

IV.C.1d Optimization of Nano-Carbon Materials for Hydrogen Sorption

Boris I. Yakobson, Ph.D.
Professor of Mechanical Engineering and Materials
Science, Professor of Chemistry
Rice University, MS 321
6100 Main Street
Houston, TX 77005
Phone: (713) 348-3572; Fax: (713) 348-5423
E-mail: biy@rice.edu
Web site: mems.rice.edu/yakobson

DOE Technology Development Manager:
Carole Read
Phone: (202) 586-3152; Fax: (202) 586-9811
E-mail: Carole.Read@ee.doe.gov

DOE Project Officer: Jesse Adams
Phone: (303) 275-4954; Fax: (303) 275-4753
E-mail: Jesse.Adams@go.doe.gov

Contract Number: DE-FC36-05GO15080

Project Start Date: February 1, 2005
Project End Date: January 31, 2010

Objectives

- Overall: Model materials structures' interaction with hydrogen, and optimize their makeup for storage and assess the volumetric and gravimetric capacity. Recommend the synthetic goals e.g., pore/channel size, metal enhancement routes.
- Identify obstacles (thermodynamic and kinetic) for the spillover, e.g. metal aggregation, and develop a conceptual model of the process for its improvement.
- Explore doping as an anchor to metal cluster, effect of dopants on spillover threshold.
- Explore the viability of metallacarborane-based metal organic frameworks (MOFs) for enhanced room temperature storage.
- Optimize the volumetric and the gravimetric capacities of the 3-dimensional (3D) foam and suggest the best pore size for the storage.
- Synthesis of metal- and electronegative-group- (F , BF_3) enhanced VANTA (vertically aligned nanotube arrays, *contrast to fibers*) for H_2 adsorption.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the

Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption

Technical Targets

Carbon-based 3D structures (including metal incorporated structures) for physical and chemi-sorption of hydrogen will be developed. Apply the gained insights towards the design and synthesis of hydrogen storage materials that can meet the DOE hydrogen storage system targets with special emphasis on:

- System Net Gravimetric: 5.5 wt%
- System Volumetric Capacity: 1.3 kWh/L

Accomplishments

- Carried out Grand Canonical Monte Carlo (GCMC) simulations to optimize the storage in 3D foams. The surface areas of foams were evaluated. Quantum corrections were incorporated to estimate realistic storage capacities.
- Hydrogen uptakes in metallacarboranes were studied. Capacities are closer to DOE goals.
- Efforts made towards optimizing the catalysts for spillover. B and N have emerged as good anchors for metal catalysts. N-doping is promising for enhancement of spillover kinetics.
- The barrier for H to move from metal to the hydrogenated phase was found to be very small and can be overcome at room temperature.
- 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.



Introduction

The search for novel materials capable of efficiently storing hydrogen for on-board energy use needs guidance from modern materials science, which includes predictive theoretical tools. In this project we combine accurate theoretical models with small-scale pilot synthesis efforts. This activity allows us to provide material design suggestions to the Hydrogen Sorption Center of Excellence partners, as well as to verify selected

experimental approaches in-house. Work done in this project helps the Center to see more promising paths to meeting its goals (e.g., 3D architectures with optimum spacing or enhancement of spillover by introduction of heterogeneous nucleation via bridges), while down-selecting some others which computational analyses do not support as feasible (e.g., densely packed raw single wall nanotube material).

Overall inexpensive 3D foams are designed with optimum porosity for enhanced storage capacity. We have provided a consistent explanation for the spillover process and recognized the key factors (catalyst saturation and improved H-receptor binding energy), which can be modified to improve storage efficiencies. This work will benefit both theoretical and experimental efforts in the center to design efficient catalysts and receptors for spillover. Furthermore, metallacarboranes are proposed as the high storage capacity material, which do not suffer from the clustering of transition metals.

Approach

The modeling approach combines quantum-chemical ab-initio and, wherever possible, classical force fields to achieve the accurate yet affordable predictions of nano-structured systems. GCMC simulations are used, with the judicious choice of interaction potentials, to estimate the storage capacities under ambient conditions. The quantum corrections as suggested by Feynman and Hibbs are included in the potentials. The synthesis approach utilizes novel VANTA growth methods and advances its flexibility towards developing materials best suited for H-storage.

Results

Carbon Foams

We have designed inexpensive carbon foams with the optimized porosity for enhanced dihydrogen binding and storage capacity that could meet DOE 2010 targets. By varying the separation and diameters, foams with different porosity are generated and their storage capacities are computed and compared as shown in Figure 1. The accessible surface areas have also been calculated using N_2 as the probe gas, which enables a direct comparison with Brunauer-Emmett-Teller specific surface area data. Among the similar mass density foams, the (5,5)+(10,0) is the optimum for storage (computed by the GCMC simulations) with the gravimetric (6 wt%) and volumetric (60 g/L) capacities at 77 K exceeding the DOE targets on a materials basis.

The effect of quantum corrections (QC) on the storage capacities has been estimated. The QC in C-H₂ and H₂-H₂ potentials essentially adds some repulsion

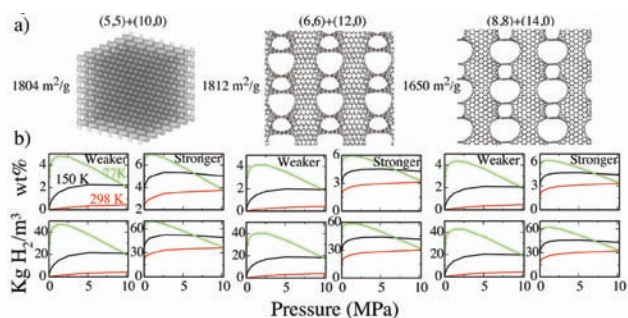


FIGURE 1. a) Optimized structure of the constant mass density 3D nano-foams. Corresponding accessible surface areas are also shown. b) The gravimetric and volumetric % of H₂ in the nano-foam obtained by GCMC. The left and right plots are obtained using weak [III] and strong [III] C-H₂ potentials.

and depends on temperature. The storage capacity computed without QC are overestimated by as much as ~5% (298 K) and ~20% (77 K). Including quantum corrections is important for accurate comparison of storage capacities with the DOE targets.

Spillover Catalysts

The effect of hydride formation on the catalytic activity of metal clusters has been evaluated. In order to assess this, we have separately calculated the chemical potential of H in the Pd-hydride crystal (PdH_{0.75}). The result is shown in Figure 2a (also shows the complete process of spillover) by the red line, which lies ~60 meV above the gray CH-line. Hence, in the case of Pd the spillover will occur before hydride formation. We also calculated the adsorption energies of the H on a Pd(111) surface, for coverage from 0.25 ML to 1 ML, shown by the red block in Figure 2a. The adsorption energy of 0.25 ML hydrogen is 0.57 eV, only slightly higher (~0.1 eV) than that in the Pd₄ cluster. Hence, with increasing cluster size the threshold of the spillover may decrease but not very significantly. The spillover analysis has been extended to Ni shown in Figure 2b. Overall the less expensive Ni behaves similarly to the Pd.

The weak binding of metal catalyst on graphene substrates leads to agglomeration, which reduces the wt% of spillover H₂. In order to maximize the storage wt% via spillover well-dispersed smaller sized catalysts are required. We show that doping of the graphene with B or N improves the binding energy of the catalyst significantly, which is desired to obtain well-dispersed catalysts on graphene. Furthermore, the effect of doping on the spillover has also been explored. Boron has very little effect on the spillover. However, in the case of N-doping, the binding energy of first H₂ is significantly reduced, and entropy-driven spillover can begin essentially from the very first adsorbed H₂, improving the net capacity. Therefore, both B and N are not only good anchors for individual transition metal (TM) atoms (as shown

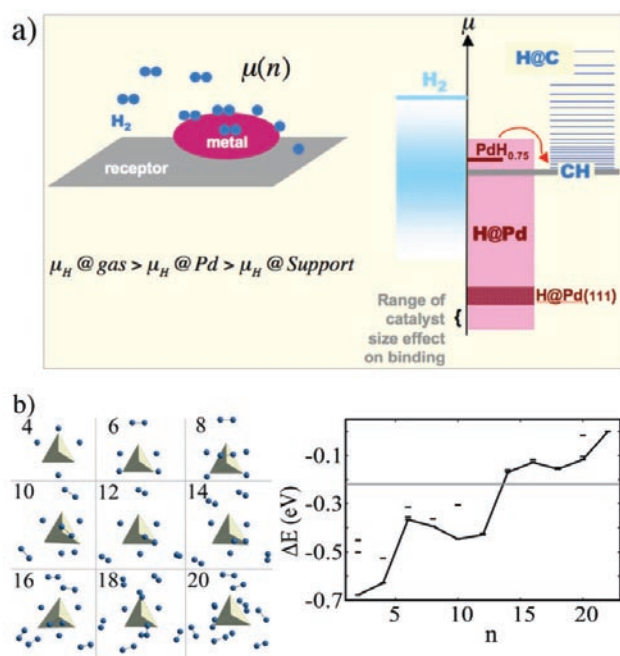


FIGURE 2. a) Left: Schematic of spillover process in real space. The inequality shows the range of chemical potential μ_H favorable for spillover. Right: model of spillover in energy space displays the relative energies (chemical potential) of H in different states. The gray, dark-red, and blue lines show the μ_H in fully hydrogenated graphene (CH), in metal hydride, and in the H_2 molecule, respectively. The pink and dark-red blocks show the range of energies of H at the catalyst and at the Pd(111) surface with the H coverage varying from 0.25 to 1 ML. The family of thin dark-blue lines corresponds to the energies of H bound to graphene. b) The optimized structure of Ni_4H_{2n} ($n = 2$ to 10). The plot of incremental energy E_{incr} versus number of H atoms. The grey line shows the H binding energy in fully hydrogenated phase. The E_{incr} crosses this line after 6th H_2 molecule, indicating the thermodynamic onset of spillover.

previously at the National Renewable Energy Laboratory) but also for spillover catalysts.

Metallacarboranes

We continue our effort in designing materials incorporating TM atoms, which can bind dihydrogen via Kubas interaction while avoiding the clustering of TM atoms. We show that a high hydrogen storage capacity can be obtained in metallacarboranes via the TM atoms reversibly binding up to 5 dihydrogen, as shown in Figure 3. Sc and Ti were found to be optimal among the first row TM atoms maximizing the H_2 storage density to ~8 wt% on the metallacarborane. The calculated binding energies are within the range needed for reversible adsorption. Being an integral part of the cage, the TMs do not suffer from clustering problems, which have been an issue for the development of TM decorated graphitic materials. Furthermore, carbon atoms in the

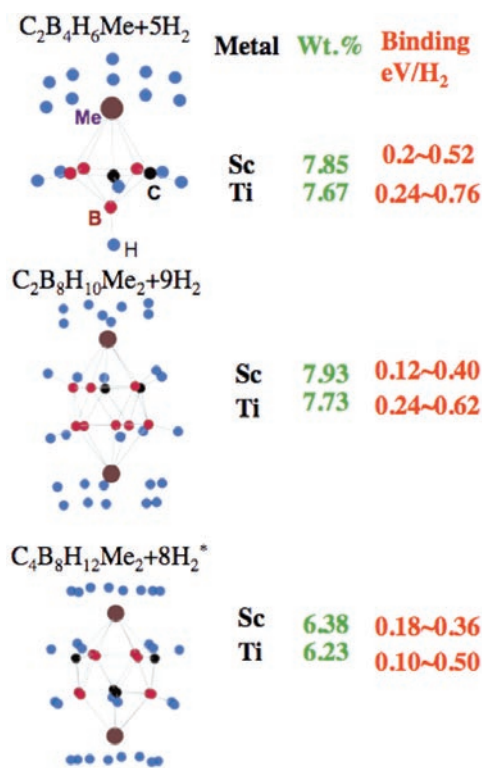


FIGURE 3. Optimized structure of fully saturated metallacarboranes, wt% and binding energies eV/ H_2 are shown.

cage can bind other metallacarboranes to form metal organic frameworks.

Superacids

High surface area carbon samples supplied by Channing Ahn, Caltech, have been converted to a carbon nanotube salt and tested for hydrogen uptake. Initial studies suggest that converting a high surface carbon substrate to a superacid with charge separation stabilized via BF_3 complexation does not improve H_2 storage significantly as shown in Figure 4, and needs further testing.

Conclusions and Future Directions

- The pore sizes of 3D foams were optimized to maximize the storage capacity. The importance of quantum corrections to the interaction potentials was demonstrated.
- The effects of hydride formation and size of the catalyst on the catalytic activity of metal clusters were investigated and are found to be minimal.
- B and N dopants help to stabilize well dispersed spillover catalyst on carbon supports. The N doping leads to enhanced kinetics.

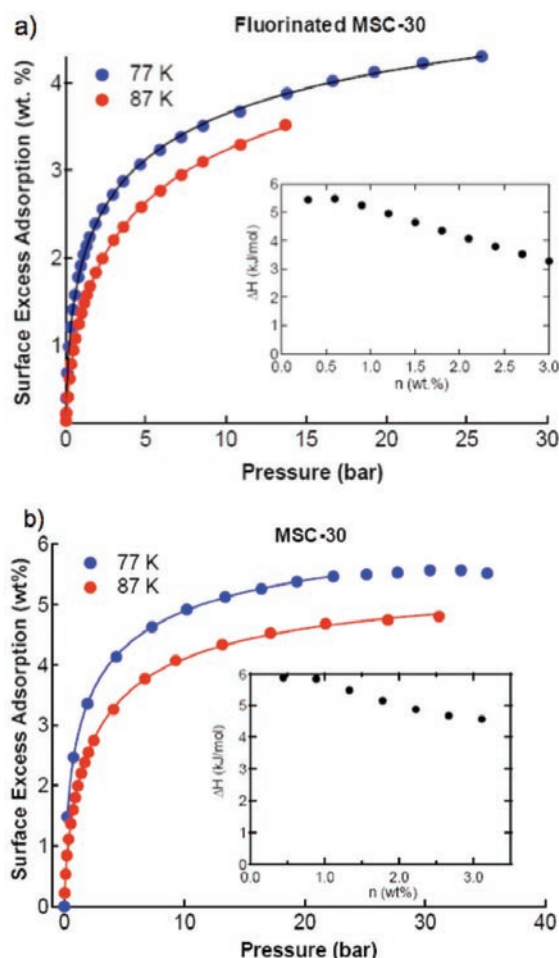


FIGURE 4. a) Adsorption isotherm of BF_3/F_2 -treated MSC-30 sample at 100°C , (wt gain 19%). Inset shows the isosteric heat as a function of surface excess adsorption. Limiting zero-coverage adsorption enthalpy is approximately 6.1 kJ/mol, consistent with that of pristine MSC-30. b) For comparison, the adsorption isotherm of pure MSC-30 ($3350 \text{ m}^2/\text{g}$). Inset: isosteric heat. The zero-coverage enthalpy for MSC-30 was approximately 6.2 kJ/mole.

- Metallacarboranes were demonstrated to store ~ 8 wt% of hydrogen and can meet the DOE targets.
- Converting a high surface carbon substrate to a superacid with charge separation stabilized via BF_3 complexation did not demonstrate significant improvement in H_2 storage but needs further testing.
- Future spillover thermodynamics work: Study the effect of surface modification on the thermodynamics and kinetics of spillover. Evaluate the effect of curvature, size of metal cluster, anchors, and bridges on the migration barriers of H from the activator to the receptor. The possibility of transport of atomic H, as the recombination will not occur due to violation of the momentum conservation.
- Use foams as a model to quickly assess the storage capacities of porous carbon materials. Optimize

both gravimetric and volumetric contents with respect to accessible surface area. Complete development of the GCMC-evaluator and include the quantum corrections for more accurate realistic isotherm. Calibrate the predicted capacities with results from known materials.

- Search for lighter metal atoms (e.g. Ca) to maximize the wt% in metallacarboranes. Effect of linkers on the wt and volume%. Suggest optimized structures for metallacarboranes-based MOFs.
- Continue our work on dynamics of the chemically bound/absorbed hydrogen atoms: barriers and sigmatropic selection rules for H-hopping. 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.
- Conversion of nitrogen doped p-delocalized carbon systems such as giant fullerenes, VANTA, and activated carbon, to superacid salts and test for hydrogen storage. High-pressure Fourier transform infrared studies of curvature dependent hydrogen spillover. Continue the testing on VANTA.

Special Recognitions & Awards/Patents Issued

1. Our work published in Nano Letters was selected as a Cover article (March 2008).
2. DOE Hydrogen Program R & D Award (June 2008).
3. B.I.Y. received 2008 Nanotech Briefs Nano 50 Innovator Award (July 2008).

FY 2009 Publications

1. "Hydrogen storage by spillover on graphene as a phase nucleation process", Y. Lin, F. Ding, and B.I. Yakobson, *Phys. Rev. B*, v 78, 041402-R (2008).
2. "Fullerene nanocage capacity for hydrogen storage", O.V. Pupyshva, A.A. Farajian, and B.I. Yakobson, Nano Letters, v 8, 767 (2008) Cover article.
3. "H-spillover through the catalyst saturation: An ab initio thermodynamics study", A.K. Singh, M.A. Ribas, and B.I. Yakobson, ACS Nano, v 3, 1657 (2009).
4. "Comparative evaluation of carbon-foams hydrogen storage capacity through Monte-Carlo simulations", A.K. Singh, J. Lu, R. Aga, and B.I. Yakobson, in preparation.
5. "Metallacarboranes: A promising new hydrogen storage material", A.K. Singh, A. Sadzadeh, and B.I. Yakobson, in preparation.

FY 2009 Presentations

1. "Nanoclusters and surfaces for H storage", Boris I. Yakobson, DOE CMSM-08 coordination meeting in Gatlinburg, TN, Oct 30 – Nov 1, 2008.

2. Lecture on “Computations for Applied Nanostructures”, Lockheed-Martin Corp. Workshop, October 13–16, 2008.
3. “Exploring nanostructures with a computer: hydrogen confinement on carbon”, Department of Mechanical Engineering, University of Houston, Texas, February 26, 2009.
4. “Carbon nanostructures for molecular hydrogen confinement”, A.K. Singh, F. Ding, R.S. Aga, B.I. Yakobson, ACS Annual Meeting, Salt Lake City, April 26, 2009.

References

1. Y. Zhao et al., Phys. Rev. Letts. 94, 155504 (2005).
2. S.C. Wang et al., J Low Temp Phys 41, 611 (1980).
3. S. Patchkovski et al., PNAS 102, 10439 (2005).