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

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Project ID # ST27

Overview

Timeline

- Project start: 12/1/04
- Project end: 11/30/09
- Percent complete: 70%

Budget

- Total funding expected: $2.9M
  - $1.8M from DOE to UC Berkeley
  - $600k from DOE to LBNL
  - $500k in cost-sharing
- Funding FY07: $400k
- Funding FY08: $600k

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 Corporation
- Electric Power Research Institute

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)

Part I* (EERE)

Metal/metal hydride nanocrystals (Alivisatos)

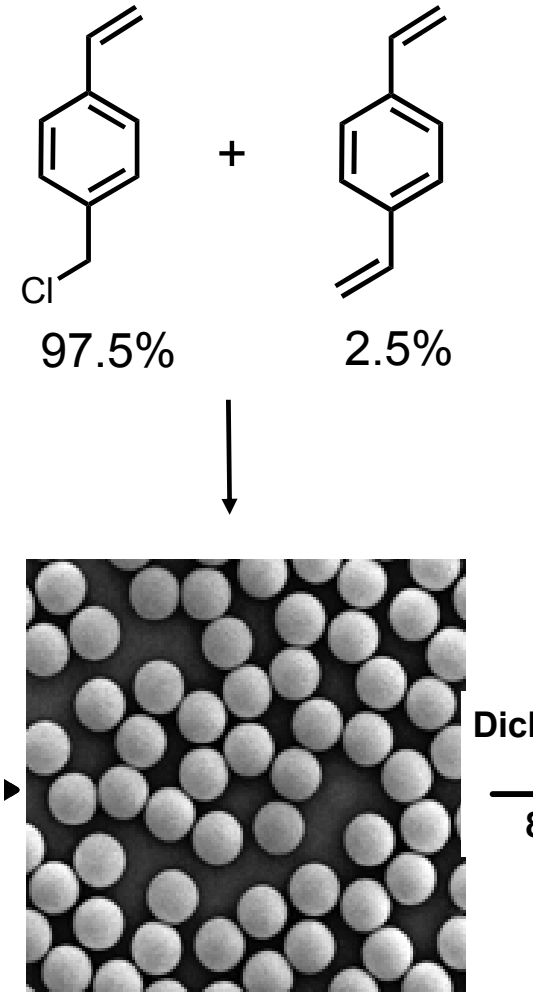
Synthesis of nanostructured boron nitrides (Zettl)

Theory for boron nitride materials (Cohen and Louie)

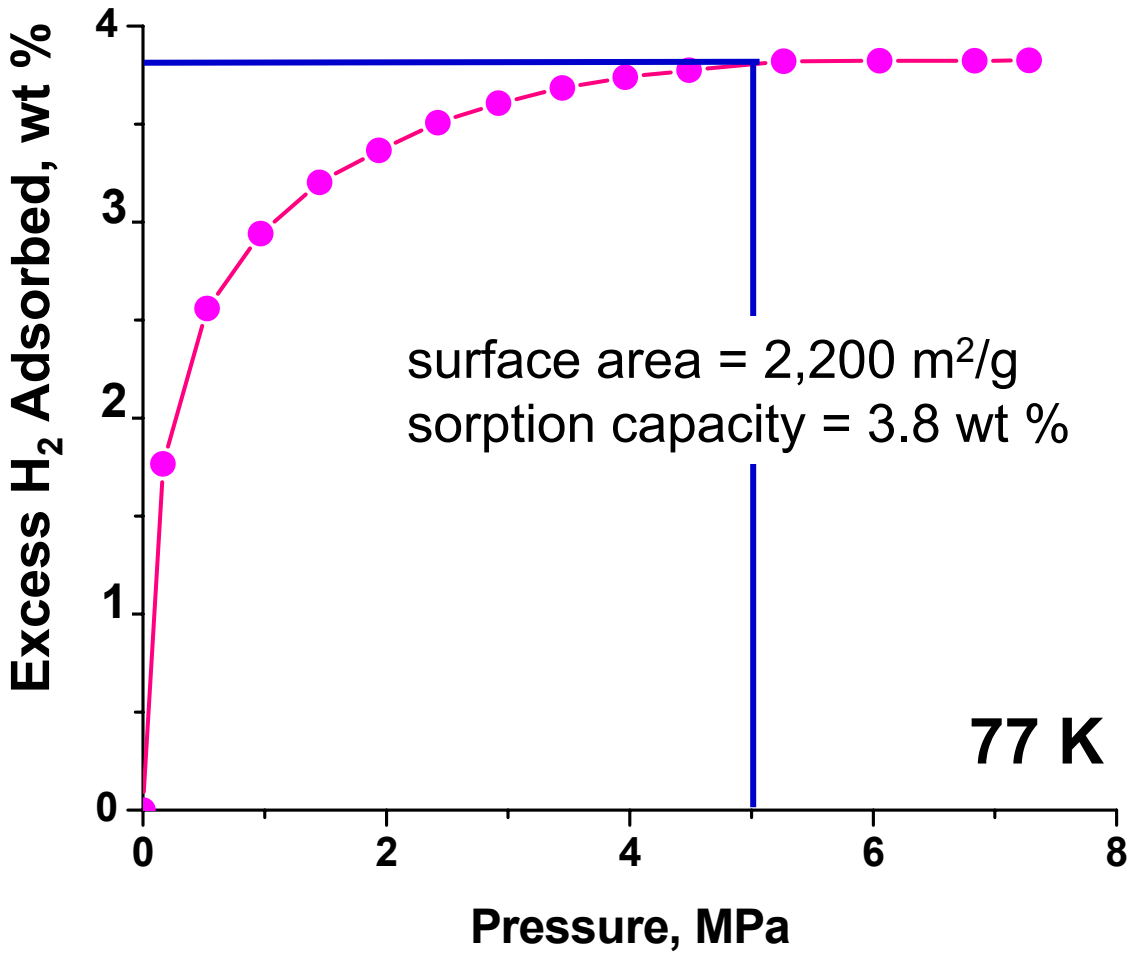
Part II (BES)

*Note that the results presented here are solely from Part I, which is funded through EERE

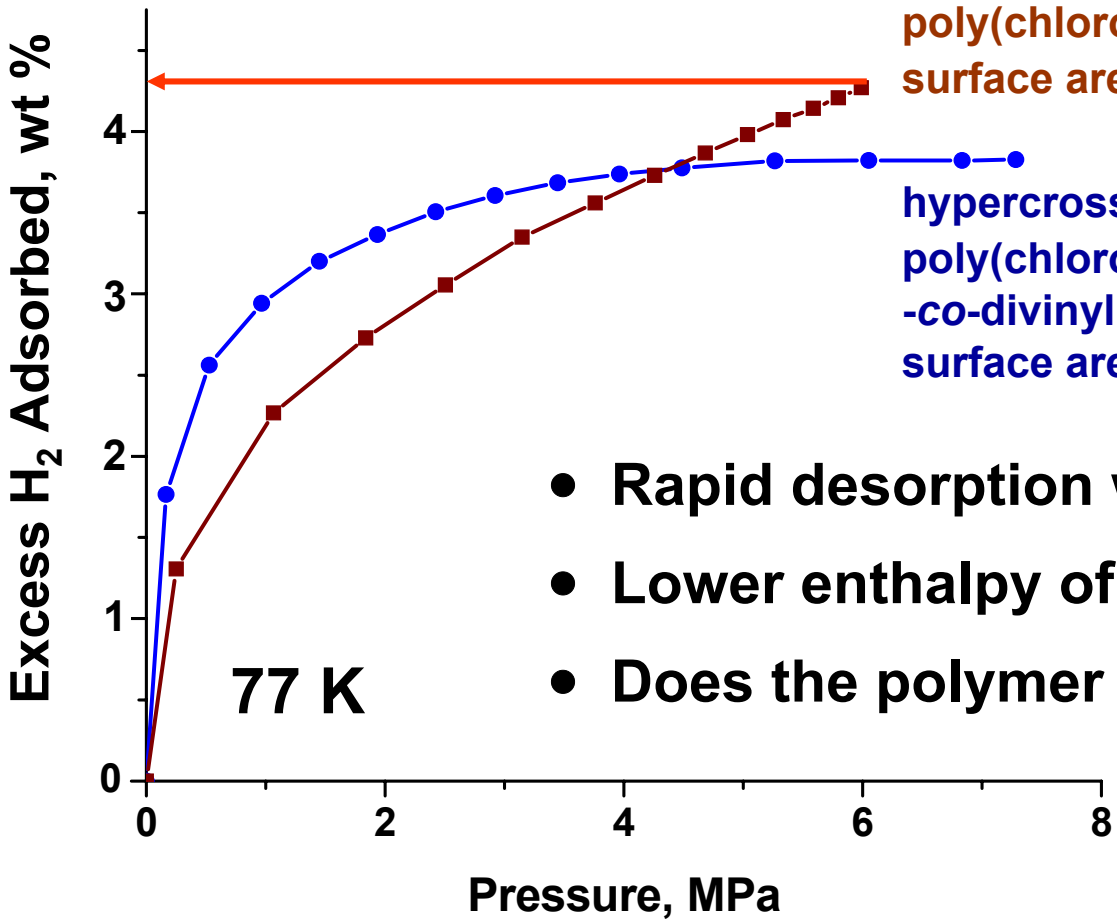
H_2 Adsorption in a Hypercrosslinked Polymer



poly(chloromethylstyrene-*co*-divinylbenzene)



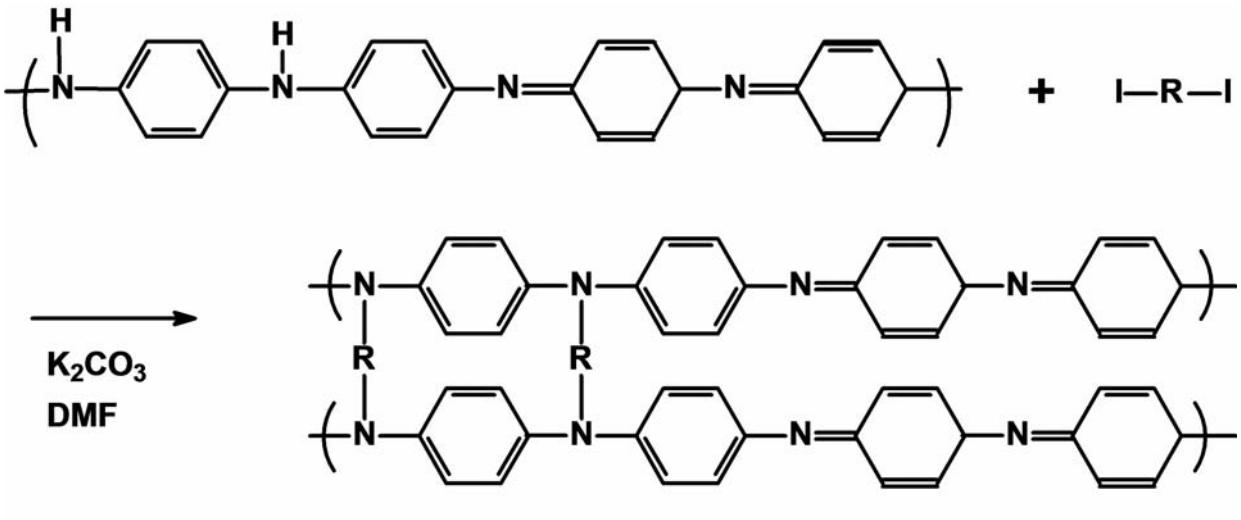
Comparison of Hypercrosslinked Polymers



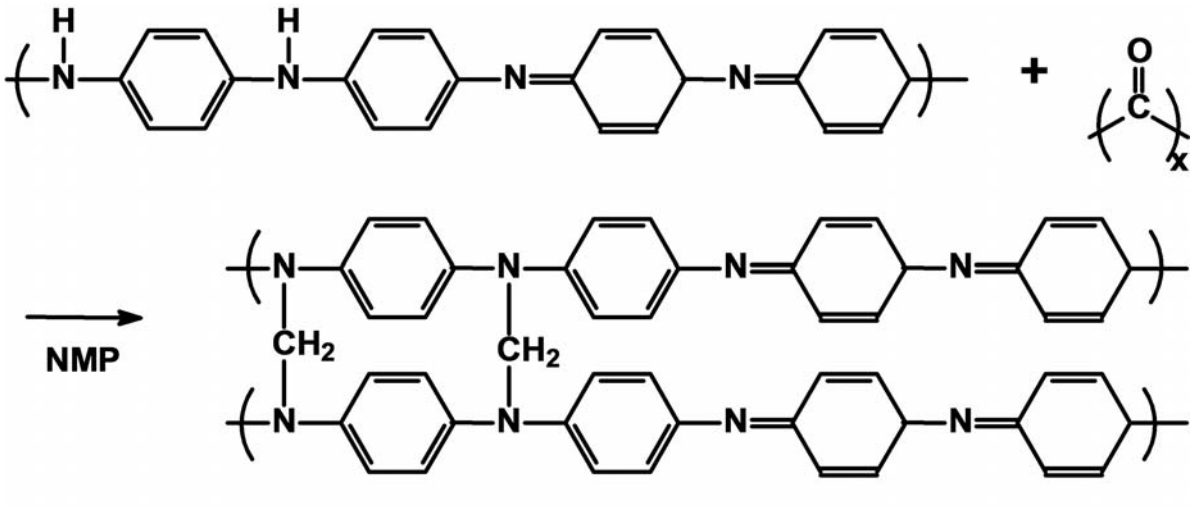
- Rapid desorption with no hysteresis
- Lower enthalpy of adsorption
- Does the polymer swell with pressure?

Hypercrosslinked Polyaniline

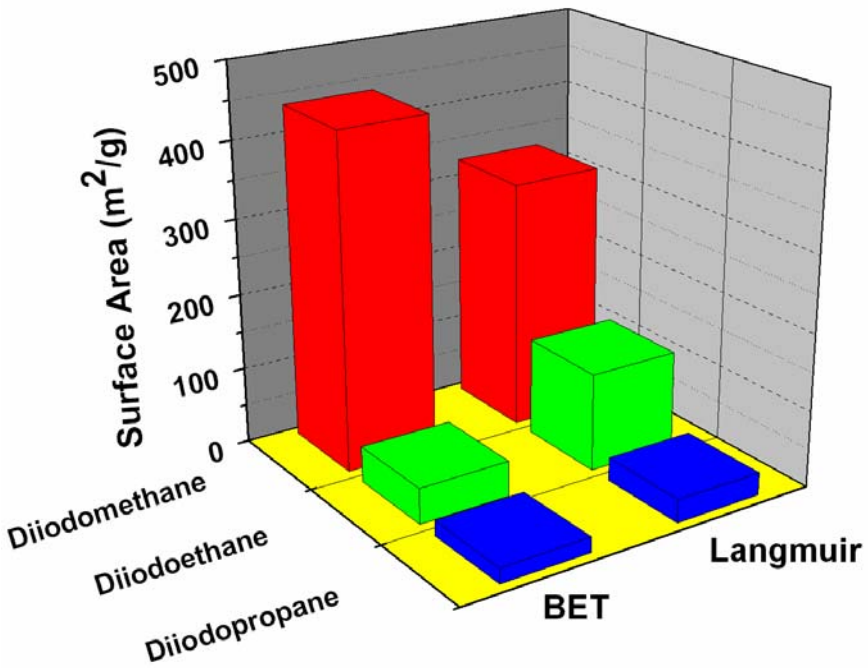
Route 1:

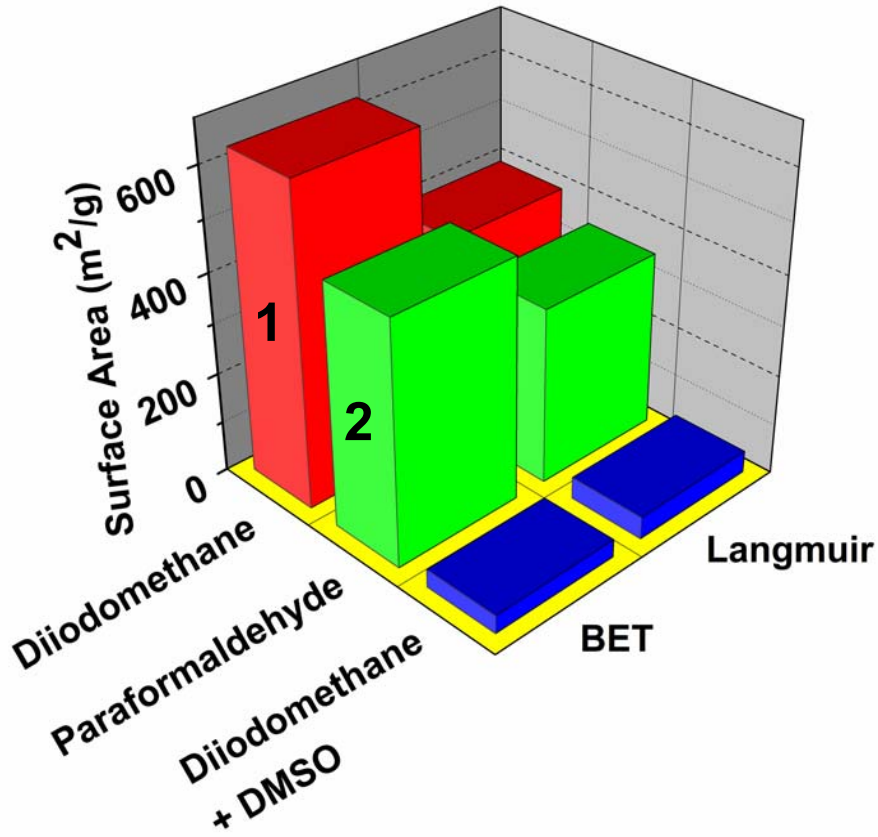


Route 2:



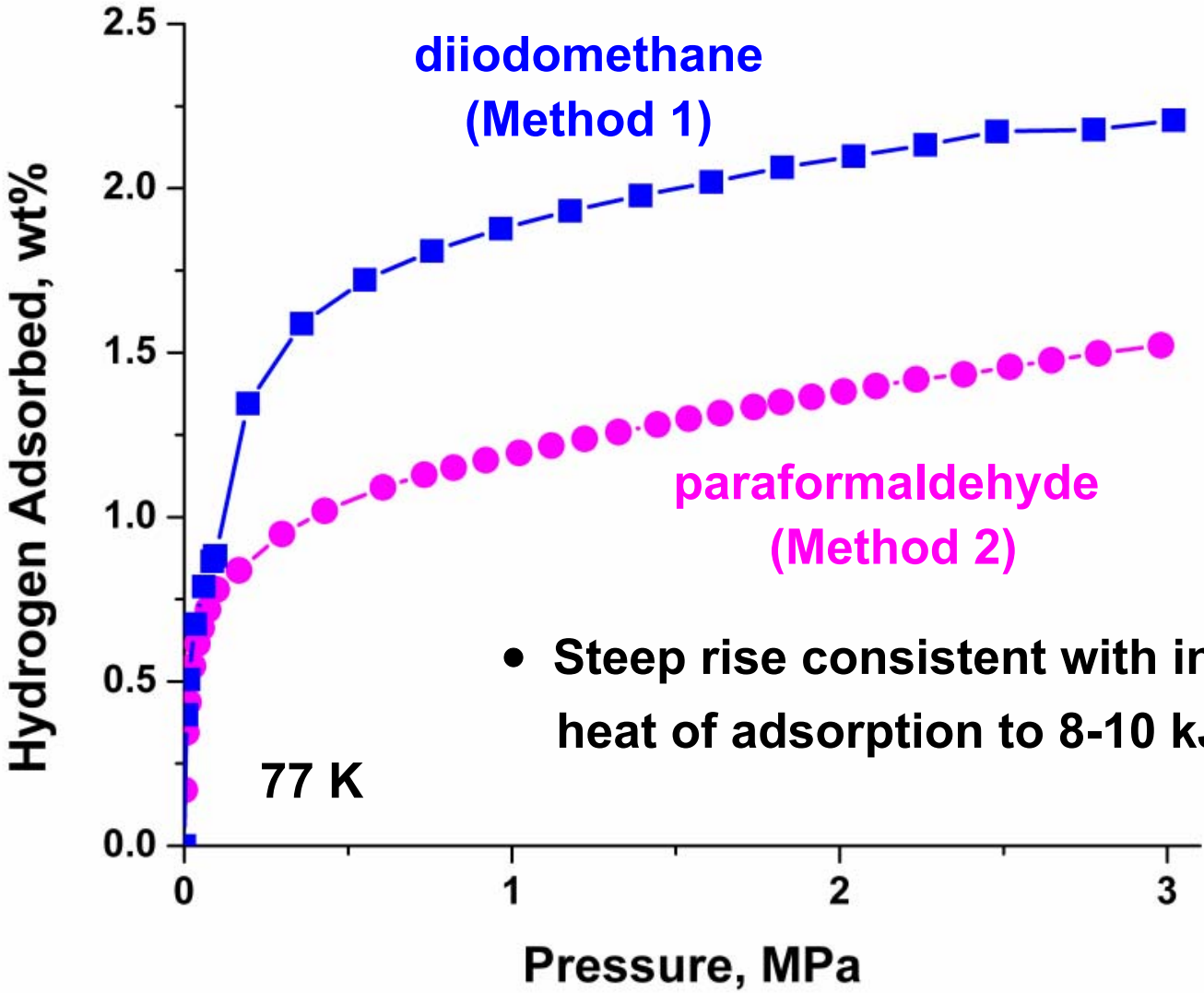
Effect of Crosslinking Route





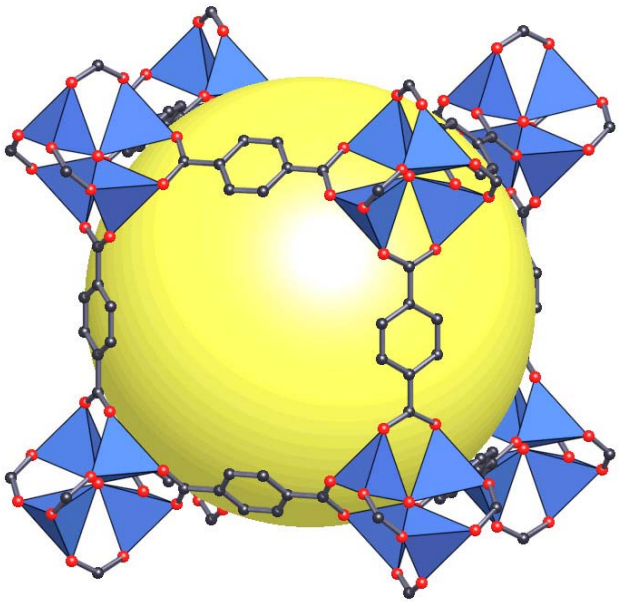
- **Crosslinking with methylene units gives highest surface areas**

H_2 Uptake in Hypercrosslinked Polyaniline



- Steep rise consistent with increased heat of adsorption to 8-10 kJ/mol

Variation of N_2 Uptake in $Zn_4O(BDC)_3$ (MOF-5)

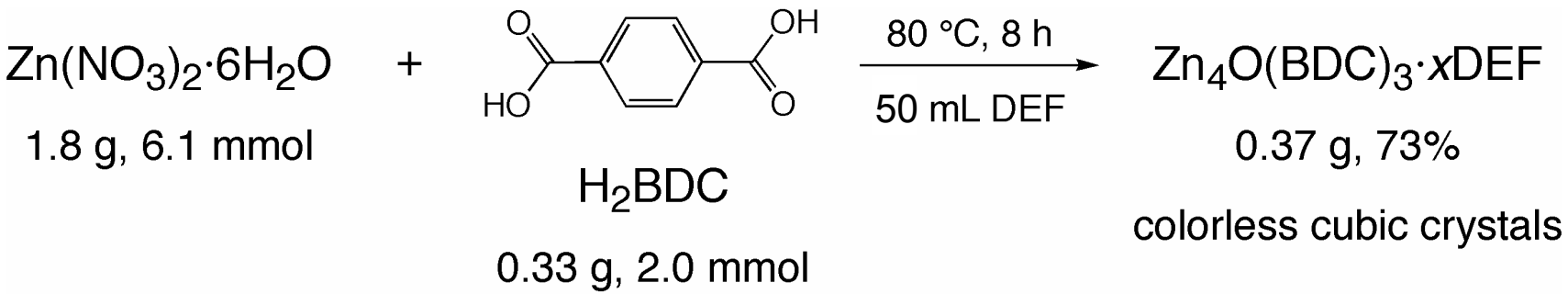


$Zn_4O(BDC)_3$

preparation	N_2 uptake (mmol/g)	SA_{BET} (m^2/g)	$SA_{Langmuir}$ (m^2/g)
1	11.8	570	1010
2	14.5	950	1250
3	29.7		2900
4	31.6		3080
5	34.4		3360
6		3530	4170

(1) Panella, Hirscher *Adv. Mater.* **2005**, *17*, 538
(2) Yan, *et al. Microporous Mesoporous Mater.* **2003**, *58*, 105
(3) Li, Eddaoudi, O'Keeffe, Yaghi *Nature* **1999**, *402*, 276
(4) Dailly, Vajo, Ahn *J. Phys. Chem.* **2006**, *110*, 1099
(5) Rowsell, Millward, Park, Yaghi *J. Am. Chem. Soc.* **2004**, *126*, 5666
(6) Wong-Foy, Matzger, Yaghi *J. Am. Chem. Soc.* **2006**, *128*, 3494

Optimized Synthesis and Activation of $Zn_4O(BDC)_3$



- Heating too high or too long gives yellow-brown crystals with reduced storage capacity

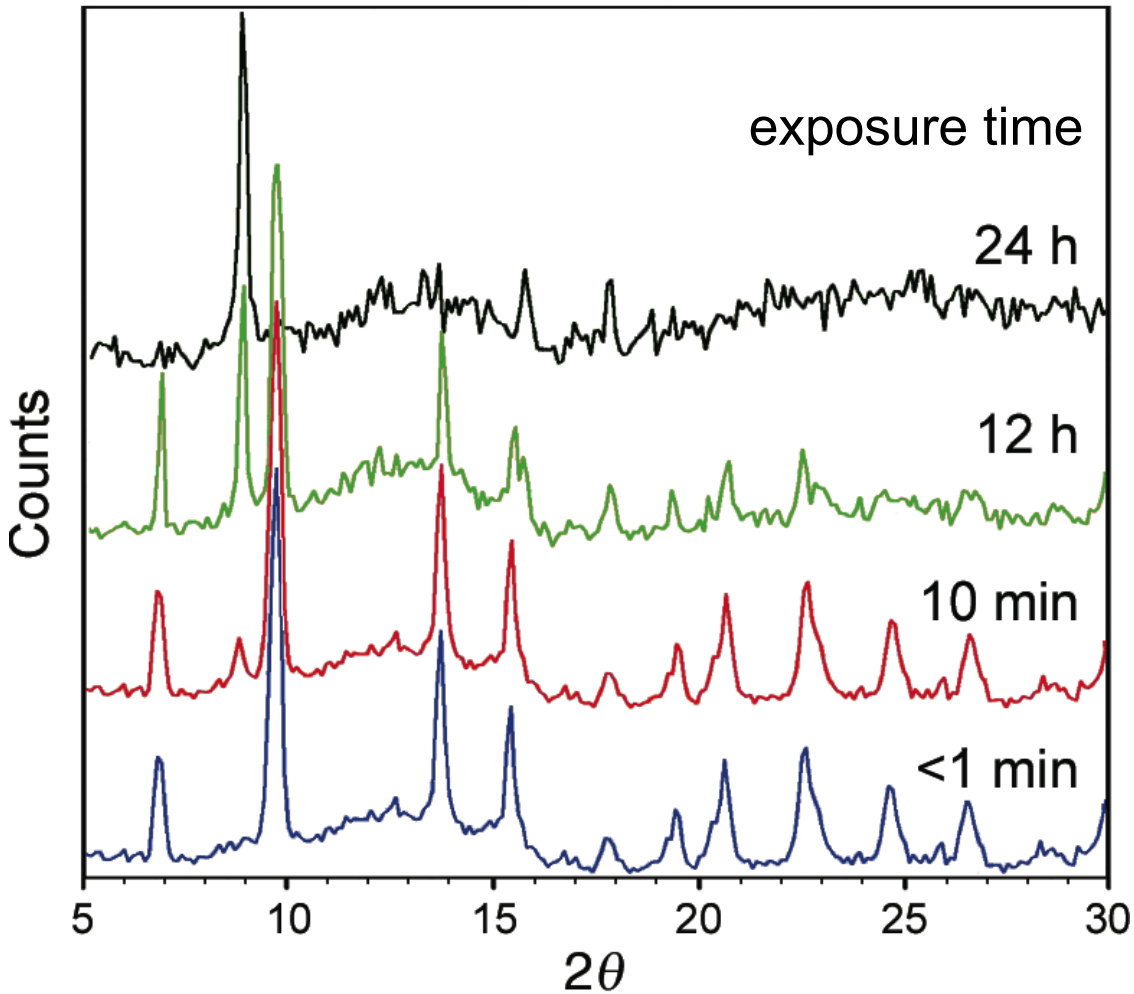
Evacuation procedure

Soak crystals in 10 mL DMF for 8 h (6 times)

Soak crystals in 10 mL CH_2Cl_2 for 8 h (6 times)

Evacuate crystals at 25 °C under dynamic vacuum until an outgas rate of <1 mtorr/min is achieved

Decomposition of $Zn_4O(BDC)_3$ in Air



$Zn_3(OH)_2(BDC)_2$ + **?**
(nonporous)

$Zn_4O(BDC)_3$

Variation of N_2 Uptake in $Zn_4O(BDC)_3$

preparation	N_2 uptake (mmol/g)	SA_{BET} (m^2/g)	$SA_{Langmuir}$ (m^2/g)
1	11.8	570	1010
2	14.5	950	1250
3	29.7		2900
4	31.6		3080
5	34.4		3360
6		3530	4170
air-free	**44.5**	**3800**	**4400**

(1) Panella, Hirscher *Adv. Mater.* **2005**, *17*, 538
(2) Yan, *et al. Microporous Mesoporous Mater.* **2003**, *58*, 105
(3) Li, Eddaoudi, O'Keeffe, Yaghi *Nature* **1999**, *402*, 276
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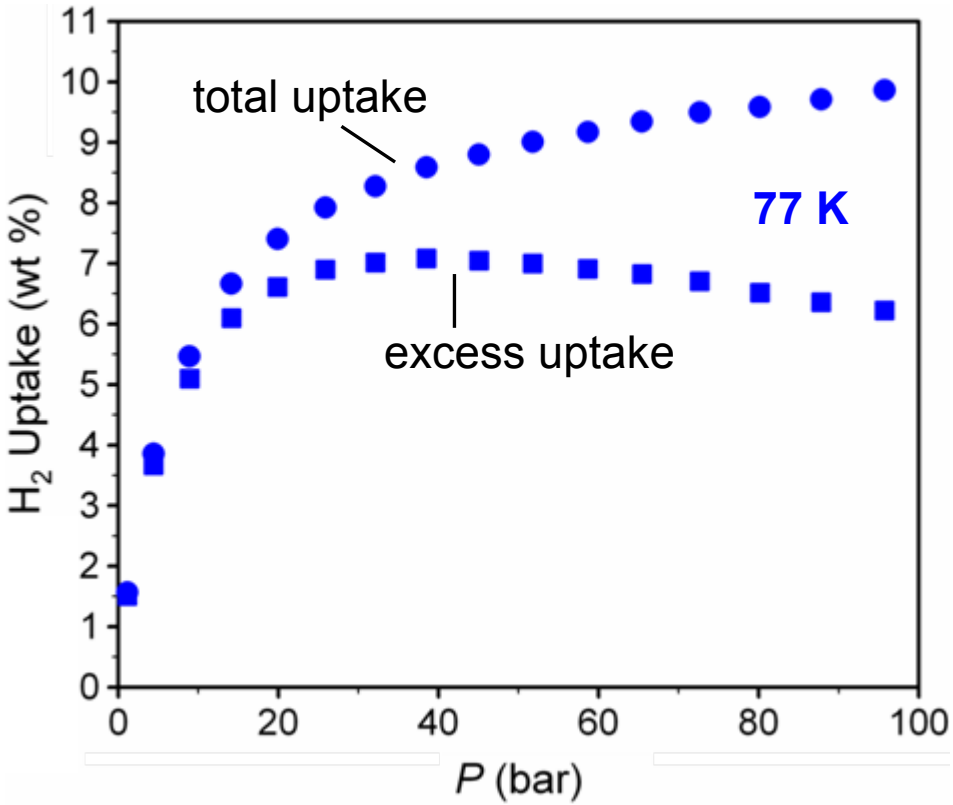
(5) Rowsell, Millward, Park, Yaghi *J. Am. Chem. Soc.* **2004**, *126*, 5666
(6) Wong-Foy, Matzger, Yaghi *J. Am. Chem. Soc.* **2006**, *128*, 3494

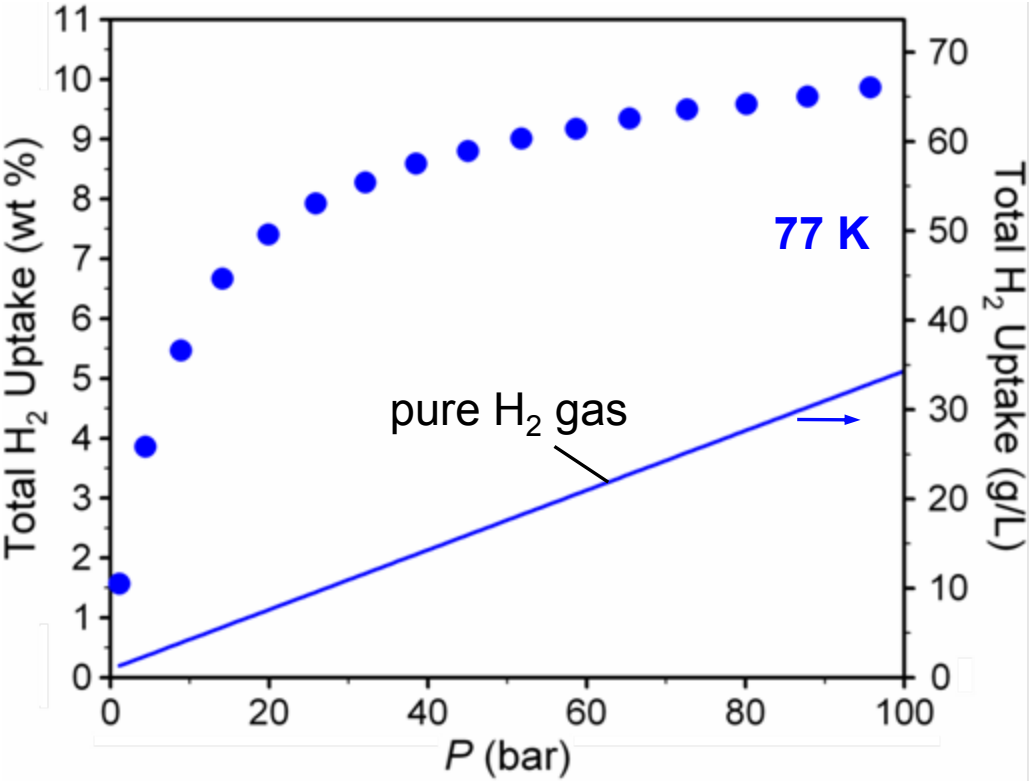
High-Pressure H_2 Uptake in $Zn_4O(BDC)_3$



- At 40 bar, a record physisorbed excess capacity of 7.1 wt % is achieved
- Total uptake is the amount of gas contained within the volume of the crystals

Kaye, Dailly, Yaghi, Long *J. Am. Chem. Soc.* **2007**, *129*, 14176

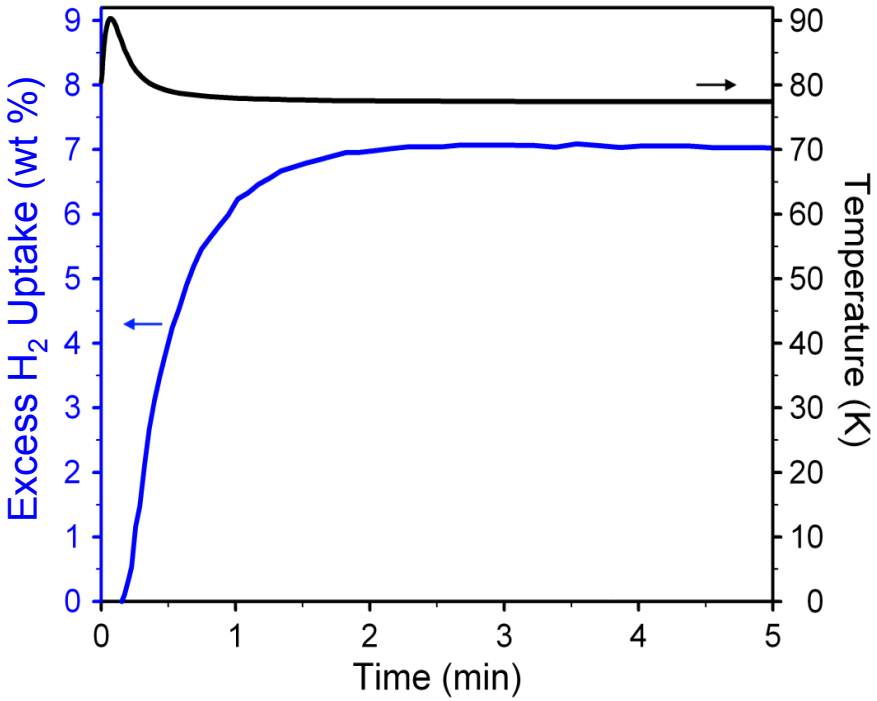
High-Pressure H_2 Uptake in $Zn_4O(BDC)_3$

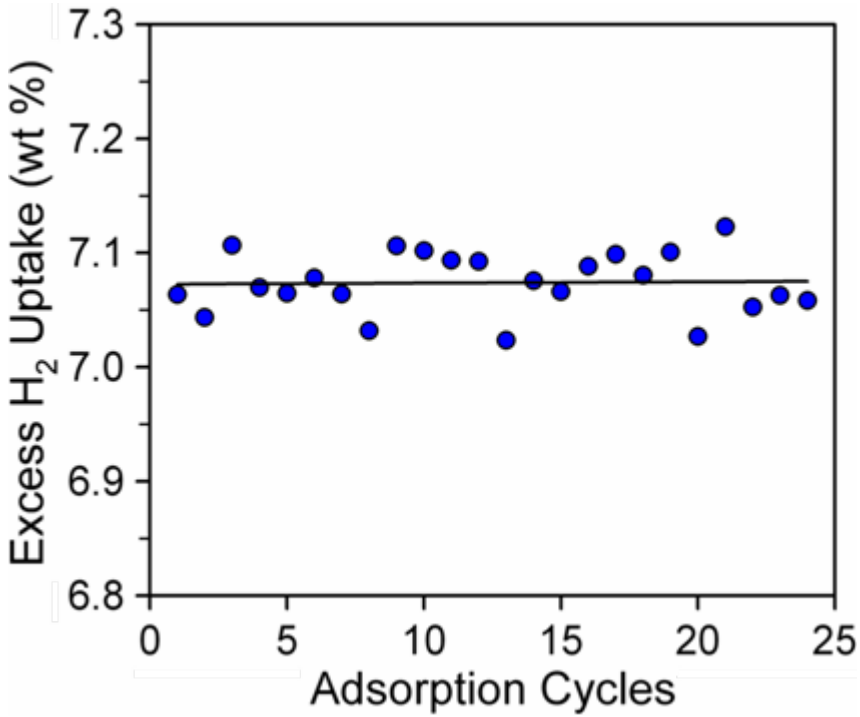


- Knowledge of total uptake permits calculation of the volumetric storage density
- At 100 bar, a record physisorbed storage density of 66 g/L is achieved

Kaye, Dailly, Yaghi, Long *J. Am. Chem. Soc.* **2007**, *129*, 14176

Kinetics and Cycling for H_2 Uptake in $Zn_4O(BDC)_3$

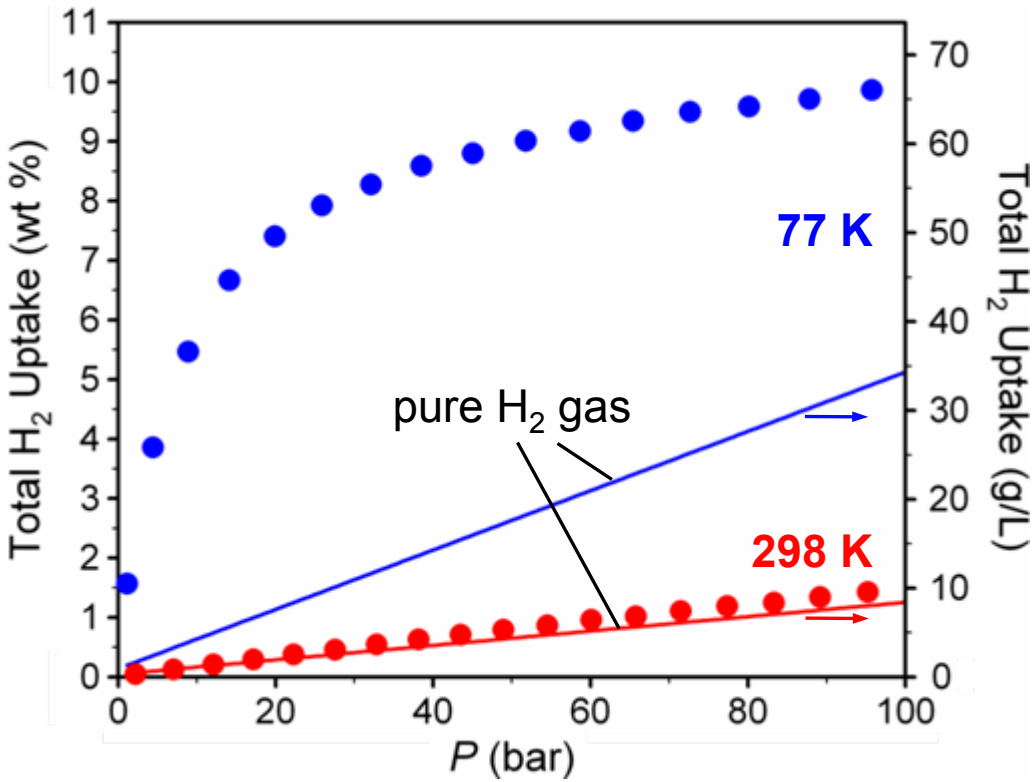




- Results are upon exposure to a manifold of H_2 gas at 45 bar and 298 K
- No detectable loss in capacity or kinetics after 24 adsorption-desorption cycles

Kaye, Dailly, Yaghi, Long *J. Am. Chem. Soc.* **2007**, *129*, 14176

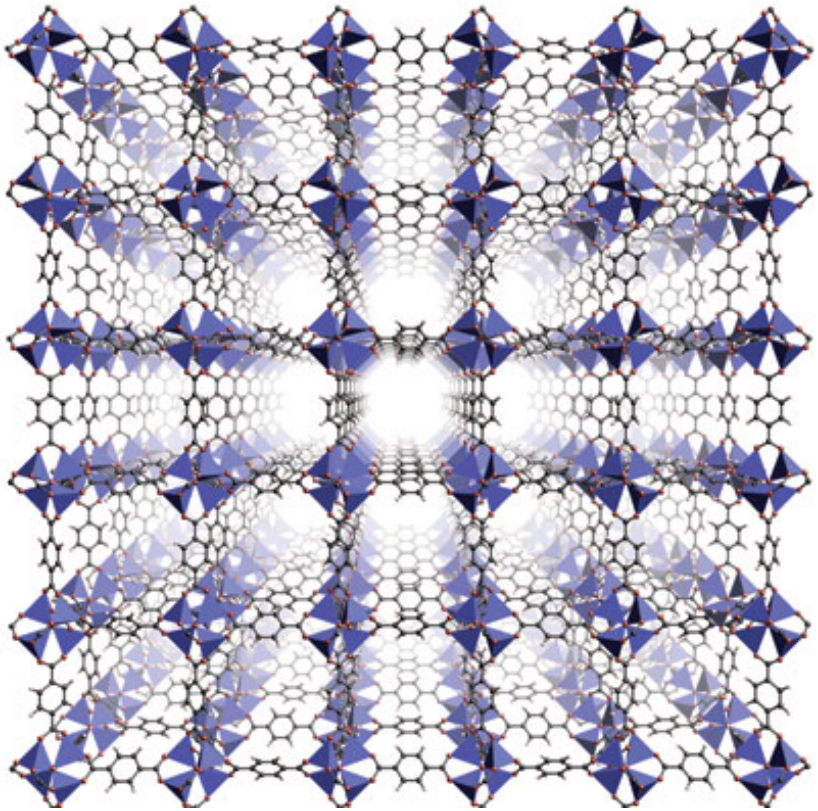
Room-Temperature H_2 Uptake in $Zn_4O(BDC)_3$

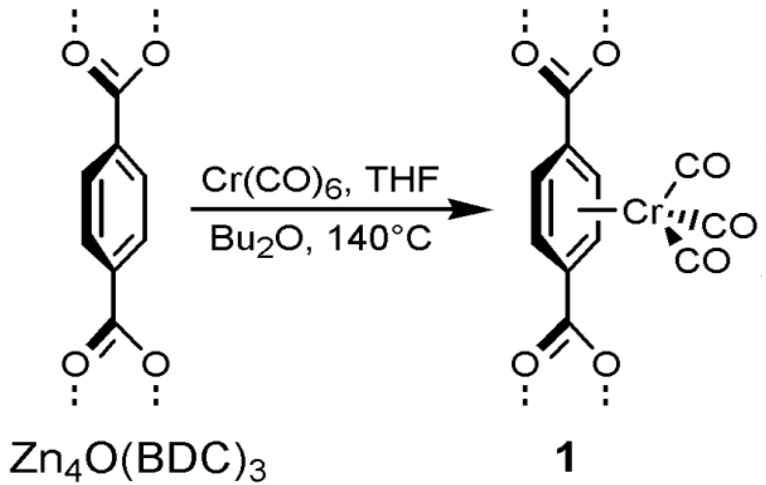


- At 298 K, framework offers little improvement over density of pure H_2 gas
- Due to very weak interaction of H_2 with the framework ($\Delta H_{ads} \approx 5$ kJ/mol)

Kaye, Dailly, Yaghi, Long *J. Am. Chem. Soc.* **2007**, *129*, 14176

Coating the Surfaces with $Cr(CO)_3$ Units

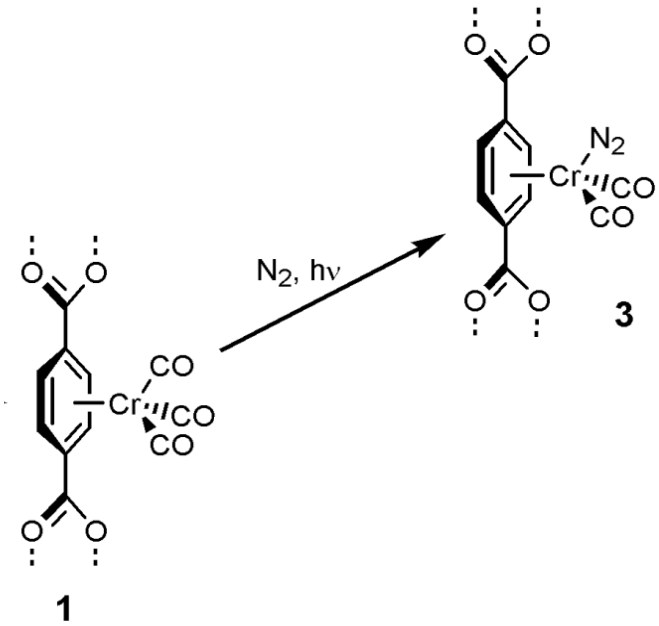


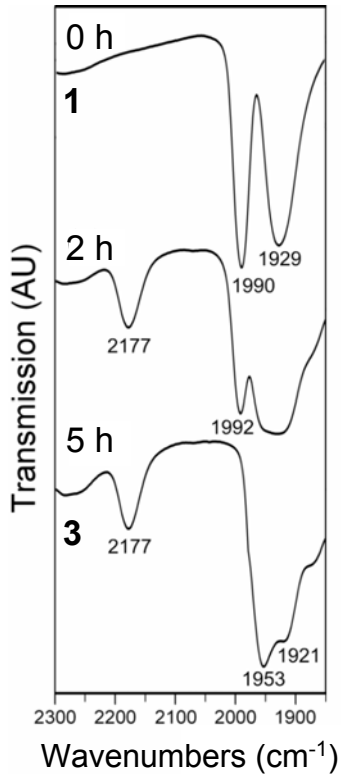


- Infrared spectrum matches that observed for molecular analogue
- Elemental analysis and NMR spectroscopy indicate attachment to all rings

Kaye, Long *J. Am. Chem. Soc.* **2008**, *130*, 806

Matrix Isolation Chemistry in a Framework

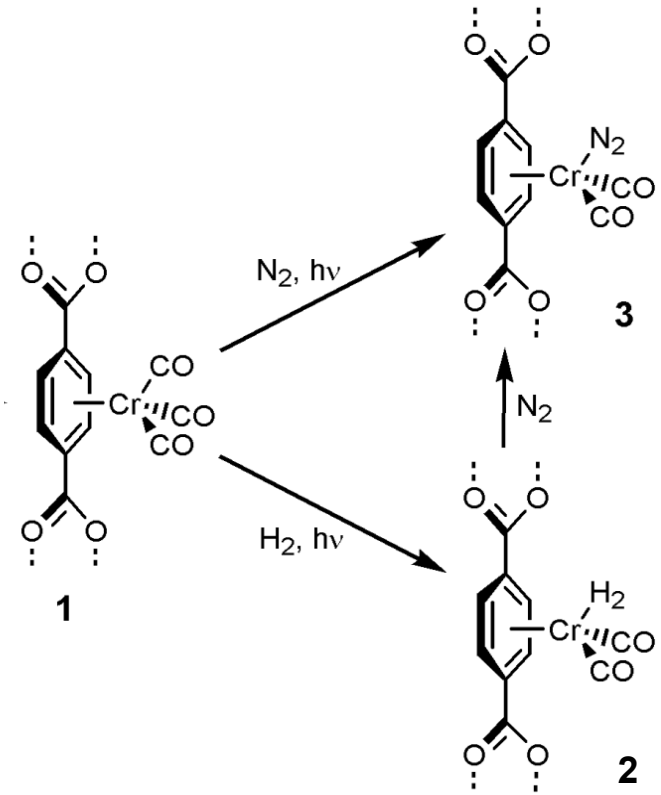


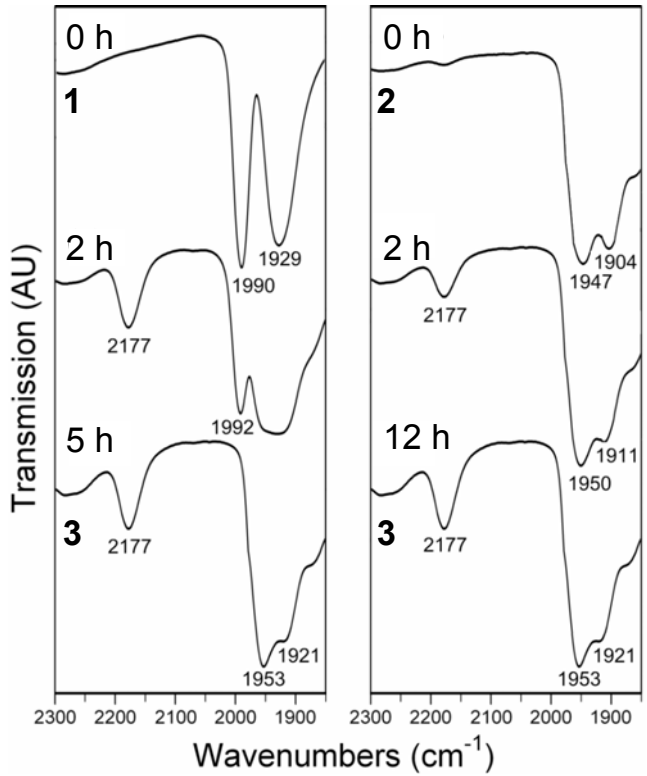


- Infrared spectra match those observed for molecular analogues
- Compound **3** is much more stable than analogue generated in frozen Xe

Kaye, Long *J. Am. Chem. Soc.* **2008**, *130*, 806

Strong H_2 Binding at Cr^0 Centers



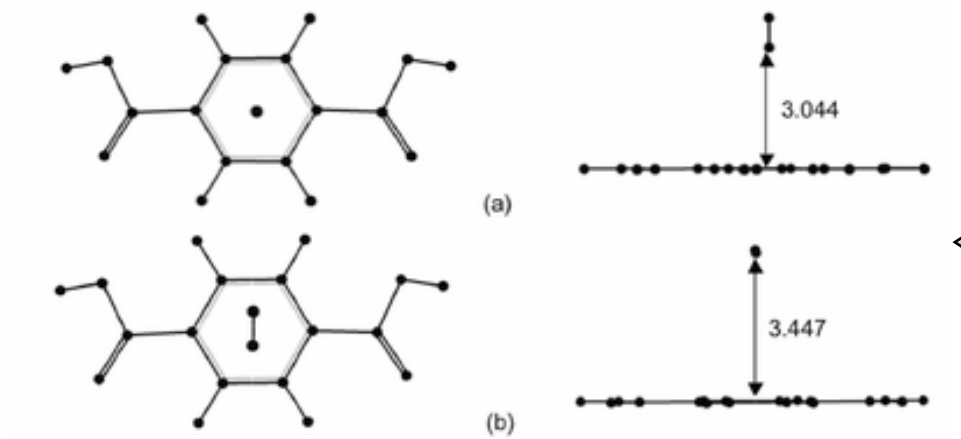


- Infrared spectra match those observed for molecular analogues
- Cr^0-H_2 complex in compound **2** is stable indefinitely at room temperature!

Kaye, Long *J. Am. Chem. Soc.* **2008**, *130*, 806

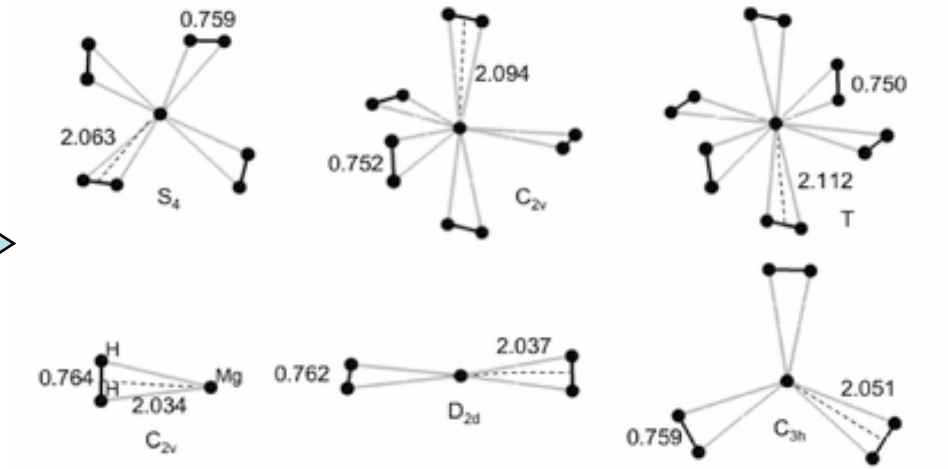
Range of H_2 Binding Interactions

dispersion < electrostatics < charge-transfer



H_2BDC-H_2
van der Waals
~ 3-5 kJ/mol

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



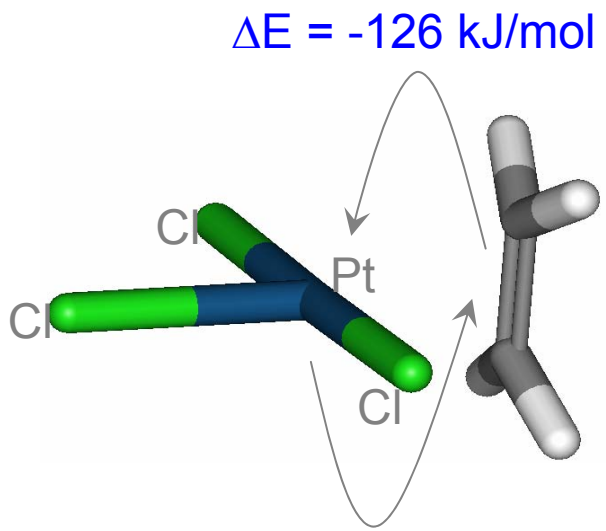
Lochan, Head-Gordon *Phys. Chem. Chem. Phys.* **2006**, *8*, 1357

Understanding H_2 Binding

A New Analysis Method

Decompose interaction energies rigorously into:

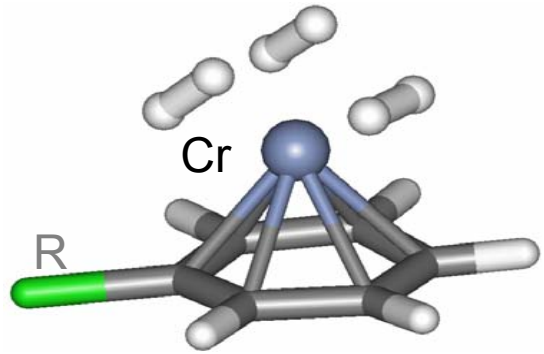
- Geometric distortion
- Frozen density interaction
- Induction
- Forward- and back-donation
- Small higher-order charge transfer

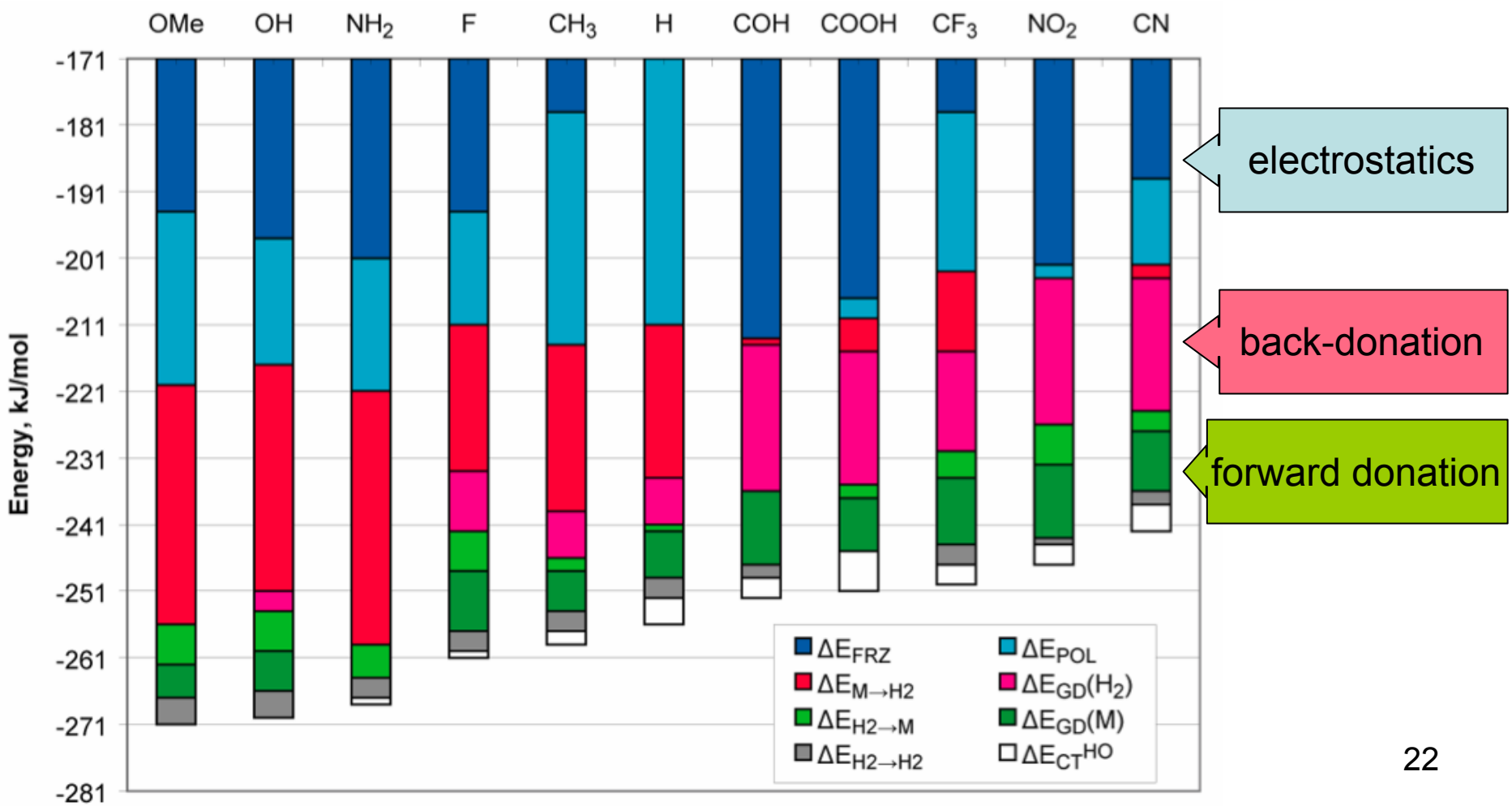


•Khaliullin, Cobar, Lochan, Bell, Head-Gordon *J. Phys. Chem. A* **2007**, *111*, 8753

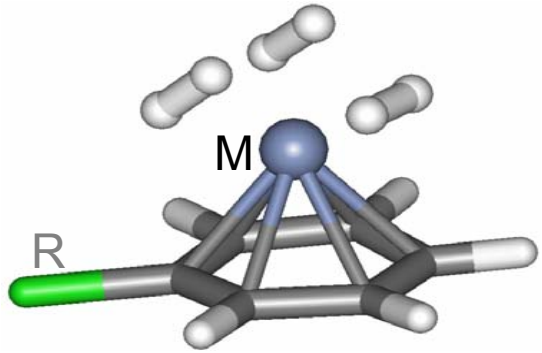
Relative Effect of Substituent

Metal chosen as Cr^0



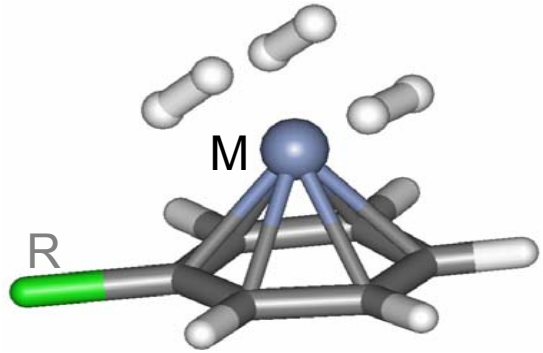


Effect of Substituent (R)



- Electron-donating groups enhance binding, while electron-withdrawing groups reduce binding
  - –Tunability is 7% of binding
  - –Energies are for three bound H_2 molecules
- Correlates with back-donation, electrostatics
- Quantitative information; qualitative insight
  - –BDC^{2-} substituents can fine-tune binding
  - –Coarse-tuning must come from different metals

Effect of Metal Substitution



- Heavier isoelectronic elements:

  $(C_6H_6)Cr(H_2)_3$ binding per H_2 of 68 kJ/mol

  $(C_6H_6)Mo(H_2)_3$ binding per H_2 of 84 kJ/mol

- Lighter transition elements:

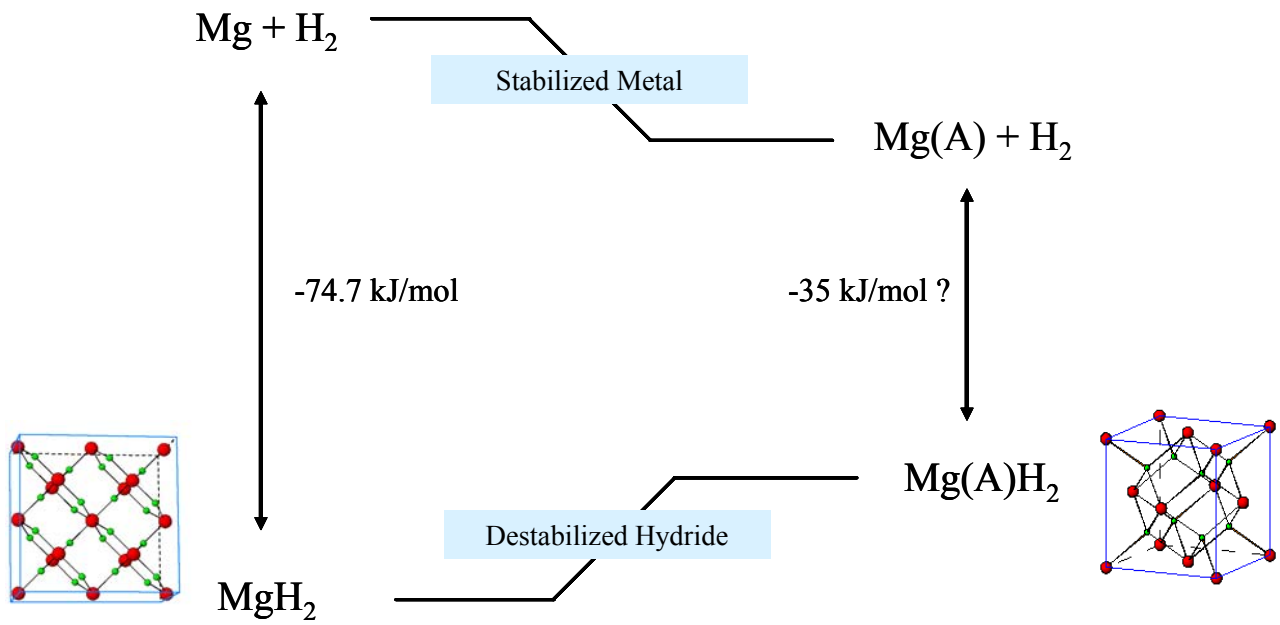
  $(C_6H_6)Cr(H_2)_3$ binding per H_2 of 68 kJ/mol

  $(C_6H_6)Ti(H_2)_4$ binding per H_2 of 32 kJ/mol

- Shows coarse tuning is possible

  Still need to examine synergy of these effects

Destabilization of Metal Hydrides



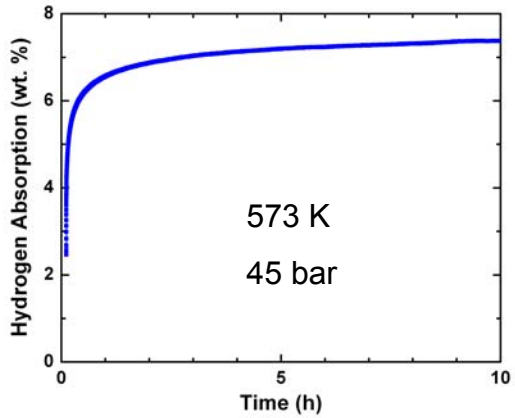
- Attempts at alloying of Mg in order to reduce ΔH
- Success in partial substitution to form $Mg_{1-x}A_x$ (A = Mn, Fe, Ni)
- Some increases in plateau pressures, but poor kinetics
- Attempts to substitute Na and Li for Mg are underway

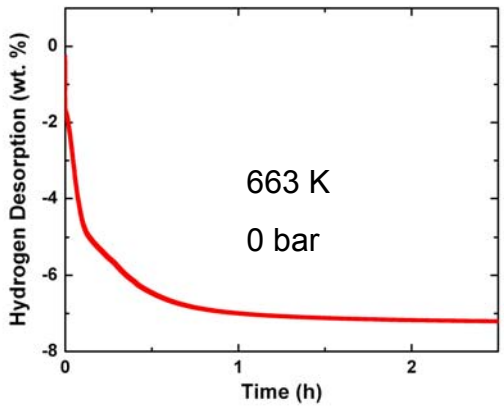
Attempts to Generate $MgH_{2-x}F_x$ Solid Solutions

Preliminary results, not yet reproduced:

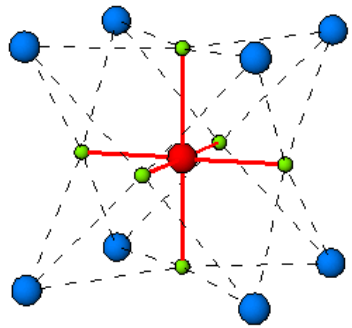
- MgH_2 + 10 mol% MgF_2 ball-milled
- 1st desorption at 663 K: 6.1 wt%
  (based on MgH_2 component)
- 1st absorption at 573 K: 7.4 wt%
- 2nd desorption at 663 K: 7.2 wt%

Does fluoride catalyze H_2 uptake and release via solid solution formation?

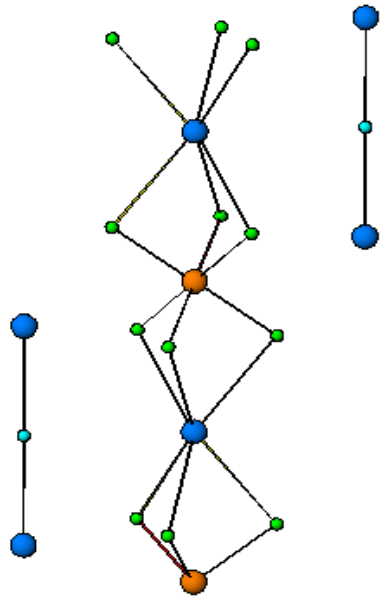




Destabilization of Complex Hydrides?



Mg_2FeH_6



Mg_3MnH_7

- Attempts at partial substitutions to adjust thermodynamics and kinetics
- Substitutions at both Mg and transition metal sites, as above
- Study effects of substituting F for H (e.g., $CaH_{2-x}F_x$ known for all x)
- Small fluoride additions reported to enhance reactivity of Mg_2Ni