DOE Carbon-based Hydrogen Storage Center of Excellence: Center Highlights and NREL Activities

NREL Team: J.L. Blackburn, C. Curtis, M. Davis, A.C. Dillon, C. Engtrakul, T. Gennett†, M.J. Heben, K.M. Jones, Y.-H. Kim, P.A. Parilla, L.J. Simpson, E.S. Whitney, S.B. Zhang, Y. Zhao

National Renewable Energy Laboratory

† Rochester Institute of Technology

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This presentation does not contain any proprietary or confidential information

ST 23 and STP 20

Overview: Timeline and Budget

Timeline

- Center of Excellence start date: FY05
- Center of Excellence end date: FY09
- Percent complete: 20%

Barriers

- See next slide

Budget

- Center funding
  - $27.5 M for five-year CoE
  - $2.5 M Contractor share (20% of Contractor budget)
- $2 M in FY05 for NREL
- $2.1 M in FY06 for NREL

Partners

Rice (J. Tour), Rice (B. Yakobson, R. Hauge), Air Products (A. Cooper), Duke (J. Liu), CalTech (C. Ahn), LLNL (J. Satcher), NIST (D. Neumann, ORNL (D. Geohegan), Penn State (P. Eklund), U. Michigan (R. Yang), University of North Carolina (Y. Wu), U. Penn. (A. MacDiarmid) + others outside of the COE

Overview: Barriers & Targets

General

A. Cost.
B. Weight and Volume.
C. Efficiency.
E. Refueling Time

Reversible Solid-State Material

M. Hydrogen Capacity and Reversibility.
N. Lack of Understanding of H Physi- and Chemisorption.
O. Test Protocols and Evaluation Facilities.

Crosscutting Relevance

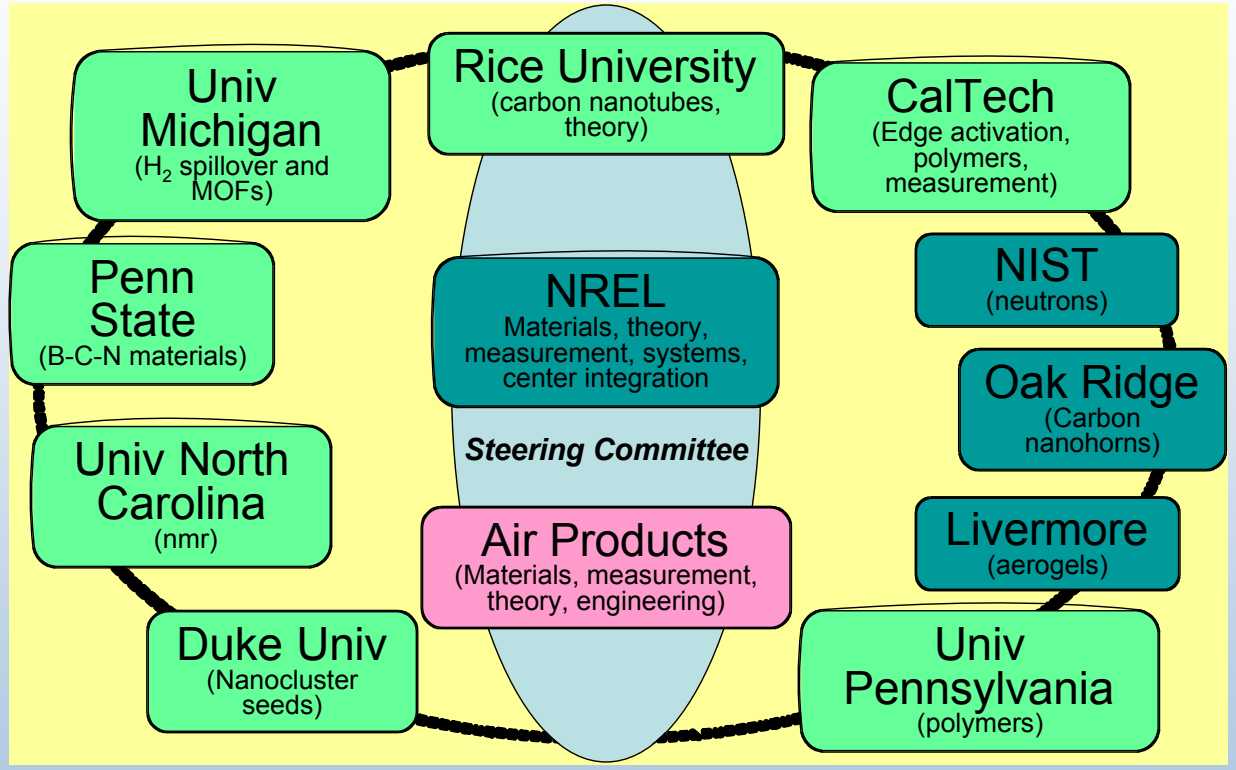
Compressed Gas Systems Barrier H: Sufficient Fuel Storage for Acceptable Vehicle Range.
Off-Board Hydrogen Storage Barriers S & T: Cost and Efficiency

DOE 2010 Technical Targets for Storage System

- Gravimetric 0.06 kg H_2/ kg
- Volumetric 0.045 kg H_2/m^3

COE Interactions & Collaborations

8 university projects (at 7 universities), 4 government labs, 1 industrial partner



Also: *IEA (R. Chahine, K. Ross), several IPHE collaborators, SwRI, Stanford GCEP, NIST, NASA, Virginia Commonwealth U. (G. Glaspell, P. Jena), Argonne National Lab (R. Ahluwalia), ATMI, synergy with two BES projects at NREL, and two BES projects at ORNL.*
Organization of Conferences: *IPHE (Lucca, 6/'05), MRS (Fall '04, Fall '05, Spring '06, Fall '07), ECS (Spring '06, Spring '07), APS '07*

Objectives

- Investigate a variety of adsorbent materials known to store hydrogen to determine limits of performance.
- Design and synthesize materials that bind hydrogen as either (i) weakly and reversibly bound atoms or (ii) as strongly bound molecules.
- Understand possible mechanisms and the interplay between structure, binding, and material and storage densities (volumetric and gravimetric).
- Develop the experimental and computational tools to speed discovery, testing, and deployment of new materials that meet DOE system goals.
- Create a collaborative, nimble environment to permit expeditious exploration, research, and deployment (sum of whole > sum of parts).
- Enable new storage system concepts possible with “smart” materials to meet DOE system targets.
  - Conformal tanks with low T and moderate P (<100 bar) operation
  - Hybrid nano-engineered systems with near STP operation

Approach: Optimize H Binding Energy, Surface Area, and Site Density

A number of advanced materials are being investigated

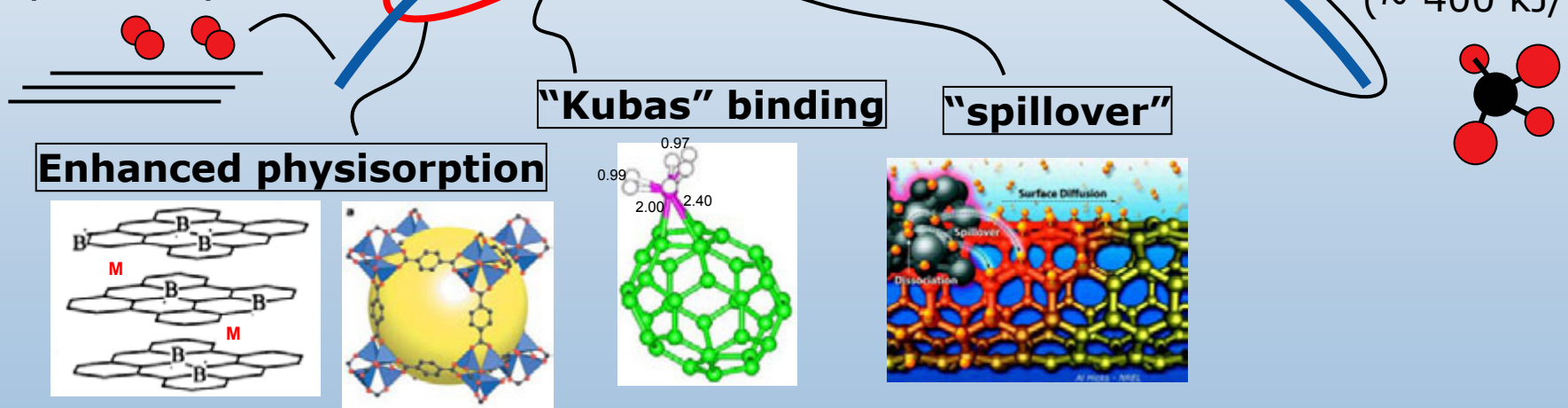
CbHS CoE
Binding energies of interest:
10 - 50 kJ/mol

Metal hydrides
50 - 100 kJ/mol

Chemical hydrides
> 100 kJ/mol

graphite-H_2
physisorption
(4 kJ/mol)

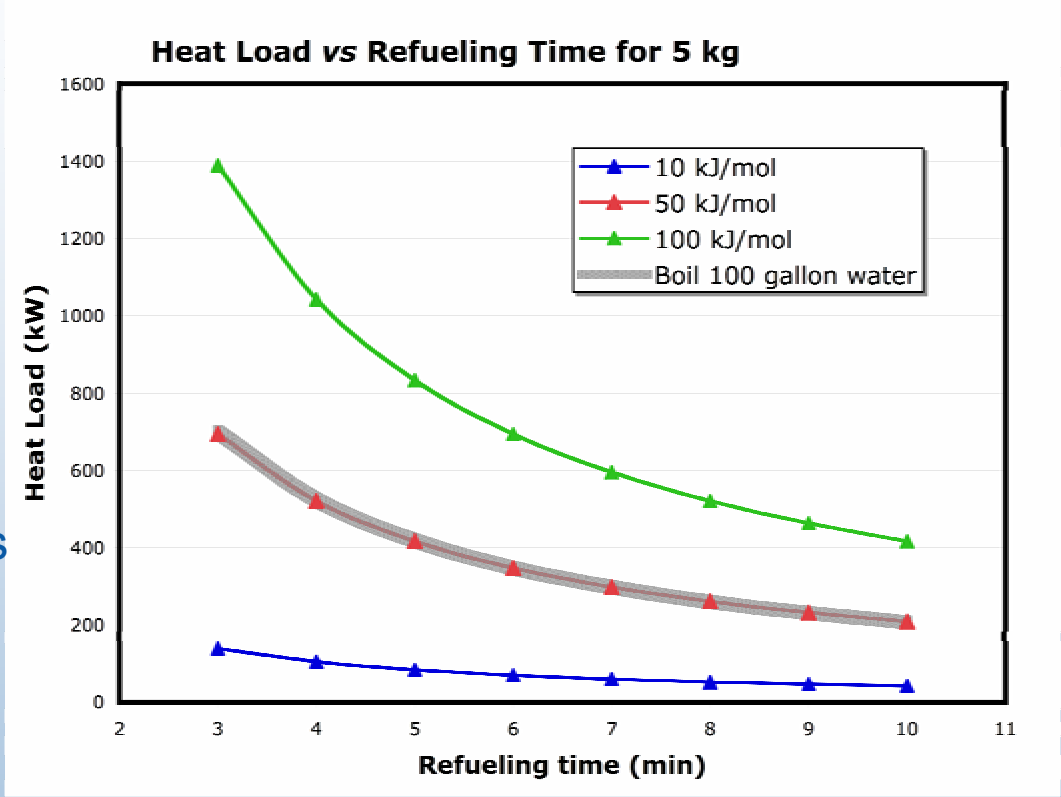
Methane
(~ 400 kJ/mol)



Materials with appropriate binding energies, sufficient surface area, low-weight and high material density will meet DOE hydrogen storage system targets and enable high-efficiency on-vehicle refueling

Approach: Binding Energy Impacts System Design

- Optimized binding is essential to enable on-vehicle refueling and reduce overall costs
  - High hydrogen capacity is typically associate with a high binding energy and/or irreversible chemical reactions
  - Properly designed materials can have high hydrogen capacities and desired intermediate binding energies (10 - 50 kJ/mol)



- *Too large of a binding energy will lead to energy penalties during charge & discharge, prohibit on-board recharging, reduce system capacities (heat exchangers), increase costs of the system and the hydrogen fuel*
- *Too low of a binding energy will reduced system capacities (cooling & insulation), increase system costs*

Approach: NREL Roles/Responsibilities

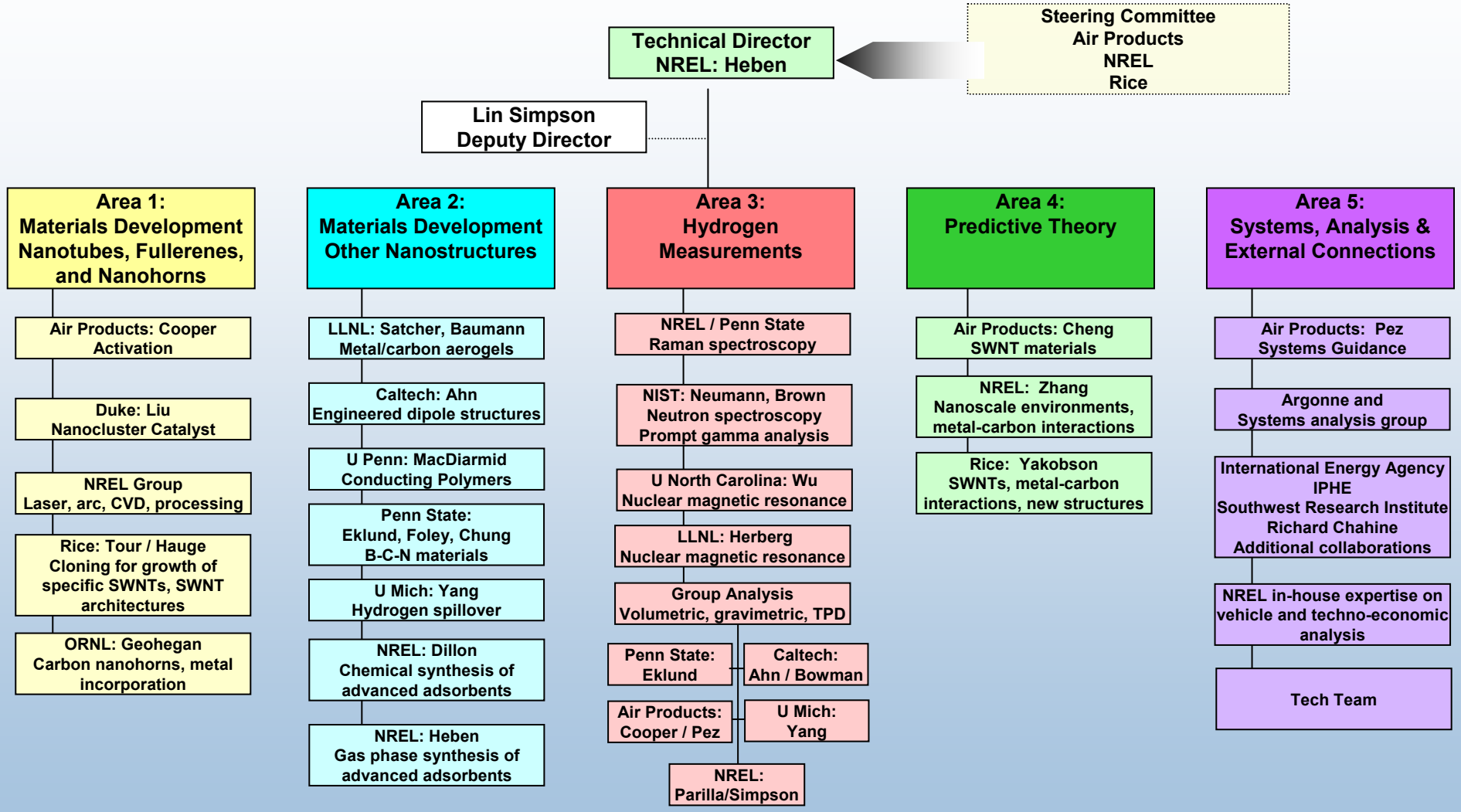
- Perform activities in five task areas in support of DOE mission
- Insure COE activities are aligned with DOE goals
- Promote communication and collaboration to expedite progress towards targets
- Create a nimble research and technology development environment to pursue new opportunities as they arise, in support of DOE

NREL in-house task areas

Task 1: Hydrogen Adsorption Measurements (Parilla)
Task 2: Gas Phase Synthesis of Nanostructured Carbon-based Adsorbents (Heben)
Task 3: Chemical Synthesis of Nanostructured Carbon-based Adsorbents (Dillon)
Task 4: Theory of Hydrogen Storage in Nanomaterials (Zhang)
Task 5: Center Integration (Simpson)

NREL performs research and development on advanced adsorbents, provides technical and scientific leadership to the COE, and serves as a resource for the COE and the larger community

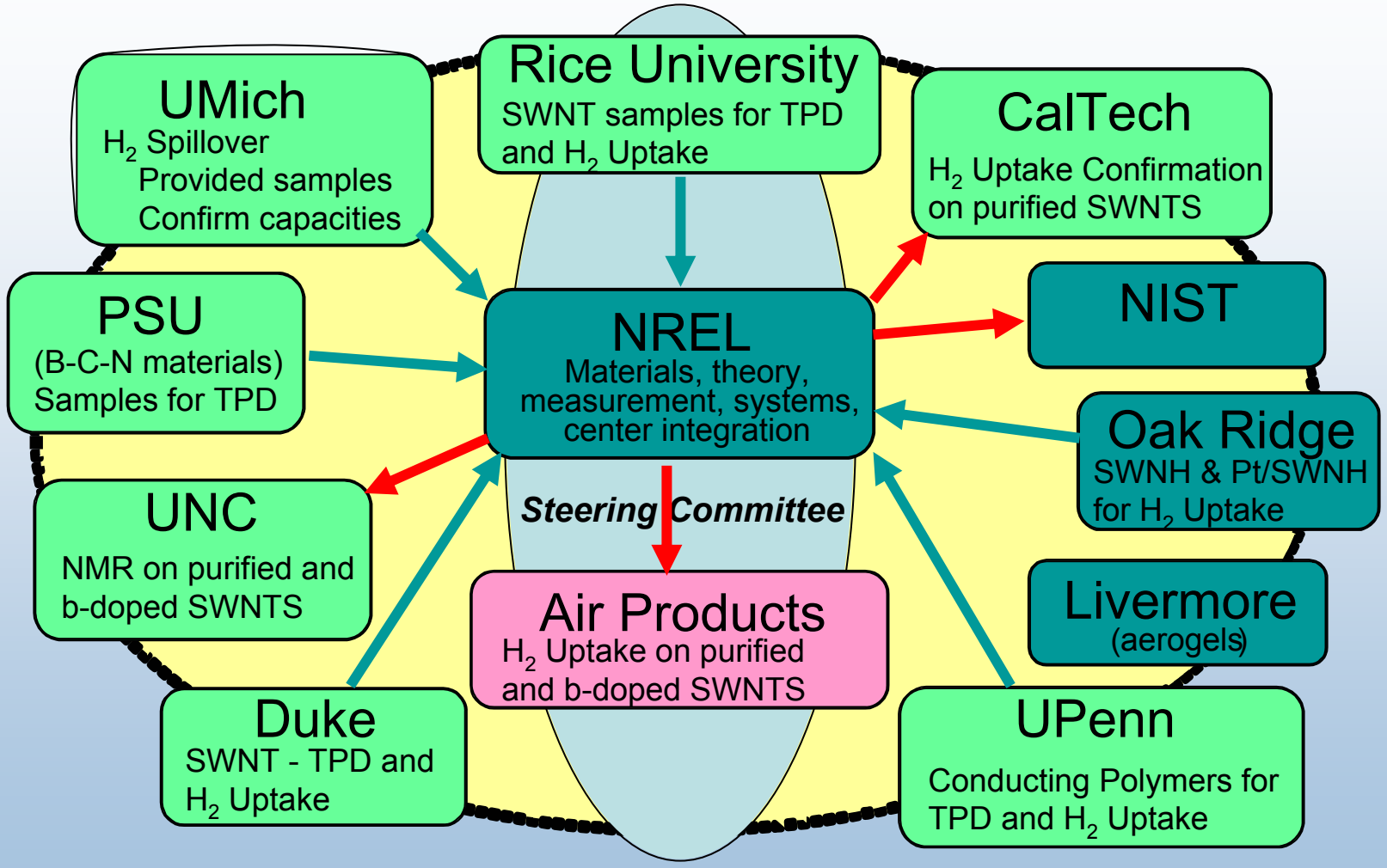
Approach: Center Organization



Center is organized into five areas - collaboration on projects across areas speeds development.

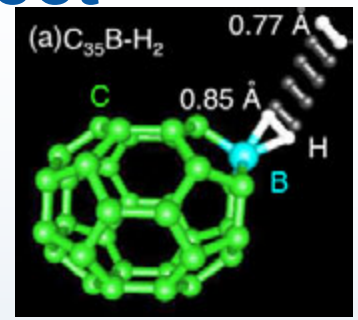
COE Accomplishment: Technical Interactions

NREL developed technical interactions with nearly all COE partners



COE mode accelerates research and development efforts to meet DOE hydrogen storage system targets. The COE is also working with SwRI, ATMI, U. Quebec, BES projects, and individuals outside of the COE.

COE Accomplishment: B-doping Project



Kim, et al., Phys. Rev. Lett. **96**, 016102 (2006)

Motivation: Enhanced H_2 binding

C-B-H_2 theory
NREL

Materials Synthesis

B-doped materials - PSU
Carbons and arc SWNTs

B-doped materials - NREL
Laser SWNTs

Measurement & Characterization

Volumetric - PSU

Small volumetric & TPD - NREL

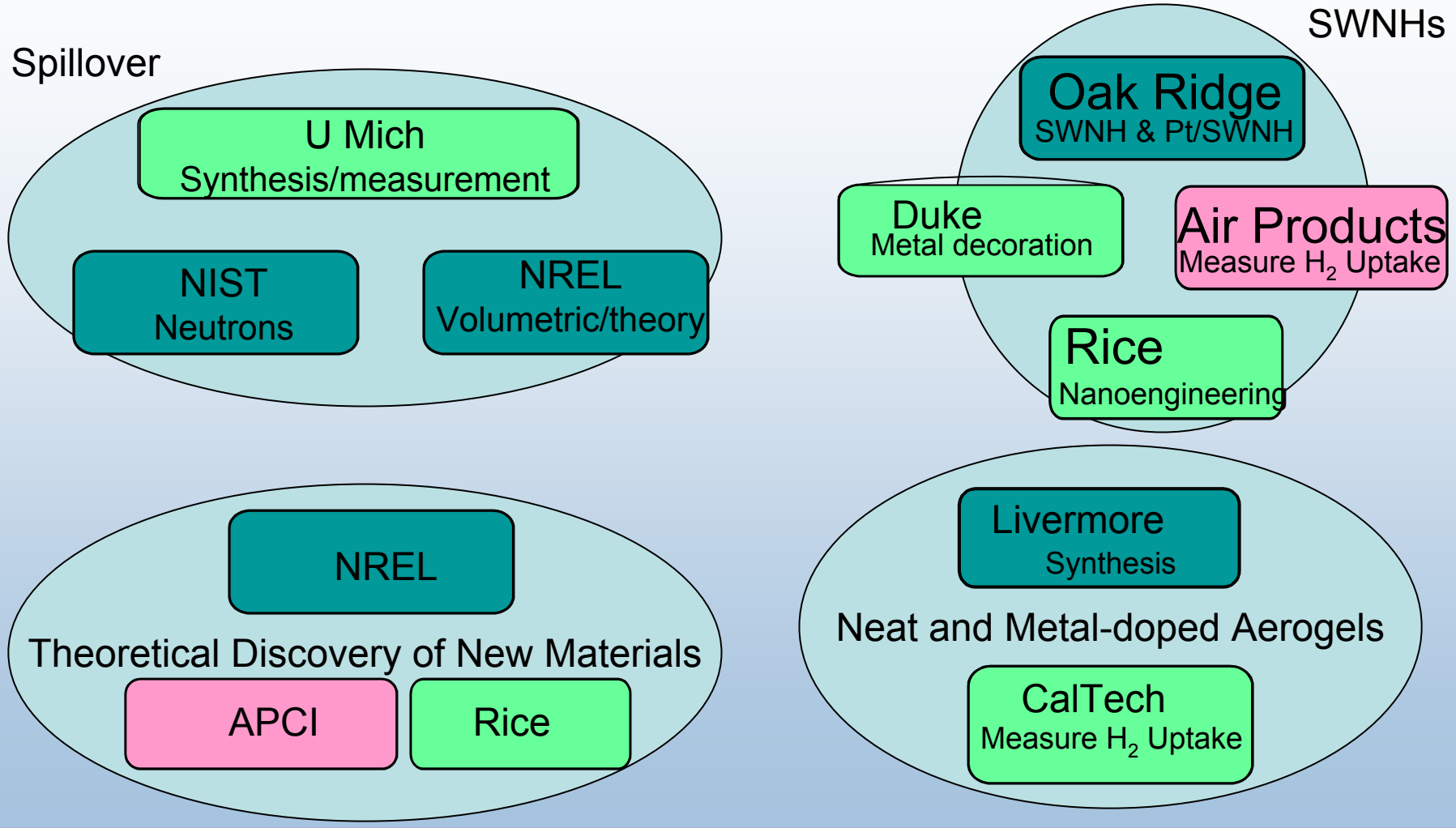
NMR - UNC

Neutron scattering
NIST

High Accuracy
Volumetric - APCI

COE technical interactions accelerate R&D efforts toward meeting DOE hydrogen storage system targets. Close interactions provide rapid feedback for development.

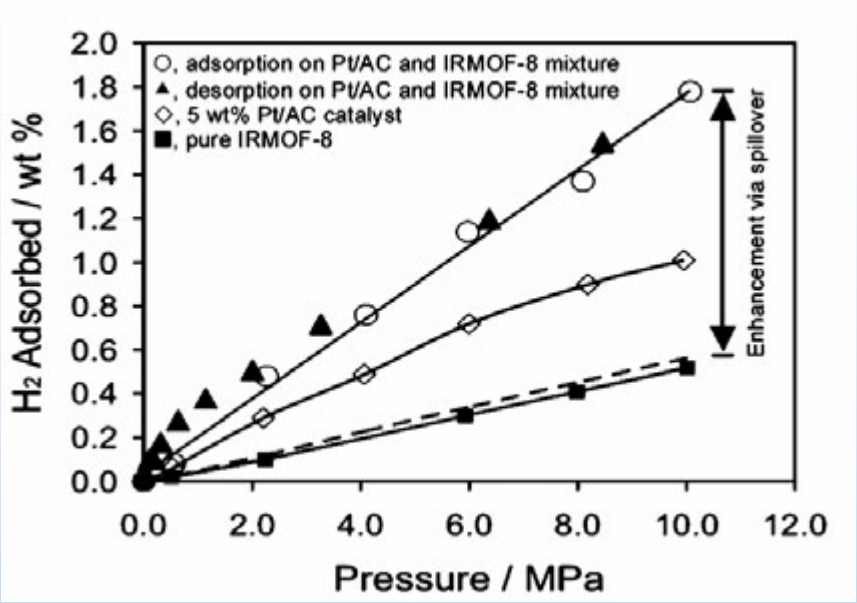
COE Accomplishments: Other Selected Accelerated Project Areas



COE technical interactions accelerate R&D efforts toward meeting DOE hydrogen storage system targets. Close interactions provide rapid feedback for development.

COE Accomplishment: Enhanced Spillover (Yang et al., U. Michigan)

- Last year's spillover result of 1.8 wt% uptake has been increased to ~ 4 wt% at room temperature and ~ 100 bar
- Key is development of "bridge" structure between catalyst and receptor components
- Volumetric capacity on materials basis is estimates to be ~41 kg H_2/m^3
- Samples currently being measured at NREL for validation



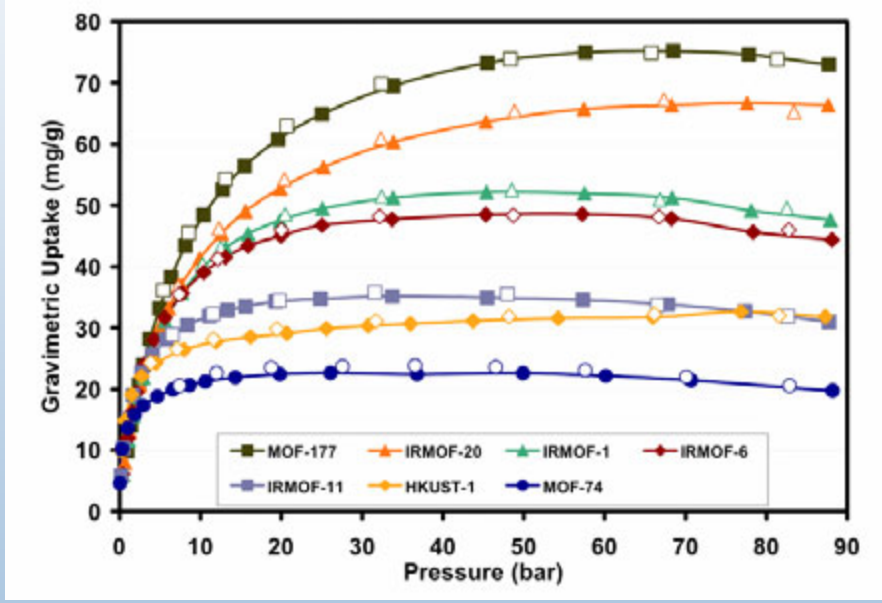
Comparison of hydrogen sorption as a function of pressure for receptor, catalyst/receptor and catalyst/bridge/receptor materials indicates a substantial enhancement when bridges are formed.
Y. Li and R.T. Yang, *JACS. 2006, 128, 726-727*

For the first time, substantial hydrogen sorption/desorption at room temperature has been demonstrated via spillover. Improved bridge forming and integration processing need to be developed to increase capacity and rates.

COE Accomplishment: Improved MOF Uptake (*Yaghi et al., U. Michigan)

- Synthesized particular MOF material with 5800 m^2/gm BET surface area
- Record 7 wt% storage at 77 K and ~ 60 bar
- Volumetric storage density in excess of 30 g/L on materials basis
- BET surface area more than twice the theoretical max for an infinite sheet of graphite (2650 m^2/gm).

A.G. Wong-Foy, A.J. Matzger, O.M. Yaghi, *JACS* (2006)



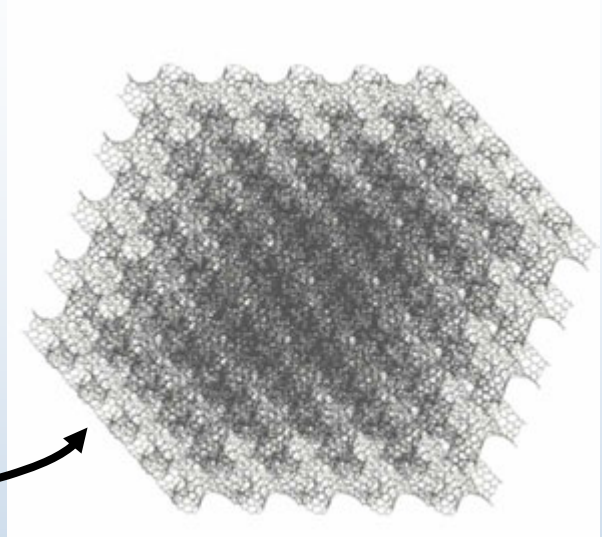
- High surface area is essential for high hydrogen storage capacities.
- Materials have hydrogen storage capacities close to that needed to meet DOE 2010 targets.
- COE partners must reproduce the results obtained on MOF structures with other nano-engineered materials, at higher T.

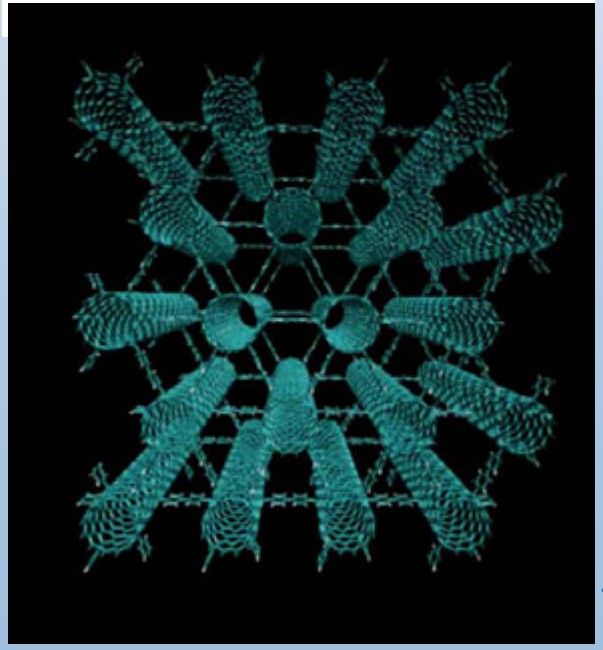
* O. Yaghi, previously at U. Michigan, is now at UCLA. His program is no longer part of the CoE.

Volumetric and gravimetric densities are close to that needed to meet 2010 system targets. Binding energy need to be increased for operation at higher temperatures.

COE Accomplishment: New Carbon Structures (Yakobson, Tour, Hauge, et al., Rice)

- Identified processing for high surface area carbon structures with opened van der Waals spaces and minimal wasted volume
  - Optimized spacing could increase hydrogen binding and capacity
    - Superposition of potentials can enhance sorption w/ optimum spacing
      - Patchkovskii, Tse, et al. PNAS 2005
    - 3D Carbon foam
      - Ding, Yakobson, et al. in progress
    - Nanoengineered SWNTs
      - Tour, Hauge, et al. in progress





Optimized nano-engineered structures may meet DOE hydrogen storage targets according to theories. Proposed routes to "propping open" normally collapsed structures outlines rational construction approach for the first time. Theoretical and process development is critical to demonstrate full potential.

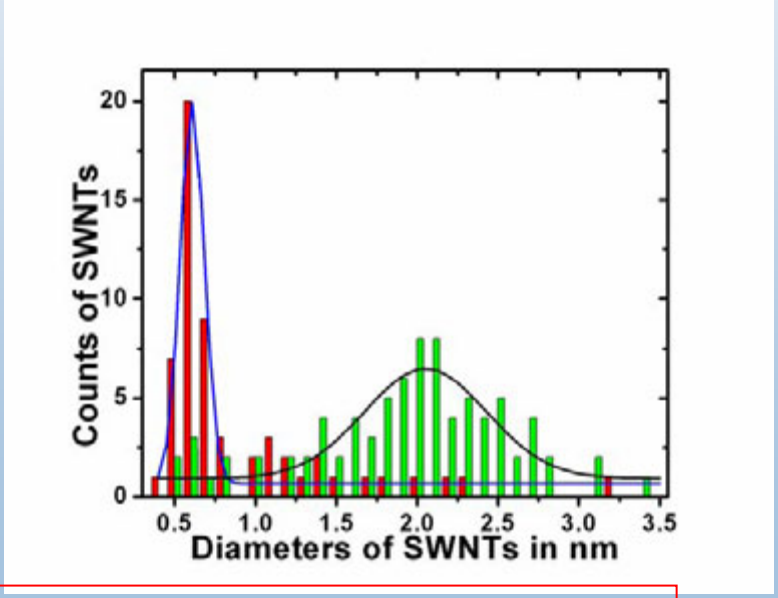
COE Accomplishment: Small Diameter Nanotube Synthesis (Liu et al., Duke)

- Theoretical calculations, from Air Products, predict that small diameter SWNTs (< 1 nm) will have higher hydrogen storage capacities and higher binding energies for dihydrogen than SWNTs with larger diameter.

  Cheng et al.,JACS *123:* 5845 (2001); Kostov et al.,PRL *89*, 2002.
- Small-diameter nanotubes have not been synthesized in high yield previously, and have not been available for testing.

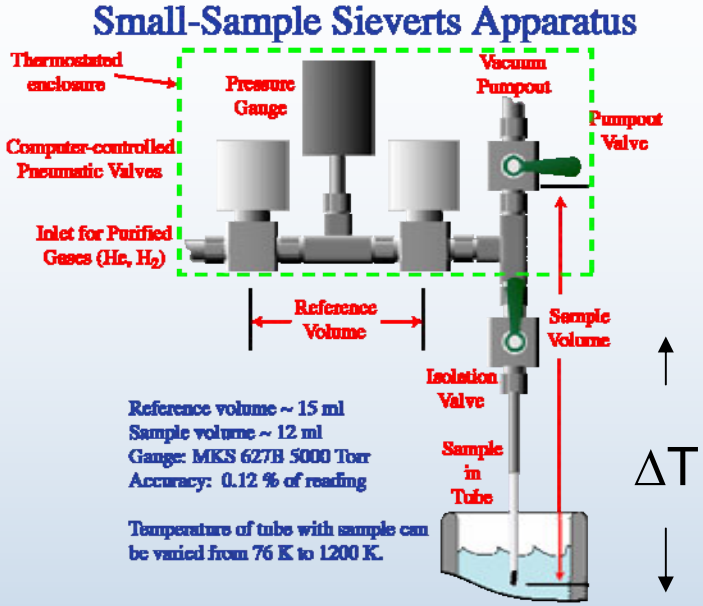
Progress:

- **Discovered that the size of SWNTs are closely related to the CVD growth conditions, most importantly carbon feeding rates.**
- **Discovered that uniform small diameter SWNTs can be produced from non-uniform catalysts if the growth condition is controlled precisely.**

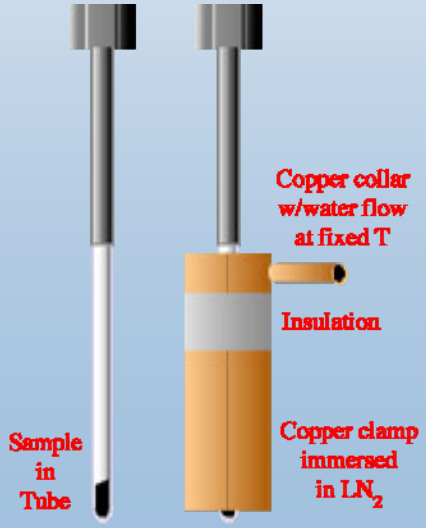


The development of methods to synthesize small-diameter SWNTs will permit testing of predictions of their improved storage characteristics

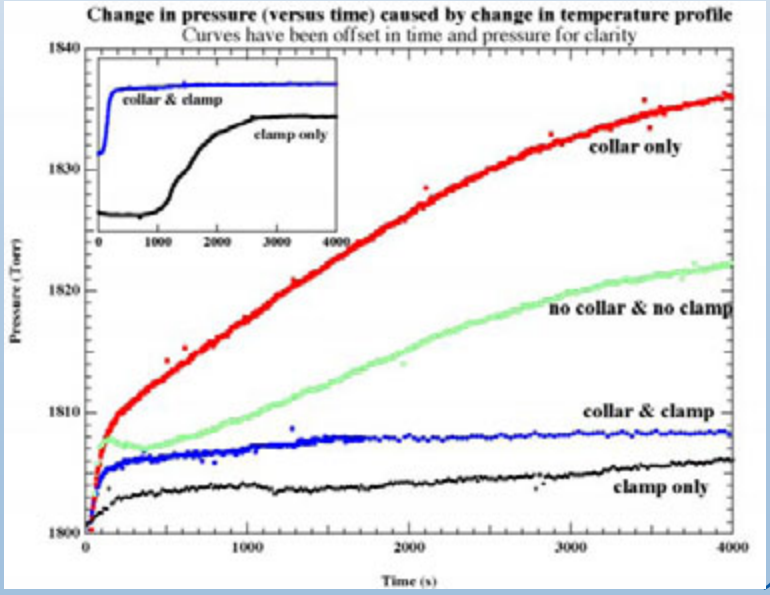
NREL Accomplishment: High Throughput, Accurate Volumetric Measurements



- Rate of materials discovery & measurement is dramatically increased by using small samples.
- Volumetric measurements, especially on small samples, are complicated by temperature gradients.
- NREL developed a simple method to improve measurement speed and accuracy
- Method is being extended to higher P, and will be transferred to partners, community and SwRI.

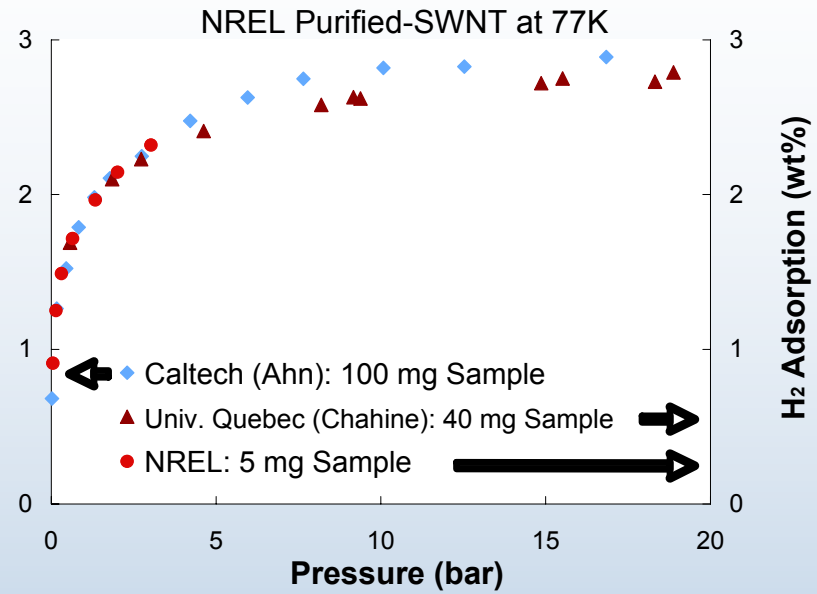


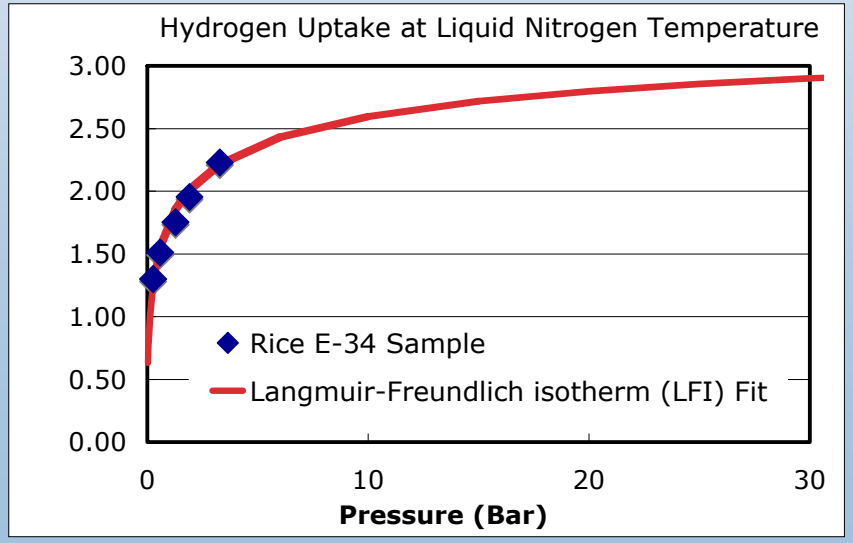
- Cu collar and clamp force ΔT to occur over a fixed distance
- Can be used with LN_2 or any fluid for variable temp measurements (ΔH)



NREL Accomplishment: Repeatable Sample Prep and Measurement

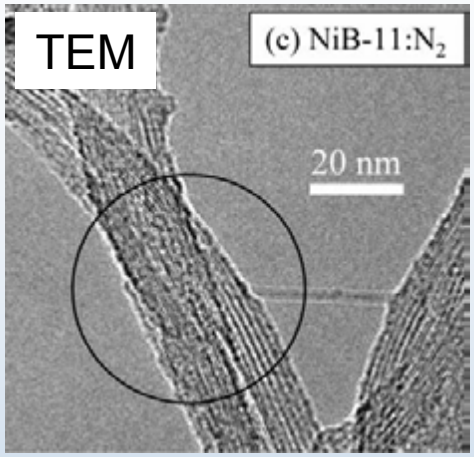
- Developed synthesis and purification processes that reproducibly produced the same H_2 uptake (~3 wt% at saturation)
  - SWNT preparation involves repeated acid and high temp. oxidation steps
    - Nitric, sulfuric, hydrochloric acids
    - Heating in air, O_3 and/or CO_2
- H_2 uptake confirmed at 4 different institutions (including SwRI)
- Different institutions using similar processing created materials with similar H_2 uptake properties`



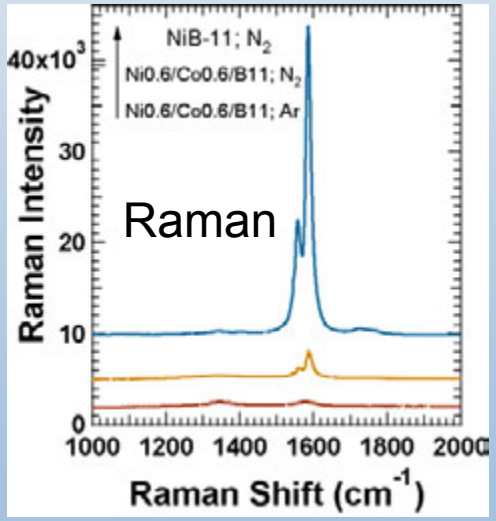


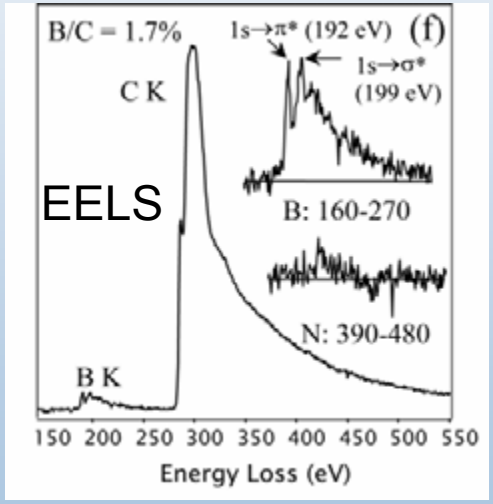
- Partners are working together to increase H_2 storage capacities of base and nanoengineered materials.
- Interactions will accelerate development to meet DOE storage targets.

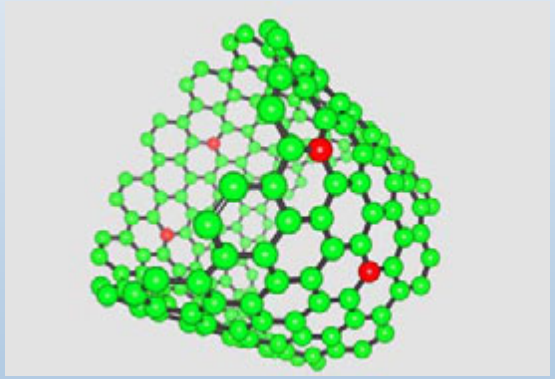
NREL Accomplishment : B-doped SWNTs made by Laser Vaporization



- B-SWNTs in high yield for first time using laser
- N_2 as carrier gas and NiB as a catalyst
- EELS spectrum indicative of sp^2-bonded B in hexagonal lattice (confirmed by ^{13}C NMR)
- Current doping level is 1-2% by EELS





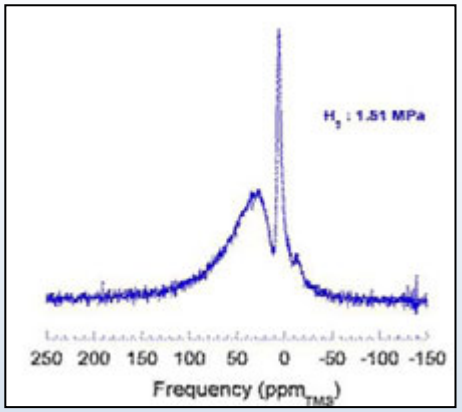


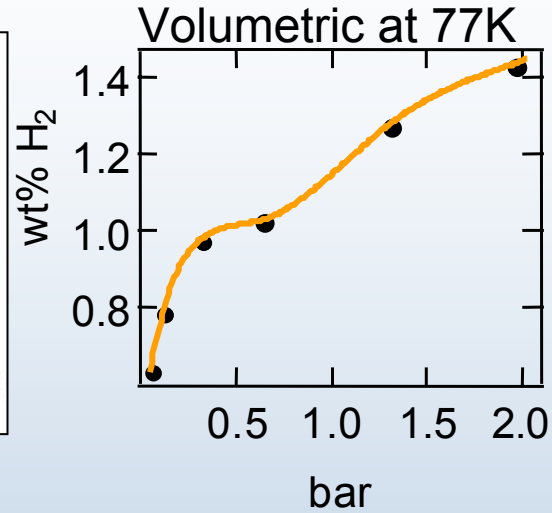
Blackburn et al., Chem. Mat. *accepted*

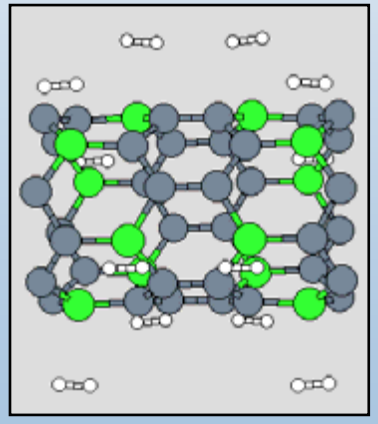
B-doped materials are needed to enhance the H_2 binding energy, point the way to better adsorbents

Joint Accomplishment (NREL/UNC/NIST): NMR, Volumetric, and Neutron Scattering Show Stronger H_2 Binding

- Variable pressure NMR spectra show adsorbed and free H_2
- Binding energy of 11.6 kJ/mol - in good agreement with theory (12 kJ/mol)
- See STP41 - Wu et al.







BC_3 nanotubes

12 kJ/mol

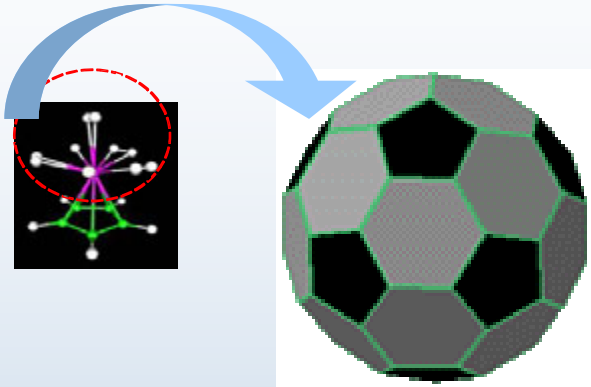
~ 4.2 wt%

Kim et al. P.R.L. 96, 016102 (2006)

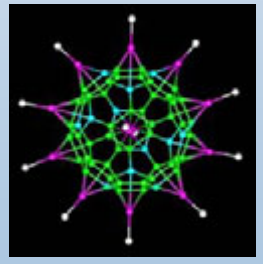
- Step in adsorption isotherm shows B sites are populated first, consistent with NMR and neutron data (see ST25 - Neumann et al.)
- Prompt gamma analysis shows B content of 1.2% in samples, consistent with EELS
- At least 25% B is possible (BC_3)

B-SWNTs and carbons will enable RT sorption at moderate pressures. Must increase boron doping content and determine affects on neighboring carbon sites

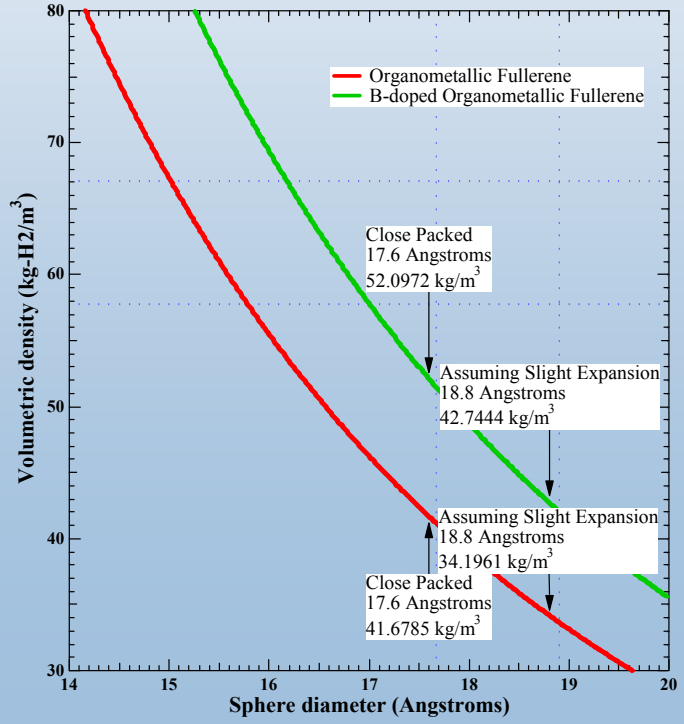
NREL Accomplishment: Volumetric Performance of Predicted OBBs (Organometallic Bucky Balls)

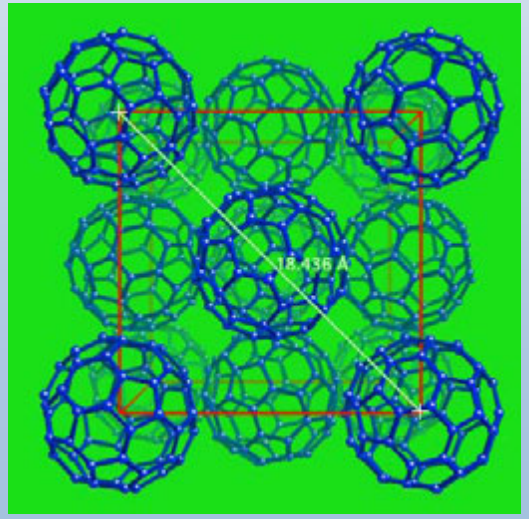


- Calculations have shown that first-row transition metals complexed to C_{60} can bind H_2 with near-optimal binding energies (20 -30 kJ/mol); Zhao et al., PRL 94, 155504 (2005)
- 8.8 wt% reversible, near ambient P and T, capacity was found for Sc complexed to B-doped fullerenes
- Assuming that OBBs form FCC crystals as does C_{60}, but with an expanded lattice parameter, a volumetric capacity between 42 and 52 kg H_2/m^3 can be expected.



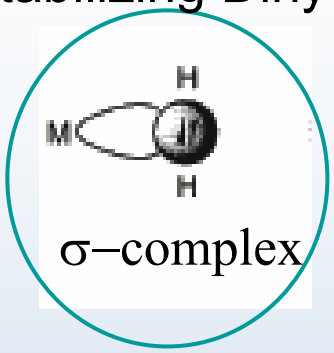
$$C_{48}B_{12}[ScH]_{12} \xrightleftharpoons{60H_2} C_{48}B_{12}[ScH(H_2)_5]_{12}$$





NREL Progress: Synthesis of OBB Adsorbents

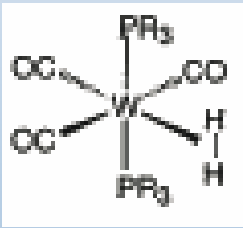
Stabilizing Dihydrogen Ligands Requires Non-classical Coordination



G.J. Kubas, *J. Organomet. Chem.* 635 (2001) 37;
G.J. Kubas, *Acc. Chem. Res.* 21 (1988) 120.

- Metal d to σ* H-H back-donation is key to σ-bond coordination and the stabilization of dihydrogen ligands.
- However, too much electron donation results in dissociation and formation of monohydride species.
- Problem: C_{60} organometallic chemistry is generally olefinic (2 e^- donor)
- But Fe η5 □□ chemistry is known

First demonstration in 1983

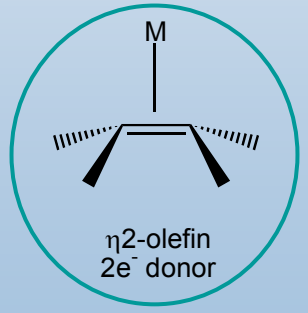


Bulky phosphine ligands allow for H_2 to be stabilized with a σ-bond.

Enhanced d-σ* metal:H_2 interaction with Ir complexes as X = I > Br > Cl

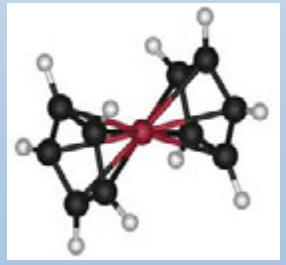
$IrXH_2(H_2)(PR_3)_2$ (X= Cl, Br, I)

T. Le-Husebo and C.M. Jensen, Inorg. Chem. 32 (1988) 3797.



Olefinic C-C addition

η5 coordination by Fe: Ferrocene

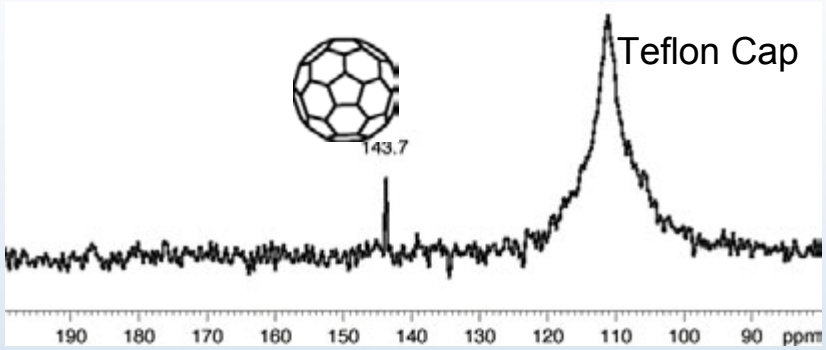


Discovered in 1954: Nobel Prize to Wilkinson and Fisher in 1974.

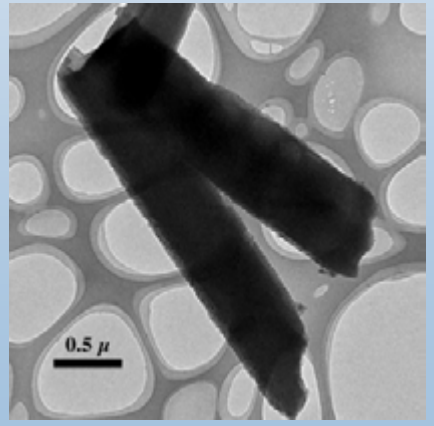
NREL Accomplishment: Non-olefinic coordination to C_{60}

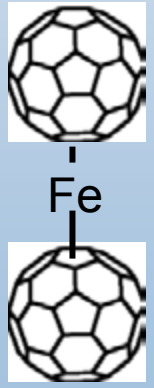
- Initial attempts with Fe due to known $\eta 5$ coordination (ferrocene)
- Reaction chemistry cannot be revealed at this time, but NMR is consistent with $\eta 5$ coordination
- Fe detected at just above detection limits by EDS in TEM
- EPR confirms the presence of Fe^{+3}
- Proposed Bucky-dumbell structure
- First metal $\eta 5$ coordination to C_{60}?

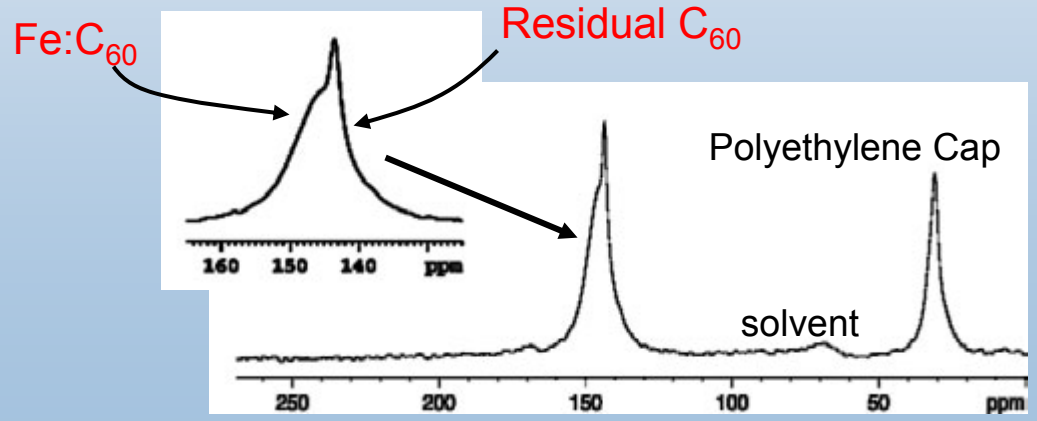
Solid State ^{13}C NMR of Starting C_{60}



After reaction: No non-fullerene related peaks in ^{13}C NMR spectrum

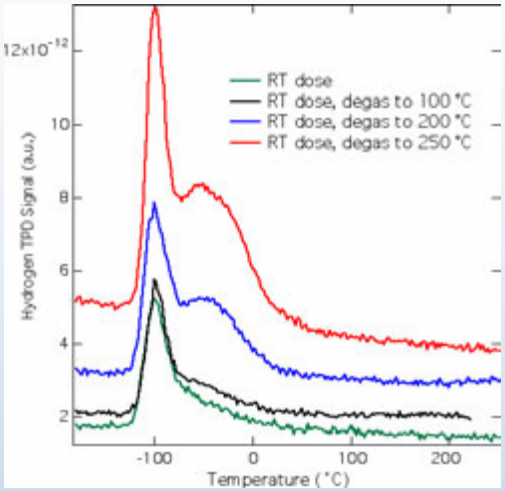


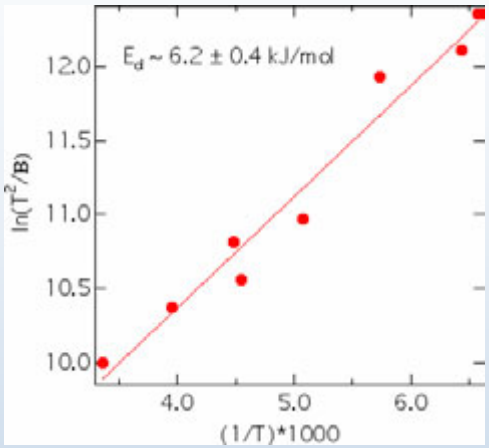




non-olefinic coordination to C_{60} is important first step to OBB synthesis.

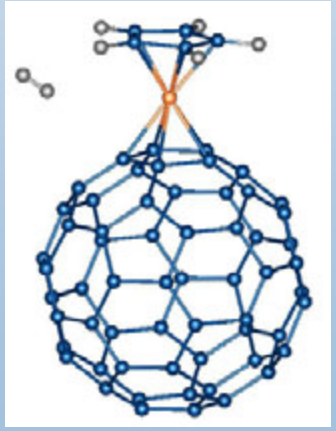
NREL Accomplishment: Temperature Programmed Desorption of C_{60}-Fe-C_{60}





- H2 adsorption sites after exposure to H2 at 500 Torr for 5 min.
- Peaks increase as sample is progressively heated in vacuum up to 250˚C.
- Measured binding energy of 6.2 kJ/mol lower than expected from DFT calculations on C_{60}-Fe-Cp.

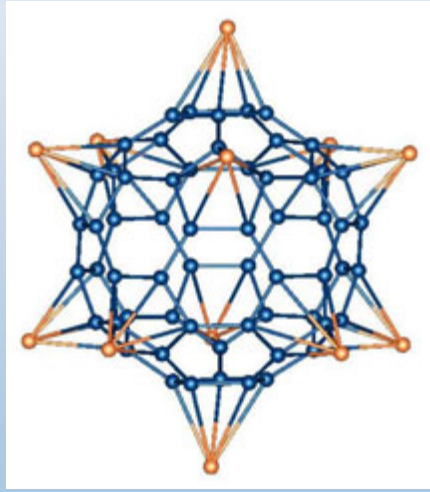
DFT over estimates physisorption binding energy: 14.27 kJ/mol



Next steps:
- Confirm structure
- Dislodge C_{60} and replace with H_2
- Increase # of Fe species
- Develop chemistries for other metals
- Demonstrate metal/structure stability

NREL Accomplishment: Avoiding Metal Coalescence in Novel Adsorbents

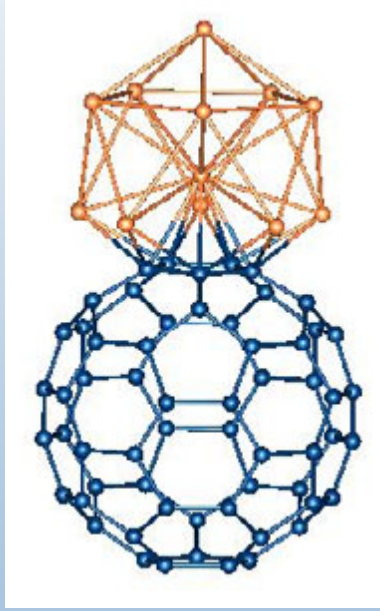
- Dihydrogen uptake by transition metals (TMs) on fullerenes and nanotubes has stimulated new thinking for designing optimal adsorbents. Zhao et al., PRL 94, 155504 (2005); Yildirim et al., PRL 94, 175501 (2005)
- Metal clustering reduces H capacity. *n* TM-TM bonds reduces dihydrogen ligands bound to TM by *n*. [1]Sun et al., JACS 127, 14582 (2005)
- The issue of clustering / disproportionation is critical for all hybrid systems (e.g Li/C), and is being investigated



- Conversion at 200° C (MD simulations) with a gain 1.22 eV/Sc, or ~2 eV/Ti[1]
- Driving force lowered with first hydride bond

$$(C_5Sc)_{12} \rightleftharpoons C_{60}Sc_{12}$$

- TM dispersal is favored with B-doping, or charged TMs, which reduces TM-TM bonding and promotes stronger TM-cage bonding

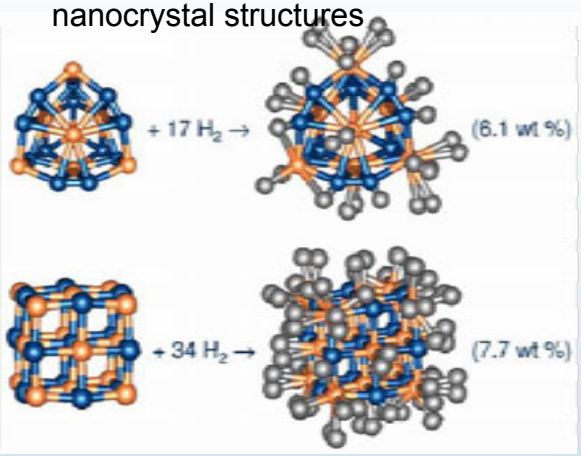


TM atoms must be kept separated for high-capacity H storage. Coalescence can be avoided by increasing TM-C bond while decreasing TM-TM interactions

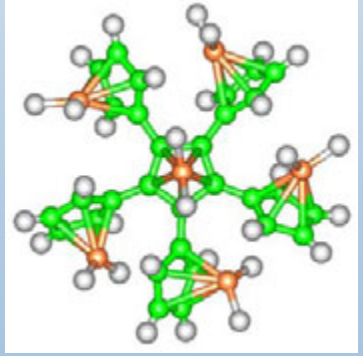
NREL Accomplishment: New Materials

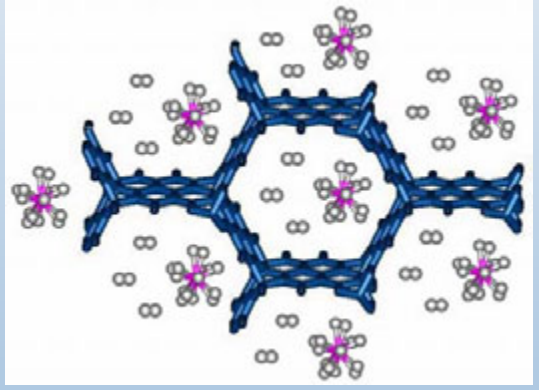
- Identified new approaches to stabilize large hydrogen capacities at STP
- Emphasis on stable materials
- Self-catalyzed H_2 dissociation with MetCar
  - Forms hydrides with barriers less than 0.25 eV
  - Potential gravimetric capacity of 7.7 wt%
  - Model system for spillover shows both H and H_2 binding (Y. Zhao et al. Chem. Phys. Lett. *accepted)*
- Dendrimers or Macroscopic Molecules
  - Yu et al., Angew. Chem. In. Ed. 45, (2006)
  - Gravimetric capacity > 5 wt%
- Porous carbons used to keep TM atoms isolated
  - High storage on TM atoms
  - Also get storage with carbon matrix

Metallocarbohedrene and nanocrystal structures



Developing new macroscopic molecules with hydrogen sorption capacities that can meet DOE system targets



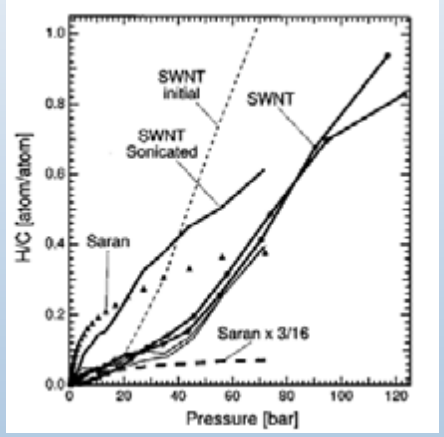


Hydrogen decorated transition metals implanted in a highly porous carbon matrix

Other hybrid structures that are easier to produce are being identified that can meet DOE hydrogen storage targets

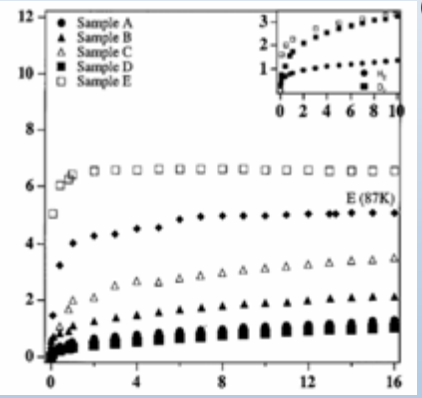
NREL Progress: 4 wt% Milestone Focused on Pure SWNTs for Reproducibility in Processing

- As previously discussed, we demonstrated reproducible processing and volumetric measurement of hydrogen uptake on SWNTs across 4 labs.
- The measured uptake was ~ 3 wt% at 30 bar and 77 K.
- Samples have been sent to R. Chahine (U. Quebec, Trois-Rivieres) to be processed by a method that should yield 4.5 wt% uptake



8 wt% on SWNTs at 80K, 100 bar
Ye, et al., APL 74, 2307 (1999)

1000 °C anneal

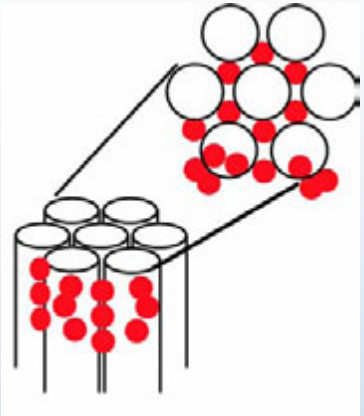


$Q_{st} \sim 0.12$ eV

6 wt% on SWNTs at 77K, 2 bar
Pradhan, et al., JMR **17**, 2209 (2002)

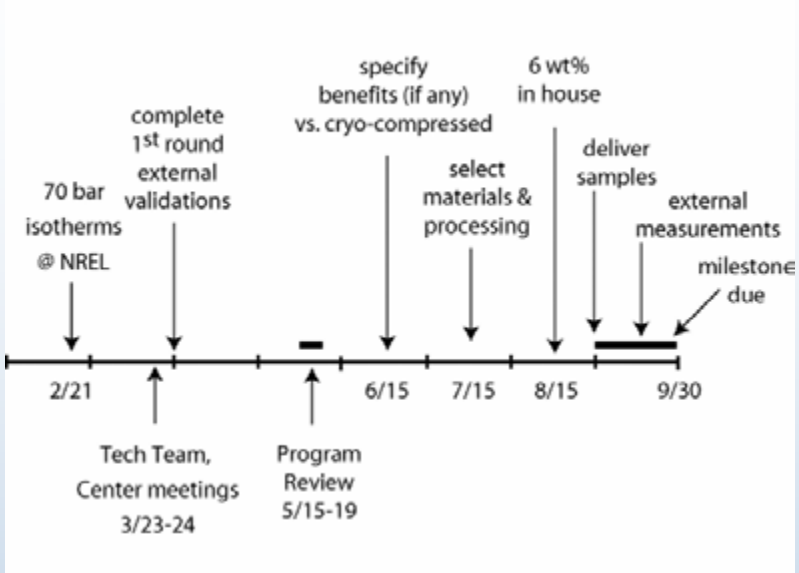
The performance reported in the literature was not found, although sample processing may have differed. Efforts to improve performance are continuing.

Plan to Meet 6 wt% SWNT Go/No-Go



6 wt% at RT means:

- BET S.A of 3000 m^2/g and increased binding energy
- According to "Chahine's Rule": 1 wt% per 500 m^2 of S.A.
- Chahine's rule may be improved upon with enhance binding energies due to a high density of small pores.



- 12 kJ/mol shown by Pradhan et al. suggests milestone can be met at RT.
- Various expected adsorption sites have not been resolved.
- The 3 wt% saturation capacity suggests that the existing surface area is not accessible.
- Directions: small diameter tubes, open ends, un-bundled, loosely bundled, or propped open tubes, cross-linking, defects, dopants, …
- If research on pure SWNT adsorbents should be stopped as a result of a No-Go decision, SWNTs should still be considered as building block components for possible nanoengineered adsorbents.

SWNTs alone or as functional components in designed adsorbents hold promise for meeting DOE storage targets if appropriate processing can be developed.

Project Summary

Technical Accomplishments and Progress:

- Substantial interactions involving all partners were established to accelerate R&D
- Strong teaming across institutions / topics / expertise
- Partner collaborations have enabled boron doped carbons that bind H_2 at ~ 12 kJ/mol: May enable ~RT and moderate pressure H_2 storage system
- MOF materials with > 5800 m^2/g surface areas where made and sorbed ~ 7 wt% hydrogen
- Small diameter tubes have been made in high yield
- Developed nanoengineering strategies to construct better adsorbents
- Demonstrated substantial (~ 4 wt%) hydrogen sorption/desorption at RT via spillover
- Theory of spillover has been developed which shows energetic pathway from gas phase dihydrogen to chemisorbed hydrogen on model Metcars systems
- Demonstrated substantial (> 4 wt%) irreversible hydrogen capacity of hybrid materials at STP
- Strong interplay between theory and experiment is identifying weaknesses in approaches, and determining new paths forward.
- Organization and management of Center has been enhanced
  - Website and ftp site are operational
  - Regular webcasts on topical areas
  - Steering Committee has been engaged
  - Milestones, Go/No-Gos, Safety plans for all partners

For other Progress, see talks and posters from COE partners!

Future FY06 Work at NREL

- Complete development/testing of commercial high pressure volumetric system for use in laboratory scale (~10 mg samples) analysis to help accelerate materials development. Transition to community.
- Continue SWNT development efforts to meet 6 wt% Go/No-Go by Sept. 2006
  - Improve purification/debundling techniques to maximize surface area
  - Develop nano-engineering to keep tubes separated and aligned in appropriate structures
  - Demonstrate that diameter and/or intrinsic doping significantly increases hydrogen uptake
    - e.g. Demonstrate B-SWNT with ~ 10 at% B with >0.5 wt% hydrogen sorption at ~ RT
- Continue developing processes to nano-engineer hybrid materials
  - Demonstrate TM-C_{60} structures that have appropriate structures close to theoretical predictions
  - Identify/demonstrate synthesis of other new materials
    - Demonstrate TM-SWNT, Catalyst-SWNT, and Alkali metal-carbon structures with room temperature hydrogen sorption significantly higher than the base materials
    - e.g. Pt/Pd decorated carbons with 2-4 X increase in hydrogen sorption at ~ RT
  - Integrate work with other spillover and materials development activities in the COE
- Perform calculations to identify new materials that could meet DOE targets
  - Complete calculations investigating the affects of alkali metal with carbon to bind H_2
  - Complete initial models for spillover in the MetCar systems. Apply to other cases.
- Continue Center activities to accelerate H_2 storage materials development
  - Work with others to provide rapid materials characterization and develop new materials
  - Work with DOE/GO to ensure optimum functioning of the Center

Future FY07 Work at NREL

- Develop new lab scale testing to accelerate H_2 materials development
  - e.g. BET surface area measurements that accurately correlate to H_2 capacity
- Develop intrinsic mat. w/ high surface areas, H_2 uptake > 6 wt%, 45 g/L
  - e.g. Nano-engineered carbon structures with enhanced binding (> 10 kJ/mol)
- Nano-engineer hybrid materials with STP H_2 uptake > 6 wt% 45 g/L
  - Develop synthetic processing to construct structures predicted to meet DOE targets
- Continue to identify new materials that meet DOE targets
  - Identify new synthetic processing to make meta-stable materials
  - Improve fundamental understanding of different adsorption processes
  - Search for good sorbent materials, both experimentally and computationally, that are readily synthesized and likely to be stable.
- Coordinate Center activities to accelerate H_2 storage materials development
  - Work with others to provide rapid materials characterization and develop new materials / approaches.
  - Work with DOE/GO and partners to ensure optimum functioning of the Center
  - Redirect activities away from unproductive materials and approaches toward more productive ones.

Summary Table of Selected CbHS COE Results

On-Board Hydrogen Storage System Targets
(**Data is based on material only, not system value)
NA: Not Available

Storage Parameter	Units	2010 System Target	MOF ** FY05	MOF ** FY06	Spillover ** FY05	Spillover ** FY06	SWNT ** FY05	SWNT ** FY06	B-SWNTs ** FY05	B-SWNTs ** FY06	FY06 Alkali Metal decorated SWNT**	FY06 Aerogels **
Specific Energy	wt. % H_2	6	2.5	7	1.6	~4	See comments	3†	NA	~3 Cold 0.5 RT	4.2	4.2
Volumetric Energy Capacity	g/L	45	NA	31	NA	41	N/A	28[a]	NA	28[a]	N/A	N/A
Comments			77K ~40 bar		RT 100 bar FY06 Results are Preliminary		77K, 20 bar Previous results inconsistent. > 6% reported in literature. † Reproduced at Different labs		77K ~20 bar B-doping level is only 1-2% presently, result is similar to C-SWNT		STP Irreversible	77K 30 bar

a. 28 g/L assuming a ~20% expanded lattice. Will be ~56 g/L at 6 wt% H_2 with this same assumption.

Summary Table of Selected CbHS COE Results (Predicted)

On-Board Hydrogen Storage System Targets
(**Data is based on material only, not system value)
NA: Not Available

Storage Parameter	Units	2010 System Target	Organometallic Fullerenes Predicted ** FY05	Organometallic Fullerenes Measured $Fe-C_{60}$ ** FY06	MetCars Predicted ** FY06	Macromolecules Predicted ** FY06	Spillover on SWNTs Predicted ** FY06
Specific Energy	wt. % H_2	6	~9	0.4	>7.7	>5	~7.7
Volumetric Energy Capacity	g/L	45	52 - 43	NA	NA	>40	~56
Comments			STP	77K 2 bar	STP	STP	STP Preliminary Result

Back-Up Slides

Response to Past Reviewer Comments

Comment: Revisiting the pseudo cold/pressure region is recommended, this may be the "sweet spot" or at least the happy medium where overall system efficiencies can be acceptable in terms of compression/cooling energies and transfer from forecourts to vehicle tanks - especially if bulk transport of hydrogen will continue to favor liquid hydrogen.

Response: We agree. High density carbon nanostructures, such as tubes or foams, may improve the volumetric performance which has hindered past adsorbents in comparison to cryo-compressed tanks. Relatively modest increases in binding energy through doping or materials engineering may permit operating pressures to be reduced or temperatures to be increased. Low pressure operation will permit conformal tanks. A combination of a portion of hydrogen stored strongly at high binding energy sites and a high capacity at lower T would improve dormancy and allow for less insulation.

Comments: (1) Should give more attention to the projected volumetric H2 density of these modified C60 structures. In a relatively optimistic case, the projected density is 43 kgH_2/m^3; do these materials have (even theoretically) a chance to meet the 2010 or 2015 goals? (2) The key issue with these materials is the volumetric storage.

Response: We agree and have insisted that volumetric performance be as important as gravimetric performance. As can be seen from the Summary Table, several systems are currently close to or predicted to exceed the 2010 targets on a materials basis. This emphasis will continue in the future.

Response to Past Reviewer Comments

Comment: Broad and well respected collaborations. Only possible concern is that there may be too many institutions working on too many things to be able to adequately manage and direct.

Response: The Center is now ~ 1 year old and we have improved the management and organization so that the participants are clustered around focus areas (e.g. enhanced physisorption, Kubas-type interactions, spillover, materials production and measurement)

Comments: (1) Should increase flexibility. (2) Need to establish the internal material selection process/criteria. (3) Ensure an appropriate mechanism is put in place for the effective management of the Center of Excellence; this could be challenging in view of the size of the consortium and the diversity of the expertise there.

Response: Sufficient time must be allotted for the partners to pursue their SOWs sufficiently that informed decision can be made. Go/No-Go decision points are in place for all projects. However, we need to be as flexible as possible to pursue new opportunities as they arise, and to enhance support of promising areas. These issues are continuously discussed with DOE HQ and GO management. Management of Center has been improved by addition of a Deputy Director (Lin Simpson), addition of dedicated manager at GO (Jesse Adams), breakdown of internal NREL work into Tasks, use of communication tools such as webcasts, and a more active Steering Committee.

Response to Past Reviewer Comments

Comment: Showed binding energy for single metal atom on a single pentagonal ring. However, is there metal-metal interaction (i.e., is the binding still strong for a fully covered C60 molecule with 12 Sc atoms?). Is the fully-doped system stable with respect to decomposition into C60 + metal or C60 + metal hydride?

Response: These concerns are valid and are generally relevant to hybrid materials being investigated here as well as those proposed elsewhere. We have addressed the specific comment above computationally, and will continue to do so, both computationally and experimentally, for other systems and new approaches as they arise

Comments: (1) The highlight of the last year is the portfolio diversification of the possible carbon-based storage molecules. It is critical to continue this pathway and create a well-balanced program with proper risk mitigation. (2) Center should continue to expand activities beyond carbon work. It seems that all materials with low bonding energy 10 to 50kJ/mol would be appropriate for this center and the systems would be similar.

Response: We agree that the concepts, techniques, and tools are well-suited to any types of materials or molecules with low binding energy and wish to expand the scope under study to include those promising adsorbents that do not contain carbon.

NREL Publications

1. "Non-dissociative adsorption of H2 molecules in light-element doped fullerenes", Y.-H. Kim, Y. Zhao, A. Williamson, M.J. Heben, and S. B. Zhang, Physical Review Letters **96**, 016102 (2006)
2. "Self-catalyzed Hydrogenation and Dihydrogen Adsorption on Metallo-Carbohedrenes and Related Nanocrystals" Yufeng Zhao, A.C Dillon, Y.-H. Kim, M.J. Heben and S.B. Zhang, Chemical Physics Letters, in press
3. "Synthesis and Characterization of Boron-doped Single-wall Carbon Nanotubes Produced by the Laser Vaporization Technique"**,** Jeff L. Blackburn, Yanfa Yan, Chaiwat Engtrakul, Philip A. Parilla, Kim Jones, Thomas Gennett, Anne C. Dillon, Michael J. Heben. Chemistry of Materials, May 2006.
4. "Development and characterization of single wall carbon nanotube–Nafion composite actuators" B.J. Landi, R.P. Raffaelle, M.J. Heben, J.L. Alleman, W. VanDerveer, T. Gennett, Materials Science and Engineering B, 116(3), 359-362, 2005
5. "Systematic Inclusion of Defects in Pure Carbon Single-wall Nanotubes and Their Effect on the Raman D-band**,"** A.C. Dillon, P.A. Parilla, J.L. Alleman, T. Gennett, K.M. Jones and M.J. Heben, Chem Phys Lett**,** 401, 522-28, 2005**.**
6. "Generalized Kubas Complexes as a Novel Means for Room Temperature Molecular Hydrogen Storage," Y.-H. Kim, Y. Zhao, M.J. Heben & S.B. Zhang, Materials for Hydrogen Storage-2004, edited by M.J. Heben, I.M. Robertson, R. Stumpf & T. Vogt, 837, N3.21 (2005
7. "The Role of Metal Catalyst in near Ambient Hydr. Adsorption on Multi-Walled Carbon Nanotubes," Y.-W. Lee, R. Deshpande, A.C. Dillon, M.J. Heben, H. Dai & B.M. Clemens, Materials for Hydrogen Storage-2004, edited by M.J. Heben, I.M. Robertson, R. Stumpf & T. Vogt, Mat. Res. Soc. Symp. Proc. 837, N3.18 (2005)
8. "An Experimental Estimate of the Free Energy of Formation of Single Walled Carbon Nanotubes," L.M. Wagg, G.L. Hornyak, L. Grigorian, A.C. Dillon, K.M. Jones, J.L. Blackburn, P.A. Parilla & M.J. Heben, Functional Carbon Nanotubes, edited by D.L. Carroll, B. Weisman, S. Roth & A. Rubio, Mater. Res. Soc. Symp. Proc. 858E, HH2.7 (2005)
9. "Systematic Inclusion of Defects in Pure Carbon Single-Wall Nanotubes and Their Effect on the Raman D-Band," A.C. Dillon, P.A. Parilla, J.L. Alleman, T. Gennett, K.M. Jones & M.J. Heben. Chemical Physics Letters 401, 522-528 (2005)
10. "Experimental Gibbs Free Energy Considerations in the Nucleation and Growth of Single-Walled Carbon Nanotubes," L.M. Wagg, G.L. Hornyak, L. Grigorian, A.C. Dillon, K.M. Jones, J. Blackburn, P.A. Parilla & M.J. Heben, Journal of Physical Chemistry B 109, 10435-10440 (2005)
11. "Hot-wire chemical vapor synthesis for a variety of nano-materials with novel applications," Dillon, A. C., Mahan, A. H., Deshpande, R., Alleman, J. L., Blackburn, J. L., Parillia, P. A., Heben, M. J., Engtrakul, C., Gilbert, K. E. H., Jones, K. M., To, R., Lee, S. H., and Lehman, J. H., Thin Solid Films 501 (1-2), 216-220, 2006
12. "Importance of Turning to Renewable Energy Resources with Hydrogen as a Promising Candidate and on-board Storage a Critical Barrier" A.C. Dillon*, B. P. Nelson, Y. Zhao, Y-H. Kim, C. E. Tracy and S. B. Zhang Mat. Res. Soc. Proc. Fall (2005), in press.
13. "High yield nanotube synthesis in a hot-zone arc-discharge apparatus", T. Gennett, C. Engtrakul, J. Blackburn, K. Franz, J. Alleman, K. Jones, A. Dillon, M. Heben, manuscript in preparation.
14. "Rapid, accurate, *in situ,* calibration of a mass spectrometer for temperature programmed desorption studies", K.E.H. Gilbert, P.A. Parilla, J.L. Blackburn, T. Gennett, A.C. Dillon, and M.J. Heben, manuscript in preparation.
15. "Competitive adsorption between carbon dioxide and methane on carbon nanotube materials" K.E.H. Gilbert, P.A. Parilla, J.L. Blackburn, T. Gennett, A.C. Dillon, and M.J. Heben, manuscript in preparation
16. "Hydrogen Storage in Novel Carbon-based Nanostructured Materials" E. S. Whitney, C. Curtis, C. Engtrakul, M. Davis, T. Su, K. M. Jones, P.A. Parilla, L. J. Simpson, J.L. Blackburn, Y. Zhao, Y-H. Kim, S. B. Zhang, M.J. Heben and A.C. Dillon Mat. Res. Soc. Proc. Spring (2006) under review.
17. "Nano-octahedra of MoS2 and MoSe2: Global Topological Constraints on Bonding and Stoichiometry", Philip A. Parilla, Anne C. Dillon, Bruce A. Parkinson, Kim M. Jones, Jeff Alleman, David S. Ginley & Michael J. Heben, extended abstract for the ECS Meeting, Denver, CO, May 2006
18. "Hydrogen Volumetric Sorption Measurements On Small Samples At Low Temperatures", P. A. Parilla, L.J Simpson, J.L. Blackburn, A.C. Dillon, T. Gennett, K.E.H. Gilbert, & M.J. Heben, manuscript in preparation
19. "H2 Sorption Volumetric Measurements of Single Wall Carbon Nanotubes", L.J. Simpson, P.A. Parilla, J.L. Blackburn, T. G. Gennett, K.E.H. Gilbert, C. Engtrakul, A.C. Dillon, and M.J. Heben. National Hydrogen Association Conference Proceedings, March 2006.
20. "Hydrogen Storage using Carbon Nanomaterials", L.J. Simpson, P.A. Parilla, J.L. Blackburn, T. G. Gennett, C. Engtrakul, A.C. Dillon, and M.J. Heben. Conference Proceedings of the Electrochemical Society Meeting May 2006

NREL Invited Presentations

1. "Using Nanoscience to Design Hydrogen Adsorbents", M.J. Heben, A.C. Dillon, Y. Zhao, J.L. Blackburn, P.A. Parilla, Y.-H. Kim, T. Gennett, C. Curtis, K.E.H. Gilbert, J.L. Alleman, K.M. Jones, S.B. Zhang, and L.J. Simpson, (invited talk), First Conference of Stanford's Global Climate and Energy Program, Stanford CA, June 13-14, 2005
2. "Using Nanoscience to Design Hydrogen Adsorbents", M.J. Heben, J.L. Blackburn, C. Curtis, A.C. Dillon, T. GennettÝ, K.E.H. Gilbert, K.M. Jones, Y.-H. Kim, P.A. Parilla, L.J. Simpson, Y.Yan, S.B. Zhang, Y. Zhao, (invited talk), TMS Symposium in Honor of Gary Sandrock, Louis Schlapbach, and Seijirau Suda, March 13-16, San Antonio TX, 2006
3. "Carbon Materials Center of Excellence: Overview and NREL Activities", M.J. Heben, A.C. Dillon, P.A. Parilla, Y. Zhao, Y.-H. Kim, T. Gennett, C. Curtis, J.L. Blackburn, K.E.H. Gilbert, J.L. Alleman, K.M. Jones, S.B. Zhang, and L.J. Simpson, (invited talk), at the DOE/Hydrogen Program Peer Review, Washington D.C., May 25, 2005
4. "DOE Carbon-based Hydrogen Storage (CbHS) Center of Excellence", M.J. Heben, J.L. Blackburn, C. Curtis, A.C. Dillon, T. Gennett, M.J. Heben, K.M. Jones, Y.-H. Kim, P.A. Parilla, L.J. Simpson, Y. Yan, S.B. Zhang, Y. Zhao, (invited talk), The FreedomCAR & Fuel Partnership Tech Team Meeting, Washington D.C., March 23, 2006
5. "Hydrogen Storage in Novel Carbon-based Nanostructured Materials" A.C. Dillon, (invited talk / session chair), Materials Research Society Meeting, April 30, 2006, San Francisco, CA.
6. "Grand Challenge of Vehicular Hydrogen Storage: Developing an Appropriate Adsorption System" A.C. Dillon, (invited talk/ session chair), Materials Research Society Meeting, November 30, 2005, Boston, MA.
7. "The Grand Challenge of the Hydrogen Cycle-Production, Storage and Fuel Cells" A.C. Dillon, (invited key note lecture / advisory panel / session chair), 2005 Taiwan Symposium on Hydrogen Storage in Carbon Nanomaterials, Oct. 18, 2005 Taipei, Taiwan.
8. "Novel Nanostructured Materials with a Variety of Applications" A.C. Dillon, (invited talk / session chair), SPIE-The International Society for Optical Engineering Nanotechnology Meeting, August 3, 2005, San Deigo, CA.
9. "Organometallic Nanostructures for Hydrogen Storage" Yufeng Zhao, Y.-H. Kim, A. C. Dillon, M.J. Heben, and S. B. Zhang, (invited colloquium talk), Dept. of Physics, University of Louisville, Kentucky, Sept. 16, 2005.
10. "Theory of Hydrogen Storage: a New Strategy within Organometallic Chemistry" Yufeng Zhao, Y.-H. Kim, A. C. Dillon, M.J. Heben, and S. B. Zhang, (invited colloquium talk), Dept. of Mechanical Engineering and Material Science, Rice University, Sept. 28, 2005.
11. "Organometallic Methods for Hydrogen Storage: Functionalization of Porous Materials" Yufeng Zhao, Y.-H. Kim, A. C. Dillon, M.J. Heben, and S. B. Zhang, (invited seminar), Dept. of Chemistry, University of Michigan, Nov. 7, 2005.

NREL Invited Presentations (Cont.)

12. "Theory of Hydrogen Storage: a New Strategy within Organometallic Chemistry" Yufeng Zhao, A. C. Dillon, Y.-H. Kim, M.J. Heben, and S. B. Zhang, (invited talk), APS March Meeting, Baltimore, March 13, 2006.
13. "Towards high wt%, room temperature reversible, carbon-based hydrogen adsorbents", S. B. Zhang (invited talk), IPHE Hydrogen Storage Technology Conference, Lucca, Italy, June 21, 2005.
14. "Activities in the DOE center of excellence for carbon-based hydrogen storage materials", S. B. Zhang, Y. Zhao, Y.-H. Kim, A. C. Dillon, M. J. Heben, (invited talk), Materials Science & Technology 2005 Conference (MS&T'05), Pittsburgh, PA, September 26, 2005.
15. "Prediction of Novel Organometallic Nanomaterials for High Weight Percent Reversible Hydrogen Storage", S. B. Zhang, (invited talk), Materials Research Society Fall Meeting, Symposium A, Boston, November 30, 2005.
16. "Novel Organometallic Nanomaterials for Room-Temperature Reversible Hydrogen Storage: A First-Principles Prediction", S. B. Zhang, (invited talk), TMS 135th Annual Meeting & Exhibition, San Antonio, TX, March 15, 2006.
17. "Fullerenes and Nanostructured Materials for Room-Temperature Reversible Hydrogen Storage: A First-Principles Study", S. B. Zhang, (invited talk), The 61th Annual Meeting of the Physical Society of Japan, Matsuyama, Japan, March 27, 2006.
18. "Fullerenes and Nanostructured Materials for Room-Temperature Reversible Hydrogen Storage: A First-Principles Study", S. B. Zhang, Y. Zhao, Y.-H. Kim, A. Williamson, A. C. Dillon, M. J. Heben, (invited talk), The 209th Electrochemical Society (ECS) Meeting, Denver, CO, May 7, 2006.
19. "NREL Activities in the DOE Carbon-based Hydrogen Storage Center of Excellence", (invited talk), A.C. Dillon, P.A. Parilla, Y. Zhao, Y.-H. Kim, T. Gennett, C. Curtis, J.L. Blackburn, K.E.H. Gilbert, J.L. Alleman, K.M. Jones, L.J. Simpson, S.B. Zhang, & M.J. Heben, DOE Annual Hydrogen Program Review, May, 2005. Also presented posters for the CbHS COE and NREL activity at the same meeting.
20. "Update on Activities for the Storage Systems Analysis Working Group", P.A. Parilla, (invited talk), Fuel Cell Seminar, Palm Springs, CA, November 2005
21. "Determining Purity and Quality of Carbon Single-Wall Nanotubes: Importance of Raman Scattering", Philip Parilla, Anne Dillon, Jeff Alleman, Tom Gennett, Kim Jones, Jeff Blackburn, Katie Gilbert, Mike Heben, (invited talk), 1st NanoScience & Applications Conference, NIST, Boulder, CO, October 17-19, 2005
22. "On-Board Hydrogen Storage—Breakthroughs and Barriers", Instructors: Tom Autrey, Weifeng Luo & Philip Parilla, Symposia 'A' (Tutorial), Fall MRS Meeting, Boston, MA, 11/27/05
23. "Carbon-Based Nanostructures for Hydrogen Storage" Thomas Gennett, Anne C. Dillon, Phillip Parilla, Jeffrey Blackburn, Sheng Bai Zhang, Michael J. Heben, (invited speaker) The 25th Annual Esther and Bingham J. Humphrey Memorial Symposium in Chemistry Saturday, September 30, 2006, University of Vermont
24. "Department of Energy Carbon-based Materials Center of Excellence", Lin Simpson, (invited talk), Hydrogen Storage Workgroup Meeting, Clean Energy Research Center, University of South Florida, November 2005

NREL Contributed Presentations

1. "Hydrogen storage in Titanium-Carbide nanoparticles" Yufeng Zhao, A. C. Dillon, Y.-H. Kim, M.J. Heben, and S. B. Zhang, (contributed talk), MRS Fall Meeting, Boston, Dec., 2005."Novel Organometallic Functionalization of Fullerenes for Hydrogen Storage Applications" A.C. Dillon, (contributed talk), Spring Electrochemical Society Meeting, May 10, 2006.
2. "New Structures for Hydrogen Storage: the Organometallic Frameworks" Yufeng Zhao, (contributed talk), CbHS Center of Excellence Techteam Meeting, Washington DC and Gathersburg, March. 23-24, 2006.
3. "Quantum Monte Carlo studies of the non-dissociative absorption of hydrogen to doped fullerenes" A. Williamson, Y.-H. Kim, and S. B. Zhang, (contributed talk), APS March Meeting, Baltimore, March 14, 2006.
4. "Hydrogen storage in Metallo-carbohedrenes" Yufeng Zhao, A. C. Dillon, Y.-H. Kim, M.J. Heben, and S. B. Zhang, (contributed talk), 230th ACS Meeting, Washington DC, Aug. 28, 2005.
5. "Hydrogen Volumetric Sorption Measurements On Small Samples At Low Temperatures", P. A. Parilla, L.J Simpson, J.L. Blackburn, A.C. Dillon, T. Gennett, K.E.H. Gilbert, & M.J. Heben, (contributed talk), Spring MRS Meeting, San Francisco, CA, April 2006
6. "Nano-octahedra of MoS_2 and $MoSe_2$: Global Topological Constraints on Bonding and Stoichiometry", Philip A. Parilla, Anne C. Dillon, Bruce A. Parkinson, Kim M. Jones, Jeff Alleman, David S. Ginley & Michael J. Heben, (contributed talk), ECS Meeting, Denver, CO, May 2006
7. "Modified Arc Discharge Chamber for the Improved Synthesis of Single Wall Carbon Nanotube Materials" T. Gennett, C. Engtrakul, K. J. Franz, J. A. Alleman, P. A. Parilla, K. M. Jones, J. Blackburn, K.E.H. Gilbert, A. C. Dillon, M. J. Heben, (poster), MRS Meeting Boston, MA December 2005
8. "Carbon-Based Nanostructures for Hydrogen Storage" Thomas Gennett, Anne C. Dillon, Phillip Parilla, Jeffrey Blackburn, Sheng Bai Zhang, Michael J. Heben, (invited talk) College of Science Colloquium Speaker, Rochester Institute of Technology, Rochester, NY, Oct 2005.
9. "Hydrogen Storage Properties of Boron-doped Carbon Nanotubes." Jeff Blackburn, Anne Dillon, Thomas Gennett, Phil Parilla, Katie Gilbert, Yong-Hyun Kum, Y. Zhaou, S.B. Zhang, Yanfa Yan, Kim Jones, Michael Heben. (contributed talk), Materials Research Society Meeting, Fall 2005, Boston, MA.
10. "Hydrogen Storage Properties of Laser-generated Boron-doped Carbon Nanotubes." Jeff Blackburn, Anne Dillon, Thomas Gennett, Phil Parilla, Lin Simpson, Katie Gilbert, Yong-Hyun Kim, Yufeng Zhao, Shangbai Zhang, Yanfa Yan, Kim Jones, Michael Heben, (contributed talk), Electrochemical Society Meeting, Spring 2006, Denver, CO.
11. "Synthesis and Characterization of Carbon Nanotube Based Structures for Hydrogen Storage" Jeff Blackburn, Chemical Sciences Seminar Series, National Renewable Energy Laboratory, March 14, 2006.
12. "H_2 Sorption Volumetric Measurements of Single Wall Carbon Nanotubes", L.J. Simpson, P.A. Parilla, J.L. Blackburn, T. G. Gennett, K.E.H. Gilbert, C. Engtrakul, A.C. Dillon, and M.J. Heben. (contributed talk) National Hydrogen Association Conference, March 2006.
13. "Hydrogen Storage using Carbon Nanomaterials", L.J. Simpson, P.A. Parilla, J.L. Blackburn, T. G. Gennett, C. Engtrakul, A.C. Dillon, and M.J. Heben. (contributed talk) Electrochemical Society Meeting, May 2006.

NREL Service

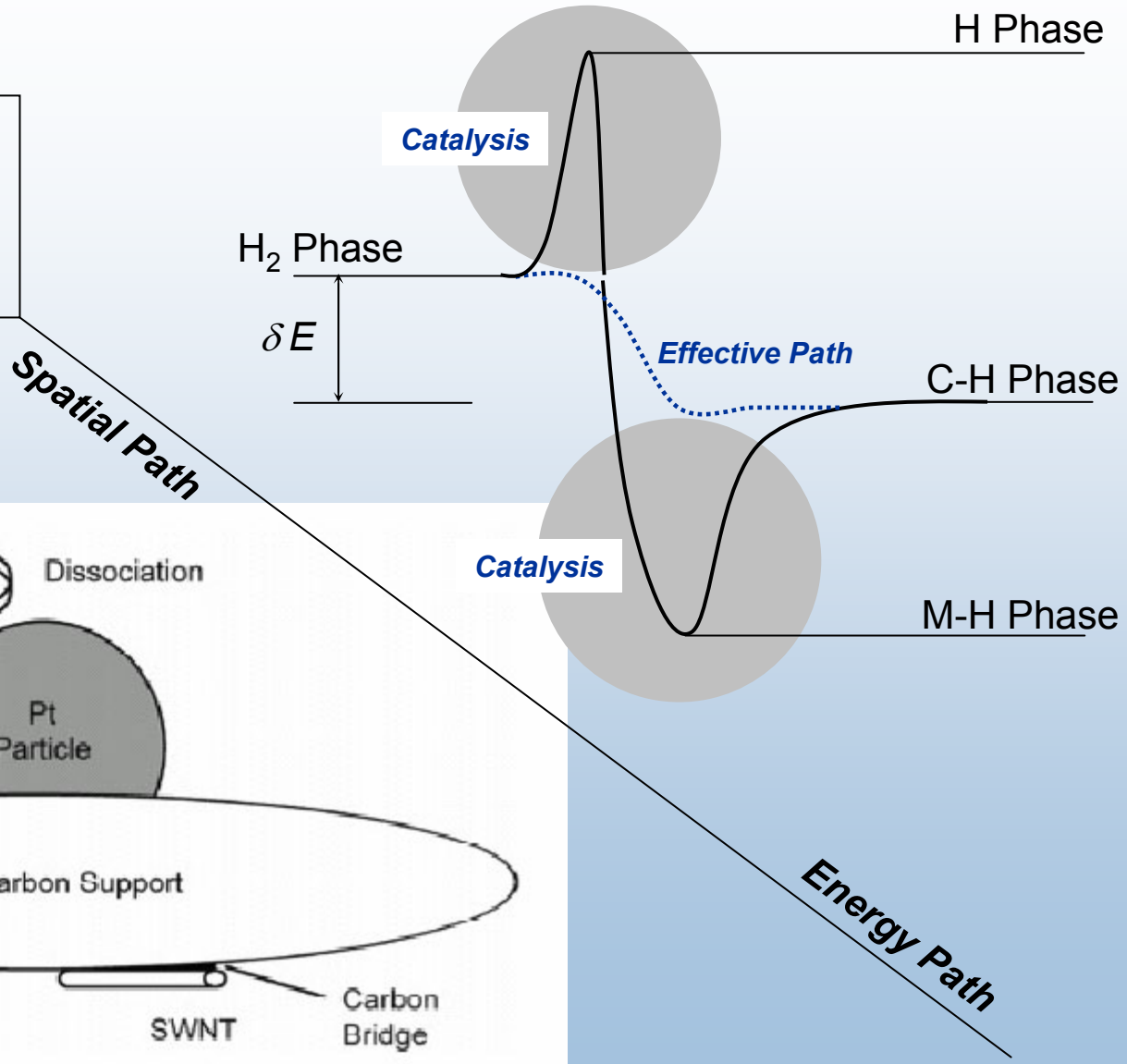
1. Lead symposium organizer, A.C. Dillon, for a six-day symposium (including tutorial) entitled “The Hydrogen Cycle-Generation, Storage and Fuel Cells” Materials Research Society (MRS) Fall Meeting, Boston , Nov. 28 – Dec. 2, 2005,
2. Co-organizer, M.J. Heben, Symposium N and Editor of Proceedings Volume" Hydrogen Storage Materials" at Fall meeting of the MRS, Boston MA, Nov. 28 - Dec. 2, 2005.
3. Co-organizer, M.J. Heben, International Partnership for Hydrogen Energy meeting on hydrogen storage held in Lucca, Italy, June 20-23, 2005.
4. Co-organizer, M.J. Heben, Symposium EE Editor of Proceedings Volume "Hydrogen Storage Materials" at Spring meeting of the MRS, San Francisco CA, April 17 -21, 2006.
5. Co-organizer, M.J. Heben, Symposium on Hydrogen Energy at the Spring meeting of the ECS, Denver CO, May 8-12, 2006.
6. Co-organizer, M.J. Heben, 1st NIST NanoScience and Applications Conference, Boulder CO, Oct. 17-19, 2005.
7. Instructor for tutorial, P.A. Parilla, “On-Board Hydrogen Storage—Breakthroughs and Barriers”, Symposia ‘A’, Fall MRS Meeting, Boston, MA, 11/27/05
8. Guest editor, P.A. Parilla, for a special edition of JMR on “Energy and the Environment”.
9. Editor, A.C. Dillon, MRS Proceedings entitled “The Hydrogen Cycle-Generation, Storage and Fuel Cells”.
10. Symposium organizer, S. B. Zhang, “Simulating Hydrogen Storage: From Current Challenges to Future Promises”, APS March Meeting, Baltimore, March 13, 2006.
11. Keynote lecture, advisory panel, A.C. Dillon, 2005 Taiwan Symposium on Hydrogen Storage in Carbon Nanomaterials, Oct. 18, 2005 Taipei, Taiwan.
12. Editor, L.J. Simpson and M.J. Heben, CbHS COE contribution to the DOE 2005 Annual Report

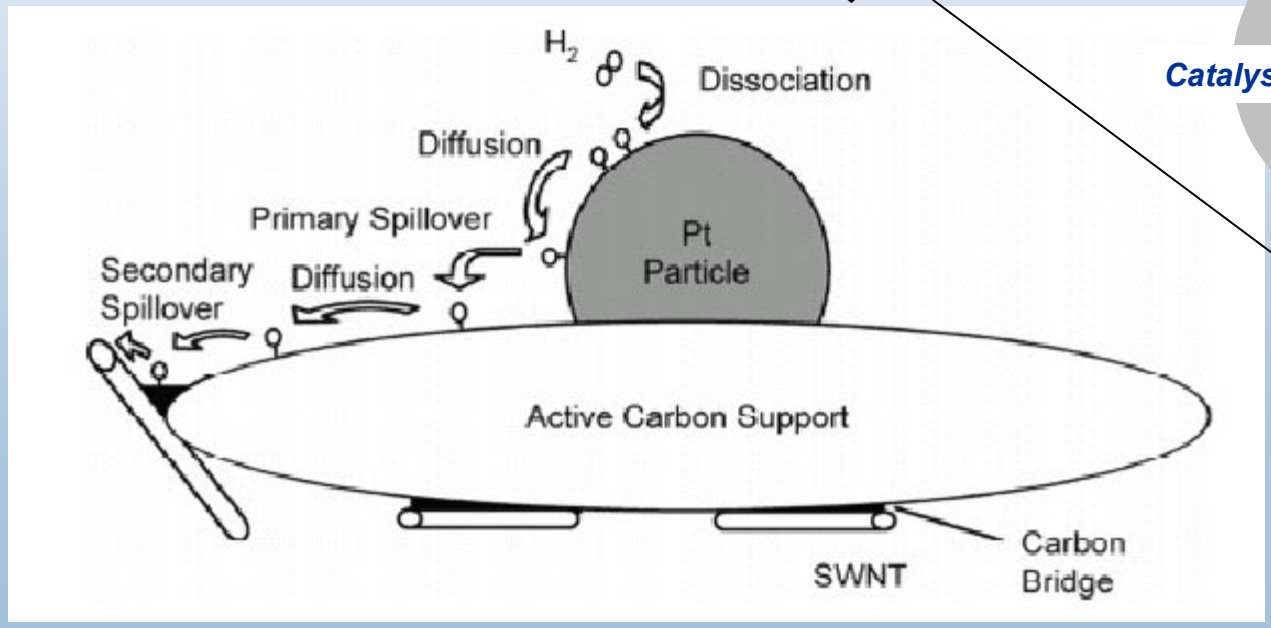
Critical Assumptions and Issues

- Success with a low binding energy approach is critical to permit efficient charge/discharge on-board vehicle and to avoid increasing the effective cost of hydrogen back through the hydrogen supply.
- Effective adsorbents can be identified which can meet all of the DOE targets when deployed in a system.
- Though our effort is research-based at this time, we assume that viable, low-cost synthesis methods can be developed once the best candidate(s) have been identified.
- The issues of stability, clustering, and disproportionation are extremely important when considering the use of dispersed metals in combination with carbons for hydrogen storage.
- The COE mode of operation is desired to accelerate discovery, research, and development of optimize adsorbents.

Spillover: A Thermal Equilibrium between the H_2 and C-H Phases

Reversible Condition (at room temperature):
δE ~ 10-30 kJ/mol-H_2





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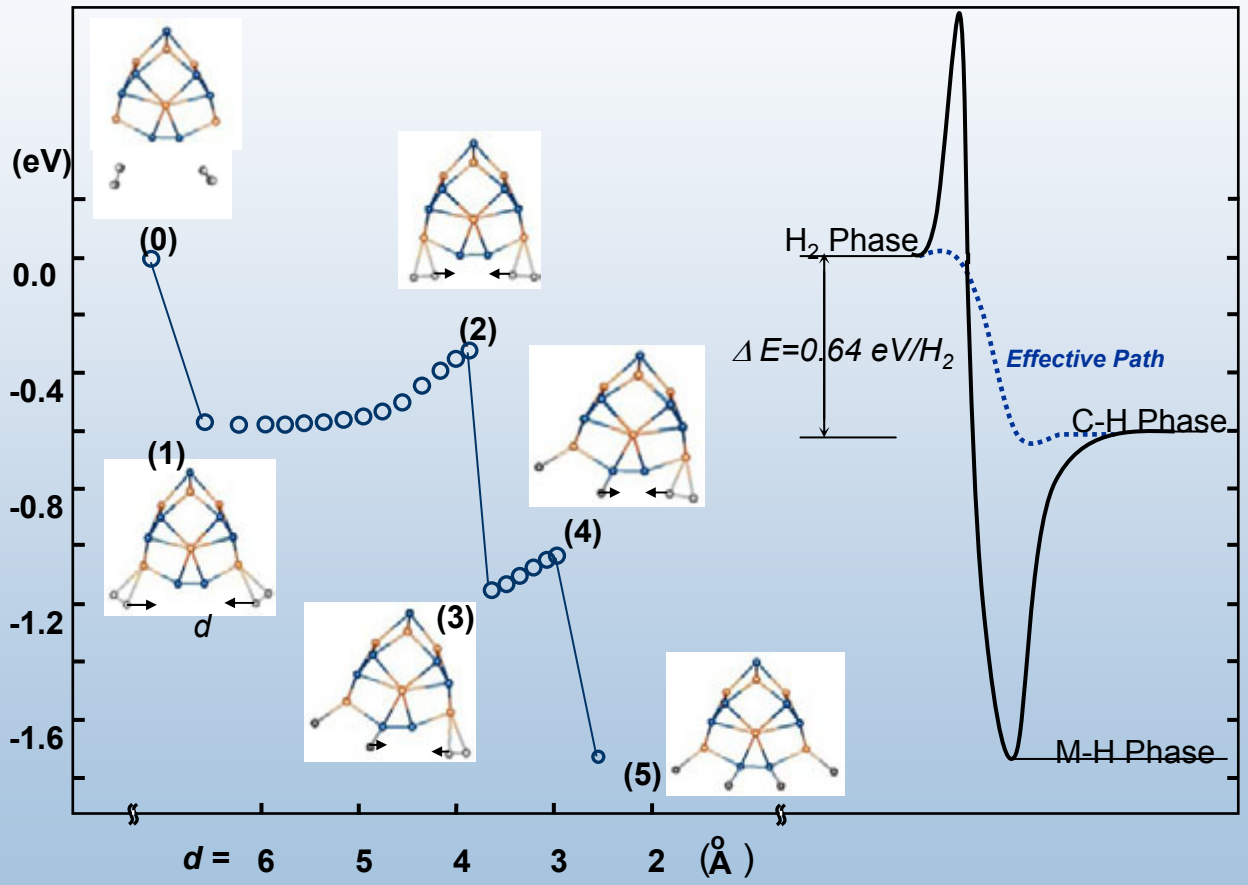
Energy Pathway Calculated for MetCars

- Dihydrogen in gas phase is first adsorbed as dihydrogen by Ti atoms
- Adsorbed dihydrogen "spills-over" onto carbon



"Self-catalyzed Hydrogenation and Dihydrogen Adsorption on Metallo-Carbohedrenes and Related Nanocrystals" Yufeng Zhao, A.C Dillon, Y.-H. Kim, M.J. Heben and S.B. Zhang, Chemical Physics Letters, in press