

Preparation and Characterization of High Surface Area BC_x Coated Carbon

Ali Qajar, BillyPaul M. Holbrook, Ramakrishnan Rajagopalan and Henry C. Foley

Department of Chemical Engineering, PennState University, State College, PA 16802

Introduction

Boron substituted carbon, BC_x , synthesized by chemical vapor deposition process has a turbostratic morphology with as high as 25% boron content [1]. The exact structure of BC_x is still largely debated. Depending on how boron is incorporated in carbon, intercalated or substituted, the boron content of final product might be different [2-3]. The accepted hypothesis is that boron can be substitutionally incorporated in carbon up to 16 at%. The presence of electron deficient boron in the carbon framework alters the electronic structure of carbon and increases the electrostatic interaction of molecules such as hydrogen. Experimental and theoretical studies show that incorporation of boron in high surface area carbon adsorbents enhances hydrogen uptake [4-5].

In this work, we have uniformly deposited BC_x thin films on high surface area supports such as mesoporous silica and activated carbon. The deposited films were characterized by several spectroscopic methods such as ^{11}B solid state MAS-NMR, XRD, and XPS to show the presence of substitutional boron in these materials.

Experimental

A schematic of the CVD reactor used for BC_x synthesis is given in Fig. 1. Prior to use, benzene (purchased from Sigma Aldrich, Inc.) was purged by UHP Ar for an hour. BCl_3 was used without further purification. A furnace setup with temperature controller was used as the reactor. UHP He was bubbled through the benzene flask and the flow of benzene and BCl_3 was controlled by a mass flow controller. Prior to each run, the reactor was purged by UHP He for at least 4 hrs. Then it was preheated to $900^\circ C$ for an hour; and then the reactant gases were introduced to the reactor at specified flow rates. The BC_x films were deposited on the sample as well as the walls of the reactor chamber. The gaseous by product, HCl, was neutralized by passing through a soda-lime solution. All of the reactions were done at $900^\circ C$, for 30 min. The BCl_3 flow rate was 24 ml/min and the benzene flow rate was 14 ml/min.

Silica aerogel and microporous carbon were selected to be used as substrates coated by BC_x films at $900^\circ C$. Microporous carbon was made in our lab by pyrolysis of polyfurfuryl alcohol as the precursor at $900^\circ C$ and activated at $900^\circ C$ by using CO_2 activation. Details of the process are explained elsewhere [6]. The microporous carbon provides surface area of $1500\text{ m}^2/\text{g}$ and a narrow pore size distribution of about 8 \AA [6].

X-Ray diffraction patterns were collected using a Scintag PADV theta-2-theta powder diffractometer. Radiation source was $Cu\ K\alpha$ with a step size of $0.02^\circ 2\theta$ and wave length of 1.5412 \AA . X-ray photoelectron spectroscopy (XPS) data were collected monochromatic $Al\ K\alpha$ source. ^{11}B solid state MAS-NMR was performed on a Varian Inova spectrometer operating at 300 MHz, observation frequency of ^{11}B . Boric acid was used as the reference material.

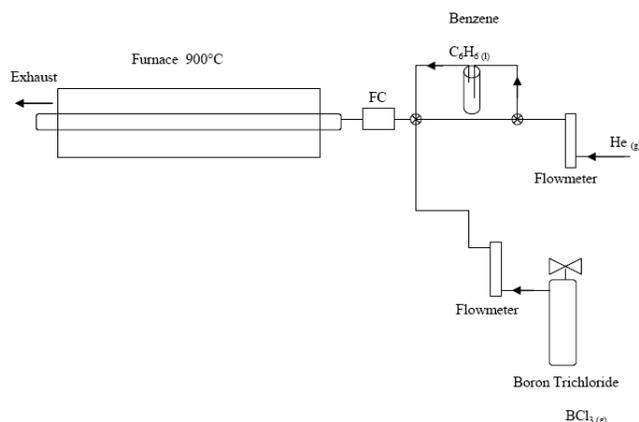


Figure. 1 Schematic of the CVD reactor used for BC_x synthesis

Results and Discussion

^{11}B Solid State MAS-NMR and XPS was used to measure the boron content and probe the state of boron in the deposited BC_x film. The results indicate the presence of 15 – 17 atomic% boron in the synthesized samples. Additionally, boron was in the trigonal configuration as indicated by a downfield shift in the NMR peak to 32 ppm. By incorporating boron into the framework, the repulsive interactions between the sheets were reduced by a global lowering of π electrons as well as Poisson contraction along the c -axis resulting in smaller lattice spacing. The material can further be considered non-porous for practical purposes due to similar lattice spacing as graphite. For this material to be used as an adsorbent it must be either synthesized with pores, modified to incorporate porosity or be used as a coating on a highly porous support.

Table 1: Boron concentration in BC_x determined by XPS, NMR and d-lattice spacing by TEM and XRD

B Concentration		B:C Ratio		d_{002} Lattice Spacing (nm)	
XPS ¹	^{11}B NMR ²	XPS	^{11}B NMR ³	XRD	TEM
17	15.9	1:3	1:4.6	0.36	0.34

BC_x was then deposited on high surface area mesoporous silica aerogel (~750 m²/g) for various periods of deposition time. ¹¹B Solid State NMR was used to determine the coordination of boron in the material. In contrast to the bulk BC_x, the BC_x coated aerogel composed of two nonequivalent sites as indicated by well resolved peaks centered at ~11 ppm and ~27 ppm, respectively. The results indicate that the BC_x coated aerogel may undergo a partial conformation change from trigonal to tetrahedral coordination. Moreover, the boron nucleus is sensitive to the local electronic environment in which it resides. For nuclei experiencing a nonzero quadrupole moment or some other underlying anisotropy, there can also be a change in the symmetry of the peak or in the peak width. Although aerogel have very large pores to start with, it was concluded that the pores begin to collapse quickly at 900°C. After only 15 minutes, the surface area had dropped by almost half and by one hour, the surface area was reduced to 90 m²/g. Hydrogen adsorption studies showed that there was an optimum deposition time for achieving the highest initial heat of adsorption of 11 KJ/mol. The heat of adsorption of BC_x coated aerogels was consistently higher than the pure silica aerogel (~4KJ/mol). The optimum deposition conditions are simultaneously influenced by the collapsing of pores in the aerogel as well as the deposition of BC_x.

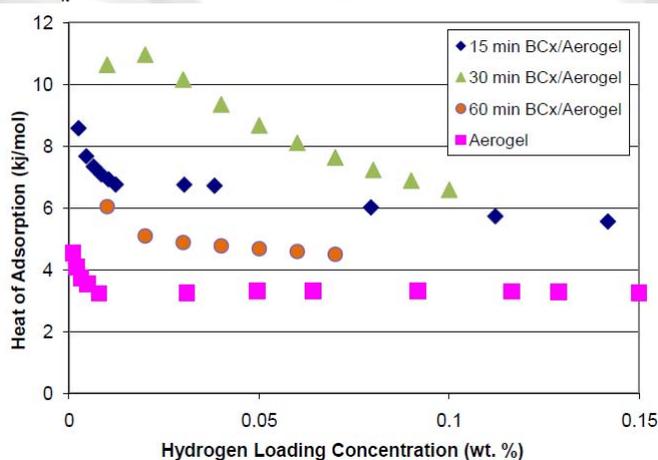


Figure 2: Hydrogen heat of adsorption for different BC_x/Aerogel samples

To overcome the problems associated with pore collapsing, high surface area activated carbons were used as templates. The initial heat of hydrogen adsorption was almost ~ 12 KJ/mol. However, there were issues related to micropore clogging of the samples. Under optimized conditions, hydrogen storage capacity of 1.6wt% @ 77K, 1 bar was achieved. Further study on mesoporous carbon templates are being carried out. Table 2 summarizes the results of the preliminary studies.

Table 2: Hydrogen uptake on different templates

Sample	SSA (m ² /g)	Initial heat of adsorption (KJ/mol)	Hydrogen uptake (wt%) @ 77K, 1bar
BC _x coated aerogel	200	11	0.2
BC _x coated activated microporous carbon	780	9	1.6
BC _x coated mesoporous templated carbons	900	8.8	1.1

Conclusions

BC_x was synthesized by CVD process and coated on high surface area templates. Our initial studies show that the coated carbons can have heat of adsorption of almost ~11 – 12 KJ/mol. However, there are limitations on the overall hydrogen adsorption capacity due to decrease in surface area owing to pore collapse or pore clogging issues. Templated approach could ideally provide an excellent method to make hydrogen adsorbents with high binding energies.

Acknowledgment. The authors acknowledge US Department of Energy and the Hydrogen Sorption Center of Excellence (DE-FC36-05GO15077).

References

- [1] Shirasaki T., et al., Synthesis and characterization of boron-substituted carbons. *Carbon* 2000, 36(10): 1461-1467
- [2] Burgess J. S., et al., Boron-doped carbon powders formed at 1000C and one atmosphere. *Carbon*, 2008 46(13): 1711-1717
- [3] Hyshiyama, Y., Inagaki M., Lattice parameter changes in graphite with boron doping, *Carbon*, 2001, 39(1): 137-158
- [4] Chung T.C.M., et al., Synthesis of microporous boron-substituted carbon (B/C) materials using polymeric precursors for hydrogen physisorption, *Journal of American Chemical Society*, 2008, 130(21): 6668-6669
- [5] Wu X., Radovich L.R., Ab Initio Molecular Orbital Study on the Electronic Structures and Reactivity of Boron-Substituted Carbon, *Journal of Physical Chemistry A*, 2004, 108(42): 9180-9187
- [6] Burket C. L., Rajagopalan R., Foley H. C., Overcoming the barrier to graphitization in a polymer-derived nanoporous carbon, *Carbon*, 2008, 46(13):501-510