

SYNOPSIS OF

**ON THE POTENTIAL OF CARBON MATERIALS FOR SOLID
STATE HYDROGEN STORAGE**

A THESIS

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ON THE POTENTIAL OF CARBON MATERIALS FOR SOLID STATE HYDROGEN STORAGE

INTRODUCTION

All the three components of the hydrogen economy, namely, production, storage and application of hydrogen have been posing challenges to the scientific community for the past several decades. At the present, storage of hydrogen in solid matrices appears to be the appropriate option. The scientific community in their anxiety and enthusiasm has come up with remarkable but not reproducible results for hydrogen storage in solid state. The desirable storage capacity for viable commercial exploitation of hydrogen as energy source is around at least 6.5 weight % as originally postulated by US-DOE. However, any figure up to 67 weight % has been claimed as possible storage capacity in solids especially in carbon based materials (Dillon *et al.*, 1997; Chambers *et al.*, 1998). This has opened up a variety of investigations dealing with modification of carbon materials like metal loading (Chen *et al.*, 1999; Yang *et al.*, 2000), preparing carbon materials in various geometrical forms and phase purity and addition of metal oxides (Liu *et al.*, 1999; Hirscher *et al.*, 2002), but however none of these studies have unambiguously established that carbon nanomaterials can store hydrogen to the extent required by the original DOE standards. This situation is critical, demanding definite and exploratory solutions from practicing scientists. The essential questions that require immediate attention are:

- (i) Are the carbon materials appropriate for solid state hydrogen storage?
- (ii) If this were to be true, what type of carbon materials or what type of treatments for the existing carbon materials are suitable to achieve desirable levels of hydrogen storage?
- (iii) What are the stumbling blocks in achieving the desirable storage of hydrogen in solid state?
- (iv) Where does the lacuna lie? Is it in our theoretical foundation of the postulate or is it in our inability to experimentally realize the desired levels of storage?

MOTIVATION AND SCOPE

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 equipotential carbon surface. While considering these aspects

heteroatoms like N, P, S and B seem to be promising as activators due to their properties like higher redox potential than that of carbon. This can result in the tuning of the electronic property of the carbon materials. Therefore, the present study is aimed at establishing the role of heteroatom for hydrogen storage in the carbon materials, both by theoretical and experimental methodology.

The thesis work focused on the following aspects.

- To develop suitable theoretical models for identifying the activating sites for hydrogen.
- To prepare carbon nanomaterials of various types and examine their hydrogen storage characteristics.
- To synthesise heteroatom containing carbon nanomaterials by various methods and evaluate their hydrogen storage characteristics.
- The final aim is to evolve conditions for the formation of carbon nanomaterials and also their hydrogen storage capacity at ambient conditions.

THEORETICAL STUDIES ON CARBON NANOTUBES

Typically three Single Walled Carbon nanotubes (SWNTs) of armchair type (4, 4) with each tube having 32 carbon atoms, making tube diameter of 5.56 Å, have been modelled for the present study. Full geometry optimization of one SWNT was carried out with DFT by using Becke's three parameter hybrid function with LYP correlation function (B3LYP) and 6-31G (d, p) basis set. This optimized SWNT has been utilized to construct an interface with three nanotubes of interstitial distance 3.64 Å (the distance between two tubes) as shown Fig 1a. The valency of each element is taken into consideration for the calculations. It is reported in literature that the hydrogen molecule has preferential interaction at the interface of the carbon nanotubes (Chan *et al.*, 2001). The model describes the interface of the three carbon nanotubes that has been optimized with Universal Force Field parameter (UFF 1.02) in Cerius² software.

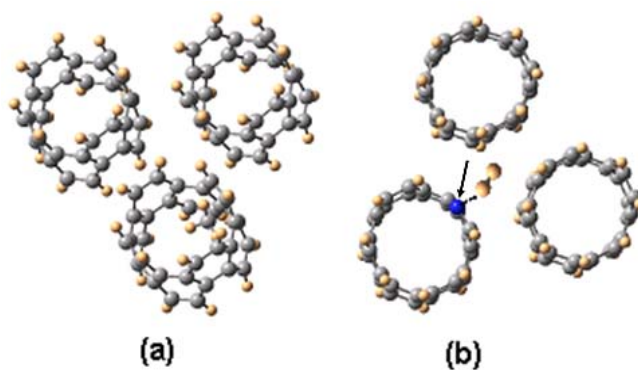


Fig. 1 (a). The side view of the UFF optimized CNT (4, 4) cluster taken for the study, (where the terminal positions are saturated with hydrogen) (b). Top view of the heteroatom (arrow indicated ball) substituted CNT cluster with the hydrogen molecule interaction.

Quantum chemical calculations

Computations using DFT have been carried out on optimized configuration obtained using UFF. The single point energy and bond population analysis were carried out by DFT on the optimized configurations by using B3LYP/6-31G (p, d) basis set. To reduce the computational cost, combined UFF / DFT method has been utilized to find the effect of heteroatom on hydrogen activation as this combined method have been effectively utilized for such large systems (Froudakis, 2001). The substitutional positions for heteroatoms in the CNT cluster model have been chosen based on the fact that the interstitial position offers minimum potential energy for the cluster and the calculations have also shown the result. The interaction of hydrogen at various sites in carbon nanotubes has been considered. The variations in dissociation energy and bond length were calculated. The results are given in Table 1.

Table 1. The bond length and dissociation energy of hydrogen on the CNTs calculated using B3LYP with 6-31g (p, d) basis set on the UFF optimized structure.

Substitution	Total Energy (Hartrees)	H ₁ -H ₂ (Å)	Dissociation Energy (eV)
H ₂	-1.175	0.708	4.76
CNT	-3686.5502	-	-
CNT + H ₂	-3687.7161	0.776	4.51
N CNT	-3702.5908	-	-
N CNT + H ₂	-3703.5989	0.835	0.22

P CNT	-3989.1694	-	-
P CNT + H ₂	-3990.2550	0.815	2.33
S CNT	-4046.0020	-	-
S CNT + H ₂	-4047.0067	0.817	0.13
B CNT	-3671.7254	-	-
B CNT + H ₂	-3672.9440	0.818	5.95
2B CNT (adjacent)	-3658.6666	-	-
2B CNT (adjacent) + H ₂	-3659.8092	0.913	3.88
2B CNT (alternate)	-3659.3491	-	-
2B CNT (alternate) + H ₂	-3660.3594	0.928	0.28

Heteroatom substituted carbon nanotubes show increase in the hydrogen bond length and decrease in dissociation energy compared to unsubstituted one, and has good correspondence with the Ellingham diagram and the standard redox potential values. The orbital contributions to the HOMO level of CNT cluster have been computed. In the case of heteroatom-substituted CNT, the contribution to HOMO level is from 2p orbital of the carbon. Upon interaction with hydrogen molecule, the contribution to HOMO level comes from both H 1s orbital and the p orbitals of heteroatom, which shows that there exists bond formation between the heteroatom and hydrogen molecule

The hydrogen molecule is activated at the heteroatom sites as deduced from the decrease of dissociation energy given in Table 1. It is believed that the activated hydrogen will migrate to equipotential carbon surface by spill over mechanism. It is deduced from the values of bond length, bond energies and wave functions that the presence of heteroatoms in carbon nanotubes activate hydrogen and lead to the absorption of hydrogen. To study the reaction mechanism of hydrogenation of carbon nanotubes, a simple cluster model with 14 carbon atoms has been considered, which is the terminal and reactive part of the SWNT as shown in Fig 1.

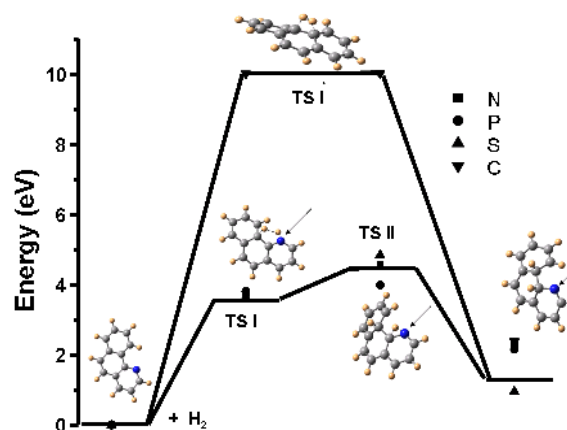


Fig. 2 The transition state energy profile of the heteroatom substituted CNTs cluster calculated by DFT method (B3LYP) with 6-31g (p, d) basis set. (the arrow indicated balls are heteroatoms like N, P and S).

Density Functional Theory has been employed to find the transition state parameter with 6-31g (p, d) basis set. The nature of stationary points thus obtained was characterized by frequency calculations. The transition state calculations were carried out for the proposed mechanism for the activation of hydrogen by heteroatom, where the initial step is dissociation of hydrogen by heteroatom and then migration of dissociated hydrogen to the carbon surface. The activation energy (ΔE_a) for this process has been obtained for CNTs using the calculated parameters. The results are given in Table 2 and the energy profile diagram for the mechanistic path way for the substituted (N, P & S) CNTs are shown in Fig. 2.

Table 2. The transition state optimized parameters of the cluster and the value of the activation energy calculated by B3LYP with 6-31g (p, d) basis set.

Substitution	E_a I (eV)	E_a II (eV)	H_1-H_2 (Å)	X-H (Å)	C-H ₁ ^b (Å)	C-H ₂ ^b (Å)
CNT	10.02	-	0.71	-	-	-
N CNT	3.84	4.58	1.45	1.11	1.70	1.94
P CNT	3.81	3.99	1.51	1.61	1.27	2.33
S CNT	3.65	4.85	1.50	1.75	1.24	2.40
2B CNT (adjacent)	2.22	2.98	1.95	1.31	2.59	2.72
2B CNT (alternate)	1.5	2.33	2.95	1.47	1.47	2.34

$E_a = E(\text{transition state}) - E(\text{reactant})$ and ^b Shortest C-H bond distance

It is clear from the results obtained that the energy for the activation of hydrogen in the first transition state is lower for the heteroatom containing CNT compared to pure CNT. In addition, the subsequent transfer of hydrogen to carbon surface is a facile process in the presence of heteroatom in CNTs. From the proposed mechanism given in Figure 2 and the results given in Table 2, the overall activation barrier has been shown less for the boron substituted in CNT at alternate positions compared to boron located at the adjacent positions. The theoretical studies have shown that hydrogenation of carbon nanomaterials require activation centers. To achieve effective hydrogenation and

hydrogen migration, the hetero atom should be incorporated into the carbon network with appropriate geometry and suitable chemical nature. The present theoretical results on heteroatom containing carbon nanomaterials opens up another avenue in the search for materials for the hydrogen storage.

THEORETICAL STUDIES ON FULLERENE

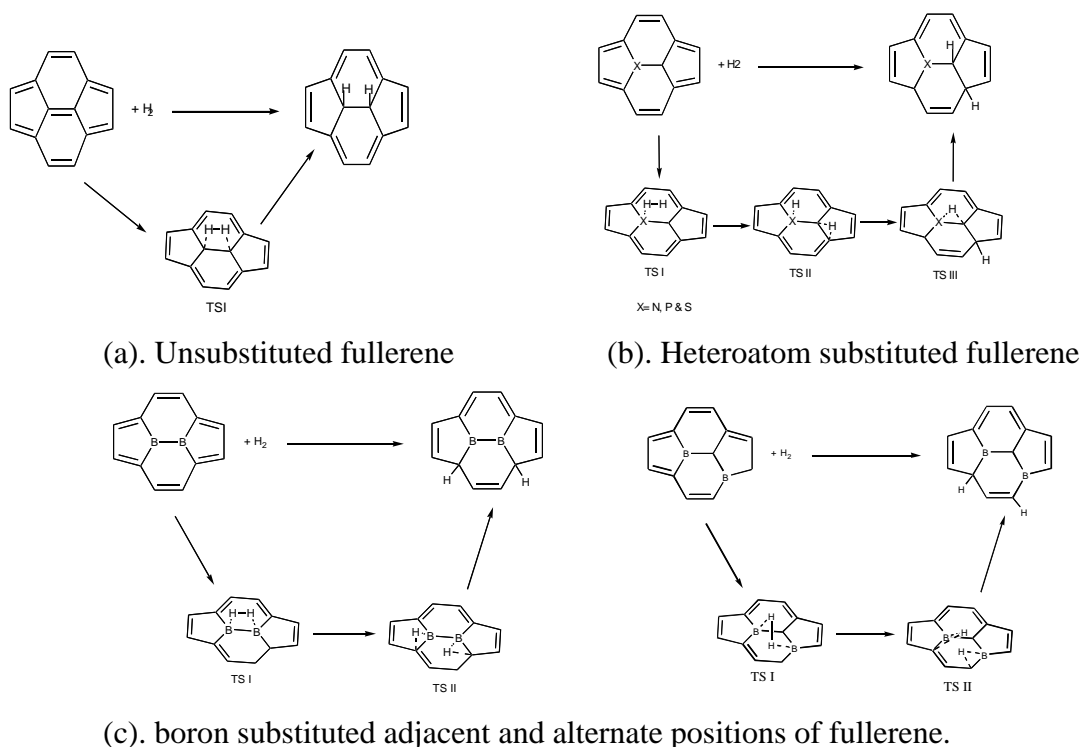
In order to exploit fullerenes and fullerene based materials for hydrogen storage, various attempts have been made, however it is shown that an activator for hydrogen is necessary in the fullerene network. For our present theoretical calculations, a single fullerene molecule (C_{60}) has been taken to study the role of heteroatom in hydrogen activation. The substitution of carbon with N, P, S and B on the fullerene network has shown to be promising for the activation and dissociation of hydrogen molecule (Table 3).

Table 3. The bond length and dissociation energy of hydrogen on the fullerene molecule is calculated using B3LYP with 6-31g (p, d) basis set on the UFF optimized structure.

Substitution	Total Energy (Hartrees)	H ₁ -H ₂ (Å)	Dissociation Energy (eV)
H ₂	-1.175	0.708	4.76
C ₆₀	-2286.042	-	-
C ₆₀ + H ₂	-2287.211	0.707	4.61
N C ₅₉	-2302.653	-	-
N C ₅₉ + H ₂	-2303.640	0.831	0.36
P C ₅₉	-2589.253	-	-
P C ₅₉ + H ₂	-2590.276	0.813	0.64
S C ₅₉	-2646.036	-	-
S C ₅₉ + H ₂	-2647.013	0.815	0.62
B C ₅₉	-2272.764	-	-
B C ₅₉ + H ₂	-2273.908	0.818	3.92
2B C ₅₈ (adjacent)	-2259.506	-	-
2B C ₅₈ + H ₂ (adjacent)	-2560.567	1.126	1.662
2B C ₅₈ (alternate)	-2259.487	-	-
2B C ₅₈ + H ₂ (alternate)	-2260.477	1.016	0.276

In order to understand the role of heteroatom on hydrogen activation in fullerene, simple cluster model has been taken which is the subunit of C_{60} molecule consisting of two pentagons and two hexagons. Essentially the hydrogen activation and the subsequent

hydrogenation of carbon atoms of fullerenes are conceived by the mechanistic pathways shown in scheme 1.



Scheme 1. Proposed transition state pathways for hydrogen storage in fullerene and heteroatom (N, P, S & B) containing fullerene.

The values of activation energy for each of the steps of hydrogen activation and migration of hydrogen have been calculated within the framework of transition state theory by using Density Functional Theory (DFT). The results of first transition state of the reaction mechanism are given in Table 4.

Table 4. The transition state optimized parameters of the cluster and the value of the activation energy calculated by B3LYP with 6-31g (p, d) basis set.

Cluster	E_a I (eV)	E_a II (eV)	H_1-H_2 (Å)	X-H (Å)	C-H ₁ ^b (Å)	C-H ₂ ^b (Å)
Carbon cluster	18.49	-	0.70	-	-	-
N substituted	3.24	3.15	1.85	1.04	1.44	1.50
P substituted	1.73	1.52	1.85	1.26	1.48	1.62
S substituted	2.56	6.48	1.13	1.60	1.70	1.70
2B substituted (adjacent)	2.26	2.68	1.98	1.19	2.52	1.43
2B substituted (alternate)	0.5	2.03	2.95	1.27	1.25	1.97

E_a = E (transition state) – E (reactant) and ^b Shortest C-H bond distance

From the values of activation energy given in Table 4, one can deduce that the heteroatoms are favourable for the hydrogen interaction dissociation and possibly favour the subsequent migration to the carbon surface. These results support our contention that heteroatoms are the appropriate sites for activation of hydrogen on fullerene.

The theoretical studies have shown that hydrogenation of carbon nanomaterials requires activation centers. Geometrically and chemically these activation sites have to be incorporated in the carbon network for effective hydrogenation and hydrogen storage applications. This opens up another avenue in the search for material for the hydrogen storage.

EXPERIMENTAL SETUP FOR HYDROGEN STORAGE MEASUREMENTS

Volumetric low pressure and high pressure hydrogen absorption measurements have been carried out using custom built volumetric and Sievert's apparatus. The high pressure absorption apparatus consists of reservoir cell and a cylindrical sample cell of known volume (33.8 cm^3). The whole system has been pressurized at the desired value by hydrogen and the change in pressure was monitored. The change in the pressure was recorded by a pressure transducer after the attainment of equilibrium. All the hydrogen absorption measurements have been carried out at room temperature. The experiments have been repeated under the same conditions for various pressures. The compressibility factor of hydrogen has been utilized.

HYDROGEN STORAGE IN ACTIVATED CARBON

To study whether modification of activated carbon enhance the storage capacity, mainly two modifications have been carried out namely, metal loading and chemical treatment. Commercial carbons Calgon and CDX-975 have been studied. Nickel metal has been loaded in various weight percentages (2, 5 & 20 wt %) by taking the physical mixture of acetate metal precursor and Calgon carbon. Subsequent reduction in hydrogen atmosphere at $450 \text{ }^\circ\text{C}$ gave nickel in carbon. The presence of nickel was confirmed by XRD analysis. Commercial CDX-975 has been modified by chemical treatment with 1M HNO_3 and treated with tri ethylene tetra amine and dried and washed. Both acid and amine treatment has been carried out the sample. BET Surface area and hydrogen absorption activity has been carried out for the fresh samples and the modified samples. The granular Calgon activity have been studied for hydrogen absorption at various

temperatures and the Van't Hoff's plot the heat of absorption was found to be -5.69 kJ / mol. Hydrogen absorption activity of 20 wt % nickel loaded carbon has been studied and their heat absorption is calculated to be -59.2 kJ / mol. The hydrogen absorption activity at 1atm (760 mm Hg) of all the activated carbon and the modified carbon with their BET surface area values are tabulated in Table 5.

Table 5. Specific surface area and amount of hydrogen adsorbed at 1 atm and different temperatures.

	Calgon	Nickel / carbon (Calgon)			CDX- 975	T-CDX	A-CDX	TA -CDX
		20 wt%	5 wt%	2 wt%				
Surface area (m ² /g)	931	616	750	1066	325	224	129	124
Hydrogen absorption (cm³/g) at 1 atm and at various temperatures (°C)								
77 K	137.7	54.4	44.5	120.8	28.1	27.3	8.2	10.4
298 K	0.70	0.5	-	-	0.53	-	-	0.7
373 K	0.43	3.14	1.4	1.53	2.83	3.17	3.03	2.97
423 K	-	1.95	1.7	2.05	4.18	4.25	4.30	-
473 K	-	-	-	-	5.0	4.60	-	-
523 K	-	-	-	-	4.80	6.36	-	-

2 wt% nickel supported on the activated carbon shows different property compared to higher loadings (5 & 20 wt %). The modifications enhanced the hydrogen absorption activity

NITROGEN CONTAINING CARBON NANOMATERIALS – PREPARATION AND HYDROGEN ABSORPTION ACTIVITY

Preparation of nitrogen containing carbon nanomaterials

a. Carbon nanotubes were prepared by taking nitrogen containing (polypyrrole) and without nitrogen containing (polyphenyl acetylene) polymer precursors. The monomer carbon precursors are polymerized in alumina membrane and the polymer/ alumina

composite has been carbonized at 900 °C and then the alumina membrane was dissolved in 48% HF.

b. Polymer was used as the structure directing agent as well as carbon source for the preparation of nitrogen containing carbon nanomaterials. Synthesis has been carried by following the gel composition in acidic medium as 1.2 SiO₂: 0.005 PVP: 4.2 HCl: 126 H₂O. Synthesis resulted in polymer derived carbon (PDC) with rod shape morphology and the nitrogen content was found to be 7.65 wt%, which is estimated from CHN analysis. The XRD pattern shows more graphitic nature of the carbon nanomaterials prepared.

c. Acetylene gas as the carbon precursor with utilizing pyridine as nitrogen source and H-Y zeolite (C/zeolite) and Al-pillared clay as template (C/Clay) were utilized to prepare nitrogen containing carbon nanomaterials by carbonization in Ar gas atmosphere at 900°C. Finally, the template was removed by HF treatment and the resulting carbon was characterized. The TEM measurements confirm that there is formation carbon nanotube with fibrous carbon.

d. Micro emulsion polymerization has been utilized to prepare nitrogen containing carbon nanomaterial and in this method polyacrylonitrile has been synthesized in micelle core environment. The nitrogen content of the prepared material is 4.5 wt%.

Carbon nanomaterials prepared have been characterized by XRD, FT-Raman, FT- IR, TEM and hydrogen absorption measurements.

Hydrogen absorption activity

To study the hydriding property, evolved gas analysis was carried and the gas evolved on the dehydrogenation was analyzed by the quadruple mass spectrometer. Ammonia evolution was noticed in the nitrogen containing carbon nanotubes (CNTppy). By independent method, the evolution of ammonia from the CNTppy was ascertained by spectrophotometry using Nessler's reagent. From the amount of ammonia evolved, it is estimated that CNTs containing 20 wt % of nitrogen is capable of taking up about 1 wt % of hydrogen. Hydrogen absorption study of polymer derived carbon (PDC) has been carried out in various temperatures. It showed different trend (increases with increase in temperature) compared to activated carbon. The specific surface area (SSA) of the samples was evaluated by BET method and the hydrogen absorption data at 760 mmHg

(i.e.) 1 atm pressure for the various carbon samples are also given in Table 6. These results show that hydrogen absorption increases with increase in temperature for carbon nanotubes, and the surface area obtained are comparable with those of reported values (Rzepka *et al.*, 2005).

Table 6. Specific surface area and amount of hydrogen adsorbed at 1 atm & different temperatures.

	Surface area (m ² /g)	Hydrogen absorption (cm ³ /g) at 1 atm and at various temperatures (°C)				
		-196	25	100	150	200
PDC	93	20.2	0.34	0.90	-	-
NC (emulsion)	182	64.4	-	2.78	-	-
C/Zeolite	633	28.0	-	3.42	4.23	-
NC/Zeolite	647	-	-	-	-	-
C/ Clay	49	-	-	3.0	3.22	-
N/ Clay	66	7.45	-	2.4	-	-
NCNT/Membrane	246	47.5	-	6.11	-	9.5

The low temperature absorption of hydrogen seems to increase with increase in surface area of the activated carbon (Calgon), CVD carbon and CDX. However at the ambient temperatures NCNT shows higher absorption with respect to other carbons.

High pressure hydrogen absorption measurements show that the hydrogen absorption increases with pressure and with the absorption capacity of 1.2 wt % at 100 bar for NCNT. The other samples CDX-975, CVD carbon and Calgon showed 0.36, 0.25 and 0.20 wt % storage respectively. However, in the second cycle, NCNT showed reduced hydrogen uptake of 0.6 wt %, which further confirms that the role of nitrogen in hydrogen activation and its subsequent absorption. Heat treatment (800 °C) in Ar atm of nitrogen containing carbon nanomaterial showed increase in hydrogen absorption activity. Nitrogen containing carbon nanomaterials prepared from the pillared clay template showed high hydrogen capacity of 1.8 wt % at 80 bar pressure of hydrogen and does not decrease significantly in the second cycle.

BORON CONTAINING CARBON NANOMATERIALS – SYNTHESIS AND HYDROGEN ABSORPTION ACTIVITY

The importance of gradation and the geometrical positions of boron substitution in carbon nanomaterials for hydrogen activation through DFT have been analyzed (see section 1

and 2). Preparation and characterization of boron containing carbon nanomaterials by different methods and their structural morphology and also the chemical environments of boron and their relevance towards hydrogen storage application are studied

Synthesis of boron containing carbon nanomaterials

(1) Boron containing carbon material has been prepared by using boron polymer as precursor by utilizing divinyl benzene and borane gas generated using sodium borohydrate and BF_3 .etherate. The polymer prepared is carbonized at $900\text{ }^\circ\text{C}$ in Ar atmosphere. The carbon (BC) obtained are showed a uniform spherical morphology with 100 nm size.

(2) Boron containing carbon material prepared by pyrolyzing phenolic resin chemically bonded with boron atoms (PBC), synthesized via an esterification reaction of the phenol hydroxyl groups by boric acid and pyrolysed at $900\text{ }^\circ\text{C}$ in Ar atmosphere (Xiang *et al.*, 2002).

(3) Boron containing carbon nanotubes (BCNT1) have been prepared by *in situ* hydroboration polymerization of divinyl benzene with borane in THF medium using alumina membrane as the template. The polymer / alumina composite has been carbonized at $900\text{ }^\circ\text{C}$ in Ar atmosphere. The carbon / alumina composite has been dissolved in 48% HF to remove the template and washed with distilled water.

(4) Other boron containing carbon nanotubes (BCNT2 and BCNT3) have been prepared by chemical vapour deposition (CVD) method by using zeolite (H-Y) and Pillered Clay respectively as template. Acetylene gas (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 $900\text{ }^\circ\text{C}$ in Ar atmosphere. The carbon/zeolite(or)Clay composite has been treated with 48 % HF for 24 h and the carbon has been washed with distilled water and dried at $100\text{ }^\circ\text{C}$.

Boron containing carbon nanomaterials have been prepared by using various templates such as Zeolite, Clay and Alumina membrane have been characterized by XRD, FT-Raman, FT- IR, CP MAS NMR, TEM and hydrogen absorption measurements.

The variation of template and the carbon precursor causes difference in the morphology and also the chemical environments of boron. ^{11}B MAS NMR experiments have been carried out to determine the environment of boron in the carbon net work. Boron

containing carbon nanotubes prepared with polymer precursor using alumina membrane as template show different boron chemical environments and structural morphology. There are two different chemical environments in which boron is present in the carbon nanotube prepared by polymer route (BCNT).

Hydrogen absorption activity

The Specific Surface Area (SSA) of the samples was evaluated by BET method and the hydrogen absorption data at 760 mm Hg pressure for the various boron containing carbon samples are given in Table 7.

Table 7. Specific surface area by BET method of various boron containing samples and their hydrogen absorption activity at 1 atm in different temperatures.

	SSA (m ² /g)	Hydrogen absorption at 1 atm (cm ³ /g) at various temperatures (°C)			
		-196	25	100	150
BC	12	3.63	0.6	3.63	4.68
PBC	430	73	-	2.90	3.02
BCNT1	523	127	-	16.5	14.8
BCNT2	62	3.22	-	2.38	4.73
BCNT3	33	1.09	-	1.7	-

Hydrogen storage capacity up to 2 wt % for BCNT1 prepared by alumina membrane template could be observed at 80 bar where as the other samples showed only 0.2 wt % at this pressure. This configuration has a bearing in hydrogen sorption characteristics.

CONCLUSIONS

- Theoretical studies have shown that the effective hydrogenation of CNTs is possible with activation centers and the heteroatom containing CNTs are able to activate the hydrogen in a facile manner compared to pure CNTs.
- For effective hydrogenation and hydrogen storage these boron atoms should be incorporated geometrically and chemically into the carbon network.
- Nitrogen containing CNTs are amenable for hydrogen absorption than other carbon materials. However, these active sites should be made catalytic in nature by various preparation methods and surface engineering so that necessary hydrogen storage may be achieved.

- Boron containing carbon nanotubes have been produced successfully by template synthesis method. For boron atoms two different environments in the carbon nanotubes have been prepared and the maximum hydrogen storage capacity of 2 Wt % has been realised. This configuration has a bearing in hydrogen sorption characteristics.
- The heteroatom substitution in the carbon nanotubes opens up another avenue in the search for materials for hydrogen storage.

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PROPOSED CONTENTS OF THE THESIS

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- Chapter 6** Boron containing carbon nanomaterials - Synthesis and hydrogen absorption activity.
- Chapter 7** Summary and Conclusions

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6. **Viswanathan, B. and M. Sankaran**, Options for hydrogen storage – the current status (invited lecture) to be presented in Indo – German Workshop on “Fuel cells and Hydrogen Energy” to be held in January 29-31, 2007, Kolkata, India.