A Synergistic Approach to the Development of New Hydrogen Storage Materials

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This presentation does not contain any proprietary or confidential information

Project ID #: ST8

OVERVIEW

Timeline

- Project start date: new start
- Project end date: FY08
- Percent complete: new start

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

Budget

- Total funding expected: $5.275M
  - $4.53M from DOE ($2.98M to UC, $1.55M to LBNL)
  - $745k in cost-sharing
- Funding received in FY05: $500k

Partners

- ChevronTexaco
- General Motors
- Electric Power Research Institute

OVERALL VISION

- Bring together a group of top 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 AND PRIORITY ORDER

1. Set-up of H_2 storage characterization instrumentation at LBNL (Mao)
2. Synthesis and characterization of nanoporous polymers (Fréchet)
3. Synthesis and characterization of nanoporous coordination solids (Long)
4. First-principles determination of H_2 binding energies (Head-Gordon)

FY05 start

5. Synthesis and characterization of destabilized hydrides (Richardson)

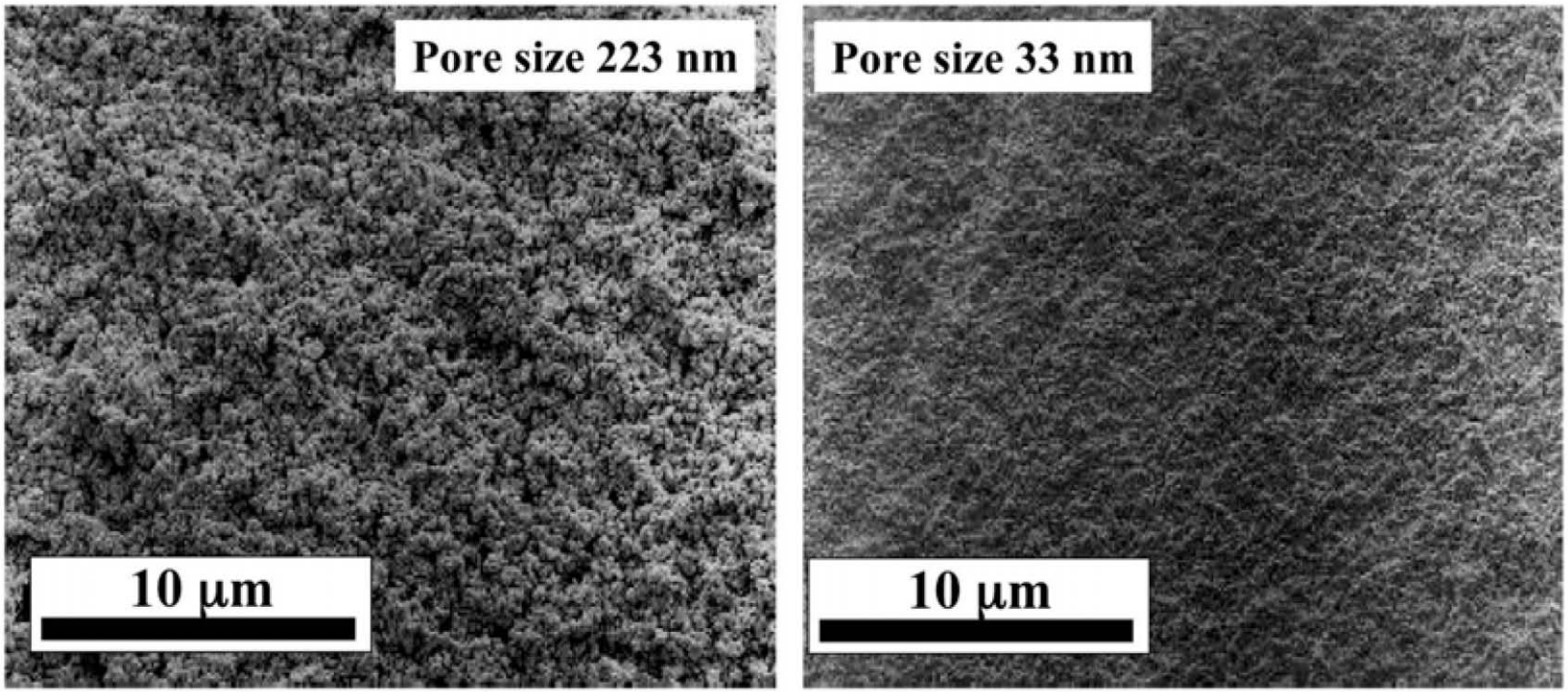
FY06 start

6. Synthesis and characterization of nanostructured boron nitrides (Zettl)
7. Theoretical predictions for nanostructured boron nitrides (Cohen and Louie)
8. Synthesis and characterization of Mg and metal alloy nanocrystals (Alivisatos)

H_2 STORAGE CHARACTERIZATION INSTRUMENT (Mao)

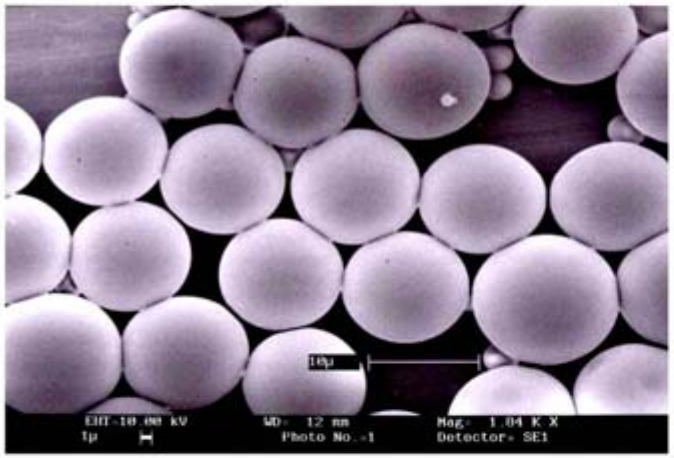
- Reliable instrumentation for measuring H_2 uptake at a variety of temperatures and pressures
- Gravimetric instrument for rapid screening of small mass samples
- Will consult closely with experts at Sandia-Livermore
- Intelligent Gravimetric Analyzer:
  Pressures: 10^{-5} mbar - 20 bar
  Temperatures: 77 -1100 K

NANOPOROUS POLYMERS (Fréchet)

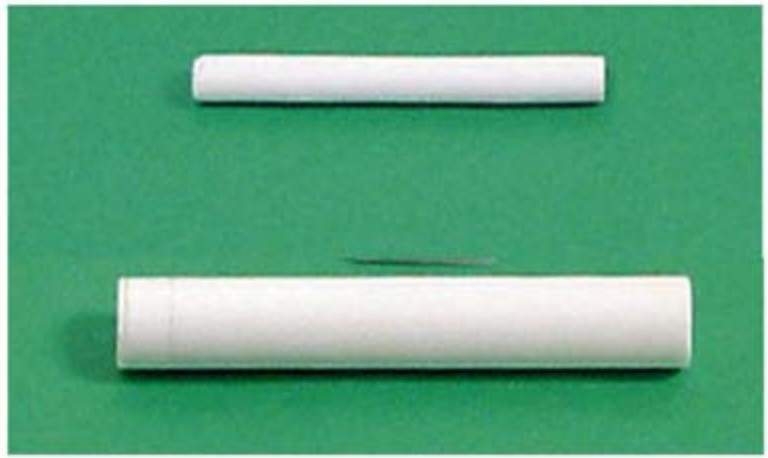


- Nanoporous polymers with specific surface areas of up to 800 m^2/g have been reported
- Fréchet group has extensive experience in the synthesis and characterization of such materials for use in liquid separations

READILY SCALEABLE AND PROCESSIBLE MATERIALS



beads



monolithic rods

- Nanoporous polymers can be manufactured reproducibly and inexpensively on a large scale in a single reaction step from polymerization mixtures comprising suitable monomers and porogens
- Resulting materials can be produced in a variety of forms and are easily molded into a desired shape

ENHANCING POROSITY AND H_2 AFFINITY

- Supercritical CO_2 will be used as a porogen to create nanoporous polymers with specific surface areas above 1500 m^2/g:

  Solvency of CO_2 readily controlled via temperature and pressure

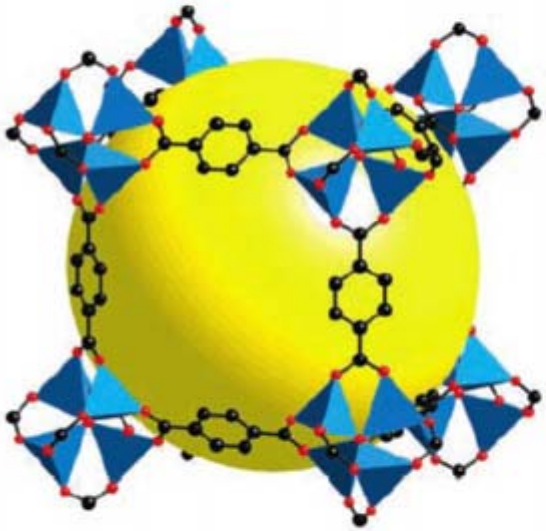
  Removal of CO_2 from pores is achieved simply by releasing pressure

- Aromatic polymer backbones and pendant groups will be utilized to enhance H_2 binding—take advantage of building units found to work in porous coordination solids (see below)

- Pyrolysis of resulting materials can potentially increase surface area and H_2 binding

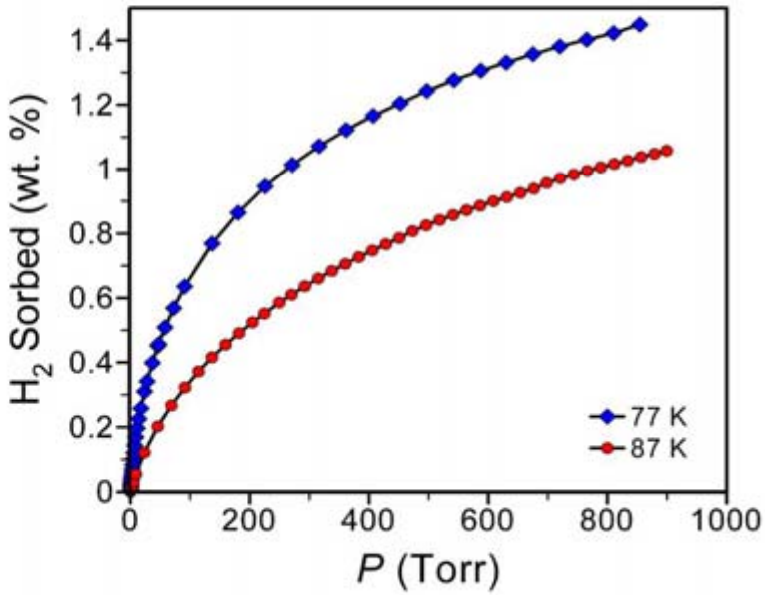
- A conductive polymer could also potentially store hydrogen via charge transfer into the conduction band, resulting in an electrically-activated uptake and release mechanism

NANOPOROUS COORDINATION SOLIDS (Long)



$Zn_4O(O_2C\text{-}C_6H_4\text{-}CO_2)_3$

Yaghi and coworkers



- Materials of this type can have surface areas as high as 4500 m^2/g
- Napthalene analogue reported to adsorb 2.0 wt. % H_2 at 10 bar and 298 K
- Application of the Clausius-Clapeyron equation gives H_2 binding enthalpies in the range 4.7-5.2 kJ/mol (would like to increase to ~40kJ/mol)

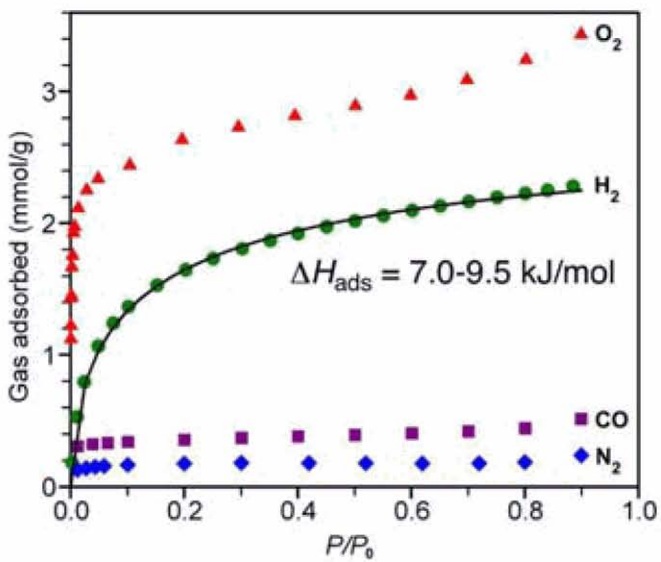
MAGNESIUM-BASED FRAMEWORKS

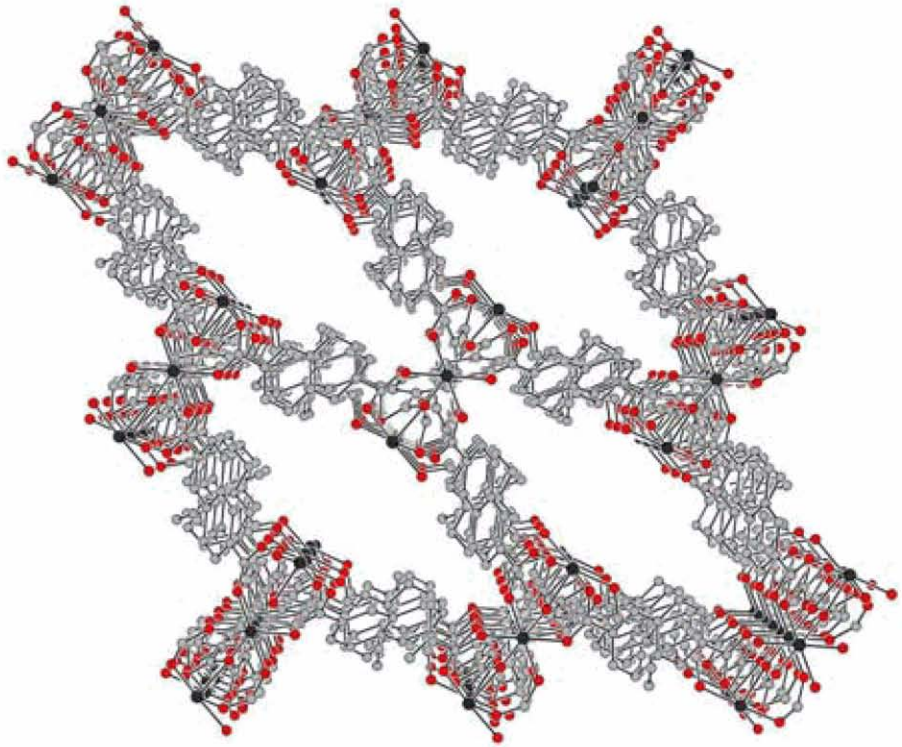
Mg^{2+}

+

$HO_2C\text{-}C_{10}H_6\text{-}CO_2H$

$\xrightarrow[\text{DEF}]{100\ ^\circ C}$



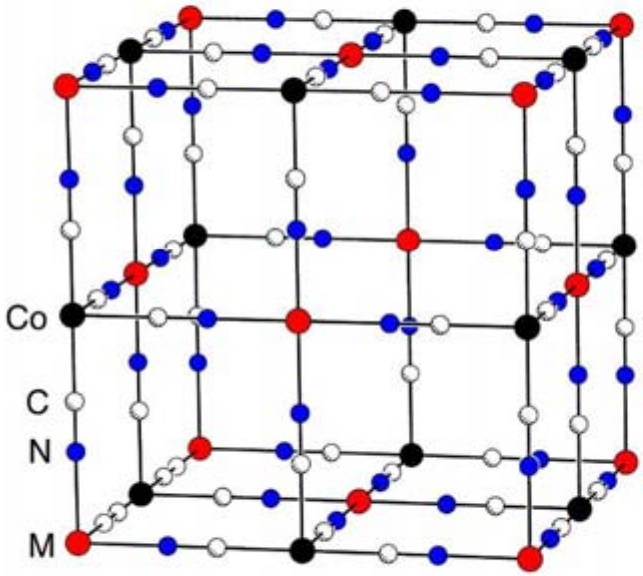


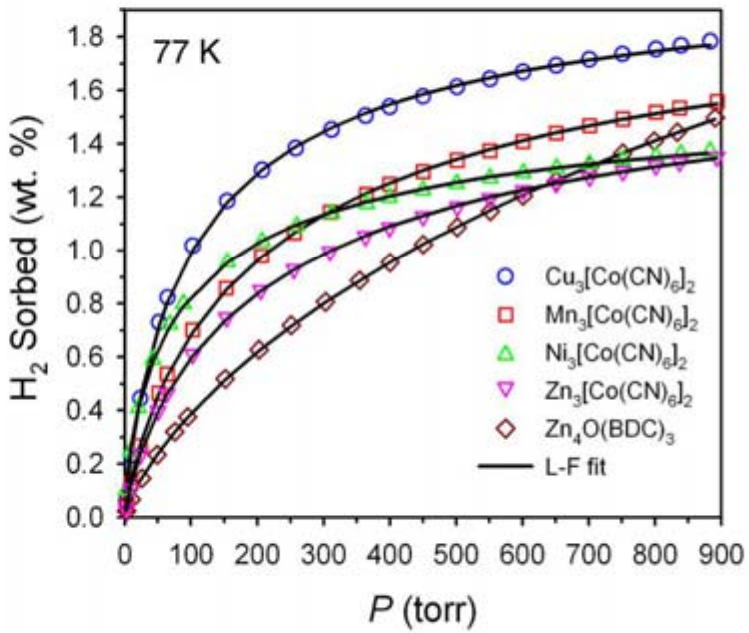
$Mg_3(O_2C\text{-}C_{10}H_6\text{-}CO_2)_3 \cdot 4DEF$

- Related reaction produces a solid containing an isostructural $Zn_3(O_2C\text{-}C_{10}H_6\text{-}CO_2)_3$ framework
- Material absorbs H_2 and O_2, but not N_2 or CO! May be useful for separations

Dinca, Long *J. Am. Chem. Soc.*, submitted

H_2 STORAGE IN $M_3[Co(CN)_6]_2$ PRUSSIAN BLUE ANALOGUES



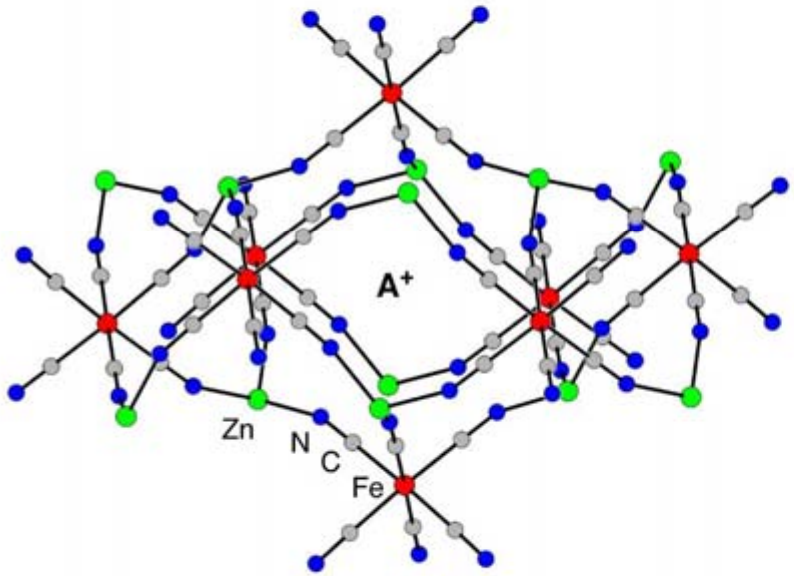


- H_2 binding enthalpies vary with changes in the coordinatively-unsaturated metal M
- Saturation at 1.9 wt. % expected for binding one H_2 at each open metal coordination site
- Incorporation of square pyramidal $[Co(CN)_5]^{3-}$ should give still further open coordination sites:

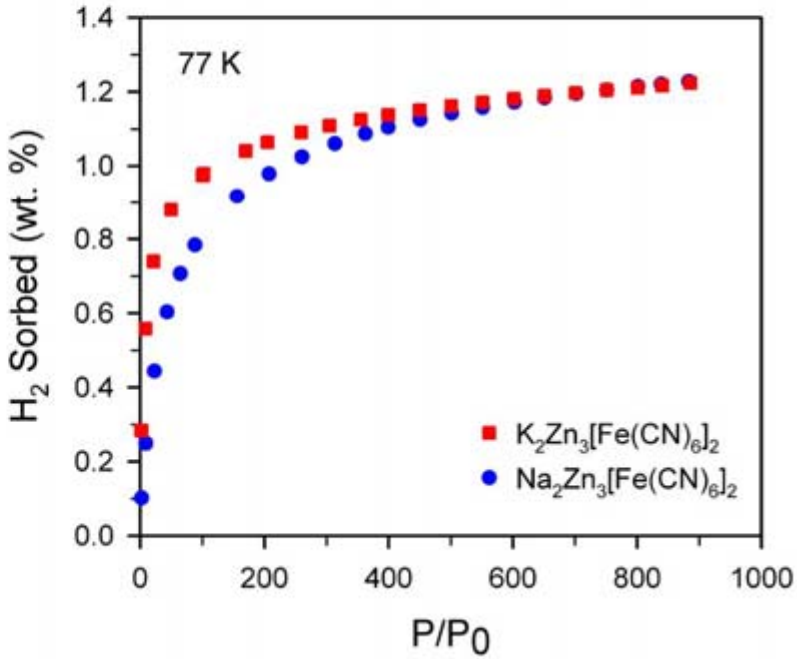
$Co_3[Co(CN)_5]_2$: 3.5 wt. %, 0.041 kg/L **$Mg_3[Co(CN)_5]_2$: 4.3 wt. %, 0.041 kg/L**

Kaye, Long *J. Am. Chem. Soc.* **2005**, *127*, ASAP

ANIONIC FRAMEWORKS

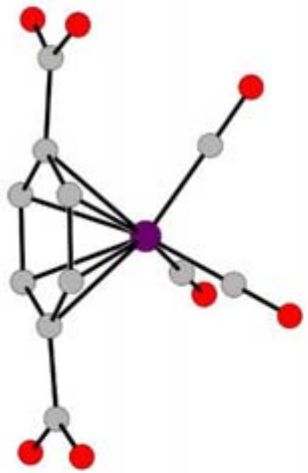


$A_2Zn_3[Fe(CN)_6]_2$

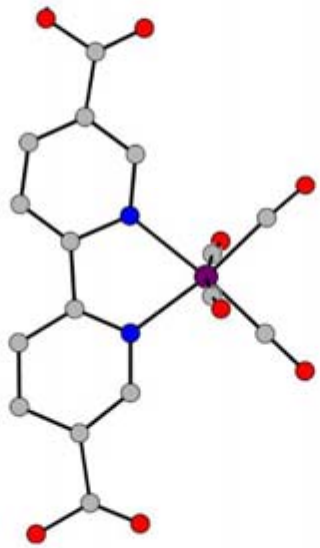


- Cations within cavities are readily varied: A = H^+, Li^+, Na^+, K^+, and possibly Mg^{2+} and Cu^+
- A = Na^+ and K^+ already measured at 6.9-7.3 and 7.1-8.5 kJ/mol, respectively
- Lighter weight main group metal-cyanide frameworks should lead to much higher storage capacities

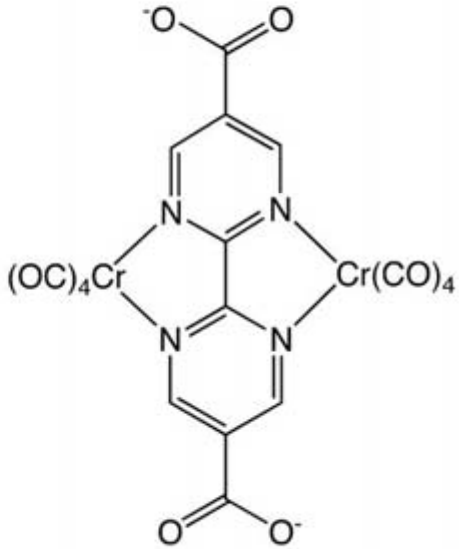
INCORPORATING METAL BINDING SITES



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; utilize light main group metal centers similarly

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 nanoporous 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)

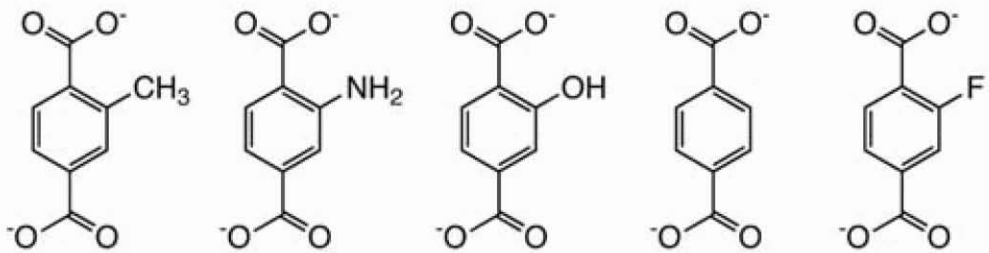
  - Use MP2 theory to correctly describe dispersion interactions (unlike DFT)

  - Use auxiliary basis expansions and local methods for efficiency

  - Correct energies for basis set superposition error

INITIAL TEST SYSTEMS

- Probe the effect of electron withdrawing/donating substituents on terephthalic acid:



Theory:	-4.33	-4.30	-4.16	-4.03	-3.77 kJ/mol

- Evaluate ligand-H_2 electrostatic interactions:

CO — H_2	-1.1 kJ/mol	(largely dispersion)
CN^- — H_2	-15.2 kJ/mol	(charge-quadrupole)
Cp^- — H_2	-15.4 kJ/mol	(charge-quadrupole)

- Longer-term objectives:
  - Characterize interaction of H_2 with transition metal and light maingroup metal ions
  - Identify ligands that display strong charge-transfer interactions with H_2
  - Complete full computational survey of relevant H_2 interactions
  - Predict infrared, NMR, and INS spectra to aide in characterizing H_2 interactions

DESTABILIZED LIGHT METAL HYDRIDES (Richardson)

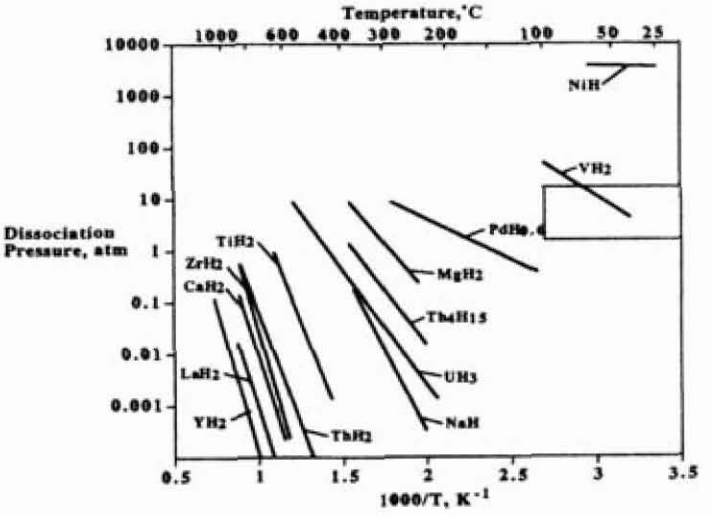
$$M + H_2 \rightleftharpoons MH_2$$

$\Delta S \sim 135$ J/molK

$\Downarrow$

$\Delta H \sim -40$ kJ/mol

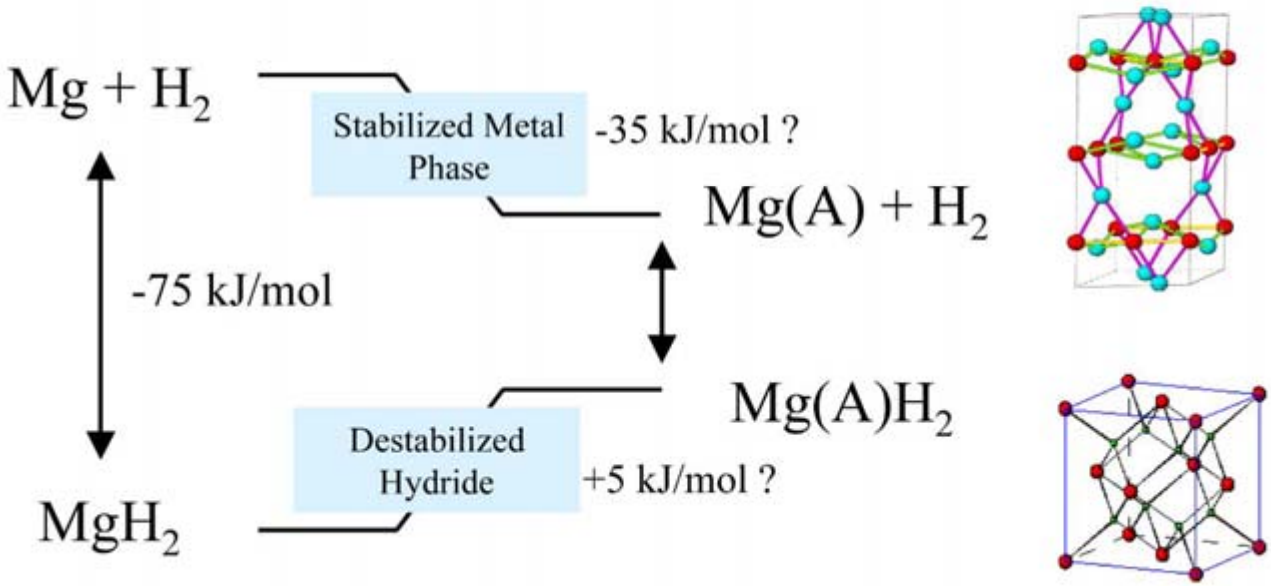
for reversibility at 1 atm and 300 K



Sandrock, *J. Alloys and Compounds*, **293**, 877 (1999).

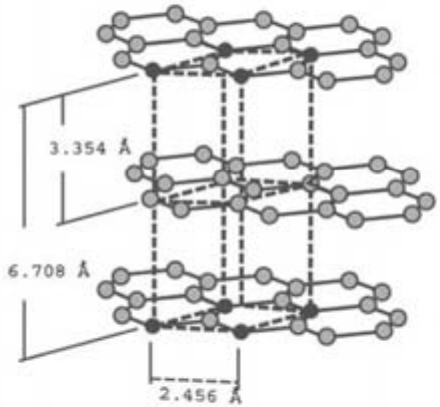
- Dissociation pressure is determined by heat of formation of the metal hydride; this also represents the heat that must be removed during refueling
- With $\Delta H = -75$ kJ/mol, MgH_2 is one of the best candidates for H_2 storage
- We will attempt to adjust ΔH via solid solution or alloy formation

MAGNESIUM ALLOY ENERGETICS

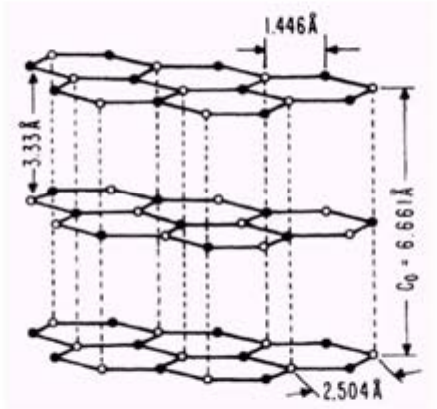


- Research in the Richardson lab has already demonstrated destabilization of MgH_2 by doping with a few atom percent of a transition metal element
- Stabilization of the magnesium alloy can likely provide a larger energy change
- Both transition and main group metals will be investigated for this purpose

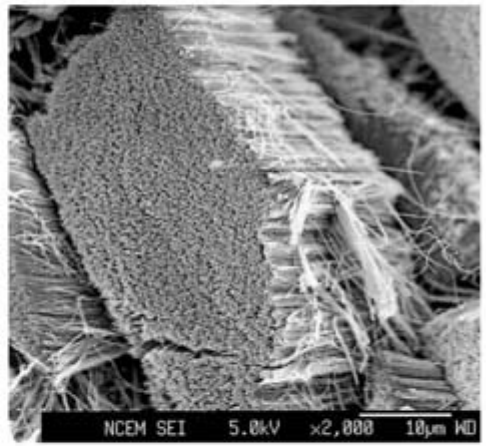
SYNTHESIS OF NANOSTRUCTURED BORON NITRIDE (Zettl)



graphite



BN

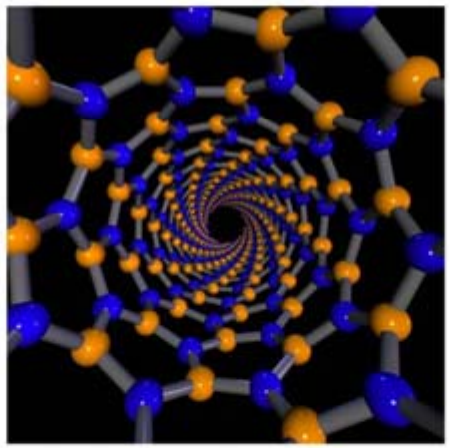


- Zettl group has discovered a CVD-like method by which carbon nanotubes can be converted directly into BN nanotubes:

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

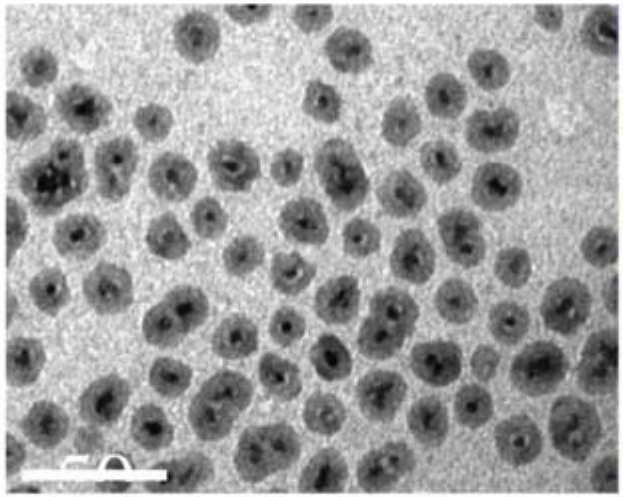
- Approach will be applied in converting other forms of carbon into nanostructured BN
- Intermediate materials of the type $C_xB_yN_z$ will also be investigated

PREDICTIVE THEORY FOR NANOSTRUCTURED BORON NITRIDE (Cohen and Louie)



- Plane wave total energy pseudopotential approach and DFT will be used in probing electronic structure of BN-based materials
- Head-Gordon's methods will be adopted for assessing H_2 binding energies within such extended systems
- Theory will then be used in predicting new structure types and morphologies with features leading to maximal coverage and a high H_2 binding affinity

MAGNESIUM AND METAL ALLOY NANOCRYSTALS (Alivisatos)



- Synthesize Mg nanocrystals via reduction of Mg^{2+} in presence of a surfactant
- Study size and shape dependence of thermodynamics and kinetics of hydrogen storage
- Investigate methods for keeping nanocrystal surfaces well-separated
- Extend synthetic methods to destabilized high-density hydrides discovered by Richardson

SUMMARY

- Purchase of an instrument for measuring H_2 uptake is in progress
- Projects on nanoporous polymers and coordination solids and accurate calculation of H_2 binding energies have begun, and work toward enhancing storage capacities and binding enthalpies is underway
- Projects on destabilized hydrides, nanostructured boron nitride, and Mg nanocrystals are planned to begin in FY06
- Go-no go decision points for the projects are planned as follows:
  - End of year 1: demonstration of utility of theory predictions
  - End of year 2: uptake of >2.0 wt. % in polymers and coordination solids
  - End of year 3: reversible storage of >4.5 wt. % in high-density hydrides
  - End of year 3: uptake of >2.0 wt. % in nanostructured boron nitride
  - End of year 3: utility of theory predicting new boron nitride materials
  - End of year 3: improvement over bulk for H_2 storage in Mg nanocrystals

The following panels contain supporting information, and will not be shown in the actual presentation.

PUBLICATIONS

"Hydrogen Storage in the Dehydrated Prussian Blue Analogues $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu, Zn)" Kaye, S. S.; Long, J. R.*J. Am. Chem. Soc.* **2005**, *127*, in press.

"Strong H_2 Binding and Selective Gas Adsorption within the Microporous Coordination Solid $Mg_3(O_2C\text{-}C_{10}H_6\text{-}CO_2)_3$" Dinca, M.; Long, J. R. *J. Am. Chem. Soc.*, submitted.

PRESENTATIONS

"Hydrogen Storage in Porous Metal-Cyanide Frameworks" Kaye, S. S.; Long, J. R. *The 229th Meeting of the American Chemical Society*, San Diego, CA, March 14, 2005.

"Hydrogen Storage in the Dehydrated Prussian Blue Analogues $M_3[Co(CN)_6]_2$ (M = Mn, Fe, Co, Ni, Cu, Zn)" Kaye, S. S.; Dinca, M.; Yu, A. F.; Long, J. R. *Pacifichem 2005*, Honolulu, HI, scheduled for December 18, 2005.

HYDROGEN SAFETY

The most significant hydrogen hazard associated with this project is in the sudden release of hydrogen cylinder contents that may result in a fire.

HYDROGEN SAFETY

Our approach to deal with this hazard is to:

(1) Keep the hydrogen gas in a fume hood, equipped with fire sprinklers.
(2) Use two point securing with non combustible chains.
(3) Have the regulator shop design and install the gas conveyance system.
(4) Control all spark and other ignition sources.
(5) Keep non compatible materials (oxidizing agents) out of the fume hood.
(6) Use a minimum quantity of hydrogen gas so that if a sudden release were to occur, the fume hood ventilation rate would dilute the resulting airborne hydrogen gas to a concentration less than 25% of hydrogen's Lower Explosive Limit of 4%.