
Inorg. Chem. **57** (2018), 6825)

3:1 ethanol:acetaldehyde reaction

- MOF-808(M), M=Zr, Hf)
- 10 bar H₂, 120 C overnight

Preliminary 2-EH selectivity results:

Pd@MOF-808-Zr	Pd@MOF-808-Hf	Amberlyst 15 + Pd/C (10 wt%)
35%	38%	< 20%

Uniform Pd distribution throughout crystals

