

IV.C.1a Overview of the DOE Hydrogen Sorption Center of Excellence

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Project Start Date: February 1, 2005
Project End Date: The current materials CoEs are scheduled to end in Fiscal Year 2010

Objectives

The Center seeks to discover and develop high-capacity sorbent materials that can operate at near ambient temperatures and be efficiently and quickly charged on-board with minimum energy requirements and minimum penalties to the hydrogen fuel infrastructure. Work is directed at overcoming barriers to 2010 DOE system goals and identifying pathways to meet 2015 goals. In particular, we strive to:

- Synthesize high-surface area sorbent materials with high volumetric packing densities such that both the volumetric and gravimetric DOE system storage targets are achieved simultaneously.
- Develop materials that utilize mechanisms that bind hydrogen with an optimal energy for room temperature operation (10-20 kJ/mol).
- Employ materials with high thermal conductivity to mitigate effects of exothermic refueling process.
- Develop catalytic processes to ensure rapid charge/discharge kinetics.
- Devise economically scalable synthetic routes for materials made of abundant, non-toxic and inexpensive materials.
- Rapidly correlate capacity, structural, and energetic information to reduce time between discovery, assessment, and down-selection of materials.
- Create a nimble, flexible yet structured, teaming environment to accelerate discovery, evaluation, and selection of promising development directions.

Technical Barriers

The Hydrogen Sorption Center of Excellence (HSCoE) is developing novel high-surface area materials and systems for on-board vehicle hydrogen storage. The HSCoE presently has 15 active projects at 14 institutions. HSCoE partners are conducting a wide range of applied research on currently available sorbent materials and developing design principles and synthetic methods for next generation materials that will meet the critical DOE 2010 system hydrogen storage targets. The technical barriers addressed by these projects from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, include:

General:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (E) Charging/Discharging Rates
- (J) Thermal Management

Reversible On Board:

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

Technical Targets

Hydrogen Sorption Storage Systems

This project focused on the development of advanced hydrogen sorption systems. Importantly a system that contains hydrogen adsorption sites with an optimized binding energy (10-20 kJ/mol) is under investigation such that a system that operates at near ambient temperatures and pressures may be achieved. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

- Cost: \$4/kWh net
- Specific energy: 2 kWh/kg
- Energy density: 1.5 kWh/L
- Charging/Discharging Rate: 3 min for a 5-kg system

Accomplishments

The HSCoE partners worked closely together to systematically accelerate the development of advanced hydrogen sorbent systems that meet the DOE 2010 targets. Representative accomplishments are listed below:

- The HSCoE synthesized and characterized many new, promising hydrogen sorption materials:
 - Duke developed simple methods to prepare microporous carbon materials by the pyrolysis of the polymer polyether ether ether ketone (PEEK), and demonstrated pore diameters smaller than 1 nm could be prepared using organic templates. A series of samples with high surface area ($>3,000 \text{ m}^2/\text{g}$) and high microporosity were prepared. An enhanced binding energy of 8.1 kJ/mol H_2 was demonstrated.
 - ORNL synthesized single-wall nanohorns (SWNHs) with tunable morphologies at scalable production rates (e.g. 10 g/h) and decorated the SWNHs with Pt and Pd nanoparticles with controlled metal loadings between 3 wt% to 20 wt%. Compressed pellets of metal-decorated nanohorns with surface areas of $2,200 \text{ m}^2/\text{g}$ showed significant room temperature storage of $\sim 0.6 \text{ wt\%}$ at 30 bar.
 - Rice (Tour) developed methodologies to disperse, functionalize, and crosslink graphene in solutions by employing the technology they developed for carbon nanotubes (CNTs). Methods to intercalate graphene and CNTs with metals are underway to extend high-density storage to room temperature (RT). Through oleum-free fluorination and crosslinking of CNT fibers, a network of 1.3 nm pore size was

achieved. This is close to the optimum pore size needed for H_2 RT uptake.

- ANL and the University of Chicago synthesized three series of new polymers with surface areas $>1,000 \text{ m}^2/\text{g}$. Gravimetric hydrogen adsorption capacities of 0.4 wt% and 3 wt% were observed at 60 bar for ambient and liquid nitrogen temperatures, respectively.
- PSU (Chung) demonstrated that the incorporation of boron into nanoporous carbon frameworks improves the uptake of nanodispersed metals. This work represents experimental validation for the NREL calculation that boron atoms will stabilize transition metals on carbon surfaces.
- ORNL developed experimental techniques to synthesize homogeneous Ca- decorated SWNHs in order to confirm theoretical predictions of $\sim 8.4 \text{ wt\%}$ with a binding energy of $\sim 30 \text{ kJ/mol H}_2$.
- Rice (Kittrell/Hauge) designed and constructed a direct elemental fluorination reactor for the synthesis of new materials with the ability to add another gas such as boron trifluoride and other strong Lewis acids. Samples can be created and handled without exposure to air.
- LLNL incorporated hydrogen dissociation catalysts (Ni and Pt) into activated carbon aerogel (CA) samples with different surface areas through a metal impregnation process. The Pt-doped CA material with Brunauer-Emmett-Teller (BET) surface area of $\sim 2,400 \text{ m}^2/\text{g}$ exhibited 1.2 wt\% H_2 uptake at room temperature and 100 bar. Hydrogen adsorption measurements were performed by HSCoE member Caltech.
- LLNL also developed novel CA scaffolds containing dispersions of carbon nanotubes and prepared Ca/ LiBH_4 nanocomposites that showed a decrease in hydrogen desorption temperature relative to bulk Ca/ LiBH_4 . Metal hydride incorporation and desorption measurements were performed by Metal Hydride Center of Excellence member HRL Laboratories.
- NREL synthesized five classes of organo-metallic fullerene compounds and evaluated them for hydrogen storage capabilities. Significant insight into the relevant chemical processes for hydrogen storage was ascertained and is employed in both experimental and theoretical methods to explore more tractable reactions. Tractable aromatic systems have been demonstrated as promising for their potential to stabilize molecular hydrogen ligands on a first row transition metal atom.

- APCi developed a method for the controlled temperature programmed desorption of BF_4^- intercalated graphite to produce samples of F/BF_4^- intercalated graphite. Measurement of hydrogen isotherms of mixed F/BF_4^- intercalated graphite shows a high adsorption enthalpy of ca. 12 kJ/mol.
- Texas A&M demonstrated that by tuning the metal alignment in metal organic frameworks (MOFs), the hydrogen binding energy can be increased. When the metal center is exposed, a binding energy of 12.5 kJ/mol is observed for coverage up to 1.7 wt%. A capacity of 3.0 wt% is observed at 77 K and 1 bar with a volumetric density of 24.6 mg/cm³.
- The HSCoE dedicated substantial effort and made progress on spillover:
 - Rice (Yakobson) developed the first thermodynamically consistent model of spillover-chemisorption considering spillover to be similar to the nucleation of a new hydrogenated phase on graphene. Spillover on pristine graphene requires the presence of a hydrogenated phase nucleus after which the spillover process becomes dramatically more favorable.
 - APCi completed a detailed computational model of the well-established, reversible hydrogen spillover process in Pt/MoO₃, and developed a predictive model for H spillover dynamics on carbon which accounts for every step of the H spillover mechanism.
 - NREL prepared spillover materials following the recipes developed at UM (*Y. Li, and R. Yang J. Phys. Chem. C 111 (2007) 11086*). A two-fold increase in hydrogen uptake was confirmed for the activated sample confirming the observation of spillover.
 - NREL also probed the mechanism of the spillover process with Na-reduced sp² hybridized carbons. Approximately 2 wt% reversible storage at RT was demonstrated.
 - PSU (Eklund) developed a hydrogen spillover test bed measurement system, the first with the ability to simultaneously measure optical and transport signatures of spillover within a highly optimized uniform planar exposed geometry.
 - UM devised a simple technique for bridge building and studied the spillover storage of the most promising MOFs. It was found that the heats of adsorption for spillover depend on the metal content of the MOF and that the spillover storage depends on both BET surface area and the heat of adsorption. A capacity of up to 4.0 wt% is observed for isoreticular metal organic framework-8 (IRMOF-8) at RT and 100 bar.
- UM also developed a thermal reduction technique for the metal doping of carbon that significantly increased the spillover storage capacity, and showed that the ambient-temperature desorption rates for spillover hydrogen on both bridged MOFs and metal-doped carbon exceeded the DOE discharge rate target (0.02 g/s/kW). Efforts to improve the slower charging kinetics are underway.
- The HSCoE made several important additional accomplishments in the area of theory and modeling:
 - ORNL theoretically investigated the strong binding of hydrogen on metal-decorated carbons and predicted optimal materials involving alkaline earth metals to avoid clustering and yet provide a dipole-induced polarization and binding of molecular hydrogen.
 - PSU performed first-principles computations and identified several new mechanisms of enhanced hydrogen bonding in the intermediate physical/chemical sorption range, exploiting concepts of zwitter ions and topological frustration.
 - Rice (Yakobson) carried out Grand Canonical Monte Carlo simulations to determine the storage capacity of previously designed 3-dimensional foams. The gravimetric and volumetric capacities of foams are found to surpass the well-separated, equivalent diameter nanotube bundles. At 77 K storage capacities up to 6.5 wt% and 65 kg H₂/m³ are observed.
 - APCi carried out calculations of H₂ physisorption energies for F⁻ anion intercalated graphite.
 - NREL performed theoretical calculations to probe a viable co-intercalation system for hydrogen storage that may be easily synthesized. Notably, the proof-of-concept synthesis was achieved in only two months. This represents a significant step forward and a first time demonstration of the synthesis of a theoretically predicted system.
- The HSCoE developed and applied advanced and new spectroscopic techniques to determine the relationships between material structure and hydrogen storage behavior:
 - NIST determined bulk elemental compositions of materials of interest to the HSCoE using prompt gamma analysis, and employed inelastic neutron scattering methods to determine the location of hydrogen binding sites and the site-specific hydrogen adsorption strength in several different materials. Materials studied include

- metal-decorated carbon-based materials, MOFs, and boron-infused carbon materials.
- Caltech measured the isosteric heat of adsorption for MOF-74 to be in the range from 8.5 to 4 kJ/mol with the initially high value attributable to binding to the coordinatively unsaturated Zn site. The binding energy of 8.5 kJ/mol H₂ is observed for coverage up to about 0.5 wt% with the binding energy decreasing as the capacity increases to 1.5 wt%.
- NIST in collaboration with Caltech determined that MOF-74 material has one of the highest known surface packing densities (SPD) of molecular H₂, in excess of the density found in solid hydrogen, with the closest H₂-H₂ distance (2.85 Å) measured at low pressure. At a high surface packing density of 4.3×10⁻⁵ g/m², a minimum surface area requirement of ≈1,400 m²/g (or ≈2,100 m²/g) is needed for a material that can reach an excess adsorption of 6 wt% (or 9 wt%).
- NREL developed instrumentation to measure pore size distribution using the BET method with H₂ as the molecular probe, and developed new calibration procedures to enable the measurement of ~40 μmoles of H₂ under high-pressure conditions. This and other advances allowed the rate of high-throughput measurement to be accelerated. The pace of measurement has been doubled over FY 2007, with more than 700 measurements performed on external and internal samples in the first eight months of FY 2008.
- UM performed deuterium isotope tracer studies and showed directly that (1) hydrogen atoms are formed in spillover storage and (2) desorption follows a reverse spillover route.
- UNC developed a ¹H nuclear magnetic resonance (NMR) technique to evaluate the porosimetry of materials using H₂ as the probe molecule, and also evaluated boron site symmetry in various boron-doped materials using ¹¹B NMR spectroscopy.
- The operational structure of the HSCoE was enhanced through the implementation of four Research Clusters (RCs): Engineered Nanospace, Doped Materials, Strong Binding of Dihydrogen, and Storage by Spillover.
 - Each RC is co-led by an NREL senior staff member and an HSCoE Steering Committee member.
 - RC “Roadmaps” were developed which are stand-alone, but roll-up to address DOE’s Multi-Year Research, Development, and Deployment Plan.

- RCs group expertise, create focus around central challenges, and permit “separation of variables” approach to this complex problem.
- Advances in individual RCs are additive, and can be combined.
- Partners have a primary home and focus in one cluster, but contribute to other clusters by collaborating across disciplines.



Introduction

The HSCoE is developing on-board reversible sorbent materials for hydrogen storage within the U.S. DOE National Hydrogen Storage Project. The HSCoE is developing the science base and technology advances required to meet DOE goals for on-board storage of hydrogen by conducting applied research on a wide range of nanostructured hydrogen adsorbents. A guiding principle in developing the required material is that a continuum of energies exists for hydrogen bound to substrates and molecules. 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 10-50 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” 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 sorption-based materials if the enthalpy for hydrogen adsorption can be designed to be in an optimal range of 10-20 kJ/mol. Heat removal upon charging 5 kg of material with H₂ adversely impacts system capacity due to the necessity of heat exchangers. Thus the adsorption enthalpy should be the absolute minimum required to store the hydrogen. Figure 1 displays a plot of optimal adsorption enthalpies calculated for adsorption temperatures of 77, 223 and 298 K and plotted for pressures up to 100 bar with a minimum outlet pressure of 1.5 bar. (The entropy changes of -8R and -10R, where R is the gas constant, are based on simulations of adsorption in slit and cylindrical pores and experimental measurements for molecular hydrogen sorption in potassium/graphite intercalation compounds, respectively.) In addition to binding energy it is also necessary to achieve efficient volumetric arrangement of a sufficient number of suitable binding sites with a low-weight material. 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

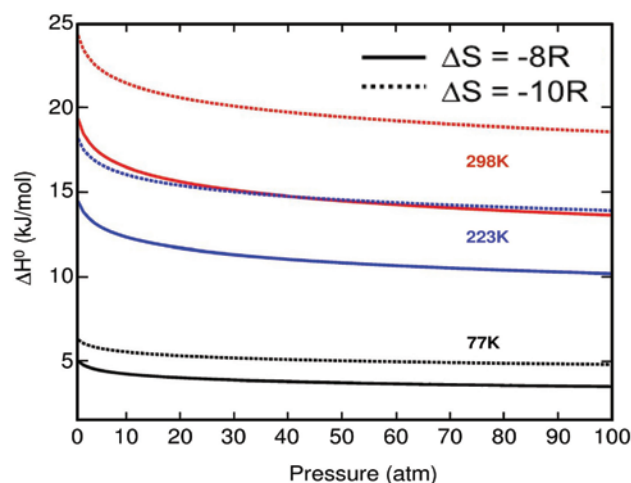


FIGURE 1. Plot of optimized adsorption enthalpies for adsorption temperatures of 77, 223 and 298 K and for pressures up to 100 bar with a minimum outlet pressure of 1.5 bar.

sites, and excessive macroporosity and poor volumetric packing.

Approach

The main goals of the HSCoE are to discover the limits of performance of high surface area adsorbents and to synthesize and test sorbents that will meet the DOE system targets for reversible, on-vehicle hydrogen storage. This involves the design and synthesis of materials that bind large amounts of hydrogen on both a per-weight and a per-volume basis as (i) weakly and reversibly bound atoms and/or (ii) strongly bound molecules. The HSCoE focuses 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 involves determining the affects of geometry, the introduction of defects, adventitious dopants, catalytic species, as well as elemental substitution. The HSCoE currently investigates a wide range of different lightweight nanomaterials and porous frameworks. In addition to the current materials systems being studied, the HSCoE strives to be nimble and flexible to incorporate promising new ideas, materials, and concepts as they arise.

Results

Numerous specific significant results from the FY 2008 HSCoE activities were listed previously. These and others will be discussed in more detail in the Partner-specific portions of this report. Here we highlight notable HSCoE progress in a few different areas.

Synthesis of Advanced Sorbent Materials with Enhanced Hydrogen Binding Energies

In FY 2008 ORNL predicted a new $\text{Ca}_{32}\text{C}_{60}$ compound theoretically having an uptake of ~ 8.4 wt% hydrogen, with a binding energy of ~ 20 -40 kJ/mol that may allow for near ambient adsorption. The strong binding is attributed to an intriguing charge transfer mechanism involving the empty d levels of the metal elements. The charge redistribution, in turn, gives rise to electric fields surrounding the coated fullerenes, which can now function as ideal attractors upon molecular hydrogen adsorption with binding strengths strong enough for potential RT applications but weak enough to avoid H_2 dissociation. Furthermore experimental efforts at ORNL have been made in order to implement this theoretical prediction, and Ca-decorated carbon nanohorns were verified using high-resolution transmission electron microscopy (TEM) and energy dispersive X-ray. Higher resolution TEM images indicate possible interstitial Ca intercalation, as evidenced by interwall spacings of ~ 0.4 nm between the walls of the nanohorns within the aggregates. The proof of concept demonstration of this Ca-decoration will be the basis for the development of Ca-based high-surface area materials with optimized volumetric packing in FY 2009. In future work, the hydrogen adsorption properties of these materials will be probed to assess the agreement with theoretical predictions and determine whether calcium hydride formation is observed.

In FY 2008 NREL has also directly probed new binding mechanisms for hydrogen with enhanced heats of adsorption using wet chemical synthesis techniques. Simple systems based on inexpensive starting materials are explored. For example, the reaction path shown in Figure 2 was designed for wet chemical synthesis of $\text{CpScH}_2(\text{H}_2)_4$. However, solution phase NMR quickly revealed that it was not possible to isolate the Cl-bridged intermediate shown in step 2 of the reaction. Hence this reaction was down-selected and not explored further. A second reaction pathway was developed to make a $\text{C}_9\text{H}_{13}\text{ScH}_2(\text{H}_2)_4$ compound. In this reaction mechanism, the reactive intermediate following a two-step process is $(\text{CH}_3\text{C}_6\text{H}_4\text{NMe}_2)_2\text{ScC}_9\text{H}_{13}$. This reactive intermediate was isolated at high yield and exposed to ~ 2 bar hydrogen in a sealed NMR tube. NMR spectroscopy indicated that the $\text{CH}_3\text{C}_6\text{H}_4\text{NMe}_2$ ligands were dislodged through the carbon linker suggesting that hydrogen is complexing with and/or dissociating on the Sc atom. However, hydrogen bound to the Sc was not detected in the NMR possibly because it was masked by the signal of the H_2 gas. This may represent the synthesis of a compound with a dihydrogen ligand bound to a first row transition metal atom. Scale-up of the synthesis as well as other techniques to detect the hydrogen interacting with the Sc will be the subject of future work. Thus tractable reactions on simple aromatic systems have

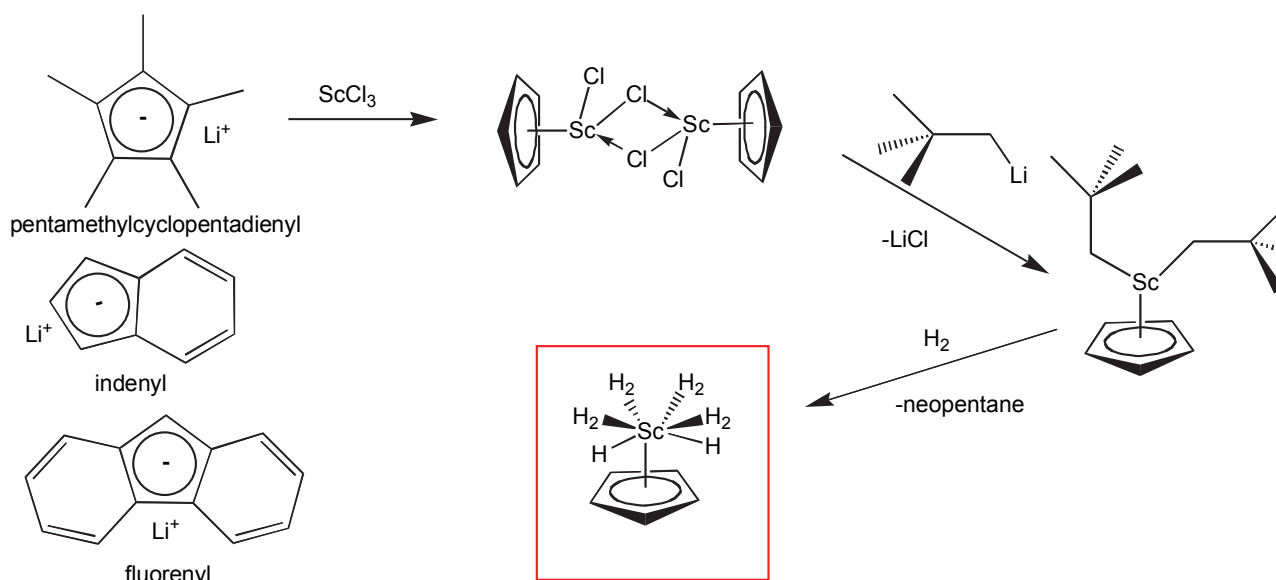


FIGURE 2. Reaction Scheme for Wet Chemical Synthesis of CpScH₂(H₂)₄

been shown promising for the development of on board hydrogen storage materials with moderate binding energies. In FY 2009 theoretical investigations of isolated reaction intermediates will be employed to guide the reactive chemistry.

Finally hydrogen bound with an enhanced binding energy has also been demonstrated for MOFs at Texas A&M. Synthesis routes were developed such that the metal atom had greater surface exposure to the interior open framework of the MOF. Specifically, in PCN-12 the binding energy of H₂ to exposed Cu atoms was measured to be 12.5 kJ/mol. Furthermore this enhanced binding energy was observed to relatively high coverage (~1.7 wt%). At 2 wt% a binding energy of 10 kJ/mol is observed. PCN-12 exhibits 3.0 wt% at 77 K and 1 bar, with a volumetric density of 24.6 mg/cm³. Thus the majority of the hydrogen is stabilized with an enhanced binding energy in the ideal range for vehicular hydrogen storage. Work in FY 2009 will focus both on increasing the total capacity and on increasing the hydrogen bound with an enhanced binding energy.

Advances in the Measurement and Characterization of Hydrogen Sorption Materials

The HSCoE, collectively, made several important advances in the area of hydrogen measurement that have revealed some exciting features of the advanced sorbents that are being developed. These findings underscore the promise of the HSCoE approach and point the way to the development of materials for future, viable, on-vehicle hydrogen storage systems.

NIST performed a collaborative HSCoE study of MOF-74 with Caltech using neutron powder diffraction

and isotherm measurements. They showed that H₂ adsorbed on the MOF-74 with a higher surface packing density at 77 K than is found for solid H₂ at ≈4 K. The results revealed the shortest intermolecular D₂-D₂ distance observed in a physisorption-based material without the application of pressure (Figure 3). At least

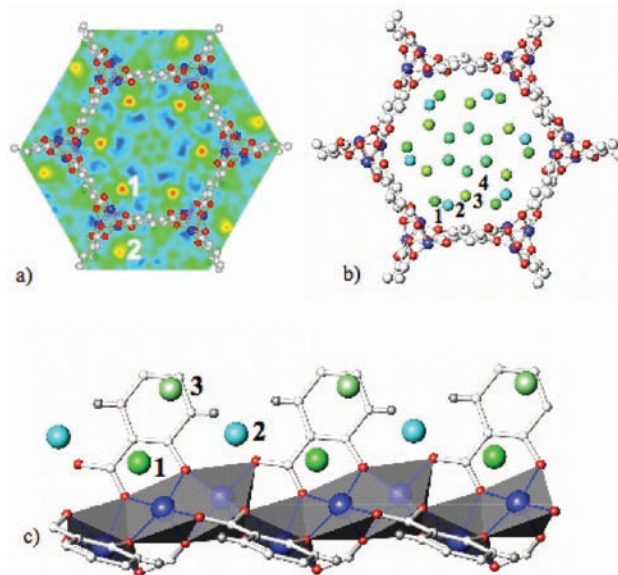


FIGURE 3. D₂ adsorption sites in MOF-74 at a loading of 4:2 D₂:Zn. a) Suppositions of Fourier difference map together with the crystal structure of MOF-74 projected down the *c*-axis. The red-yellow regions indicate the high scattering regions of the first two adsorption sites. b) The four D₂ adsorption sites identified by neutron powder diffraction (labeled 1-4, spheres of green and light blue). c) The first three D₂ adsorption sites are shown with the first site directly interacting with the Zn²⁺ ions (blue balls) at a distance of 2.6 Å.

part of the high density can be attributed to the presence of coordinatively unsaturated Zn^{2+} centers that promote intermolecular deuterium distances of about 2.85 Å at 4 K. This observation, along with results from other systems with coordinatively unsaturated metal centers that exhibit large SPDs, presents an avenue to increase the surface density of adsorbed hydrogen in this class of materials. The low SPD of many carbon materials at technically relevant temperatures has limited their sorption capabilities. For example, if H_2 in MOF-177, (surface area $\approx 4,500 \text{ m}^2/\text{g}$), had a similar hydrogen surface density to that of hydrogen in activated carbons, its excess adsorption would reach $\approx 9.0 \text{ wt}\%$ rather than 7.5 wt% at 77 K. In order to understand how an attractive surface potential decreases the H_2 - H_2 distance and to determine if sorbent-sorbate interactions can significantly increase the SPD beyond that in MOF-74, quantum mechanical calculations on a model system were performed. The combined results of experiment and calculation indicate that the adsorption potentials for a hydrogen molecule in framework structures are large enough to induce a high SPD at 77 K. The SPD of $4.3 \times 10^{-5} \text{ g}/\text{m}^2$ calculated from the model system is roughly the upper limit for the SPD of a physisorption system, which in turn sets a minimum surface area required for a working material based on surface physisorption methods. The estimate indicates a minimum surface area requirement of $\approx 1,400 \text{ m}^2/\text{g}$ (or $\approx 2,100 \text{ m}^2/\text{g}$) for a material that can reach an excess adsorption of 6 wt% (or 9 wt%).

Additionally, UNC has developed an expanded suite of NMR-based techniques for probing the interactions between molecular hydrogen and sorbents. In addition to providing quantitative information on H_2 storage and microscopic insight into the adsorption process, ^1H NMR contributes information on the pore size and pore size distribution of light-weight storage materials. Establishing clear correlations between synthesis, processing, pore structures, and H_2 storage is essential for optimizing the H_2 storage capacity of sorbent materials. Within a sample, H_2 is found in the space between grains of material, designated voids, with dimensions on the order of grain sizes ($\sim \mu\text{m}$) and in the pores that permeate the grains with dimensions that are characteristic of the material, usually in the micropore or mesopore range. Within a pore of width d the local magnetic field sensed by a H_2 molecule strongly depends on the distance between pore surface and molecule (r): $\Delta B_0 \sim (1/r^3 + 1/(d-r)^3)$. The difference in magnetic field translates to a different observed shift in the spectrum. There are basically two different values of shift, δ_{ads} for adsorbed H_2 and δ_{gas} for not adsorbed H_2 as depicted in Figure 4. Because of rapid adsorption and desorption on the NMR timescale, the observed line shift, δ_{obs} , is the weighted average given by relative contributions of adsorbed and free hydrogen making up the H_2 population within the pore:

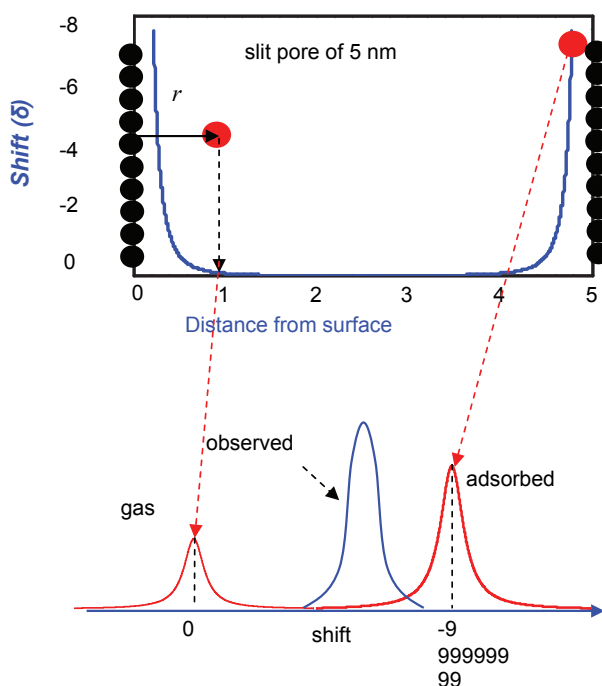


FIGURE 4. Magnetic field distribution within a slit pore and the resulting observed line shift, δ_{obs} , for H_2 rapidly exchanging between wall and pore interior.

$$\delta_{\text{obs}}(P) = \frac{\delta_{\text{gas}} n_{\text{gas}}(P) + \delta_{\text{ads}} n_{\text{ads}}(P)}{n_{\text{gas}}(P) + n_{\text{ads}}(P)} \quad (\text{Equation 1})$$

Since the number of adsorbed (n_{ads}) and not adsorbed (n_{gas}) hydrogen depend on pressure P differently, δ_{obs} depends on P unless one or the other contribution dominates. H_2 in macro pores ($n_{\text{gas}} \gg n_{\text{ads}}$) and H_2 in micropores of width $\sim 1 \text{ nm}$ ($n_{\text{ads}} \gg n_{\text{gas}}$) will produce NMR lines that do not shift with pressure while H_2 in larger micropores and mesopores will show a pressure dependence.

The ^1H NMR techniques were applied to a variety of materials within the HSCoE. Several materials with slit pores of width of approximately 1 nm were readily identified. Such materials show a strongly shifted NMR signal since H_2 is always located near the pore surface: only two H_2 can be fit next to each other between adjacent walls. The observed line shift will not change with pressure. Materials with homogeneous distributions of pores of width around 1 nm are:

- Boron-doped graphitic material (M. Chung; PSU)
- Activated PEEK with short activation times (J. Liu; Duke University)
- CNs with small diameters (D. Geohegan; ORNL)

A preliminary analysis using a Langmuir formalism showed adsorption energy of 6.5 and 8.1 kJ/mol for CN and activated PEEK, respectively. Only CN samples

opened through a mild oxidation procedure show hydrogen adsorption indicating that it is indeed the sample preparation method that creates pores that will adsorb hydrogen.

Advances in Storage by Spillover

Finally, the HSCoE continued to advance spillover technology this year. In addition to the specific accomplishments in theory and experiment listed above, UM studied spillover on various MOFs including COF-1, HKUST-1, MIL-101, MOF-177 and IRMOF-8. An example is shown for MIL-101 in Figure 5. It is seen that the storage capacity for pure MIL-101 was about 0.4 wt% at 100 bar and 298 K. The capacity was nearly doubled by mixing with 10 wt% added catalyst (5 wt% Pt/activated carbon), and it was further increased to 1.5 wt% storage by adding 10% carbon bridges between the MOF and the catalysts. As shown previously, the isotherms for all bridged MOFs were reversible at 298 K. The simple bridge-building technique has been described in previous reports. A capacity of up to 4.0 wt% is observed for IRMOF-8 at RT and 100 bar.

The isosteric heats of adsorption for the bridged MOFs were measured based on the temperature dependence. The heats of adsorption depended on the metal content. COF-1 had no metal and had the lowest heat of adsorption. IRMOF-8 and MOF-177 had the same metal oxide clusters ($[Zn_4O]^{6-}$), while IRMOF-8 had a higher metal content, and showed higher heats of adsorption. The metals were Cr for MIL-101 and Cu for HKUST-1. Thus enhanced binding energies are again linked to structure of the adsorbent.

In order to better understand the spillover mechanism theoretical investigations were performed.

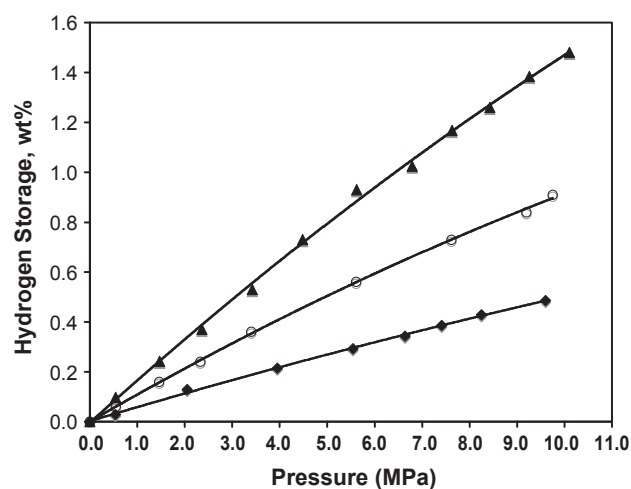


FIGURE 5. H_2 Isotherms at 298 K on MIL-101 bridged with 10% added catalyst (5% Pt/AC): MIL-101 (\blacklozenge); physical mixture of 90% MOF and 10% Pt/AC (\circ); bridged sample with 10% carbon bridges (\blacktriangle).

A predictive model for H spillover dynamics including every stage of the spillover process was developed by APCi. It was shown that the efficiency of hydrogenation of graphitic materials is enhanced by using carbon materials with curved surfaces. Also, Rice studied the activity of the metal catalyst, as an important constituent of spillover process, by calculating the binding energies of H_2 on free as well as graphene-supported Pd_4 clusters. These energies serve as the chemical potential for H, and determine the onset of the spillover. The migration barriers (0.68 eV) for the motion of H from metal cluster to the H-graphene phase were computed. The results show that the presence of a hydrogenated phase of graphene makes the spillover step from metal to receptor thermodynamically favorable. Understanding the underlying spillover mechanisms is of essential importance for the design and development of improved materials that will assist in meeting the DOE hydrogen storage system targets.

Conclusions

- The HSCoE partners worked closely together to systematically accelerate the development of advanced hydrogen sorbent materials. Four RCs were created to provide focus on core research challenges. However activity in the clusters is additive and will be combined to enable the development of a sorption material that meets the DOE system targets.
- The HSCoE developed and applied advanced and new spectroscopic techniques to determine the relationships between material structure and hydrogen storage behavior. Development of these techniques enables systems with higher surface packing densities and desired pore width to be developed.
- The HSCoE dedicated substantial effort and made substantial progress on spillover. Importantly it was shown that the ambient-temperature desorption rates for spillover hydrogen on both bridged MOFs and metal-doped carbon exceeded the DOE discharge rate target (0.02 g/s/kW). Theoretical investigations reveal the spillover mechanism and will enable improved material development in FY 2009.
- The HSCoE synthesized and characterized multiple new, promising hydrogen sorption materials including: microporous carbons with a binding energy of 8.1 kJ/mol H_2 , metal-decorated nanohorns with room temperature storage of ~0.6 wt%, polymers with 3 wt%, carbon aerogels with 1.2 wt% uptake at RT, as well as crosslinked graphine structures, polyaromatic organo-metallic structures with ligands that are dislodged by H_2 , Boron-doped carbons with nanodispersed metals and BF_4^- intercalated graphite materials showing a high binding energy of 12 kJ/mol.

Future Directions

- The gap between theory and experiment will be closed. Iterative, intimate interactions in the HSCoE have already taught theoreticians what is possible experimentally, and *vice versa*. Theoretical work will be focused on providing feed back to calibrate the modeling with observed experimental data.
- The co-intercalation of graphite will continue to be developed as demonstration of the theoretical trend was easily done. Next steps include completing the degree of intercalation, and remove trapped, unneeded solvent species to expose active sites.
- Intercalation of BC₃ will be probed by: introducing intercalating species, such as F and K, into BC₃ to induce both physisorption and chemisorption; enhancing H₂ adsorption kinetics; performing ab initio molecular dynamics simulations and minimum energy path calculations on BC₃-intercalated compounds; and exploring the optimal concentration of intercalating species in both BC₃ and N-doped F- intercalated graphite.
- Organo-metallic structures for strong binding of hydrogen will be studied with more tractable reactions schemes enabling rapid identification of atomic structures as well as non-equilibrium reactive syntheses in gaseous and condensed phase environments to “trap” structures in desired, active configurations.
- Boron-doping and metal decoration of porous carbons produced with zeolite templates, propped graphenes, carbon and non-carbon aerogels will be accelerated. Partners will work to interactively to characterize the structure properties, analyze the optimal pore effect, and investigate the highest potential for H storage through B-doping and metal decoration.
- Efforts in spillover will include: determination of the contributions of bridges and receptor to kinetic limitations; identification of features leading to reproducible sample prep; preparing samples on the multi(tens)-gram scale for system testing; performing very high pressure measurements (>350 bar) to determine saturation capacities.
- Further enhance H₂-MOF interactions by preparing materials with a higher density of coordinatively unsaturated metal centers, improve H₂ uptake at temperatures higher than 77 K by ligand and MOF design, increase MOF thermal stability while maintaining its porosity and increase volumetric performance using denser H₂ packing.
- Take lessons learned through extensive experience with carbon-based materials and extend to determine if other light elements can be used to implement mechanisms more straightforwardly, or if brand new, more desirable approaches may be found.
- The HSCoE will work directly with the National Research Center Demokritos, Greece to validate the spillover material with 8 wt% capacity at room temperature using a volumetric method as well as to assist in new materials development.