Advanced Boron and Metal Loaded High Porosity Carbons

T. C. Mike Chung
Vincent Crespi
Peter Eklund
Hank Foley

The Pennsylvania State University

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Overview

Timeline

- Project start: 2/1/05
- Project end: 1/31/10
- % complete: 80%

Budget

- Total funding for PSU team
  - DOE share: $1,485,000
  - Contractor share: $371,250
- FY08 $ 333,000
- FY09 $ 333,000

Partners

- Dispersed throughout HSCoE: NIST (neutron), NREL (TPD), Air Products (vol. ads.), UNC (NMR)
- M Dresselhaus (MIT)
- Carbolex, Inc

Barriers

A: *System Wt & Vol:* Hydrogen volumetric (1.5 kWh/L) and gravimetric (6wt%) storage density goals for 2010

B: *Absorbents:* Hydrogen binding energy 10-20 KJ/mol and SSA >2000m^2/g

C: *System Cost:* High-volume low-cost synthesis routes (via pyrolysis, molecular reaction, and arc)

D: *Energy Efficiency:* Moderate temperature operation (via enhanced binding energy)

E: *Charge/Discharge Rate:* via Mixed micro/mesopore structures through precursor design

F: *Thermal Management:* via designed moderate binding energies of physisorption

G: *Improved Understanding:* via calculations in coupling with fundamental measurements on well-characterized, well-ordered systems

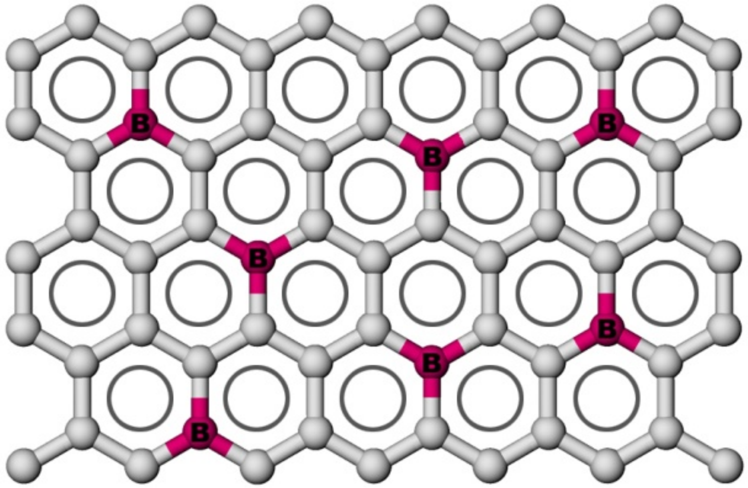
Three complementary approaches to prepare B-substituted carbon (BC_x) materials

- B-Containing Polymer Precursors and Pyrolysis *(Chung)*
  - *New precursors to prepare BC_x with high B content, acidity, and SSA*
  - ***Accomplishment:*** *15% substitutional B in BC_x structure. Data show the incorporation of B in C doubles the H_2 binding energy and absorption capacity. BC_x shows enhanced dispersion of Pt nanoparticles for spill-over study. Developing new route to prepare the well-defined B-framework that could further enhance B acidity, content, exposure, and SSA.*
- Molecular Reaction and Pyrolysis *(Foley)*
  - *Combinations of precursors to control complex pyrolitic decomposition*
  - ***Accomplishment:*** *Synthesis of BC_3 coated aerogel that shows increase of H_2 binding energy and adsorption capacity due to BC_3 surface modification.*
- Electric arc vaporization from M-B-C Electrodes *(Eklund)*
  - *Non-equilibrium high-energy conditions*
  - ***Accomplishment:*** *Production of highly ordered uniform high SSA B-doped carbon nanotubes with boron doping up to 3%, which shows enhancement of H_2 binding energy by inelastic neutron scattering. Production of Al-B-nanocarbon particles from Al-B-C electrodes.*

Objectives and Approaches

Achieving DOE 2010 H_2 storage goal with 60 mg H_2/g (gravimetric) and 45 g H_2/L (volumetric) by developing advanced H_2 adsorption materials with moderate binding energy (10-20 kJ/mol) and high SSA (> 2000 m^2/g)

Synthesis of Microporous <u>Boron Substitutional Carbon Materials (BC_x)</u> and its derivatives, closely coupled to adsorption measurements and first-principles materials theory



B Features

- ✓ *Lightness of Boron*
- ✓ *Abundant*
- ✓ *Enhancing H_2 interaction*
- ✓ *Tunable acidity*
- ✓ *Stabilizing atomic metal*

Project Activities and Schedule

Year 06

- Studying three synthesis routes (polymer precursor, molecular reaction, and electric arc vaporization) to prepare B-substitution C (BC_x) materials.

Year 07

- Synthesizing and Characterizing new BC_x materials with B content up to 7% and SSA 1000 m^2/g, and their H_2 adsorption.
- Theoretical prediction of M/BC_x materials M (Pt, Pd, etc.).
- GO decision for the program

Year 08

- Optimizing the methods to prepare the desirable BC_x materials with B content (>10%), including BC_3 coated aerogels.
- Identifying (experiments and calculation) the most suitable H_2 binding sites (binding energy 10-20 kJ/mol H_2).
- Investigating new synthesis routes to prepare metal dispersion (M-intercalation) in BC_x materials for spill-over study.
- Exploring new synthesis route for the well-defined B-Framework.

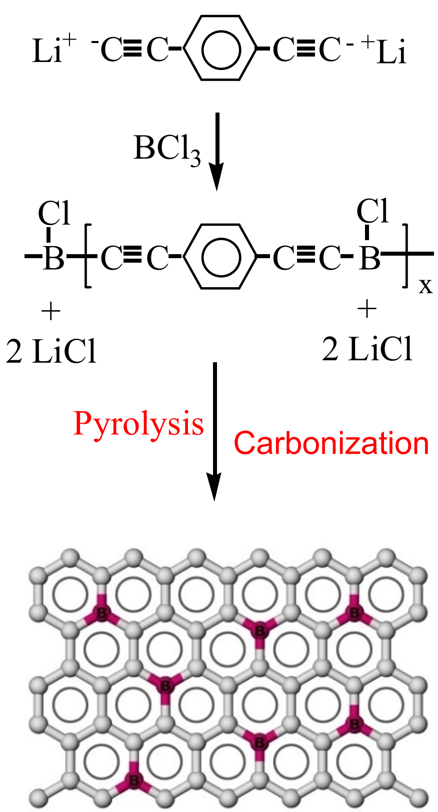
Year 09

- Preparing BC_x materials with a combination of high B content (>15%), acidity, exposure, and surface area (SSA >2000 m^2/g).
- Developing well-defined B-Framework with strong B acidity and high H_2 binding energy >20 kJ/mol.
- Studying storage mechanism for spill-over in M/C, M/BC_x materials M (Pt, Pd, etc.).

BC_x Materials Prepared by B-Polymer Precursor

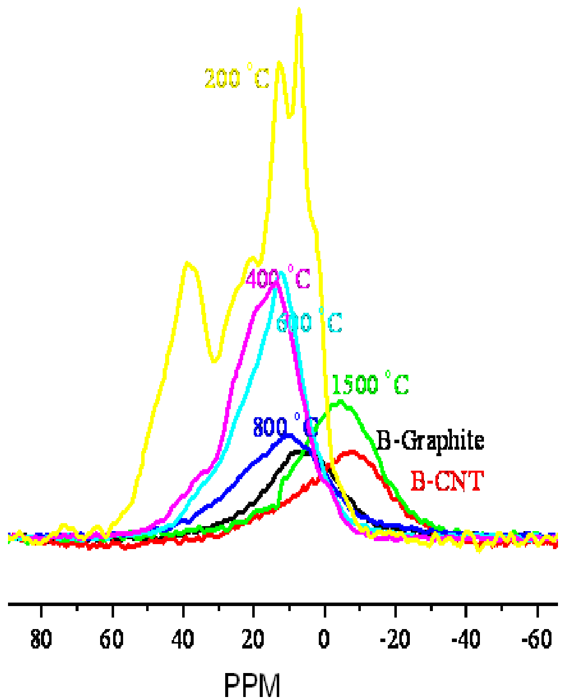
J. Am. Chem. Soc. 2008, 130, 6668

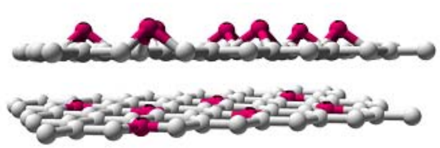
Synthesis route



BC_x material

Solid State ^{11}B NMR





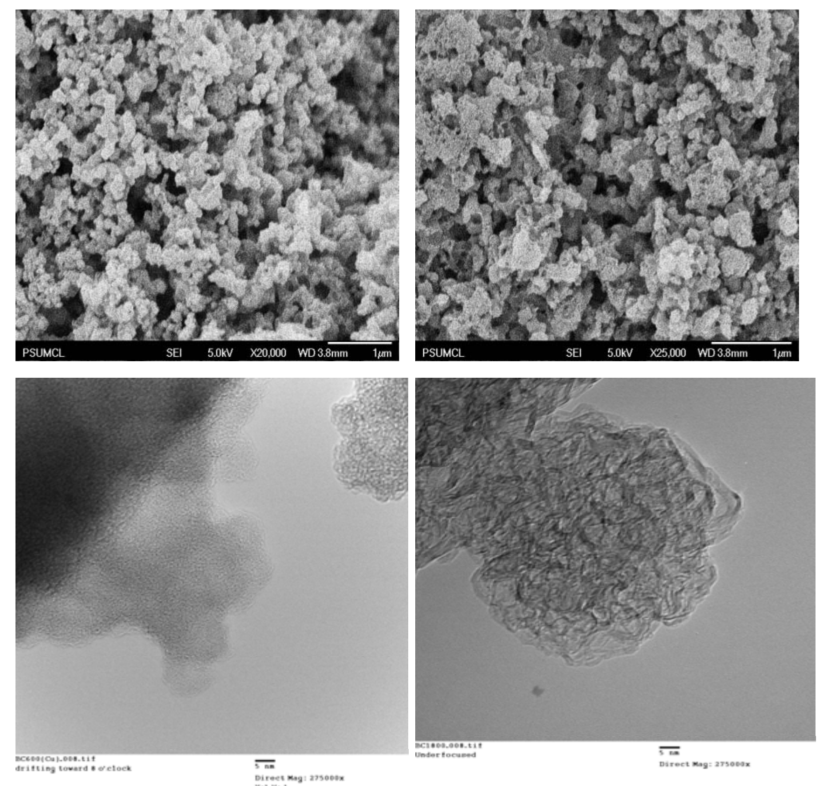
SEM and TEM

BC_x-600

7.6% B; 780 m²/g

BC_x-1500

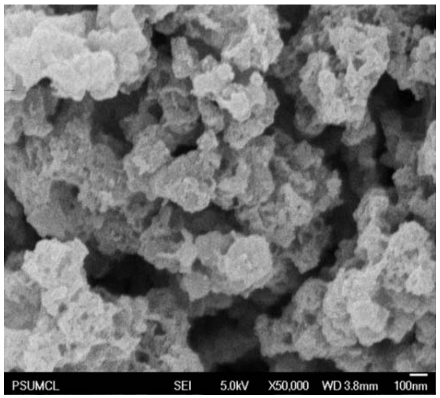
3.8% B; 33 m²/g

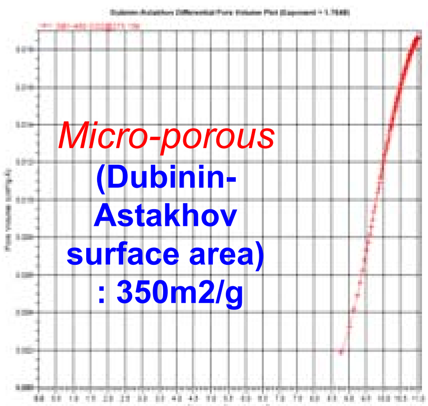


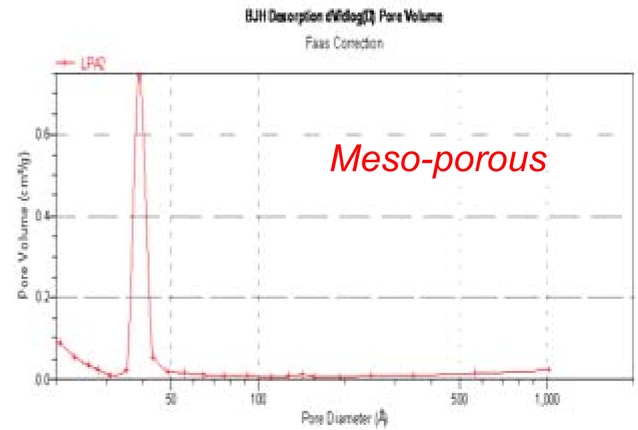
- ***BC_x microstructure and acidity are dependent on pyrolysis temperature.***
- ***BC_x-600 contains 7% B and 780 m²/g porosity (only 1/3 of B are accessible).***

BC_{12}; Pore Structure and H_2 Adsorption

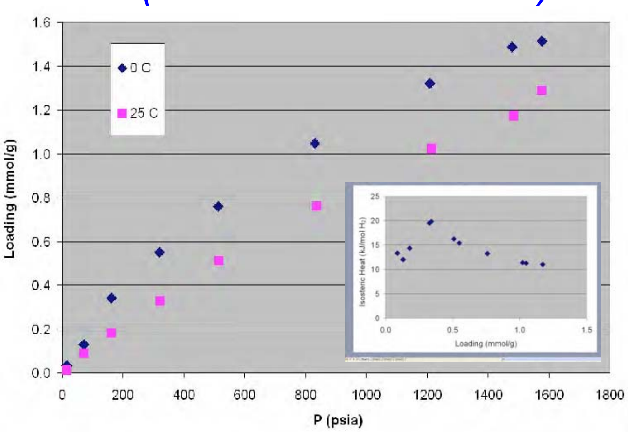
B content: 7.6%; SSA: 780 m^2/g

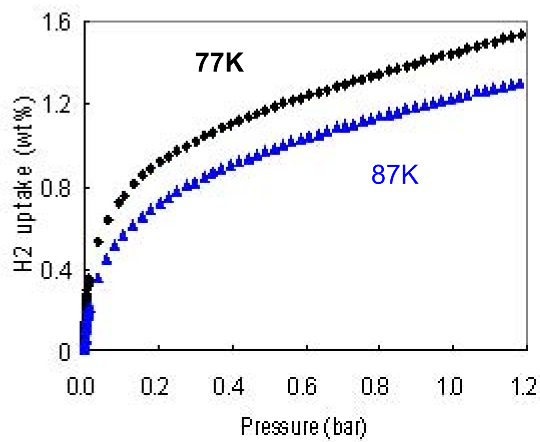


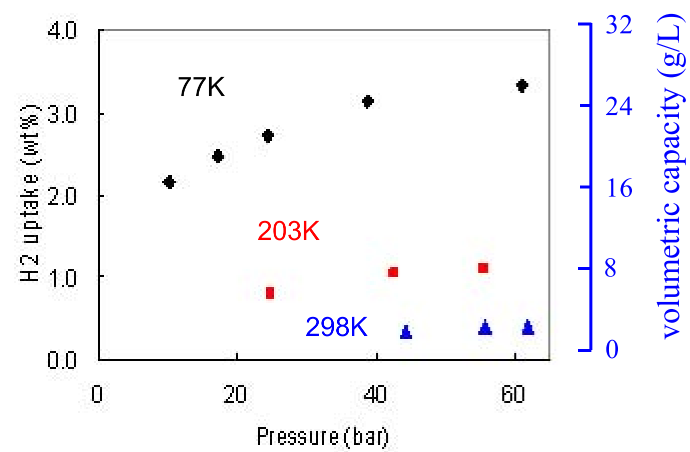




(Measured at Air Products)

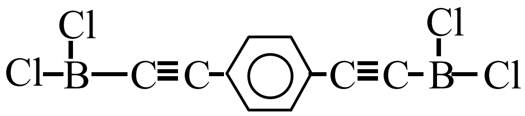
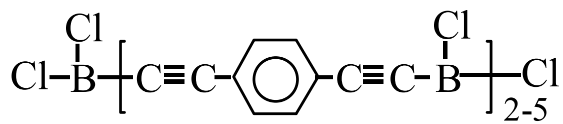
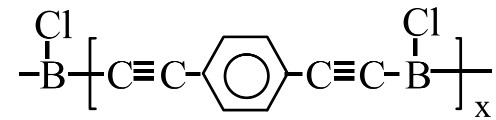




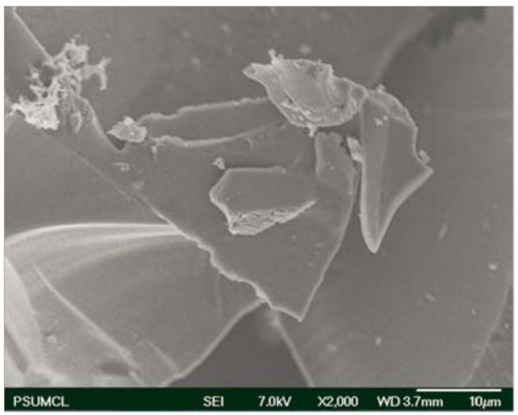


BC_x-600 shows both micro- and meso- porous structures, heat of adsorption 10-20 kJ/mol, and more than double H_2 adsorption capacity vs. C with the same SSA.

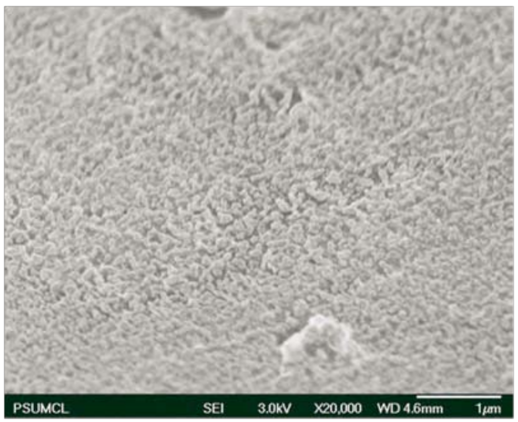
Increase B Content in BC_x; BC_8 and BC_6

Organic precursor (Liquid)	Oligamer precursor (Wax)	Polymer precursor (Solid)
		 + 2 LiCl
B/C ratio= 2/10	B/C ratio= 1.5/10	B/C ratio= 1/10

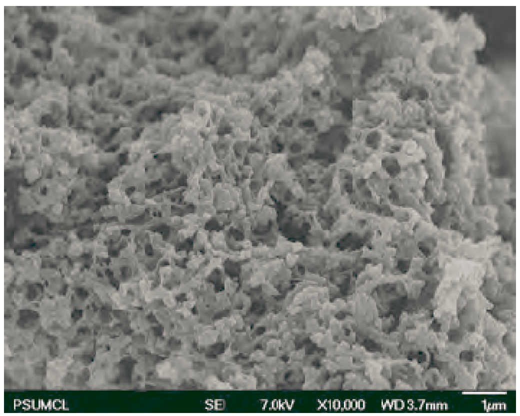
(Pyrolysis at 600 ^oC for 12 hours to form B/C with >60% yield)



B Content: 14.5 %
SSA: 5 m^2/g



B content: 11.6%
SSA: 330 m^2/g (microporous)

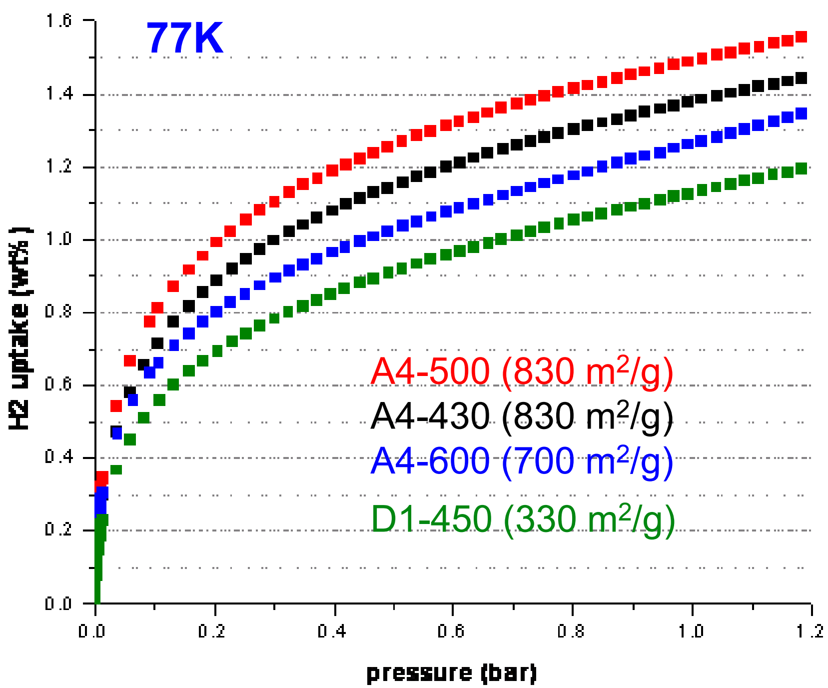


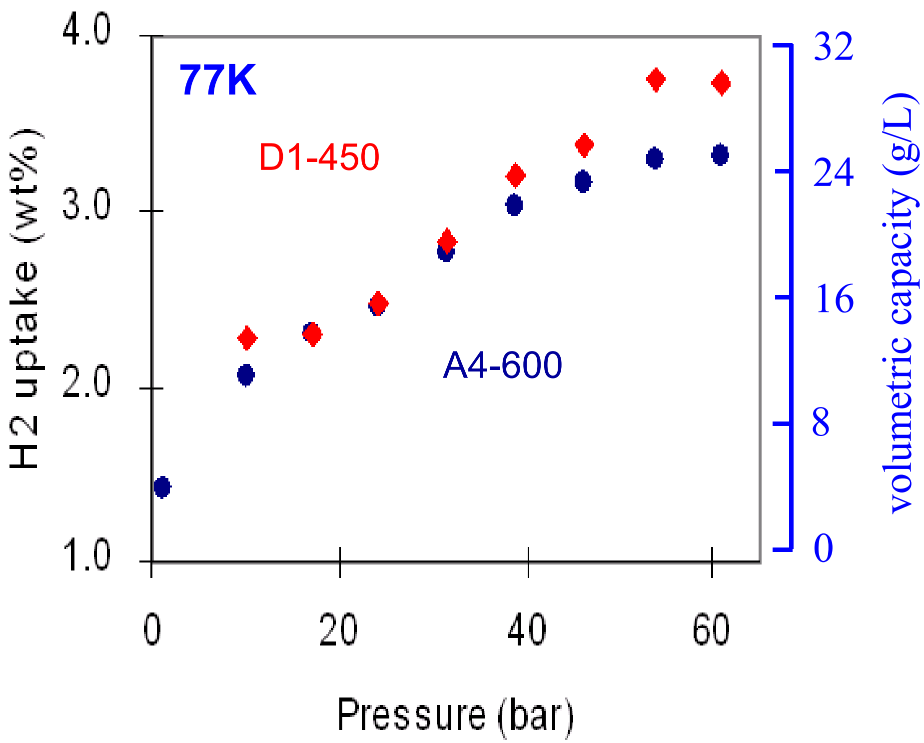
B content: 7.6%
SSA: 780 m^2/g

BC_6 and BC_8 materials have been prepared using liquid precursors. However, the resulting BC_x materials exhibit lower surface areas.

H_2 Adsorption Capacities for BC_8 and BC_{12}

A4 samples (7.6% B) are prepared from polymer precursor
D1 sample (11.6% B) is prepared from oligomer precursor



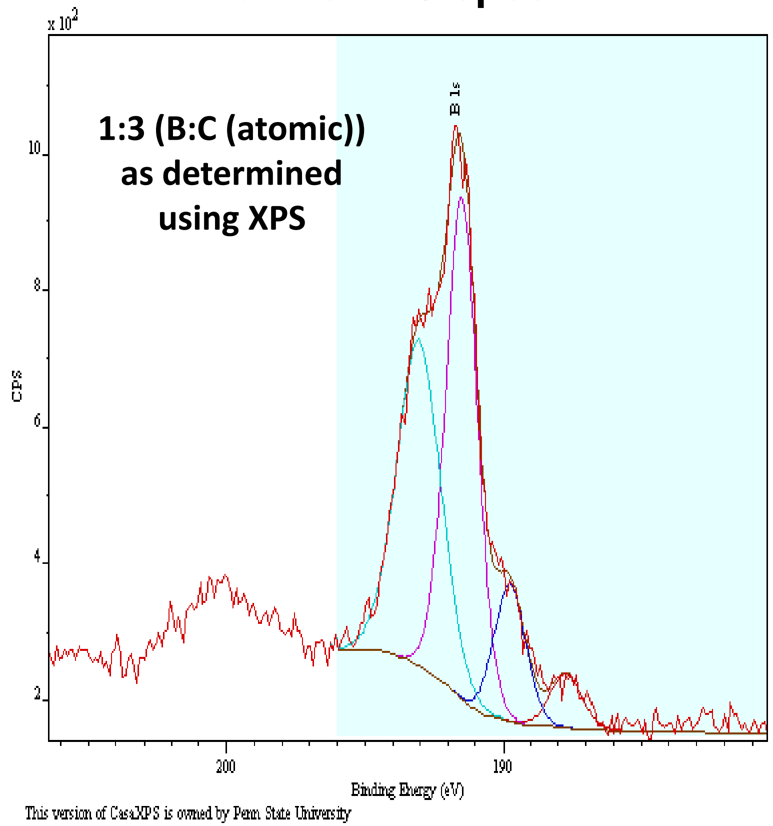


Despite low surface area, the D-1 sample with higher B content (11.6%) shows significantly higher H_2 adsorption capacity per surface area.

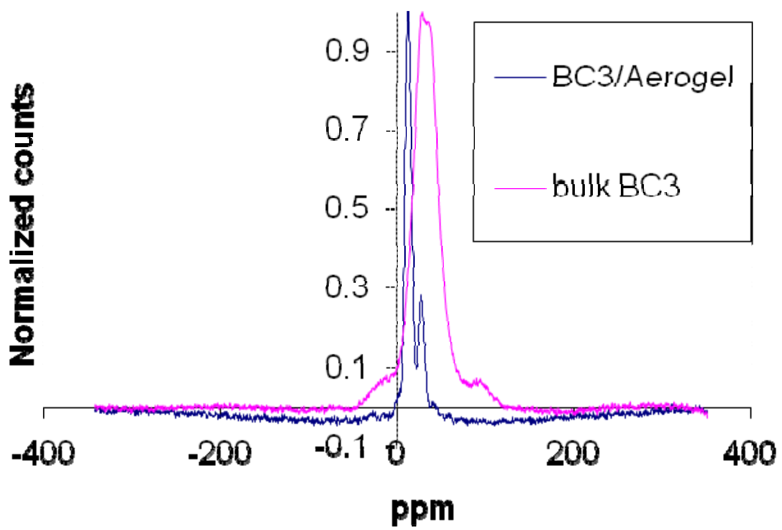
Further Increase B Content; BC_3

$$2BCl_3 + C_6H_6 \xrightarrow{900^oC} 2BC_3 + 6HCl^{a,b,c}$$

Boron 1s XPS spectrum



Solid state B NMR spectroscopy

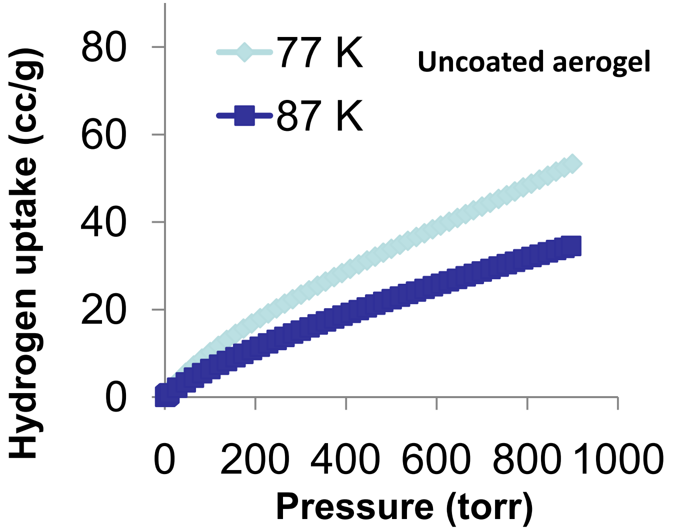


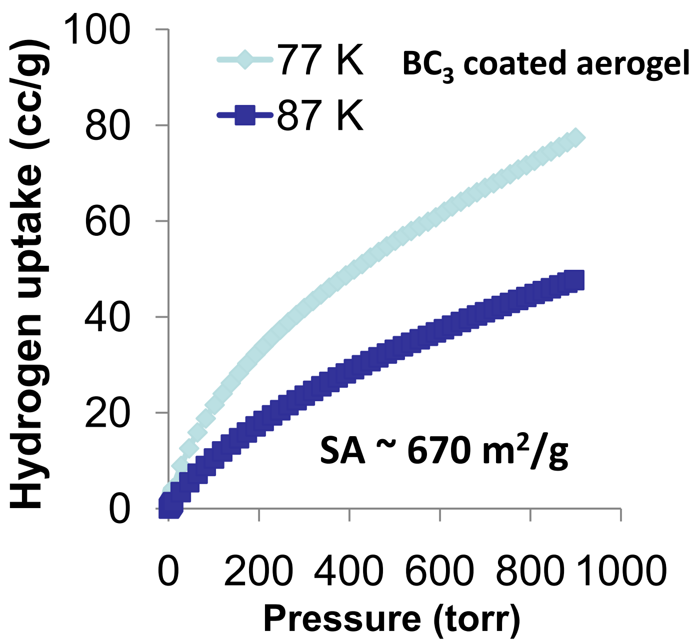
Presence of trigonally bonded boron also confirmed using 900 MHz solid state B-NMR done at PNNL

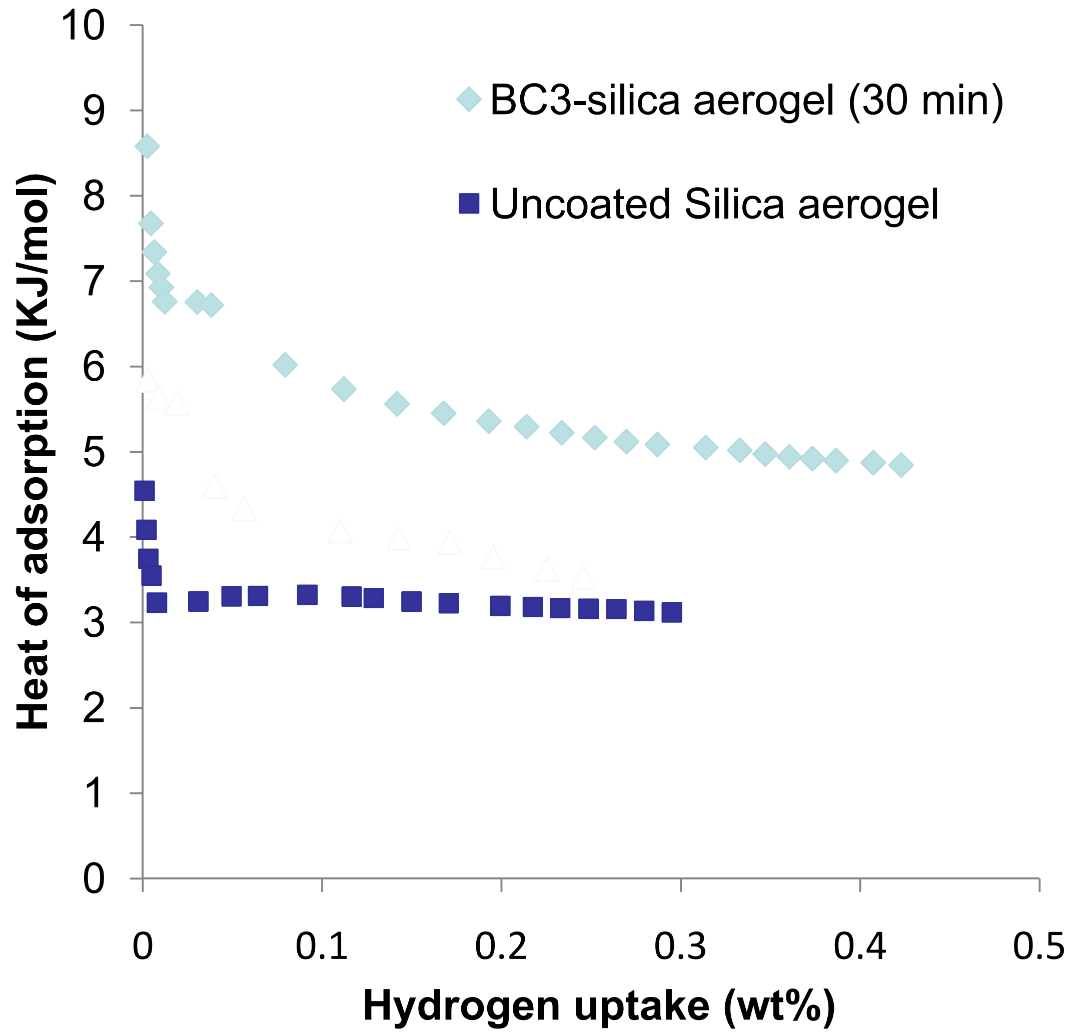
- ***Synthesis of BC_3 reproduced successfully***
- ***BC_3 was successfully deposited on high surface area mesoporous silica (~670 m^2/g)***

[a] Kouvetakis et al., *JCS Chem. Comm.*, (1986), 1758-1759
[b] Fecko et al., *Carbon*, 31 (1993) 637 -644
[c] Cermignani et al., *Carbon*, 33 (1995) 367-374

Hydrogen Uptake on BC_3 Coated Aerogel





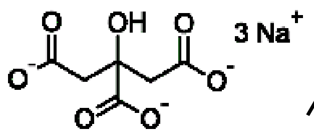


Initial heat of adsorption almost doubled (~9KJ/mol) after 30 min. of deposition of BC_3 on aerogel.

Metal-decorated BC_x materials for Spill-over

Synthesis Routes

Activated C + H_2PtCl_6

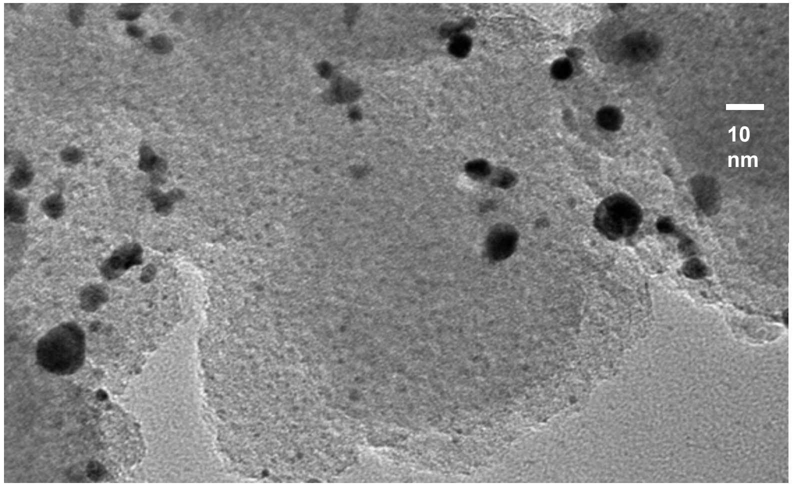


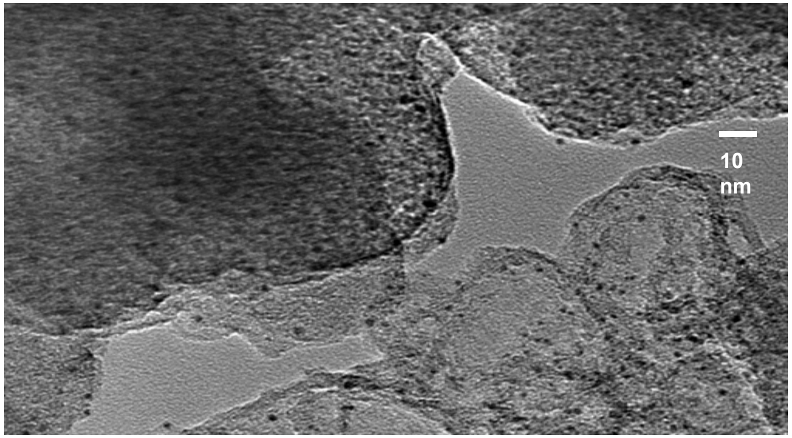
$/H_2O \xrightarrow{NaBH_4}$ **Pt/C**

E. Bekyarova et al. *J. of Physical Chemistry B Letters*, 109 (2005) 3711-3714

BC_{12} Material + H_2PtCl_6 $\xrightarrow{\text{filtration}}$ **H_2PtCl_6/BC_{12}** $\xrightarrow[H_2]{\triangle}$ **Pt/BC_{12}**

TEM Micrographs



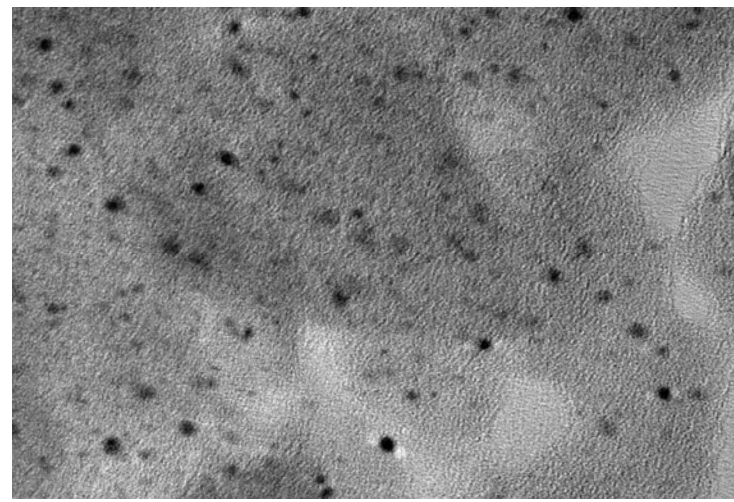


B/C material offers active surfaces; absorbing H_2PtCl_6 in aqueous solution and forming Pt nano-particles (<2 nm) after reduction.

Zr and Ti nanoparticle on BC_{12} Materials Using Metallocene Reagents

BC_{12} material $\xrightarrow[\text{Homogeneous Toluene solution}]{Cp^*_2ZrCl_2}$ $\xrightarrow[\text{then drying}]{\text{Washing}}$ $\xrightarrow[600\ ^oC]{\Delta}$ **Zr/BC_{12} Material**

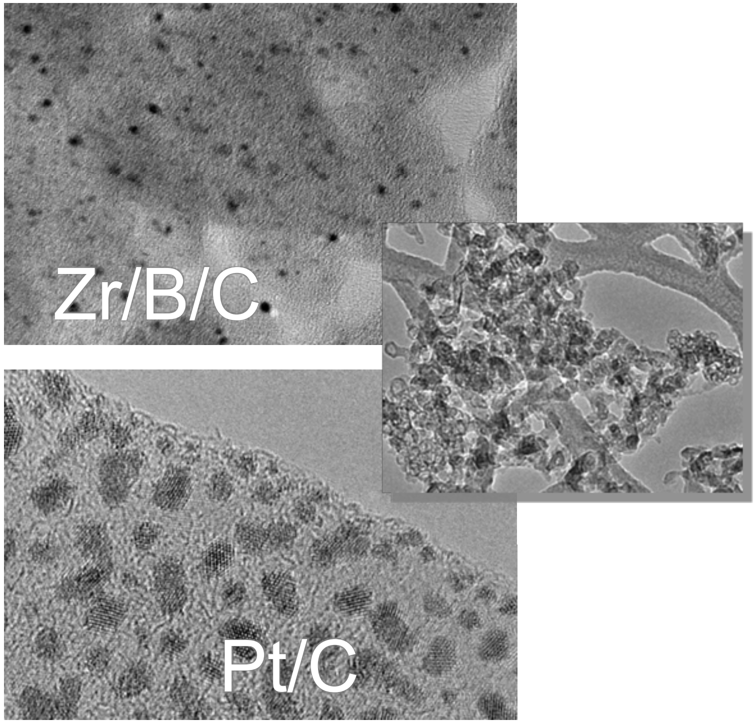
Metal Containing Reagents	Activated C (200 mg, 600 m²/g)	B/C Material (200 mg, 500 m²/g)
	After metal loading (mg)	After metal loading (mg)
$N(C_4H_9)_3$	200	279
Cp_2TiCl_2	200	309
$Cp^*_2ZrCl_2$	205	222
$[(\eta^5\text{-}Cp^*)SiMe_2(\eta^1\text{-}NCMe_3)]TiCl_2$	203	272

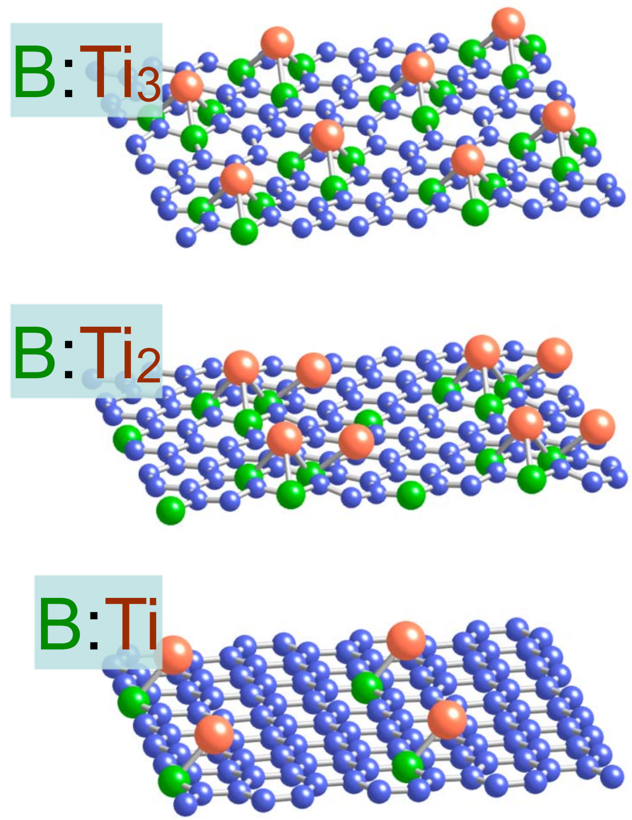


Uniform Zr particles on B/C (size < 2nm)

- ***Several early transition metal (Ti and Zr) nanoparticles (< 2nm) have also been formed and well-dispersed on BC_{12} surfaces.***
- ***Pt/BC_{12} material shows <u>Spill-over phenomenon</u> with significant H2 adsorption at ambient temperature.***

Theory Work: Increasing B doping in BC_x stabilizes dispersed metals





~7 eV gained by depositing Ti on surface

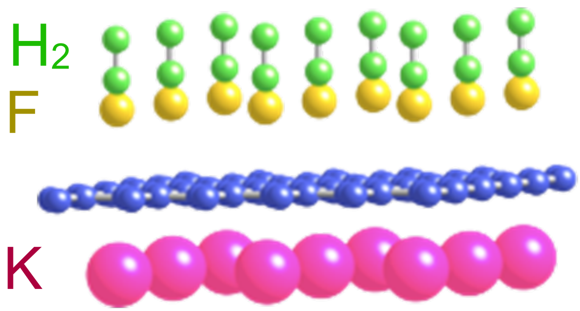
~5 eV

~2 eV

Calculations suggest that boron doping stabilizes **atomically** dispersed metals (Sc, Mg, Ti, Pd, Be...) against aggregation. Stabilization is both thermodynamic (charge transfer) and kinetic (due to variations in local B content). These metals then provide highly-coordinate H_2 binding sites.

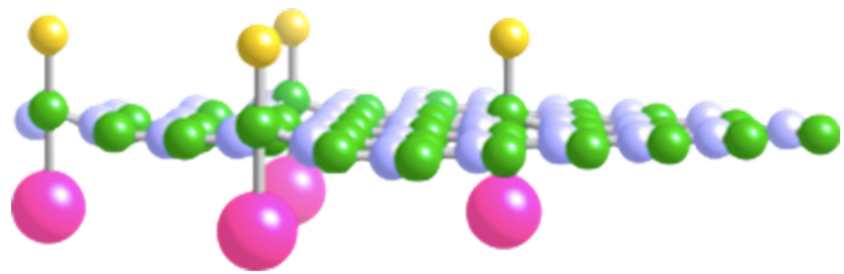
Theory Work: Long-range electrostatic effects due to topological frustration modulate H_2 bonding

0.28 eV per H_2

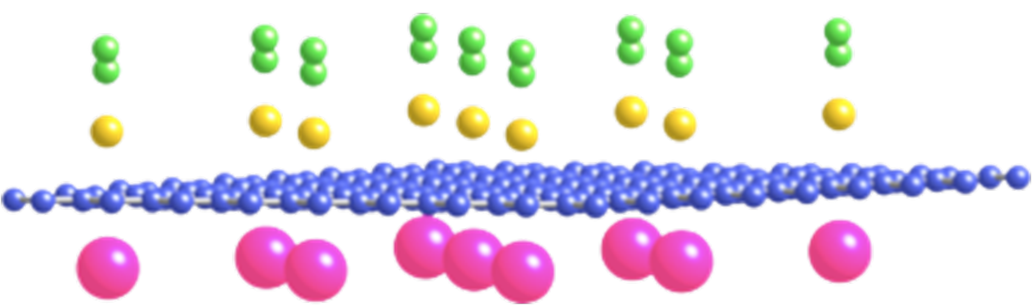


high density

BN barriers enable stronger cross-sheet charge transfer due to weaker screening.



0.1 eV per H_2



low density

Closure of the alkali half-space by sheet curvature (closed fullerene-like structure) would produce a high SSA bulk material.

Future Work

Plan for the rest of FY09

- ***Increasing surface area of BC_x materials***

  Continuing the development of BC_x materials to achieve a combination of high B content , acidity, and exposure, and surface area (>2000 m^2/g), which could further increase H_2 storage capacity at ambient temperature.

- ***Studying spill-over on the metal-doped BC_x materials during H_2 adsorption-desorption.***

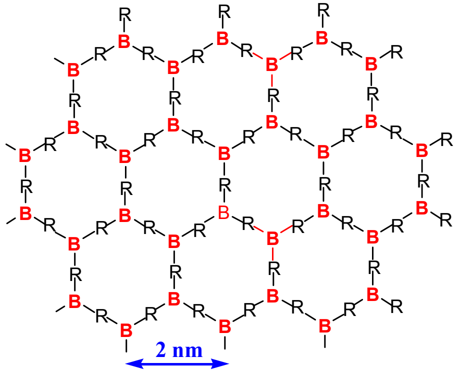
- ***Improving Boron-framework to achieve well-defined microporous structure and high surface area.***

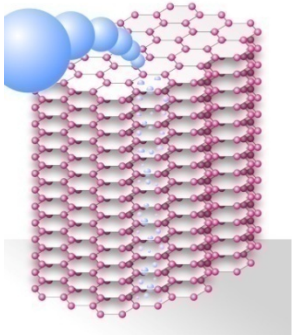
High B content (12-20%)

Good B exposure

Highly acidic B species

SSA > 2000 m^2/g





Summary

- **Relevance:** Increase reversible hydrogen binding energy by developing new storage materials through B-substitutional carbon (BC_x) structures.
- **Approach:** Three complementary synthesis techniques closely coupled to adsorption measurements and first-principles materials theory.
- **Technical accomplishments:**
  - Developing new chemical routes to prepare boron-substituted carbon (BC_x) materials with a broad range of B content and acidity.
  - Understanding BC_x structure from puckered to graphitic controlled by pyrolysis temperature.
  - BC_{12} material with SSA= 780 m^2/g shows H_2 binding energy 20-10 kJ/mol and more than doubles H_2 absorption capacity per surface area.
  - BC_8 material with SSA=330 m^2/g shows even higher H_2 adsorption capacity per surface area (3.8 wt% at 77K).
  - BC_6 material with 15% B has been prepared, but having very low SSA.
  - BC_3 coated aerogel also shows increase of H_2 binding energy (6 kJ/mol)
  - Transition metal doped BC_x materials (M/BC_x) exhibit well-dispersed Pt, Ti, Zr nano-particles (size < 2nm) and Spill-over phenomenon.
  - Studying new synthesis route to prepare new B-frameworks that have high microporous surface area and high B acidity.

Summary Table

Material Systems	Surface Area (m^2/g)	Binding Energy (KJ/mol H_2)	H_2 Adsorption Capacity			
			Gravimetric (mg H_2/g)	Volumetric (g H_2/L)	Temperature (K)	Pressure (atm)
BC_{12}	**780**	**10-20**	**3** **34**	**2.4** **27.2**	**298** **77**	**100** **50**
BC_8	**330**		**5.2** **38**	**4.2** **30.4**	**298** **77**	**83** **50**
NPC (derived from PFA)	**1590**		**6.5** **23**	**4.875** **17.25**	**298** **77**	**100** **1**
BC_3 Coated Aerogel	**670**	**6-9**	**6.9**	**3.45**	**77**	**1**

B substitution in C shows the significant increase of H_2 binding energy (20-10 kJ/mol) and H_2 absorption capacity per surface area. To meet the 2010 goals, our research focus is on the greater microporous surface area.