

Possibility of Hydrogen Storage by Boron Substituted Carbon nanotubes

M.Sankaran*, B.Viswanathan* and S.Srinivasamurthy#

* National Centre for Catalysis Research, Department of Chemistry and
Department of Mechanical Engineering, Indian Institute of Technology, Madras
Chennai-600 036,INDIA

The possibility of exploiting boron substituted carbon nanotubes for hydrogen storage is examined. The importance of geometrical location of Boron atoms in the nanotubes is also brought out.

Introduction:

A major difficulty in utilizing hydrogen as energy carrier has been the absence of a practical means for hydrogen storage. Developing safe and reliable hydrogen storage technology that meets performance and cost requirements is critical to use hydrogen as a fuel for both vehicular and for stationary power generation applications. Current on-board hydrogen storage approaches involve compressed hydrogen gas tanks, liquid hydrogen tanks, metal hydrides, carbon-based materials/high surface area sorbants such as metal-organic frameworks, and chemical hydrogen storage using complex hydrides. The current state of art does not seem to provide a solution for the problem of finding appropriate economically viable hydrogen storage medium. But it appears that the carbon nanomaterials may show promising potential towards storage capacity of hydrogen to achieve the original requirement of DOE standard of 6.5 wt% and 62% volumetric densities for mobile application [1]. For last one-decade carbon nanotubes have been extensively studied for hydrogen storage options by both experimentally and theoretically, but the results are not prompt and promising [2-7]. Even varying the experimental limits and the

growth conditions could not attain the DOE requirement. Doping carbon nanomaterials with of alkali metal (Na, K), transition metals (Fe) and alloys ($\text{TiAl}_{0.1}\text{V}_{0.04}$, Ti-6Al-4V and NiO-MgO) where the storage mechanism is different, as the metals are involved forms hydride and the metal hydride could not store greater than its number atomic combinations [8-11] has not yielded the requisite material. Against this background, the need for an activator for hydrogenation in carbon materials is realized, which should be easily hydridable than carbon and facilitate migration of the dissociated hydrogen to carbon surface. While considering these aspects heteroatoms like N, P, S and B seem to be promising as activators [12-14]. The substitution of heteroatom at the required gradation and the geometrical positions are the important criteria for hydrogen activation. The boron substitution in the carbon materials has received special attention with respect to their geometrical positions and the recent theoretical reports reveal that the substitution of boron in alternate position is more effective for hydrogen activation compared to adjacent substitution positions [15, 16]. In this communication, attempts to synthesize boron containing carbon nanotubes and

the relevance to hydrogen storage are reported.

Experiments and Results:

Boron containing carbon nanotubes (BCNT1) have been prepared by using the boron containing polymer as the carbon precursor, stable cross linked π - conjugated organoboron polymer prepared by hydroboration polymerization of 1, 4-divinylbenzene and diborane in THF medium. In situ polymerization has been carried out over the alumina membrane template (0.2 μm pore diameter and 60 μm thick) in THF medium. After the polymerization, the membranes are removed and polished with alumina powder to remove the adhered polymers. The polymer/alumina composite membranes have been carbonized at 900 $^{\circ}\text{C}$ in Ar atmosphere and the carbon/alumina composite treated with 48% HF for 24 h to remove the template. Finally undissolved carbon materials has been washed with distilled water and dried at 100 $^{\circ}\text{C}$. Other boron

containing carbon nanotube (BCNT2) has been prepared by chemical vapour deposition (CVD) method by using zeolite (NaY) as template and acetylene (5 ml/min) as carbon source and in situ generation of borane gas by addition of conc. H_2SO_4 in NaBH_4 in THF medium, carbonized at 900 $^{\circ}\text{C}$ in Ar atmosphere. The carbon/zeolite composite has been treated with 48% HF for 24 h and the undissolved carbon has been washed with distilled water and dried at 100 $^{\circ}\text{C}$. The BCNTs obtained were characterized by Transmission electron microscopy (TEM). The micrographs shown in Fig.1 shows that the procedure adopted leads to the formation of nanotubes. ^{11}B MAS NMR experiments have been carried out to determine the environment of boron in carbon net work. From the Fig. 2, it is seen that there exist two different chemical environments for boron present in the carbon nanotube prepared by polymer route (BCNT1) where as in BCNT2 show a single environment of boron.

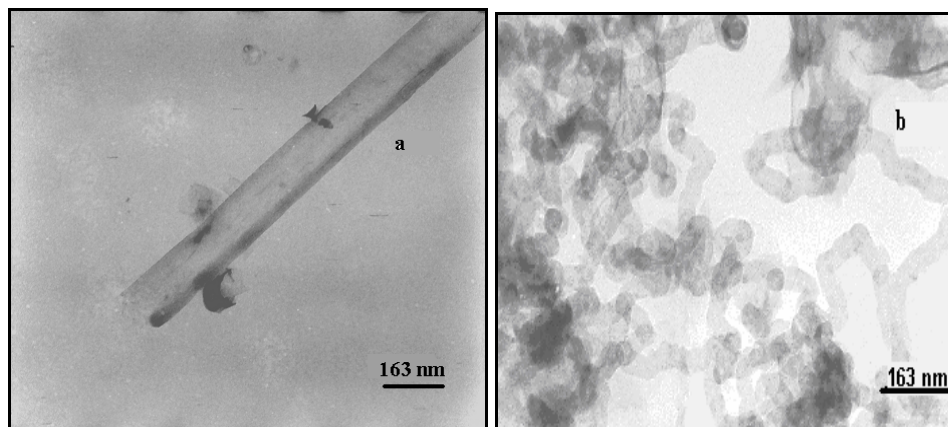


Figure 1. (a). TEM picture of boron containing carbon nanotube (BCNT1) prepared from polymer and (b). Boron containing carbon nanotubes prepared by CVD method (BCNT2).

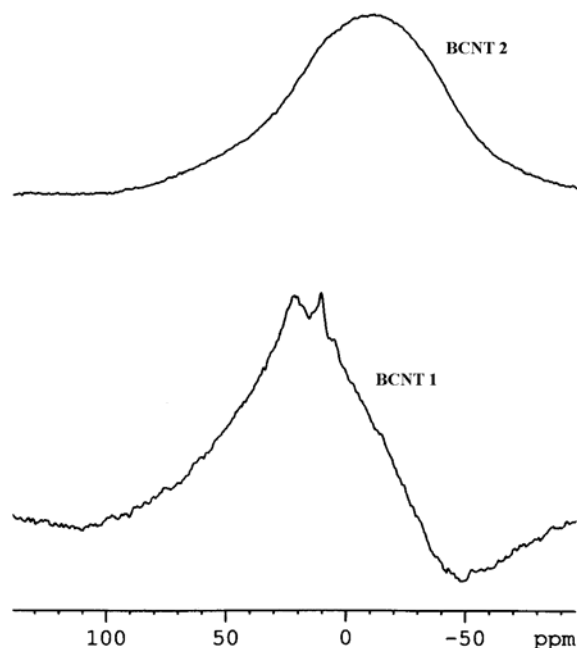


Figure 2. ^{11}B MAS NMR spectrum of boron containing carbon nanotubes prepared by different methods (BCNT1 and BCNT2).

Volumetric high pressure hydrogen adsorption measurement has been carried out using custom built Sievert's apparatus. The high pressure adsorption apparatus consists of reservoir cell and a cylindrical sample cell of known volume (33.8 cm^3). All possible care for the possible sources of leak was carefully taken and long blank run tests were carried out. Care has been taken to avoid the errors due to factors such as temperature instability, leaks and additional pressure and temperature effects caused by expanding the hydrogen from the reservoir to the sample cell. The volume of the system was determined by measuring accurately those of the single components at lower pressures using helium gas. The measurements were carried out by utilizing the systematic procedure as

follows: Typically the mass of the carbon samples used for hydrogen storage measurements is in the region of 100–300 mg. Prior to measurement, the samples are degassed and heated at 450°C for approximately 6 h in vacuum of 10^{-5} Torr. The whole system has been pressurized at the desired value by hydrogen and change in pressure was monitored. The change in the pressure was recorded by a pressure transducer, when no more pressure change is observed, it is assured that the equilibrium has been reached. All the hydrogen adsorption measurements have been carried out at room temperature. The experiments have been repeated under the same conditions for various pressures. The hydrogen compressibility factors were utilized for the calculations.

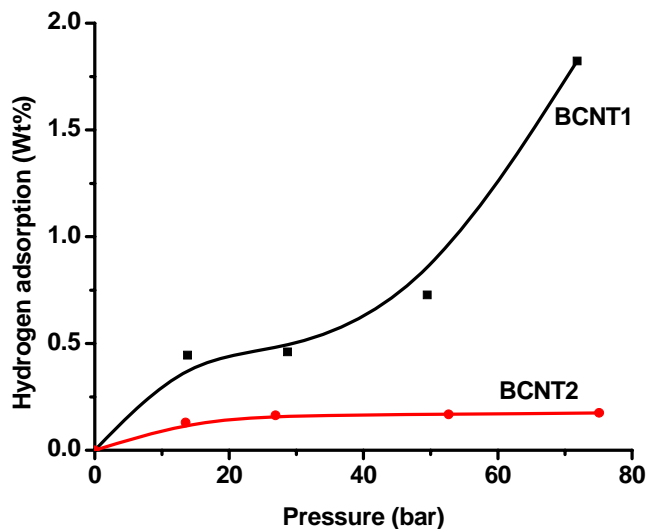


Figure 3. High pressure hydrogen adsorption activity of boron containing carbon nanotubes.

High pressure hydrogen adsorption measurements (Fig. 3) show that the hydrogen adsorption increases with pressure. Adsorption upto 2 wt% for BCNT1 could be observed at 80 bar where as the other sample BCNT2 shows out 0.2 wt% at this pressure.

In summary, boron containing carbon nanotubes prepared with polymer precursor, show different boron chemical environments for boron. This configuration has a bearing in hydrogen sorption characteristics.

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