Advanced Boron and Metal Loaded High Porosity Carbons

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Project ID # ST080

Overview

Timeline

- Project start: 2/1/05
- Project end: 06/30/10
- % complete: 100%

Budget

- Total funding for PSU team
  - DOE share: $1,485,000
  - Contractor share: 371,250
- FY09: $444,000
- FY10: $0

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 (6 wt%) storage density goals for 2010

B: Absorbents: Hydrogen binding energy 10 – 20 KJ/mol and SSA > 2000 m^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

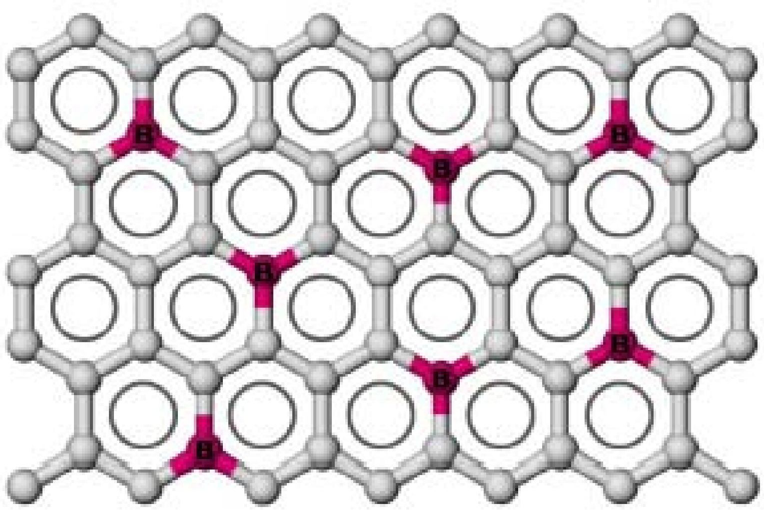
Three complementary approaches to prepare B-substituted carbon (BC_x) materials

- 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_x coated carbon templates that show increase of H_2 binding energy and adsorption capacity*
- 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 Boron Substitutional Carbon Materials (BC_x) and its derivatives, closely coupled to adsorption measurements and first-principles materials theory



Boron 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 m2/g, and their H2 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 synthetic routes to prepare metal dispersion (M-intercalation) in BC_x materials for spill-over study.

Year 09

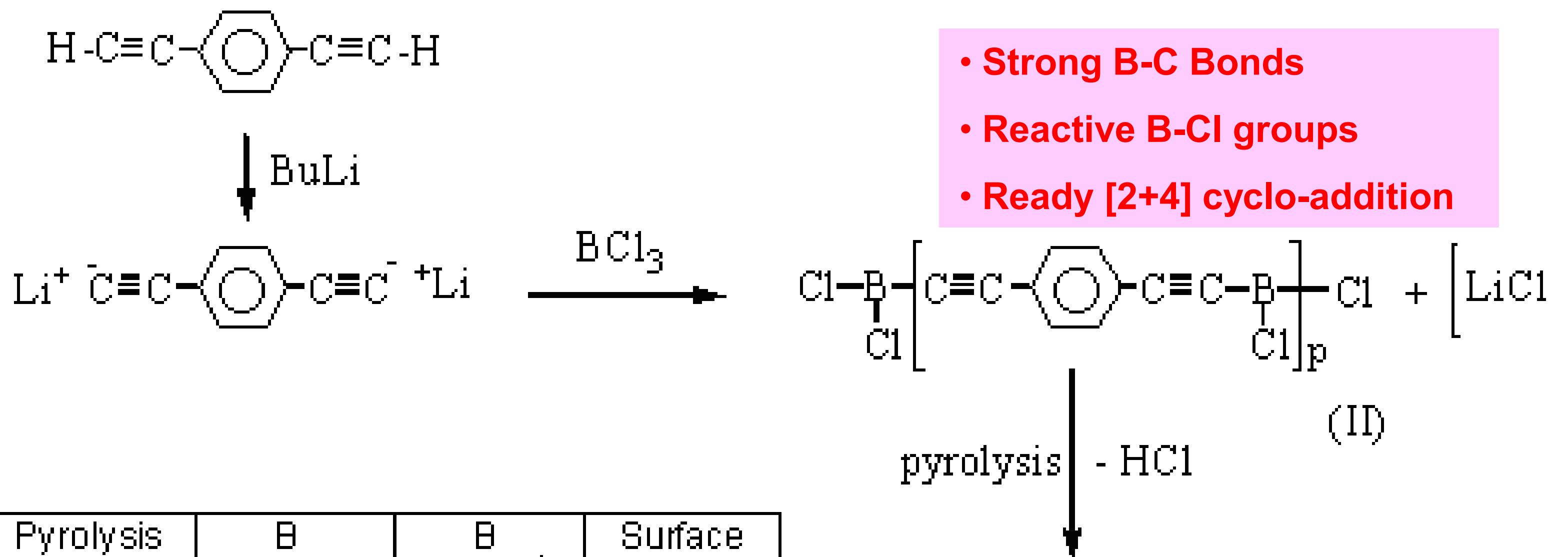
- Exploring new synthesis route for the well-defined B-Framework.
- Developing well-defined B-Framework with strong B acidity and high H2 binding energy > 20 KJ/mol.
- Studying storage mechanism for spill-over and direct H-M binding in M/C, M/BC_x materials M (Pt, Pd, etc.)

Year 10

- Developing new processing routes to deposit BC_x materials on high surface area templates
- Studying the interaction of hydrogen with BC_x materials using various characterization techniques including DRIFTS and NMR
- Preparing BC_x materials with a combination of high B content (> 15%), acidity, exposure and surface area (SSA > 1000 m2/g)
- Developing means to stabilize highly dispersed metals on BC_x supports.
- Developing new concepts in storage exploiting electron-deficient frameworks, topological constraints

Synthesis of BC_x with Porous Structure by B-Polymer Precursor

- **Strong B-C Bonds**
- **Reactive B-Cl groups**
- **Ready [2+4] cyclo-addition**



BC_x Material
(Containing LiCl molecules)

water washing (- LiCl)

Porous BC_x material

Run	Pyrolysis temp (°C)	B content[a] (wt%)	B content[b] (wt%)	Surface ares (m^2/g)
1	600	7.7	7.7	760
2	800	6.7	7.1	650
3	1100	4.2	4.5	40
4	1500	3.1		3

a. B content was determined by Prompt γ-ray Activation Analysis
b. B content was determined by 11B NMR.

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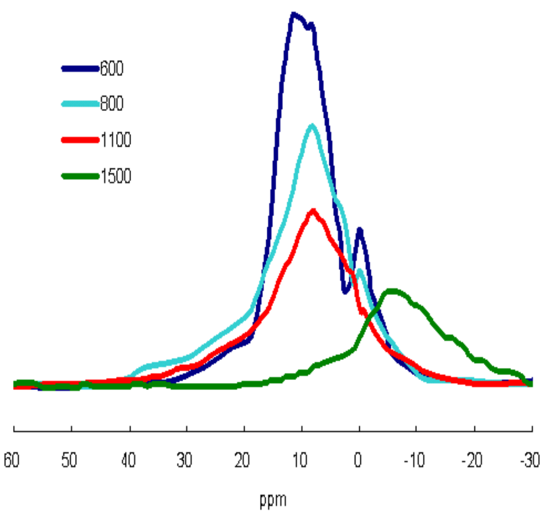
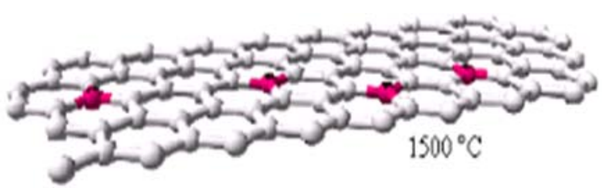
➢ ***BC_x microstructure and porosity are dependent on pyrolysis temperature***

BC_x Molecular Structure

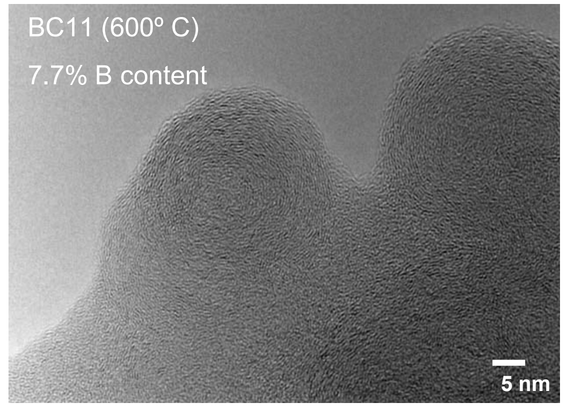
MAS-[11]B NMR

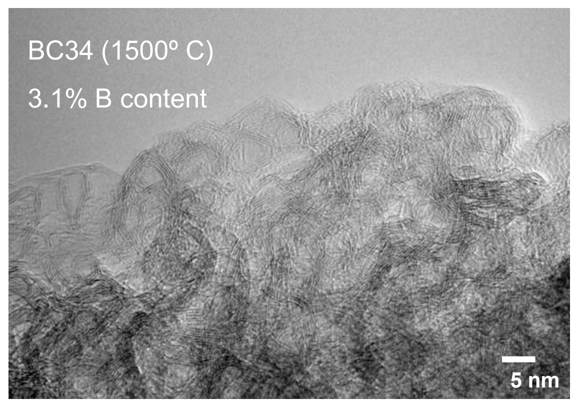




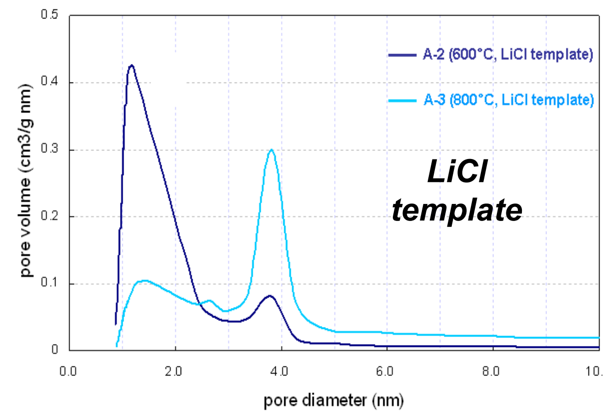
Carbon (29 March 2010)

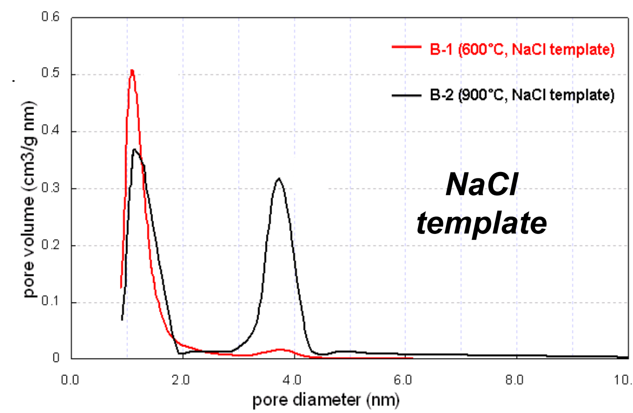
TEM Micrographs





Pore size distribution

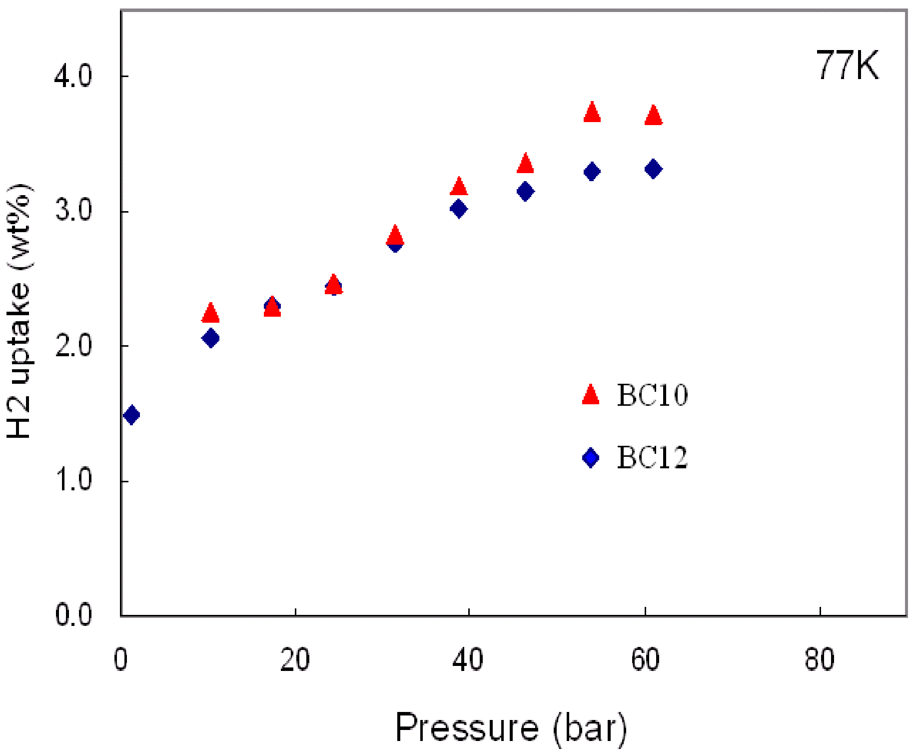


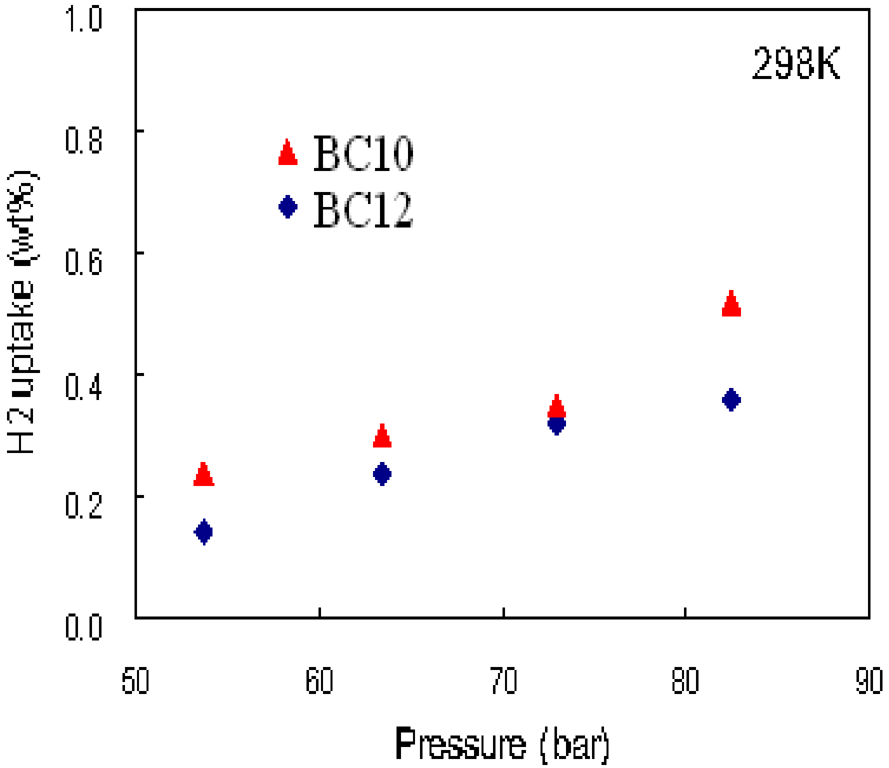


Template	N_2 sorption at 77K			CO_2 sorption at 273K	
	Surface area[a] (m^2/g)	Micropore volume[b] (cm^3/g)	Cumulative pore volume[b] (cm^3/g)	Surface area[c] (m^2/g)	Micropore volume[c] (cm^3/g)
LiCl	780	0.38	0.43	873	0.33
LiCl	528	0.10	0.29	569	0.16
NaCl	634	0.34	0.34	828	0.32
NaCl	405	0.16	0.29	762	0.25

a. Calculated by BET equation. b. Estimated by BJH method. c. Estimated by D-R method.

H_2 Adsorption in Porous BC_{10} and BC_{12}





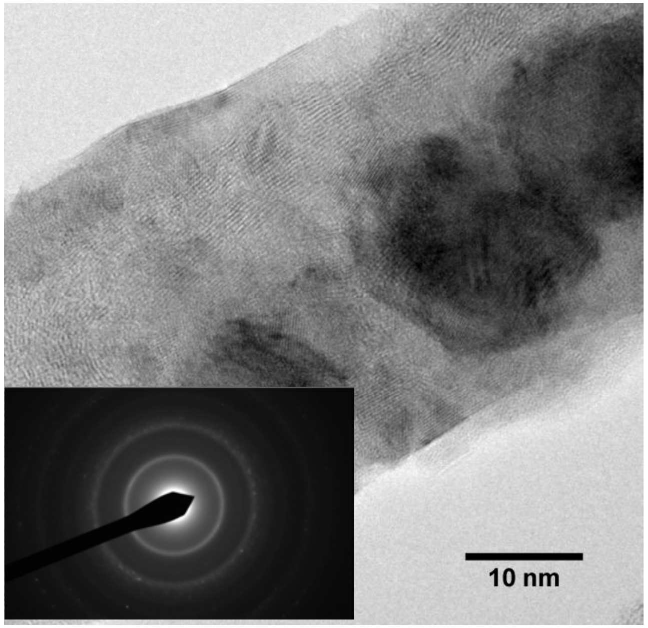
BC_{10} (SSA=609 m^2/g) ***BC_{12} (SSA=780 m^2/g)***

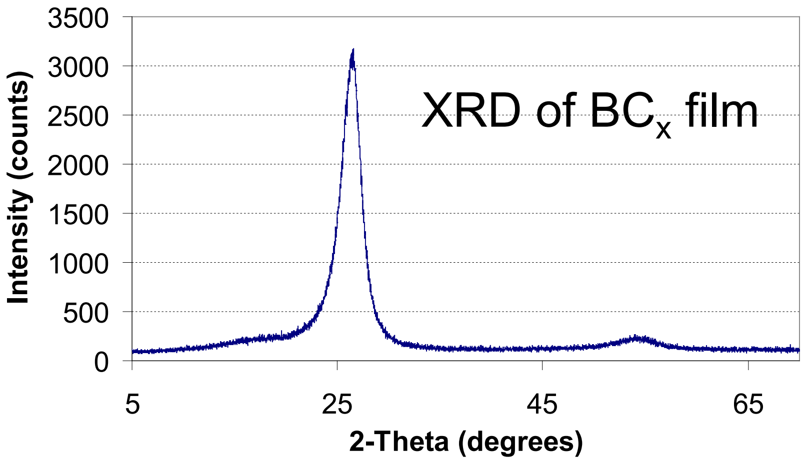
➢ ***Despite low surface area, the samples show significantly higher H_2 adsorption capacity per surface area***

Synthesis of BC_x by CVD process

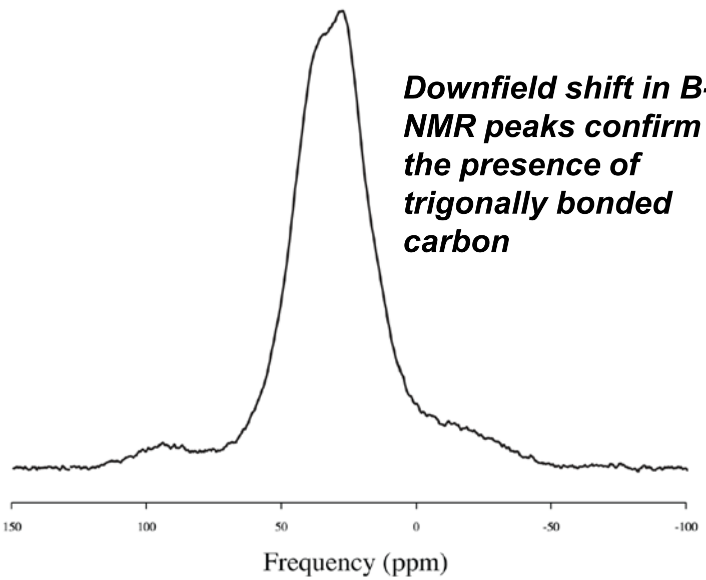
$$2BCl_3 + C_6H_6 \rightarrow 2BC_3 + 6HCl$$

B Concentration		B:C Ratio		d_{002} Lattice Spacing (nm)	
XPS[1]	^{11}B NMR	XPS	^{11}B NMR	XRD	TEM
17	15.9	1:3	1:4.6	0.36	0.34



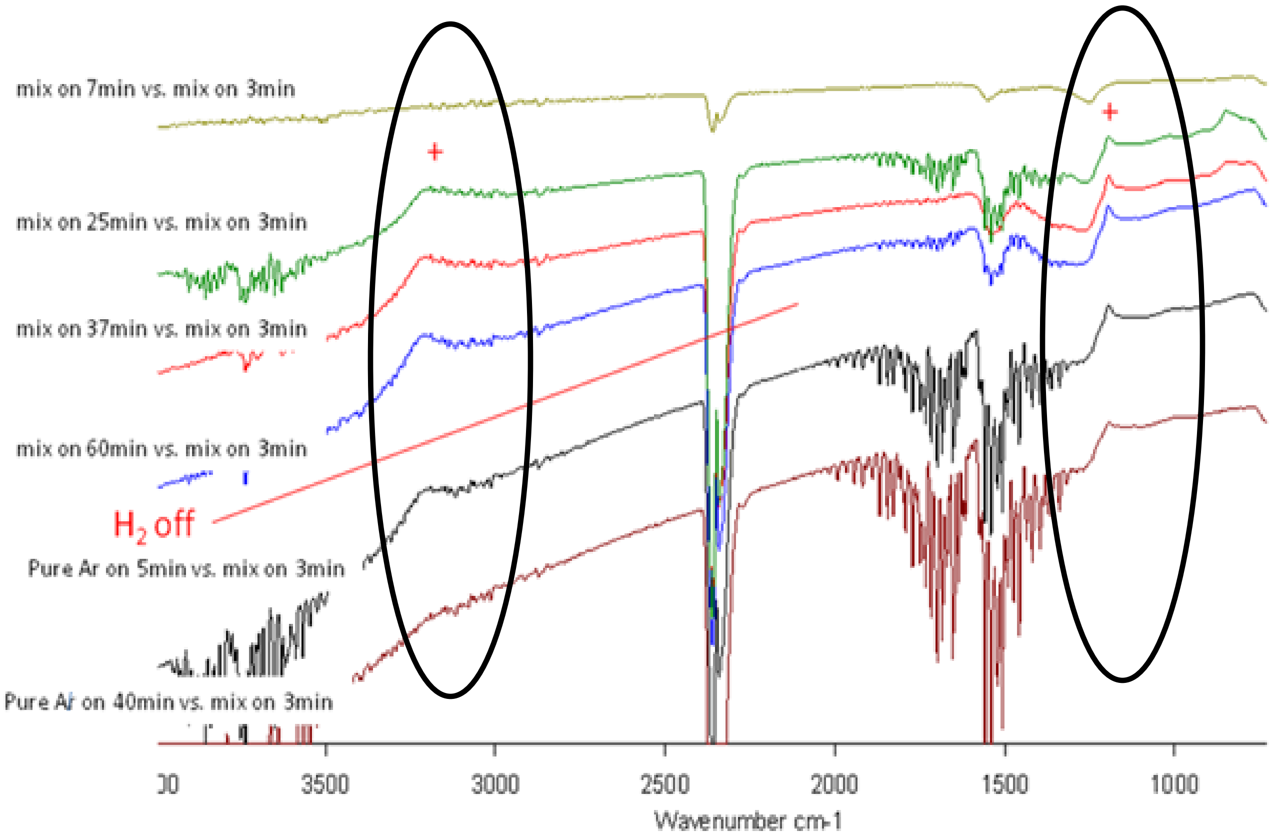


- ***BC_x films synthesized by chemical vapor deposition are turbostratic in nature with little or no accessible porosity***
- ***Presence of 16 – 17 at% substitutional boron confirmed by XPS (surface) and B-NMR (bulk) techniques***



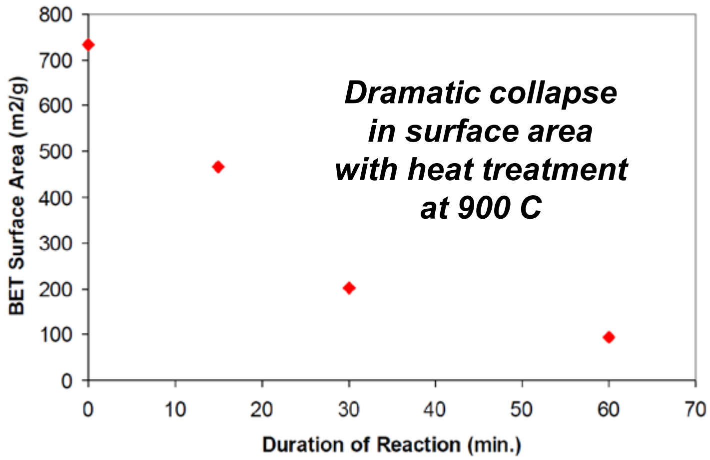
Downfield shift in B-NMR peaks confirm the presence of trigonally bonded carbon

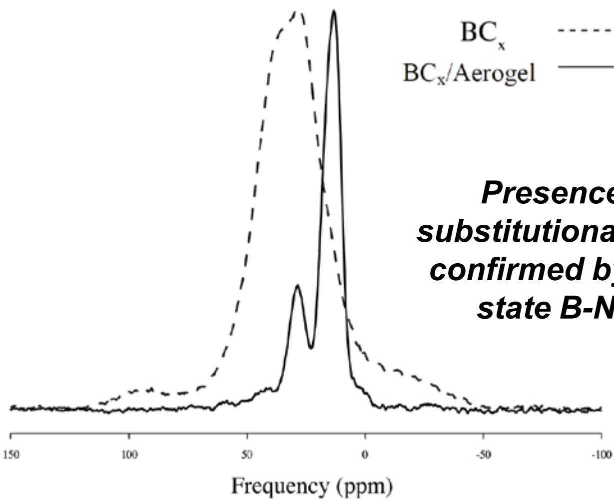
DRIFTS study: Probing interaction of hydrogen with BCx films

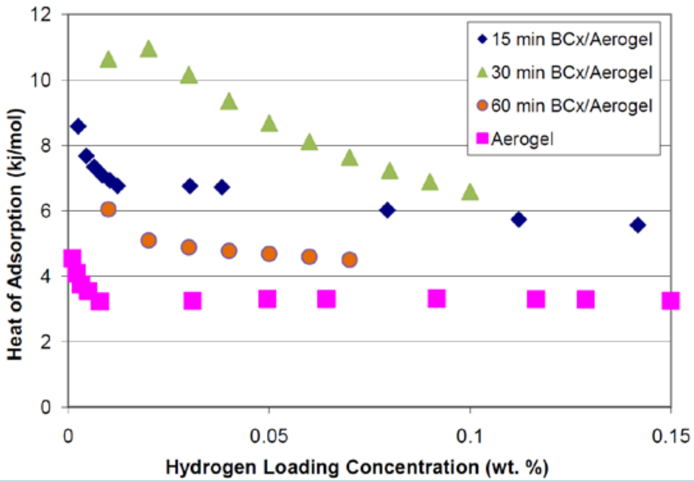


- ➢ ***Two peaks at 3200 and 1190 cm-1 appear as BCx is exposed to 5% H2/Ar gas mixture and the peak intensity increases with time of exposure***
- ➢ ***The peaks start to disappear when the sample is purged with helium indicating reversible desorption of hydrogen***
- ➢ ***The peaks may be due to formation of B-H str. (1190 cm-1). Further study is underway to understand the origin of these peaks using high pressure DRIFTS accessory***

Depositing BC_x on mesoporous silica template



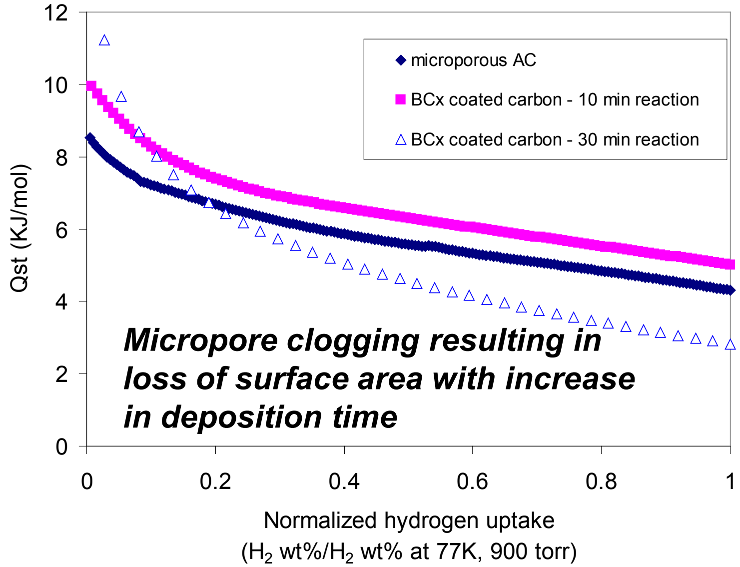


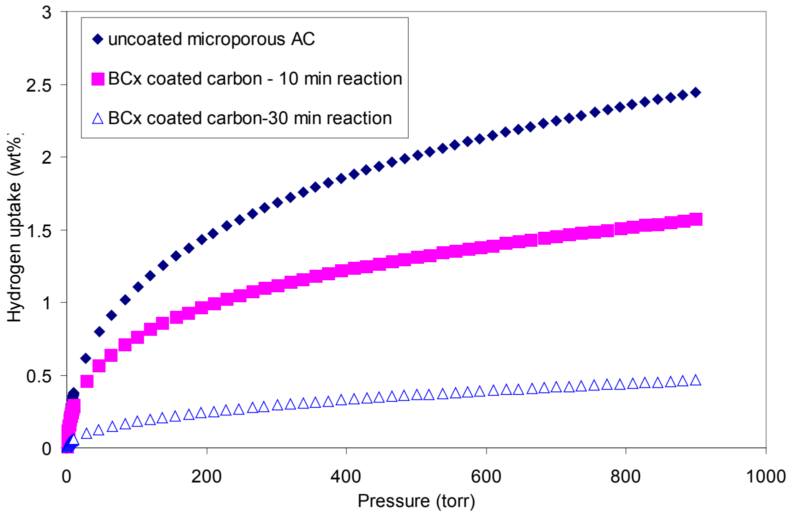


Aerogel	Initial hydrogen ΔH_{ads}
15 minute coated	6.1
30 minute coated	10.9
60 minute coated	6.1
Uncoated	4.5

- ***Downselected the use of mesoporous silica template for BC_x deposition due to pore collapsing issues upon heat treatment***
- ***Hydrogen uptake was very low due to low accessible surface area, however initial heat of adsorption of BC_x coated aerogels under controlled synthesis conditions were ~ 11KJ/mol, three times higher than the silica aerogel supports***

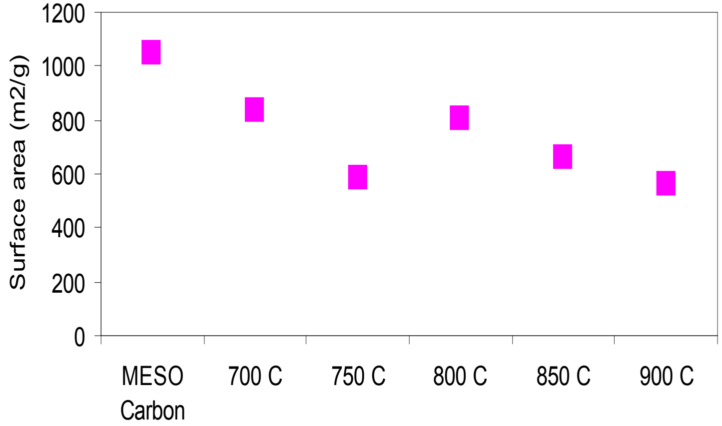
BC_x on Activated carbons

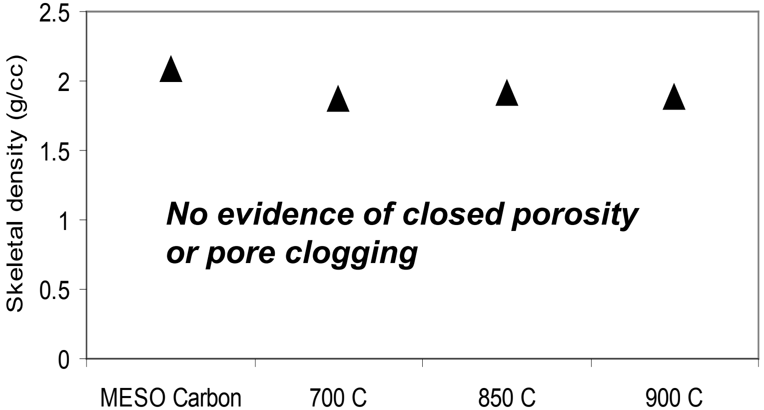




H_2 adsorption measurements done at 77K, 1bar

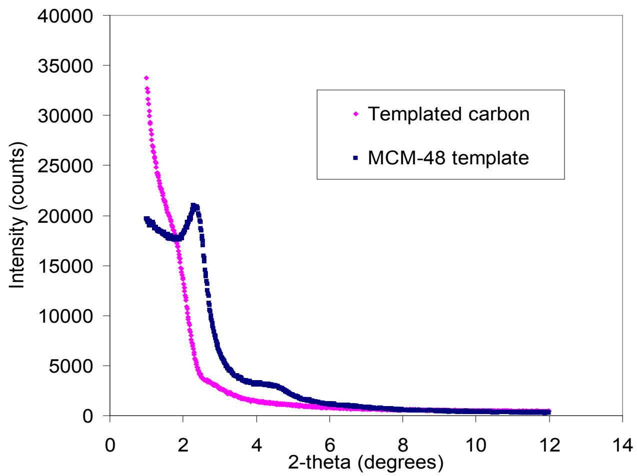
Studies of BC_x deposition on commercially available mesoporous activated carbons

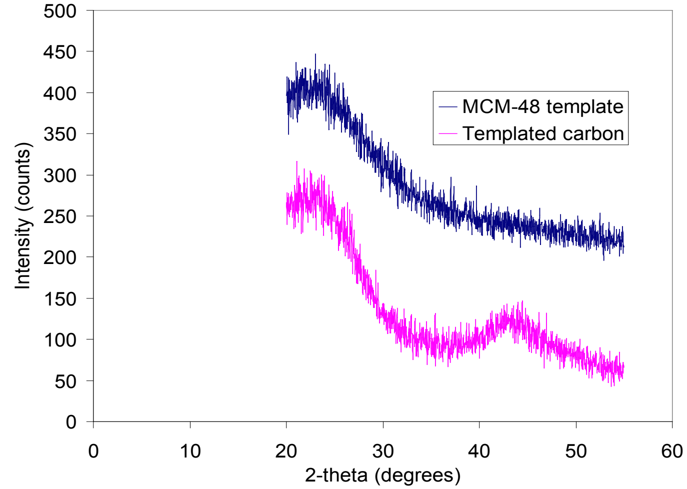




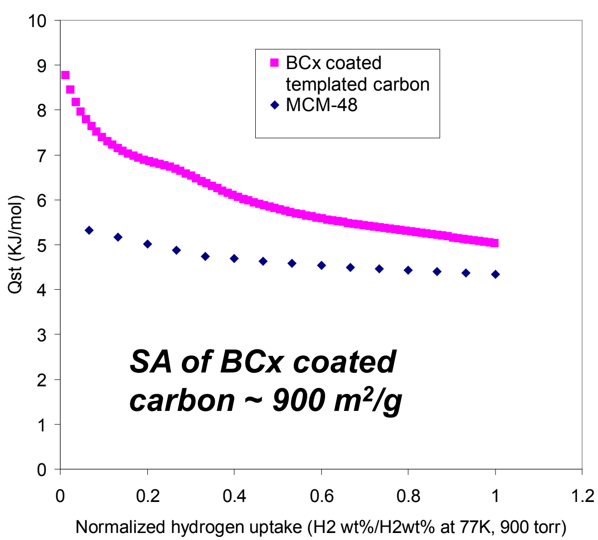
- ***BC_x deposition showed slight increase in the heat of adsorption of microporous carbons, however the uptake is limited due to micropore clogging***
- ***BC_x deposition on mesoporous carbon accomplished without significant pore clogging and accessible surface area of 800 m^2/g***
- ***Studies underway to measure the effect on hydrogen adsorption on mesoporous activated carbons***

BC_x on MCM-48 templated carbons

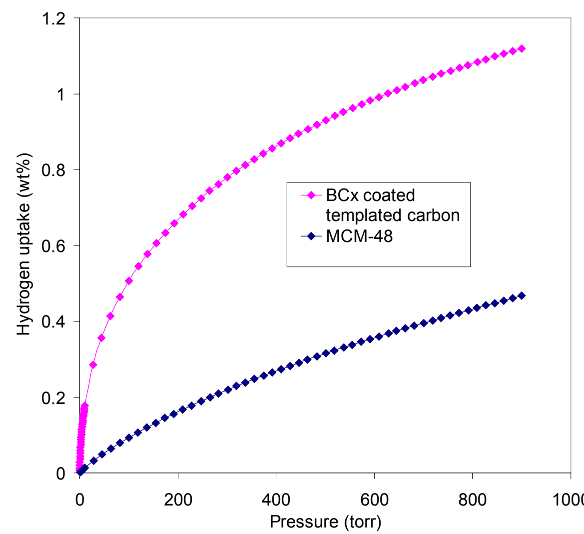




XRD of synthesized templated carbons show long range ordering of mesopores as seen from the presence of peaks at 1.6º and 2.7º respectively



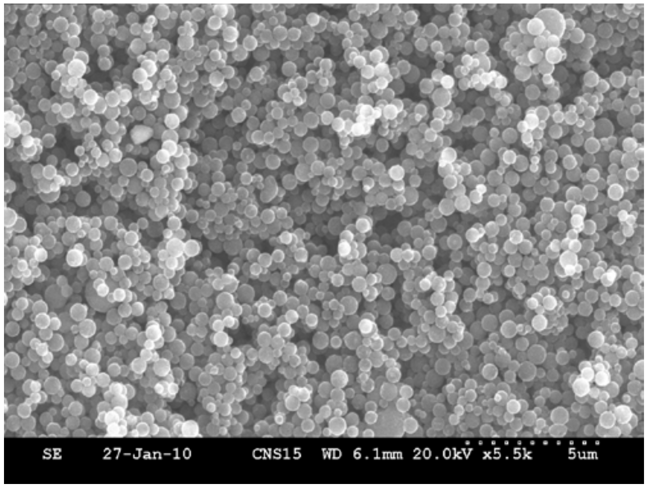
SA of BCx coated carbon ~ 900 m^2/g

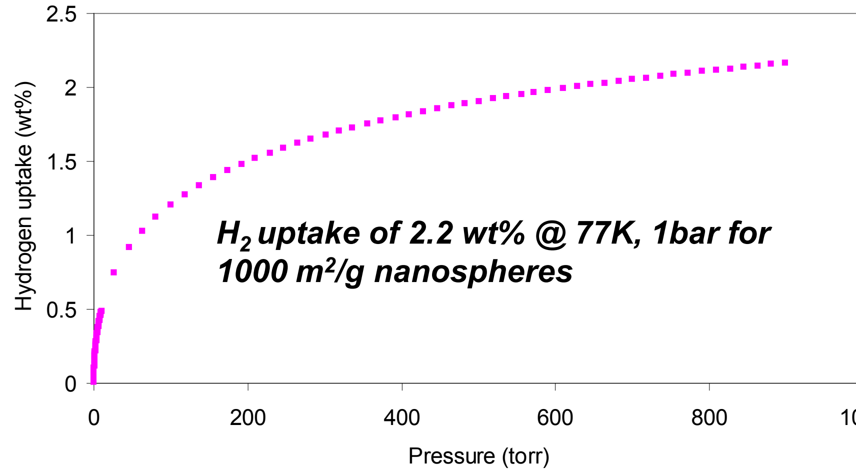


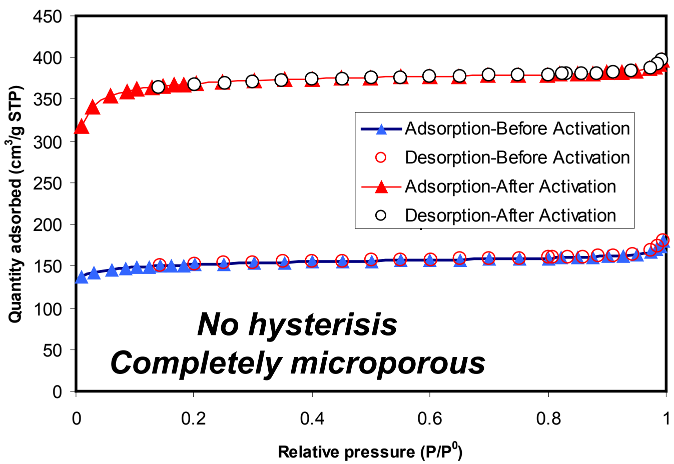
All H_2 adsorption measurements done at 77K, 1bar

➢ ***Initial Heat of adsorption almost doubled with BC_x coated templated carbon as compared to MCM-48 template***

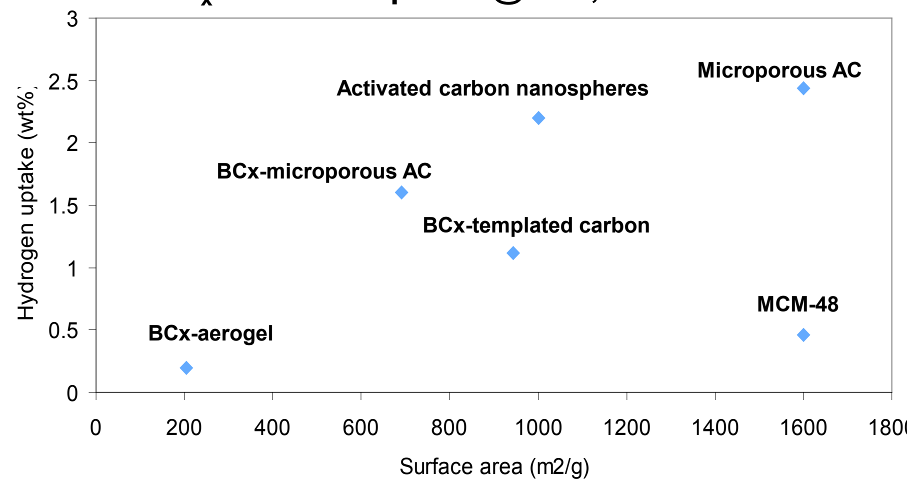
Carbon nanosphere templates







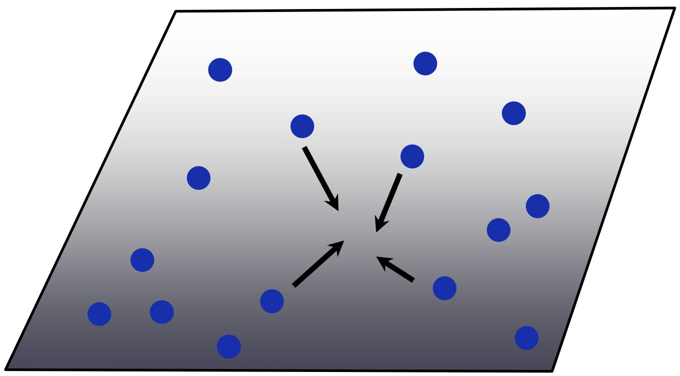
Hydrogen adsorption capacity for various BC_x coated templates @ 77K, 1bar



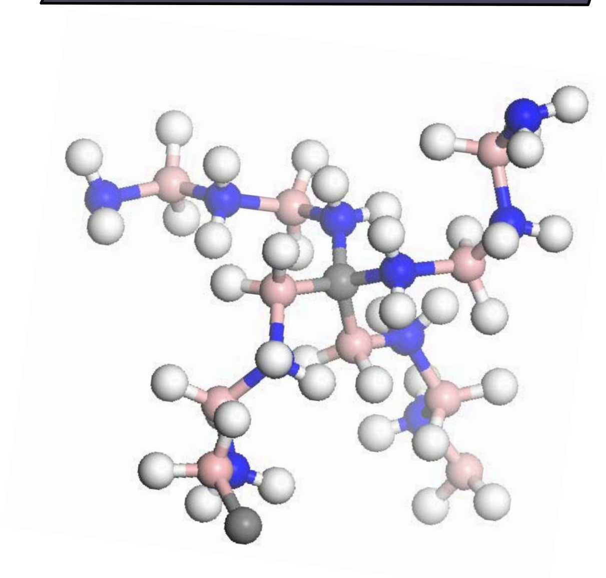
- ***Carbon nanospheres in the order of 500 nm in diameter with large extrinsic surface area was synthesized***
- ***Activated carbon nanospheres with large extrinsic surface area show initial hydrogen heat of adsorption of ~ 10 KJ/mol***
- ***Currently exploring the use of these carbons as templates for BC_x deposition***

Theory: Metal dispersion & New frameworks

When metals are dispersed onto BC_x sheets, they preferentially stick to the B-rich regions. Using percolation theory and first-principles calculations, we have estimated the activation barrier against metal atom aggregation across a range of B concentrations. (At the higher B concentrations, the metal is actually thermodynamically stable against aggregation).



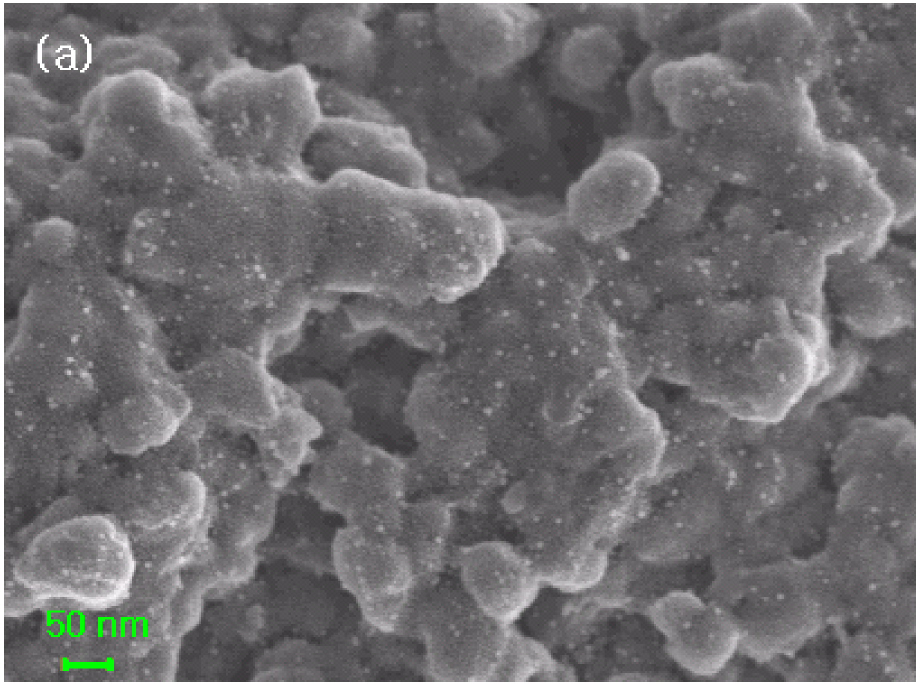
B concentration	Barrier against Ti aggregation
5%	3.8 eV
10%	2.4 eV
20%	1.3 eV



In additional work, we have demonstrated that novel BN-based *framework* compounds can reversibly release H_2 without irreversible collapse into a BN end-state.

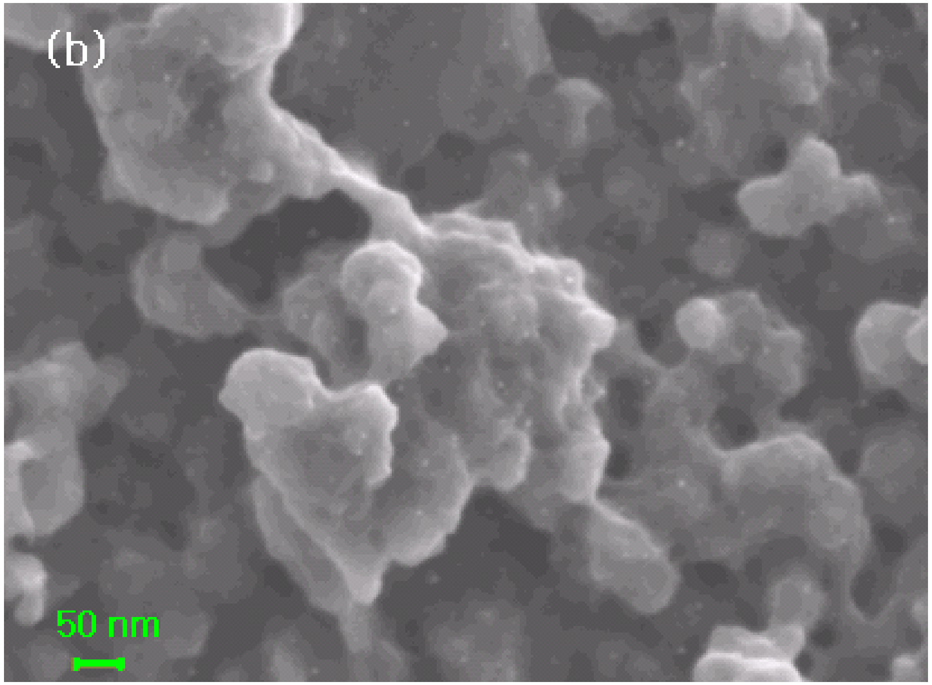
Metal nanoparticles decorated BC_x (FE-SEM Micrographs)

Pd/BC_{12} (Pd: 1.65 wt%)



SSA: 650 m^2/g

Pt/BC_{12} (Pt: 0.7 wt%)



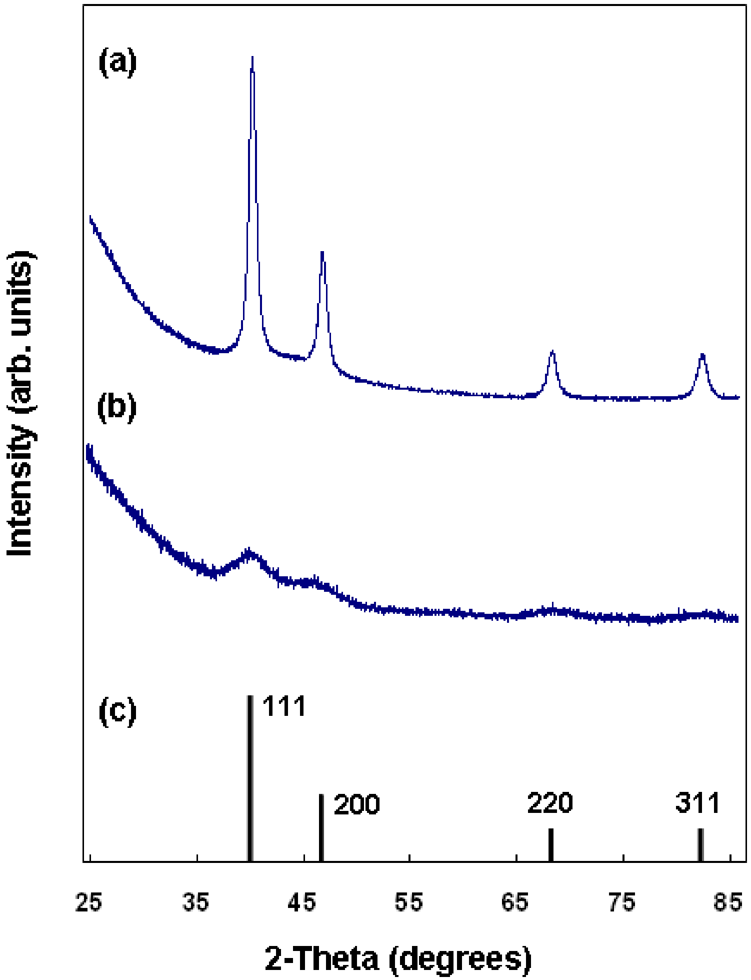
SSA: 644 m^2/g

(Starting BC_{12}: 650 m^2/g)

Nano Letters (submitted)

Comparison of Pt/C and Pt/BC_x

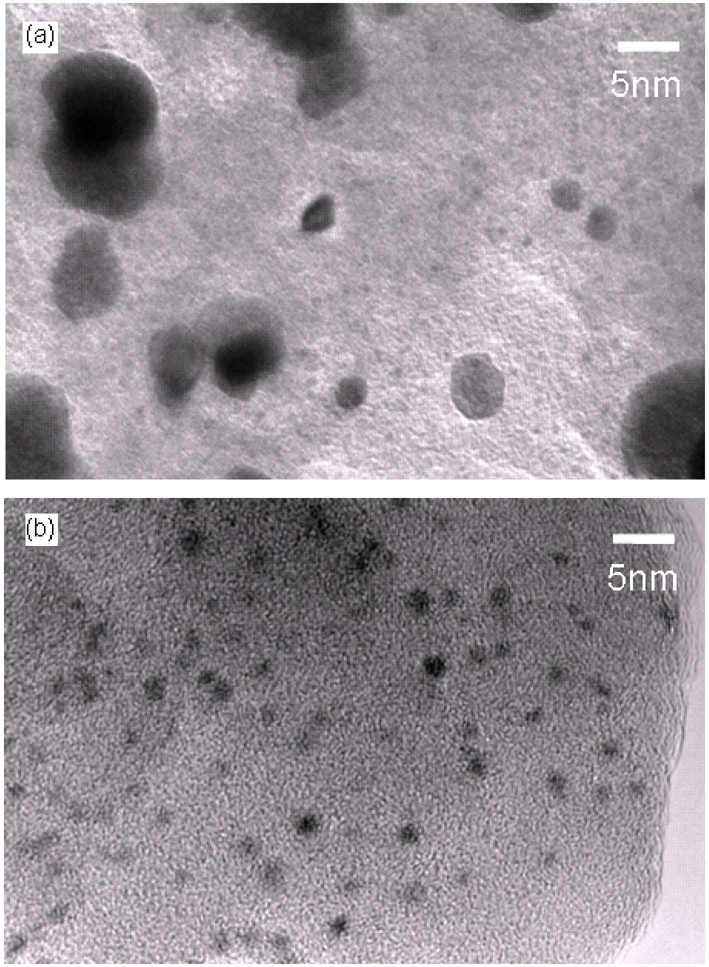
XRD



TEM

(a)
Pt/C

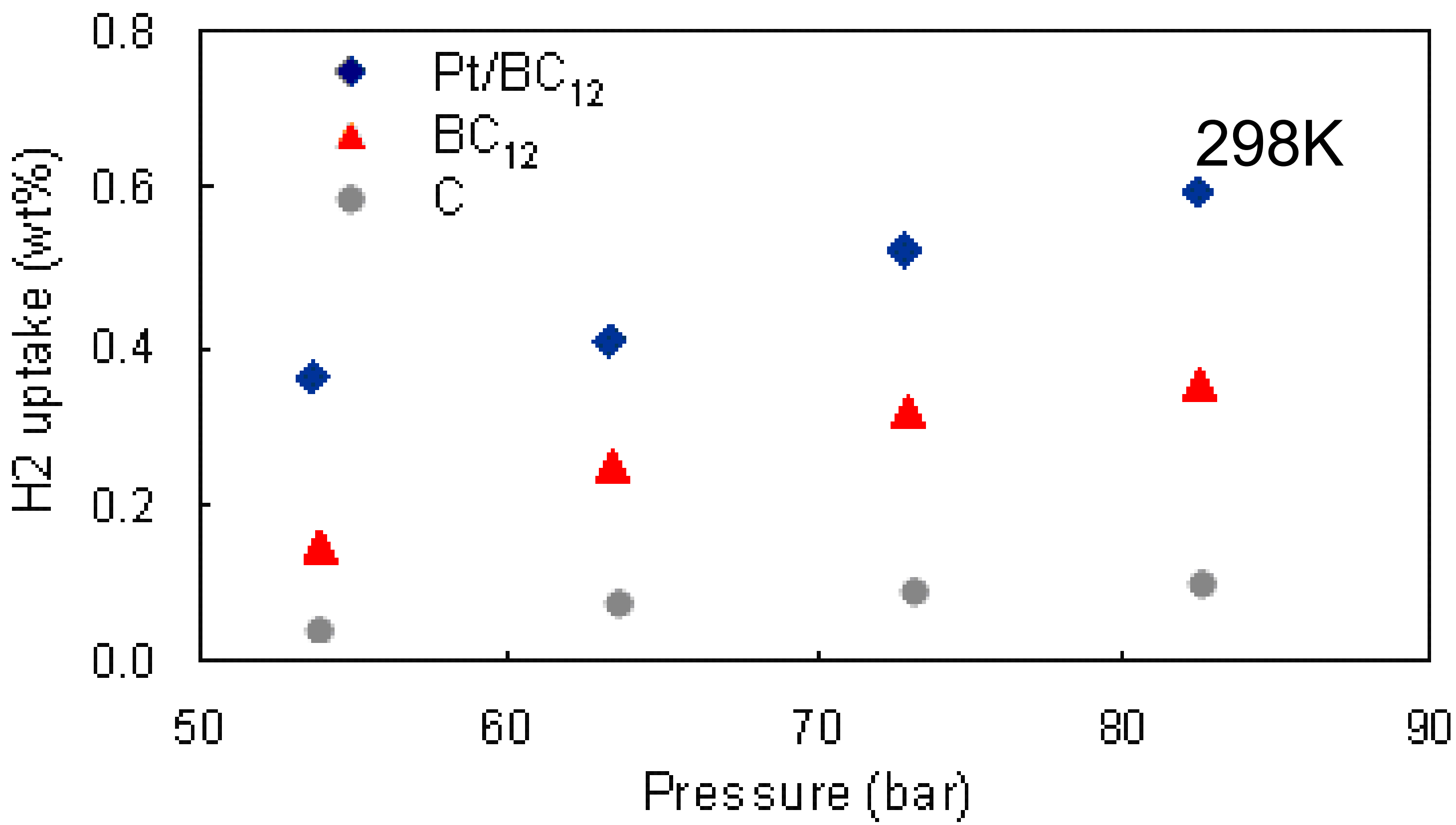
(b)
Pt/BC_x



> ➢ ***Platinum nanoparticles were better dispersed on BC_x support as compared to carbon support of similar surface area***

Comparison of Hydrogen adsorption Pt-BC_{12} (0.7 wt% Pt), BC_{12} and C

(SSA=650 m^2/g)



➢ ***Evidence of increased hydrogen adsorption capacity on Pt/BC_{12} as compared to BC_{12} and porous carbon of similar surface area***

Future Work

Plan for the rest of FY10

- ***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) using templated approach, which could further increase H_2 storage capacity at ambient temperature

- ***Probe the interaction of hydrogen with BC_x materials***

  Characterize interaction of hydrogen with BC_x coated carbons using DRIFTS and NMR

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:**
  - Developed new synthetic approaches to deposit BC_x films with 16 at% boron content onto high surface area supports
  - Showed increased heat of adsorption for BC_x coated templates
  - Theory work predicted better metal dispersion on BC_x material with high boron content
  - Pt/BC_{12} with SSA=650 m^2/g has increased hydrogen adsorption capacity of 0.6wt% at 298K, 85 bar as compared to BC_{12}
  - Studying interaction of hydrogen with BC_x using spectroscopic techniques