IV.C.1 DOE Carbon-Based Hydrogen Storage Center of Excellence

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Objectives of the Center

- Investigate a variety of adsorbent materials known to store hydrogen to determine limits of performance.
- Design and synthesize materials that bind hydrogen reversibly as either (i) weakly bound atoms or (ii) as strongly bound molecules.
- Understand possible mechanisms and the interplay between structure, binding, and material and storage densities (volumetric and gravimetric).
- Develop the experimental and computational tools to speed discovery, testing, and deployment of new materials that meet DOE system goals.

- Create a collaborative, nimble environment to permit expeditious exploration, research, and deployment (sum of whole > sum of parts).
- Enable new storage system concepts possible with "smart" materials to meet DOE system targets, e.g. conformal tanks with low temperature and moderate pressure (<100 bar) operation using hybrid nanoengineered systems with near standard temperature/pressure (STP) operation.

Technical Barriers Addressed by the Center

This project addresses the following On-Board Hydrogen Storage Technical Barriers specified in the Hydrogen Storage section of DOE's HFCIT Program Multi-Year RD&D Plan:

General

(A) System Weight and Volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rates
(G) Materials of Construction
(J) Thermal Management
(K) System Life-Cycle Assessments
(L) High-pressure Conformability

Reversible Materials-Based Storage Systems (Regenerated On Board)

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(Q) Reproducibility of Performance

Technical Targets Addressed by the Center

The Carbon-based Hydrogen Storage (CbHS) Center of Excellence (CoE) is developing novel carbon-based and high-surface area materials and systems for on-board vehicle hydrogen storage. The CoE presently has thirteen active projects at twelve institutions. CoE partners are conducting a wide range of applied research and engineering studies on currently available adsorbent materials and developing design principles and synthetic methods for next generation materials that will meet the following critical DOE 2010 system hydrogen storage targets:

- Specific Energy: 2 kWh/kg (6 wt%)
- Energy Density: 1.5 kWh/L (45 g H_2/L)
- Storage System Cost: $4/kWh

Overall Approach of Center

- Design, synthesize and test a number of promising sorbent materials for reversible, on-vehicle hydrogen storage. The focus is on developing materials that bind and desorb hydrogen at close to room temperature under moderate pressure conditions to mitigate thermal management demands during refueling and normal operation.
    - Conduct detailed experimental and computational investigations to determine the limits of performance of specific materials and extract general mechanistic information. Theoretical efforts are performed to enable material design/synthesis and explain experimental results.
    - Develop a fundamental understanding of the factors affecting adsorbent synthesis and stability to permit fabrication of materials optimized for on-vehicle hydrogen storage.
    - Optimize hydrogen binding energies and material surface areas to meet DOE hydrogen storage system targets, enabling high-efficiency on-vehicle refueling.
    - Perform reproducible and accurate hydrogen storage capacity measurements as a function of pressure and temperature to characterize material properties and hydrogen storage behaviors.
    - Develop methods to reproducibly synthesize, activate and handle materials to permit scale-up and validate hydrogen uptake/release.
    - Create an environment that facilitates teaming, communication, discovery, and rapid advancement toward hydrogen storage objectives.
    - Share advances in measurement, synthesis, and computational science to speed CoE progress.
    - Develop and test system configurations that can meet DOE RD&D Plan goals for on-vehicle reversible hydrogen storage.

FY 2006 Center Accomplishments

The CbHS CoE partners worked closely together to systematically accelerate the development of advanced hydrogen sorbent materials. Specific materials development results for FY 2006 are listed in Table 1 and 2. Specific accomplishments are listed below.

- The University of Michigan demonstrated multiple routes to enhanced hydrogen storage via spillover, including: 1.8 wt% hydrogen storage at 298K and 10 MPa using AX-21 activated carbon and bridged Pd/carbon catalyst, and isoreticular metal organic framework (IRMOF)-8 and Pt/carbon catalyst; and preliminary indications of 4 wt% at 298K and 10 MPa for IRMOF-8 and bridged Pt/carbon catalysts.
- NREL performed detailed calculations to identify new hybrid materials (e.g. MetCars and dendrimers) with the high hydrogen sorption capacities needed to meet DOE hydrogen storage system targets. In addition, advanced models were used to identify potential processing pathways to form high performance metastable materials.
- Air Products and Chemicals Inc. developed a new computational approach for modeling Gibbs excess adsorption on carbon-based materials.
- NREL improved reproducible purification processes to produce and test single-walled nanotubes (SWNTs) at different institutions. The hydrogen storage capacities of the different materials were within 10% as measured at different laboratories.
- Pennsylvania State University developed arc-generated B-SWNTs and B-doped carbons from polymer precursors. NIST confirmed the boron doping by prompt gamma activation analysis, and measured an enhance binding energy for dihydrogen by neutron scattering.
- NREL developed arc- and laser-based processes to generate boron doped SWNTs. Boron doping was confirmed by a number of techniques including prompt gamma activation analysis at NIST, and ^{13}C nuclear magnetic resonance (NMR) and electron energy loss spectroscopy (EELS) at NREL. ^{1}H NMR and neutron scattering measurements performed at University of North Carolina and NIST, respectively, indicated an enhanced hydrogen binding energy of ~12 kJ/mol for the B-SWNTs. This binding energy may be sufficient to produce full saturation of the B sites at room temperature and moderate to high pressures.
- Penn State, Air Products and Chemicals, and NREL developed advanced models for the B-doped materials to identify potential hydrogen sorption capacities and thermodynamically stable structures.
- NREL developed chemical processing to form precursor materials that may provide a synthetic route to the organometallic buckyballs that have been predicted to stored nearly 9 wt% hydrogen.
- NREL demonstrated processing to decorate SWNTs and other porous carbon materials with metals such as Na, Cr, Rh, Pt, Sc, Pd, Ni, Co, or Ti. The Cr-SWNTs demonstrated near room temperature hydrogen sorption. Since Cr is not a hydride forming element, the hydrogen sorption behavior may be a result of the Cr-SWNT interactions. The hydrogen uptake behavior of other metal-decorated

TABLE 1. Summary of Selected FY 2006 Materials Performance

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value) NA: Not Available												
Storage Parameter	Units	2010 System Target	MOF **		Spillover **		SWNT **		B-SWNTs **		FY06 Alkali Metal decorated SWNT**	FY06 Aerogels **
			FY05	FY06	FY05	FY06	FY05	FY06	FY05	FY06		
Specific Energy	wt. % H_2	6	2.5	7	1.6	~4	See comments	3†	NA	~3 Cold 0.5 RT	4.2	4.2
Volumetric Energy Capacity	g/L	45	NA	31	NA	41	N/A	28a	NA	28a	N/A	N/A
Comments			77K ~40 bar		RT 100 bar FY06 Results are Preliminary		77K, 20 bar Previous results inconsistent. > 6% reported in literature. † Reproduced at Different labs		77K ~20 bar B-doping level is only 1-2% presently, result is similar to C - SWNT		STP Irreversible	77K 30 bar

a 28 g/L assuming a ~20% expanded lattice. Will be ~56 g/L at 6 wt% H_2 with this same assumption.

TABLE 2. Summary of FY 2006 Predicted Hydrogen Storage Materials

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value) NA: Not Available							
Storage Parameter	Units	2010 System Target	Organometalic Fullerenes Predicted ** FY05	Organometalic Fullerenes Measured Fe-C_{60} ** FY06	MetCars Predicted ** FY06	Macromolecules Predicted ** FY06	Spillover on SWNTs Predicted ** FY06
Specific Energy	wt. % H_2	6	~9	0.4	>7.7	>5	~7.7
Volumetric Energy Capacity	g/L	45	52 - 43	NA	NA	>40	~56
Comments			STP	77K 2 bar	STP	STP	STP Preliminary Result

SWNTs/carbons also demonstrated enhanced dihydrogen sorption characteristics.

- Caltech, working with carbon aerogel materials synthesized at LLNL, performed detailed analyses of the surface area dependence of hydrogen physisorption and validated the 77K linear dependence of 1 wt% gravimetric density for every 500 m^2/g of Bruner-Emmett-Teller (BET) surface area.

- Duke University developed an understanding of the relationship between the carbon feeding rate and the diameter of produced nanotubes. Duke also identified multiple conditions under which small diameter CNTs can be prepared. Very small diameter CNTs may have sufficient binding energy to meet DOE hydrogen storage targets at room temperature and moderate pressure.

- Rice University demonstrated regrowth of SWNTs from the end of dense, aligned SWNT fibers. Rice also developed processing to synthesize vertically aligned SWNT carpets. Routes to densified carpets and spun fibers were also demonstrated. These technical developments are required to construct functional SWNT-based sorbent materials for H_2 storage systems.

- Rice also identified potential synthesis paths to make 3D nanoengineered arrays of pure SWNT with optimum spacing to enhance hydrogen storage. The initial processing to form the requisite crosslinking was demonstrated.

- ORNL synthesized and processed single-walled carbon nanohorns (SWNHs) with tunable porosity, size and metal nanoparticle decoration. Processing was developed to make gram quantities and increased surface areas to 1,890 m^2/g. SWNHs demonstrated ~2.5 wt% hydrogen sorption at 77K. In addition, neutron scattering measurements at NIST of metal decorated SWNHs provided evidence of spillover.

- University of Pennsylvania demonstrated reversible H_2 uptake on conducting, doped-polyaniline nanofibers with applied potential.

- University of North Carolina developed NMR capabilities up to 100 atm to quantitatively measure H_2 adsorption amounts and the corresponding hydrogen binding energy.

- Carbon based materials were synthesized with over 5000 m^2/g surface areas and over 7 wt% hydrogen uptake by Dr. Yaghi's group at the University of Michigan before his effort left the CoE.

- Air Products developed and validated a new hydrogen storage measurement method – the "capsule" method – in which hydrogen is weighed in a lightweight capsule.

Future Directions of Center for FY 2007

Develop efficient, safe, and cost-effective sorbent-based technologies with greater than 6 wt% and 45 g H_2/L hydrogen uptake and binding energies lower than ~40 kJ/mol that can meet the goals for on-vehicle hydrogen storage applications. This includes:

- Advancing theoretical modeling of hydrogen interactions with materials for different sorption mechanisms to enhance understanding and provide guidance for materials development.

- Theoretically predicting the strength of non-dissociative dihydrogen binding on nanostructured materials by varying the metal elements, adsorption site coordination, and structure.

- Developing synthetic methods using gas phase, solution phase and other approaches where carbon, metal, and hydrogen (or other stabilizing ligands) may coalesce to form targeted C:M:H nanomaterials like the high hydrogen storage complexes theoretically predicted.

- Incorporating B into carbon aerogels and other carbon materials at significantly higher concentrations than the 1-3 atomic (at)% that has been achieved to date to increase the adsorption enthalpy beyond the 4 kJ/mole typical of most carbon-based systems.

- Increasing material surface area to maximize available sorption sites for enhanced hydrogen storage capacity.

- Validating the "spill-over" effect on carbon materials, and studying and understanding the binding energies and mobility barriers for H on carbon substrates, and at the metal-carbon interface.

- Developing synthetic methods to construct new 3D nanoengineered hydrogen storage structures.

- Developing and implementing synthesis/combinatorial approaches to rapidly identify and test the hydrogen storage performance characteristics of promising materials.

Introduction

Significant improvements over currently available hydrogen storage technologies are required if hydrogen is to become a viable energy carrier. The hydrogen storage targets presented in DOE's Multi-year Research Development and Demonstration (RD&D) Plan for the Hydrogen, Fuel Cells, and Infrastructure Technologies (HFCIT) Program state the critical needs and goals (*http://www.eere.energy.gov/hydrogenandfuelcells/ mypp/*). At this time, no known storage system can meet the mass, volume, cost, safety, and efficiency requirements for vehicular hydrogen storage systems.

Consequently, DOE is investigating solid-state storage options such as metal hydrides, chemical hydrides, and carbon-based adsorbent materials. Nanostructured carbon and other high surface area materials containing carbon, metals, oxygen, and other elements, show tremendous promise for break-through performance in vehicular hydrogen storage. However, the capabilities of these materials remain unclear due to a lack of understanding of both the factors governing their performance and the design principles for fabricating viable adsorbent systems.

NREL is leading the initiative to develop reversible sorbent materials for hydrogen storage within the U.S. DOE National Hydrogen Storage Project. A guiding principle in developing the required material is that a continuum of energies exists for hydrogen bound to substrates and molecules (Figure 1). On the weak side of the continuum is non-dissociative physisorption due purely to van der Waals (vdW) forces (4 kJ/mol). On the strong side is the full C-H chemical bond in methane with an energy of ~400 kJ/mol. Between these two limits, with binding energies between 10 and 50 kJ/mol, are: (i) stronger physisorption (due to modification of the key parameters effecting vdW forces), (ii) dihydrogen binding via the formation of complexes that exhibit Kubas-type [1] interactions, and (iii) weak, reversible chemical bonding of mono-atomic hydrogen to strained C-C and other matrices ("spillover"). The DOE goals can be met with carbon-based materials if (i) the energy for hydrogen adsorption can be designed to be in an optimal range (10–50 kJ/mol), and (ii) efficient volumetric packing of a low-weight skeletal material can be achieved without compromising the density of adsorption sites. These goals are difficult to reach in conventional high-surface-area adsorbents

that are limited by low physisorption binding energies, heterogeneity of the adsorbent surfaces and adsorption sites, and excessive macroporosity and poor volumetric packing.

Approach of the Center

The nanostructured sorption-based materials that are the current focus of this effort offer tremendous potential for a break-through in hydrogen storage performance. For example, reliable data from NREL, Penn State, NIST, and UNC showed that dihydorgen binding energies of SWNTs can be increased from ~4 kJ/mol to ~12 kJ/mol with boron doping [2]. In addition, experimental results from Penn State [3] and the University of Quebec (Trois Rivieres) [4] show 4–6 wt% H_2 adsorption under a few atmospheres of pressure at 77K. Similarly, recent work by Yaghi's group at the University of Michigan has demonstrated metal-organic framework (MOF) structures with greater than 5,000 m^2/g surface areas and ~7 wt% H_2 adsorption at 77K [5]. Furthermore, Yang's group at the University of Michigan has demonstrated 4 wt% reversible hydrogen storage at room temperature and moderate pressures via spillover using a Pt-MOF system [6]. In addition to the experimental results, recent calculations from NREL predict that certain carbon-transition metal hybrid structures can achieve room temperature hydrogen storage densities near 9 wt% with high volumetric storage densities (~52 kg H_2/m^3) [7]. These results, along with recent theoretical calculations from NIST [8] on Ti-doped nanotubes, and from the Steacie Institute for Molecular Sciences [9] on H_2 physisorption between pure graphene layers, provide a firm theoretical foundation for developing sorption-based materials to meet the DOE hydrogen storage system targets.

The main goal of the CbHS CoE is to discover the limits of performance of high surface area adsorbents and to synthesize and test adsorbents that will meet the DOE system targets for reversible, on-vehicle hydrogen storage. This will involve the design and synthesis of materials that bind large amounts of hydrogen on both a per-weight and a per-volume basis as either (i) weakly and reversibly bound atoms or (ii) strongly bound molecules. An additional task will be the design and testing of appropriate containers for the selected adsorbents. For example, conformal tanks capable of lower temperature and moderate pressure (<100 bar) operation may be required. Initially, the CbHS CoE will focus on determining hydrogen binding mechanisms and energies, and the manner in which suitable sites may be organized in space to achieve a high volumetric density using low-weight frameworks. This will involve determining the affects of geometry, the introduction of defects, adventitious dopants, catalytic species, as well as elemental substitution. The CoE currently investigates
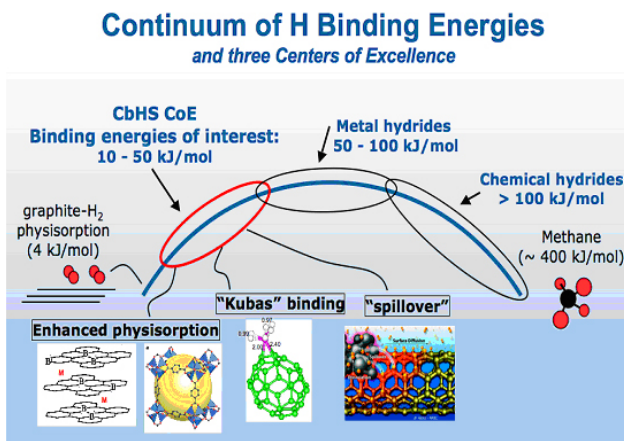

FIGURE 1. Depiction of the Range of Binding Energies and Several of the Nanostructured Materials of Interest to the CbHS Center of Excellence

a wide range of different light-weight sorption-based nanomaterials. These include pristine, metal-doped and metal-decorated graphitic materials, carbon aerogels, carbon nanohorns, graphite nanofibers, conducting and boron-doped polymers, metal organic frameworks, pure and defective SWNTs, and SWNT-metal and fullerene-metal hybrid materials. In addition to the current materials system being studied, the CoE will strive to be nimble to incorporate promising new ideas, materials, and concepts as they arise. Figure 2 shows the participants in the CoE and highlights the primary research mission of each partner.

Results of the Center

As previously indicated, the CoE is interested in a wide array of materials, the study and development of the hydrogen storage capabilities of these materials, as well as the discovery and development of new, more promising materials. The CoE effort is driven by a synergistic interaction between computational modeling, materials synthesis, hydrogen adsorption/desorption characterization, and systems-related engineering concerns. Numerous specific significant results from the FY 2006 CoE activities were listed previously. These and others will be discussed in more detail in the Partner-specific portions of this report. Here we highlight three notable CoE accomplishments.

Enhanced Physisorption of Matrix Materials

To improve physisorption, as discussed above, both the surface area and binding energy of carbon-based materials must be increased in comparison to typical porous carbons. Recent work using MOF-124 [5] at the University of Michigan demonstrated that surface areas of greater than 5,000 m^2/g are achievable with a carbon-based material. An infinite graphene sheet has a theoretical surface area of ~2,600 m^2/g. In addition,

the MOF-124 had a correspondingly higher hydrogen uptake of ~7 wt% at 77K and ~30 bar pressure. This represents a substantial increase in both surface area and hydrogen sorption compared to previously measured MOF or carbon-based matrix material.

In addition to increased surface area, the binding energy of carbon-based materials (typically 4 kJ/mol) must be increased to attain substantial hydrogen sorption capacities at non-cryogenic temperatures. Last year, NREL predicted that the substitutional doping of boron in a carbon graphene matrix will increase binding energies to approximately 12 kJ/mol [10]. These theoretical results were verified by Penn State University and elsewhere. Progress in this area was clearly enhanced by the Center of Excellence approach. Figure 3a depicts how CbHS CoE partners worked closely together to discover, experimentally synthesize, and validate substitutionally doped boron SWNTs and other carbon materials. Once the boron-doped carbon materials were synthesized and purified at NREL and Penn State, the materials were sent to
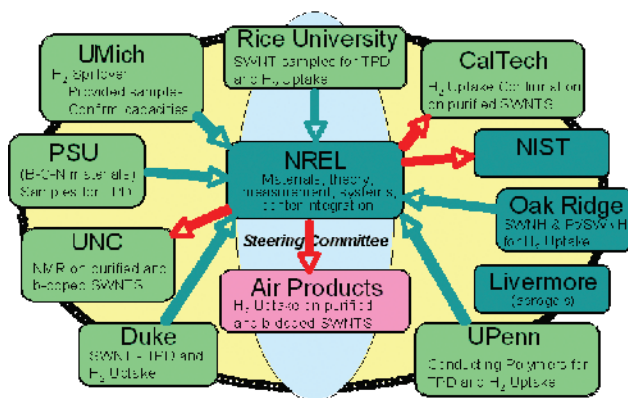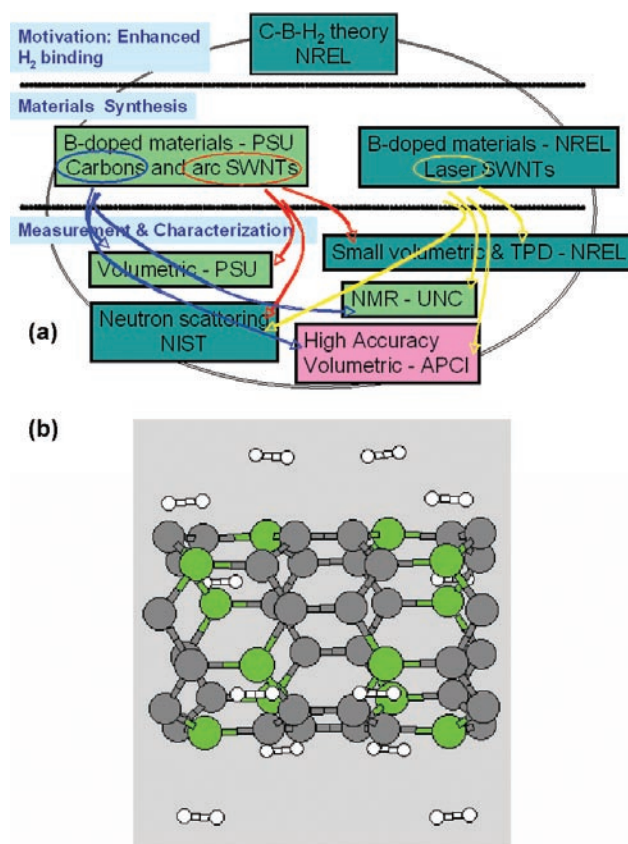

FIGURE 3. (a) Diagram showing the synergistic interactions between CoE partners to perform the complex research needed for developing B-SWNTs. This is just one example of how the CoE concept accelerates materials development. (b) Model of a BC3 SWNT structure that is predicted to store over 5 wt% hydrogen at room temperature and moderate pressure with a binding energy of 12 kJ/mol. Green spheres represent B, white dumbbells are H_2 molecules.

FIGURE 2. Diagram Showing the Organization of the Carbon-based Hydrogen Storage Center of Excellence, Partner Institutions, and Primary Responsibilities

NIST and University of North Carolina for neutron scattering and NMR measurements, respectively. Initial prompt gamma analysis measurements confirmed that boron was incorporated in the SWNTs at 1 to 3 at%. In addition, neutron scattering measurements clearly identified preferentially stronger binding of dihydrogen at the boron sites. Similarly, NMR measurements identified enhanced binding compared to a pure carbon matrix and confirmed an approximate 12 kJ/mol binding of dihydrogen by the boron-doped SWNTs. Additional theoretical work at NREL (Figure 3b) and Penn State indicated that BC_3 should be a thermodynamically stable composition if synthetic routes can be determined. Additional theoretical efforts at NREL are now investigating how the binding of hydrogen to the carbon atom sites might be affected by boron incorporation to 25 at%. Importantly, and depending on site-to-site interactions, a 12 kJ/mol binding energy may be sufficient for adsorption storage at room temperature at moderate pressures. Subsequent research will strive to increase the boron loading in carbon materials and to quantify the enhanced hydrogen storage properties. Fortuitously, boron doping stabilizes dispersion of partially coordinated metal atoms and may therefore be useful for building next generation adsorbents such as the organometallic bucky balls and metal decorated nanotubes [7].

New Dihydrogen Sorption Materials

In FY 2005, NREL developed a rational theoretical model for constructing organometallic bucky balls capable of storing nearly 9 wt% H_2 at near ambient pressure and temperature [7]. The key to this advance was the insight that thermodynamically metastable, but kinetically stable materials could have the enhanced hydrogen storage capacities required, with binding energies in the 10 to 40 kJ/mol range. Further theoretical efforts in FY 2006 identified additional materials/structures that also have the potential to meet DOE hydrogen storage goals at room temperature. For example, the adsorption of hydrogen on metallocarbohedrene (MetCar) Ti_8C_{12}, and nanocrystal $Ti_{14}C_{13}$ was studied using first-principles calculations [11]. Based on these calculations, NREL predicts hydrogen capacities of 6.1 wt % for Ti_8C_{12} and 7.7 wt% for $Ti_{14}C_{13}$ (Figure 4) at moderate temperatures and pressures. The nanocrystals store a portion of the hydrogen as molecules and a portion as atoms. The metal atoms in these nanostructures enable self-catalyzed dissociation of H_2 to form hydrides (i.e. via spillover) with barriers less than 25 kJ/mol. Thus, in addition to being new target materials for further investigation and development, these materials offer a complete description of spillover. In addition to the MetCars and nanocrystals, NREL also calculated that porous carbon implanted with transition metal atoms (e.g. using an ion beam) might be sufficiently reactive
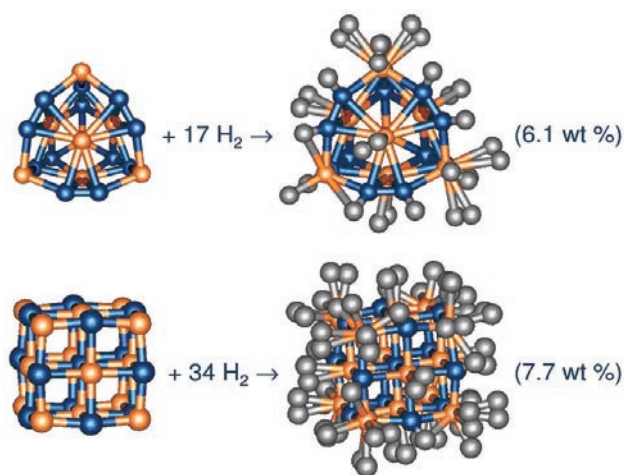

FIGURE 4. Schematic drawings of MetCar Structures that have the potential to meet DOE hydrogen storage system targets and that have demonstrated synthesis routes.

to bind hydrogen, and that the transition metal (TM)-hydrogen complex could modify the porosity further to enhance physisorption of additional hydrogen. The other key developments from this set of activities are the identification of materials that are potentially easier to synthesize and routes for creating materials with high hydrogen storage but lower binding energies (10 to 40 kJ/mol).

Room Temperature Hydrogen Sorption/Desorption on Carbon Matrix Material

Dr. Yang's group at the University of Michigan achieved ~4 wt% reversible hydrogen storage at room temperature via spillover (Figure 5). Spillover, involves the dissociation of dihydrogen via a catalyst followed by transport of the mono-atomic hydrogen onto a receptor lattice (e.g. carbon SWNTs, porous carbon, MOFs, etc).

The University of Michigan work developed a simple and effective technique to build carbon bridges that serve to improve contact between a spillover source and a secondary receptor. In this work, a supported catalyst (e.g. Pt/C, Pd/C, Ni/C, etc.) served as the source of hydrogen atoms via dissociation and primary spillover. Initial efforts that formed carbonized bridges between the catalysts and AX-21 or SWNT secondary spillover receptors increased the hydrogen adsorption amount by a factor of 2.9 for the AX-21 receptor and 1.6 for the SWNT receptor at 298K and 100 kPa. However, subsequent work involving Pt/C catalysts and carbonized bridges with a MOF-8 receptor increased the spillover of hydrogen to ~4 wt%, compared to the ~1.8 wt% previously measured with an AX-21 receptor. Reversibility was demonstrated through desorption and re-adsorption all at 298K. The key bridge-building process appears to be receptor specific and optimization
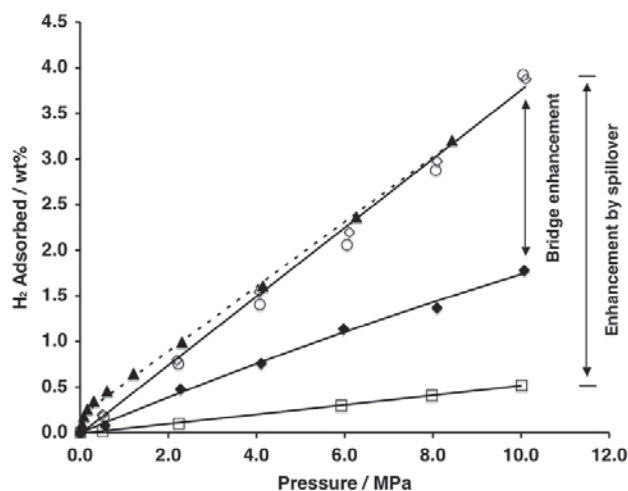
FIGURE 5. High-pressure hydrogen isotherms at 298 K for pure IRMOF-8 (□), Pt/AC and IRMOF-8 physical mixture (1:9 weight ratio) (◆), and for bridged sample of Pt/AC-bridges-IRMOF-8: first adsorption (○), desorption (▲) and second adsorption (◇).

and/or use of other receptors may yield even greater hydrogen storage capacities. These results are currently being validated through close collaboration with CoE partners and Southwest Research Institute.

Additional details for each of the CbHS CoE Partners are provided in this report and including a summary of FY 2006 results and FY 2007 plans for each partner.

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