The Pennsylvania State University
The Graduate School
Department of Materials Science and Engineering

SUPER ACTIVATED CARBON CONTAINING SUBSTITUTIONAL BORON:
SYNTHESIS, CHARACTERIZATION AND APPLICATIONS
IN HYDROGEN STORAGE

A Dissertation in
Materials Science and Engineering

by
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**ABSTRACT**

Boron substituted carbon material ($\text{BC}_x$) is a new class of activated carbon that contains substitutional boron homogeneously distributed throughout the entire hexagonal carbon structure with three covalent bonds. The $\text{BC}_x$ produced with porous structures has been suggested as a promising candidate for onboard hydrogen storage application. Nanoporous $\text{BC}_x$s with varying boron content, surface area, and morphology were synthesized. The chemistry involves a designed boron containing precursor, i.e. poly(diethynylphenylborane chloride) containing in situ formed inorganic salts that serve as the templates for forming the porous morphology. The MAS solid state $^{11}$B NMR were conducted to reveal the boron content and electron delocalization in the fused hexagonal ring structures. Morphologies including pore size and distribution were examined by high resolution TEM, FE-SEM, XRD, and surface area and pore size distribution were examined by nitrogen and carbon dioxide sorption method. One $\text{BC}_{12}$ with 780 m$^2$/g of surface area showed an extended fused hexagonal ring structure with boron puckered curvature. This off-planar boron moiety maintains its high acidity (electron deficiency), due to limited $\pi$ electron delocalization, and serves as an internal p-type dopant for activating $\text{BC}_x$ surfaces that exhibit super-activated interactive properties. Such activation
can enhance both hydrogen binding energy (up to 13 kJ/mole) and adsorption capacity. Additionally, the nanoporous BC$_x$ played a unique role in metal particles dispersion in the BC$_x$ support. The disposed metal compounds are stabilized by the substitutional boron moiety of BC$_x$ support and therefore maintained highly monodisperse and small particles without additional surface stabilizers. This stabilization is due to the interaction between the d orbital of transition metal atom and the p orbital of boron atom on the BC$_x$ surface, which enable a 0.7 wt.% Pt/BC$_{12}$ to show the catalytic activity in the hydrogen physisorption system even with extremely low levels of metal content.
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Chapter 1

Introduction

1.1 Hydrogen Storage System

Hydrogen, as an alternative energy source, is strategically important to minimize our dependency on fossil fuels and to eliminate greenhouse gas emissions because of its non-limited and non-polluting properties. The desire to utilize hydrogen energy has led many advances in hydrogen production, storage, and the fuel cell system. The development of onboard hydrogen storage technology for hydrogen-fueled vehicles is a particular major challenge in realizing hydrogen energy potential.\textsuperscript{1-3} However, currently available hydrogen storage methods including compressed gas, cryogenic liquid, and hydrides (metal hydrides or chemical hydrides), show significant deficiencies and limitations in practical applications. An approach to overcome the drawbacks of those storage methods above is using an absorbent via gas-on-solid physisorption mechanism but practical usage has still failed to reach the DOE goal of: gravimetric capacity $>6$ wt.% of H\textsubscript{2} and volumetric capacity $>45$ g H\textsubscript{2}/L.
1.1.1 Amount of Required Hydrogen Fuel for Onboard Storage.

Primary consideration is given to the volume of the systems needed to store sufficient hydrogen for a vehicle as compared to corresponding conventional internal combustion engine (ICE) vehicles using gasoline. In order to travel 300 miles after fueling, assuming an average energy consumption rate is approximately 0.34 kWh/mile, the required energy would be 102 kWh. Typical voltage to operate each fuel cell is 0.6 V.

\[ E = VIt \]  \hspace{1cm} [1-1]

where \( E \) is electrical energy, \( V \) is potential difference, \( I \) is the current and \( t \) is the time.

From the fact that 102 kWh is 0.6 times \( It \) in Eq. [1-1], \( It \) becomes 170 kAh. From the Faraday’s first law (Eq. [1-2]), the mass of the hydrogen fuel required can be calculated.

\[ m = \frac{M}{zF} It \]  \hspace{1cm} [1-2]

where \( m \) is the mass of hydrogen, \( M \) is the molar mass of hydrogen, \( z \) is number of electrons transferred per ion, and which \( F \) is the Faraday constant of 96,485 C or 96485 A·second or 26.80 A·hour. Therefore 6,343 grams of hydrogen is required for 300 miles of driving using the current fuel cell system.
1.1.2 Comparison of Various Hydrogen Storage Systems

1.1.2.1 Metal Hydrides and Chemical Hydrides

Hydrogen storage using metallic hydrides such as MgH$_2$ and Mg$_2$NiH$_4$ can attain high gravimetric storage densities of 3.6 – 7.7 wt.%; but heating to 235 °C is required to release hydrogen from direct decomposition.\(^5\) Chemical hydrides such as LiBH$_4$ and NaBH$_4$ release even more hydrogen gas (10 - 18 wt.%) than metallic hydrides, however they require relatively high temperature (above 400 °C) due to their strong ionic bond between the metal ion and the borate ion.\(^6\) Although only 2.5 L of internal volume for would be required for Mg$_2$NiH$_4$ to release 6.343 kg of hydrogen gas, through a density of Mg$_2$NiH$_4$, 2,530 kg/m$^3$,\(^7\) a more complex system required to operate at high temperature as well as its own weight probably preclude its use in light-duty vehicles. Moreover, the higher energy required to form metal to hydride bond (Mg$_2$NiH$_4$ $\rightleftharpoons$ Mg$_2$Ni + 2H$_2$) to recover the original hydride after hydrogen gas release from direct decomposition of a hydride should be considered.
1.1.2.2 Cryogenic Liquefied Hydrogen, Compressed Hydrogen Gas and Physical Absorbents

As opposed to hydrides which are used via chemical process, liquefied hydrogen, compressed gas, and physisorbents are utilized through physical processes. Given that the density of liquid hydrogen is 70.8 g/L, the internal volume of liquefied hydrogen would be 90 L, but due to the additional 6 L of shell and liner and 32 L of insulation volume needed to contain in a liquefied hydrogen storage system, the total volume of 128 L. Liquefied hydrogen systems are close to the DOE target if you consider only the volume parameter. However, the cost of using liquid hydrogen as a transportation fuel is currently nearly twice that of gaseous hydrogen, due to the liquefaction process at 20 K, increased fuel transportation costs and the more complex manipulation of the fuel. Table 1.1 show liquefaction energy for hydrogen gas compared to other gases.

Table 1.1. Ideal liquefaction energies for various gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temperature (deg K)</th>
<th>Energy (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>77.8</td>
<td>777</td>
</tr>
<tr>
<td>Methane</td>
<td>111.8</td>
<td>1,147</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>20.4</td>
<td>12,190</td>
</tr>
<tr>
<td>Helium</td>
<td>4.2</td>
<td>8,389</td>
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</tbody>
</table>
Considering a density of compressed hydrogen gas is 23.5 kg/m$^3$ (or g/L) at 5000 psi, 6.343 kg of hydrogen would require a volume of 262 L for the hydrogen gas with 5000 psi of pressure, not including the gas tank and other equipment. The estimated volume of a storage tank affording 5000 psi of pressured gas is 28 L,\textsuperscript{8} therefore the total volume of a storage facility for compressed gas would be 290 L at 5,000 psi. If the volume of hydrogen gas tank at 5,000 psi is 290 L, then at least 15,000 psi of hydrogen gas pressure would be required to satisfy an acceptable volume (less than 100 L) for a hydrogen gas tank for fuel cell vehicles, which is not practical at all.

Storing hydrogen in a physical absorbent such as carbon material provides an intermediate choice between compressed hydrogen and liquid hydrogen. If an absorbent material which has a 6 wt.% of hydrogen capacity is stored in a tank, the internal volume of hydrogen physisorbed on an absorbent might be 148.7 L (assuming density is 1.8 kg/L from an example of amorphous carbon\textsuperscript{10}). When 8.18 L of volume from liner and shell and 32 L of insulation volume are added to this internal volume,\textsuperscript{8} the total volume of physisorbed hydrogen system would be 189 L, which has a greater than 100 L volume advantage over compressed hydrogen gas system.
Figure 1.1 illustrates the volume of the tanks needed to store 6 kg of hydrogen fuel as a compressed gas (5000 psi), as a liquid (20 K), and as adsorbed on a physical adsorbent (with 6 wt.% of hydrogen capacity).

1.2 Materials for Adsorption-based Storage System

The storage of liquid hydrogen by physisorption is an inherently safe and energy efficient method due to its ease and its fast reversible adsorption and desorption kinetics. An important criterion for effective physisorption is a high surface area in which lots of sorption sites are exposed to hydrogen molecules.¹¹
1.2.1 Carbonaceous Materials

Carbon based adsorbent materials such as carbon nanotubes, carbon aerogels, carbon nanofibers, and activated carbons make promising candidates for hydrogen storage materials because they possess low density, chemical stability, diverse structure and pore distribution, and easy control of surface modification. An extensive search of hydrogen uptake by carbon adsorbents was conducted in 1997, but only one of the ten carbon adsorbents tested showed hydrogen adsorption at 200 bar. Significant improvement in hydrogen adsorption capacity was achieved when Orimo et al. (1999) created a porous structure on graphite by mechanical milling to break up its normally crystalline structure. The first report in 1997 of hydrogen adsorption using carbon nanotubes revealed that single-walled carbon nanotubes (SWCNTs) can store 5 to 10 wt.% of hydrogen at ambient temperature. This result stimulated conducting active research on graphite nanofibers, multi-walled carbon nanotubes (MWCNTs) and nanostructured graphite (NSG). Furthermore, several references reported that carbon nanotubes and nanofibers exhibited a high hydrogen storage capacity. This brightened the prospects of carbon nanomaterials for hydrogen storage until some theoretical approaches used to interpret that those experimental results did not confirm the large
uptake reported for SWCNTs and nanofibers and, additionally, other researchers were not able to reproduce previous results. The large discrepancies in storage capacities can be attributed not only to experimental errors in initial measurement of hydrogen uptake but to incomprehension of the specific surface areas of the absorbents. Once the relationship between the conflicting hydrogen capacity data and various carbon materials was illuminated through systematic experiments and calculations, most of the research accomplished thereafter was centered on producing high surface area. Traditional methods to produce porous carbons were studied such as chemical or physical activation, carbonization of polymer blends composed of a carbonizable polymer and a pyrolyzable polymer, carbonization of a polymer aerogel, and templated process.

Higher storage capacity can be obtained by lowering the temperature according to the basic gas adsorption kinetics, in which adsorption rate relies on temperature with the function of \( e^{-\frac{\Delta E}{RT}} \). The hydrogen uptakes of SWCNTs, activated carbons, and activated carbonized aerogels with various specific surface areas were measured at cryogenic temperature (77 K) under high pressure (up to 70 atm). The specific surface area is related well with the hydrogen gravimetric storage capacity of about 1 wt.\% H\(_2\) per 500
m²/g surface area, independently of the nature or shape of the carbon materials and regardless if a carbon material was modified with the metal incorporation (Figure 1.2 and Figure 1.3).

Figure 1.2. Relation between hydrogen storage capacities of the different carbon samples at 77 K and their specific surface area. The slope of the fit is 1.91x10⁻³ wt.% / m² g.⁴⁰
Figure 1.3. Excess gravimetric density (H₂ wt.%) saturation value at 77 K as a function of BET surface area. The line is 1 mass % sorption per 500 m²/g, converted to wt.%.  

1.2.2 Non-Carbonaceous Materials

Only limited experimentation has focused on the hydrogen adsorption of non-carbonaceous materials such as zeolites and boron-nitride (BN) nanotubes. While hydrogen capacity in zeolites looked strongly dependent upon exchanged cation type, systematic summarized data indicated hydrogen uptake at 77 K was linearly dependent on the BET surface area of zeolites. A slope of 1 wt.% H₂ per 500 m²/g surface area at 77 K and 20 bar of pressure was achieved, no matter what type of zeolite was used in carbonaceous materials (Figure 1.4). Meanwhile BN nanotubes with high surface area also showed significantly high hydrogen capacity at ambient temperature although
conventional BN nanotubes didn’t effect hydrogen adsorption much. This research indicates that the desirable hydrogen absorbent should have high surface area regardless of whether the materials are carbonaceous or non-carbonaceous.

Figure 1.4. Correlation between hydrogen adsorption at 77 K and BET surface area for a series of zeolite materials.

1.3 Binding Energy of Hydrogen

As shown in Section 1.2, high surface area is a key issue to achieve efficient physisorption based hydrogen storage. However, a chief problem is that effective hydrogen physisorption even with a high surface area of carbon material requires its
operation at cryogenic temperature due to a weak binding energy between adsorbate
(hydrogen molecule) and adsorbent material (carbon atom). Typically, hydrogen retains
its molecular form and binds only weakly with a carbon surface via van der Waals
interactions.\textsuperscript{44} Another thermodynamic consideration (density functional theory)
validated that the binding energy of hydrogen molecule on a carbon atom in a graphene
layer ranged 4.2 to 7.2 kJ/mole.\textsuperscript{45} Since adsorption experiments indicate the associated
isosteric heat of adsorption of hydrogen onto graphene surface was 4 kJ/mole,\textsuperscript{46} the
hydrogen adsorption is directly affected by the binding energy between hydrogen
molecule and carbon surface in carbonaceous materials. Moreover, it would seem that the
slope in the linear relationship (in Figure 1.2 and Figure 1.3) should be relevant to the
binding energy. Accordingly, the constant slope shown in all carbon hydrogen uptakes
indicates that the binding energy between hydrogen molecule and carbon surface is a
certain value irrespective of the nature of carbon materials (the van der Waals
interaction).

Enhanced binding energy can be a solution to achieve effective on-board storage
application. For instance, adsorbed natural gas storage system using an activated carbon
can be operated at room temperature due to its higher binding energy while typical
hydrogen physisorbent system requires cryogenic temperature. Binding energy of methane to porous carbon materials was provided by both experimental and theoretical ways. Isosteric heat of adsorption\textsuperscript{47} and NMR\textsuperscript{48} measurements demonstrated that binding energy ranged from 10.1 to 18.2 kJ/mole and a thermodynamic calculation resulted 22.7 kJ/mol.\textsuperscript{49} Therefore, experimental and thermodynamic considerations indicate that the hydrogen binding energy of 10-25 kJ/mol should be achieved in order for ambient temperature operation under moderate pressure.

One approach to increase binding energy of hydrogen is functionalization of carbon surface. Activated carbon is a form of carbon with a large surface area and a surface functionality which usually includes a combination of several oxygen functional groups, such as carboxylic acid, phenol, quinone, lactone, anhydride, and cyclic peroxide,\textsuperscript{50,51} as illustrated in Figure 1.5. Unfortunately, the isosteric heat of adsorption from oxygen functionalized carbons and nitrogen functionalized carbons has been demonstrated to be 4-7 kJ/mol,\textsuperscript{52} which is typically the value found in a graphene structure.\textsuperscript{46} It is known that the surface functionality of the activated carbon is located only on the edge area of the carbon planar structure due to the stable carbon hexagonal framework as illustrated in Figure 1.5 and Figure 1.6. Even though activation of
amorphous carbon increases disordered structures and provides more edge area resulting in a large propensity for oxygen functionalities, it is not enough to enhance the binding energy because the desired heteroatom functions are not homogeneously distributed throughout the entire carbon structure.

Figure 1.5. Molecular structure of oxygen functionalized activated carbon.\textsuperscript{50}

Enhanced binding energy would be feasible if the functional groups or dopants are placed in the same phase with carbon surfaces and distributed homogeneously, which
might induce polarization of carbon surfaces. Boron has unique properties that are noteworthy for this application. First, based on the atomic size, boron may be the only element that can be effectively substituted in the hexagonal carbon structure without significantly distorting its planar structure. Second, acidic boron, which has an electron deficiency, should engage in electron delocalization in the fused ring structures and serve as a p-type dopant (internal) to effectively activate the entire surface area for interaction or adsorption of hydrogen molecule. Therefore, it can be predicted that hydrogen binding to the boron site results in an H-H bond elongation and a partial charge transfer from the occupied $H_2 \sigma$ orbital to the empty $p_z$ orbital of boron, leading to an enhancement of hydrogen physisorption.

Theoretical works validated enhancement of binding energy due to the substitutional doping with nitrogen,$^{54, 55}$ boron,$^{54, 56}$ and other elements.$^{57-59}$ Compared to a substitutional dopant which is fused in hexagonal carbon ring structure, an endohedral dopant which is located at edge area of a carbon surface doesn’t show significant interaction energy. The most prominent increase in binding energy was obtained in the substitutional doping of boron to fullerene $C_{36}$, $C_{54}$, and carbon nanotubes, which were quantified at approximately 20 kJ/mole within the ideal range (10-25 kJ/mole) for
ambient temperature $\text{H}_2$ adsorption. In contrast nitrogen substituted fullerene ($\text{C}_{36}\text{N}$) with a hydrogen molecule showed lower binding energy than in a non-substituted fullerene-$\text{H}_2$ system.

In conclusion, the desirable hydrogen absorbent requires enhancement in binding energy which can be achieved by boron substitution in carbon hexagon ring structure. A strongly localized, empty $p_z$ orbital of a boron atom is essential for the enhanced interaction with an occupied $\sigma$ orbital of hydrogen molecule. This leads to a partial charge transfer from the hydrogen molecule to the boron substituted carbon (see $\text{BC}_x$ in Figure 1.7).

![Figure 1.7. Molecular structure of boron substituted carbon ($\text{BC}_x$).](image_url)

**1.4 Boron Substituted Carbon Materials ($\text{BC}_x$)**

In some early reports, there have been discussions on boron substitution in the graphitic carbon by doping graphite with boron-containing inorganic chemicals, such as
boron powder, boron carbide, boron nitride, etc., via solid state diffusion under very high temperature. Typically, the doping of well-ordered crystalline graphite is difficult. The substitution usually requires the presence of vacancies in the graphite. Several researchers reported that inhomogeneous distribution arises during the doping process because boron preferentially enters into the most disordered regions of the carbon.\textsuperscript{63, 64} Lowell determined that the solid solubility of boron in carbon approached a maximum value of 2.35 mol\% at 2350 °C, which was believed to be the thermodynamic limit.\textsuperscript{60} More recently, a similar post-carbonization process—with the aids of high energy sources (such as arc and laser)—has been applied to boron doping in new, well-defined carbon structures, including fullerene\textsuperscript{65} and nanotubes.\textsuperscript{66-70} However, when boron components from boron doped SWCNTs were analyzed systematically by Gai \textit{et al.} (2004),\textsuperscript{69} it was shown that the majority of boron was found to be not homogeneous boron substitution, but uniform mixture of $\text{B}_4\text{C}$ and $\text{B}_2\text{O}_3$ particles in the carbon matrix. Generally, this high temperature post-carbonization process produces inhomogeneous products that contain either very high boron content (such as a stable $\text{B}_4\text{C}$ structure) or very low boron content (<3 wt.\%) in the graphitic structure.
On the other hand, there are a few reports\textsuperscript{71-73} reporting the preparation of BC\textsubscript{x} material by the chemical vapor deposition (CVD) process using organic precursors. Kouvetakis \textit{et al.} (1986) reported the preparation of graphite-like BC\textsubscript{3} (~25 wt.% of boron content) via the chemical vapor reaction between BCl\textsubscript{3} and benzene at 800 °C.\textsuperscript{71} Another report\textsuperscript{72} showed depositing a thin film of BC\textsubscript{3} on the C surface improves its oxidative stability. Evidently, BC\textsubscript{3} is an inert material because the graphite-like structure with excellent electron delocalization, may completely neutralize boron acidity. Satishkumar, \textit{et al.} (1999) used a C\textsubscript{2}H\textsubscript{2}-B\textsubscript{2}H\textsubscript{6} reagent and a similar CVD process with the presence of cobalt nanoparticles to prepare boron-carbon nanotubes, which showed local graphitic layer structure with an average C\textsubscript{35}B composition of < 3 mol% of boron content.\textsuperscript{74} Overall, both the solid state diffusion process (using inorganic precursors) and the CVD process (using organic gases) will prepare either stable B\textsubscript{4}C and BC\textsubscript{3} with very high boron content (>25 mol%) or the B-substituted graphite with <3 mol% boron content, or a mixture of both.

In the past decade, we have been studying a facile precursor/pyrolysis method\textsuperscript{75-78} to prepare BC\textsubscript{x} materials, with the objective of expanding its compositions and microstructures. The chemistry involves the designed organic precursors containing
boron moieties, such as 9-chloroborafluorene (9-CBF), which are favorable in thermo-transformation to form the fused ring structure containing substitutional boron atoms.\textsuperscript{75} By controlling the pyrolysis temperature, the precursors slowly evolve into BC\textsubscript{x} with various boron contents and microstructures, from amorphous to highly crystalline materials. Therefore maintaining a relative low temperature compared to the arc or laser treatment and the CVD process mentioned above, can be a good strategy to achieve BC\textsubscript{x} with desirable boron contents for hydrogen adsorption. However, all the resulting structures from both the low temperature approach via precursor synthesis as well as from the high temperature approach utilizing the arc, laser, or CVD processes are well-ordered structures with very low surface areas, which are not suitable for hydrogen physisorption.

As mentioned in an earlier section, a porous structure with high surface area is essential for hydrogen adsorption.\textsuperscript{32, 40} Templated process\textsuperscript{34-39} is one of the methods to produce porous carbon structures and it requires the carbonization of the mixture of carbon precursors and inorganic templates such as zeolites of porous aluminas, followed by removing inorganic templates using hydrofluoric acid. Regardless, it is hard to remove the inorganic templates completely using hydrofluoric acid because zeolites or aluminas
hardly dissolve in general solvents, even hydrofluoric acid. An advanced synthetic method would come out to produce porous carbon structures with interactive boron moieties, when the idea of designing organic precursor containing boron moieties and the templated method with better template which dissolves in solvent such as water combine.

1.5 Conclusions

Hydrogen storage is a major challenge in realizing hydrogen energy. Physisorption would be an ideal method if the adsorbent material could show sufficient adsorption capacity at ambient temperature and moderate pressure, and perform fast adsorption-desorption kinetics at convenient conditions. The effective physisorption of hydrogen requires high surface area of adsorbents and an optimum binding energy of 10 – 25 kJ/mole). BC\textsubscript{x} material with high surface area is promising candidate because the boron moiety maintains its high acidity (electron deficiency), and serves as an internal p-type dopant for activating BC\textsubscript{x} surfaces. In conclusion, new synthetic strategies should be developed to make the ideal structure feasible for hydrogen storage applications.
Chapter 2
Synthesis and Characterizations of Nano-Porous BC\textsubscript{x}
via Polymeric Precursors and Inorganic Templates Approach

2.1 Introduction

In Chapter 1, boron substituted carbon material (BC\textsubscript{x}) was suggested as a promising candidate for onboard hydrogen storage application. Theoretical results\textsuperscript{54, 56} demonstrated that enhancement in binding energy can be achieved by boron substitution in carbon hexagon ring structure. Experimental efforts in our group revealed that formation of boron substituted carbon structures could be realized by pyrolysis of designed organic precursors containing boron moieties (Figure 2.1)\textsuperscript{75-78}.

![Figure 2.1](image-url)  
(a)  
(b)

Figure 2.1. Structures of boron containing organic precursor of (a) 9-chloro-borafluorene\textsuperscript{75} (b) dichloro(phenylacetylide)borane.\textsuperscript{77}
With a boron-conjugated \( \pi \) electrons delocalized structure, most of the boron elements in the precursor were incorporated by substitution into the carbon during the carbonization process. As a preliminary experiment, two BC\(_x\) samples are prepared by the carbonization of 9-chloro-borafluorene\(^{75}\) and dichloro(phenylacetylide)borane\(^{77}\) at 800 °C to examine the feasibility of the application of BC\(_x\)s for onboard hydrogen storage. The resulting BC\(_x\) materials, however, showed dense morphology with extremely low surface area (3.1 m\(^2\)/g), which are not suitable as hydrogen storage material. Since a porous structure with high surface area is essential for hydrogen adsorption\(^{32,40}\), a new synthetic strategy to produce porous structures with interactive boron moieties is required. In this chapter, I will systematically discuss how to prepare various porous BC\(_x\) materials with controllable molecular structure and morphology, including boron content, boron microstructure (electron-deficiency), and nano/meso porous structures.

### 2.2 Experimental Details

#### 2.2.1 Materials and Instruments

1,4-diethynylbenzene, n-butyl lithium (2.5 M solution in hexanes), sodium borohydride, and boron trichloride (1 M solution in hexane) were purchased from Sigma-Aldrich\(^{\circ}\) and used without further purification. Sodium lump in paraffin oil was
purchased from Sigma-Aldrich® and washed with purified hexane and dried and stored in a glove box. Reagent grade hexane and 1,4-dioxane were purchased from Sigma-Aldrich®, dried over calcium hydride, and then distilled into a Schlenk flask and stored in a glove box.

All solution \(^1\)H and \(^{11}\)B NMR spectra of boron-precursors were recorded on a Bruker AM-300 spectrometer. Quartz NMR tubes were used for the \(^{11}\)B NMR measurements. The typical sample size was 15 mg of polymer dissolved in 0.5ml of deuterated solvent. The internal standard for the \(^{11}\)B NMR was boron trifluoride diethyld etherate which has a chemical shift of 0 ppm. The magic-angle-spinning (MAS) \(^{11}\)B NMR spectroscopy at 9.4 Tesla was used to measure the solid BC\(_x\) materials, determining the boron chemical shifts and boron contents. The composition of BC\(_x\) materials were also determined by prompt gamma ray activation analysis (PGAA) in the NIST neutron facility. During exposure of the sample in a neutron beam, neutrons hit the nuclei in the sample and formed neutron captured compounds. The unstable compounds immediately de-excite and emit a gamma ray (prompt gamma). By analyzing the prompt gamma ray spectra, the sample’s elemental identity and number can be ascertained. Powder X-ray diffraction (XRD) data were collected on a Bruker GADDS three-circle X-ray
diffractometer using Cu Kα (λ = 0.15406 nm) radiation. High resolution transmission electron microscopy (HR-TEM) images were obtained via a bright field TEM micrograph using JEOL JEM-1200 equipment operating at 120 kV. TEM samples were prepared by sonicating the powders in hexane and then dropping a small volume of this onto a copper grid. Scanning Electron Microscopy (SEM) images were acquired using a Topcon International Scientific Instruments ISI-SX-40 with secondary electron imaging, and a Leo 1530 Field Emission Scanning Electron Microscope (FE-SEM). Surface area and pore size distribution were measured with a Micromeritics ASAP 2010 Brunauer-Emmet-Teller (BET) surface analysis instrument using N₂ and CO₂ gases at 77 and 273 K, respectively. Thermogravimetric–mass spectral (TGA-MS) analysis was performed with a TA Instruments TA 2050 attached to a Pfeiffer Thermostar mass spectrometer. TGA measures weight changes in materials as the temperature is increased and simultaneously the Thermostar mass spectrometer provides information about decomposition and volatilization.

### 2.2.2 Synthesis of diethynylphenyldilithium (LiC≡C(C₆H₄)C≡CLi)

In a 250 mL flask, equipped with a magnetic stirrer, 2.52 g (20 mmol) of 1,4-diethynylbenzene and 125 mL of dried hexane were added and mixed under an argon
atmosphere. After cooling the solution to -78 °C, 48 mmol of n-butyllithium (30 mL of a
1.6 M solution in hexane) was slowly added over a period of 30 minutes. A yellow-white
suspension was immediately observed. The mixture was continuously stirred at -78 °C
for 30 minutes before warming up to room temperature. After isolating the yellow-white
solid powder by filtration and washing using fresh hexane three times, the resulting solid
powder was dried under a vacuum overnight to obtain about 2.66 g (yield > 95%) of the
diethynylphenyldilithium product.

2.2.3 Synthesis of diethynylphenyldisodium (NaC≡C(C₆H₄)C≡CNa)

In a 250 mL flask, equipped with a magnetic stirrer and 100 mL of dried 1,4-
dioxane, about 0.5 g of sodium lump was added under an argon atmosphere and heated
up to 100 °C. To the sodium dispersion in 1,4-dioxane, 2.52 g (20 mmol) of 1,4-
diethynylbenzene dissolved in 50 mL of 1,4-dioxane was added and kept at 100 °C for 24
hours. Silver colored liquid sodium dispersed in 1,4-dioxane gradually disappeared and a
dark brown solid precipitated during the reaction. After cooling the suspension to room
temperature, dark brown powder was isolated by filtration and washing using fresh 1,4-
dioxane three times. The resulting solid powder was dried under a vacuum overnight to
obtain about 2.38 g (yield 80%) of the diethynylphenyldisodium product.
2.2.4 Synthesis of Diethynylphenylborane chloride Olgomer (1)

A suspension of 1.38 g of diethynylphenyldilithium (10 mmole) was made in 100 mL of 1,4-dioxane in a 250 mL of air-free flask equipped with a magnetic stirrer. In another air-free flask, 25 mmole of boron trichloride (25 mL of 1 M solution in 1,4-dioxane) was, cooled by placing it in an ice-water bath. Two flasks were connected through a side-arm. The suspension of diethynylphenylldilithium in 1,4-dioxane was added dropwise into the solution of boron trichloride via the side-arm. The off-white suspension rapidly turned brown in color upon the addition of boron trichloride. The reaction was kept cold during the course of the addition and then stirred for an hour. The soluble fraction was isolated by filtration, and ultimately a viscous gel of 67 wt.% (2.50 g) yield was obtained by evaporation of 1,4-dioxane on a vacuum line. Samples were stored in a glove-box under an atmosphere of argon prior to carbonization. Mass spectrometry was performed and the gel yielded 555 of mass per charge which corresponds to the trimer when diethynylphenylborane chloride trimer was exposed to the air and exchanged to two chain-end hydroxyl groups ((OH)\textsubscript{2}B-(C=C(C\textsubscript{6}H\textsubscript{4})C≡C-BCl)\textsubscript{2}-C≡C-(C\textsubscript{6}H\textsubscript{4})-C≡C-B(OH)\textsubscript{2}).
2.2.5 Synthesis of Poly(diethynylphenylborane chloride) containing lithium chloride (2), (3) and sodium borohydride (4)

A suspension of 1.38 g of diethynylphenylidilithium was made in 100mL of hexane in a 250 mL air-free flask equipped with a magnetic stirrer. The flask was cooled by placing it in an ice-water bath, and 12 mmole of boron trichloride (12 mL of 1 M solution in hexane) was added dropwise into the flask from a gastight syringe. The off-white suspension rapidly turned brown in color upon the addition of boron trichloride. The reaction was kept cold with ice (0 °C) during the course of the addition, and then allowed to slowly warm to room temperature. After stirring for an additional hour, the reaction flask was warmed to 80 °C and kept stirring for 6 hours. After cooling down the reactor and removing the solution fraction by filtration, the resulting polymer solid which contained in situ formed lithium chloride salts was isolated and dried by vacuum to obtain a brown solid product (2). The solid sample (2) was stored in a glove-box under an atmosphere of argon prior to carbonization.

About 0.5 g of lithium chloride was added to 2.56 g of the solid sample (2) and the mixture was grounded in a mortar (3). Another 2.56 g of the solid sample (2) was mixed with 0.38 g of sodium borohydride. The solid mixture was also ground in a mortar
(4). All solid samples were stored in a glove-box under an atmosphere of argon prior to carbonization.

2.2.6 Synthesis of Poly(diethynylphenylborane chloride) containing sodium chloride (5)

A suspension of 1.70 g of diethynylphenylkisododium (10 mmole) was made in 100 mL of hexane in a 250 mL air-free flask equipped with a magnetic stirrer. The flask was cooled by placing it in an ice-water bath, and 12 mmole of boron trichloride (12 mL of 1 M solution in hexane) was added dropwise into the flask from a gastight syringe. The reaction was kept cold with ice (0 °C) during the course of the addition, and then allowed to slowly warm to room temperature. After stirring for an additional hour, the reaction flask was warmed to 80 °C and kept stirring for 6 hours. After cooling down the reactor and removing the solution fraction by filtration, the resulting polymer solid which contained in situ formed sodium chloride salts was isolated and dried by vacuum to obtain a dark brown solid product (5). The solid sample (5) was stored in a glove-box under an atmosphere of argon prior to carbonization.
2.2.7 Synthesis of porous BC\textsubscript{x} Materials

A systematic study (Table 2.1) was conducted to evaluate the effect of pyrolysis conditions on the BC\textsubscript{x} materials, especially boron content, boron moieties, and porous structure. Pyrolysis was performed in one step through a Lindberg split-tube furnace by placing poly(diethynylphenylborane chloride) and inorganic mixtures (2), (3), (4), and (5). The sample was loaded in a quartz (or ceramic holder for $>1000$ °C pyrolysis assays) and sealed from exposure to the atmosphere by closing valves at both ends of the quartz tube. After ensuring a positive pressure of argon existed in the quartz tube, the sample was heated in the tube furnace under a flowing stream of argon. The high temperature ($>1000$ °C) pyrolysis reactions were performed in a graphite resistance type furnace manufactured by Centorr Vacuum Technology. The furnace was evacuated to a vacuum of 150 mtorr and then pressurized to 2 psi with ultra high purity argon. This process was repeated twice thereafter to ensure the elimination of air from the furnace before any heating took place. The temperature was increased to about 300 °C at a rate of about 1 °C/min and held there for about 3 hours. After holding at 300 °C, the temperature was increased to about 600 °C at a rate of about 1 °C/min, and then held at 600 °C for about 12 hours. The samples turned into completely black solids after heating at $>550$ °C. The
yield was usually very high (about 80 wt.%), with good boron retention in the resulting \( \text{BC}_x \) product. After water-washing to remove lithium chloride or sodium chloride molecules, porous \( \text{BC}_x \) materials were attained.

### 2.3 Results and Discussion

As discussed in Chapter 1, most of the commercial activated carbons contain oxygen (electron rich atom) functional groups, located on the outer edge areas of carbon planar hexagonal ring structure. Few reports discussed whether the activated carbon with boron (electron deficient atom) moieties could be substitutionally incorporated into the fused ring structure. Regardless, early methods involving high energy processes offer \( \text{BC}_x \) materials with boron content that is either too low (lower than 3 mol\%) or too high (higher than 25 mol\%) through the production of \( \text{BC}_3 \) and \( \text{B}_4\text{C} \) materials, respectively. Both materials show graphite-like (crystalline) structures with good electron delocalization and very low surface area and activity.

Our initial motivation for expanding \( \text{BC}_x \) composition by the boron containing precursor approach was guided by the favorable notion that boron is similar in atomic size as carbon and forms a strong tri-valence bonding structure with carbon. Evidently, boron atom can replace carbon atom in the fused hexagonal rings (Figure 2.2)—either in
amorphous carbon or crystalline graphite—to form BC$_x$ materials with a broad range of boron content and microstructures. Varying the pyrolysis process from a low to high temperature on different templates offers the opportunity to manipulate the BC$_x$ microstructure into amorphous, crystalline, or porous structures. The amorphous BC$_x$ materials, prepared under low pyrolysis temperature, are also predicted to be more adaptable to a wide range of boron content. The small lattice distortion caused by the substituted boron may post no problem in an amorphous carbon that contains many small sizes of disordered planar structures. However, the highly crystalline material prepared at high temperatures has a large planar multi-layer structure and therefore the tolerance for even just a small lattice distortion will be reduced. The boron content can be changed with pyrolysis temperature. Both boron content and microstructure determine the acidity (electron deficiency) of boron moieties in BC$_x$ materials, which can greatly affect their surface activities.
2.3.1 Synthesis of BC\(_x\) Materials

Figure 2.3 illustrates the synthesis scheme in the preparation of porous BC\(_x\) materials, via the designed boron-containing precursors (2) and (5), which contain inorganic pore-forming additives and pyrolysis procedures. By taking into account the chemistry of boron and the mechanism of carbonization, we tailor the boron-precursor molecular structure (I) containing reactive B-Cl and phenylethynyl moieties, and then thermally transform them into the fused hexagonal ring structures with high boron and carbon yields.
The boron-precursor (I) is prepared by a polycondensation reaction between 1,4-diethynylphenyldimetal and BCl₃, which contains two boron species including several in-chain di(phenylethynyl)chloroborane moieties and two chain-end (phenylethynyl) dichloroborane moieties. As expected in the polycondensation reaction, the degree of polymerization is largely controlled by the stoichiometric mole ratio between dimetallized 1,4-diethynylbenzene and BCl₃. A trimer was obtained when a 1 to 2.5 ratio of stiochiometry was used, and the 1 to 1.2 ratio yielded a decamer. The resulting boron-
precursor (I) can be either in viscous gel or solid form, depending on its molecular weight (trimer or decamer). Figure 2.4 shows a solution $^{11}$B NMR spectrum of a boron-precursor oligomer (I) that is soluble in 1,4-dioxane, exhibiting two $^{11}$B chemical shifts peaked at 23 and 29 ppm, corresponding to in-chain and chain-end borane moieties, respectively. Slightly up-field chemical shifts for two boron moieties imply some complexization between the acidic boron and 1,4-dioxane solvent. The relative peak intensity between two chemical shifts provides the mole ratio of two borane moieties: the estimated average polymer molecular weight is about 629 g/mole.
Figure 2.4. Solution $^{11}$B NMR spectrum of poly(diethynylphenylborane chloride) oligomer.
Since the *in situ* formed inorganic salts (LiCl or NaCl) are insoluble in organic solvents (hexane or dioxane), the viscous boron-precursor gel (soluble liquid in solvent) naturally excludes inorganic additives and gradually aggregates to form dense BC$_x$ material, and the pyrolysis process keeps inorganic salts out of the BC$_x$ phase. In contrast, the high molecular weight boron-precursor (insoluble solid) contains some inorganic salts, including the *in situ* formed salts and occasionally the externally added lithium chloride (LiCl) or sodium borohydride (NaBH$_4$). For some comparative studies, both gel and solid forms of the boron-precursor were pyrolized and only the gel boron-precursor produced BC$_x$ without any porous structure. During pyrolysis, the boron-precursor (I) involves a facile thermal transformation to convert to a BC$_x$ fused ring structure and since LiCl or NaCl salts are inert, they serve as the pore-forming templates in producing porous BC$_x$ morphology. The inorganic salt distributions in the BC$_x$ matrix therefore determine the pore structures. Additional LiCl to the boron-precursor as well as *in situ* formed LiCl molecules can provide more pores. On the other hand, the external NaBH$_4$ additives—decomposed at about 600 °C $^{79, 80}$ to form reactive B-H species and Na particles—may serve both as a B content-enhancing agent and a pore-forming template.
Figure 2.5 shows two typical TGA weight loss vs. pyrolysis temperature profiles, including (a) boron-precursor (I) containing *in situ* formed LiCl salts and (b) the resulting porous BC$_x$ material prepared following pyrolysis at 600°C and water-washing to remove all LiCl salts. In boron-precursor (I), the combination of alkynyl and B-Cl moieties is very favorable for inter-polymer reactions at low temperature (<150°C), which should involve chloroboration and cyclization (2$\pi$ + 4$\pi$ electrons). The precursor (I) changes color from brown to dark brown, also increasing molecular mass without losing weight. Both reactions offer an important stabilization step to assure a high pyrolysis yield at high temperatures. Beyond 150°C, the precursor quickly deepens in color with the continuous evolution of HCl gas, which may be related to electrophilic substitutions on aromatic rings involving B-Cl moieties during incorporation of B elements in the fused ring structures. The route by which the boron element gets into the thermally stable cyclized structure is similar to the Friedel-Crafts reaction (Figure 2.6)$^{81}$. A proposed mechanism showing how the boron-precursor (I) transforms into BC$_x$ structure, is presented in Figure 2.7.
Figure 2.5. TGA curves of (a) B-precursor (I) containing *in situ* formed LiCl salts and (b) the resulting porous BC$_x$ material after pyrolysis at 600°C and LiCl removal.
Figure 2.6. Friedel-Crafts alkylation

Figure 2.7. Proposed mechanism of the stabilization and further cyclization of poly(diethynylphenylborane chloride) to form the thermally stable BC\textsubscript{x} structure.
As shown in Figure 2.5(a), following the initial weight loss seen below 800°C—mostly due to loss of the HCl by-product—the weight loss begins to taper off as the temperature rises. At 600 °C, the total weight loss is about 20%, which is close to the value expected when removing all H and Cl atoms in the boron-precursor (I) which originally contained some \textit{in situ} formed LiCl salts. In fact, the PGAA measurement of the resulting porous BC\textsubscript{x} material—after water-washing to remove LiCl salts—shows practically only B and C elements in a BC\textsubscript{11} composition (Run A-3 in Table 2.1). This material possesses 7.7 wt.% of boron, which is slightly below the 8.4 wt.% observed in the starting boron-precursor (I) considering boron to carbon ratio. Above 800 °C, a dramatic weight loss was observed due to the evaporation of white LiCl salts that were deposited outside of the furnace, and this evaporation of LiCl was detected by TGA-MS and DSC (Figure 2.8 and Figure 2.9).
Figure 2.8. (a) Weight loss profile of TGA curves of B-precursor (I) containing \textit{in situ} formed LiCl salts and (b) a profile of TGA-Mass spectometry showing released Cl gas from (I).
To understand the weight loss due to the boron-precursor (I) at high temperatures, a porous BC$_{12}$ (the predicted composition based on $^{11}$B NMR result) material was first prepared by pyrolysis at 600°C, subsequently underwent water-washing to remove all LiCl salts, and was finally subjected to the TGA measurement. Figure 2.5(b) shows almost no additional weight loss at below 600°C, but a slight and continuous weight reduction at higher temperatures. The overall results indicate a slow, but continuous evolution of the BC$_x$ structure under higher pyrolysis temperatures (higher than 600°C).

Table 2.1 summarizes several resulting porous BC$_x$ materials prepared under various pyrolysis conditions containing different inorganic salts (pore-forming additives) that were removed by water-washing after thermal treatment. Considering a series of Run A set in Table 2.1, the boron content slowly decreases with the further increase of the
pyrolysis temperature. The composition changes from $\text{BC}_{12}$ at 600 °C to $\text{BC}_{17}$ at 800 °C, and $\text{BC}_{21}$ at 1100 °C, respectively. As will be discussed later, the evolution of the $\text{BC}_x$ composition coincides with the development of its planar fused ring structure and crystallinity. It is interesting to note that the composition becomes quite constant after 1500 °C, with slightly above 2 wt.% boron content that is close to the reported maximum value of substitutional boron content in the crystalline graphite structure. Additionally added LiCl enabled $\text{BC}_x$ to create more porous structure without composition change. Addition of another external additive, NaBH$_4$ can significantly increase boron content at low temperatures (600-1000 °C range). However, after pyrolysis at 1500 °C, the resulting $\text{BC}_x$ materials also exhibit about 3 mol% of boron content.
Table 2.1. A summary of porous BC$_x$ materials prepared by B-precursors containing inorganic salts under various pyrolysis conditions.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Pore forming additives</th>
<th>Pyrolysis temp. (°C)</th>
<th>B content (wt.%)</th>
<th>Surface area (m$^2$/g)</th>
<th>Composition (BC$_x$)</th>
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<td></td>
<td></td>
<td></td>
<td>$^{11}$B NMR</td>
<td>PGAA</td>
<td></td>
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<tr>
<td>A-1</td>
<td>LiCl</td>
<td>550</td>
<td>7.0</td>
<td>-</td>
<td>780</td>
</tr>
<tr>
<td>A-2</td>
<td>LiCl</td>
<td>600</td>
<td>7.0</td>
<td>7.7</td>
<td>650</td>
</tr>
<tr>
<td>A-3</td>
<td>LiCl</td>
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<td>6.0</td>
<td>528</td>
</tr>
<tr>
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<td>LiCl</td>
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<td>3.7</td>
<td>212</td>
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</tr>
<tr>
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</tr>
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<td>2.0</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
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<td>NaCl</td>
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<td>8.0</td>
<td>-</td>
<td>536</td>
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<td>NaCl</td>
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<td>405</td>
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<td>10.0</td>
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<td>LiCl/NaBH$_4$</td>
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<td>8.2</td>
<td>387</td>
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<tr>
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<td>LiCl/NaBH$_4$</td>
<td>1500</td>
<td>3.3</td>
<td>-</td>
<td>-</td>
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<tr>
<td>D-1</td>
<td>LiCl/LiCl(ex)</td>
<td>800</td>
<td>5.5</td>
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<td>740</td>
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2.3.2 BC\textsubscript{x} Molecular Structures

Solid state magic angle spinning (MAS) \textsuperscript{11}B NMR, X-ray diffraction, and high resolution transmission electron micrograph (HR-TEM) were used to monitor the boron moieties and crystalline structure development during the pyrolysis. Figure 2.10 shows the \textsuperscript{11}B MAS-NMR spectra of several resulting porous BC\textsubscript{x} materials, which were prepared by pyrolysis of boron-precursor (I) containing \textit{in situ} formed LiCl salts at various temperatures and water-washed to remove all LiCl additives. The resulting porous structure in the BC\textsubscript{x} material essentially mirrors the structure of the impregnated LiCl aggregates in the matrix.

![Solid state MAS \textsuperscript{11}B NMR spectra of BC\textsubscript{x} materials prepared from pyrolysis of B-precursor (with LiCl salts) at (a) 600 °C, (b) 800 °C, (c) 1100 °C, and (d) 1500 °C.](image)

Figure 2.10. Solid state MAS \textsuperscript{11}B NMR spectra of BC\textsubscript{x} materials prepared from pyrolysis of B-precursor (with LiCl salts) at (a) 600 °C, (b) 800 °C, (c) 1100 °C, and (d) 1500 °C.
After pyrolysis at 600 °C, the resulting porous BC\textsubscript{12} (Run A-2) shows one distinctive broad chemical shift centered at 10 ppm, corresponding to trivalent boron moieties that involve some $\pi$ electron delocalization in the carbon fused rings. There is a minor peak centered at 0 ppm, which may be associated with a few boron moieties located at the edge area of the porous BC\textsubscript{12} structure. During water-washing, any remaining B-Cl groups should change to B-OH groups. As the pyrolysis temperature increases from 600 to 800 °C, the major trivalent boron peak slowly moves up-field, indicating a gradual increase of electron density at boron and better $\pi$ electron conjugation in the BC\textsubscript{16} material (Run A-3). In contrast, the edge area boron moieties sharply decrease in its intensity. At 1100 °C, only a trivalent boron peak at 8 ppm was observed in BC\textsubscript{21} (Run A-4). Evidently, the BC\textsubscript{x} fused ring structure increases its size as the pyrolysis temperature increases, and most of boron moieties become the substitutional trivalent species inside the BC\textsubscript{x} structure (Figure 2.2). Upon further annealing the sample at higher temperatures (1500 °C), the BC\textsubscript{x} material appears to graphitize on a larger scale, with a single B chemical shift abruptly moving up-field to -5 ppm in the BC\textsubscript{36} material (Run A-6), which indicates that boron is highly involved in $\pi$ electron delocalization to form very weak acidic (or even basic) boron moieties.

It is interesting to examine the effects of inorganic salts (pore-forming additives) to the structure evolution of boron-precursors (I) during the pyrolysis. Figure 2.11 depicts the $^{11}$B MAS-NMR spectra of porous BC\textsubscript{x} materials prepared by the boron-precursor (I) containing \textit{in situ} formed NaCl salts at 600 °C (Run B-1) and 900 °C (Run B-2). Figure 2.12 presents the $^{11}$B MAS-NMR spectra of porous BC\textsubscript{x} materials obtained from a boron-precursor (I) containing \textit{in situ} formed LiCl and externally added NaBH\textsubscript{4} salts at 600 °C.
(Run C-1) and 800 °C (Run C-2), respectively. After pyrolysis, the inorganic salts were removed by water-washing, resulting in porous BC\textsubscript{x} structures which were then measured with NMR. In Figure 2.11(a), we observed the same two NMR chemical shifts centered at 10 and 0 ppm, corresponding to the substitutional (trivalent) boron moieties in the BC\textsubscript{x} fused ring structure and the boron moieties on the edge area, respectively. Similarly, the front (major) peak shifts slightly toward high-field and the later minor peak reduces its intensity at 900 °C. The major difference between LiCl and NaCl experiments is the concentration of edge area boron moieties at 600 °C. In the NaCl case (Run B-1), a significantly higher number of boron moieties are located on the edge area of the resulting porous BC\textsubscript{10.5} material. This may be associated with the higher melting temperature (800 °C) of the NaCl additive, which maintains good interaction between boron moieties and NaCl at 600 °C (but not at 900 °C) to slow down the increasing size of BC\textsubscript{x} fused ring structure. As will be discussed later, the morphology and crystalline structure in the two cases are very different, and the NaCl salts are well-dispersed in the BC\textsubscript{x} matrix after pyrolysis at 600 °C.
Figure 2.11. Solid state MAS $^{11}$B NMR spectra of BC$_x$ materials prepared from pyrolysis of B-precursor containing NaCl salts at (a) 600 °C and (b) 900 °C.
Figure 2.12. Solid state MAS $^{11}$B NMR spectra of BC$_x$ materials prepared from pyrolysis of B-precursor containing LiCl and NaBH$_4$ salts at (a) 600 °C and (b) 800 °C.

It is interesting to compare Figure 2.10 with Figure 2.11 at 600 °C and 800 °C pyrolysis temperatures. The addition of the external NaBH$_4$ additive into the boron-precursor (I) that already contains internal (in situ formed) LiCl salts, not only boosts the boron content, but also increases B moieties on the edge area of the resulting BC$_x$ materials (Run C-1 and Run C-2 in Table 2.1). The boron chemical shift at -45 ppm, corresponding to NaBH$_4$, completely disappeared at 600 °C, which may have been thermally decomposed to form a reactive boron species that immediately involved the
reaction with forming the BC$_x$ material and locating them mostly at the edge area (high reactivity) of the developing BC$_x$ structure. Significantly high concentrations of boron moieties remained on the edge area, even after increasing the pyrolysis temperature to 800 °C.

Figure 2.13 depicts the X-ray diffraction patterns of the porous BC$_x$ materials at different pyrolysis temperatures. The BC$_{12}$ material (Run A-2) is almost completely amorphous, and the BC$_x$ material gradually shows small order domains as the pyrolysis temperature increases to 1400 °C (Run A-5), with two broad (100) and (101) peaks which merge usually in the amorphous carbon structure. It is noteworthy that a small amount of boron carbide (B$_4$C) was also observed at 1500 °C (Run A-6). As discussed, the boron content in BC$_x$ material at 1500 °C (Table 2.1) dramatically reduced to 2.5 wt.%, which is close to the maximum boron solubility level in the graphitic structure.\textsuperscript{60} Evidently, at this temperature, some small crystallites were formed with a short-range order structure, which ejects excess boron in the form of B$_4$C from the matrix. Using Bragg’s equation (Eq. [2-1]) and Scherer’s equation (Eq. [2-2]), X-ray crystallite parameters can be calculated.\textsuperscript{82, 83}

\begin{equation}
    n\lambda = 2d \sin(2\theta) \tag{2-1}
\end{equation}

\begin{equation}
    L = \frac{K\lambda}{h_{1/2} \cos \theta} \tag{2-2}
\end{equation}

where $\lambda$ is the wavelength of the X-rays, $\theta$ is the diffraction angle, $K$ is the shape factor which is 0.9 at (002) plane, and 1.84 at (10) reflection, and $h_{1/2}$ is the peak width at half maximum intensity. $L_c$ is provided from (002) plane and $L_a$ is obtained from (100) or (101) plane. Therefore, $L_c$ and $L_a$ result in the volume of crystallites.
Table 2.2 summarizes the Lattice parameters of interlayer spacing ($d$), crystallite size ($L_c$), and crystallite width ($L_a$). Generally speaking, the $d$-spacing decreases with heat treatment temperature, while both $L_c$ and $L_a$ increase with temperature. However, both crystallite size and crystallite width remain relatively small even after pyrolysis at 1800 °C, which means BC$_x$ materials basically resemble disordered non-graphitizable carbons that limit the expansion of crystallite domains and prevent long-range order. The $d$-spacing of Run A-7 is 0.339 nm which is very close to the 0.335 nm width seen in ideal graphite. Despite the relatively low pyrolysis temperature at 1800 °C, the highly short-range ordering may be associated with having boron in the precursor, a supposition which is verified by the TEM images (Figure 2.14).

High-resolution transmission electron micrographs provide a direct observation of microstructures. Figure 2.14 presents TEM images of both BC$_{12}$ (Run A-1) and BC$_{45}$ (Run A-7) materials. In the BC$_{12}$ material, prepared at 600°C, we observed fingerprint patterns with short and curved fringes, and randomly-oriented fringes between fingerprint patterns. On the other hand, the randomly-oriented stacks of several layers with extended, straight, and parallel organized fringes were observed in the BC$_{45}$ material prepared at 1800°C. The stack thickness ($L_c$; crystallite size) is about 2-3 nm, and the stack length (crystallite width) is in the range of 5-7 nm, which are consistent with the X-ray results (Table 2.2). Figure 2.14(c) shows the TEM micrograph for the BC$_7$ material (Run C-1), prepared at the same pyrolysis temperature 600 °C using the B-precursor (I) that contains both in situ formed LiCl and the externally added NaBH$_4$ salts. Comparing with Figure...
2.14(a), it shows a completely random configuration (no fingerprint patterns) with short and curved fringes. Evidently, the additional NaBH$_4$ salts were mixed well with boron-precursor (I) and provide an additional boron source. Although NaBH$_4$ salts don’t interfere in the carbonization process of converting boron-precursor (I) into the BC$_x$ material, their presence in the matrix do effectively prevent any development of a local ordering structure by maintaining a high edge area, consistent with the solid state $^{11}$B NMR results shown in Figure 2.11.
Figure 2.13. X-ray diffraction patterns of porous BC$_x$ materials prepared at various pyrolysis temperatures (a) 600 °C, (b) 800 °C, (c) 900 °C, (d) 1100 °C, (e) 1400 °C, (f) 1500 °C, and (g) 1800 °C.
Table 2.2. Lattice parameters of BC\textsubscript{x} materials measured by X-ray diffraction patterns and the parameters are obtained by Bragg’s equation and Scherer’s equation.

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<td>(\theta) (rad)</td>
<td>(d) (nm)</td>
<td>FWHM</td>
<td>FWHM (rad)</td>
<td>(L_c) (nm)</td>
<td>(L_a) (nm)</td>
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<td>(\theta) (rad)</td>
<td>(d) (nm)</td>
<td>FWHM</td>
<td>FWHM (rad)</td>
<td>(L_c) (nm)</td>
<td>(L_a) (nm)</td>
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<td>(d) (nm)</td>
<td>FWHM</td>
<td>FWHM (rad)</td>
<td>(L_c) (nm)</td>
<td>(L_a) (nm)</td>
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<td>(\theta) (rad)</td>
<td>(d) (nm)</td>
<td>FWHM</td>
<td>FWHM (rad)</td>
<td>(L_c) (nm)</td>
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<td>(\theta) (rad)</td>
<td>(d) (nm)</td>
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Figure 2.14(a). TEM micrographs of BC$_x$ material prepared by pyrolysis of B-precursor containing LiCl at 600 °C.
Figure 2.14(b). TEM micrographs of BC₅ material prepared by pyrolysis of B-precursor containing LiCl at 1800 °C.
Figure 2.14(c). TEM micrographs of BC₃ material prepared by pyrolysis of B-precursor containing LiCl and NaBH₄ at 600 °C.
2.3.3 Morphology of BC\textsubscript{x} Materials

It is noteworthy to understand how the pyrolysis temperature and inorganic salts (pore-forming additives) affect BC\textsubscript{x} morphology. Since the inorganic additives serve as the pore-forming templates, removed after pyrolysis, the pore structure also reveals the distribution of inorganic salts in the BC\textsubscript{x} matrix during pyrolysis. Figure 2.15 shows an X-ray diffraction (XRD) pattern of the impregnated LiCl during the pyrolysis of boron-precursor (I), which provides the direct evidence of LiCl agglomeration at a high pyrolysis temperature. At the temperature <400 °C, the dispersed LiCl molecules show no diffraction peak. As the pyrolysis temperature increases up to 450 °C, several broad diffraction peaks suddenly appeared which are associated with the LiCl crystals and hydrated LiCl (formed when exposed to air). The broad peaks become sharp when the pyrolysis temperature increases to 600 °C which can be explained by LiCl crystallite gradually growing according to the Scherer’s equation.\textsuperscript{82} Evidently, the dispersed LiCl molecules start to melt flow at 450 °C although the temperature is below the melting point (605 °C) of LiCl crystal, and aggregate progressively into bigger particles at higher temperature. The melting temperature of a bulk material is not dependent on its size. However, as the dimensions of a material decrease towards the atomic scale, the melting temperature scales with the material dimensions.\textsuperscript{84-86} The melting temperature depression of LiCl crystal was supported by DSC measurement of B-precursor (I) with in situ formed LiCl salts (Figure 2.16) and it indicates that LiCl salts are distributed in atomic scale (or nano scale). It is important to note that the in situ formed LiCl molecules in B-precursor (I) were conveniently used as the internal pore-forming additives to prepare
various porous structures in the BC$_x$ material, which can be completely removed by water-washing. The resulting pore structure in BC$_x$ is the mirror image of the impregnated LiCl aggregates in the matrix.

Figure 2.15. X-ray diffraction patterns of LiCl salts in B-precursor after pyrolysis at various temperatures (a) 150 °C, (b) 400 °C, (c) 450 °C, and (d) 600 °C.
Figure 2.16. High temperature DSC of LiCl salts in B-precursor.
Figure 2.17 shows Scanning Electron Microscopy images of BC$_x$ materials, including BC$_{12}$ (Run A-2), BC$_{30}$ (Run A-5), and BC$_{45}$ (Run A-7), from three temperatures. The *in situ* formed LiCl salts should maintain good dispersion in the BC$_x$ matrix (Figure 2.17(a)) and create porous structure after being washed out by water (Figure 2.17(b)). These macro-porous structures are clearly the result of LiCl aggregates in the matrix, which are formed (phase separated from BC$_x$) during pyrolysis. Despite very different pyrolysis temperatures, BC$_{12}$, BC$_{30}$ and BC$_{45}$ materials show similar macro-phase morphology with many continuous micron-width channels (Figure 2.17(b), (c) and (d)).

One control sample was prepared by pyrolysis (600 °C) of oligomer boron-precursor (I) without any inorganic salt and the completely dense BC$_x$ material, with no surface area checked by BET, was observed (Figure 2.18(a)). Figures 2.19–2.21 present high-resolution FE-SEM micrographs of three BC$_x$ materials which were pyrolyzed by the boron-precursor with different *in situ* formed inorganic salts and at different temperatures. The NaCl salts, having a higher melting temperature (800 °C), remain in a well-dispersed phase in the BC$_x$ matrix at 600 °C (Figure 2.20) and gradually aggregate at higher temperature (900 °C) to create the continuous micron-width channels, which produce similar morphology to BC$_{12}$ obtained from LiCl templates in Figure 2.17 (Figure 2.20). Clearly, the combination of additives and pyrolysis temperature offers a unique tool to control BC$_x$ morphology.
Figure 2.17(a,b). SEM micrograph of BC\textsubscript{x} materials obtained after pyrolysis of B-precursor (a) at 600 °C before removing LiCl and (b) at 600 °C after removing LiCl.
Figure 2.17(c,d). SEM micrograph of BC\textsubscript{x} materials obtained after pyrolysis of B-precursor (c) at 1400 °C after removing LiCl, and (d) at 1800 °C after removing LiCl.
Figure 2.18. SEM micrograph of BC₃ materials obtained after pyrolysis of (a) oligomer B-precursor (gel) without LiCl at 600 °C and (b) polymer B-precursor (solid with LiCl) at 600 °C.
Figure 2.19(a). High resolution FE-SEM micrograph of porous BC₃ materials obtained after pyrolysis of B-precursor with LiCl at 600 °C at low magnification (20,000 times).
Figure 2.19(b). High resolution FE-SEM micrograph of porous BC₃ materials obtained after pyrolysis of B-precursor with LiCl at 600 °C at high magnification (100,000 times).
Figure 2.20(a). High resolution FE-SEM micrograph of porous BC₃ materials obtained after pyrolysis of B-precursor with NaCl at 600 °C at low magnification (20,000 times).
Figure 2.20(b). High resolution FE-SEM micrograph of porous BC₅ materials obtained after pyrolysis of B-precursor with NaCl at 600 °C at high magnification (100,000 times).
Figure 2.21(a). High resolution FE-SEM micrograph of porous BC \( x \) materials obtained after pyrolysis of B-precursor with NaCl at 900 °C at low magnification (20,000 times).
Figure 2.21(b). High resolution FE-SEM micrograph of porous BC$_x$ materials obtained after pyrolysis of B-precursor with NaCl at 900 °C at high magnification (100,000 times).
It is useful to know how much LiCl salt is dispersed in the BC\textsubscript{x} matrix, which may result in pore distribution. Based on high-resolution FE-SEM results, both micropores (nanopores, less than 2 nm of diameter) and mesopores (between 2 nm and 50 nm of diameter) clearly exist in the BC\textsubscript{x} matrix. However, the resolution does not allow for the determination of pore size and distribution.

The specific pore sizes and pore size distributions in the BC\textsubscript{x} materials were examined by a BET surface area analyzer using N\textsubscript{2} and CO\textsubscript{2} gases. Figure 2.22 and Figure 2.23 compare four pore size distributions of BC\textsubscript{12} (Run A-2), BC\textsubscript{16} (Run A-3), BC\textsubscript{10.5} (Run B-1), and BC\textsubscript{13} (Run B-2) prepared by pyrolysis of the boron-precursor (I) containing LiCl or NaCl salts. Both A-2 and A-3 materials, obtained from boron-precursor (I) with LiCl salts at 600 °C and 800 °C, respectively, contain nanopores (with pore diameter centered at 1.2 nm) and mesopores (with pore diameter centered at 3.75 nm), but at very different proportions. The significant shift of the nanopore-dominated A-2 sample (83 vol% of nanopores in Figure 2.22(a)) to the mesopore-dominated higher temperature A-3 sample (66 vol% mesopores in Figure 2.22(b)) implies some local LiCl agglomeration occurs during pyrolysis, beyond the melting temperature of LiCl at 605 °C. As expected, the BET surface area was also reduced from 650 to 528 m\textsuperscript{2}/g. Similar shifting of pore size was found in samples B-1 to B-2 when pyrolysis temperature increased from 600 °C to 900 °C due to some local NaCl agglomeration (Figure 2.23). It is interesting to see that the pores are mainly in the nanopore range in the B-1 sample while 51 vol% of mesopores are distributed in B-2 sample, which can be attributed to high NaCl salts having a higher melting temperature (800 °C). Considering the fact\textsuperscript{87} that unit cell size of LiCl is 0.538 nm and that of NaCl is 0.564 nm, nanopore diameter of
1.2 nm from the pore size distribution is a reasonable size derived by aggregation of several LiCls and NaCls.
Figure 2.22. Pore size distributions of $\text{BC}_x$ materials obtained after pyrolysis of B-precursor with LiCl salts at (a) 600 °C and (b) 800 °C.
Figure 2.23. Pore size distributions of BC\textsubscript{x} materials obtained after pyrolysis of B-precursor with NaCl salts at (a) 600 °C and (b) 900 °C.
2.4 Conclusion

Early methods of gas phase CVD and solid state diffusion have previously been used to prepare BC\textsubscript{x} materials with either B\textsubscript{4}C/BC\textsubscript{3} with a >25% B content or a graphitic product with <3% B content. The resulting dense structures were not suitable for hydrogen storage applications. In this study, we have developed a versatile method to prepare a broad range of porous BC\textsubscript{x} materials, bridging the boron content and microstructure, by using a specifically-designed boron-containing polymer (boron-precursor) that contains some inorganic additives (pore-forming templates). By taking into account the chemistry of boron and the mechanism of carbonization, most of the boron moieties in the boron-precursor were substitutional incorporated in the fused hexagonal ring structure. The morphology and crystalline structure were determined after treatment by a combination of pyrolysis temperature and inorganic additives. As illustrated in Figure 2.24, the chemical structure of BC\textsubscript{x} changes from a disordered (less $\pi$ conjugated) state, or a boron-puckered configuration at 600-800 °C to an ordered (highly $\pi$ conjugated) state, that is a planar and multilayered configuration at 1500 °C. The resulting planar layers can only accommodate a reduced amount (<3%) of boron content which is consistent with the thermodynamic observation at high temperature (1500 °C to
2500 °C). After pyrolysis, the inorganic salts dispersed in the resulting BC\textsubscript{x} matrix are removed by water washing, which creates pore structures in the BC\textsubscript{x} material.

![Figure 2.24. Schematic presentation of planar BC\textsubscript{x} materials (left) top view and (right) side view.](image)

Some resulting amorphous BC\textsubscript{x} materials (created by pyrolysis at 600-800 °C) show controllable nanopore and mesopore structures with high surface area, and contain a boron content of up to 12 wt.% with acidic (electron-deficient) boron moieties. The combination provides super-activated surfaces useful for physical interactions with various molecules.
Chapter 3

Interaction of Nanoporous BC\textsubscript{x} with Other Molecules including Hydrogen

3.1 Introduction

Nanoporous BC\textsubscript{x}s with various boron contents and surface areas, which are expected to have strong interactions with hydrogen molecules, were synthesized using a combination of designed boron containing polymeric precursors (boron-precursor) with \textit{in situ} formed inorganic templates and pyrolysis.\textsuperscript{88,89} Careful studies were performed to develop an understanding of how the boron moiety affects hydrogen sorption properties. Methods to obtain quantitative measurement of sorption behavior of other compounds besides hydrogen were also developed.

3.2 Interaction between BC\textsubscript{12} and tert-Dodecyl Amine

3.2.1 Experimental

3.2.1.1 Materials and Instruments

Tridodecylamine and boron trichloride (1.0 M solution in hexane) were purchased from Sigma-Aldrich\textsuperscript{®}. Activated carbon with 670 m\textsuperscript{2}/g and 1000 m\textsuperscript{2}/g of surface area...
were purchased from an activated carbon Darco® and Darco® KB from Sigma-Aldrich®. Various BC\textsubscript{x} materials were synthesized in accordance with a published procedure\textsuperscript{88,89}

Thermogravimetric–mass spectral (TGA-MS) analysis was performed with a TA Instruments TA 2050 attached to a Pfeiffer Thermostar mass spectrometer. Thermogravimetric analysis (TGA), which measures weight changes in materials as the temperature is increased, provides an excellent way of characterizing amine-BC\textsubscript{x} complexes. However, while TGA readily provides quantitative weight change information about decomposition and volatilization, it does not generally provide information about the identity of specific off-gas materials. Hence, TGA is coupled with mass spectroscopy in order to obtain this qualitative data.

3.2.1.2 Procedures

An excess of tridodecylamine (2 mL, 3.15 mmole) was added dropwise to 345.5 mg of porous BC\textsubscript{12} (2.23 mmole) powder mixed with a magnetic stir bar in a dry 100 mL round bottomed flask. After addition, the mixture was stirred for 12 hours at room temperature. The slurry mixture was filtered and residue was rinsed with pure hexane and then dried at 80 °C under a vacuum. The resulting dried powder (BC\textsubscript{12} sample interacted with tridodecylamine) was weighed. 20 mg of this powder was run using TGA-MS. 5 mL
of BCl$_3$ solution (1.0 M in hexane) was added to the dried powder and stirred for 2 hours at room temperature. The slurry mixture was filtered and residue was rinsed with pure hexane and then dried at 200 °C under a vacuum. The resulting powder was weighed once completely dried.

3.2.2 Results and Discussion

A porous BC$_{12}$ sample was subjected to a B-N complexization study with tridodecylamine at ambient temperature, in order to examine the available boron sites. The procedure and results of mass increase are schematically shown in Figure 3.1.
Figure 3.1. Schematic drawing of B-N complexization between BC\textsubscript{12} and amine compound.

Based on the weight increase, one-third of the boron sites in the BC\textsubscript{12} sample interact with tridodecylamine. A more complete analysis of C\textsubscript{12}B-N(C\textsubscript{12}H\textsubscript{25})\textsubscript{3} complexes in argon atmosphere was obtained by coupling TGA to a mass spectrometer so that the evolved compound from BC\textsubscript{12} during thermal dissociation could be identified. TGA
weight loss profiles in Figure 3.2(a) indicates that half of C\textsubscript{12}B-N(C\textsubscript{12}H\textsubscript{25})\textsubscript{3} complexes are quantitatively erupting between the temperature range of 300-450 °C. Released methyl (CH\textsubscript{3}) fragments from tridodecylamine were detected by the coupled mass spectrometer in Figure 3.2(b). At this point, tridodecylamines are not physically mixed but form a complexation with the BC\textsubscript{12} (C\textsubscript{12}B-N(C\textsubscript{12}H\textsubscript{25})\textsubscript{3}) which is quite stable until 300 °C. Furthermore, since boron trichloride forms stronger complexes with amine than the boron moiety in BC\textsubscript{12}, the recovered mass of free BC\textsubscript{12} separate from the C\textsubscript{12}B-N(C\textsubscript{12}H\textsubscript{25})\textsubscript{3} complex was obtained.

Figure 3.2. A profile of TGA-Mass spectrum from C\textsubscript{12}B-N(C\textsubscript{12}H\textsubscript{25})\textsubscript{3} in argon atmosphere (a) weight loss profile of C\textsubscript{12}B-N(C\textsubscript{12}H\textsubscript{25})\textsubscript{3} and (b) ion intensity of a fragment with 15 m/e matching methyl ion (CH\textsubscript{3}+) in releasing gas.
3.3 Interaction between BCₙ and Hydrogen Molecules

3.3.1 Hydrogen Physisorption

3.3.1.1 Apparatus

An important step for conducting hydrogen storage research is analysis of hydrogen sorption efficiency. Thermogravimetric analysis (TGA) and volumetric analysis are the main techniques used to evaluate hydrogen storage capacity. TGA uses a microbalance to measure the variation of the sample mass which adsorbed hydrogen and is the only direct gas uptake measurement technique. Theoretically, the adsorbed hydrogen could be calculated from the additional mass after adsorption equilibrium under each pressure. However, the balance stabilization required for this measurement would be disturbed by the hydrogen current after hydrogen was admitted into the chamber. Another problem is that the effect of buoyancy, which changed with pressure variations, and the effect of water and other gas impurity have a less than trivial impact on the results.⁹⁰, ⁹¹

Volumetric analysis²³, ⁹², ⁹³ is the most versatile approach for hydrogen storage capacity measurement. Hydrogen uptake from the sample material is calculated by measuring pressure changes in a reference volume, remote from the sample, held at a fixed temperature. Hydrogen storage over a wide range of pressures can be measured by
employing a wide range pressure transducer. However, small samples (~ 1 mg) present
difficulty due to the small pressure changes in the typical reference volumes. The
accuracy of volumetric techniques is potentially greater compared to that of TGA
techniques only if large amount of samples are used. Therefore 150 mg of sample was
loaded in a chamber in which large changes in gas pressure are measured rather than
measuring small changes in mass as in TGA techniques. The commercial instrument
Micrometrics ASAP 2010 is available and permits low pressure operation (up to 1.2 bars)
at various temperatures using a bath.94 A volumetric apparatus designed for high pressure
operation (up to 60 bars) was built and is shown in Figure 3.3 as a schematic diagram.
3.3.1.2 Measurement of Hydrogen Adsorption Isotherms

Volumetric hydrogen adsorption measurements were carried out under various temperatures and pressure conditions. Samples for adsorption measurement were loaded in a quartz sample cell within an argon glove box and attached to the ASAP 2010 instrument. The samples were then heated at a rate of 30 °C per min under a vacuum,
held at 400 °C for 2 hours, and then cooled down. Following the degassing procedure under a vacuum, a sorption experiment was initiated by charging the chamber with gas (helium and hydrogen) at the thermal equilribriums of 77 K and 87 K obtained through the use of liquid nitrogen and liquid argon baths, respectively. The gas was subsequently expanded after reaching equilibrium and 60 to 100 points of adsorption data were collected at points ranging from 0.001 to 1.2 bar.

The same procedure was repeated and data ranging from 20 bar up to 80 bar were collected using the apparatus shown in Figure 3.3. Thermal equilibrium of 77 K and 87 K was obtained by liquid nitrogen and liquid argon baths, 203 K using a dry ice and methanol bath, and room temperature. Helium gas was used to determine the free volume of the sample cell assuming no helium adsorption or interaction with the solid substrate during the free space analysis at those temperatures.

3.3.1.3 Results and Discussion

To compare BC<sub>x</sub> materials with activated carbon materials at a glance, hydrogen adsorption isotherms at 77K were measured and the result is presented in Figure 3.4. In all samples, the adsorption increased as hydrogen pressure increase and surface area
increase. The figure clearly shows how the boron substitution affects enhancement in hydrogen adsorption.

Figure 3.4. Hydrogen adsorption isotherms at 77 K for BC$_{12}$ with a 780 m$^2$/g of specific surface area, BC$_{12}$ with a 650 m$^2$/g of specific surface area, activated carbon with a 1000 m$^2$/g of specific surface area, and activated carbon with a 670 m$^2$/g of specific surface area.

The BC$_{12}$ sample, having a specific surface area of 780 m$^2$/g (BC$_{12}$-780), was further examined at different temperatures under various pressures. Figure 3.5 shows hydrogen adsorption at 77 K and 87 K under low pressure, and Figure 3.6 presents
hydrogen adsorption at these same temperatures under high pressure. Hydrogen uptake follows an almost linear relationship with hydrogen pressure, which is quite different from carbon materials that reach a saturation level in relatively low pressure.\textsuperscript{24,32,96}

Figure 3.5. Hydrogen adsorption isotherms at 77 K and 87 K under low pressure for sample BC\textsubscript{12} with 780 m\textsuperscript{2}/g of specific surface area.
Figure 3.6. Hydrogen adsorption isotherms at 77 K, 203 K and 298 K under high pressure for sample BC12 with 780 m$^2$/g of specific surface area.

About 0.52 wt.% hydrogen adsorption was observed in the BC12-780 at ambient temperature under 80 bars of hydrogen pressure, which is about double that of corresponding carbonaceous materials with similar surface areas. Temperature has a marked effect on the increase of the hydrogen adsorption capability. At 77 K, hydrogen adsorption reaches the 3.45 wt.%, which is the highest found using our experimental technique and is more than six times that found at ambient temperature. The value, 3.45 wt.% is more than double of that found for the corresponding carbonaceous materials.
with similar surface area considering a capacity of about 1 wt.% H$_2$ per 500 m$^2$/g surface area.$^{32, 40, 93, 98}$

Further investigation of BC$_x$ with various boron contents was completed. Figure 3.7 depicts adsorption isotherms of six BC$_x$ materials with various boron contents and specific surface area at 77 K. Compared to BC$_{16}$, hydrogen adsorption capacity of BC$_{12}$ clearly increases, despite reduction of surface area in the case of BC$_{12}$-650. Evidently, the substituted boron elements are essential in hydrogen adsorption. The low hydrogen capacity of BC$_{10.5}$ can be attributed to its low internally substituted boron content; despite the fact that its total boron content is higher than that of BC$_{12}$, and moreover it has a lower surface area. BC$_6$ can be understood in the same context as well as its lower surface area.
Figure 3.7. Hydrogen adsorption isotherms at 77 K under low pressure for sample BC_{12} with 780 m\(^2\)/g, BC_{12} with 650 m\(^2\)/g, BC_{16} with 740 m\(^2\)/g, BC_{7} with 600 m\(^2\)/g, BC_{10.5} with 536 m\(^2\)/g, and BC_{16} with 528 m\(^2\)/g of specific surface area.

Detailed experimental results of high pressure hydrogen adsorption of BC_{10.5} and BC_{7}, compared to BC_{12} are depicted in Figures 3.8–3.11. Both isotherms of BC_{10.5}, having a specific surface area of 536 m\(^2\)/g (BC_{10.5-536}), and BC_{7} with a 600 m\(^2\)/g of specific surface area (BC_{7-600}) show low adsorption values than those of BC_{12} at 77 K and 298 K. It is interesting to note that the internally substituted boron content, and surface area of BC_{12} is higher than that of BC_{10.5-500}, or similar with BC_{7-600}, although
total boron content is low considering $^{11}\text{B}$ NMR result in Chapter 2. The results suggest that the internally substituted boron rather than total boron content contributes to the hydrogen uptake. In addition, the boron atoms located at the edge area of BC$_x$ either sparingly influence or possibly deteriorate hydrogen adsorption in some degree if the boron atoms are saturated with oxygen atoms. Surface area shows more significant influence on adsorbing hydrogen at 77 K.

Figure 3.8. High pressure hydrogen adsorption isotherms at 77 K for sample BC$_{12}$ with 780 m$^2$/g, and BC$_{10.5}$ with 536 m$^2$/g of specific surface area.
Figure 3.9. High pressure hydrogen adsorption isotherms at 77 K for sample BC$_{12}$ with 780 m$^2$/g, and BC$_7$ with 600 m$^2$/g of specific surface area.

Meanwhile, at ambient temperature the higher boron content BC$_x$ compounds (BC$_{10.5}$ and BC$_7$) have hydrogen adsorptions that increase at a higher rate and eventually exceed the amount of hydrogen adsorbed into BC$_{12}$ at higher than of 83 bar pressure (see Figure 3.10 and Figure 3.11). Therefore it is noteworthy that total boron content enhances hydrogen adsorption especially at high pressure and room temperature (298 K) although surface area and internally substituted boron is more important at low temperature because this enhances the surface energy for binding hydrogen.
Figure 3.10. High pressure hydrogen adsorption isotherms at 298 K for sample BC$_{12}$ with 780 m$^2$/g, and BC$_{10.5}$ with 536 m$^2$/g of specific surface area.

Figure 3.11. High pressure hydrogen adsorption isotherms at 77 K for sample BC$_{12}$ with 780 m$^2$/g, and BC$_{7}$ with 600 m$^2$/g of specific surface area.
3.3.2 Binding Energy of $\text{BC}_x$ with hydrogen molecule

The quantitative hydrogen binding energy on the $\text{BC}_x$ compounds was estimated by measuring isosteric heat of adsorption using hydrogen adsorption isotherms at two temperatures (77 and 87 K) at low surface coverage (satisfying monolayer adsorption). The term “heat of adsorption” describes the energy released when a molecule of gas (in this case hydrogen) attaches to a solid surface. Calculation of the isosteric heat of adsorption was based on the Clausius-Clapeyron equation.\(^{99-102}\)

$$\left( \frac{\partial \ln P_i}{\partial T} \right)_{n_i} = \frac{Q}{RT^2} \quad [3-1]$$

where $Q$ is the heat of adsorption of component $i$ of an ideal gas mixture at a specific absorbate loading of $n_i$ for that component, and $T$ and $P_i$ are system temperature and partial pressure of component $i$ in equilibrium, and $R$ is the universal gas constant. For a certain $n_i$ value, $Q$ was calculated by applying the integral format of the Clausius-Clapeyron equation.

$$\ln \left( \frac{P_i}{P_2} \right) = -\frac{Q}{R} \left( \frac{1}{T_i} - \frac{1}{T_2} \right) \quad [3-2]$$

The sorption experiments for the heat of adsorption were performed on $\text{BC}_{12^{-}}^{-780}$, $\text{BC}_{12^{-}}^{-650}$, $\text{BC}_{10.5^{-}}^{-536}$, and $\text{BC}_{7^{-}}^{-600}$ at 77 K and 87 K and the results compared to carbon-670 are shown in Figures 3.12–3.16 and in Tables 3.1–3.5.
Figure 3.12. Hydrogen adsorption isotherms of sample BC$_{12}$ with 780 m$^2$/g of specific surface area at 77 K and 87 K in order to estimate isosteric heat of adsorption.
Table 3.1. Isosteric heat of adsorption measurements of BC$_{12}$ with 780 m$^2$/g of specific surface area from 77 K and 87 K.

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Figure 3.13. Hydrogen adsorption isotherms of sample BC\textsubscript{12} with 650 m\textsuperscript{2}/g of specific surface area at 77 K and 87 K in order to estimate isosteric heat of adsorption.
Table 3.2. Isosteric heat of adsorption measurements of BC$_{12}$ with 650 m$^2$/g of specific surface area from 77 K and 87 K.

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Figure 3.14. Hydrogen adsorption isotherms of sample BC\textsubscript{10.5} with 536 m\textsuperscript{2}/g of specific surface area at 77 K and 87 K in order to estimate isosteric heat of adsorption.
Table 3.3. Isosteric heat of adsorption measurements of BC\textsubscript{19.5} with 536 m\textsuperscript{2}/g of specific surface area from 77 K and 87 K.

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</table>
Figure 3.15. Hydrogen adsorption isotherms of sample BC$_7$ with 600 m$^2$/g of specific surface area at 77 K and 87 K in order to estimate isosteric heat of adsorption.
Table 3.4. Isosteric heat of adsorption measurements of BC$_7$ with 600 m$^2$/g of specific surface area from 77 K and 87 K.

<table>
<thead>
<tr>
<th>$Q$(wt.%)</th>
<th>$P_1$(77K)</th>
<th>$P_2$(87K)</th>
<th>Ln($P_1/P_2$)</th>
<th>$(1/T_1-1/T_2)$</th>
<th>$\delta H$(kJ/mol)</th>
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<td>0.0015</td>
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</table>
Figure 3.16. Hydrogen adsorption isotherms of an activated carbon sample with 670 m$^2$/g of specific surface area at 77 K and 87 K in order to estimate isosteric heat of adsorption.
Table 3.5. Isosteric heat of adsorption measurements of an activated carbon with 670 m$^2$/g of specific surface area from 77 K and 87 K.

<table>
<thead>
<tr>
<th>Q(wt.%)</th>
<th>P1(77K)</th>
<th>P2(87K)</th>
<th>Ln(P1/P2)</th>
<th>(1/T1-1/T2)</th>
<th>$\delta$H(kJ/mol)</th>
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</thead>
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</tr>
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<td>0.0015</td>
<td>5.08</td>
</tr>
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</table>
The initial isosteric heat of adsorption for the BC$_{12}$-780 is 13.47 kJ/mole and remains higher than 11 kJ/mole level to higher surface coverage (Table 3.1). The BC$_{12}$ with reduced surface area (BC$_{12}$-650) also has a quite high heat of adsorption (12.47 kJ/mole) and which is maintained over 11 kJ/mole (Table 3.2). It is interesting that the isosteric heat of adsorption is independent on the surface area which is in accordance with previous report on carbon materials. The results indicate that the isosteric heat of adsorption is dependent on the composition and independent on surface area. BC$_{10.5}$-500 resulted in 7-9 kJ/mole of isosteric heat of adsorption and BC$_{6}$-600 maintained higher than a 9 kJ/mole level, which might be explained by the interaction energy related to the boron content fused in hexagon ring because both BC$_{10.5}$-500 and BC$_{6}$-600 contain quite large portion of edge area boron moieties. All in all, the values of isosteric heat of adsorption from 77 K and 87 K are significantly higher than those observed in the activated carbon (6.66 kJ/mol in Table 3.5) which is close to the value of 4-7 kJ/mole from other activated carbons.$^{52}$

Meanwhile supporting information of the isosteric heat of adsorption of BC$_{12}$-780 from other than 77 K and 87 K was provided by the facility in Air Products which is shown in Figure 3.17.
Figure 3.17. Hydrogen adsorption isotherms of a BC_{12-780} at 0 °C and 25 °C and isosteric heat of adsorption.

The initial isosteric heat of adsorption from 273 K and 298 K, close to 20 kJ/mole is significantly high and supports that boron substituted carbon samples maintain high hydrogen adsorption energies than those observed in undoped carbonaceous materials, and the increase of boron content increases the hydrogen binding energy.

3.4 Conclusions

In summary, the experimental approaches were performed to validate the interaction of nanoporous BC_{x} with polar compound and hydrogen molecules. The substitutional boron elements in BC_{x} served as internal p-type dopants and polarized the
surface of BC$_x$, and they exhibit significantly higher hydrogen adsorption capacity than carbon materials. A porous BC$_{12}$ material exhibits a reversible hydrogen physisorption capacity of 0.5 and 3.5 wt.% H$_2$ at 293 and 77 K, respectively, under moderate hydrogen pressure (<100 bars). Both values are 2.3 times higher than H$_2$ absorption capacities in the corresponding carbonaceous materials. The physisorption results were further warranted by absorption isotherms, indicating a binding energy of hydrogen molecules between 10 and 20 kJ/mole, significantly higher than the 5-7 kJ/mole observed on an activated carbon surfaces.
Chapter 4

Colloidal Synthesis of Metal Nanoparticles on a BC\textsubscript{x} Material

4.1 Introduction

4.1.1 Synthesis of Metal Nanoparticles disposed on BC\textsubscript{x}

Transition metals, such as platinum, palladium, titanium and zirconium are often used as catalysts for organic reactions\textsuperscript{103-105} as electrocatalysts in the fuel cell systems\textsuperscript{106-108} and for olefin polymerizations\textsuperscript{109-111} and hydrogen physisorption\textsuperscript{112-117}. For efficient metal utilization, these metals are often prepared as particles dispersed in a suitable support, such as carbon materials, to increase the surface to mass ratio. Furthermore, the stability of these dispersed metal particles in the carbon support is crucial for effective catalytic activity of the supported metal catalysts.

One typical way to synthesize supported metal particles uses a solution method called incipient wetness impregnation\textsuperscript{114-117}. The aqueous metal precursor solution is soaked into a porous carbon support in the impregnation system and then the solvent is gradually evaporated, followed by the reduction of the metal ion with hydrogen gas at 300 °C. At high temperatures, however, powder metal particles diffuse together to form
clusters because the van der Waals interaction between metal particles and carbon support is not enough to prevent metal clustering or sintering.

Another synthetic route is the chemical reduction of the metal precursor with the aid of a surface stabilizer. The stabilizers such as commercialized surfactants, sodium citrates, or polyvinylpyrrolidones (PVPs) provide the stability of the dispersed metal particles-support colloidal system and control over the size of metal particles. In fact, the stabilizer protected metal particles are not catalytically active and post-thermal treatment is needed to activate metal sites, which results in the agglomeration of the metal particles.

This sintering or agglomeration of metal particles is prevented by dispersing metal particles in the support materials in order to reduce the chance of metal utilization. Even though many of strategies for overcoming the metal clustering have been directed toward changing the reduction method or selecting fortuitous better stabilizers, there has been relatively little effort to change the carbon structure to create a polarized surface. However, incorporation of a functional group on the carbon surface is challenging because of the stable frame of graphene structure. While useful in many other applications, traditional chemical activation produces surface modification of activated
carbon with a heteroatom, usually oxygen, but is not effective to avoid the metal clustering because the oxygen is bonded only to peripheral carbon atoms at the edges of the activated carbon structure. Another approach is to modify the morphology of carbon structure to a carbon nanohorn, but this doesn’t change the interaction between the intrinsic carbon and metal particles other than the van der Waals interaction.

The boron atom, which is similar to carbon in its size and ability to form trivalent bonds, has a vacant p orbital which can be strongly hybridized with a d orbital of the transition metal atom. This hybridization suggests to us an advanced and direct synthetic route to the metal particles on the surface of the carbon support having substitutional boron atoms (BC$_x$ material). Due to the enhanced interaction between a metal atom and a substitutional boron atom in the BC$_x$ materials, metal particles keep energetically favorable sites around the boron atoms and will resist being agglomerated even at high temperature. This route should lead to a significantly small and monodisperse distribution in the BC$_x$ matrix, even without the aid of stabilizers.

Recently a published thermodynamic study revealed that the binding energy between platinum and a one boron substituted carbon nanotube (CNT) structure increased by 0.48 eV relative to an intrinsic CNT reference, with a 1.33 eV and 1.58 eV increase...
being demonstrated in a two boron and a three boron substituted CNT, respectively. (Figure 4.1)

Similar results are reported with a palladium and boron substituted CNT system.\textsuperscript{125}

Figure 4.1. Schematic diagram of binding energies of a platinum atom and a carbon nanotube and boron substituted carbon nanotubes.\textsuperscript{124}

Meanwhile, previous research in our group presented how to synthesize the boron substituted carbon materials from boron containing organic precursors\textsuperscript{75, 77, 88, 89} and experimentally proved that the substitutional boron strongly interacted with hydrogen or amine compounds.\textsuperscript{89} Intuitively, this BC\textsubscript{x} material should provide a unique opportunity for a metal atom to connect to a boron atom in the BC\textsubscript{x} strongly enough to prevent the
agglomeration from occurring even at high temperatures (over 500 °C). The highly monodispersed small metal particles synthesized using BC\textsubscript{x} material as a support should show improved property in the catalysts application\textsuperscript{126} including hydrogen physisorption systems.

4.1.2 Hydrogen Physisorption in Metal Disposed BC\textsubscript{x}

Late transition metal including platinum or palladium has already been shown experimentally to enhance in hydrogen physisorption of support materials.\textsuperscript{112-117} The increase in hydrogen adsorption by metal deposition is explained theoretically by the hybridization of the d orbital of transition metal atom with the σ orbital of hydrogen molecule via a stable structure complex (Figure 4.2).\textsuperscript{127}

![Diagram of Electrophilic and Nucleophilic Metal]

Figure 4.2. Generalized scheme of transition metal hydride via σ complex of hydrogen molecule to metal atom.\textsuperscript{127}
Platinum or palladium metal easily forms metal hydride with a hydrogen molecule due to the back donation of electrons from the occupied d orbital of the metal to the empty $\sigma^*$ (anti-bonding) orbital of hydrogen molecule, thus leading to hydrogen destabilization and eventually to the dissociation of hydrogen molecule.\textsuperscript{127,128} However, if the d orbital of metal atom is coupled to p orbital of boron atom in $\text{BC}_x$, this considerably reduces back donation into the empty $\sigma^*$ anti-bonding orbital of hydrogen molecule, resulting in a reduction of hydrogen destabilization and preventing $\sigma$ donation of the hydrogen molecule to d orbital of the metal atom.

On the other hand, a general electrophillic metal such as titanium and zirconium induces strong $\sigma$ donation of hydrogen molecule due to its electron deficient properties, thus forming metal hydride and protons by the charge polarization mechanism\textsuperscript{129}. In the case of zirconium or titanium disposition onto $\text{BC}_x$, the electrophilic characteristic of the metal is reduced by hybridization with polarized surface of $\text{BC}_x$, and therefore maintaining stable $\sigma$ complex (less charged polarized hydrogen complexes with the metal atom) without further dissociation. The interaction between early transition metal and hydrogen may be able to enhance the physisorption characteristic although no experimental results have been reported yet.
4.2 Experimental Details

4.2.1 Materials and Instruments

Hexachloroplatinic acid hexahydrate and palladium(II) nitrate hydrate were purchased from Sigma-Aldrich. Bis(pentamethylcyclopentadienyl)zirconium dichloride were obtained from Strem Chemicals Inc. (Dimethylsilyl)(tetramethylcyclopentadienyl) (t-butylamido)titanium dimethyl was purchased from Boulder Scientific Company. Acetone and toluene from Sigma-Aldrich were further distilled with Na-benzophenone ketyl. Pure carbon material was obtained from an activated carbon Darco® (Sigma-Aldrich®) after thermal treatment at 600 °C. Two BC\textsubscript{x} materials (BC\textsubscript{12} and BC\textsubscript{6}) were synthesized in accordance with a published procedure.\textsuperscript{88,89}

Powder X-ray diffraction (XRD) data were collected on a Bruker GADDS three-circle X-ray diffractometer using Cu K\textalpha\ (\(\lambda = 0.15406\) nm) radiation. High resolution transmission electron microscopy (HR-TEM) images were obtained using a JEOL JEM-2010. TEM samples were prepared by sonicating the powders in hexane and then dropping a small volume onto a copper grid. Field Emission scanning electron microscopy (FE-SEM) images were acquired using a Leo 1530 FE-SEM.
The metal contents were verified by thermogravimetric analysis (TGA) in air atmosphere on a TA Instruments Q600 SDT and were supported by prompt gamma ray activation analysis (PGAA) in the NIST Neutron facility. During exposure of the sample in a neutron beam, neutrons hit the nuclei in the sample and form neutron captured compounds. The unstable compounds immediately de-excite and emit a gamma ray (prompt gamma). By analyzing the prompt gamma ray spectra, we can identify what element and how much of them are in a sample.

A Micrometrics ASAP 2010 analyzer was used to measure nitrogen adsorption at 77 K using liquid nitrogen, carbon dioxide adsorption at 273 K using ice water, and hydrogen adsorption at 77 K and 87 K using liquid argon. Hydrogen adsorption data were collected at 77 K and 298 K at high pressure by a Sievert type volumetric apparatus.23

4.2.2 Synthesis of Pt/BCx

4.2.2.1 Pt/BC12 (1)

While being stirred in a 100 mL of flask at room temperature, 200 mg of BC12 was dispersed in 40 mL of acetone. Twelve mg of hexachloroplatinic acid hexahydrate (37.64 wt.% of Pt) suspended in 10mL of acetone was added dropwise to the above solution under agitation and stirred for 12 hours. The solid fraction was filtered, dried
under vacuum at room temperature for 12 hours, and then transferred to a quartz holder in a tube furnace. The filtrate solution of hexachloroplatinic acid was reused for further experiment. The platinum ion loaded on BC\textsubscript{12} material was reduced at 500 °C under a flowing stream of argon.

4.2.2.2 Pt/BC\textsubscript{12} (2)

As an alternative, 48 mg of hexachloroplatinic acid hexahydrate was loaded onto 200 mg of BC\textsubscript{12} and same procedure was repeated as described with Pt/BC\textsubscript{12} (1) in order to produce Pt/BC\textsubscript{12}.

4.2.2.3 Pt/BC\textsubscript{6} (3)

The same procedure followed in Section 4.2.2.1 was carried out with 200 mg of BC\textsubscript{6} and 48 mg of hexachloroplatinic acid hexahydrate.

4.2.2.4 Pd/BC\textsubscript{12} (4)

While stirring in a 100 mL of flask at room temperature, 200 mg of BC\textsubscript{12} was dispersed in 40 mL of acetone. Following this, 25.2 mg of palladium(II) nitrate hydrate (38.9 wt.% of Pt) in 10 mL of acetone was added dropwise to the above solution under agitation and stirred for 12 hours. The solid fraction was filtered, dried under vacuum at
room temperature for 12 hours, and then transferred to a quartz holder in a tube furnace. The filtrate solution of hexachloroplatinic acid was reused for further experiment. The platinum ion loaded on BC\textsubscript{12} material was reduced at 500 °C under a flowing stream of argon.

4.2.2.5 Ti/BC\textsubscript{12} (5)

Two hundred mg of BC\textsubscript{12} was dispersed in 40 mL of toluene and was stirred in a 100 mL of flask at room temperature in a glove box filled with highly purified argon. Following this, 29.4 mg of Bis(pentamethylcyclopentadienyl)zirconium dichloride in 10 mL of toluene was added dropwise to the above solution under agitation and stirred for 12 hours. The solid fraction was filtered, dried under vacuum at room temperature for 12 hours, and then transferred to a quartz holder in a tube furnace. The titanium ion loaded on BC\textsubscript{12} was reduced to metallic Ti at 500 °C under a flowing stream of argon.

4.2.2.6 Zr/BC\textsubscript{12} (6)

Two hundred mg of BC\textsubscript{12} was dispersed in 40 mL of toluene and was stirred in a 100 mL of flask at room temperature in a glove box filled with highly purified argon. Following this, 40 mg of Bis(pentamethylcyclopentadienyl)zirconium dichloride in 10
mL of toluene was added dropwise to the above solution under agitation and stirred for 12 hours. The solid fraction was filtered, dried under vacuum at room temperature for 12 hours, and then transferred to a quartz holder in a tube furnace. The zirconium ion loaded on BC$_{12}$ was reduced to metallic Zr at 500 °C under a flowing stream of argon.

4.2.2.7 Pt/AC (7, 8)

For comparison, the mixture of a pure carbon and hexachloroplatinic acid hexahydrate solution was filtered. After the filtrate was removed, the residue solid was dried under vacuum in order to check the mass increase. No more mass increased and only pure carbon was obtained. A 5.6 wt.% of Pt supported by an activated carbon (Pt/AC (7)) was prepared using an activated carbon Darco®, hexachloroplatinic acid hexahydrate, sodium citrate as a stabilizer, and sodium borohydride as a reducing agent in accordance with Zeng et al. (2006). Another 5.6 wt.% of Pt supported by an activated carbon (Pt/AC (8)) was prepared using an activated carbon Darco®, hexachloroplatinic acid hexahydrate in acetone solution in accordance with Li et al. (2007).
4.3 Results and Discussion

4.3.1 Pt Particles Supported by BC$_x$ Materials using Hexachloroplatinic acid

Hexachloroplatinic acid dissociates to hexachloroplatinate anion in water or acetone solvent. While the strong hybridization between the d orbital of a platinum atom and p orbital of a boron atom enables stable metal platinum particles to be disposed on the BC$_x$, driving force for platinum precursors to adsorb on the substrate is related to the electrostatic interaction between a hexachloroplatinate anion and an electropositive center on the surface of BC$_x$. The electrostatic interaction assists adsorption of hexachloroplatinate anion on the BC$_x$ surface and keeps tight connection of the palatinate anion to a boron atom even after filtration with an unreacted metal solution. The chlorinated platinum anions (PtCl$_6^{2-}$) display repulsive force toward each other, which makes it possible for the palatinate anion to interact with BC$_x$ surface at the atomic level, and then arrest growth even under the high temperature treatment used for reduction platinum. Figure 4.3 shows a visualization of the electrostatic interaction between metal and BC$_x$ compared to the corresponding carbon.
Figure 4.3. General scheme of deposition of platinum particles onto a surface of BC$_x$ material using hexachloroplatinate precursor. Carbon substrates are included for comparison.
Table 4.1. Summarized data for metal particles disposed on a support material based on 200 mg of BC\textsubscript{x} (BET surface area of BC\textsubscript{12} is 650 m\textsuperscript{2}/g and BC\textsubscript{7} is 600 m\textsuperscript{2}/g).

<table>
<thead>
<tr>
<th>Material</th>
<th>Metal Precursor</th>
<th>Loading metal (mmol)</th>
<th>Loaded metal (mmol)</th>
<th>Loading efficiency (mol%)</th>
<th>Metal content (wt.%)</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/BC\textsubscript{12} (1)</td>
<td>0.46 mM H\textsubscript{2}PtCl\textsubscript{6}·6(H\textsubscript{2}O)</td>
<td>0.023</td>
<td>0.007</td>
<td>30</td>
<td>0.7</td>
<td>644</td>
</tr>
<tr>
<td>Pt/BC\textsubscript{12} (2)</td>
<td>1.84 mM H\textsubscript{2}PtCl\textsubscript{6}·6(H\textsubscript{2}O)</td>
<td>0.092</td>
<td>0.031</td>
<td>34</td>
<td>3.0</td>
<td>590</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.46 mM H\textsubscript{2}PtCl\textsubscript{6}·6(H\textsubscript{2}O)</td>
<td>0.023</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>670</td>
</tr>
<tr>
<td>Pt/BC\textsubscript{7} (3)</td>
<td>1.84 mM H\textsubscript{2}PtCl\textsubscript{6}·6(H\textsubscript{2}O)</td>
<td>0.092</td>
<td>0.058</td>
<td>63</td>
<td>5.7</td>
<td>460</td>
</tr>
<tr>
<td>Pd/BC\textsubscript{12} (4)</td>
<td>1.84 mM Pd(NO\textsubscript{3})\textsubscript{2}·(H\textsubscript{2}O)</td>
<td>0.092</td>
<td>0.020</td>
<td>22</td>
<td>1.65</td>
<td>650</td>
</tr>
<tr>
<td>Ti/BC\textsubscript{12} (5)</td>
<td>1.80 mM Me\textsubscript{2}Si(tBuN)Cp*TiMe\textsubscript{2}</td>
<td>0.090</td>
<td>0.064</td>
<td>71</td>
<td>1.5</td>
<td>612</td>
</tr>
<tr>
<td>Zr/BC\textsubscript{12} (6)</td>
<td>1.84 mM Cp\textsuperscript{2}ZrCl\textsubscript{2}</td>
<td>0.092</td>
<td>0.050</td>
<td>54</td>
<td>2.3</td>
<td>610</td>
</tr>
</tbody>
</table>
The amounts of disposed platinum on a BC\textsubscript{x} material analyzed by the TGA and PGAA methods are summarized in Table 4.1. When more boron atoms are substituted in the BC\textsubscript{x} matrix (BC\textsubscript{12} vs. BC\textsubscript{6} in (2) and (3)), the adsorption of platinum on the surface of BC\textsubscript{x} is further increased, which explains why no platinum on the pure carbon surface is observed following loading at low concentration of the precursor and subsequent filtration.

The powder X-ray diffraction (XRD) pattern, shown in Figure 4.4 indicates that platinum ions in the precursor solution adsorbed on a BC\textsubscript{x} surface were successfully reduced to metallic platinum after heating to 500 °C under argon atmosphere even without any additional reducing agent. In this case, the hydrogen atoms at the edge of BC\textsubscript{x} served as a source of reduction. While Pt/C synthesized via the typical colloidal solution method using a stabilizer\textsuperscript{104} depicts sharp peaks in (a), the peaks of Pt/BC\textsubscript{12} in (b) are significantly broad, which indicates a big size difference between two samples because the full width at half maximum (FWHM) is related to the metal size.\textsuperscript{82} Such similar sharp patterns of the XRD in (a) are often found in typical carbon supported platinum particles.\textsuperscript{104, 107, 114-116, 130, 131} Size of the platinum particle determined by the Scherer’s equation,\textsuperscript{82} results in a diameter of 10 nm for the Pt/C and 2.5 nm for the
Pt/BC$_6$. More accurate size information is obtained by high resolution transmission electron microscopy (HR-TEM).

Figure 4.4. Powder XRD data for (a) Pt/C (7) reduced by a chemical reducing agent with a stabilizer, and (b) Pt/BC$_{12}$ reduced at 500 °C under argon stream without a stabilizer. The simulated XRD pattern for Pt is shown for comparison in (c).
Platinum nanoparticles synthesized with various BC\textsubscript{x} support materials are showed in HR-TEM images (Figure 4.5). All particles are fairly monodisperse with a mean diameter of less than 2 nm. Evidently, the substitutional boron atoms which interacted with hexachloroplatinate anion, prevented migration and clustering of the platinum particles under high temperature reduction, and provided a synthetic way to produce highly dispersed platinum particles with the desired small size.
Figure 4.5(a,b). HR-TEM images of (a) 0.7 wt.% of Pt/BC$_{12}$ and (b) 3.0 wt.% of Pt/BC$_{12}$. 
Figure 4.5(c,d). HR-TEM images of (c) 5.7 wt.% of Pt/BC$_6$ and (d) 5.6 wt.% of Pt/C (7).
Figure 4.5(e). HR-TEM images of 5.6 wt.% of Pt/C (8).

4.3.2 Pd Particles Supported by BC$_x$ Materials using Palladium nitrate hydrate

In contrast to the case of platonic acid, the precursor compound for palladium particles dissociates to palladium cations (Pd$^{2+}$). Given the different charging mechanism, a palladium cation without any stabilizing ligands is less favorable for interacting with the surface of BC$_x$. Comparison of the loading efficiency of Pt/BC$_{12}$ (2) and Pd/BC$_{12}$ (4), demonstrates palladium cations were less adsorbed onto BC$_x$ surface.

The amount of reduced metallic palladium on a BC$_{12}$ matrix after thermal treatment at 500 °C is 1.6 wt.% and the size is characterized by FE-SEM (Figure 4.6). Compared to 0.7 wt.% of the Pt/BC$_{12}$ sample, palladium particles are much bigger, and
therefore more similar to conventional carbon supported metal particles. Although a polarized $\text{BC}_{12}$ surface promoted the adsorption of palladium cations, the interaction between palladium cation and $\text{BC}_x$ surface might not be strong enough to prevent migration and clustering. However, there is one more factor to be considered. Since platinum ions are surrounded by six chlorine ligands which will stabilize the platinum ion, as opposed to bared cations of the palladium ions, the resulting repulsive force among hexachloroplatinate ions should enable each anion to keep separate and stuck in the boron center on the $\text{BC}_x$ surface. Therefore, anionic ligands are essential to achieve monodispersal of small metal particles on the $\text{BC}_x$ support.
Figure 4.6. FE-SEM images of (a) 1.65 wt.% of Pd/BC$_{12}$ and (b) 0.7 wt.% of Pt/BC$_{12}$ in same magnification. (c) is a higher magnification image of 0.7 wt.% of Pt/BC$_{12}$ showing more detail of the particles.
4.3.3 Zr particles Supported by BC<sub>x</sub> Materials using Zirconocene dichloride

As shown in Table 4.1, the substituted boron in BC<sub>x</sub> assisted adsorption of zirconium compounds. The loading efficiency of zirconocene dichloride onto BC<sub>12</sub> (6) is doubled, compared to that in hexachloroplatinic acid. Reduced zirconium metal particles are fairly small (1-2 nm of diameter) from the HR-TEM image in Figure 4.7. The relatively bigger particles found in the image may be attributed to the formation of oxidized zirconium when the air sensitive zirconium particles were exposed to the air during sample preparation for TEM measurement.

Figure 4.7. A HR-TEM image of 2.3 wt.% of Zr/BC<sub>12</sub>. 
Zirconocene dichloride dissociates to zirconocenium (Cp*₂Zr^{2+}) cation.\(^{132-135}\) While bared palladium cations without stabilizing ligands are unfavorably interact to BC\(_x\) surface, zirconocenium cations interact strongly with the BC\(_x\) surface because a zirconocenium cation can be stabilized by its interaction with the boron mediated carbon configuration. Molecular orbital calculation\(^{133}\) explains that the d orbital of a zirconium atom in a zirconocenium cation is hybridized with the p orbital of a carbon atom activated by neighboring boron atom (Figure 4.8); these stabilized complexes are found in the olefin polymerization.\(^{132-135}\) Consequently, a zirconium atom which is stabilized by two cyclopentadienyl rings is drawn toward a boron induced polarized BC\(_x\) surface and maintains a quite stable configuration, resulting in efficient adsorption. The adsorbed zirconium atoms surrounded by bulky cyclopentadienyl groups are kept separate due to the repulsive interaction between each of the zirconocenium ions derived by steric hindrance of bulky cyclopentadienyl rings. For similar reasons, titanium with a cyclopentadienyl ligand (5) is considered as good adsorbate material. When comparing the adsorption of zirconocenium (Cp*₂Zr^{2+}) and half titanocenium (Me₂SiCp\(^*\)(t-BuN)Ti^{2+}) cations to the BC\(_x\) substrate, the titanocenium cation was found to have higher
adsorption, which might be attributed to the increased space it has available with which to approach the $\text{BC}_x$ surface. (Figure 4.10)

Figure 4.8. Interaction diagram between $(\eta_5\text{-C}_5\text{H}_5)_2\text{ZrCH}_3^+$ fragment and $\text{F}_3\text{BCH}_3^{-133}$. 
To summarize, the efficiency of metal loading into BC$_x$ surface and the metal particle size can be controlled by type of metal precursor. Metal compounds stabilized by
bulky ligands produced small metal particles highly monodispersed in the BC\textsubscript{x} matrix, which is a unique property achieved by the boron substituted carbon structure.

### 4.3.4 Hydrogen Adsorption of Metal Disposed on BC\textsubscript{x} Material

Metal nanoparticles have distinct differences in their catalytic activity including hydrogen physisorption when compared with their bulk counterparts.\textsuperscript{136} Main reason is because the surface area of metal catalyst to utilize is significantly increase in the case of nano particles. Therefore, the smaller particle will be expected to achieve more hydrogen adsorption with the same amount of metal. Figure 4.11 gives several information about hydrogen adsorption of metal loaded BC\textsubscript{x} at 77 K and low pressure (lower than 1.2 bar). When using platinum with the same particle diameter (0.7 wt.% of Pt/BC\textsubscript{12-644} vs. 5.7 wt.% of Pt/BC\textsubscript{7-460}), the amount of hydrogen adsorption measured varied depending on the specific surface area of the sample, and similar trend is found with different metal loaded BC\textsubscript{x} in Figure 4.12. Considering the sample of 5.6 wt.% of Pt/C has higher surface area (800 m\textsuperscript{2}/g) than Pt/BC\textsubscript{x} did, small sized platinum particles disposed on BC\textsubscript{x} apparently have enhanced physisorption of hydrogen (Figure 4.12).

Figure 4.12 depicted hydrogen uptake of various metal particles on a BC\textsubscript{12} support at 77 K under low pressure. The trend of hydrogen adsorption shown
continuously over an extended pressure range appears to follow in order of surface area of samples. Among 0.7 wt.% of Pt/BC\textsubscript{12}, Pd/BC\textsubscript{12} and BC\textsubscript{12} without metal loading, there was no difference despite 1.65 wt.% of Pd particles on BC\textsubscript{12} displayed bigger size and this trend continues at further pressure range (Figure 4.13).

Figure 4.11. Hydrogen physisorption of Pt/BC\textsubscript{x} samples at 77 K under low pressure. 5.6 wt.% Pt/C synthesized\textsuperscript{104} is shown here for comparison.
Figure 4.12. Hydrogen physisorption of various metal Pt/BC\textsubscript{12} samples at 77 K under low pressure.

Figure 4.13. Hydrogen physisorption of BC\textsubscript{12}, 0.7 wt.% of Pt/BC\textsubscript{12} and 1.65 wt.% of Pd/BC\textsubscript{12} at 77 K. Three samples have similar surface area (about 650 m\textsuperscript{2}/g).
Figure 4.14. Hydrogen physisorption results of BC$_{12}$, 0.7 wt.% of Pt/BC$_{12}$ and 1.65 wt.% of Pd/BC$_{12}$ at 298 K. Three samples have similar surface area (about 650 m$^2$/g).

Although not much difference of hydrogen uptake at 77 K among three samples was observed, a significant difference was seen at ambient temperature (298 K) under high pressure (Figure 4.14) In case of 0.7 wt.% of Pt/BC$_{12}$ sample, the overall hydrogen adsorption capacity clearly increases by 64% compared to 1.6 wt.% of Pd/BC$_{12}$ and BC$_{12}$. In fact, the enhancement in hydrogen uptake at ambient temperature under high pressure of supported metals has been reported frequently.$^{114-116}$ A 6 wt.% of Pt/C was reported to exhibit a 60% enhancement in hydrogen uptake at room temperature$^{116}$, a 50% increase was observed in a 3 wt.% of Pt/C material$^{115}$, and a 5.6 wt.% of Pt/C showed doubled hydrogen capacity compared to the carbon base sample$^{114}$. Considering all the reported data, a 64% increase in hydrogen capacity due to 0.7 wt.% of platinum, even when using
an extremely low metal content, indicates that highly monodisperse and small nanosized platinum particles have a predominant role in the enhancement of hydrogen physisorption. Not much of a difference in hydrogen capacity at 77 K conditions was shown despite the significant enhancement observed in the hydrogen adsorption at ambient temperature.

Figure 4.15. Comparison of hydrogen physisorption of 0.7 wt.% of Pt/BC and 5.6 wt.% of Pt/C at 298 K.

In Figure 4.15, hydrogen physisorption of 0.7 wt.% of Pt/BC is compared to 5.6 wt.% of Pt/C at ambient temperature (298 K). It is interesting to note that the adsorption measurement after each data point in the Pt/C sample, required serious pre-activation treated by vacuum at 200 °C for 4 hours in order to completely remove the hydrogen molecules adsorbed onto Pt/C surface from the previous measurement. This pre-
activation was not necessary when BC$_x$, activated carbon samples, and even Pt/BC$_x$ samples were run for hydrogen adsorption, which indicates reversible adsorption and desorption kinetics. This supports that strong interaction between hydrogen and Pt on the carbon support, which was explained theoretically by the hybridization of the d orbital of platinum atom with the σ orbital of hydrogen molecule and additionally the back donation of electrons from the occupied d orbital of the platinum to the empty σ* (anti-bonding) orbital of hydrogen molecule in Figure 4.2 in Section 4.1.2. In the case of Pt/BC$_x$ sample, it can be explained that the d orbital of platinum atom is coupled to p orbital of boron atom in BC$_x$, this considerably reduces back donation into the empty σ* anti-bonding orbital of hydrogen molecule, resulting in a reduction of interaction of hydrogen to the platinum on BC$_x$ surface, and eventually it makes reversible adsorption and desorption easy and fast.

4.4 Conclusions

Conventional supported metal particles are typically prepared by adsorbing precursors into a porous carbon support by aid of a stabilizer in the colloidal system or by incipient wetness impregnation into a porous carbon support, followed by a reduction process. Thermal treatment is necessary to generate active metal particles which
often involve reduction of the metals by hydrogen gas, but this causes metal clustering and loss in surface area of the metal particles.

Here we synthesized highly monodispersed nanosized metal particles without the use of stabilizers via colloidal stabilization by aid of $BC_x$ materials. The particle size can be controlled by precursor type. A platinum or zirconium atom which is stabilized by bulky ligands was drawn toward a boron induced polarized $BC_x$ surface and maintained a quite stable configuration, resulting in efficient loading and small and uniformly dispersed particles after reduction process even at high temperature (500 °C). The particle size information, characterized using XRD, FE-SEM and HR-TEM provided a mean diameter of less than 2 nm.

A 60% enhancement in hydrogen physisorption was observed at the ambient temperature in the $BC_{12}$ sample supported with 0.7 wt.% of platinum, compared to $BC_{12}$ without metal particles. The big difference seen in palladium and platinum system can be explained by the resulting total surface area of metal particles because much smaller platinum particles have many chance to react with hydrogen molecules due to higher surface area. While metal doping effect on hydrogen adsorption increase was observed at ambient temperature, not much of a difference in hydrogen capacity at 77 K conditions
was shown. At 77 K, the maximum condensation of hydrogen molecules on a monolayer of ideal graphene sheet is $1.25 \times 10^{-5}$ mole of $H_2/m^2$ of substrate, which corresponds to 0.4 of hydrogen atom per a surface carbon atom, or 2.5 wt.% of $H_2$ per 1000$m^2/g$ of a graphene sheet.\textsuperscript{3} Considering the fact, the amount of hydrogen adsorbed at 77 K by BC$_x$s or metal loaded BC$_x$ materials already have exceeded their maximum value at the given surface area. That might be reason why rather surface area of adsorbents than metal particle size or substituted boron content, is a major variable to control the hydrogen adsorption.

In fact, most commercialized platinums or palladiums on activated carbons from Strem Chemicals Inc. range from 5 wt.% to 10 wt.% of metal content because a critical platinum content of above 5 wt.% is required to exhibit appropriate catalytic activity within the range of conventional metal particle size. Considering a highly effective enhancement in hydrogen capacity with an extremely low level of metal content was achieved from the metal loading on BC$_x$, the synthetic approach of metal particles on BC$_x$ supports will be able to maximize the efficiency in metal utilization. Applications for this synthetic process can be expanded to other applications such as metal catalysts systems for organic reactions or for fuel cell system, as well as for hydrogen storage applications.
Chapter 5
Conclusions and Suggested Future Work

5.1 Summary of Present Work

5.1.1 Boron Substituted Carbon (BC\textsubscript{x}) Materials

Hydrogen storage is a major challenge in realizing hydrogen energy. Physisorption would be an ideal method if the adsorbent material could show sufficient adsorption capacity at ambient temperature and moderate pressure, and perform fast adsorption-desorption kinetics at convenient conditions. The effective physisorption of hydrogen requires high surface area of adsorbents and an optimum binding energy of 10 – 25 kJ/mole. BC\textsubscript{x} material with high surface area is promising candidate because the boron moiety maintains its high acidity (electron deficiency), and serves as an internal p-type dopant for activating BC\textsubscript{x} surfaces. Therefore, new synthetic strategies should be developed to make the ideal structure feasible for hydrogen storage applications.

Early methods of gas phase CVD and solid state diffusion prepared BC\textsubscript{x} materials with either B\textsubscript{4}C/BC\textsubscript{3} (>25% B content) or the graphitic product with <3% B content. The resulting dense structures were not suitable for hydrogen storage applications. In this
study, we have developed a versatile method to prepare a broad range of porous BC\textsubscript{x} materials, bridging the gap of boron content and microstructure, by using a specifically-designed boron-containing polymer (boron-precursor) that contains some inorganic additives. By taking into account the chemistry of boron and the mechanism of carbonization, most of the boron moieties in the boron-precursor were substitutional incorporated in the fused hexagonal ring structure. The morphology and crystalline structure are determined by a combination of pyrolysis temperature and inorganic additives. As illustrated in Figure 2.24, the chemical structure of BC\textsubscript{x} changes from a disordered (less $\pi$ conjugated) state, or a boron-puckered configuration at 600-800 °C to an ordered (highly $\pi$ conjugated) state, that is a planar and multiple-layered configuration at 1500 °C. The resulting planar layers can only accommodate a reduced amount ($<3\%$) of boron content which is consistent with the thermodynamic observation at high temperature (1500 °C to 2500 °C). After pyrolysis, the inorganic satss dispersed in the resulting BC\textsubscript{x} matrix are removed by water washing, which creates pore structures in the BC\textsubscript{x} material.

Some resulting amorphous BC\textsubscript{x} materials (pyrolysis at 600-800 °C) show controllable nanopore and mesopore structures with high surface area, and containing up
to 12 wt.% of boron content with acidic (electron-deficient) boron moieties. The combination provides super-activated surfaces for physical interactions with various molecules.

5.1.2 Hydrogen Physisorption and Binding Energy with BC_x Materials

The experimental approach to validate the interaction between nanoporous BC_x and hydrogen molecule is measuring hydrogen isotherm physical adsorption and obtaining isosteric heat of adsorption. The substitutional boron elements in BC_x served as internal p-type dopants and polarized the surface of BC_x, and they exhibited significantly higher hydrogen adsorption capacity than carbon materials. The physisorption results were further supported by isosteric heat of absorption, indicating a binding energy of hydrogen molecules between 9 and 14 kJ/mole, significantly higher than the 4 kJ/mole reported on most graphitic carbon and activated carbon surfaces.

5.1.3 Metal Doped BC_x Materials

Conventional supported metal particles are typically prepared by adsorbing precursors into a porous carbon support by aid of a stabilizer in the colloidal system or by incipient wetness impregnation into a porous carbon support, followed by a reduction
process. Thermal treatment is necessary to generate active metal particles which often involve reduction of the metals by hydrogen gas, but this causes metal clustering and loss in surface area of the metal particles.

Here we synthesized highly monodispersed nanosized metal particles without the use of stabilizers via colloidal stabilization by aid of BC\textsubscript{x} materials. The particle size can be controlled by precursor type. A platinum or zirconium atom which is stabilized by bulky ligands was drawn toward a boron induced polarized BC\textsubscript{x} surface and maintained a quite stable configuration, resulting in efficient loading and small and uniformly dispersed particles after reduction process even at high temperature (500 °C). The particle size information, characterized using XRD, FE-SEM and HR-TEM provided a mean diameter of less than 2 nm. Based on the fact\textsuperscript{137} that atomic diameter of platinum is 0.27 nm, that of palladium is 0.28 nm, and zirconium has 0.31 nm of diameter, the size information of metal particles on BC\textsubscript{x} support materials gives us intuitive understanding that several metal atoms agglomerated during the reduction process although we have tried to promote atomic interaction between boron atom and metal atom.

A 64% enhancement in hydrogen physisorption was observed at the ambient temperature in the BC\textsubscript{12} sample supported with 0.7 wt.% of platinum, compared to BC\textsubscript{12}
without metal particles. This similar improvement can be achieved only when more than 5 wt.% of Pt on carbon materials are used under same conditions. The big difference seen in palladium and platinum system can be explained by the resulting total surface area of metal particles because much smaller platinum particles have many chance to react with hydrogen molecules due to higher surface area. While metal doping effect on hydrogen adsorption increase was observed at ambient temperature, not much of a difference in hydrogen capacity at 77 K conditions was shown. At 77 K, maximum condensation of hydrogen molecules on a monolayer of ideal graphene sheet is $1.25 \times 10^{-5}$ mole of $\text{H}_2$ / m$^2$ of substrate, which corresponds to 0.4 of hydrogen atom per a surface carbon atom, or 2.5 wt.% of $\text{H}_2$ per 1000m$^2$/g of a graphene sheet.$^3$ Considering the fact above, the amount of hydrogen adsorbed at 77 K by BC$_x$s or metal loaded BC$_x$ materials already have exceeded their maximum value at the given surface area. That might be reason why rather surface area of adsorbents than metal particle size or substituted boron content, is a major variable to control the hydrogen adsorption.

In fact, most commercialized platinum or palladiums on activated carbons from Strem Chemicals Inc. range from 5 wt.% to 10 wt.% of metal content because a critical platinum content of above 5 wt.% is required to exhibit appropriate catalytic activity
within the range of conventional metal particle size. Considering the fact that BC_{12} sample achieved 64% of increase in hydrogen uptake with only 0.7 wt.% of Pt loading, uniform nanosized platinum particles have distinctive advantages and will be able to maximize the efficiency in the application of metal utilization.

Applications for this synthetic process can be expanded to other applications such as metal catalysts systems for organic reactions or for fuel cell system, as well as for hydrogen storage applications.

5.2 Final Conclusions

In this study, a novel approach to the preparation of nanoporous BC_{x} materials has been developed. Due to electron-deficient boron moieties and limited \( \pi \) electron delocalization, the boron atom in BC_{x} serves as an internal p-type dopant that exhibits interactive properties with hydrogen molecules. Such boron doping can enhance both hydrogen binding energy and adsorption capacity. The synthesized nanoporous BC_{x} is a new class of activated carbon and has shown enhanced hydrogen adsorption which can give feedback on many theoretical predictions about the importance of the substituted boron in the carbon structure for hydrogen storage technologies.\(^{54, 56}\) The interaction between nanoporous BC_{x} and other chemicals such as amine compounds and metal
compounds with stabilizing ligands shows that the utilization of the nanoporous BC\textsubscript{x}s have distinctive advantages for possible applications such as the synthesis of nanosized metal particles, selective permeation of gas molecules, new electrode materials for lithium battery,\textsuperscript{138} and double-layer capacitor\textsuperscript{139} as well as hydrogen physical adsorbents.

5.3 Suggested Future Work

Although the approach of designing \textit{in situ} inorganic templates in the synthetic process is simple and advantageous way, there is a limitation to increase surface area if higher surface area than 1000 m\textsuperscript{2}/g is required to enhance hydrogen adsorption capacity. Therefore, further effort to achieve higher surface area of BC\textsubscript{x} should be necessary. Synthetic methods of the preparation of porous carbon materials can be divided into two categories: activation processes and template methods. Activation processes have frequently been employed for the synthesis of porous carbon materials. However, it is not recommendable for increase in the surface area of BC\textsubscript{x} material because oxidation of the substituted boron atom is possible during the activation process, which was confirmed from the preliminary experiments. Classical template methods using external inorganic template such as high surface area of zeolites can be tried. In an attempt to utilize the zeolites as templates, the preparation of suitable B-precursor should be crucial. Since the
solid polymeric B-precursor, poly(diethynylphenylborane chloride) is considered difficult to diffuse into the highly porous zeolites, the liquid oligomeric B-precursor whose synthesis was discussed in Section 2.2.4, can be used. However, the template method using zeolites still has problem that hydrofluoric acid, which is not easy to handle with, should be used to remove zeolite templates after carbonization of the mixture of B-precursor and zeolites because of very low solubility of zeolites in typical solvent. Regardless of the shortcoming, it is worth trying the approach via liquid B-precursor and zeolite templates to achieve advanced BC$_x$ material with increased surface area.
35. Han, S.; Sohn, K.; Hyeon, T., "Fabrication of New Nanoporous Carbons through Silica Templates and Their Application to the Adsorption of Bulky Dyes", Chemistry of Materials 2000, 12, 3337.


Preparation and X-ray Crystallographic Characterization of \([\text{Cp}^*\text{Al}]^+\text{[Me(Ph)B(\text{η}^5-C_5H_4)ZrCl}_2]\) and \([\text{PPN}]^+\text{[Cl(Ph)B(\text{η}^5-C_5H_4)ZrCl}_2]\)"", \textit{Organometallics} \textbf{1999}, \textit{18}, 5432.


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