A Synergistic Approach to the Development of New Hydrogen Storage Materials

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OVERALL VISION

- Bring together a group of scientists with a broad range of perspectives and experiences in materials discovery, and get them thinking about and working on the problem of 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

PROGRAM OVERVIEW

Synthesis and characterization of metal/metal hydride nanocrystals (Alivisatos)

Synthesis and characterization of nanostructured boron nitrides (Zettl)

Theory predictions for nanostructured boron nitrides (Cohen and Louie)

Set-up of H_2 storage characterization instrumentation at LBNL (Mao)

Synthesis and characterization of microporous polymers (Fréchet)

Synthesis and characterization of microporous coordination solids (Long)

First-principles determination of H_2 binding energies (Head-Gordon)

Synthesis and characterization of destabilized hydrides (Richardson)

9/05 start

BES

EERE

12/04 start

H_2 STORAGE CHARACTERIZATION INSTRUMENTS (Mao)

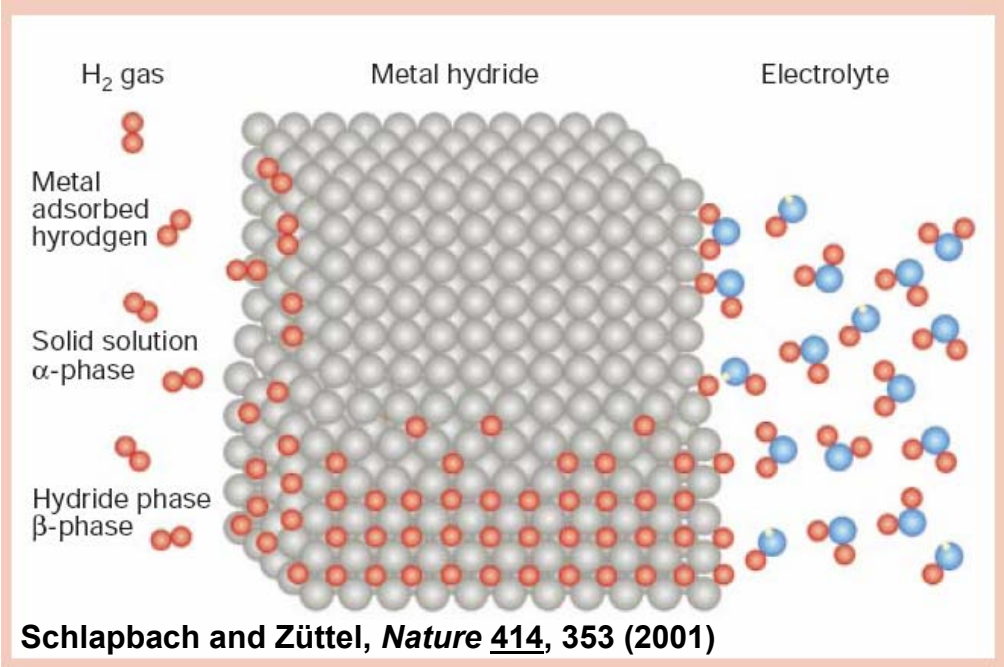
Hiden Isochema IGA

installed 7/05

Hy-Energy PCTPro-2000

delivery expected 7/06

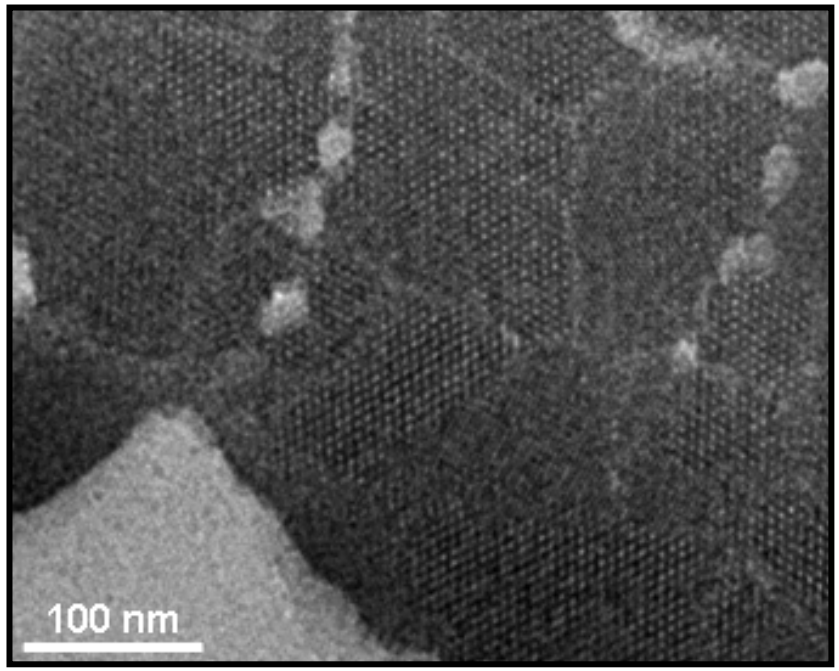
H_2 UPTAKE IN METAL NANOCRYSTALS (Alivisatos)

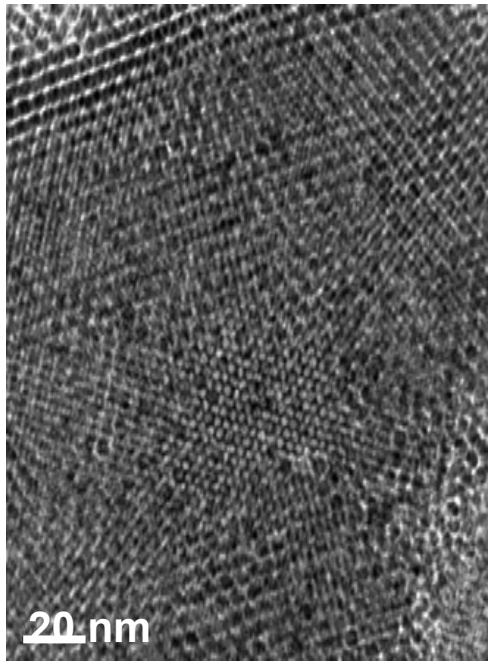


Schlapbach and Züttel, *Nature* 414, 353 (2001)

- High surface area to volume ratio can alter kinetics and maybe thermodynamics
- Study effects of manipulating nanocrystal size, shape, and capping ligands
- Start with well-understood Pd system and move to lighter metals (e.g., Mg, Al)

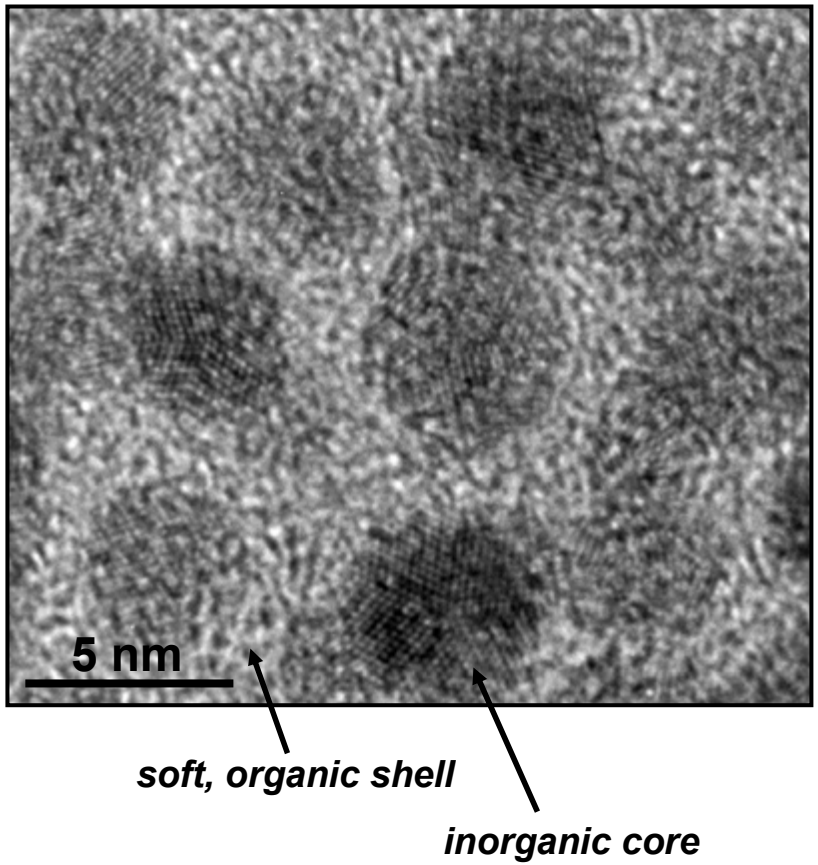
3-D SUPERLATTICES OF 5-nm Pd NANOCRYSTALS

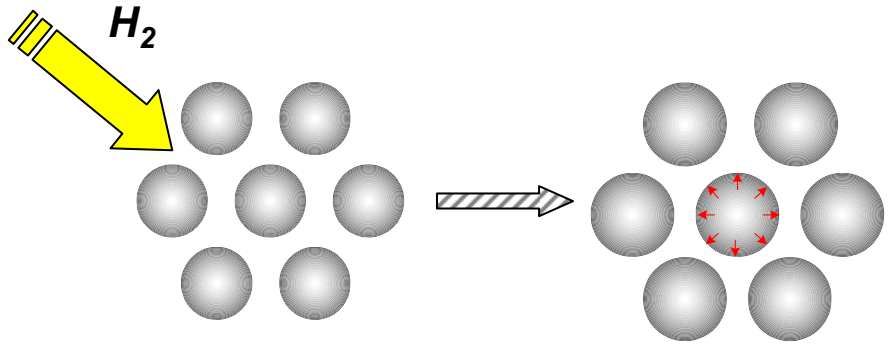




- Superlattices may reduce strain, combating embrittlement and hysteresis
- Goal is to monitor nanocrystal shape and volume during H_2 uptake and release
- Then optimize system by adjusting nanocrystal size and interparticle spacing

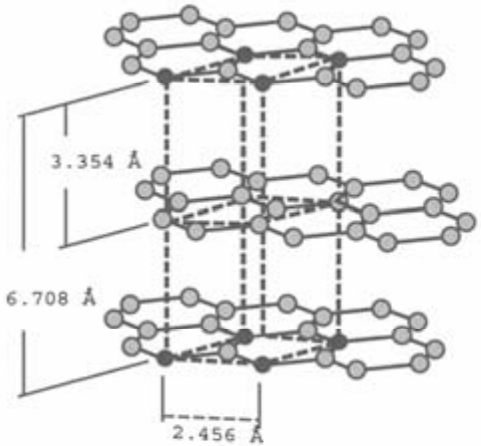
CHARACTERIZATION OF H_2 ADSORPTION IN 3-D ARRAYS



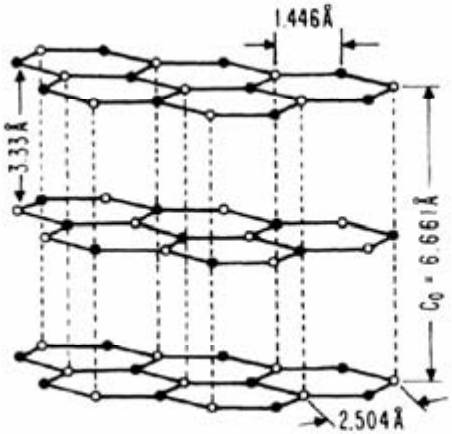


- *In situ* X-ray diffraction and TEM
- Pressure-composition isotherms
- Thermogravimetric analysis
- X-ray photoelectron spectroscopy

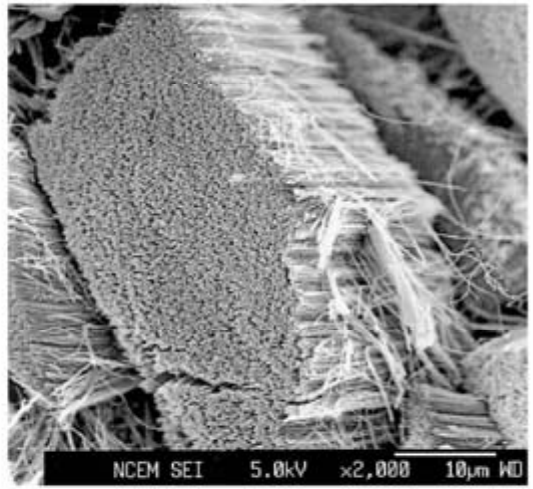
SYNTHESIS OF NANOSTRUCTURED BORON NITRIDE (Zettl)



graphite



BN

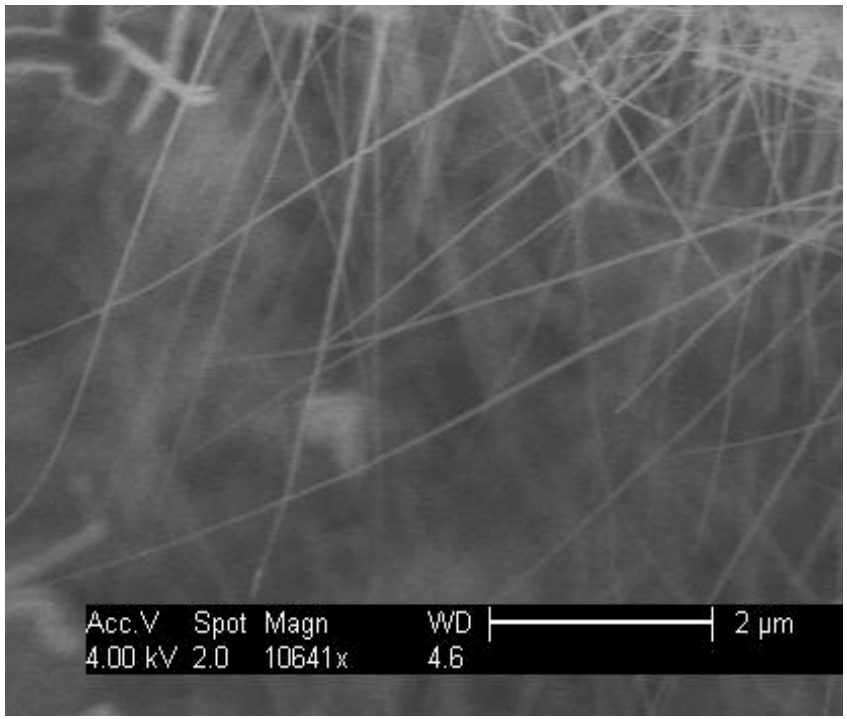


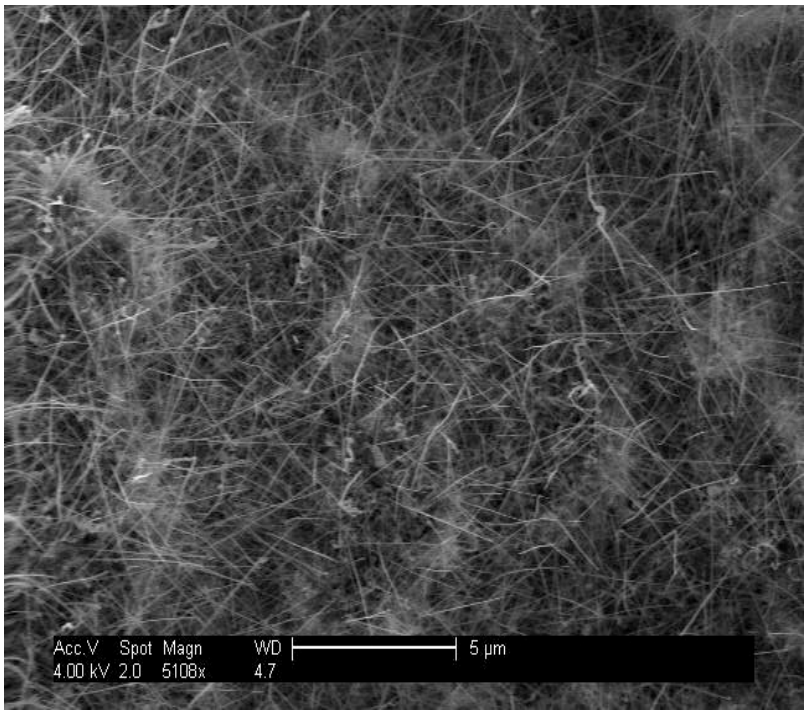
- Zettl group has discovered a CVD-like method by which carbon nanotubes can be converted directly into BN nanotubes:

$$C + B_2O_3 + 2NH_3 \longrightarrow 2BN + CO + 2H_2O + H_2$$

- Approach will be applied in converting other forms of carbon into nanostructured BN
- Intermediate materials of the type $C_xB_yN_z$ will also be investigated

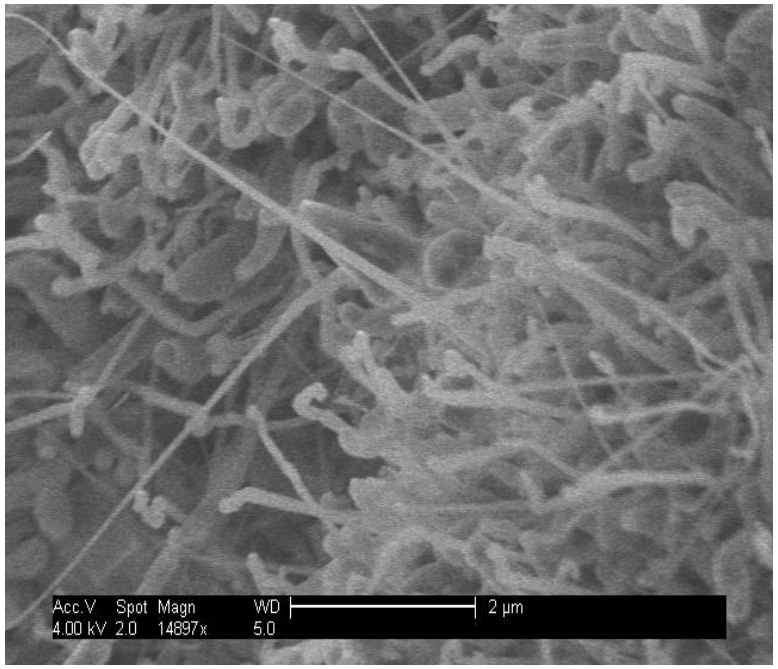
LARGE-SCALE PRODUCTION OF PURE BN NANOTUBES

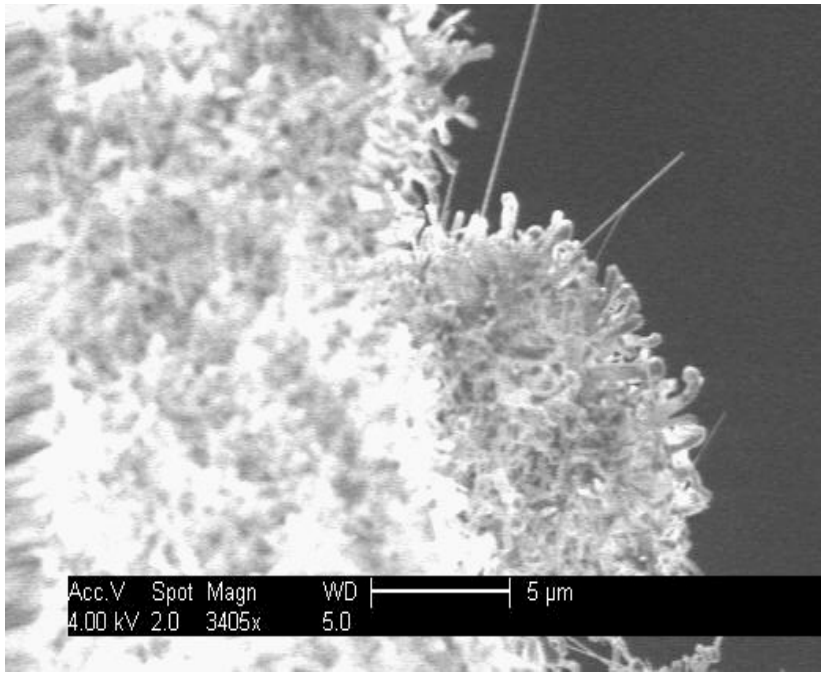




- Both CVD and induction furnace methods have been refined

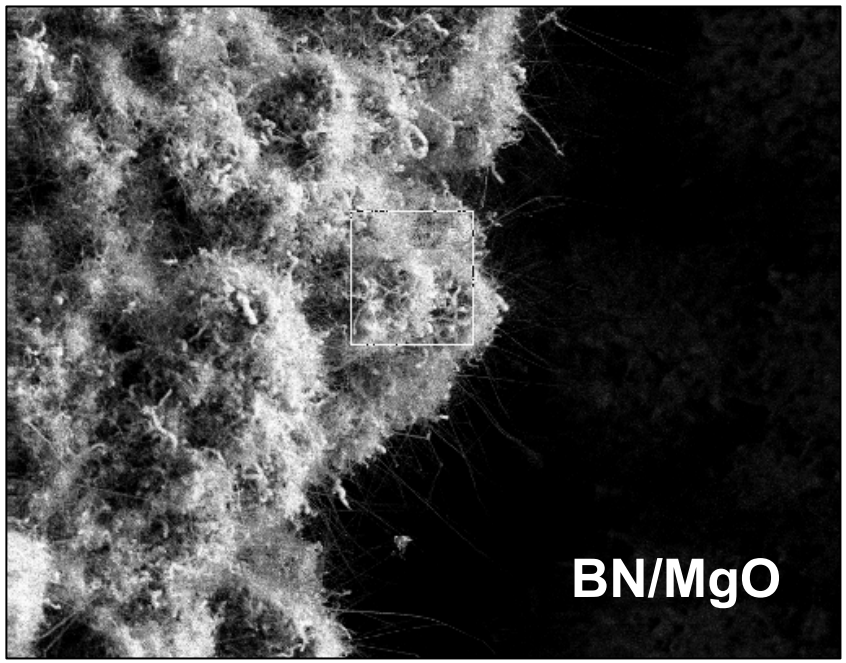
VARYING THE MORPHOLOGY OF BN NANOPARTICLES

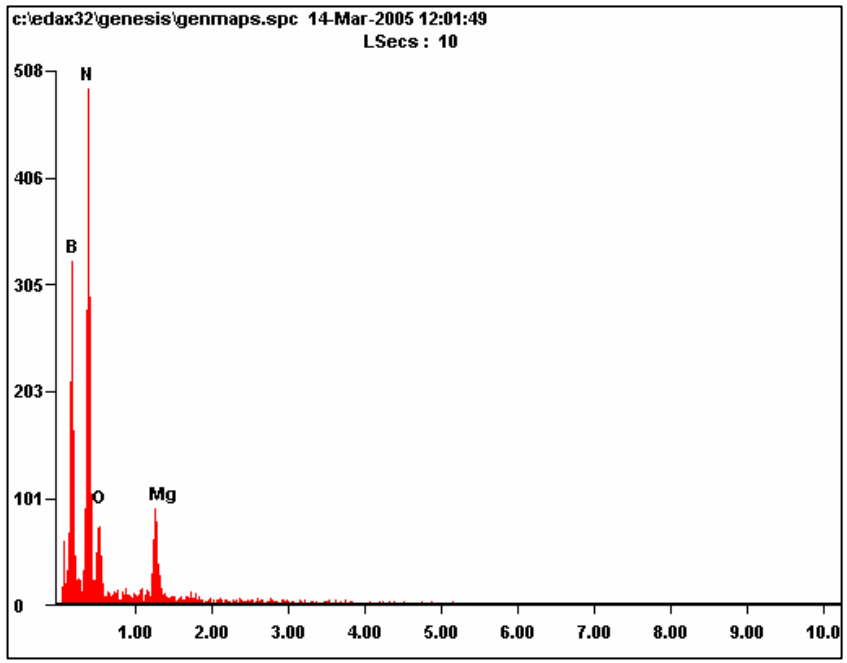




- Initial form of the carbon nanostructure can be used to adjust BN morphology
- Gas sorption measurements underway to compare surface areas and H_2 storage

SYNTHESIS OF BN-NANOPARTICLE COMPOSITES





- CVD methods also being developed to produce composites with metal and metal oxide nanoparticles

COMPUTATIONAL METHODS FOR BN SOLIDS (Cohen and Louie)

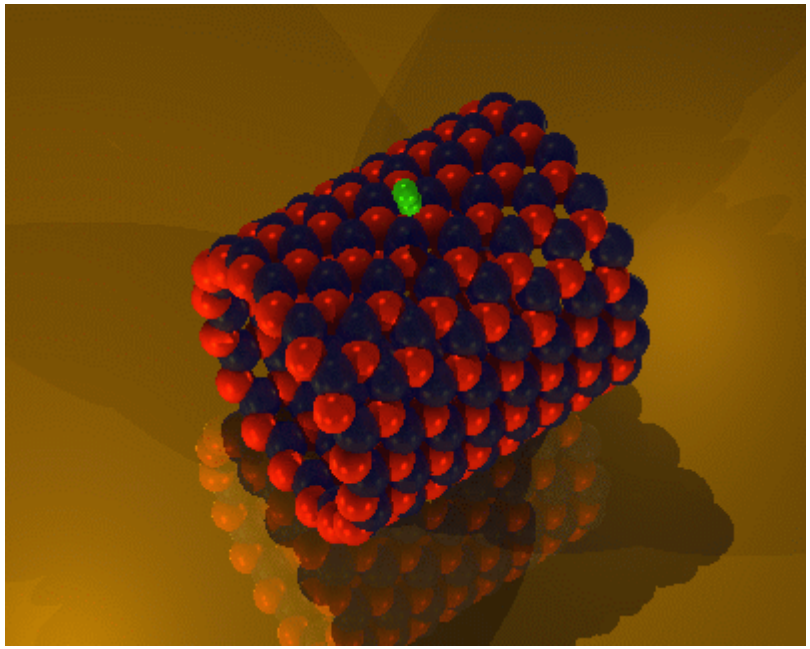
Ab initio density functional theory for H_2 binding energy calculations:

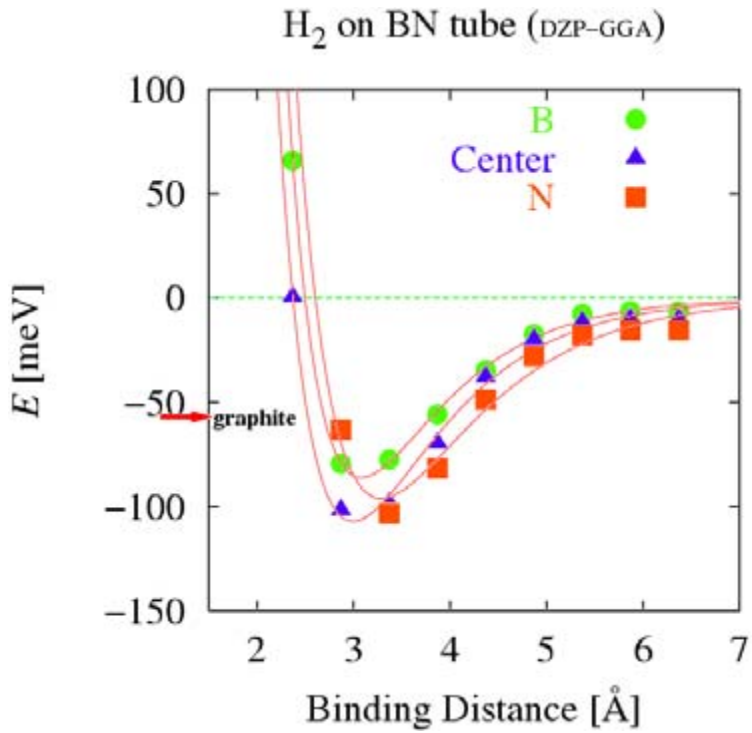
- Pseudopotential method; basis = atomic orbitals/planewaves
- Exchange-correlation $V_{e\text{-}e}[\rho]$: generalized gradient approximation (GGA)
- Variation principle to $E[\rho]$
- One-particle Schrödinger equation: $[-\nabla^2 + v(r) + V_H(r) + V_{XC}(r)]\,\psi(r) = \varepsilon\psi(r)$

Adsorption theory for calculating H_2 storage capacities:

- van't Hoff equation: $\ln p_0 = -\Delta H/kT + \Delta S/R$
- Langmuir isotherms: $\theta = \dfrac{p/p_0}{1 + p/p_0}$

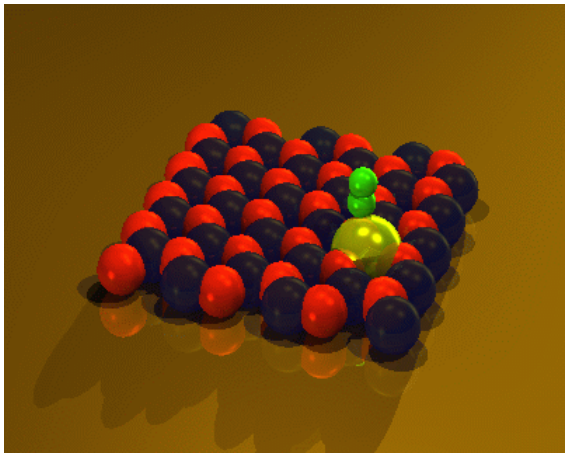
H_2 ADSORPTION ON BN NANOTUBES

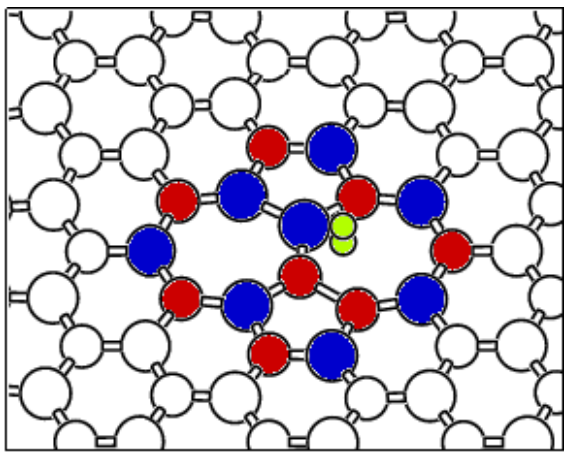




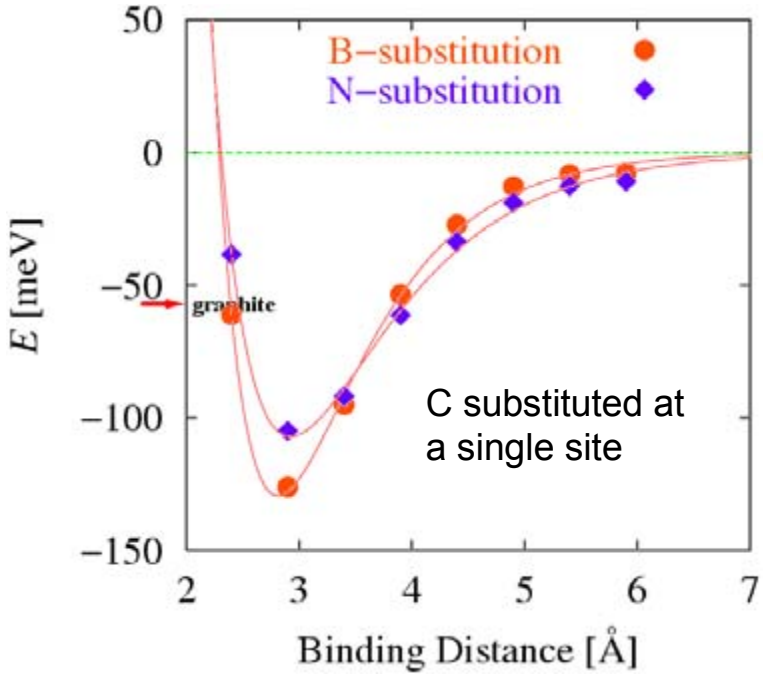
- Strongest binding sites are over N atoms and above ring centers
- Enhanced binding of 10 kJ/mol compared with ~7 kJ/mol for carbon tubes

H_2 ADSORPTION AT DEFECT SITES IN BN NANOTUBES





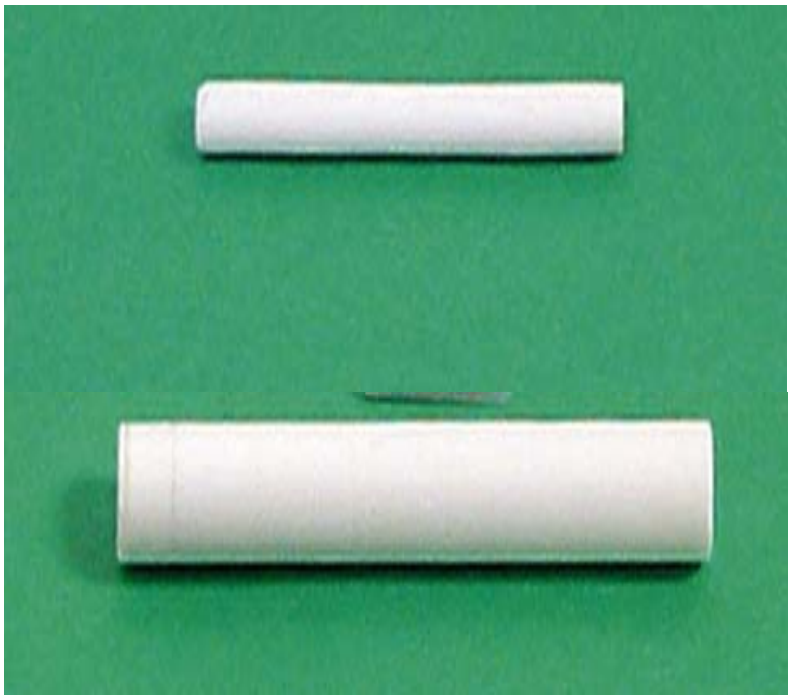
Stone-Wales defect

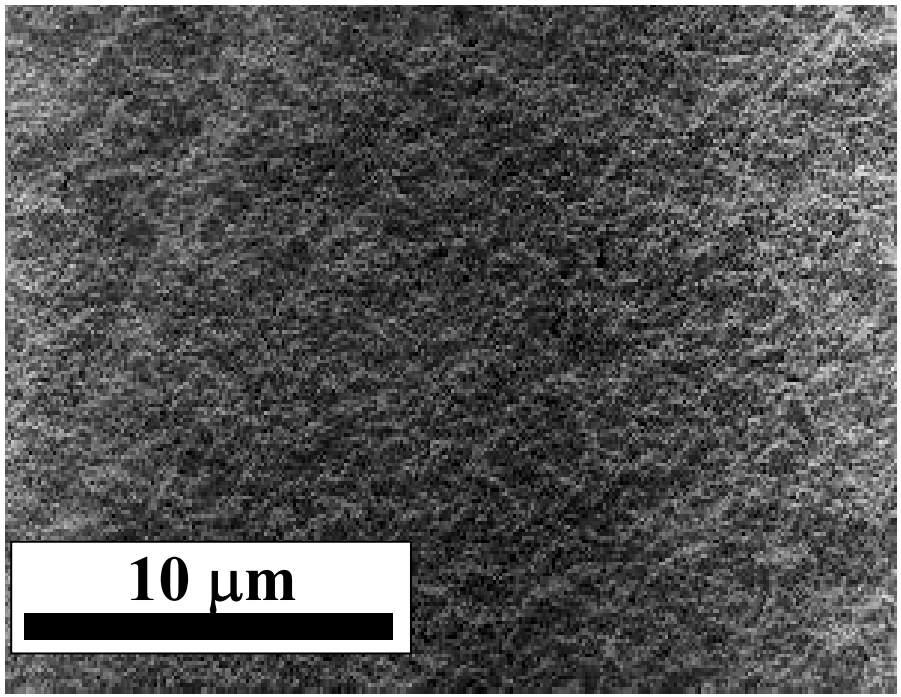


- Binding energies increase by

  10-30% relative to perfect tubes

MICROPOROUS POLYMERS (Fréchet)



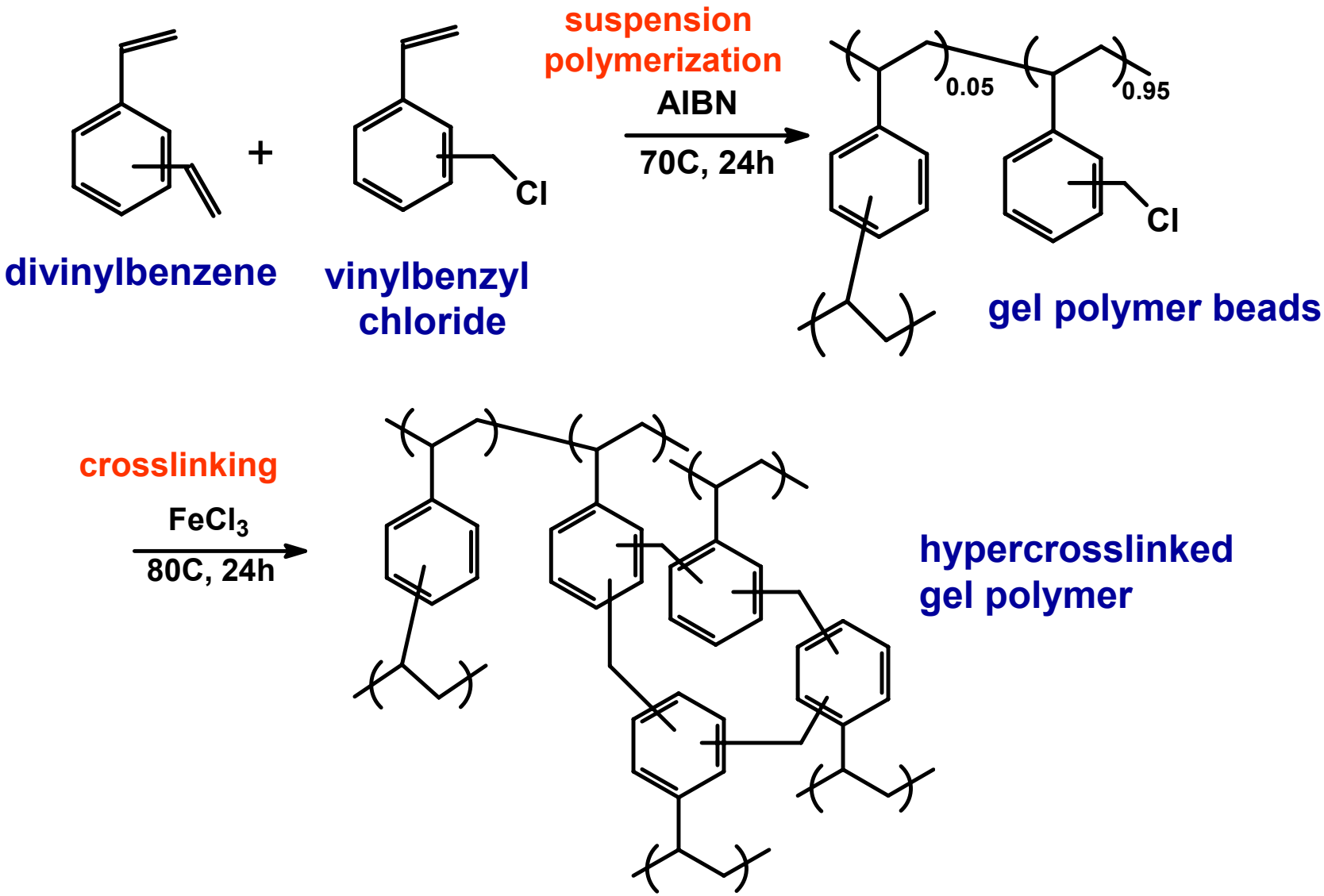


- Generally inexpensive materials that can be produced on a large scale
- Readily processed: can be molded to produce monoliths of any shape and size
- Surface characteristics can be tuned using well-established molecular chemistry

GAS SORPTION IN POROUS FORMS OF COMMERCIAL RESINS

Trade name	Composition	BET surface area (m^2/g)	H_2 capacity at 77 K and 1 bar (wt%)
Amberlite XAD4	poly(styrene-co-divinylbenzene)	1,060	0.8
Amberlite XAD16	crosslinked aliphatic polymer	770	0.6
Lewatit EP63	poly(styrene-co-divinylbenzene)	1,200	1.3
Haysep N	poly(divinylbenzene-co-ethylene dimethacrylate)	460	0.5
Hypersol-Macronet MN200	hypercrosslinked polystyrene	840	1.3

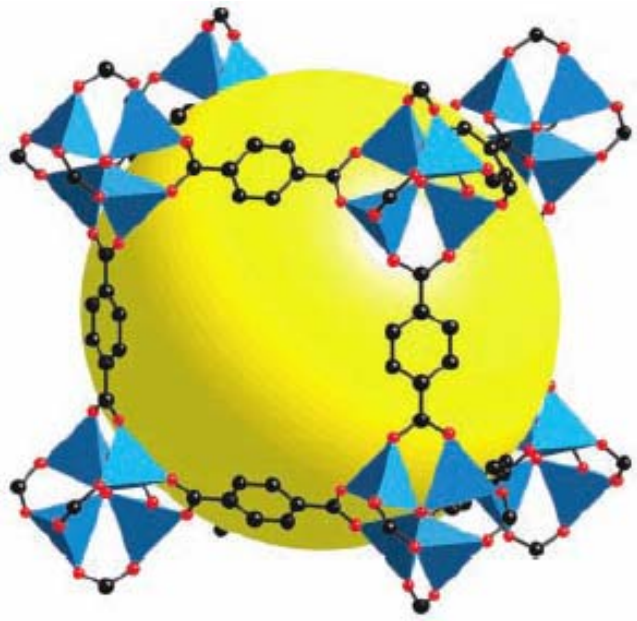
SYNTHESIS OF HYPERCROSSLINKED POLYMERS



GAS SORPTION IN HYPERCROSSLINKED POLYMERS

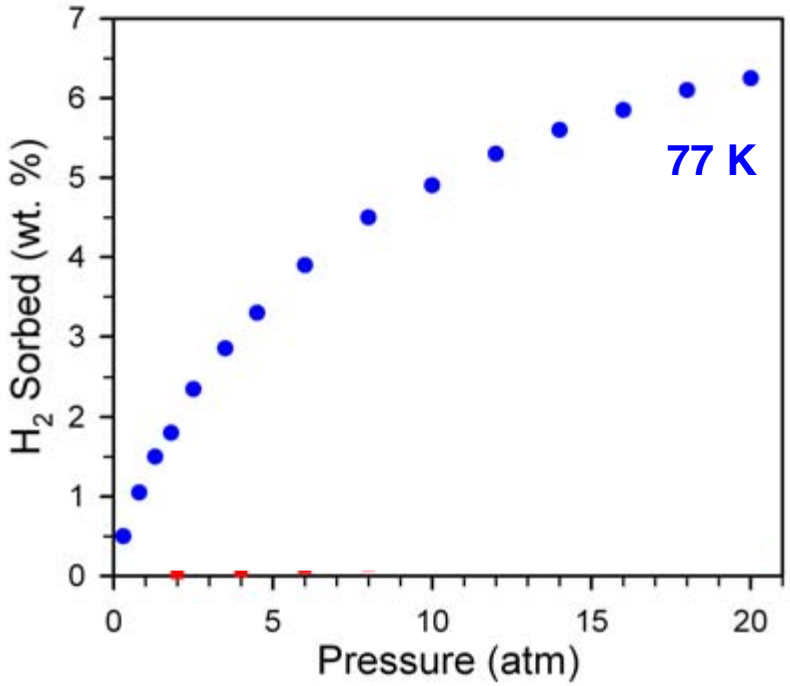
Precursor	Composition (%)	Character	BETsurface area (m^2/g)	H_2 capacity at 77 K and 1 bar (wt%)
Poly(vinylbenzyl chloride -co-divinylbenzene)	40.0 : 60.0	macroporous	310	0.4
		↓		
		hypercrosslinked polymer	1,300	1.20
Poly(vinylbenzyl chloride -co-divinylbenzene)	2.5 : 97.5	gel	0	0
		↓		
		hypercrosslinked polymer	1,930	1.55

MICROPOROUS COORDINATION SOLIDS (Long)



Zn_4O(1,4-benzenedicarboxylate)$_3$

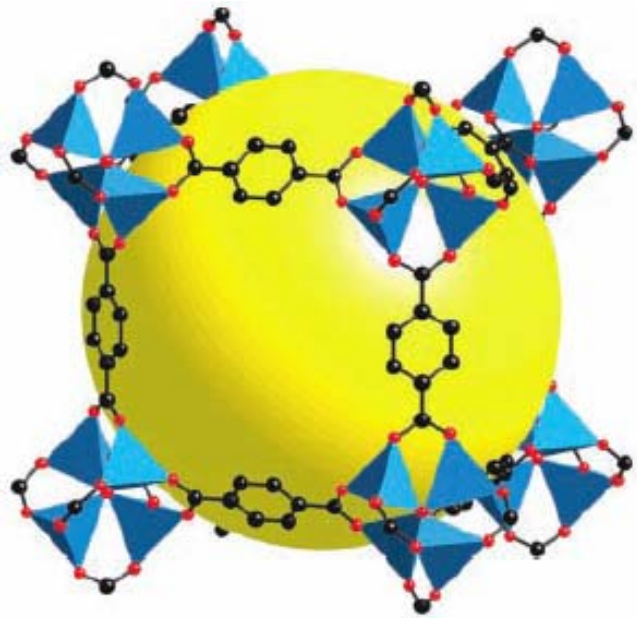
Yaghi and coworkers



Our results agree with Yaghi's

- Gravimetric storage capacity is quite high
- No strong binding sites, leads to adsorption enthalpy of just 5 kJ/mol
- Our goal is to create materials of this type with exposed metal coordination sites

MICROPOROUS COORDINATION SOLIDS (Long)



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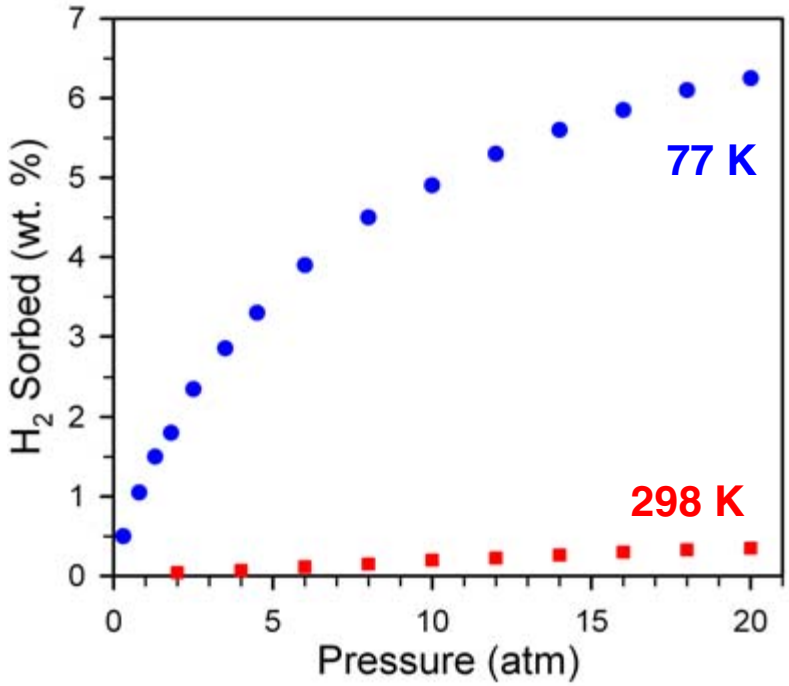


Our results agree with Yaghi's

- Gravimetric storage capacity is quite high, but only at low temperature
- No strong binding sites, leads to adsorption enthalpy of just 5 kJ/mol
- Our goal is to create materials of this type with exposed metal coordination sites

H_2 BINDING ENTHALPIES

$$MH_2 \rightleftharpoons M + H_2 \qquad \Delta H$$

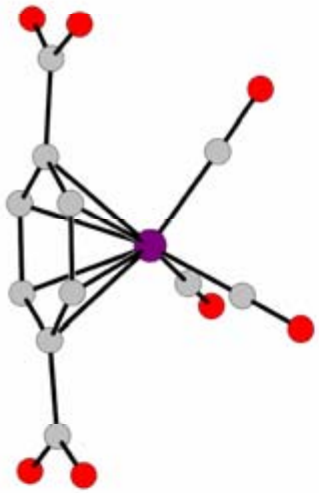
- Wide variation in binding enthalpy, depending upon character of metal and surrounding ligands
- For a storage material that operates at room temperature and moderate pressures would like to acheive:

ΔH = 10-20 kJ/mol

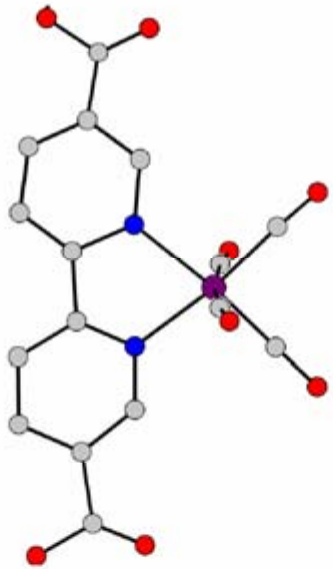
- Target lightweight metal ions that can potentially sustain many exposed coordination sites

M	ΔH (kJ/mol)
$Li^+_{(g)}$	27
$Na^+_{(g)}$	10
$K^+_{(g)}$	6
$Ti^+_{(g)}$	37
Cu^+ in chabazite	56
CuCl surface	93
$Cr(CO)_5$	78
$Mo(CO)_5$	81
$Cr(CO)_3(PCy_3)_3$	31
$Mo(CO)_3(PCy_3)_3$	27
$W(CO)_3(PCy_3)_3$	42
$OsH_2(CO)(P^iPr_3)_2$	82

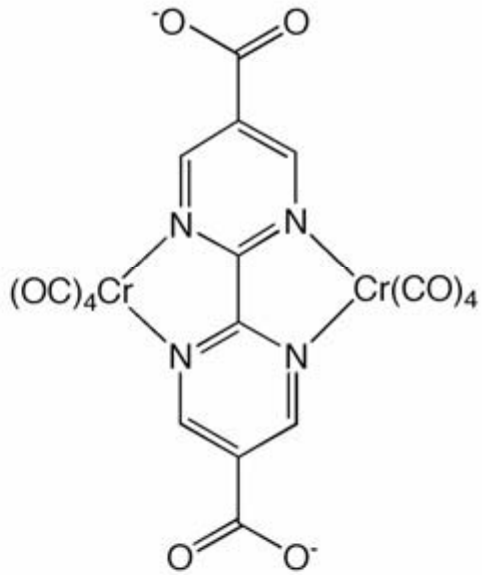
INCORPORATING METAL BINDING SITES



2.8 %



4.2 %



6.1 %

$$LCr(CO)_n \xrightarrow{\Delta/h\nu} LCr \underset{-\,H_2}{\overset{+\,H_2}{\rightleftharpoons}} LCr(H_2)_n$$

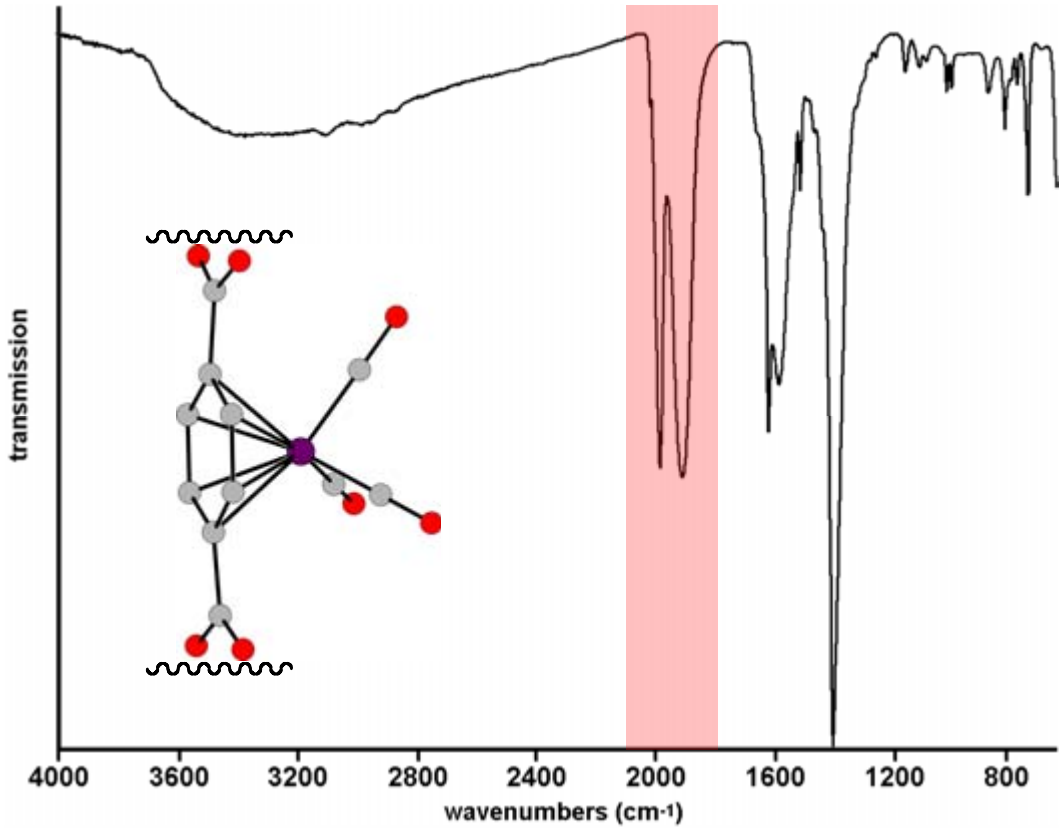
- Rigid framework will pin coordinatively-unsaturated metal centers, preventing aggregation
- Adjust binding affinity by varying metal center and/or ligand substituents

SYNTHESIS OF $Zn_4O(BDC\text{-}Cr(CO)_3)_3$

$Zn(NO_3)_2$

+

$(H_2BDC)Cr(CO)_3$



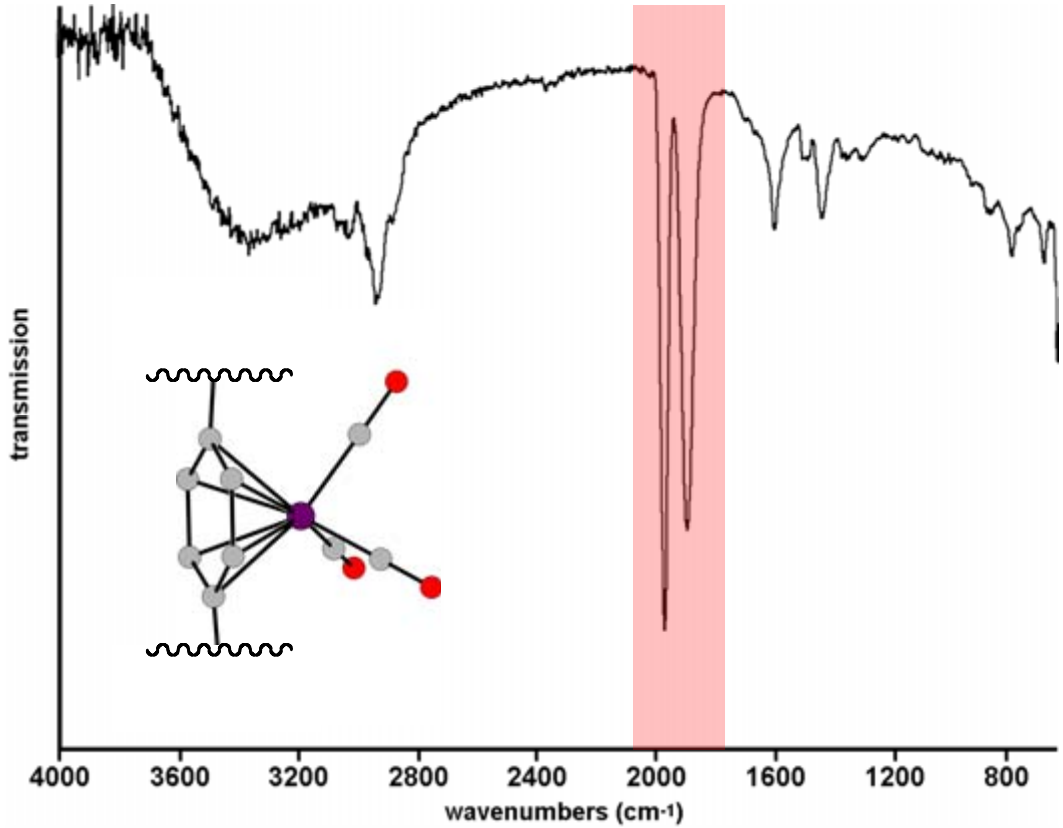
- Dark orange-red solid with the usual cubic structure by powder X-ray diffraction
- Intense CO stretches in IR spectrum are very similar to those of molecular precursor

METALLATION OF A MICROPOROUS POLYMER

$[CH_2CH(C_5H_6)]_n$

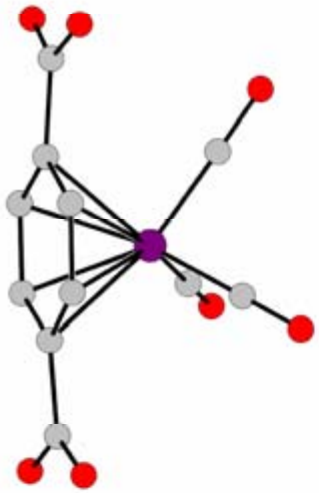
+

$Cr(CO)_6$



- Polymer turns dark orange-red in color and BET surface area drops to 650 m^2/g
- Appearance of CO stretches and comparison with model complex indicate incorporation

INCORPORATING METAL BINDING SITES



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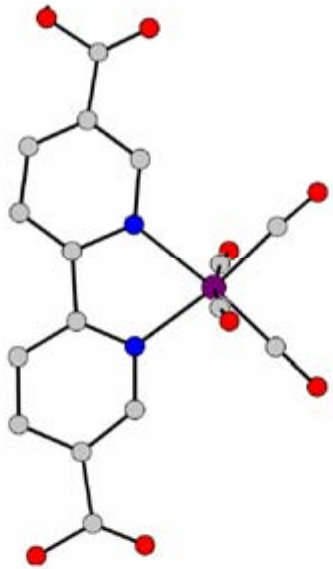
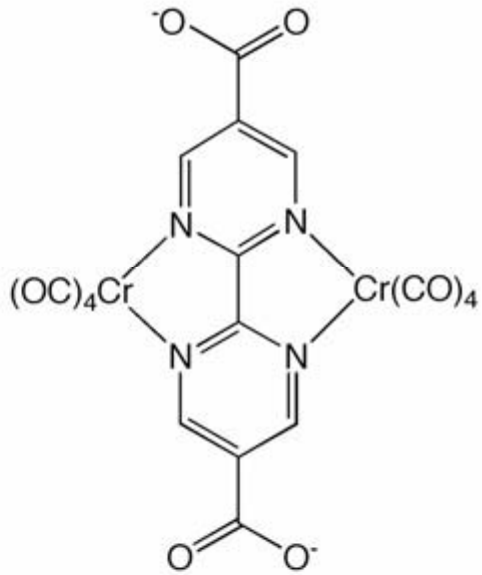


4.2 %



6.1 %

$$LCr(CO)_n \xrightarrow{\Delta/h\nu} LCr \underset{-\,H_2}{\overset{+\,H_2}{\rightleftharpoons}} LCr(H_2)_n$$

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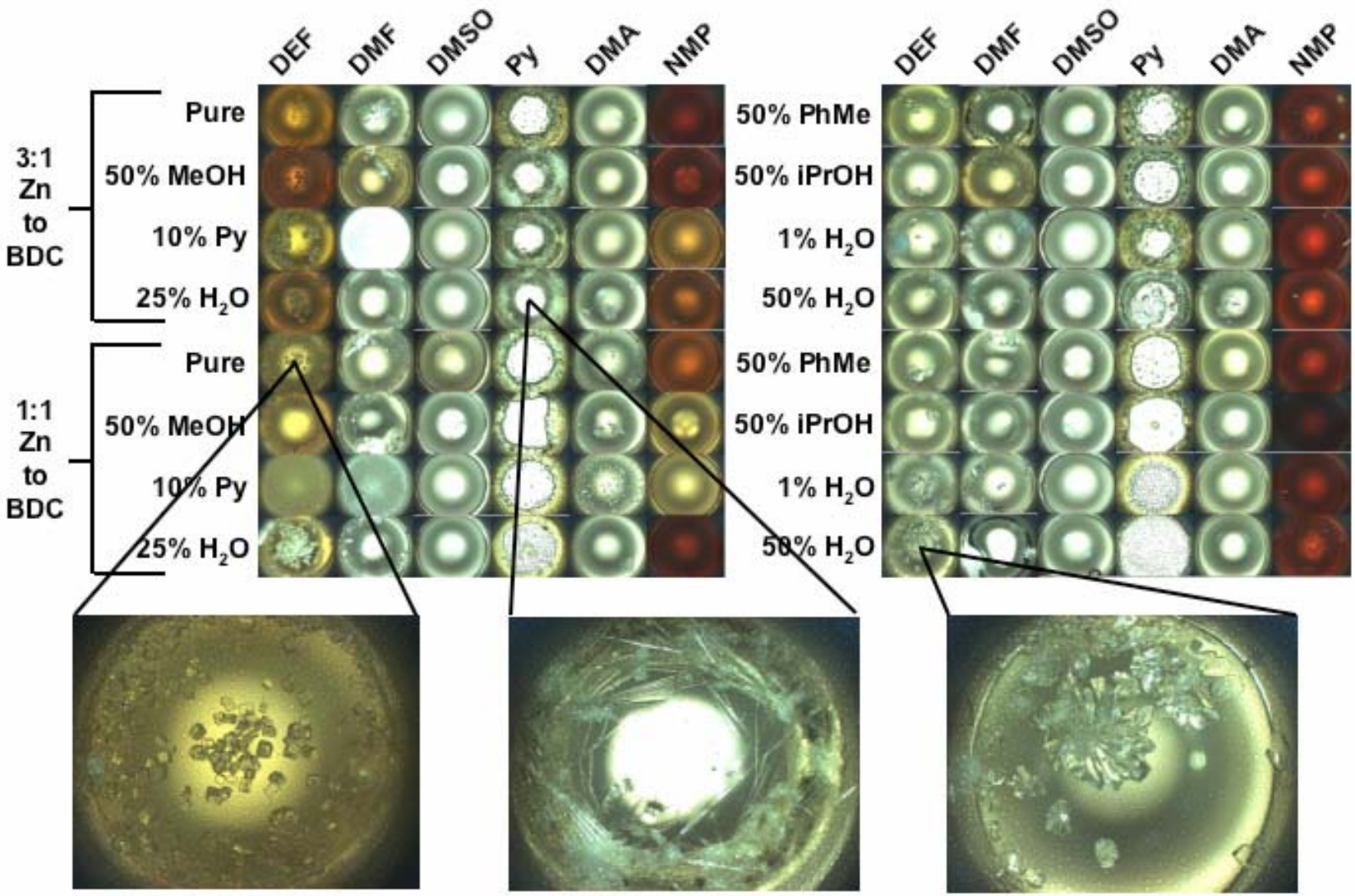
- Adjust binding affinity by varying metal center and/or ligand substituents

HIGH THROUGHPUT FRAMEWORK SYNTHESIS



with Tom Boussie and Dawn Verdugo at Symyx Technologies

CALCULATION OF H_2 BINDING AFFINITIES (Head-Gordon)

- **Goal:** Apply first-principles electronic structure calculations to evaluate interactions of H_2 with ligands and metals employed in microporous polymers and coordination solids

- Theory must accurately assess a range of possible effects:

  - Dispersion interactions (weak)

  - Interactions with localized charges (charge-quadrupole interactions)

  - Charge-transfer interactions involving forward and/or back donation

- Technical details:

  - Use our own optimized code (Q-Chem)

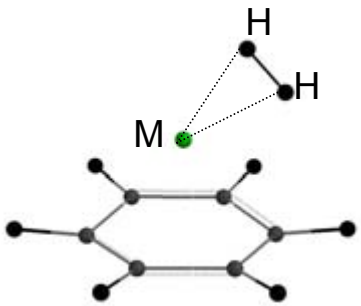
  - Use MP2 theory to correctly describe dispersion interactions (unlike DFT)

  - Use auxiliary basis expansions and local methods for efficiency

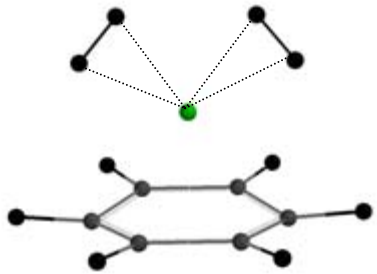
  - Correct energies for basis set superposition error

H_2 BINDING TO METAL-BENZENE COMPLEXES

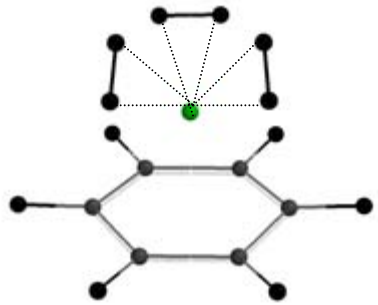
BP86/SRSC/6-311G** results for $(C_6H_6)M(H_2)_n$ complexes:



n = 1



n = 2



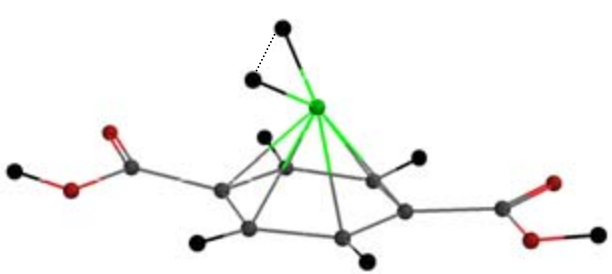
n = 3

M = Cr D_0:	16.0 kcal/mol	12.9 kcal/mol	12.5 kcal/mol
H-H:	0.906 Å	0.868 Å	0.888 Å
M = Mo D_0:	25.1 kcal/mol	13.4 kcal/mol	15.8 kcal/mol
H-H:	1.525 Å	0.895 Å	0.915 Å

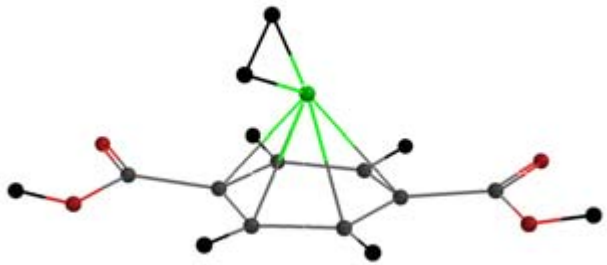
- Binding energies are a factor of 4 larger than desired
- Calculations on other first-row transition metals are in progress

H_2 BINDING TO METAL-H_2BDC COMPLEXES

BP86/SRSC/6-311G** results for $(H_2BDC)M(H_2)_n$ complexes:



M = Cr

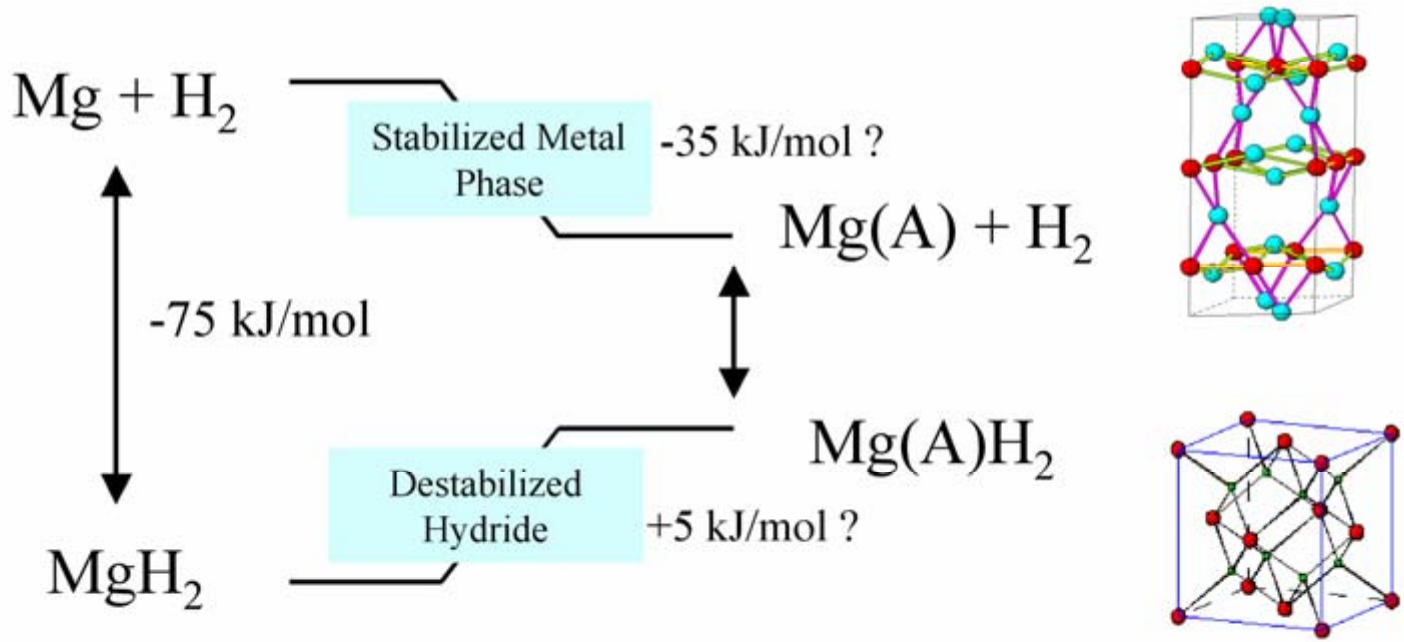


M = Mo

D_0:	14.8 kcal/mol	22.6 kcal/mol
H-H:	0.885 Å	1.013 Å

- Carboxylic acid substituents lower binding energy by ~2 kcal/mol
- Calculations will study effects of utilizing other benzene substituents

STABILIZED LIGHT METAL ALLOYS (Richardson)



- Research in the Richardson lab has already demonstrated destabilization of MgH_2 by doping with a few atom percent of a transition metal element
- Stabilization of the magnesium alloy can likely provide a larger energy change
- Both transition and main group metals are under investigation for this purpose

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