



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

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Project ID # ST27



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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 H₂ binding energies (Head-Gordon)

Synthesis of destabilized hydrides (Richardson)

H₂ storage characterization instrumentation (Mao)

Metal/metal hydride nanocrystals (Alivisatos)

Synthesis of nanostructured boron nitrides (Zettl)

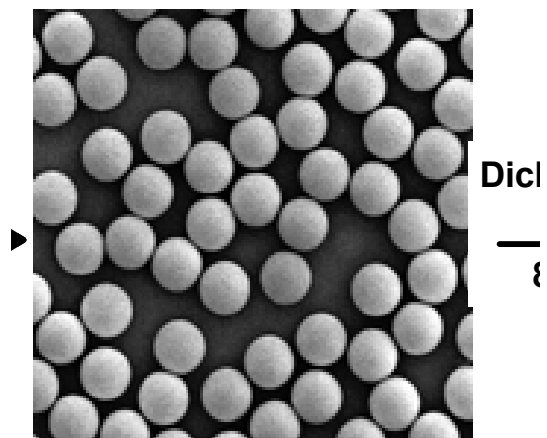
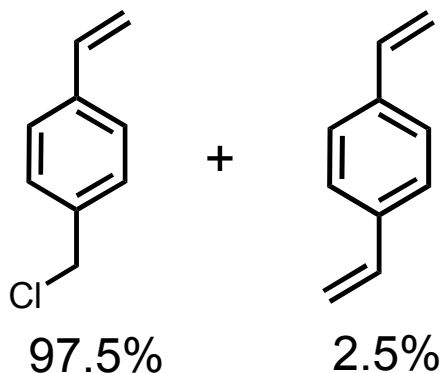
Theory for boron nitride materials (Cohen and Louie)

Part I*
(EERE)

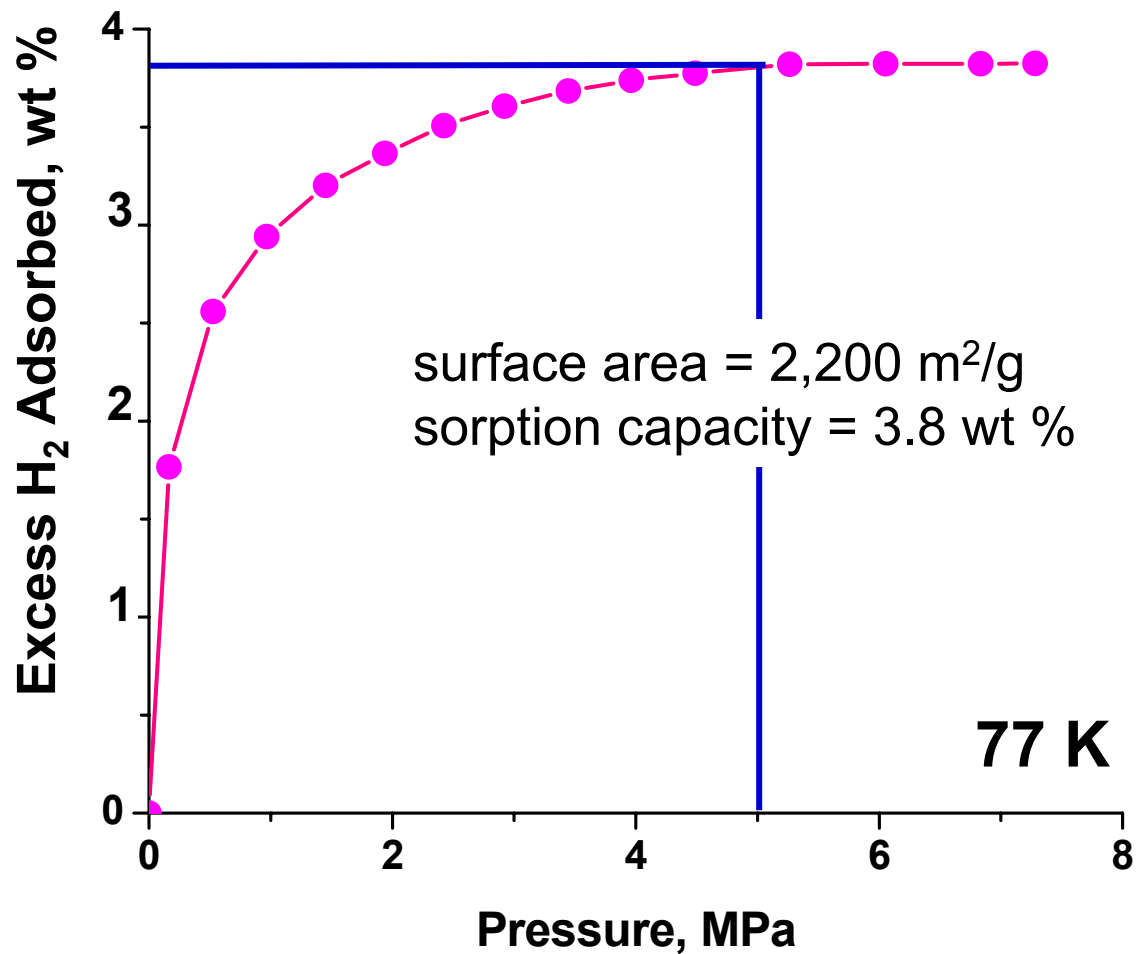
Part II
(BES)

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

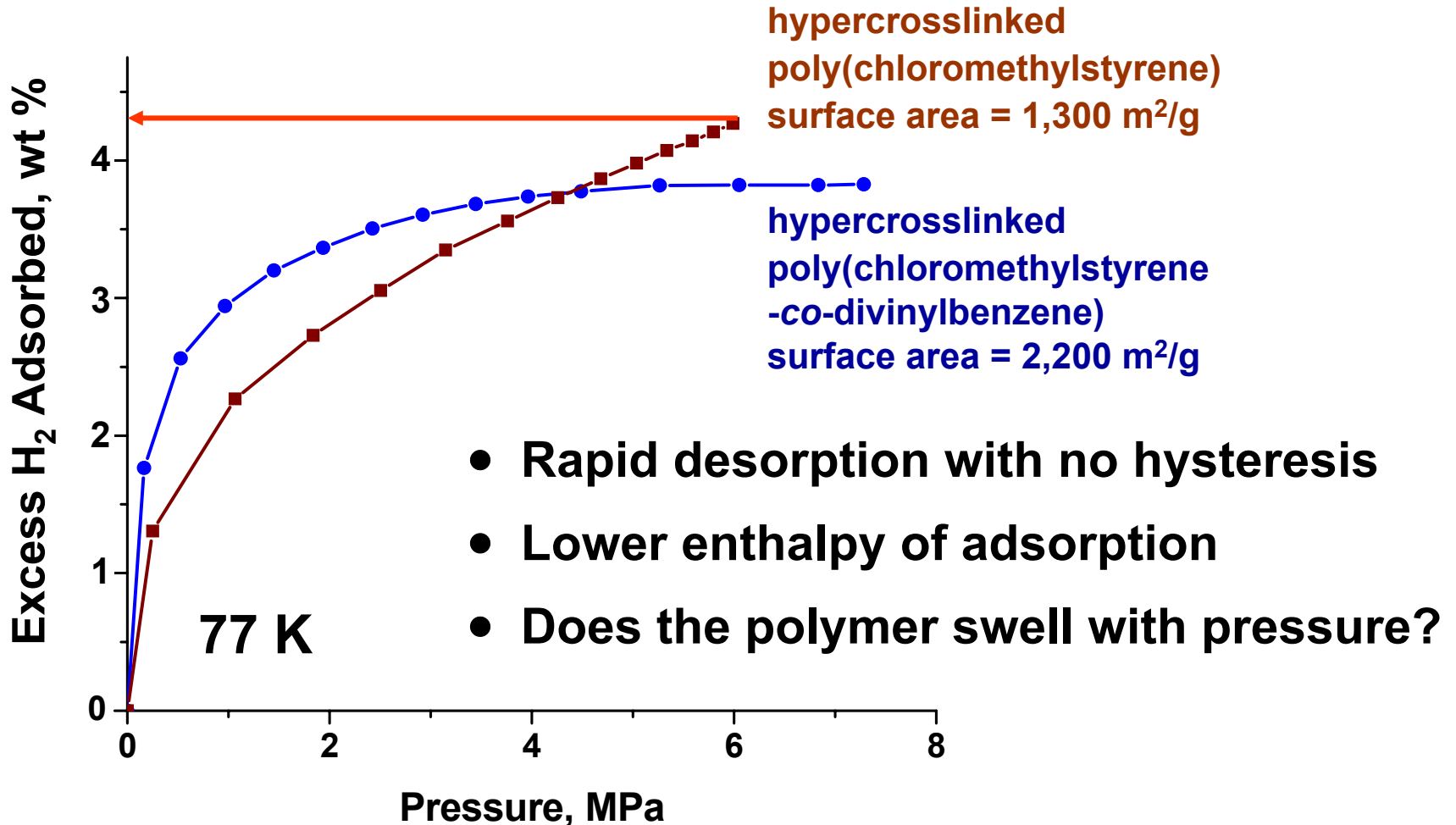
H₂ Adsorption in a Hypercrosslinked Polymer



poly(chloromethylstyrene-co-divinylbenzene)

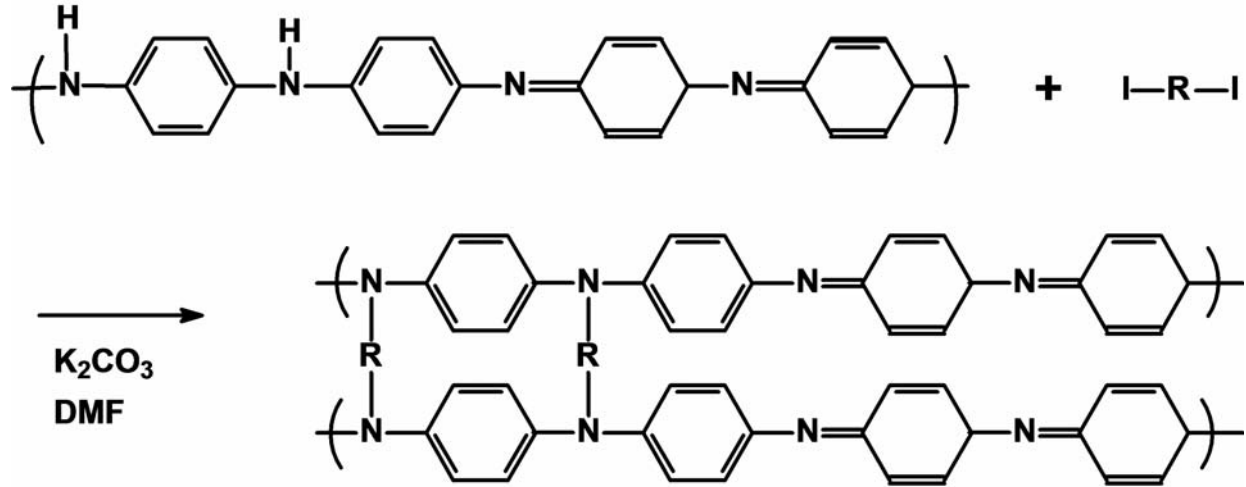


Comparison of Hypercrosslinked Polymers

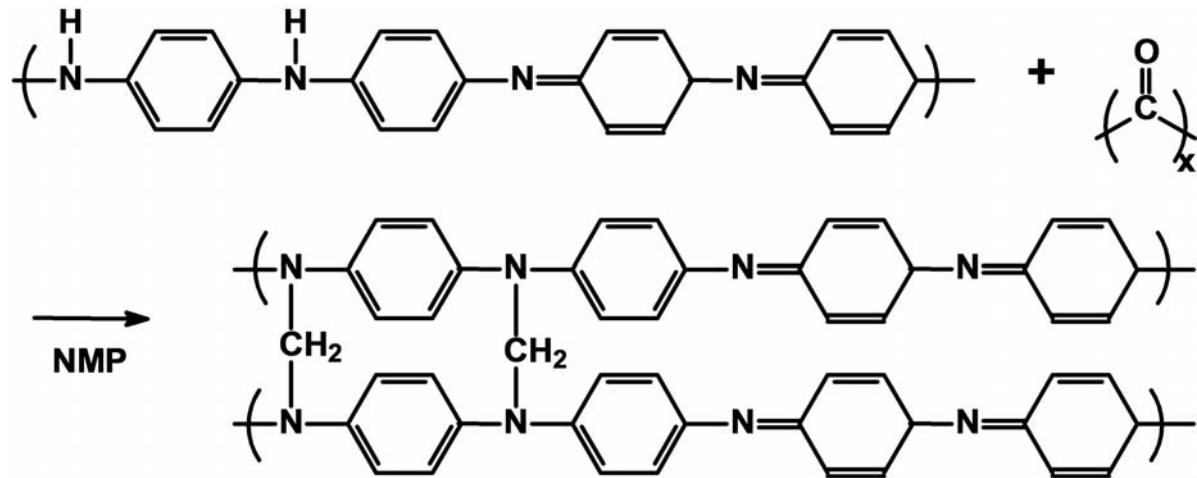


Hypercrosslinked Polyaniline

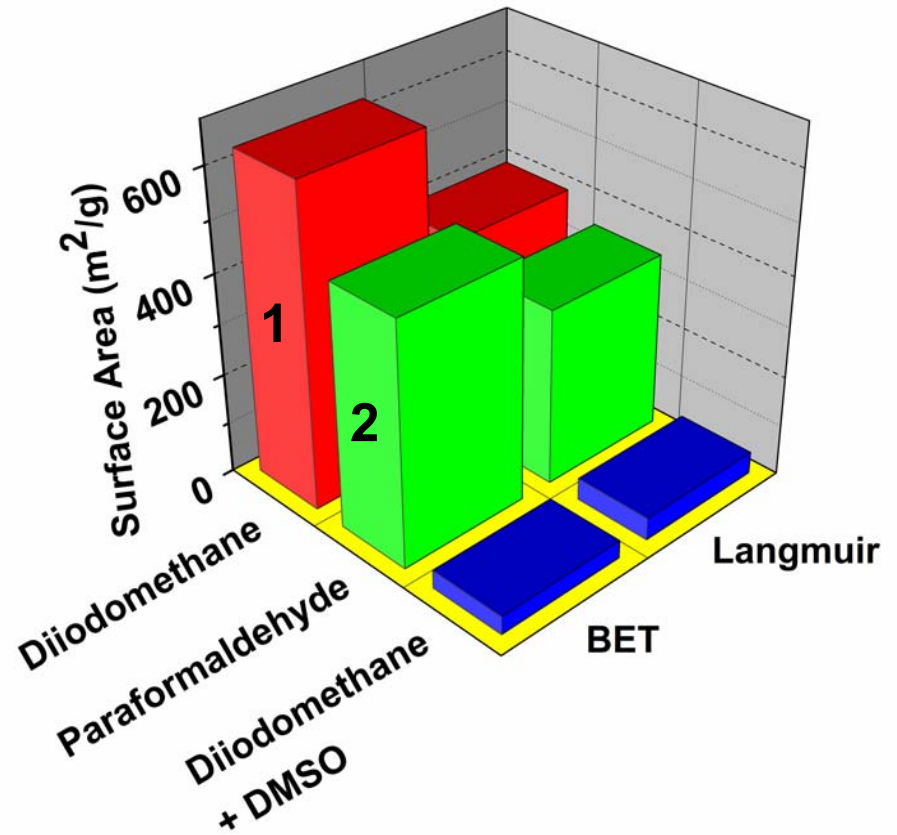
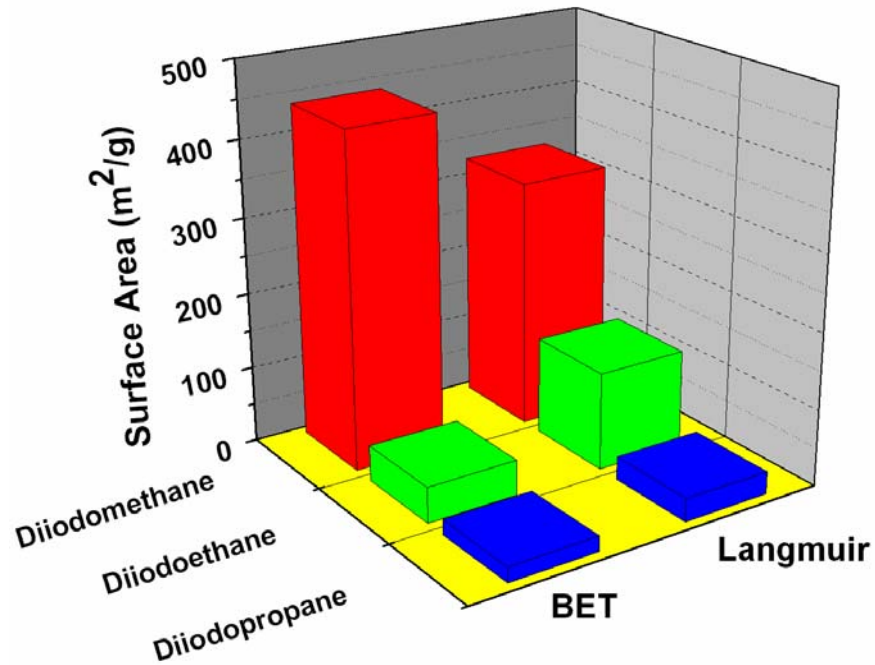
Route 1:



Route 2:

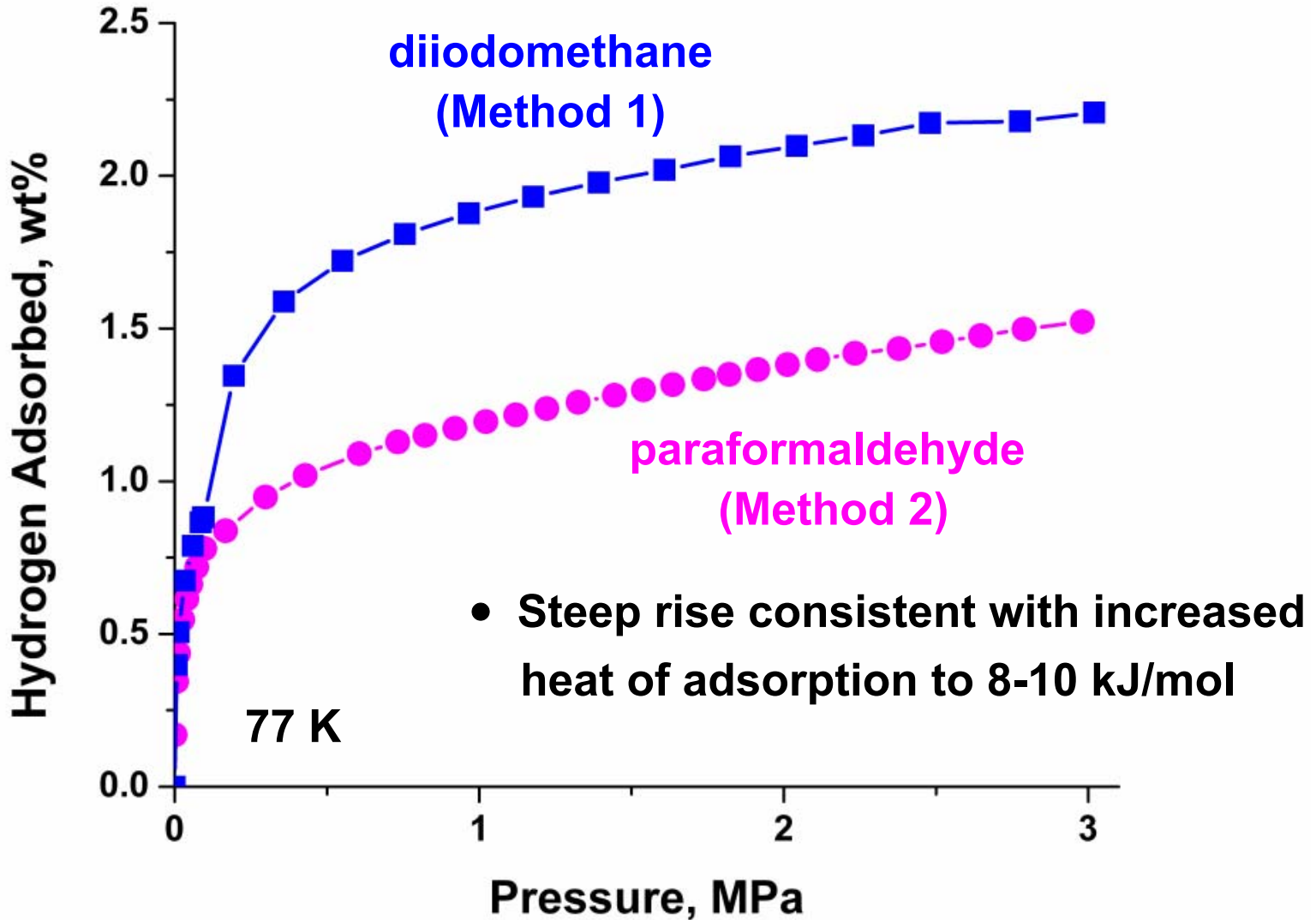


Effect of Crosslinking Route

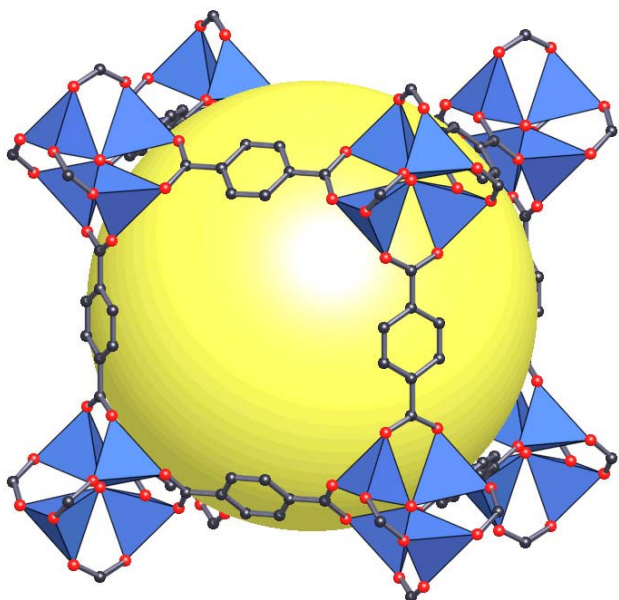


- Crosslinking with methylene units gives highest surface areas

H₂ Uptake in Hypercrosslinked Polyaniline



Variation of N₂ Uptake in Zn₄O(BDC)₃ (MOF-5)

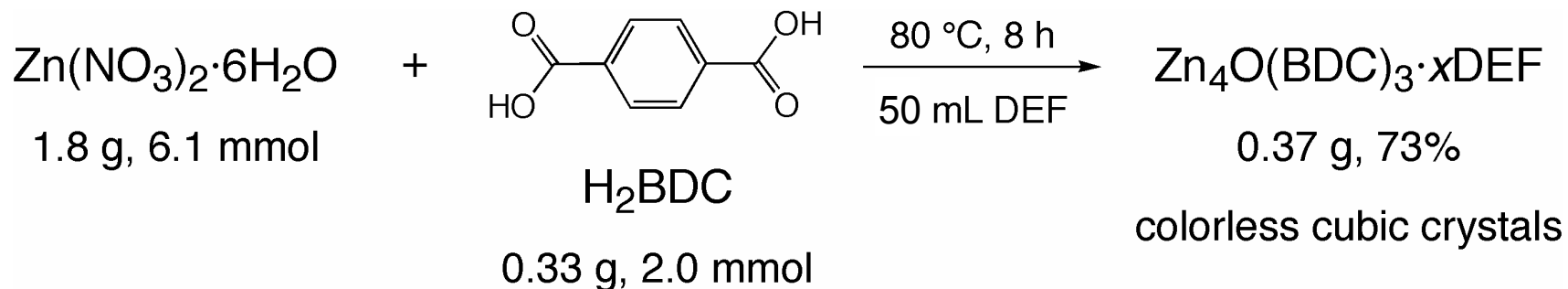


Zn₄O(BDC)₃

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 $\text{Zn}_4\text{O}(\text{BDC})_3$



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

Evacuation procedure

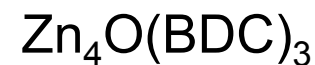
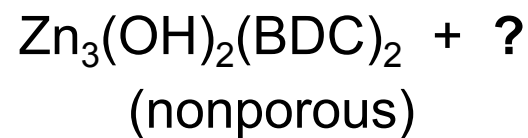
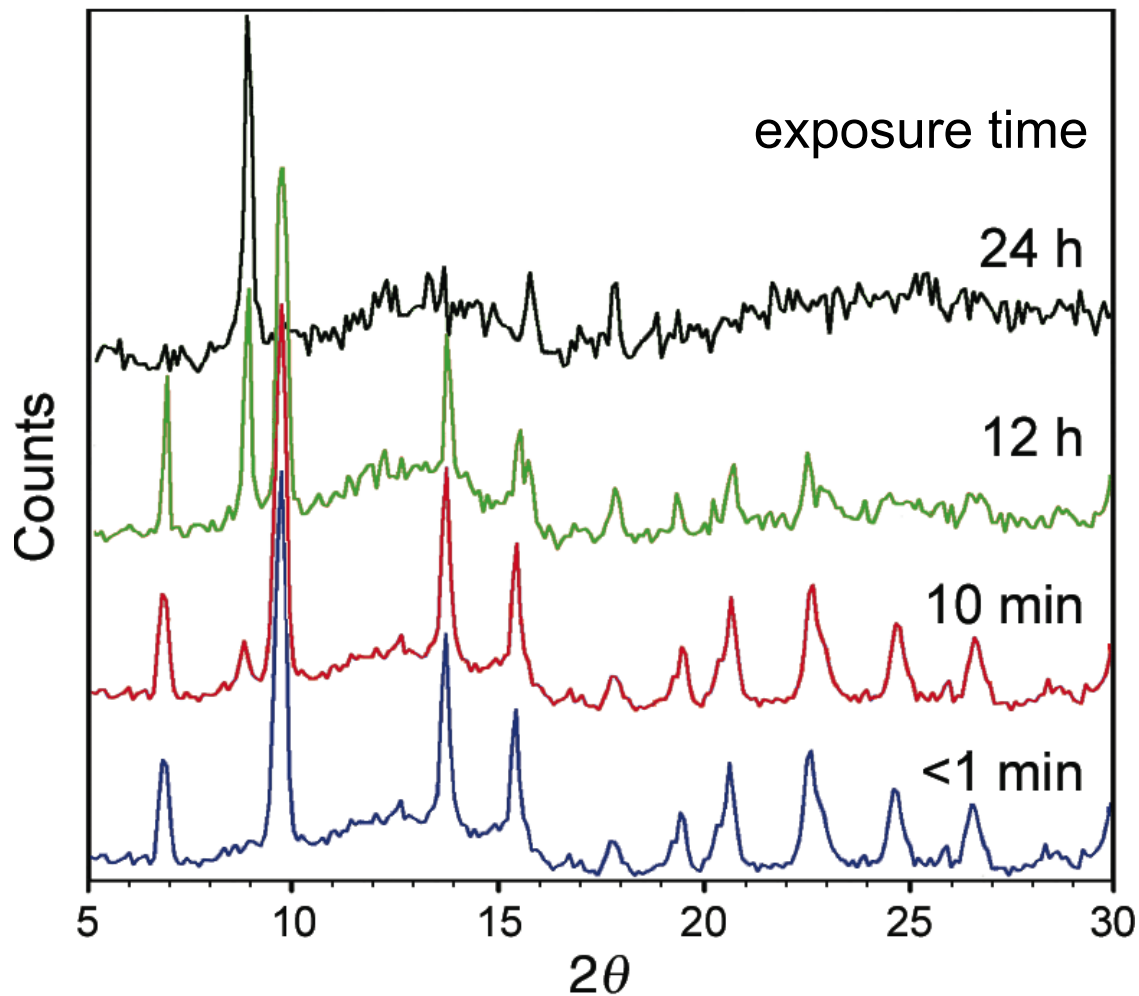
Soak crystals in 10 mL DMF for 8 h (6 times)

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 $\text{Zn}_4\text{O}(\text{BDC})_3$ in Air



Variation of N₂ Uptake in Zn₄O(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

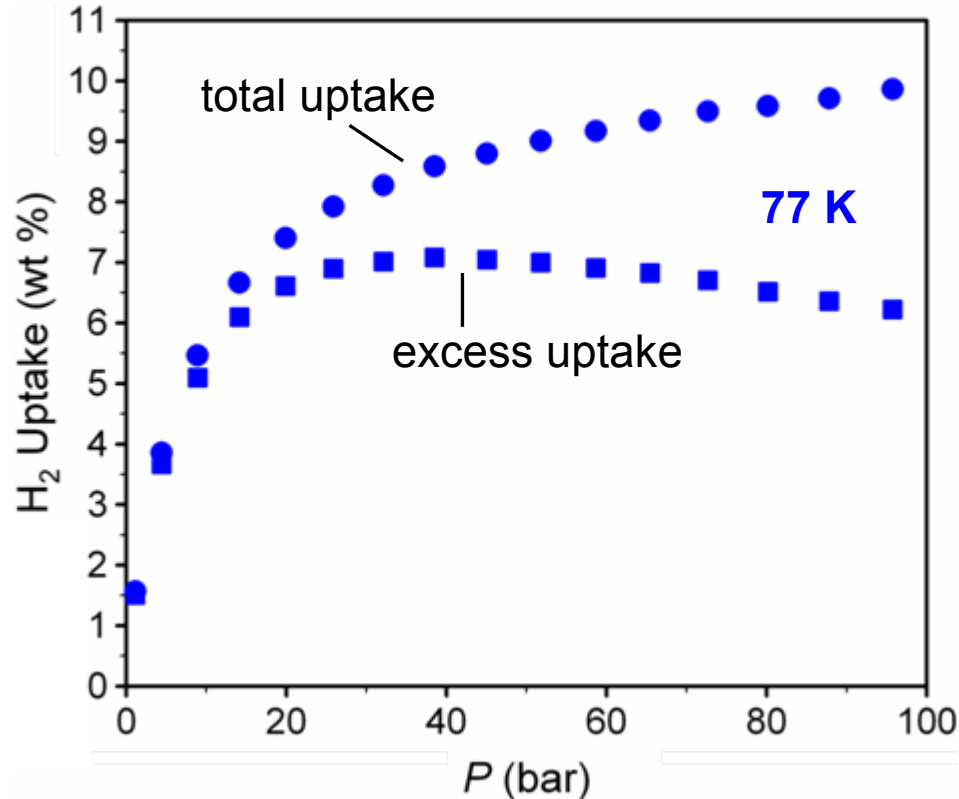
(3) Li, Eddaoudi, O'Keeffe, Yaghi *Nature* **1999**, *402*, 276

(4) Dailly, Vajo, Ahn *J. Phys. Chem.* **2006**, *110*, 1099

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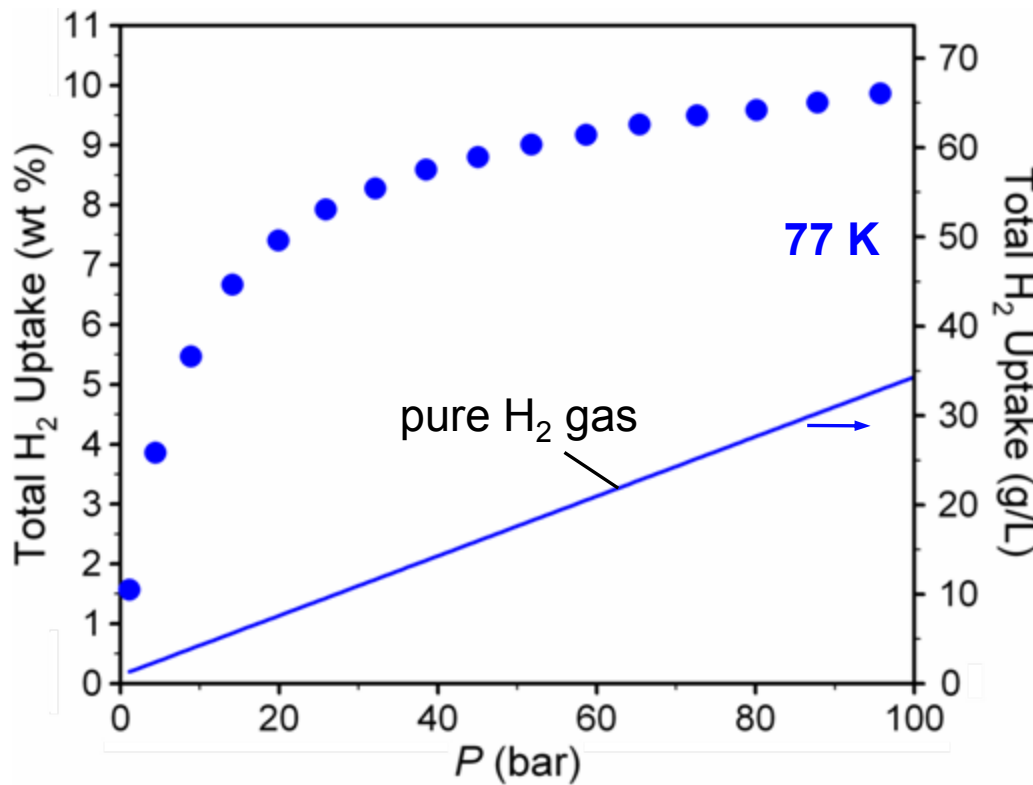
(6) Wong-Foy, Matzger, Yaghi *J. Am. Chem. Soc.* **2006**, *128*, 3494

High-Pressure H₂ Uptake in Zn₄O(BDC)₃



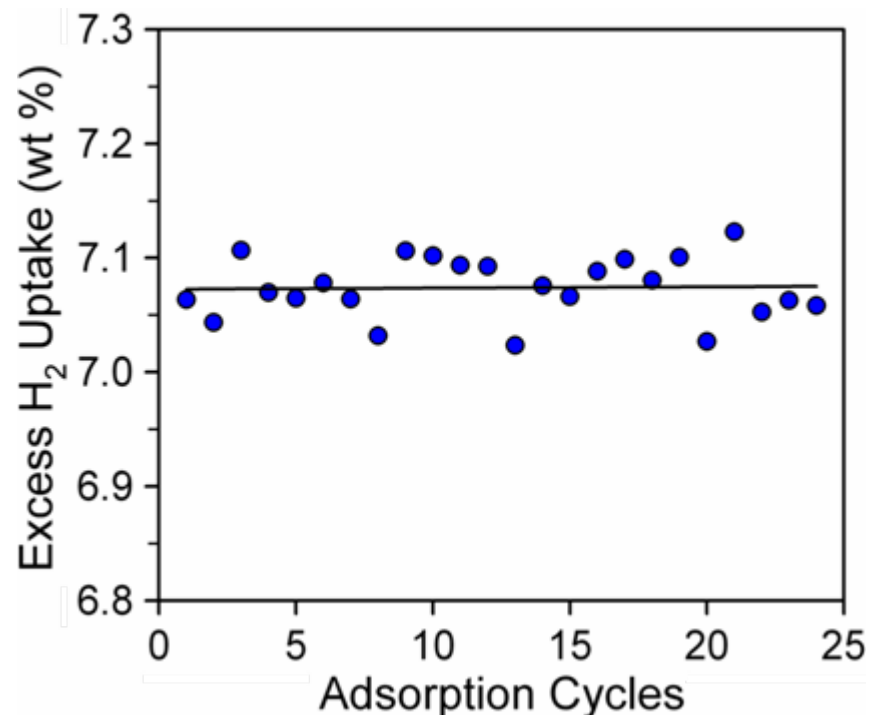
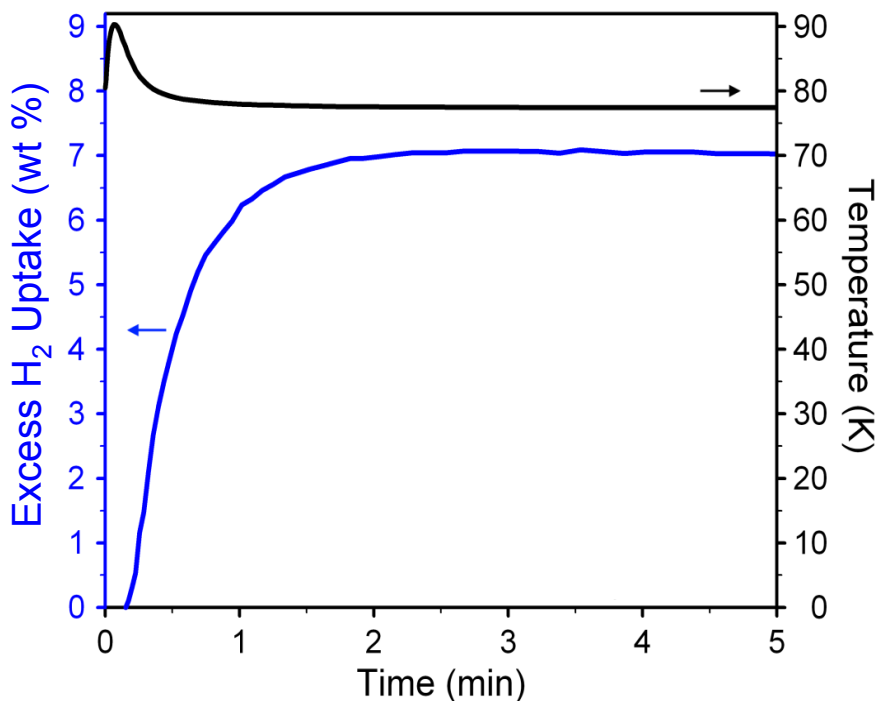
- At 40 bar, a record physisorbed excess capacity of 7.1 wt % is achieved
- Total uptake is the amount of gas contained within the volume of the crystals

High-Pressure H₂ Uptake in Zn₄O(BDC)₃



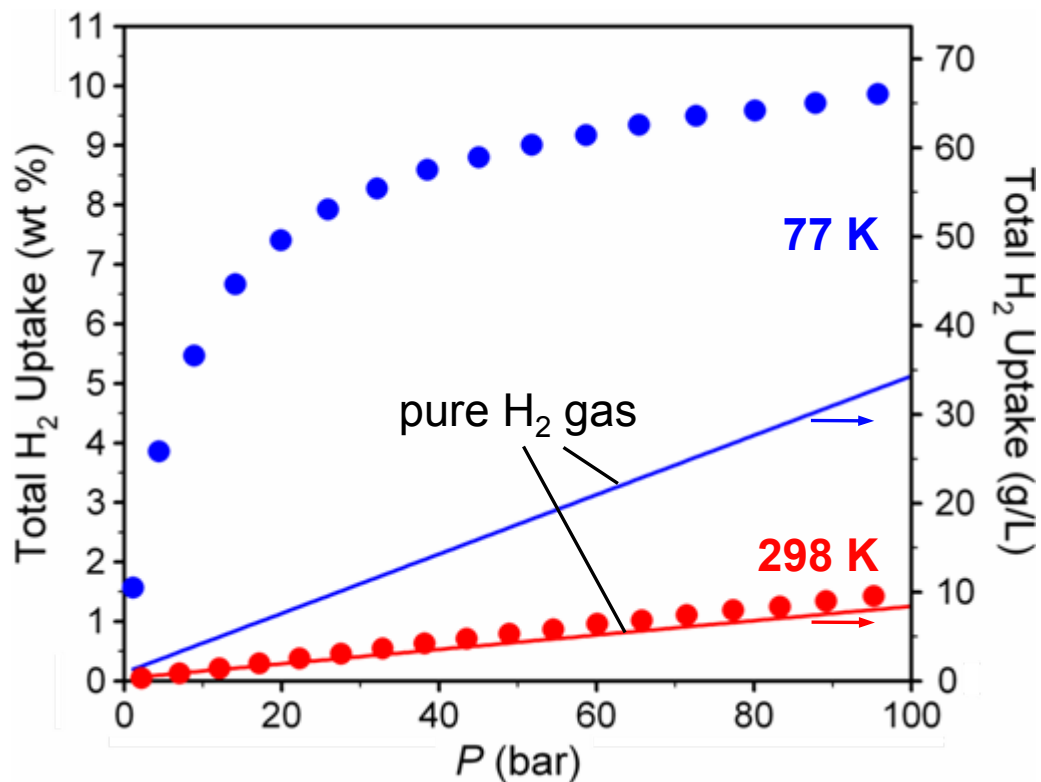
- Knowledge of total uptake permits calculation of the volumetric storage density
- At 100 bar, a record physisorbed storage density of 66 g/L is achieved

Kinetics and Cycling for H₂ Uptake in Zn₄O(BDC)₃



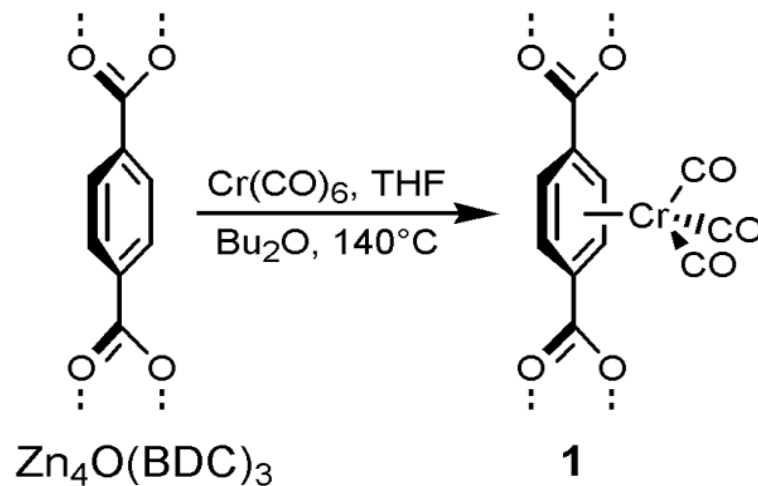
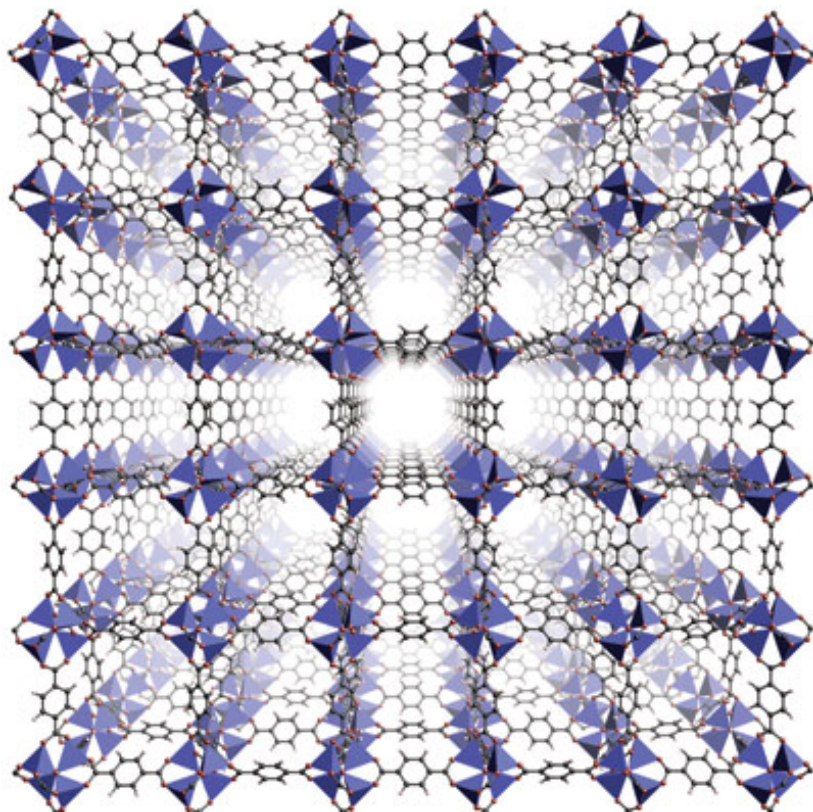
- Results are upon exposure to a manifold of H₂ gas at 45 bar and 298 K
- No detectable loss in capacity or kinetics after 24 adsorption-desorption cycles

Room-Temperature H₂ Uptake in Zn₄O(BDC)₃



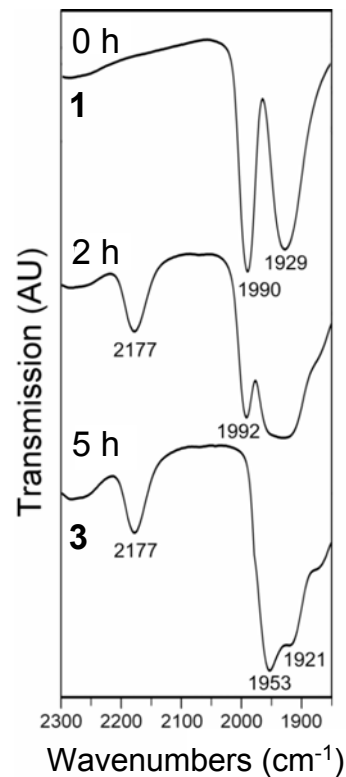
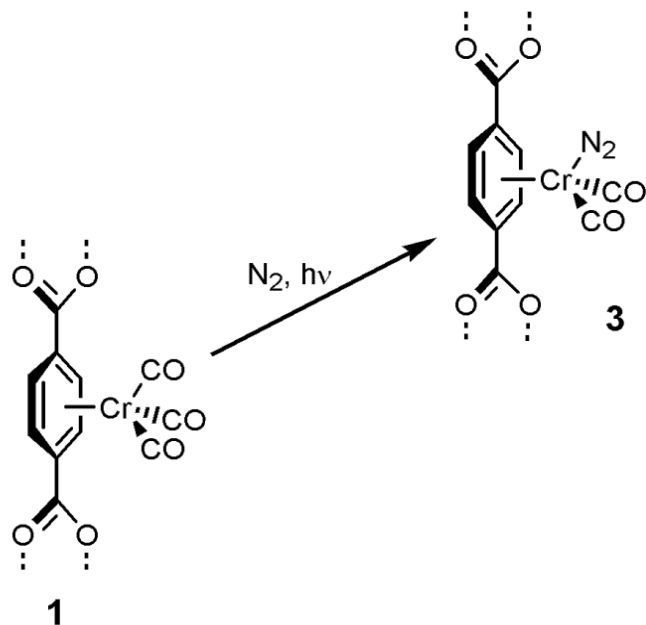
- At 298 K, framework offers little improvement over density of pure H₂ gas
- Due to very weak interaction of H₂ with the framework ($\Delta H_{\text{ads}} \approx 5$ kJ/mol)

Coating the Surfaces with Cr(CO)₃ Units



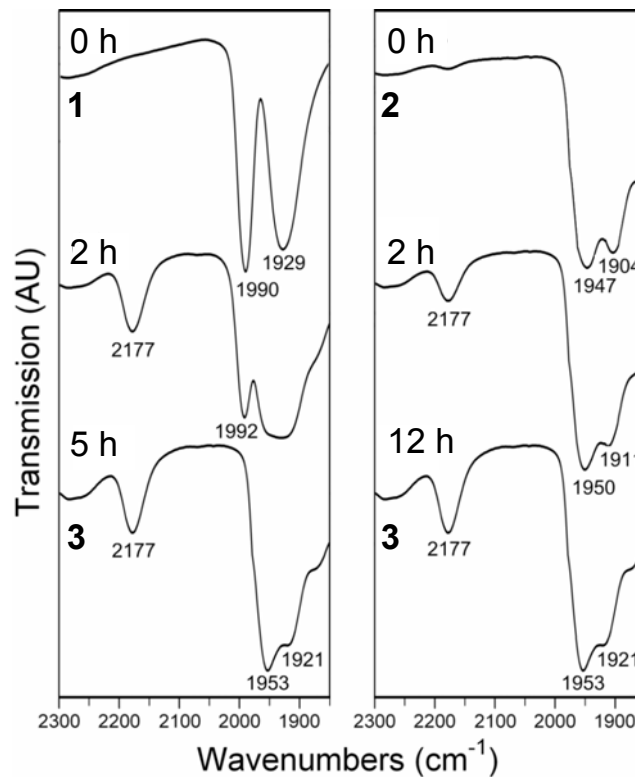
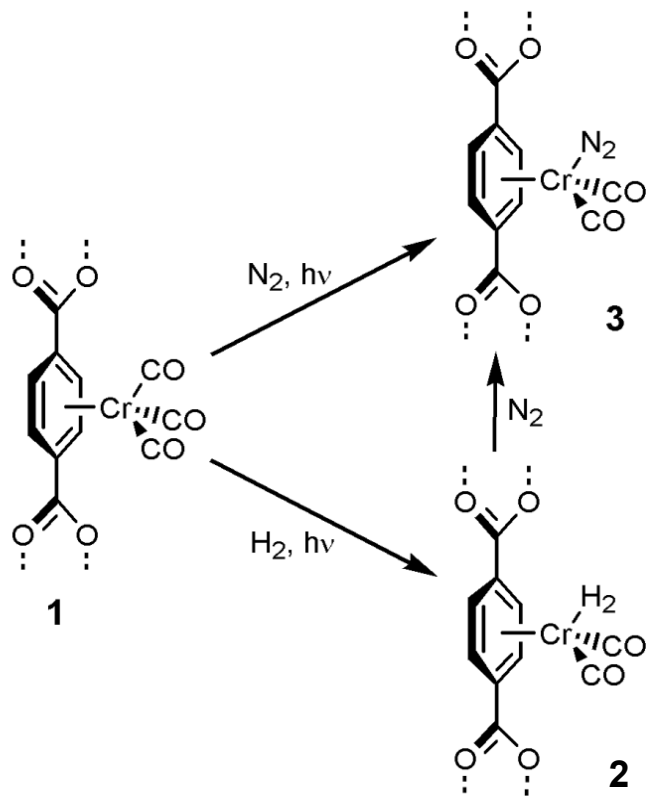
- Infrared spectrum matches that observed for molecular analogue
- Elemental analysis and NMR spectroscopy indicate attachment to all rings

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

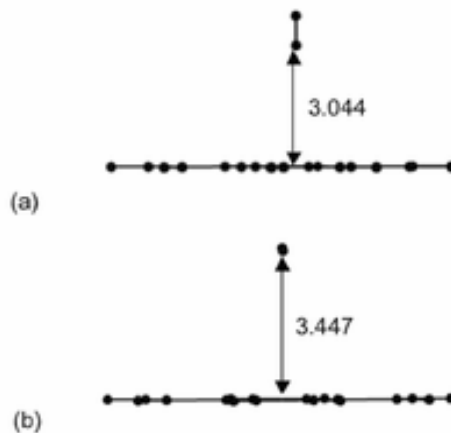
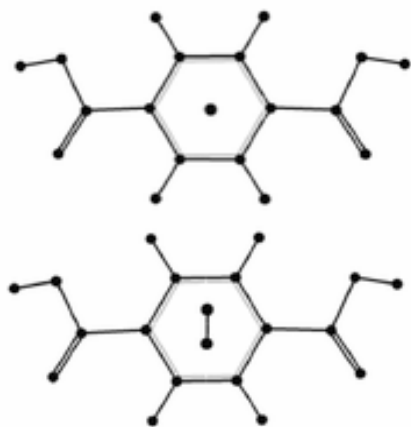
Strong H₂ Binding at Cr⁰ Centers



- Infrared spectra match those observed for molecular analogues
- Cr⁰-H₂ complex in compound **2** is stable indefinitely at room temperature!

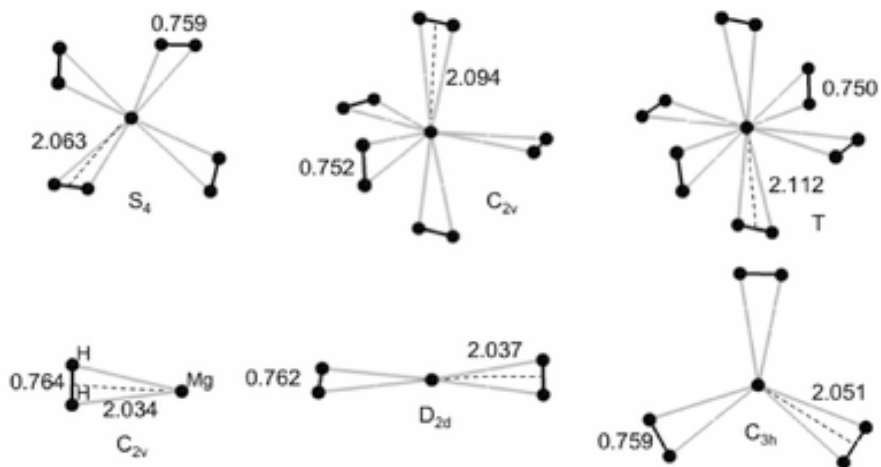
Range of H₂ Binding Interactions

dispersion < electrostatics < charge-transfer



H₂BDC-H₂
van der Waals
~ 3-5 kJ/mol

Mg²⁺-H₂
electrostatic
~ 45 kJ/mol

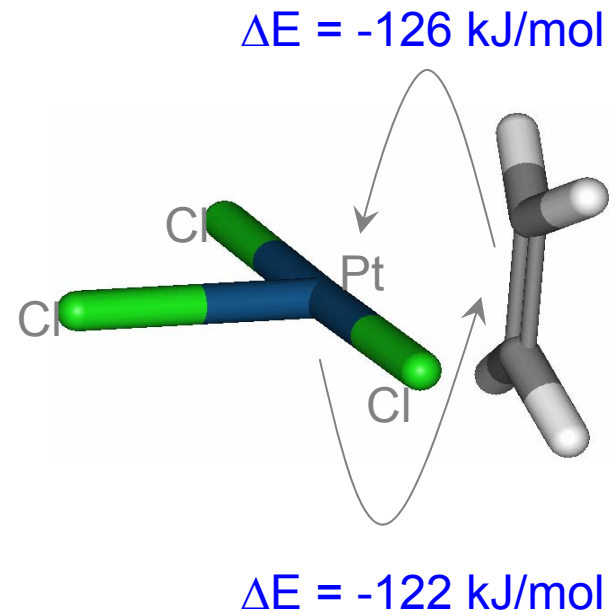


Understanding H₂ Binding

A New Analysis Method

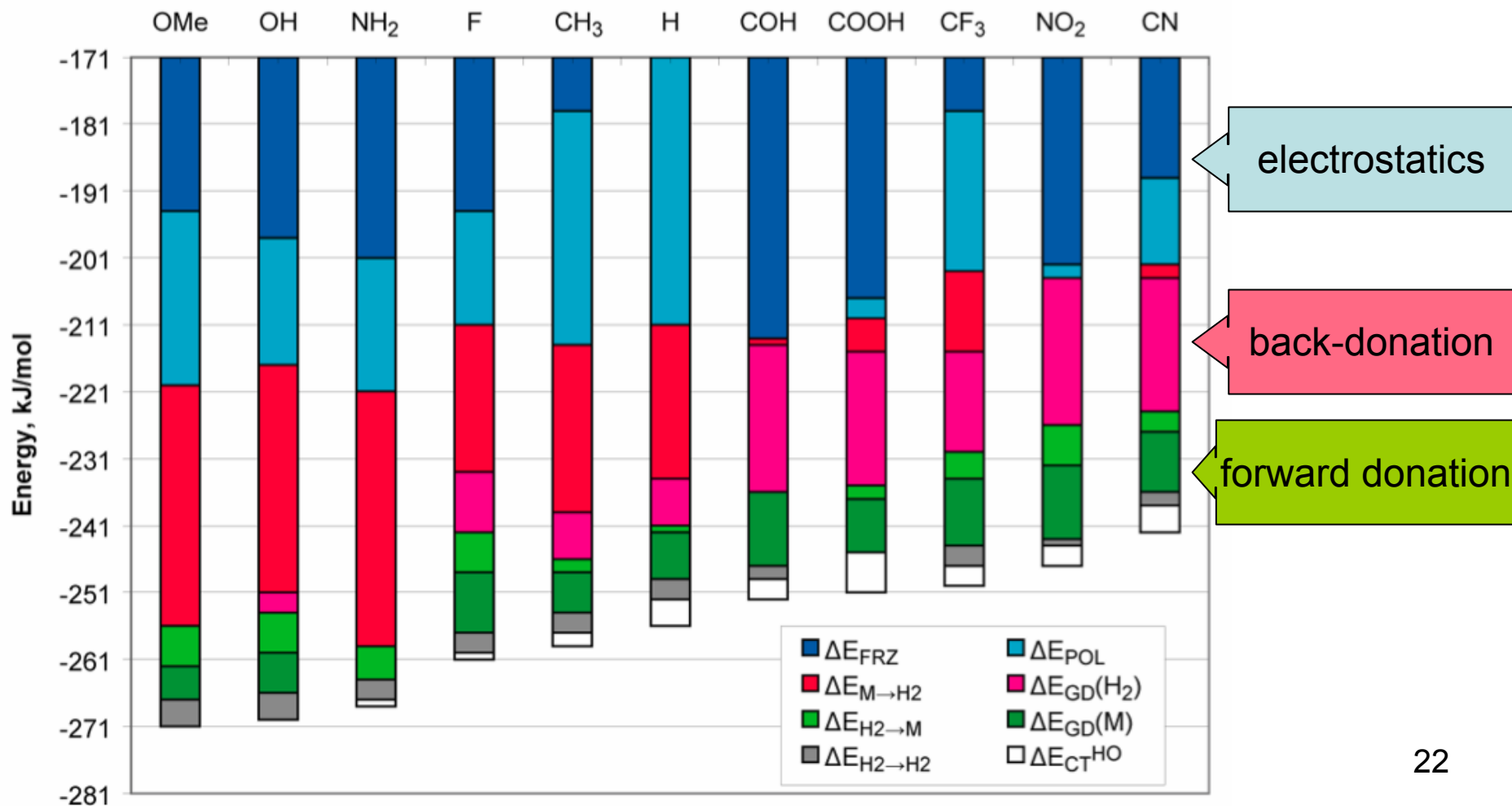
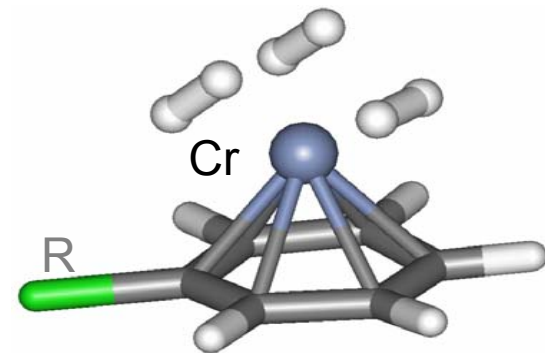
Decompose interaction energies rigorously into:

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

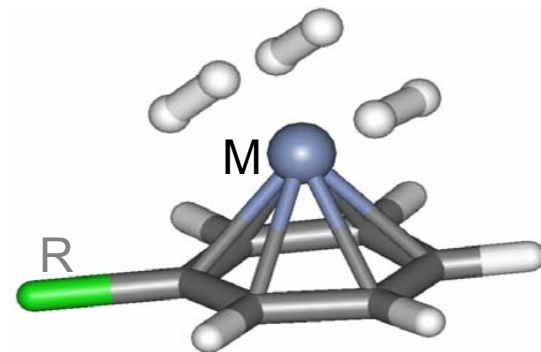


Relative Effect of Substituent

Metal chosen as Cr⁰

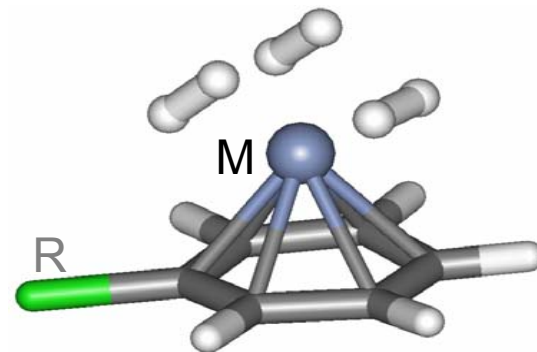


Effect of Substituent (R)



- Electron-donating groups enhance binding, while electron-withdrawing groups reduce binding
 - Tunability is 7% of binding
 - Energies are for three bound H₂ molecules
- Correlates with back-donation, electrostatics
- Quantitative information; qualitative insight
 - BDC²⁻ 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:

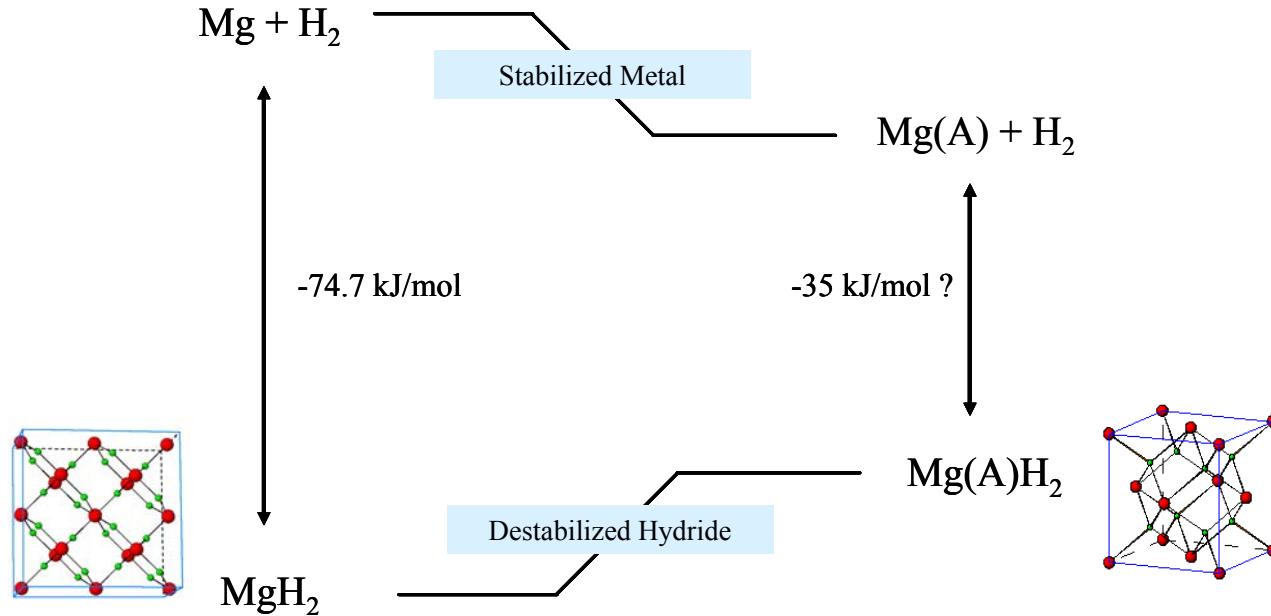
$(C_6H_6)Cr(H_2)_3$ binding per H_2 of 68 kJ/mol

$(C_6H_6)Ti(H_2)_4$ 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



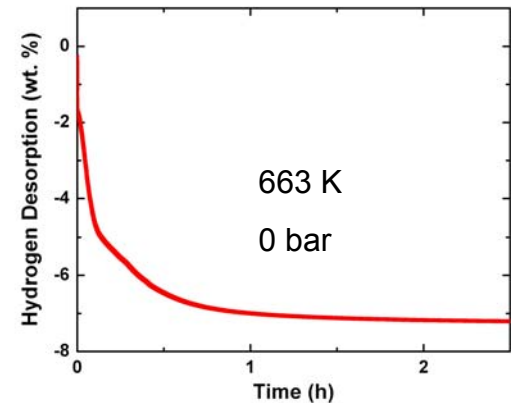
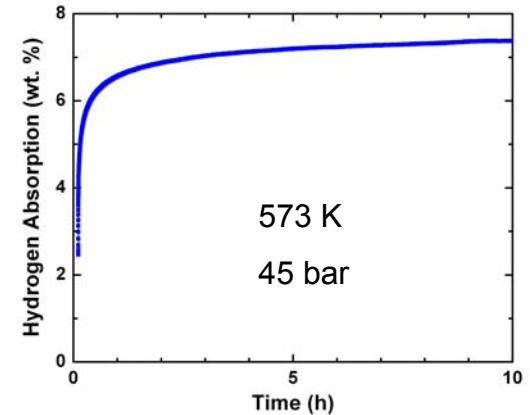
- Attempts at alloying of Mg in order to reduce ΔH
- Success in partial substitution to form $\text{Mg}_{1-x}\text{A}_x$ (A = Mn, Fe, Ni)
- Some increases in plateau pressures, but poor kinetics
- Attempts to substitute Na and Li for Mg are underway

Attempts to Generate $\text{MgH}_{2-x}\text{F}_x$ Solid Solutions

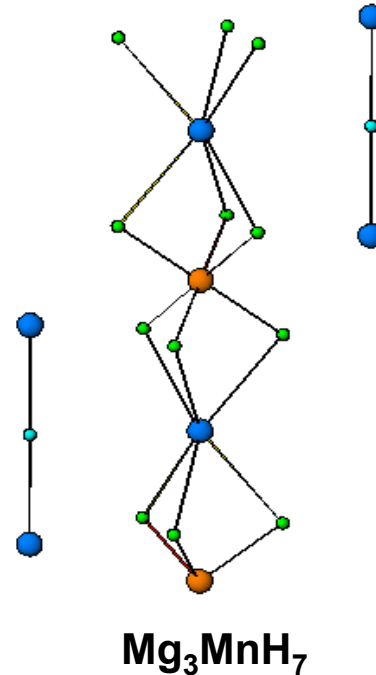
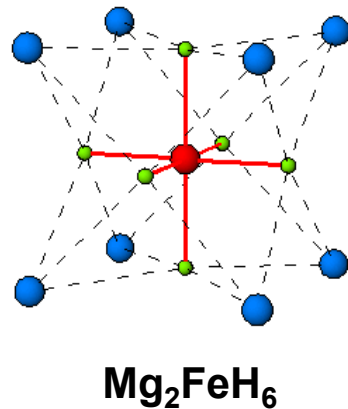
Preliminary results, not yet reproduced:

- 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?



- 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., $\text{CaH}_{2-x}\text{F}_x$ known for all x)
- Small fluoride additions reported to enhance reactivity of Mg_2Ni