IV.C.1e Advanced Boron and Metal-Loaded High Porosity Carbons

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Objectives

- Identify a new class of high surface area boro-carbon and metal-boro-carbon material systems with surface chemistry tuned for a stronger hydrogen binding interaction that will enable 2015 DOE-target volumetric and gravimetric reversible hydrogen storage capacity, through a synergistic combination of materials synthesis, characterization and first-principles computation.
- Synthesize highly porous boro-carbons and metal boro-carbons with simultaneous ultra-high boron content, high surface area, tuned and optmized pore distributions, controlled spillover effects, metal loading, and tunable curvature.
- Enhance the stability of highly dispersed metals on carbon frameworks, including atomic-level dispersion that is stable against aggregation, by means of tuned electron deficiency.
- Maintain these properties in a system with low-to-moderate economic cost of raw materials and stability over many cycles.

Technical Barriers

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

(A) System Weight and volume
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharge Rates
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption
(Q) Reproducibility of Performance

Technical Targets

This project is conducting fundamental studies of the hydrogen-substrate interaction to develop a novel class of highly electron deficient carbon frameworks, and a subclass thereof with light metal atoms dispersed on the same framework. We have recently demonstrated substantial enhancement in the interaction of hydrogen with such a modified surface, increasing the adsorption energy from 4-6 to 12.5 KJ/mol (the target adsorption energy is in the range of 15-30 KJ/mol). In the previous year, we have demonstrated that boron incorporation facilitates uptake of nanodispersed metals, and have developed techniques to control curvature-induced enhancements to hydrogen binding in highly porous low-cost substrates. We have developed a testbed for inducing, understanding and exploiting spillover effects with novel in situ measurement modalities, including simultaneous measurements of transport and optical signature of stored hydrogen in a well-characterized nanoscale geometry. We are continuing towards the goal of developing sorbents which can meet the DOE 2015 hydrogen storage targets for gravimetric and volumetric storage densities at reasonable cost in a reversible system, although further breakthroughs in synthesis will be necessary to increase boron content, tune local geometries, maintain and increase porosity, exploit spillover, control chemical frustration, and obtain optimal properties in a homogeneous material.

Accomplishments

- The binding energy for hydrogen as measured by isosteric heats of adsorption has been increased to 12.5 kJ/mol, much higher than in conventional activated carbons (4-6 kJ/mol), due to the presence of boron in the samples. These values begin to approach those necessary for high-capacity reversible room temperature hydrogen storage (15-30 kJ/mol), and enhance the probability to meet DOE 2010 storage targets.
- Demonstrated that incorporation of boron into nanoporous carbon framework improves the uptake of nanodispersed metals, in accord with

goals in atomic dispersion of metals for enhanced wt% and volumetric hydrogen storage, following computational predictions for hydrogen binding energies of 30 kJ/mol in light-weight frameworks designed to be resistant to aggregation.

• First-principles computations have identified several new mechanisms of enhanced hydrogen bonding at levels of 20 to 40 kJ/mol (i.e. in the desired intermediate physical/chemical sorption range), exploiting concepts of zwitterionicity (the ability to capture hydrogen in the spaces between separated positive and negative charges) and topological frustration (forcing atoms to arrange themselves in structures that are highly active towards hydrogen binding due to geometrical constraints that prevent the atoms from attaining more familiar, lower-binding structures).

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Introduction

A new class of hydrogen sorbents with substantially enhanced hydrogen binding energies in a low-mass framework shows potential to meet DOE gravimetric targets, with further optimization. The introduction of boron into a curved high-surface-area carbon framework induces electron deficiency in the framework and so increases the propensity to bind H_2 reversibly at energies intermediate between traditional physical and chemical adsorption. Additionally, we have demonstrated through first-principles calculations that this same electron deficiency can help stabilize the atomic dispersion of light metal atoms. The exposed orbitals of these atoms then provide another venue for new binding chemistry, importantly, in a geometry that is naturally resistant to aggregation due to the continuous rigid nature of the porous framework. We also continue to develop improved means to control porosity and activate surface area in heavily boron-doped carbons.

Approach

Our approach is to intimately couple the synthetic, computational and characterization efforts locally at Penn State with the world-leading characterization tools (and also synthetic and computational efforts) available throughout the Center to break new ground in the discovery of new materials systems that modify the binding chemistry towards hydrogen at a fundamental level by controlling electron content and spillover geometry in a rigid framework. The starting point, a carbon-based nanoporous framework, provides a robust, lightweight, high surface area, mechanically rigid, low-cost system with the structural cohesiveness to withstand the substantial variations in local chemistry that are necessary to induce enhanced hydrogen

adsorption. These modifications include withdrawing substantial numbers of electrons from the structure, dispersing exposed metal atoms onto the structure, and forcing topologically or topographically frustrated geometries that have the potential to generate very large local electric fields and open-shell configurations. Pyrolysis of the designed boron-containing polymeric precursors, which are the polyaddition adducts of phenylene diacetylene (with and without lithiation) and BCl_3 has shown significantly higher hydrogen binding energy and physisorption capacity, compared with the corresponding carbonaceous materials. Each of these final states: electron deficiency, exposed uncompensated orbitals, and uncompensated local fields, provides a distinct fundamental means to generate new classes of adsorptive interaction that is intermediate between traditional chemical and physical adsorption and in the optimal range for reversible room-temperature hydrogen storage. In all stages of this process careful attention is paid to DOE goals in materials cost, volumetric and gravimetric density, and stability over multiple cycles.

Results

To carry forward successes in the previous year in producing highly boron-loaded porous boro-carbon materials, we have engaged a sustained effort towards creating dispersed metals with unprecedented levels of stability and small (near-atomic) particle size. For enhanced H_2 physisorption it is very important to obtain micro-porous B/C material with a high surface area and substantial electron deficiency, to stabilize dispersed metals whose open orbitals then provide sites for enhanced hydrogen binding. The original metal-free samples provide about 0.7 wt% hydrogen adsorption with an initial isosteric heat of adsorption of 12.5 kJ/mol and maintain a high adsorption energy level to higher surface coverage (10.8 kJ/mol for 0.62 wt% H_2 uptake). At 77 K, the H_2 adsorption reaches 3.2 wt%; this is almost double that of the corresponding carbonaceous materials. In comparison, our advanced tuned small-pore-size carbons exhibited a hydrogen binding energy of 9.5 kJ/mol (Figure 1, extracted from adsorption isotherms at 0, 20 and 40°C from Air Products and Chemicals, Inc. data), also much higher on conventional activated carbons (4-6 kJ/mol).

Recently, transition metals have been doped into these microporous B/C materials (Figure 2) to obtain a new transition metal decorated M/B/C material, with good control of metal particle size. The current objective is to further enhance the binding energy or exhibit spill-over effects in the resulting M/B/C materials. Figure 3 compares transmission electron microscopy (TEM) micrographs of two Pt/B/C materials, which were prepared by traditional Pt loading procedure (top) and our new (simpler) procedure (bottom), started with the same B/C material. The first material was prepared by
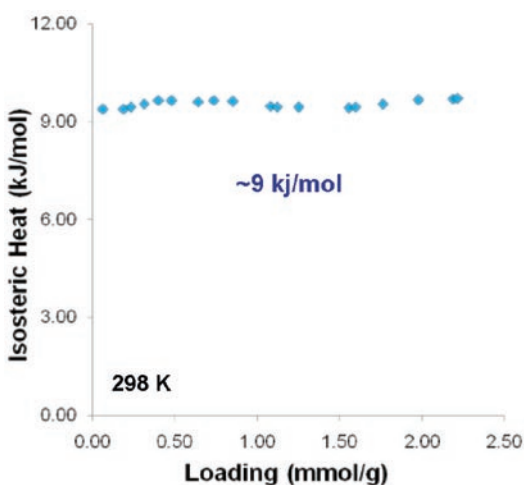
FIGURE 1. Pure carbons with optimized pores show an enhanced heat of adsorption for H_2 and maintain a high adsorption energy for moderate loadings. Boron loading further increases the heat of adsorption to >12 kJ/mol, and investigations of metal loading and spillover proceed.

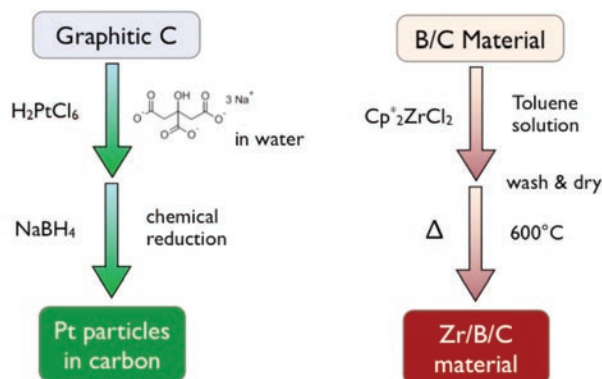## Metal Loading in Micro-porous B/C material

FIGURE 2. Several Strategies are Being Pursued to Obtain Metal-Impregnated Nanoporous Boro-Carbons

FIGURE 3. TEM Micrographs of Pt/B/C Materials Prepared by Doping with H_2PtCl_6 (top) with Surfactant and (bottom) without Surfactant

doping B/C material in an H_2PtCl_6 aqueous solution with the presence of sodium citrate (surfactant), then chemical reducing by $NaBH_4$ to obtain Pt nanoparticles. The resulting Pt/B/C material contains 13 wt% of Pt with particle size 1-4 nm, very similar to reported results obtained in the Pt-doped C (Pt/C) material. Apparently, the size of Pt particles was controlled by the size of micelles in solution, with little effect from the substrate. In contrast, the Pt particles in Figure 3 (bottom) are much smaller (<0.5 nm) and more uniform in size. Our new procedure simply immerses the B/C material in the same H_2PtCl_6 aqueous solution, without any surfactant. After rinsing with water and drying in vacuum, the doped sample is subjected to thermal treatment at 600°C to obtain Pt particles. Evidentially, the B/C
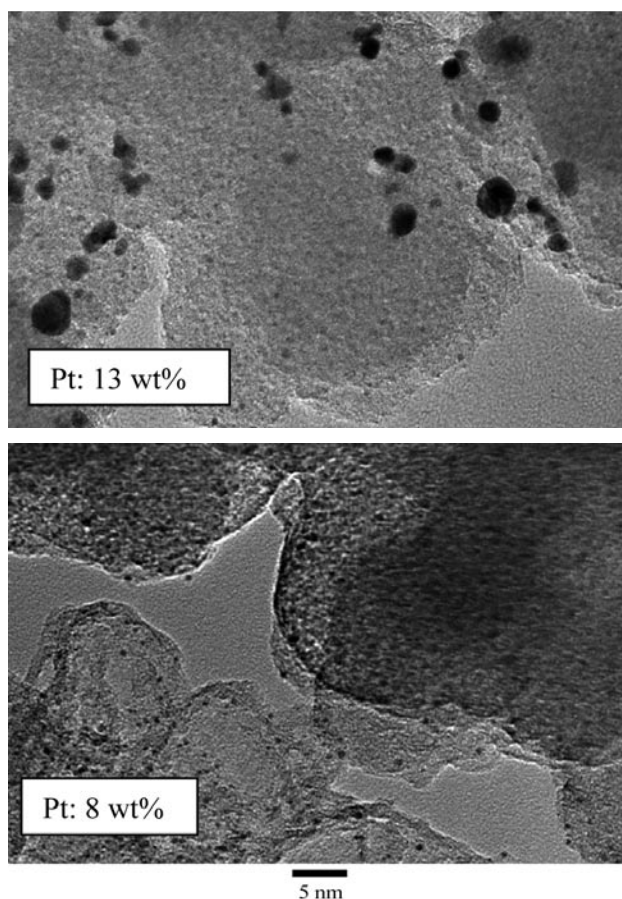
material shows good interaction with H_2PtCl_6 in aqueous solution, as anticipated by the team's computational simulations of B-doped carbons. It is technologically important for storage to obtain such small Pt particles and uniform distribution. In an alternative metal loading route, platinum acetylacetonoate was reduced to platinum nanoparticles using ethanol using ultraviolet radiation on the surface of high surface area nanoporous carbon derived from perfluoroalkoxy with a mean pore size of ~0.8 nm. X-ray diffraction results showed that the platinum nanoparticles were less than 2 nm. Pore size distribution showed that the 10 wt% Ptx/ nanoporous carbon (NPC) was still microporous. The hydrogen spillover effect on the catalyst was confirmed by passing pure hydrogen over a mixture of tungsten oxide (WO_3) and Ptx/NPC. As an alternative low-cost porous starting framework for further modification by e.g. metal loading, coal tar pitch precursor was also modified using H_2SO_4, resulting in an NPC with mean pore size of about 5 Å and pore volume of 0.15 cc/g. CO_2 activation of this carbon yielded a carbon which was completely microporous with a mean pore size of 6 Å and a N_2 Brunauer-Emmett-Teller surface area of 660 m^2/g. The sample showed an uptake of 1.4 wt%

at 77 K and 1 atm, which is twice the storage per unit surface area of typical activated carbons, which show uptake of only 1.1 wt% at a larger surface area of 1,000 m^2/g. This material therefore shows promise as a new framework for subsequent chemical modifications along the lines described above.

Nanoparticles of Zr have also been successfully incorporated into the boro-carbon materials via this post-synthesis processing technique wherein the high-surface-area borocarbon framework is first produced and then impregnated in a second distinct synthesis step. These efforts have yielded dispersed nanoparticulate metals in the borocarbon structures, and increased boron in the starting structure is correlated with increased metal uptake in the final material. Table 1 shows detailed data that demonstrates that the boron is facilitating metal uptake. Since thermally induced mobility of the dispersed metals would enable aggregation, the thermal history of the sample will be critically important to minimize aggregation. Further work will focus (among other issues) on developing as gentle as possible thermal processing histories to enable highly dispersed metals, bound to boron-rich sites, to remain highly dispersed.

A new testbed device has been developed to elucidate the critical mechanism of spillover, particularly the binding of hydrogen, whether atomic or molecular, to the high specific surface area framework. To this end, a single-graphene-layer device, with a well-characterized structure and geometry, has been developed which can be simultaneously monitored with electronic transport and Raman scattering probes of the spillover mechanism. This device, with well-dispersed catalyst particles of well-defined uniform size may enable use to determine the chemical state of the spilled over hydrogen directly in a controlled environment. This insight will then be directly applied to optimization of spillover-based hydrogen storage materials. We have successfully dispersed uniform Pt naocatalyst particles on a single graphene sheet (see Figure 4) and have the techniques in hand to pattern electrodes on these systems. We also have a demonstrated ability to acquire the needed resonant Raman measurements from single-atomic-layers of graphene. Patterning of contacts and exposure of the systems to hydrogen are proceeding, while monitoring transport and Raman simultaneously
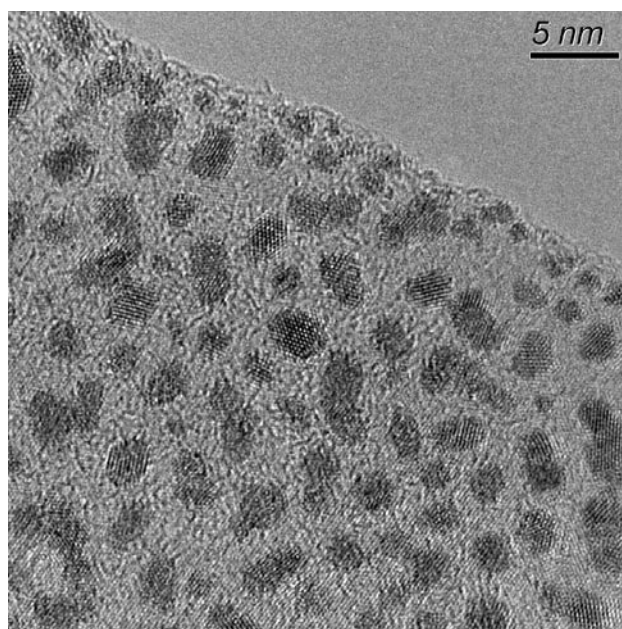

FIGURE 4. Dispersed Pt nanoparticle catalysts on a single graphene layer support, suitable for simultaneously monitoring of Raman and transport signatures of spillover, the first time that this has been performed.

to determine both the chemical state of the hydrogen and the hybridization state of the carbon.

As experimental efforts are currently focused on the previously predicted metal/boro/carbon systems, theory efforts are focused on predicting the next synthetic targets. In addition to first-principles calculations that establish that curvature plays a critical role in the enhanced binding of H$_2$ (at e.g. 0.15 eV/molecule), we have designed into substrates large static electric dipole moments, so that the hydrogen/substrate interaction is enhanced by a static dipole (of the substrate) with an induced dipole (of the H$_2$). Zwitterionic crystals (Figure 5), wherein charge separated species are covalently bound to a unitary rigid covalent framework to form regions of enhanced electric field that may form enhanced binding sites. Preliminary band-structure calculations demonstrate that ammonium groups can be covalently attached to high surface area carbons to form structures that heavily electron-dope the carbon, to densities comparable to those achieved by alkali doping.

Conclusions and Future Directions

Our synthesis approaches to produce high surface area materials with high boron content have advanced to a natural point of extension to metal dispersion and incorporation: nuclear magnetic resonance, inelastic neutron scattering and H$_2$ storage experiments show that boron substitution into the sp^2 lattice produces an increased binding energy for H$_2$, one that may be

TABLE 1. Boron-Doping of the Framework Facilitates the Incorporation of Metals into Micro-Porous Carbons

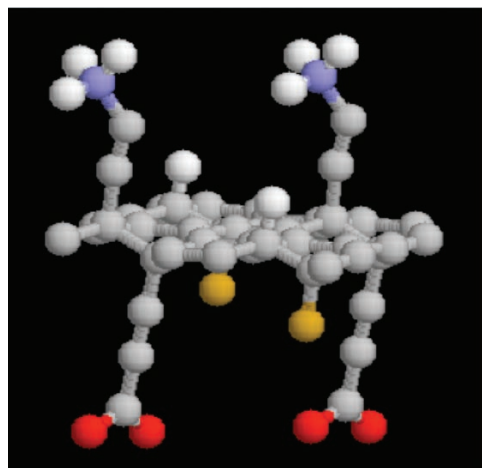| Metal-containing reagent	Mass of activated C after metal loading (200 mg, 600 m²/g before)	Mass of B/C material after metal loading (200 mg, 500 m²/g before)	Loaded in:
H$_2$PtCl$_6$	230 mg	234 mg	surfactant & water
Cp$_2$TiCl$_2$	200	309	toluene
Cp'$_2$ZrCl$_2$	205	222	toluene
[(η^5-Cp')SiMe$_2$ (η^1-NCMe$_3$)]TiCl$_2$	203	272	toluene

FIGURE 5. Charge-separated planar zwiterion have been designed computationally to enhance local fields and improve hydrogen sorption.

further enhanced by highly dispersed metals. We will continue to increase the boron content (>10 wt%), porosity (>2,500 m^2/g), and hydrogen binding in these nanoporous borocarbons, with computational guidance on optimizing surface chemistry via induction of high curvature, electron deficiency, large local fields, and exposed metal orbitals that are resistant to aggregation. The choices of low-Z metals or spillover catalysts to disperse in our materials will be guided computationally via modeling of the interaction with boron. These efforts are focused on obtaining very large densities of homogeneously distributed binding sites of 15-30 KJ/mol binding energy in a lightweight framework, which will enable attainment of DOE 2010 targets for gravimetric and volumetric storage and provide a pathway to 2015 goals. Work to date has led to ~120% improvement in binding energy (halfway to the goal) and recent work on incorporating metals has demonstrated 50% increased uptake in boron-substituted samples, validating the underlying design concept for these new advanced sorbents. The team will focus these efforts on further reducing the particle sizes of the metals by optimizing loading conditions and thermal budgets. The effect of increased binding energy on high surface area nanoporous boro-carbons on processes such as hydrogen spillover from noble metals like Pt is also being examined in detail with new highly metal-dispersed substrates and new testbed geometries.

FY 2008 Publications/Presentations

1. "X-ray Diffraction and H-Storage in Ultra-Small Palladium Particles", Kishore, D.G. Narehood, H.Goto, J.H. Adair, J.A. Nelson, H. R. Gutiérrez, P.E. Sokol, and P.C. Eklund, Adv. Materials (under review).

2. "Transparent Boron-doped Nanotube Films", X.M. Liu, H.E. Romero, K.Adu and P.C. Eklund, NanoLetters (accepted).

3. R. Rajagopalan, H. Foley, "A simple approach to synthesize nanoporous carbons with high heats of adsorption for hydrogen", (in preparation).

4. M. Chung, V.H. Crespi, P. Eklund, and H. Foley, Advanced Boro-carbon Sustrates and Spillover Dynamics, The 2008 DOE HSCoE Team Meeting, February 2007, Houston, TX (oral presentation).

5. V.H. Crespi, M. Chung, P. Eklund, and H. Foley, Advanced Hydrogen Storage Sustrates, The 2008 DOE HSCoE Tech Team Team Meeting, February 2007, Exxon-Mobile, TX (oral presentation).

6. Z. Huang, V. Crespi, Advanced hydrogen sorbents using geometrical constraints, (in preparation).

7. Physisorption of Hydrogen on Boron-Containing Carbon (B/C) Material Prepared by Organoborane Precursor, Z.C. Zhang, W. Chen, and T.C. Mike Chung, ECS Transactions, 2008.

8. Synthesis of Micro-Porous Boron-Substituted Carbon (B/C) Materials Using Polymeric Precursors for Hydrogen Physisorption", T.C. Mike Chung, Youmi Jeong, Qiang Chen, Alfred Kleinhammes, and Yue Wu, J. Am. Chem. Soc. 2008, 130 (21), 6668.