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Hydrogen Sorption Center of Excellence

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Executive Summary

An efficient, cost-effective hydrogen storage system is a key 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, recognized this need and responded to the DOE "Grand Challenge" solicitation (DOE Solicitation DE-PS36-03GO93013) under Category 1 as an industry partner and steering committee member with the National Renewable Energy Laboratory (NREL) in their proposal for a center-of-excellence on Carbon-Based Hydrogen Storage Materials. This center was later renamed the Hydrogen Sorption Center of Excellence (HSCoE). Our proposal, entitled "Designing Microporous Carbons for Hydrogen Storage Systems," envisioned a highly synergistic 5-year program with NREL and other national laboratory and university partners.

The solicitation was directed at developing hydrogen containment concepts for hydrogen-powered vehicles. Our initial model for meeting the storage system requirements was based upon a temperature/pressure swing adsorption (TPSA) system consisting of a lightweight container where H_2 is in equilibrium with a solid, porous sorbent. Our sorbent design was dictated by the primary technical targets, which are the H_2 capacity and hydrogen charge/discharge rates for the system. The most demanding target, gravimetric hydrogen capacity, is inexorably linked to the heat (ΔH) and the entropy (ΔS) of H_2 sorption, which determine the strength and extent of equilibrium binding to the sorbent, and to the volumetric space per unit mass of sorbent that is accessible to hydrogen capture.

From the use of thermodynamic models of hydrogen adsorption on porous adsorbents, it became apparent that no known materials exhibited the requisite heat of adsorption (ca. 15-20 kJ/mol H_2) to allow for a TPSA system that would operate at ambient temperatures and moderate pressures. Therefore, we used predictive computational modeling to evaluate a number of new materials that might demonstrate higher heats of adsorption relative to the 'conventional' hydrogen sorbents (e.g., activated carbons; $\Delta H = 4-6$ kJ/mol H_2). Several candidate materials emerged from these modeling efforts.

Building from our previous experimental and computational studies of hydrogen storage using single-walled carbon nanotubes (SWNT), we initially studied the limits of practical hydrogen storage with SWNT. The main objective of this study was to guide the experimental work within the HSCoE to identify SWNT with the appropriate type (chirality) and size (diameter, aspect ratio) that give rise to the optimal H_2 adsorption energy and maximum capacity. When our computational efforts and the experimental efforts of partners within the HSCoE determined that SWNT would not demonstrate a sufficient heat of adsorption to meet the storage system targets, the use of pure (i.e., non-doped) SWNT was down-selected within the HSCoE.

Using computational modeling, we showed that use of certain 'dopants' in carbon-based materials would increase the heat of adsorption. In this context, the doping process is the introduction of elements or ions other than carbon into the materials. For example, we investigated the effect of introducing lithium ions into the SWNT on the hydrogen capacity of the materials. Our findings showed that doping of SWNT with lithium resulted in a desirable

increase in the heat of adsorption. However, the inclusion of lithium in the material ultimately lowered the space per unit mass of sorbent that was accessible to hydrogen capture, resulting in a minimal increase in the hydrogen capacity of the material.

Another example of "doped" carbon materials that was evaluated are fluoride-graphite intercalation complexes (F-GIC). Graphite was modified by the addition of fluoride ions through an oxidative chemical process. From computational modeling data, the F-GIC was expected to show a substantial increase in the heat of adsorption vs. undoped graphite. In addition, the introduction of ions in the graphite created porosity in the otherwise completely non-porous starting material. We were successful in synthesizing and evaluating a broad range of F-GIC samples. Our results showed that certain F-GIC samples displayed very high heats of adsorption (ca. 12 kJ/mol H₂). However, the porosity that could be generated through introduction of fluoride ions was not sufficient to support high hydrogen capacities.

The substitution of boron atoms into carbon materials is another example of doping that was expected to result in enhanced hydrogen capacity. Our computational modeling studies suggested that boron-doped carbon (e.g., material with the chemical formula BC₃) could spontaneously react with hydrogen to form carbon-hydrogen bonds in a chemical reaction that may be reversible. Unfortunately, the known BC₃ materials are largely non-porous in nature. In collaboration with other HSCoE partners, we developed synthetic routes to boron-containing carbon materials that exhibited substantial porosity. These materials were shown to be promising leads for the development of new hydrogen storage materials.

Within the HSCoE, alternate mechanisms involving the reversible chemical adsorption of hydrogen have been explored for high-density hydrogen storage. We engaged with HSCoE partners in the development of hydrogen spillover processes for hydrogen storage. Hydrogen spillover is a well-known phenomenon in catalysis, but the mechanism of hydrogen storage via spillover is poorly understood. Therefore, we initiated a systematic computational analysis of the complete hydrogen spillover process in an effort to guide the experimental efforts of the HSCoE partners involved in materials development. The first comprehensive model for hydrogen spillover in carbon-based materials was developed and published in a series of eight publications for the larger hydrogen storage community.

Accurate characterization of hydrogen storage materials was a key factor in the success of the HSCoE. Issues such as small sample sizes, inexperience with sorption measurements, and a lack of consensus regarding how to communicate hydrogen measurement results led to the publication of many false and misleading results in the literature by the larger hydrogen storage community. With our recognized experience in adsorption characterization, we engaged in a task dedicated to the development of an accurate technique for high-pressure isotherm measurement (differential pressure adsorption) and a low-cost, high-throughput technique for hydrogen storage material screening (pressure capsule technique). Details on these techniques were published in peer-reviewed journals.

Several broad conclusions can be drawn from the collective output of the HSCoE:

- 1) The HSCoE was successful in the challenge of advancing hydrogen storage materials development. Due to the collaborative model inherent in the HSCoE and the coordination of partners with different technical capabilities and strengths, the output of the HSCoE was almost certainly greater than the sum of the individual projects. A significant number of publications and ongoing collaborations are a tangible sign of the success of the HSCoE.
- 2) While the simplicity of an adsorption-based system would be a significant advantage for practical hydrogen storage, it is unclear whether materials with sufficient properties can be engineered for adsorption-based systems that would operate at ambient temperatures. Operation at ambient temperatures would require materials with a combination of significantly higher heat of adsorption and surface area than have been discovered in this project or disclosed in the literature. Certain materials (e.g., metal-organic framework materials) may be suited to adsorption-based systems that operate at cryogenic temperatures.
- 3) Several promising mechanisms for hydrogen storage emerged from the HSCoE and could benefit from additional development. For example, hydrogen spillover materials show potential for reversible, high-density hydrogen storage at ambient temperatures and moderate hydrogen pressures. More fundamental research on the hydrogen spillover mechanism and maximization of the capacity and reversibility of the process will be needed to realize the full potential.

CHAPTER 1

Introduction

Project Background

An efficient, cost-effective hydrogen storage system is a key 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, recognized this need and strategically focused on developing new hydrogen storage technology using novel reversible H₂-sorbent materials that would be suitable for containment in robust, light-weight, low-cost containers.

Reversible metal hydrides have long been studied as reversible H₂-sorbent materials, but with the possible exception of the recently developed complex hydrides (e.g., Alanates), they all suffer from a limited gravimetric capacity. Microporous, activated carbons can reversibly adsorb large quantities of hydrogen, but only at cryogenic temperatures. Carbons are inherently much lighter materials with the potential of a high hydrogen sorption capacity, but unfortunately the H₂-carbon interaction energy (heat of adsorption (ΔH) of approximately -4 kJ/mol H₂) is far too small for a significant capture of the gas at ambient conditions. In a seminal paper¹, Dillon, Heben *et al.* reported a remarkable room temperature adsorption of H₂ on a single-walled carbon nanotube (SWNT) containing material with a ΔH of about -20 kJ/mol H₂. While the associated claim of 5-10 wt.% capacity for the very minor SWNT component stimulated a great deal of research initiating the new and somewhat controversial²⁻⁵ field of H₂ storage with carbons, we were intrigued by the careful experimental determination of an unusual ΔH for the adsorption of hydrogen.

We therefore responded to the DOE "Grand Challenge" Solicitation (DOE Solicitation DE-PS36-03GO93013) under Category 1 as an industry partner and steering committee member with the National Renewable Energy Laboratory (NREL) in their proposal for a center-of-excellence on "Carbon-Based Hydrogen Storage Materials." Our proposal, entitled "Designing Microporous Carbons for Hydrogen Storage Systems," envisioned a highly synergistic 5-year program with NREL and other national laboratory and university partners in which the Phase 1, 3-year deliverable was a proof of feasibility of a hydrogen storage concept using a carbon-based material, and the Phase 2 objective was a 1 kg H₂ storage system prototype.

The Solicitation was directed at developing hydrogen containment concepts for fuel cell and hydrogen vehicles. From a H₂ sorbent material design perspective, the most significant technical targets for the FreedomCAR storage and delivery system for the year 2010 were a 6 wt % gravimetric and 45.6 g/L volumetric system hydrogen capacity and a rapid refilling rate of 1.5 kg H₂/min. The specified maximum H₂ delivery temperature of 85°C was assumed to be available for releasing hydrogen at the specified rate (0.2 g/sec/kW) from a containment tank. Also specified was an aggressive total storage system cost target of ~\$8/kg.

Technical Summary of the Project Objectives

Our initial model for meeting the FreedomCAR storage system requirements was based upon a temperature/pressure swing (TPSA) adsorption⁶ H₂ storage system consisting of a lightweight container where H₂ at some pressure is in equilibrium with a solid porous sorbent, in this case a carbon-based microporous solid. Associated with this "tank" are pressure and gas flow measurement and control devices for delivering the H₂ to the fuel cell or IC engine, and a capability of heating and cooling the system. The required capacity targets for delivered H₂ (not simply the contained gas) are achieved by a containment of the gas in a bound, yet labile state by the sorbent. This ideally made possible the achievement of both the gravimetric and volumetric goals, but with greater safety margins because of 1) the much lower H₂ pressures than conventional compressed hydrogen storage, and 2) the heat transfer-limited, self-retarding H₂ desorption kinetics in the event of an unwanted release of the contained hydrogen. The design, discovery, and development of the enabling hydrogen sorbent material constituted the major effort of Phase 1 of the research in this project.

Sorbent Hydrogen Capacity

Our sorbent design was dictated by the primary technical targets, which are the H₂ capacity and hydrogen charge/discharge rates for the system. The most demanding, gravimetric hydrogen capacity is inexorably linked to the heat (ΔH) and the entropy (ΔS) of H₂ sorption, which determine the strength and extent of equilibrium binding to the sorbent, and to the volumetric space per unit mass of sorbent that is accessible to hydrogen capture. The sorbent (S) and H₂ equilibrium is expressed as:

The terms in square brackets represent the concentration of H₂-bound $[S \cdot H_2]$ and of empty "sites" $[S]$ of the sorbent at a given pressure of hydrogen, P_{H_2} . The equilibrium constant K is related to the Gibbs free energy (ΔG), heat (ΔH), and entropy (ΔS) of sorption by the familiar thermodynamic relationship: $\Delta G = -RT \ln K = \Delta H - T \Delta S$. It is assumed that the envisaged reversible H₂/sorbent interaction can be represented by a simple Langmuir isotherm model⁷, where the heat of sorption is independent of the extent of H₂ binding:

$$[S \cdot H_2] = K[S_T]P_{H_2} / (1 + KP_{H_2})$$

(where $S_T = [S \cdot H_2] + [S]$ represents the maximum gravimetric H₂ capacity of the sorbent).

The Langmuir model permits us to quantitatively (as a first pass) visualize an H₂ sorption/desorption cycle, tank filling and emptying within the DOE/FreedomCAR specified range of operating conditions. Assume a H₂ sorption equilibrium where the maximum H₂ loading (Gibbs excess adsorption, *vide infra*) at very high pressures is 10 wt % in the sorbent and that 80% of this loading is achieved at 20°C and 50 atm of hydrogen overpressure. This results in the upper (20°C) curve in Figure 1-1, for which $K = 0.19 \text{ atm}^{-1}$. We have no *a priori* knowledge of the entropy of adsorption, ΔS , which is needed for arriving at some estimate of the heat. However,

some experimental guidance was available from the reversible physisorption of H_2 at cryogenic temperatures (77 K to 90 K) by the potassium-graphite intercalation compound for which Watanabe *et al.*⁸ report a ΔH of -9.5 kJ/mol H_2 and a ΔS of -85 J/mol $\cdot$ K; this represents the loss of most of the translational component (118 J/mol $\cdot$ K) of the entropy of H_2 . Our molecular dynamics computational model⁹ of H_2 intercalated along with K in $C_{24}K\cdot 2H_2$ provided a picture of a highly mobile layer of fluxional K atoms and H_2 molecules between the sheets of graphite. The ideal adsorbent we were visualizing, where the H_2 is more strongly held, should display a ΔS of sorption that is somewhat larger than that for $C_{24}K$. Assuming a ΔS of -105 J/mol $\cdot$ K for our model H_2 sorbent leads to a ΔH of -25 kJ/mol H_2 (using the equations shown above). From the assumed entropy, we calculate the isotherm for an 80°C temperature, which is shown as the lower curve in Figure 1. At 3 atm (the specified desorption pressure) and 80°C , 0.44 wt % H_2 remains in the sorbent; the tank can thus deliver 7.56 wt % hydrogen *vis-à-vis* the weight of sorbent at the stated TPSA process conditions. This leaves a sufficient allowance for the weight of the container (26% of the weight of the sorbent) for possibly meeting the previous target for 2010 total system hydrogen capacity of 6 wt % (deliverable).

Figure 1-1. Simulated isotherms derived from the Langmuir model.

Alternatively, a purely pressure-swing process where the sorbent remains at $\sim 20^\circ\text{C}$ during desorption (with heat supplied from the fuel cell) could be used to store hydrogen. To arrive at the same 7.56 wt % delivered hydrogen would require bringing the system to a residual pressure of 0.24 atmospheres. H_2 would then have to be compressed to the required delivery pressure. The obvious drawbacks of this concept are the required extra equipment (e.g., compressor) and the potential safety concern of having the tank at sub-atmospheric pressure.

Thus far in this discussion, the hydrogen loading has been expressed only in terms of the Gibbs excess adsorption capacity. This is defined as the amount of gas contained by the system that is in excess of what would be present in the absence of the adsorptive surface.¹⁰ In practice, the determination of excess adsorption requires a knowledge of the skeletal density (d_s) of the porous sorbent. This is usually obtained by helium pycnometry with the assumption that there is no He adsorption. The bulk or maximum packing density of the sorbent in the tank, d_b will be somewhat lower, leaving a volume/per unit mass, $V_s = 1/d_b - 1/d_s$ which could be occupied by non-adsorbed H_2 at the system pressure. This quantity is additive to the Gibbs excess loading, and while difficult to predict precisely, it can be measured gravimetrically for the total (tank + sorbent + H_2) system for a given H_2 equilibrium pressure.

The volumetric hydrogen capacity (g H_2 /l) of the tank with sorbent will be the total Gibbs excess loading for the packed sorbent, plus the free hydrogen mass, per unit volume of the container. For a carbon with $d_s=1.2$ g/cc (as is reasonable for graphitic carbons), a total (Gibbs+"free") H_2 capacity of 8 wt % ($\text{H}_2/\text{C}+\text{H}_2$) as a packed bed with $d_b=1.0$ g/cc would leave a 23% void volume for accommodating the gas and container material volume and a volumetric H_2 capacity of 80 g/l.

Hydrogen Loading and Unloading Kinetics

A second significant hurdle was achieving the DOE 2010 target refueling rate of 1.5 kg H_2 /min. deliverable hydrogen. For the ΔH of adsorption of approximately -25 to -30 kJ/mol H_2 , this almost requires a capture of the gas by a strong physisorption mechanism, i.e., where the H-H bond may be slightly lengthened, but essentially remains intact. This H_2 uptake is expected to have little or no activation energy and is likely to be diffusion limited (ΔE diff. ~ 16 -40 kJ/mole). Activation energies for chemisorption, where the H-H bond is ruptured and there are accompanying significant structural changes, will be higher (ΔE of 65–150 kJ/mol H_2). Chemisorptive processes are thus likely to be slower, but their potential utilization was not excluded, particularly if all the H_2 desorption takes place at 80°C or higher. Note also that the physisorption processes being the less disruptive at the molecular level are the more likely to meet the specified (1000, $\frac{1}{4}$ tank to full) cycle life.

For both the "strong physisorption" or "weak chemisorption" models in the absence of engineering controls, the H_2 refueling time will be limited by the heat-transfer kinetics; this is the rate at which the approximately -25 kJ that is generated per mole of sorbed hydrogen, corresponding at a 7.54 wt % available H_2 delivery to ~ 925 kJ/kg of sorbent, is discharged from the storage tank. The very considerable ($>200^\circ\text{C}$) temperature rise under adiabatic conditions

would greatly inhibit the sorption of H_2 , and a rapid transfer of heat from the bed will be essential.

A schematic representation of the heat management system of a FC vehicle is shown in Figure 1-2. The fueling is done with a multiple-duty supply "hose," which delivers not only pressurized H_2 (at 50 atm. in our model), but also a two-way flow of a suitable heat-transfer fluid. Charging our model tank with 4 kg of H_2 , deemed sufficient for a 300-400 mile trip with a compact FC vehicle¹¹, would require coping with 50,000 kJ of released heat of sorption and up to 400-1200 kJ of sensible heat. While this total is not large, dealing with it during the desired <3 min. refueling time presents a high heat removal rate issue that will have to be addressed by appropriate engineering.

Figure 1-2. Schematic of heat flows within the hydrogen storage system.

The storage tank has to be designed with the means to efficiently transfer this cooling capacity to the sorbent during refueling and to transfer a portion of the waste heat from the FC to the sorbent bed when the FC becomes operational. Designs and models for efficient heat transfer have been devised for metal hydride H₂-storage beds.¹² For some carbon materials, a mitigating factor is their high thermal conductivity. Aligned bundles of SWNT display a thermal conductivity of >200 W/m·K¹³ compared to the in-plane thermal conductivity of graphite (19.5 W/m·K) and copper (4.01 W/m·K) at 300 K.

For vehicle operation, a minimum specified full-flow rate of 0.02 g/sec/kW for 50 kW FC would require an input to the sorbent bed of ~750 kJ/minute, far less than the cooling duty during refueling. This input could be supplied from PEM fuel cell waste heat, which at 50% efficiency for an H₂ lower heating value of 245 kJ/mol H₂ would provide an ample 122 kJ/mole H₂ *vis-à-vis* approximately 25 kJ/mol H₂ required for H₂ desorption, as long as the FC is at a higher operating temperature than the tank. The storage system would thus actually lighten the load of the fuel cell radiator (Figure 2).

Materials Development Background

With the engineering limitations and DOE storage system goals in mind, we sought to develop materials that demonstrated potential for reaching hydrogen capacity and thermodynamics that could enable reversible, high-density hydrogen storage.

Building from our previous experimental and computational studies of hydrogen storage using SWNT, we initially studied the limits of practical hydrogen storage with carbon nanotubes. The main objective of this study was to guide the experimental work within the HSCoE to identify SWNT with the appropriate type (chirality) and size (diameter, aspect ratio) that give rise to the optimal H₂ adsorption energy and maximum capacity. There were at least five fundamental questions that needed to be addressed: (1) For a given H₂ loading and a nanotube type, what is the H₂ distribution in the nanotube bundle? (2) For a given nanotube type, what is the optimal loading, balancing capacity and adsorption energy? (3) What is the appropriate diameter range of nanotubes at which H₂ adsorption is most energetically favorable? (4) What chiral type of SWNT gives the highest H₂ adsorption energies? (5) What are the adsorption isotherm and H₂ diffusion coefficient for a given nanotube?

At the time of the project start, we had recently developed atom-atom potential functions that are explicitly curvature-dependent.¹⁴ These functions were derived based on the existing force fields for inter-atomic potential functions for carbon atoms with sp² and sp³ hybridizations, which have been developed using either experimental or high-level *ab initio* results. Although the basic idea is applicable to both bonding and non-bonding interactions, the curvature effect has the most pronounced influence on the physisorption energies via the non-bonding interactions, which was the main focus of our study. Following convention, we describe the non-bonding forces with the Lennard-Jones (L-J) potential. However, the L-J parameters σ and ϵ are made explicitly dependent on the radius of the nanotube, r , using the following equations:

$$\sigma(r) = f(r)\sigma_{sp^2} + [1 - f(r)]\sigma_{sp^3} \quad (1)$$

$$\varepsilon(r) = \begin{cases} f(r)\varepsilon_{sp^2} + [1 - f(r)]\varepsilon_{sp^3}^{head-on} & \text{exohedral} \\ f(r)\varepsilon_{sp^2} - [1 - f(r)]\varepsilon_{sp^3}^{side-on} & \text{endohedral} \end{cases} \quad (2)$$

where $f(r) = \left(1 - \frac{r_0}{r}\right)^\lambda$ and r_0 is a reference constant. It is obvious from Equations (1) and (2) that the non-bonding interactions in a nanotube with a large radius are similar to those in a graphite sheet, while these forces can be substantially enhanced in small radius nanotubes. This novel force field allowed us to include a large number of atoms (~1,000-100,000) in the unit cell with a long time scale for molecular dynamics (MD) or a large sampling space for Monte Carlo simulations.

Using the curvature-dependent force field, we carried out extensive MD simulations for H₂ adsorption in SWNT, selecting 3 armchair nanotubes with diameters ranging from 4 Å to 12 Å, 3 zigzag nanotubes with diameters similar to the armchair examples and 1 chiral nanotube (8.28 Å). We focused mainly on H₂ uptake of 0.4 wt %, 3.0 wt % and 6.5 wt % for each of the nanotubes included in our study. In each case, we first determined the optimal H₂ distribution in the lattice that gives the lowest energy among the possible distributions.

Table 1-1. The calculated optimal distribution of H₂ and the average adsorption energy (kJ/mol) per H₂. The uncertainty with the averaged adsorption energy is approximately ± 2 kJ/mol.

nanotube	d(Å)	0.4 wt %		3.0 wt %		6.5 wt %	
		endo/exo ratio	ΔE_{ad}	endo/exo ratio	ΔE_{ad}	endo/exo ratio	ΔE_{ad}
(3,3)	4.068	0:100	23.9	0:100	20.6	0:100	15.5
(5,5)	6.780	0:100	21.4	20:80	10.0	30:70	7.1
(9,9)	12.204	0:100	16.0	40:60	5.9	50:50	4.6
(5,0)	3.914	0:100	22.3	0:100	21.4	0:100	11.8
(10,0)	7.828	0:100	20.2	20:80	8.8	30:70	3.8
(15,0)	11.743	0:100	13.9	30:70	4.6	50:50	2.5
(8,4)	8.285	0:100	18.1	20:80	8.0	30:70	2.5

From Table 1-1, it is important to note that H₂ adsorption becomes increasingly favorable at the exohedral site as the tube diameter decreases. In addition, at low H₂ loading for all nanotubes, the molecular adsorption is exclusively in favor of the exohedral site, in good agreement with published experimental results.¹⁵

Brief Technical Summary of the Project Achievements

Our computational modeling of hydrogen adsorption in SWNT, detailed in Chapter 2, ultimately led to the conclusion that “pure” SWNT could never achieve the hydrogen capacity and thermodynamics necessary to meet the DOE storage system targets. Therefore, we developed a concept to increase the heat of adsorption of hydrogen on SWNT by intercalation of lithium in the nanotube bundles. This intercalation was found to increase the electron density of the nanotubes by charge transfer, ultimately leading to higher heats of adsorption (Chapter 2). However, the lithium cations in the intercalated SWNT bundles also occupied valuable pore volume, leading to decreased hydrogen capacity relative to undoped SWNT.

Our materials development task evolved over the course of the project period to study the adsorption of hydrogen with materials containing Lewis acids. In Chapter 3, we detail the predictive computational modeling and experimental synthesis and testing of carbon materials containing “naked” fluoride anions. Our preliminary gas-phase calculations and calculations of solid-state, periodic materials such as graphite fluoride suggested very high heats of adsorption of hydrogen were possible due to charge transfer from the fluoride anion to molecular hydrogen. While there was good evidence for synthesis of the desired hydrogen adsorbents, the experimental heats of adsorption were found to be substantially lower than predicted by the computational modeling. This appears to be due to lower charge density of the “semi-ionic” fluoride anions in the experimental materials.

A computational study in the literature¹⁶, in addition to the activities of several partners in the HSCoE (NREL, Penn State University), led us to collaborate on the synthesis and testing of boron-containing carbons as hydrogen adsorbents. The inclusion of boron in graphitic materials can be considered to generate Lewis acidity that was suggested to increase the heat of adsorption of hydrogen and even lead to hydrogen dissociation. Our initial studies used computational models that extended the literature study to known materials such as BC_3 . Our results (Chapter 4) showed that hydrogen would dissociate within the layers of BC_3 and that the relatively weak C-H bonds could be labile at moderate temperatures. In collaboration with HSCoE partners, we developed strategies to increase the surface area of boron-containing carbons using a modified templating method.

Throughout the duration of the project, we collaborated with HSCoE partners at the University of Michigan (R. Yang), NREL, and Rice University (B. Yakobson) to develop models for the storage of hydrogen via hydrogen spillover. These models provided valuable insight to the materials developers to increase the capacity of the hydrogen adsorbents and optimize the charging and discharging kinetics. In Chapter 5, we detail the first comprehensive study of hydrogen spillover on carbon-based materials. The initial studies used a well-known metal oxide spillover receptor, MoO_3 , to test the computational models.

Another important task within the project was the development and use of advanced techniques to accurately measure the hydrogen capacity of storage materials (Chapter 6). Prior to the start of the project, Air Products had designed and constructed a unique differential pressure adsorption unit (DPAU) in our laboratories in Allentown, PA. This fully automated instrument demonstrated many advantages over the absolute pressure volumetric adsorption equipment

commonly used for measurement of hydrogen adsorption. The design (shown in Figure 1-3) elaborated on a basic concept, as described by Browning *et al.*¹⁷, involving the use of a set of identical adsorption volumes that are used to quantify adsorption through the measurement of differential pressure.

Figure 1-3. Schematic of the Differential Pressure Adsorption Unit (DPAU).

In Chapter 6, we also detail the development a new, practical method for the measurement of hydrogen adsorption. This static adsorption technique had been successfully demonstrated for the adsorption of gases and vapors on sorbents at high pressures.¹⁸ Unlike other gravimetric techniques, where the mass of the sample is monitored from inside a pressurized vessel, with the static sorption technique the entire pressure vessel is weighed before and after the experiment to determine the amount of gas uptake. This technique allowed adsorption measurements to be conducted at high pressures at lower cost and with less complexity than other methods.

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CHAPTER 2

Computational and Experimental Studies of Hydrogen Adsorption on Carbon Nanotube Materials

Introduction

Molecular physisorption is an important surface phenomenon arising from van der Waals forces. A physisorbed molecule may adsorb statically to a specific adsorption site, move dynamically between adsorption sites, or desorb from the surface in equilibrium with a reservoir of gaseous molecules. In all cases, the adsorption strength is usually characterized by an average enthalpy (heat) of adsorption, where the average is over all of the particles interacting with the surface. However, this average heat does not fully characterize the specific adsorbate/substrate interactions, since for each particle of a molecular assembly the adsorption strength is dependent on the distance of the molecule from the adsorption sites and the local environment. Individual molecules located far from adsorption sites on surfaces contribute only negligibly to the total adsorption energy and ought to be excluded in the energy average if a desired output of the simulation is the strength of adsorbate/substrate interactions. To more precisely describe the physisorption phenomenon, we devised a novel methodology that allows simultaneous determination of adsorption strength and effective adsorption population (i.e., surface coverage) of a molecular adsorbate in proximity to the substrate surfaces. To demonstrate the concept, this procedure was applied to the physisorption of H_2 molecules in a finite bundle of single-walled carbon nanotubes (SWNT). We show that at a given H_2 loading, a heat of adsorption can be averaged according to the distance of gaseous H_2 from the SWNT surface. This simple procedure is readily applicable to other physisorption systems, providing a new way of characterizing relative strength of physisorption for molecules on surfaces.

Hydrogen adsorption in SWNT has been a subject of considerable interest, both experimentally and theoretically since SWNT was first reported as a promising hydrogen storage material by adsorption of a large amount of H_2 .¹⁻⁶ SWNT differs from graphite in that its carbon atoms adopt a quasi- sp^2 hybridization arising from curvature. As a consequence, the exohedral interaction of H_2 with SWNT is significantly stronger than with graphite, which was shown to have a heat of adsorption of ca. 4 kJ/mol H_2 at 77 K.⁷ To more accurately describe the interaction between H_2 and SWNT, we previously developed a curvature-dependent force field, based on quantum mechanical calculations, that allows large-scale molecular dynamics (MD) simulations in a canonical ensemble. This novel force field is applied in the present work of using constant-NVT MD to study H_2 physisorption in a finite bundle of SWNT.

Shi and Johnson have performed simulations of adsorption of CH_4 , Ar and Xe onto both homogeneous and inhomogeneous SWNT bundles and showed that the calculated isosteric heats of adsorption in the inhomogeneous, but not homogeneous, bundles are in good agreement with the experimental data.⁸ That study suggests that the packing inhomogeneity of SWNT plays an important role in adsorbing gas molecules due to the enhanced volume and pore size of the interstitial channels between SWNT. A larger interstitial pore size certainly

should give rise to better accessibility and diffusion of the gas molecules. However, additional porosity does not necessarily translate into higher adsorption capacity, since the magnitude of adsorption is dictated largely by the strength of the interaction between the adsorbed molecules and SWNT. A fundamental question concerning the effectiveness of adsorption thus arises: for a given packing of SWNT and a molecular loading, what percentage of gas molecules are effectively adsorbed? Intuitively, the closer the molecules get to the nanotube walls, the more these molecules “feel” the attractiveness/repulsiveness of SWNT. Therefore, molecular adsorption is a distance-dependent phenomenon. To address this issue, we devised a computational procedure that allows calculations of effective adsorption energy for molecular physisorption for a given loading of gas molecules. This procedure was utilized in the present molecular dynamics (MD) simulation study of H₂ adsorption in finite SWNT bundles. Following Shi and Johnson, we also studied adsorption in both homogeneous and inhomogeneous SWNT bundles.

Typically, SWNT are fabricated with a diameter ranging from 5 to 30 Å^{9,10}, of which the majority have a radius of ~ 10 Å^{11,12}. In an ideal bundle, homogeneous nanotubes are held together by van der Waals forces with hexagonal packing similar to the shape of a honeycomb. The packing scheme of an inhomogeneous bundle is more complicated, depending on the maximum of cohesive energies. These energies are derived from the intertube interactions, which are in principle size-dependent.¹³ Upon adsorption of gas molecules, the nanotube packing of both homogeneous and inhomogeneous bundles is also subject to change.¹⁴ In the present study, we first performed energy minimization for the selected SWNT bundles by running MD simulation at 0 K for 10 ps. Subsequently, we loaded 6.5 wt % H₂ in the optimized structure of SWNT bundles followed by additional energy minimization. We then performed MD simulations at near-ambient temperature to study the adsorption dynamics and energetics. We showed that both nanotube packing inhomogeneity and thickness have a significant effect on the H₂ adsorption strength and that the effective adsorption capacity of the nanotube bundles can be estimated based on the dynamic adsorption patterns.

It is also possible to increase the heat of adsorption of H₂ on carbon-based materials such as SWNT by alkali metal doping. This is illustrated by a second stage graphite intercalation complex, KC₂₄, which reversibly adsorbs ~1.2 wt % H₂ at 77 K with an isosteric heat of ~8 kJ/mol. The intercalated layers of KC₂₄ show an increase in the interlayer spacing (from 3.35 Å to 5.35 Å), which allows H₂ molecules (kinetic diameter 2.89 Å) to access the interlayer spaces. The increased isosteric heat of adsorption exhibited by KC₂₄ is ascribed to the strongly polarizing electric field that is generated by charge transfer from intercalated potassium to the graphene. It begets the question of whether this enhanced heat of adsorption on alkali metal intercalated graphite could be reflected in alkali metal intercalated nanotubes. Recent theoretical calculations predicted that the hydrogen physisorption binding energies on Li doped graphene and Li doped nanotubes should be about twice that of its undoped counterpart.¹⁵ It has been suggested that a practical adsorbent storing and discharging H₂ at near-ambient temperatures and moderate pressures would require a heat of adsorption of approximately 15 kJ/mol.¹⁶

In this chapter, we report the intercalation of SWNT samples using lithium naphthalide in 2-methyltetrahydrofuran (MeTHF) and the effects of Li intercalation on the isosteric heat of H₂ adsorption and the H₂ storage capacity. This solution-based method for lithium doping of carbon nanotubes using organic radical anions in ether solvents was previously reported by Petit et al.¹⁷ and was selected for the simplicity (all synthetic steps were performed using standard glassware at room temperature) and straightforward isolation of the product. The solvent MeTHF was used instead of the more common tetrahydrofuran, since it exhibits a lower tendency to co-intercalate with the lithium cation.¹⁸

Computational and Experimental Methods

Molecular dynamics (MD) simulations were performed using a modified version of the AIREBO code. The AIREBO potential¹⁹ is based on the REBO potential developed by Brenner²⁰, and has been used to simulate many hydrocarbon systems where non-bonding interactions are important.^{20,21} In the AIREBO potential, a Lennard-Jones (L-J) 12-6 potential is used to calculate intermolecular interactions. Of particular importance in the potential parameters is the ability to account for the curvature effect of SWNT by simply modifying the Lennard-Jones parameters for carbon-carbon and carbon-hydrogen interactions. The curvature-dependent parameters enable classical simulations to deal with a variety of nanotubes, with diameter-dependent interaction strengths.

A finite bundle of SWNT was created containing 3, 4, or 7 tubes. The homogeneous bundle consists of only (9,9) nanotubes. The inhomogeneous bundles are packed in the following fashion. A 3-tube inhomogeneous bundle consists of hexagonally packed (7,7), (9,9) and (12,12) SWNT. A 4-tube inhomogeneous bundle is composed of a single (5,5), (7,7), (9,9), and (12,12) SWNT. Finally, a 7-tube inhomogeneous bundle consists of a single (5,5) SWNT, a single (7,7) SWNT, three (9,9) SWNT, and two (12,12) SWNT. The intertube distance in the homogenous bundle was initially set to 3.4 Å.²² The inhomogeneous bundles are packed in a similar manner to the homogeneous bundles. However, different radii between tubes make it difficult to maintain a 3.4 Å distance between a tube and all of its neighboring tubes in the 7-tube bundle. In this case, a distance of 3.4 Å is maintained between the center tube and the six surrounding SWNT, as shown in Figure 2a. The packing of inhomogeneous tubes in this case plays a large part in the amount of surface area exposed for adsorption. The placement of a smaller diameter tube next to a much larger diameter tube would allow for more surface exposure than would be available if two tubes of the same size were placed next to one another.

In principle, H₂ can be adsorbed in both exohedral and endohedral sites with a relative distribution population, depending on the radius of the nanotube. In previous simulations, we used a curvature dependent potential²³ to study the optimal distribution of endohedral/exohedral H₂ loading in a variety of nanotubes. The basic idea was to systematically sample the endohedral/exohedral H₂ distribution for a given H₂ loading in each nanotube bundle to select the one that is energetically most favorable. This approach was considered in the selection of

the endohedral/exohedral H₂ distributions in the present study. However, we slightly adjusted the distributions in order to facilitate comparison of the adsorption capacity between homogeneous and inhomogeneous nanotube bundles. This was done by first making the average diameters of the inhomogeneous bundles approximately the same as those in the homogeneous bundles and then assigning the H₂ distributions in the inhomogeneous bundles to be similar in magnitude to those in the homogeneous bundles. The average diameters of the SWNT bundles per nanotube as well as the endohedral/exohedral H₂ distributions used in our simulations are shown in Table 2-1.

Table 2-1. Finite nanotube bundles used in the MD simulations at various H₂ loadings and distributions.

Bundle Composition	Homogeneous			Inhomogeneous		
	Average Diameter (Å)	H₂ Loading (wt %)	endo/exo ratio	Average Diameter (Å)	H₂ Loading (wt %)	endo/exo ratio
3 tubes	12.204	1.21	20:80	12.656	1.46	20:80
		3.57	40:60		3.85	30:70
		6.5	50:50		6.5	43:57
4 tubes	12.204	1.27	28:72	11.937	1.50	26:74
		3.35	35:65		3.64	30:70
		6.5	40:60		6.5	42:58
7 tubes	12.204	1.51	23:77	12.204	1.30	25:75
		3.57	40:60		3.54	39:61
		6.5	46:54		6.5	46:54

Molecular dynamics simulations were performed using the Langevin thermostat at 300 K for 30 ps on both the homogenous and inhomogeneous SWNT bundles with an integration time step of 0.25 fs. The equations of motion were integrated with the velocity Verlet algorithm. The total volume of each system was fixed such that the total number of H₂ molecules was treated as an ideal gas at 100 atm. A simulation box was then created with a periodicity along the nanotube axis. The dimensions of the selected boxes are shown in Table 2-2.

Table 2-2. Dimensions of simulation box used for each nanotube distribution.

Bundle Composition	Homogeneous		Inhomogeneous	
	H ₂ Loading (wt %)	Simulation Cell (Å)	H ₂ Loading (wt %)	Simulation Cell (Å)
3 tubes	1.21	51.57x51.57x22.14	1.46	57.65x57.65x22.14
	3.57	89.32x89.32x22.14	3.85	94.74x94.74x22.14
	6.5	122.31x122.31x22.14	6.5	127.63x127.63x22.14
4 tubes	1.27	60.77x60.77x22.14	1.50	63.45x63.45x22.14
	3.35	99.86x99.86x22.14	3.64	100.05x100.05x22.14
	6.5	141.23x141.23x22.14	6.5	135.22x135.22x22.14
7 tubes	1.51	82.44x82.44x22.14	1.30	81.54x81.54x22.14
	3.57	136.44x136.44x22.14	3.54	137.65x137.65x22.14
	6.5	187.23x187.23x22.14	6.5	186.83x186.83x22.14

H₂ adsorption in SWNT is not a static process, but rather a dynamic process. Therefore, the adsorption energy of each H₂ molecule depends on the local environment in which it resides. Individual molecules located far from the substrate contribute only negligibly to the total adsorption energy, while those close to the SWNT surface are interacting more strongly with the substrate. To determine the effective capacity and adsorption energy of hydrogen around a SWNT bundle, we have devised a novel method for calculating the average adsorption energy per hydrogen molecule that is dependent on the distance of a molecular gas from the substrate surface by defining the distance-dependent adsorption energy as

$$\Delta E_{ad}(r) = n(r)\epsilon_{H_2} + \epsilon_{tube} - \{\epsilon_{tube+H_2} - [N - n(r)]\epsilon'_{H_2}(r)\} \quad (1)$$

where $n(r)$ is the number of molecules within a distance r of the substrate and N is the total number of H₂ molecules in the unit cell. ϵ_{H_2} is the energy of H₂ molecule. ϵ_{tube} and ϵ_{tube+H_2} are the total average energies of SWNT bundle and the bundle loaded with N H₂ molecules in the unit cell, respectively. Finally, $\epsilon'_{H_2}(r)$ denotes the average energy of a H₂ molecule beyond r , which takes the form:

$$\epsilon'_{H_2}(r) = \left(\epsilon_{H_2} - \frac{\epsilon_{tube+H_2} - \epsilon_{tube}}{N} \right) \frac{n(r)}{N} + \frac{\epsilon_{tube+H_2} - \epsilon_{tube}}{N} \quad (2)$$

It is clear that:

$$\frac{\epsilon_{tube+H_2} - \epsilon_{tube}}{N} \leq \epsilon'_{H_2}(r) \leq \epsilon_{H_2} \quad (3a)$$

$$\Delta E_{ad}(r) \rightarrow \begin{cases} 0, & r \rightarrow 0 \\ N\epsilon_{H_2} + \epsilon_{tube} - \epsilon_{tube+H_2}, & r \rightarrow \infty \end{cases} \quad (3b)$$

where the second expression of Eq. (3b) represents the conventional approach for calculating the total adsorption energy.

The number of H₂ molecules within r can be readily calculated by first computing a minimum distance distribution function, $A(r)$, which counts the number of adsorbate molecules whose center of mass is a distance r from the *closest* substrate atom. This function can be evaluated by averaging over the MD trajectories. Subsequently, $n(r)$ can be obtained using

$$n(r) = \int_0^r A(r') dr', \quad (4)$$

from which the H₂ content within a given radius can also be evaluated.

Equations (1)-(4) allow adsorption energy to be explicitly expressed in terms of a given distance between the gas molecule and the substrate. The number of gas molecules within the distance can also be calculated, and thus the effective adsorption capacity of the substrate can be readily evaluated.

Single-walled carbon nanotubes were purchased from CNI (Houston, TX). Lithium (99.99% granules) and 2-methyl tetrahydrofuran (anhydrous, 99.9%) were purchased from Sigma-Aldrich. The as-purchased carbon nanotubes had <3 wt % Fe catalyst residue as determined by thermogravimetric combustion analysis under flowing air. The nanotubes were dried and deoxygenated by heating to 800°C in a quartz tube for 3 hrs under a flow of argon gas. After cooling, the tube was sealed under argon and opened inside an argon-filled glove box. MeTHF was stored over activated molecular sieves following degassing using a freeze-pump-thaw procedure.

All of the synthetic procedures were conducted in an argon-filled glove box. A mixture of 0.126 g of lithium granules (18 mmol, excess) and 0.641 g of naphthalene (5.0 mmol) was placed in 25 ml of MeTHF and stirred for 3 hours to yield a purple solution. The excess Li granules were then filtered using a sintered glass funnel, and the colored solution was added to a Schlenk flask containing the nanotube sample (0.25 g) and a glass-coated magnetic stir bar. After five days of stirring at room temperature, the suspension was filtered through an alumina membrane (Whatman, 0.2 micron), and the nanotube cake was rinsed with MeTHF until the washings were colorless. The resulting product was dried under vacuum (10⁻² Torr) for 16

hours. Li doped nanotubes (Li-SWNT) are highly sensitive to air and moisture and were thus kept under an argon atmosphere at all times. Elemental analyses were performed by Schwarzkopf Laboratory, Woodside, NY. For Li-SWNT as prepared: C 65.87%, H 2.36%, Li 8.21%, Fe 0.98%. For Li-SWNT after 500°C activation (Li-SWNT-5): C 62.17%, H 0.95%, Li 8.05%, Fe 0.99%.

Thermal analyses were performed using a TA Instruments 2960 SDT enclosed in a glove bag. The carrier gas was N₂ at 100 sccm and the temperature ramping rate 10°C/minute. A Pt pan was used. Raman spectroscopy was performed using a Kaiser Hololab Series 5000 microscope with 10mW power at the sample with a 20x Olympus MsPlan objective. The integration time was 10 seconds and signals were averaged over 8 scans. Samples were examined in 0.5 mm glass capillaries sealed with fluorocarbon grease.

For gas adsorption measurements, samples were pretreated by activation at elevated temperatures under high vacuum. Typically, a 100-200 mg sample was loaded in a quartz sample cell within an argon filled glove box and attached to an ASAP 2010 manometric apparatus (Micromeritics, Inc.). The samples were then activated under dynamic vacuum at various temperatures from 100°C to 500°C until a pressure of 10⁻⁵ Torr was reached. Measurements were made on Li-doped nanotubes activated at 300°C (Li-SWNT-3) and 500°C (Li-SWNT-5). Helium was used to measure free space. The total pore volume and BET surface area were calculated from the N₂ isotherm, and the temperature dependence of the H₂ isotherm was used to estimate the isosteric heat using the Clausius-Clapeyron relationship.

Results and Discussion

Computational Modeling of Hydrogen Adsorption in SWNT

In order to estimate the effective adsorption capacity of the nanotube bundles, we first calculated the H₂ density around the homogeneous and inhomogeneous systems at three similar weight percentages for a total of 25 ps of simulation time. The results are shown in Figure 2-1. Several main features can be readily observed:

1. The highest density of H₂ molecules is located at ~3 Å from the closest carbon atom, and this distance is independent of the H₂ loadings contained in the system. As the amount of adsorbed H₂ molecules (coverage) increases, the surface area of the SWNT bundle is eventually saturated with hydrogen, leading to weaker adsorption featured at about 5 Å from the closest carbon.
2. For a given loading, the H₂ density increases with the nanotube thickness near the SWNT surfaces. This is expected, since the surface area of the nanotube bundle increases with the bundle thickness. For a given nanotube bundle, the H₂ density increases with the H₂ loading, since there are more H₂ molecules interacting with the surface.

Figure 2-1. The calculated density of H_2 vs. the distance of H_2 from SWNT sidewalls at various H_2 loadings. (a) 3-tube homogeneous bundle; (b) 4-tube homogeneous bundle; (c) 7-tube homogeneous bundle; (d) 3-tube inhomogeneous bundle; (e) 4-tube inhomogeneous bundle; (f) 7-tube inhomogeneous bundle.

The H_2 density appears to be considerably higher in the inhomogeneous bundle than the homogeneous bundle. However, particular caution needs to be taken when assessing the relative adsorption strength, since the nanotube radii of the inhomogeneous bundles are different from those of the homogeneous bundle. To understand the main difference in the adsorption property, we used the case of 7-tube homogeneous/inhomogeneous bundles to gain insight into the effect of inhomogeneity on adsorption. The calculated trajectories of H_2 at 6.5 wt % loading in these bundles are projected into the density map shown in Figure 2-2. The average diameter of the inhomogeneous bundle is the same as that of the homogeneous bundle (Table 2-1). At 6.5 wt % H_2 loading, the endohedral/exohedral distributions in the homogeneous and inhomogeneous nanotube bundles are also identical. It is apparent in Figure 2-2 that due to the packing inhomogeneity arising from different diameters of nanotubes, more H_2 molecules are populated near the surface in the inhomogeneous SWNT bundle than in the homogeneous bundle. In particular, the interstitial channels, which are barely accessible to H_2 molecules in the homogeneous bundle, and the groove sites are now densely populated in the inhomogeneous bundle. The incommensurate packing geometry in the inhomogeneous bundle creates a significantly larger surface area for H_2 molecules to access.

Figure 2-2. Density map of H_2 molecules over the course of 25 ps for the (a) inhomogeneous and (b) homogeneous tube bundles. The scale bar shows distance in angstroms.

Figure 2-3. The calculated effective H_2 storage capacity vs. the distance of H_2 from SWNT sidewalls at various H_2 loadings. (a) 3-tube homogeneous bundle; (b) 4-tube homogeneous bundle; (c) 7-tube homogeneous bundle; (d) 3-tube inhomogeneous bundle; (e) 4-tube inhomogeneous bundle; (f) 7-tube inhomogeneous bundle.

Figure 2-3 shows the calculated weight percentages of H_2 in the homogeneous and inhomogeneous SWNT bundles at various H_2 loadings as a function of distance between H_2 and SWNT surfaces. At the same H_2 loading, H_2 weight percentage increases much more quickly in the inhomogeneous bundles than in the homogeneous bundles. At the low loadings (~ 1.5 wt % and ~ 3.5 wt %), slightly over 90% of H_2 molecules in the inhomogeneous bundles are within 4 Å of the surfaces. In the homogeneous bundles, H_2 molecules must be summed over a larger H_2 -SWNT distance in order to equal the same adsorption capacity. Note that in both cases, the lower the H_2 loading, the faster the nanotube bundles can reach their full loading capacity because more surface area becomes accessible. Furthermore, the effective capacity increases as the bundle thickness decreases. This is clearly illustrated in Figures 2-3(c) and 3(f) for 6.5 wt % loading. For both the homogeneous and inhomogeneous bundles, smaller bundles are capable of achieving a higher weight percentage of adsorption due to higher surface areas exposed to the gas molecules. However, neither the homogeneous bundles nor the inhomogeneous bundles at 6.5 wt % loading can reach a storage capacity for H_2 molecules within a H_2 -SWNT distance at which the interaction between H_2 and SWNT bundles is appreciable. Nevertheless, the effective loading capacity of the inhomogeneous bundles at a given distance is considerably larger than that of the homogeneous bundles.

Figure 2-4. The calculated average adsorption energy vs. the distance of H₂ from SWNT sidewalls at various H₂ loadings. (a) 3-tube homogeneous bundle; (b) 4-tube homogeneous bundle; (c) 7-tube homogeneous bundle; (d) 3-tube inhomogeneous bundle; (e) 4-tube inhomogeneous bundle; (f) 7-tube inhomogeneous bundle.

One factor that ultimately determines whether an adsorbent is useful as a storage medium with a sufficient capacity at a given temperature is the adsorption energy. For a given H₂ loading and temperature, a low adsorption energy may correspond to low capacity, while a high adsorption energy may give rise to irreversible adsorption. Using Eq. (1), we evaluated the effective adsorption energy as a function of the distance between H₂ and nanotube walls. The results are shown in Figure 2-4, from which several important features can be observed:

1. The adsorption energy decreases rapidly as the H₂-SWNT distance increases. This indicates that H₂ molecules quickly lose their attractive interaction with the nanotube bundles as they move away from the surface.
2. At the same distance from the SWNT surfaces and similar bundle thickness, the adsorption energy decreases as the H₂ loading increases. This is expected because a higher H₂ loading forces individual C atoms to interact with more H₂ molecules, which leads to a smaller adsorption strength.
3. For the same distance from the SWNT surfaces and similar bundle thickness, the adsorption energy in the inhomogeneous bundles is higher than in the homogeneous bundle. This is consistent with the higher H₂ density and weight percentage shown in Figures 2-1 and 2-3 due to more surface area available for H₂ adsorption.

4. For the same distance from the SWNT surfaces and H₂ loading, the calculated adsorption energy decreases slightly as the thickness of nanotube bundles increases, again due to the fact that a thinner bundle provides more surface area, and particularly more groove sites for H₂ adsorption. The inhomogeneous bundles have larger groove sites and more interstitial pore volume than the homogeneous bundles, and thus the H₂ adsorption energies in the inhomogeneous bundles are higher.
5. In all cases, the adsorption energies are relatively small at near-ambient temperature. Only at a low loading with H₂ molecules within 3 Å from the nanotube outer walls is the average adsorption energy above 8 kJ/mol. However, for $r < 3$ Å, the effective storage capacity is much smaller than the loading, as shown in Figure 2-3. For example, for the 7-tube inhomogeneous bundle at 1.30 wt % of H₂, the calculated adsorption energy at $r = 3$ Å is 7.8 kJ/mol; from Figure 2-3(d), however, the effective storage capacity is only 0.65 wt %. Clearly, as r increases, the effective storage capacity increases, but the average adsorption energy decreases. Figures 2-3 and 2-4 provide a direct correspondence between the effective storage capacity and the average adsorption energy, both of which depend on the distance of H₂ molecules from surfaces of nanotube bundles.

It is important to estimate the energy of the H₂ molecule in an interactive environment in the regime beyond r in order to gain understanding on the average adsorption energy. As shown in

Equation 3(a), for a small r , $\epsilon'_{H_2}(r) \rightarrow \frac{\epsilon_{tube+H_2} - \epsilon_{tube}}{N}$ and for a large r , $\epsilon'_{H_2}(r) \rightarrow \epsilon_{H_2}$. Figure 2-5 displays the calculated $\epsilon'_{H_2}(r)$ vs. r for various H₂ loadings in the nanotube bundles. The results show that at a small r , $\epsilon'_{H_2}(r)$ deviates from ϵ_{H_2} significantly, implying that H₂ molecules are interacting strongly since a considerable amount of H₂ is near the nanotube sidewalls. The influence of nanotube bundles diminishes rapidly as the distance between H₂ molecules and the exterior nanotube sidewalls increases. Finally, the results shown in Figure 5 indicate the sensitivity of $\epsilon'_{H_2}(r)$ to the H₂ loading, i.e., the variation of $\epsilon'_{H_2}(r)$ increases as H₂ loading decreases.

Figure 2-5. The calculated average energy of a single H_2 in an interactive environment in the regime beyond r vs. the distance of H_2 from SWNT sidewalls at various H_2 loadings. (a) 3-tube homogeneous bundle; (b) 4-tube homogeneous bundle; (c) 7-tube homogeneous bundle; (d) 3-tube inhomogeneous bundle; (e) 4-tube inhomogeneous bundle; (f) 7-tube inhomogeneous bundle.

Experimental Studies of Hydrogen Adsorption on Lithium-doped SWNT

Dried and deoxygenated SWNT samples were treated with an excess of lithium naphthalide in MeTHF. After reaction, filtration, and drying under vacuum, the Li-doped nanotube samples had a composition of $LiC_{4.6}H_{2.0}$ by elemental analysis. This corresponds to the empirical formula $LiC_{3.6} \cdot 0.2$ MeTHF using the assumption that all of the hydrogen in the Li-doped nanotubes originates from co-intercalated solvent. The amount of lithium incorporation here is unprecedented, although higher doping levels (LiC_3) have been claimed using electrochemical charging of cut nanotubes.²⁴

Lithium-doped nanotubes (Li-SWNT) under flowing nitrogen (Figure 2-6) exhibited a decrease of *ca.* 10.5% in weight upon heating from 100°C – 500°C using thermogravimetric analysis (TGA). If a formula of $LiC_{3.6} \cdot 0.2$ MeTHF is assumed and all the solvent is removed, the expected weight loss should be ~25%. This suggests that the removal of solvent is incomplete and/or polymerization or carbonization of the solvent has occurred. The decrease in weight is not linear and, as indicated by the derivative plot in Figure 2-6, there are maxima at 229°C, 300°C and 383°C, which are likely indicative of different coordination sites for the solvent molecules.

Figure 2-6. TGA plot of Li-doped nanotubes (Li-SWNT) in flowing nitrogen. The temperature ramping rate is 10°C/minute.

Guided by this TGA data, we prepared samples of Li-doped nanotubes for additional characterization and H₂ adsorption studies by activation under flowing N₂ at 300°C and 500°C. The former was chosen as the temperature corresponding to the second (middle) peak in the derivative plot in Figure 2-6, and the latter as the upper limit for activation where little further weight loss was observed. After activation at 500°C, the elemental composition was LiC_{4.5}H_{1.0} (or LiC₄*0.1 MeTHF). The calculated weight loss from LiC_{3.6}*0.2 MeTHF to LiC₄*0.1 MeTHF is 6.3% compared to the observed 10.5% in the TGA plot.

The Raman spectra of pristine nanotubes, Li-doped nanotubes, and Li-doped nanotubes after 500°C activation are shown in Figure 2-7. Noticeable upshifts are evident in the G (11 cm⁻¹) and G' (13 cm⁻¹) bands of the Li-doped samples before and after thermal activation. Similar shifts in the G and G' bands for Li-doped nanotubes have been reported previously.²⁴ This implies that the carbon was still doped even after high-temperature activation. Interestingly, the D band located at 1320 cm⁻¹ did not increase in intensity for the doped samples, demonstrating that intercalation did not lead to a significant increase in graphitic disorder.

Figure 2-7. Raman spectra (532 nm) of pristine nanotubes (SWNT) and Li-doped nanotubes before activation (Li-SWNT) and after 500°C activation (Li-SWNT-5). The inset is an enlargement of the portion of the Raman spectrum containing the radial breathing modes.

The radial breathing modes (RBM; observed at 100-300 cm^{-1}) are very sensitive to interactions between nanotubes, and there was a change in these modes upon lithium intercalation. However, the RBM features of the pristine SWNT were largely recovered after activation at 500 °C.

Hydrogen isotherms measured at 77 K for pristine nanotubes and Li-doped nanotubes activated at 300 °C and 500 °C are presented in Figure 2-8. It is evident that the pristine, unmodified nanotube samples adsorbed a greater amount of hydrogen at 77 K than Li-doped materials. Raising the activation temperature from 300 °C to 500 °C increased the amount of adsorbed H_2 in the activated samples, likely due to more effective removal of solvent molecules occupying pore volume. The amount of hydrogen adsorbed at 77 K and 1 atm. by the activated Li-doped nanotubes (54 cm^3/g or 0.48 wt %) is about half that of the pristine counterpart (96 cm^3/g or 0.86 wt %) and is mirrored by a concomitant decrease in the N_2 BET surface area from pristine (784 m^2/g) to lithium-doped (334 m^2/g). This strongly suggests that the decrease in the amount of hydrogen adsorbed by the Li-doped nanotubes is due to a loss in accessible surface area/pore volume and associated adsorption sites compared to the pristine nanotubes.

Figure 2-8. Hydrogen isotherms at 77 K for pristine nanotubes and lithium-doped nanotubes activated at 300°C (Li-SWNT-3) and 500°C (Li-SWNT-5). Volumes are normalized to standard temperature and pressure (STP). The N₂ BET surface areas for pristine nanotubes and Li-SWNT-5 are shown adjacent to the isotherm data.

For the calculation of the isosteric heats of adsorption, hydrogen isotherm data for pristine and Li-doped nanotubes was also obtained at 87 K (Figure 2-9). It is at least qualitatively evident from this isotherm data that there is a more marked effect of temperature on hydrogen adsorption for the Li-doped nanotubes *vis-a-vis* the pristine nanotubes. This observation is suggestive of a higher isosteric heat of adsorption of hydrogen for the Li-modified material.²⁵ The isosteric heats of adsorption as a function of H₂ loading were calculated using the Clausius-Clapeyron relationship and are presented in the insets of Figure 2-9. For both Li-doped and pristine nanotubes, the isosteric heats diminish with increasing H₂ coverage. At low coverage, the isosteric heat of the Li-doped nanotubes (10.5 kJ/mol) is about 2 kJ/mol higher than pristine nanotubes (8.4 kJ/mol). More definitive adsorption measurements using larger sample quantities and preferably a variable temperature cryostat to obtain measurements at additional temperatures will be needed to more confidently quantify these apparent differences in heats of adsorption for the two samples.

Figure 2-9. H_2 adsorption isotherms for pristine (upper panel: SWNT) and doped nanotubes (lower panel: Li-SWNT-5) at 77 and 87 K. The volumes are normalized to STP. The insets display plots of isosteric heats vs. loading.

Nitrogen adsorption isotherms at 77 K were obtained for both the Li-doped, heat-treated samples and for a pristine sample to provide additional data on the materials' inherent porosity characteristics. Both samples shown in Figure 2-10 exhibited Type IV isotherms with small H3-

type hysteresis loops. The Gurvitch volume ($P/P_0 = 0.98$) of the Li-doped nanotube sample ($0.649 \text{ cm}^3/\text{g}$) was considerably less than for the pristine material ($1.384 \text{ cm}^3/\text{g}$), and the micropore volume ($P/P_0=0.05$) is approximately a third lower. Thus, the microporosity is greatly affected by the combination of lithium doping and heat treatments.

Figure 2-10. Nitrogen adsorption isotherms at 77 K for pristine (SWNT) and Li-doped, 500°C activated nanotubes (Li-SWNT-5). The inset displays an enlargement of the low-pressure ($P/P_0 \leq 0.1$) region of the isotherms.

If we consider the diameter of a Li^+ ion to be $1.80 \text{ \AA}$ and the intertube spacing at its maximum to be similar to the interlayer spacing of graphite ($3.35 \text{ \AA}$), it is possible to see how intercalation of Li^+ in the interstitial sites²⁶ could lead to pore blockage and a large decrease in micropore volume, even if all the intercalated solvent were removed.

Conclusions

We have developed a theoretical model to describe molecular physisorption on a solid substrate and applied it to the detailed analyses on H_2 adsorption in homogeneous/inhomogeneous finite SWNT bundles. This model explicitly associates the effective H_2 storage capacities and

average adsorption energies with the distance between H₂ molecules and the sidewalls of these nanotube bundles using the calculated quantities from molecular dynamics simulations. It provides detailed physical insight into the interactions between H₂ and nanotube bundles and among H₂ molecules. More important, given a desired value of average adsorption energy at a given H₂ loading, the model allows one to predict the effective adsorption capacity.

We show that the highest H₂ density appears at around $r = 3$ Å, regardless of H₂ loading, bundle thickness, and nanotube packing patterns (homogeneous or inhomogeneous). However, at this distance the calculated effective capacities in all cases are much lower than their theoretical values determined by H₂ loadings, and a considerable number of H₂ molecules are unable to interact effectively with the nanotube sidewalls. The corresponding adsorption energies at $r = 3$ Å are relatively small, roughly 8 kJ/mol. The adsorption energy decreases rapidly as the H₂-SWNT distance increases. In general, we found that a higher H₂ loading leads to a lower adsorption energy and that a thicker bundle provides a smaller surface area with which H₂ can interact. The effective adsorption capacity and average adsorption energy of an inhomogeneous nanotube bundle are higher than that of the homogeneous nanotube bundle with similar thickness.

In order to explore the effect of lithium intercalation of SWNT on the heat of hydrogen adsorption, lithium intercalation of single-walled carbon nanotubes was effected using lithium naphthalide in 2-methyltetrahydrofuran. The intercalation of lithium, accompanied by co-intercalation of solvent, induced pore blockage and resulted in decreased surface area and pore volume. The hydrogen adsorption capacity was also reduced as a result of lithium intercalation. There is some evidence, however, of a small increase in the isosteric heat of adsorption. It has been recently shown that in systems with larger pore volumes, such as metal organic frameworks, lithium intercalation results both in an increased hydrogen uptake and heat of adsorption.²⁷ Therefore, the determination of hydrogen uptake in lithium-doped pillared nanotubes or lithium-doped exfoliated nanotubes²⁸, where the possibility of pore blockage is less, should be of interest.

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CHAPTER 3

Hydrogen Storage Using Graphite Intercalation Complexes

Introduction

It has been widely recognized that a prototypical hydrogen storage device requires lightweight materials capable of interacting with molecular hydrogen via either physisorption or chemisorption.^{1,2} This interaction must occur with an appropriate strength to enable the “capture” of hydrogen to be reversible under practical operating conditions of temperature and/or pressure. Porous hydrogen storage materials that store H₂ via physical adsorption have a perceived advantage for system engineering of heat removal during filling relative to most metal hydrides and chemical hydrides due to the relatively low enthalpy associated with physisorption. Most hydrogen storage materials in this class rely on physical adsorption due to van der Waals forces and/or electron density donation from the σ orbital of H₂ to an electrophile (“Kubas-type binding”).³ In this chapter, we report a combined theoretical and experimental study of H₂ physisorption in graphite intercalation compounds (GIC) of fluoride anions. In contrast to Kubas-type binding, the dominating mechanism of hydrogen binding in these materials is donation of electron density from a nucleophile to the σ^* orbital of H₂. We show that these compounds exhibit significantly higher heat of adsorption than other porous H₂ storage materials, such as graphitic nanofibers and metal organic framework compounds, at near-ambient temperatures and thus they could potentially serve as practical H₂ storage media.

In gas-phase calculations, “naked” fluoride anions have been shown to interact strongly with molecular hydrogen.⁴ Charge separated ammonium fluoride salts have also shown enhanced binding affinities for hydrogen in gas-phase calculations.⁵ Sweany et al. have reported an experimental characterization of simple adducts of H₂ with CsF ion pairs in a solid argon matrix at 10 K.⁶ The normally infrared-silent H₂ was perturbed by the salt, giving rise to spectra interpreted as arising from H₂ and CsF adducts, with as many as 3 H₂ molecules per CsF, where H₂ interacts primarily with the F⁻ anion. Based on H-H stretching frequency shifts showing a lengthening of the H-H bond, the interaction was attributed to the donation of electron density from the F⁻ anion to the H₂ anti-bonding σ^* orbital.

A conceptual challenge is to devise solid-state materials which incorporate both the strong hydrogen interactions of “naked” fluoride and sufficient porosity for diffusion of gaseous H₂. Chemical intercalation of graphite has been demonstrated to increase H₂ adsorption capacity by rendering the crystalline graphite porous through intercalation and separation of the graphene layers, as well as increasing the hydrogen affinity of the graphite through increased electron density. For example, the second-stage graphite intercalation complex KC₂₄ has been shown to adsorb 2 H₂/K at 77 K corresponding to 1.2 wt % H₂.⁷ Electron transfer from K to the graphene layers in this “donor type” GIC increases the heat of adsorption from 4 kJ/mol in native graphite to ca. 10 kJ/mol in KC₂₄. To date, there have been no examples of “acceptor type” GIC with a demonstrated appreciable hydrogen adsorption. Graphite fluorides represent a well-studied subset of acceptor GIC. A range of fluorination levels are accessible and the nature of the C-F

interaction evolves from ionic to semi-ionic to covalent as the decreasing C:F ratio approaches 1:1.⁸

A concept to induce higher electron density on the fluoride ions to make them more attractive to H₂ has motivated us to consider doping the graphite lattice with n-type species that would allow more electrons to delocalize via the π -conjugation network intrinsic to graphitic carbons. Atomic nitrogen can be considered as such a species. Upon replacement of a C atom with an N in the graphitic network, two *p*-electrons of the N atom can participate in the π -bonding via the π -conjugation, and thus the fluoride ion is expected to be further enriched with more electron density. H₂ adsorption in the N-doped partially fluorinated GIC complexes was then simulated using *ab initio* molecular dynamics.

Computational and Experimental Methods

Computational Methods

In order to investigate H₂ adsorption, we carried out *ab initio* molecular dynamics (MD) simulations at room temperature on H₂ in a GIC intercalated with fluoride anions and subsequently synthesized a fluoride-GIC followed by isotherm measurements. The electronic energy was calculated with periodic density functional theory (DFT) under the local density approximation (LDA) employing the Perdew-Zunger exchange-correlation functional⁹ coupled with a plane-wave basis set, while the MD simulation was performed in the constant NVE canonic ensemble using the Nosé thermostat¹⁰. The selected unit cell in our simulations contains 32 C and 8 F atoms. To maximize the hydrogen capacity, only stage-1 GIC was studied with 24, 12, 2 H₂, and 1 H₂ molecules per unit cell, corresponding to 8.2 wt %, 4.3 wt %, 0.74 wt .% and 0.37 wt % of adsorbed H₂, respectively.

The electronic energy was calculated with periodic density functional theory (DFT) under the local density approximation (LDA) employing the Perdew-Zunger exchange-correlation functional coupled with a plane-wave basis set, while the MD simulation was performed in the constant NVE canonic ensemble using the Nosé thermostat. Ultrasoft pseudopotentials were used to describe the core electrons with a cutoff energy of 425eV. The Brillouin zone integration was performed using the Monkhorst and Pack points of 2×2×4. All structures including cell parameters were fully equilibrated prior to MD simulations. The forces acting on the atoms, derived from the ground state electronic energies, were calculated using the Hellmann-Feynman theorem at each time step and are subsequently utilized in the integration of Newton's equation of motion. The mass of tritium was used for H, which allows us to use a time step of 1 femtosecond to simulate the dynamic systems for up to 5 picoseconds at room temperature.

Experimental Setup and Methods

Apparatus and Method for BF_4^- intercalation

The synthesis of C_xBF_4 has been reported through different methods by several groups.^{11,12} In this study, graphite was exposed to a gas mixture of BF_3 and F_2 at room temperature to make the fluoroborate salt. Native carbons were heated at 900 °C for 4-6 hours under vacuum to remove water and oxide / hydroxide functional groups. For Alfa Aesar, Timrex, graphite fiber, and carbon black samples, the 20% F_2 (in N_2) and BF_3 were purified before use. F_2 was purified by flowing it through a bed of anhydrous NaF , and BF_3 was purified by trap to trap distillation. For the other carbons, unpurified 20% F_2 and BF_3 were used directly from the cylinders. The Alfa Aesar and first Timrex samples were synthesized with the two gases premixed in a ballast containing a 1:2 F_2 to BF_3 molar ratio. In subsequent syntheses, the BF_3 and F_2 were separately pressurized through the stainless steel manifold and into the reactor.

Carbon was loaded into a fluorinated ethylene propylene (FEP) tube reactor in a glove box. After connecting to a stainless steel (SS) manifold, the reactor was evacuated and then pressurized with the 20% F_2/BF_3 mixture to between 900 and 2000 torr. (In the cases where BF_3 and F_2 were introduced separately, BF_3 was always introduced first to decrease the likelihood of exothermic combustion of high surface area carbons with F_2 to make CF_4 . A 1:2 or 1:1 F_2 to BF_3 ratio was employed.) The FEP reactor was evacuated several times a day and refilled with fresh F_2/BF_3 for a total of 4 days with continuous mild agitation. In total, a stoichiometric excess of F_2/BF_3 to carbon was ensured. In the final cycle, the reactor was evacuated for several hours to remove any gases adsorbed to the carbon surface.

Apparatus and Method for PF_6^- Intercalation

Synthesis of C_xPF_6 was performed in the same manner as C_xBF_4 and according to literature reports. PF_5 was used instead of BF_3 – trap to trap distillation was performed with PF_5 ; however, HF impurities were not completely removed, as shown in the elemental analysis.

Apparatus and Method for HF_2^- and F^- Intercalation

Carbon, previously heated to 900 °C under vacuum for 4-6 hours, was loaded into a FEP reactor in a glove box. The reactor was then connected to the flow system and evacuated. HF was then forced into the reactor from the HF reservoir until the liquid level was slightly above the carbon (about 30-40 mL). N_2 was allowed to flow through the reactor at 50 mL/min, and the back pressure regulator was set to 25 psig. After the system had equilibrated, 20% F_2 was flowed at 50 mL/min into the reactor together with the N_2 . This method effectively reduces the F_2 concentration to 10%. This ratio of gases was flowed for 2 hours, after which the N_2 flow was stopped, leaving only 20% F_2 flowing at 50 mL/min. The 20% fluorine was flowed for an additional 4 hours. During this reaction time, HF was recycled back into the reactor about once every hour due to the volatility of HF at room temperature. After reaction, the FEP reactor was evacuated to the scrubber to remove the majority of excess HF. C_xHF_2 was synthesized at this point. To decompose C_xHF_2 (through removal of intercalated HF) to make C_xF , the reactor was

heated in a water bath at 50 °C overnight while being evacuated through a FEP cold trap (using liquid nitrogen).

Apparatus and Method for Thermal Decomposition of Intercalated Graphite

C_xMF_y ($M = B, P, H$) were thermally decomposed by placing synthesized powder in a quartz boat and loading the boat into a quartz tube (sealed with Kontes-type valves) in a glove box. The quartz tube was transferred from the glove box to a tube furnace (Lindberg Blue M Mini-Lite), and connected to a vacuum manifold equipped with a diffusion pump and LIN cold trap. Vacuum was slowly achieved in the quartz tube by opening the Kontes valve incrementally. Once pressures of 10^{-3} torr were achieved, the furnace was ramped to specified temperatures. Out-gassing from samples was monitored by mass spectrometry (Balzers Prisma).

Apparatus and Method for Synthesis of C_xN Graphite Fibers

Ni powder was loaded onto a quartz boat in the glove box due to the pyrophoricity of small particle size Ni. The boat was placed in a quartz tube which was inserted into a Haynes alloy metal tube. The entire system was sealed, brought out of the glove box and placed into a horizontal tube furnace. Argon was purged through the tube while it was heated to 400 °C. After equilibrating at 400 °C, 100% H_2 was introduced to the tube and allowed to reduce any oxide impurities of the Ni catalyst for 1 hour. The H_2 flow was terminated and Ar was purged through the tube while it was heated to 900 °C. After reaching 900 °C, the Ar flow was redirected through a sparger containing acetonitrile. The CVD process at 900 °C was performed for 5-6 hours before switching back to pure Ar and allowing the furnace to cool.

Chemicals and Reagents

Carbons:

Alfa Aesar graphite powder, crystalline -300 mesh, 99%

Timrex SFG6, Timcal (6 micron flake graphite, sample #AB-222M)

Graphite fibers, Showa Denko VGNF

Graphitized carbon black, Columbian Chemical Co.

Amoco AX-21 (Supersorb activated carbon)

Kynol ACF-1603-20 (activated carbon fiber)

Penn State carbon made by Dr. Ram Rajagopalan (Foley group partner in the HSCoE)

Fluoride sources:

20% fluorine in nitrogen, Air Products and Chemicals, Inc.

Boron trifluoride (electronic grade 99.99%), Air Products and Chemicals, Inc.

Phosphorous pentafluoride, SynQuest 99%

Anhydrous hydrogen fluoride (electronic grade), Air Products and Chemicals, Inc.

Starting materials for C_xN synthesis:

Ni powder (3 micron, 99.7%), Aldrich

Ni nanopowder (<100 nm, 99.9%), Aldrich

Acetonitrile (anhydrous, 99.8%), Aldrich

Analytical Tools and Methods

X-ray Diffraction (XRD)

C_xBF₄ and other graphite fluoro-complexes were loaded into thin (0.7 mm) quartz capillaries in a glove box. They were plugged with grease and then sealed prior to XRD scans. Typical scans ranged from 3-80 degrees 2-theta. C_xN materials were scanned normally without any additional loading requirements.

Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC)

Due to their sensitivity to moisture, graphite fluoro-complexes (~4-10 mg) were loaded into crimped aluminum pans in the glove box prior to TGA and DSC measurements. A small hole was punctured in the top of the pan, which was transferred to the analytical instrument sealed in a capped glass vial. The transfer was made as quickly as possible and the instrument chamber closed and purged with either N₂ or He. For DSC measurements, the reference pan was also punctured for consistency. It was discovered that aluminum fluoride was being made in the pan surfaces upon release of BF₃ during thermal decomposition of the materials. This can significantly affect the observed thermal behavior, especially in the DSC. Thus, gold was sputtered as a coating onto all aluminum pans used for the DSC data shown in this report.

Fourier Transform Infra-red (FTIR) Spectroscopy

Carbon fluoro-complexes were loaded onto BaF₂ or ZnSe plates in a glove box by sprinkling mg quantities onto one plate and carefully rotating the second plate to evenly disperse the powder. Plates were secured in a holder and transported in a capped plastic jar. IR spectra were obtained with the sample chamber purged by N₂.

Raman Spectroscopy

Powders were loaded in the glove box into glass capillaries (~1 mm diameter) and plugged with grease before transportation in a sealed glass jar to the measurement lab. Spectra were obtained with a 532 nm light source.

Solid State Nuclear Magnetic Resonance (NMR) Spectroscopy

Carbon fluoro-complex powders were loaded into 3.2 mm zirconia rotors in a glove box prior to measurements. Spectra were obtained primarily on a Bruker 300 instrument, with magic angle spinning (MAS) frequencies ranging from 10-20 kHz.

Transmission Electron Microscopy (TEM) / Electron Energy Loss Spectroscopy (EELS)

C_xN materials were ground in a mortar and pestle, dispersed in acetone or methanol and dropped onto a holey carbon Cu grid.

Iodometric Titration

10% NaI or KI solution was prepared fresh (within ~1-2 days) for each titration. 0.1 N Na₂S₂O₃ standard was diluted in a volumetric flask to 0.01 N. Approximately 50 mg each of carbon fluoro-complex was weighed and sealed in a glass vial in the glove box. Vials were transported to a fume hood, where about 10 mL of 10% NaI or KI solution was added quickly to the vial. 0.01 N thiosulfate was titrated into the vials until the color of the solution turned clear. A color progression of dark yellow/orange to faint yellow to clear occurred during titrations. Due to slow kinetics (presumably from poor access within graphene planes), titrations required up to 2 weeks before reaching the endpoint. Stirring and sonicating between doses of thiosulfate did not appreciably increase reaction rates. Vials were stored by wrapping in aluminum foil between titration doses to prevent light induced oxidation of I⁻ to I₂.

N₂ and H₂ Isotherm Measurements

N₂ isotherms at 77 K were performed through a volumetric method using a Micromeritics Accelerated Surface Area and Porosimetry (ASAP 2010) analyzer.

High pressure H₂ adsorption isotherms were performed using our Differential Pressure Adsorption Unit (DPAU; see Chapter 6). Samples were loaded in a glove box and evacuated on the DPAU to a pressure of <10⁻⁴ torr. Samples were heated on the DPAU to enhance degassing of the sample prior to measurements. Heating temperatures were varied to stay below the decomposition temperature of each particular sample.

Temperature Programmed Desorption (TPD)

50-100 mg of carbon fluoro-complex powder was loaded in a glove box into a quartz boat, which was further loaded into a quartz tube sealed with Kontes-type valves. The quartz tube was placed in a Lindberg Blue 'clam-shell' type tube furnace (M Mini-Lite) and evacuated through a vacuum manifold. When pressures were < 10⁻³ torr, the valve to the mass spectrometer (Balzers Prisma) was opened. Temperatures were ramped at 2-10 degrees/min. to various soak temperatures.

X-ray Photoelectron Spectroscopy (XPS)

XPS data for C_xBF₄ materials were inconsistent and are thus not presented in this report. The heating lamp in the chamber stage of the XPS instrument produced enough heat to possibly

decompose C_xBF_4 , making it difficult to correlate the measurements to a particular sample stoichiometry.

Elemental Analysis

Graphite fluoro-complex samples were sent to Schwarzkopf Analytical (now Galbraith Laboratories, Inc.) for fluorine, boron and carbon elemental analysis. ~100 mg was sent of each sample loaded in a glove box into either a glass tube sealed with a Kontes type valve, or glass vials capped and sealed with vinyl tape and shipped inside another glass jar also capped and sealed with vinyl tape. C_xN materials were sent to Prevalere Life Sciences for CHN analysis. ~100 mg of each sample were sent in capped glass vials.

Results and Discussion

Computational Modeling of Hydrogen Adsorption on Graphite Intercalation Complexes

To simulate H_2 interactions in GIC of fluoride anions, we selected a unit cell of a GIC containing 32 C and 8 F atoms. To maximize H capacity, only a stage-1 GIC was studied with 24, 12, 2 and 1 H_2 molecules per unit cell, corresponding to 8.22 wt %, 4.29 wt %, 0.74 wt % and 0.37 wt % of H_2 loading, respectively.

We first calculated the structures of the partially fluorinated GIC and the GIC containing the selected numbers of H_2 molecules by performing full optimization of cell structure and cell parameters. The super cell structure of the GIC replicated by $2 \times 2 \times 2$ is shown in Figure 3-1, and the optimized cell parameters are listed in Table 3-1. Initially, the F atoms were distributed evenly in the GIC lattice and intentionally placed above the graphene plane to determine if F atoms could be stabilized above the surface without forming a bond with the C atoms. Non-covalent F atoms in the lattice are expected to maintain the highest anionic character to maximize the interaction with H_2 molecules. Upon energy minimization, all F atoms were found to strongly interact with C atoms. Four F atoms form bonds with C atoms of the bottom layer, and another four are linked with C atoms of the upper layer (Figure 3-1). These F atoms are separated by at least 2.4 Å. In addition, significant lattice expansion in the c-axis (~2.3 Å) occurs. The F atoms intercalated in the graphite form long C-F bonds with the graphene sheets. However, compared with the typical C-F bond lengths in organofluoro compounds and perfluorinated graphite (~1.35 Å), the C-F bonds in the partially fluorinated graphite GIC are considerably longer, ranging from 1.417 Å to 1.533 Å. The significantly elongated bond lengths arise from the bond angle distortions resulting from the partial fluorination as the C atoms associated with the F atoms change their electronic configuration from sp^2 to sp^3 . Since these fluorinated C atoms are also linked to the adjacent sp^2 C atoms in the graphitic network, which inherently prevents them from being completely “puckered” out of the graphene plane, the seemingly covalent bonding between the F atoms and the C atoms in the present case is not as stable as in organofluoro compounds and perfluorinated graphite and exhibits a significant ionic character. As has been suggested by Watanabe et al., the C-F bonding is in fact semi-ionic in nature.¹¹ Indeed, as shown in Table 2, the Bader population analysis indicates that the average

charge on the F atoms is between -0.655 and -0.659. The negative charge built up on F atoms allows them to interact strongly with H_2 molecules.

Figure 3-1. Selected supercell of the partially fluorinated GIC replicated by $2 \times 2 \times 2$.

Table 3-1. The H_2 gravimetric density, the calculated lattice spacing, the average Bader charge on F and the average H_2 adsorption energy at 300 K for fluoride GIC complexes.

Complex	H_2 wt %	d (Å)	Q_F	ΔE (kJ/mol· H_2)
$C_{32}F_8$	-	5.698	-0.659	-
$C_{32}F_8 \cdot H_2$	0.37	5.613	-0.656	-23.3
$C_{32}F_8 \cdot 2H_2$	0.74	5.602	-0.655	-19.6
$C_{32}F_8 \cdot 12H_2$	4.29	6.556	-0.657	-10.5
$C_{32}F_8 \cdot 24H_2$	8.22	7.723	-0.656	-3.6

Table 3-2. The H₂ gravimetric density, the calculated lattice spacing, the average Bader charge on F and the average H₂ adsorption energy at 300 K for N-containing fluoride GIC complexes.

Complex	H ₂ wt %	d (Å)	ΔE (kJ/mol·H ₂)
C ₂₄ N ₈ F ₈	-	5.303	-
C ₂₄ N ₈ F ₈ ·H ₂	0.36	5.599	-14.2
C ₂₄ N ₈ F ₈ ·2H ₂	0.72	5.641	-14.5
C ₂₄ N ₈ F ₈ ·12H ₂	4.17	6.547	-10.1
C ₂₄ N ₈ F ₈ ·24H ₂	8.0	7.962	-5.3

At lower H₂ loadings, the spacing between adjacent graphene layers in fluoride GIC shrinks slightly relative to the GIC lattice (Table 3-1). This shrinkage is due to the fact that the H₂ molecules interact strongly with several F atoms simultaneously and are thus capable of holding the graphene sheets closer together. The optimized structure is displayed in Figure 3-2(a). The calculated MD trajectories indicate a high mobility of H₂ molecules in the lattice, and H₂ is capable of interacting with several F⁻ anions simultaneously.

Figure 3-2. Perspective view of the fully optimized structure of a partially fluorinated GIC with 1 H₂ (a), 2 H₂ (b), 12 H₂ (c), and 24 H₂ (d).

Figure 3-3 displays the calculated radial distribution functions (RDFs) of C-F, H-H, H-C and H-F distances at the given H₂ loadings. The RDF of C-F distances exhibits a large peak centered around 1.45 Å, which is significantly longer than the conventional C-F bond length, reflecting the semi-ionic nature of the bond. The H-H bond marginally shifts up from its gas phase value of 0.74 Å, indicating slight activation of the bond resulting from the interaction with the GIC. The RDF of C-H distance shows that H₂ molecules are rarely close to graphene sheets. The shorter C-H distances at low H₂ loading are partially attributed to the smaller spacing between graphene sheets. As the loading increases, the H₂ molecules move farther away from C atoms. The RDF

of F-H distances reveals that H_2 molecules interact with the F atoms in a surprisingly close distance. At a low H_2 loading, contacts start at 1.9 Å and peak at around 2.5 Å. The shortest F-H distance in the GIC lattice is similar to the calculated gas phase value of 1.867 Å, suggesting that the interaction between F and H_2 arises from the partial charge transfer from F to H_2 as in the gas phase calculations. The calculated RDFs confirm that H_2 molecules reside primarily between F layers.

Figure 3-3. Radial distribution function of the selected bond parameters at low H_2 loadings ($C_{32}F_8 \cdot H_2$, and $C_{32}F_8 \cdot 2H_2$). (a) H-H. (b) C-F. (c) C-H. (d) F-H.

The calculated average adsorption energy per H_2 molecule, based on the room temperature *ab initio* MD simulation results, for a 0.37 wt % of H_2 loading is -23.3 kJ/mol (Table 3-1), substantially higher than the reported heat of adsorption of H_2 on graphite at liquid nitrogen temperature (ca. 4 kJ/mol¹³). We note here that it is known that the LDA method used in our simulation tends to overestimate the adsorption energy by about 30 - 40%, based on our previous simulations.¹⁴ Nevertheless, even upon discounting the over-binding of H_2 in the lattice, the calculated heat of adsorption is still significantly higher than what has been reported for H_2 adsorption in most porous carbon-based materials at near-ambient temperatures.¹⁵⁻¹⁸ However, compared with the calculated adsorption energy of H_2 on a gas-phase F^- anion, which

is approximately -30 kJ/mol, the average H₂ adsorption energy in the GIC of F⁻ anion is significantly reduced. As expected, the semi-covalent C-F bond effectively prevents the charge from being built entirely around the F atom. Furthermore, our MD results suggest that doubling the H₂ loading to 0.74 wt % only gives rise to a slightly lower average adsorption energy of -19.6 kJ/mol, and the inter-sheet spacing is reduced marginally (Table 1), suggesting that the interaction between H₂ molecules and the GIC still remains strong. The calculated RDFs of C-F, H-H, H-F and H-C distances shown in Figure 3-3 exhibit similar features as in the case of 0.37 wt % of H₂ loading. Quantitatively, the shortest C-H and F-H distances for the higher H₂ loading are slightly longer, consistent with the weaker interaction energy between H₂ and the GIC.

In contrast to the case of small H₂ loading, the interlayer distance increases substantially at higher H₂ loading to accommodate the large number of H₂ molecules. Figures 3-2(c) and 3-2(d) display the fully equilibrated structures of the partially fluorinated GIC with 12 and 24 H₂ molecules in the selected unit cell, respectively. The interlayer spacing between graphene sheets increases substantially with the large H₂ loadings in the lattice. At 4.29 wt % H₂ loading, the calculated interlayer spacing is 5.602 Å, while doubling the H₂ loading it further increases to 7.723 Å (Table 3-1). Our results indicate that the increased H₂ molecules are mostly confined between F layers. A detailed analysis of the MD trajectories indicates that H₂ molecules in the lattice are again highly mobile in the interlayer spaces between fluoride anions at 300 K, similar to the case of low H₂ loadings. The H₂ molecules are confined to the interlayer spaces between F atoms and are rarely in close contact with graphene sheets. The calculated RDFs of C-F, H-H, H-F and H-C distances are shown in Figure 3-4. No dissociative chemisorption of H₂ was observed in the entire course of the MD simulations. Our results suggest that the calculated average H₂ adsorption energy decreases as H₂ loading increases. Because of the large concentration of H₂ molecules between F layers, as shown in Figures 3-2(c) and 3-2(d), the H₂-H₂ repulsion becomes a significant factor in determining H₂ adsorption strength in the lattice and is largely responsible for the decrease of H₂ adsorption energy. At 4.29 wt % H₂ loading, the calculated heat of adsorption is drastically reduced to -10.5 kJ/mol. Further increase of H₂ loading to 8.58 wt % results in virtually no attractive interaction with the GIC lattice.

Figure 3-4. Radial distribution function of the selected bond parameters at high H_2 loadings ($C_{32}F_8 \cdot H_2$, and $C_{32}F_8 \cdot 2H_2$). (a) H-H. (b) C-F. (c) C-H. (d) F-H.

These results suggest that while the formation of semi-ionic C-F indeed helps improve the heat of adsorption of H_2 molecules, the material unfortunately fails to provide a sufficiently high H_2 capacity and high heats of adsorption for H_2 storage. The smaller capacity is partially due to the small surface area of the material and, more important, it is due to the significantly reduced electron density on the F atoms upon intercalation in the graphite and the strong repulsion between H_2 molecules at a high loading. To enhance the electron density on the atoms, we considered an n-doping procedure by replacing some of the carbon atoms on graphite with N atoms. The main idea is that the n-doping with N would allow the lone pair of the N atoms to be delocalized in the entire lattice through the π -conjugation already available in the graphene network. Consequently, the F atoms would be able to withdraw more charges from the graphitic sheets, potentially making the C-F bonds more ionic, which is expected to further enhance the attractive interactions between fluoride ions and H_2 molecules.

We reconstructed the original unit cell by replacing 8 C atoms with 8 N atoms. The supercell now contains 24 C atoms, 8 N atoms and 8 F atoms. The N atoms were intentionally made to be separated from each other as much as possible in the lattice, and their energetically preferred positions were sampled by performing energy minimization calculations. It was found that the α -positions to the C atoms with which F atoms form semi-ionic bonds are most

favorable. The calculated C-F bond distances range from 1.403 Å to 1.487 Å, slightly shorter than the range of C-F bond distances in the fluorinated GIC without the N-doping, but still longer than the conventional C-F bond length of approximately 1.35 Å. This implies that the C-F bonds in the case of N-doping are slightly less ionic than without N-doping, but still are semi-ionic in nature. In no situation is an N-F bond formed. The optimized unit cell structure, replicated by 2×2×2, is displayed in Figure 3-5. We subsequently uploaded the same numbers of H₂ molecules as in the case without N-doping in the supercell, followed by structural equilibration. The resulting lattice structures with H₂ adsorption are shown in Figure 3-6, and the calculated lattice spacing is listed in Table 3-2.

Figure 3-5. Supercell lattice containing 24 C atoms, 8 N atoms and 8 F atoms.

The slight shortening of the C-F bonds upon doping with N atoms in the partially fluorinated GIC is unexpected and undesirable because our original intention was to further promote polarization of the C-F bonds to enhance the interaction with H₂ molecules through delocalization of the electron lone pair of the N atoms via the π -conjugation network. To understand the origin of the C-F bond shortening, we studied the local binding structure by allowing H₂ to interact with a selected small portion of N-doped graphene, consisting of six fused rings, fluorinated by one F atom. The edges are terminated with H atoms (Figure 3-7). To examine the effect of the doping sites on H₂ adsorption strength, we placed the F atom at the α -, β - and γ -sites next to the N atom, respectively. We then performed full geometry optimization with and without H₂ and evaluated the relative interaction energies of H₂ with these molecules. The calculation was done at the level of B3LYP/6-311+G** using Jaguar 4.1¹⁹. The computational results are displayed in Table 3-3, where the main structural parameters, the

Mulliken charges on F and N atoms and interaction energies between the aromatic species and H_2 are listed.

Figure 3-6. Perspective view of the fully optimized structure of partially fluorinated, nitrogen-containing GIC with 1 H_2 (a), 2 H_2 (b), 12 H_2 (c), and 24 H_2 (d).

Figure 3-7. Structure of a small portion of N-doped graphene, consisting of six fused rings, fluorinated by one F atom.

We first compare the relative stability of N-doping at the α -, β - and γ -sites. Our calculation suggests that fluorination at the α -site is 66.1 kJ/mol more stable than at the β -site and 84.5 kJ/mol more stable than at the γ -site, indicating the tendency of dipole minimization. For the F atom placed at the α -site, the C atom is puckered out of the plane to form a semi-ionic bond with F with a torsional angle of 27.24° . Correspondingly, the N atom is pushed considerably inside the plane with a torsional angle of -6.71° . The calculated Mulliken charge in N indicates that the atom is virtually charge neutral with little electron delocalization from the lone pair, resulting from the structural distortion. The N atom thus adopts an electronic configuration of pseudo sp^3 hybridization, leading to its diminished π -conjugation effect on the F atom. The C-F bond is significantly longer than the conventional C-F bond due to the structural stress. In addition, the N-C $_{\alpha}$ bond, where C $_{\alpha}$ represents the C atom at the α -site, is also longer than the conventional N=C bond, again indicating the weakening of the π -conjugation around the N atom. Upon introduction of H $_2$, changes in the calculated bond parameters and charge distribution are marginal.

Table 3-3. The calculated structural parameters, the calculated Mulliken charges on F and N atoms prior to and post H₂ absorption and H₂ absorption energies in the selected portion of N-doped graphene fluorinated by a F atom. Here, torsion (C) is the torsional angle around C which comes out of the plane to form a semi-ionic C-F bond, and torsion (N) is the torsional angle around N, which goes to the opposite site of the plane.

	α		β		γ	
	prior	Post	prior	post*	prior	Post
C-F (Å)	1.495	1.506	1.611	1.509	1.577	1.608
N-C _a (Å)	1.449	1.447	1.380	1.447	1.400	1.400
H-H' (Å)	-	0.746	-	0.747	-	0.749
H-F (Å)	-	2.530	-	2.521	-	2.388
torsion (C) (degree)	27.24	26.91	24.61	26.81	25.56	24.61
torsion (N) (degree)	-6.71	-6.56	-0.50	-6.49	-0.44	-0.41
Q _F	-0.126	-0.101	-0.210	-0.101	-0.180	-0.136
Q _N	-0.035	-0.023	0.135	-0.023	0.182	0.191
ΔE_{ad} (kJ/mol)	-1.8		not meaningful		-3.3	
	-1.4					

* The optimized post H₂ absorption structure indicates that the F atom shifts from the β -site to the α -site upon H₂ absorption.

For the F atom placed at the β -site, the optimized structure shows that the C _{β} atom is pulled out of the plane with a torsional angle of 24.61° by F (Table 3-3). However, the *sp*² configuration of N is only marginally distorted by 0.5° upon fluorination. Consequently, the effect of π -conjugation is increased, as shown by a calculated positive charge on the N atom and a shorter N-C _{α} bond. Correspondingly, the F atom becomes more negatively charged, as expected. As a consequence, the C-F bond is significantly elongated, reflecting the stronger semi-ionic nature of the bond. Upon interacting with H₂ molecule followed by energy minimization, however, the F atom shifts from the β -site to the α -site, and the optimized structure is nearly identical to the one obtained by placing the F atom directly at the C _{α} atom. The migration is essentially barrierless, indicating the strong energetic preference of fluorination at the α -site. Finally, we placed the F atom at the γ -site. Again, the N atom adopts a nearly perfect *sp*² configuration without significant structural distortion. As a result, the π -conjugation effect of the lone pair of the N atom on the polarization of the C _{γ} -F bond, although not as strong

as in the case at the β -site, is still readily visible. The above results suggest that the charge enhancement on the F atom can be done at only the γ -site, but fluorination at this site is much less energetically favorable than at the α -site.

Having understood the interactions between H_2 and the small N-doped fluorinated fragment of graphene, we proceeded to perform MD simulations on the fully equilibrated supercells (Figure 3-6), containing both N atoms and F atoms at the selected H_2 loadings. In all cases shown here, fluorination takes place at the α -site. Similar to the situations without N-doping, H_2 molecules were found to be highly mobile in the lattices, confined primarily between F layers. The distances between the graphitic layers expand slightly at low H_2 loadings and increase substantially at high loadings. The calculated RDFs of the H-H, C-F, N-F, F-H, C-H and N-H distances are shown in Figure 3-8. In all cases, the H-H bond distance is centered around 0.75 Å. At high H_2 loadings, the H_2 molecules are separated by at least 2.4 Å. The RDF of C-F indicates that the C-F bonds are approximately in the range of 1.4-1.5 Å, reflecting the semi-ionic nature of the bond. The first peak of the N-F RDF indicates that the distance between N atoms and the F atoms at the α -site is about 2.5 Å. For each N atom in the lattice, there is at least one F atom at the α -site (Figure 3-5). The RDF of H-F distances exhibits a broad distribution, ranging from 1.8 Å to 4.0 Å and peaked around 2.5 Å. Here, the H_2 molecules can approach the F atoms more closely than in the gas phase, in which the calculated F-H distances vary from 2.388 Å to 2.530 Å, because each H_2 molecule is now interacting with several F atoms in the case of low loading. At high H_2 loading, most of the H_2 molecules cannot effectively interact with F atoms, and only a few molecules are in proximity to the F atoms. Consequently, the main feature of the F-H RDF shifts up slightly. Similar to the case without N-doping, the H_2 molecules stay away from the graphitic sheets by at least 2.8 Å.

Our MD simulations on H_2 storage in the selected N-doped fluorinated GIC yield significantly smaller average adsorption energies at low H_2 loadings compared with the average adsorption energies of H_2 in the non-doped fluorinated GIC (Tables 3-1 and 3-2). As analyzed above, the substantially reduced average adsorption energies are due to the fluorination at the α -site, leading to diminished π -conjugation of the N atoms, which prevents enhancement of negative charges on the F atoms. At high H_2 loadings, most H_2 molecules are unable to be in close contact with the F atoms, giving rise to small average adsorption energies. Our MD simulation results indicate that the N-doped, partially fluorinated GIC does not achieve enhanced higher heat of adsorption for H_2 via π -conjugation. The key obstacle is that fluorination occurs at the α -sites instead of β - or γ -sites.

Figure 3-8. Calculated RDFs of the H-H, C-F, N-F, F-H, C-H and N-H distances for hydrogen in the $C_{24}N_8F_8$ GIC.

Synthesis of Graphite Fluoroborate from Flake Graphites

C_xBF_4 provides a route towards fluorinated graphite based on Nikonorov's report²⁰ on the thermolysis of graphite fluoroborate. BF_3 is released from C_xBF_4 at 148-200°C, resulting in C_xF . However, data and details are scarce in this report, such that the nature of the decomposed material remains poorly understood. A schematic of the synthesis and thermal decomposition is shown in Figure 3-9. The desired product is the mixed anion material, $C_x(BF_4/F)$, highlighted by the dotted line. The residual BF_4^- anions are envisioned to prop graphene layers open for easier H_2 access towards the F atoms.

Figure 3-9. Synthesis and thermal decomposition of graphite fluoroborate.

The first materials were synthesized using larger particle flake graphite for ease of characterization. High surface area in the carbon precursor was not believed to be necessary because this could be achieved through the expansion of graphite layers through intercalation of anions. The greater crystallinity of large particle graphite facilitated the use of X-ray diffraction (XRD) to characterize changes in structure upon intercalation and subsequent thermal decomposition.

Alfa Aesar synthetic flake graphite (40-60 micron particle size) was used in the initial intercalation reactions. Exposure of graphite to a mixture of BF_3 and 20% F_2 over 4 days resulted in a second stage material, where every other graphite layer is intercalated with anions. The chemical formula determined through elemental analysis was $C_{25}BF_4$. This BF_4 concentration is less than the 2nd stage materials reported by Rosenthal and others ($C_{16}BF_4$).^{21,22} However, lattice parameters determined from XRD are consistent with Rosenthal's 2nd stage fluoroborate, displaying a c-axis spacing of 10.9 Å. $C_{25}BF_4$ was heated to 185 °C to thermally decompose the fluoroborate salt into a carbon fluoride. The XRD patterns of the as-produced BF_4 intercalated graphite and the heated material are shown in Figure 3-10.

Figure 3-10. Powder XRD (Mo K α) is shown for Alfa Aesar C_xBF₄ as synthesized, and after heating to 185°C. Approximately 1-3 mg of powder was loaded into a 0.7 mm diameter sealed glass capillary for measurement. The capillary gives a broad background amorphous peak centered around 22° 2 θ .

A clear shift of the peak centered around 24° 2 θ to a higher angle after heating indicates a decrease in the average layer thickness (from 3.63Å to 3.49Å). Thermal decomposition was further studied by thermogravimetric analysis (TGA) and temperature programmed desorption (TPD). As shown in Figures 3-11 and 3-12, C_xBF₄ made from Alfa Aesar graphite lost roughly 22 wt % upon heating, due to decomposition of the fluoroborate to form BF₃ and CF₄ gas.

Figure 3-11. TGA plot of C_xBF_4 from Alfa Aesar graphite, heated at 2 °C/min. under flowing N_2 .

Figure 3-12. TPD plots of C_xBF_4 from Alfa Aesar graphite, heated at 2 °C/min. under flowing N_2 .

BF_3 evolves from the GIC in two stages, at just under 100 °C and around 375 °C. The different decomposition stages are heavily reliant on the type of graphite used, as will be discussed later. The environment of the BF_4^- anions within the materials is still not well understood. However, the presence of CF_4 production indicated that C-F bonds were indeed being formed with decomposition of BF_4^- .

Differential scanning calorimetry (DSC) on Alfa Aesar C_xBF_4 is displayed in Figure 3-13, verifying the endothermic reaction of BF_4^- decomposition to BF_3 between 100 and 200 °C. A signature for CF_4 evolution is not observed in the DSC, perhaps due to the small quantity of material (about 3-8 mg) used in the measurement.

Figure 3-13. DSC data on C_xBF_4 with Alfa Aesar graphite. The DSC cell was purged with helium during a 10 °C/min. ramp to 600 °C.

These experiments indicated that a C_xBF_4 material heated to between 100-200 °C could yield a partially decomposed material containing F^- and residual BF_4^- anions. Infrared (IR) spectroscopy on a Alfa Aesar C_xBF_4 material also supports this observation. Shown in Figure 3-14 are IR absorption spectra on the neat C_xBF_4 powder heated under N_2 purge to various temperatures.

Figure 3-14. IR spectra of C_xBF_4 with Alfa Aesar graphite heated at different temperatures in a Harrick cell. CaF_2 plates are responsible for rising background with increasing temperature.

The broad peak at $\sim 1050\text{ cm}^{-1}$ corresponds to the B-F stretch in a BF_4^- anion. Upon heating, different components of this broad peak become visible, suggesting that different environments of B-F species are present during the thermal decomposition. Broad peaks centered around 1200 cm^{-1} are visible at 225°C , consistent with IR stretches reported for covalent C-F bonds.²³ At 300°C , both B-F and C-F stretches disappear, concurrent with the decomposition of C_xBF_4 to BF_3 and CF_4 gas. The differences in decomposition temperature observed between TGA, DSC, TPD, and IR measurements are attributed to differences in thermocouple positioning in relation to the sample and variations in heat mass transfer between these methods.

Raman spectra (532 nm) were obtained for these materials, revealing peaks corresponding with the G (graphite, 1580 cm^{-1}) and D (defect, 1360 cm^{-1}) bands known for graphitic materials.²⁴ The ratios of these bands changed with heating, indicating qualitative changes in the number of defect sites in the material. However, any further insights on the structure of C_xBF_4 based on this information were limited.

Based on the above evidence that a graphite fluoride could be generated from decomposing Alfa Aesar C_xBF_4 , we postulated that smaller graphitic domains would lead to faster decomposition of BF_4 and yield a greater F/ BF_4 ratio (greater fluoride content). Therefore, smaller particle carbons were used in place of the Alfa Aesar material in subsequent intercalation reactions.

Timrex SFG6 Graphite Fluoroborate – Synthesis and Thermal Decomposition

Timrex SFG6 is a synthetic flake graphite with uniform size distribution (average of 6 μm). This graphite was chosen as an intermediate carbon having enough crystallinity for XRD studies, yet increased surface area ($\sim 15 \text{ m}^2/\text{g}$) for faster intercalation. BF_3 / 20% F_2 exposure over 4 days resulted in intercalated graphite with molecular formula of $\text{C}_{20}\text{BF}_{4.7}$ as determined by elemental analysis. This material was analyzed by temperature programmed desorption (TPD) where off-gassing of the sample upon heating it in a tube furnace was analyzed by mass spectrometry. Intensity of signals for various atomic masses is plotted in Figure 3-15 versus increasing temperature.

Figure 3-15. TPD of C_xBF_4 made from Timrex graphite. Thermal decomposition products from heating the graphite fluoroborate are analyzed by mass spectrometry and plotted versus temperature. Major fragments are listed in the legend (e.g., $\text{BF}_3 = \text{BF}_2^+$).

BF_3 is observed to decompose from the sample in stages at different temperatures. CF_4 is generated at $\sim 400^\circ\text{C}$, indicating that C-F bonds were indeed being formed with decomposition of the BF_4^- anion. The relative intensity of peaks in the Timrex TPD differs from the Alfa Aesar graphite fluoroborate, likely due to differences in graphite morphology. However, the exact

nature of this decomposition, especially in correlating the shape and temperature of the TPD peaks with the type of graphite, is still not fully understood. To verify that the off-gassed BF_3 is coming from the intercalated BF_4 rather than adsorbed BF_3 on the carbon surface, XRD (shown in Figure 3-16) was employed to monitor changes in the lattice spacing.

Figure 3-16. Powder XRD (Mo $K\alpha$) of Timrex graphite and C_xBF_4 heated to different temperatures. Approximately 1-3 mg of powder was loaded into a 0.7 mm diameter sealed glass capillary for measurement. The capillary gives a broad background amorphous peak centered around $22^\circ 2\theta$.

The powder patterns in Figure 3-16 show the development of carbon layer spacing (determined from 00l reflections) upon intercalation and subsequent thermal decomposition. Native hexagonal graphite (space group $P6_3/mmc$, #194) exhibits a large 002 peak, corresponding to the $3.35 \text{ \AA}$ spacing between ABAB stacked graphene sheets. The 001 peak, corresponding to a c-axis unit cell size of $6.7 \text{ \AA}$, would be nonexistent in a perfect graphite crystal due to extinction of this reflection based on the structure factor.²⁵ Intercalated graphites, with anions incorporated between graphene layers, display an increase in average layer spacing, along with varied position and intensity of 00l reflections, depending on the staging, stacking sequence and crystallinity. Second stage intercalated graphite can also be indexed with a hexagonal cell, but the structure factor gives highest intensity to the 003 reflection rather than 002.²⁶ Loss of c-axis order upon intercalation can decrease the intensity or shift the positions of 00l reflections.^{27,28}

The sharp 002 peak at around $27^\circ 2\theta$ of the graphite starting material corresponds to an expected d-spacing of 3.35 Å. After intercalation, the largest peak at $\sim 24^\circ 2\theta$ corresponds with a 003 reflection for a 2nd stage C_xBF_4 with an increased d-spacing of 3.66 Å, consistent with an expansion of the graphene layers. The low angle 001 peak, which gives information about the sandwich layer spacing, and the 002 peak are not visible in this data due to the poor crystallinity of the material. The relatively small 6 micron particle size graphite loses much of its c-axis stacking order due to defects introduced upon intercalation. After heating to 150 °C, the 003 peak decreases in d-spacing to 3.55 Å, corresponding to a narrowing of the graphite layers following BF_3 decomposition. This gives strong evidence that the BF_3 originates from intercalated molecules within graphite layers and is not simply adsorbed to the carbon surface. At 600 °C, the C-F bonds are decomposed to CF_4 (as seen in the TPD), resulting in a XRD pattern similar to the graphite starting material (albeit with poor crystallinity). The broad peak centered roughly around $22^\circ 2\theta$ is common to all the patterns and is due to X-ray scattering from the amorphous quartz capillaries containing the samples.

The fluoride intercalation in these materials was investigated using solid state nuclear magnetic resonance (NMR). NMR analysis can provide chemical shift and line-shape information. Chemical shift is sensitive to changes in the local environment of a studied nucleus. Line-shape analysis can provide information regarding the mobility and distribution of species. The ^{19}F NMR chemical shift is extremely sensitive to small changes in local structure, making it suitable for monitoring the evolution of fluorine species in graphitic materials at various synthesis conditions and heat treatments. Variation in electron charge density on the F atoms will affect their response to an applied magnetic field. Different chemical environments, ranging from covalent to ionic C-F interactions, will change the relative charge density and mobility on intercalated fluorine species. The ^{19}F chemical shift and peak shape measured for different graphite fluorides can therefore be used to compare the relative ionic character of the fluoride atoms. ^{11}B NMR can provide coordination number information as it can be used to identify three- and four coordinated boron species. Finally, ^{13}C NMR can be used to monitor any structural changes in the graphitic layers. As an example, solid state NMR spectra of $C_{19}BF_4$ (as determined by elemental analysis), made from Timrex SFG6 heated to different temperatures, is displayed in Figures 3-17 and 3-18.

Figure 3-17. Solid state magic angle spinning (MAS) NMR spectra for ^{19}F and ^{11}B nuclei within Timrex C_xBF_4 materials heated to different temperatures. Tentative peak assignments are labeled. Peak intensities have been adjusted to relatively similar values for clarity. Frequencies are relative to CFCl_3 .

^{13}C MAS NMR

Figure 3-18. Solid state magic angle spinning (MAS) NMR spectra of ^{13}C nuclei within Timrex C_xBF_4 materials heated to different temperatures. Peak intensities have been adjusted to relatively similar values for clarity. Frequencies are relative to CFCl_3 .

The ^{19}F NMR spectra of synthesized and heated Timrex C_xBF_4 exhibited many peaks, of which most are only tentatively assigned at this time. The relative broadness of peaks in these spectra, and the more unpredictable chemical shift effect of a graphitic cation in solid state NMR make the assignments challenging. For the room temperature spectra, the main peak at about -145 ppm is likely representative of fluorine atoms in BF_4^- anions. This assignment is made based on the 148-152 ppm for BF_4^- in ionic liquids^{29,30} (it may not be an appropriate comparison due to a strong interaction between Na and BF_4^- ion; the chemical shift of NaBF_4 is -163 ppm from our study); it is also based on the elemental analysis which showed the composition of the anions to be BF_4^- rather than B_2F_7^- . B_2F_7^- is a cluster formed from the coordination of a BF_3 molecule to a BF_4^- anion, and is known to exist in ionic liquids. The strong Lewis acidity of BF_3 lends itself to coordinate with electron rich species. This can include any BF_4^- anions it encounters while diffusing out from the middle of a graphite domain, producing B_2F_7^- or higher ordered clusters. Additional coordination may even occur with any residual oxide functional groups bonded to carbon. B-F clusters, formed from coordinating BF_3 , may contribute to the smaller peaks in the NMR spectra shifted to the left of the BF_4^- peak. A weaker carbon

interaction with $B_2F_7^-$ versus BF_4^- results in this higher chemical shift. Note that the chemical shift of $B_2F_7^-$ at -150°C were reported at -117 ppm for bridging F and at -151.4 ppm for terminal F.³¹ The average chemical shift at room temperature should be about -147 ppm, which agrees with our assignment.

From literature reports on C_xF materials, semi-ionic C-F bonds have ^{19}F chemical shifts in the -150 to -160 ppm range.³²⁻³⁴ Therefore, peaks to the right of the BF_4 signal were tentatively assigned to C-F bonds being generated as BF_4^- anions were decomposing. Covalent C-F bonds, as in perfluorinated graphite, have shifts in the -190 to -200 ppm range, which were not observed until 375°C .^{35,36} However, changes in the ^{19}F spectra with heating are in correspondence with subtle changes in the ^{11}B NMR spectra, suggesting that most of the ^{19}F peaks at 25 , 150 and 250°C are still related to B-F species rather than substantial C-F bonding. These various B-F chemical environments observed in the NMR data may correspond with the different stages of BF_3 decomposition seen in the TPD plots. Absence of signal enhancement via cross polarization experiments from ^{19}F to ^{11}B NMR suggests that these BF species are mobile. The ^{11}B signals in Figure 3-17 are centered around -2 to -4 ppm, and correspond to a typical 4-coordinated boron species. No evidence of three coordinated species exists (usually these are located at 15 ppm). Still, at 375°C , the ^{11}B signal becomes broad, with low intensity, suggesting that the ^{19}F signal at this temperature is representative of mostly C-F interactions; because this chemical shift at -155 ppm is also present in the 150°C ^{19}F spectra, we were led to believe that C_xBF_4 heated to 150°C contains some of the desired mixed anion material, $C_x(BF_4/F)$. The elemental analysis does not confirm a large presence of C-F at 150°C , with the stoichiometry resulting in $C_{26}BF_{4.2}$. It is worth mentioning that the decrease in ^{19}F chemical shift of BF_4^- species at higher temperatures may be due to a stronger interaction between C and BF_4^- species. At a certain point, the BF_4^- structure is no longer stable, and semi-covalent C-F forms coincident with the out-gassing of BF_3 . More discussion on ^{19}F NMR spectra with respect to other materials made in this study will be provided below.

^{13}C NMR displayed two closely spaced peaks, indicative perhaps of different carbon environments associated with 2nd stage intercalated materials. Carbon layers with intercalant and those without may give slightly different chemical shifts. As the BF_4 intercalant is decomposed with heat, the system is similar to a pure graphitic material with higher conductivity, which may be the cause for the observed broadening in the NMR line-shape as was seen in un-intercalated graphitic materials.

Iodometric titrations were performed on the series of heated Timrex C_xBF_4 to help determine the relative ionicity of fluoride between samples. Samples with more ionic character, and therefore more moles of positively charged carbon, would be stronger oxidizers towards iodide. The reactions occur in the titration of generated I_2 as follows:

Moles of thiosulfate required to titrate iodine back to iodide were used to calculate moles of C^+ present in the materials, assuming the stoichiometry of $2C^+ + 2I^- \rightarrow I_2$. Chemical formulas were then determined by assuming a C_xBF_4 stoichiometry for all samples. These relative formulas can be compared to roughly determine the oxidative activity of the materials, which are directly related to their degree of ionicity. Formulas determined for Timrex graphite fluoroborate treated at 25, 150, 250, and 375 °C were $C_{43}BF_4$, $C_{51}BF_4$, $C_{72}BF_4$, and $C_{147}BF_4$, respectively. A sharp decrease in active C^+ content is evident with the increase in heat treatment temperature. This is likely due to the C-F interactions becoming more covalent with higher temperatures. Indeed, covalent perfluorinated graphites are synthesized by the direct fluorination of graphite at temperatures $>400^\circ\text{C}$. To maintain a more ionic C-F bond, thermal decomposition of C_xBF_4 must be performed at as low a temperature as possible.

H₂ Adsorption of Alfa Aesar and Timrex SFG6 Graphite Fluoroborates

Hydrogen adsorption isotherms were measured at near-ambient temperatures on both the Alfa Aesar and Timrex C_xBF_4 materials heat treated at relatively low temperatures. The series of plots are shown in Figure 3-19.

a)

b)

c)

d)

e)

f)

g)

h)

Figure 3-19. H_2 adsorption isotherms and isosteric heat vs. capacity, respectively, are displayed for Alfa Aesar 2nd stage C_xBF_4 (a, b), Timrex 2nd stage C_xBF_4 (c, d), Timrex 2nd stage C_xBF_4 (e, f), and Timrex 1st stage C_xBF_4 TMX F2-3 (g, h). The Alfa Aesar sample was heat treated at 185°C, while the Timrex materials were heated to 150°C.

All materials showed small capacities, <0.2 wt %, but with heats of H_2 adsorption of ~2 kcal/mol (~8 kJ/mol), a value much higher than native graphite (~4 kJ/mol¹³), and on par with Amoco Supersorb activated carbon (GX-31). One Timrex 2nd stage C_xBF_4 sample showed a ~3 kcal/mol (~12 kJ/mol) heat of adsorption; however, this result was not been reproduced in other 2nd stage materials. The large variability in thermal decomposition between batch syntheses is likely the cause. The last sample in Figure 3-19 represents a 1st stage C_xBF_4 . The overall capacity is not as high as the 2nd stage material, but the initial heat of H_2 adsorption is slightly higher. The decrease in isosteric heat upon loading may be attributed to loss of active binding sites as more H_2 becomes adsorbed. The demonstration of two samples with heats of H_2 adsorption well above that observed for activated carbons supports the hypothesis that fluoride anions significantly increase the affinity for hydrogen.

It was never apparent if the mild activation procedure used just before isotherm measurements (25-50 °C heating under vacuum for several hours or overnight) results in insufficient degassing, and thus affects the H₂ adsorption data.

Analyses of Other Graphite Fluoro-complexes

Several materials were synthesized to compare the differences in thermal decomposition between various carbons intercalated with BF₄ and other fluoride species. Because of the low crystallinity displayed by many of these materials, the most important analytical experiments included TPD, elemental analysis, and solid state NMR. TPD data for all samples synthesized in this report are presented here (Figure 3-20), while other analyses are summarized in the following section.

a)

b)

c)

d)

e)

f)

g)

h)

i)

j)

Figure 3-20. TPD plots showing mass spectroscopy signals of various masses as a function of temperature. TPD were performed on C_xBF_4 materials synthesized from graphite fibers (a), graphitized carbon black (b), UCAR carbon (c), Kynol carbon fibers (d), and carbons from the Foley Research group at Penn State University (e). Also shown are TGA-IR plots of C_xPF_6 made from Timrex (f, g) and graphite fibers (h, i). The final TPD illustrates the thermal decomposition products of C_xF made from Timrex C_xHF_2 (j).

The TPD plots presented here clearly show a large variability of thermal decomposition characteristics between BF_4^- intercalated materials made with different carbons. Because different B-F species were observed in the NMR data, we believed initially that the low temperature ($\sim 100^\circ C$) BF_3 decomposition was indicative of weakly bound coordinated BF_3 molecules, rather than decomposition of BF_4^- anions. It followed that this low temperature peak was missing from the TPD plots of higher surface area carbons because coordinated BF_3 would be easily evacuated by vacuum pumping. However, C_xBF_4 made with Kynol carbon fibers had the highest surface area of any carbons used in this study, and only the low temperature BF_3 decomposition is present in its TPD. Also, the presence of significant amounts of coordinated BF_3 would imply that B_2F_7 or higher order clusters are present after synthesis at room temperature. Elemental analysis on all samples made thus far have resulted in BF_4 or $BF_{>4}$ compositions, not the $BF_{3.5}$ ratio expected for B_2F_7 . All syntheses were performed with stoichiometric or excess F_2 , making the generation of coordinated BF_3 unlikely. The variation in

BF₃ decomposition between samples is due most likely to the interaction of intercalated BF₄ anions with the type of graphitic domains present in each carbon. Without detailed knowledge of the domain morphologies, it remains difficult to predict the nature of the thermal decomposition.

Summary of Graphite Fluoro-complexes

Table 3-4. Summary and comparison of various intercalated graphite fluoride complexes.

No.	Formula – C, H, B, P, F elemental analysis	Act. Temp. (°C)	Carbon Type	Surface Area (carbon, in m ² /g)	Surface Area (after F, in m ² /g)	H ₂ Capacity (wt. % at room temp, ~100 atm.)	Heat of Ads. (kJ/mol)	I ₂ titration derived formula (mmol C ⁺ /g)	¹⁹ F shifts (-ppm)	Notes
1	C ₂₀ BF _{4.7}	None	Timrex	14.7					146	First sample made with Timrex.
2	C ₂₅ BF ₄	150	Timrex	14.7	75	0.12 %	12		140, 152	Made from heating #1. Only sample to exhibit 12 kJ/mol isosteric heat.
3	C ₂₈ BF _{4.1}	None	Timrex	14.7						Exposed to less than stoichiometric amounts of BF ₃ , F ₂ .
4	C ₃₅ BF _{5.8}	150	Timrex	14.7		0.09 %	9			Made from heating #3.
5	C ₁₉ BF ₄	None	Timrex	14.7	117.6			C ₄₃ BF ₄ (1.6)	138, 144, 150	Attempt at repeating synthesis of #1.
6	C ₂₆ BF _{4.2}	150	Timrex	14.7	15.9	0.17 %	8	C ₅₁ BF ₄ (1.4)	140, 148, 151, 156	Made from heating #5.
7	C ₂₆ BF _{4.2}	150	Timrex	14.7		0.32 %, 77 K (1 atm)	8	C ₅₁ BF ₄ (1.4)	140, 148, 151, 156	Same sample as #6, just measured at 77 K.

8	$C_{37}BF_{5.3}$	250	Timrex	14.7	16.9	0.14 %		$C_{72}BF_4$ (1.1)	144, 148, 152	Made from heating #5.
9	$C_{72}BF_{7.7}$	375	Timrex	14.7	16.7			$C_{147}BF_4$ (0.54)	156	Made from heating #5.
10	$C_{18.5}BF_{5.3}$	None	Graphite fibers	18.3	25.0			$C_{20}BF_4$ (3.1)	137, 148	
11	$\sim C_{77}BF_{12}$	375	Graphite fibers	18.3		0.10 %			150, 185	Made from heating #10.
12	$C_{40}BF_{4.5}$	None	Carbon black	79.4	80.0			$C_{29}BF_4$ (2.3)	146	Excess oxidant in titration result.
13	$C_{27}H_{2.1}BF_{6.4}$	None	UCAR	25.6					148	Use of unpurified F_2 cause for presence of HF.
14	$C_{25.5}BF_{5.3}$	150	UCAR	25.6	13.4	0.06 %	8		154	Made from heating #13.
15	$C_{40}PF_9H_4$	25	Timrex	14.7	101.1	0.06 %		$C_{46}PF_6$ (1.4)	72, 75	Use of unpurified F_2 cause for presence of HF.
16	$\sim C_xPF_6$	200	Timrex	14.7	82.5					
15	$C_{36.3}PF_{11}H_{1.5}$	25	Graphite fibers	18.3						
16	C_xBF_4	25	Hard Carbon							Li Battery carbon
17	$C_{3.4}F$	50	Timrex	14.7	17.6	0.04 %	~ 5	$C_{187}F$ (0.44)	144, 183	Matches literature reported structural properties. Isotheric heat is calculated based on poor 0 C isotherm data.
18	$\sim C_8F$	50	PSU carbon	145		0.20 %	2		150, 199	Adsorbed HF likely present. Slow (>4 hr) H_2 equilibration in

										isotherm data.
19	C ₂₀₇ BF ₃₂	150	PSU carbon	145	474.7	~0	~0	C ₁₆ BF ₄ (3.6)	150, 199	Heated to remove adsorbed HF. Evidence of adsorbed F ₂
20	C ₁₅₂ BF ₁₈	50	MWNT	297	298.2			C ₁₄ BF ₄ (3.9)	138, 152, 175, 200	3.6% metals present, NiF ₂ , FeF ₃ likely
21	C ₂₅ BF ₄	40	PSU carbon	145	5.7			C ₂₉ BF ₄ (2.3)	147	
22	C ₄₄ BF ₁₂	40	Kynol	1800	798.5			C _{1.3} BF ₄ (9.8)	155, 159	Presence of adsorbed F ₂ likely
23	C ₁₆ BF ₃	40	Amoco AX-21	2500	1947.7			C ₁₂ BF ₄ (4.2)	154	Evidence of adsorbed F ₂
24	Pt/C	300/3 %H ₂	PSU after DPAU		1474.4	0.57 %	2.0-9.2			19 point DPAU run to concentrate on low P spill over
25	C ₁₅₄ BF ₃₁	150	Kynol BF ₄	1800	775.3	0.20 %	0	C ₁₂₅ BF ₄ (0.6)		
26	C ₅₁ BF ₅	250	PSU carbon	145	20.7	0.18 %	7.1	C ₄₆ BF ₄ (1.6)	145, 152	
27	C ₁₂₃ BF ₈	150	Amoco AX-21	2500	2387.0	0.60 %	7.9	C ₃₅₁ BF ₄ (0.2)		
28	C _x BF ₄	50	Timrex	14.7					138, 149	Pure F ₂ / @ RT; 3 days – XRD 2 nd /1 st stage; 25% loss on heating to 600C
29	C _{8.2} BF _{4.2}	50	Timrex	14.7	11.7			C _{9.7} BF ₄ (4.9)	138, 149	Continued Pure F ₂ treatment, 1 st stage by XRD, 58% loss on 600C TPD
30	C ₉₇ BF ₁₃	150	Timrex	14.7	13.0	0.05 %	7.7-13.8	C ₃₁ BF ₄ (2.2)	147, 180	TMX-F2-2 treated at 150C, 48% loss on heating

31	Native Carbon	900	Graphite Fibers	18.3		~0	~0			Isotherm too small for accurate measurement of uptake or heats
32	C _{16.3} BF _{7.3}	50	Graphite Fibers	18.3	21.0			C _{11.3} BF ₄ (4.5)		Pure F2 until XRD 1 st stage
33	C _x BF ₄	150	Graphite Fibers	18.3		0.08 %	5.1-10.0	C ₄₁ BF ₄ (1.5)		GFib-F2-1 treated at 150C
34	C ₁₃ B	300	BCx	700		0.34%	11.0-16.2			Mike Chung PSU – 8%atom Boron, Activated 300C – 500mg supplied
35	C _x BF ₄	150	Timrex	14.7						
36	C _x BF ₄	375	Carbon Black	79.4						
37	C _x PF ₆	25	Timrex	14.7						
38	C _x BF ₄	50	SWNT			0.24 %	3.3-7.4	C ₁₂ BF ₄ (4.2)		Tensimetric uptake to est C ₁₀ BF ₄
39	C _x BF ₄	100	SWNT			0.24%	9.6-11.5	C ₁₈ BF ₄ (3.2)		FSWNT treated at 100C for further activation
40	C _x BF ₄	118	Timrex	14.7		0.11%	7.6-12.5	C ₂₂ BF ₄ (3.1)		TMX-F2-2 Treated at 115 for specified BF3 loss of ~50%

Chemical formulas denoted by '~' are rough estimates calculated from gravimetric analyses.

* Liquid HF phase synthesis, with bubbled 20% F₂ followed by 50 °C overnight evacuation.

PSU carbon indicates carbon obtained from Foley research group at Penn State Univ.

Summary of H₂ Adsorption Testing and Characterization

Ambient temperature hydrogen adsorption isotherms were measured for several BF₄⁻ and F⁻ intercalated graphites at pressures up to 100 atm. Isosteric heats were determined from isotherms measured at 0 and 25°C based on the Clausius Clapeyron equation. As shown in Table 3-1, the highest isosteric heat (12 kJ/mol) was obtained for a Timrex C_xBF₄ material heated to 150°C. This result could not be reproduced, however, due to the batch-to-batch variability inherent to these materials. It is worth noting that the surface area for the initial sample of C_xBF₄ (entry #2 in Table 4), heated to 150°C, was 75 m²/g, while later samples of

heated Timrex C_xBF_4 gave surface areas only around 16-17 m^2/g . The surface area of a later sample (entry #5 in Table 3-4) immediately after intercalation showed an increase from 15 to 118 m^2/g , but somehow lost nearly all the excess surface area after heating. This may be due to the variability in thermal decomposition as discussed earlier with the TPD plots. It is uncertain at this time whether some intercalated molecules become trapped during decomposition, due to the collapse of the graphene sheet edges. This would be consistent with a decrease in surface area after heat treatment, but further study would be necessary to determine the exact microstructure of the heated materials.

The ambient temperature capacities for heated Timrex C_xBF_4 materials in general were in the 0.1 to 0.2 wt % range, with isosteric heats around 8 kJ/mol. While these levels are well below the DOE targets, they are relatively high given the low measured surface areas. By comparison, activated carbon can have surface areas around 2000 m^2/g and adsorb 0.6 wt % H_2 at ambient temperature with heats of adsorption around 8 kJ/mol.

From these initial results, two different strategies were pursued. The first strategy was to vary the type of fluoride intercalant, and the second was to intercalate high surface area carbons. HF_2^- and PF_6^- were intercalated into Timrex graphite as a direct comparison to BF_4^- . C_xHF_2 decomposes upon mild heating under vacuum (50°C) to give C_xF . This material resulted in poor H_2 adsorption, with a capacity of 0.04 wt % and a heat of adsorption of 5 kJ/mol. C_xPF_6 has larger gallery spacing than C_xBF_4 and was hoped to improve H_2 storage through this increase in surface area. While this sample did show an increase in surface area ($\sim 100 m^2/g$), it only obtained a H_2 capacity of 0.06 wt %, below even the low capacities of the BF_4 materials. This PF_6 sample, however, was measured as synthesized (without any heat treatment). The intercalated anions are therefore composed of PF_6^- and a small amount of HF_2^- (bifluoride was present due to the use of unpurified F_2).

Fluoride intercalation into a high surface area carbon was initially believed to be difficult due to the amorphous nature of these carbons (small graphitic domain sizes). Graphite intercalation occurs via a charge transfer reaction, where the graphene sheets are either reduced or oxidized. In the case of C_xBF_4 , for example, graphite is oxidized by F_2 to make F^- and C^+ . This oxidation is possible at ambient temperatures (rather than higher temperatures if only F_2 was used) due to the strong Lewis acidity of BF_3 , which facilitates the reaction by reacting with the F^- to form a BF_4^- complex. The heat of formation is large enough to overcome the Van der Waals forces that hold the graphene sheets together and thus allows the BF_4^- anions to intercalate. Without large graphite domains, we imagined that physical access between graphene sheets as well as electronic factors for charge transfer would be hindered. Indeed, C_5N , an amorphous nitrogen doped carbon, could not be significantly intercalated with BF_4^- . Several different carbons were treated with BF_3/F_2 , and they all seemed to gain mass and have measured ^{19}F NMR signals consistent with successful BF_4^- intercalation. While graphite fibers, graphitized carbon black, and UCAR carbon have some degree of graphitic character, the Amoco AX-21, Kynol ACF-20, and Penn State materials are more amorphous carbons that appeared initially to intercalate with BF_4^- anions. Titration results and elemental analysis give evidence that adsorbed F_2 may be responsible for the major increase in weight. Still, it was unexpected that any BF_4^- intercalation would occur.

Graphite fibers and UCAR carbon, with surface areas comparable to Timrex graphite, resulted in C_xBF_4 materials with H_2 adsorption capacities and heats of adsorptions no better than Timrex C_xBF_4 . However, the measured surface areas were still below the $75\text{ m}^2/\text{g}$ obtained for the first Timrex C_xBF_4 heated to 150°C . Graphitized carbon black, which has a native surface area of $80\text{ m}^2/\text{g}$ before intercalation, had not been measured for H_2 adsorption. It would be interesting to see if a C_xBF_4 material with graphitized carbon black would increase the heat of adsorption due to the higher surface area. However, the BF_4^- concentration was a factor of two lower than Timrex C_xBF_4 .

H_2 adsorption capacities are shown in Table 3-4 for C_xBF_4 materials made from higher surface area carbons. Despite the high native surface area of $1800\text{ m}^2/\text{g}$, Kynol C_xBF_4 heated to 150°C obtained only a capacity of $0.2\text{ wt } \%$, and displayed a negligible heat of adsorption for hydrogen. The surface area after BF_4 intercalation decreased to $800\text{ m}^2/\text{g}$ and fell further to $775\text{ m}^2/\text{g}$ after heating, indicating that intercalation filled some available pore volume, resulting in decreased H_2 capacity. Iodometric titration indicated that excess oxidant was present in the intercalated material, suggesting that a significant amount of F_2 was adsorbed in the carbon. After heating, the titration results revealed a significant loss of oxidative capacity, suggesting the C-F bonds created were mostly covalent. Upon heat treatment, the adsorbed F_2 may have directly reacted with the carbon to give more covalent type C-F bonds, filling available active sites and decreasing the affinity for H_2 . A similar titration result was observed for Amoco AX-21 C_xBF_4 ; however, its surface area did not decrease as much with intercalation, and thus the H_2 isotherms showed better capacities ($0.6\text{ wt } \%$, 8 kJ/mol heat of adsorption). The elemental analysis for Amoco AX-21 C_xBF_4 showed that the fluorine concentration dropped significantly after heating to 150°C , yet its surface area actually increased after heating. This result indicated that the adsorbed F_2 may have desorbed on heating instead of reacting with carbon, and resulted in essentially unmodified activated carbon.

The Penn State carbon (provided by Dr. Ramakrishnan Rajagopalan; native surface area of $145\text{ m}^2/\text{g}$) intercalated with BF_4 with subsequent 250°C heating (temperature chosen based on TPD data) resulted in a H_2 capacity of $0.2\text{ wt } \%$, with a heat of adsorption of 7 kJ/mol . The surface area after intercalation was quite low, $5.7\text{ m}^2/\text{g}$, but increased to $20\text{ m}^2/\text{g}$ after heating. Both surface areas are much lower than that of the native carbon, suggesting that intercalation in this case also takes up potential H_2 binding sites. Any increase in H_2 affinity provided by the fluoride is negated by the loss in surface area. Still, although this material represents another example of similar H_2 adsorption characteristics to Timrex C_xBF_4 , it helps illustrate the improvement of H_2 adsorption between fluorides made from BF_4 versus HF_2 . C_8F made from the thermal decomposition of C_xHF_2 synthesized from the PSU carbon displayed a capacity of $0.2\text{ wt } \%$ as well, but a heat of adsorption of only 2 kJ/mol . After heating to 150°C to remove any HF or adsorbed F_2 , both the capacity and heat essentially measured zero.

The C_xBF_4 materials made with higher surface area carbons did not improve the capacities or the heats of adsorption for H_2 . This may be due to the type of C-F bonds being generated in the high surface area materials. If the mass increase was due mostly to adsorbed F_2 and not BF_4 intercalation, then the direct reaction of F_2 with carbon at higher temperatures would result in covalent C-F. ^{19}F NMR spectra on these heated materials are necessary to reveal the effects of

heat treatment. However, based on the iodometric titration results, we have evidence that the C-F bonds generated are of a covalent nature. Also, the similar capacities could be due to available active sites for H₂ adsorption. Intercalation of high surface area materials apparently fills what used to be available pore volume for H₂ adsorption. A further reason for the lack of distinction in capacity between low and higher surface area C_xBF₄ materials may be the measurement of H₂ isotherms at ambient temperatures. Isotherms measured at 77 K could have resulted in a greater distinction.

¹⁹F NMR Analysis for Different Carbons

Figure 3-21 displays a stack plot of ¹⁹F solid state NMR spectra for the various graphite fluorides synthesized in this study. As discussed earlier, the chemical shift can be related to the ionic character of the fluoride anions. The first group of spectra shows data for Timrex C_xBF₄. Sample batch variability is evident, despite similar compositions as determined from elemental analysis (see Table 3-4). Subtle variations in fluoride composition may affect how the anions interact with carbon in the graphite sheets, resulting in a slightly different chemical shift.

Further variability exists in the ¹⁹F spectra measured on C_xBF₄ materials synthesized with different carbons. The second group includes materials made with higher surface area carbons, and fewer peaks are observed that may correspond with B₂F₇⁻ clusters. We hypothesize that the shorter graphitic domains present within these higher surface area carbons allow coordinated BF₃ to be more easily removed on the final evacuation step during synthesis. Elemental analysis on almost all samples of C_xBF₄ has indicated BF₄⁻ anions rather than B₂F₇⁻, even in the Timrex materials. However, solid state NMR may be more sensitive to small concentrations of coordinated BF₃ (i.e., B₂F₇⁻). The chemical shift related to BF₄⁻ was observed to vary between -140 and -160 ppm, depending on the type of carbon used. The interaction of the BF₄⁻ anion with the graphene sheets may be responsible for these differences. Shorter sheet lengths, present in the amorphous carbons such as Amoco AX-21 and Kynol fibers, limit the mobility of the BF₄⁻ ions, and effectively result in a stronger interaction with carbon. This results in a lower peak shift (more negative, towards the right). Carbons that exhibit longer graphene sheet morphologies, such as Timrex and graphite fibers, allow BF₄⁻ anions more mobility, resulting in a less effective interaction with carbon.

Figure 3-21. ¹⁹F NMR spectra of various graphite fluorides.

The last group of spectra was measured for C_xF materials synthesized through C_xHF_2 for comparison to C_xF made from C_xBF_4 (the carbon fluorides made from the graphite bifluoride intercalate were produced by heating C_xHF_2 to about 50 °C under vacuum). It is clear that the NMR spectra for C_xF produced through C_xHF_2 have much wider peaks, even when compared to Timrex C_xBF_4 heated to 375 °C. The peak widths can be correlated with relative ionic character, with the narrower the peak corresponding with more ionic fluoride species. In this report, the peak centered at around -150 ppm represents the “semi-ionic” C-F bonds, and the small peak, near -190 ppm, indicates the presence of more ionic F^- . Confusion arises from the fact that covalent C-F in CF_x or $(C_2F)_x$ materials also give ^{19}F shifts around -170 to -200 ppm. The important distinction between these two is attributed to the difference in peak widths. Covalent C-F, with low mobility, results in much wider peak widths in solid state NMR compared to ionic C-F. Ionic F^- species are isolated mobile ions that are non-interactive with carbon and thus have a more isotropic chemical environment, giving one sharp peak in the NMR spectra (similar to mobile ions in liquid state NMR). The less mobile fluorine nuclei in covalent C-F bonds have greater anisotropy present in their nuclear magnetic interactions with carbon. Despite the sample being spun at high frequency to reduce this affect, it still manifests in the apparent presence of multiple chemical shifts, resulting in a broadened peak.

The broadness of the -185 ppm peak suggests that the semi-covalent C-F species are disordered (with variety of C-F bond lengths). C_xF made from the Penn State carbon has a sharper peak at around -200 ppm. However, the peak is significantly reduced in intensity upon heating, and it is in the approximate range for adsorbed HF. It is likely HF that had not been evacuated successfully. A weight loss was not observed after heating this sample, and it could not be detected by TPD. We concluded that just a small amount of surface or inter-sheet adsorbed HF is enough to be detected by NMR.

In summary, the C_xF materials made from C_xHF_2 had more disordered semi-covalent C-F bonds than that made from C_xBF_4 heated to 375 °C, suggesting the BF_4 route is more favorable toward synthesizing an ionic graphite fluoride with semi-covalent C-F bond with more ordered bond length. However, two factors need to be considered that temper this conclusion:

- 1) The major ^{19}F peak signal for Timrex C_xBF_4 heated to 375 °C has not been definitively assigned as a C-F interaction rather than B-F. The ^{19}F peak of C_xF from C_xBF_4 being sharper than that of C_xF from C_xHF_2 may only be indicative of a small amount of intercalated BF_4^- that overwhelms a lower intensity, broad signal of any covalent C-F present.
- 2) If the fluorine signal in Timrex C_xBF_4 heated to 375 °C is entirely due to C-F interactions, the fluorine content is still relatively low (about $C_{20}F$) compared to C_xF made from C_xHF_2 ($C_{3.4}F$). Higher values of x have been reported to correspond to more covalent C-F, while lower concentrations are more ionic.

Still, the BF_4 materials gave higher H_2 capacities and heats of adsorption than HF_2 samples made with the same carbons. We conclude that C_xF derived from HF_2 is either too covalent or too limited in gallery size for H_2 access to F atoms. The relatively low concentration of F in the heated C_xBF_4 materials also prevents us from reaching definitive conclusions in this study.

C_xN Graphite Fibers

Nitrogen doped graphite synthesized using Nakajima's CVD method³⁷ resulted in the highest observed level of nitrogen incorporation of C₁₉N (GN-43). Synthesis involved passing acetonitrile vapor over nickel powder catalyst at 600-900 °C. Several conditions were varied in attempts to improve the nitrogen doping level and scale up this reaction to produce enough C_xN for BF₄ intercalation. The results are presented in Table 3-5.

Table 3-5. Synthesis conditions and products of C_xN graphite fibers

ID	Growth Temp. (°C)	Size of Ni catalyst	Amt of Ni catalyst (mg)	Temp. of CH ₃ CN sparger (°C)	Argon flow rate (cc/min)	Time of H ₂ at 400 °C (hr)	Time of growth (hr)	Outlet check valve press. (psig)	Amt of carbon (mg)	C/N atomic ratio
GN-43	900	3 μm	112	25	25	1	5	1	244	C ₁₉ N
GN-47	900	100 nm	86	25	25	1	6	1	407	C ₁₂₆ N
GN-52	600	100 nm	85	25	25	1	4	1	41	C ₁₆ N
GN-55	700	100 nm	124	25	25	1	5	1	72	C ₃₆ N
GN-56	900	3 μm	361	25	25	2	5	1	421	C ₁₁₂ N
GN-59	900	3 μm	1510	25	25	2	5	1	810	C ₇₃ N
20968-72	900	3 μm	117	60	25	1.5	7	10	415	C ₇₂ N
20968-73	900	3 μm	1102	70	25	4	7	10	4858	C ₈₈ N
20968-76	900	3 μm	95	25	50	1.5	8.5	1	1318	C ₂₆ N

The results shown in Table 3-5 demonstrate that increasing the argon carrier gas flow rate resulted in the best yield and maintained a relatively high N-doping level. Increasing the acetonitrile vapor concentration in the reactor through heating the sparger and increasing the check valve pressure gave better yields, but drastically reduced the nitrogen incorporation. This result may be due to the effects of annealing the fibers in hydrogen at high temperature. H₂ is likely present during the pyrolysis of CH₃CN, and decomposes C_xN through formation of HCN. Increasing the vapor concentration of acetonitrile adversely affects the N incorporation by also increasing the concentration of hydrogen in the reactor.

Using 100 nm Ni catalyst at lower temperatures ($\sim 600^\circ\text{C}$) improved the N-doping, but yields were extremely low. Synthesis with increased carrier gas flow rate using the 100 nm Ni at lower growth temperatures (600°C) may be worthwhile to attempt. X-ray photoelectron spectroscopy (XPS) data on sample GN-43 is shown in Figure 3-22.

Figure 3-22. XPS spectra of C_{19}N fibers.

The N 1s peak has two major components corresponding to quaternary N incorporated into the graphene sheets, and pyridinic N bonded to the edge of the sheets. More of the N doping appears to be quaternary, the desired result. Binding energies and quaternary/pyridinic N ratios agree closely with Nakajima's published values.

The Ni metal catalyst should be removed from the carbon fibers before BF_4 intercalation is attempted, due to the formation of NiF_2 which would complicate further material characterization. While refluxing fibers in acid is the reported purification technique for carbon

nanotubes³⁸, we attempted simply stirring or sonicating metal catalyzed carbon fibers in hydrochloric acid to observe if this would be sufficient to remove most of the metal particles.

GN-43 was stirred in 17% hydrochloric acid overnight. TGA combustion of the fibers in flowing air before and after acid treatment showed that most of the Ni had been removed by HCl washing. A drop in the residual weight (corresponding to remaining Ni metal) after carbon combustion of 35% to 4% was observed after overnight HCl treatment (Figure 3-23).

Figure 3-23. TGA data comparing combustion in air of C₁₉N before and after acid treatment. Residual weight at >700°C indicates amount of Ni remaining.

Electron microscopy and spectroscopy were performed on C_xN fibers to determine the nature of the nitrogen in these materials. Nitrogen atoms doped into the plane of the graphene sheets were preferred – pyridinic nitrogen incorporated at the edges of the sheet would not represent true incorporation of extra electrons into the graphene planes. By using transmission electron microscopy (TEM) coupled with electron energy loss spectroscopy (EELS), we hoped to map the location of nitrogen atoms within the microstructure of the fibers. TEM and EELS analysis of C₁₉N fibers are shown in Figures 3-24 and 3-25.

Figure 3-24. TEM images of C₁₉N fibers with a progression towards increasing magnification.

Figure 3-25. EELS spectra display the carbon and nitrogen K-edges (bottom right TEM micrograph in Figure 3-24 shows the region where EELS spectra were measured).

TEM images showed that C_xN fibers (diameter ~ 0.3 microns) are composed of smaller entwined graphite-like ribbons with diameters/widths of approximately 5 nm. The graphene sheet spacing in this material is between 3-4 angstroms, as expected for a graphitic fiber. The ribbon morphology leads to the potential for a high surface area material. EELS spectra indicated that the variety of different morphology fibers in the C_xN mix all contain carbons that are C_{60} -like and doped nitrogen atoms that have some sp^2 character.

$C_{30}N$ fibers were subjected to the same BF_3/F_2 treatment as has been used for regular graphite. A weight increase of $\sim 20\%$ was observed, which was below the 31% required for 2nd stage $C_{16}BF_4$ and 47% required for 1st stage C_8BF_4 . Subtracting the 10% weight of Ni in the C_xN fibers, and assuming the BF_3/F_2 did not react with Ni, the weight increase was still only 22.6 %. TPD of this material after fluorination is shown in Figure 3-26.

Figure 3-26. Temperature programmed desorption of $C_{30}N$ fibers treated with BF_3/F_2 .

The BF_3 (49) peak has a similar decomposition behavior as seen in regular graphites. However, very little CF_4 (69) is seen in the out-gassing, and a small baseline of N_2 (28) is observed upon heating. The TPD suggests a low concentration of BF_4^- intercalation, similar to what was seen in the large batch of Timrex C_xBF_4 . Intercalation of C_xN fibers with higher pressures of BF_3/F_2 and more pump/refill cycles of fresh gas mixtures could increase the amount of BF_4^- incorporation.

Despite the low BF_4^- concentration, TEM/EELS was used to analyze this intercalated $C_{30}N$ material. As shown in Figure 3-27, graphitic fringes were observed after intercalation, and appear to be ~12 angstroms apart, consistent with a 2nd stage $C_{16}BF_4$ material. EELS spectra suggest that the incorporation of B and F was uniform throughout the material. However, the low concentration of N made the EELS detection difficult for nitrogen atoms. This data provided encouraging information that these smaller graphitic domains intercalate in a similar manner to bulk flake graphite.

Figure 3-27. High resolution TEM image of $C_{30}N$ intercalated with BF_4^- . Circled regions highlight graphitic domains where layer spacings were measured to be ~ 12 Å.

Conclusions

In this chapter, we attempt to address the issue of hydrogen physisorption using *ab initio* molecular dynamics simulations at room temperature; we proposed utilizing negatively charged species to attract molecular H_2 to enhance heat of adsorption via partial charge transfer from the anions to the anti-bonding σ^* -orbital of H_2 . From this computational study, fluoride ions are shown to interact with H_2 molecules strongly at lower H_2 loadings. To devise a practical solid state material, we consider partially fluorinated graphite compounds as the storage media. These GICs are unique bonding structures with geometric stress in the lattice due to partial fluorination of the graphene planes to yield semi-ionic C-F bonds. The negative charges built on the F atoms then provide the driving force for the physisorption of molecular hydrogen in the material.

Our simulation results indicate that the C-F bonds are significantly longer than the C-F bonds found in small organo-fluoro compounds and in perfluorinated graphite and thus are considerably more polarized. Hydrogen molecules are largely confined between F layers in the lattice. We show that H_2 molecules can interact with the GIC at low H_2 loading, yielding heats of adsorption energy significantly higher than what was found for H_2 in pristine graphite at liquid N_2 temperature (ca. ~ 4 kJ/mol). Our results suggest that the average H_2 adsorption energy decreases with H_2 loading. At high H_2 loadings, the average adsorption energy diminishes likely

due to lack of a sufficient number of interaction sites and to the repulsive interactions among H₂ molecules at high density. A higher average adsorption enthalpy and a larger surface area would offset some of the decrease in the average adsorption energy at higher loadings.

Compared with the gas-phase fluoride ion, the negative charges on the F atoms are substantially smaller. To further enhance the ionic character of the C-F bonds in the selected GIC, we considered doping N atoms in the lattice to replace some of the C atoms and expected that the π -conjugation effect would allow the lone pair of N atoms to delocalize into the graphene plane to enhance the negative charges on F atoms. This attempt failed to achieve the goal, since fluorination at the α -sites is energetically preferred, and the F atoms residing at these sites force the N atoms to adopt a pseudo- sp^3 hybridization, which essentially diminishes the π -conjugation effect of the N atoms. As a consequence, the N-doped, partially fluorinated GIC significantly underperforms the compound without N-doping in terms of interaction strength with H₂ molecules.

Our experimental efforts showed that tetrafluoroborate GICs could be produced from graphitic materials. Careful thermal decomposition, guided by TPD data, was used to generate GIC containing mixed BF₄⁻/F⁻ anions. Extensive characterization was used to assign the semi-ionic character of the intercalated BF₄⁻/F⁻ anions.

Unfortunately, despite the observation of high hydrogen adsorption enthalpies for certain GIC samples (~8 kJ/mol), the low surface area of these materials resulted in low hydrogen capacity at near-ambient temperature and high hydrogen pressure. Our attempts at using graphitic materials with higher native surface area (e.g., Kynol graphite fibers) were limited by the poor graphitization of these materials. Intercalation of the high-surface-area carbons was limited, and the ultimate hydrogen capacity of the intercalated materials was diminished relative to the starting materials.

Preliminary computational data motivated a short-term study on the use of nitrogen-containing precursors to generate graphitic carbon materials containing nitrogen. Various levels of nitrogen could be incorporated into the materials, and some evidence of intercalation by BF₄⁻ was noted. However, due to the discouraging nature of later computational modeling data, no hydrogen adsorption was attempted with the N-containing GICs.

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CHAPTER 4

Enhancement of Hydrogen Adsorption by Boron-doped, Carbon-based Materials

Introduction

Recent reports of hydrogen storage in boron-doped, carbon-based materials have shown significant promise for considerably higher capacities and heats of absorption than in analogous carbon materials.¹ Boron doping was found to be beneficial because of the potential to induce stronger interactions with H₂, the ability to increase H retention², and higher oxidation resistance vs. graphite.³ Boron-containing, carbon-based materials can be prepared with a variety of techniques.^{1,4,5} If boron substitution is solely carried out via solid state diffusion, the solubility in graphite is limited to only 2.35 at. % at 2350°C.⁴ However, significantly higher boron content can be achieved by using carbonization of polymeric precursors¹ or chemical vapor deposition.⁵ Chung and co-workers recently reported that carbon materials with high substitutional boron content exhibit an enhanced H₂ binding energy (~11 kJ/mol H₂)¹ and a hydrogen storage capacity nearly twice that of similar carbonaceous materials at 77 K.⁶ First principles calculations based on local density approximation (LDA) by Kim et al. suggest that H₂ can be strongly activated upon interacting with boron in doped fullerenes.⁷ Ferro *et al.* performed density functional theory (DFT) calculations to examine hydrogen interactions with boron-doped graphite surfaces and reported a significant increase in the H binding energy.⁸ They found that boron substitution can lead to an increase in graphite reactivity toward H⁹ and a reduction in the activation barrier for H diffusion by half.¹⁰ Many studies have attributed the increase in hydrogen absorption energy upon B substitution to the destabilization of the graphene structure, the increase in electron density around the substitutional boron atoms, and the lower electrostatic potential.¹¹⁻¹³

Graphite-like BC₃ was originally synthesized by Kouvetakis and coworkers by reacting benzene with BCl₃ in a high temperature process.⁵ An interesting recent study by Zhang and Alavi using DFT/LDA calculations examined H absorption, H₂ dissociation, and H diffusion in bulk BC₃.¹⁴ Their calculations indicate that H₂ molecules undergo nearly spontaneous dissociative chemisorption at low coverage, forming C-H bonds with the C atoms inside the BC₃ layers. This reactivity is in sharp contrast to what was found for H₂ absorption on a single BC₃ sheet, which has a large activation barrier along the dissociation pathway. The chemisorbed H in bulk BC₃ is reportedly capable of diffusing in the lattice with a relatively modest activation barrier. At high coverage, their LDA calculations predict formation of strong covalent C-H bonds in the lattice, assuming that all C atoms adopt the most energetically favorable configurations. Of course, high chemisorption energies resulting from these stable configurations would inherently disallow reversible absorption under near-ambient conditions. However, it may be anticipated that the absorption process is largely kinetically controlled; thus, it is unlikely that the hydrogenated structure would adopt the lowest energy configuration. Nevertheless, the absorption energies of these most stable configurations can serve as the upper bound of kinetically controlled absorption structures.

In Zhang and Alavi's calculations, H_2 molecules were placed in positions between the BC_3 layers.¹⁴ However, it remains unclear whether bulk BC_3 can intercalate H_2 molecules without encountering a significant barrier; the structure of bulk BC_3 resembles the structure of graphite in which H_2 diffusion from the gas phase into the lattice is known to be impossible in the absence of co-intercalated species (*e.g.*, potassium in KC_{24}). Direct permeation through the layers is of course energetically and physically prohibitive.¹⁴ The only rational possibility for H_2 molecules to enter into the bulk BC_3 layers is via the slit pores at the edges of the crystalline material. The conclusions derived from Zhang and Alavi's results are based on LDA calculations, which give a better interlayer distance in comparison with experiment. However, LDA is known to overestimate chemical bonding strength.¹⁵ The effective hydrogen storage process in bulk BC_3 involves chemisorption and diffusion of H atoms in the lattice, which inherently leads to numerous events of formation and breaking of C-H bonds, and such processes are usually better described with generalized gradient approximation (GGA). In this paper, we use first principles calculations to address two issues: 1. the energy barrier to the transit of H_2 molecules from the gas phase into bulk BC_3 and 2. the comparison of H_2 dissociative chemisorption in bulk BC_3 between LDA and GGA results.

Our Center of Excellence colleagues at Penn State University (PSU) have demonstrated that boron-containing carbons (or BC_x) display significant improvements in the energies of hydrogen sorption when compared to analogous carbons. These benefits are attributed to the electron-deficient nature of the boron in addition to its inherent low molecular weight. Currently, however, the PSU BC_x materials do not possess sufficient surface area or boron content to quantitatively evaluate the true activity of the boron. Therefore, as partners in the U.S. Department of Energy (DOE) Hydrogen Sorption Center of Excellence (HS CoE), Air Products and PSU have agreed to collaborate on the improvement of both boron content and surface area of the materials. Using the BC_x precursors developed by our colleagues at PSU, we set out to develop methods for controllably increasing the surface area of the products and retaining more boron in the process. This was accomplished using porous templating and nanocasting methods. During the study, we uncovered mechanisms for boron loss related to increased surface area and template removal, both of which were partially remedied by making subtle changes to the preparative chemistry and template removal processes, both of which were leveraged by Air Products' intimate knowledge and handling abilities related to fluorine and halogen chemistry.

Computational and Experimental Details

Computational Details

The first-principles calculations were performed using density functional theory with a periodic boundary condition as implemented in the Vienna *ab initio* simulation package (VASP).^{16, 17} The Kohn-Sham equation was solved iteratively using a plane wave basis set with a cutoff energy of 600 eV to describe the valence electrons. The electron-ion interactions were described by the projector augmented wave (PAW) method.^{18, 19} The exchange-correlation effects were

incorporated in both the local spin density approximation and the spin-polarized generalized gradient approximation using the Perdew-Wang (PW91) functional.²⁰ To facilitate direct comparison with the results obtained by Zhang and Alavi, we chose the Perdew and Zunger parametrization of the numerical results of Ceperley and Alder for the LDA calculations, which is the same method used by Zhang and Alavi in their earlier calculations.¹⁴ To model the bulk solid, a supercell containing 4 B atoms and 12 C atoms was used, and the number of H atoms in the selected unit cell varies with H loading. The Brillouin zone (BZ) integration was sampled within a 4×4×3 Monkhorst-Pack *k* point mesh²¹, and electron smearing was employed using the Methfessel-Paxton technique²² with a width of 0.1 eV to minimize the errors in the Hellmann-Feynman forces. To model H₂ diffusion into the BC₃ lattice from the edge, we selected a rectangular supercell structure containing 2 graphitic layers with the cell size of 20 Å × 5.11 Å × 6.79 Å, which includes 8 B and 24 C atoms; the edge atoms are terminated by H and the nearest distance between the atoms on the edges and the atoms in the adjacent repeating image is set to be greater than 11 Å to avoid lateral interactions. A smaller 2×4×3 *k* point mesh was used to sample the edge structure. All the calculated energies were extrapolated to T = 0 K. Full structural optimizations on both lattice parameters and atomic coordinates were performed until the total energy of the system converged to less than 10⁻³ eV. We used the nudged elastic band (NEB) method²³ to calculate the minimum energy profiles along the prescribed diffusion pathways, with the initial and final states chosen based on the optimized absorption structures.

Materials

Phenylacetylene was obtained from Aldrich and was distilled immediately prior to use. 1,4-bis(ethynyl)benzene was obtained from Aldrich and was purified by vacuum sublimation immediately prior to use. 1M solutions of HCl, BCl₃, and BBr₃ were obtained from Aldrich and used without further purification. 2.5M butyllithium was obtained from Aldrich, the concentration was confirmed by quantitative ¹³C NMR analysis, and it was used without further purification. Lithium chloride was obtained as 99.99% pure from Aldrich and was dried by fusion under high vacuum; the fused pellets were crushed to a fine powder in an argon-purged glove box immediately prior to use. Anhydrous toluene was obtained from Aldrich, confirmed to have less than 1 ppm moisture by potentiometric Karl Fisher titration, and used without purification. Inhibitor-free, anhydrous ethyl ether from Aldrich was also used without purification, as long as Karl Fisher analysis indicated less than 1 ppm moisture. 50% aqueous sodium hydroxide and 48% hydrofluoric acid were obtained from Fisher Scientific and used without purification. Electronic-grade anhydrous HF was obtained from Air Products and was dispensed without purification using an all-metal vacuum manifold. Hexagonal MCM-41 was obtained from Aldrich, dried under high vacuum at 600°C, and stored under argon. Zeolites NaY and 13X were obtained from Aldrich, dried under high vacuum at 300°C and stored under argon. All chemicals were handled and transferred by schlenk, syringe, cannula, or glove box techniques under dry argon.

Analytical Methods

All activated materials were handled under dry argon. Electron microscopy samples were prepared by dispersion of the powdered samples in pentane, sonicated for 10 seconds and spread as a slurry over copper grids. Scanning electron microscopy (SEM) observation was performed using a Hitachi S-4800 field-emission SEM. Images were obtained at X100, X1000, X5000, and X20,000 magnification using the upper secondary electron detector, mixing in 50% low angle backscattered electrons. All images were obtained using an accelerating voltage of 2 kV with 10 micro amps of beam current. Energy-dispersive x-ray microanalysis (EDS) was performed in the Hitachi S-4800 using a Thermo Noran System Six EDS system. EDS spectra of typical areas were acquired at 10 kV accelerating voltage for routine samples and at 5 kV when attempting to observe boron in high beam current mode using the Noran Point & Shoot method with a spectrum acquisition time of approximately 40 seconds per point or area.

Elemental analysis for C, H, O, and B was performed by Galbraith Laboratories. Nitrogen BET surface area measurements were contracted to Micromeritics and Air Products' adsorption lab. The near-ambient hydrogen adsorption capacities are reported as comparative excess to that measured with helium using a Differential Pressure Adsorption Unit (DPAU) as described in Chapter 6. Cryogenic adsorption of hydrogen is reported as comparative excess to that measured with helium using an HPA-300 automated adsorption unit from VTI Corporation.

Simultaneous DSC-TGA (or SDT) was conducted using a TA Instrument Model 2960 with a 10°C/min ramp to 1000°C, after loading the sample into platinum pans under a nitrogen atmosphere; volatile decomposition products in the effluent were observed using an AVATAR FTIR. TGA analyses were conducted using a TA Instrument Model 2950 with a nitrogen purge and a standard ceramic element oven; the instrument is housed in a nitrogen-purged glove box maintained to less than 1 ppm each of oxygen and moisture to facilitate transfer of air-sensitive reagents. Platinum pans were used for all thermal analyses. Liquid-phase ^1H , ^{11}B , and ^{13}C NMR experiments were performed using a Bruker™ DMX-500 FT-NMR spectrometer with a 5 mm liquids probe. Samples were run unlocked in their preparation solvents using valved J. Young tubes. ^1H and ^{13}C chemical shifts were corrected to TMS, and ^{11}B chemical shifts were corrected to boron trifluoride. Powder XRD was performed on samples loaded and sealed into 0.7mm glass capillaries; also used were a Panalytical X'Pert PRO MRD with a Cu X-ray tube, an X-ray mirror equipped with an automatic 0.2mm Cu/Ni beam attenuator and $\frac{1}{2}^\circ$ divergence slit on the incident beam, a parallel-plate collimator with 0.09° of collimation on the diffracted beam, and a proportional gas-ionization detector with a detection efficiency of 84% and a linear range up to 10^6 cps.

Experimental Procedures

Activation of BC_x Substrates: In an argon-purged glove box, the BC_x analyte was loaded into a quartz boat that is inside a 1" diameter quartz furnace tube closed at both ends with valved ball joints. Outside the glove box, the tube was installed in a 1.5" diameter by 12" long Blue-M programmable tube furnace and attached to a vacuum manifold with high vacuum capability.

The tube was evacuated via the manifold to a pressure of less than 1×10^{-5} torr, indicating a sufficiently leak-tight system. The tube was then heated to 300°C at a rate of 2°C per minute and held for 4 hours at a pressure below 1×10^{-5} torr. The tube was closed and returned to the glove box for storage and further analysis.

Lithiation of Phenylacetylene: In an argon-purged glove box, 1 g (9.8 mmol) of purified phenylacetylene was added to a 250 mL schlenk flask containing a PTFE stir bar. The valve of the flask was closed, and a rubber septum was secured to the flask neck opening with a plastic clamp. The flask was removed from the glove box and attached to a vacuum manifold via heavy-walled vinyl tubing, which was secured with hose clamps. The tubing connection was evacuated to less than 10^{-3} torr and refilled with dry argon three times before the valve was opened to the argon source of the manifold to maintain about 900 torr (~ 3 psig) of absolute argon pressure to protect the reagent from air contamination. 100 mL of ethyl ether or toluene were transferred into the flask by cannula. The resulting solution was stirred rapidly. Using an external dry-ice/acetone slush bath, the flask contents were cooled to -78°C . Using a gas-tight syringe, 4.11 mL of 2.5M butyllithium in hexanes (5% excess relative to alkyne or 10.3 mmol) were added with a syringe pump down the side of the flask at a rate of ca. 2 drops per second. Once the addition was complete, the flask contents were stirred at low temperature for 30 minutes, and then allowed to warm to room temperature and stirred for an additional 30 minutes. Ether solutions were homogeneous, while those in toluene gave thick slurries.

Lithiation of 1,4-Bis(ethynyl)benzene: In an argon-purged glove box, 1 g (7.9 mmol) of purified 1,4-bis(ethynyl)benzene was added to a 250 mL schlenk flask containing a PTFE stir bar. The valve of the flask was closed, and a rubber septum was secured to the flask neck opening with a plastic clamp. The flask was removed from the glove box and attached to a vacuum manifold via heavy-walled vinyl tubing, which was secured with hose clamps. The tubing connection was evacuated to less than 10^{-3} torr and refilled with dry argon three times before the valve was opened to the argon source of the manifold to maintain about 900 torr (~ 3 psig) of absolute argon pressure to protect the reagent from air contamination. 100 mL of ethyl ether or toluene was transferred into the flask by cannula. The resulting solution was stirred rapidly. Using an external dry-ice/acetone slush bath, the flask contents were cooled to -78°C . Using a gas-tight syringe, 6.66 mL of 2.5M butyllithium in hexanes (5% excess relative to alkyne substituents or 16.6 mmol) were added down the side of the flask with a syringe pump at a rate of ca. 2 drops per second. Once the addition was complete, the flask contents were stirred at low temperature for 30 minutes, and then allowed to warm to room temperature and stirred for an additional 30 minutes. Ether solutions were homogeneous, while those in toluene gave thick slurries.

Condensation of Boron Trihalide With Phenylethynyllithium: An oven-dried 250 mL schlenk flask with PTFE stir bar was attached to a vacuum manifold via heavy-walled vinyl tubing, which was secured with hose clamps. The flask was evacuated to less than 10^{-3} torr and refilled with dry argon three times, then maintained at about 900 torr (~ 3 psig) of absolute argon pressure to protect the system from air contamination. Using a gas-tight syringe, 10.28 mL of 1M BCl_3 or BBr_3 (5% excess relative to alkyne or 10.3 mmol) were introduced into the flask. The contents of the flask were cooled to -50°C using an external dry-ice-cooled bath of acetone. With rapid stirring of both flasks, the phenylethynyllithium solution/slurry was transferred drop-wise via

cannula directly into the boron trihalide solution. Quantitative transfer of the remaining lithium reagent residues was facilitated by rinsing the originating flask with small amounts of the solvent and transferring it to the boron trihalide solution. Once the transfer was complete, the resulting product solution was stirred for 30 minutes at low temperature, and then allowed to warm to room temperature and stirred for an additional 3 hours. These solutions usually possess an orange color. Initial purification of the product incorporated filtration of salts or insoluble polymers through a schlenk filter and captured in yet another schlenk flask. At this stage, the solution was concentrated under reduced pressure to about 10% of its original value to precipitate additional electrolyte byproduct and polymer. The resulting solution was filtered again. The final solution was stored in a schlenk flask in the glove box.

Condensation of Boron Trihalide With Benzene-1,4-bis(ethynyllithium): An oven-dried 250 mL schlenk flask with PTFE stir bar was attached to a vacuum manifold via heavy-walled vinyl tubing, which was secured with hose clamps. The flask was evacuated to less than 10^{-3} torr and refilled with dry argon three times, then maintained at about 900 torr (~3 psig) of absolute argon pressure to protect the system from air contamination. Using a gas-tight syringe, 16.6 mL of 1M BCl_3 or BBr_3 (5% excess relative to alkyne groups or 16.6mmol) were introduced into the flask. The contents of the flask were cooled to -50°C using an external dry-ice-cooled bath of acetone. With rapid stirring of both flasks, the phenylethynyllithium solution/slurry was transferred drop-wise via cannula directly into the boron trihalide solution. Quantitative transfer of the remaining lithium reagent residues was facilitated by rinsing the originating flask with small amounts of the solvent and transferring it to the boron trihalide solution. Once the transfer was complete, the resulting product solution was stirred for 30 minutes at low temperature, and then allowed to warm to room temperature while being stirred for an additional 3 hours. These solutions are usually an orange color. Initial purification of the product incorporates filtration of salts or insoluble polymers through a schlenk filter. At this stage, the solution is concentrated under reduced pressure to about 10% of its original value to precipitate additional electrolyte byproduct and polymer. The resulting solution is filtered again. The final solution is stored in a schlenk flask in the glove box.

Template Impregnation of Alkynylboron Dihalides: In an argon-filled glove box, 3 g of dried MCM-41 were added to a 100 mL schlenk flask containing a PTFE stir bar. A solution of the precursor (any of the preparations listed above) was placed in a separate, stoppered schlenk dropping funnel which was secured to the opening of the 100 mL flask, sealed with Apeizon N grease and secured with an Ace spring. The MCM-41 was evacuated to a static pressure of less than 10^{-3} torr, and the precursor solution was carefully degassed under slow evacuation until the solvent would reflux rapidly when a piece of dry ice was placed against the upper portions of the funnel. Under static vacuum, the precursor solution was dropped into the MCM-41 at room temperature and allowed to stir for at least 48 hours. Aliquots of the slurry were then filtered and monitored by NMR for the absence of precursor, taken as an indication that the impregnation was complete.

Selective Lithium Chloride Templating of BC_x : As a test for porosity effects in comparison with the templated media, some precursor was templated using ground LiCl. In a glove box, an estimated 1 g of precursor in concentrated ether solution was added to a quartz boat. To the same was added the powdered LiCl (0.25 g for the mono-alkynyl derivative and 0.30 g for the di-alkynyl derivative). The boat was placed on a rocker plate and stirred until enough ether evaporated to solidify the dispersion, at which point a 0.1M ether solution was added to polymerize, as described in the following sections. Carbonization was performed, as described in later sections.

On-Template Preparation of BC_x : The following was performed in a glove box. To a slurry of alkynyllithium as prepared from 1 gram of alkyne precursor (discussed in earlier sections) were added 3 g of MCM-41. The slurry was stirred for 24-48 hours and monitored by NMR for disappearance of the lithiated precursor, indicating desired impregnation. At room temperature, the commensurate amount of 1M BX_3 solution (amount provided in earlier sections) was added to the slurry with rapid mixing. The NMR again was monitored for disappearance of the BX_3 , which was usually complete within 24 hours. The on-template prepared precursor could be isolated by simple filtration. Polymerization was performed as described in later sections.

Polymerization of BC_x Precursors: To a solution of precursor or a slurry of templated precursor estimated to have ca. 1 g of precursor was added 1 mL of 0.1M HCl solution in ether. The slurry was stirred vigorously under argon for 24-48 hours. If desired, the solvent could be removed either under argon purge or by evacuation on a vacuum manifold. For solutions of precursor, immediate precipitation of a brown, sticky substance was observed instantaneously upon acid addition. For templated precursors, rapid darkening of the solid was observed upon addition of the acid.

Carbonization of BC_x in Bulk: In an argon-purged glove box, polymerized BC_x substrate (either templated or not) was loaded to a quartz boat inside a 1" diameter quartz furnace tube closed at both ends with valved ball joints. Outside the glove box, the tube was installed in a 1.5" diameter by 12" long Blue-M programmable tube furnace and attached to a vacuum manifold. Flow of argon at 50 sccm was established through the tube. Carbonization under high vacuum was also feasible, but we found this to diminish the boron content. The tube was then heated at 2°C/min to 150°C and held for thirty minutes to force out volatile materials, and then heated at the desired heating rate (typically 1°C/min) to the final carbonization temperature and held for at least two hours. The tube was closed and returned to the glove box for storage and further analysis.

Micro-Scale Carbonization of BC_x : A number of rapid screening studies were done by performing the carbonization in a TGA at a reduced scale and evaluating the products by SEM-EDS. A typical experiment was conducted by bringing a sealed vial of templated or non-templated substrate into the nitrogen purge box containing the TGA. Using a zirconia-ceramic spatula, ca. 50-100 mg of material were loaded to the tared, flame-dried platinum balance pan. The pan was loaded to the TGA and heated under the desired conditions with a balance purge of 10 sccm and a furnace purge of 90 sccm nitrogen. Immediately following the run, the sample was removed and sealed in a clean, dry vial for transport to the glove box or analytical lab.

Template Removal With Anhydrous HF: This task was performed in a glove box: To a 1" or 3/4" O.D. FEP™ tube reactor heat-sealed at one end and capped on the other with a 316 SS Swagelok™ reducing union fixed with a 316 SS Swagelok™ SS-1KS4 needle valve was added the desired templated or non-templated substrate to be treated with HF. The reactor tube was sealed and attached to a metal vacuum manifold. The reactor was evacuated to less than 1 torr to eliminate the static attraction of any fine powders adhering to the reactor walls, at which point the tube was lightly tapped to settle all solids into the bottom of the reactor. Still under dynamic vacuum, the tube was immersed in a dry-ice/acetone slush bath to cool the contents to -78°C. To ensure complete cooling of the solids, the reactor was allowed to cool for one hour. Under static vacuum, aHF was slowly admitted to the reactor at a rate that would not allow condensation of droplets that could cause a high localized heat of reaction upon contact with the solid. Immediately upon admission of the HF, a light yellow cloud of gas formed above the solid, indicating formation of SiF₄. Infrared analysis of the gases indicated that they were primarily SiF₄ with tiny traces of BF₃. The HF introduction was ceased, the byproduct gases were evacuated from the reactor, and this process was repeated several times until the cloud did not form over the solid. At this point, liquid HF was allowed to condense to a point sufficient to cover the solid, which was always black at this stage. This was allowed to stand for 15 minutes, at which point the HF was evacuated under vacuum. Once solid HF was observed collecting at the upper liquid interface (indicating a liquid temperature of ca. -84°C), the solution was moved to a -50°C bath in a vacuum dewar, ensuring maintenance of temperature below -50°C as long as HF continued to be removed. After no more HF was removed at -50°C (as evident by settling of the solid; "dancing" for moving solids is indicative of gas evolving), the bath was allowed to slowly warm to room temperature overnight (or about 18 hours), at which point the water byproduct and HF adduct were removed. The exposed solid was moved to the glove box for further processing, activation, or analysis.

Results and Discussion

Revisiting Hydrogen Storage in Bulk BC₃ by Computational Modeling

Following Zhang and Alavi,¹⁴ we first performed DFT-LDA calculations to examine whether it is energetically possible to move H₂ molecules into bulk BC₃ through the edge planes. We performed NEB calculations to map out the minimum energy profile of moving one H₂ molecule into the bulk BC₃ from the edge. Given an equilibrated initial position for the H₂ molecule of about 3.5 Å away from the edge (Figure 4-1(a)), we gradually moved the molecule toward the slit pore, passing through the edge, and ending in a location between two B atoms of adjacent BC₃ layers in the middle of the selected unit cell (Figure 4-1(b)).

The calculated minimum energy profile, the corresponding changes of the lattice parameter in the c direction, and the H-H bond distance along the prescribed pathway are shown in Figure 4-2. The potential energy increases as the molecule approaches the edge and reaches the transition state where the H₂ molecule is slightly activated (bond distance of 0.77 Å) at the edge of the BC₃ lattice. The c-axis spacing expands by 1.28 Å at the transition state in order to

accommodate H₂ with a slightly tilted horizontal orientation. Continuing on this pathway, the c-axis spacing increases by an additional 0.36 Å beyond the transition state spacing as the H₂ molecule orientation changes to a tilted vertical alignment with the BC₃ layers to interact more effectively with the two B atoms residing in the two adjacent layers near the edge. At this point, the H-H bond distance again increases slightly, and the potential energy is reduced by *ca.* 10 kJ/mol from the transition state energy. It is remarkable that the lattice parameter *c*, which is twice the interlayer distance, increases substantially to 8.44 Å from its initial value of 6.79 Å. Commensurately, the potential energy continues to decrease as the activated H₂ molecule moves toward the center of the unit cell. The c-axis spacing then gradually decreases to nearly its original value. At the site of chemisorption, the H-H bond becomes significantly elongated, and the two H atoms form covalent bonds with C atoms adjacent to the B atoms. The calculated C-H bond distance is 1.18 Å, which is considerably longer than the typical C-H bond found in most hydrocarbons. The apparently modest strength of this bond is likely due to the geometric bond angle strain on the C and B atoms next to the binding sites, imposed by the change of carbon atom hybridization from sp² to sp³ upon forming the C-H bonds. H diffusion from this configuration into the bulk has been previously postulated by Zhang and Alavi to be facile at near ambient conditions.¹⁴

Figure 4-1. Initial (a) and transition state (b) configurations for a H₂ molecule migrating into bulk BC₃ through the edge of the crystalline lattice.

Figure 4-2. The evolution of the energy (a), lattice parameter along the c direction (b), and the H-H distance (c) for H_2 to diffuse through the BC_3 edge into the bulk.

As illustrated in Figure 4-2(a), the overall calculated activation barrier for H_2 migration and dissociative chemisorption in bulk BC_3 is quite modest (~ 30 kJ/mol). Thus, it is expected that H_2 diffusion through the slit pore into the bulk BC_3 lattice would be facile at near ambient conditions. This is in sharp contrast to the analogous process in graphite where H_2 diffusion from the gas phase into the bulk is known to be very difficult.²⁴ Within the BC_3 lattice, the H_2 molecule is partially activated upon arrival at the transition state, as evidenced by the elongated H-H bond distance. This quasi-dissociated state is maintained as the H_2 molecule continues its

migration toward the center of the unit cell where the H-H bond is abruptly ruptured to form the C-H bonds. The relaxation of the C atom where H is chemisorbed is relatively modest, and the neighboring B atom moves out of the BC₃ plane toward the opposite direction of the absorbed H. The lattice relaxation upon H absorption in BC₃ is significantly smaller than the relaxation upon H absorption in graphite, in which the C atom that forms a bond with H protrudes out of the plane by several tenths of an angstrom.²⁵ Thus, the hydrogen dissociation and C-H bond formation has a very low energy barrier, confirming the conclusions of Zhang and Alavi.¹⁴

Our results using LDA suggest that H₂ diffusion into the slit pore of BC₃ is facile and the intercalated H₂ will undergo spontaneous dissociation to form covalent bonds with C atoms. These C-H bonds might be sufficiently labile to allow the H atoms to diffuse throughout the lattice in a thermally activated process, which would make BC₃ a highly promising hydrogen storage material with good capacity and facile desorption kinetics.¹⁴ In particular, we note that BC₃ would be an ideal media to store hydrogen via hydrogen spillover. It should be more efficient than the materials that have been used as hydrogen spillover substrates to date, because it would require no metal catalyst to promote the release of storage hydrogen by the dissociation of molecular H₂. Thus, a critical issue is related to the reliability of the LDA calculations because LDA is known to overestimate binding energies. Furthermore, since the intercalation of H₂ into the BC₃ lattice leads to H-H bond dissociation and C-H bond formation, GGA should be a more appropriate method to describe the energetics. Figure 4-2(a) shows the calculated energy profile with the GGA method along the LDA-optimized minimum energy pathway that leads to H₂ diffusion from the edge into bulk BC₃. In contrast to the exothermic process predicted by the LDA calculation, this process was found to be moderately endothermic by approximately 46 kJ/mol. The calculated energy barrier of *ca.* 60 kJ/mol is also higher than the value obtained with LDA. Nevertheless, both the GGA-calculated thermo-chemistry and the activation barrier are modest, suggesting that H₂ diffusion into bulk BC₃ and the subsequent dissociative chemisorption near the edge could be facile at near ambient conditions.

Having addressed the behavior of H₂ near the *edge* of bulk BC₃, we further set out to calculate the average energies of H₂ sequential absorption, the activation energies of H₂ dissociative chemisorption, and H diffusion barriers *inside* bulk BC₃ with both LDA and GGA methods. For the purpose of comparison, we also computed the average absorption energies of sequential H₂ adsorption in graphite with the same methods.

In our selected supercells, each unit cell of BC₃ will accommodate a maximum of 6 chemisorbed H atoms, while the cell of graphite will allow 8 chemisorbed H atoms. We assumed that all the hydrogenated structures will adopt the lowest energy configurations, i.e., the C-H bonds are formed at adjacent carbon atoms, but disposed in opposite directions with respect to the graphite plane, providing the least geometric stress. The average absorption energy is defined by:

$$E_{absorp} = \frac{2}{n} [E(H_n A) - E(A) - \frac{n}{2} E(H_2)]$$

where $E(A)$, $E(H_2)$ and $E(H_nA)$ are the total energies of the substrate (bulk BC_3 or graphite), hydrogen molecule, and the hydrogenated substrate, respectively. The calculated average absorption energies for sequential H_2 absorption in both BC_3 and graphite are shown in Figure 4-3.

Figure 4-3. Hydrogenation energy in bulk graphite and BC_3 as a function of the number of H_2 molecules chemisorbed. The results using both LDA and GGA approximations as exchange and correlation functional in DFT calculations are presented.

Significant differences between the LDA and the GGA results are revealed. First, the average absorption energies calculated with GGA are considerably smaller than the corresponding LDA values by amounts ranging from 25 to 50 kJ/mol. For BC_3 , dissociative chemisorption of H_2 at the selected loadings is exothermic. The calculated absorption energy increases with the loading as more C atoms are relaxed to the lowest energy configuration upon H_2 chemisorption. In particular, we note that the GGA values are very modest, in a range of -4 to -27 kJ/mol, which should facilitate the desorption of chemisorbed hydrogen. This is in sharp contrast to the LDA results, which predict much stronger bonding upon chemisorption. A similar trend for the relationship between the calculated average absorption energies of H_2 and hydrogen loading is

also found for H_2 chemisorption in graphite. The GGA results predict that unless every C atom in the selected graphite unit cell is hydrogenated with the lowest energy configuration, the process is endothermic or close to thermo-neutral. However, the LDA calculations suggest that the chemisorption process becomes energetically favorable after only 25% of C atoms in the lattice are hydrogenated and the full hydrogenation of graphite is highly exothermic, with a calculated average absorption energy of -75 kJ/mol. The fact that hydrogenation of graphite has never been realized experimentally may indicate that the thermo-chemical process is not as favorable as the LDA data indicates, but rather is more consistent with the GGA results. DFT calculations of the thermo-chemical energy for hydrogenation of benzene to form cyclohexane yield a hydrogenation energy of -273 kJ/mol with LDA and -186 kJ/mol with GGA. Compared with the experimental value of -208 kJ/mol, we conclude that the GGA results for hydrogen absorption in BC_3 are more reliable. Figure 4-3 also shows that for comparable H_2 loadings, absorption in BC_3 is significantly more exothermic than in graphite. This is particularly the case for low loadings in which hydrogen absorption in BC_3 is substantially stronger than in graphite. As Zhang and Alavi have suggested, the favorable absorption strength in BC_3 is largely due to the weaker, more flexible B-C bonds, which allow the lattice to relax more easily upon hydrogen absorption.

Figure 4-4. Energy profile for H_2 molecules to dissociate in bulk BC_3 along the most energetically favorable pathway using LDA (solid line with open circles) and GGA (dotted line with open stars) approximations.

Figure 4-4 displays the calculated energy profiles of the minimum energy pathway for H_2 dissociative absorption inside bulk BC_3 using both LDA and GGA methods. Dissociation of a H_2 molecule leads to formation of two C-H bonds next to the B atoms in two separate BC_3 planes. This pathway was also explored by Zhang and Alavi with LDA. Our LDA energy profile is in agreement with theirs, which suggests that H_2 dissociation in the BC_3 lattice is exothermic and virtually barrierless. In contrast, the GGA data indicates that the dissociation is moderately endothermic by roughly 26 kJ/mol and requires traversing an activation barrier of approximately 50 kJ/mol. Since the calculated GGA adsorption energies shown in Figure 4-3 appear to be more reliable than the LDA data, we believe that the energy profile calculated with GGA more reliably describes the energetics required to hydrogenate BC_3 . Nevertheless, both the thermochemical energy and the activation barrier calculated with GGA are relatively modest, which is in sharp contrast to the much higher barrier for the hydrogenation of graphite.²⁶ Hydrogenation of BC_3 could thus more readily occur under near-ambient conditions.

Figure 4-5. Schematic showing the several sites (from 1 to 4) in bulk BC_3 involved in the H diffusion study.

Finally, we performed NEB calculations to examine H migration along several low-energy pathways in bulk BC_3 . The selected paths, shown in Figure 4-5, include a H atom breaking the covalent bond with a C atom at site 1 to migrate to sites 2, 3, and 4, respectively. The calculated energy profiles are shown in Figure 4-6. H atoms can migrate readily between two adjacent C atoms along the C-C bond with a relatively small barrier (0.47 eV for LDA and 0.49

eV for GGA), consistent with the reported LDA value of 0.41 eV¹⁴, but significantly smaller than the diffusion barriers of 0.8-0.9 eV required for the same process in graphite.²⁷ The calculated migration barriers for H to move along the C-B bond and to jump from site 1 to site 4 are moderately higher (~0.6-0.7 eV). H atom migration along these pathways might still be possible at near-ambient conditions.²⁸

Figure 4-6. Energy profile for H to diffuse in bulk BC_3 along several low-energy prescribed pathways. The LDA (solid line with filled circles) and GGA (dashed dot line with open stars) results for H diffusion from site 1 to 2, as well as LDA results for H diffusion from site 1 to 3 (dotted line with asterisks) and from site 1 to 4 (dashed line with open diamonds) are represented. The sites involved in H diffusion are shown in Figure 4-5.

Boron-containing Carbons

With the notable exception of boron carbide (B_4C , which is unattractive for H_2 storage applications), nearly all reported attempts to produce boron-containing carbons (BC_x) suffer from the products possessing limited quantities of boron. One method of preparing BC_x is based on thermal or deposition techniques that are limited by the actual solubility of boron in

graphite at temperatures low enough to avoid B_4C formation.²⁹ Other work has produced BC_x materials via etching of active carbon with boron oxides, but always contains boron-oxygen species in the product.³⁰ The thermolysis of a plethora of polymeric organoboranes³¹ has also yielded BC_x materials, but there are losses of significant amounts of boron in the carbonization process due to the ability of organic boron to undergo rearrangements facilitating loss of volatile boranes as a kinetically favorable process.³² Another strategy includes favoring the elimination of HCl from organo-boron dichlorides and is also problematic regarding the thermodynamic driving force for HCl to liberate boron in the form of BCl_3 .³³ There is also a report of BC_x preparation by electrochemical deposition.³⁴ One exception to these trends is related to earlier work in Neil Bartlett's group^{5,35-37} on ordered, graphite-like BC_3 which, based on our extensive evaluation by computational methods is believed to represent a unique class of graphitic materials that should reversibly chemisorb H_2 without a catalyst or pillaring spacer. While BC_3 is of interest to members of the HS CoE, it is not considered in the work related to this report, which was derived based on the carbonization of a novel class of organo-boron compounds, as discussed in the following section.

Background of PSU BC_x Materials

Prof. T.C. Chung of PSU is a partner in the HS CoE. His group is dedicated to applying BC_x materials as H_2 sorbents with enhanced sorption energetics that are based on the electron-deficient nature of the incorporated boron. Prof. Chung has a long-standing knowledge of boron-containing polymers and BC_x materials derived from their thermolysis.³⁸⁻⁴⁰ The culmination of this work is the ingenious realization that isolation of boron in an organic precursor by an alkynyl group reduces the propensity for borane rearrangements, which leads to boron loss by evolving volatile organo-boranes under carbonization conditions. The PSU group's most recent efforts¹ were directed towards maximizing the boron content by developing precursors with multiple alkynylboron linkages via carbonization of the substrates (II) shown here:

When the carbonization of the BC_x precursor (II) is performed directly without removal of the lithium chloride byproduct, natural-unregulated porosity is obtained by aqueous leaching of the

remaining salt. It is such a BC_x material possessing *ca.* 7% atom boron and a reported surface area of 700 m^2/g (sample designated HPA18-500) that was shipped to Air Products for H_2 adsorption evaluation using our Differential Pressure Adsorption Unit (DPAU, described in Chapter 6). Initial results of the material activated at 300°C under high vacuum indicated a significant hydrogen uptake (0.23% by weight at 25°C and 100 atm.), given the reported surface area and a remarkably increased (30-50%) isosteric heat of adsorption (range: 8.4-12.6 kJ/mol H_2) for H_2 compared to pure carbon analogs (Figure 4-7). Because of the uncertainty of the heat values obtained from only 2 isotherms, a more thorough investigation was conducted using temperatures ranging from -196°C to 40°C, giving heat values ranging in the lower half of the preliminary data (Figure 4-8). The SEM-EDS of the PSU material (Figure 4-9) does confirm non-ordered porosity, but also indicates an alarming amount of oxygen (not considered beneficial for H_2 adsorption), which despite meticulous handling at Air Products, was not reported by the PSU group.

Figure 4-7. H₂ isotherms and isosteric heat plots for PSU BC_x (7% atom B) sample HPA18-500.

Figure 4-8. Full H₂ isotherms and heat plots for PSU BC_x (7% atom B) sample HPA18-500.

A second sample received from the Chung group with a reported stoichiometry of BC_6 was also evaluated for H_2 storage properties using the DPAU (Figure 4-10), but could not be completed because the sample suffered from extremely poor inherent surface area, as evident from the SEM-EDS evaluation (Figure 4-11). Our colleagues at PSU also reported (verbally) that they had attempted the preparation of porous product by templating BC_x using the smallest units of their precursor (II) on zeolite NaY, but derived a product of poor surface area that was also devoid of boron. At this stage, Air Products entered a collaboration with the PSU group to aid in the development of high-surface-area and high-boron-content BC_x materials for hydrogen storage using precursors of composition (II) shown in the scheme above.

PSU BC10 – X 100K

PSU BC10 – X 100K

PSU BC10 – X 200K

PSU BC10 – X 200K

Full scale counts: 518 BC 10 porous BCx 5 kV (1)_pt1

Figure 4-9. SE/TEM-EDS of PSU BCx (7% atom B) sample HPA18-500.

Figure 4-10. PSU BC₆ Sample DPAU H₂ Isotherms.

PSU BC₆ – X 50K PSU BC₆ – X 200K

Full scale counts: 2105 BC₆ porous BC_x 5 kV (1)_pt1

Figure 4-11. SEM-EDS Analysis of PSU BC₆ Sample.

Computational Evaluation of BC_x Materials

There are indications that the active nature of the BC_x for hydrogen adsorption is related to the acidity of the boron, which is believed to be even more profoundly affected by the planarity of the sp² hybridized atom.¹ Aside from NMR chemical shift comparison and the predisposition of the chemistry, there is little support for this concept. In order to gain greater insights, we evaluated the activity of the boron in small molecule models toward H₂ and compared them to the corresponding carbon-based material (for comparative examples, see Table 4-1). As expected, the empty orbital of the sp² hybridized boron weakly attracts the σ-bond of H₂ in a side-on configuration (Figure 4-12). Interestingly, the binding energy of a single H₂ toward a slate of small organoboranes is about 20-30% higher than that for the corresponding hydrocarbon, the same value of increase as observed for PSU's BC_x over standard carbons. When the cone angle of the trigonal boron face was decreased in the model compounds, there did not appear to be any advantages as might be expected from substrates such as boranobornane and the boron-substituted analog of quinuclidine. Only at the extremes of acidity for sp² hybridization of the boron atom, such as with borabenzene (which has never been

synthesized as a stable material), will the energy increase further, but it proceeds so energetically that instead of coordination, an irreversible chemical reaction takes place.

Figure 4-12. Computational modeling of H₂ with boranes (boron – orange, carbon – green, hydrogen – white).

With the challenge of finding solid adsorbents for H₂ that will meet the DOE targets, it is becoming clear that many different factors need to be addressed in order to optimize the performance of any adsorbent. Maximizing surface area should not only increase exposure of the adsorbing gas to active boron atoms in the material, but should also yield higher hydrogen storage capacity due to conventional physisorption. The surface area alone does not only improve capacity, but the size of the pore⁴¹ is also of integral importance and can offer additional energetic benefits in a storage application. Thus, while a 30% increase in energy of adsorption may not seem significant, this increase in compilation with other effects such as surface area and pore size optimization can give a material with additive beneficial effects. This is why the current work is important in order to develop reproducible, controllable ways to increase the porosity of BC_x materials.

Table 4-1. Computational comparison of H₂ binding energies toward gas-phase boron and organoboron compounds.

Molecule	ΔE (kcal/mol H ₂)	Molecule	ΔE (kcal/mol H ₂)
-3.29		-2.21
-2.06		-2.10
-1.97		-2.19
-2.31		-2.25
-2.12		-2.13

-2.06		-1.86
-1.96		-2.86
-2.05		-2.40
-2.03		-1.96
-2.09		

Template Selection

Some of the highest surface area carbons ever reported were prepared by templating methods.⁴² This incorporated the use of furfuryl alcohol in zeolite NaY. Before beginning the evaluation it is critical to ensure the selection of the appropriate template. Furfuryl alcohol is the model carbonization precursor because it is inexpensive, it is readily available, it is stable at room temperature, can be polymerized with gentle heating, has incorporated oxygen which aids in the carbonization process, and is small and flexible enough to penetrate and fill the pores of a zeolite. On a closer examination, it becomes readily apparent that BC_x could not be templated on zeolite NaY using the PSU-based precursors.

Zeolite NaY has a limiting pore diameter of 7.4 Å, while the minimum Van der Waals cross-section distance of the PSU precursor (Cl₂B-C₂-Ph-C₂-BCl₂) is about 7.6 Å, with a long-axis distance of 16.5 Å. Although moving to larger pore sizes brings with it more limitations to the attainable surface area and pore volumes of the ideal products, it became apparent that using commercially available mesoporous silicas of MCM-type represented an excellent starting point for concept development. Specifically, hexagonal MCM-41 with pore diameters ranging from 15-25 Å was obtained for use. It is conceivable that the analogous MCM-48 could also be used as a template for smaller pore variations, while allowing pore filling from all directions based on the inter-connecting pore structure. It is beneficial that templated carbons from these systems have also been produced⁴⁶, offering the expectation for surface areas of 1200 m²/g or higher. These silicas are thermally resilient and can be thermally dried at very high temperatures.

There is some concern that the surface oxygen atoms of the silica⁴⁴ may react or coordinate strongly with the alkynylboron dihalides of the PSU-type. This could introduce boron-oxide species which are believed to provide detractive effects on H₂ adsorption properties. There were no indications throughout the experimentation that this is a problem; however, it should not be discounted in future studies, while thorough drying and annealing of the silicas should be observed. Should the oxidic nature of the silica template prove to be problematic, one might attempt to cap or graft the active oxide surface with reagents such as hexamethyldisilane.

Ultimately, once a reproducible method has been developed for the templating of BC_x it will be desirable to drive the surface area to considerably higher values. This will require the development of smaller organic precursors that will fit the appropriate pores. One may consider the alkynyl boron derivatives of acetylene or butadiene that are stabilized for impregnation into the selected porogen, and then polymerized as needed (see later sections).

It is also important to project the development of such concepts to a commercial scale and realize that templating methods may not be economically or materially feasible. It is also a possibility that the template removal process as currently performed may yet prove to have detrimental effects on the activity and boron content of the product. PSU's use of the LiCl byproduct as an in-situ porogen is not a novel concept.^{45,46} However, it does appear that conceptually there is considerable room for improvement. Our recommendations would be to evaluate such factors as different concentrations of the electrolyte, alternate electrolytes (i.e., CaCl₂ or CsCl) considering melting point and coordinating capacity, mixed electrolytes, or even some of the more recently developed water-soluble zeolites⁴⁷.

Selection and Preparation of the PSU BC_x Substrate

Rigorous no-air handling and schlenk techniques⁴⁸ were employed to protect the intermediates and products from interaction with oxygen or water. Based on the selection of the PSU BC_x precursors described in the introduction and the desire to use microporous structured materials, it is important that we select precursors that are smaller in order to allow impregnation into the template and provide the greatest boron content based on the boron-to-carbon ratio (B/C). This distills the choice to two obvious candidates, (1) and (2) alkynyl groups, as shown here:

Our colleagues at PSU represent the only group to have reported a successful preparation of these materials by lithiation followed by condensation with boron trichloride. Other groups who indicate this to be problematic report the preparation of this material class via the more selective condensation between the boron trihalide and the corresponding alkynylstannane⁴⁹. The first step of the sequence (for the reaction scheme shown in the introduction) is selection of a solvent. Following the strategy of the PSU group, we initially attempted to avoid ether solvents, as there was a general concern that they may incorporate oxygen into the BC_x product. While convenient for their lack of reactivity, alkane solvents do not afford solubility of the aryl alkyne precursors. Because benzene and toluene afford suitable solubility, toluene was initially utilized for the relative toxicological safety. Ether solvents gave variable results in terms of oxygen incorporation into the carbonized product. Tetrahydrofuran (THF) presented several challenges as it tends to polymerize in an acidic environment, thus giving rise to significant amounts of oxygen in the carbonized product. Stabilizer-free ethyl ether was found to be beneficial in producing added solubility, while at the same time it could be completely removed from the substrate before carbonization, thus avoiding oxygen incorporation. It is also suggested that dimethyl ether, despite the challenges of handling at room temperature, might also be a suitable solvent for the reactions.

The lithiation of the alkyne substrate was not directly described by our PSU colleagues, and the reference cited for its preparation⁵⁰ described only that for the lithiation of phenylacetylene using ether as a solvent. For preparation of the dilithiated dialkynyl derivative, we referred to the reports of another group.⁵¹ The researchers at PSU indicate that a slurry of the alkynyllithium in benzene was used. Based on this it is not clear whether the researchers at PSU used ether for the preparation of the lithium reagent, removed the solvent and replaced it with benzene or if the lithiation was performed directly using benzene as the solvent. In the former situation, ether

would have undeniably remained coordinated with the lithium⁵² and carried through the synthesis, which could have induced beneficial effects as discussed later in this section.

Lithiation of the alkyne could be performed with lithium hydride, which is convenient for separation methods; however, the convenience of commercial 2.5M butyllithium in hexanes as used by the PSU group was the reason for its selection as the base. A 5% excess stoichiometric amount of base was used for each alkyne group (to compensate for impurities and adventitious moisture), and lithiations were conducted at -78°C. With toluene as a solvent, the lithiated alkynes were highly insoluble. With ether as a solvent, phenylethynyllithium was soluble, the monolithium diacetylene derivative was soluble, but the dilithiated diacetylide derivative was insoluble. Because of the volumetric bulk imposed by the insoluble organometallics, it was imperative to introduce extensive dilution of nearly 1-2% by weight alkyne precursor in solvent, which was required in order to effect efficient mixing and transfer of the slurries. In the case of both solvents, deuteration experiments and subsequent analysis by GC-MS indicated quantitative conversion of the alkyne to the fully lithiated products with no evidence of addition of the alkynyllithium to the alkyne. The slurries of alkynyllithium were stable at room temperature.

The alkynyllithium must then be reacted with a boron trihalide to provide the BC_x precursors (1) and (2). The PSU group employed the strategy of adding the boron trihalide to the alkynyllithium slurry at ice temperatures based on convenience of the addition. This order of addition, however, is not conducive to the preparation of (1) and (2), but rather the tetrahedral coordinated borate ion product, since the reaction is expected to be very rapid.⁵² Instead we opted to employ large-bore cannula techniques to slowly add the alkynyllithium slurry to a cold solution of the boron trihalide. Again, we selected different thermal conditions than those reported by the PSU group (0°C) based on the tendency for the trihalide and the dihalide adducts to perform haloboration addition chemistry;⁵³ we chose to run the addition of the alkynyllithium at -50°C to bias the desired metathesis reaction and then allowed it to warm to room temperature to complete the reaction and equilibrate.

Boron trihalides are commercially available as 1M solutions in solvents of heptanes, hexanes, or toluene. When toluene was used as the solvent for dissolution of the alkyne, the use of toluene as the boron trihalide solvent was preferred as it allowed direct isolation of the products without a change of solvents. Otherwise, if ether was used as the preparation solvent, alkane solvents were preferred because they are more easily removed under mild heating or vacuum conditions.

Following PSU's example as well as considering general availability and cost of reagents, we chose to initially use BCl₃ as the boron trihalide. We did, however, notice in both our experiments as well as those of the PSU group that an increase in surface area appeared to give lower boron contents. We theorize that as surface area increases, the HCl byproduct of carbonization (discussed in later sections) should react readily with exposed boron sites to liberate BCl₃ as the thermodynamic product. Based on thermodynamic comparison with BBr₃ (see Tables 4-2 and 4-3) and loss of HBr, the bromide appears to be about 10 kcal/mol more stable toward the loss of HBr than HCl. Although boron bromides are considered more reactive toward olefins and alkynes, the bromide derivatives of precursors (1) and (2) appear to have

similar stability in ether solutions as their chloride counterparts. Results discussed later confirm that this shift in thermodynamics is helpful in retaining some boron, even though the LiBr byproduct remains soluble in ether. Given the trend of thermodynamic stabilities toward loss of HX, one might also consider using BI_3 in the preparation.⁵⁴

At this point of the reaction, there appears to be a delineation in the solvent that one should use in order to obtain (1) and (2). We discovered that the strict use of toluene gave rise to products (1) and (2), which were stable only in solution for periods of only 24-48 hours as observed by NMR. The decomposition invariably produced sticky, tar-like polymers that were insoluble in all solvents but strong acids, indicating cleavage of boron-carbon bonds leading to destructive depolymerization, which is known for many poly(organoboranes)^{32,55}. It is theorized that the polymer byproduct is the result of haloboration polymerization of the multivalent products (1) and (2).

Tables 4-2 and 4-3. Thermodynamic comparison of boron-loss via reaction with HCl versus HBr. Calculations were performed using HSC 5.1.

T (C)	ΔH (kcal)	ΔS (cal/K)	ΔG (kcal)	K	Log K
0	22.854 1	9.778	17.451	1.087E-014	-13.964
100.000	22.554	18.844	15.522	8.090E-010	-9.092
200.000	22.264	18.155	13.674	4.824E-007	-6.317
300.000	21.987	17.623	11.886	2.932E-005	-4.533
400.000	21.731	17.210	10.145	5.079E-004	-3.294
500.000	21.506	16.898	8.441	4.110E-003	-2.386
600.000	21.323	16.675	6.763	2.028E-002	-1.693
700.000	21.183	16.523	5.103	7.141E-002	-1.146
800.000	21.081	16.424	3.456	1.977E-001	-0.704
900.000	21.014	16.364	1.817	4.586E-001	-0.339
1000.000	20.978	16.334	0.183	9.303E-001	-0.031

T (C)	ΔH (kcal)	ΔS (cal/K)	ΔG (kcal)	K	Log K
0.000	30.162	19.357	24.875	1.247E-020	-19.904
100.000	29.984	18.805	22.967	3.526E-014	-13.453
200.000	29.785	18.333	21.111	1.770E-010	-9.752
300.000	29.568	17.917	19.299	4.370E-008	-7.359
400.000	29.345	17.558	17.525	2.040E-006	-5.690
500.000	29.134	17.266	15.785	3.449E-005	-4.462
600.000	28.946	17.037	14.070	3.006E-004	-3.522
700.000	28.788	16.865	12.375	1.661E-003	-2.780
800.000	28.661	16.741	10.696	6.632E-003	-2.178
900.000	28.564	16.654	9.026	2.081E-002	-1.682
1000.000	28.495	16.597	7.364	5.443E-002	-1.264

These unstable product mixtures are consistent with early reports⁵⁶ that such alkynylboron reagents generally decompose. This decomposition or polymerization was found to be too accelerated to enable effective impregnation into the template (discussed in later sections). Thus, as taught in the literature⁵⁷, a Lewis base should stabilize the alkynyl boranes and prevent further reactions of haloboration as well; in our case use of ethyl ether as a solvent appeared to be sufficient, enabling stabilization of products (1) and (2) in solution for 4 weeks or longer at room temperature. It must be noted that removal of the solvent results in immediate polymerization. Again, we found that ethyl ether did not bring on oxygen contamination of the carbonized product, thus deeming it a suitable solvent, as long as it was degassed of oxygen, dry, free of peroxide, and free of inhibitors.

Before moving to the templating stages of the current preparation, it is important to perform a purification that removes any polymeric, insoluble salt, or tetrahedral coordinated borate adducts that might block the pores of the template or act as a secondary templating surface. This was done by a simple schlenk-type filtration. LiX salt content could further be reduced by concentrating the solution to 10% of its original volume and filtering again. The resulting solutions were used directly to perform templating, as described in later sections.

Based on NMR analysis and gravimetric evaluation of the product from solvent removal, it was determined that static yields of 62% and 37% crude product were obtained when using toluene versus ether, respectively. However, the purity of each was ca. 65% for toluene and ca. 85% for ether, with the balance presumed to be BX_3 and some halo-addition products, as reported by the PSU literature. Given this disparity in bulk yield, it was preferred to use the ether solvent due to its stability-inducing effects and apparent higher purity of the product.

Again, based on the selectivity and yields of the current preparation incorporating the combination of a boron halide with alkynyllithium, there appears to be considerable room for improvement. Aside from improvements around the HX elimination thermochemistry already discussed, there may still be some boron loss and selectivity issues around the continued ability for boron to migrate where C-H bonds may still exist. In terms of selectivity while avoiding the

toxic stannic alkynes as derivatives, there is precedence that commercially available trimethylsilylacetylenes can readily and selectively react with boron halides to directly give the products (1) and (2) in high yields near ambient temperatures.⁵⁸ Silanes are of particular benefit because they are among the only readily prepared functional groups that are thermodynamically pre-disposed to displacement by boron halides or even simple boranes. One may even attempt the direct preparation of inorganic BC_x of high boron content by employing this methodology to commercially available compounds such as bis(trimethylsilyl)acetylene⁵⁹ or 1,4-bis(trimethylsilyl)-1,3-butadiyne as precursors to BC₃ and BC₆, respectively. As these preparations facilitate the complete loss of all organic carbon via liberation of R₃SiX, there will be no remaining C-H bonds to facilitate rearrangements and loss of volatile boranes. In addition, BF₃ now becomes an attractive reagent of choice as HF loss is not a concern in the carbonization process, and facilitation of the reaction energetics is even more favorable due to the formation of Si-F bonds.

Filling the Template with Precursors

As covered in the introduction, there are a number of methods for performing templating of carbons; however, because we have selected to work with solutions of relatively sensitive substrates (1) and (2), the options become limited. These solutions are only suitable to absorption impregnation into the templates. This means that the template must be evacuated of all gases to facilitate filling of the pores with solution. Intuitively, it seems reasonable to expect the arylalkynylboron halides to be selectively absorbed into the pores over dissolution in the employed solvents. The degassed solutions of compounds (1) and (2) are introduced to the template and stirred until the precursor is absorbed, as determined by IR or NMR analysis of the liquid phase. Indeed, the signals for the precursors subside within 24-48 hours, as long as an excess of free volume inside the template is provided. By calculation, we attempted to provide at least a three-fold excess of free volume in the MCM-41 to incorporate the precursor with possible coordinated solvent.

Once the absorption of the precursor was confirmed analytically, the impregnated MCM-41 was washed with a small amount of solvent to prevent particle-coating effects. Powder X-ray diffraction (pXRD) data for the treated template was obtained to confirm filling of the pores (Figure 4-13), as observed by loss of the reflections indicating regulated pore structure. This is not evidence that the pores were completely filled with the precursor alone, but undoubtedly included solvent. While better templating results (discussed in later sections) were obtained by this method when ethyl ether was used as a solvent, we discovered a second method of performing the reaction condensation directly on the template that allowed use of the toluene solvent; we refer to this concept as “on-template” synthesis. This was accomplished by preparing the alkynyllithium intermediate as a slurry in toluene. Although the solubilities of the lithiated derivatives are quite low in toluene, they are significant enough to be detected by NMR in solution. The MCM-41 template was added to the slurry of alkynyllithium and stirred vigorously. The NMR signal for the lithiated intermediate was found to subside within 72 hours at room temperature. At this stage, the impregnated solid adopted a light-blue color for both

alkynyllithium intermediates that was not observed for any other impregnation experiments; the nature of the color is not fully understood. At room temperature, a 5% stoichiometric excess of BCl_3 per equivalent of alkynyllithium was added all at once and allowed to stir. Monitoring of the reaction was conducted by ^{11}B -NMR. According to this measure, all of the BCl_3 was consumed within 18 hours, giving rise to a deep-purple solid. The solvent can be easily removed under reduced pressure, exposing the purple solid. Because the preparation is performed in toluene, it is likely that the product polymerized inside the template, so stability of the precursor is of little concern. It is important to point out that the on-template synthesis of BC_x differs from the direct templating method in that it does not incorporate the purification step to remove undesirable byproducts, including LiCl . It is possible that the LiCl may aid in the development of additional porosity.

Figure 4-13. pXRD progression of attempted MCM-41 templated BC_x .

Polymerization of Precursors

Once the precursor has been impregnated into the template, it must be polymerized in order to fix it into place and avoid sublimation or being otherwise ejected from the pore. The PSU group reports that heating the precursors (1) and (2) to 350°C effectively dries and hardens the material. In our experience, polymerization of the precursors occurs readily without heating when toluene is used as the solvent. However, when ether is used as the stabilizing solvent, volatilization of the precursor with ether generally precedes polymerization in a thermally-based process. It appears that the stabilizing mechanism employed affords excessive protection against polymerization. While evaluating alternative solvents⁶⁰ that would allow more facile polymerization upon removal, we chose an alternative route.

We know from the literature³² that neutral and acidic environments support hydroboration and haloboration additions across unsaturated systems, and bases tend to coordinate the boron center, causing re-hybridization and loss of reactivity. Based on this information it was postulated that a protic acid may catalyze the haloboration polymerization that is desired in order to fix the precursor in place. Indeed, we discovered that catalytic amounts⁶¹ of HCl were conducive to nearly-instantaneous polymerization of the precursors in solution. It is important to minimize the quantity of protic acid, as there is the possibility it may liberate BCl₃, causing undesirable boron loss. The polymers formed were insoluble in all solvents except strong protic acids. The on-template preparations should not intuitively require acid-catalyzed polymerization if they were prepared in the absence of ether. However, as described in later sections, we did find that acid treatment of these intermediates assisted in obtaining better carbonization yields.

Carbonization of BC_x and Microscopic Comparison

Carbonization of the precursor is accomplished by thermolysis in the absence of air and moisture, namely under purge of argon or high vacuum. During the carbonization process, it is desirable to eliminate hydrogen halide from the precursor or polymerized precursor to obtain a thoroughly inorganic BC_x. As shown in the schemes below, the stoichiometry of the dialkynyl precursor ideally suits a perfect condensation to BC_x, with no halogen or hydrogen remaining as the mono alkynyl compound leaves an excess of hydrogen (not to indicate that elemental hydrogen is the actual byproduct), opening the viability for boron migration and elimination chemistry (facilitating loss of boron):

It would be ideal to have a condensation reaction in which no bound hydrogen remains, as it can facilitate rearrangements that allow boron loss as volatile small molecules in the heating process. Our colleagues at PSU do not report exact conditions for the carbonizations of their most recent precursors, but do have older work that discusses the development and selection of conditions, including an annealing step at 350°C and a carbonization step which takes place up to ca. 600°C. Beyond that it is reported that boron loss becomes a problem or that the boron activity drops significantly.

We were able to confirm the stages of various thermal processes in the carbonization by TGA and TGA-IR analysis of precursor (1), PhC₂BCl₂ (Figure 4-14). It is evident that the etherate of the precursor becomes volatile and produces very low yields upon heating as the unpolymerized material. The value of proper polymerization (see previous sections) is also clear, as it dramatically improves the net yield of the carbonized product. Identical results were obtained for the dialkynyl precursor (2), Cl₂BC₂PhC₂BCl₂.

Another differentiation in yield was observed by varying the heating rate. Higher heating rates gave greater net yields, which indicate that faster heating rates kinetically advance the elimination of HCl over rearrangement chemistry, creating larger volatile byproducts of carbon and boron. A comparison of the various TGA plots in Figure 4-14 clearly shows the stages where solvent and volatile materials are removed up to 150°C, which is followed by the chemical condensation zone up to ca. 400°C, where most of the XH elimination chemistry and rearrangements will take place. Because many of the BC_x materials covered in this study are high melting pitches, heating them to 600°C and holding for a time (about 4 hours) is sufficient to anneal the carbonized product and provide graphitic BC_x. Similar results were obtained for the dialkynyl precursor (2) and related polymer.

Figure 4-14. TGA study of Ph-C₂-BCl₂.

A similar evaluation was performed on the bromide precursor derivatives of (1) and (2) (see Figure 4-15). This study was conducted in a significant presence of byproduct salt⁶², LiBr, causing a shift in absolute mass comparison relative to the chloride substrates. Nonetheless, one can see that the chemical condensation regime for the bromide is shifted ca. 50-100°C lower, contrary to thermodynamic postulation, but commensurate with the higher reactivity of the bromide. This is indicative that carbonizations may be feasible at lower temperatures with the

higher halogens. For the materials reported here, we extended the thermal annealing range to 600°C to ensure the ability to directly compare results with the chloride analogs and that annealing was properly conducted. One interesting aspect of these thermal analyses is that LiBr appears to develop a substantial vapor pressure at around 800°C, well below its boiling point (1290°C), becoming volatile and exiting the system. This was verified with pure LiBr.

The direct carbonization of the precursors (1) and (2) or their related polymers at 600°C consistently produced boron-containing products of a graphitic nature, as exemplified by the electron micrographs in Figure 4-16. The SEM/TEM analyses were very useful in screening for porosity on the scale expected for MCM-41. EDS was also useful in discerning purity and screening for boron. While it is usually not suitable to evaluate light elements such as boron, we pioneered methods incorporating low incident beam energies (~5kV) to obtain information about boron. Although none of the EDS results were quantitative and elemental analysis was required to obtain such values, we have observed that a small (non-resolvable) shoulder or tail on the carbon peak of such EDS (Figure 4-17) is coincident with boron values of at least 3% compared to elemental analysis.

TGA of PhC_2BBr_2

TGA of $\text{Br}_2\text{BC}_2\text{PhC}_2\text{BBr}_2$

Figure 4-15. TGA analyses of PhC_2BBr_2 and $\text{Br}_2\text{C}_2\text{PhC}_2\text{BBr}_2$.

Figure 4-16. SE/TEM of graphitic BC_x.

Carbonization of the bromide derivatives (1) and (2) was also performed; however, it must be noted that these preliminary results are from starting material containing a measurable amount of the LiBr salt byproduct. The microscopy results (Figure 4-18) indicate a low porosity grain-like structure for the dialkynyl substrate, while the monoalkynyl derivative strictly yielded high-density graphitic structures, despite the presence of copious amounts of LiBr; it is noted that the EDS indicates the presence of silicon, but is very likely due to bromide remaining in the sample (Figure 4-19). Both products were found to have a B/C ratio superior to that obtained for the chloride derivatives.

Attempts to template precursors (1) and (2) with toluene as a solvent gave similar results to that noted above without a template. The conclusion is that polymerization takes place too quickly to obtain a templated material, though there are some examples of disrupted structure that look as though they may have resulted from carbonization at the edge or surface of the MCM-41 (Figure 4-20). Surface areas were very poor (<100 m²/g) for materials thus obtained.

Image Name: BCx-5 Ext-600 no template(1)

Accelerating Voltage: 30.0 kV

Magnification: 10000

Full scale counts: 334 BCx-5 Ext-600 no template(1)_pt1

Full scale counts: 421 BCx-5 Ext-600 no template(1)_pt2

Figure 4-17. SE/TEM of Graphitic BCx.

Figure 4-18. SE/TEM-EDS of BC_x obtained from polymerization/carbonization of $Br_2BC_2PhC_2BBr_2$.

Figure 4-19. SE/TEM-EDS Of BC_x obtained from polymerization/carbonization of $Br_2BC_2PhC_2BBr_2$.

Figure 4-20. Attempted MCM-41 templating carbonization with $Cl_2BC_2PhC_2BCl_2$ in Toluene.

The most successful structural templating attempts to date were accomplished by the on-template preparations discussed in earlier sections. The result (Figures 4-21 and 4-22) is a quantitative preparation of a porous solid with mixed morphology from that of literature MCM-41 templating and that of the salt-leaching templating employed by PSU. It is very simple to describe this based on the MCM-41 template and the fact that the salt byproduct is not removed in the on-template preparations. With surface areas approaching 600 m²/g, this method represents one of the more promising methods.

The templating of the chloride materials on MCM-41 employing stabilizing ether as a solvent provided considerably more interesting results and confirmed the requirement for stabilization of the precursor in the templating process. Although further optimization is still needed, considerably more structured porogens were observed. While a measurable percentage of the observed field still contained non-porous, graphitic products, two other morphologies presented themselves as first examples of templated BC_x. The first morphology representing about 20% of the particulate field is a tube-like structure consistent with wall coating of the major pores of MCM-41, as described in the literature⁶³ for materials that do not diffuse into the mesopores as readily due to surface effects and size. The other useful morphology is represented by a dense, interpenetrating porous solid that closely resembles those reported⁴³ for inverted mesostructures of MCM-41 (Figure 4-23). The bulk surface area of this mixture is on the order of 230 m²/g, an indication that optimization around template fixing is needed and appears to be possible based on other learnings described herein.

Figure 4-21. Results of the Nn-template preparation of BC_x from $LiC_2PhC_2Li + BCl_3$.

Image Name: BCx insitu-
2 MCM 5 kV (1)

Accelerating Voltage: 5.0 kV

Magnification: 20000

Full scale counts: 1556 BCx insitu-2 MCM 5 kV (1)_pt1

Figure 4-22. On-template preparation of BC_x from LiC₂PhC₂Li + BCl₃.

Figure 4-23. Literature example of MCM-41 templated carbon (Ref. 43).

Finally, in an attempt to separate the issue of boron loss from possible template effects and removal based on HF, it was important to find another way to increase surface area and not offer chemical changes. In order to accomplish this comparison, we first isolated the chloride derivative (2) from the lithium chloride and other insoluble byproducts. Freshly dried and powdered LiCl was then added back to the purified substrate, which was polymerized and carbonized side-by-side with the same precursor free of LiCl. The result of the elemental analysis clearly shows that the material containing salt has measurably less boron under exactly the same treatment conditions. With the LiCl salt removed (next section), the morphology of the product is represented by large, folded cells of graphitic BC_x (Figure 4-24).

Figure 4-24. BC_x templated from $Cl_2BC_2PhC_2BCl_2$ with added $LiCl$.

Template Removal

The final step of the templating process is selective removal of the template, leaving behind the cast material, preferably unchanged in the process. Zeolitic and mesoporous silica templates are routinely removed with either concentrated aqueous hydrogen fluoride or concentrated aqueous hydroxide. Some of our earliest work with the PSU BC_x material confirmed expectations that conditions sufficient to etch zeolites or porous silica⁶⁴ with these reagents also completely compromises the boron content. This would provide our PSU colleagues with a tangible explanation why they did not observe boron in the products of their attempts to template their precursors on zeolites using classical methods.

Because the aqueous etching is out of the question in terms of preservation of the boron in the product, Air Products has taken a different approach by leveraging its experience and capabilities with anhydrous HF (aHF). We discovered that aHF can instantaneously convert silica to volatile SiF_4 at temperatures (-78°) near the melting point of HF and preserve some of the boron content of templated BC_x , as long as the HF is removed below $-50^\circ C$ and the residual

water byproduct-HF adduct is removed under high vacuum between -50°C and 0°C .⁶⁵ While the study was ultimately incomplete, there are indications that the HF does compromise up to half of the boron content in the material during this process, as validated through the low-temperature HF treatment of the PSU higher-surface-area BC_{10} product. Rather than evacuation of the HF reagent, it might be more efficient and conducive to boron retention to isolate the de-templated product by filtration (see experimental section). Further investigation of the treatment conditions or possibly the use of alternative fluoride sources⁶⁶ might also prove useful in improving the retention of boron. We did observe that none of the HF etching affected the product morphologies in any way when performed at low temperature, but found that the morphology was completely destroyed when conducted at room temperature (Figure 4-25). We have not attempted to see if the boron removal introduced additional porosity to the carbons that might prove useful for H_2 storage and improvement of surface areas in materials.

As described earlier, there remains some concern whether the silica-based templating with aHF removal will best provide good high-surface-area BC_x with high boron contents. As recommended in earlier sections, the salt-based templating employed by PSU also offers considerable room for improvement by varying the treatment conditions and even the salt porogen. One definite recommendation for future work related to the salt templating method is to apply every precaution to avoid contact of the active BC_x with oxygen or other oxidizing media. In our final studies of the program, we attempted to template precursors (1) and (2) on finely powdered LiCl crystallized from the ether solution. We did obtain results similar to those of the PSU BC_{10} ; however, we washed the LiCl crystals out of the matrix in side-by-side experiments with deionized water that was handled in air and with deionized water that was carefully degassed of oxygen and treated to remove traces of peroxide.⁶⁷ We discovered that the thermally dried material washed with the carefully prepared water did not contain any oxygen by XPS and EDS analysis, while the material handled in air did contain oxygen. Future work could also consider other anhydrous and aprotic solvents for removal of the electrolyte, such as ethers, alkyl carbonates, nitriles, or even supercritical CO_2 .

Image Name: BC10 plus HF(1)

Accelerating Voltage: 5.0 kV

Magnification: 10000

Full scale counts: 1973

BC10 plus HF(1)_pt1

Figure 4-25. SE/TEM-EDS of BC_x treated with HF at room temperature.

Conclusions

We were able to make significant inroads towards the structured templating of high-surface-area, high-boron-content BC_x materials. This was accomplished by first realizing the size limitations of the PSU boron-containing precursors and adjusting the structured template pore size appropriately, specifically by using commercially available hexagonal MCM-41. Second, it was important to address the general effect that increased surface area BC_x materials suffered more boron loss than low surface area ones, an effect that was partially remedied by addressing the thermodynamic balance of ejecting BX_3 versus HX . While BBr_3 is effective at this, it is possible that BI_3 could be even more so, although it is much more reactive toward alkynes. The third major hurdle was removing the template without compromising the boron content. The fortuitous selection of a silica-based template enabled the development of a low-temperature removal with aHF. This method did enable retention of boron, but did affect the removal of some active boron, indicating a need for method improvement or evaluation of alternative templates and removal strategies.

Recommendations for improvements in the area of BC_x were also covered. Template selection is very important, and the salt leaching method still has merits and could benefit from some development efforts that could include evaluating alternative salts. Suggestions for alternative homogeneous chemistries for preparation of the PSU precursors are also provided, which include application of alkynyl silanes rather than organometallic compounds. It may also be helpful for the PSU researchers to closely evaluate the depolymerization products of the BC_x pre-polymer, which can directly confirm assembly mechanisms and structure. Another suggestion is to prepare a carbon analog (i.e., no boron, templated in the exact same fashion) of the current BC_x to validate the absolute contributions of boron in these new materials.

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CHAPTER 5

A Comprehensive Computational Model of Hydrogen Storage Via Spillover

Introduction

Recently, pioneering studies by our partners in the HSCoE, R. Yang and co-workers, revealed a novel process to store substantial quantities of hydrogen via hydrogen spillover.¹⁻¹¹ Unusually high hydrogen storage capacities at near-ambient conditions were achieved, and were subsequently validated in several independent experiments.¹²⁻²⁰ Hydrogen spillover has been investigated using many carbon-based materials, such as carbon nanofibers,¹⁴ amorphous activated carbon,¹⁸ graphite,^{21,22} single walled carbon nanotubes,^{1,2,7,13,20,23} and metal organic framework complexes.^{5,6,11,24} In one example, Lachawiec *et al.* reported a hydrogen spillover-induced increase of hydrogen storage capacity for activated carbon and single-walled carbon nanotubes by factors of 2.9 and 1.6, respectively.³ Thus, metal catalyst doping of carbon should significantly enhance hydrogen spillover and storage.⁹ It has been suggested that the stored hydrogen atoms in the carbon-based materials are 'loosely adsorbed' on surfaces of substrates via spillover upon H₂ dissociation on nickel catalyst.¹⁶ Inelastic neutron scattering spectroscopy directly identified spillover hydrogen on a carbon support.²² The proposed spillover mechanism^{5,6,24} can be briefly summarized as follows. At a given pressure of H₂ gas, the H₂ molecules undergo dissociative chemisorption upon interacting with a supported transition metal catalyst, e.g., nanoparticles of platinum. The generated H atoms then migrate from the catalyst particles to the storage material through a 'bridge' built of carbonized sugar molecules and further diffuse throughout the entire bulk solid. Obviously, in order for the spillover process to occur to any significant extent in solid materials, it is essential that the H atoms should be able to move from the vicinity of catalyst particles to substrate sites far from where the catalysts reside. While active research efforts are being made to understand the hydrogen spillover processes, to date, there has been no general consensus on the spillover mechanisms that can satisfactorily explain the observed large storage capacity (up to 4 wt % of H₂) or facile hydrogen desorption kinetics from the carbon-based storage compounds at near-ambient temperatures.²⁴⁻

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Hydrogen spillover on solid-state materials is not a newly discovered phenomenon. The concept of hydrogen spillover has its genesis in fundamental studies with heterogeneous metal catalysts, particularly with such systems as are used for chemical hydrogenation reactions.^{27,28} Within catalytic processes, the metal has the role of "activating" hydrogen by reversibly dissociating H₂ into metal-H atom (hydride) species on its surface. It has been observed that, for instance, by heating Pt dispersed on carbon at 350 °C, Pt/Al₂O₃ at 200-300 °C, Pd/C at 200 °C, and Pt/WO₃, under hydrogen pressure the amount of H₂ absorbed is in excess of the known H₂-sorption capacity of the metal alone.²⁹ In these seminal reports, the 'excess quantity' of this hydrogen on the support is usually very small, amounting to only several atoms of H for every H that is bound to the metal. In this context, we have reported that intimate combinations of hydrogen reactive metals, metal alloys, or metal hydrides with various forms of substantially

graphitic carbon, i.e., carbon-metal hybrids, display an uptake of hydrogen at near-ambient conditions and are useful as pressure-swing and temperature-swing sorbents for the storage of hydrogen.³⁰ The observed reversible, facile hydrogen reactivity is theorized to occur either by a hydrogen spillover mechanism or by a partial reversible metal catalyzed hydrogenation of the unsaturated graphitic carbon structures.

Another well-known hydrogen spillover phenomenon is the formation of hydrogen bronzes from metal oxides³¹⁻³³ (e.g., MoO₃ and WO₃) and metal sulfides^{34, 35} (e.g., ZnS and MoS₂). Ritter and co-workers have applied solid-state NMR techniques to study the bonding properties, location, and mobility of hydrogen in H_xMoO₃.³⁶ They found that the activation energies for hydrogen diffusion are on the order of 15 to 30 kJ/mol and also concluded that hydrogen atoms reside on a line connecting the vertex sharing oxygen atoms within the (MoO₆)_n layers.^{37, 38} An atomic force microscopy study by Smith and Rohrer unraveled the evolution of the MoO₃ (010) surface during reduction in H₂-N₂ mixtures at 425 °C.^{39, 40} The results demonstrate that MoO₃ intercalates H atoms during the gas-phase reactions, resulting in protonation, which in turn leads to precipitates of hydrogen molybdenum bronze. In an additional example, an increase in hydrogen storage capacity by spillover on CeO₂ in the presence of Pt catalysts was recently reported, and NMR studies indicated the presence of protonic hydrogen on the oxide surfaces.²² The hydrogen bronze complexes can be prepared most effectively via hydrogen spillover in the presence of Pt or Pd catalysts. The solid metal oxide compounds are generally semiconductors, but are transformed into metals (conductors) immediately upon hydrogen bronze formation via hydrogen spillover.²⁶ Unfortunately, to date, there have been very few theoretical studies of the formation of H_xMoO₃ precipitates, and the detailed energetics associated with the hydrogen bronze formation via hydrogen spillover still remain poorly understood.

A mechanistic understanding of the well-known hydrogen spillover processes in metal oxides would help the efforts in determining the mechanism of hydrogen spillover in carbon-based materials. Successful modeling of the widely studied hydrogen spillover on metal oxides also provides validation for the theoretical methods that are used to model the poorly understood hydrogen spillover on carbon-based materials. We note that many of the recent advances in lightweight metal hydride syntheses have been also partially attributed to hydrogen spillover-type phenomena.⁴¹ However, the primary driving force that dictates hydrogen atom diffusion in metal hydrides is completely different than in metal oxides. For example, the H atoms in the hydrogen bronzes are best described as protons, while in the classical metal hydrides, these H atoms withdraw electrons from the metal atoms and are thus negatively charged.

Theoretically, a comprehensive description of the spillover process is highly challenging, since the computational model must account for the effects of at least the metal catalyst, used to split H₂ molecules into H atoms, the substrate, on which the H atoms should be able to diffuse freely both on surfaces and in the bulk, and the interplay at the catalyst-substrate interface. Computationally, rigorous quantum mechanical calculations on realistically sized transition metal catalyst particles, which contain thousands of atoms, are prohibitively difficult. Instead, we have chosen a Pt cluster to represent the catalyst particle. While the size of the cluster is exceedingly small compared with the size of real catalyst particles, previous studies have shown

that at full saturation of H atoms on Pt clusters, the threshold H_2 dissociative chemisorption energy and the H desorption energy do not vary significantly with the cluster size.⁴² This is relevant since in a typical catalytic hydrogenation process the catalyst surfaces are fully covered by H atoms at a constant, high H_2 pressure. Therefore, a fully saturated (H-saturated) small Pt cluster could serve as a model to mimic the dissociative chemisorption of H_2 on Pt catalyst particles and the migration of H atoms from Pt to the substrate at the catalyst-substrate interface. We next placed the fully H-saturated Pt cluster on a $MoO_3(010)$ surface and on a few selected graphitic carbon nanostructures such as graphene and single walled carbon nanotubes to examine hydrogen spillover at the catalyst-substrate interface. Subsequently, we explored a variety of possible diffusion pathways of H atoms on the substrate surfaces and calculated the corresponding energy barriers. Effects of carbon material surface curvature on hydrogen spillover capacity were also discussed.

Computational Methods

H_2 Dissociative Chemisorption on Small Pt Clusters

We first examined H_2 dissociative chemisorption on Pt clusters, used as a model to represent Pt catalyst particles. The calculations were performed using density functional theory (DFT) under the generalized gradients approximation (GGA) with the Perdew-Wang's exchange-correlation functional (PW91)⁴³ as implemented in the DMol³ package.⁴⁴ The spin-polarization scheme was employed to deal with the electronically open-shell systems. A double numerical basis set augmented with polarization functions was utilized to describe the valence electrons. The core electrons were described with an effective core potential, which also accounts for the relativistic effect that is important for heavy elements such as platinum. Full electron calculations were also previously performed for several selected Pt clusters⁴⁵, and no significant differences in cluster structures, relative stability and chemisorption energies were found. Full structural optimizations were performed until the energy was converged to less than 2×10^{-4} eV, with the maximum force and displacement less than 0.05 eV/Å and 0.005 Å, respectively. Population analysis was performed based on the Hirshfeld charge partitioning scheme.

Hydrogen Spillover onto MoO_3 and Nano-structured Carbons

For calculations on hydrogen spillover in solid state materials, we used DFT with periodic boundary conditions with the PW91 functional plus spin polarization. The electron-ion interactions are described by projector augmented wave (PAW) pseudopotentials.^{46,47} The valence electrons were described with a plane wave basis set. The Brillouin zone was sampled within the Monkhorst-Pack mesh scheme⁴⁸, which varies with the size of the selected unit cells. For the finite aromatic systems, the selected box size is large enough so that the closest atomic distance between two adjacent boxes is larger than 8.0 Å. The cell parameters along with the K-points and energy cutoffs used in our calculations can be found in Table 5-1. All atoms were fully relaxed, with the forces converged to less than 0.03 eV/Å. Electron smearing was

employed using Methfessel-Paxton technique⁴⁹, with a smearing width of $\sigma = 0.1$ eV, in order to minimize the errors in the Hellmann-Feynman forces due to the electronic free energy. All calculated energies were extrapolated to $T = 0$ K. The computational method is implemented in the Vienna *ab initio* simulation package (VASP).^{50, 51} The nudged elastic band (NEB) method of Jónsson and co-workers⁵² was used to examine the activation energy profile along prescribed diffusion pathways. Initial and final states were chosen based on the adsorption calculation, and the number of images was chosen to achieve smooth curves. To understand the dynamics of hydrogen spillover in graphitic carbon materials, we performed first principles molecular dynamics simulations. A constant-volume canonical ensemble was simulated using the Nosé thermostat⁵³ with the initial temperature of 300 K. We utilized the Verlet algorithm to integrate the Newton's equations of motion with a time step of 1 femtosecond for about 5 picoseconds.

Table 5-1. The cell parameters of the selected rectangular unit cells, the K-points and the energy cutoffs used in the calculations.

	Cell Parameters	K-points	Energy Cutoff (eV)
Pt ₆ /MoO ₃	7.4 Å×7.9 Å×25 Å	3×3×1	400
Pt ₆ /Graphite	12.2 Å×12.2 Å×16 Å	2×2×1	400
SWNT	20 Å×20 Å×7.4 Å	1×1×2	400
Hexabenzocoronene	20 Å×20 Å×20 Å	1×1×1	400

Results and Discussion

Hydrogen Dissociative Chemisorption on Small Pt Clusters

Transition metal catalysts, such as Pt and Pd, play a critical role in hydrogen spillover processes where H₂ molecules undergo dissociative chemisorption on the catalyst particles, and the resulting H atoms then migrate to the substrate. Substantially higher hydrogen capacities of storage materials via catalyst-mediated spillover have been reported.^{3,6} Given a sufficiently high H₂ pressure, the surfaces of the catalyst particles are fully covered by H atoms upon dissociative chemisorption of H₂. In many theoretical studies of gas-solid interactions, the catalyst particles are represented with large, flat crystalline surfaces with low hydrogen coverage. While such a surface slab model is capable of providing useful information about catalytic activities, it is known that in many cases catalytic activity occurs primarily at surface defect sites such as sharp corners, edges, and kinks. As an alternative to the approach using a crystalline surface model, we used small Pt clusters to investigate the critical physicochemical properties of Pt in catalyzing H₂ dissociative chemisorption and subsequent H migration onto the

selected substrates at full H saturation, which mimics the catalytic condition at a constant H₂ pressure.⁵⁴

Figure 5-1. The fully optimized Pt clusters saturated with H atoms.

We first investigated the most energetically stable small Pt_n clusters for n=2-9. Next, we examined H₂ dissociative chemisorption on these clusters using the sequential addition of hydrogen until the clusters were fully saturated with H atoms (maximum stable H:Pt ratio). Cluster saturation was ensured by performing *ab initio* molecular dynamics (MD) simulations at 300 K. We identified cluster saturation as the point at which additional loading of H atoms on the saturated clusters resulted in spontaneous recombination of H atoms to form H₂ molecules, which were subsequently desorbed from the cluster during the MD simulation. Figure 5-1

displays the fully optimized Pt clusters saturated with H atoms. The MD trajectories indicate that the H atoms are well-separated from each other, with H-H distances of at least 2 Å. On average, each Pt atom is capable of covalently binding with 4 H atoms, as shown in Figure 5-2. Of course, the maximum H:Pt ratio for small Pt clusters is substantially higher than what is possible for substantially larger Pt particles. This is because all of the Pt atoms in small clusters are exposed to H₂ molecules and are able to form Pt-H bonds. In more realistic, larger catalyst particles, most of the Pt atoms are embedded underneath the catalyst surfaces and thus are inaccessible to gas molecules. Therefore, these Pt atoms do not directly participate in the catalytic reactions.

Figure 5-2. The average number of chemisorbed H atoms per Pt atom in small Pt clusters.

Under the conditions of full H atom saturation, two critical properties of the small Pt clusters that determine the catalyst activities can be evaluated. The first property is the threshold H₂ dissociative chemisorption energy, which describes the energy required to liberate a molecule of hydrogen from the cluster. The second property is the threshold H atom desorption energy, which determines how much energy is required to remove one H atom from the fully saturated cluster. Again, under a constant H₂ pressure, once a H atom desorbs from the cluster, a H₂ molecule will immediately undergo dissociative chemisorption to occupy the vacant site to maintain an overall cluster saturation equilibrium. Figure 5-3 displays the calculated H₂

dissociative chemisorption energies and H desorption energies at full H saturation for the small Pt clusters. We note that these energies do not change significantly as a function of cluster size. This is important and certainly deserves further investigation, since it seems to imply that these two threshold properties may remain more or less the same for large Pt particles, despite possessing much lower H:Pt aspect ratios, as for small clusters. We also note here that the threshold H desorption energy is the energy required to transfer a H atom from a fully H-saturated Pt cluster to the gas-phase as an atom, which is very large as anticipated. In the presence of an acceptor in close contact with the saturated Pt cluster where a concerted atom-transfer can occur, the H desorption energy would be expected to be significantly lower. In this case, H atom transfer energies will depend partially on the chemical properties of the specific substrate. Nevertheless, the calculated threshold H desorption energy is an important quantity that may serve as a reference for measuring catalytic activity.

Figure 5-3. (a) H₂ dissociative chemisorption energies at full H coverage; (b) H threshold desorption energies at full H coverage.

Because of the remarkably small variation of the threshold H desorption energies with respect to the Pt cluster size, we decided to choose an octahedral Pt₆ cluster to model the Pt particles for hydrogen spillover. The simple catalyst model, upon full H saturation, can greatly facilitate computational studies on hydrogen spillover at the catalyst-substrate interface and yield useful physical insight into the spillover mechanisms. Figure 5-4 displays the calculated density of

states for sequentially chemisorbed H atoms up to full cluster saturation. The Fermi level is shifted to zero and the main components of atomic orbitals that contribute to the low lying states are projected. For the bare Pt_6 cluster, the 6s orbitals contribute only slightly to the valence band, which is largely dominated by the d -band. Upon H_2 dissociative chemisorption, contribution of the Pt d -band to the valence band decreases with the H coverage, while contribution of the H 1s orbital to the valence band increases. In parallel, the d -band component in the conduction band increases considerably. The change of the electronic structure suggests that the d -electrons from the Pt_6 cluster are partially but sequentially ionized, and the H atoms act as the charge acceptor. It is also noteworthy that the valence band and the conduction band become increasingly separated with the H coverage as the bonding nature in the cluster changes from the metal-metal bonding to more covalent metal hydride bonding.

Figure 5-4. The calculated density of states for sequentially chemisorbed H atoms up to full cluster saturation.

Hydrogen Spillover In MoO_3

The structure of a MoO_3 single crystal comprises layers of slabs in the (010) orientation (Figure 5-5(a)). Each slab contains 4 layers of O atoms and 2 layers of Mo atoms. We selected a supercell containing one (2×2) MoO_3 (010) layer and a 18 Å wide vacuum space to study

spillover at the Pt cluster-MoO₃ (010) interface (Figure 5-5(b)), and subsequently investigated H diffusion between the slabs to understand the bulk diffusion phenomenon. The validity of a one layer slab model for surface study is sustained by the fact that the MoO₃ interlayer interactions are dominated by the van der Waals forces. Furthermore, our optimized Mo-O bond lengths in the relaxed single slab are virtually identical to those in bulk MoO₃.^{55,56}

Figure 5-5. (a) The structure of a MoO₃ single crystal comprises layers of slabs in the (010) orientation. Each slab contains 4 layers of O atoms and 2 layers of Mo atoms. (b) The selected supercell containing one (2×2) MoO₃ (010) layer and 18 Å vacuum space for the study of hydrogen spillover at the Pt cluster-MoO₃ (010) interface.

Hydrogen Atom Imigration from the Catalyst to the Surface

We first carefully placed a fully H-saturated Pt₆ cluster (shown in Figure 5-1), with the bottom 4 H atoms removed, on the MoO₃ (010) slab, followed by structural optimization. Subsequently,

we performed minimum energy path calculations to allow an H atom near the bottom of the cluster to migrate onto the substrate to form an O-H bond with a terminal O atom. The calculated energy profile is displayed in Figure 5-6, and shows that a H atom can readily move, with a low activation energy barrier of 0.37 eV, from the H_{20}Pt_6 cluster to a terminal oxygen atom to form an O-H bond. This indicates that the H atom desorption energy from the H-saturated Pt_6 cluster can be significantly reduced by close contact with a substrate and a concerted atom transfer process. This hydrogen migration (H-migration) process is exothermic, with thermochemical energy of 0.21 eV. It is understood that there are numerous possible H adsorption configurations on the Pt_6 cluster; however, our extensive computational tests suggest that the calculated H-migration barriers fluctuate only in a small range around 0.35 eV. The Bader charge analysis⁵⁷ revealed that this barrier is a result of charge flows and protonation. In the initial state, each hydrogen atom adsorbed on Pt_6 gains 0.05-0.15 electrons from Pt-5d bands, depending on its location on Pt_6 . The terminal oxygen atoms in MoO_3 are negatively charged by 0.8-1.2 electrons. Thus, initially, the interaction between the H atoms on the saturated Pt cluster and the terminal O atoms is electrostatically repulsive. Upon the H migration onto the terminal oxygen, the electrons begin to transfer from the H-1s orbital to the O-2p orbital. The migrated H atom loses its electron and thus is positively charged (+0.96 electrons), essentially becoming a proton, in the final optimized conformation. Accordingly, the O atom gains an extra electron, which reduces the Mo-O bond strength, resulting in partial reduction of the Mo ion. The system undergoes a transition from repulsive O-H interactions to attractive proton-oxygen interactions along the migration pathway, resulting in a relatively small H-migration barrier. The calculated low activation energy clearly demonstrates the effectiveness of spillover in the H-migration process from the catalyst to the substrate.

Figure 5-6. The calculated energy profile for H atom migration from the fully H-saturated Pt cluster to the terminal oxygen to form an O-H bond at the catalyst-MoO₃(010) interface.

The energy profile shown in Figure 5-6 describes only one of the H-migration pathways from the fully H-saturated Pt₆ cluster to the MoO₃(010) surface. Several other adsorption sites on the slab are also capable of binding with the H atom with similar migration profiles. The selected MoO₃ slab comprises two symmetric Mo-O sheets (upper and lower) linked by strong Mo-O bonds. There are three structurally distinct lattice oxygen atoms on each sheet, i.e., terminal oxygen, symmetric bridging oxygen and asymmetric bridging oxygen, as shown in Figure 5-7. The sites labeled as A_{upp,i} and A_{low}, which are symmetrically equivalent, were found to be most favorable for H adsorption with an adsorption energy of 2.91 eV. The hydrogen atom bonds with the upper asymmetric oxygen via a strong covalent bond (0.97 Å bond length) and also interacts with the lower asymmetric oxygen via weaker H-bonding (at a distance of 1.7 Å). These results are consistent with the previous NMR and neutron diffraction studies by Ritter^{36, 37} and Dickens³⁸ which identified protons residing between the lower and upper asymmetric oxygens. Our results verify that it is thermodynamically and kinetically facile to form H_xMoO₃ bronze at the vicinity of Pt catalyst particles.

Figure 5-7. Three structurally distinct lattice O atoms on each slab, i.e., terminal oxygen, symmetric bridging oxygen and asymmetric bridging oxygen.

Hydrogen Diffusion from Surface to Lattice

Perhaps the most important step for realizing substantial hydrogen spillover on materials is the step in which the H atoms proximal to the catalyst particles migrate to sites away from where the metal particles are located. To study this step, we first explored the surface diffusion paths of an H atom within the selected slab. Figure 5-8 displays the calculated minimum energy profile following one potential diffusion pathway of an H atom on MoO₃. The first barrier corresponds to the diffusion across two adjacent terminal oxygen atoms. This calculated activation energy is 0.51 eV. This is a relatively low activation barrier and suggests that H atom migration on the MoO₃ surface is facile at a moderate temperature. For example, the hopping rate of hydrogen between two adjacent terminal oxygen atoms is about 2.0 s^{-1} at room temperature, assuming a typical prefactor of 10^{13} s^{-1} .⁵⁸ The second barrier corresponds to the movement of the H atom from a terminal oxygen onto an upper asymmetric oxygen. This calculated activation energy is 0.6 eV. This slightly higher energy indicates that the diffusion from the terminal surface oxygen atom into the second layer is the rate-limiting step for the hydrogen bronze formation. The two binding modes are identified on the asymmetric oxygen

atoms: $A_{\text{upp,p}}$ and $A_{\text{upp,i}}$. Our calculation of the H-migration in the lattice reveals that the H atom is able to rotate around the $\langle 001 \rangle$ direction by 120° from $A_{\text{upp,p}}$ to $A_{\text{upp,i}}$ with nearly zero activation energy. The last activation barrier, corresponding to the migration from $A_{\text{upp,i}}$ to A_{low} , is 0.35 eV. NMR experiments have suggested that at a low hydrogen content, protons in MoO_3 reside between the lower and upper asymmetric oxygen sites, and the diffusion activation energy was reported to be in the range of 0.1-0.3 eV.^{36,59} Our calculated H diffusion barriers and the predicted relative thermodynamic stability of H adsorption sites in the lattice are in good agreement with these experimental observations. In the entire proton migration pathway, the highest activation barrier is no more than 0.6 eV, which clearly explains the high mobility of H in hydrogen bronze.

Figure 5-8. The calculated minimum energy profile following the selected diffusion pathways.

To understand the low barriers for this H atom diffusion mechanism, we monitored the O-H distances during the H-diffusion process following the proton migration pathway. The calculated O-H distance distribution is displayed in Figure 5-9, which reveals a massive H-bonding environment along the proton migration pathway in the lattice. The first peak at around 1.0 Å is attributed to the strong covalent O-H bonds at the stable binding modes. The second peak at 1.5 Å, which indicates a weaker O-H interaction, can be attributed to non-covalent hydrogen bonding at or near the transition states. This suggests that the H-bonding interactions play a

critical role in facilitating the proton migration in the lattice by reducing the activation barriers and increasing the H atom mobility. The shoulder in the plotted O-H distance distribution at 1.8-2.0 Å and the broad bands at distances greater than 2.0 Å are attributed to long-range oxygen-proton interactions with lower strengths. The extensive H-bonding network in the lattice provides a low energy barrier diffusion channel and thus enables the hydrogen atom to move between oxygen atoms at near-ambient temperatures. These results clearly indicate that H diffusion within the selected MoO₃ slab is facile.

Figure 5-9. The calculated O-H distance distribution.

To further understand the diffusivity of the H atom in the MoO₃ bulk lattice, we continued our investigation of H migration through identification of pathways between two adjacent slabs. Figure 5-10 displays the calculated minimum energy pathway to transfer one proton from the terminal oxygen located at the bottom T1 site of the upper slab to the top terminal site of the lower slab. These results indicate that diffusion of protons between slabs is energetically feasible and, therefore, H atoms can diffuse from the surface layers into the subsurface layers of bulk MoO₃.

Figure 5-10. The calculated minimum energy pathway to transfer one H atom from the terminal oxygen located at the bottom T1 site of the upper slab to the top terminal oxygen site of the lower slab.

Hydrogen Diffusion in Bulk MoO₃

We examined the structural and electronic properties of bulk α -MoO₃, which has orthorhombic symmetry composed of layers aligned in the (010) orientation. The optimized lattice parameters, $a=3.721$ Å, $b=3.965$ Å, and $c=14.673$ Å, are in reasonable agreement with the experimental data of 3.696, 3.963, and 13.855 Å.⁶⁰ The calculated c parameter is slightly longer than the experimental value due to the fact that the structure of bulk α -MoO₃ is composed of MoO₃ slabs along the c -axis packed together via van der Waals interactions, and GGA is known to underestimate such interaction forces. There are three structurally distinctive types of oxygen atoms in bulk MoO₃: one-coordinate terminal oxygens, O_t; two-coordinate asymmetric bridging oxygens, O_a; and three-coordinate symmetric bridging oxygens, O_s, as shown in Figure 5-11. The optimized Mo-O bond lengths, shown in Table 5-2, are in good agreement with available experimental data⁶⁰ and previous calculations.^{61,62}

Figure 5-11. The optimized structure of bulk α -MoO₃, where the terminal, symmetric bridging, and asymmetric bridging oxygen sites are denoted by Ot, Os, and Oa, respectively.

The calculated band structure and electronic density of states (DOS) are displayed in Figure 5-12, with the Fermi level shifted to zero. The valence band directly below the Fermi level has a width of 5.8 eV, and the gap between the conduction band and the valence band is about 1.9 eV, both in good agreement with previous DFT calculations.^{62,63} Experimentally, MoO₃ was found to be an *n*-type semiconductor with a band gap of 3.3 eV.⁶⁴ It is not uncommon for DFT calculations to underestimate the band gap of transition metal oxides, since the relative energies of occupied and unoccupied electronic levels are not well described.⁶⁵

Figure 5-12. Band structure and electronic density of state of bulk α -MoO₃. All of the energies are relative to the Fermi level.

The DFT+U method was proposed to address the on-site Coulomb interactions more accurately in the localized *d* or *f* orbitals in strongly correlated systems by adding an additional Hubbard-type term.^{66,67} Wang *et al.* performed detailed comparisons of the calculated magnetic moments and band gaps for many transition metal oxides using GGA and GGA+U methods, and reported significant improvements with the GGA+U calculations compared with experimental data, especially for ferromagnetic and anti-ferromagnetic oxides.⁶⁸ For diamagnetic transition metal oxides, such as Cu₂O, V₂O₅, and CrO₃, the change in band gap by adding the Hubbard term was relatively modest. We performed GGA+U calculations for bulk α -MoO₃ with the U and J parameters at 6.4 and 0.95 eV, respectively.⁶⁹ As shown in Figure 5-13, GGA+U only slightly increased the calculated band gap of bulk α -MoO₃ by about 0.1 eV, similar to what was found in several other diamagnetic metal oxides.⁶⁸ Coquet and Willock reported a band gap of 2.1 eV for

bulk α -MoO₃ based on their DFT+U study, consistent with our results.⁶³ Since the GGA+U calculations did not show significant improvements to the predicted electronic structure characteristics, we employed only GGA calculations in our H atom absorption and diffusion studies.

Figure 5-13. Electronic density of state of bulk α -MoO₃ calculated from GGA+U method, in comparison to the GGA results.

The calculated Bader charges of Mo and O atoms in the optimized bulk α -MoO₃ (Table 5-2) clearly indicate that the Mo atoms are significantly oxidized by O atoms, with the symmetric bridging oxygen bearing the largest negative charge due to its high coordination number. The terminal oxygen, however, is more strongly electron withdrawing because of its unsaturated valence, and both the symmetric and asymmetric bridging oxygen atoms exhibit considerable ionic character. The calculated charges agree with the previous Bader population analysis by Coquet and Willock,⁶³ and the slight differences likely arise from the fact that while we used fully optimized structures, the lattice parameter along the *c* direction was fixed at the experimental value in Coquet and Willock's calculations. Electron population analysis based on the Milliken

scheme also led to similar conclusions.⁷⁰ The calculated electronic density differences between bulk α -MoO₃ with respect to the atomic densities clearly show that all O atoms are withdrawing electrons from their neighboring Mo atoms, as shown in Figure 5-14.

Figure 5-14. The calculated electronic density distributions in optimized α -MoO₃ structure. The locations of Mo and O atoms are denoted by green and red spheres.

The charges around the asymmetric oxygen are unequally distributed toward two neighboring Mo atoms due to the different Mo-O bond lengths, and the charges around the symmetric oxygen atoms are evenly distributed toward two neighboring Mo atoms in the plane. Most of the electron density around the terminal oxygen lies along the Mo-O bond, indicating a considerably covalent character for this bond.

Table 5-2. The bond parameters and Bader atomic charges in the optimized bulk MoO₃ structure, in comparison to experimental data.

		Calculations	Experiment
Bond length (Å)	Mo-O _t	1.702	1.671
	Mo-O _a	1.774	1.734
		2.211	2.251
	Mo-O _s	1.962	1.948
		2.429	2.332
Bader charge	Mo	2.29	-
	O _t	-0.56	-
	O _s	-0.95	-
	O _a	-0.77	-

Energetics of Hydrogen Diffusion and Desorption

To understand the relative reactivity of MoO₃ toward hydrogen spillover and the hydrogen desorption dynamics from the bronzes, we next examined the structural, energetic and electronic properties for H atoms residing in the MoO₃ lattice at various H atom concentrations. The fully optimized absorption configurations are shown in Figure 5-15. The calculated lattice parameters and the average absorption energies of H atoms at various concentrations are listed in Table 5-3. Here, the average absorption energies are defined as:

$$E_{\text{absorp}} = \frac{1}{x} [E(\text{MoO}_3) + xE(\text{H}) - E(\text{H}_x\text{MoO}_3)]$$

where $E(\text{H}_x\text{MoO}_3)$, $E(\text{H})$, and $E(\text{MoO}_3)$ are the total energies of the H_xMoO_3 bronze, gas phase atomic hydrogen, and bulk $\alpha\text{-MoO}_3$, respectively. At higher H atom concentrations, the lattice parameters of a and b change only modestly, while the c parameter increases more rapidly. For $\text{H}_{0.25}\text{MoO}_3$, the bronze has the same orthorhombic crystal structure as bulk $\alpha\text{-MoO}_3$, with the lattice angles α , β and γ all at 90° . Further increases in the hydrogen concentration lead to a

slight deviation of β from 90° , while α and γ stay at 90° , making the bronze structure monoclinic. Experimentally, the molybdenum bronze was found to have a maximum x value of 2.0. Four different hydrogen molybdenum bronze phases were identified, depending on the H atom concentration. Phases I ($0.25 < x < 0.40$) and II ($0.85 < x < 1.04$) are both blue with orthorhombic and monoclinic crystal structures, respectively. Phases III ($1.55 < x < 1.72$) and IV ($x=2.0$) are monoclinic with red and green colors, respectively.⁷¹

Figure 5-15. Fully optimized configurations for hydrogen molybdenum bronze, H_xMoO_3 , at different H atom concentrations and binding sites and modes. Mo, O and H atoms are represented by green, red, and white spheres, respectively.

Table 5-3. Lattice parameters and H absorption energies of $H_x\text{MoO}_3$ at various H atom concentrations, in comparison to available experimental data.

		a(Å)	b(Å)	c(Å)	$\beta(^{\circ})$	$E_{\text{absorp}}(\text{eV})$
$\alpha\text{-MoO}_3$	Calculations	3.721	3.965	14.673	90	-
	Experiment	3.696	3.963	13.855	90	-
$H_{0.25}\text{MoO}_3$	Ot	3.769	3.824	15.544	90	2.90
	Os	3.799	3.800	15.615	90	2.32
	Oa, up	3.734	4.055	14.853	90	2.45
	Oa, down	3.760	3.914	15.429	90	2.87
	Experiment* $H_{0.28}\text{MoO}_3$	3.718	3.890	14.18	90	-
$H_{0.5}\text{MoO}_3$	Calculations	3.772	3.821	15.769	90.5	2.85
	Experiment* $H_{0.6}\text{MoO}_3$	3.769	3.852	14.543	90.7	-
$H_{0.75}\text{MoO}_3$	Calculations	3.759	3.827	16.113	90.4	2.79
$H\text{MoO}_3$	Calculations	3.727	3.834	16.196	90.3	2.73
	Experiment* $H_{0.9}\text{MoO}_3$	3.794	3.862	14.519	93.7	-
$H_{1.25}\text{MoO}_3$	Calculations	3.765	3.892	16.264	90.6	2.57
$H_{1.5}\text{MoO}_3$	Calculations	3.784	3.983	16.058	91.0	2.42
	Experiment** $H_{1.67}\text{MoO}_3$	3.774	4.059	19.927	93.94	-

* Ref. 72.

** Ref. 73.

Compared to the experimentally available lattice parameters with similar H atom concentrations,^{72, 73} our GGA calculations consistently overestimate the *c* values due to the intrinsic inaccuracy of the method in describing weak van der Waals interactions between the layers, but the calculated bonding structures within the MoO₃ layers are in good agreement with the experimental results.

At a low H atom concentration of H_{0.25}MoO₃, we calculated the absorption energies and configurations for H atoms on all three types of oxygen atoms in the lattice and found the following:

1. On the symmetric bridging oxygen, the hydrogen is bound in the (010) plane with an absorption energy of 2.45 eV. H atom absorption lengthens the Mo-O bonds between the symmetric bridging oxygen and its neighboring Mo atoms, increasing the Mo-O bond length from 1.96 to 2.05 Å in the plane and from 2.43 to 2.68 Å between the symmetric O with Mo atom in the adjacent plane.
2. On the asymmetric bridging oxygen, the hydrogen is bound in two different modes: perpendicular to the (010) plane or at an angle pointing directly toward the inside of the layer, with H binding energies of 2.32 and 2.87 eV, respectively. Substantial lattice relaxation occurs upon H atom absorption in both cases, with the two unequal Mo-O bond lengths of 1.77 Å and 2.21 Å in bulk α -MoO₃ becoming essentially equal at 2.03 Å.
3. On the terminal oxygen, the H atom is bound with an angle of 60° normal to the (010) plane, with a relatively high binding energy of 2.90 eV due to the unsaturated valence of the O atom. The Mo-O bond length between the terminal oxygen and its neighboring Mo is significantly elongated from 1.70 Å to 1.88 Å.

The H atom coordination in the bulk exhibits significant differences from what was observed on the (010) surface. First, the terminal oxygen is the most favorable H atom absorption site in the bulk, but only a metastable, weak binding site on the surface due to different lattice bonding environments.⁷⁴ In the bulk, H atoms not only bind directly with oxygen via a strong O-H bond (ca. 0.98 Å), but also interact with the two terminal oxygen atoms in the adjacent layers via a weaker hydrogen bond (2.33 Å). The latter bonding mode is absent on the (010) surface. Despite the experimental studies to date, the exact locations of the H atoms in the bronze materials remain an open topic of research. Ritter *et al.* suggest that H atoms first fill the intralayer positions on the asymmetric bridging oxygen atoms at an angle oriented toward the inside of the layer, and then start to fill the terminal oxygen sites when the H atom concentration (*x*) is greater than 0.85.³⁶ However, a recent combined theoretical and experimental study suggests no hydrogen occupation on the intralayer sites, even at high H atom concentrations in Phase III.⁷³ Adams examined the location of absorbed H atoms using a combination of time resolved X-Ray diffraction with molecular mechanics simulations and derived a structural model for Phase II hydrogen bronze with H atoms absorbed on terminal oxygens.⁷²

Table 5-4. Bond length changes introduced by the absorption of H at low concentration in $\text{H}_{0.25}\text{MoO}_3$. Different Mo and O sites, from Mo1 to Mo3, and O1 to O4, are denoted in Figure 5-11.

H absorption site	Bond length (Å)		
		$\alpha\text{-MoO}_3$	$\text{H}_{0.25}\text{MoO}_3$
Terminal oxygen O1	Mo1-O1	1.702	1.876
	Mo1-O2	1.774	1.895
	Mo1-O3	2.211	1.929
	Mo1-O4	1.962	1.932
Symmetric oxygen O4	Mo3-O4	2.429	2.681
	Mo1-O4	1.962	2.054
	Mo1-O3	2.211	1.921
	Mo1-O2	1.774	1.948
Asymmetric oxygen O2, up	Mo1-O2	1.774	2.028
	Mo2-O2	2.211	2.047
	Mo1-O1	1.702	1.712
	Mo1-O3	1.962	1.950
Asymmetric oxygen O2, down	Mo1-O2	1.774	2.024
	Mo2-O2	2.211	2.023
	Mo1-O1	1.702	1.685
	Mo1-O3	1.962	1.946

Our results indicate that the calculated H binding energies on the terminal and asymmetric oxygen atoms differ only by 0.03 eV, suggesting that these two sites can both be populated upon hydrogen spillover. In practice, the distribution of the absorbed H atoms would likely depend on the preparation of the samples, which is probably one of the reasons why the locations of H atoms in the bronze materials found in different experiments differ from each other.^{36,72,73} The calculated average H atom absorption energies shown in Table 4-3 indicate that as the H atom content in the lattice increases, the H atom binding strength decreases, assuming that at a given H atom concentration the H atoms always fill the lowest energy absorption sites first.

We found that the O-H bond lengths (0.99 Å) in the optimized $\text{H}_{0.25}\text{MoO}_3$ structure are essentially independent of the absorption site. However, the absorption significantly changes the nature of the Mo-O bonding near the absorption sites. As shown in Table 5-4, the Mo-O bond length between the oxygen where H is absorbed and the neighboring Mo atoms is generally elongated. In $\alpha\text{-MoO}_3$, Mo forms bonds with two neighboring asymmetric oxygen atoms with distinctively different bond lengths of 1.774 and 2.211 Å, respectively. Upon H absorption, the two unequal Mo-O bond lengths become essentially equal, with 1.91, 1.93 and 2.03 Å for H absorption on the terminal, symmetric and asymmetric oxygen sites, respectively. To model higher H atom concentrations in the molybdenum bronze materials, we adopted a procedure to place H atoms in the lattice based on the energetic preference of absorption sites. Specifically, the most favorable terminal oxygen sites are populated first, followed by the asymmetric oxygen sites. Table 5-5 shows the distribution of H atoms in the selected hydrogen bronze materials. The average adsorption energy decreases significantly with the increase in H atom loading, as shown in Table 5-3, while the optimized O-H bond distances are relatively unaffected.

Table 5-5. Distribution of H atoms on different oxygen sites in the unit cell of hydrogen molybdenum bronze with 4 Mo and 12 O atoms at various concentrations of H_xMoO_3 . The terminal, symmetric bridging, and asymmetric bridging oxygen sites are denoted by O_t , O_s , and O_a , respectively.

	O_t	O_a	O_s
$H_{0.25}MoO_3$	1	0	0
$H_{0.5}MoO_3$	2	0	0
$H_{0.75}MoO_3$	3	0	0
$HMoO_3$	4	0	0
$H_{1.25}MoO_3$	4	2	0
$H_{1.5}MoO_3$	4	2	0

Figure 5-16. Band structures and electronic densities of state for several hydrogen molybdenum bronzes, $\text{H}_{0.25}\text{MoO}_3$, $\text{H}_{0.5}\text{MoO}_3$, HMoO_3 , and $\text{H}_{1.5}\text{MoO}_3$. The energies are relative to the Fermi level.

The calculated band structures and densities of states for several selected hydrogen bronzes are shown in Figure 5-16. In contrast to the semiconductor-like band structure of bulk α -MoO₃, the band structures of all the hydrogen bronzes exhibit strong metallic features with considerably widened valence bands across the Fermi level into the conduction bands. The abrupt change of electronic structures of the hydrogen bronzes arises from the strong H-bonding network formed upon H absorption and the subsequent charge transfer. The highly polarized bonding environment in the lattice gives rise to higher electron mobility, which makes the bronzes strongly metallic. This agrees well with the experimental findings, which show that semiconducting molybdenum oxide becomes a metallic conducting hydrogen bronze upon H atom absorption.⁷⁵

Table 5-6. Bader atomic charges in hydrogen molybdenum bronze, H_xMoO₃, in comparison to bulk MoO₃.

	H_{0.25}MoO₃	H_{0.5}MoO₃	H_{0.75}MoO₃	HMoO₃	MoO₃
H	0.67	0.67	0.66	0.69	-
Bond O_t	-0.97	-0.96	-1.07	-0.96	-0.56
Neighboring Mo	2.25	2.19	2.20	2.18	2.29

We next performed Bader charge analysis on the hydrogen bronzes with various H atom concentrations, as shown in Table 5-6. Upon H atom absorption onto the terminal oxygen, charge transfer occurs from the H-1s orbital to the O-2p orbital, and the H atom becomes essentially protonic. The terminal O atom then transfers the extra charge to the Mo atoms in direct coordination. Consequently, the Mo atoms are moderately reduced and the Mo-O bond strength is slightly decreased. The Bader charge analysis is consistent with the calculated electron density maps shown in Figure 5-17. At all four selected H atom concentrations, there is clearly charge transfer from the absorbed H atom toward the neighboring terminal oxygen. The charge on the terminal oxygen is readjusted accordingly, and the charges around its neighboring Mo atoms are much more evenly distributed due to the charge transfer and lattice reconstruction induced by the absorption of the H atoms. The charge transfer and lattice reconstruction are not localized to only the immediate vicinity of the absorption site. For H atom absorption on terminal oxygen atoms, the electron density around the nearby asymmetric bridging O atoms is evenly distributed toward their neighboring Mo atoms, significantly different than the uneven electron density distribution in bulk α -MoO₃ due to the highly in-equivalent Mo-

O bond lengths (Figure 5-14). A previous atomic force microscopy and X-ray diffraction study by Smith and Rohrer demonstrated that MoO_3 intercalates H and the protonation of H leads to the precipitation of hydrogen bronze.⁷⁶ Eda *et al.* examined the locations of protons in $\text{H}_{0.26}\text{MoO}_3$ by line-shape analysis and suggested that 3- to 5-proton clusters may exist in the bronze.⁷⁷ The formation of protonic hydrogen and the enhancement of hydrogen spillover has also been studied by NMR spectroscopy in other transition metal oxides such as CeO_2 .⁷⁸ Our results are consistent with these experimental observations.

Figure 5-17. The electronic density distributions in an optimized $\text{H}_{0.25}\text{MoO}_3$ structure, with the H atom absorbed on a terminal oxygen site. The locations of the Mo, O and H atoms are denoted by green, red, and white spheres, respectively.

Figure 5-18. Schematic plot of H atom diffusion pathway in bulk MoO_3 .

To gain insight into hydrogen spillover and the mechanism of H atom migration within a crystalline metal oxide lattice, we performed nudged elastic band calculations to examine the minimum energy pathways for an H atom to diffuse in the lattice of molybdenum hydrogen bronze. Due to the computational intensity of these calculations, we performed this analysis only for $\text{H}_{0.25}\text{MoO}_3$. At this low H atom concentration, the terminal oxygen atoms and asymmetric oxygen atoms with an angle pointing inside the layer are the two most favorable H atom absorption sites with calculated H binding energies of 2.90 eV and 2.87 eV, respectively. These two sites are most likely involved in the H atom diffusion processes, since H atom binding on other adsorption sites is much less energetically favorable. The diffusion pathway selected in our minimum energy path calculations is shown schematically in Figure 5-18. The H atom, initially adsorbed on a terminal oxygen (O_{t1}), first transfers to another terminal oxygen site (O_{t2}) in the adjacent layer; it continues migrating inside the layer to an adjacent asymmetric site (O_{a1}),

then moves again to the next neighboring asymmetric site (O_{a2}), ceasing diffusion at another terminal oxygen site (O_{t3}). The migration of hydrogen between O_{a2} and O_{t3} is the reverse process from O_{t2} to O_{a1} with essentially the same diffusion barrier. We first performed NEB calculations to estimate the activation energy barrier for a chemisorbed H on the terminal oxygen to rotate around the axis parallel to the (010) layer. The calculated activation energy was found to be essentially zero. Similarly, the calculated activation barrier for the H atom on the asymmetric oxygen to rotate along the direction pointing to the inner layer is also negligible. We subsequently carried out minimum energy path calculations along the H atom diffusion route defined by $O_{t1} \rightarrow O_{t2} \rightarrow O_{a1} \rightarrow O_{a2}$ in Figure 5-18. The calculated energy profile is displayed in Figure 5-19. The H atom migrates readily from one terminal oxygen to the nearest terminal oxygen of the adjacent layer with a low energy barrier of 0.13 eV. The barrier for an H atom to move from O_{t2} to O_{a1} is estimated to be only 0.10 eV and the barrier for migration from O_{a1} to O_{a2} is even smaller (0.06 eV). Ritter *et al.* have performed solid state ^1H NMR studies to examine the bonding properties, location, and H atom mobility in H_xMoO_3 , and reported an activation energy for H diffusion on the order of 0.1-0.3 eV.³⁶ Our calculated activation barriers are in good agreement with this experimental value range. The small migration barriers for protons in the lattice indicate that H atom diffusion in the MoO_3 lattice is feasible. Therefore, this is the ultimate reason why hydrogen spillover occurs with such facility in this class of materials.

Figure 5-19. The calculated energy profile for H atoms to migrate within the hydrogen molybdenum bronze, $\text{H}_{0.25}\text{MoO}_3$, from one terminal oxygen to its neighboring terminal oxygen in an adjacent layer (a) and between two second most favorable absorption sites (b).

Figure 5-20. The evolution of H-O and Mo-O bond distances for H migration from one terminal oxygen, O_{t1} , to its neighboring oxygen, O_{t2} , in the adjacent layer. Mo_1 and Mo_2 are the two neighboring Mo atoms to the terminal oxygen atoms O_{t1} and O_{t2} , respectively.

To explore the geometric and electronic structural evolution during the H atom diffusion process, we monitored the variation of the main bond parameters and Bader charges as an H atom diffuses from one terminal oxygen atom, O_{t1} , to its neighboring terminal oxygen in the adjacent layer, O_{t2} . This is likely the rate determining step of the spillover process.

The change of primary bonding parameters during this diffusion step is shown in Figure 5-20. The $H-O_{t1}$ distance remains essentially steady until the transition state is reached, at which point the $H-O_{t1}$ bond is partially broken to form a new $H-O_{t2}$ bond. The evolution of the $H-O_{t2}$ distance is essentially the reverse of the $H-O_{t1}$ distance. The H atom transfer thus adopts a “jumping” mode, which explains why the barrier is the highest along our prescribed diffusion pathway. As hydrogen migrates from O_{t1} to O_{t2} , the Mo_1-O_{t1} bond is shortened from 1.87 Å to 1.72 Å, while the Mo_2-O_{t2} bond becomes elongated, representing a stronger Mo_1-O_{t1} bond and a weaker Mo_2-O_{t2} bond, respectively. The variation of the Mo-O bonds reflects the change of the oxidation states of the Mo atoms upon H migration. Figure 5-21 displays the calculated Bader charges along the H atom diffusion pathway. The charge on the mobile hydrogen fluctuates only slightly in a range between 0.65 e and 0.7 e, indicating that the hydrogen remains essentially protonic. The terminal oxygen gains an extra 0.4 e upon H absorption, and the charge is reduced to ~ -0.6 e after the H release. Consequently, the Mo atom adjacent to the site where H is absorbed gains approximately 0.14 e, indicating that the metal atom is partially reduced and thus the Mo-O bond becomes slightly weaker. In contrast, the Mo atom without H absorption on the adjacent O atoms is more positively charged, suggesting a higher oxidation state and hence a stronger Mo-O bond. At the transition state, the Mo_1 and Mo_2 atoms share essentially the same Bader charge and so do the O_{t1} and O_{t2} atoms, consistent with the equal Mo-O and H-O bond lengths at the transition state.

Figure 5-21. The change in the Bader atomic charge for H, Mo, and O atoms for H migration from one terminal oxygen, O_{t1}, to its neighboring oxygen, O_{t2}, in the adjacent layer. Mo₁ and Mo₂ are the two neighboring Mo atoms to the terminal oxygen atoms O_{t1} and O_{t2}, respectively.

Hydrogen Desorption

For hydrogen storage purposes, molybdenum and tungsten hydrogen bronzes are not practical, since the gravimetric storage capacity is relatively low because of the presence of ‘heavy’ elements with high atomic weights. However, because of the ability to reversibly capture

hydrogen, MoO_3 has been used as a hydrogen reservoir in hydrogenation catalysis,^{79,80} and for the study of other spillover-based hydrogen storage materials, it is important to understand the desorption of hydrogen from metal oxides. As a measure of hydrogen desorption capability, we calculated the average sequential desorption energy to form H_2 molecules from several selected hydrogen bronzes with varying H atom concentrations, defined by:

$$\Delta E_{des}^x = 8 \left[E(\text{H}_{x-0.25}\text{MoO}_3) + \frac{1}{8} E(\text{H}_2) - E(\text{H}_x\text{MoO}_3) \right]$$

We assume that at a given H atom concentration the H atoms always occupy the most stable absorption sites first. This assumption is justified in light of the fact that H atom diffusion in the lattice is facile, and thus thermal equilibration can be reached quickly. The calculated results are displayed in Figure 5-22. As expected, the sequential desorption energy decreases as H loading increases, and desorption becomes an exothermic process at H loading higher than $x=1$, indicating that it becomes increasingly difficult for the lattice to accommodate the H atoms and the materials are in a thermally unstable condition. The results thus suggest that desorption is facile at medium to high H loading.

Figure 5-22. The calculated sequential desorption energies for hydrogen molybdenum bronze at different H atom concentrations.

Electronic Structure

The electronic structure of MoO_3 exhibits a well-separated semiconductor-like band gap of 3.3 eV.⁸¹ It has been observed in many experiments that this semiconducting material is turned into a metal upon the formation of hydrogen bronze. To understand this transition, we calculated the energy band structure of MoO_3 and $\text{H}_{0.25}\text{MoO}_3$. The calculated band structure for MoO_3 (Figure 5-23) exhibits a band gap of approximately 1.8 eV, in agreement with the experimental⁸¹ and previous *ab initio* computational^{82,83} results. Upon the hydrogen bronze formation, substantial change in the electronic structure is observed. The valence band is significantly widened, across the Fermi level into the conduction band. The electronic structure thus exhibits the typical band structure of a metal, in excellent agreement with the experimental observations. The origin of the change of electronic structure lies again in the extensive H-bonding environment, in which the protons bridge over the surrounding oxygen atoms for electron hopping.

Figure 5-23. The calculated energy band structure of bulk MoO_3 and $\text{H}_{0.25}\text{MoO}_3$.

Hydrogen Spillover in Carbon-based Materials

To examine hydrogen spillover in carbon-based materials, we selected several nanostructured carbon materials as the spillover substrates including a single graphene sheet, single walled carbon nanotubes (SWNTs), fullerenes, and hexabenzocoronene.^{56,84,85} The key issues we attempted to address in our computational studies were:

1. The minimum energy pathways for an H atom to migrate from the H-saturated Pt_6 cluster to the substrates;
2. The minimum energy pathways for an H atom to diffuse from a chemisorption site to another chemisorption site;
3. The nature of H adsorption in graphitic carbon materials and dynamics;
4. The influence of carbon material surface curvature on hydrogen storage capacity via spillover.

For simplicity, we will focus the majority of our discussions on hydrogen spillover on a graphene sheet. In the experiments conducted by Yang and co-workers, the Pt catalyst nanoparticles are attached to the substrate using a bridge material made of carbonized sugar, which is not incorporated in our theoretical model since its exact composition and structure are unknown.

Figure 5-24. The calculated minimum energy pathway for two H atoms near the bottom of the fully saturated Pt_6 cluster migrating to the graphene sheet to form two C-H bonds.

Similar to the study on hydrogen spillover in MoO_3 , we first performed minimum energy pathway calculations by allowing two H atoms near the bottom of the fully saturated Pt_6 cluster to migrate to the graphene sheet to form two C-H bonds. The calculated potential energy curve is shown in Figure 5-24. The migration process is slightly endothermic with an average reaction energy of 0.23 eV per H atom. The calculated average activation barrier for the migration is 0.48 eV per H atom, which is moderate, indicating that the process is kinetically facile as well. These results suggest that H migration from a Pt catalyst to a graphene sheet in the vicinity of the catalyst could occur at moderate conditions, and the close contact between the fully saturated Pt cluster and the graphene sheet can result in C-H bond formation.

Figure 5-25. The graphene sheet showing H adsorption and diffusion sites.

A key question is whether the H atoms, upon C-H bond formation, are capable of breaking the C-H bonds to diffuse to other sites of the graphene sheet. In Figure 5-25, we label the C atoms to which an H atom chemisorbed on site 1 would migrate. For simplicity, only the case in which there is one C-H bond in the selected supercell was studied. It is anticipated that both the calculated reaction energies and activation barriers will be higher if more C-H bonds are present in the supercell, since a higher number of C-H bonds can result in more energetically favorable conformations for the hydrogenated graphene. Figure 5-26 displays the calculated potential energy curves for an H atom to move from a C atom (site 1) to an adjacent C atom (site 2) and from site 1 to site 4, as shown in Figure 5-25. The calculation yields an activation energy of

0.78 eV for diffusion from site 1 to site 2, which is close to the adsorption energy, but only slightly lower than the activation energy required to desorb an H atom from the carbon surface.

Figure 5-26. The calculated potential energy curves for an H atom to move from a C atom (site 1) to an adjacent C atom (site 2) and from site 1 to site 4.

It might have been anticipated that a concerted atom-transfer reaction to move a hydrogen between adjacent carbon atoms on the sheet could lower the energy barrier relative to the H atom dissociation energy. However, this result indicates that the C-H bond needs to be broken in a largely non-concerted process in order for the H atom to move. This stringent requirement of course hinders the H diffusion. After the completion of H atom diffusion, the 'puckered' (out of the graphene plane) carbon atom from the original C-H bond moves back toward its original lattice site. Simultaneously, the adjacent carbon atom is pulled out of the graphene plane to form a new C-H bond. For H diffusion from site 1 to site 3, the calculated minimum energy pathway indicates that the H atom must pass through site 2. Therefore, the calculated potential energy curve for the diffusion pathway is simply a duplicate of the energy curve for diffusion from site 1 to site 2. For H diffusion from site 1 to site 4, the calculated potential energy exhibits a double-hump shape representing essentially three consecutive steps. First, the H atom is desorbed from the surface. Second, the H atom is adsorbed at a metastable site above the center of the hexagonal ring. Finally, the H atom reaches its destination by forming a strong C-H bond at site 4. The rate-limiting step is the transition from the chemisorption state to the metastable site with a barrier of 0.95 eV, which is slightly higher than the activation energy of diffusion between two adjacent sites. Considering the small energy difference of 0.17 eV between the diffusion pathways for site 1 to site 2 and site 1 to site 4, it is likely that the two diffusion pathways could coexist at high temperatures. We have also investigated several

possible diffusion routes for two H atoms chemisorbed on opposite sides of two neighboring C atoms in graphene starting from the optimized co-adsorption structure. It was found that even the lowest activation energy is larger than 1.5 eV. We thus conclude that the concerted motion of two H atoms is not energetically feasible. Our results are consistent with the recent report using scanning tunneling microscopy and DFT calculations to study diffusion of two separated H atoms on a graphite (0001) surface, which concluded that simultaneous diffusion of two H atoms is energetically unfavorable.⁸⁶

We performed the same diffusion pathway calculations for H atom diffusion along the longitudinal (from site **1** to **3**) and horizontal (from site **1** to **2**) directions on (5,5) and (9,9) armchair SWNT surfaces. The calculated minimum energy profiles for H atom diffusion on SWNT are similar to those for graphene. However, the calculated diffusion barriers on SWNTs are considerably higher than those in graphene. The calculated results are shown in Table 5-7, where the H atom adsorption energies along with the C-H bond lengths are also listed. The calculated diffusion barriers are very close to the corresponding adsorption energies, which again indicates the need for complete C-H bond dissociation for diffusion. The calculated energy profiles reflect a strong influence of the SWNT curvatures on the barriers to H atom surface diffusion. A high nanotube curvature positively enhances the adsorption strength (C-H bond energy) and thus also significantly reduces the possibility of mobility of H atoms on the surface. When compared with the results for the graphene sheet, it appears that it is more difficult for the H atom to diffuse on the carbon atoms in SWNT with sp^3 -like C-C-C bond angles.

Table 5-7. The calculated H adsorption energies and the C-H bond lengths.

	Graphite	(5,5) SWNT	(9,9) SWNT
H diffusion barrier (eV)	0.78	1.09	1.42
H adsorption energy (eV)	0.82	1.07	1.43
C-H bond length (Å)	1.12	1.11	1.12

Finally, we considered H diffusion from an inner site to the edge of hexabenzocoronene. The calculated energy landscape diagram of adsorption and transition states is shown in Figure 5-27. The calculated diffusion activation energies from site **1** to site **2** and from site **2** to site **3** are 1.52 and 1.42 eV, respectively. These activation energies are much higher than those calculated for the graphene sheet, but similar to the activation energies for H atom diffusion on the exterior wall of (5,5) SWNT. The diffusion is accompanied by considerable structural changes in the molecule in order to accommodate the change of electronic configuration of the carbon atom in the C-H bond from sp^2 to sp^3 hybridization. The bond angle changes within the molecule, as well as the diffusion on the sp^3 carbons, significantly increase the activation energy. In contrast, H atom diffusion on the flat graphene sheet and exterior walls of SWNTs causes more localized bond angle deformations and a smaller extent of structural relaxation in

these more rigid structures, in which only the carbon atom in the C-H bond and a few adjacent carbon atoms are involved.

Figure 5-27. H diffusion from an inner site (site 1) to the edge of hexabenzocoronene and the calculated energy landscape diagram of adsorption and transition states.

These results for surface diffusion of a chemisorbed H atom on graphene, SWNTs and a small polyaromatic molecule clearly demonstrate that hydrogen spillover based on a chemisorption mechanism would be energetically difficult. Therefore, we explored another possibility for H atom diffusion via physisorption. It was recently reported by Ye and Chiu that atomic hydrogen is mobile on graphite at room temperature, based on their observation in the experiment of graphite mediated reduction of azoaromatic compounds with elementary iron in dialysis cells.⁸⁷ DFT calculations by Sha and Jackson⁸⁸ suggest that there is an energy barrier to forming a C-H bond of approximately 0.2 eV when a H atom approaches a graphite surface. The barrier arises from the structural stresses induced by pulling the C atom out of the graphene plane. If the H atom remains “hot” (i.e., has enough kinetic energy) after dissociation, transfer from the catalyst, and diffusion across the surfaces of the support and bridges, this activation barrier can be readily overcome and a C-H bond would then be formed. However, if the atom becomes kinetically “cold,” it will be blocked by the activation barrier, located approximately 2.5 Å above the graphene plane, and the H atom can only be physisorbed.^{89,90} We suspect that the high mobility of the H atoms observed in Ye and Chiu’s experiment is due to the diffusion of physisorbed H atoms. Indeed, our calculated physisorption energy for an H atom on the graphene sheet and the selected SWNTs is less than 0.1 eV. Figure 5-28 displays the calculated potential energies in the physisorption region. The potential energy is rather flat, indicating a site-independent behavior. In other words, if the H atom is physisorbed on graphene, it can move across the plane with minimal energy changes. It is important to point

out that H atom physisorption arising from the van der Waals force cannot be accurately described by DFT. Nevertheless, regardless of the computational methods used in the calculations, the adsorption energy is obviously very small, as qualitatively indicated in our results. Therefore, we believe that the only viable mechanism for hydrogen spillover in graphitic carbon materials is via H physisorption.

Figure 5-28. The calculated potential energies for the movement of a physisorbed H atom across the graphene surface.

How stable are the weakly bound physisorbed H atoms on the graphitic carbon materials? To understand their thermal and chemical stability, we attempted to qualitatively address the dynamics of these atoms by performing *ab initio* molecular dynamics simulations at room temperature. A key issue is how fast and to what extent these atoms will remain highly mobile free radicals, recombine to form molecular hydrogen, or form C-H bonds with the substrates. An additional interesting issue is whether the substrate structures influence the spillover efficiencies. To simplify the simulations, we selected a single graphene sheet and C₆₀ to examine the dynamic behavior of an assembly of physisorbed H atoms.

Figure 5-29. The unit cell selected for MD simulations of physisorbed H atoms interacting with a graphene sheet.

We performed a MD simulation of H atoms in a sufficiently large rectangular box containing a single graphene sheet. The unit cell, shown in Figure 5-29, contains 50 C atoms in the graphene sheet sandwiched by 4 H atom layers, two above and two below. Each H atom layer includes 9 physisorbed H atoms separated at least 4.0 Å from each other to prevent the atoms from rapid recombination to form H₂ molecules. The vacuum spacing separating the sheets was set at a distance of 25 Å to minimize inter-sheet interactions. With the activation barrier for H atom chemisorption on the substrate in mind,^{88,89} we set the initial position of the inner H atom layers at distances of 2.5, 2.75 and 3 Å from the substrate, respectively, and the outer H layers at a spacing of 4 Å from the inner H layers. Admittedly, these initial structural arrangements are rather arbitrary; however, other physisorption configurations should not change the total potential energies significantly as long as the H atoms remain in the physisorption region. Nevertheless, kinetically, reactive events may vary, depending on the relative positions of atoms in the unit cell. In addition, MD simulations on such a small unit cell are not statistically significant. Our main interest here is to find out qualitatively whether an assembly of physisorbed H atoms is capable of interacting with these substrates, including forming C-H

bonds, at a near-ambient temperature. Our MD simulation results indicate that for the inner H-layers located at 2.5 Å from the substrate, the strong attraction between H atoms and the substrate steers the H atoms in the inner layers towards the graphene immediately, and most of the H atoms in these two layers become chemisorbed after 0.25 ps (Figure 5-30(a)). The substrate structure undergoes substantial relaxation, and the interacting C atoms pucker out of the plane to form C-H bonds with a bond length of approximately 1.15 Å, consistent with the previous DFT study.^{88,91} In parallel, most of the H atoms in the outer layers rapidly form H₂ molecules, which subsequently become weakly physisorbed on the graphene sheet. For the chemisorbed H atoms, no further diffusion to other chemisorption sites was observed during the 4 ps simulation time. However, Eley-Rideal recombination,^{92,93} in which a gas-phase H atom strikes a C-H bond to form an H₂ molecule, was observed, indicating that the surface C-H bonds are rather weak compared with the C-H bonds in organic molecules. We found that Eley-Rideal recombination on the graphene sheet is a significant process that results in depletion of the chemisorbed H atoms from the substrate. Indeed, at 4 ps, the number of the surface H atoms is actually reduced compared with the number at 0.25 ps (Figure 5-30(b)). The remaining C-H bonds are not well ordered with respect to each other on the graphene sheet, despite the fact that the structural configuration with alternative C-H bonds on graphene, i.e., one C-H bond above the plane adjacent to another C-H bond below the plane, is thermodynamically more favorable than the structure with randomly distributed isolated C-H bonds.⁹⁴ This suggests that the chemisorption process is kinetically controlled.

Table 5-8. The H distributions on graphite and C₆₀ during the first principles molecular dynamics simulations. N_H is the number of initial H atoms, and D_{C-H} is the nearest initial C-H distance.

Substrate	N _H	D _{C-H} (Å)	time (ps)	Chemisorbed State	Physisorbed State	Molecular State
Graphite	36	2.5	0.25	15	7	14
			1	10	8	18
			4	10	2	24
		2.75	0.25	4	6	26
		3.0	0.25	1	7	28
			1	1	3	32
C ₆₀	50	3.2	0.1	1	23	26
			1	4	24	22
			1.5	6	8	36

Figure 5-30. MD simulation snapshots for H atoms on a graphene sheet at (a) 0.25 and (b) 4 picoseconds for the initial configuration with nearest C-H layer distance at 2.5 Å, and at 0.25 picoseconds for an initial distance at 2.75 (c) and 3.0 (d) Å.

Moving the layers of H atoms from their original positions by 0.25 Å and 0.5 Å, respectively, along the direction away from the graphene sheet yielded a drastically smaller number of chemisorbed H atoms on the graphene sheet in our MD simulations (Figures 5-30(c) and (d)). This is largely due to fact that the hydrogen atoms are now located at a distance from the

graphene, which is outside of the distance associated with the C-H bond formation energy barrier (ca. 2.5 Å) and, more important, the recombination of H atoms to form H₂ molecules is barrierless and thus a thermochemically and kinetically more favorable competitive process. Therefore, the kinetics of C-H bond formation will be sensitive to the relative initial distance between H atoms and C atoms in the MD simulations. A short distance increases the probability for an H atom to form a C-H bond, and a long distance gives rise to a higher probability for H₂ recombination reaction. Morisset et al. examined the formation of the H₂ molecule through two initially physisorbed atoms on a graphite surface via quantum wave packet method, and reported that the reaction occurs with a significant probability,^{95,96} which is consistent with what is observed in our MD simulations. The calculated numbers of events are summarized in Table 5-8. Despite the lack of statistical significance of the current method due to a small number of atoms used in the theoretical model and the relatively short simulation time, it can be qualitatively concluded that the transition from physisorbed H atoms to a chemisorption of hydrogen atoms on a graphene sheet can occur at room temperature. In a closed system with a metal catalyst (as in the published hydrogen spillover experiments), H₂ molecules formed via H atom recombination could again interact with the metal catalyst to regenerate H atoms.

To understand the structural effects of the carbon substrates on H spillover, we performed a MD simulation for an assembly of H atoms on C₆₀ confined in a sufficiently large box at 300 K. The unit cell parameters were set at 27.34 Å and the number of H atoms in the box was set at 50. The initial positions of the H atoms were 4.0 Å from each other, and the distance between H atoms and C₆₀ was set to be at least 3.2 Å. Similar to the case of the simulation involving graphene, all H atoms exhibit high mobility upon the start of the MD simulations, suggesting that H diffusion in the physisorption state is facile. However, shortly after MD initiation, both H chemisorption that leads to formation of C-H bonds and H recombination to form H₂ take place almost simultaneously. Of the 50 H atoms in the box, 6 of them become chemisorbed and the rest form H₂ molecules (Table 5-8). Figure 5-31 displays several snapshots of the MD trajectory. The chemisorption of hydrogen atoms on C₆₀ appears to be much easier compared to chemisorption on graphene, as evidenced by the fact that more H atoms form C-H bonds on C₆₀. This is likely due to a lower barrier to C-H bond formation for adsorbed H atoms and more favorable thermochemical C-H bond energy resulting from carbon curvature.^{97,98}

Figure 5-31. MD simulation snapshots for H atoms on C_{60} at (a) 0, (b) 0.1, (c) 1, and (d) 1.5 ps.

The MD studies of H spillover dynamics on graphene and C_{60} qualitatively indicate that physisorption of H atoms facilitates H diffusion and ultimately leads to either H chemisorption or H_2 formation as time evolves. The spillover efficiency (i.e., the percentage of adsorbed H atoms that form C-H bonds) depends on the curvature of the substrates. Our MD simulations indicate that the efficiency of hydrogenation of graphitic materials could be enhanced with carbon materials with curved surfaces (e.g., fullerenes). To gain additional understanding of this "curvature effect," we examined the hydrogenation energies of fullerenes with various sizes where the hydrogenation takes place at the exohedral sites.

Figure 5-32. The calculated average C-H bond energy as a function of hydrogenation percentage in several selected fullerene molecules.

To understand the energetics required to partially or fully hydrogenate fullerenes, we calculated the average C-H bond energies at various levels of hydrogenation. The results are shown in Figure 5-32, and the optimized fully hydrogenated fullerene structures are displayed in Figure 5-33. Upon hydrogenation, the C-C bond distances of fullerenes increase slightly as the hybridization of the C atoms changes from sp^2 to sp^3 , and the C-H bond lengths (1.095 Å) are similar for all the nine fully hydrogenated fullerenes. To form only one C-H bond per fullerene, the C-H bond energy essentially decreases with fullerene size, reflecting the strong influence of carbon material curvature on the C-H bond strength. The only exception is C₃₂, on which the C-H bond is in fact weaker than on C₄₄. A detailed analysis indicates that the surprisingly weaker C-H bond in C₃₂ arises from the exceptionally stable electronic structure of C₃₂. C₃₂ has been known to be much more stable than other small fullerene molecules except C₆₀.^{99,100} Ultraviolet photoelectron spectroscopy of C₃₂ and C₆₀ exhibits unusually large HOMO-LUMO gaps of 1.3 eV and 1.6 eV, respectively.¹⁰¹ In contrast, the HOMO-LUMO gaps of other fullerene molecules are much smaller, ranging from 0.70-0.80 eV.

Figure 5-33. Optimized configurations for nine fully hydrogenated fullerenes, $C_{20}H_{20}$, $C_{28}H_{28}$, $C_{32}H_{32}$, $C_{36}H_{36}$, $C_{40}H_{40}$, $C_{44}H_{44}$, $C_{48}H_{48}$, $C_{60}H_{60}$, and $C_{70}H_{70}$.

Table 5-9. Calculated HOMO-LUMO gaps of nine selected fullerene molecules. The experimental gaps are determined from photoemission spectra.

Molecules	HOMO-LUMO gap (eV)	
	Calculation	Experiment
C ₂₀	0.37	-
C ₂₈	0.78	-
C ₃₂	1.43	1.3
C ₃₆	0.45	0.8
C ₄₀	0.88	0.7
C ₄₄	0.85	0.8
C ₄₈	0.73	-
C ₆₀	1.67	1.6
C ₇₀	1.72	1.3

The calculated HOMO-LUMO gaps of the selected fullerenes, shown in Table 5-9, compare well with the experimentally measured values. We also note that the C-H bond energy in C₂₀ is substantially larger than those in other fullerenes, resulting from the highly acute C-C-C bond angles of the carbon atoms, causing these atoms to behave like radicals. For higher percentages of hydrogenation of the fullerenes, the calculated C-H bond energies decrease monotonically with the fullerene size. For larger fullerenes, the average C-H bond energy varies in a relatively small range, roughly within 0.4 eV, with respect to hydrogenation percentage; a considerably larger variation of C-H bond energies vs. hydrogenation percentage for smaller fullerenes, particularly C₂₀, was found since these fullerenes exhibit higher reactivity. Compared with the typical C-H bond energy in organic molecules (~4.3 eV), the average C-H bond energies in fullerenes, except C₂₀, are much smaller. Nevertheless, our results suggest that hydrogenation of fullerenes by physisorbed H atoms is a highly exothermic process. As the fullerene size decreases, the well-depth of C-H bond formation increases. It is therefore anticipated that hydrogenation of the fullerenes will become increasingly facile as the fullerene

size decreases, but dehydrogenation will be increasingly more difficult. Table 5-10 displays the calculated average energy of forming H₂ molecules from the selected hydrogenated fullerenes (C_nH_m) at a given capacity, defined by:

$$\Delta E_{des} = \frac{2}{m} \left[E(C_n) + \frac{m}{2} E(H_2) - E(C_n H_m) \right]$$

In all cases, desorption is an endothermic process and, as expected, the desorption energy decreases with increasing fullerene size. In particular, at 80% to full hydrogen saturation, the required desorption energy for C₆₀ and C₇₀ appears to be quite small. Of course, the key challenge to make these materials useful for hydrogen storage is to find a catalytic process that allows the C-H bonds to be broken easily.

Table 5-10. Calculated average desorption energies for several selected hydrogenated fullerene molecules at different hydrogenation percentages.

Molecules	Hydrogenation Percentage				
	20%	40%	60%	80%	100%
C ₂₀	2.34	2.96	1.98	2.3	2.68
C ₃₂	1.58	1.3	1.1	1.3	1.6
C ₄₄	0.86	0.56	0.44	0.8	1.06
C ₆₀	0.12	0.32	0.06	0.3	0.46
C ₇₀	0.02	0.2	-0.04	0.18	0.26

Conclusions

Understanding the underlying spillover mechanisms is of essential importance for the design and development of novel hydrogen storage materials that will assist in meeting the DOE hydrogen storage system targets. Mechanistically, the hydrogen spillover process includes three consecutive steps. In the first step, H₂ molecules undergo dissociative chemisorption upon interacting with metal catalysts. Subsequently, H atoms on the catalyst surfaces migrate

to the substrate in the vicinity of the catalyst particles. Finally, H atoms near the catalysts diffuse freely to the surface or bulk sites far from where the catalyst particles reside. We attempted to address every step of the spillover process, and our combined quantum-mechanical first-principles calculations and catalytic hydrogenation and dehydrogenation experiments for solid state polycyclic aromatic hydrocarbon compounds represent a comprehensive description of the hydrogen spillover process in the chosen solid state materials.

Theoretically, we first employed a simple Pt cluster model to represent the Pt catalyst nanoparticles and examined H₂ dissociative chemisorption on the cluster until it was fully saturated by H atoms. The small cluster model is, of course, a gross simplification of the realistic size of catalyst particles and does not resemble the catalyst particles used in practice. However, it has the following advantages over the conventional crystalline surface model, which has been widely used in computational modeling of heterogeneous gas-solid catalytic reactions in the literature:

1. The cluster model possesses sharp corners, edges and kinks, which are often found to be the most active catalytic sites in experimental and computational studies.
2. The cluster model allows us to computationally investigate the effects of full coverage of chemisorbed gas species on catalytic activities. At a given gas pressure, the active catalyst surfaces are expected to be fully covered with hydrogen.
3. The cluster model provides an opportunity to examine chemistry at the catalyst-substrate interface, which would be otherwise very difficult to model computationally.

Our computational results from H₂ dissociative chemisorption on the selected small Pt clusters suggest that at full H-saturation, the H₂ dissociative chemisorption energy and the H-desorption energy do not change significantly with the cluster size. This is very important because it allows us, with more confidence, to use a small cluster to explore how H atoms are transferred from the catalyst to the solid substrate, thus gaining insight into the interface chemistry. Due to computational limitations, the present study deals with only small Pt clusters at the subnano scale. Further in-depth investigations on the catalytic properties of larger Pt clusters at full saturation of H atoms are necessary in future studies to gain full understanding of the catalyst size effects.

We utilized a fully H-saturated Pt cluster to explore the energetic profiles of H migration from the cluster to its vicinity on the substrate surfaces. On the MoO₃(010) surface, the H-migration was found to be facile with a moderate activation barrier and an exothermic reaction energy. As the H atom migrates from the Pt cluster to the substrate, it gradually loses its electron to the accepting O atom and becomes a proton upon forming H_xMoO₃. Consequently, the Mo atom bonded to the accepting O atom is reduced. We showed that H atoms can readily diffuse on the surfaces of a MoO₃ slab and between the adjacent slabs into the bulk lattice. Assisting the facile hydrogen spillover is an extensive H-bonding network inherent to the MoO₃ lattice capable of accommodating protons after H atom transfer from the Pt catalyst surfaces. Our calculated H-diffusion barrier in bulk MoO₃ is in excellent agreement with the available NMR experimental

data. Upon formation of the hydrogen bronze, the semiconductor-like electronic structure of MoO_3 was found to exhibit a zero band gap, consistent with experimental observations. For the first time, the complete mechanism that dictates hydrogen spillover processes in the transition metal oxides is conclusively understood.

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CHAPTER 6

Development of Advanced Techniques for the Characterization of Hydrogen Adsorption

Introduction

Hydrogen storage materials such as those developed within the HSCoE are currently being sought after to provide a means to effectively store hydrogen for fuel cell powered applications. Such new technology would help minimize world-wide dependence on fossil fuels and mitigate local and global environmental issues. An effective storage material will require a high hydrogen sorption capacity, relatively high isosteric heats of adsorption, and sufficiently fast kinetic uptakes. All three of these intrinsic properties are critical to the success of such a storage medium.

Unfortunately, the literature has many dubious claims of large H₂ sorption capacities which have not been confirmed by other investigators. This confusion in the literature is due predominantly to: (1) the variability in carbon samples from one laboratory to another, and (2) the inherent difficulties in measuring H₂ sorption on small samples (< 100 mg) at very high (up to 120 atm.) H₂ gas pressures.¹

The focus of a portion of the project work presented in this chapter is the development of a highly accurate sorption apparatus which can be applied to understand the true storage capacities of candidate materials. The heart of our experimental design lies in the measurement of the differential pressure between a reference cell and a sample cell that contains a sorbent.

The development of the “capsule method” for hydrogen storage uptake measurements was targeted at high-throughput and rapid determination of hydrogen storage material capacity. If solid adsorbents are placed within a gas cylinder, they occupy a portion of the volumetric space. Despite this loss of gas-phase volume, if the gas-solid interactions are sufficiently favorable, there is the potential to reversibly store more total molecules of adsorbate within this type of a system than within a conventional pressurized gas cylinder. Alternatively, one may be able to store the same amount of H₂ in a container holding adsorbent at lower pressures than in a pressurized empty container, thereby yielding a storage system that is inherently safer (i.e., is at lower pressure) and which has less of a wall thickness requirement for the container. In turn, the reduction of wall thickness would lead to lower cost containers. The successful implementation of such an adsorbent-based storage system is centered on the development of adsorbent materials which have sufficient reversible H₂ sorption characteristics.

Many experimental techniques have been developed to measure gas-solid equilibrium data based on knowledge of the total moles of adsorbate contained within a system and an experimental assessment of the moles of the adsorbate residing in the gas phase by techniques

such as IR spectroscopy², NMR spectroscopy³, GC headspace analysis^{4,5} and through simple use of a pressure transducer⁶. The moles of gas adsorbed on the solid phase, therefore, can be inferred by differences in these two quantities.

In this chapter, we present our experimental methodology for a sorption capsule technique and provide benchmarking data to examine its effectiveness in measuring the total loading of a gas within a pressurized vessel. We also discuss the more difficult experiment of evaluating a sorption isotherm, using a pressure transducer to evaluate the amount of adsorbate in the gas phase. Experimental limitations will be discussed, along with conditions under which the presence of the adsorbent is found to hinder the total storage capacity.

Experimental Details

Materials

NaA (4A) zeolite pellets were obtained from UOP, and GX-31 activated carbon was obtained from Amoco. All the gases used were obtained from Airgas. The hydrogen used was Research Grade (99.9995%), the helium was ultra-pure He BIP[®] PLUS (< 20 ppb water, <10 ppb O₂), and the methane was ultra-high purity (99.99%). Hydrogen and methane were further purified by passing the gases through an active metal point-of-use purifier (Matheson TriGas, Model MN-12).

Sample Preparation

Differential Pressure Adsorption Unit (DPAU)

Samples for adsorption testing with the DPAU were activated by degassing the materials during a series of temperature ramps and isothermal soaks while under a dynamic vacuum. For carbon samples, typically 100-500 mg of sample were loaded in a sample cell within an argon glove box and attached to an ASAP 2010 (Micromeritics). The samples were then heated at a rate of 10°C/min. to 100°C and held at that temperature for 30 minutes. The temperature was subsequently increased to either 300 or 750°C at the same ramp rate and held there until a vacuum reading of less than 10⁻⁴ torr was achieved. The 4A zeolite pellets were activated under dynamic vacuum while ramping at 1°C/min. with one hour holds at 100, 150, 200, and 250°C, and then holding at 400°C until a vacuum of less than 10⁻⁴ torr was achieved.

During the sample activation procedure, the gas phase within the sample cell could be continuously monitored with a quadrupole mass spectrometer so that a temperature desorption profile could be obtained. This process enabled us to determine when all the oxygen-containing functional groups were removed from the samples under the high-temperature (750°C) activation.

After the activation, samples were transferred back into the argon glove box and accurately weighed into a high-pressure cell for gas sorption studies. The activated sample was then removed from the glove box, connected to the differential sorption apparatus and outgassed at ambient temperature to remove the argon adsorbed while the sample was loaded into the sample cell.

Capsule

Samples for adsorption testing using the capsule technique were activated by degassing the materials during a series of temperature ramps and isothermal soaks while under a dynamic vacuum. Typically ~1.5-2.0 g of sample were loaded in an activation cell within an argon glove box and attached to an ASAP 2010 (Micromeritics, Inc.). The samples were then heated at a rate of 10°C/min to 100°C and held at that temperature for 30 minutes. The temperature was subsequently increased to 300°C at the same ramp rate and held there until a vacuum reading of less than 10^{-4} torr was achieved.

After the activation, samples were transferred back into the argon glove box and weighed into a high-pressure sorption capsule cell for gas sorption studies. The activated sample was then removed from the glove box, connected to the sorption capsule apparatus and outgassed at ambient temperature to remove the argon adsorbed while the sample was loaded into the capsule cell. Final weighing of the sample was performed using a five place analytical balance. Both the analytical balance and sorption capsule reside in a nitrogen-purged Lexan box to avoid complications associated with weight changes based on condensation of humidity on the external surface of the sorption capsule.

Results and Discussion

Differential Pressure Adsorption Apparatus Design

The experimental sorption device developed during the project is a DPAU. This apparatus is a volumetric adsorption device that determines the amount of gas adsorbed by a material based on a differential pressure change between a reference cell and a sorption cell containing sample. A schematic of the DPAU is provided in Figure 6-1. Sorption experiments are initiated by charging the sample and reference side manifolds with gas, allowing time to come to thermal equilibrium, and subsequently expanding to the sample and reference cells. After equilibration, the manifolds are re-pressurized and expanded again. This sequential dosing process is typically performed so that isotherm data are collected from 12 to 1600 psia. Sorption capacities are determined via mass balance, taking into account the non-ideality of the gas phase in various regions of the DPAU through the use of an equation of state and from knowledge of the system free space. Desorption experiments are conducted in an analogous fashion, i.e., by equilibrating the manifold sections to a reduced pressure relative to the prior

isotherm point and expanding the sample and reference cell pressures to the manifold section. We consider equilibrium as a differential pressure transducer (DPT) change of less than 0.01 psia observed over a period of an hour.

The individual manifold-, as well as the reference- and sample-leg, volumes are all approximately 50 cm³. The manifold volumes were accurately measured by gas-phase expansions using a very accurate 300 psia transducer (Paroscientific Digiquartz 6000-300A). The manifold section of the DPAU is housed in a thermostated chamber, which is maintained at 35°C. This chamber is also nitrogen purged to eliminate safety hazards associated with leaking of high-pressure flammable and/or combustible gas. The reference and sample temperatures were controlled by immersing these sections into a common Dewar whose temperature was regulated by recirculating an aqueous ethylene glycol mixture from a controlled temperature bath.

The DPT (Rosemont model 3051CA4A22A1A) is capable of detecting pressure changes as low as 0.01 psi. Since a sorption isotherm is a comparison of a quantity of gas adsorbed at a particular pressure, the system requires two absolute pressure transducers in addition to the DPT. All three transducers are Class II and are designed for use in flammable gas atmospheres. Since the basis of the sorption determination for the DPAU is *differential* pressure, isotherms measured with the DPAU are equally accurate in the high pressure regime as they are at low pressures. This is not so for typical Sieverts devices, which employ absolute pressure transducers whose accuracy depends on a percentage of the full-scale reading. Since differential pressure can be measured with approximately two orders of magnitude more accuracy than absolute pressure, the DPAU is able to accurately characterize the sorption of a gas with as little as ~100 mg of material.

The DPAU has been fully automated, enabling unattended operations for standard isotherm measurements. The automation program was written in LabView[®] to be user-friendly and allows for variable entry of experimental parameters and criteria for defining the equilibrium condition. The pressure tables are completely programmable in that they are created off-line, using a spreadsheet application, and saved so they can be used repeatedly for future experiments. The software enables the DPAU to be monitored at all times. Critical raw data are collected into a master file that is used to evaluate system free space and gas isotherms.

Figure 6-1. Schematic of the Differential Pressure Adsorption Unit (DPAU).

The use of differential pressure readings in the characterization of adsorption isotherms allows for a greater tolerance of laboratory/instrument temperature fluctuations during the course of data collection vs. a conventional Sieverts apparatus. In Figure 6-2 we illustrate the stability of our differential pressure readings over a period of 60 hours (Fig. 6-2a) while maintaining the sample and reference cell temperatures at 25°C and the system pressure at ~1000 psia. During the 60 hour period, the laboratory temperature was observed to undergo substantial variation. While the absolute pressure (Fig. 6-2b) is seen to vary by as much as 5 psia due to the temperature fluctuations during this period, the variation in the DPT response is observed to be only ~0.02 psia.

Figure 6-2. Stability test of the readings from the (a) differential pressure transducer and (b) absolute pressure of the DPAU at 25°C and ~1000 psia. The data clearly reveal much smaller variations in the DPT readings than the absolute pressure readings.

While absolute temperature fluctuations are well tolerated by the DPAU, it is of the utmost importance to maintain “temperature symmetry” during the isotherm analyses. That is, each relative volume (i.e., reference manifold and sample manifold; reference cell and sample cell) must be maintained at the same **relative** temperature. Any deviation of relative temperature between manifold volumes, sample cells, or “legs” connecting the manifold and cells will cause shifts in the DPT readings and affect the isotherm data collection.

Free Space Determination

In traditional sorption studies, experiments are typically conducted by first performing a sorption experiment with the gas of interest and subsequently performing a helium free-space analysis. Performed in this manner, the adsorbent is not “contaminated” by exposure to helium prior to experimentation. Although the experiment is performed in this order, the following discussion will first present the helium free-space analysis and subsequently will discuss the analysis of adsorption. The logic of the adsorption calculation is more understandable when presented in this manner.

A series of helium expansions is performed by first evacuating the system, pressurizing the manifold section to a desired pressure, and then expanding the manifolds into the sample and reference chambers simultaneously. If one considers the DPAU as two independent traditional volumetric sorption units, the mole balance for the sample and reference sections of the DPAU at the first expansion step can be written as:

$$\frac{P_{MS1}V_m}{Z_{MSi1}T_m} = \frac{P_{S1}V_m}{Z_{MSF1}T_m} + \frac{P_{S1}V_S}{Z_{S1}T_S} \quad (1)$$

$$\frac{P_{MR1}V_m}{Z_{MRi1}T_m} = \frac{P_{R1}V_m}{Z_{MRF1}T_m} + \frac{P_{R1}V_R}{Z_{R1}T_R} \quad (2)$$

Here, M refers to the manifold, S refers to the sample section and R refers to the reference section. P_{MS1} and P_{MR1} are the pressures in the sample and reference manifolds, respectively, prior to expansion. P_{S1} and P_{R1} represent the post-expansion pressures. V_M , V_S , and V_R are the volumes of the respective sections of the DPAU; T_M , T_S , and T_R are the absolute temperatures in the respective sections of the DPAU; and Z_{MSi1} , Z_{MRi1} , Z_{MSF1} , and Z_{MRF1} represent the individual gas-phase compressibility factors, which are functions of pressure, temperature, and chemical species.

It should be noted that the sample and reference manifold pressures prior to expansion are approximately equal (although because of unsymmetrical seating of the manifold valve, they are experimentally not equal). Since the sample sizes are generally small and the sample and reference cells are approximately the same volume, the sample-side and reference-side pressures post-expansion are comparable. These observations enable us to make the following approximations: 1) The compressibility factors in the manifold sections are equal prior to expansion, i.e., $Z_{Mi1}=Z_{MSi1}=Z_{MRi1}$, 2) the compressibility factors in the manifold sections are equal post-expansion, i.e., $Z_{MF1}=Z_{MSF1}=Z_{MRF1}$, 3) the temperature in the sample and reference sections are equal, i.e., $T=T_S=T_R$, and, consequently, and 4) the compressibility factors in the sample and reference sections are equal post-expansion, i.e., $Z_1=Z_{S1}=Z_{R1}$. All of these approximations are excellent.

If we define the pre-expansion manifold differential pressure (δ_i) and the post-expansion system differential pressure (ΔP_{Ti}) to be:

$$\delta_i = P_{MSi} - P_{MRi} \quad (3)$$

$$\Delta P_{Ti} = P_{Si} - P_{Ri} \quad (4)$$

we can then combine Eqs. 3 and 4 with Eqs. 1 and 2 and write:

$$\frac{\delta_1 V_m}{Z_{m1} T_m} - \frac{\Delta P_{T1} V_m}{Z_{mF1} T_m} - \frac{\Delta P_{T1} V_R}{Z_1 T} = \frac{P_{S1}}{Z_1} \left[\frac{V_S}{T} - \frac{V_R}{T} \right] \quad (5)$$

Subsequent helium expansions are performed by isolating the sample and reference sides from the manifold, repressurizing the manifold, and expanding again to the lower sections of the DPAU. The general expression for the differential pressure change after the i^{th} helium expansion is:

$$\frac{V_m}{T_m} \sum \frac{\delta_i}{Z_{mii}} - \frac{V_m}{T_m} \sum \frac{\Delta P_{Ti}}{Z_{mFi}} - \frac{\Delta P_{Ti} V_R}{Z_i T} = \frac{P_{Si}}{Z_i} \left[\frac{V_S}{T} - \frac{V_R}{T} \right] \quad (6)$$

The two unknown free-space parameters which need to be determined are: 1) $V_S/T - V_R/T$ and 2) V_R/T . Although Eq. 6 can be rearranged to linear form, enabling the evaluation of $V_S/T - V_R/T$ and V_R/T , it requires dividing by a very small differential pressure reading, thereby leading to large errors. To circumvent this problem, we recognize that V_R/T can be determined with the use of an absolute pressure transducer through manipulation of Eq. 2.

With V_R/T evaluated, all of the terms on the left hand side of Eq. 6 are known. Consequently, a plot of y vs. P_{Si}/Z_i yields a straight line which passes through the origin with a slope of $V_S/T - V_R/T$. The key parameters required for the differential adsorption analysis, i.e., $V_S/T - V_R/T$ and V_R/T , have therefore been determined.

We emphasize again that Eq. 6 makes the explicit assumption that helium does not adsorb on the sample during free space evaluations. When helium adsorption is considered, Eq. 1 must be modified such that,

$$\frac{P_{MS1} V_m}{Z_{MS1} T_m} = \frac{P_{S1} V_m}{Z_{MSF1} T_m} + \frac{P_{S1} V_S}{Z_{S1} T_S} + K_{He} P_{S1} R W_S \quad (7)$$

Here, K_{He} is the Henrys constant for helium, which must be evaluated in separate investigations, and W_S is the weight of the sample used in the experiment. Since helium adsorbs only on the

sample, the equation for the reference cell mass balance, i.e., Eq. 2, remains unaffected. Propagating this result in the DPAU analysis leads to the ultimate equation used to determine the key free space factor, $V_S/T - V_R/T$, namely,

$$\frac{\delta_1 V_m}{Z_{m1} T_m} - \frac{\Delta P_{T1} V_m}{Z_{mF1} T_m} - \frac{\Delta P_{T1} V_R}{Z_1 T} - K_{He} P_{Si} R W_S = \frac{P_{S1}}{Z_1} \left[\frac{V_S}{T} - \frac{V_R}{T} \right] \quad (8)$$

The equations for the following hydrogen adsorption analysis are unaffected by whether or not helium adsorption is considered during free space evaluations. The resulting hydrogen capacities are influenced by the method of free-space evaluation due to differences in the value of $V_S/T - V_R/T$ determined.

Gas Adsorption/Desorption Analysis

The first step of the analysis of gas adsorption occurs in precisely the same way that the helium free space measurement is performed, i.e., the entire system is initially evacuated, the manifold section is then pressurized with hydrogen, and then the gas in the manifold sections is expanded to the reference and sample chambers. The reading on the differential pressure transducer after expansion represents the change in pressure based on expansion (as witnessed by helium) and the extra pressure change due to adsorption. The amount of uptake after step 1 can be determined from:

$$n_{ADS1} R = \frac{\delta_1 V_m}{Z_{m1} T_m} - \frac{\Delta P_{T1} V_m}{Z_{mF1} T_m} - \frac{P_{S1}}{Z_1} \left[\frac{V_S}{T} - \frac{V_R}{T} \right] - \frac{\Delta P_{T1} V_R}{Z_1 T} \quad (9)$$

As in the case of helium, subsequent experiments are performed by isolating the sample and reference sides from the manifold, repressurizing the manifold, and expanding again to the lower sections of the DPAU. The general expression for the total uptake after the i^{th} step of the DPAU experiment is:

$$n_{ADSi} = \frac{V_m}{RT_m} \sum \frac{\delta_i}{Z_{Mii}} - \frac{V_m}{RT_m} \sum \frac{\Delta P_{Ti}}{Z_{MFi}} - \frac{P_{Si}}{Z_i R} \left[\frac{V_S}{T} - \frac{V_R}{T} \right] - \frac{\Delta P_{Ti} V_R}{Z_i RT} \quad (10)$$

Finally, the capacity is determined by dividing the amount adsorbed by the sample weight. Since the manifold pressure prior to expansion (P_{MSi}) can either be greater or less than the pressure for the previous isotherm point (P_{Si-1}), Eq. 10 is applicable to both adsorption and desorption experiments.

As a further refinement in the sorption calculation, the helium free space data are reanalyzed as if they were true adsorption/desorption data with the use of Eq. 10, using the free space factors calculated previously. Any systematic deviance in capacity (mmoles/g) observed from the helium data is noted and subtracted from the isotherm values calculated with the adsorbate gas. This empirical correction ensures that a null isotherm is produced in the case of a presumed non-adsorbing system and that systematic errors inherent in the equipment do not contribute to apparent isotherm loadings. Neglecting helium adsorption onto adsorbates, under certain conditions, can lead to appreciable errors in adsorption isotherms. This topic is addressed in a subsequent section of this manuscript.

Sample Testing Using the DPAU

As pointed out by Tibbets and coworkers, it is critical to perform complete adsorption and desorption measurements to assure that data are collected at equilibrium. We have found that, depending on the sample type, the time required to achieve equilibrium can be well over an hour.

Figure 6-3. Differential pressure readings as a function of time from an automated methane adsorption/desorption experiment conducted at 30°C with NaA (4A) zeolite.

As an example of this observation, and to illustrate the functionality of the DPAU, in Figure 6-3 we provide the raw DPT data for methane on 4A zeolite at 30°C as a function of time for a typical automated sorption/desorption experiment. The data reveal that each of the sorption steps for this system requires approximately 80 minutes to achieve equilibrium, and that the duration of the entire adsorption/desorption experiment is approximately 38 hours. It is important to note here a significant benefit of the differential pressure method for obtaining kinetic data during the time needed to reach equilibrium. In a conventional Sieverts apparatus, the expansion of gas from a manifold (dosing) volume into a sample cell will cause a rise in the temperature of the gas due to the heat of expansion. The subsequent cooling of the gas will result in an observed decrease of the absolute pressure in the apparatus in addition to the pressure decrease due to gas adsorption. In this situation, it may be impossible to determine whether the rate of pressure equilibration is controlled by the thermal equilibration (heat of expansion) or adsorption kinetics (rate of equilibration of adsorbed gas vs. non-adsorbed gas). By contrast, during isotherm measurements with the DPAU, an equal number of moles of gas are expanded from the reference and sample manifolds into largely equal reference and sample cells, causing an equal heat of expansion on both sides of the instrument. This has the positive effect of cancelling the heat of expansion contribution to the equilibration data collected by the DPT and allows the adsorption kinetics to be characterized, including the amount of time necessary to reach equilibrium.

In Figures 6-4a and 6-4b we provide the results for several benchmarking tests of the DPAU by comparing hydrogen adsorption and methane adsorption/desorption results from our laboratory, measured with a standard Sieverts volumetric apparatus from VTI, using 4A zeolite. Also included in Figure 6-4a is a datum from the literature.⁷ A comparison of the 30°C sorption isotherms clearly reveals the excellent agreement of the DPAU results with independent measurement techniques.

Figure 6-4. Benchmarking tests of the DPAU for (a) hydrogen adsorption ($\circ$) and (b) methane adsorption ($\circ, +$)/desorption ($\bullet$) measured on NaA (4A) zeolite at 30°C. The DPAU data are compared with results from our laboratory measured with a standard Sieverts volumetric apparatus from VTI (Δ) as well as a datum from the literature ($\blacksquare$).⁷ To illustrate the importance of accounting for helium adsorption in free space evaluations, we also include in Figure 6-4b the resulting methane isotherm assuming that helium adsorption on 4A zeolite is comparable to that of 5A (open diamonds).

Figure 6-5. Comparison of 25°C hydrogen isotherms on Amoco Supercarbon (GX-31) measured on the DPAU with 112 mg (Δ), 580 mg ($\circ, \bullet$), and 514 mg (open diamond) samples and on a Rubotherm gravimetric sorption balance with a 1014 mg sample (+). Hydrogen weight % is defined as $g(H_2)/g(\text{sample}) \times 100$.

In Figure 6-5, we compare 25°C H_2 sorption isotherms from the DPAU with gravimetric sorption data measured on a Rubotherm balance using 1014 mg of Amoco Supercarbon GX-31. The data from the DPAU demonstrate: 1) the repeatability of the unit from two sequential runs using a 580 mg sample and 2) the ability of the unit to precisely measure an isotherm with as little as 112 mg of sample. The excellent agreement with the Rubotherm data suggests that our DPAU protocols yield accurate data as well.

We emphasize again that helium adsorption was not accounted for in the isotherm calculations. As will be shown in the next section, properly accounting for helium sorption during free space analyses leads to higher sorption capacities which, in turn, will affect the values of ΔH calculated from a Clausius-Clayperon analysis of the isotherm data. A more detailed discussion of this topic has been presented in a recent article featuring the application of the DPAU to measure credible hydrogen sorption isotherms on a series of well-defined, single-walled carbon nanotubes.⁸

Helium Sorption Considerations

When helium adsorption is not considered in the DPAU analysis, the experimental procedure is completely analogous to conventional volumetric experiments, i.e., the system free space is evaluated by a series of helium expansions, and hydrogen isotherm measurements are subsequently performed. Recent work⁹⁻¹¹, however, has shown that the common practice of ignoring helium adsorption during measurements of void space in volumetric analyses can lead to large errors in estimating sorption capacities at high pressures. As the surface area of the adsorbent increases, it is expected that this problem will be aggravated.

Since the protocol for accounting for helium adsorption has already been documented,^{10,11} the procedure will not be repeated in detail here. Suffice it to say, however, that evaluation of accurate sample densities at conditions where helium sorption is negligible is required to facilitate the analysis. Due to the small sample sizes for the materials we have previously examined (< 100 mg) and the relatively large volume of the DPAU (100 cm³), consistently accurate measurement of sample densities is generally not achievable. A low-volume high-temperature pycnometer was constructed in our laboratory to enable variable temperature density, and consequently, helium gas Henrys constant evaluations.

As an illustration of the importance of accounting for helium adsorption in free space evaluations, we re-examine the methane-4A data presented in Figure 6-4b. If we make the assumption that helium adsorption on 4A is comparable to that on 5A, we can then employ a Henrys constant and heat of adsorption previously evaluated¹³ and use those values to evaluate a new isotherm for this system. The revised methane-4A isotherm, included in Figure 6-4b, clearly indicates that methane adsorption is noticeably underestimated at pressures greater than ~400 psia when helium adsorption is presumed to be negligible.

The result also demonstrates that neglecting helium sorption in free space analyses renders artificially low sorption capacities. Accounting for helium sorption on high surface area materials will be essential in order to: 1) accurately measure high-pressure sorption isotherms and 2) calculate meaningful isosteric heats of adsorption.

Sorption Capsule Apparatus

The basis of the sorption capsule technique lies in the ability to accurately quantify the amount of gas contained within a vessel by comparing the weight of the evacuated vessel to the weight of the vessel when it contains pressurized gas. The difference in these two weights directly gives the amount of gas stored within the container at a known pressure, P, and a temperature, T.

The effect that a solid adsorbent has in either enhancing or hindering the amount of gas able to be stored can also be easily discerned by a similar procedure. First, a solid adsorbent is loaded into the sorption capsule and the system is evacuated. A comparison of the weight of the evacuated capsule, which contains solid, to the evacuated weight when empty, yields the sample weight. When gas is introduced to the system containing adsorbent to the same

pressure as in the empty sorption capsule experiment, P , and allowed to achieve equilibrium, gas resides both in the free space and on the adsorbent. A comparison of the weight of the pressurized capsule containing adsorbent with that of a pressurized capsule containing no solid reveals the enhancement (or hindrance) that the solid plays in terms of its gas storage capability. As described, this experiment provides the total amount of gas contained within a pressurized vessel containing solid. It does not directly yield information regarding the partitioning of the adsorbate between the solid phase and the gas phase.

It is interesting to note that neither the empty capsule volume, the free space volume, nor the sample weight are needed in order to assess whether the presence of the solid improves or impedes gas sorption within the vessel by the method outlined. These quantities, however, are essential if a sorption isotherm is desired. The explicit relationship between the extent of sorption, the volume occupied by the adsorbent, and the system free space is developed in the next section of this manuscript.

A schematic of the capsule apparatus is provided in Figure 6-6. Two key components of the apparatus employed in our studies are the two capsules, which are hooked to a gas handling system, and the analytical balance used for weighing them. The analytical balance employed was a Sartorius Research Series MC1 balance which has a weighing limit of 210 grams and a readability of 0.05 mg. The capsules were constructed of T-316 stainless steel and were orbitally welded to a $\frac{1}{4}$ " VCO male tube weld gland. The capsules were $\sim 7 \text{ cm}^3$ in volume possessing an O.D. of 12.8 mm and an I.D. of 9.5 mm and were hydrostatic tested to 3200 psig. The shut-off valves on the capsules, (Swagelok SS-IRVCO4-SC11), are constructed of stainless steel and have a maximum pressure rating of 6000 psia. The capsules were sized so that the total weight of a capsule, with a valve attached, was ~ 180 grams. This enables one to perform weighing measurements with the 5-place Sartorius balance, even with an appreciable sample size.

Figure 6-6. Schematic of the Sorption Capsule Unit. The sorption capsules, gas manifold, pressure transducer, and analytical balance are contained in a temperature-regulated (25°C), nitrogen- purged Lexan box. The nitrogen flow rate was regulated so that the relative humidity was maintained at ~10%.

Performing weight measurements accurately to 5 decimal places can be challenging when one considers changes in laboratory temperature and humidity levels. To circumvent these problems, the entire capsule apparatus is housed in a temperature controlled Lexan box which is nitrogen purged so that the relative humidity (RH) is maintained at a steady 10%. The box is also equipped with two rubber gloves so that the capsules can be transferred from the gas manifold system to the analytical balance without exposure to laboratory atmosphere or direct contact with human hands, which can contaminate the outside of the sorption capsules and alter their weight.

Calculations of Sorption Capacity Using the Sorption Capsule

The number of moles of gas, n , which can be contained in an empty vessel of volume, V_E , at pressure, P , and temperature, T , can be expressed as:

$$n = \frac{PV_E}{zRT} \quad (11)$$

where z is a compressibility factor which accounts for gas-phase non-idealities, and R is the universal gas constant.

If the vessel is filled with an adsorbent material and is again pressurized with an adsorbate gas, the total number of moles of gas within the container has contributions from both the gas phase and the solid phase such that:

$$n = \frac{PV_{FS}}{zRT} + KPM_S \quad (12)$$

Where V_{FS} is the free space (gas-phase) volume, M_S is the mass of the solid adsorbent, and K is a partition coefficient indicating the distribution of adsorbate between the gas phase and the solid phase, such that

$$n_{ADS} = KPM_S \quad (13)$$

Here, n_{ADS} is the Gibbsian excess moles adsorbed on the solid. In the case of a Langmuirian isotherm, the partition coefficient is given as:

$$K = \frac{mb}{1 + bP} \quad (14)$$

The parameters m and b are termed the saturation capacity and adsorption coefficient, respectively. As indicated in Equation 14, the partition coefficient can be a function of pressure; however, in the low-pressure limit, K ceases changing with pressure and equals the Henry's constant, K_H , which is also equal to the product mb .

Since V_{FS} represents the difference between the empty capsule volume and the volume occupied by the solid adsorbent, one can write:

$$V_{FS} = V_E - \frac{M_S}{\rho_S} \quad (15)$$

where ρ_S is the skeletal density of the solid adsorbent. Substitution of Eq. 15 into Eq. 12 yields a second, and somewhat more insightful, expression for the total adsorbate contained within a pressurized vessel, namely:

$$n = \frac{PV_E}{zRT} + M_S P \left[K - \frac{1}{\rho_S zRT} \right] \quad (16)$$

The first term on the right hand side of Eq. 16 represents the number of moles of gas that would be contained in an empty pressurized capsule. The second term, therefore, represents the effect the solid has on the total loading within the capsule. Since the bracketed term is a difference, it can be either positive or negative. To increase the amount of gas within the container holding solid above that amount in the empty container, the sorption capacity (as indicated by the partition coefficient) must be sufficiently large to overcome the free-space volume loss due to the physical presence of the solid. Thus, if $K > 1/\rho_S zRT$, the solid increases the total gas capacity; otherwise the space that the solid occupies contains more gas molecules when the container is empty.

To illustrate this point further, in Figure 6-7 we present calculated results for the weight of hydrogen contained within a 42.2 liter volume, i.e., the size of a commercial BX H₂ cylinder, at 21°C and as a function of pressure, for the cases when the cylinder is empty or contains 66 lbs of Amoco GX-31 activated carbon. The weight of GX-31 is assumed to be the maximum loading based on a skeletal density of ~2 g/cm³ and a packing density of 0.71 g/cm³.ⁱ The H₂ weight contribution due to adsorption onto GX-31 was calculated from a dual-site Langmuir (DSL) isotherm correlation of sorption data measured for this system. The DSL model is given as:

$$n_{ADS} = \left[\frac{m_1 b_0 \exp\left(\frac{Q_b}{RT}\right)}{1 + b_0 \exp\left(\frac{Q_b}{RT}\right)P} + \frac{m_2 d_0 \exp\left(\frac{Q_d}{RT}\right)}{1 + d_0 \exp\left(\frac{Q_d}{RT}\right)P} \right] PM_s \quad (17)$$

The model parameters for the H₂-GX31 system are provided in Table 6-1. The bracketed term provides the temperature and pressure dependence of the partition coefficient, K.

Table 6-1. DSL parameters for the system H₂ - GX31

m ₁	4.486 mmoles/g
m ₂	4.733 mmoles/g
b ₀	4.198 x 10 ⁻⁶ psia ⁻¹
Q _b	2584.9 cal/mol
d ₀	2.459 x 10 ⁻⁵ psia ⁻¹
Q _d	1550.9 cal/mol

The dotted line in Figure 6-7 indicates the grams of H₂ contained in the empty vessel as a function of pressure. As one might expect, higher pressure results in higher H₂ loading. For comparison, the specifications for a fresh BX H₂ cylinder are 6000 psia at 21°C, which corresponds to ~1140 g (2.5 lbs) H₂. Since a BX cylinder weighs ~300 lbs, the storage of H₂ is 0.8% by weight (2.5 lbs/302.5 lbs) and 27 g H₂/liter by volume.

Figure 6-7. Variable pressure hydrogen loading calculations for a BX H₂ cylinder volume (42.2 liters) at 21°C. The dotted line indicates the H₂ contained in the system when there is no adsorbent in the capsule. The solid line (a) illustrates the H₂ capacity when 66 lbs of Amoco GX31 are loaded into the capsule. The solid line (b) represents the total H₂ loading in the system if the adsorbent capacity were tripled. The calculations have assumed that the skeletal density, ρ_s , is 2.0 g/cm³ and that the packing density is 0.71 g/cm³.

The solid line in Figure 6-7, indicated as “a,” represents the total H₂ loading within the 42.2 liter vessel when it contains 66 lbs of GX31. Notably, at low pressures the presence of the adsorbent aids the storage capacity, with the vessel while at pressures above 4700 psia the GX31 is expected to hinder hydrogen storage. The maximum improvement in storage capacity at a fixed pressure occurs at 1700 psia, where the enhancement is ~71 g (0.16 lbs). This is a minimal improvement over simply pressurizing the empty container and is clearly not sufficient enhancement for a practical device.

An alternate way of viewing the sorption enhancement is to examine the largest pressure savings one can obtain for a particular gas loading. At 2000 psia the total H₂ capacity in the empty capsule is ~448 g. With GX31 loaded into the storage capsule, the same total H₂ capacity is achieved at 1665 psia, which is a savings of 335 psia. Being able to store comparable H₂ loadings at lower pressures implies savings in the wall thickness (and,

consequently, weight) of the container used for storage. In addition, storage of a lower pressure gas is inherently safer than storage of a high pressure gas.

Also included in Figure 6-7 is a solid line (“b”) which indicates the total expected storage capacity of the system if the adsorbent isotherm were tripled. Clearly, this increase in the H_2 isotherm has a profound impact -on the extra amount of H_2 that can be stored at a fixed pressure and the pressure savings at a fixed loading. For this scenario, the energy density at 6000 psia is 45 g H_2 /liter.

If the same BX cylinder were used as the storage container, however, the gravimetric capacity would still only be 1.1 wt %, since the 66 lbs of adsorbent must be added to the 300 lbs weight of the cylinder to fairly consider the *system* storage capability. Clearly, developing storage devices that are light-weight and high-strength is critical to the H_2 storage effort.

Total Capacity Measurements (Empty Capsule)

The sorption capsule is ideally suited for performing measurements of the total loading of a gas within a pressurized container. Initially, an evacuated capsule is attached to the gas handling system (GHS) and evacuated until a pressure of 10^{-2} torr is reached. The shut-off valve on the evacuated capsule is then closed, and the capsule is removed from the GHS and weighed on the analytical balance. This procedure is used whether the sample capsule is empty or contains an adsorbent material. The capsule is then reattached to the gas handling system, the valve is opened, and the system is pressurized with the gas of interest. Once equilibrium is established, as indicated by the pressure transducer on GHS, the valve is once again shut off, and the capsule is detached from the GHS and weighed on the analytical balance. This procedure directly measures the weight of the gas introduced into the sample chamber.

To test our experimental protocol for weighing gas, the volume of the manifold, V_m , (indicated in Figure 6-6) was evaluated by performing pressure expansions using a calibrated standard volume. Our manifold volume was determined to be 9.6 cm³. The volumes of our empty sample capsules, V_E , were subsequently evaluated by performing pressure expansions from the manifold volume. The two sample capsules employed in this investigation had volumes of 6.8 and 7.1 cm³, respectively.

The two empty sample capsules were then pressurized with helium and hydrogen, respectively, at isothermal conditions. Since the system pressure, temperature, and volume within each sample capsule was known, the weight of gas within the sample capsule could be calculated from an equation of state (EOS).¹²⁻¹⁴ In Figure 6-8, we provide a comparison between the weight predicted by the equation of state and our experimental data. The data are found to agree with the EOS to within ~1% error.

Figure 6-8. Comparison of the experimentally measured total mass of helium (○) and hydrogen (●) contained in pressurized capsules at 25°C to that expected from an equation of state analysis based on knowledge of the pressure, temperature, and system volume.

Total Capacity and Isotherm Measurements (Adsorbent Present)

In traditional volumetric sorption studies, helium expansions are performed to assess the free-space within a sample capsule. Since the manifold volume and individual capsule volumes of the sorption capsule unit have been calibrated, this traditional method can be applied to assess the free space once an adsorbent is loaded into the system. There are two alternatives by which the free space volume can be determined in the sorption capsule experiment.

In the first method, the capsule can be pressurized with helium to a known pressure at a known temperature, and the capsule can be weighed to gauge the mass of helium within the capsule. This helium is presumed to reside exclusively in the gas phase, since helium is generally considered a non-adsorbing gas. Since pressure and temperature are known, the helium density can be determined from an equation of state. Consequently, the capsule free space volume can be determined by dividing the mass of helium measured by the helium gas density.

Figure 6-9. Comparison of the experimentally measured total mass of methane ($\circ$) at 25°C in a system containing 1.6235g Amoco GX31. The solid line indicates the contribution of gas-phase methane to the total methane weight in the system.

The second method requires knowledge of the skeletal density of the adsorbent, ρ_s . If a known mass of solid, M_s , is loaded in the sample capsule, the free space volume can be calculated directly from Eq. 14. All three of these techniques have been employed to estimate the free space volume using quartz as the “adsorbent” and have been found to agree to within ~1%.

To benchmark the sorption capsule technique using a real adsorbent, CH₄ and H₂ adsorption experiments at 25°C were performed using Amoco GX31 as the solid adsorbent. For the CH₄ experiments, 1.6235 g of GX31 were loaded into the sample chamber, the free space volume was analyzed by helium expansions and the system was subsequently pressurized with methane and allowed to equilibrate. The total amount of methane contained in the system was determined by closing the valve on the sample chamber and weighing the entire sorption capsule. The capsule could then be reattached to the system and exposed to methane at a new pressure. In this way the total loading of methane could be determined as a function of pressure. The free space volume does not need to be known to determine the total amount of methane contained within the system. This result is provided in Figure 6-9.

Figure 6-10. Isotherm data at 25°C for methane adsorption on Amoco GX31 measured by the sorption capsule technique (○) and by a differential pressure adsorption unit (●). Five repeat runs were performed at 250 psia to illustrate the reproducibility of the sorption capsule method.

Although V_{FS} is not needed to determine the total amount of methane in the system, it is needed if a sorption isotherm is desired. Included in Figure 6-9 is the calculated amount of methane in the gas phase of the sorption capsule using an equation of state and knowledge of P , T , and V_{FS} . By dividing the mass of methane on the solid adsorbent by the mass of solid, one can determine the sorption capacity (mmoles/g), i.e., surface excess at the corresponding P and T .

The methane isotherm resulting from the measurements shown in Figure 6-9 is provided in Figure 6-10, along with a literature isotherm and an isotherm from our differential pressure adsorption unit. Five repeat points were measured at 250 psia to illustrate the reproducibility of the sorption capsule method. The agreement between the two experimental data sets is excellent and highlights the capability of the relatively inexpensive sorption capsule unit.

One point that needs to be highlighted is the magnitude of the y-axis in Figure 6-10. The mass of methane weighed in these experiments is on the order of 100 mg, which is easily accomplished with a 5-place analytical balance that has a readability of 0.05 mg. For the methane/GX31 system, on average ~60% of the total methane mass within the system is found to reside on the solid phase. In this case, it is relatively simple to evaluate both the isotherm data and the total methane loading.

Since methane is eight times heavier than hydrogen, conducting weight measurements with methane is appreciably easier than with hydrogen. To assess the utility of the capsule

technique to perform hydrogen measurements, an experimental investigation comparable to that of CH_4 was performed using hydrogen as the adsorbate and employing a fresh 1.7726 g sample of GX31. The total H_2 loading in the system at 25°C was measured by the procedure outlined previously, and the results are provided in Figure 6-6. For comparison, the amount of hydrogen residing in the gas-phase of the system is also provided as a function of pressure. In this experiment ~80% of the total gas weight within the system is due to gas-phase hydrogen, and the magnitude of the total H_2 weight contained within the system is approximately an order of magnitude lower than for CH_4 .

Figure 6-11. Comparison of the experimentally measured total mass of hydrogen ($\circ$) at 25°C in a system containing 1.7726 g Amoco GX31. The solid line indicates the contribution of gas-phase hydrogen to the total hydrogen weight in the system.

Subtracting out the gas-phase contribution from the total hydrogen loading data in Figure 6-11 enables one to establish a hydrogen isotherm. In Figure 6-12, isotherm data from the capsule unit based on the experimental data shown in Figure 6-11 are compared to literature data for the H_2 -GX31 system measured by a traditional gravimetric sorption technique and our differential pressure adsorption unit. In addition, data are included for a second, completely independent, capsule investigation using a 1.6787 g sample. The agreement between the capsule data and the literature data is outstanding and highlights both the accuracy and repeatability of our experimental protocols.

Figure 6-12. Comparison of 25°C hydrogen adsorption isotherms on Amoco GX-31 measured on the sorption capsule unit with 1.7726 g (Δ) and 1.6787 g samples ($\blacktriangle$), on the DPAU with a 0.580 g sample ($\circ$), and on a Rubotherm gravimetric sorption balance with a 1.014 g sample (+).

In order to gauge the limitation of the capsule technique in its application to screening hydrogen storage materials, we consider the weighing capabilities of the analytical balance employed. The Sartorius analytical balance used in these experiments has a readability of 0.05 mg, meaning that the fifth decimal place is either 0 or 5. To best capitalize on the measurement capability of this unit, a calibration standard was maintained within the sorption capsule chamber and was weighed prior to each experimental measurement to within 0.05 mg. Since this calibration standard could be weighed accurately, and all experiments were performed within a nitrogen purged Lexan box with a constant relative humidity, the *total hydrogen loading* within the capsule could be measured to ± 0.05 mg.

Measuring a hydrogen sorption isotherm is appreciably more challenging than measuring the total hydrogen loading because it requires distinguishing how the hydrogen contained in the system is partitioned between the gas phase and the solid phase. In order to investigate the limits of the capsule technique in its application to measuring hydrogen isotherms, we draw attention to the data in Figure 6-11, particularly the *difference* between the total hydrogen loading data (represented by circles) and the gas-phase contribution (represented by the solid line). As pressure decreases, the total gas-phase contribution, as a percentage of the total hydrogen content, increases. Thus, the lower the pressure, the more difficult it is to measure a point on the isotherm accurately.

There are several predominant considerations to measuring H₂ isotherms with the capsule technique. These include: 1) the sorption capacity, 2) sample size, i.e., adsorbent mass, and 3) the bulk density. The bulk density limits the amount of adsorbent that can be physically loaded into the sample capsule. Maximizing the amount of solid employed or, conversely, minimizing the free-space volume is clearly a main objective. For the GX31 experiments, the packing density achieved was 0.24 g/cm³ which is relatively low. This value could have been increased by grinding or compacting the material, but this was not attempted.

Based on the experiments with GX31, we estimate that 2 mg of H₂ uptake by the adsorbent were required, while using 1.6787 g of this material, to effectively characterize the H₂ partitioning between the adsorbent and gas phases. To illustrate this experimental sensitivity limit, in Figure 6-13 we have constructed a plot of sorption capacity versus sample mass. Figure 6-13 indicates that an adsorbent mass smaller than 1.6787 g can be used if a new material being examined has a higher sorption capacity than GX31. Alternatively, capacity values lower than 1.19 mg/g (= 2 mg/1.6787 g) can be measured, if larger sample sizes are employed.

Included in Figure 6-8 are two isotherm data points measured at 255 psia and 1484 psia, respectively. These data points reveal that isotherm measurements at higher pressures are far removed from the sensitivity limit of the capsule technique, while at low pressures the sensitivity limit is approached. The *total* hydrogen contained within the system, however, can be easily measured at either pressure.

Finally, care should be taken if sub-ambient temperature measurements are undertaken with the capsule unit, both from the standpoint of condensation on the capsule, which is simply an operational problem, and over-pressurization upon warming the capsule back to room temperature, which is a more important safety consideration. For example, if a capsule were pressurized to 100 atm. at 77 K and subsequently warmed to room temperature, the pressure within the capsule would climb to ~390 atm. This estimate does not account for any contribution from gas desorbing from a contained adsorbent, which would tend to increase the pressure further. Since some piping and valves may not be able to withstand this elevated pressure, we do not recommend performing any measurements with the capsule technique at sub-ambient temperatures.

Figure 6-13. Sensitivity limit for measuring isotherms with the capsule technique based on sorption data on GX31. The solid curve is based on a limiting capacity value of 1.19 mg/g on a 1.6787 g sample at a packing density of 0.24 g/cm³. The curve indicates that accurate isotherm data can be measured with samples exhibiting a lower capacity, if larger sample sizes are used, and with smaller sample masses, if the adsorbent capacity is higher.

Conclusions

To support the development of advanced hydrogen storage materials and processes, we developed a methodology for using a differential pressure adsorption apparatus to conduct sorption measurements with hydrogen and other flammable (or inert) gases. The key to this unit is a dual manifold symmetrically arranged so the sample and reference legs have nearly identical volumes, thereby enabling differential pressures during adsorption (and desorption) experiments to be measured accurately. Contrary to conventional volumetric sorption equipment, the DPAU enables sorption measurements at both low and high pressures with equal accuracy, since the measurement is based on a differential measurement rather than on absolute pressures. Changes as small as 0.01 psia (0.6 torr) can be measured at total pressures of 2000 psia.

A comparison of DPAU results with those from a conventional volumetric apparatus (VTI) for hydrogen sorption on Amoco GX-31 and NaA zeolite reveal excellent agreement with independent measurement techniques. Furthermore, methane experiments with NaA zeolite demonstrate the precision with which adsorption and desorption measurements can be conducted.

Experimental sensitivity analyses have clearly revealed that the DPAU can measure H₂ uptakes very accurately on samples as small as 100 mg. This is a critical feature since in many cases the amount of specific well-characterized hydrogen storage materials available for analysis is appreciably less than a gram.

The sorption capsule technique, an accurate and relatively inexpensive experimental method, has been successfully applied to measure the total gas content within a storage volume containing adsorbent at a function of pressures and at a fixed temperature (25°C). Both hydrogen and methane were employed as adsorbates. A comparison of these experimental data to the total adsorbate mass anticipated from equation of state calculations, based on the empty capsule volume, has proven to be an effective means of evaluating whether the presence of the solid aids gas storage and is a reasonable candidate as a storage material. Since a capsule assembly system can be designed to have multiple capsules operating simultaneously, this technique enables one to perform a high-throughput evaluation of candidate storage materials.

The gas-phase volume loss due to the physical volume of the sorbent and extent of adsorption based on the partition coefficient of the gas-solid pair have been shown to be two competing effects in determining whether a solid promotes or hinders gas storage within a container (see Eq. 6). If the magnitude of K is greater than $1/p_s zRT$, then the presence of the solid increases the total gas capacity within the system; otherwise the space that the solid occupies contains more gas molecules when the container is empty.

Lastly, the gas-solid isotherm data were successfully measured by distinguishing how the total gas loading in the storage system is divided between the gas phase and the adsorbent phase. Methane and hydrogen isotherm data were measured at 25°C with GX31. The hydrogen data were benchmarked against gravimetric data measured with a Rubotherm balance and volumetric data measured with the differential pressure adsorption unit. An empirical error analysis based on our GX31 data has revealed that ~2 mg of uptake on a 1.6787 g sample is the approximate limiting weight uptake required to measure a sorption isotherm accurately at a bulk packing density of 0.24 g/cm³. For materials exhibiting sorption capacities less than GX31, measurements can be made if a larger sample size is used. Likewise, smaller sample sizes can be employed if the sorption capacity is greater than that of GX31. The use of smaller sample weights also could be achieved by minimizing the system free space volume, maximizing bulk packing density, and creating smaller sample capsules.

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Appendix 1

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2. Molecular Dynamics Simulations of Hydrogen Adsorption in Finite and Infinite Bundles of Single Walled Carbon Nanotubes. Cheng, H.; Cooper, A.C.; Pez, G.P. Kostov, M.K.; Knippenberg, M.T.; Piotrowski, P.; Stuart, S.J. in *Molecular Materials with Specific Interactions: Modeling and Design*; Sokalski, W. A., Ed.; Springer, New York, 2007.
3. A Simple Technique for the Measurement of H₂ Sorption Capacities. Zielinski, J.M.; McKeon, P.; Kimak, M.F. *Ind. Eng. Chem. Res.* **2007**, *46*, 329.
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5. Mechanistic Study on Hydrogen Spillover onto Graphitic Carbon Materials. Chen, L.; Cooper, A.C.; Pez, G.P.; Cheng, H. *J. Phys. Chem. C* **2007**, *111*, 18995.
6. High Pressure Sorption Isotherms via Differential Pressure Measurements. Zielinski, J.M.; Coe, C.G.; Nickel, R.J.; Romeo, A.M.; Cooper, A.C.; Pez, G.P. *Adsorption* **2007**, *13*, 1.
7. Molecular Dynamics Simulations on Hydrogen Adsorption in Finite Single Walled Carbon Nanotube Bundles. *J. Mol. Model.* **2008**, *14*, 343.
8. Dynamics of Hydrogen Spillover on Carbon-Based Materials. Sha, X.; Knippenberg, M.T.; Cooper, Alan C.; Pez, G.P.; Cheng, H. *J. Phys. Chem. C* **2008**, *112*, 17465.
9. A Mechanistic Study of Hydrogen Spillover in MoO₃ and Carbon-Based Graphitic Materials. Chen, L.; Pez, G.; Cooper, A.C.; Cheng, H. *J. Phys. Condens. Matter* **2008**, *20*, 064223/1.
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12. Hydrogen Storage with Graphite Anion Intercalation Compounds. Pez, G.P.; Cheng, H.; Cooper, A.C.; Foo, M.-L. U.S. Pat. Appl. Publ. 20080175780 A1.
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 14. An Enhanced Hydrogen Adsorption Enthalpy for Fluoride Intercalated Graphite Compounds. Cheng, H.; Sha, X.; Chen, L.; Cooper, A.C.; Foo, M.-L.; Lau, G.C.; Bailey III, W.H.; Pez, G.P. *J. Am. Chem. Soc.* **2009**, *131*, 17732.
 15. Revisiting Hydrogen Storage in Bulk BC₃. Sha, X.; Cooper, A.C.; Bailey III, W.H.; Cheng, H. *J. Phys. Chem. C* **2010**, *114*, 3260.

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1. "Designing Microporous Carbons for Hydrogen Storage Systems". Alan C. Cooper, Hansong Cheng, Guido P. Pez; 2005 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Annual Merit Review (5/24/05).
2. "Advanced Hydrogen Sorption Measurement Techniques: Application to Tailored Singlewalled Carbon Nanotubes". Alan C. Cooper, Mary K. Haas, John M. Zielinski, Peter McKeon, Gennady Dantsin, Charles G. Coe, Guido P. Pez; 2005 Materials Research Society Fall Meeting (11/29/05).
3. "Enabling Discovery of Materials With Higher Heat of Adsorption". Guido Pez, Hansong Cheng, Alan Cooper; FreedomCAR Tech Team Review (3/23/06).
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5. "Analysis of Process Energies and Energy Efficiencies for Carbon-Based Hydrogen Storage Systems". Guido Pez, Dan Tyndall; Hydrogen Storage Systems Analysis Working Group (SSAWG) Meeting (5/19/06).
6. "Mechanistic Understanding of Hydrogen Storage in Carbon-based Materials". Hansong Cheng, Liang Chen, Alan C. Cooper, Guido P. Pez; 2006 Materials Research Society Fall Meeting (11/29/06).
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8. "Enabling Discovery of Materials With a Practical Heat of H₂ Adsorption". Alan Cooper, Hansong Cheng, Maw-Lin Foo, John Zielinski, Charles Coe, Guido Pez; 2007 DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Annual Merit Review (5/15/07).
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 13. "Discovery of Materials with a Practical Heat of H₂ Adsorption". Alan C. Cooper; 2010 DOE Fuel Cell Technologies Program Annual Merit Review (6/9/10).