Communication

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Synthesis of Microporous Boron-Substituted Carbon (B/C) Materials Using Polymeric Precursors for Hydrogen Physisorption

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Hydrogen storage is a major challenge in realizing hydrogen energy, especially for onboard automotive applications.[1] Current methods, including compressed gas, cryogenic liquid, metal hydrides, chemical hydrides, and adsorbents, all show significant deficiencies in practical usages. Physisorption would be an ideal method if the adsorbent material could show sufficient adsorption capacity at ambient temperature and low pressure. Despite tremendous efforts on many carbonaceous materials,[2] including carbon nanotubes, recent results show a low binding energy (~4 kJ/mol)[3] between hydrogen and the carbon surface. The effective physisorption of hydrogen requires 77 K and 100 bar, with the capacity[4] of 1 wt % H_2 per 500 m^2/g surface area. To increase the binding energy, several approaches,[5] by incorporating functional groups or dopants on C surfaces that may polarize and dissociate the H_2 molecule, achieved some interesting results. Few early papers[6] discuss the doping of C with B via solid state diffusion under high temperature and long residence time. The B incorporation is limited with a maximum value of 2.35%, and the dispersion of B elements is often inhomogeneous. More recently, BC_3 and B substituted C-nanotubes[7] were also prepared, as well as the theoretical prediction of B effect to the H_2 binding energy.[8] A few years ago, we reported a method to prepare boron-substituted carbon (B/C) materials, containing up to 7 mol% of boron atoms substitutionally incorporated in the C structure, by using boron-containing organic precursors and a pyrolysis process.[9] The resulting B/C material at pyrolysis > 1500 °C becomes a stable, graphilic crystalline structure with an extremely low surface area (<3 m^2/g). For hydrogen adsorption, it is essential to have a microporous structure with a high surface area and interactive B moieties.

In this communication, we discuss a new class of polymeric B-containing precursors that can be thermally transformed to microporous B/C materials having interactive B moieties. Scheme 1 illustrates two polymeric precursors, including the polyaddition adduct (I) of phenyldiacetyene and BCl_3 and the polycondensation adduct (II) between the lithiated phenyl diacetylene and BCl_3. The *in situ* formed LiCl molecules in precursor (II) were uniformly dispersed in the matrix. Both polymeric precursors (brownish solids) were subjected to the pyrolysis. They turned to complete black solids after heating at >600 °C. The detailed procedures of the precursor preparation and pyrolysis are provided in the Supporting Information.

Table 1 summarizes the results of boron content and surface area. Generally, precursor (II) offers a higher B/C yield (>60%), with a better B conversion, and a higher surface area. The combination of alkynyl and B–Cl moieties is very favorable in the interpolymer reactions (stabilization step at low temperature), via chloroboration and cyclization ($2\pi + 4\pi$) reactions. On the other hand, the stable vinylidene chloride group in precursor (I) may slow down both

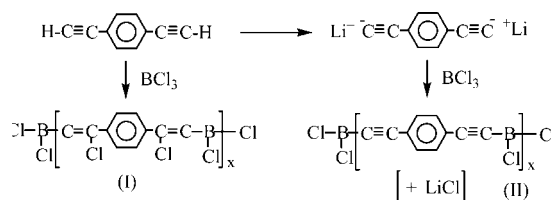**Scheme 1.** Synthesis of Two Polymeric B-Containing Precursors

Table 1. A Summary of B/C Materials Prepared under Various Conditions

sample	precursor	pyrolysis temp (°C)	B content[a] (wt %)	B content[b] (wt %)	surface area[c] (m^2/g)
BC-I-800	I	800	1.5	-	150
BC-I-1200	I	1200	1.2	-	35
BC-II-600	II	600	7.2	7.6	780
BC-II-800	II	800	5.7	7.1	528
BC-II-1100	II	1100	4.2	3.0	40

[a] B content was determined by Prompt Gamma-ray Activation Analysis. *[b]* B content was determined by ^{11}B MAS NMR spectra. *[c]* Surface area was determined by BET method using N_2 gas at liquid N_2 temperature.
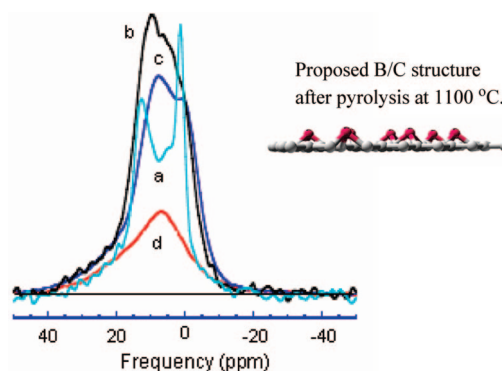

Figure 1. ^{11}B MAS NMR spectra of B/C materials prepared from pyrolysis of precursor (II) at (a) 150, (b) 600, (c) 800, and (d) 1100 °C (Inset: the proposed B/C structure after pyrolysis at 1100 °C).

reactions. In fact, some of the BCl_3 byproduct from the (reverse) dechloroboration reaction was observed during the pyrolysis of precursor (I). Figure 1 shows the ^{11}B MAS NMR spectra of several B/C materials obtained from precursor (II) after pyrolysis at various temperatures. All spectra can be decomposed into and simulated by two components (see Supporting Information). The downfield one associated with boron sites of trigonal (planar) symmetry may contain three conjugated olefinic and alkynyl ligands, formed after low temperature interchain chloroboration. The upfield one represented by spectrum (d) relates to boron sites in a nonplanar boron puckered C configuration, as illustrated in the inset of Figure 1. With increasing annealing temperature, the cyclization (carboniza-

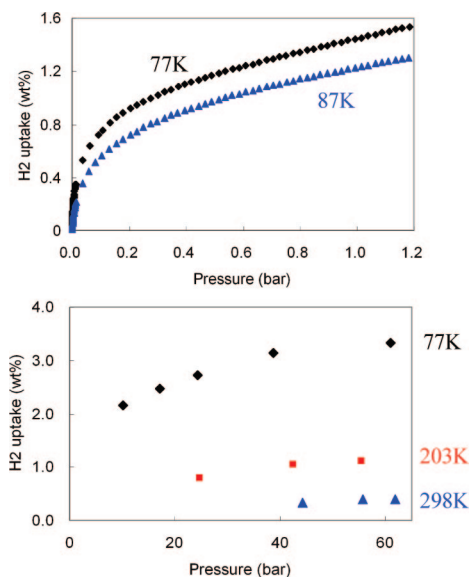† The Pennsylvania State University.
‡ University of North Carolina.

Figure 2. Hydrogen adsorption for sample B/C−II-600, (top) absorption isotherms (gravimetric measurement) and (bottom) hydrogen adsorption vs pressure (volumetric measurement).

tion) reaction gradually changes the trigonal structure toward the puckered configuration, and the number of trigonal sites vanishes once samples are annealed at 1100 °C. Samples annealed at higher temperatures (1400 to 1800 °C) appear to graphitize on a larger scale[10b] (see Supporting Information).

The presence of LiCl molecules in precursor (II), which were removed after pyrolysis by water washing, offers a convenient way to obtain microporous B/C material. Figure 1S (Supporting Information) shows the porous size distribution of sample B/C−II-800, exhibiting a narrow peak centered at a 3.5 nm pore diameter. The *in situ* formed LiCl molecules (mp: 605 °C and bp = 1300 °C) should maintain good dispersion in the matrix up to 600 °C (sample B/C−II-600). Upon heating the precursor (II) above 605 °C (sample B/C−II-800), liquid LiCl molecules may start to diffuse and merge into microphase domains. Beyond 1300 °C (sample B/C−II-1500), LiCl molecules could be evaporated out from the matrix and most of the porous structures become, instead, a much denser B/C product. The porous B/C−II-800 sample was also subjected to the B−N complexization study with tributylamine at ambient temperature, in order to examine the available B sites. Based on the weight increase, we estimated about one-third of the B sites in the B/C−II-800 sample interacting with tributylamine. The resulting B−N complexes were quite stable until >300 °C. After tributylamine removal, the regenerated B/C material shows almost the same weight and surface area.

The quantitative H_2 binding energy on the B/C materials was estimated by adsorption isotherms (at 77 and 87 K) under low hydrogen pressure (1.2 bar). Figure 2 (top) shows the hydrogen uptake vs hydrogen pressure for sample B/C−II-600. The volume adsorbed at different pressures was converted to the heat of adsorption, using the Clausius−Clapeyron equation $\Delta H_i = RT^2(\mathrm{d}(\ln P_i)/\mathrm{d}t)_{n_i}$, wherein ΔH_i 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.[11] The initial isosteric heat of adsorption for the B/C material is 12.47 kJ/mol and maintains quite a high adsorption energy level to higher surface coverage (10.8 kJ/mol for 0.62 wt % H_2 uptake). They are significantly higher than those observed in the undoped and some metal doped C materials.

Figure 2 (bottom) shows H_2 adsorption on the B/C−II-600 sample at 293, 203, and 77 K, under various H_2 pressures. About 0.4 wt % H_2 adsorption was observed at ambient temperature under 56 bar of H_2 pressure, which is ∼50% higher than that of carbonaceous

materials[12] with similar surface areas. Temperature has a marked effect on the increase of the H_2 adsorption capability. At 77 K, the H_2 adsorption of B/C−II-600 reaches the 3.2 wt % mark; this is almost double that of the corresponding carbonaceous materials.[13]

In summary, we have developed an effective route, using a combination of designed B-containing polymeric precursors and pyrolysis, to prepare microporous B/C materials with a high B content (7.2%) and high surface area (780 m^2/g). The substitutional B elements in B/C material serve as internal p-type dopants and polarize the C surface, which exhibit a significantly higher hydrogen binding energy (∼11 kJ/mol).

Supporting Information Available: Synthesis of precursors, the pyrolysis process, surface area of B/C materials, and hydrogen binding energy measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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