

Optimization of Nano-Carbon Materials for Hydrogen Sorption

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

Overview

Timeline

- Start: 01 February 2005
- End: 30 June 2010
- 95% complete

Budget

- Total project funding
 - DOE: \$1,065,209
 - Contractor: \$269,181
- Funding for FY09 \$235,000
- Funding for FY10 \$80,000

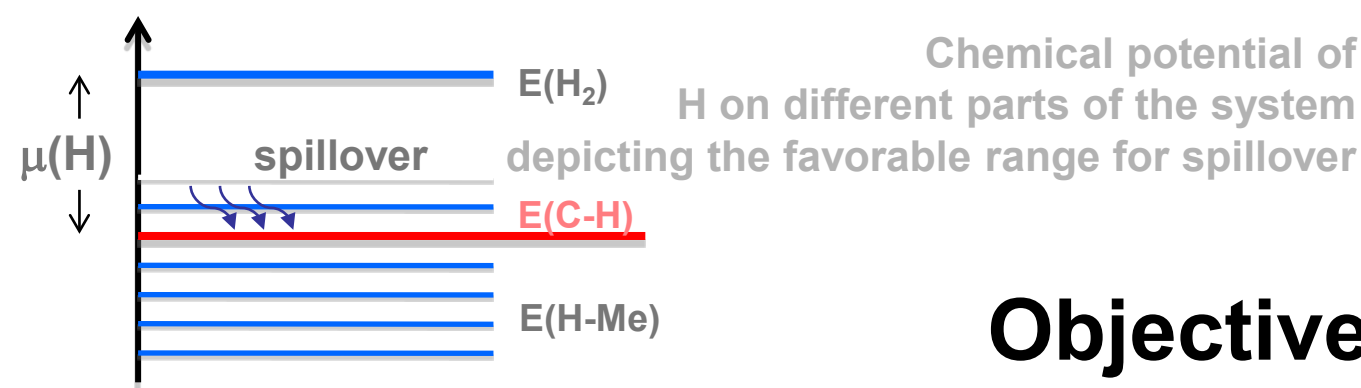
Barriers

Barriers to be addressed

- A** -- System weight and volume
- E** -- Charging/discharging rates
- P** -- Lack of understanding of hydrogen physisorption

Partners

NREL, Air Products Corp, NIST, U Michigan, Caltech, regular teleconferences, face-to-face meetings (Houston, Golden, CO, Washington, Gaithersburg, ORNL TT, MRS meetings).



Objectives-Relevance

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

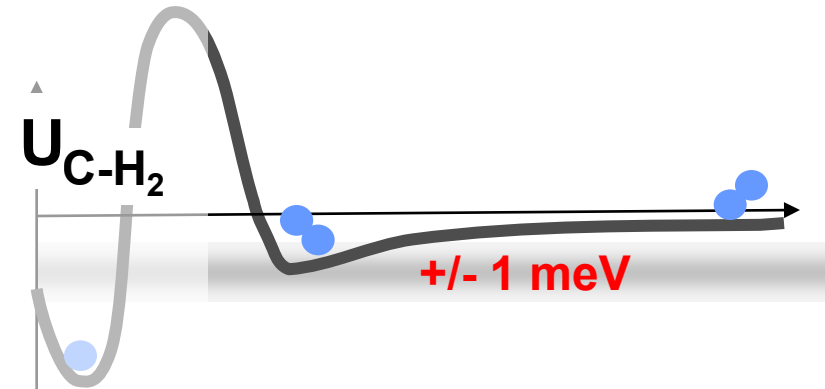
2009:

- Identify the obstacles (thermodynamics and kinetic) for the spillover and suggest/design the materials to overcome them
- Explore doping as an anchor to metal cluster, effect of dopants on spillover threshold
- Assess the effect of impurities and environment on the spillover
- Complete experiments with electronegative-group (F , BF_3) enhancement
- Sorption on foams, and novel B-structures including metallacarborane-MOFs

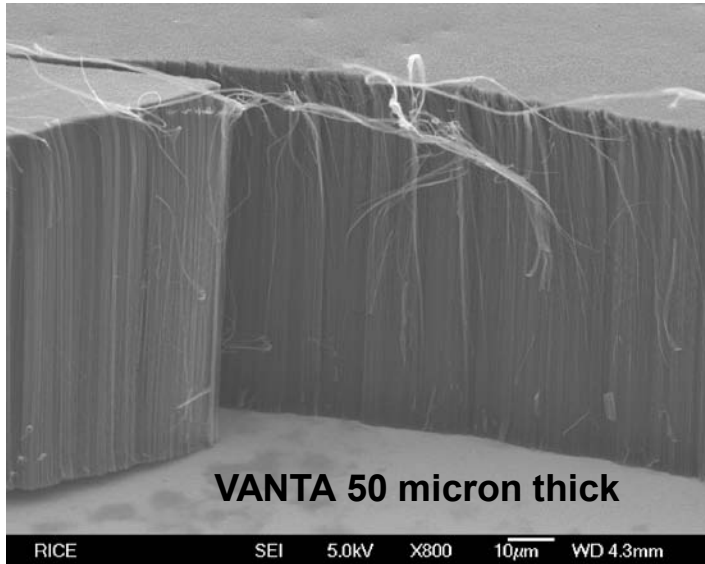
2010:

- continue the above and
- Complete conditioning of graphitic substrates, by adding O, B, organic molecules
- Study possibility of H atom diffusion on graphitic receptors
- Complete experiments with electronegative-group (F , BF_3) enhancement

APPROACH



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



1 Rapid computation of storage capacity

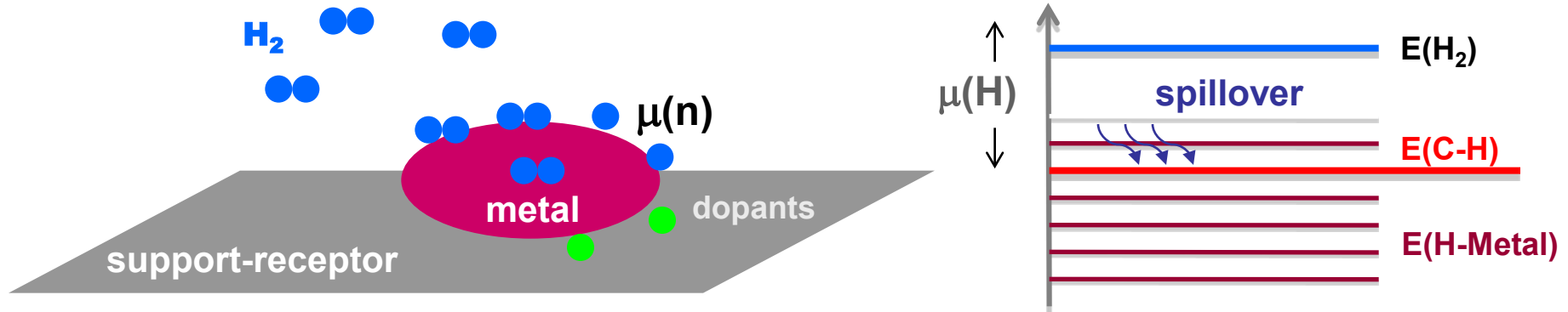
- via Grand Canonical Monte Carlo simulations for structures of interest (100%)
- judicious choice of potential of paramount importance, perform GCMC with **both** potentials to determine the range for the storage capacity (100%)
- consider quantum corrections via Feynman-Hibbs effective field (100%)
- add the similar-foam family analysis (80 %)

2 Experimental

- **VANTA** of nitrogen doped C-nanotubes, can be grown in large amounts with CVD methods. The alignment enhances gas transport into the array
- The aligned nature also lends itself to insertion of bulky anions, e.g. **BF₃⁻** as does nitrogen doping. Test same for **AC** (from Channing Ahn, Caltech)

3 Catalytic spillover “nano-thermodynamics”

- Analysis of H-binding energies in the presence of dopants. Compute diffusion barriers for an H atom through DFT calculations. (Role of bridges, defects and dopants and impurities on the overall process of spillover.)



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

- Identify thermodynamically favorable and kinetically accessible paths. Reconcile strong H binding to Me with possibility of spillover: compare chemical potential of H on metal to that on receptor (90% done, various metals added)
- These steps help in determining the key elements for spillover that can later help designing more efficient systems—support, catalyst, bridges (100%)

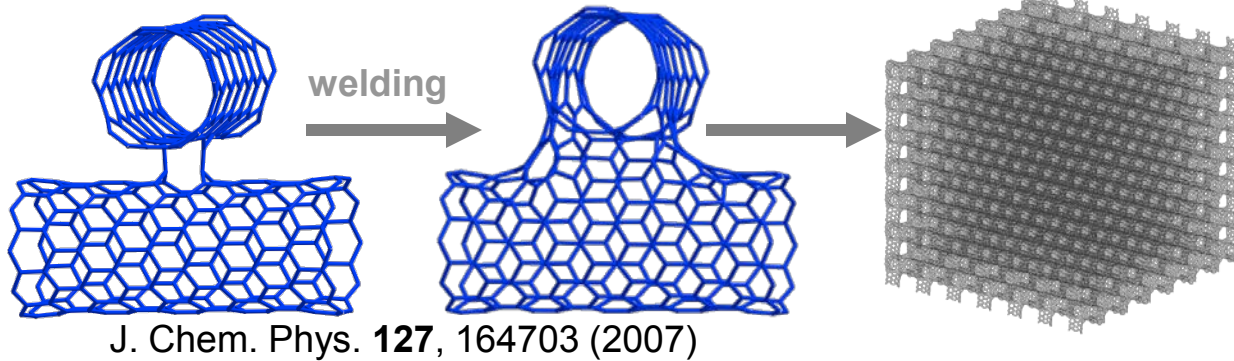
4 Metallocarboranes

- Calculate hydrogen sorption *energies*, identify metal atoms best to adsorb maximum *number* of H₂ (98%)
- Generate metallocarborane-based MOFs, using semi-empirical methods, and estimate storage capacity at ambient conditions (60%)

technical accomplishments 1

Highlights of the project

Acquire ability to generate 3d foams by experimentally realizable welding process



Foams can be produced in systematic manner, to model the adsorption in C-based materials with known surface area but little knowledge of structure

Grand Canonical Monte Carlo code further developed, to take various form of interaction potentials

Weak

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

$$\sigma = 3.0 \text{ \AA}$$

$$\varepsilon = 3.7 \text{ meV/molecule}$$

Wang et al J L. T. Phys 41, 611

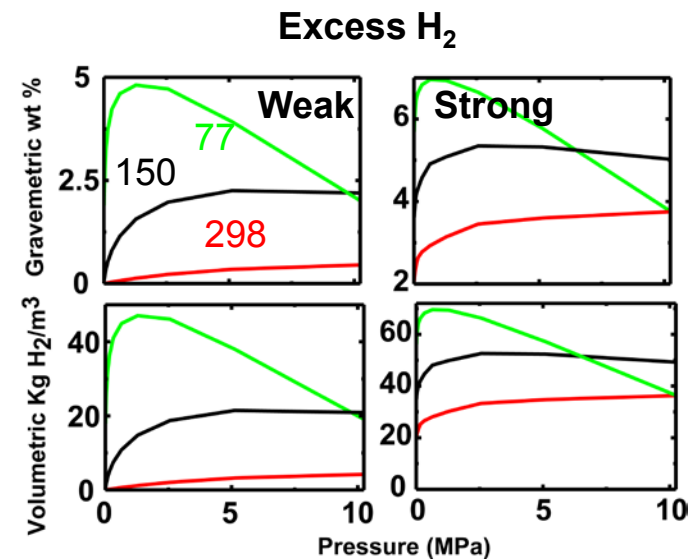
Strong

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

$$A = 1100 \text{ eV/molecule}$$

$$C_6 = -17 \text{ eV \AA}^6/\text{molecule}$$

Patchkovski et al PNAS 102 10439



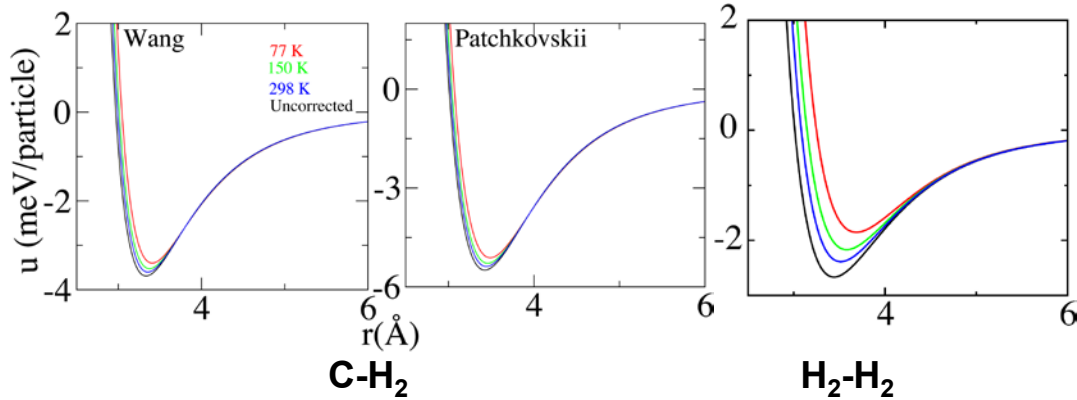
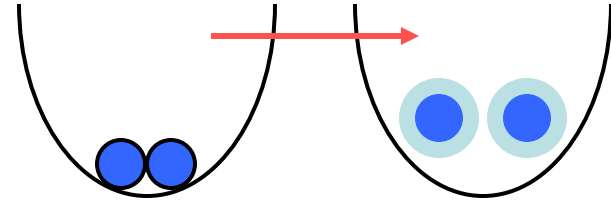
The effect of interaction on the storage capacity evaluated, which is largely responsible for the spread of the sorption data in the literature

Quantum corrections via Feynman-Hibbs formulation

Highlights of the project

Quantum-fluid molecule as Gaussian wave-packet, effective interaction potential

$$U_{FH}(r) = U(r) + \frac{\beta \hbar^2}{24\mu} \left[U''(r) + \frac{2U'(r)}{r} \right]$$



Classical overestimates by (%)

T	C-H ₂ and H ₂ -H ₂ with QC wt total	H ₂ -H ₂ with QC wt excess
298 K	5.6-5.8 (10 MPa)	7.8-12
150 K	12-13 (~5 MPa)	14-16
77 K	18-23 (~1 MPa)	21-24

Essentially, quantum corrections add a repulsion

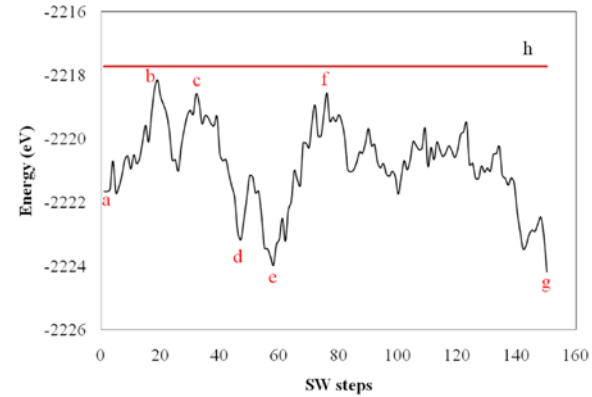
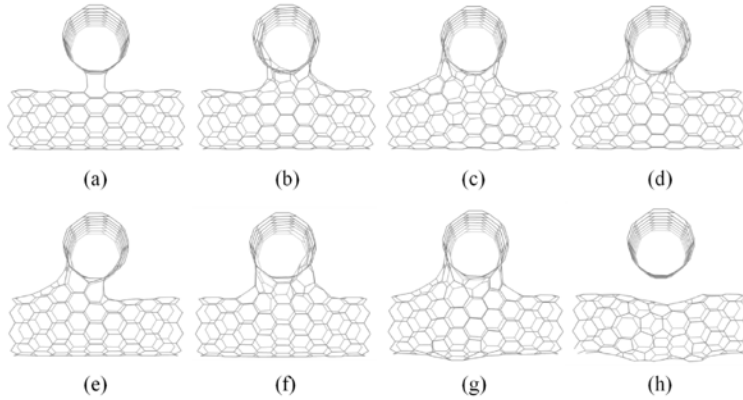
The incorporation of QC is important even at room temperature

Code developed to evaluate effective surface area for a particular probe gas, permits comparison to BET data

Overall a formidable tool to study sorption in nanoporous carbon materials

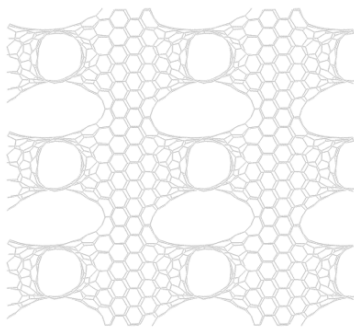
Foams as model structures

Serve to model nanoporous materials whose structures are poorly determined



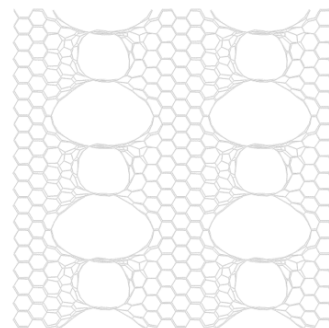
Total energy decreases upon welding supporting thermodynamic feasibility of such structures

Foams with **same geometry ratio** generated



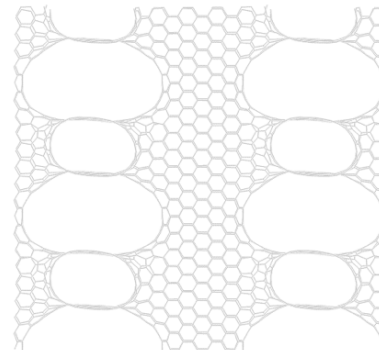
5,5-9,0

$\rho = 1.027 \text{ g/cm}^3$



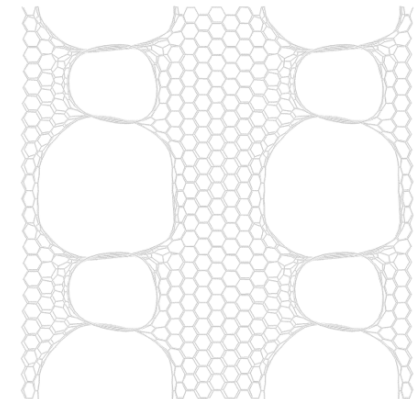
6,6-10,0

$\rho = 1.005 \text{ g/cm}^3$



8,8-14,0

$\rho = 0.81 \text{ g/cm}^3$



10,10-17,0

$\rho = 0.57 \text{ g/cm}^3$

Uniform geometry structure, where both tubes and pores scale up similar

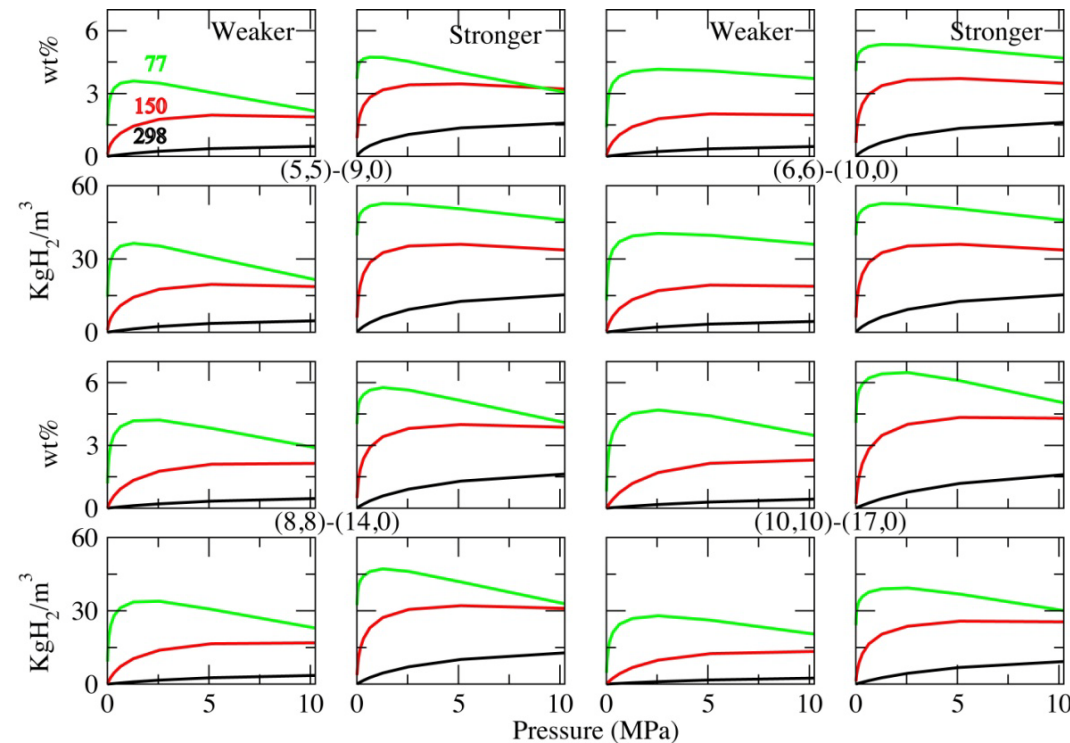
Storage capacities of foams:

Designed scalable C-foams with optimized porosity for enhanced dihydrogen binding, storage capacity could meet DOE 2010 targets

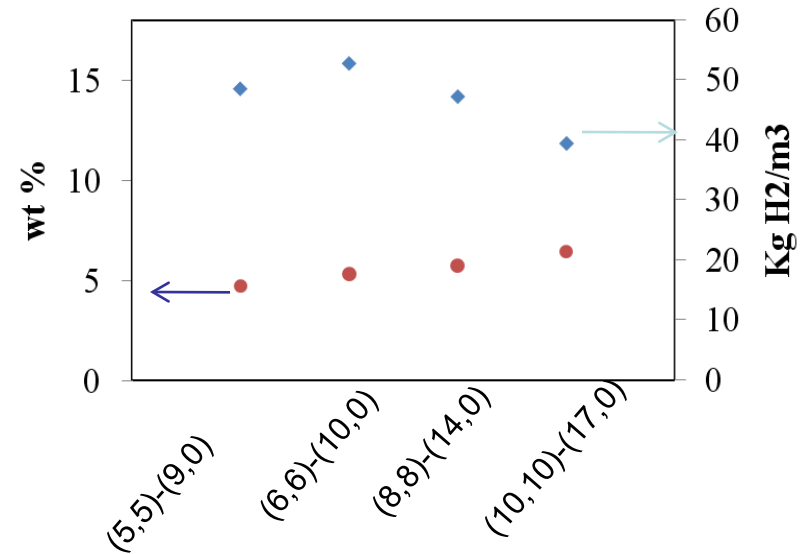
technical accomplishments 1

Progress 2009-2010

Excess Capacity



Maxima of storage in foams

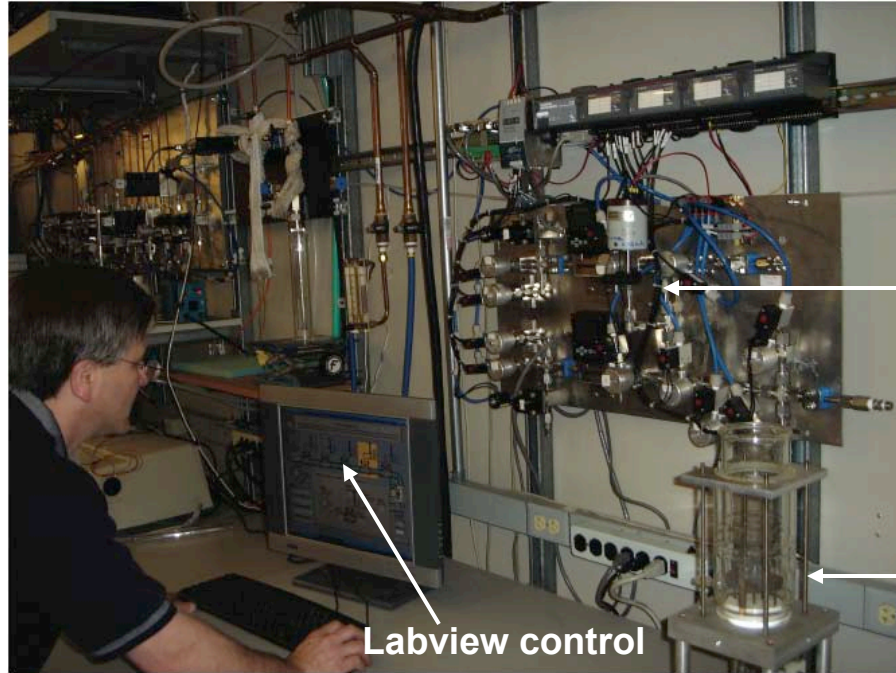


Although, storage capacities are dependent upon the choice of the interaction potential yet the trend in change of storage capacity with the change in pore size is almost independent of the choice of potential.

Excess gravimetric capacity increases with increasing potential, however the volumetric capacity peaks for (6,6)-(10,0) foam

The pore size in the (6,6)-(10,0) is optimal for hydrogen storage

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 H_2 polarization for storage

technical accomplishments 2

Highlights of the project

Parameters for best growth of VANTA scaffolds have been defined

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

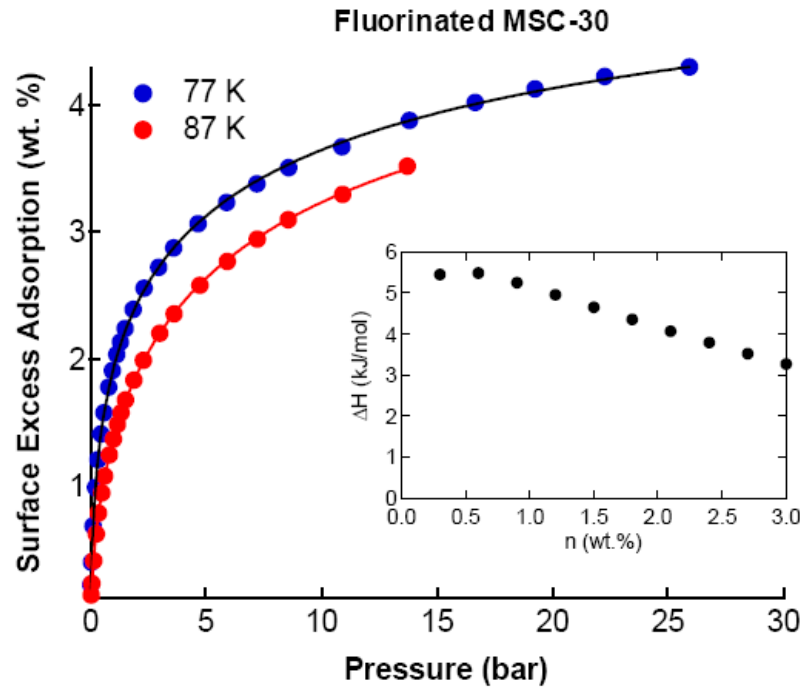
VANTAs are available for addition of electronegative groups for enhanced H_2 adsorption.

Samples up to gram quantities can be easily converted to a carbon nanotube salt and can be tested for hydrogen uptake at NREL and Air products.

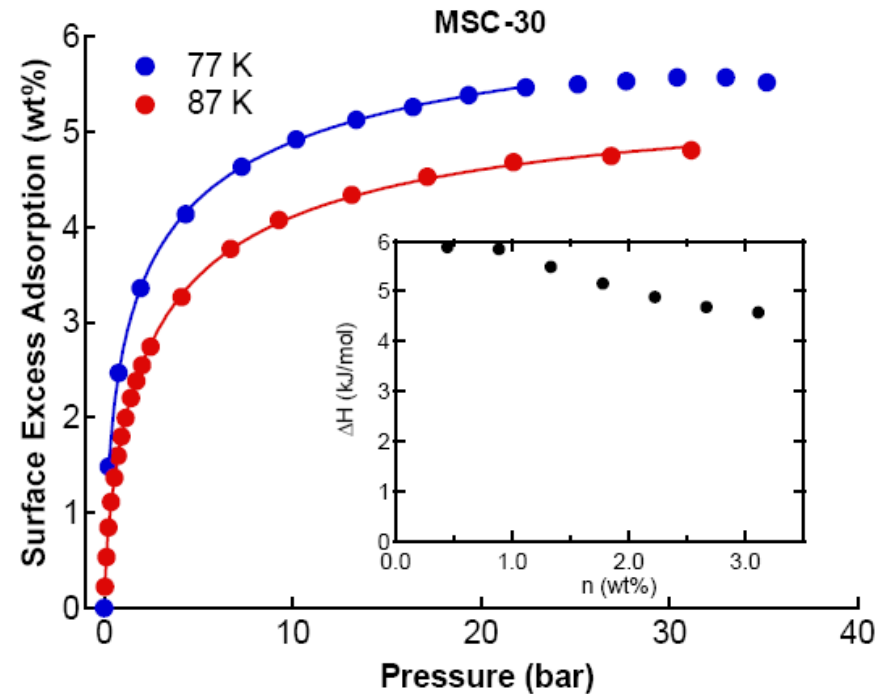
Experiments on storage in electro-negative-group- (F , BF_3) enhanced VANTA and AC

technical accomplishments 2

Progress 2009-2010



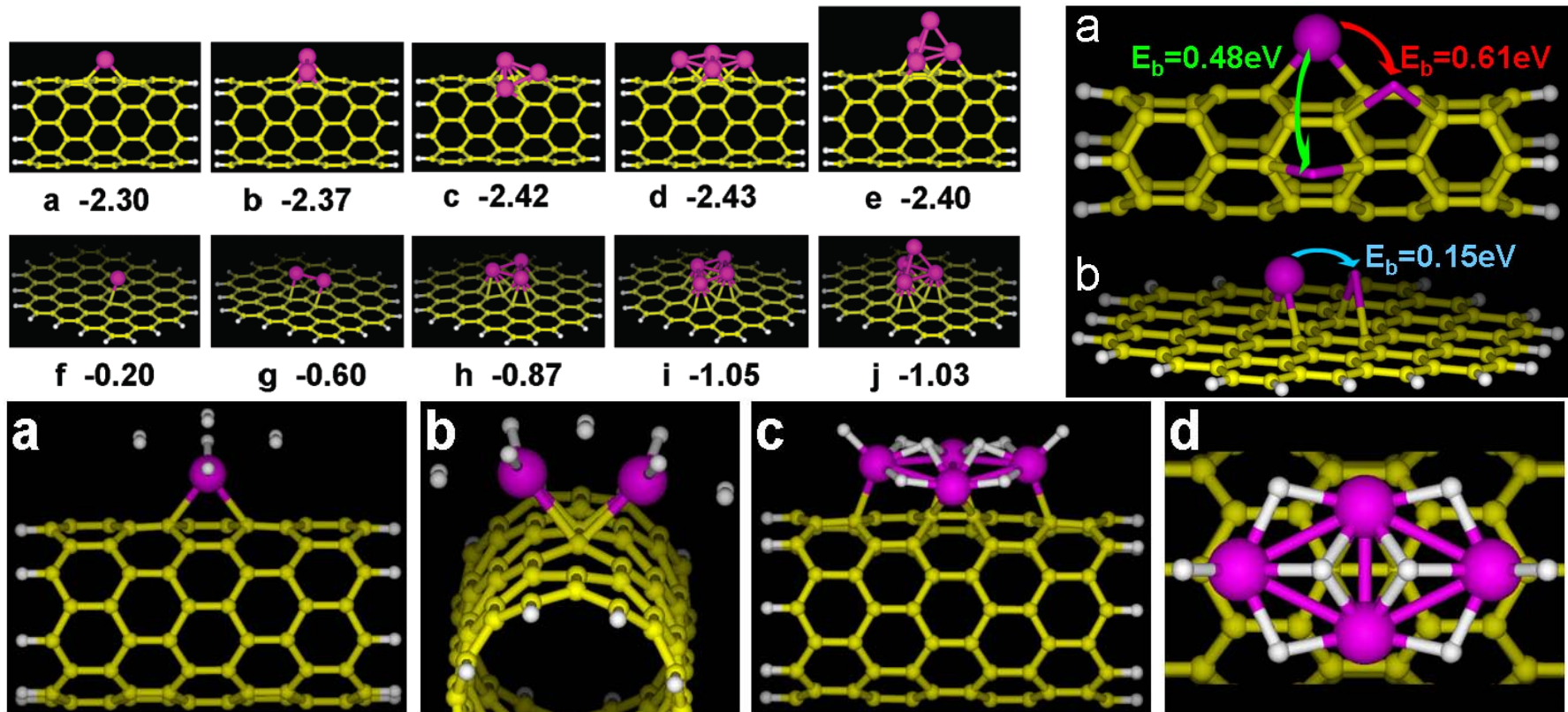
Adsorption isotherm of BF_3/F_2 -treated MSC-30 sample at 100 °C, (wt gain 19 %). Inset shows the isosteric heat as a function of surface excess adsorption. Limiting zero-coverage adsorption enthalpy is approximately 6.1 kJ/mol, consistent with that of pristine MSC-30



For comparison, the adsorption Isotherm of pure MSC-30 (3350 m²/g). Inset: isosteric heat. The zero-coverage enthalpy for MSC-30 was approximately 6.2 kJ/mole. *Adsorption data provided by Channing Ahn, Caltech*

Initial studies suggest that converting a high surface carbon substrate to a superacid with charge separation stabilized via BF_3 complexation needs further testing

Metal clustering and reduction of H₂ capacity



- Metal clustering is both energetically and kinetically favorable at room temperature
- The diffusion frequency is $\sim 10^{12} \exp(-E_b/k_b T) \sim 10^5\text{-}10^{10} \text{ s}^{-1}$ at room temperature
- Transition from Kubas adsorption to metal hydride on large Me-clusters can lead to spillover
- Pinning via doping (Zhao et al PRL 94, 155504 (2005))

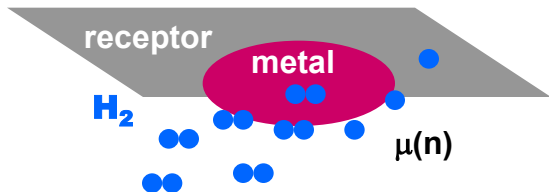
Krasnov, Ding, Singh, and Yakobson, JPCP, 2007, 111, 17977; method: B98/6-31G, Gaussian03

Care should be exercised to avoid metal aggregation

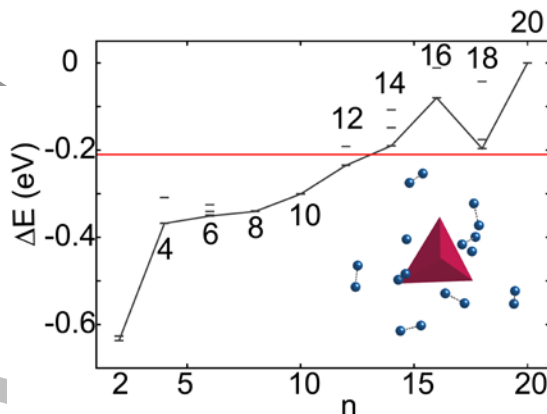
technical accomplishments 4

Highlights of the project

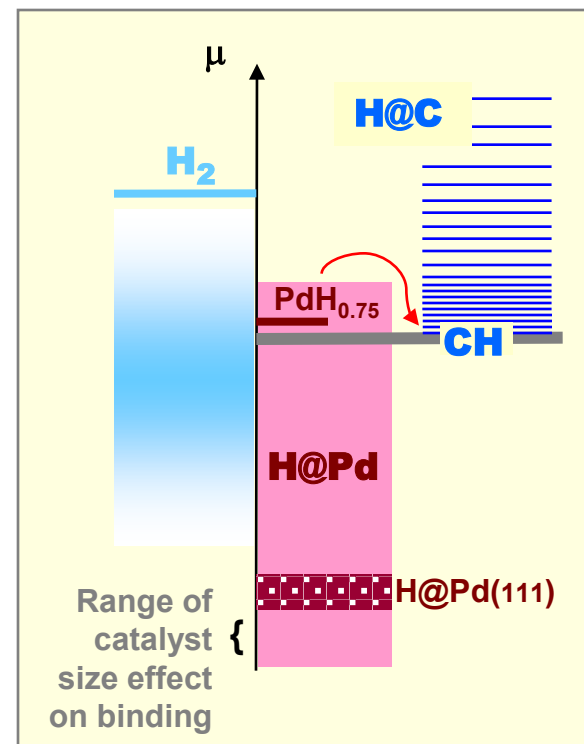
Spillover: Catalyst as a pump



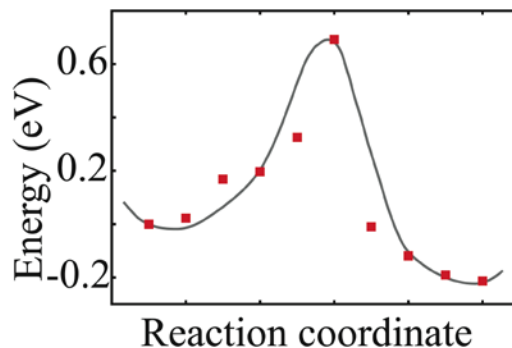
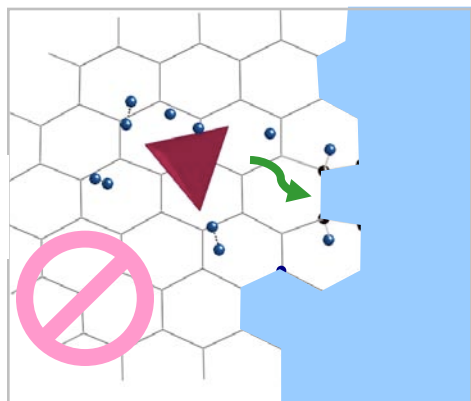
Storage-phase CH and its nucleation barrier identified [Phys Rev B 78 041402-R 2008]



Chemical potential $\mu(n)$ rises with saturation, to permit spillover onto receptor [ACS Nano, 3, 1667, 2009]



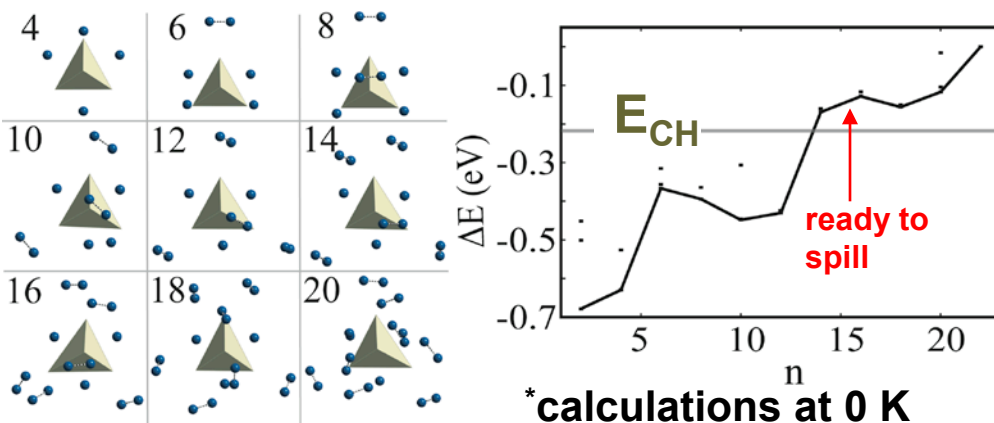
Observed: Reversible hydrogenation of graphene [Novoselov et al. Science 2009; Brus et al. NL 2008]



H shows clear affinity towards “storage phase”, and low activation barrier

Computations of binding energies in the key-states— gas, catalyst, storage-phase on the receptor—reveal the internal “machinery” of spillover, reaching up to 7.7 wt% storage, with potential to exceed 2015 DOE goals

Spillover-saturation window for Ni

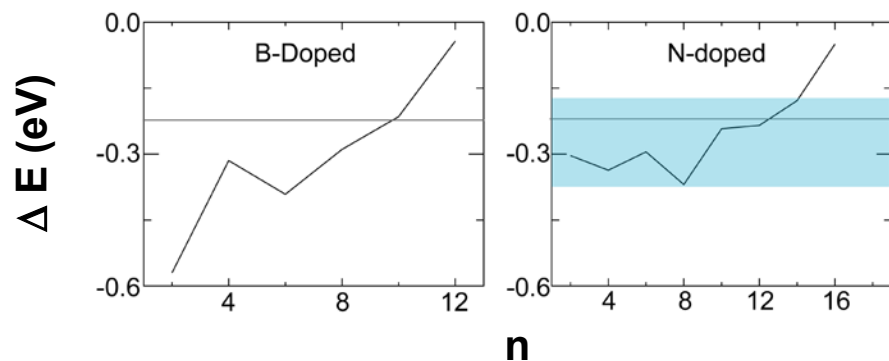


Find the energy levels for H on free Ni₄. Watch for crossover with the “storage phase”. Explore larger more realistic catalyst cluster.

Spillover is possible at n > 12 after the adsorption of 7th H₂

Overall, less expensive Ni behaves similar to Pd as the same-column elements

B-anchors for metal clusters in spillover

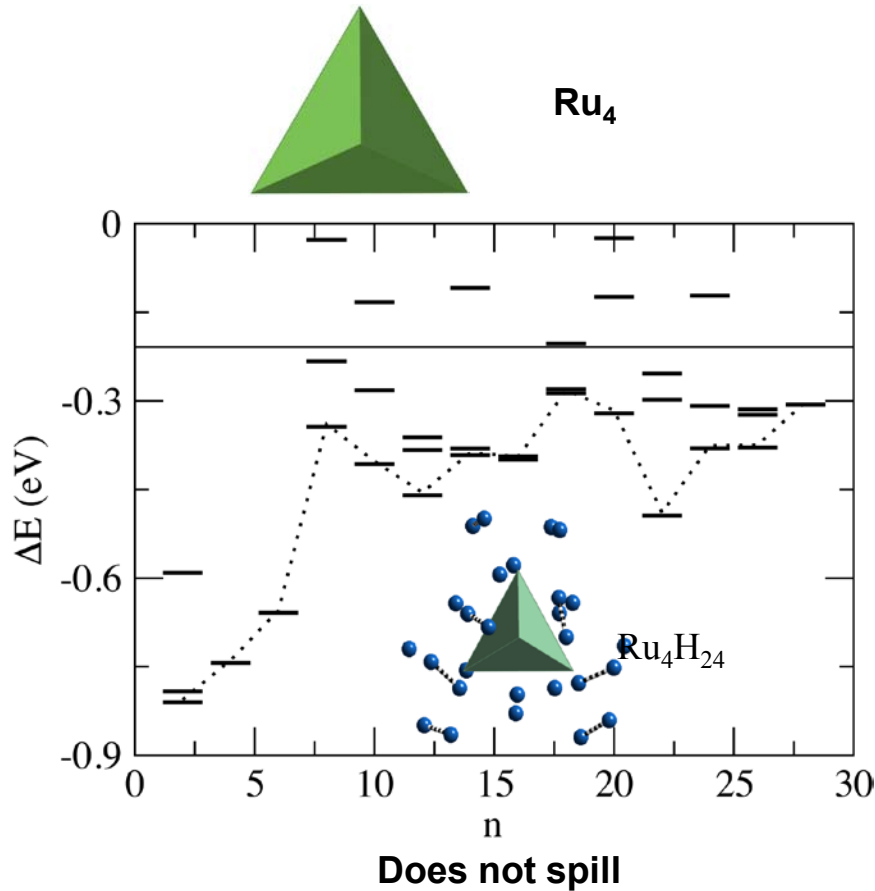


B-doping has very little influence on the catalytic activity of metal, threshold for spillover for B-doping remains unchanged

N-doping, threshold of spillover shifts to higher number of H₂

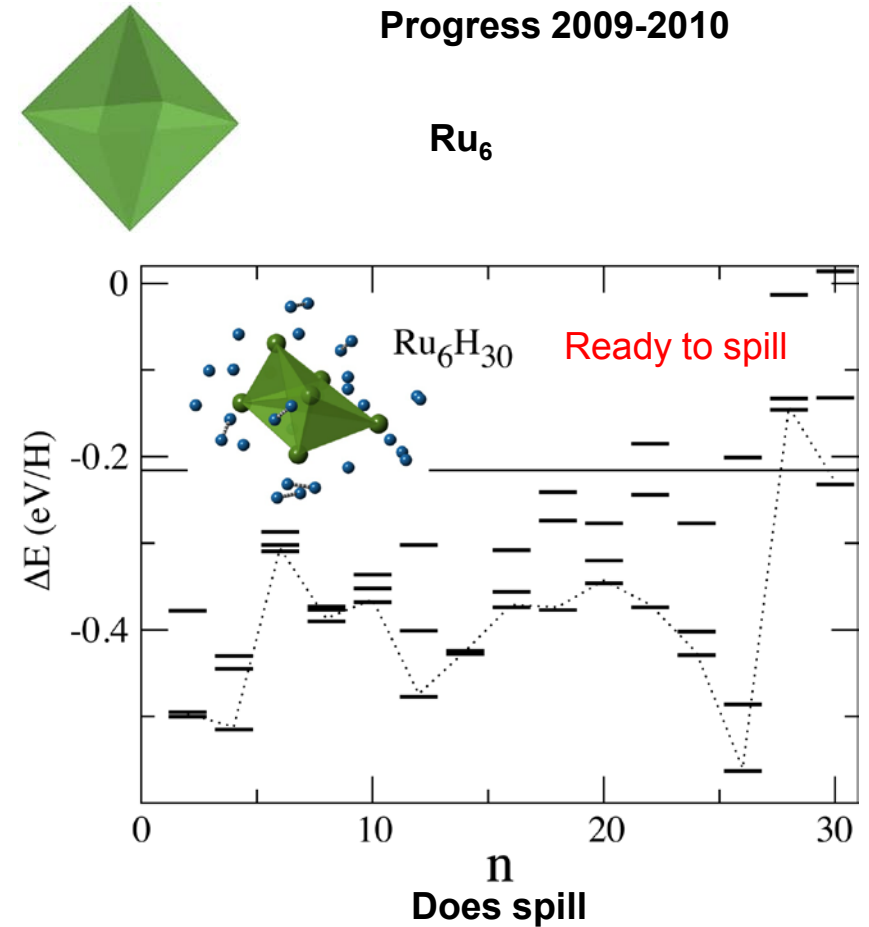
The binding energy of first H₂ is reduced, and entropy-driven spillover can begin from the very first adsorbed H₂

Effect of catalyst size



technical accomplishments 4

Progress 2009-2010

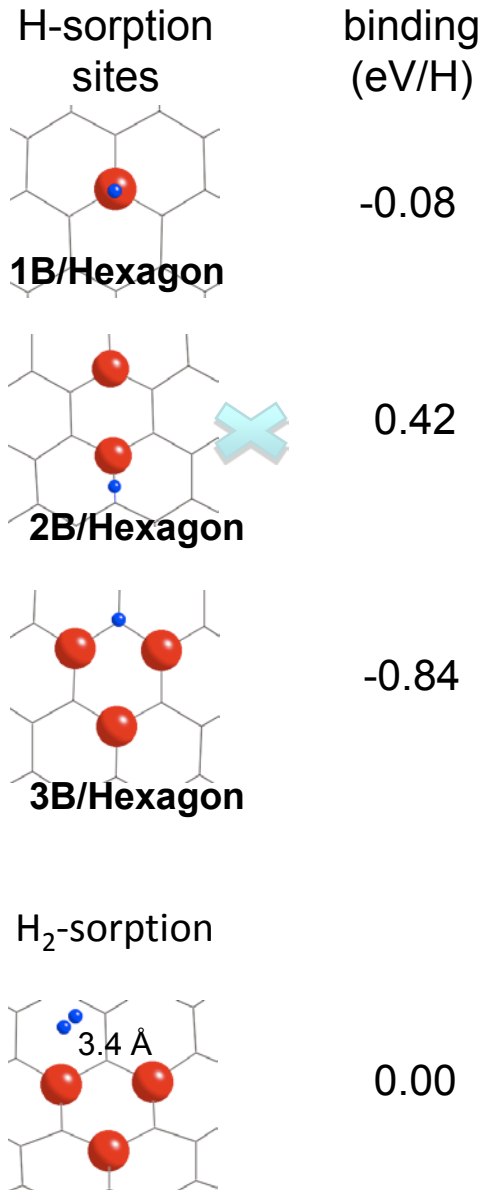


Ru has been considered promising as spillover catalyst

Adsorbs significantly higher amount of H₂ than Ni or Pt, a good candidate for dual purpose catalyst, where adsorbed hydrogen on the catalyst can also be utilized for reversible storage

Catalytic properties of Ru are size dependent and definitely promising

Progress 2009-2010



Boron doped graphene is a good spillover receptor

Binding depends on the site and concentration of dopant

Energies are towards higher side of required range

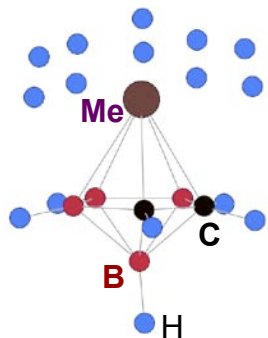
H₂ does not chemically bind

Overall mixed behavior, more investigation recommended

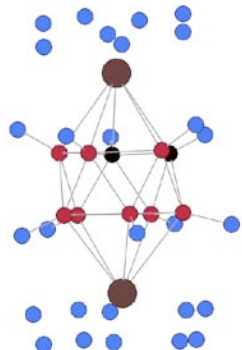
Towards metallocarborane based MOF

technical accomplishments 5

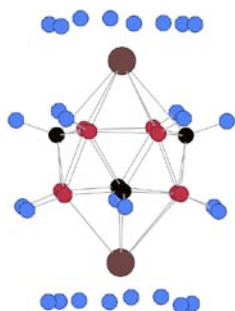
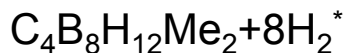
Highlights of the project



Metal	Wt.%	Binding eV
Sc	7.85	0.2~0.52
Ti	7.67	0.24~0.76



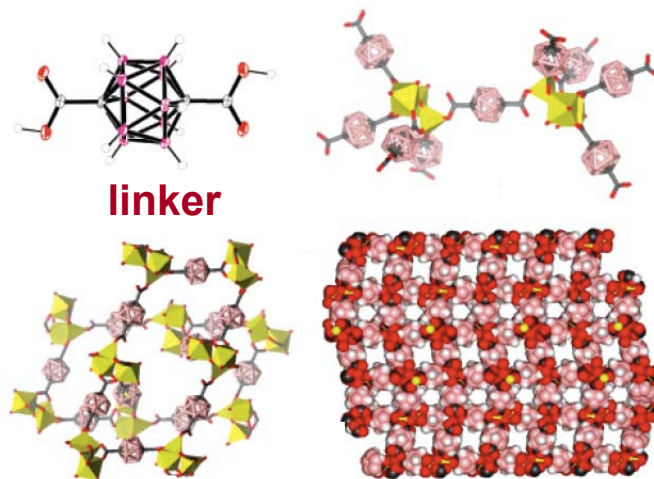
Sc	7.93	0.12~0.40
Ti	7.73	0.24~0.62



Sc	6.38	0.18~0.36
Ti	6.23	0.10~0.50

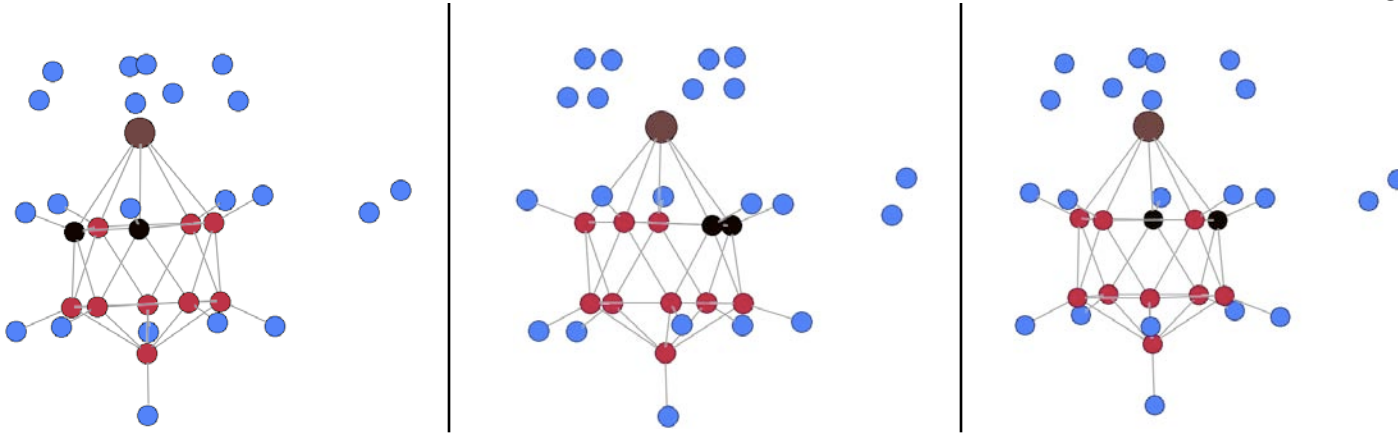
Improves binding energy and H₂ uptake

- Sc and Ti are the optimum for storage
- Manifold increase in hydrogen uptake
- Me-centered capacity adds on top of the already measured for carborane-MOF
- Binding energies are optimal for reversible storage
- Two C available to be linked into the MOFs architecture



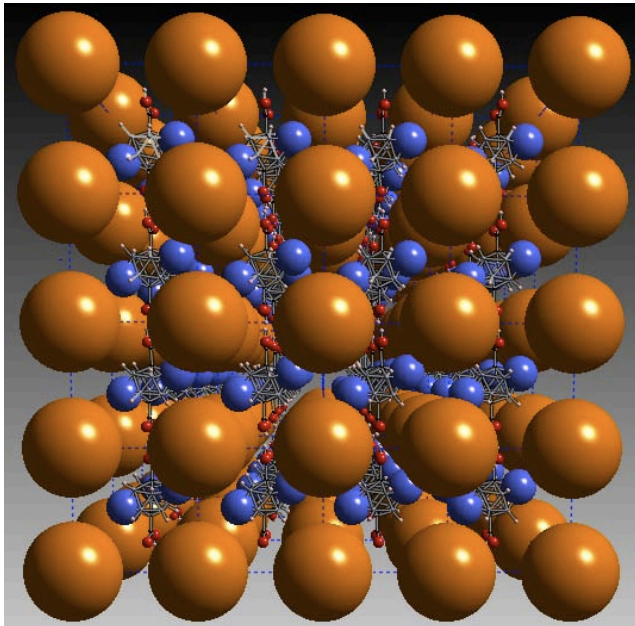
Adsorption of H₂ on the non-metal “surface” of the linker

Progress 2009-2010



Three non equivalent sites on cluster considered. Only physisorption on cluster surface

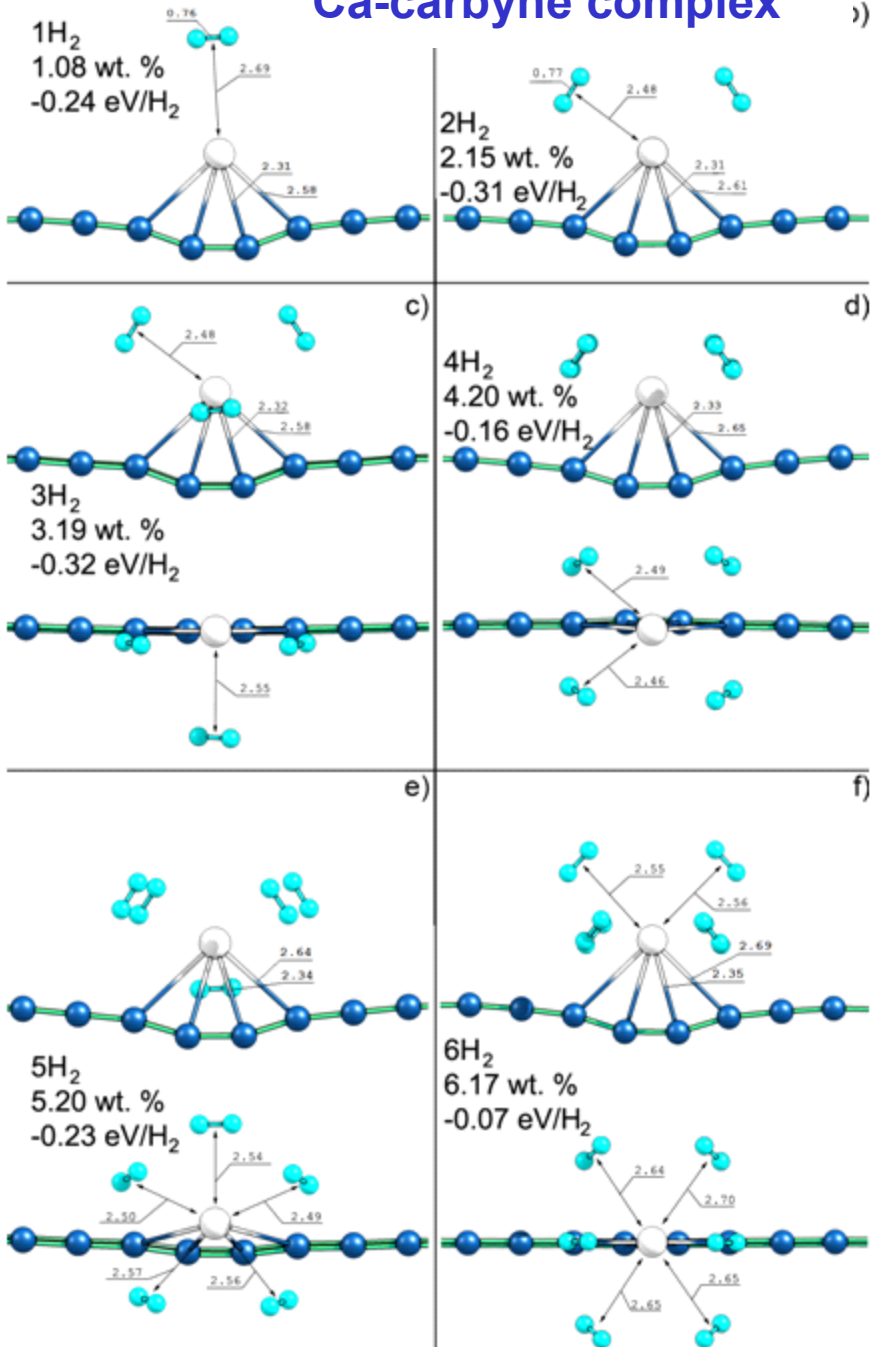
MCB-based MOF



- Structure is based on experimentally produced carborane MOF (Fraha et al.)
- Both of the Ti atoms face the voids
- Reduced steric hindrance
- Effective 6.32 wt% (Kubas)
- Additional storage in voids via physisorption

Ca-carbyne complex

)



technical accomplishments 5

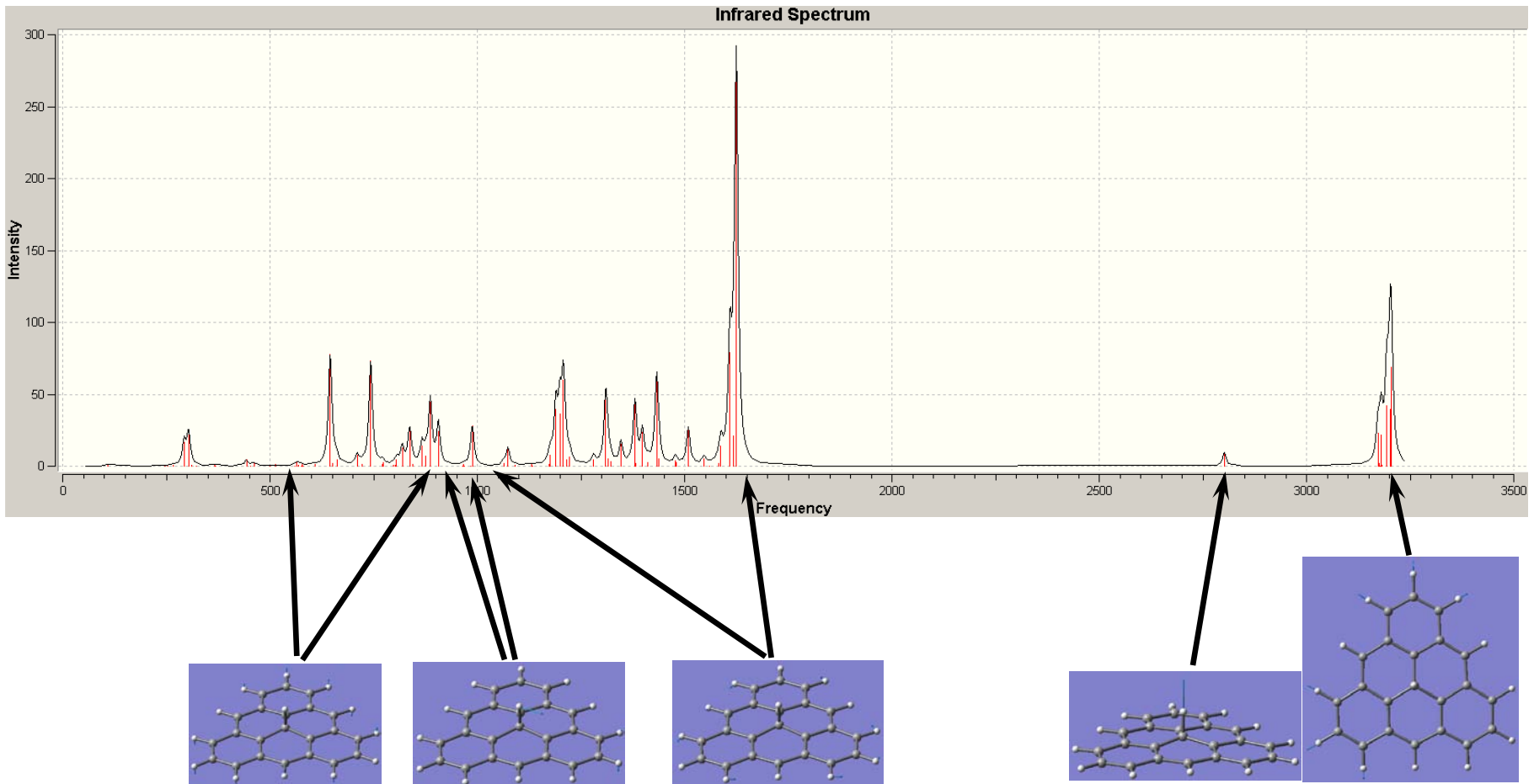
Progress 2009-2010

Carbyne is the thinnest possible experimentally observed carbon nanostructure.

Metals do not segregate on carbyne

Ca@carbyne could adsorb up to 5 H₂
5.20 wt% with binding energy **-0.23 eV/H₂**,
optimal for reversible storage

Vibration frequencies of chemically absorbed H atoms, computed for the Center's team at NIST, for n-scattering diagnostispillover cs (local signature)



Fit of theoretical and experimental spectra offers evidence of H sorption and localization

Collaborations

Within the Center

Caltech – samples testing for H-storage capacity

U Michigan – comparison with available experiments, reciprocal visits

NIST – computations for vibrational spectroscopy signature of H-binding

Air Product, Inc. – nanotube scaffolds, spillover dynamics theory

NREL – exchange of ongoing results on boron-rich structures

Outside of the Center

Wright State University – Grand Canonical Monte Carlo simulations

Hong Kong Polytechnic University – spillover kinetics

ORNL – storage phase studies in spillover

University of Nevada Las Vegas – computations of scaffolds capacities

3D-foams

- 1. Use foams as model to quickly assess the storage capacity of carbon porous materials. Improve interaction potentials to incorporate the unsaturated metal sites in the nanoporous materials. Combined experimental and theoretical investigation towards the validation of the GCMC tool needed, which will make it a reliable estimator of storage capacity.

Metallacarboranes

- 2. Having shown the suitability of the metallacarborane based cluster as hydrogen storage media, other experimentally feasible clusters with TM as constituents should be explored.

B-doped materials

- 3. B-doped materials show promise, but require extensive work to address the barriers like strong dependence of binding energies upon the position and concentration of B. Physisorption enhancement due to B-doping to be explored.

Spillover dynamics

- 4. Having developed the understanding of thermodynamics and kinetics of spillover process, the dynamics of the chemically bound/absorbed hydrogen atoms must be tackled. Directions to look are: barriers and selection rules for H-hopping; possibility of transport of H atoms, as the recombination is suppressed by momentum conservation; diffusion of H atom from catalyst to graphene, and the rate of spread, quantitative front propagation model in contrast to conventional $\langle r^2 \rangle \sim D \times t$ diffusion.

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

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

Technical Accomplishments and Progress:

- 3D-foams of similar geometry optimized for storage. Quantum corrections are incorporated to estimate storage capacities.
- Metallocarborane MOF are generated, with capacities closer to DOE goals.
- Ru shows size dependent catalytic activity. Adsorbs more hydrogen than Ni or Pd.
- The binding energy of hydrogen on B-doped graphene improves significantly, however the spread is too large and depends upon the position and concentration of B.
- The frequency for hydrogen on graphene has been calculated and compared with the experiments.
- High surface area carbon converted to superacid salts and tested for enhanced hydrogen storage. So far no enhancement of hydrogen storage due to conversion to a superacid has been revealed.

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

Future Research: ● Use foams as accurate storage capacity estimator for nanoporous materials. ● B-doped graphene is promising however, requires more studies. Nitrogen doped carbon materials, large fullerenes and graphene sheets as high area superacid materials for hydrogen storage ● Emphasis on theory of spillover dynamics, including other material-receptors. ● Explore thermodynamic stability of metallocarborane based MOFs.

Additional back-up slides

Impact across the Center

Concept of 3D-foams proposed and computationally demonstrated – Direct impact on Rice’s project (PI Tour), and beyond (UNLV).

Me atom aggregation issues addressed. – Impacts all Kubas’ interaction based enhancement work (NREL, Rice, NIST). Suggests special care and possible anchor-sites for Me attachments.

Moreover, performed analysis can bridge *Kubas’ type enhancement* with the *spillover function* on (aggregated) metal clusters.

VANTA synthesis and chemical enhancement offers material for further processing for storage by other center members (NREL, Air Products).

Spillover theory, after fundamental kinetics is understood, should yield recommendations for better receptor and bridges design (in collaboration with Center’s R Yang’s team at Michigan).

Miscellaneous: Computation of H vibration signatures assists neutron-scattering diagnostics of spillover at NIST.