Hydrogen Storage in Carbon-based Materials

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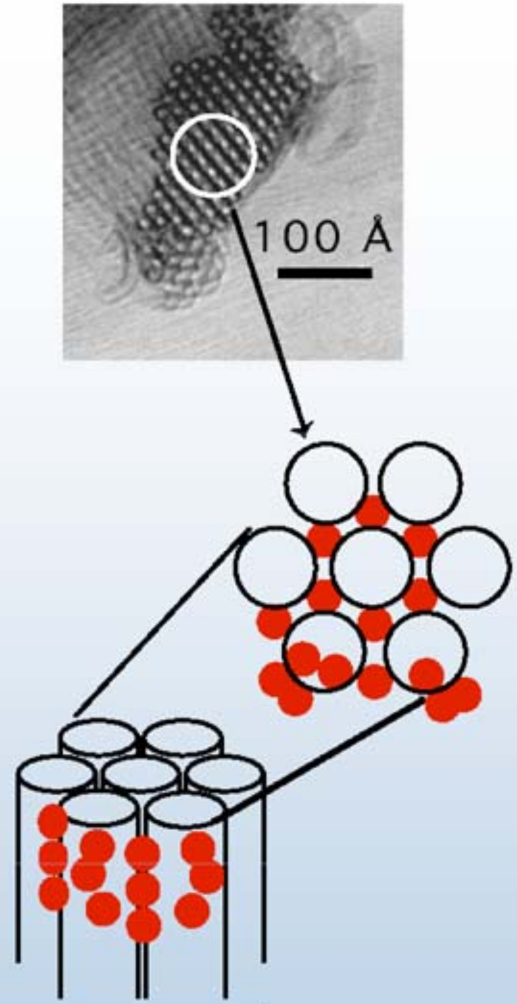
May 26, 2004

This presentation contains no proprietary information

Objective

- Advance performance of on-board adsorbents in support of DOE Multi-year Program Plan.
- Demonstrate accuracy of hydrogen measurements on adsorbent materials.
- Develop methods to reproducibly activate and handle materials to permit scale-up and validation of hydrogen uptake.
- Widen scope and throughput to develop scientific and technical basis for adsorbent use in hydrogen storage.



DOE 2010 Technical Targets for Storage System

- Gravimetric	0.06 kg H_2/ kg system
- Volumetric	0.045 kg H_2/ kg

Budget

Budget/Actual Spending ($k)

	Qtr 1		Qtr 2		Qtr 3		Qtr 4		YTD Total	
	Plan	Actual	Plan	Actual	Plan	Actual	Plan	Actual	Plan	Actual
NREL	268	291	386	361	391	0	473	0	654	652
Subcontractors	0	0	8	2	62	0	63	0	8	2
Total	268	291	394	363	453	0	536	0	662	654

- Subcontract funds support:
  - Prof. T. Gennett on two-year sabbatical at NREL from RIT
  - T. McDonald, graduate student from Columbia U., performing PhD Thesis work at NREL
- Total FY04 budget: $2 M

On-Board Hydrogen Storage Barriers & Targets

General:

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

Reversible Solid-State Material

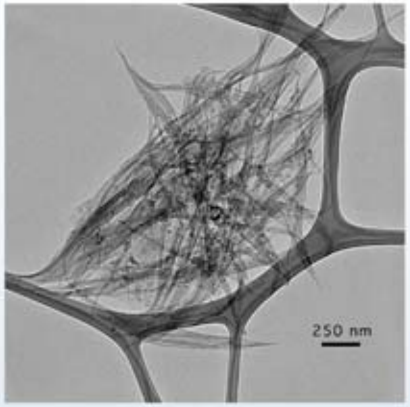
M. Hydrogen Capacity and Reversibility.
N. Lack of Understanding of H Physi- and Chemisorption.
O. Test Protocols and Evaluation Facilities.

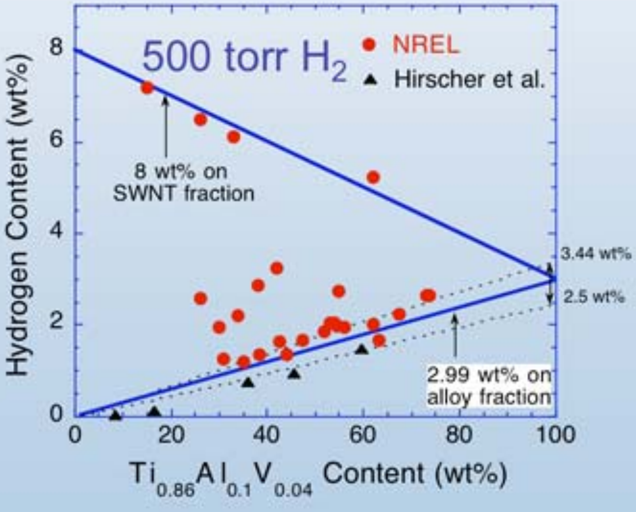
Crosscutting Relevance

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

Approach

- Develop carbon-based materials for high volumetric and gravimetric hydrogen storage
  - Reproducibility
    - In-house review of measurement techniques
    - Repeatable methods to prepare high-capacity samples
    - Validation in external lab
  - Understand physics/chemistry of adsorption
    - Discern mechanisms with computational methods
    - Experimentally probe mechanisms
    - Broaden investigation beyond carbon nanotubes
  - Engineer and fabricate best H_2 adsorbent





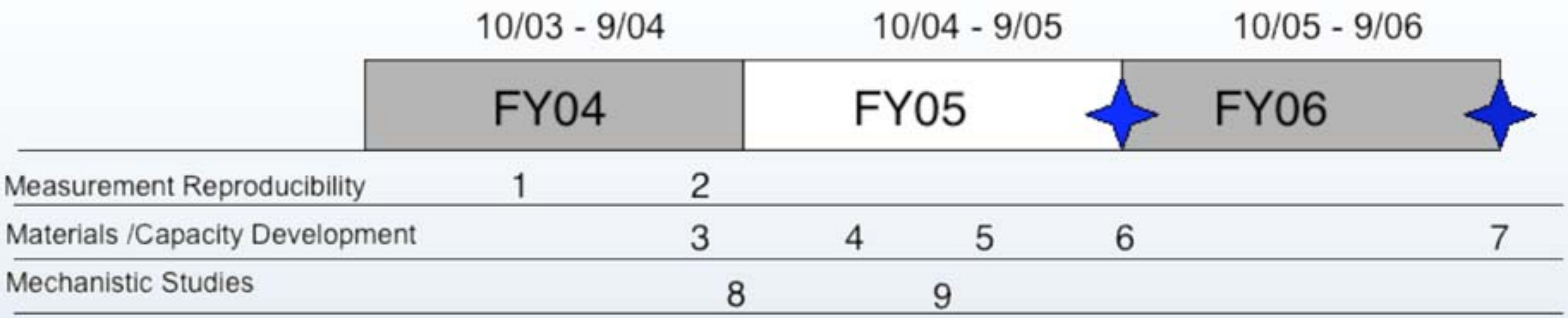
Heben, M.J., et al. AIP, Vol. CP671, 77 (2003)

Project Safety

- Adsorbents under investigation are not pyrophoric or highly flammable.
- In application, adsorbents will operate at lower pressures (< 100 bar) than compressed gas storage (680 bar), thereby reducing physical hazards.
- NREL uses rigorous safety controls for H_2, applying experience gained from handling flammable, toxic, and pyrophoric gasses for solar cell research.
- Liquid-suspended nanotubes and other nanoparticles have shown some potential for toxicity[1]. Proper handling in the lab avoids these concerns, and these issues should not be of great importance in application.

[1] R.F. Service, *Science* **300**, 243 (2003)

Project Timeline



Measurement Reproducibility

- 1 - In-house review of measurement techniques
- 2 - Agreement with measurements at external lab

Reproducible Capacity

- 3 - 3 wt% at room temperature
- 4 - 3 wt% verified externally
- 5 - Assess low-T, High-P capabilities
- 6 - 4 wt% at room temperature (verified externally)
- 7 - 6 wt% at room temperature (verified externally)

Mechanistic Studies

- 8 - Develop working theoretical model
- 9 - Identify most promising materials / mechanisms

Review of Measurement Accuracy

Tech Team Recommendation

Performed week of 1/19 to 1/23/04 by Dr. M. Miller (SwRI) and Prof. R. Gorte (U. Penn), with Dr. S. Satyapal (DOE) in attendance.

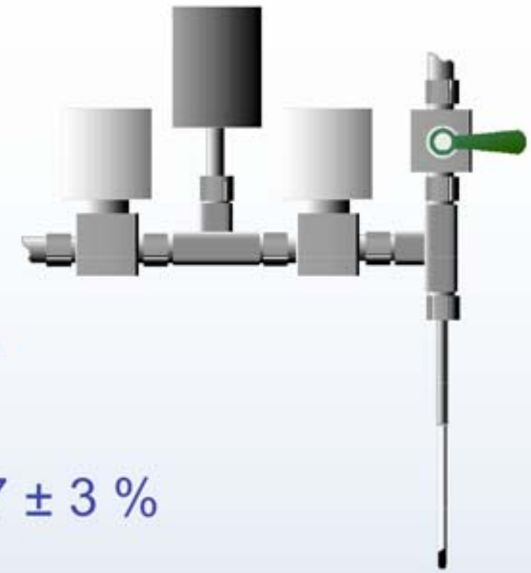
Pre-Review Concerns

- Use of TPD
- Potential contamination
- Calibration
- Alloy fraction determination
- Data reduction methods

Approach to Resolve Issues

- Use volumetric to confirm TPD
- Employ mass spectroscopy - use D_2 and H_2
- Blind analysis of TiH_2 standards
- Specify & demonstrate alloy fraction analysis
- Establish accuracy of each step, apply error analysis

Equipment Accuracy

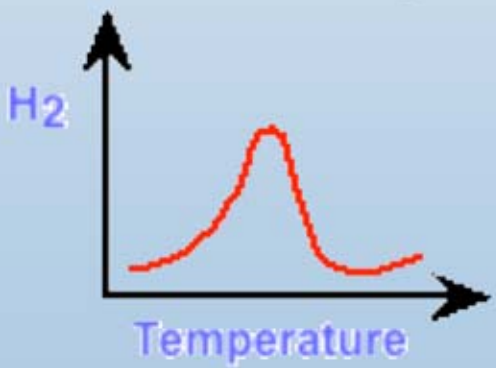


Excellent agreement between TPD and volumetric measurements for probe metal alloy

TPD	2.40 wt%		
Volumetric	2.49 (adsorption)	→	2.47 ± 3 %
	2.54 (desorption)		

Excellent accuracy in blind analysis of samples

- Systems calibrated by primary methods
- H_2 recovered from unknown weight of TiH_2 standard
- Weight determined from known H/M ratio for TiH_2



	Measured	Unknown	Difference
Vol.	11.11 mg	11.40 mg	-2.57%
	5.48 mg	5.55 mg	-1.46%
TPD	1.56 mg	1.54 mg	1.3%
	1.76 mg	1.73 mg	1.73%

Preparation of metal-doped SWNTs

Step 1: laser generation of SWNTs

produces a synthesis batch

Step 2: purification of SWNTs

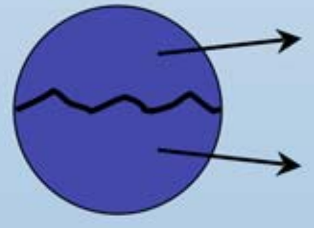
Reflux in HNO_3, collect on filter, oxidize in air
produces a purification batch (e.g. pure #1)

Step 3: Ultrasonic cutting

produces a "cut" batch, introduces metal
(e.g. cut #1)

Step 4: Collect by filtration

Bucky paper



pure #1, cut #1, piece #1

pure #1, cut #1, piece #2

Data Reduction: wt% H on SWNTs

(1): $X_{alloy} + X_{SWNT} = 1$

where X_{alloy} and X_{SWNT} are weight fractions

(2) $(wt\%\ H_{SWNT} * X_{SWNT}) + (wt\%\ H_{alloy} * X_{alloy}) = wt\%\ H_{sample}$

$$\mathbf{wt\%\ H_{SWNT} = \frac{wt\%\ H_{sample} - (X_{alloy} * wt\%\ H_{alloy})}{(1 - X_{alloy})}}$$

Requires accurate measurement of:

- ✓ Weight of sample
- ✓ Total amount of hydrogen adsorbed
- ✓ Weight of alloy in sample
- ✓ Hydrogen capacity of alloy

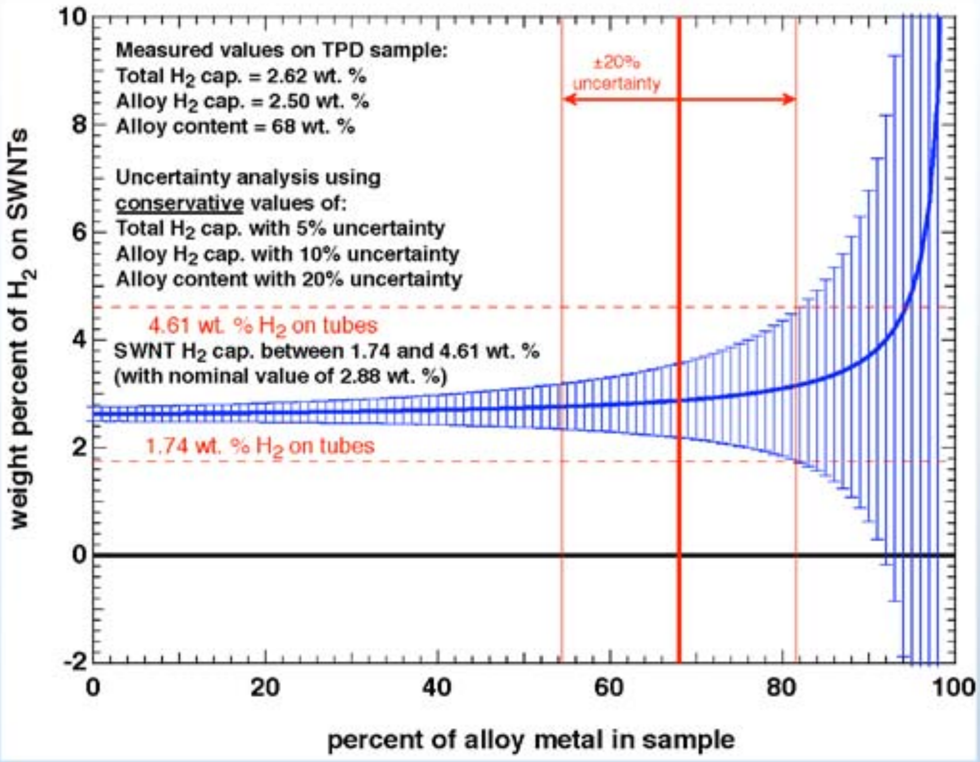
Data Obtained During Review

Sample	Technique	Wt% H_2 total	Wt% alloy	Wt% H_2 tubes
Pure #1, cut #1, piece #1	TPD	2.62	68.0	2.88
Pure #1, cut #1, piece #2	TPD	2.39	66.4	2.17
Pure #1, cut #1, piece #3	Vol (abs)	1.93	63.9	0.92
Pure #1, cut #1, piece #3	Vol (des)	2.13	63.9	1.48
Pure #1, cut #2, piece #1	TPD	1.90	41.0	1.48
Pure #2, cut #1, piece #1	TPD	1.09	22.4	0.68
Pure #2, cut #2, piece #1	Vol (abs)	1.51	45.8	0.67
Pure #2, cut #2, piece #1	Vol (des)	1.50	45.8	0.65
Pure #2, cut #2, piece #2	TPD	1.18	40.4	0.29
Pure #3, cut #1, piece #1	TPD	1.06	43.3	-0.04
Pure #3, cut #1, piece #2	Vol (abs)	0.87	35.7	0.00
Pure #3, cut #1, piece #2	Vol (des)	1.19	35.7	0.46

- Reasonable agreement between TPD and volumetric
- Differences due to degas methods, not accuracy
- Data in red show SWNT uptake after uncertainty analysis

Uncertainty Analysis

Tech Team Recommendation



Conservative estimate of possible errors

- Analysis shows significant SWNT uptake on 2 of 9 samples
- Lower metal contents desired for less uncertainty, and higher overall gravimetric performance

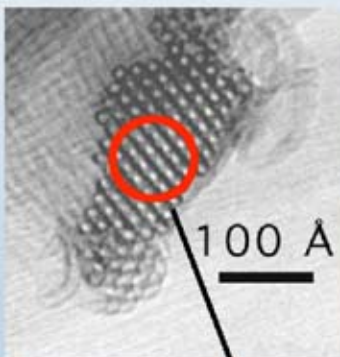
Conclusions from External Review

- H_2 uptake values for alloyed SWNTs as reported by the NREL team during peer review are credible
- Analytical methodologies are well established
- TPD and volumetric techniques were demonstrated to be accurate and repeatable based on reference standard
- Excellent correlation between techniques using similar samples
- Large variances in H_2 uptake for SWNT materials not related to analytical methodologies
  - Likely attributed to the stochastic nature of sample processing (synthesis, purification, cutting, dopant uptake)
  - Sensitivity of samples to degradation during degas cycle
- Next steps: Demonstrate 4 wt% capacity

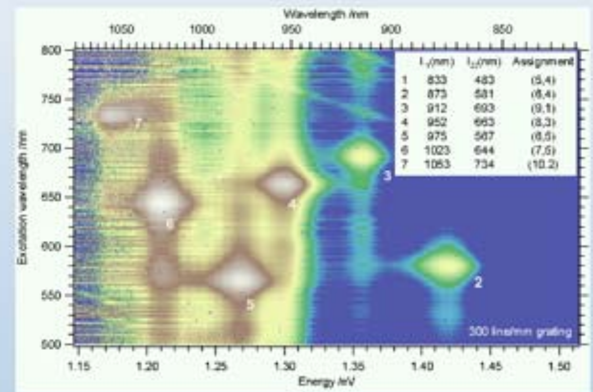
The in-house review met a critical Jan. 04 milestone on time.

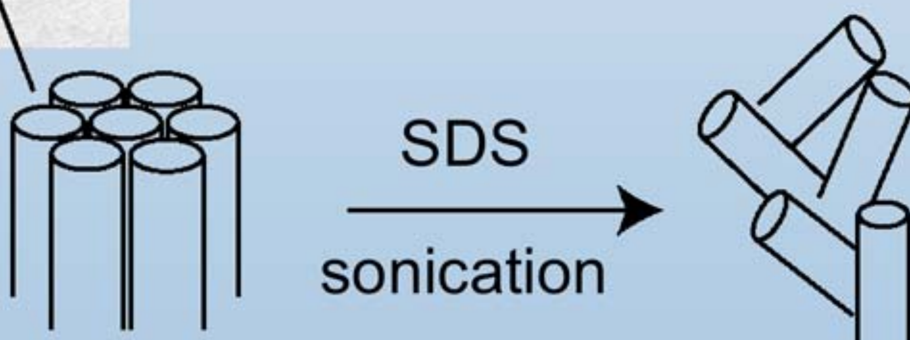
Towards Reproducible Activation

- Use surfactants to prepare fully solubilized, cut SWNTs
- Incorporate metal particles via sonication, or use solubilized SWNTs as precursors for more controlled carbon/metal hybrid syntheses
- Tube diameters and chiralities measured by luminescence, allowing structure and function to be linked



First results with SDS and high-power sonication show 3 wt% on a total sample weight basis, and 3.6 wt% on tube fraction.

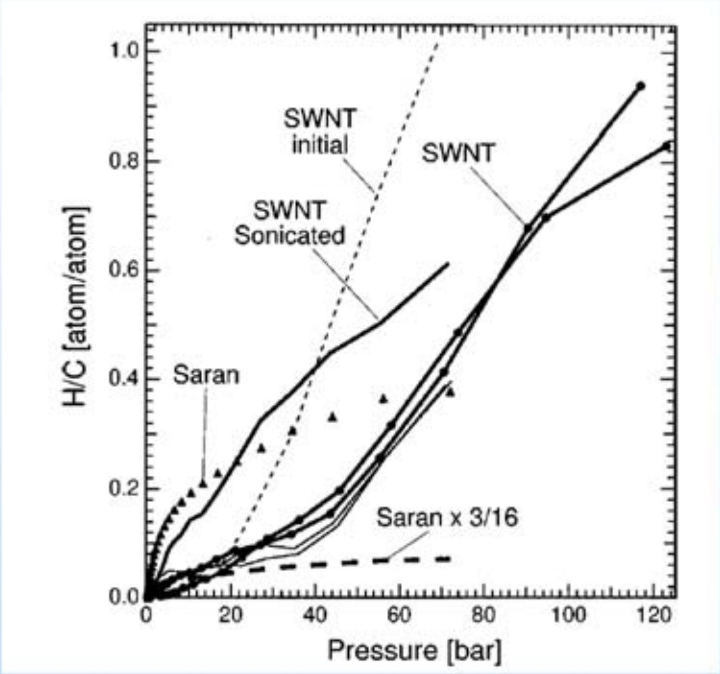




After Bachilo, et al. *Science* **298** (2002), 2361. Acknowledgements to M. Jones, C. Engtrakul, and G. Rumbles at NREL.

Low-T, Low-pressure Adsorption

- SWNTs, MOFs, graphite fibers are more effective than activated carbons available in the 1980s and 1990s
- E_B of 10 - 20 kJ/mol would permit high-density storage at cold temperatures and P < 100 bar.
- Lower pressure operation would permit the use of conformal tankage
- Early results: CO_2 treated raw SWNTs 0.8 wt% H_2 at 510 torr and 77 K
- Other materials, generated internally and from collaborators, are now under investigation



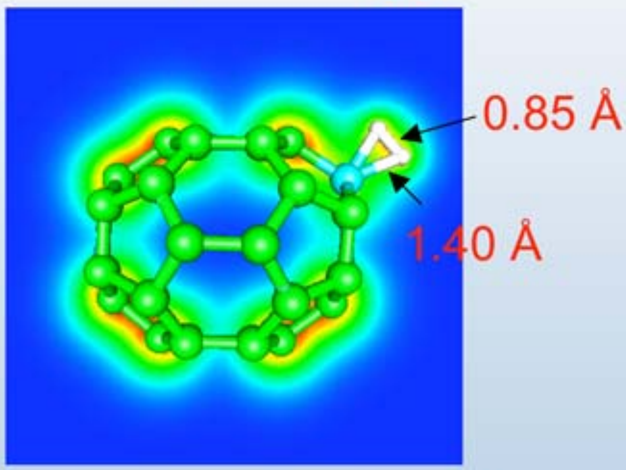
8 wt% storage on SWNTs at 80K
Ye, et al., APL 74, 2307 (1999)

Application of Computational Chemistry

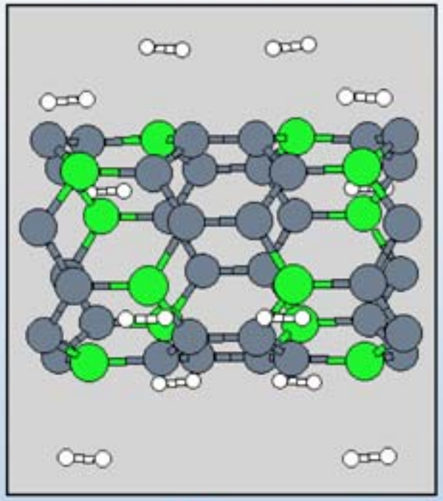
- Search for intermediate binding (10 - 50 kJ/mol) between H_2 physisorption (~ 4 kJ/mol) and C-H bond (~400 kJ/mol)

B-doped C_{36}

37 kJ/mol



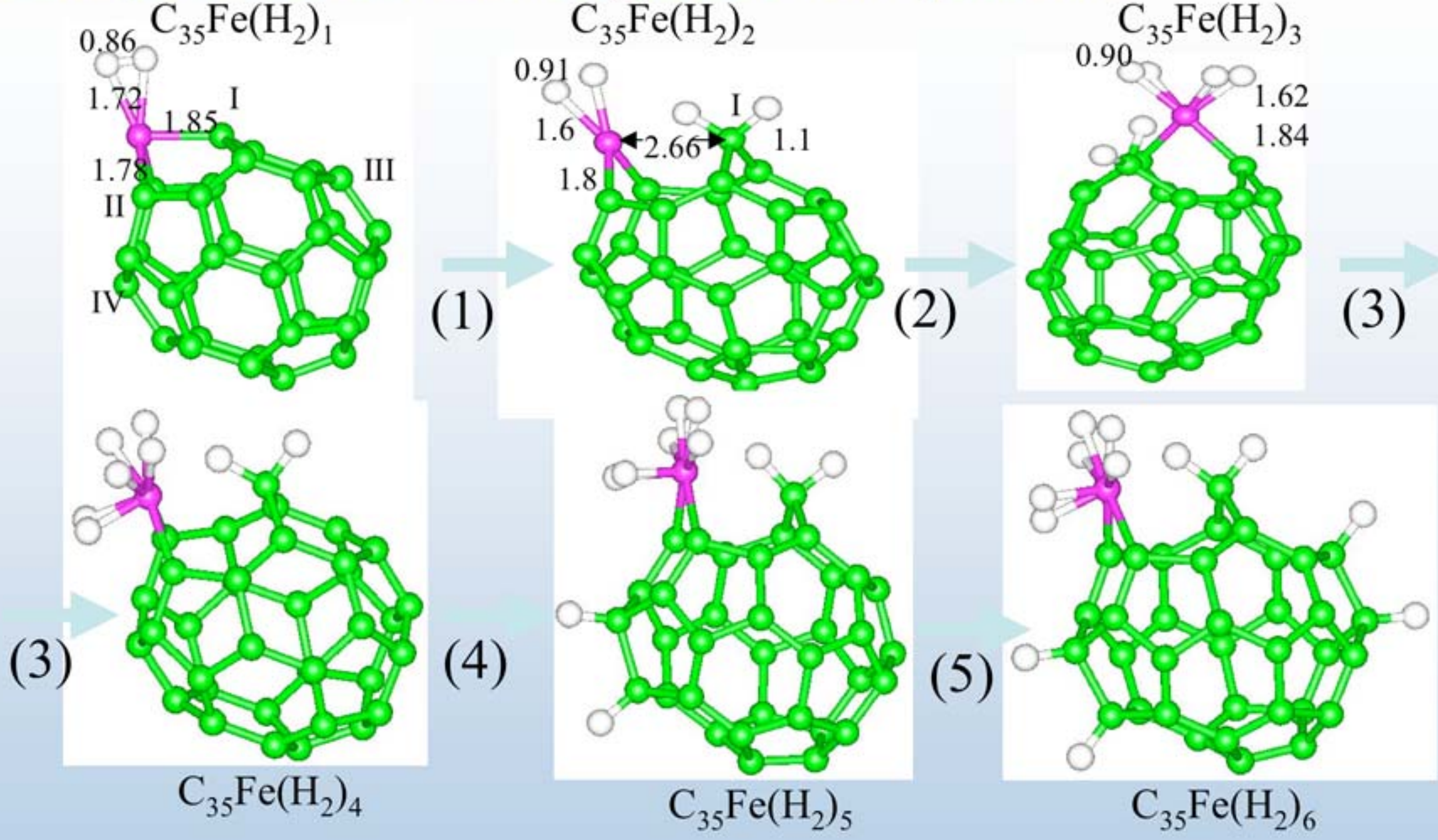
BC_3 nanotubes



12 kJ/mol
~ 4.2 wt%

- 3-center, 2-electron binding between H_2 and adsorbents
- Manipulation of binding by doping, charging & curvature
- H_2 bond lengthened vs. free H_2 (0.75 Å)
- Binding between physi- and chemisorption

Computational Investigation of Spillover

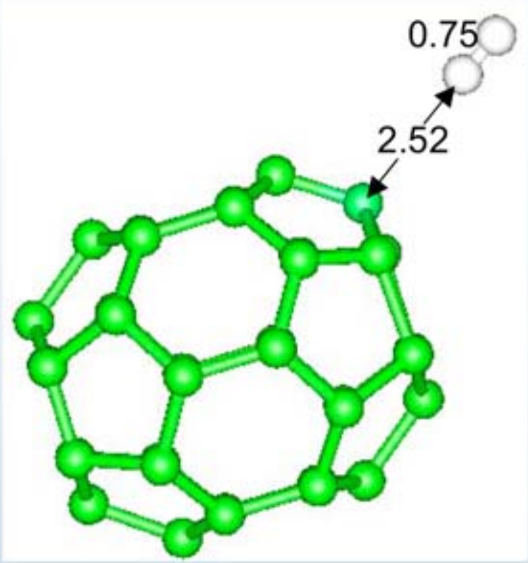


H_2 molecules first adsorb on Fe only. After three pairs, H_2 starts to dissociate and chemisorb on distant carbon as well, which was not possible without the substitutional Fe. Binding Energy to Fe is ~ 50 kJ/mol but C-H binding energy is ~170 kJ /mol.

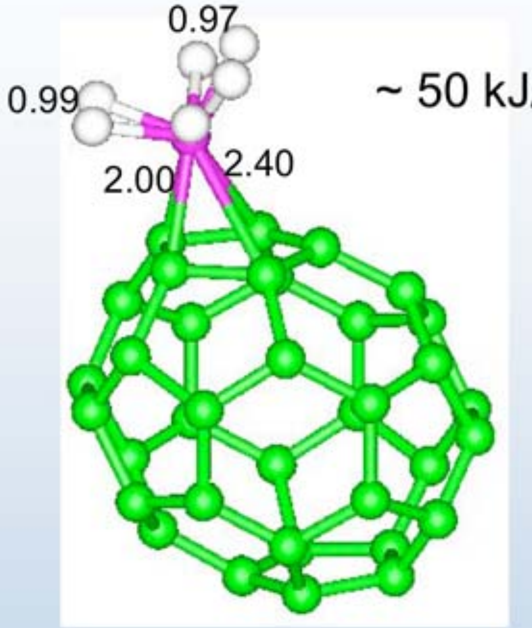
*Bond-distances are in Angstroms

Effect of Fe Adatom on Hydrogen Adsorption on C_{36}

$C_{36}(H_2)_1$



$C_{36}Fe(H_2)_3$



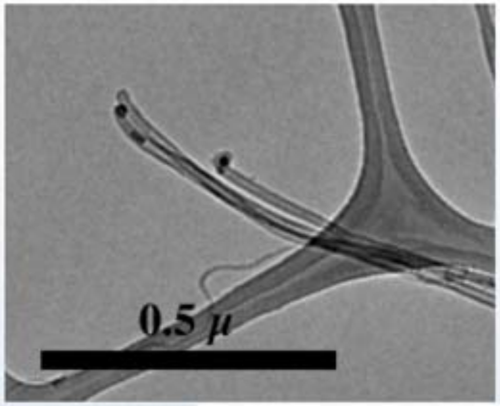
H_2 on pure C_{36}: only weak physisorbtion (~ 4 kJ/mol)

*Bond-lengths are in Angstroms

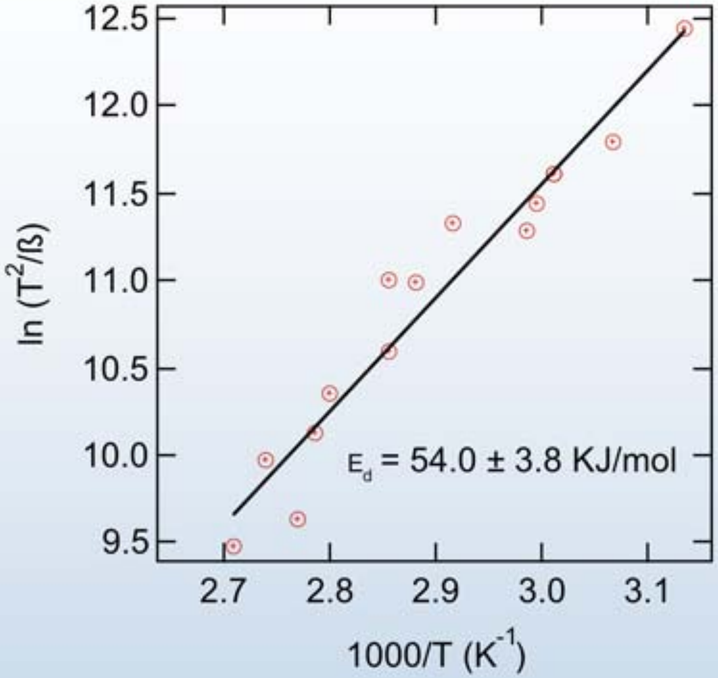
Fe adatom can complex with H_2, but does not result in hydrogen chemi- or physi-sorption on the carbon.

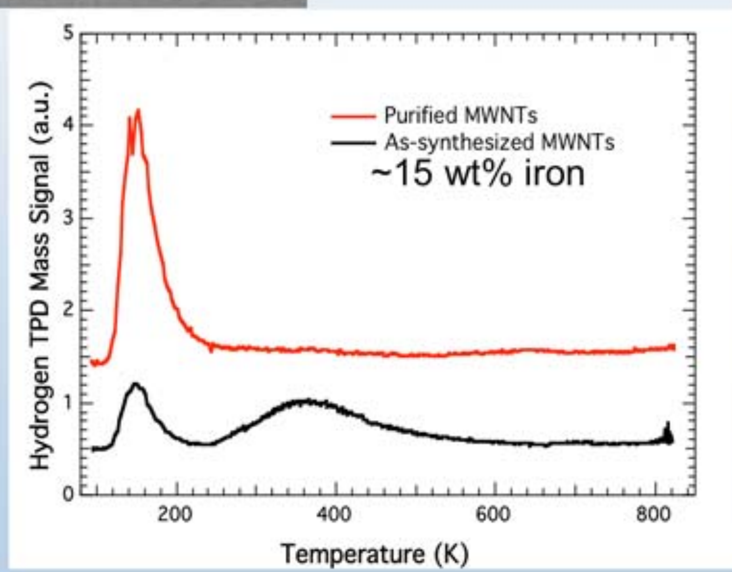
Similar to Kubas Complexes: G.J Kubas, J. Organo-metallic Chem. 635 (2001) 37-68.

Hydrogen Storage in MWNT Materials



As-synthesized MWNTs have iron nanoparticles at tips





Desorption activation energy described by: $\ln T_m = E_d/RT_m$ indicates very desirable binding energy!

Iron is not a known metal hydride. Hydrogen adsorption at near ambient conditions is also **not** anticipated on MWNTs

Interactions and Collaborations

Participation in IEA Annex 17 on Hydrogen Storage

Co-organization of Hydrogen Storage Conferences

Spring 2005 MRS symposium (Dillon)
Fall 2005 MRS symposium (Heben)
DOE/IPHE/EC/IEA workshop - June 2005 (Heben)

Synergy with two DOE/Office of Science projects

CNT Membranes & Adsorbents for CO_2 Removal (BES/DMS)
Linking Quantum Dots with SWNTs (BES/DCS)

Collaborations

Rice University (Smalley, Hauge, Yakobson), U. North Carolina (Wu, Zhou), U. Michigan (Yahgi, Yang), Caltech (Ahn, Bowman, Grubbs), Air Products (Pez, Cooper, Cheng), LLNL (Satcher, Baumann), ORNL (Geohegan, Pennycook), LBL (Zettl), NIST (Neumann), Duke (Liu), Penn State (Eklund, Foley, Crespi, Chung), U. Penn (A. MacDiarmid), SwRI (Miller, Page), BNL (Vogt, Wong), SRTC (Zidan), Stanford's GCEP Program

Multiple Presentations (NHA, MRS, ACS) & Several Publications

Response to Reviewers and Tech Team

- ✓ Employ computational methods (Reviewers)
- ✓ Widen scope (Reviewers)
- ✓ Accuracy of in-house methods (Reviewers & TT)
- ✓ Employ volumetric to confirm TPD results (TT)
- ✓ Uncertainty analysis (TT)
- ✓ Estimate volumetric performance (Reviewers & TT)

Working on:

- External validation w SwRI (Reviewers & TT)
- High-throughput experimentation (Reviewers)
- Increasing capacity on SWNT from ~2.8 (observed at peer review) to 4 wt% at room T, low P

Future Work

- Improve correspondence between volumetric and TPD data through flow-through degas (July '04)
- Use solubilized SWNTs and apply organomettalic chemistry methods for activation
- Decouple cutting/metal incorporation steps, and investigate activation without metals
- Develop and study materials for high Low-T, Low-P storage
- Externally validate uptake results at SwRI (August '04)
- Reproducible 3% uptake in-house (August '04)
- Adapt current measurement systems to, and develop new techniques for, high throughput experimentation (Sept. '04)
  multisample manifolds, optical and nmr spectroscopies, computational chemistry, combinatorial syntheses
- Discover light frameworks, with a high site density per volume, with the correct energies, to achieve DOE/HFCIT storage goals