

IV.C.1f Enabling Discovery of Materials With a Practical Heat of Hydrogen Adsorption

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Objectives

- Development and testing of new materials with high H₂ storage density and appropriate enthalpy of hydrogen adsorption.
- Development of enabling technologies for H₂ storage materials development.
 - Accurate, predictive computational methodologies for new materials discovery and mechanistic understanding.
 - Characterization tools for accurate H₂ storage measurements.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (C) Efficiency
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is conducting fundamental computational and experimental studies of hydrogen storage in carbon-based materials. 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

Accomplishments

- Porous nitrogen-doped graphite intercalation complexes that show practical H₂ adsorption enthalpies (-20 kJ/mol H₂ at 7.4 wt% H₂ loading) have been identified by predictive computational modeling.
- Synthetic routes to produce the porous nitrogen-doped graphite intercalation complexes have been identified. Nitrogen-doped carbon materials have been prepared by chemical vapor deposition.
- The first complete mechanistic computational modeling study of hydrogen spillover has been initiated.



Introduction

An efficient, cost-effective hydrogen storage system may well be an enabling technology for the widespread introduction of hydrogen fuel cells to the domestic marketplace. Air Products, an industry leader in hydrogen energy products and systems, has recognized this need, and has strategically focused on developing new hydrogen storage technology using novel, reversible H₂-sorbent materials that will be held in suitable robust, light-weight, low-cost containers. We are collaborating with partners in the Hydrogen Sorption Center of Excellence (HSCoE) to identify, synthesize, and test novel materials that exhibit heats of adsorption of hydrogen superior to known materials. This involves predictive computational modeling, materials synthesis, and advanced methods of hydrogen adsorption characterization.

Approach

The project approach is designed to enable and execute discovery of materials with “practical heats” of hydrogen adsorption. These practical heats are hydrogen adsorption enthalpy ranges which allow for the charging and discharging of hydrogen storage materials at near-ambient temperatures and reasonable hydrogen pressures (i.e. 3-100 bar).

Our approach utilizes the development of general quantitative computational models for new materials discovery. The accuracy of these methods is very important in order to realize a more practical overlap between computational and experimental work (e.g. modeling the mechanism of hydrogen spillover). Ultimately, the goal is to translate our predictive computational modeling to development and testing of new H₂ storage materials. Our current, novel hydrogen storage materials development is based upon theoretical predictions of high H₂ storage density and enthalpy for porous nitrogen-doped graphite intercalation complexes. Obtaining the materials for adsorption testing will require exploratory materials syntheses and may require entirely new synthetic strategies.

Once well-characterized samples of the potential hydrogen storage materials have been synthesized, accurate measurement techniques are employed to obtain hydrogen isotherms and heats of adsorption. When needed, advanced techniques such as correction for helium adsorption effects on H₂ isotherms may be employed.

Results

Computational Modeling of Hydrogen Spillover.

Hydrogen storage via hydrogen spillover on metal/carbon hybrid materials remains one of the most promising areas of investigation in the HSCoE (e.g. References 1 and 2; published work by HSCoE partner Professor R. T. Yang). In a collaborative process with other members of the HSCoE, we have begun computational modeling studies towards an ambitious goal - modeling every step of a H₂ spillover process. The spillover of hydrogen on carbon-based materials is proposed to proceed via a mechanism with five basic steps: 1) activation of molecular H₂ on a nanoparticle metal catalyst; 2) sequential formation of metal hydride cluster; 3) spillover of the hydrogen from the metal hydride to an acceptor; 4) migration of hydrogen across the surfaces or within the bulk acceptor material; and 5) a reversible capture of hydrogen at “resting sites” within the material. We report here the results of computational modeling studies for this proposed mechanism.

Supported metal nanoclusters play an important role in many heterogeneous catalytic reactions such as catalytic hydrogenation via hydrogen spillover. To

understand the fundamental mechanism governing the spillover process, we undertook systematic theoretical studies using density functional theory and *ab initio* molecular dynamics. We attempted to address the entire spillover processes theoretically by mapping out the energetics required for hydrogen atoms to migrate onto the graphitic carbon surfaces located in the vicinity of a platinum catalyst subnano particle and subsequently to diffuse to other sites of the materials. To simplify the description of spillover on the graphitic materials, we used a small platinum cluster, Pt₆, to represent the catalyst particle. Our results show that H₂ molecules can undergo sequential dissociative chemisorption of the selected Pt₆ cluster up to a Pt/H ratio of 1:4, at which point the cluster is fully saturated. The on-top sites were identified as the energetically most favorable adsorption sites followed by the bridge sites and then the 3-fold hollow sites. Unlike H₂ dissociative chemisorption on smooth, crystalline Pt surfaces, the reaction on the selected Pt₆ cluster is much more exothermic at a low H coverage with a calculated chemisorption energy nearly twice that on a Pt(111) surface with zero coverage. This underscores the importance of the cluster model since small catalyst nanoparticles used in practice are not smooth; instead, they exhibit sharp corners, steps, defects, vacancies, etc. In fact, it is widely believed that the catalytic activity arises mainly from these surface defects. Under typical catalytic conditions, the Pt cluster is fully saturated with hydrogen atoms. Our calculations have identified the threshold H-desorption energy from the cluster to be approximately 2.4 eV, which is the minimum energy required to pull an H atom out of the fully saturated Pt catalyst. The calculated H₂ dissociative chemisorption energy at full cluster coverage is about 0.9 eV.

In order to study the important step of hydrogen migration across surfaces or within bulk materials, our computational methods were tested using H_xMoO₃ (known in the literature as a “hydrogen bronze”), which is a well-characterized hydrogen-spillover acceptor material [3]. Hydrogen spillover on the MoO₃ (010) surface in the presence of a platinum catalyst was modeled using periodic density functional theory. The migration of H from a saturated Pt₆ cluster to MoO₃ (010) surface was found to undergo a transition from repulsive electrostatic to attractive proton-oxygen interactions. The hydrogen is able to move nearly freely on the surface and diffuse into the bulk lattice at ambient temperatures, leading to the formation of a hydrogen molybdenum bronze, the reversible “resting state” for hydrogen. We show that the high proton mobility is largely attributed to the massive H-bonding network in the MoO₃ lattice.

For the first time, the detailed H_xMoO₃ formation and proton migration mechanisms were unraveled. We show that the H atoms can readily migrate from the Pt catalyst to the MoO₃ (010) surface, followed by

protonation, to form strong, but apparently reversible, covalent bonds with the terminal oxygen atoms. Subsequently, the protons can readily migrate into the lattice via low energy barrier pathways to form hydrogen bronze (Figure 1). Our results suggest that the H adsorption and migration are facilitated by the massive H-bonding network in the lattice and the hydrogen bronze formation can occur at moderate temperatures. The calculated diffusion barriers are in quantitative agreement with the data measured by nuclear magnetic resonance [4,5] and the predicted relative thermodynamic stability of adsorption sites is consistent with experimental observations. The study reveals that H atoms supplied locally by a Pt catalyst can nearly freely flow into the entire lattice, which is precisely the essence of the so called spillover phenomenon. The unraveled spillover mechanisms presented in this study provides useful insight into other hydrogen spillover phenomena, such as spillover onto carbon-based materials for hydrogen storage.

While the mechanism of hydrogen transfer from a hydrided metal cluster to MoO_3 is well understood, the mechanism of transfer to carbon materials is still unclear. In an effort to study potential mechanisms of hydrogen transfer and diffusion on graphene surfaces, a number of computational studies were performed. Direct spillover of hydrogen from the Pt cluster to graphene is only possible with formation of C-H bonds. However, these bound hydrogen atoms are not easily mobile. The studies find that there are high barriers (0.8-1.0 eV) to diffusion of this chemisorbed hydrogen and it is not a viable mechanism for hydrogen diffusion. However, given a H atom source, hydrogen atoms could physisorb on graphite and diffuse on the surface with minimal activation energies. This diffusion

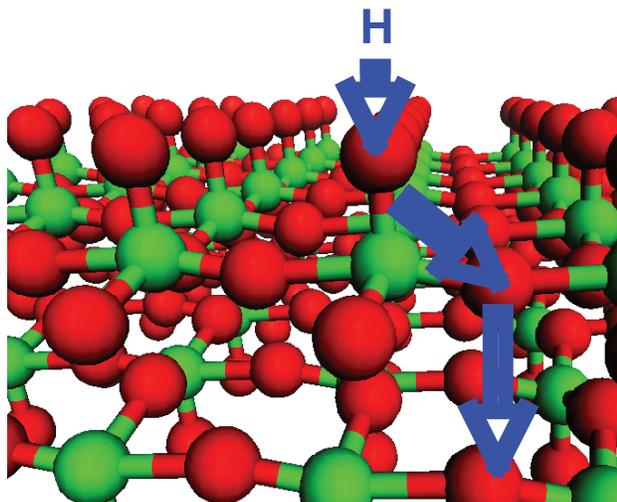


FIGURE 1. Schematic of Calculated Hydrogen Diffusion Pathway in H_xMoO_3 "Hydrogen Bronze" (Oxygen Atoms are Red, Molybdenum Atoms are Green)

of physisorbed atomic hydrogen on graphene could result in the necessary hydrogen mobility to achieve the hydrogen storage observed for spillover materials, but the nature of the ultimate reversible "resting sites" for hydrogen in these carbon materials is an issue for continued studies.

Synthesis and Adsorption Testing of Hydrogen Storage Materials. A general method for lithium doping of graphitic carbon materials would be useful to HSCoE partners because lithium doping is expected to enhance hydrogen adsorption in carbon materials [6]. We have developed a solution-based route to Li-intercalated carbon materials that was tested using single walled carbon nanotubes (SWNT). In tetrahydrofuran (THF) solvent, lithium metal is allowed to react with naphthalene, forming a partially soluble lithium naphthalide salt. Upon addition of the graphitic carbon material, the lithium is transferred to the carbon, forming a lithium graphite intercalation complex. While the method was shown to be efficient at lithium intercalation of the carbon materials, removal of co-intercalated THF solvent from Li intercalated nanotubes was difficult. Suitable thermal activation procedures were developed to remove co-intercalated THF solvent prior to hydrogen adsorption testing. Our hydrogen adsorption testing (Figure 2) found significantly lower H_2 uptake in Li-doped SWNT than previously measured for pure SWNT and we were unable to determine the heat of adsorption of hydrogen on Li-doped SWNT due to the low uptake. Our hypothesis for the lower H_2 uptake in Li-doped SWNT is that the Li^+ ions may be blocking pores in the SWNT and/or occupying substantial micropore volume. This is confirmed by the measurements of micropore volumes of $0.106 \text{ cm}^3/\text{g}$ for a pristine SWNT sample and only $0.0183 \text{ cm}^3/\text{g}$ for a Li-doped SWNT sample. While a detrimental effect of Li

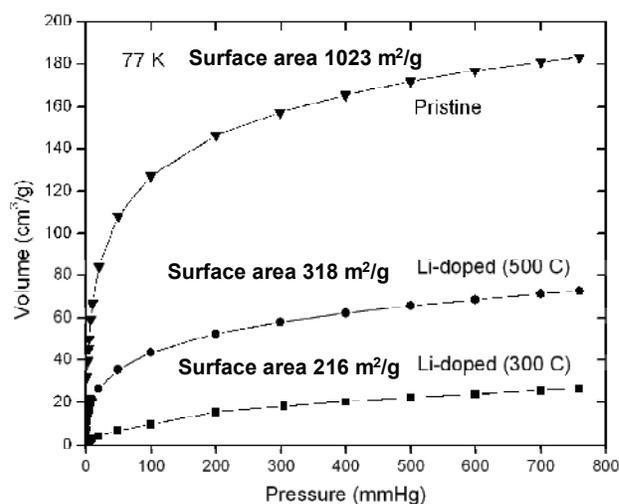


FIGURE 2. Hydrogen isotherms at 77 K of pristine and Li-doped SWNT after thermal activation under vacuum. The surface areas of these samples are shown next to the isotherm data.

doping was observed for SWNT, Li doping may be more effective for carbon-based materials with larger pore sizes (e.g. Rice University “pillared” SWNT currently under investigation within the HSCoE).

A New Concept in H₂ Storage Materials: Nitrogen-doped Graphite Intercalation Compounds. The interaction of molecular hydrogen with ionic materials has the potential for resulting in an effective hydrogen storage with relatively high adsorption enthalpies, even at high hydrogen loadings. Our calculation at 0 K of interactions of H₂ with F⁻ in the gas phase show energies in the range of 25-33 kJ/mol H₂ for ratios of 1-3 H₂/F⁻. Cesium fluoride ion pairs in the gas phase also show strong interactions with molecular hydrogen (16-22 kJ/mol H₂). This finding is consistent with experiments on hydrogen-alkali metal salt interactions as observed by infrared spectroscopy in a matrix at 10 K [7].

Our challenge is to translate the promising gas-phase calculations of strong fluoride-dihydrogen interactions to a condensed-phase material, while retaining high H₂ capacity and appropriate H₂ adsorption enthalpy. Through our predictive computational modeling we have identified a nitrogen-doped graphite intercalation compound of formula (C₆N₂)_n²ⁿ⁺ 2nF⁻ with strong H₂ – F⁻ interactions. To quantify the adsorption energy at hydrogen loadings relevant to meeting the 2010 DOE hydrogen storage system targets, we performed molecular dynamics (MD) simulations at 300 K of 7.4 wt% hydrogen adsorption in porous (C₆N₂)_n²ⁿ⁺ 2nF⁻ (Figure 3). The MD simulation showed several interesting phenomena, including a large lattice expansion upon H₂ adsorption and F⁻ interaction with carbon leading to non-planarity of the nitrogen-doped graphene sheets. A calculated average H₂ adsorption energy of -20 kJ/mol H₂ at 7.4 wt% H₂

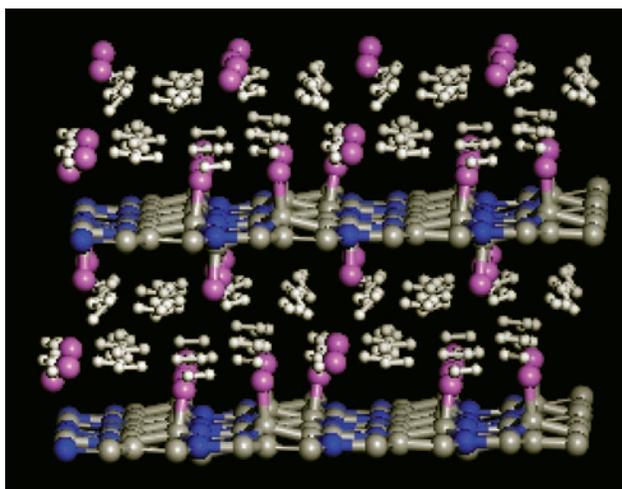


FIGURE 3. Snapshot of the Molecular Dynamics Simulation of 7.4 wt% Hydrogen Adsorption in Porous (C₆N₂)_n²ⁿ⁺ 2nF⁻ (Hydrogen Atoms are White, Fluorine Atoms are Purple, Nitrogen Atoms are Blue, Carbon Atoms are Gray)

loading was determined by the MD simulation. This very high hydrogen adsorption energy from the MD simulation of the solid-state material is important for establishing the viability of reversible hydrogen adsorption at near-ambient temperatures.

Our experimental efforts towards hydrogen adsorption testing of nitrogen-doped graphite intercalation compounds has begun with the synthesis of nitrogen-doped carbons as a starting material for the N-doped graphite fluoride intercalation complex. Using a procedure from the literature [8], nitrogen-doped carbon materials, albeit with still low (<1 atomic %) levels of nitrogen, have been synthesized by chemical vapor deposition from acetonitrile (CH₃CN) on alumina-supported Ni catalyst at 800°C (Figure 4).

Conclusions and Future Directions

- Synthesize fluoride intercalation complexes of cationic nitrogen-doped graphite and measure the hydrogen adsorption properties.
 - Challenge: Incorporation of high levels of nitrogen into graphitic materials. We will collaborate with HSCoE partners to find productive synthesis routes.
- Use our predictive computational modeling capabilities to discover new materials with high hydrogen adsorption capacities and enthalpies.
 - Focus on evaluation of new intercalated anions in N-doped graphite intercalation complexes.
- Continue collaboration with other HSCoE partners on understanding the mechanism of hydrogen storage by spillover and use this knowledge to

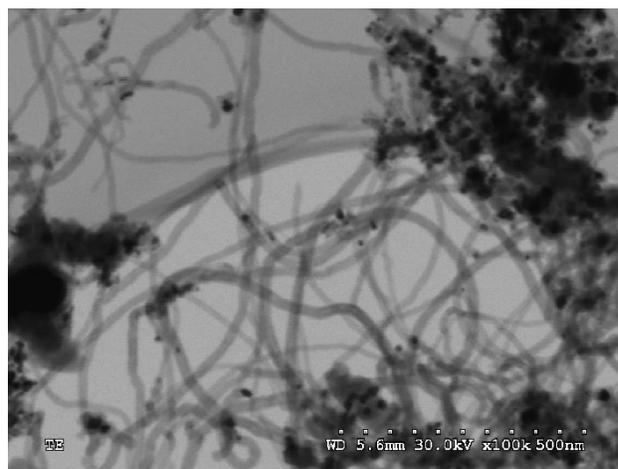


FIGURE 4. Transmission Electron Microscopy of Nitrogen-Doped Carbon Materials Synthesized by Chemical Vapor Deposition of Acetonitrile (CH₃CN) on Alumina-Supported Ni Catalyst at 800°C

increase hydrogen storage densities towards meeting 2010 DOE system-level storage targets.

FY 2007 Publications/Presentations

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2. “Density Functional Study of Sequential H₂ Dissociative Chemisorption on a Pt₆ Cluster”, Liang Chen, Alan C. Cooper, Guido P. Pez, Hansong Cheng; *J. Phys. Chem. C*, **111**, 5514 (2007).
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6. “Mechanistic Understanding of Hydrogen Storage in Carbon-based Materials”; Hansong Cheng, Liang Chen, Alan C. Cooper, Guido P. Pez; 2006 MRS Fall Meeting, November 29, 2006.
7. “Hydrogen Storage: From Carbon Nanotubes to H₂-Reversible Liquid Carriers”; Guido Pez, Alan Cooper, Bernard Toseland; SAE Hydrogen Storage Challenges for Mobility Symposium, December 7, 2006.
8. “A Mechanistic Study of Hydrogen Spillover onto Carbon Based Materials”, Hansong Cheng, invited talk at “Theory Meets Industry” workshop, Vienna, Austria, June 14, 2007.

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