

Enabling Discovery of Materials With a Practical Heat of H₂ Adsorption

Alan Cooper, Hansong Cheng, Maw-Lin Foo,
John Zielinski, Charles Coe, Guido Pez
Air Products and Chemicals, Inc.

5/15/07

ST 7

Overview

Timeline

- Project start date FY05
- Project end date FY10
- ~35% complete

Budget

- Total project \$3,948,220
 - DOE share \$3,158,575 (80%)
- FY06 funding \$475,000
- FY07 funding (phase 1) \$431,820
- FY07 funding (phase 2) \$143,180

Partners

- Current collaborations: NREL, ORNL, Penn State
- Anticipated/other interactions: Rice University, Duke University, University of North Carolina, NIST

Barriers

- Technical Barriers- Hydrogen Storage
 - A. System Weight and Volume
 - C. Efficiency
 - P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

Objectives

- **Development of enabling technologies for H₂ storage materials development**
 - **Accurate, predictive computational methodologies for new materials discovery and mechanistic understanding**
 - **Characterization tools for accurate H₂ storage measurements**
- **Development and testing of new materials with high H₂ storage density and appropriate enthalpy of hydrogen adsorption.**
- **Our goal: reversible adsorption of hydrogen at near-ambient temperatures at densities that will enable meeting the 2010 DOE system-level targets for hydrogen storage**

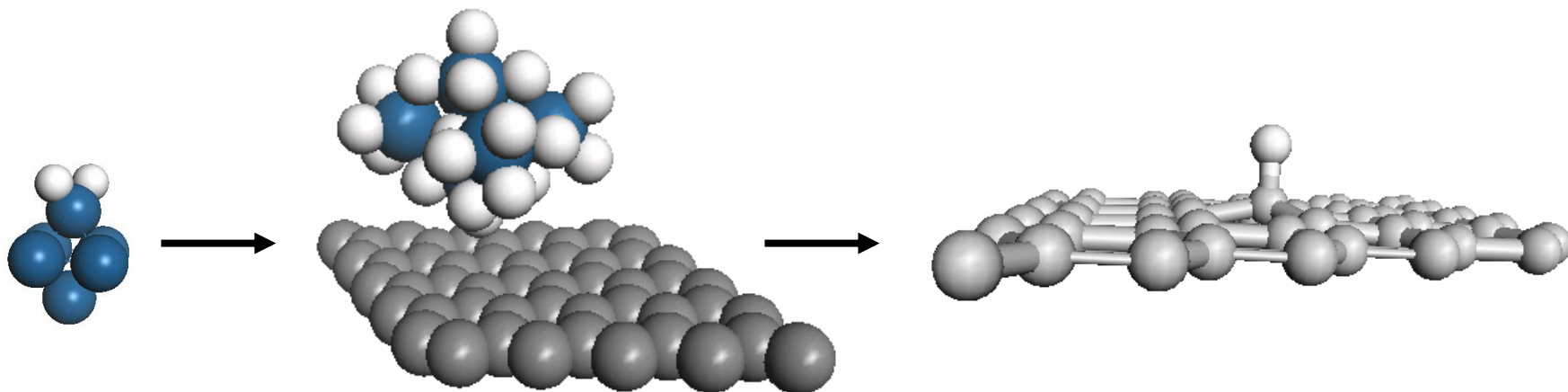
Approach: How can we enable and execute discovery of materials with a higher heat of H₂ adsorption?

- General quantitative computational models for new materials discovery
 - Realize a more practical overlap between computational and experimental work (eg. modeling mechanism of hydrogen spillover)
- Translate predictive computational modeling to development and testing of new H₂ storage materials
 - Novel materials development based upon theoretical predictions of high H₂ storage density and/or enthalpy
 - Materials synthesis (may require entirely new strategies!)
- Accurate measurement techniques
 - Correction for helium adsorption effects on H₂ isotherms

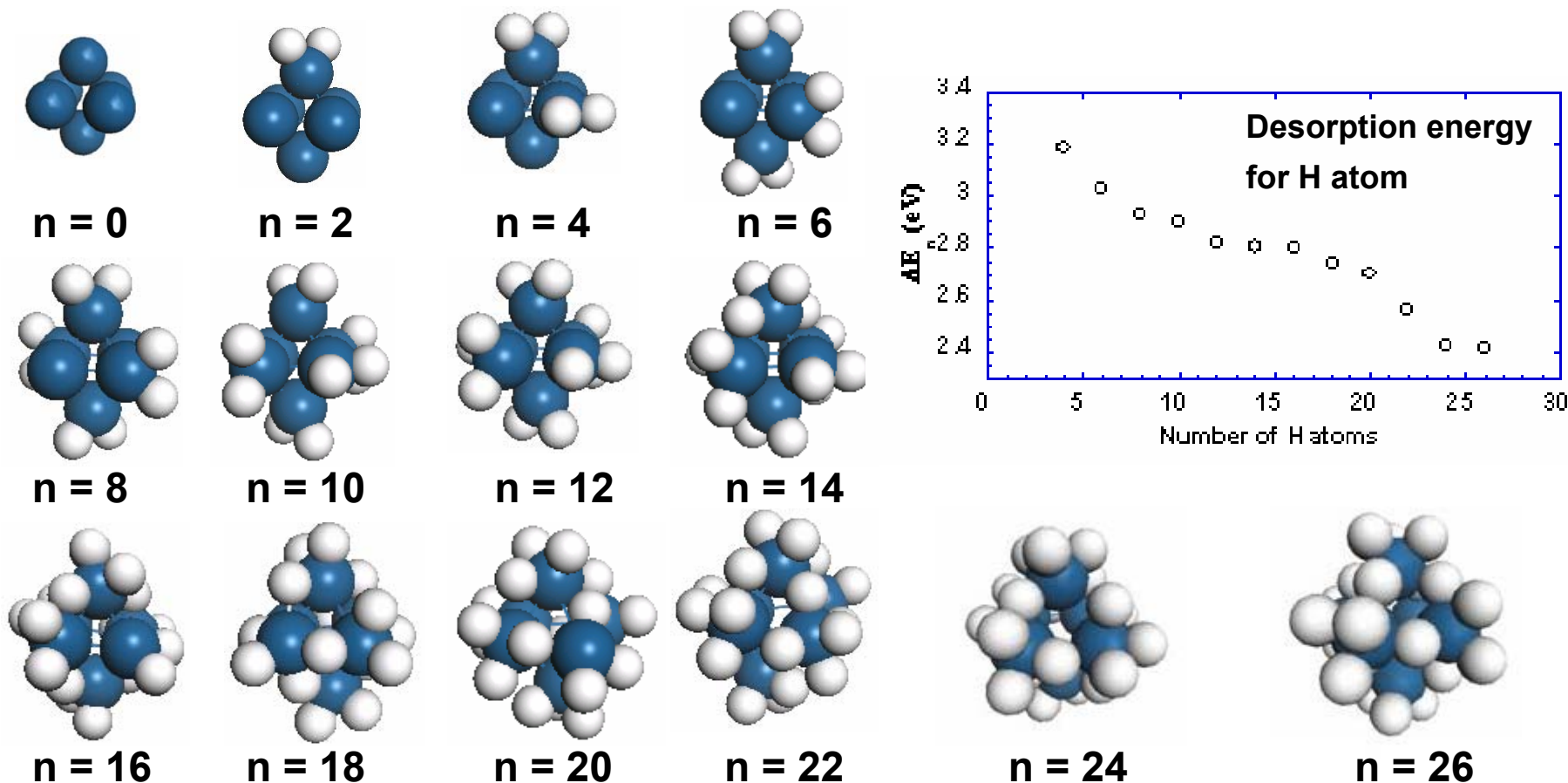
Technical Accomplishments:

An ambitious goal - modeling every step of a H₂ spillover process

- 1) Activation of molecular H₂ on nanoparticle metal catalyst
- 2) Sequential formation of metal hydride cluster
- 3) Spillover of hydrogen from metal hydride to acceptor
- 4) Migration of hydrogen across surfaces or within bulk material
- 5) Formation of labile bonds? (as reversible H₂ “sink”) – still under investigation...



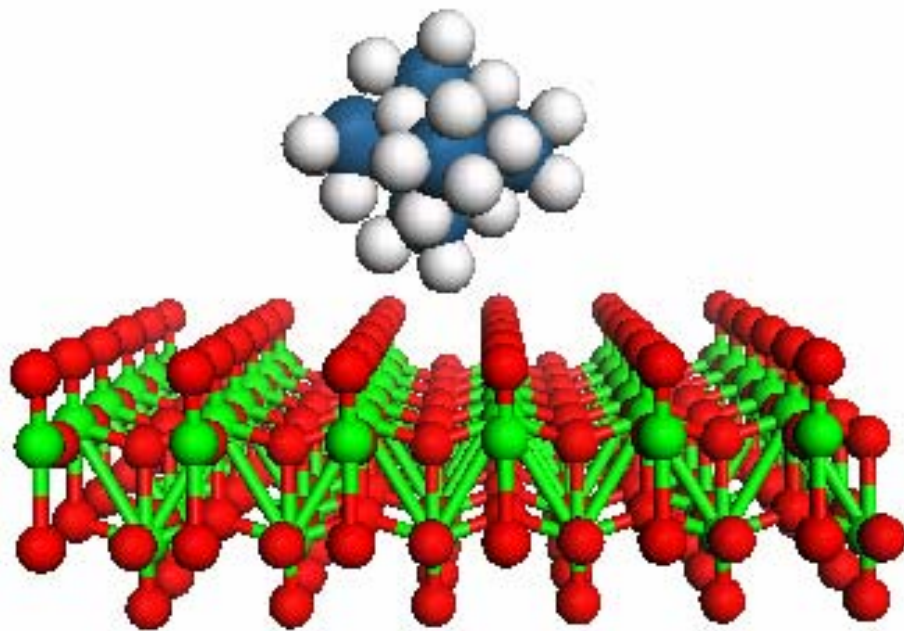
H₂ dissociative chemisorption on Pt nanoparticle: The first step of hydrogen spillover



**Pt₆ reaches saturation at 26 hydrogen atoms with minimum H atom
desorption energy of 2.4 eV**

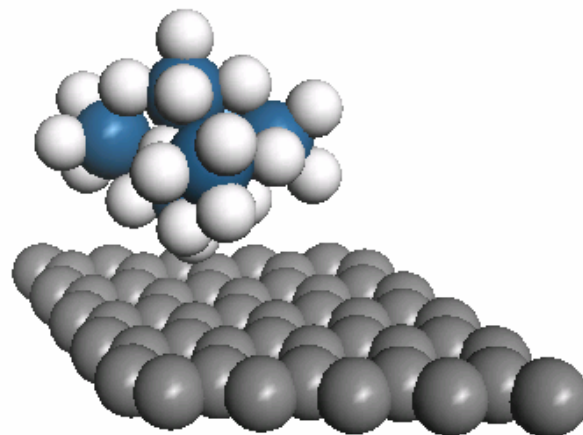
Chen, et al. *J. Phys. Chem. C* 111, 5514 (2007)

Spillover to H acceptor at catalyst-surface interface



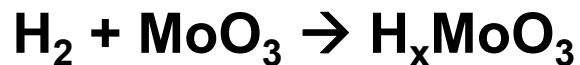
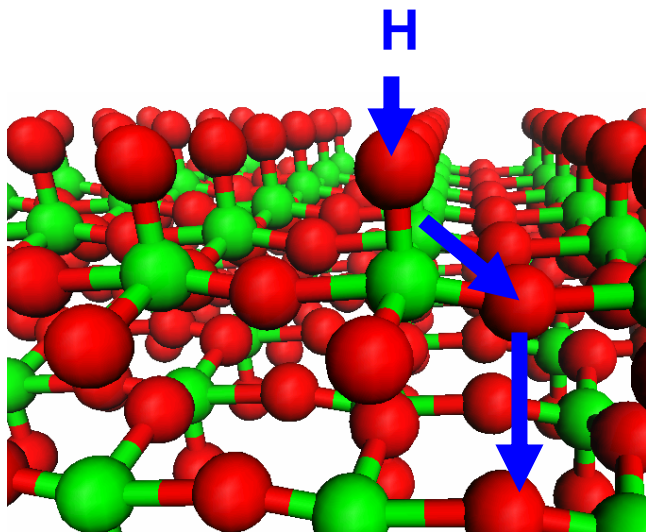
Hydrogen-saturated Pt_6 cluster on
 MoO_3 H-acceptor

- Long range: repulsive due to electrostatic interaction
- Short range: $\text{H} \rightarrow \text{O}$ charge transfer to form O-H bond lowers barrier to spillover

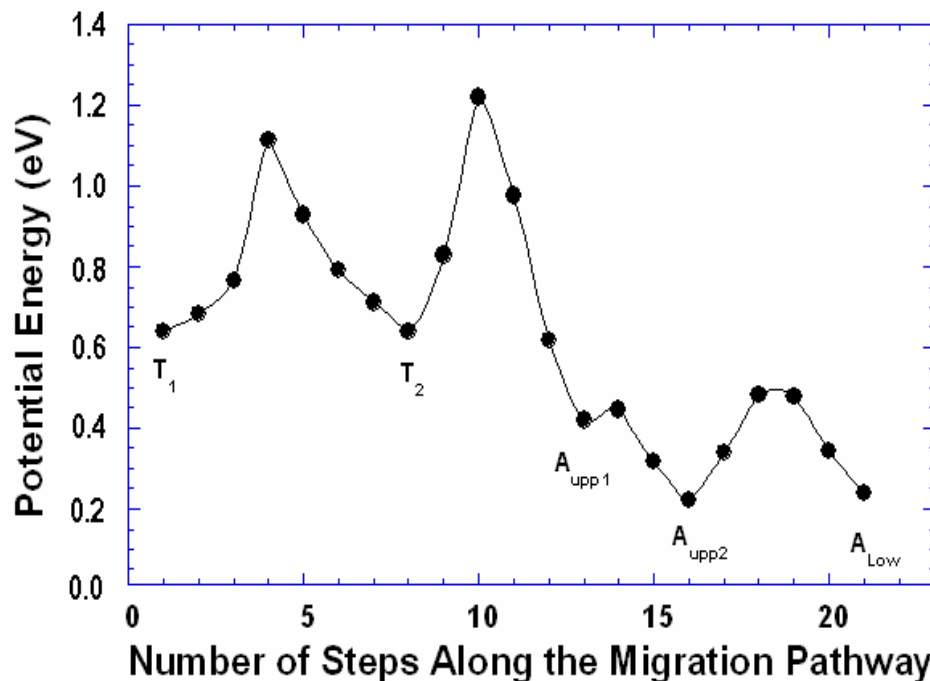


- Hydrogen-saturated Pt_6 cluster on graphene as H-acceptor
- Barrier to H atom spillover from cluster to graphene is only 0.4 eV with C-H bond formation

Mechanistic understanding of H₂ migration in a known H₂-spillover material

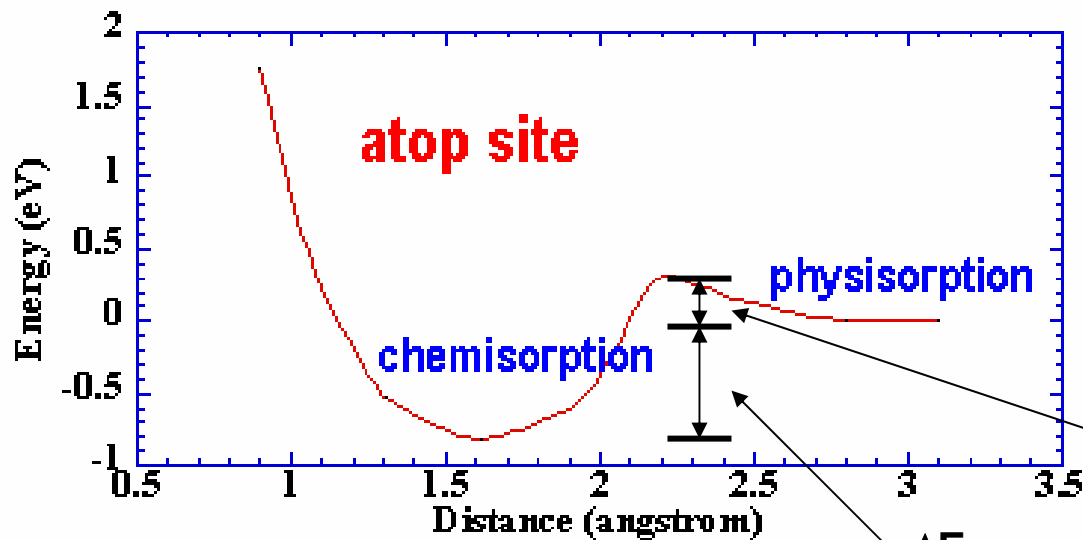
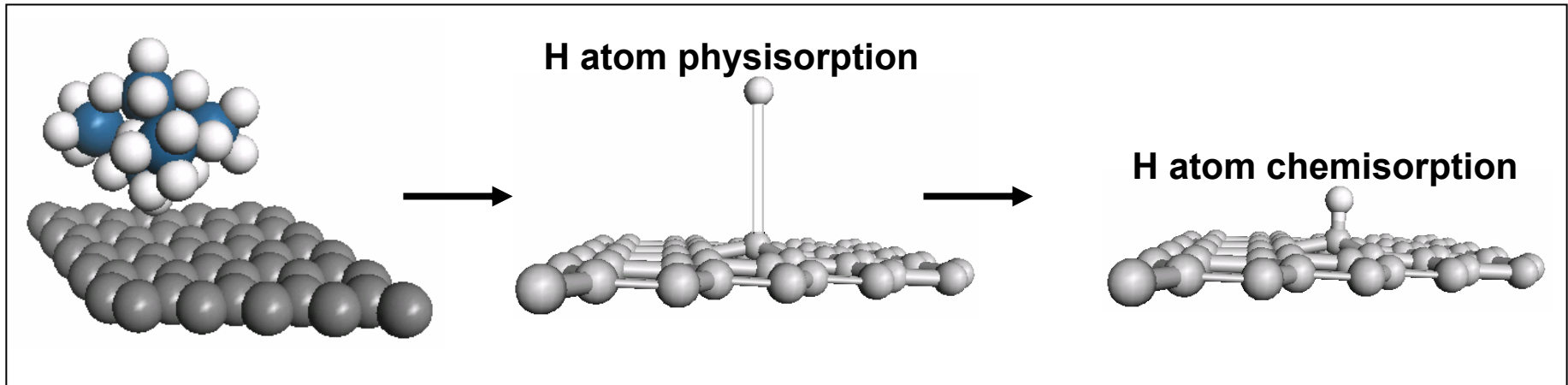


Our computational methods were tested using H_xMoO₃ (known in the literature as a “hydrogen bronze”): a well-characterized hydrogen-spillover acceptor material



- Our calculated energy barriers for specific steps in the H migration match very well with experimental measurements: C. Ritter et al., J. Chem. Phys. 83, 6130 (1985); K. Eda et al., J. Solid State Chem. 141, 255 (1998).

Towards understanding the hydrogen spillover mechanism: energetics of formation of a C-H bond

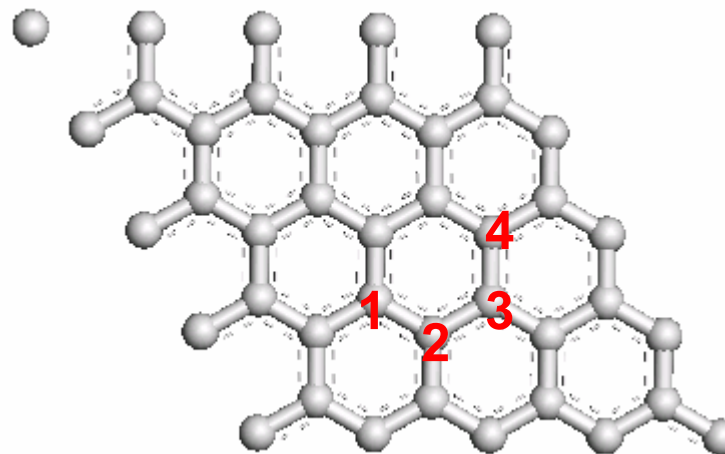
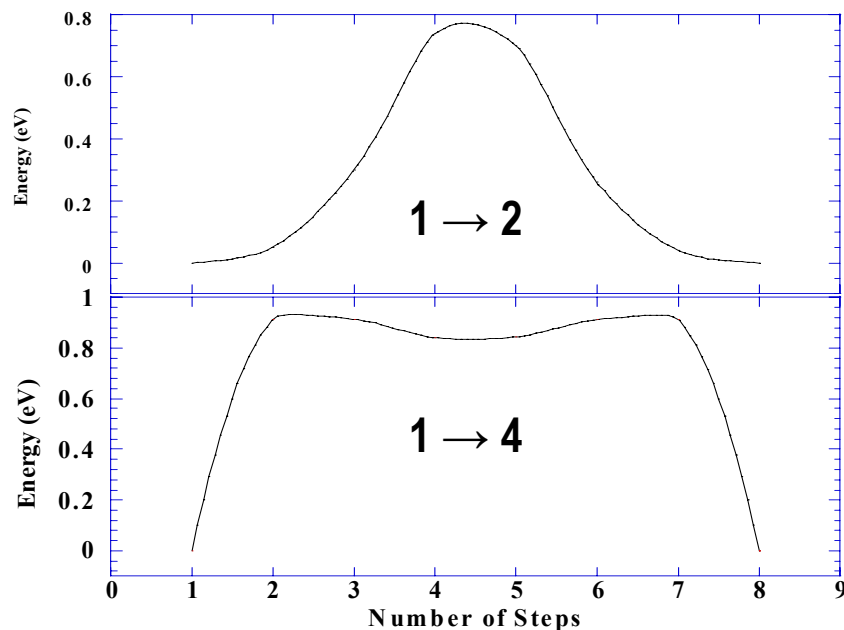


- Strong C-H bonds (chemisorption) are formed by hydrogen spillover

$$\Delta E_{\text{phys}} = 0.2 \text{ eV}$$

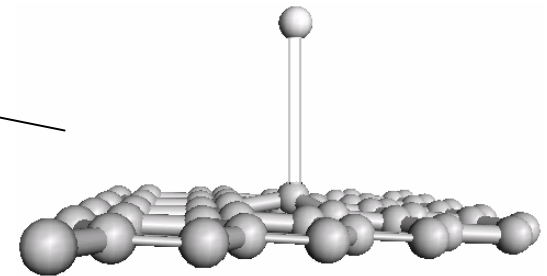
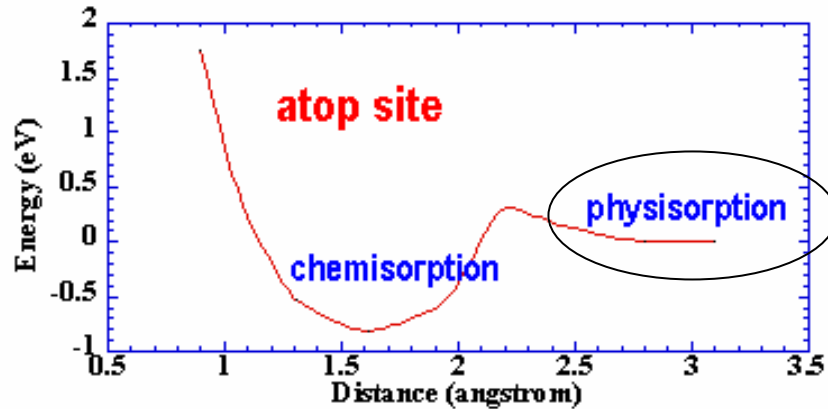
$$\Delta E_{\text{chem}} = 0.8 \text{ eV}$$

Towards understanding the hydrogen spillover mechanism: diffusion of chemisorbed hydrogen on graphene surface

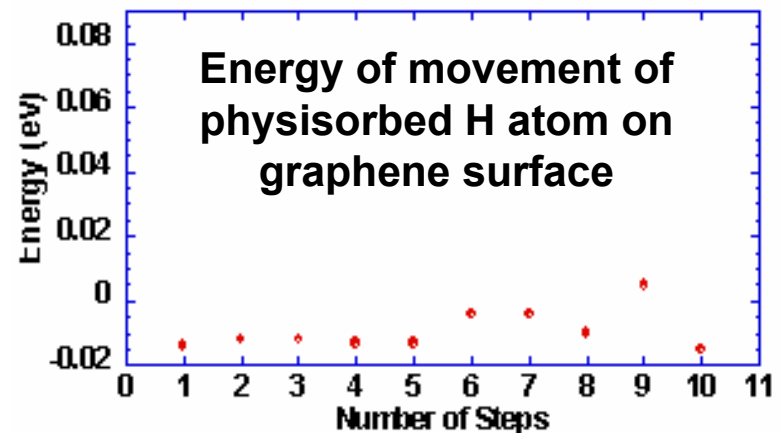


- There are high barriers (0.8-1.0 eV) to diffusion of chemisorbed hydrogen → this is not a viable mechanism for hydrogen diffusion

Towards understanding the hydrogen spillover mechanism: diffusion of physisorbed hydrogen on graphene surface



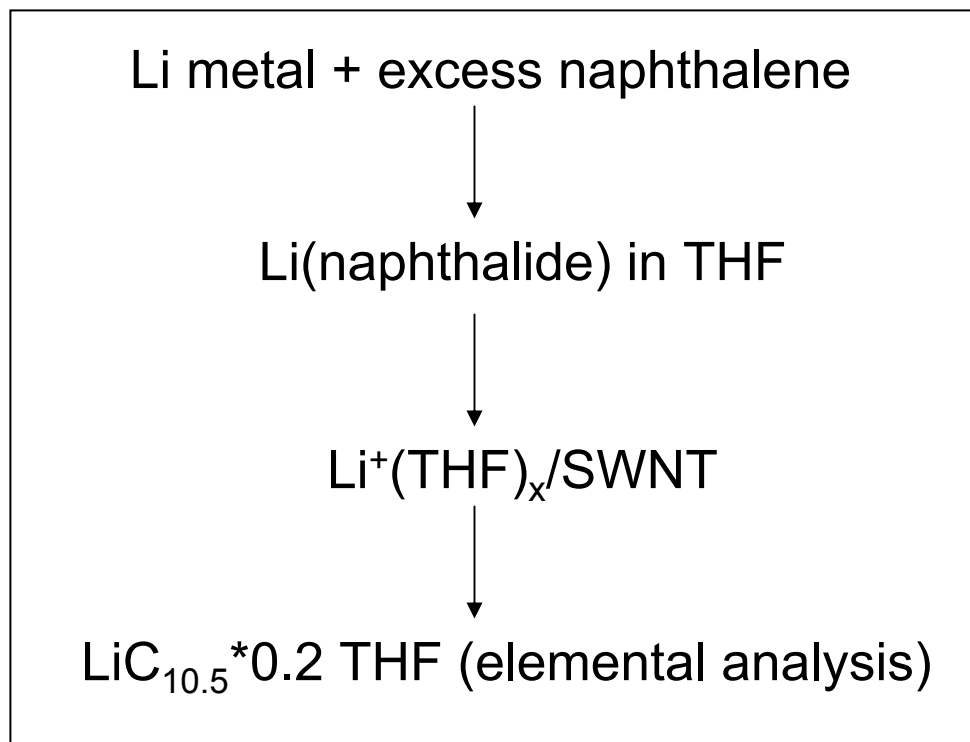
Given an H atom source, hydrogen atoms can physisorb on graphite and diffuse on the surface with minimal activation energies



Summary / Direction to HS CoE partners engaged in testing and optimization of H₂-spillover materials

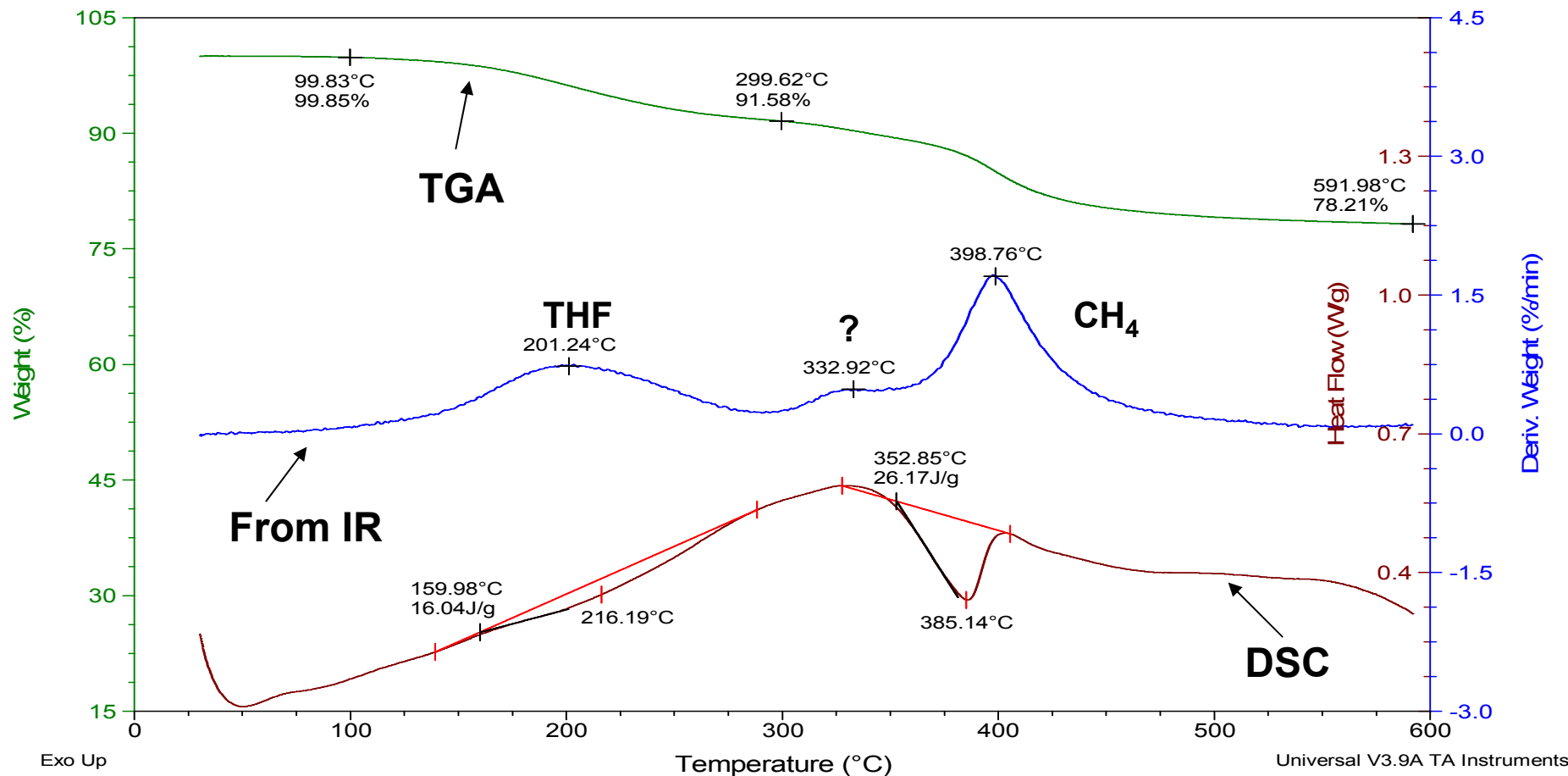
- Spillover of hydrogen from the Pt cluster to graphene is only possible with formation of C-H bonds. However, these bound hydrogen atoms are not easily mobile.
- Materials that form labile bonds with H atoms (eg. MoO₃) allow for rapid diffusion within the bulk of the material: A possible role for amorphous carbon “bridge” materials in experimental results of R. Yang at Univ. of Michigan (HS CoE partner).
- Suggestion: Use of light-metal oxide materials for “bridge” materials and/or hydrogen storage media for hydrogen storage via spillover

Technical Accomplishments: Solution-based route to Li-intercalated carbon materials



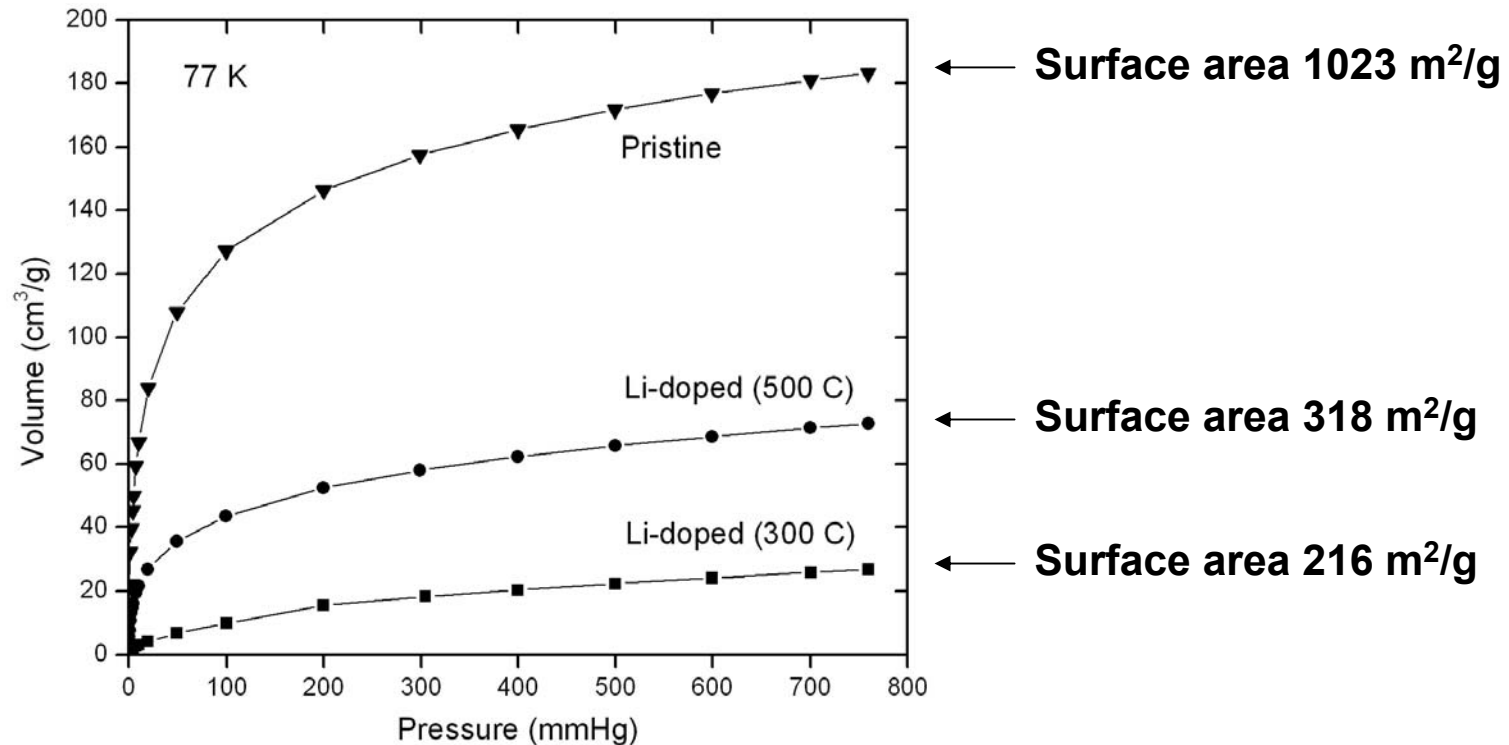
- A general method for use with graphitic carbon materials would be useful to HS CoE partners because...
- Lithium doping is expected to enhance hydrogen adsorption in carbon materials: *Phys. Rev. Lett.* 92, 166103/1-4 (2004).

TGA/DSC/IR analysis of Li/SWNT activation



Removal of THF solvent from Li intercalated nanotubes is difficult

Hydrogen isotherms of Li-doped SWNT after thermal activation under vacuum

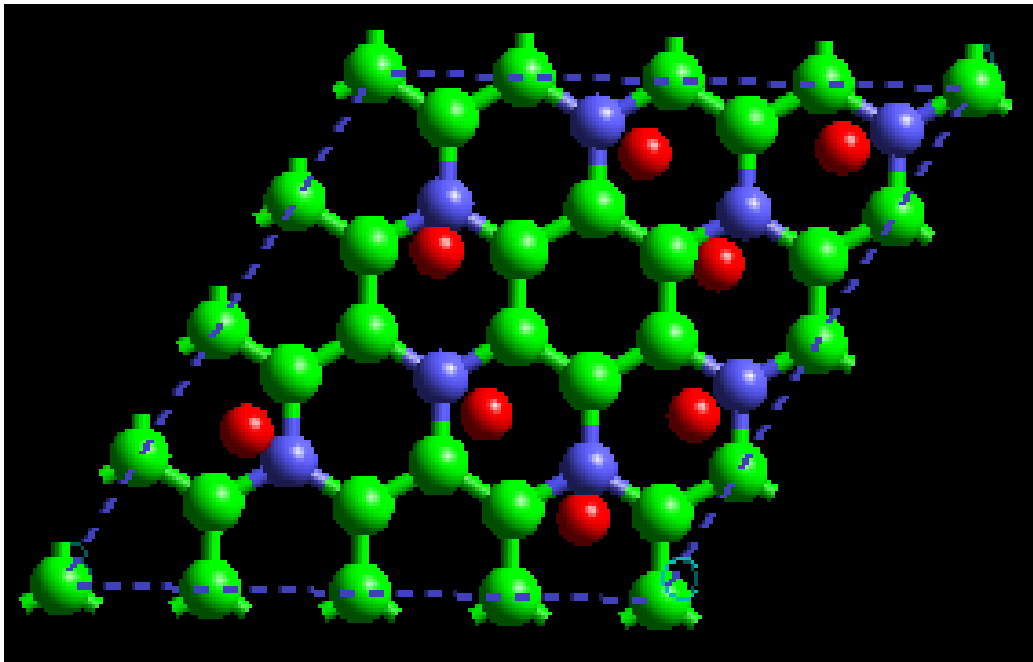


Significantly lower H₂ uptake in Li-doped SWNT; unable to determine ΔH due to low uptake

Li⁺ may be blocking pores and/or occupying substantial micropore volume. However, Li doping may be more effective for carbon-based materials with larger pore sizes (eg. Rice University “pillared” SWNT)

A new concept in H₂ storage materials:

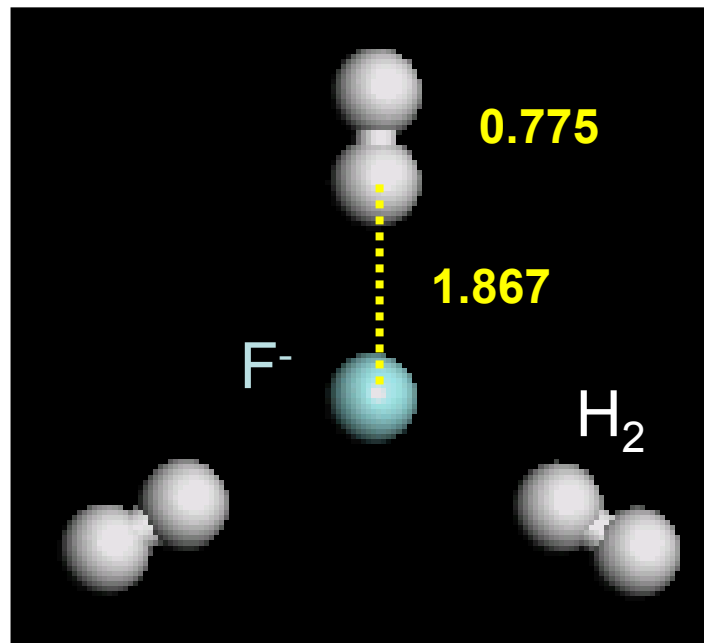
a nitrogen-doped graphite intercalation compound of formula $(\text{C}_6\text{N}_2)_n^{2n+} 2n\text{F}^-$ with strong H₂ – F⁻ interactions



- Carbon atoms (green) in graphite are replaced by an isoelectronic N⁺ atom (blue)
- Positive charge is balanced by the fluoride anions (red) intercalated in the lattice

Our challenge: translate the promising gas-phase calculations of strong fluoride-dihydrogen interactions to a condensed-phase material with high H₂ capacity and appropriate H₂ adsorption enthalpy

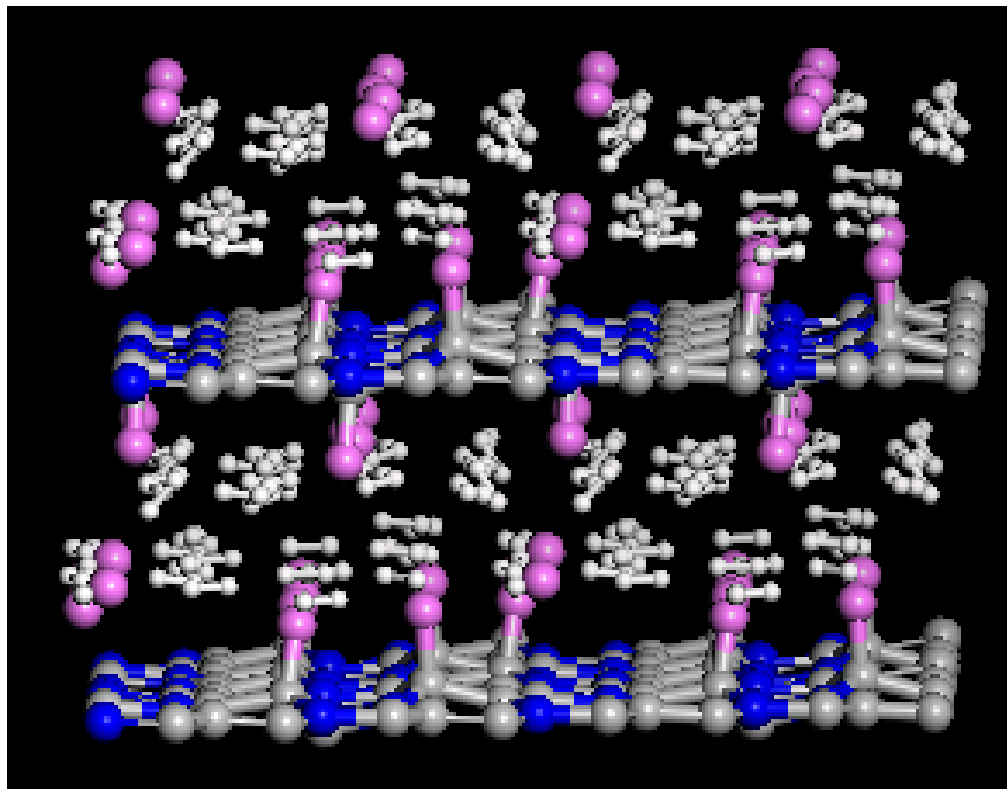
Calculation at 0 K of
strong interactions of
 H_2 with F^- in the gas
phase (kJ/mol H_2)



	B3LYP/6-311++**	B3LYP/cc-pvtz(-f)++	LACVP++
$\text{F}^-\cdots\text{H}_2$	-33.3	-30.6	-
$\text{F}^-\cdots 2\text{H}_2$	-29.9	-27.1	-
$\text{F}^-\cdots 3\text{H}_2$	-27.0	-24.3	-
$\text{CsF}\cdots\text{H}_2$	-	-	-21.8
$\text{CsF}\cdots 2\text{H}_2$	-	-	-20.2
$\text{CsF}\cdots 3\text{H}_2$	-	-	-16.3

Hydrogen-alkali metal salt interactions have been observed by
IR spectroscopy in a matrix at 10 K: *J. Phys. Chem. A.*,
106, 11440 (2002)

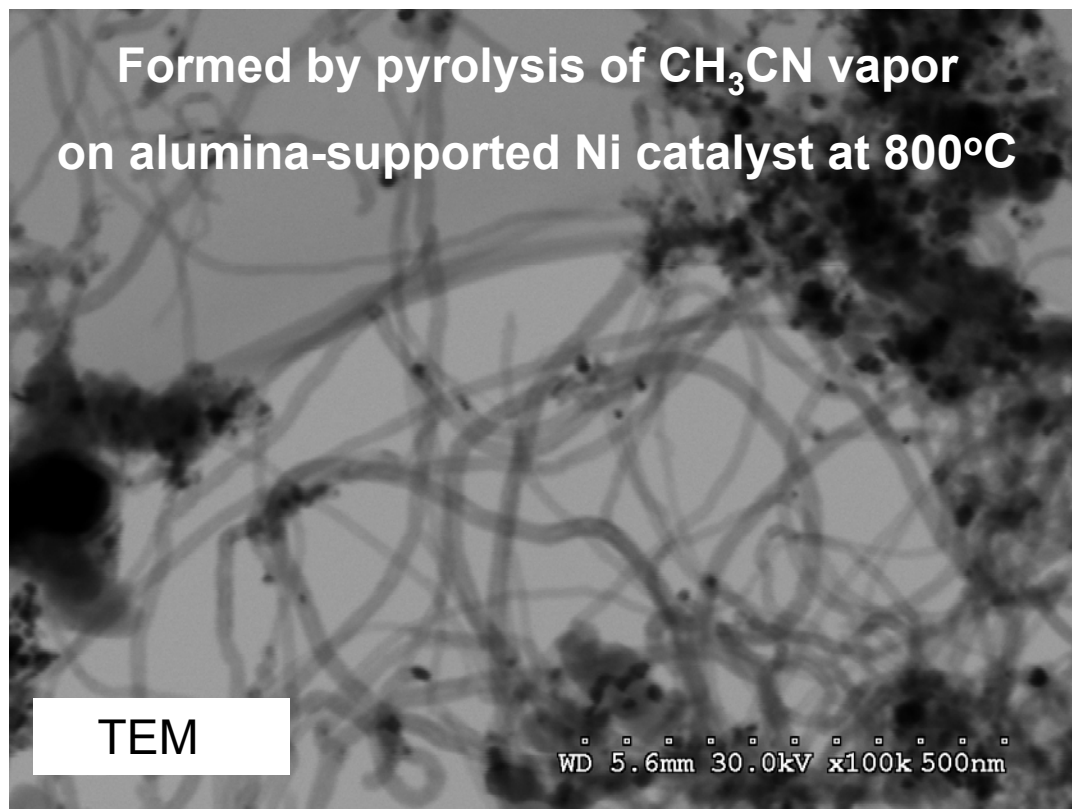
Molecular Dynamics (MD) simulation at 300 K of 7.4 wt. % hydrogen adsorption in porous $(\text{C}_6\text{N}_2)_n^{2n+} 2n\text{F}^-$



- Large lattice expansion upon H_2 adsorption
- F- interaction with carbon leading to non-planarity
- **Calculated average H_2 adsorption energy of -20.2 kJ/mol H_2 at 7.4 wt. % H_2 loading**

A high hydrogen adsorption energy results from the MD simulation of the solid-state material → important for reversible hydrogen adsorption at near-ambient temperatures

Step 1 towards experimental testing of F- GIC materials concept: Synthesis of N-doped carbons



**A starting material for the N-doped graphite fluoride
intercalation complex**

Nakajima and Koh, *Carbon* 35, 203 (1997)

Future Work

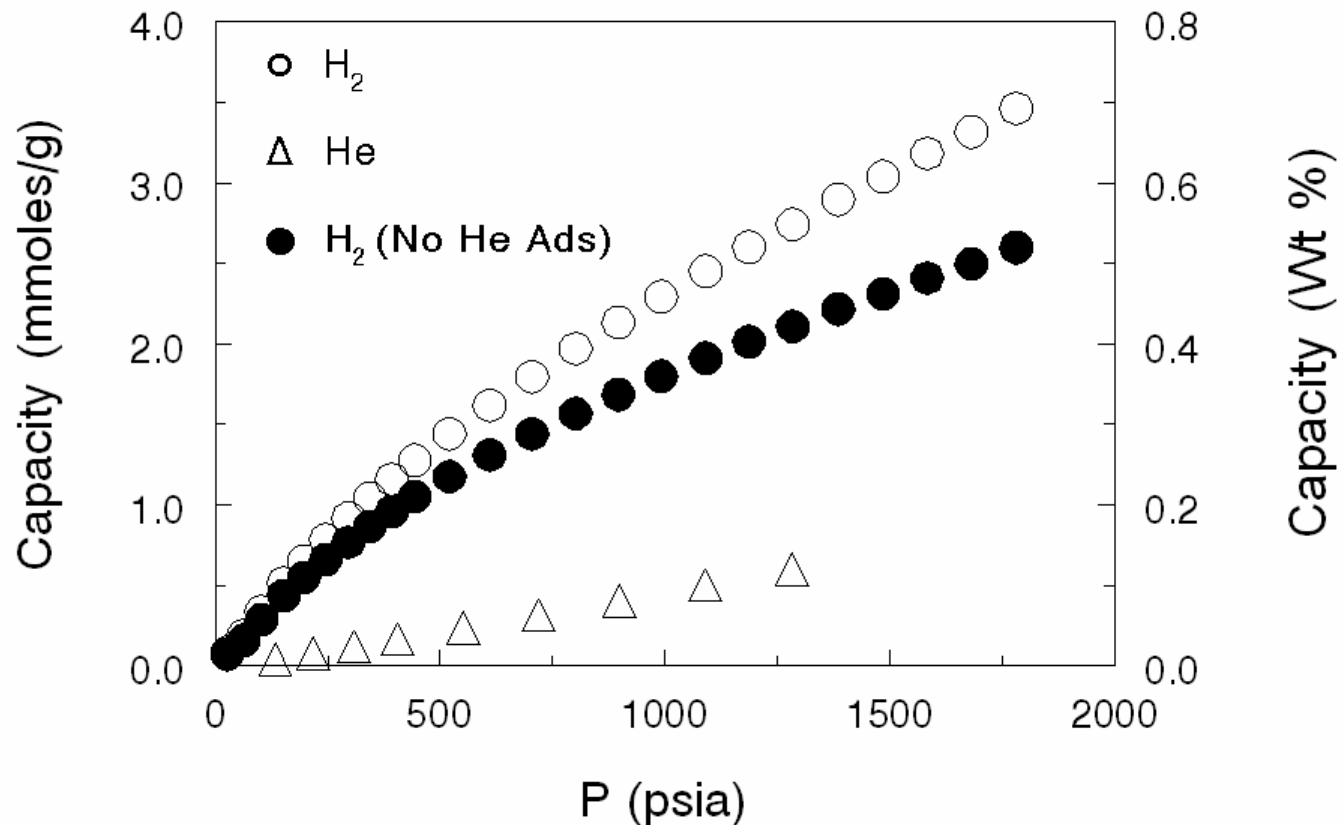
- Synthesize fluoride intercalation complexes of cationic nitrogen-doped graphite and measure the hydrogen adsorption properties
 - Challenge: Incorporation of high levels of nitrogen into graphitic materials. We will collaborate with HS CoE partners to find productive synthesis routes
- Use our predictive computational modeling capabilities to discover new materials with high hydrogen adsorption capacities and enthalpies
 - Focus on evaluation of new intercalated anions in N-doped graphite intercalation complexes
- Continue collaboration with other HS CoE partners on understanding the mechanism of hydrogen storage by spillover and use this knowledge to increase hydrogen storage densities towards meeting 2010 DOE system-level storage targets

Summary

- Relevance: High-density hydrogen storage materials with appropriate enthalpies are needed to reach the 2010 DOE system-level storage targets.
- Approach: Predictive computational modeling is used to identify promising materials. Materials are synthesized and tested using our accurate adsorption testing capabilities.
- Technical progress: Porous nitrogen-doped graphite intercalation complexes that show practical H₂ adsorption enthalpies at high H₂ loadings have been identified by computational modeling. Possible synthetic routes to produce the materials have been identified. The first complete mechanistic picture of hydrogen spillover has been initiated.
- Future work: Complete synthesis of graphitic carbon materials with high nitrogen doping levels. Use these materials to generate fluoride intercalation complexes for adsorption testing.

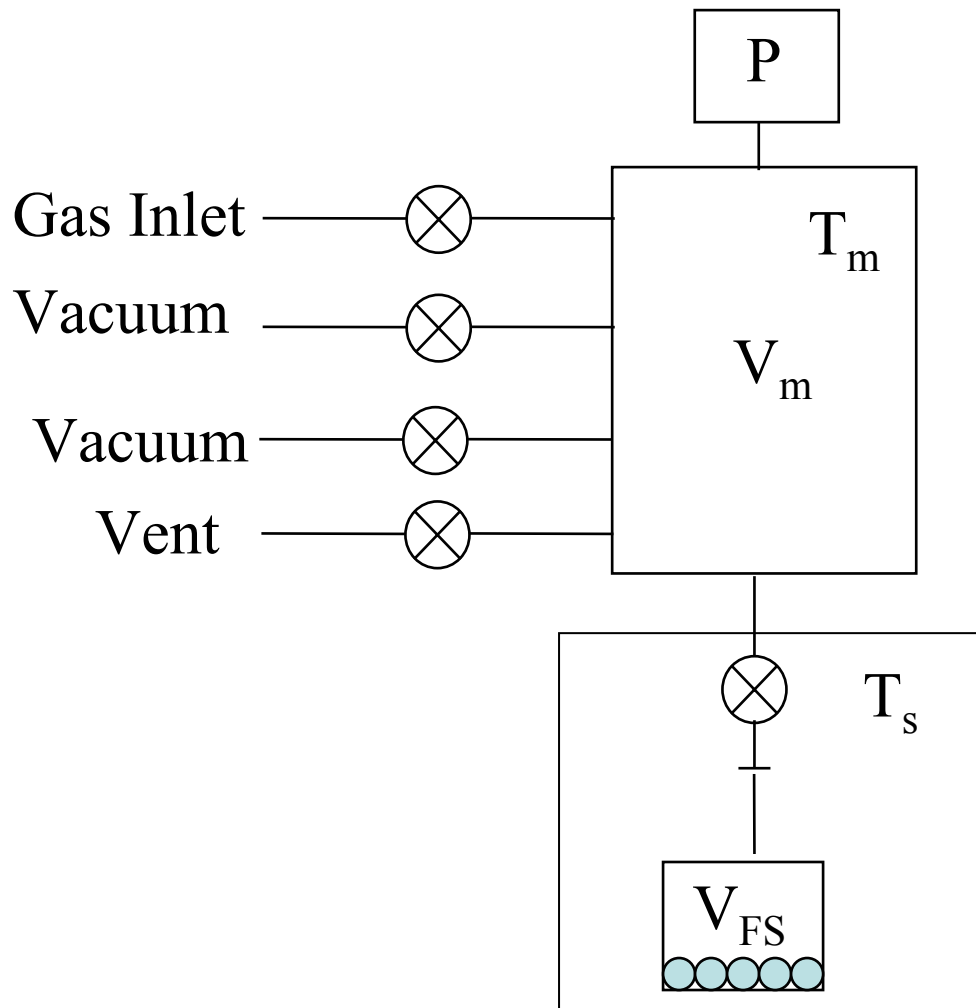
Backup Slides

Effect of helium adsorption on hydrogen isotherm measurement



- Helium adsorption during adsorption “free-space” measurement causes an underprediction of the hydrogen isotherm (filled circles)

High Temperature Helium Pycnometer



- Measures density of sample via helium expansions at high sample temperature
- At high temperature (eg. 300 °C), helium adsorption on sample is diminished relative to ambient temperature
- The density is used in the calculation of hydrogen isotherms on the sample from separate hydrogen expansion experiments

High Temperature Helium Pycnometer

Design Features:

$$V_m = 1 \text{ cm}^3$$

$$V_C = 1.8 \text{ cm}^3$$

$$P < 1000 \text{ torr}$$

$$10^\circ\text{C} < T_s < 300^\circ\text{C}$$

$$T_m = 30^\circ\text{C}$$

