Optimization of Nano-Carbon Materials for Hydrogen Sorption

Boris I. Yakobson[1,2], Robert H. Hauge[2]
[1]Department of Mechanical Engineering & Materials Science, and
[2]Department Chemistry
Rice University

Hydrogen Sorption Center of Excellence

June 11, 2008, Washington DC Project ID#: ST18

The presentation contains no proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Start: 01 February 2005
- End: 31 January 2010
- 60% complete

Budget

- Total project funding
  - DOE: $1,065,209
  - Contractor: $269,181
- Funding in FY07 $235,000
- Funding for FY08 $235,000

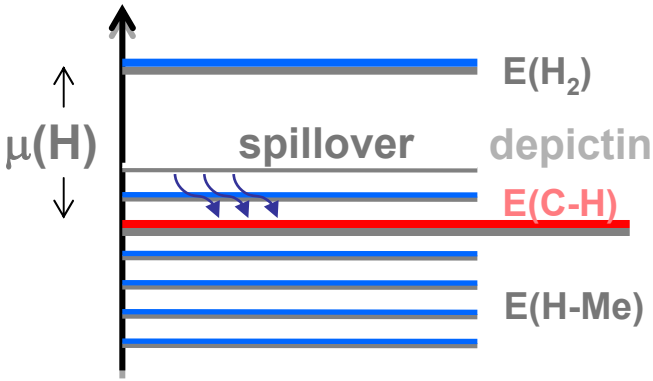
Barriers

Barriers to be addressed

- Estimating hydrogen storage capacity of 3D-foams near ambient conditions
- Conversion of VANTA into solid superacids with high surface area and charge by introduction of electronegative tetrafluoroborate
- Identifying the catalytic role of metal on support for hydrogen adsorption and its spillover
- Understanding thermodynamics and kinetic mechanisms of spillover

Partners

- **NREL, Air Products Corp,** regular teleconferences, face-to-face meetings (Houston, Golden, CO, Washington, Gaithersburg, ORNL TT, MRS San Francisco, MRS Boston).



Chemical potential of H on different parts of the system depicting the favorable range for spillover

OBJECTIVES

OVERALL: Model materials structures' interaction with hydrogen, optimize their makeup for storage and assess the volumetric and gravimetric capacity. Provide recommendations for the synthetic goals (e.g. pore/channel size, metal enhancement routes).

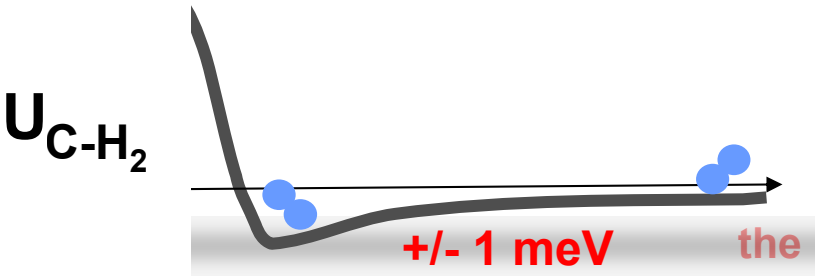
2007:

- **Identify the obstacles (thermodynamics and kinetic) for the spillover for suggesting the materials design to overcome them**
- **Implications of metal aggregation on the hydrogen storage**
- **Estimator of volumetric and gravimetric capacities of foam, comparison with NT-bundles**
- **Enhance binding of H_2 by introducing charge into the carbon lattice by adding a highly stable superacid anion that also acts as a spacer**

2008:

- **continue the above and**
- **Synthesis of metal- and electronegative-group- (F^-, BF_3^-) enhanced VANTA (vertically aligned nanotube arrays, *contrast to fibers*) for H_2 adsorption**
- **Explore doping as an anchor to metal/metal cluster, role of bridges, and dopants on the threshold of spillover**
- **Hydrogen sorption on novel structure of B (fullerenes, sheets, nanotubes)**

APPROACH



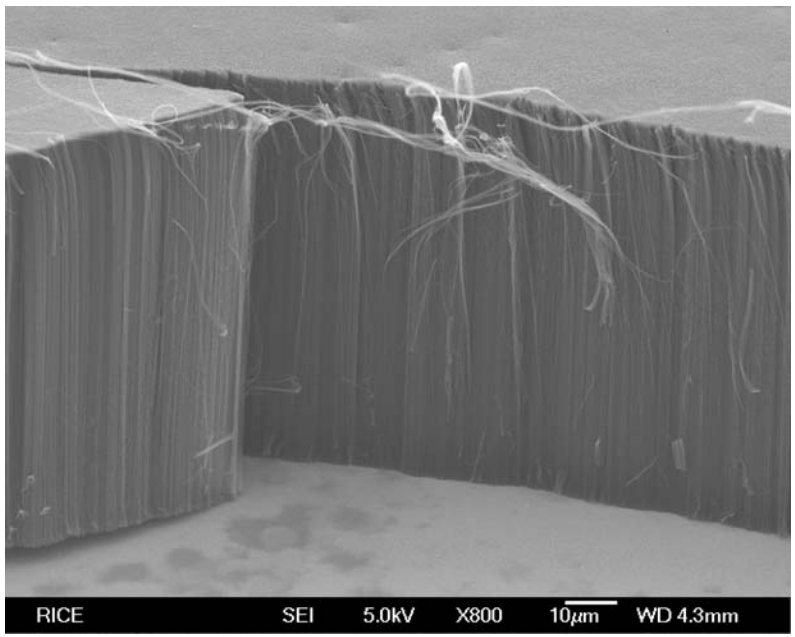
1 Rapid computation of capacity

- via Grand Canonical Monte Carlo simulations for the structures of interest
- based on judicious choice of potential (of paramount importance)

the depths of potential obtained from experiment (weaker) and *ab initio* calculations (stronger) differ by 2 meV, greatly affecting the capacity estimates

- perform GCMC with both potentials to determine the range where the storage capacity is.

For technical accomplishment 2



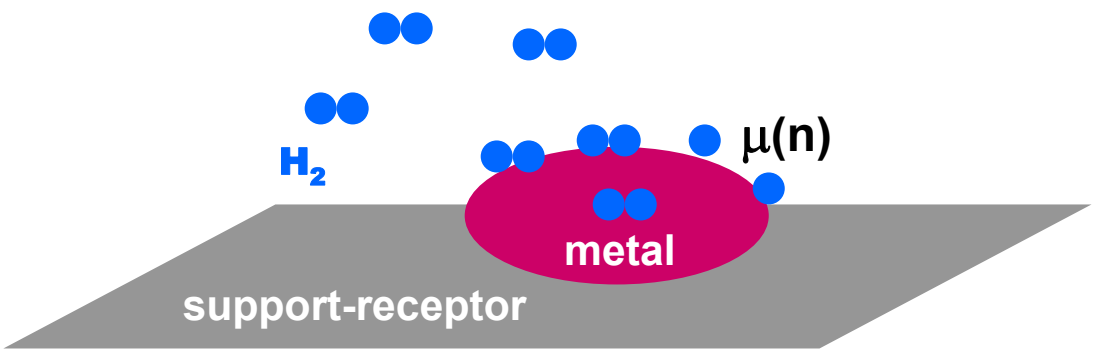
2 Experimental

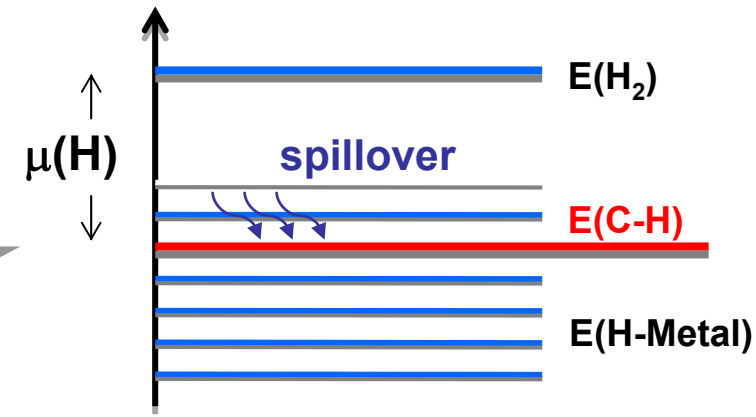
- VANTA arrays of 100 μm long carbon nanotubes, grown in large amounts with CVD methods. The alignment enhances gas transport into the array and thermal conduction.
- The aligned nature also lends itself to insertion of bulky anions, e.g. BF_3^-

APPROACH

Me-enhanced sorption on carbon receptors

3 Spillover thermodynamics, kinetic paths





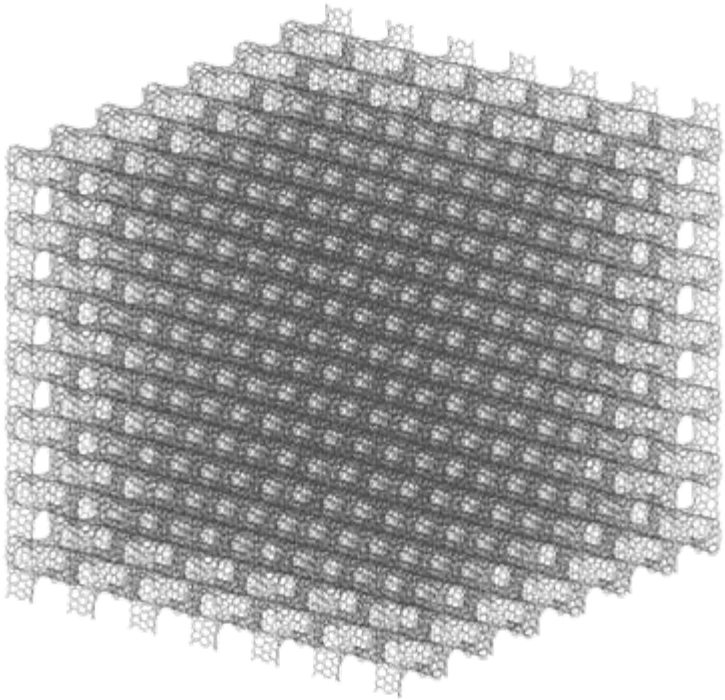
$\mu(H_2\text{-gas}) > \mu(H@metal) > \mu(H@support)$

Identify thermodynamically favorable and kinetically accessible paths
Reconcile strong H binding to Me with possibility of spillover, by comparing the chemical potential of H on metal to that on receptor
Role of bridges, defects and dopants on the overall process of spillover

4 Stability of Me-atom anchors against aggregation, analysis of binding energies and diffusion barriers through DFT calculations

Energy states and barriers calculated with DFT and using NEB method

Capacity of 3D-foams for H_2 storage



Ding et al JCP 127, 164703 (2007)

$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$$

ε = 3.7 eV/molecule

σ = 3.0 Å

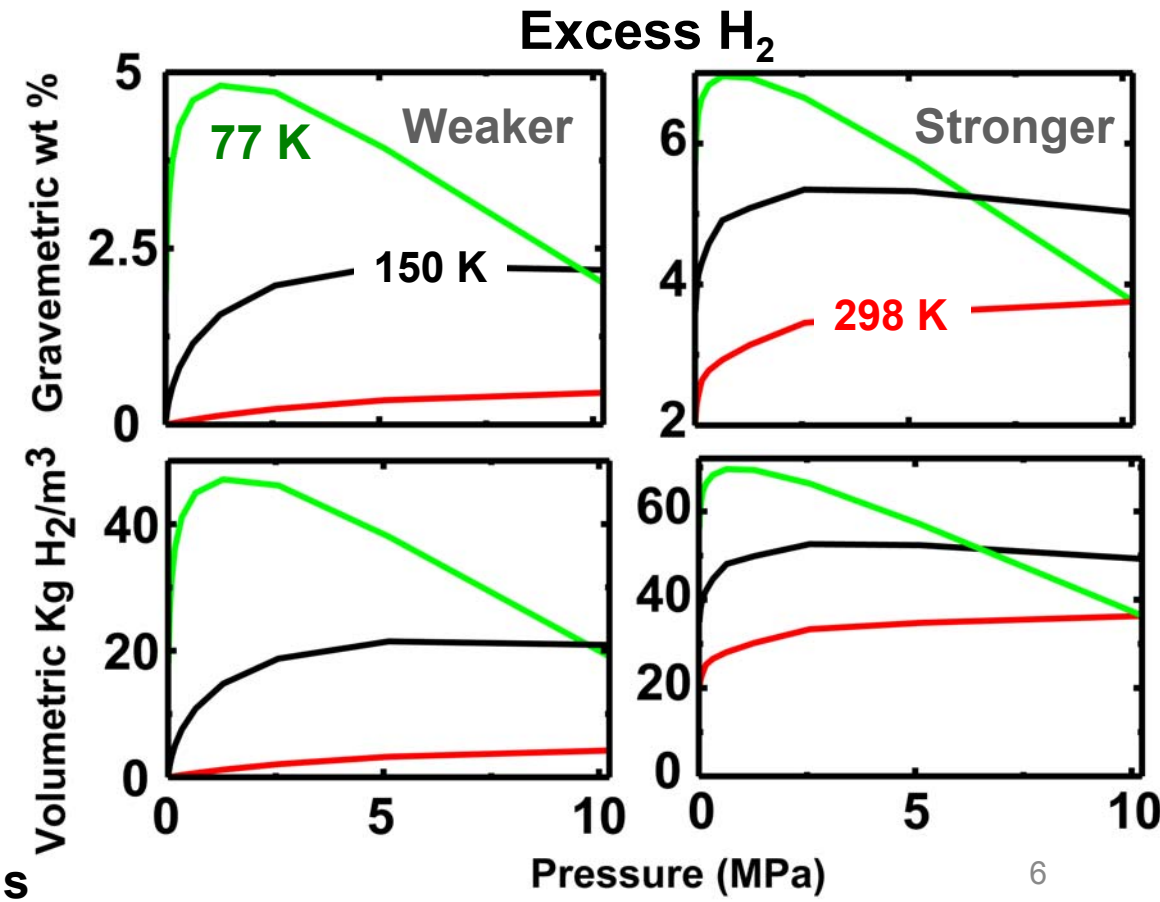
Wang et al J Low Temp Phys 41, 611

$$u(r) = Ae^{-\alpha r} + C_6 r^{-6}$$

A = 1100 eV/molecule

C_6 = −17 eV Å^6/molecule

Patchkovski et al PNAS 102 10439

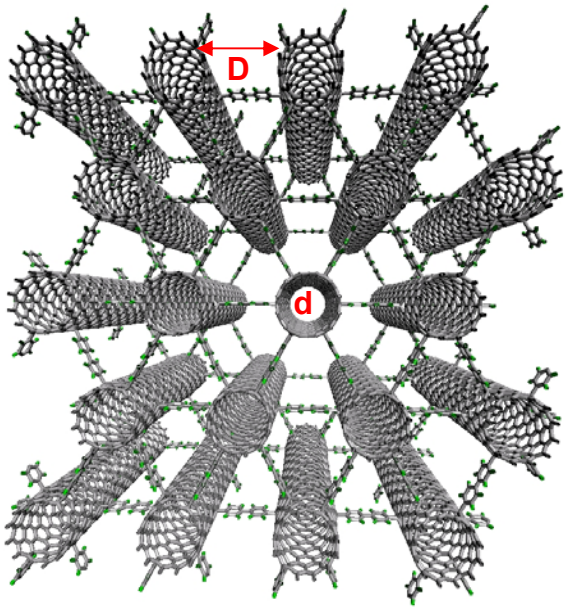


- Nanometer pores and channels
- Geometrical surface ~2600 m^2/g fully accessible

Capacity
- Sensitive to choice of potential
- At 77 K is comparable to MOF's

Foams could meet both volumetric and gravimetric goals

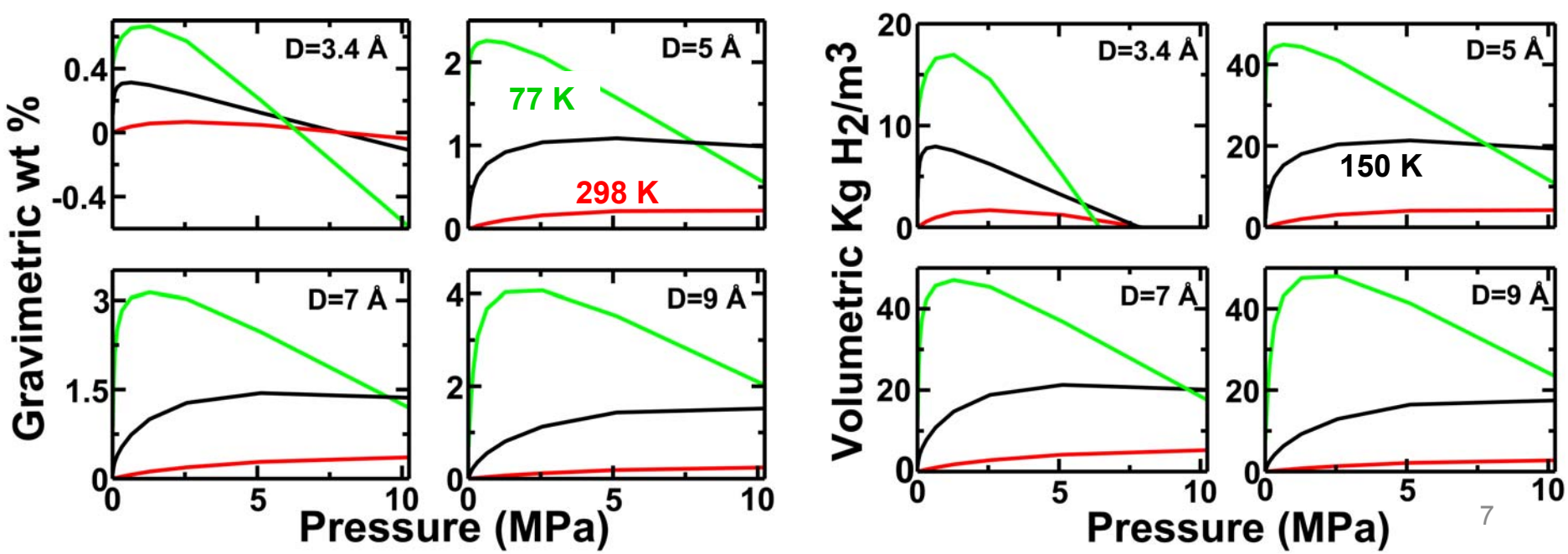
Comparison of foam with (10,0)-NT bundle



Storage capacity as function of wall-wall distance D
Volumetric % peaks at wall-wall distance of D ~ 7 Å
agrees with previous studies

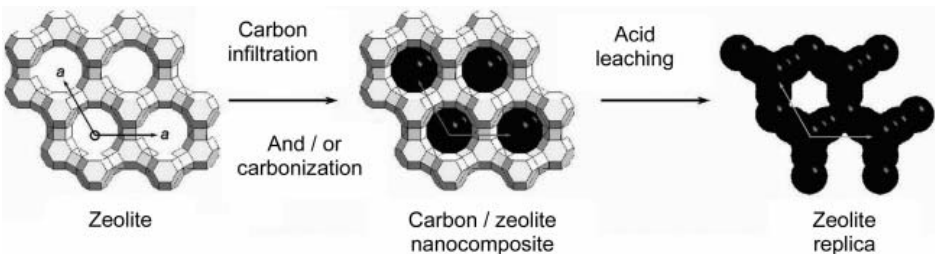
Storage capacity of foams is superior to best-separated, similar diameter nanotubes bundle (easier to synthesize)

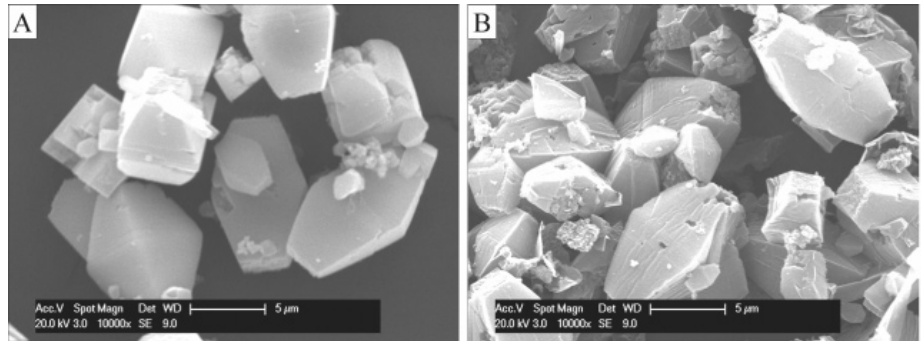
Excess H_2



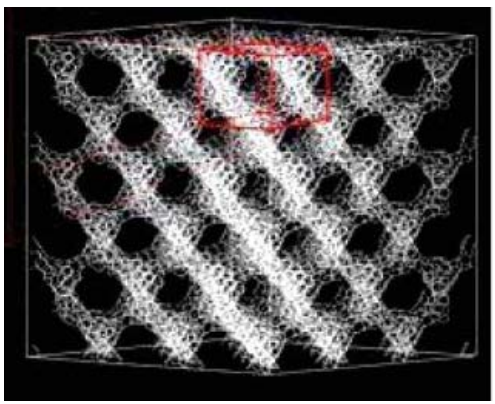
Experimental analogues produced

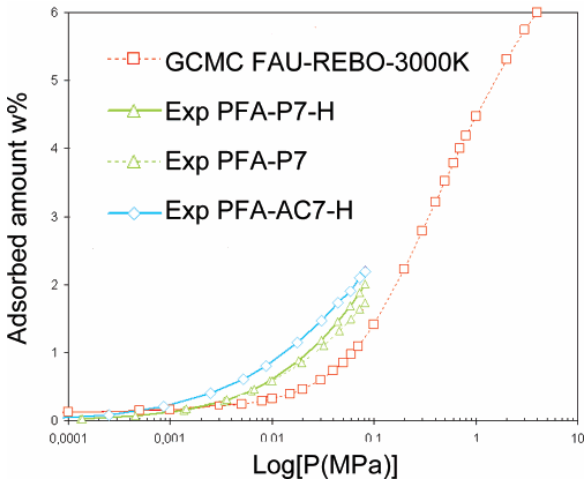
Zeolite-templated nanostructured carbon materials

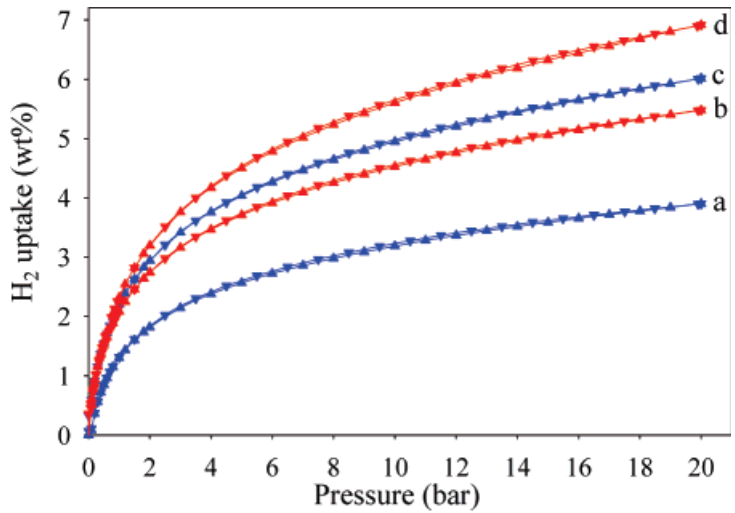




Z. Yang, Y. Xia, and R. Mokaya, J Am Chem Soc 129, 1673 2007; T. Roussel, et al J Phys Chem C 2007, 111, 15863



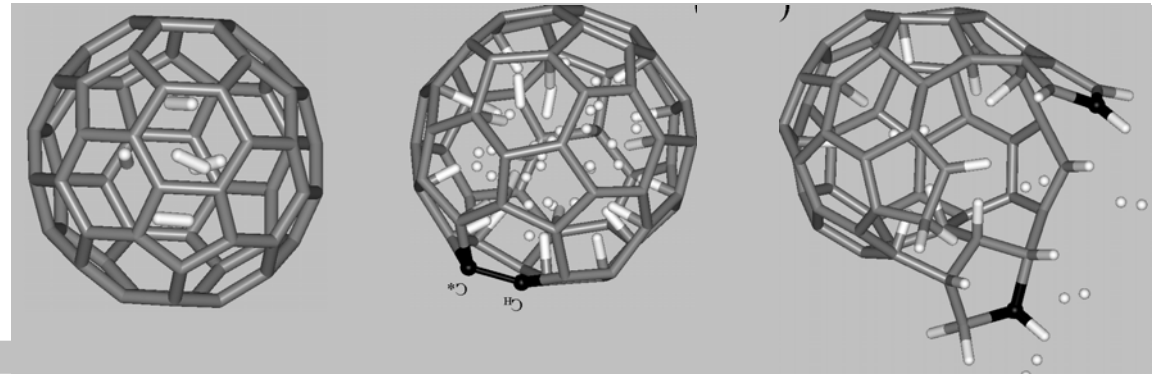


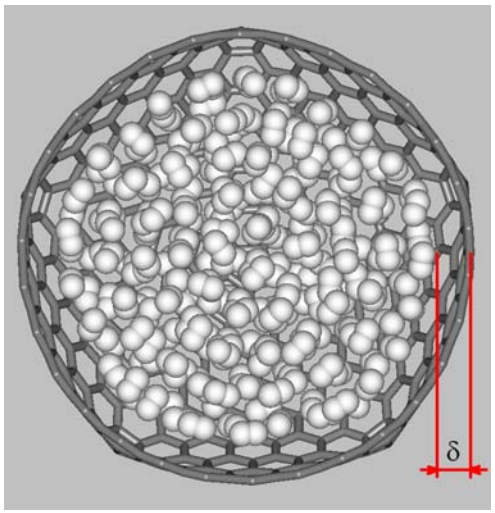


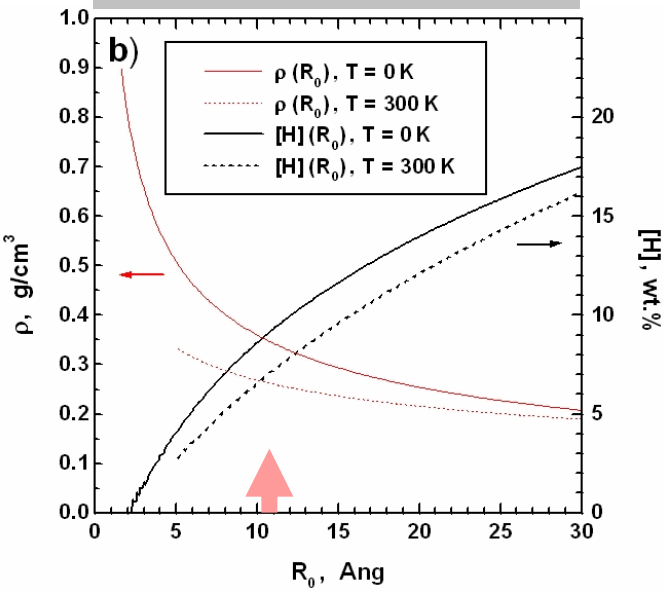
Hydrogen uptake at 77 K

Which is "ideal pore" ?
C_{60} interior *attracts* one H_2

What if we could utilize the *repulsion* for storage

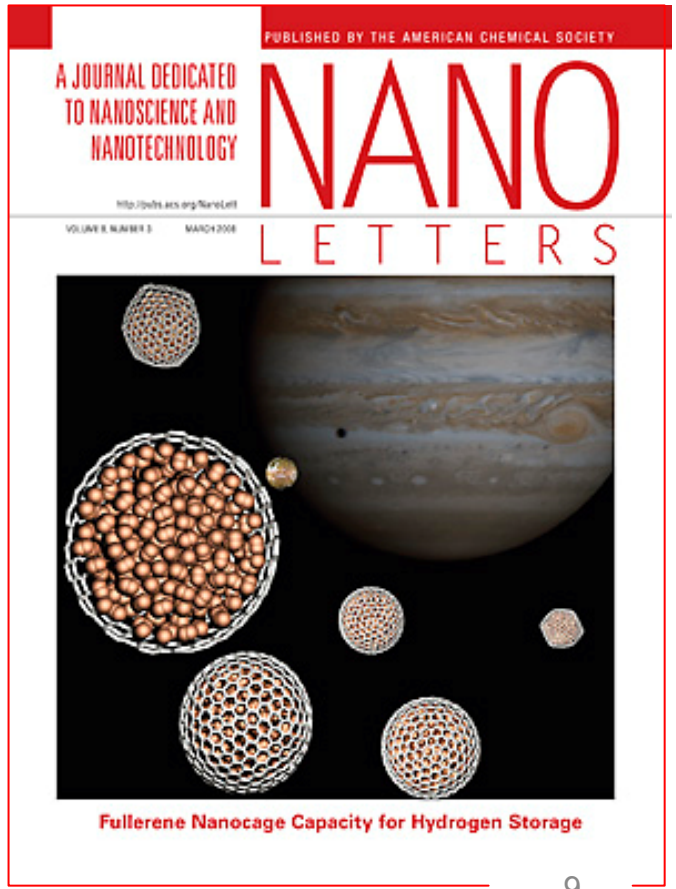




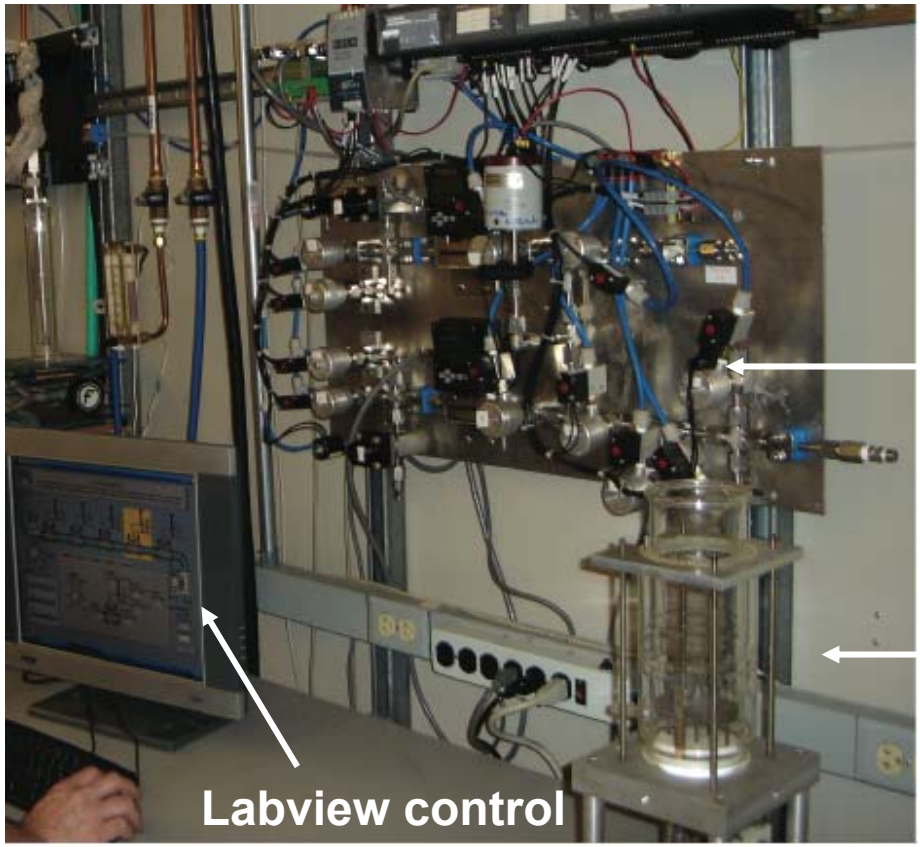


Existing giant fullerenes as ~C_{1000} sustain great internal pressure, permitting H storage.

How it can be placed there remains yet unexplored



System for synthesis of metal- and electro-negative-group- (F^-, BF_3^-) enhanced VANTA



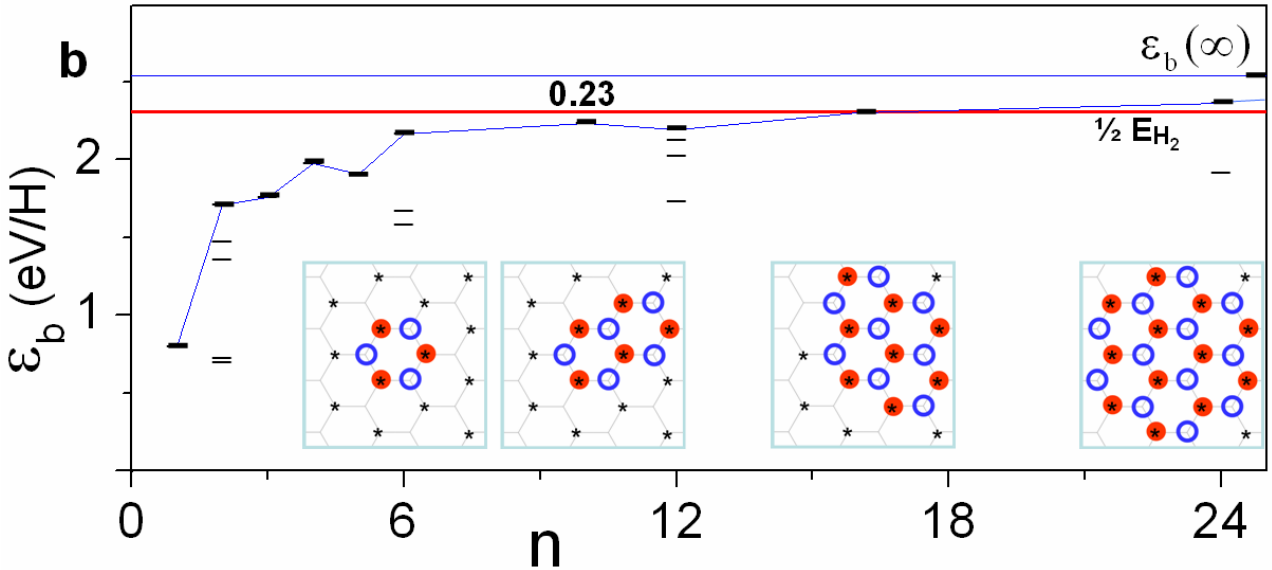
Reaction system for generation of fullerene superacid boron tetrafluoride salts, to enhance H2 polarization for storage

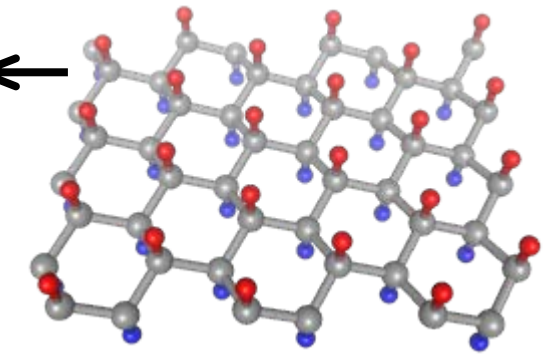
Parameters for best growth of VANTA scaffolds have been defined and VANTA are now available for addition of electronegative groups for enhanced H_2 adsorption.

A variable temperature reactor has been built and tested for controlled exposure of samples to fluorine and boron trifluoride.

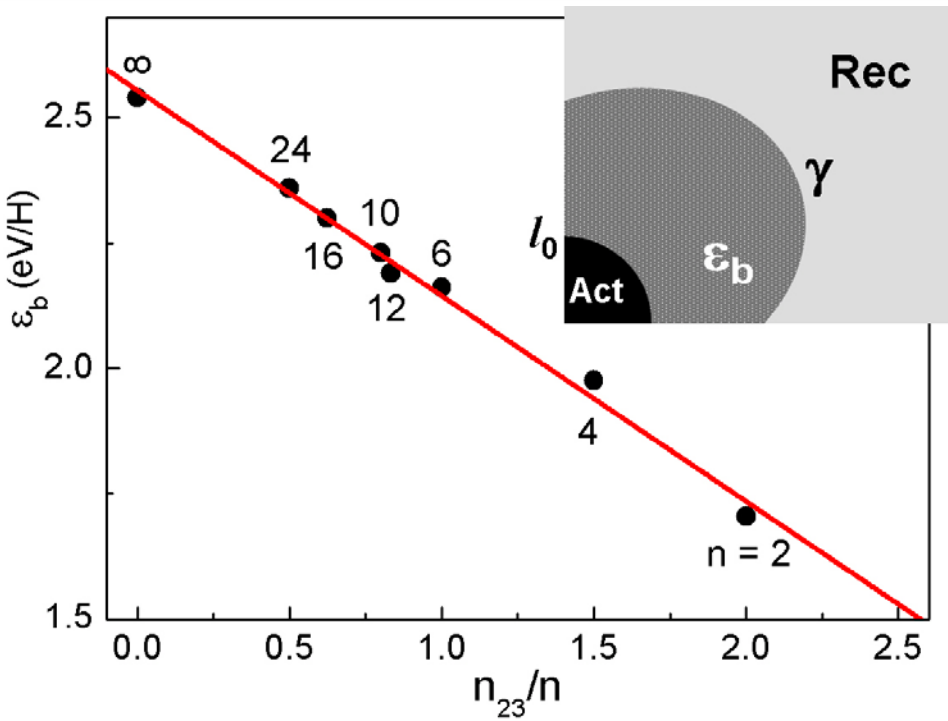
One gram samples have been converted to a carbon nanotube salt and will be tested for hydrogen uptake in collaboration with NREL and Air Products.

Spillover kinetics





H tends to form even-numbered, compact, counter-layered clusters with H_2 energy crossover near n = 20

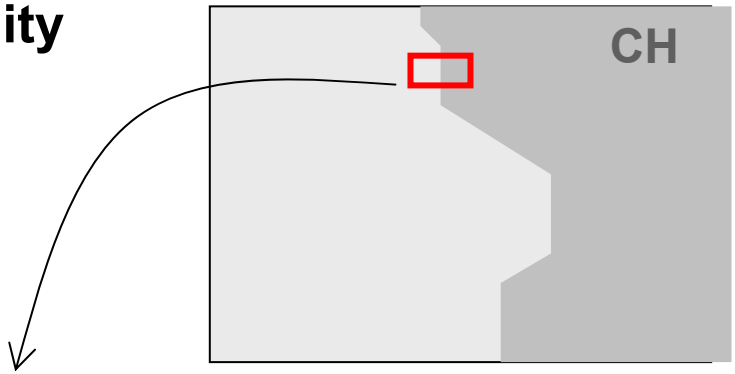


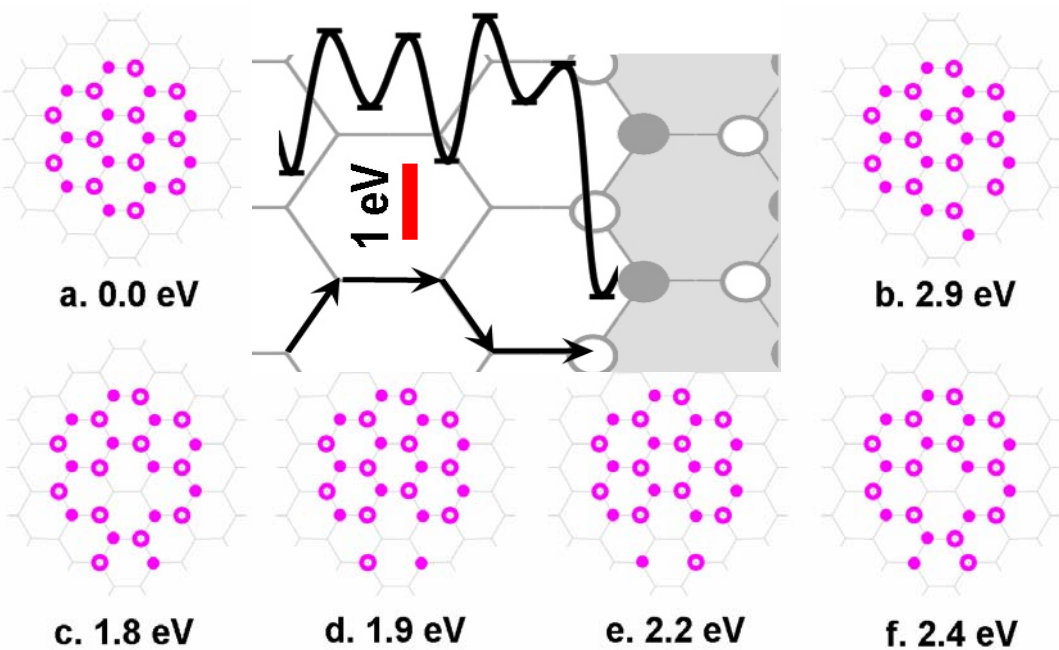
remarkably linear dependence

$\varepsilon_b(n) = \varepsilon_b(\infty) - \gamma \cdot (n_{23}/n)$

supports the notion of hydrogenated phase nucleation, with effective 0.23 eV binding, proper for H_2 adsorption/desorption

Vacancy formation and front stability



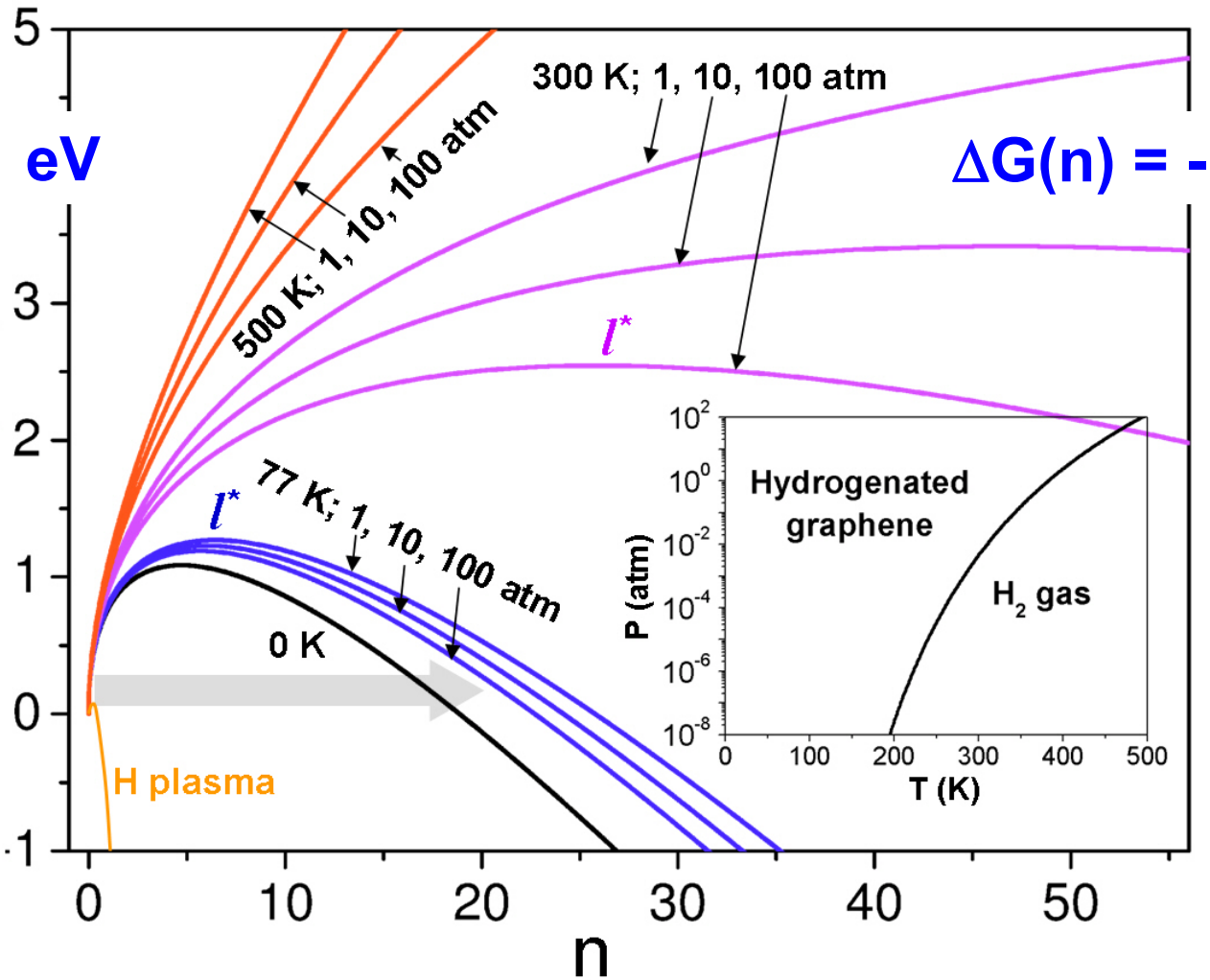


* calculations at T = 0

- Near-front kinetics and stability of the hydrogenated graphene island have been tested
- The new CH phase can absorb H around it
- Formation energy of vacancy (or DV) is high, rendering the front propagation via vacancy diffusion unlikely at storage temperatures

- Metal mobility role to be investigated

Overcoming nucleation barrier of spillover

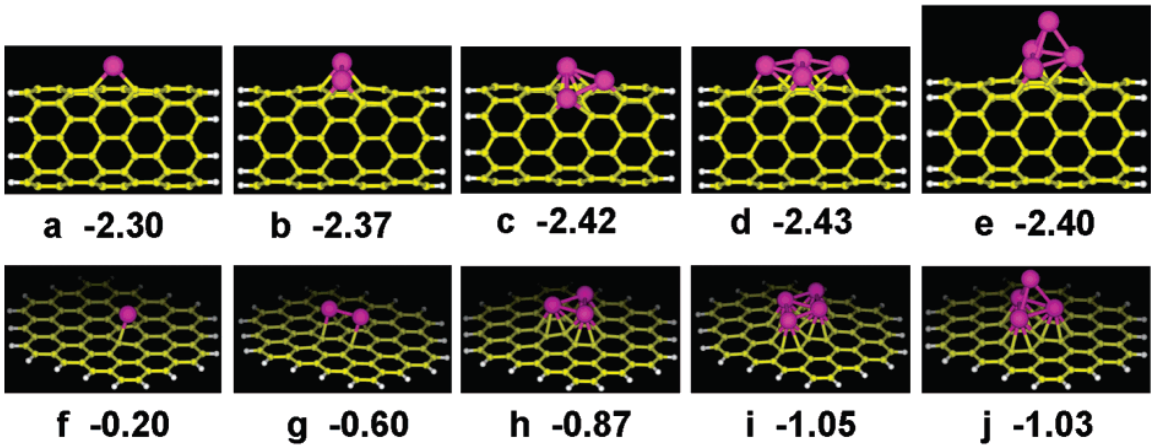


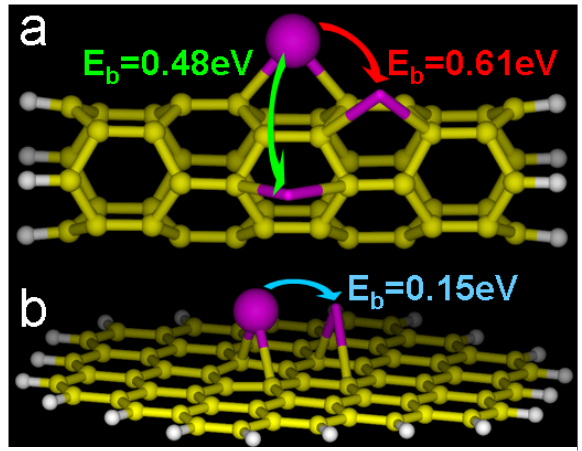
$$\Delta G(n) = -[\varepsilon_b(\infty) + \mu_H]\, n + \gamma\sqrt{n}$$

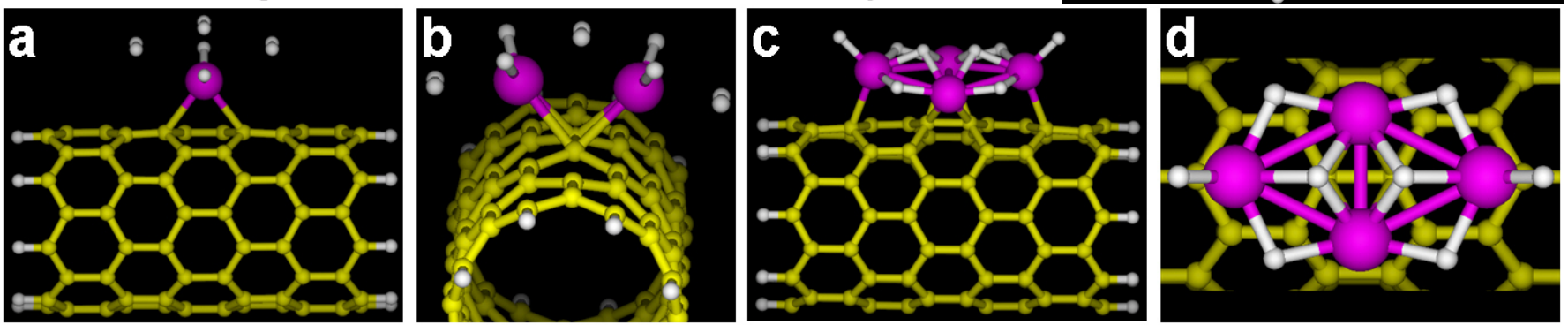
Phase diagram of the chemisorbed H, may occur at normal conditions, e.g. 380 K, 1 atm

Nucleation barrier decreases with lower T and higher P
Can be overcome by possibly "bridges" [R Yang] and the precursor H-patches [NREL work]

Metal clustering and effect on H_2 capacity







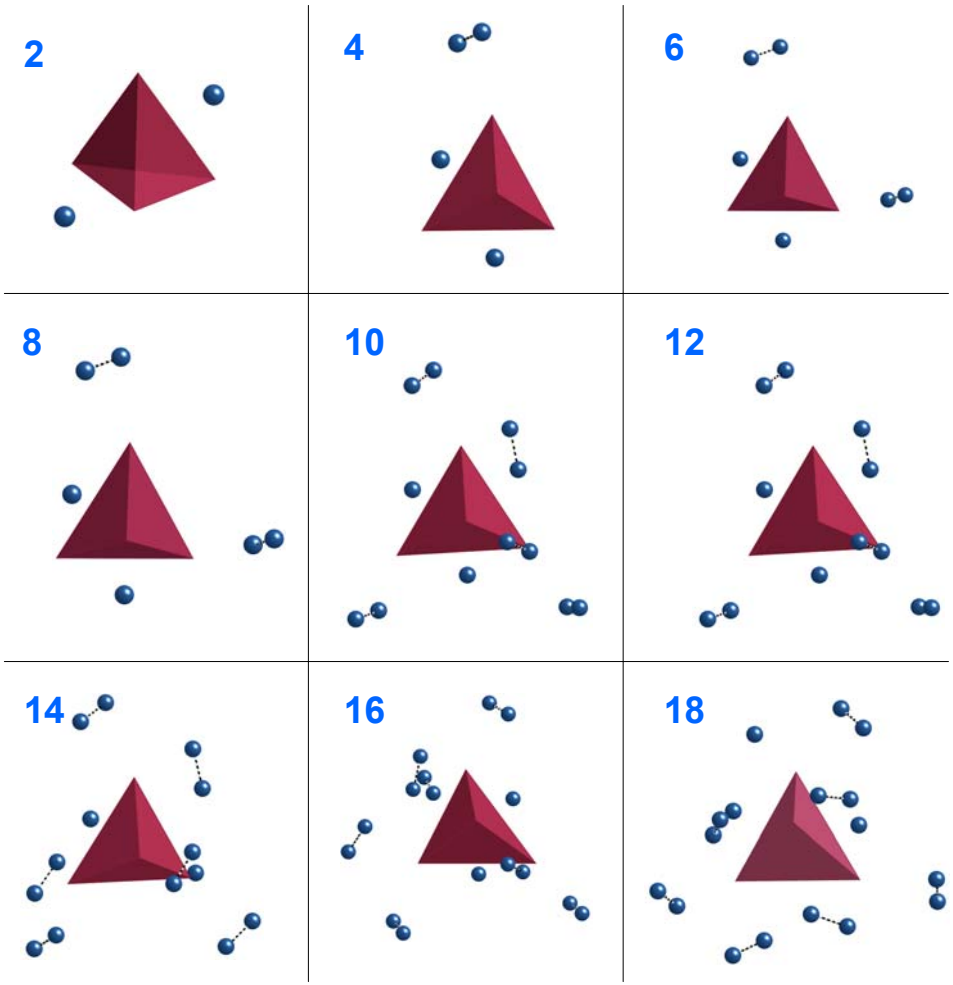
- Metal clustering is energetically and kinetically feasible at room temperature
- The diffusion frequency is ~10^{12} exp($-E_b/k_bT$)~10^5-10^{10} s^{-1} at room temperature

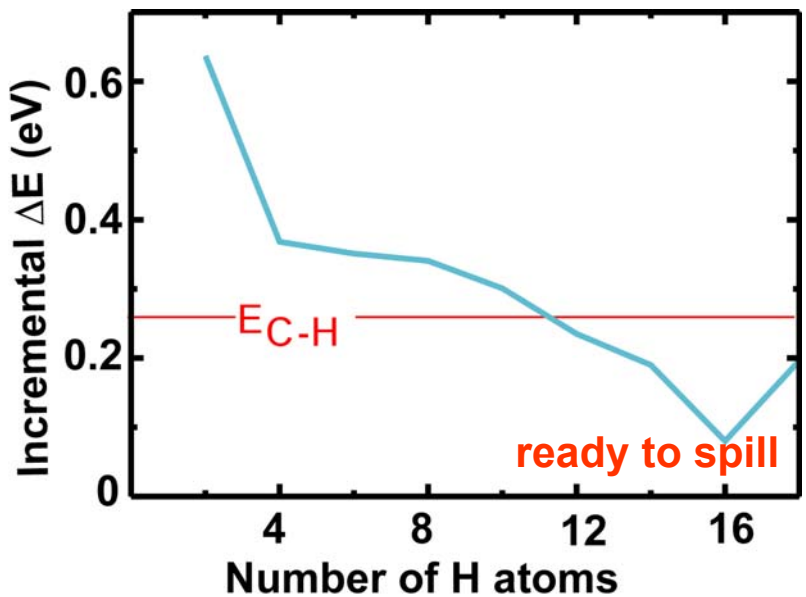
Krasnov, Ding, Singh, and Yakobson, JPCC, 2007, 111, 17977; method: B98/6-31G, Gaussian03

- Can be prevented by pinning on defects or via doping [NREL: Zhao et al PRL 94, 2005]
- Transition from Kubas sorption to H on large Me-clusters can lead to spillover

H on catalyst: spillover-saturation window

Determine the energy levels for H on free Pd_4 cluster and compare it with the onset of spillover onto C-receptor





- Several isomers were studied, only lowest energy ones are shown

- First H_2 gets adsorbed via dissociation, subsequent H_2 via Kubas type of interaction

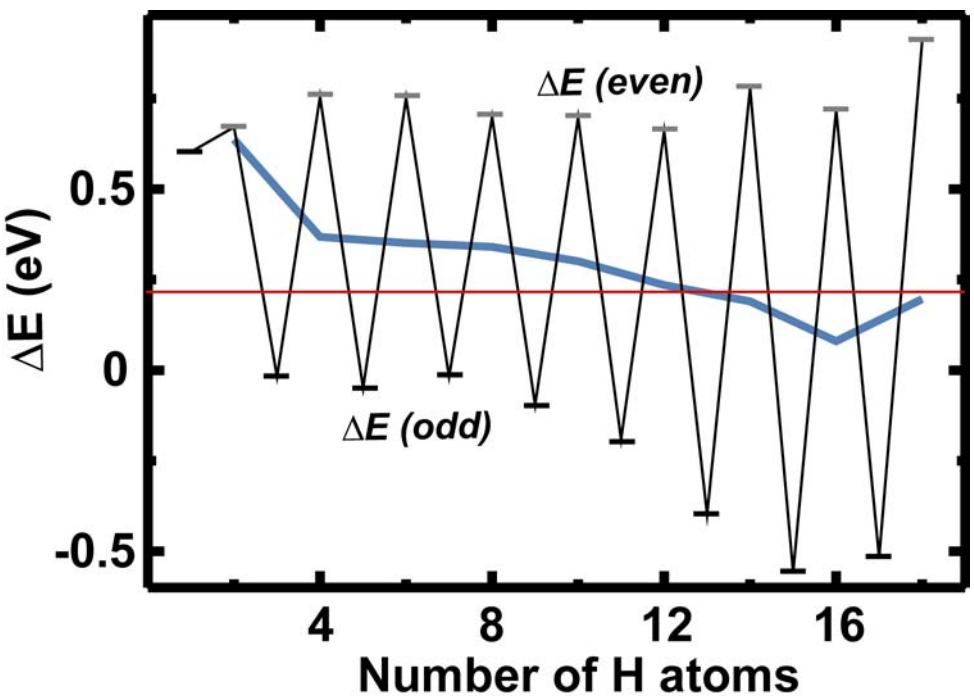
* calculations at 0 K, free cluster

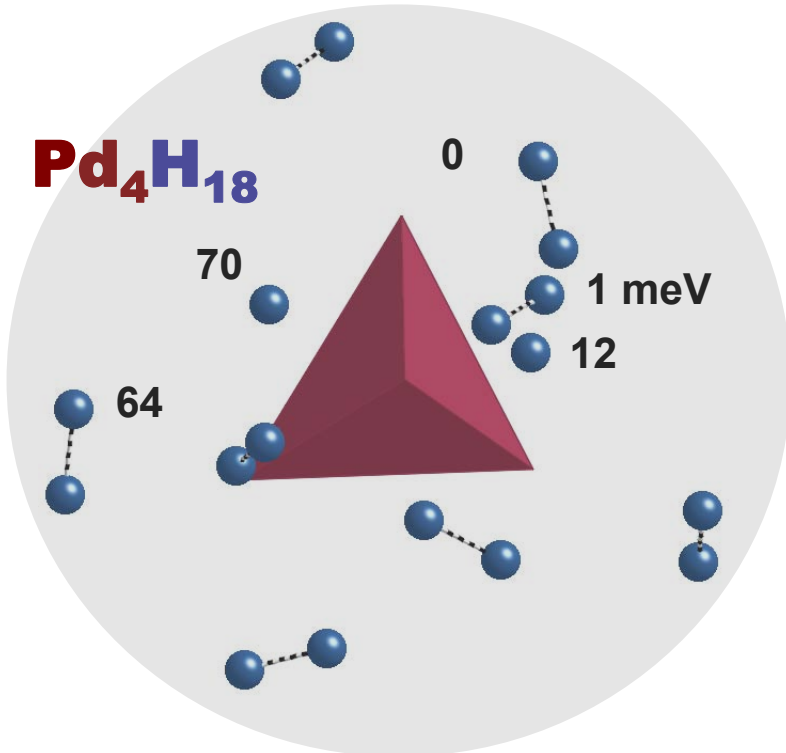
Cluster saturates with $9H_2$ (n = 18), spillover is favored after $6H_2$ (n = 12)

H desorption from catalyst

Here we answer the following questions:

What would be the energy cost to remove H atom from saturated cluster?
Does it depend on the type of H dissociative/Kubas?

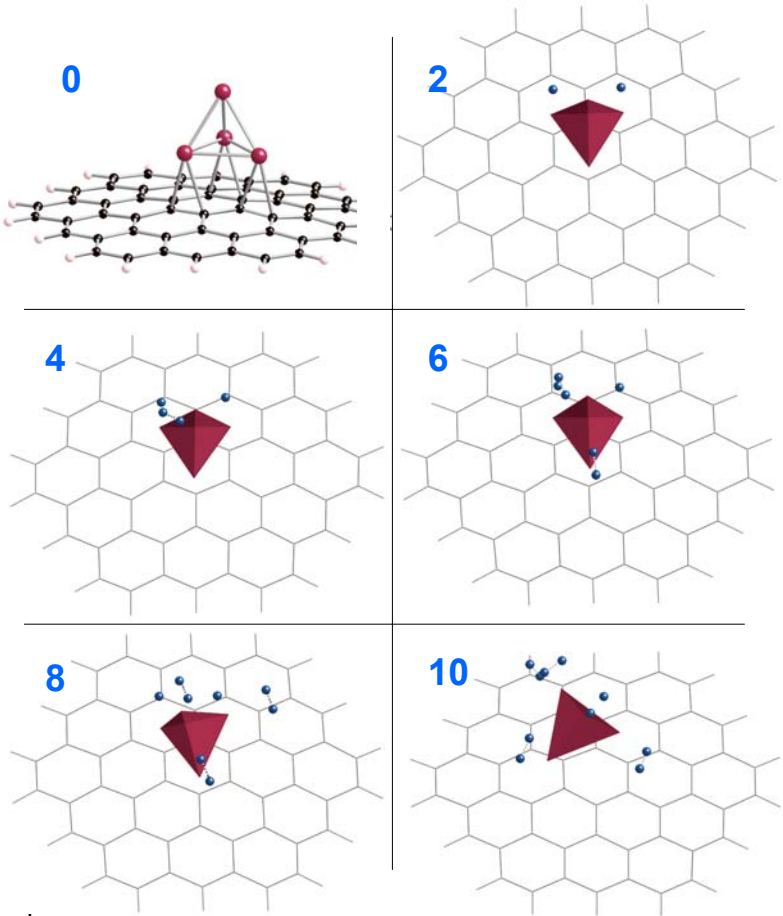


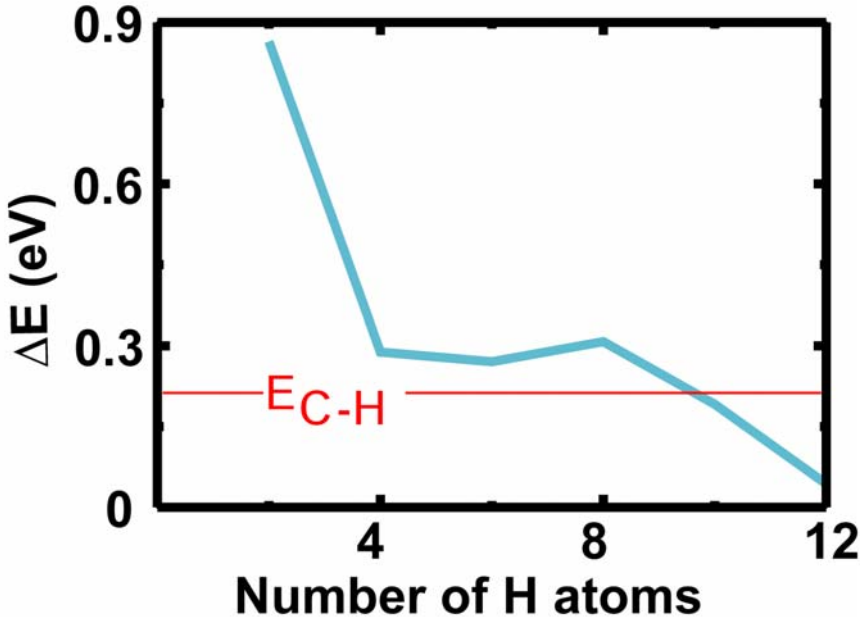


- **Cost to remove dissociated (H) and non-dissociated (Kubas H-H) H is almost same**
- **Removing odd number of H costs more energy, we believe that the difference will go down for the larger size clusters, this could be a bottle neck for the sustainable spillover through smaller clusters**

H on catalyst on receptor/support: spillover-saturation window

Effect of support on the H energy on metal





Spillover Threshold:

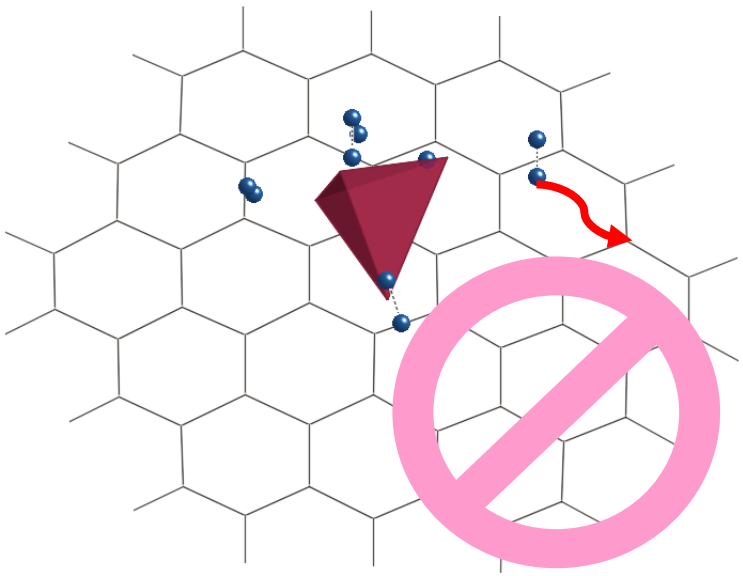
- On graphene metal saturates sooner than in the free cluster
- Onset of spillover is very close to metal full saturation

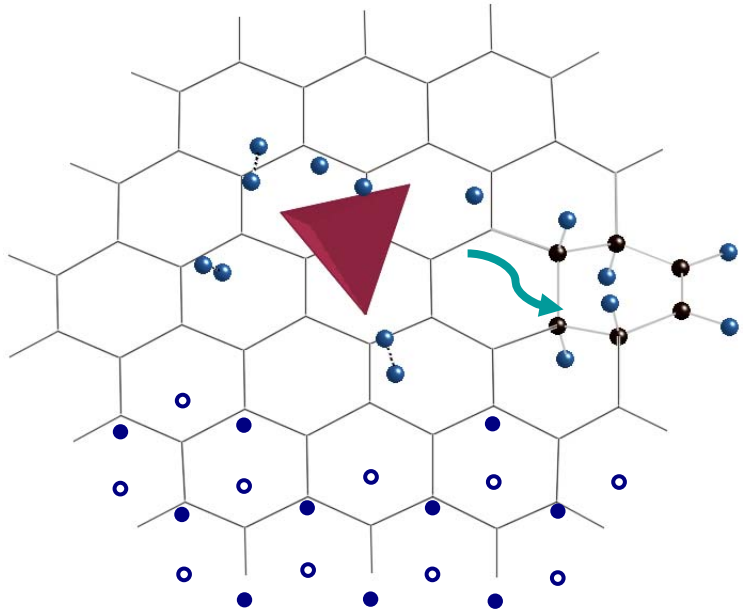
* calculations at 0 K, free cluster

- First H_2 again gets adsorbed via dissociation, subsequent via Kubas
- The cluster saturates with $5H_2$

Kinetics: activation barriers for spillover

Can metal hop from saturated cluster onto pristine graphene?





- Final state is not stable. H atom returns to metal spontaneously (implies possibility of reverse spillover)

- H further away from metal is stable, but high in energy (2.54 eV). Spillover on a pristine graphitic surfaces would be difficult. Curvature, defects, or modifications can facilitate

- Dramatic decrease in energy, H on the phase 0.15 eV more stable—first sign of possibility of spillover

- The combination of saturated metal cluster with the hydrogenated phase formation would enhance the spillover process

future work FY08-FY09

spillover dynamics

- 1 Further energy and thermodynamics calculations: effects of size of metal cluster, dopants, bridges, on the H migration barriers from activator to receptor (along with ν-signatures for experimental detection). Extend to other receptor geometry/materials (MOF, Met-Car).
- Quantitative analysis of the front propagation model in contrast to conventional $\langle r^2 \rangle \sim D \times t$ diffusion. Compute the mobility barriers for the metal cluster to study the "scooter" effect, in which the chemically adsorbed H does not move, rather the metal moves.

3D-foams

- 2 Generate several foams and optimize the storage capacity, using GCMC code for evaluating experimentally accessible surface areas. Ability to generate isotherms "on the fly" for any C-based structure. Consider doping the 3D-foams for better capacity.

VANTA synthesis

- 3 Optimization of VANTA for area and H_2 storage. Conversion of π-delocalized carbon systems (e.g. giant fullerenes, graphene sheets) and nitrogen doped carbon systems, to superacid salts. Test for hydrogen storage.

Me-centers stability

- 4 Generate tailor made yet experimentally feasible C-based materials to achieve stronger metal binding, on defects or dopant-sites of the carbon lattice.

summary

Relevance: Path-finding to reach DOE goals by modeling of major options: *spillover,* sorption on *3D-foams*, *metal-enhancement*, *doping*

Approach: Quantum *ab initio* and empirical representations of H-carriers interaction, to assess their retaining ability. Selectively test synthesis options.

Technical Accomplishments and Progress:

- Storage capacity of 3D-foam assessed, found to be comparable with the best MOFs.
- Catalytic activity of metal clusters, relevant to spillover was determined and onset of spillover both in air and at receptor was computed
- Hydrogenated phase and saturated clusters are identified as the key element for spillover.
- Reactor constructed for conversion of carbon systems to superacid salts, VANTA's have been converted to superacid salts
- Addressed aggregation of metal atom at elevated temperatures, detrimental for storage

Tech Transfer/Collaborations: Partnership with NREL, Air Products, NIST (spectroscopy). Partnership with U Michigan and U Nevada Las Vegas (external).

Future Research: ● Emphasis on theory spillover dynamics, including other material-receptors (in collaboration with Yang's project) ● Optimized 3D-foam generation for storage and large surface and screening of Me-centers via doping and defect for stability against aggregation. ● Nitrogen doped carbon materials, large fullerenes and graphene sheets as high area superacid materials for hydrogen storage.

Boris I Yakobson
713-348-3572
biy@rice.edu