A Synergistic Approach to the Development of New Hydrogen Storage Materials, Part I

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Overview

Timeline

- Project start: 12/1/04
- Project end: 11/30/09
- Percent complete: 50%

Budget

- Total funding expected: $2.9M
  - $1.8M from DOE to UC Berkeley
  - $600k from DOE to LBNL
  - $500k in cost-sharing
- Funding FY06: $546k
- Funding FY07: $400k

Barriers

- Identify new materials enabling a hydrogen storage system achieving:
  - 2 kWh/kg (6 wt %)
  - 1.5 kWh/L (0.045 kg/L)
  - 4 $/kWh

Partners

- ChevronTexaco
- General Motors
- Electric Power Reserach Institute

Approach and Objectives

- Bring together a group of scientists with a broad range of perspectives and experiences in materials discovery, and get them working on new approaches to hydrogen storage
- Utilize theory as much as possible in guiding experiments
- Ensure that the exchange of new ideas and results is facile
- Ensure that the instrumentation for measuring hydrogen storage is immediately accessible to the primary researchers—this will be the rate-limiting step in discovering new materials

Overall Program

Synthesis of porous polymers (Fréchet)

Synthesis of porous coordination solids (Long)

Calculations of H_2 binding energies (Head-Gordon)

Synthesis of destabilized hydrides (Richardson)

H_2 storage characterization instrumentation (Mao)

Metal/metal hydride nanocrystals (Alivisatos)

Synthesis of nanostructured boron nitrides (Zettl)

Theory for boron nitride materials (Cohen and Louie)

Part I (EERE)

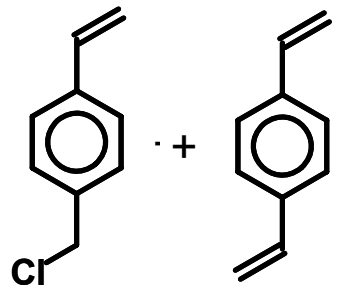
Part II (BES)

Screening Porous Aromatic Polymers

Commercial resin	surface area m^2/g	H_2 wt.%*
Hyesep-S	510	0.5
Hypersol Macronet MN 200	840	1.3
Amberlite XAD 16	770	0.6
Amberlite XAD 4	1060	0.8
Lewatit EP63	1205	1.3

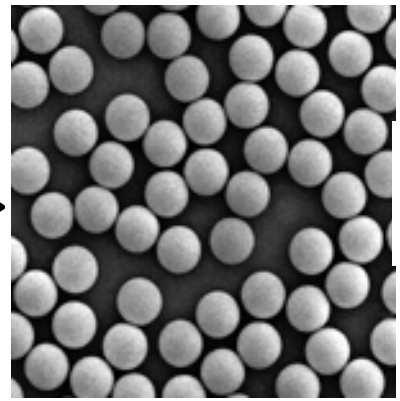
***Excess uptake at 77 K and 0.1 MPa (1 atm)**

Synthesis of Hypercrosslinked Nanoporous Polymer Beads

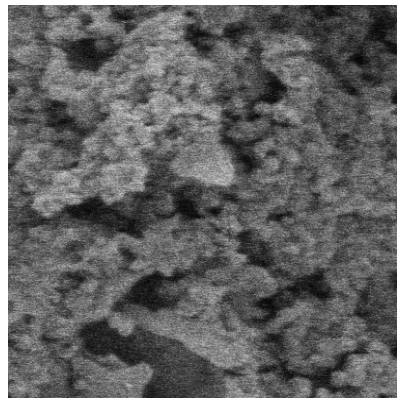


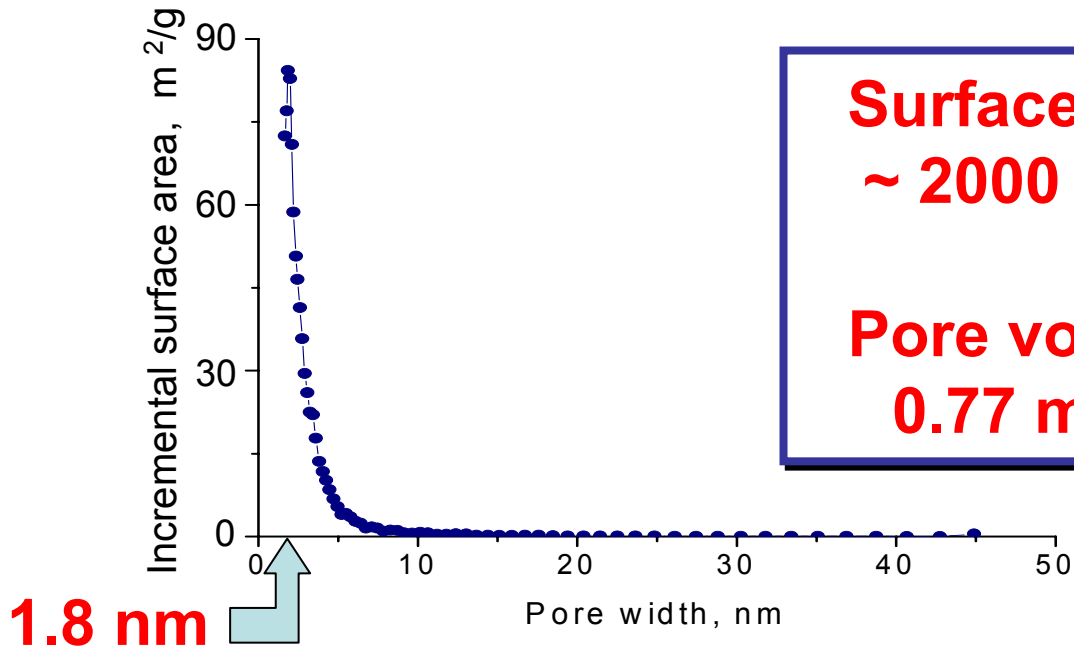
Chloromethyl-styrene (97.5%) · + Divinylbenzene (2.5%)

AIBN → 80°C, 24 h



Dichloroethane, $FeCl_3$ → 80°C, 24 h



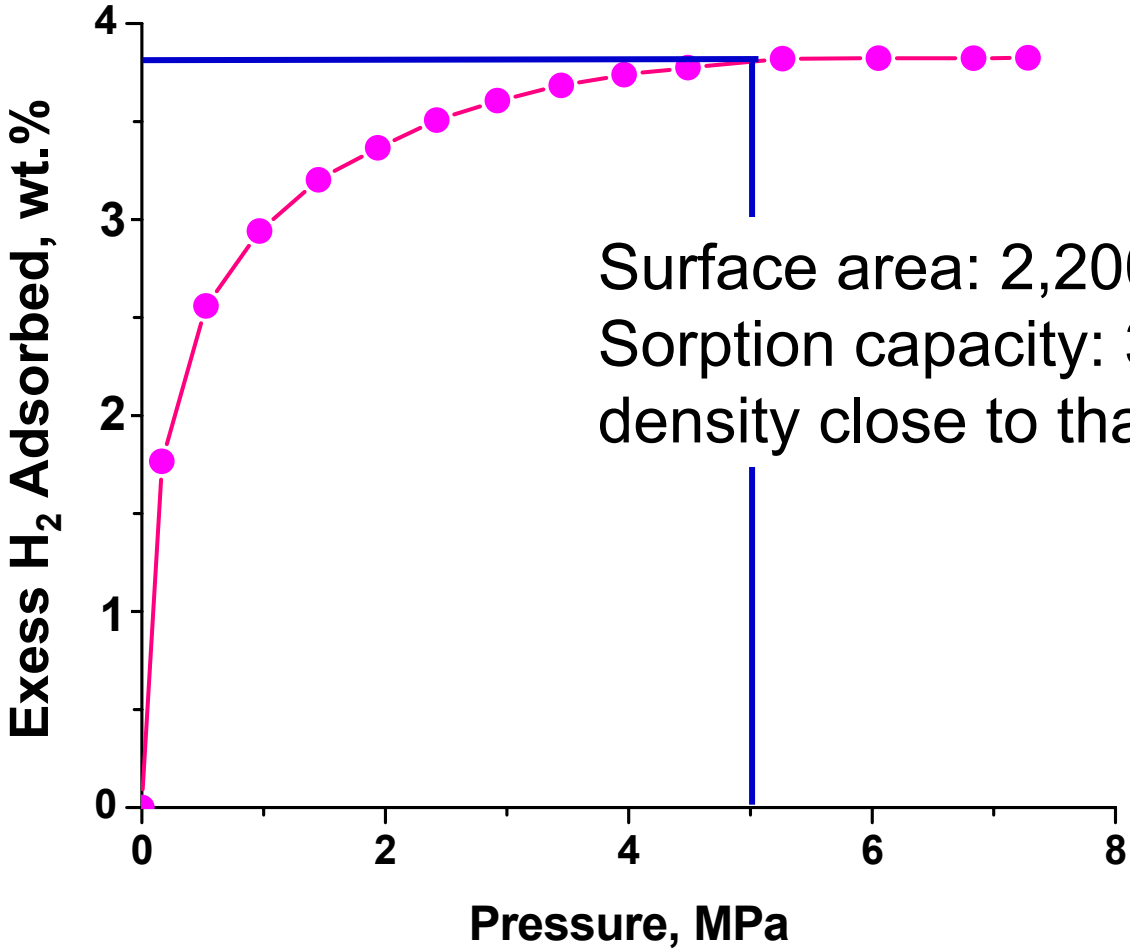


Surface area ~ 2000 m^2/g

Pore volume 0.77 mL/g

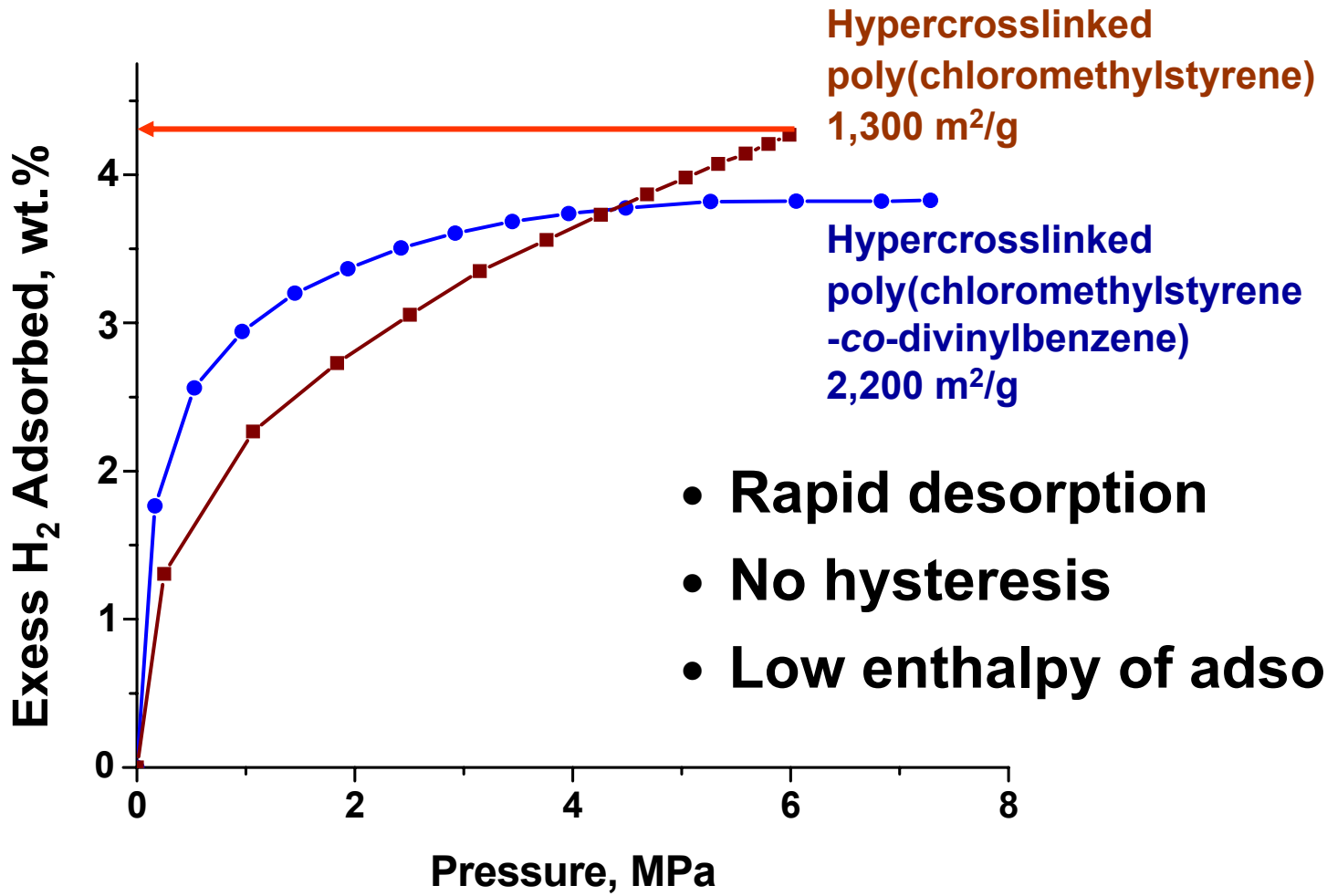
Hydrogen Adsorption in a Hypercrosslinked Nanoporous Polymer

Poly(chloromethylstyrene-*co*-divinylbenzene)



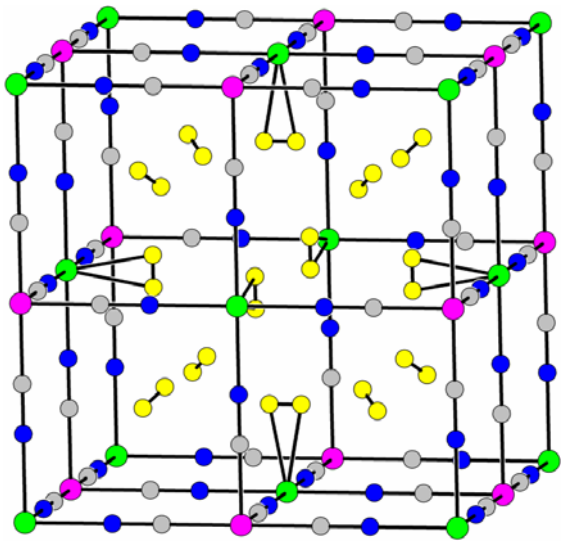
Surface area: 2,200 m^2/g
Sorption capacity: 3.8 wt% at 5 MPa, 77 K
density close to that of liq. H_2 (71 g/L)

Comparison of Hypercrosslinked Nanoporous Polymers

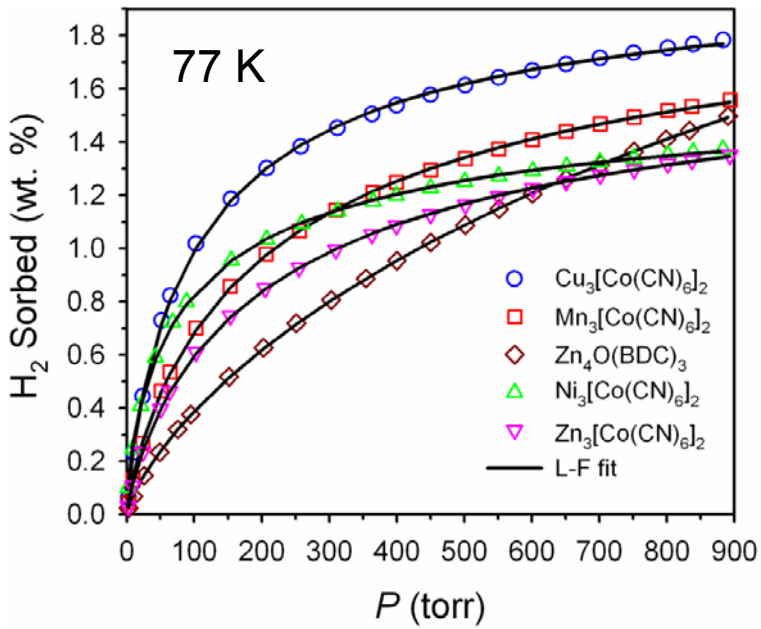


- Rapid desorption
- No hysteresis
- Low enthalpy of adsorption

Hydrogen Storage in Prussian Blue Analogs



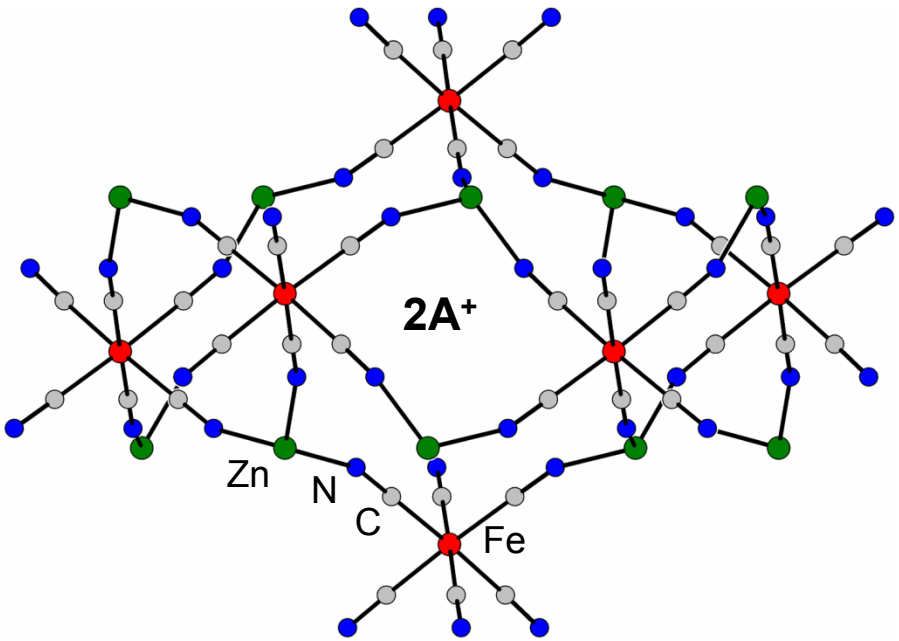
$Cu_3[Co(CN)_6]_2 \cdot 3D_2$



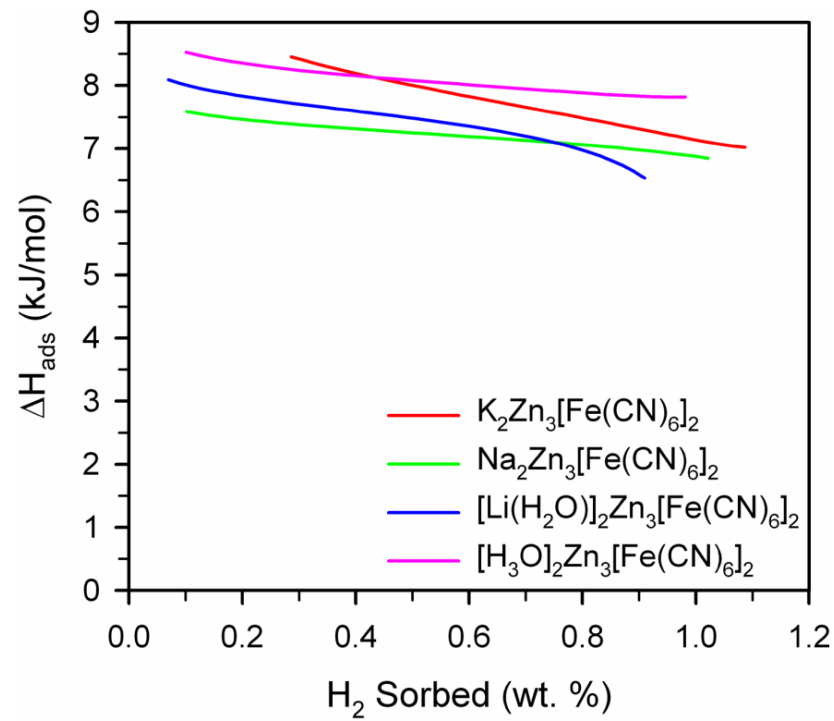
The first materials we studied were the Prussian blue analogs, cubic coordination solids composed of M^{x+} ions bridged by $[M'(CN)_6]^{y-}$ complexes. Hydrogen adsorption isotherms were measured for $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu, Zn). The excess H_2 uptake ranged from 1.3 wt. % for M = Zn to 1.8 wt. % for M = Cu at 77 K and 890 torr and enthalpy of adsorption ranged from 6.0 kJ/mol for M = Mn to 7.5 kJ/mol for M = Ni.

Powder neutron diffraction of $Cu_3[Co(CN)_6]_2$ under a D_2 pressure corresponding to 3 D_2 per formula unit shows that 75% of D_2 resides at the (0.25, 0.25 , 0.25) site and 25% coordinates to the open sites on Cu^{2+}. This suggests that in $Cu_3[Co(CN)_6]_2$, H_2 interaction with the corners of the unit cell is stronger than H_2 binding to the Cu^{2+} ions.

Hydrogen Storage in $A_2Zn_3[Fe(CN)_6]_2$

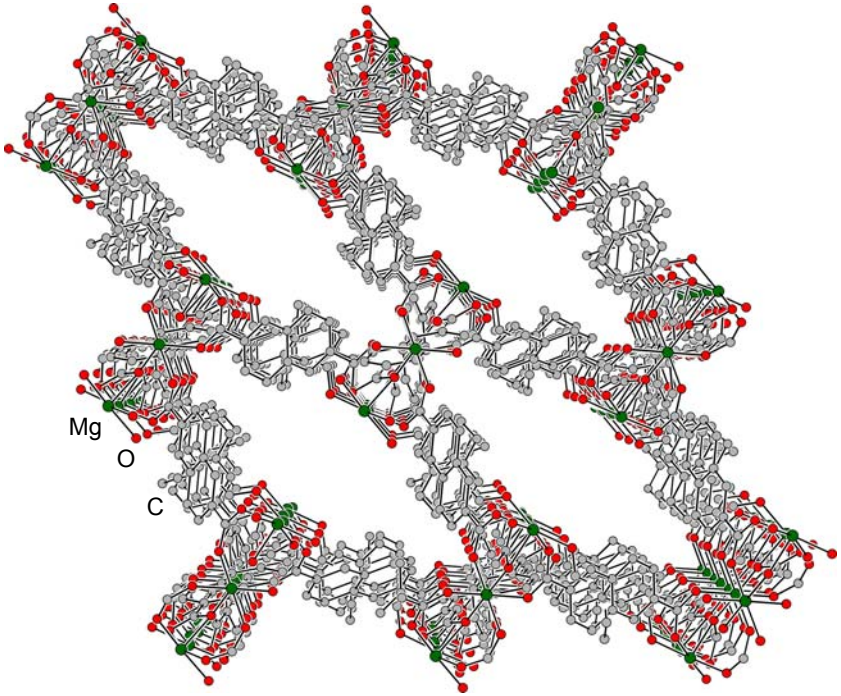


$A_2Zn_3[Fe(CN)_6]_2 \cdot nH_2O$

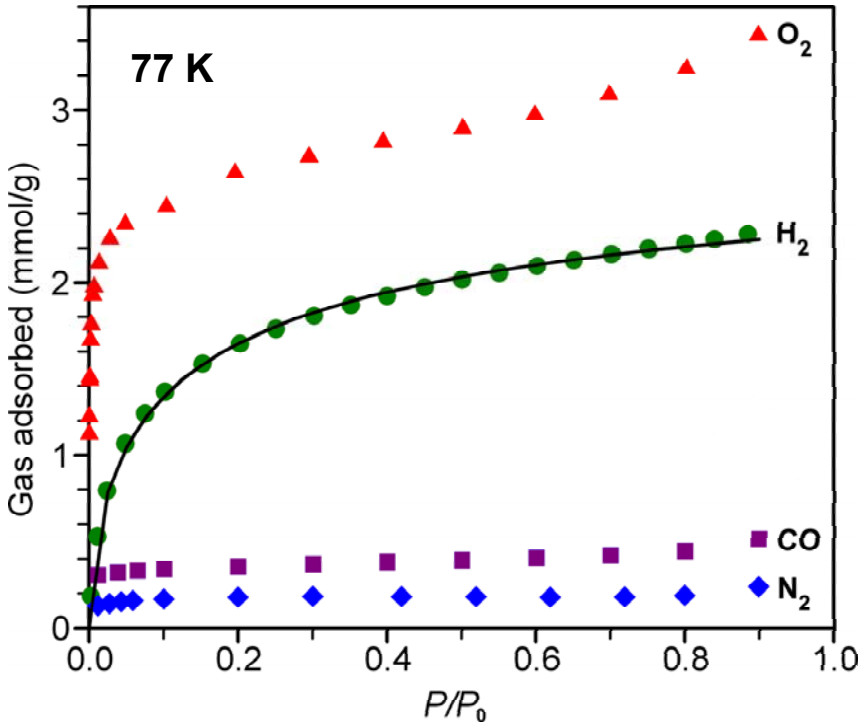


In an attempt to further increase ΔH_{ads}, we investigated the porous cyanometallates of the type $A_2Zn_3[Fe(CN)_6]_2$. In these materials, charge balance leads to the inclusion of two monovalent cations in the pores of the framework that can potentially bind H_2. Hydrogen adsorption isotherms were measured for the series A = H_3O^+, $Li(H_2O)^+$, Na^+, K^+. The excess hydrogen uptake ranged from 1.1 wt. % for A = $Li(H_2O)^+$ to 1.2 wt. % for A = K^+ at 77 K and 890 torr. The observed trend in ΔH_{ads} does not vary as much as the H_2 binding energies for the gas phase cations, suggesting that charge donation from the framework significantly mitigates the affinity of the cation for H_2.

Lightweight Magnesium-Based Frameworks



$Mg_3(NDC)_3$



Reaction of $Mg(NO_3)_2$ with 2,6-napthalenedicarboxylic acid (H_2NDC) in diethylformamide yields $Mg_3(NDC)_3(DEF)_4$. The compound is desolvated by heating at 190 °C to give the microporous solid $Mg_3(NDC)_3$, exhibiting a BET surface area of 500 m^2/g. Adsorption isotherms measured at 77 K and 87 K indicate high H_2 adsorption enthalpies in the range 7.0-9.5 kJ/mol, depending on the degree of loading. In addition, the material displays selective adsorption of H_2 or O_2 over N_2 or CO, suggesting possible applications in gas separation technologies.

Increasing Pore Size by Varying Solvent

$Mg(NO_3)_2$ + NDC^{2-}

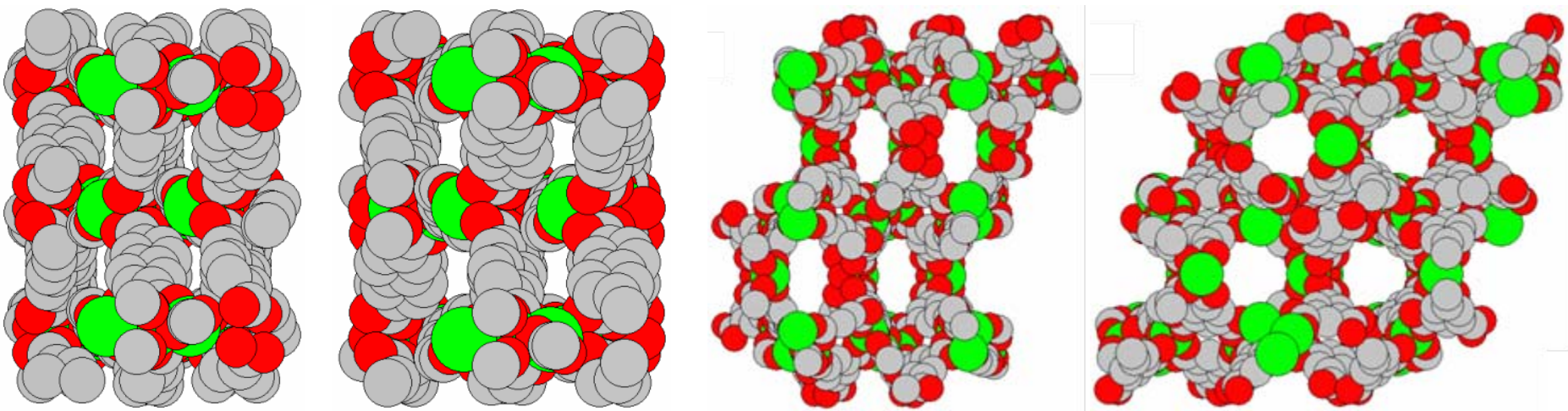
HCON**Me**$_2$ (DMF) → **$Mg_3(NDC)_3(DMF)_4$**, SA = 0 m^2/g

HCON**Et**$_2$ (DEF) → **$Mg_3(NDC)_3(DEF)_4$**, SA = 500 m^2/g

$Mg(NO_3)_2$ + BTC^{3-}

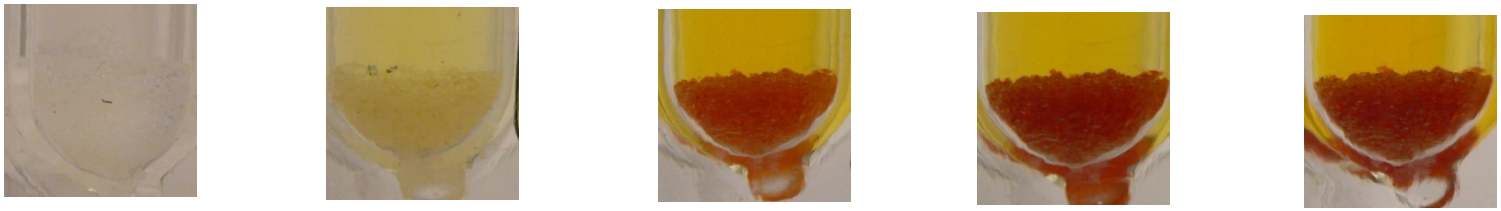
HCON**Et**$_2$ (DEF) → **$Mg_6(BTC)_4(DEF)_4$**

HCON**iPr**$_2$ (D^iPrF) → **$Mg_6(BTC)_4(D^iPrF)_4$**



As part of our investigation into the synthesis of high surface-area metal-organic frameworks, we've found that increasing the steric bulk of the solvent can lead to more porous crystalline frameworks for a given metal-ligand combination. For example, increasing the size of the solvent alkyl group in $Mg_3(NDC)_3(DMF)_4$ and $Mg_6(BTC)_4(DEF)_4$ led to a different spatial arrangement of the linkers around the metal cluster and a significant increase in pore size.

Binding Hydrogen to Electron-Rich Metals



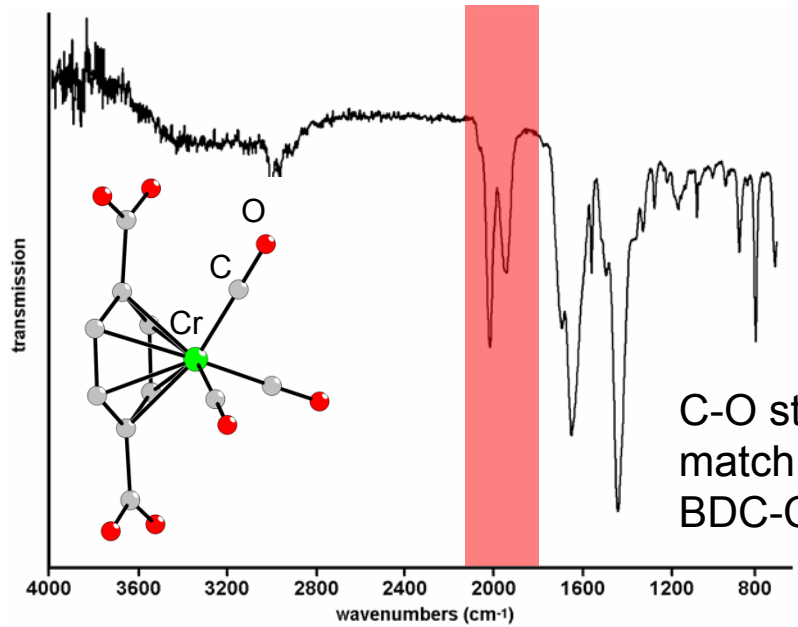
initial | 1 day | 2 days | 4 days | 5 days

$Zn_4O(BDC)_3$

+

$Cr(CO)_6$

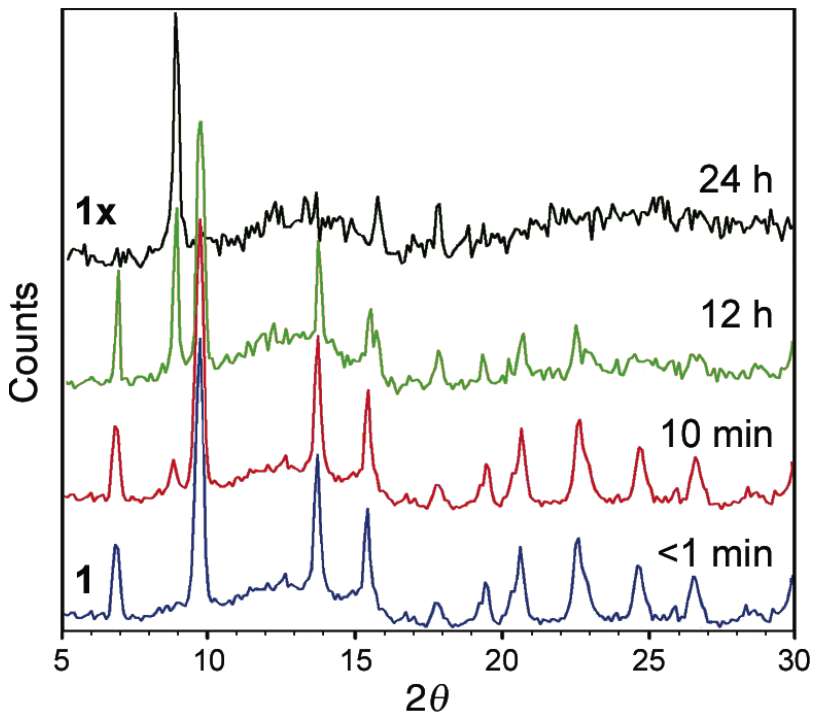
$\xrightarrow[\text{solvent}]{130\ °C}$

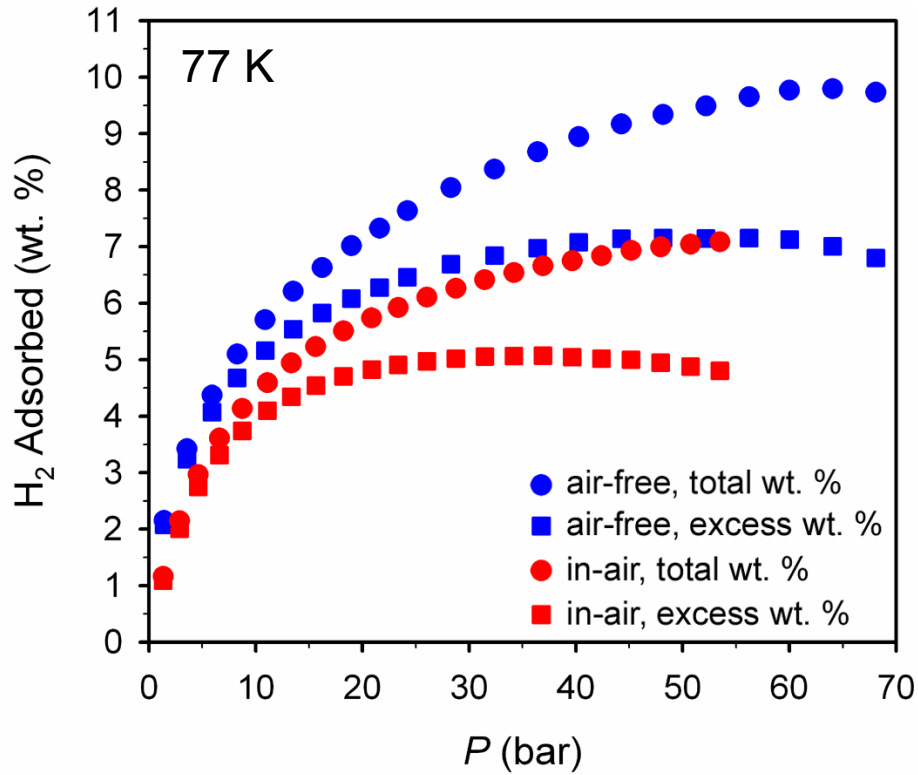


C-O stretches match those of BDC-$Cr(CO)_3$

Another approach to increasing the metal-H_2 interaction is to use more electron rich transition-metal centers, which will have stronger metal-H_2 π-backbonding compared with the Prussian blue analogs. Towards this end, reaction of $Cr(CO)_6$ with $Zn_4O(BDC)_3$ attaches a $Cr(CO)_3$ group to each of the benzene rings in the framework. Attempts to remove CO via photolysis are underway.

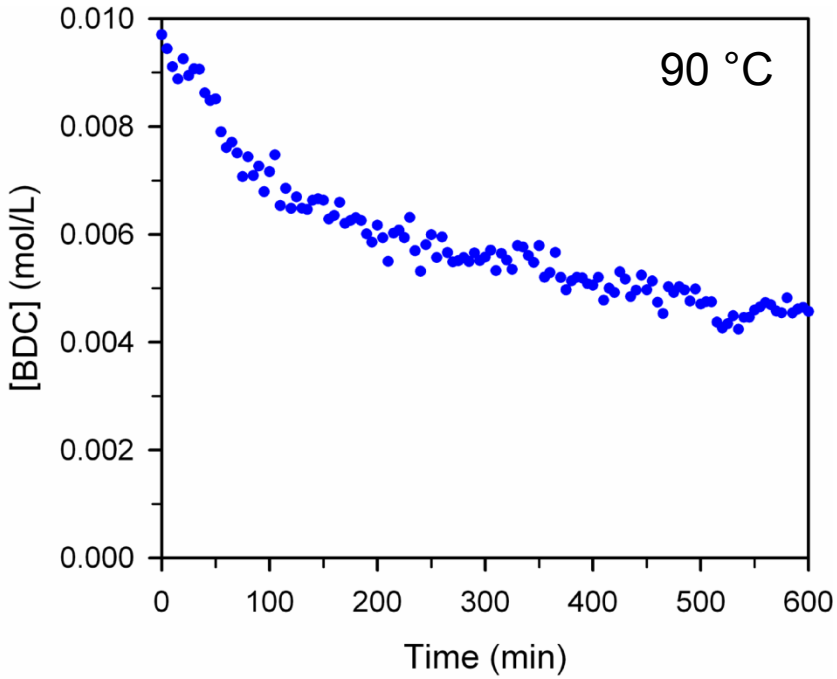
Air-Sensitivity of $Zn_4O(BDC)_3$



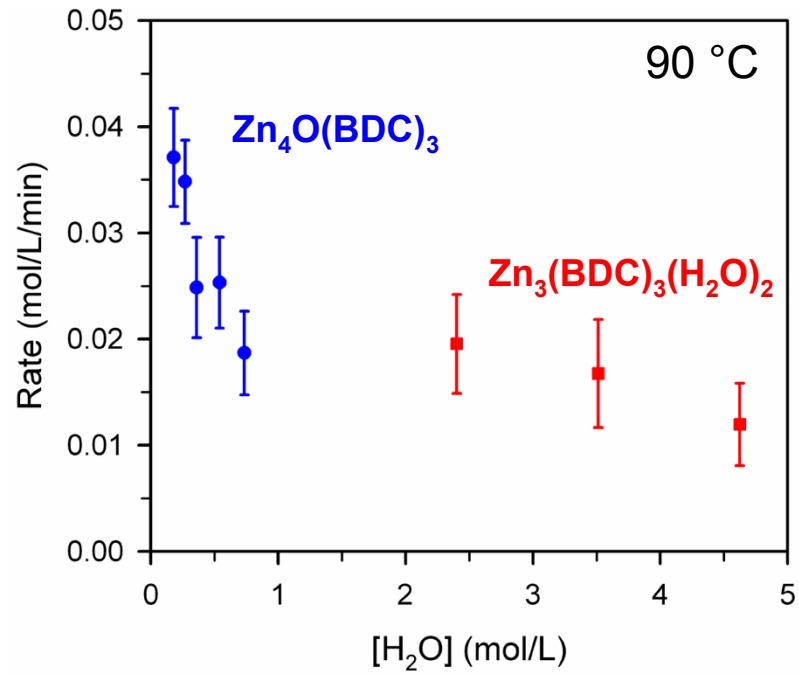


While working with $Zn_4O(BDC)_3$, it was observed to decompose slowly upon exposure to atmospheric moisture. To determine the effect of water exposure on the hydrogen sorption properties of the material, $Zn_4O(BDC)_3$ was prepared using an air-free purification and activation procedure. Hydrogen adsorption measurement of the material prepared air-free showed an uptake of 10 total wt %, an increase of ~3 wt % over the material prepared in air.

Kinetics of Framework Formation



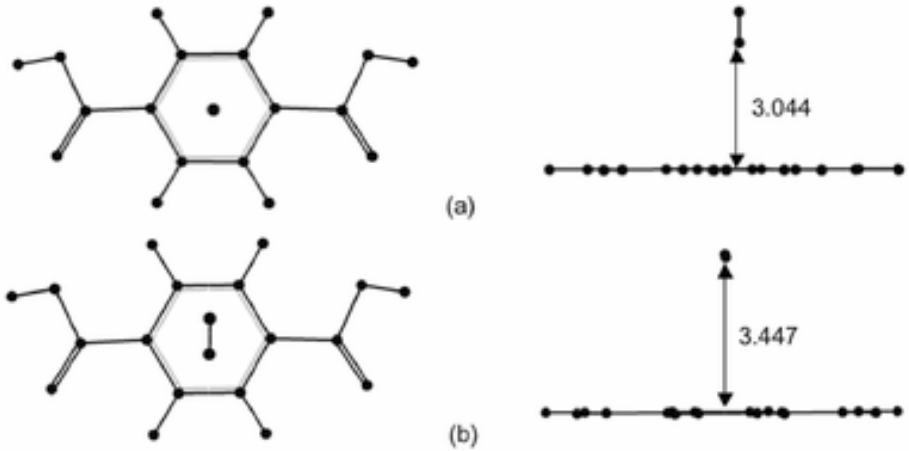
Concentration of BDC^{2-} vs. time during the synthesis of $Zn_4O(BDC)_3$.



Rate of formation of $Zn_4O(BDC)_3$ and $Zn_3(BDC)_3(H_2O)_2$ vs. $[H_2O]$.

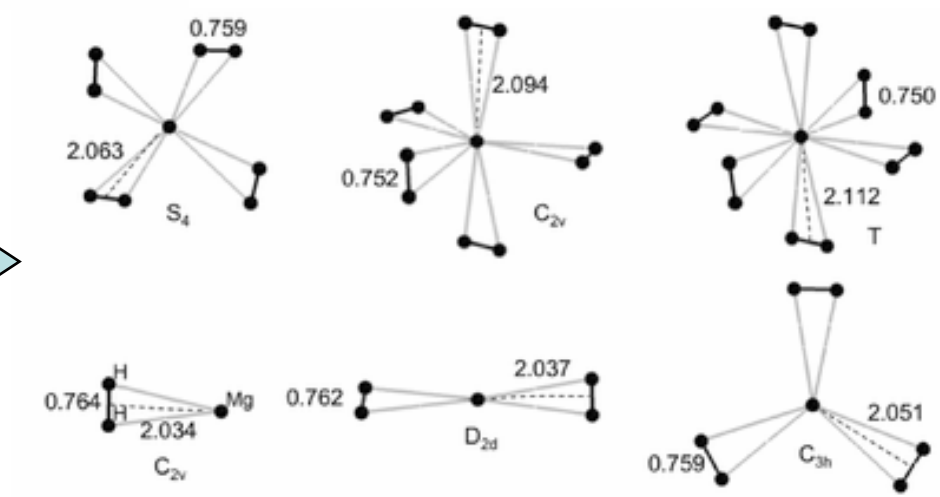
In order to better understand how to synthesize metal-organic frameworks for hydrogen storage, the kinetics of the formation of these materials are being studied. In our initial investigations, the reaction of zinc nitrate and H_2BDC in diethylformamide was monitored by measuring the concentration of BDC^{2-} vs. time using NMR spectroscopy. The rate of formation was found to slow significantly with increasing concentration of water. Preliminary experiments suggest that this effect is general, and can be observed for a wide variety of metal-organic frameworks.

Computation of M^{n+}-H_2 Interactions



BDC-H_2
van der Waals
~ 3-5 kJ/mol

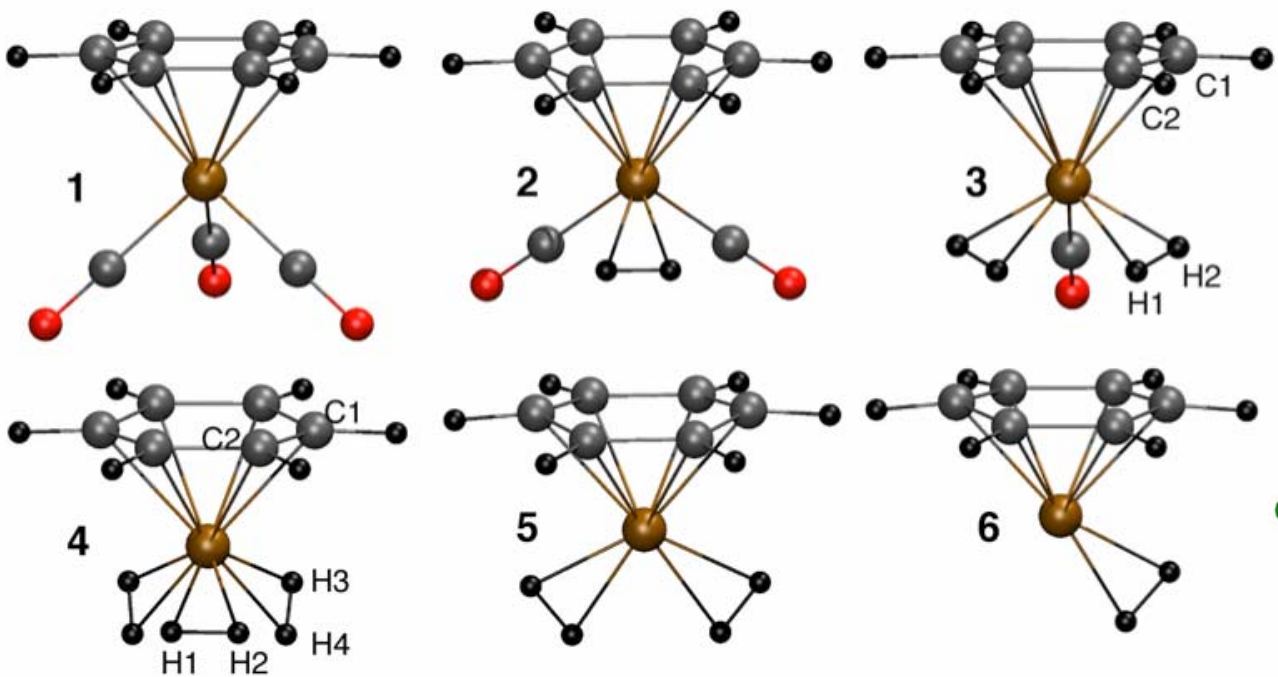
Mg^{2+}-H_2
electrostatic
~ 45-90 kJ/mol

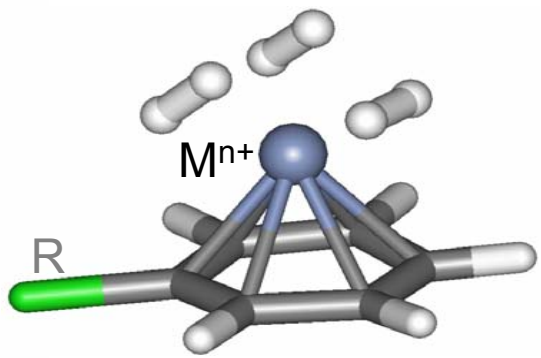


- **From van der Waals to electrostatics to charge transfer**

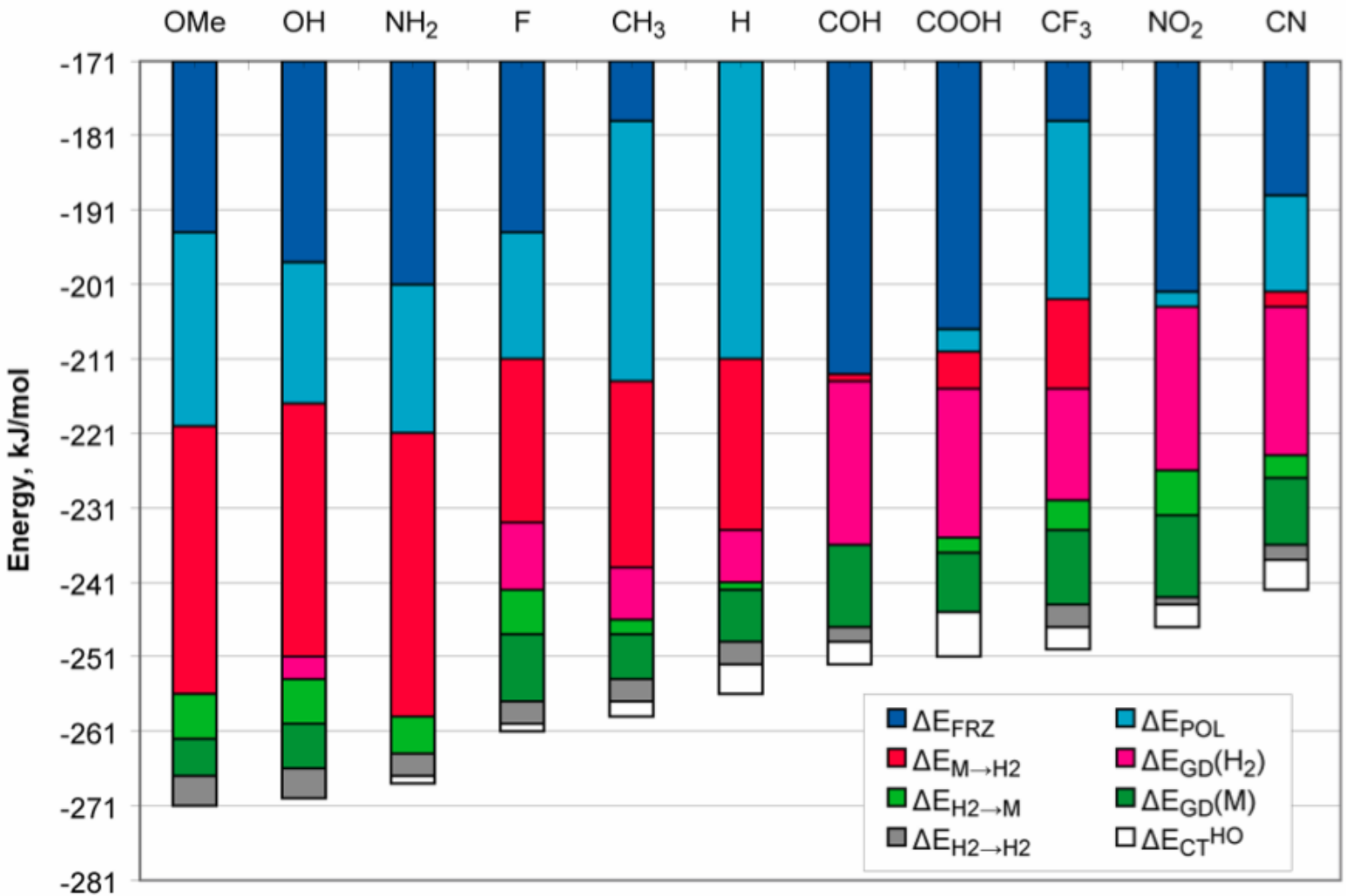
Computation of (BDC)M-H_2 Interactions

- Explore use of Cr centers bound to BDC linker
- Provides binding sites for up to three H molecules
- Adjust binding energy via metal M^{n+} and substituent R



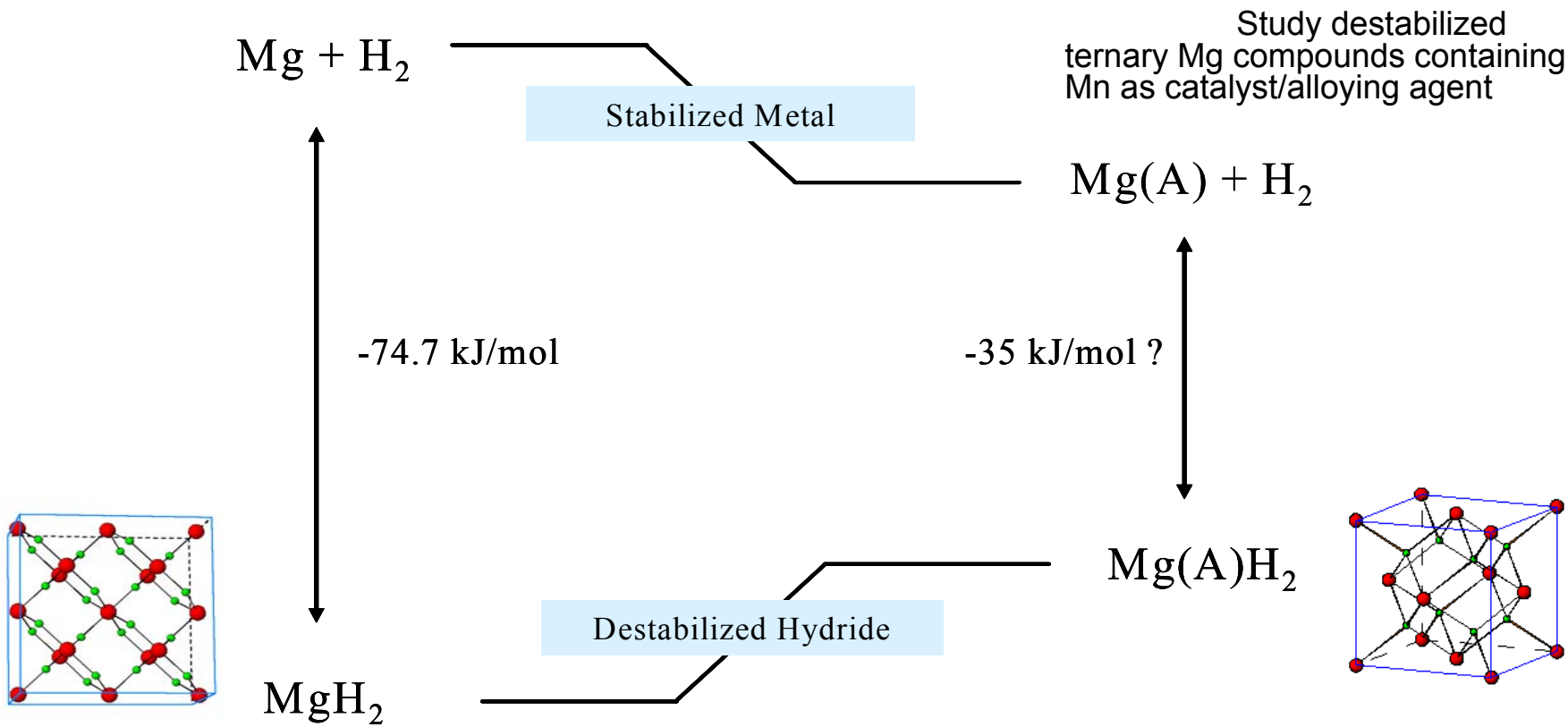


Origins of BDC Substituent Effects



Richardson and coworkers

Stabilized Light Metal Alloys for Hydrogen Storage



Heat Value of H_2 = **241.8** kJ/mol

- Smaller ΔH_f increases plateau pressure, reduces heating and cooling requirements

Future Work

- Continue to increase surface areas for hypercrosslinked polymers
- Add metal complexes (e.g. $Cr(CO)_3$) to aromatic polymer surfaces
- Evaluate means of desolvating magnesium-based frameworks to maximize exposed metal sites capable of binding H_2
- Explore thermolysis and photolysis routes to removing CO from $Cr(CO)_3$ units in microporous polymers and metal-organic frameworks
- Test impact of rigorous protection form air on uptake properties of other Zn_4O-based frameworks
- Attempt to utilize kinetics studies in identifying conditions suitable for forming stable, Mg_4O-based frameworks
- Extend theory effort to include predictions on paramagnetic metal ions
- Use thin film techniques in identifying dopants suitable for generating stabilized magnesium alloys with destabilized hydrides