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: 70%

Budget

- Total funding expected: $2.9M
  - $1.8M from DOE to UC Berkeley
  - $600k from DOE to LBNL
  - $500k in cost-sharing
- Funding FY08: $600k
- Funding FY09: $567k

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)

Metal/metal hydride nanocrystals (Alivisatos)

Synthesis of nanostructured boron nitrides (Zettl)

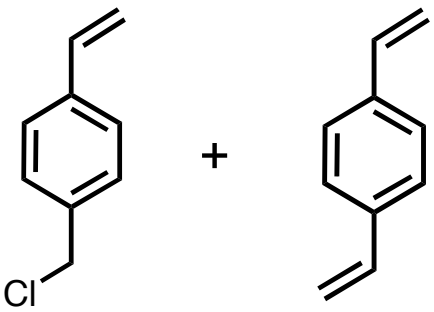
Theory for boron nitride materials (Cohen and Louie)

Part I* (EERE)

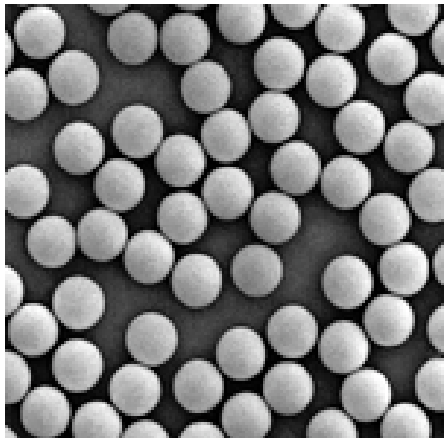
Part II (BES)

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

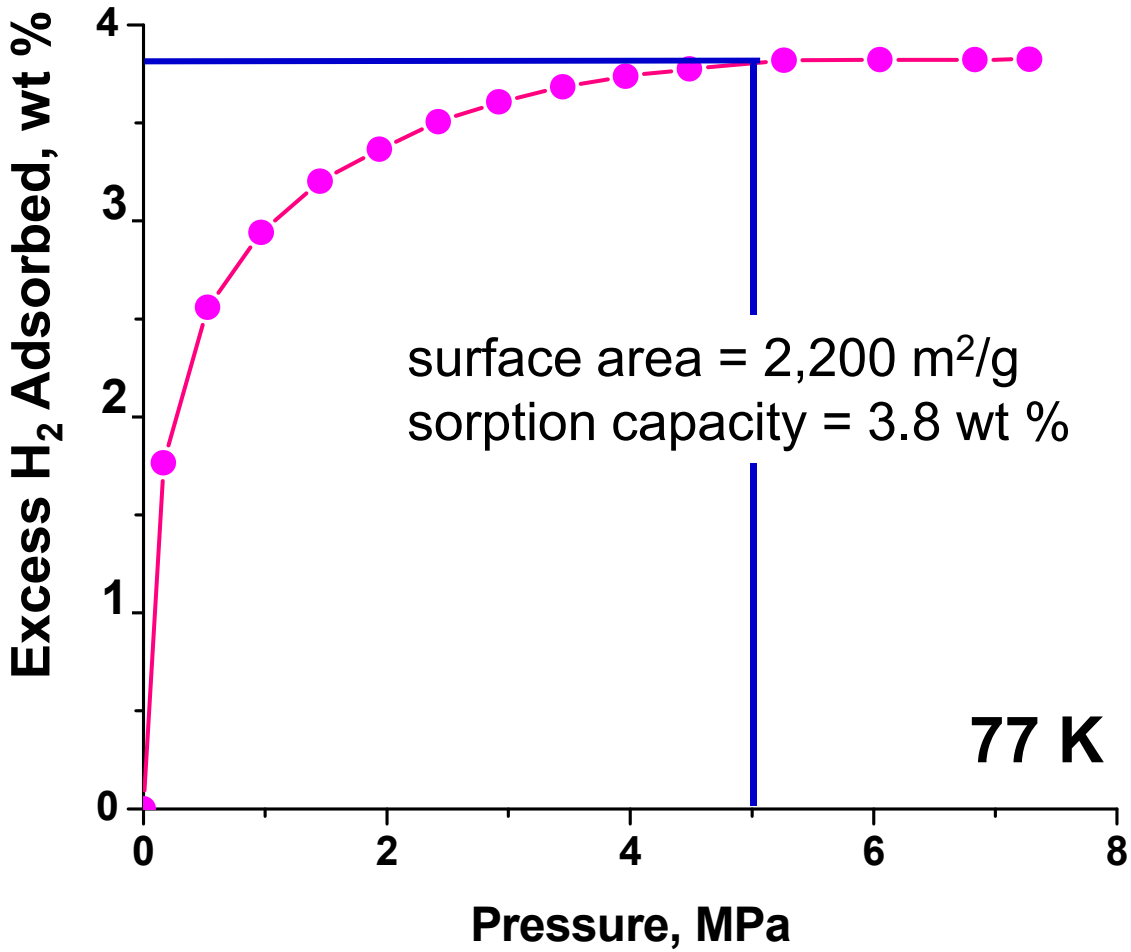
H_2 Adsorption in a Hypercrosslinked Polymer



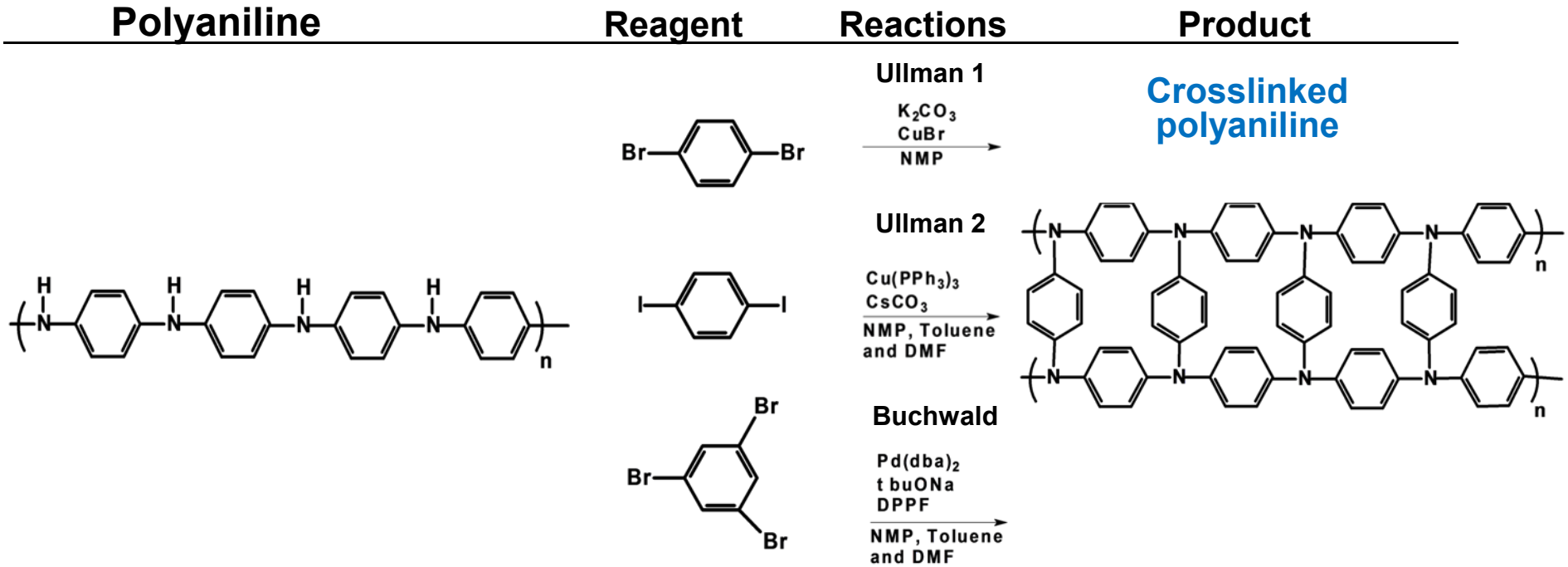
97.5% 2.5%



poly(chloromethylstyrene-*co*-divinylbenzene)

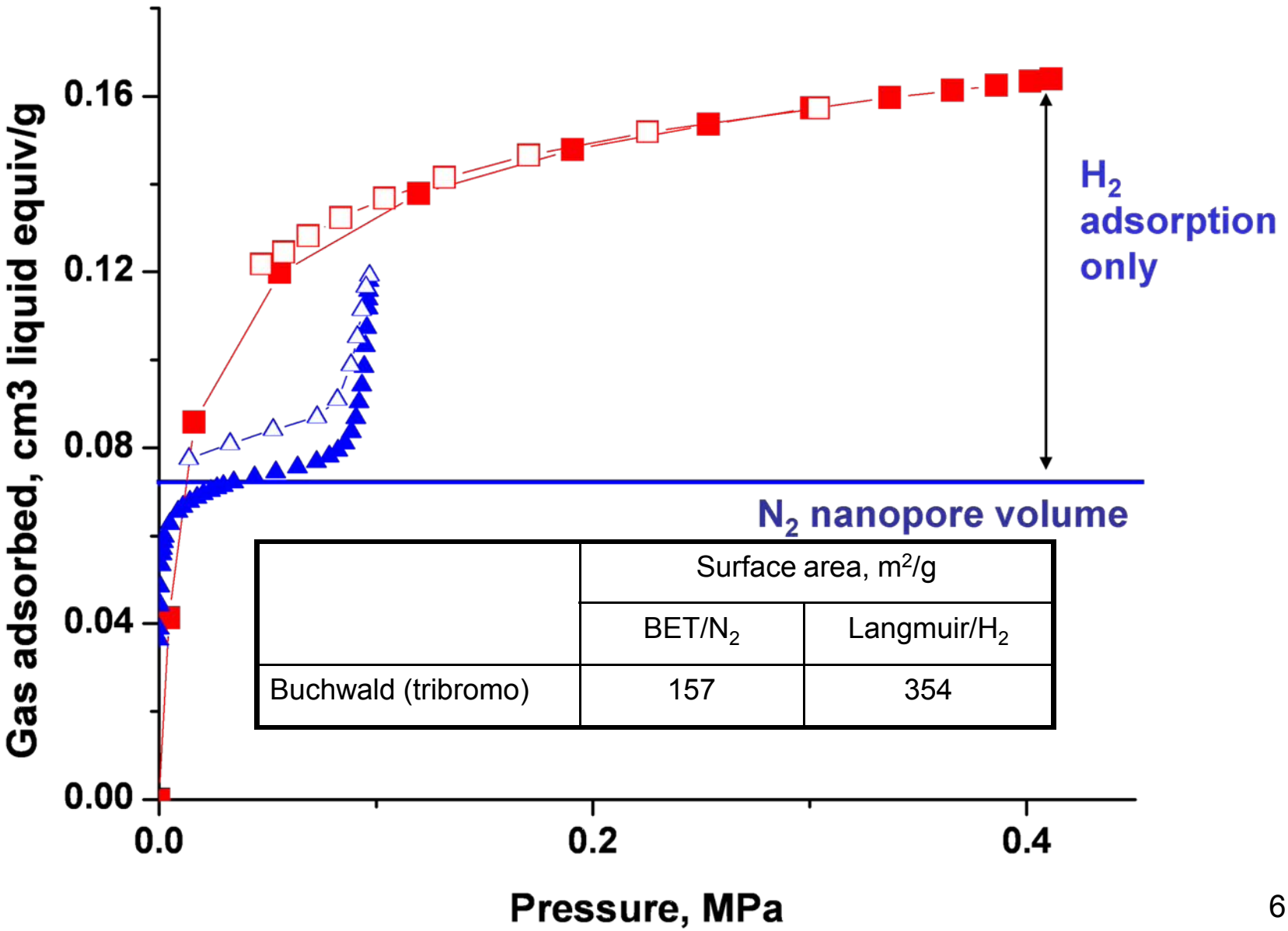


Hypercrosslinked Polyaniline



Reaction	Surf. area, m^2/g Langmuir	Pore volume, mL/g Total	Nano
Ullman 1 (dibromo)	156	0.13	0.03
Ullman 2 (diiodo)	96	0.04	0.01
Buchwald (diiodo)	343	0.25	0.13
Buchwald (tribromo)	368	0.25	0.11

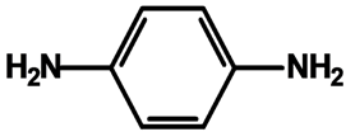
Size Exclusion of Gases in Ultrananopores

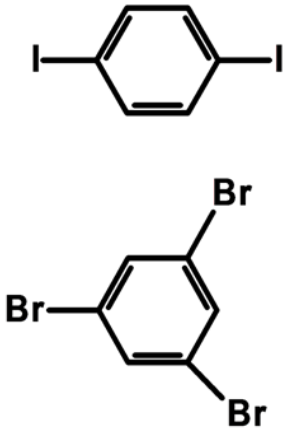


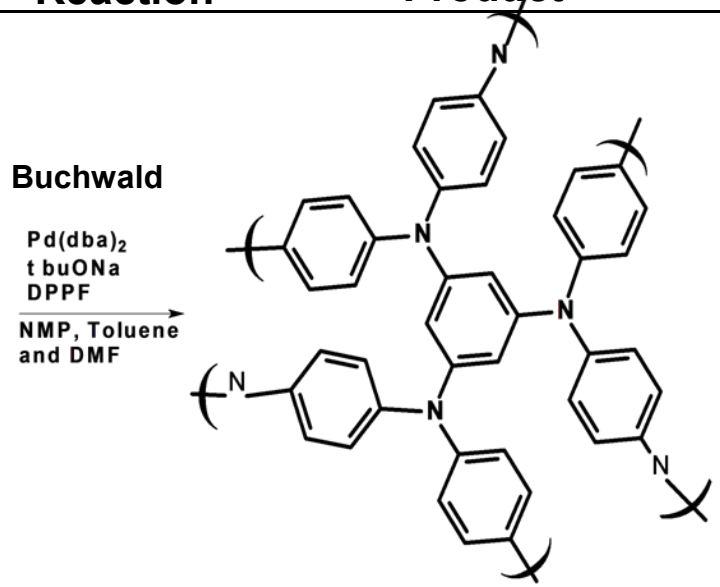
	Surface area, m^2/g	
	BET/N_2	Langmuir/H_2
Buchwald (tribromo)	157	354

Nanoporous Nitrogen-Containing Polymers

1,4-Diaminobenzene **Reagent** **Reaction** **Product**



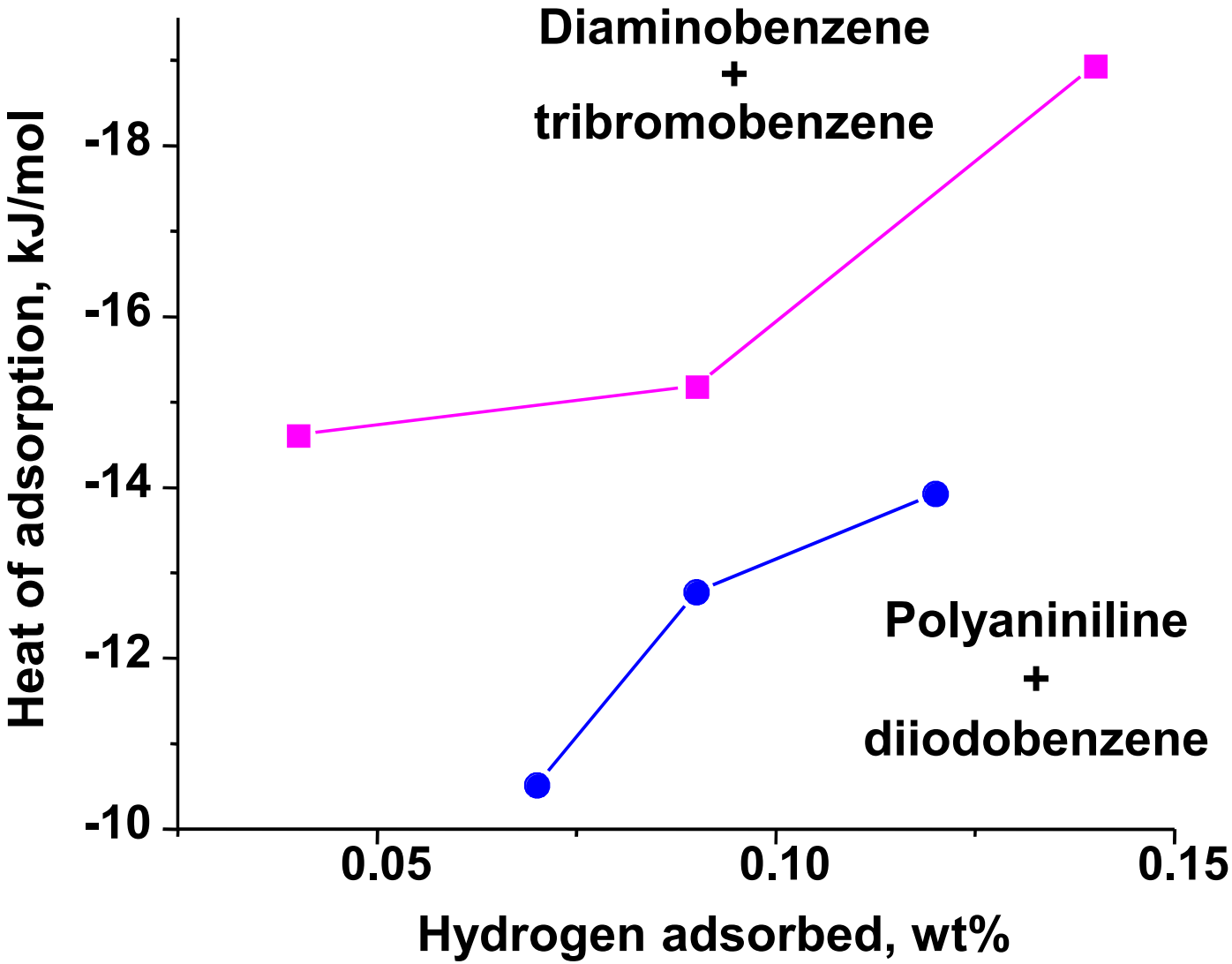




Crosslinked aromatic rings

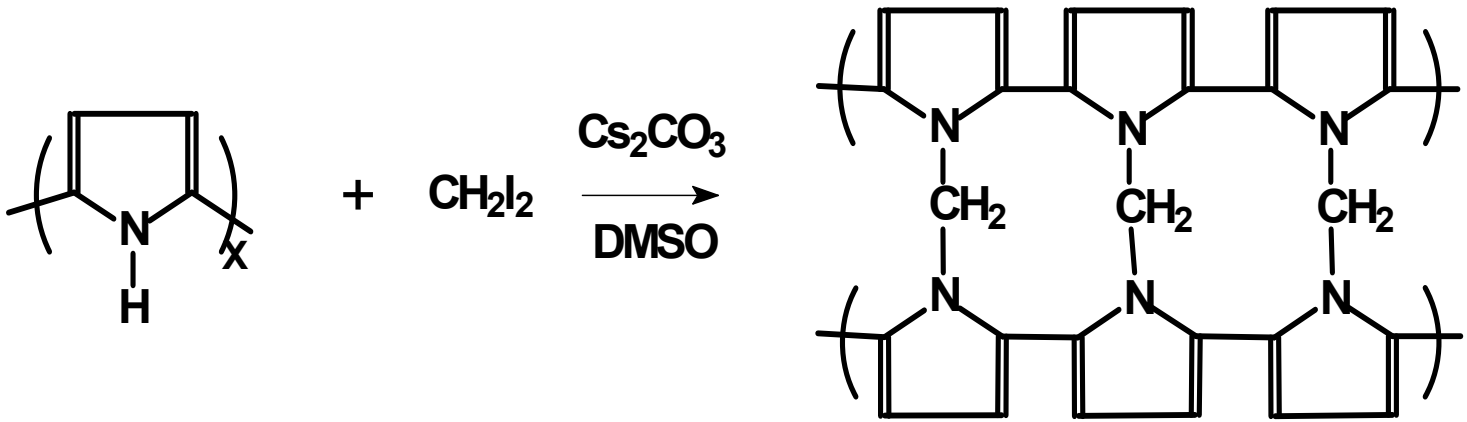
Reagent	Surf. area, m^2/g Langmuir	Pore volume, mL/g		
		Total	Nano	Ultra
Diiodobenzene	192	0.01	0.01	0.09
Tribromobenzene	384	0.13	0.11	0.06

Stronger H_2 Adsorption

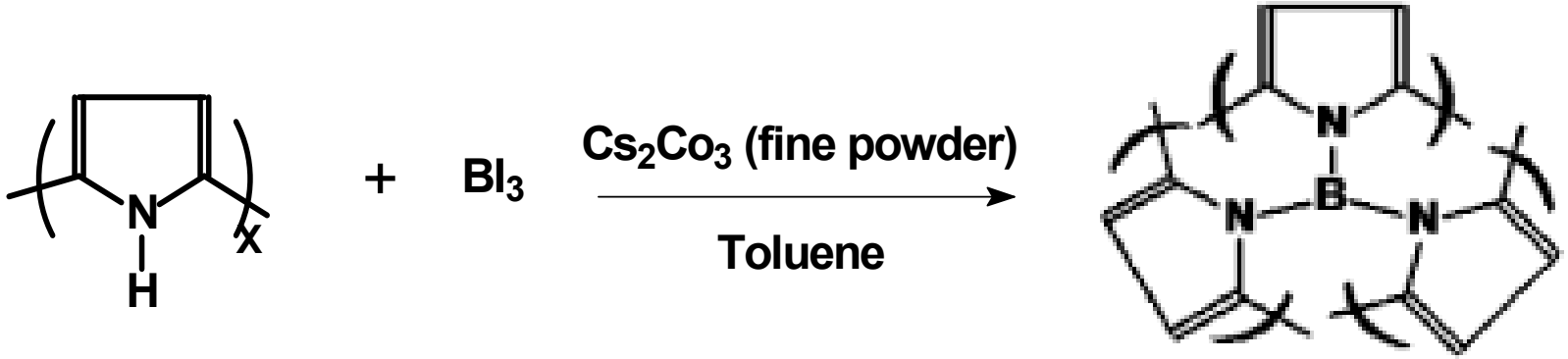


Hypercrosslinked Polypyrrole

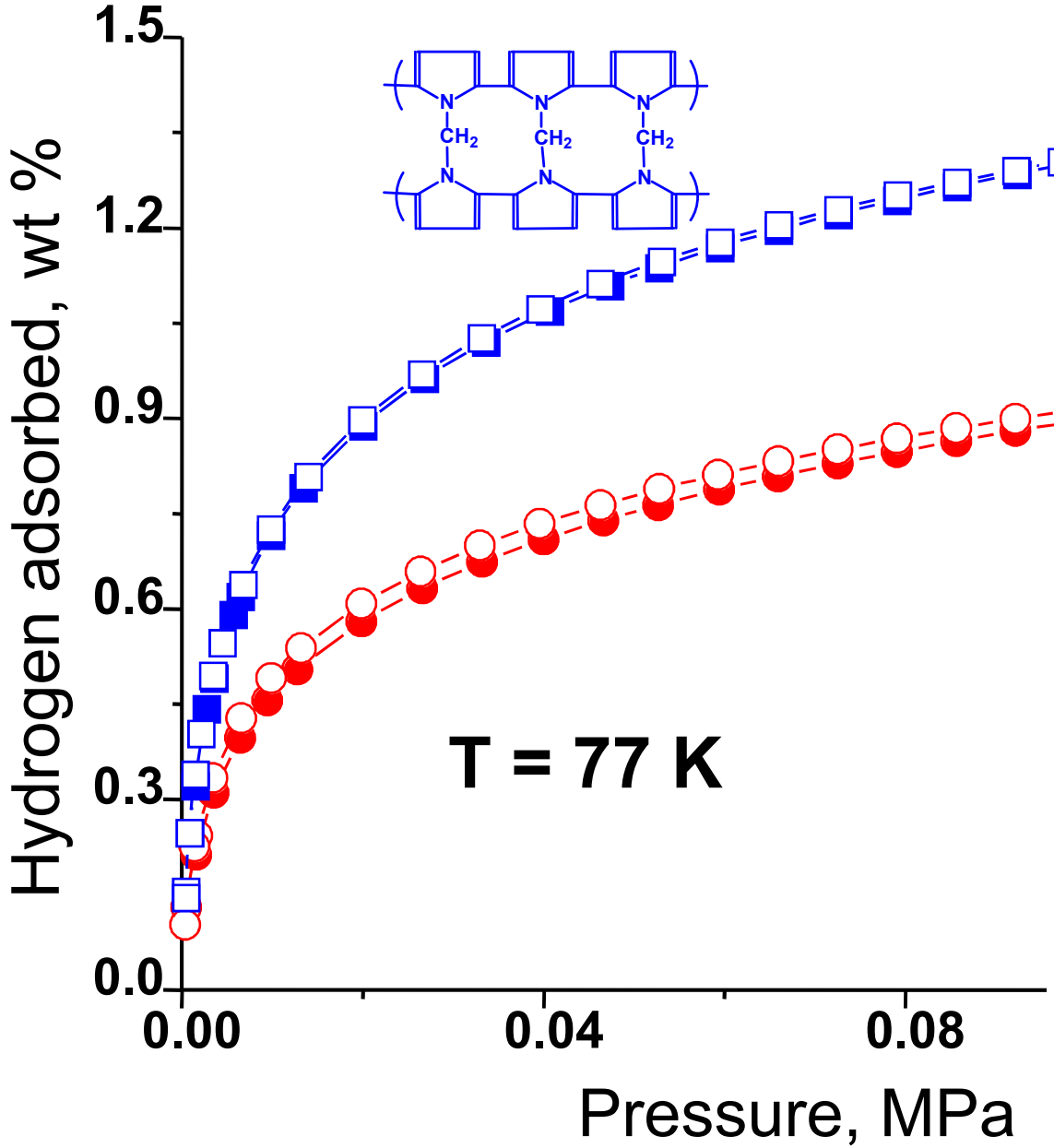
Crosslinking with alkyl groups:

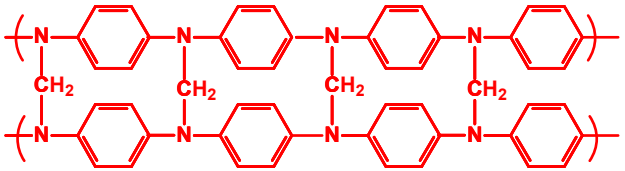


Crosslinking with boron:



Increased H_2 Adsorption Capacity

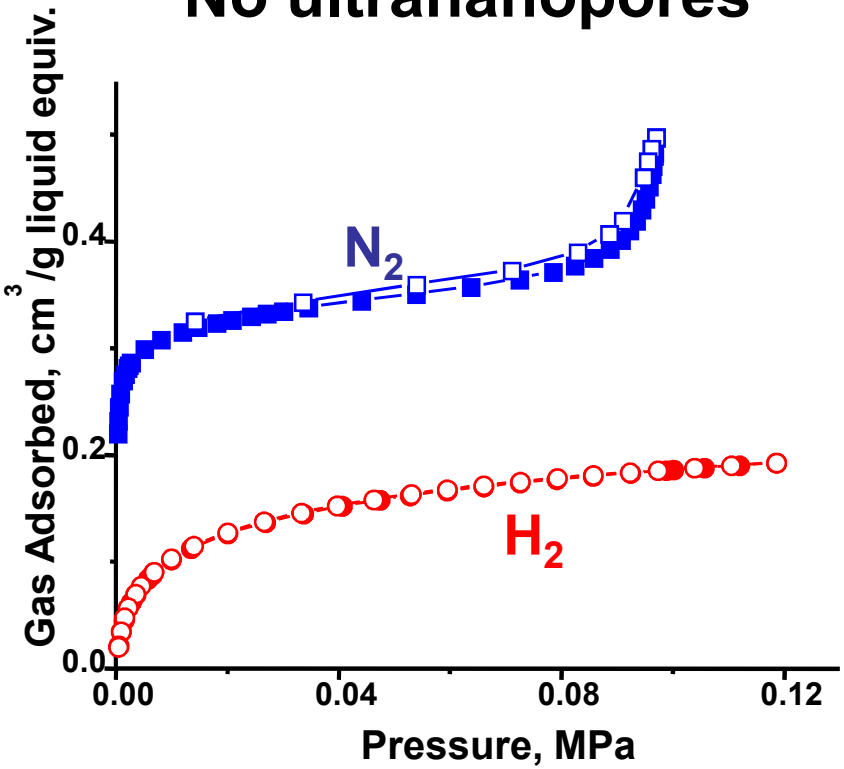




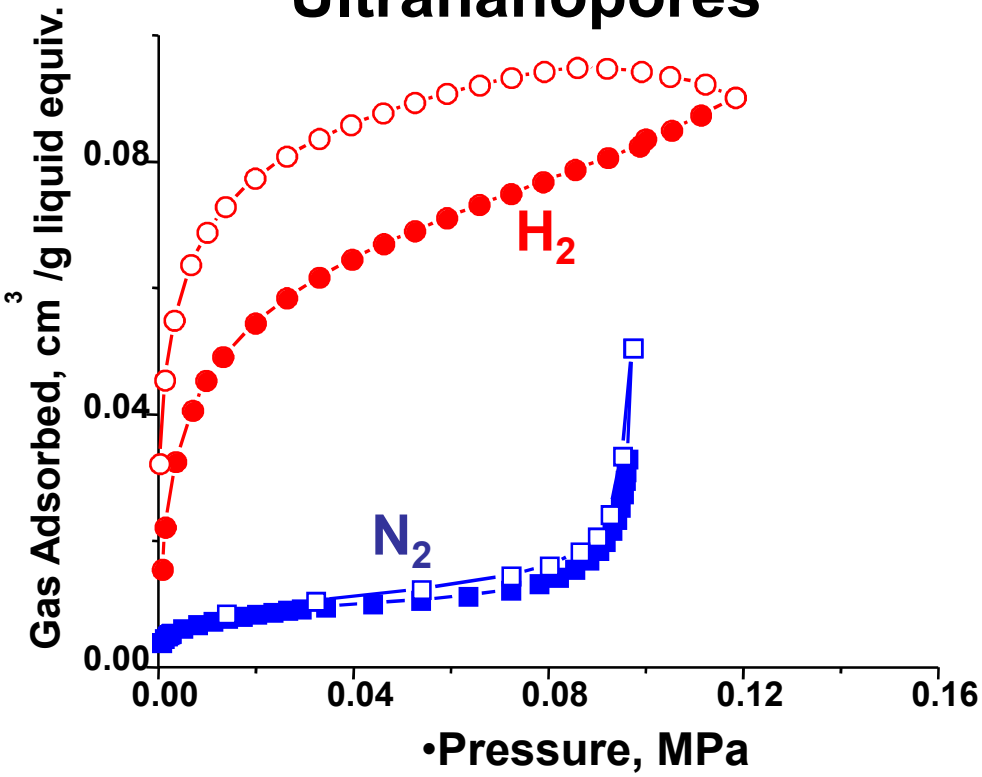
	Surface Area	
	BET/N_2	Langmuir/H_2
Ppy	738 m^2/g	558 m^2/g
Pani	630 m^2/g	400 m^2/g

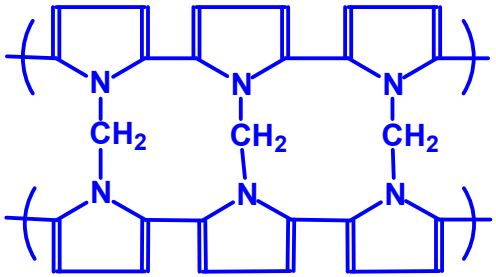
Size Exclusion of Gases in Ultrananopores

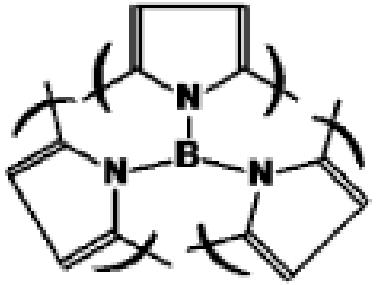
No ultrananopores



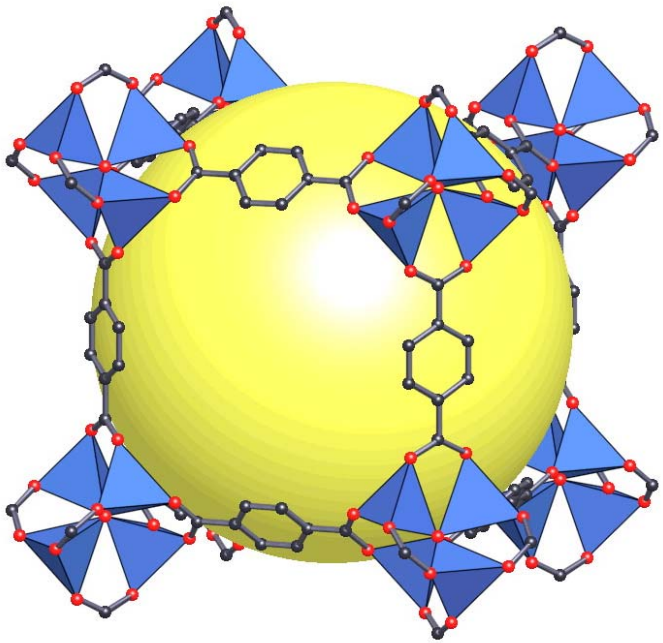
Ultrananopores



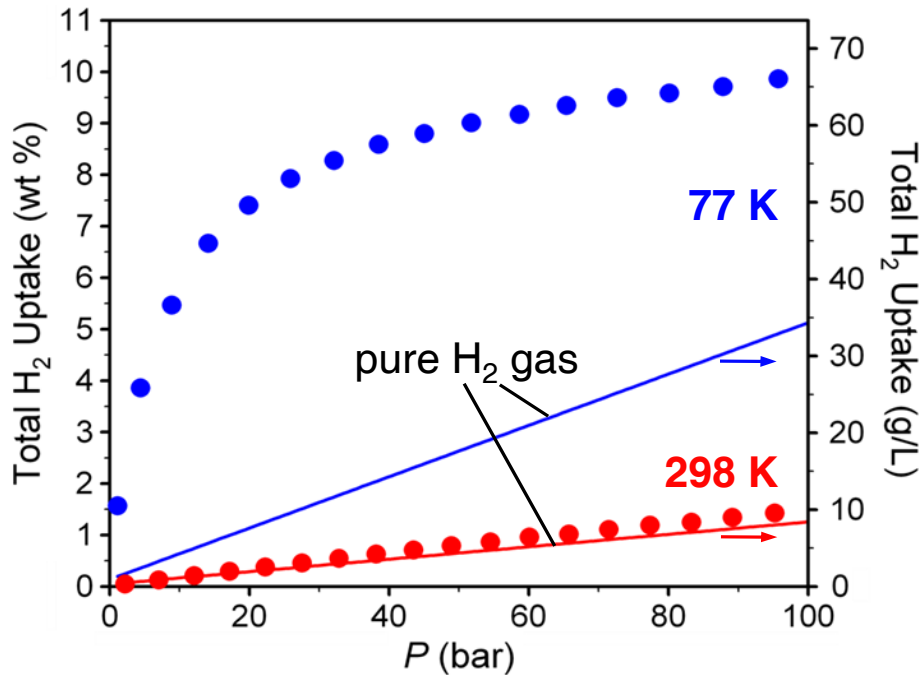




Hydrogen Storage in Completely-Activated MOF-5



$Zn_4O(BDC)_3$

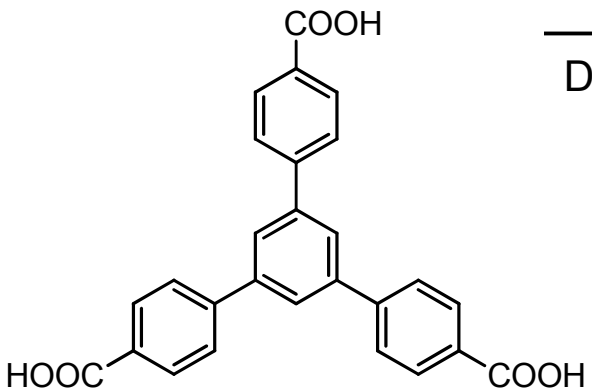


- Currently best known material for cryogenic hydrogen storage at 77 K
- Performance at 298 K is poor owing to weak interaction of H_2 with surface

A Beryllium-Based Metal-Organic Framework

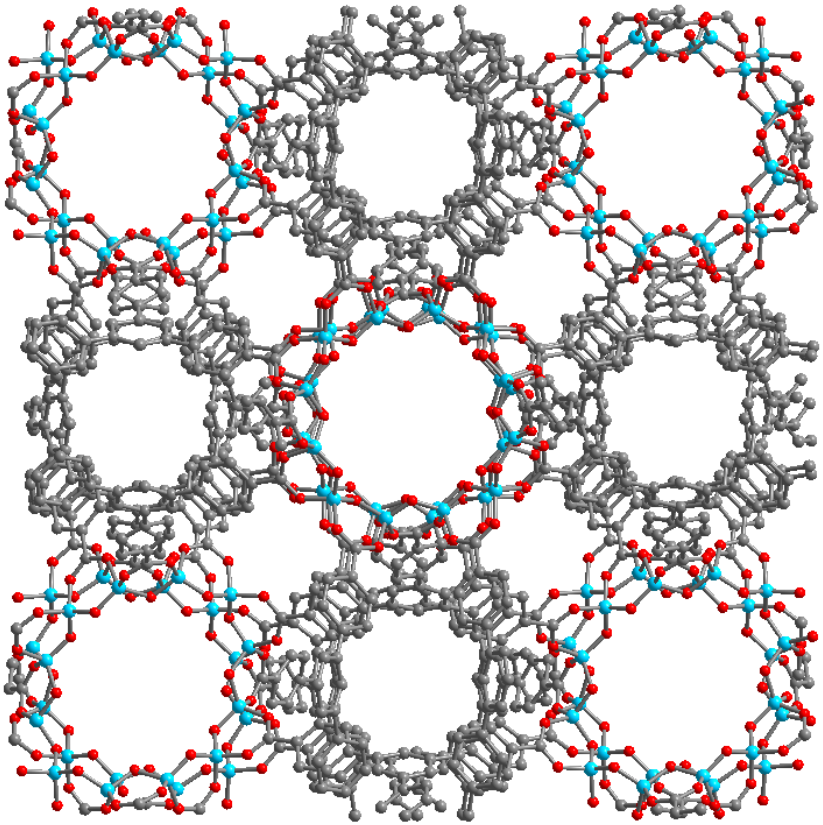
$Be(NO_3)_{2\,(aq)}$

+



H_3BTB

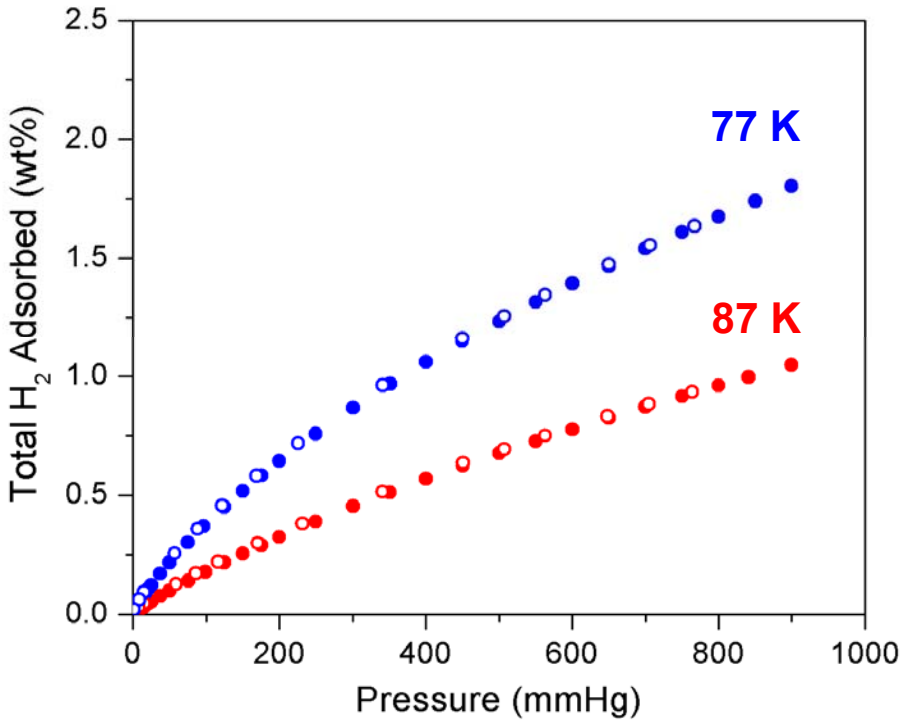
$\xrightarrow[\text{DMSO/DMF}]{\Delta}$

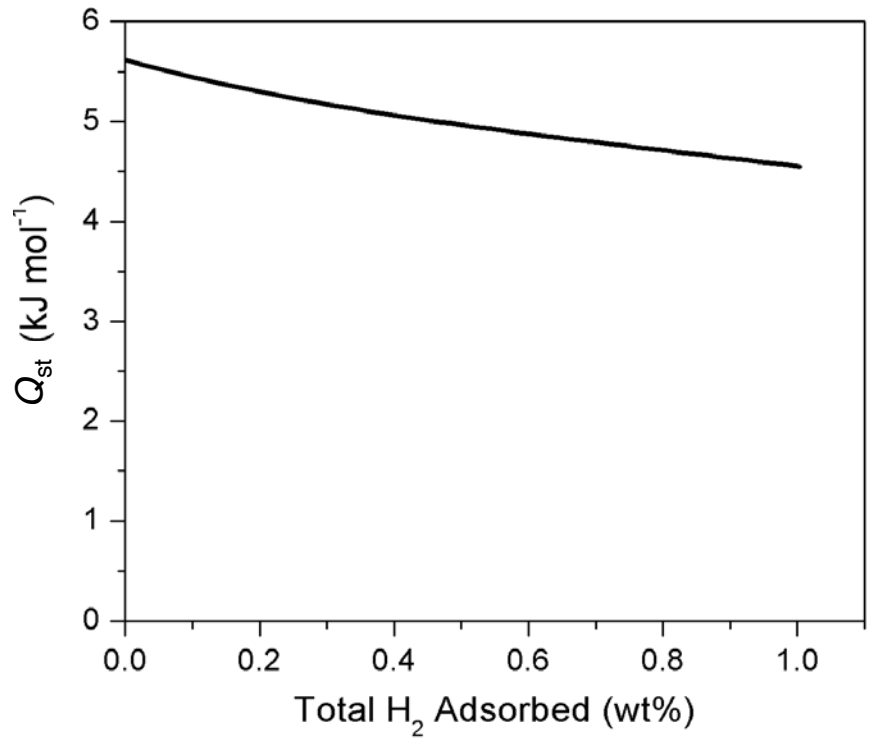


$Be_{12}(OH)_{12}(BTB)_4$

- Unprecedented structure with $Be_{12}(OH)_{12}$ rings and 12 and 15 Å channels
- Nitrogen adsorption isotherm affords BET surface area of 4020 m^2/g

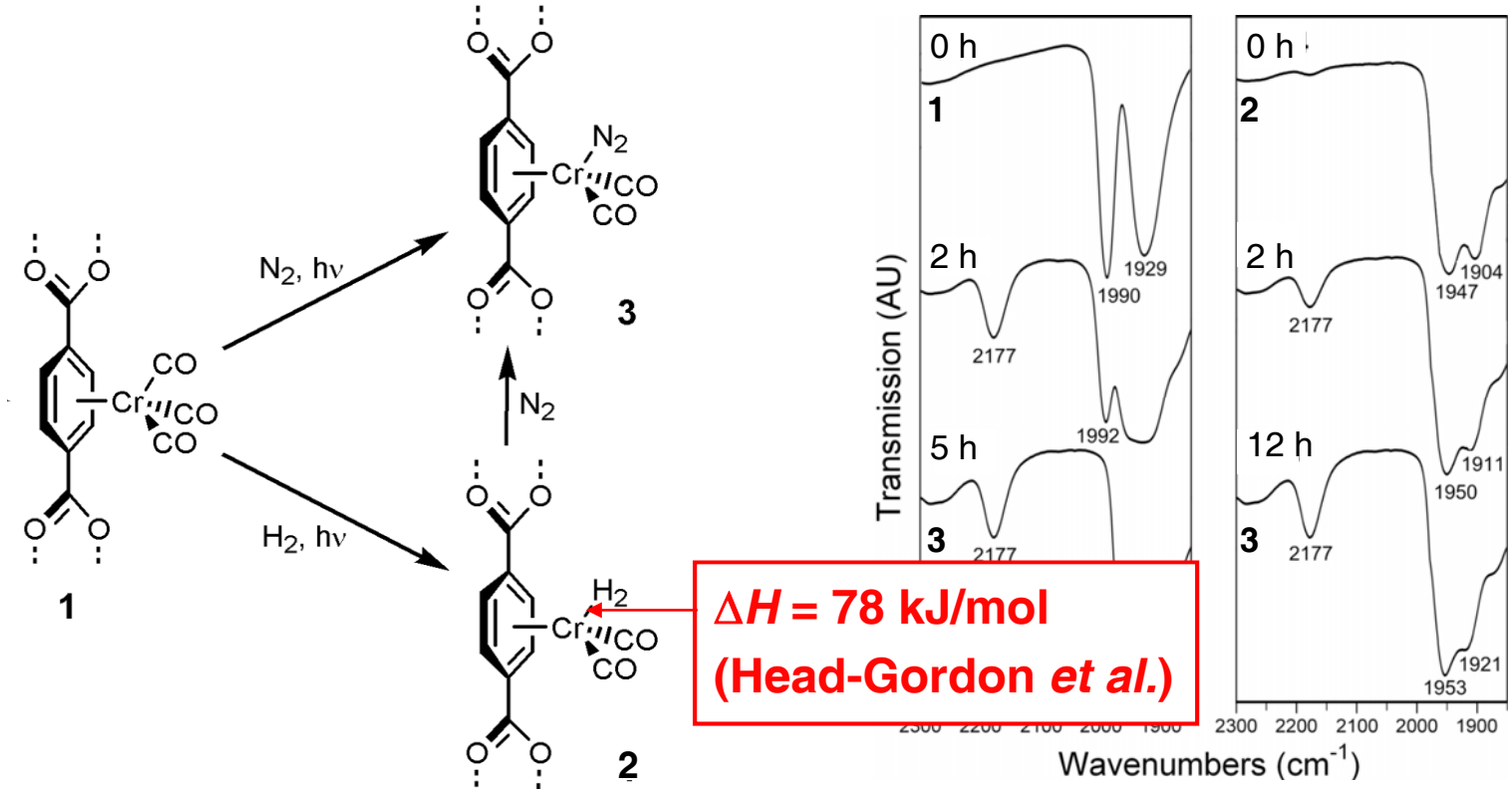
Low-Pressure H_2 Uptake in $Be_{12}(OH)_{12}(BTB)_4$





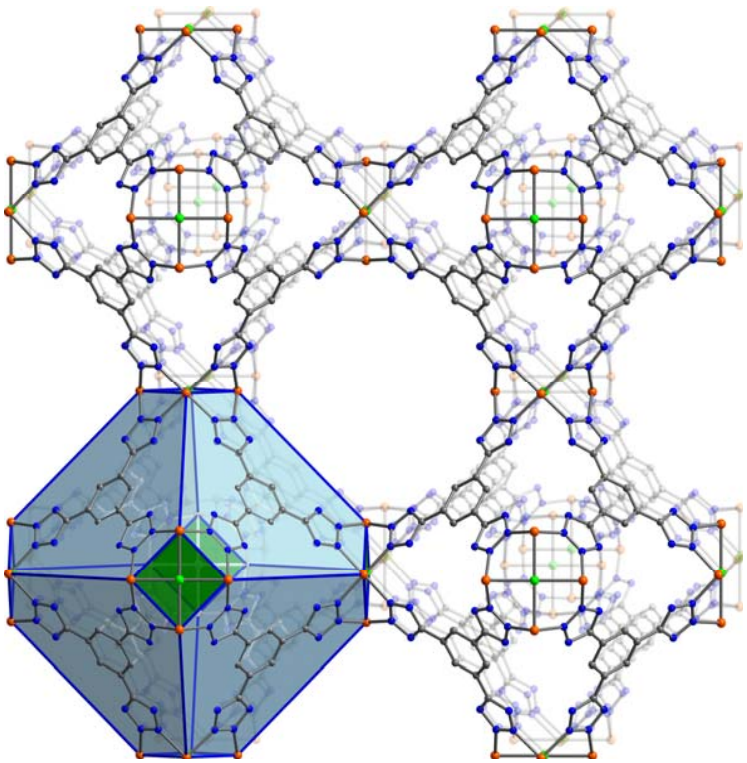
- Weak interaction of H_2 with surface, as desired for cryogenic storage
- At pressures up to 100 bar, expect gravimetric storage above MOF-5

Strong H_2 Binding in MOF-5 Functionalized with Cr^0

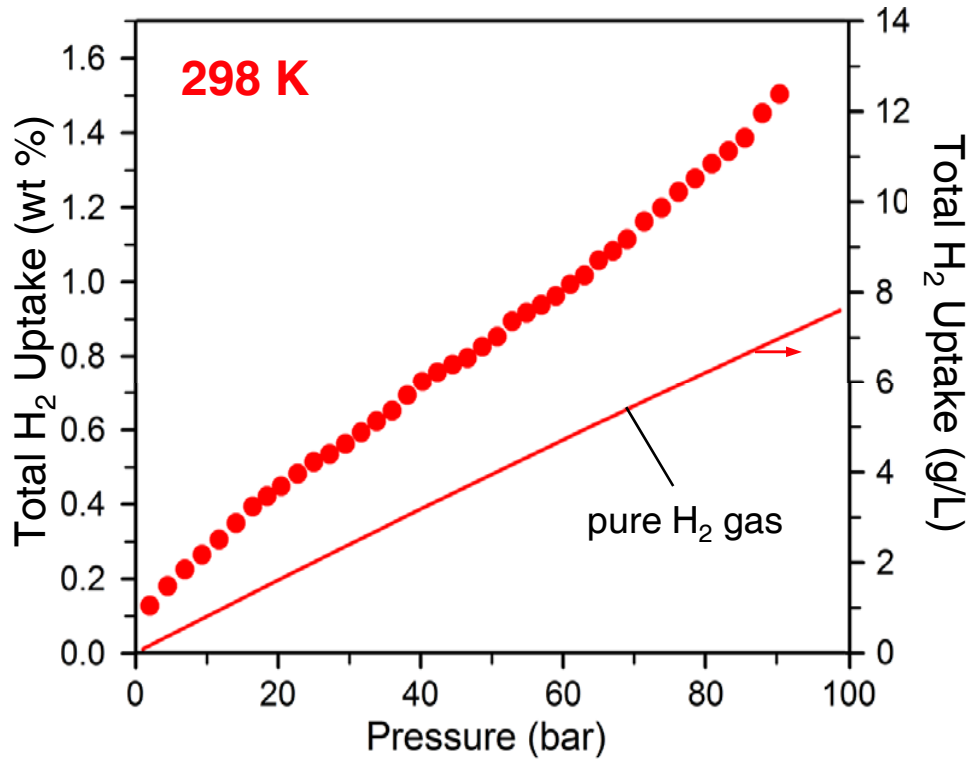


- Orbital interactions lead to strongly-bound H_2 complex that is too stable
- Need to generate charge-induced dipole interaction of 15-20 kJ/mol

Room Temperature H_2 Uptake in Mn-BTT*



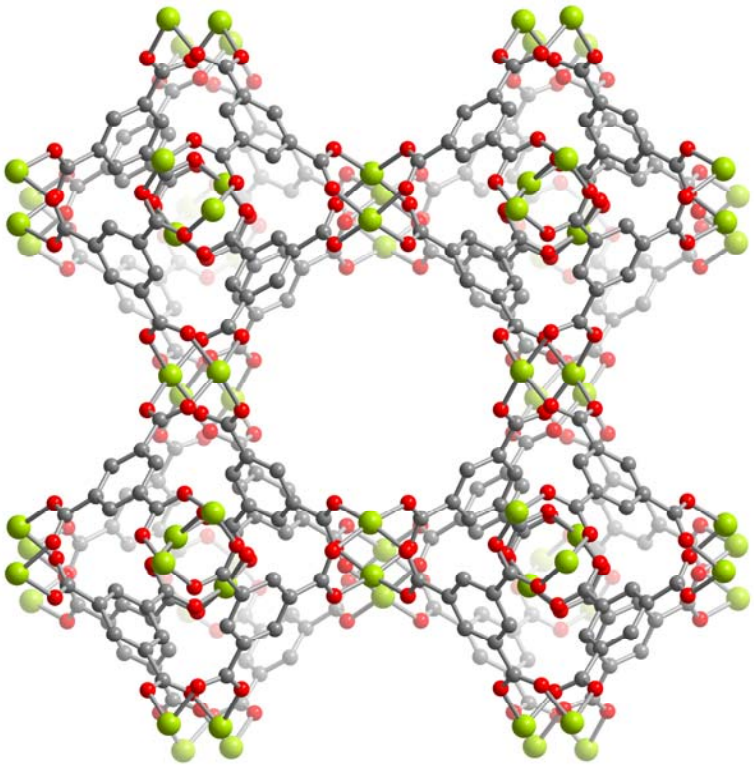
$Mn_3[(Mn_4Cl)_3(BTT)_8]_2 \cdot 20MeOH$



- Exposed Mn^{2+} sites lead to isosteric heat of adsorption of up to 10.1 kJ/mol
- Need to increase strength of binding and concentration of open metal sites

*GM-supported research

Paddlewheel Frameworks



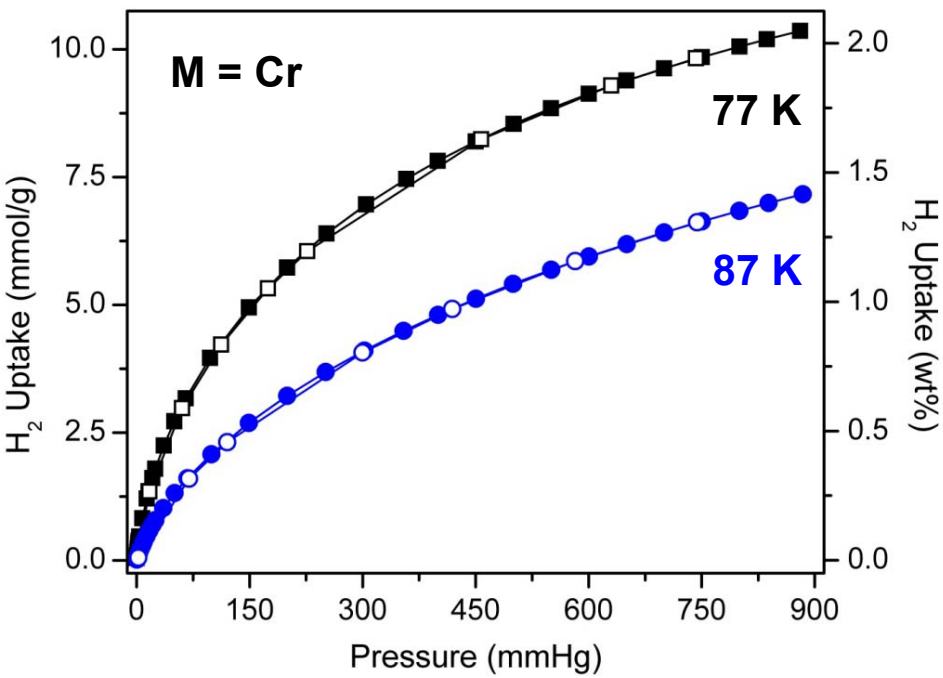
$M_3(BTC)_2$ (M = Cr, Cu, Zn, Mo)

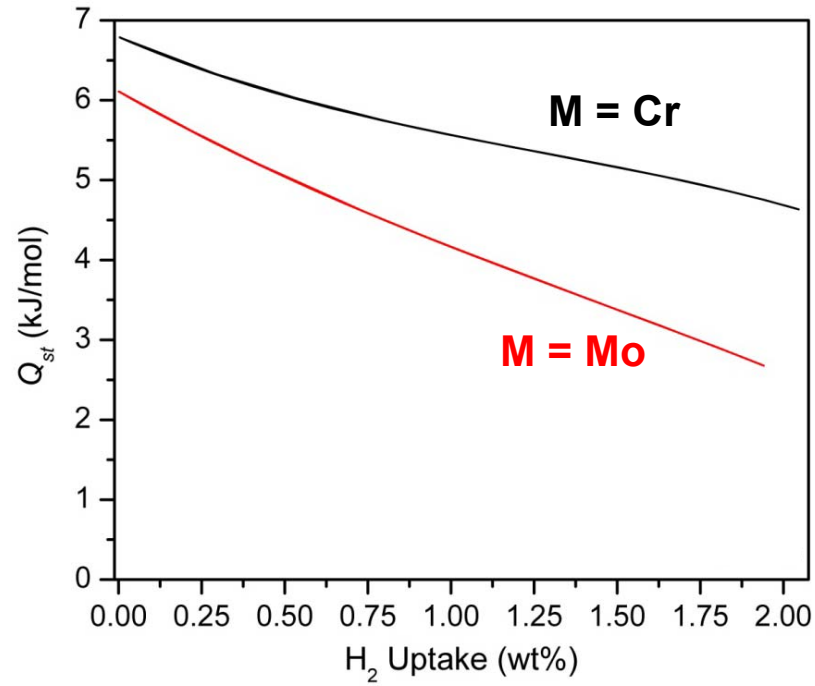
	surface area (m^2/g)	
	BET	Langmuir
$Cr_3(BTC)_2$	2340	2720
$Cu_3(BTC)_2$ [a]	1944	2260
$Zn_3(BTC)_2$	*collapsed*	
$Mo_3(BTC)_2$ [b]	1280	2010
$Mo_3(BTC)_2$	1800	2100

[a] *J. Am. Chem. Soc.* **2006**, *128*, 3494
[b] *J. Mater. Chem.* **2006**, *16*, 2245

- Preparation of $Cr_3(BTC)_2$ is new and activation of $Mo_3(BTC)_2$ is improved
- Enables comparison of H_2 binding at the open M^{II} coordination sites

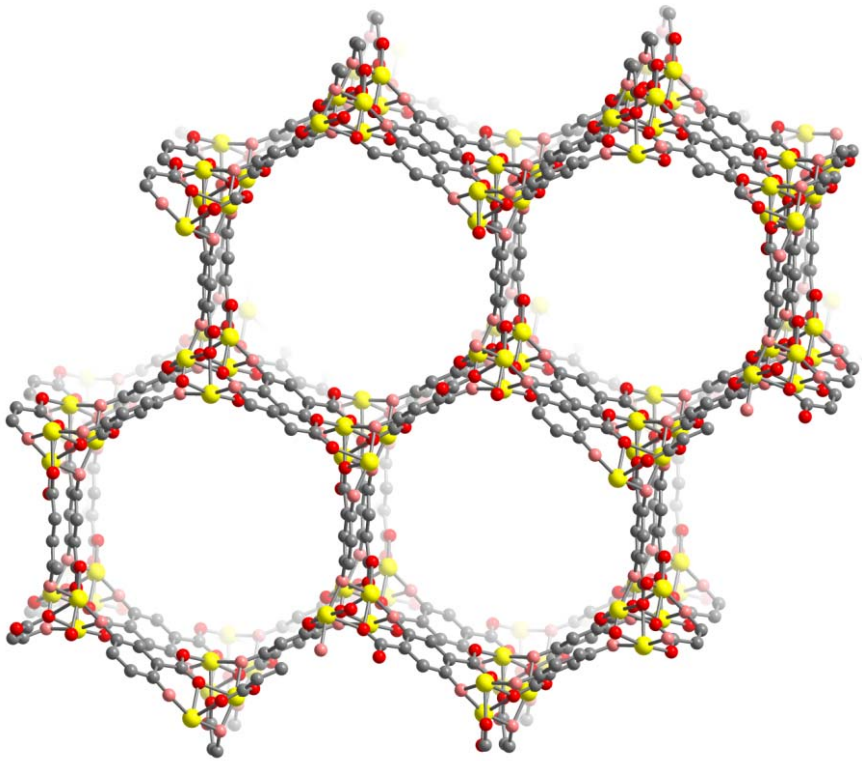
H_2 Uptake in $M_3(BTC)_2$ (M = Cr, Mo)





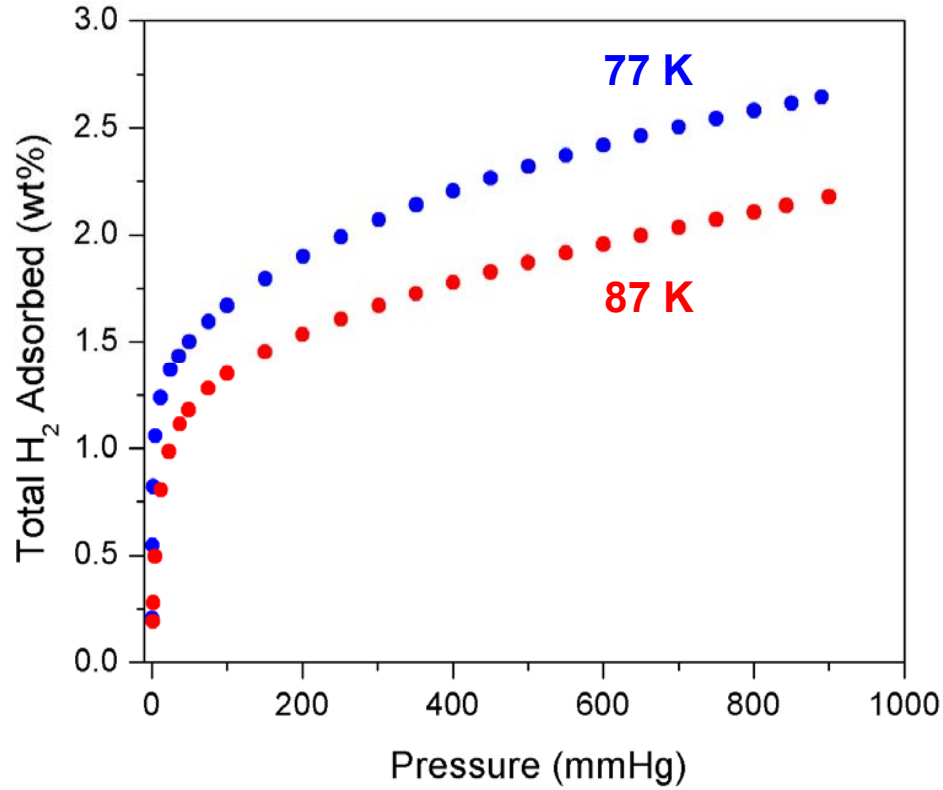
- First assessment of strength of H_2 binding to a Cr^{2+} center
- Expect better results for Co^{2+} and Ni^{2+} owing to a smaller ionic radius
- Attempts to synthesize analogues with other metal ions are underway

H_2 Uptake in Mg_2(DOBDC)



Mg_2(DOBDC)

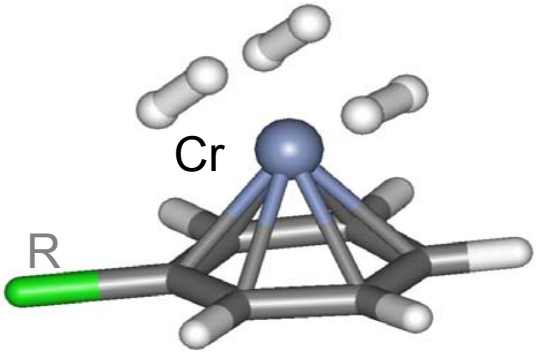
Matzger *et al. J. Am. Chem. Soc.* **2008**, *130*, 10870

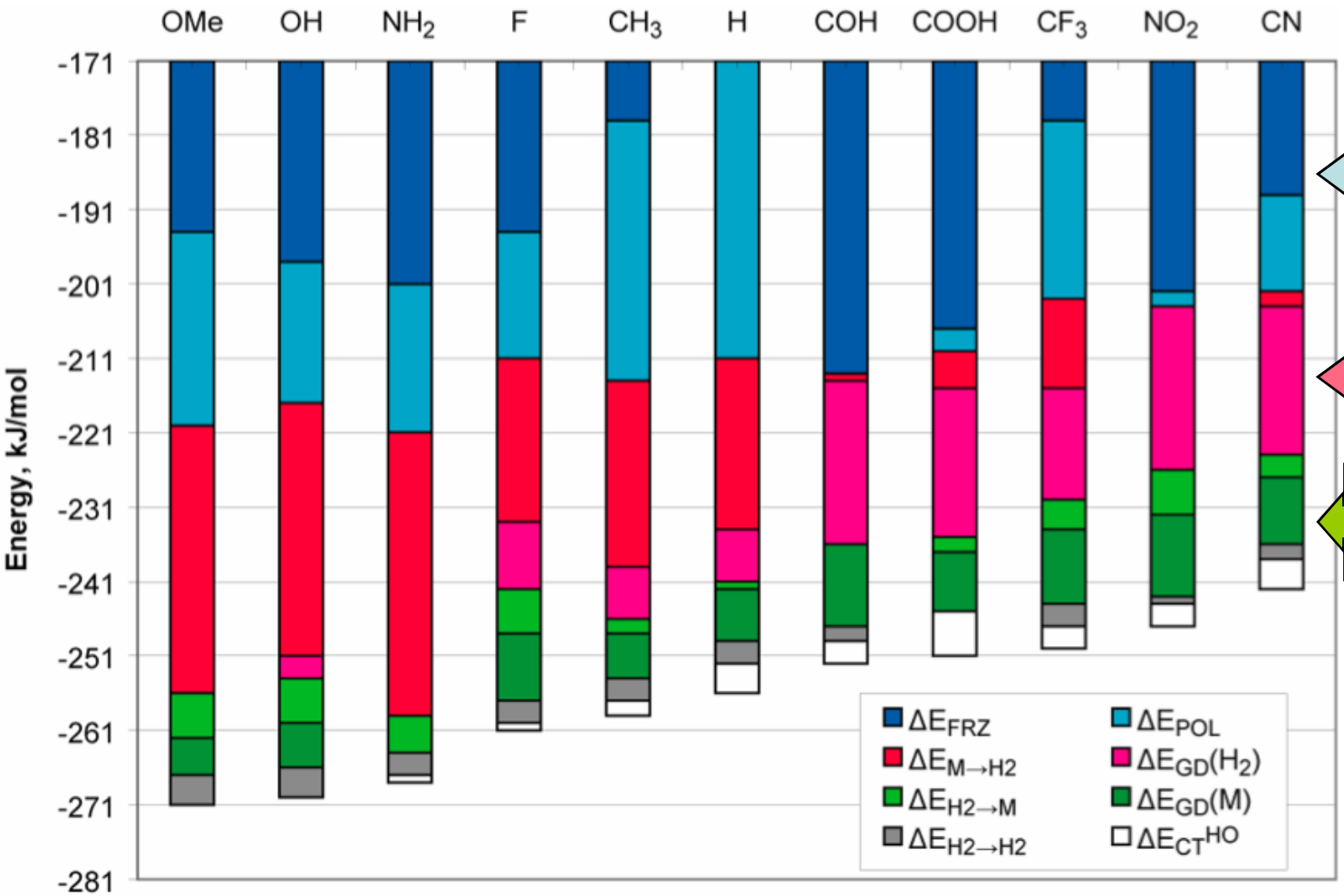


- Open Mg^{2+} sites lead to an isosteric heat of adsorption as high as 12.8 kJ/mol
- Neutron diffraction (Craig Brown, NIST) shows Mg···D_2 distance of 2.5 Å

Calculation of Substituent Effects

Metal chosen as Cr^0



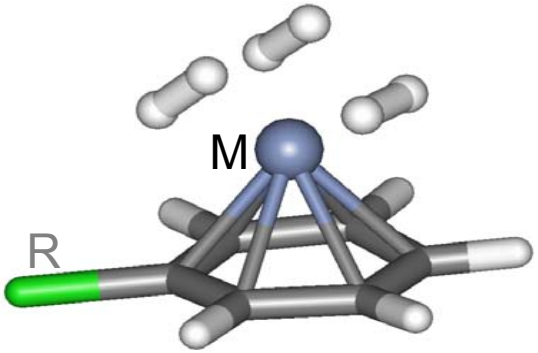


electrostatics

back-donation

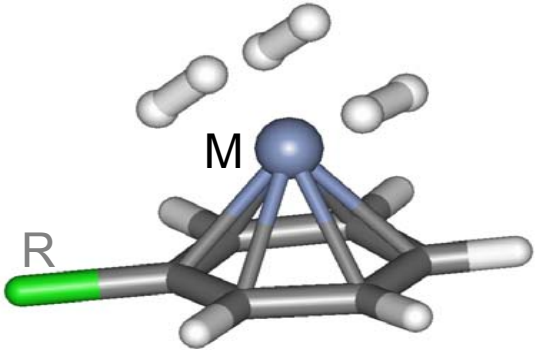
forward donation

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:

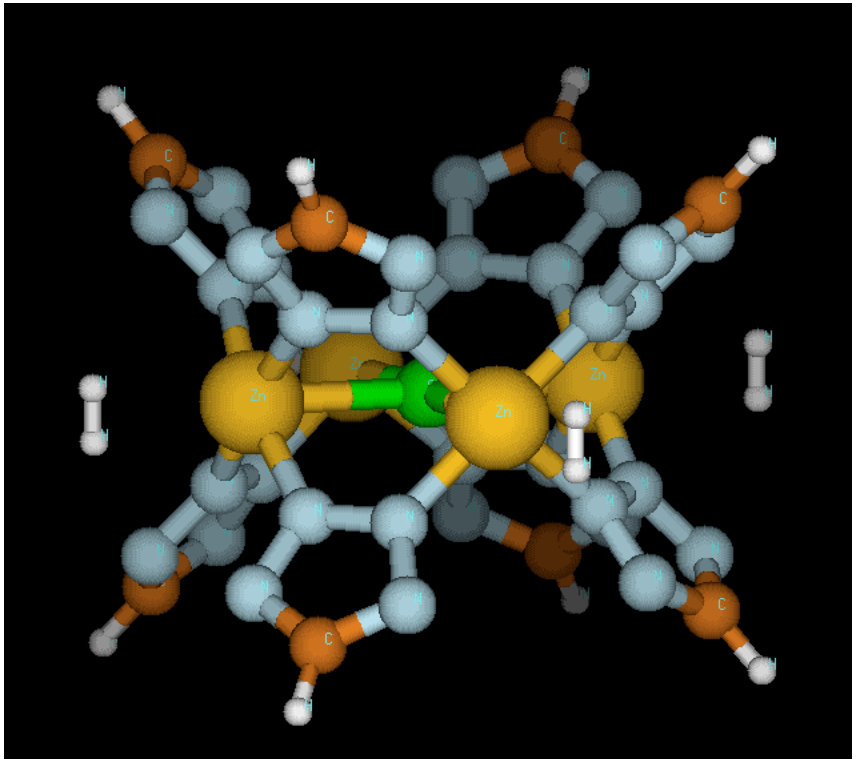
  $(C_6H_6)Cr(H_2)_3$ binding per H_2 of 68 kJ/mol

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

- Shows coarse tuning is possible

  Still need to examine synergy of these effects

Computational Study of H_2 Binding in Cu-BTT



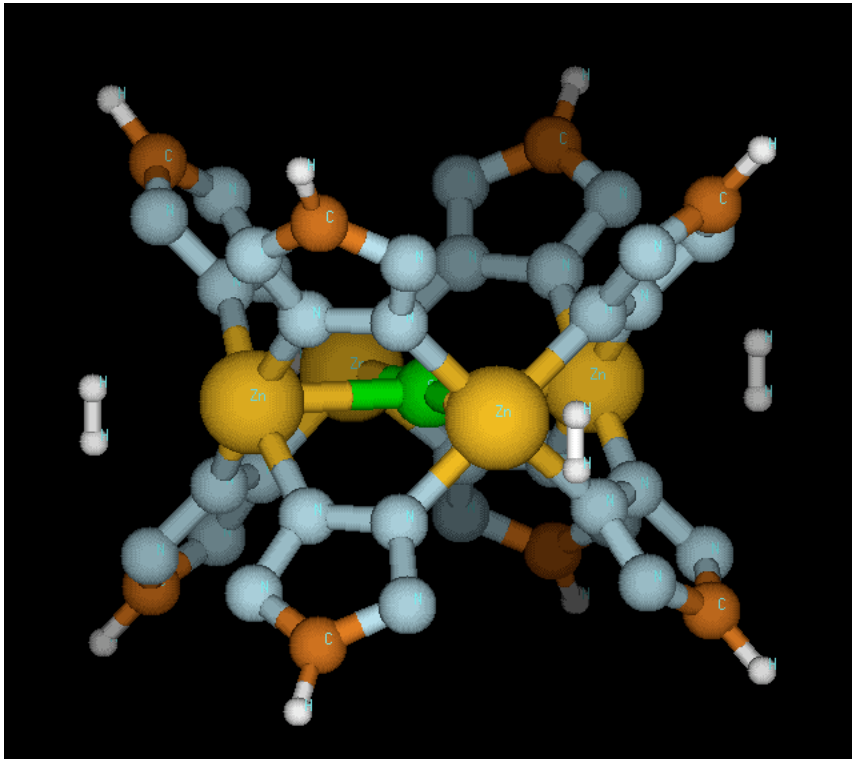
$[Cu_4X(N_4CH)_8]^-$ fragment

ωB97X-D/6-31G* calculations:

X	E/kJ/mol
F	-10.9
Cl	-10.9
Br	-13.0
I	--

- Measurements of H_2 binding energy within $HCu[(Cu_4Cl)_3(BTT)_8]$ underway
- We will attempt to synthesize $HCu[(Cu_4Br)_3(BTT)_8]$

Computational Study of H_2 Binding in "Zn-BTT"



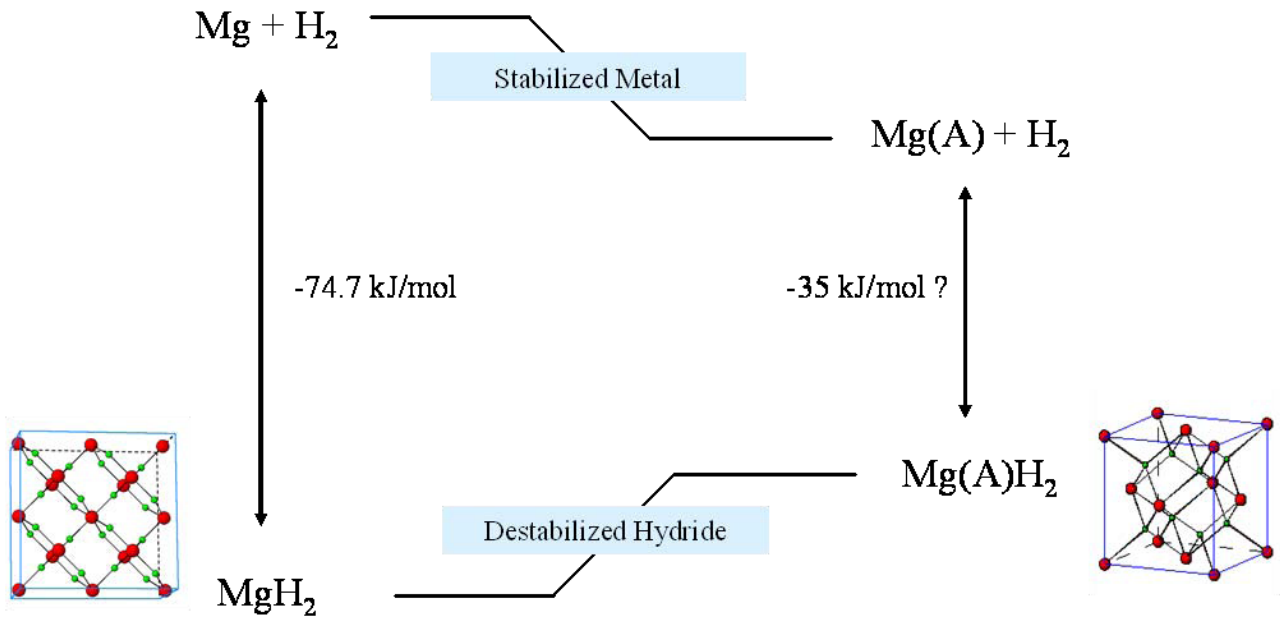
$[Zn_4X(N_4CH)_8]^-$ fragment

ωB97X-D/6-31G* calculations:

X	E_{Cu}/kJ/mol	E_{Zn}/kJ/mol
F	-10.9	-13.8
Cl	-10.9	-15.9
Br	-13.0	-16.3
I	--	--

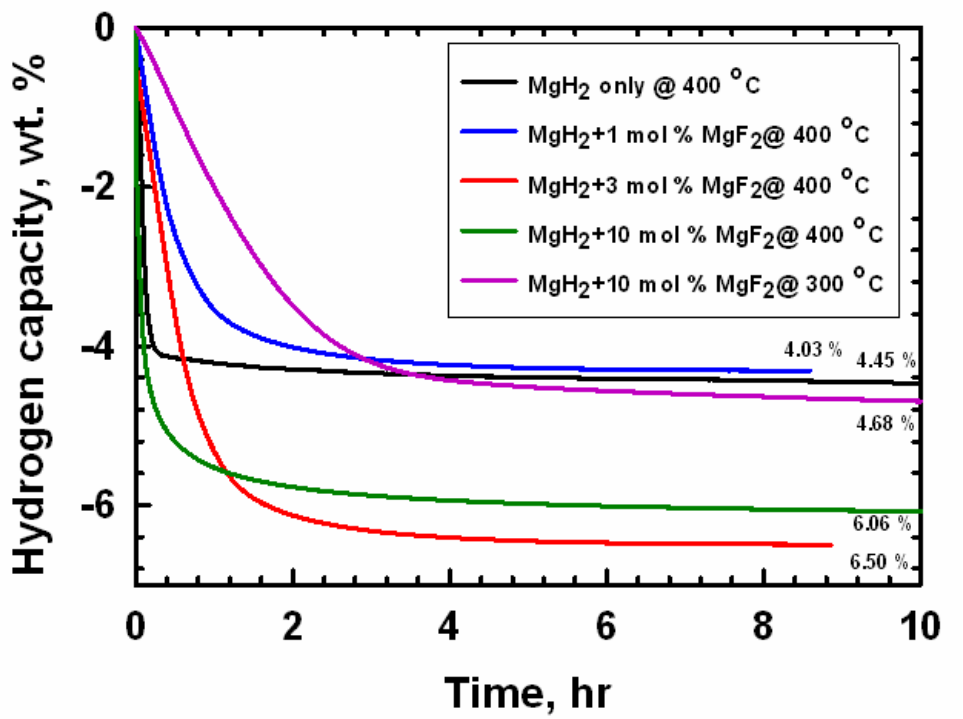
- Suggests significant improvement in binding energy for Zn-BTT frameworks
- We will therefore attempt to synthesize $Zn_3[(Zn_4Cl)_3(BTT)_8]_2$

Destabilization of Metal Hydrides

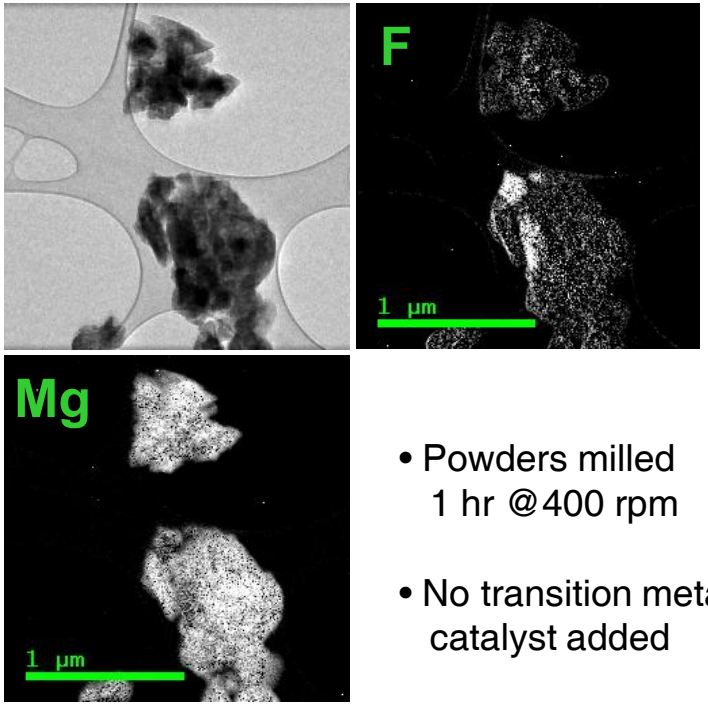


- Attempts at alloying of Mg in order to reduce ΔH
- Success in partial substitution to form $Mg_{1-x}A_x$ (A = Mn, Fe, Ni)
- Some increases in plateau pressures, but poor kinetics
- Attempts to substitute Na and Li for Mg are underway

Addition of MgF_2 Enhances Utilization of MgH_2



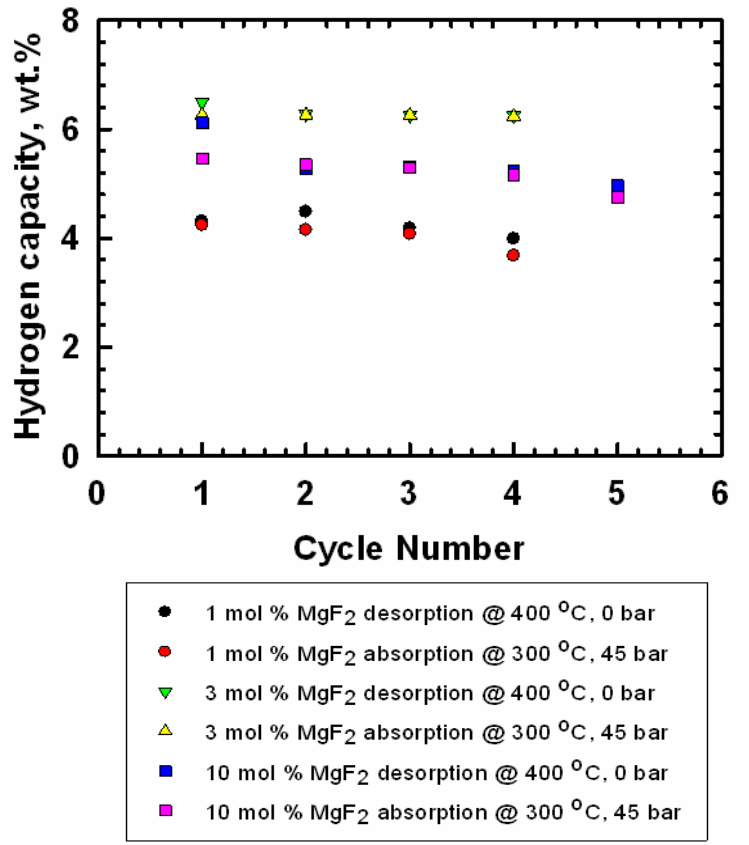
Elemental Mapping (EELS)

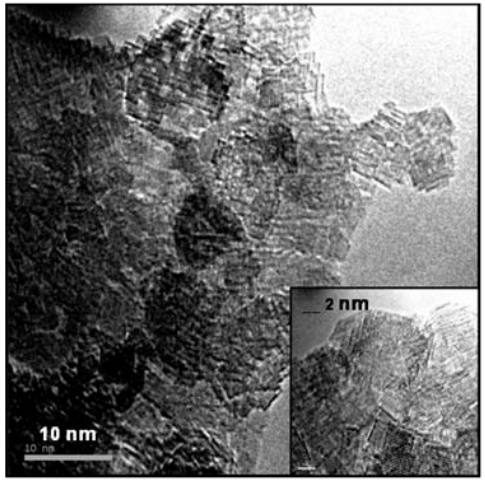


- Powders milled 1 hr @400 rpm
- No transition metal catalyst added

- MgF_2 slows desorption, but increases amount desorbed despite added weight
- Fluoride is distributed over particle surface; no evidence for bulk substitution (XRD)

Fluoride Effect Persists through Repeated Cycling

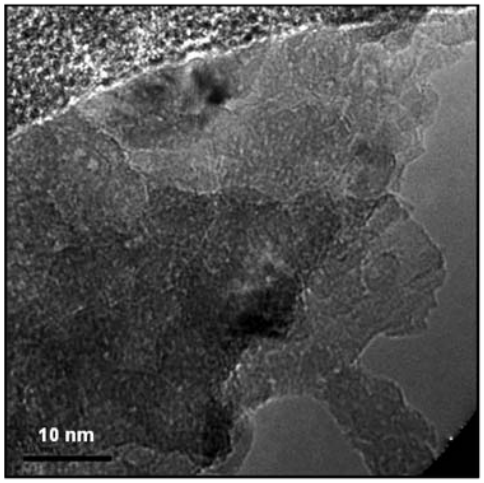




MgH_2 + 3 mol% MgF_2 after 2nd desorption @ 300° C

High-resolution TEM shows sharp faceting and marked inhibition of Mg grain growth in fluoride-containing samples.

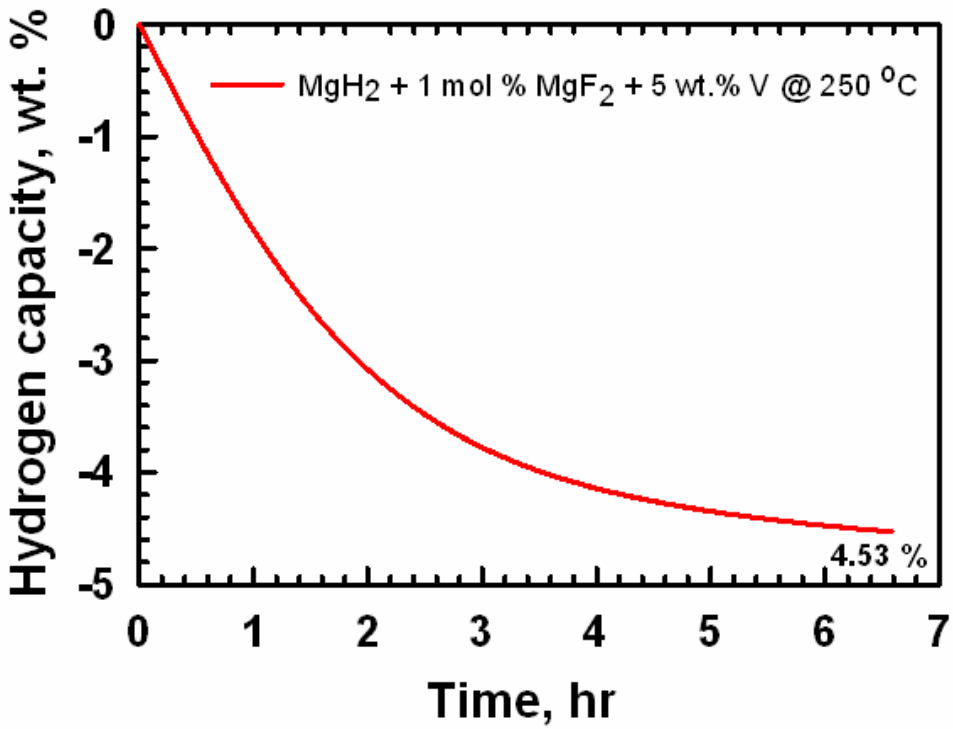
Without fluoride, sintering and coarsening reduce surface area and contribute to Mg isolation



MgH_2 after 2nd desorption @ 300° C

- Best results are for 3 mol% MgF_2 added

Metal Catalyst Activity not Inhibited by Fluoride



5wt .% V+ MgH_2 milled for 2hrs(300 rpm)
1 mol % MgF_2 added (600 rpm for 1hr)

Activity of added vanadium not inhibited by the presence of fluoride

Good utilization at 250 °C

Still below 1 wt % at 200 °C

- Future work: higher energy milling and alternative fluoride sources
- In addition, the effect of fluoride addition on ternary hydrides will be studied