ON THE POTENTIAL OF CARBON MATERIALS FOR SOLID STATE HYDROGEN STORAGE

M. Sankaran
CYD01012

Content of the thesis

- **Chapter 1 - Introduction**

- **Chapter 2 – Materials and methods**

- **Chapter 3 – Theoretical studies on carbon nanotubes and fullerenes**

- **Chapter 4 – Hydrogen storage in activated carbon**

- **Chapter 5 – Nitrogen containing carbon nanotubes – synthesis, characterization and hydrogen absorption activity**

- **Chapter 6- Boron substituted carbon nanotubes- synthesis, characterization and hydrogen absorption activity**

Situation and Questions

❖ **Production, storage and application - challenges of hydrogen economy**

❖ **Solid state storage – remarkable but not reproducible**

❖ **6.5 wt% - desired level (DOE)**

❖ **Demands consistent and innovative practice**

(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 solid state hydrogen storage?

(iii) What are the stumbling blocks in achieving the desirable solid state hydrogen storage?

(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?

Why carbon materials for solid state hydrogen storage?

- ❖ **Coordination number is variable/expandable**
- ❖ **Promote new morphologies**
- ❖ **Covalent character retention**
- ❖ **Variable hybridization possible**
- ❖ **Geometrical possibilities/size considerations**
- ❖ **Meta-stable state**
- ❖ **Similar to biological architectures "Haeckelites"**
- ❖ **Boron and nitrogen doped graphitic arrangements promise important applications.**
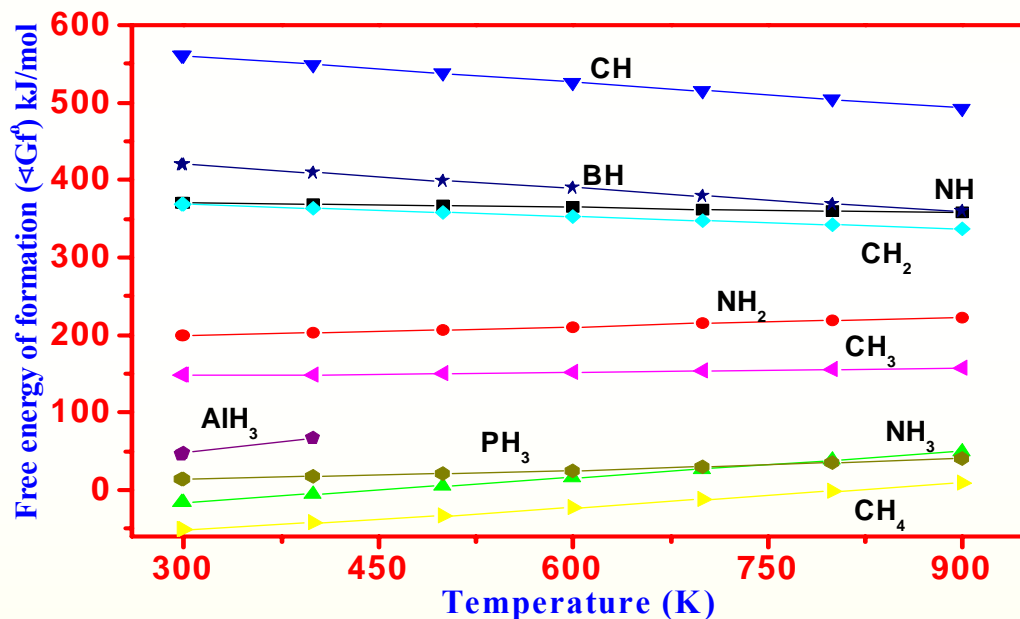
Objectives

✤ **Necessity of active sites**

✤ **Heteroatom containing carbon materials - appropriate candidates?**

✤ **Gradation of the carbon materials containing various heteroatoms**
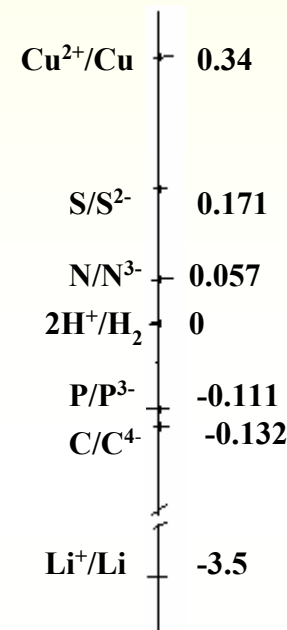
✤ **Geometrical positions of the heteroatoms**

Heteroatom in carbon materials

🌼 **Equipotential sites**

🌼 **Sites themselves hydridable**

Ellingham diagram for various species

Standard redox potential (V) for various couples

| Couple	Potential (V)
Cu^{2+}/Cu	0.34
S/S^{2-}	0.171
N/N^{3-}	0.057
$2H^+/H_2$	0
P/P^{3-}	-0.111
C/C^{4-}	-0.132
Li^+/Li	-3.5

❖ **Catalytic or Stoichiometric? & Possible combinations**

6

Effect of Heteroatoms on Hydrogen interaction

❖ **Activating sites -** **hydrogen adsorption/absorption**

❖ **The role of heteroatom substitution in carbon materials**
  – **Density Functional Theory (DFT)**

❖ **The effect of various heteroatoms like N, P, S and B for hydrogen activation**

❖ **Geometrical positions of heteroatoms**

7

➢ **Three Single Walled Carbon nanotubes (SWNTs) of armchair type (4, 4)**
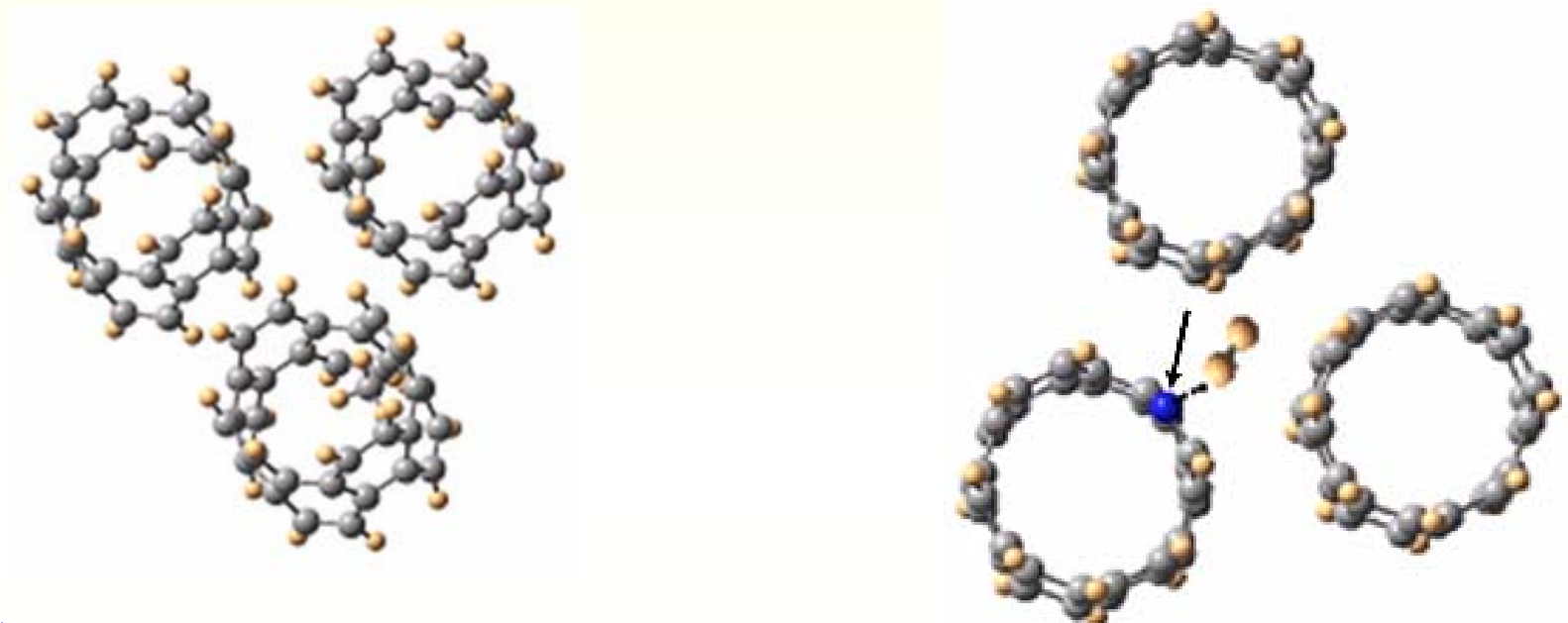
➢ **Each tube having 32 carbon atoms**

➢ **Tube diameter - 5.56 Å**

Interface with three nanotubes – intertubular distance - 3.64 Å

Energy minimization – UFF 1.02 (Cerius2 Software)
Single point energy and bond population analysis – DFT (B3LYP/6-31G*)

8

Bond length and dissociation energy of H_2 on NCNT

Substitution	Total Energy (Hartrees)	H_1-H_2 (Å)	Dissociation Energy (eV)
H_2	-1.175	0.708	4.76
CNT CNT + H_2	-3686.5502 -3687.7161	- 0.776	- 4.51
NCNT NCNT + H_2	-3702.5908 -3703.5989	- 0.835	- 0.22

Character of HOMO

HOMO (Hartrees)	% orbital contribution					
	C		N		H	
	s	p	s	p	s_b	s_t
CNT (-0.1612)	0	100	-	-	-	-
CNT + H_2 (–0.1613)	0	100	-	-	0	0
NCNT (– 0.1617)	1	98.30	0	0.18	-	0.56
NCNT + H_2 (– 0.1371)	0.52	37.39	1.37	31.91	26.66	2.15

* b- bonded hydrogen to nitrogen   and   t- terminal hydrogen in the cluster

Bond length and dissociation energy of H_2 on PCNT

Substitution	Total Energy (Hartrees)	H_1-H_2 (Å)	Dissociation Energy (eV)
H_2	-1.175	0.708	4.76
CNT CNT + H_2	-3686.5502 -3687.7161	- 0.776	- 4.51
PCNT PCNT + H_2	-3989.1694 -3990.2550	- 0.815	- 2.33

Character of HOMO

HOMO level (Hartrees)	% of orbital contribution					
	C		P		H	
Contribution	s	p	s	p	s_b	s_t
CNT (-0.1612)	0	100	-	-	-	-
CNT + H_2 (–0.1613)	0	100	-	-	0	0
PCNT (– 0.1611)	1	96.85	0	1.71	-	0.53
PCNT+ H_2 (– 0.1516)	1	85.62	0.04	8.06	4.83	0.49

* b- bonded hydrogen to phosphorus and   t- terminal hydrogen in the cluster

# Bond length and dissociation energy of H₂ on SCNT

Substitution	Total Energy (Hartrees)	H_1-H_2 (Å)	Dissociation Energy (eV)
H_2	-1.175	0.708	4.76
CNT CNT + H_2	-3686.5502 -3687.7161	- 0.776	- 4.51
SCNT SCNT + H_2	-4046.0020 -4047.0067	- 0.817	- 0.13

Character of HOMO

HOMO level (Hartrees)	% of orbital contribution					
	C		S		H	
	s	p	s	p	s_b	s_t
CNT (-0.1612)	0	100	-	-	-	-
CNT + H_2 (–0.1613)	0	100	-	-	0	0
SCNT (– 0.1375)	1	76.87	0	21.17	-	1.16
SCNT + H_2 (– 0.1207)	0.45	41.80	0.35	41.65	14.87	0.88

* b- bonded hydrogen to sulphur and   t- terminal hydrogen in the cluster

11

Energy profile for hydrogen interaction with heteroatom substituted CNT clusters
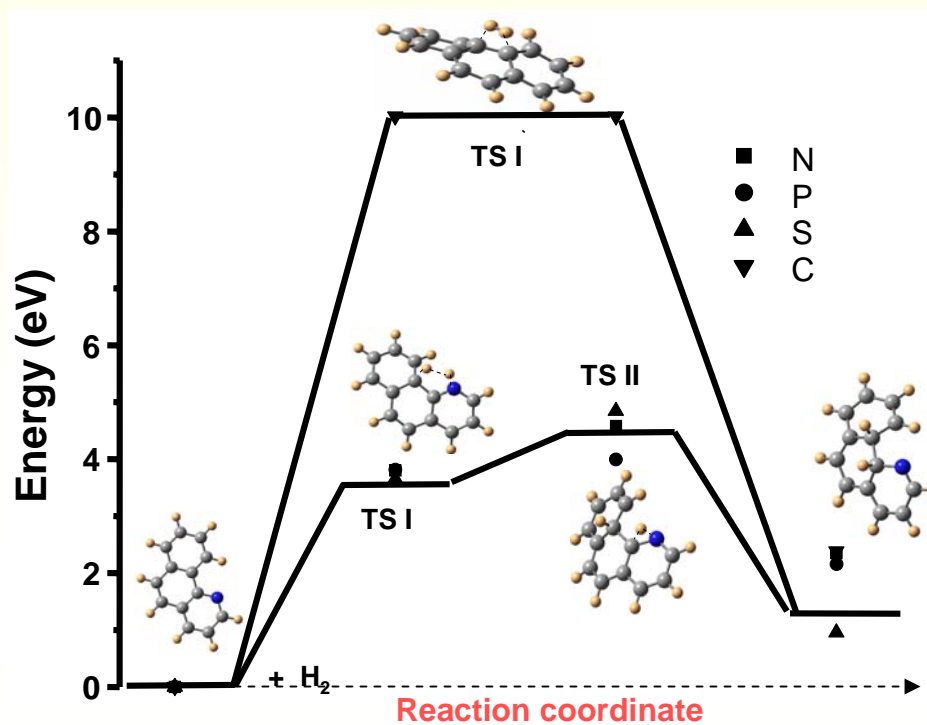
Substitution	E_a I (eV)	E_a II (eV)	H_1-H_2 (Å)	X-H (Å)	C-H_1^* (Å)	C-H_2^* (Å)
CNT	10.02	-	0.71	-	-	-
N CNT	3.84	4.58	1.45	1.11	1.70	1.94
P CNT	3.81	3.99	1.51	1.61	1.27	2.33
S CNT	3.65	4.85	1.50	1.75	1.24	2.40

E_a = E (transition state) – E (reactant)   * Shortest C-H bond distance

12

Bond length and dissociation energy of H$_2$ on BCNT

Substitution	Total energy (Hartrees)	H$_1$-H$_2$ (Å)	Dissociation energy (eV)
H$_2$	-1.175	0.708	4.76
CNT CNT + H$_2$	-3686.5502 -3687.7161	- 0.776	- 4.51
B CNT B CNT + H$_2$	-3671.7254 -3672.9440	- 0.818	- 5.95

Character of HOMO

HOMO level (Hartrees)	% of orbital contribution					
	C		B		H	
Contribution	s	p	s	p	s$_b$	s$_t$
CNT (-0.1612)	0	100	-	-	-	-
CNT + H$_2$ (–0.1613)	0	100	-	-	0	0
BCNT (–0.1576)	1	94.87	0	3.59	-	0.5
BCNT + H$_2$ (– 0.1534)	1	96.26	0.10	1.12	1	0.54

* b- bonded hydrogen to boron and   t- terminal hydrogen in the cluster

Bond length and dissociation energy of H$_2$ on BCNTs

Substitution	Total energy (Hartrees)	H$_1$-H$_2$ (Å)	Dissociation energy (eV)
H$_2$	-1.175	0.708	4.76
CNT CNT + H$_2$	-3686.5502 -3687.7161	- 0.776	- 4.51
2B CNT (adjacent) 2B CNT (adjacent) + H$_2$	-3658.6666 -3659.8092	- 0.913	- 3.88
2B CNT (alternate) 2B CNT (alternate) + H$_2$	-3659.3491 -3660.3594	- 0.928	- 0.28
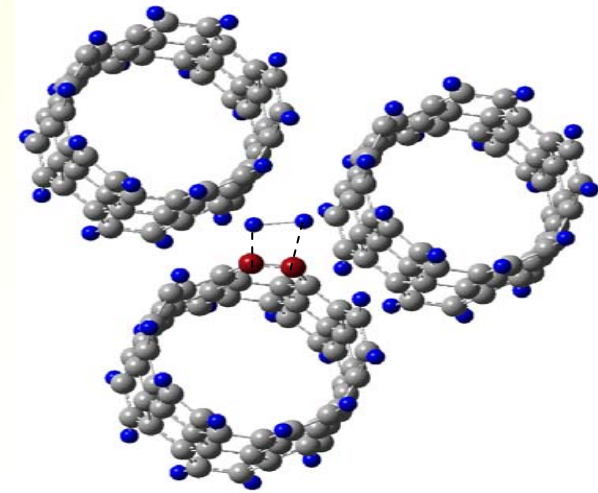
Adjacent position
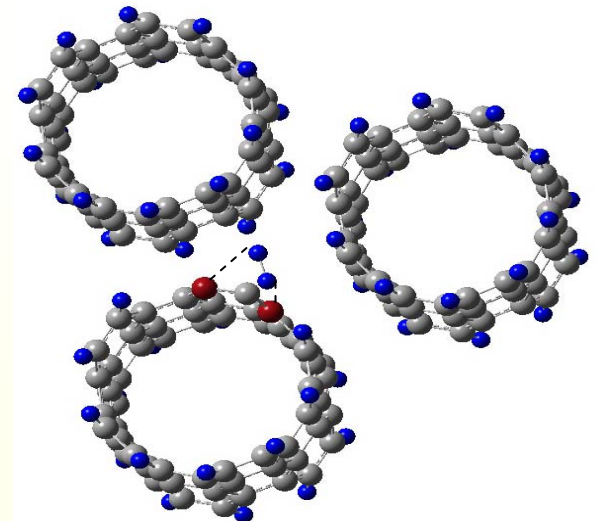
Alternative position

Energy profile of boron substituted CNT clusters
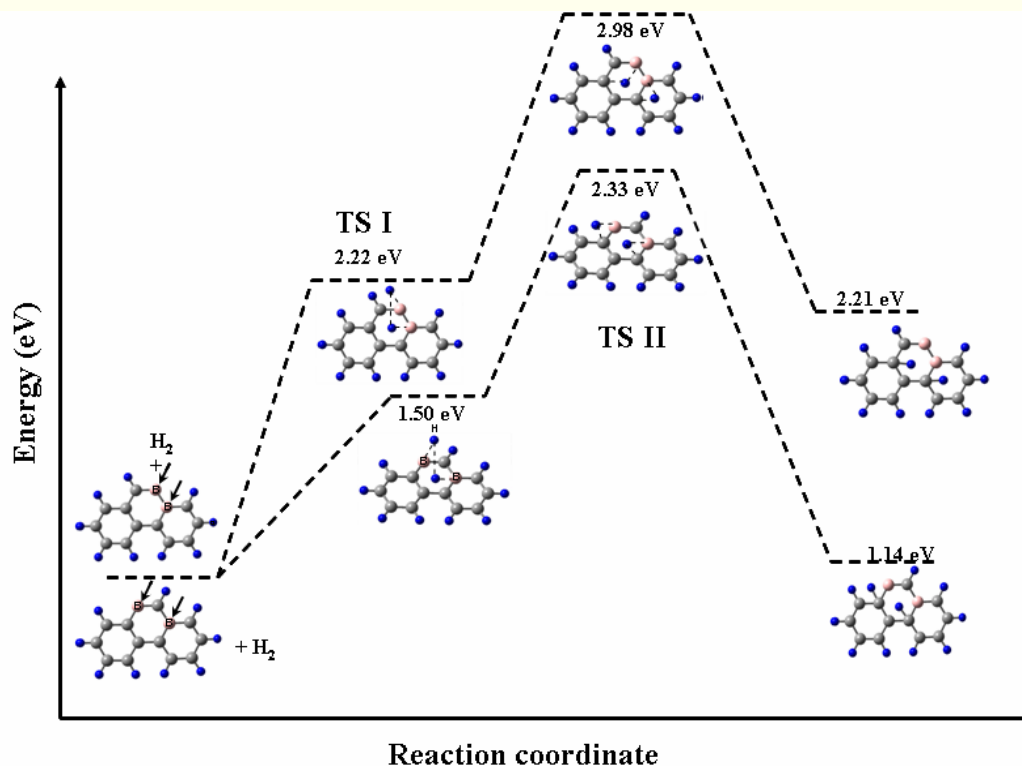
Substitution	$E_a\,I$ (eV)	$E_a\,II$ (eV)	$H_1\text{-}H_2$ (Å)	X-H (Å)	$C\text{-}H_1$* (Å)	$C\text{-}H_2$* (Å)
CNT	10.02	-	0.71	-	-	-
2B CNT (adjacent)	2.22	2.98	1.95	1.31	2.59	2.72
2B CNT (alternate)	1.5	2.33	2.95	1.47	1.47	2.34

E_a = E (transition state) – E (reactant) * Shortest C-H bond distance

15

Hydrogen activation in heteroatom substituted fullerene

METHODOLOGY

Energy minimization – UFF 1.02 (Cerius2 Software)
Single point energy – DFT (B3LYP/6-31G*)

Bond length and dissociation energy of H_2
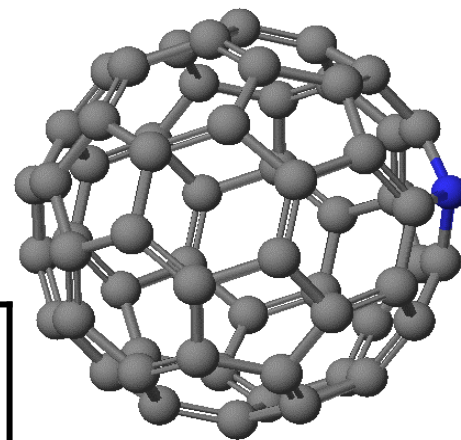
	Total Energy (Hartrees)	(H_1-H_2) Å	H_2 Dissociation energy (eV)
H_2	-1.175	0.708	4.74
C_{60}	-2286.042	-	-
C_{60}+H_2	-2287.211	0.707	4.61
NC_{59}	-2302.653	-	-
NC_{59} +H_2	-2303.640	0.831	0.36
PC_{59}	-2589.253	-	-
PC_{59} +H_2	-2590.276	0.813	0.64
SC_{59}	-2646.036	-	-
SC_{59} +H_2	-2647.013	0.815	0.62

16

Transition state path ways for hydrogen interaction

Unsubstituted fullerenes

X= N, P & S

Substituted fullerenes
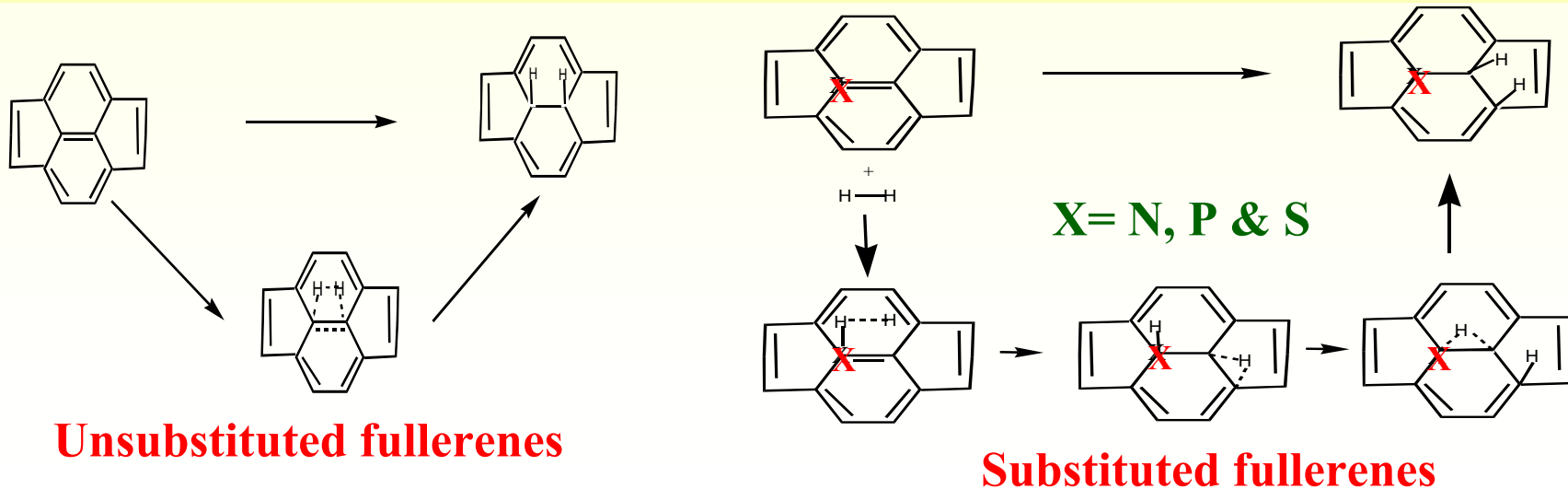
Substitution	*E_a I (eV)	E_a II (eV)	E_a III (eV)	H_1-H_2 Å	X-H_1 Å	C_1-X Å	C_2-X Å	C_3-X Å
Carbon	18.49	-	-	0.70	-	-	-	-
Nitrogen	3.24	3.15	3.08	1.85	1.04	1.44	1.50	1.50
Phosphorus	1.73	1.52	1.52	1.85	1.26	1.48	1.62	1.62
Sulphur	2.56	6.48	1.86	1.13	1.60	1.70	1.70	1.70

* = E (each transition state) – E (reactant)

Boron substituted fullerene
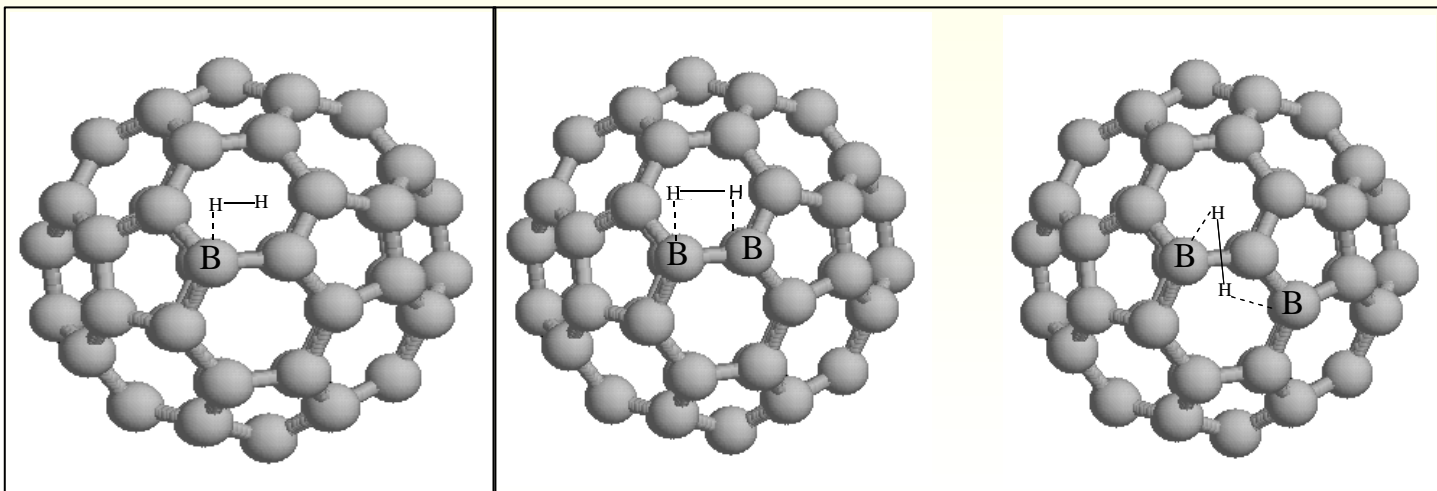
Substitution	Total energy (Hartrees)	(H-H) Å	H_2 dissociation energy (eV)
H_2	-1.175	0.708	4.74
C_{60}	-2286.042	-	-
C_{60} + H_2	-2287.211	0.707	4.61
BC_{59}	-2272.764	-	-
BC_{59} +H_2	-2273.908	0.818	3.92
$2BC_{58}$ (Adj)	-2259.506	-	-
$2BC_{58}$ (Adj) +H_2	-2560.567	1.126	1.66
$2BC_{58}$ (Alt)	-2259.487	-	-
$2BC_{58}$ (Alt) +H_2	-2260.477	1.016	0.28

Transition state optimized parameters and the E_a for the proposed pathway

Substitution		$E_a I$ (eV)	H_1-H_2 (Å)	B_1-H_1 (Å)	B_2-H_2 (Å)	C-H_1* (Å)	C-H_2* (Å)
Adjacent	(X, 2)	2.26	1.98	1.19	1.29	2.52 (C_2)	1.43 (C_4)
Alternate	(X, 3)	0.50	2.95	1.27	1.23	1.25 (C_2)	1.97 (C_5)
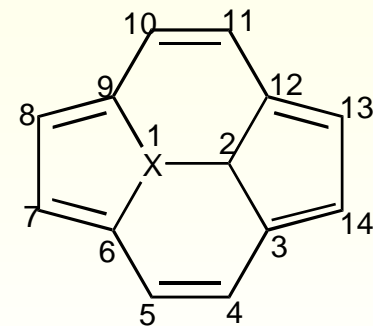
E_a = E (each transition state) – E (reactant)   * = Shortest C-H bond distance

Outcome

➤ **Substituted heteroatom acts as an active centre for hydrogen activation**

➤ **For the effective hydrogenation and hydrogen storage, the heteroatoms should be incorporated geometrically and chemically into the carbon network**

19

High Pressure adsorption apparatus

Vacuum system

RC

33.8 mL (V_1)

TC

NV

Vent

V_2 (18.64 mL)
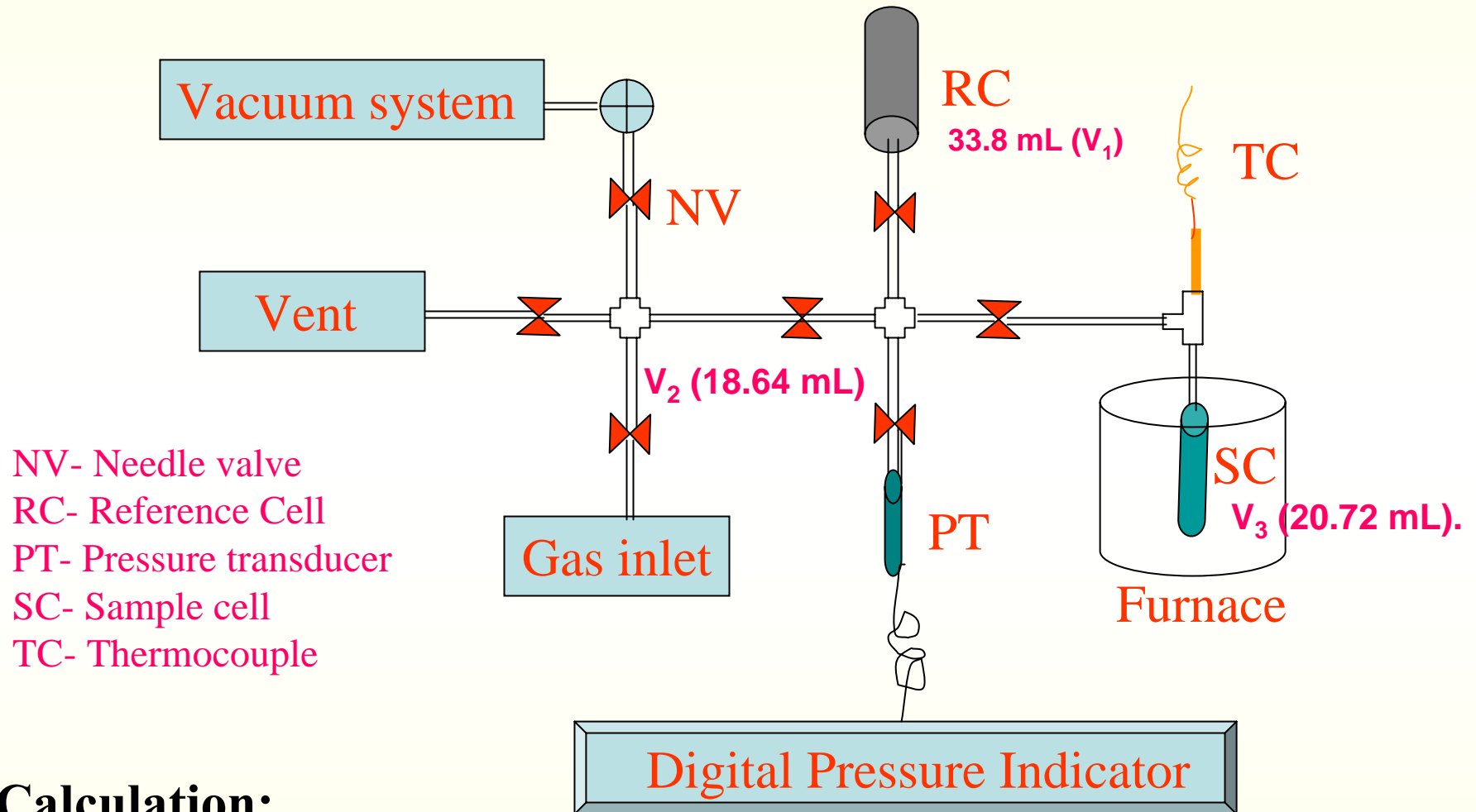
NV- Needle valve
RC- Reference Cell
PT- Pressure transducer
SC- Sample cell
TC- Thermocouple

Gas inlet

PT

SC

V_3 (20.72 mL).

Furnace

Digital Pressure Indicator

Calculation:

$$P_iV_i = P_f (V_1+V_2+V_3+ V_{ads})$$

$$V_{ads}\ Z = V_{correct}$$

Where Z = Compressibility factor

20

Activated Carbon and their modifications

❖ **Activated carbon**

(CALGON & CDX-975)

❖ **Metal supported on CALGON**
Nickel metal - (2, 5 & 20 wt %) - physical mixture of acetate metal precursor - reduction in hydrogen atmosphere at 450 °C

❖ **Chemical treatment on CDX-975**
Chemical treatment with 1M HNO_3 for acid treatment and for amine treatment tri ethylene tetra amine.

Hydrogen absorption capacity at 1 atm pressure

	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 at 1 atm (cm^3/g)								
77K	137.7	54.4	44.5	120.8	28.1	27.3	8.2	10.4
298K	0.70	0.5	-	-	0.53	-	-	0.7
373K	0.43	3.14	1.4	1.53	2.83	3.17	3.03	2.97
423K		1.95	1.7	2.05	4.18	4.25	4.30	
473K					5.0	4.60		
523K					4.80	6.36		

High pressure hydrogen absorption activity of activated carbon
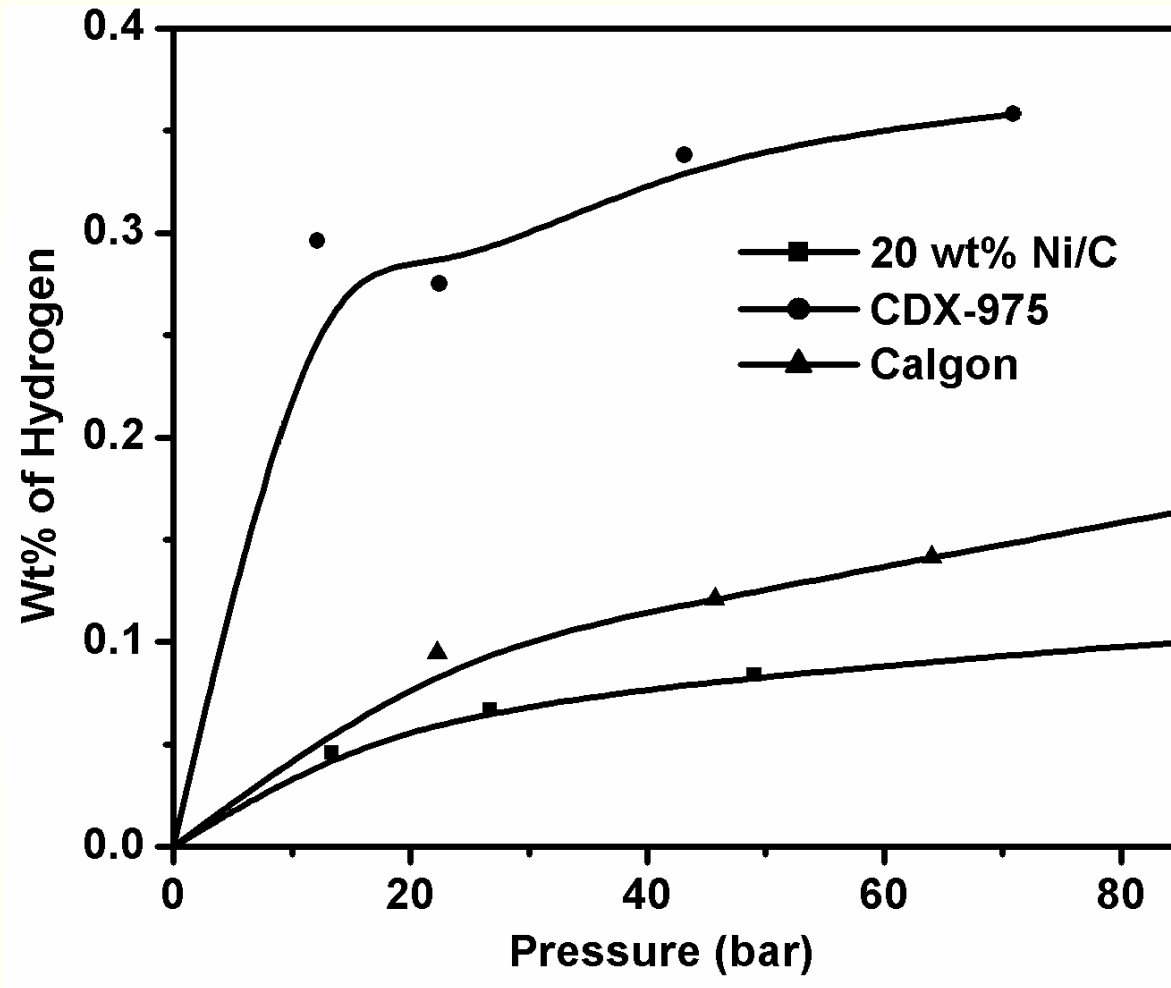
Chapter 5. Nitrogen containing carbon nanotubes – synthesis, characterization and hydrogen absorption activity

Carbon materials	Template	Carbon Source	Technique	Morphology
PDC	Silica	PVP	Precipitation	Rod shape
MEC	Silica	PAN	Insitu precipitation	Coiled and fibers
CNT1 & NCNT 1 (6.4 %)	Alumina membrane	PPA PPY	In-situ polymerization	Tubular
CNT2 & NCNT2 (2.5%)	Zeolite	Acetylene Acetylene + Pyridine	Chemical vapor deposition	Tubes and fibers
CNT3 & NCNT3 (1.8%)	Clay (pillared)	Acetylene Acetylene + pyridine	Chemical vapor deposition	Tubes and fibers

Characterization of Carbon Nanotubes

26
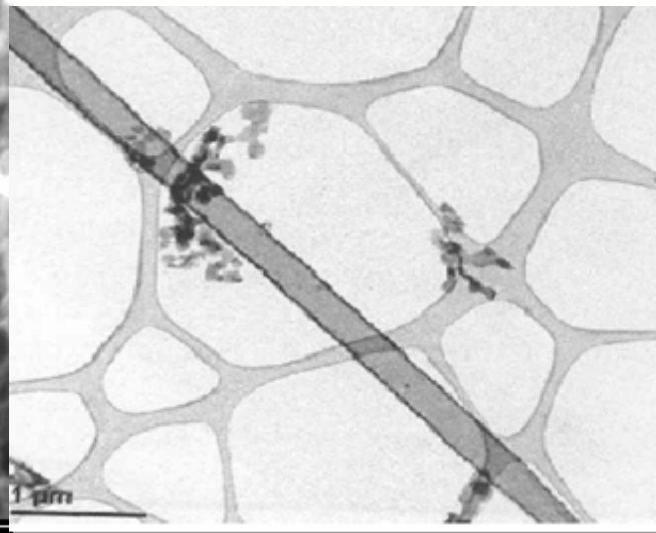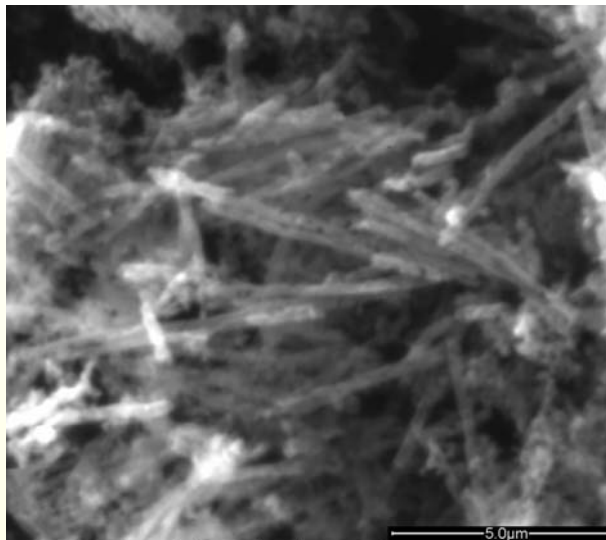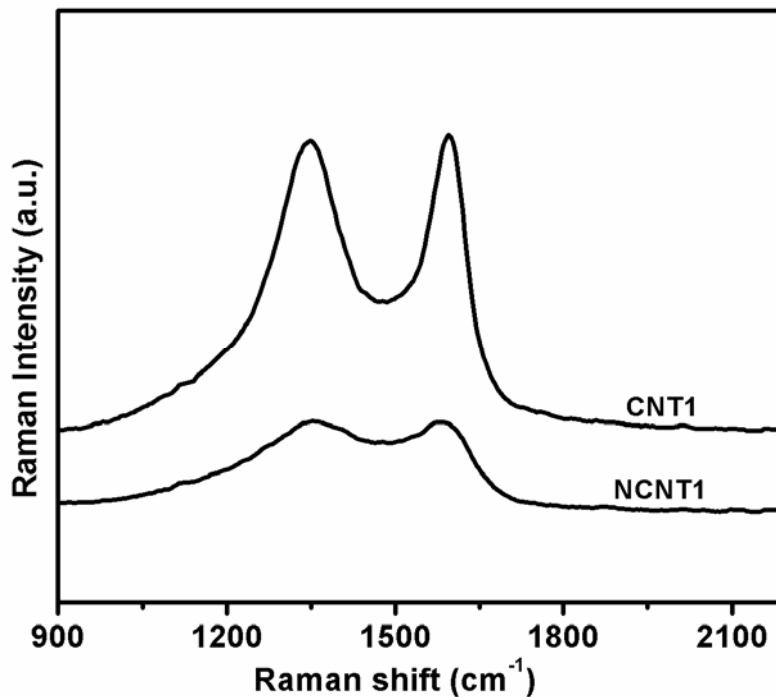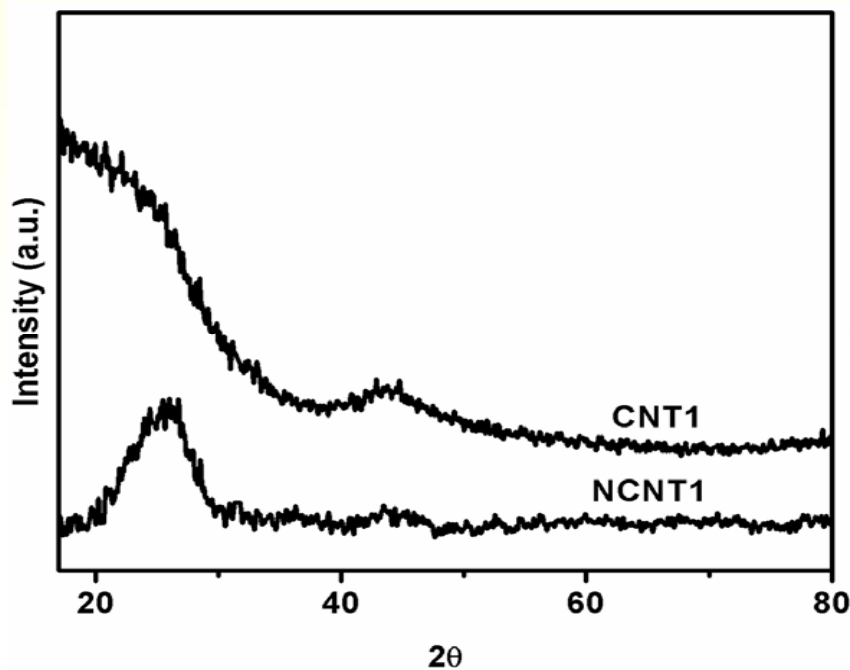
Hydrogen interaction study

- **METHODS**

  ❖ **Hydrogen storage capacity of CNTs - Measured by   Evolved Gas Analysis (EGA)**

  ❖ **Desorbed gases - quadruple mass spectrum**

- **EXPERIMENTAL CONDITIONS FOR EGA**

  ❖ **Absorption of hydrogen at room temperature and 1 atm pressure**

  ❖ **Evacuation of the chamber - 10^{-5} Torr**

- **PRETREATMENT CONDITIONS**
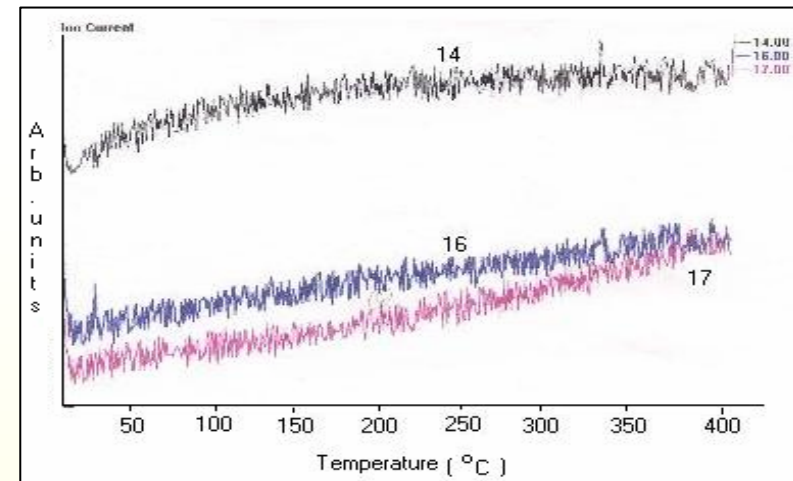
  ❖ **Heated 120 °C for 15 min – remove moisture**

EGA profiles
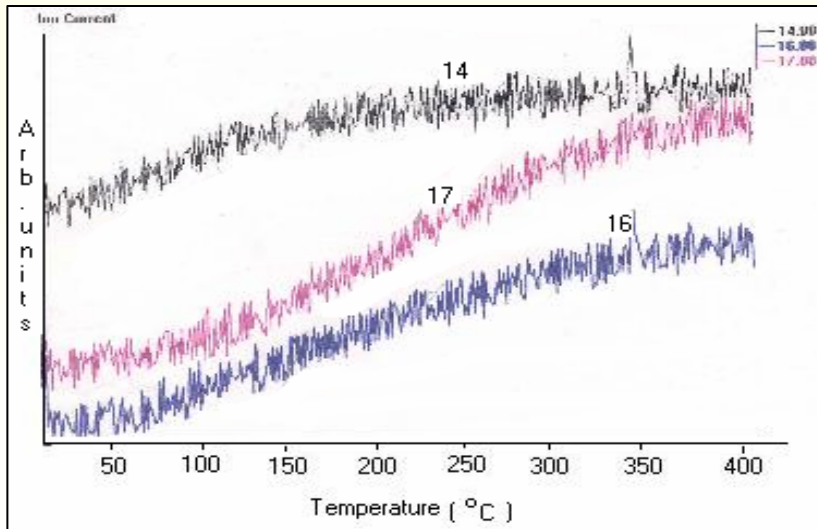
NCNT1
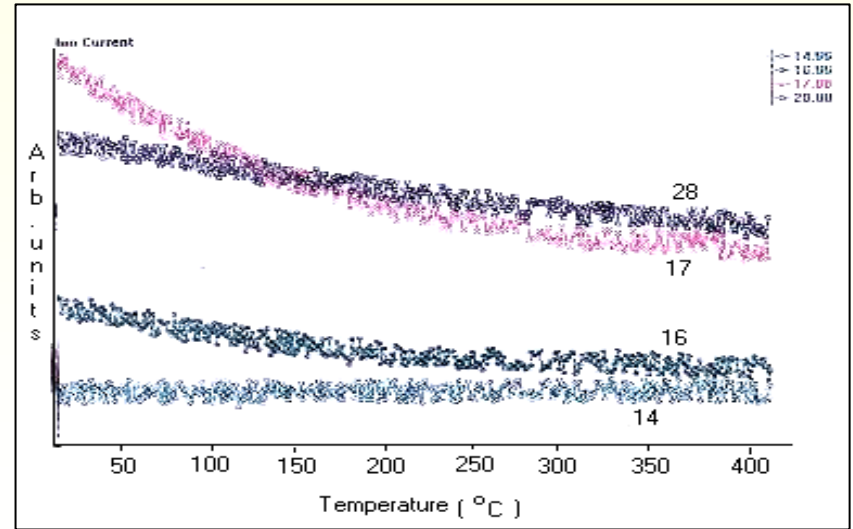
CNT1

❖ **Formation of ammonia observed from EGA**

❖ **Interaction of Nitrogen with Hydrogen - Formation of Ammonia**

❖ **Recycling of catalyst-decrease of Ammonia participation of Nitrogen.**

NCNT1 recycled

28

INDEPENDENT EXPERIMENT

✽ **Confirmation of ammonia by spectrophotometry using Nessler's reagent 0.085mL/mg (in gas phase volume).**
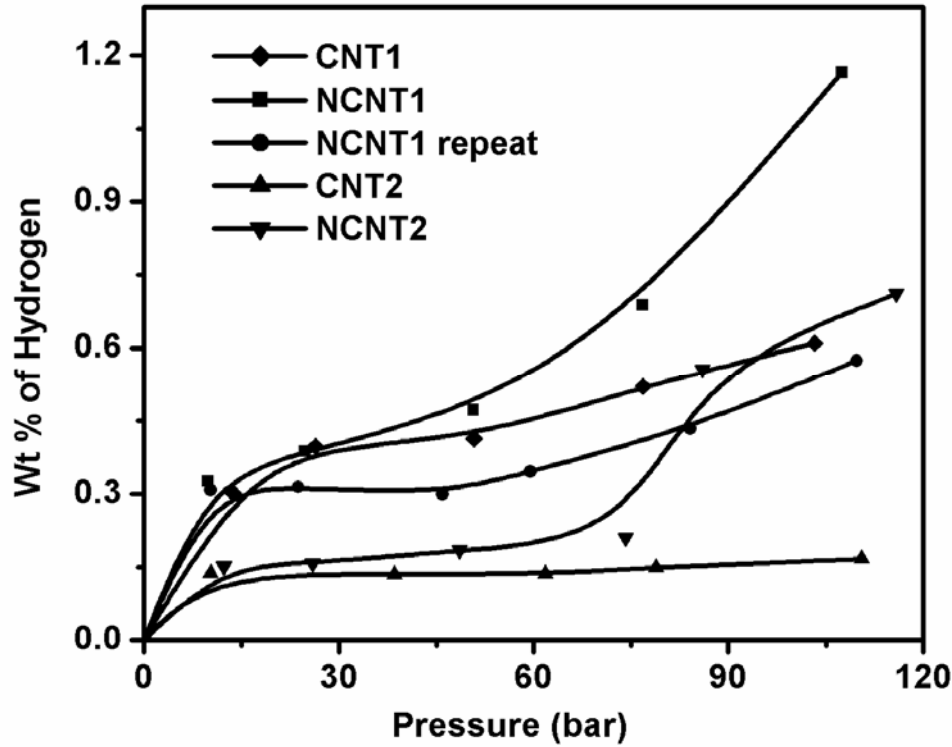**(1/3rd of the total nitrogen content in the sample)**

Nitrogen content 4.3 % by CHN analysis

✽ **Theoretically about 1wt% of hydrogen could be absorbed for 20% of Nitrogen present in the carbon network.**

Specific surface area and amount of hydrogen absorbed at 1 atm & different temperatures

Sample	SSA (m²/g)	Hydrogen absorption at 1 atm (cm³/g) at various temperatures (K)		
		77	298	373
PDC	93.0	20.2	0.34	0.90
MEC	182	64.4	-	2.78
NCNT1	246	47.5	-	6.11
CNT2	633	28.0	-	3.42
NCNT2	646.5	-	-	-
CNT3	48.8	-	-	3.0
NCNT3	66.4	7.45	-	2.4
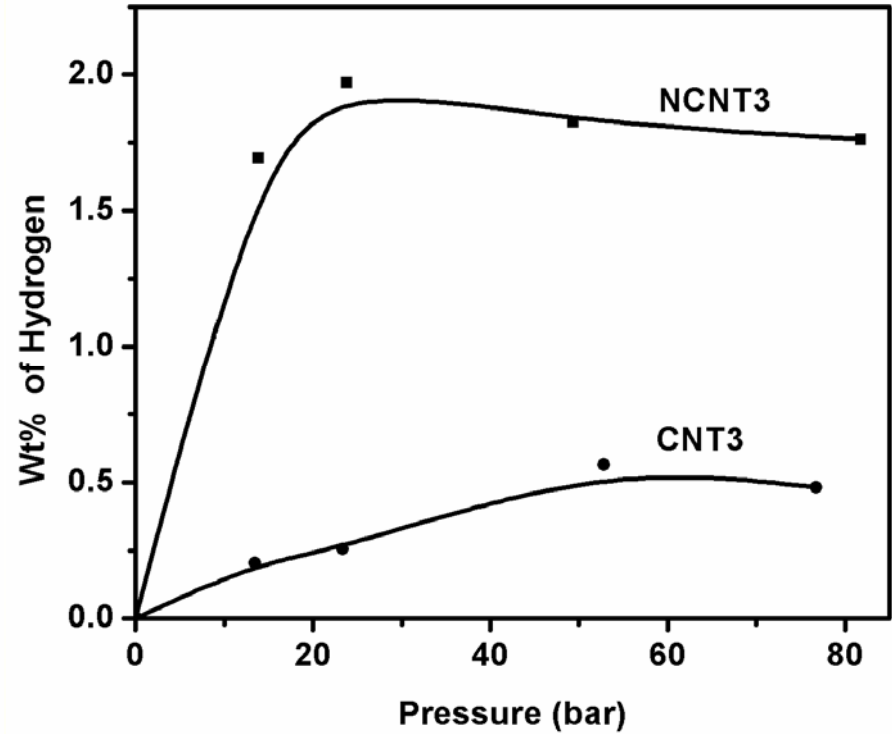
Chapter 6. Boron substituted carbon nanotubes- synthesis, characterization and hydrogen absorption activity

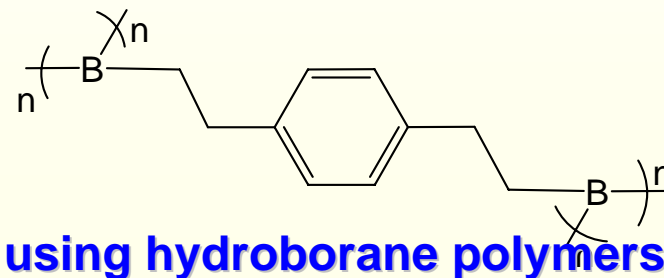| Template	Carbon Source	Technique	Morphology
Alumina membrane (BCNT1)	Polymer (hydroborane)	In-situ polymerization	Tubular
Zeolite (BCNT2)	Hydrocarbon (Acetylene + borane gas)	Chemical vapor deposition	Tubes and Fibers
Clay (pillared) (BCNT3)	Hydrocarbon (Acetylene + borane gas)	Chemical vapor deposition	Tubes and Fibers

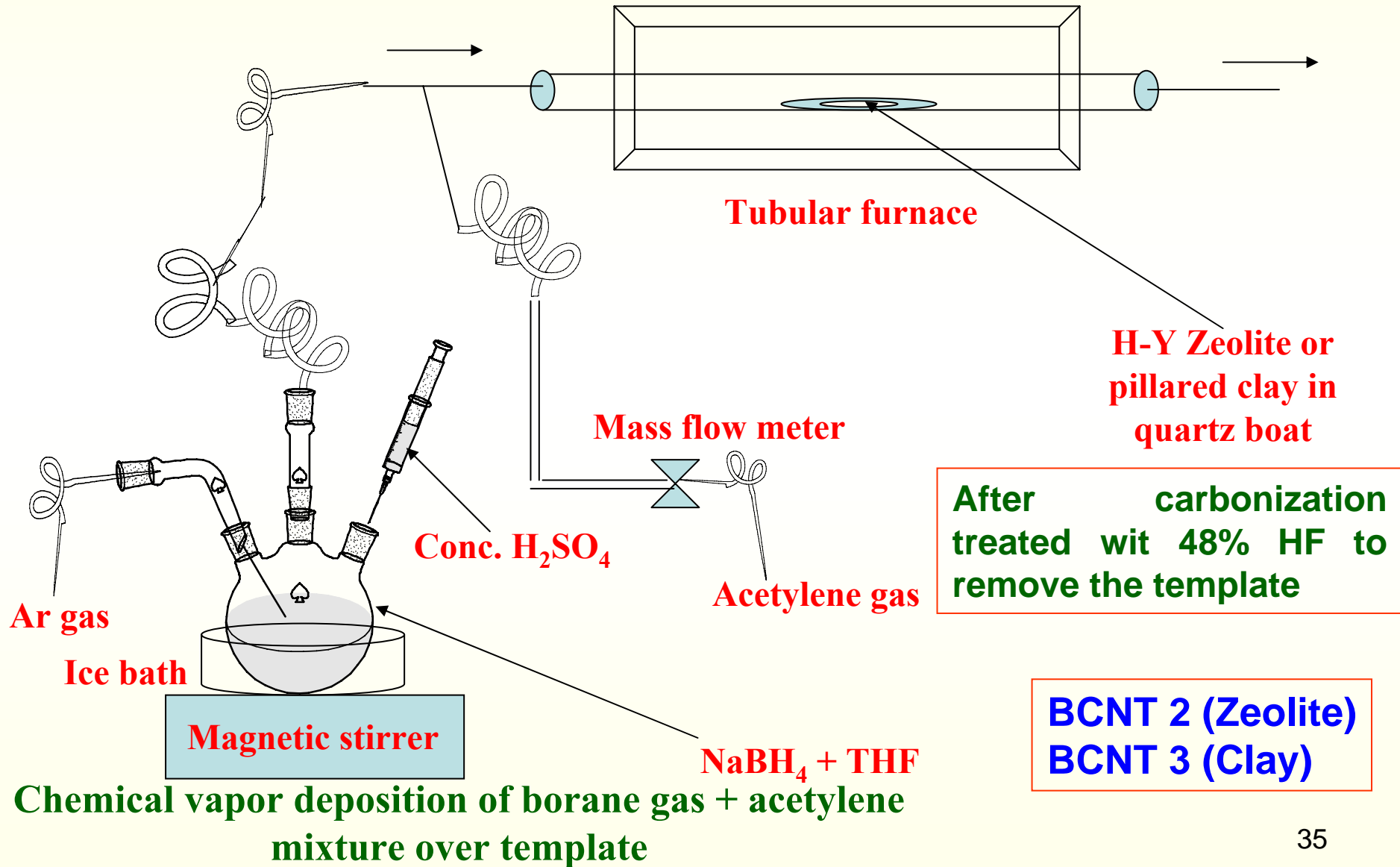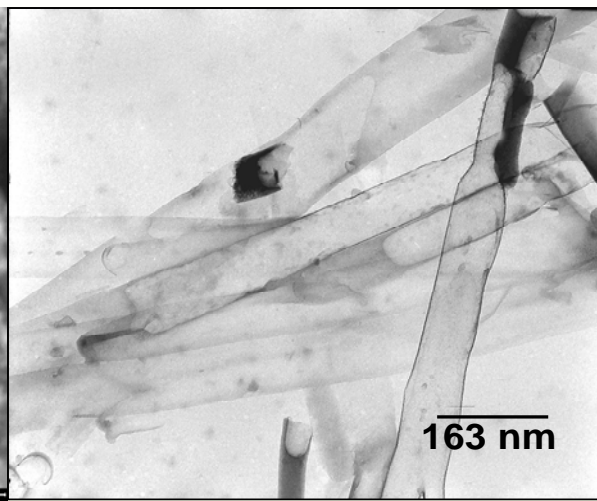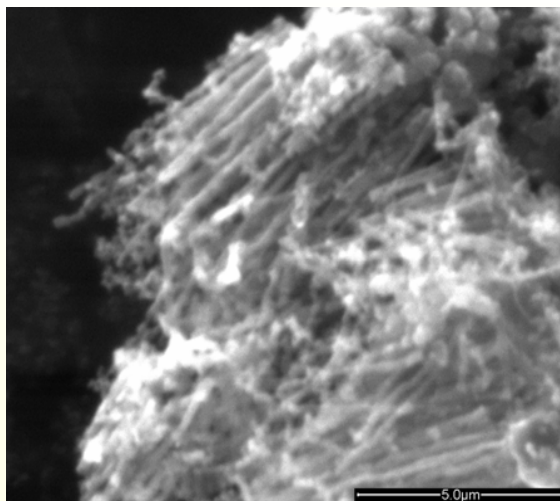# Boron containing carbon nanotubes prepared using alumina membrane

Alumina membrane (0.2μm pore size) in THF

Borane (BH$_3$.THF)

Divinyl benzene

↓

Stirred 273 K

Polymerization at RT 3h

↓

Polymer /Alumina

Carbonization 1173K Ar,4h

↓

Carbon / Alumina

↓

48% HF 24h → Carbon nanotubes (BCNT1)
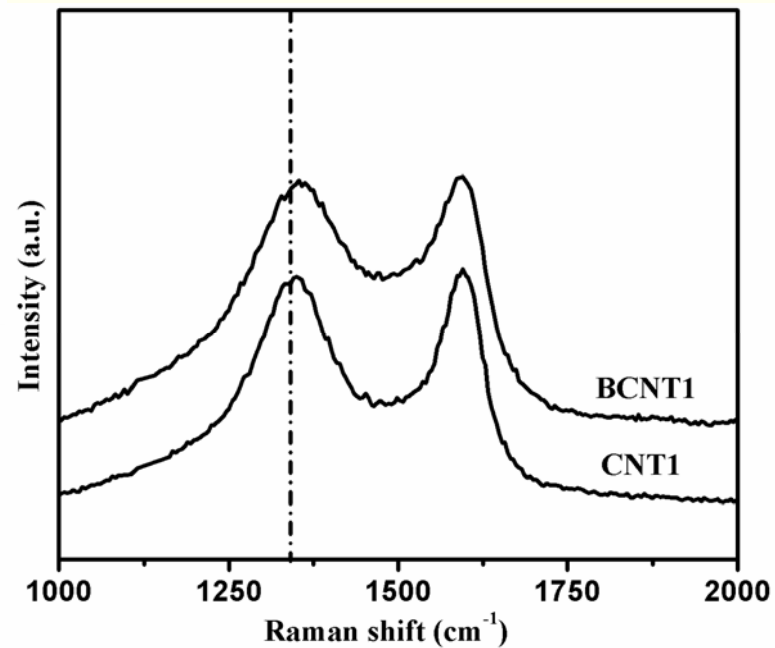
0°C
THF
solvent
N$_2$ atm

+ BH$_3$:THF

using hydroborane polymers
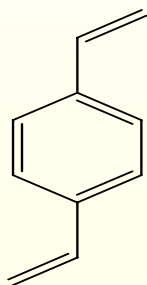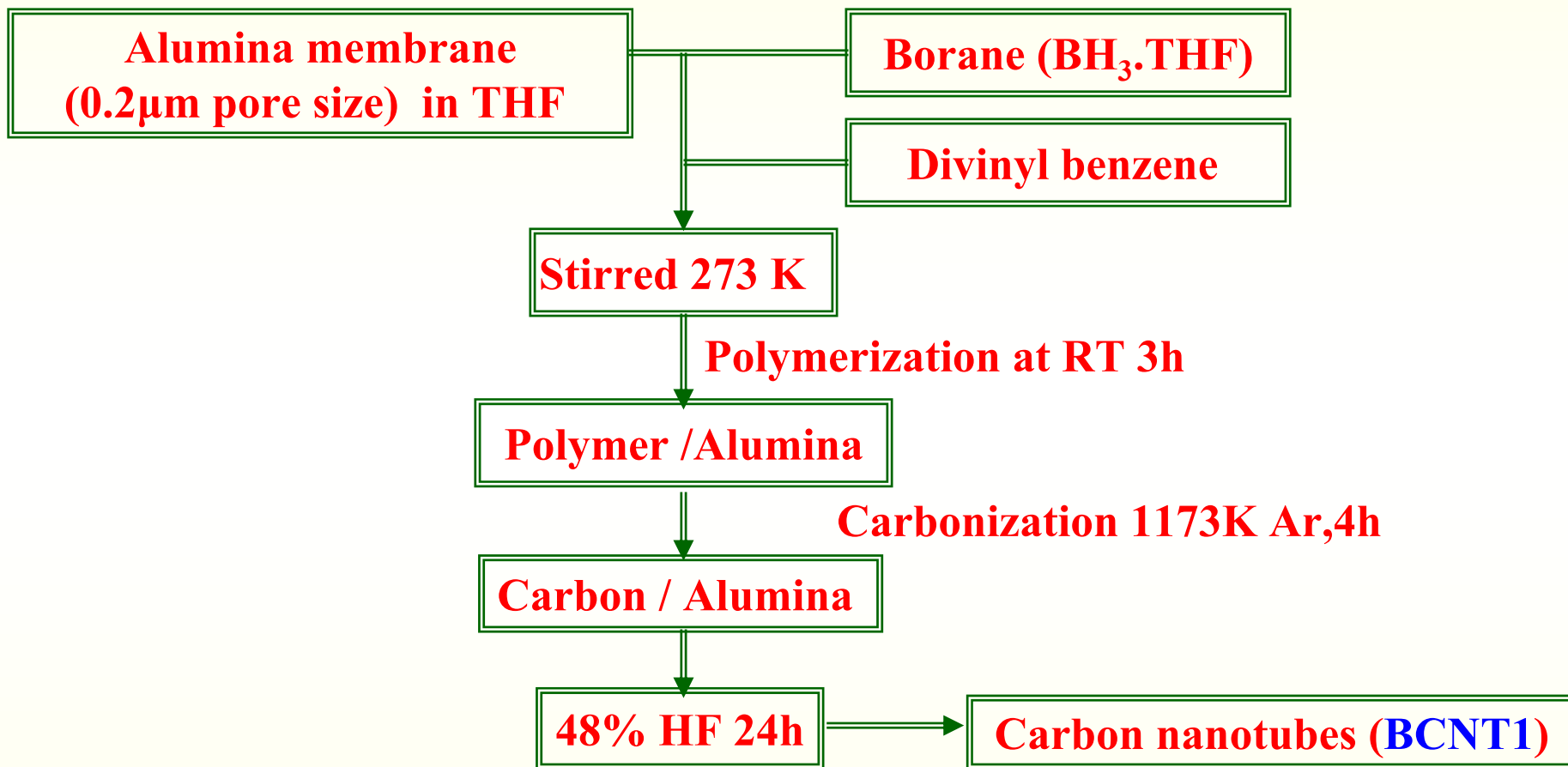
Preparation of boron containing carbon nanomaterials using zeolite and pillared clay
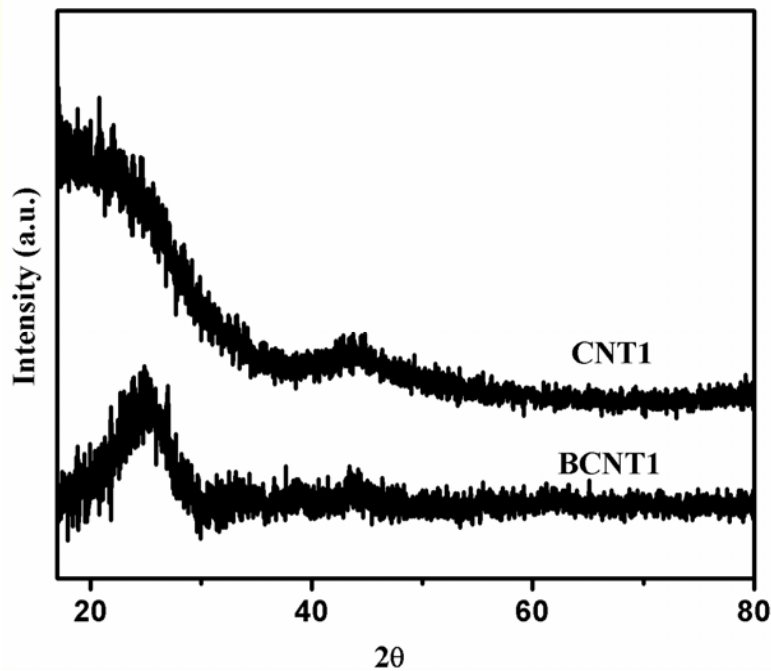
Tubular furnace

H-Y Zeolite or pillared clay in quartz boat

Mass flow meter

Conc. H_2SO_4

Acetylene gas

Ar gas

Ice bath

Magnetic stirrer

$NaBH_4$ + THF

Chemical vapor deposition of borane gas + acetylene mixture over template

After carbonization treated wit 48% HF to remove the template

BCNT 2 (Zeolite)
BCNT 3 (Clay)

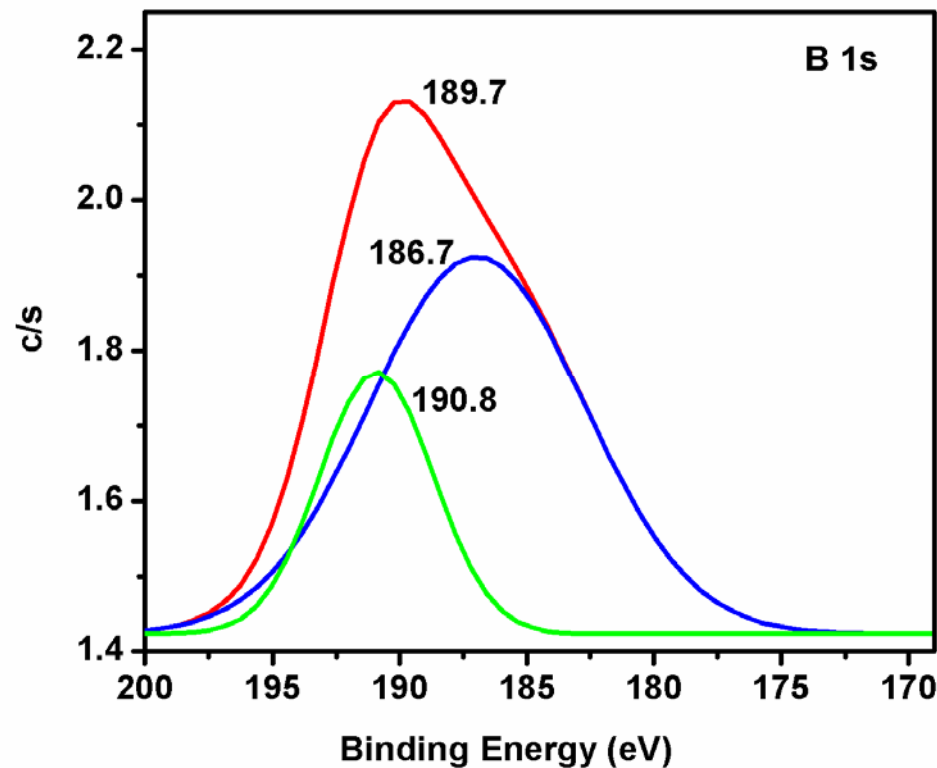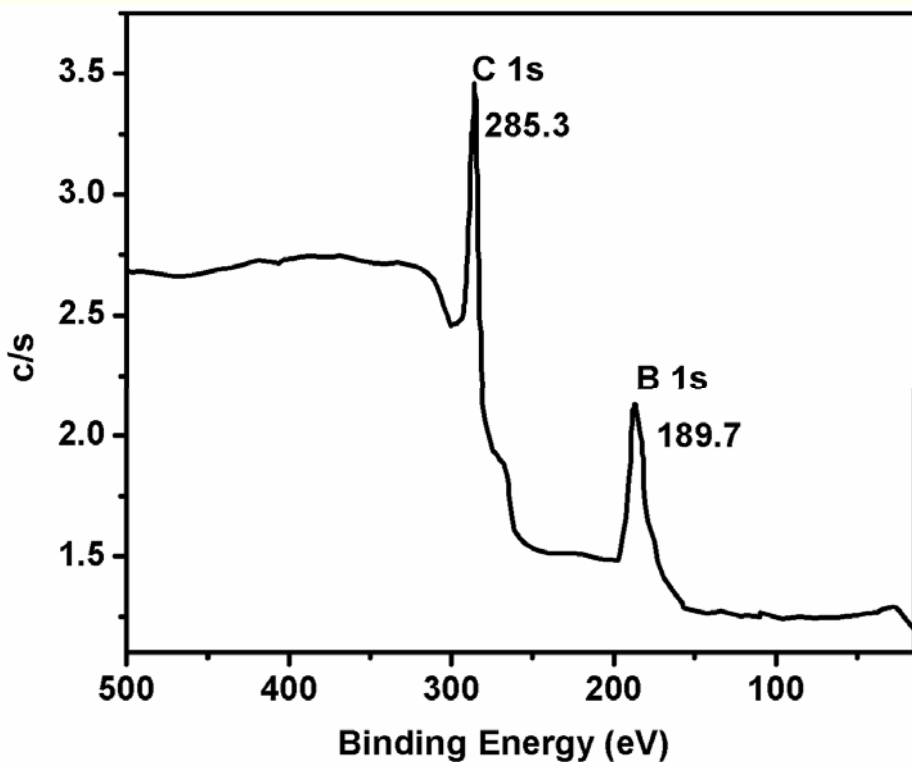# Characterization of Carbon Nanotubes
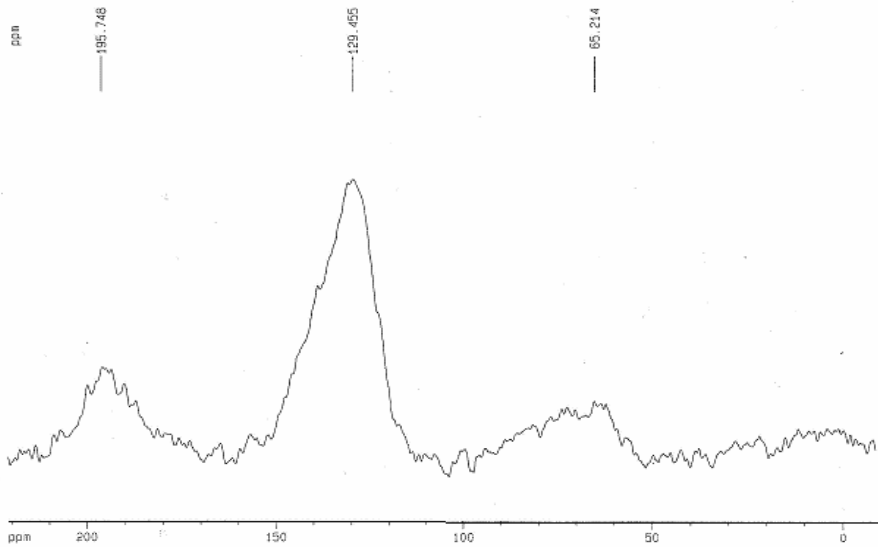
^{13}C CP MAS NMR of BCNT1
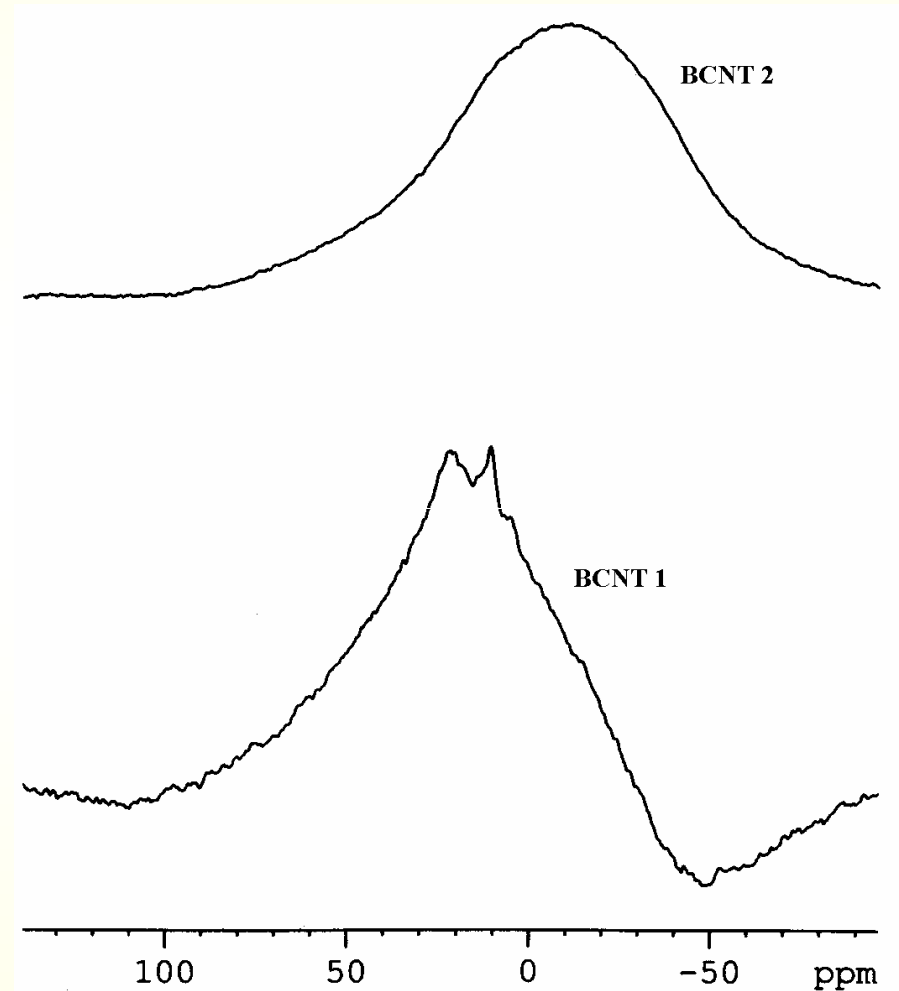
**^{11}B CP MAS NMR of BCNT1 & BCNT2**

XPS of BCNT1

(a). The service X-ray photoelectron spectrum of boron substituted carbon nanotube. (b). The deconvoluted XPS spectrum of B1s.

Confirms the presence of two different chemical environment of boron

Hydrogen absorption activity of boron containing carbon nanomaterials at 1 atm
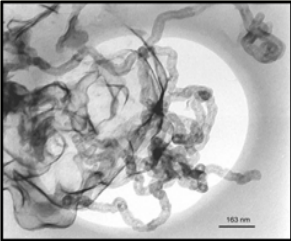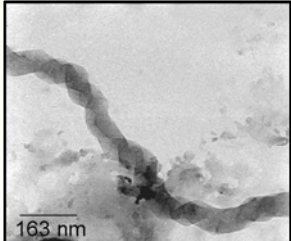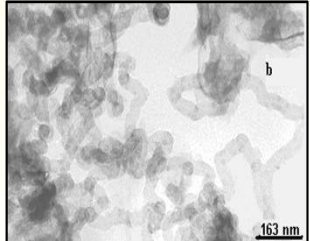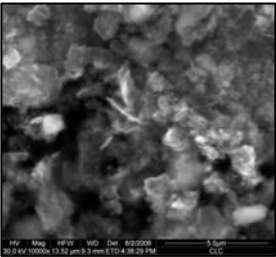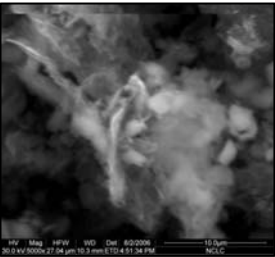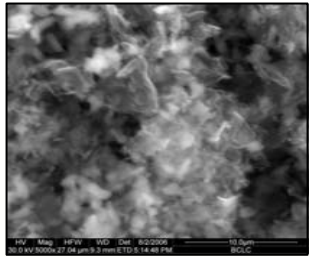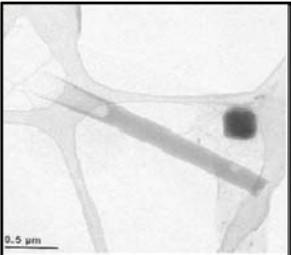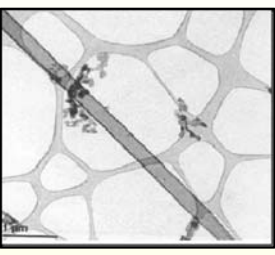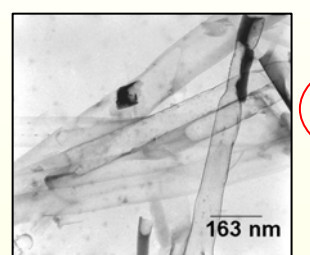
Carbon nanomaterial	Surface area (m²/g)	Amount of hydrogen absorbed (cm³/g) at 1 atm & at various temperatures (°C)			
		-196	25	100	150
BC	11.9	3.63	0.6	3.63	4.68
PBC	429.9	73	-	2.90	3.02
BCNT1	523	127	-	16.5	14.8
BCNT2	62.3	3.22	-	2.38	4.73
BCNT3	32.7	1.09	-	1.7	-

Hydrogen storage capacity of boron containing carbon nanotubes
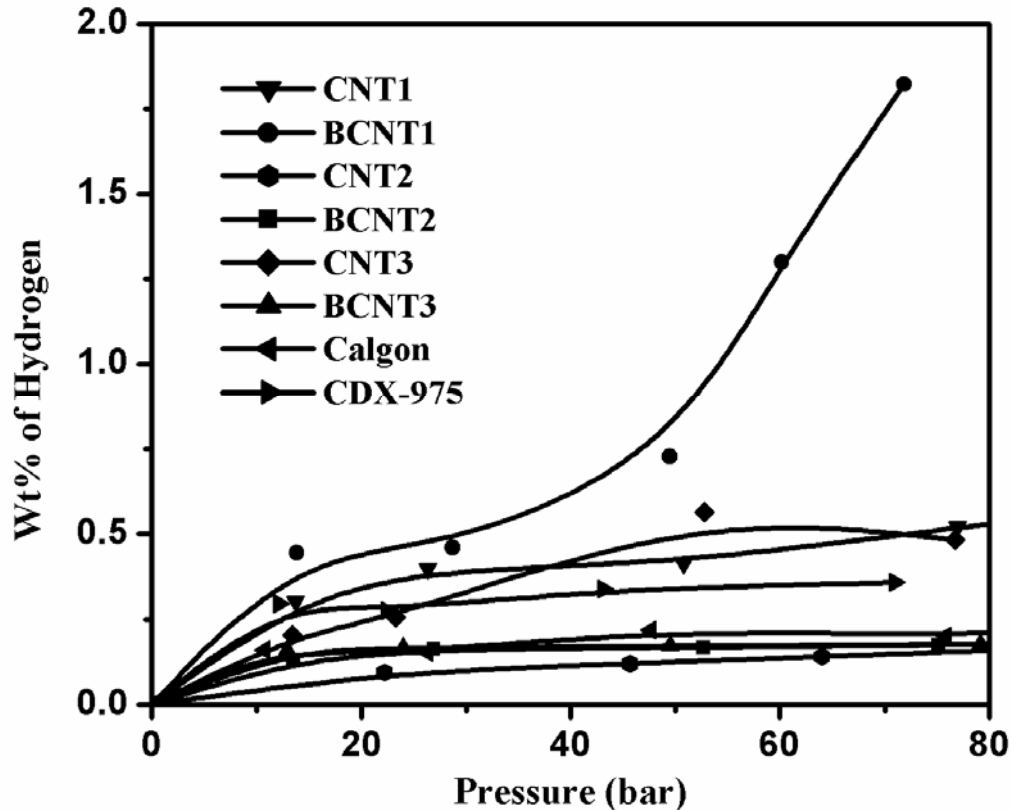
Boron containing carbon nanotubes prepared with polymer precursor, show different boron chemical environments and structural morphology. This configuration has a bearing on hydrogen sorption characteristics.

Morphology and the hydrogen storage capacity

C/Zeolite	NC/ Zeolite	BC/ Zeolite
0.2 Wt %	0.17 (0.72) Wt%	0.18 Wt%
C/ Clay	NC/ Clay	BC/ Clay
0.48 Wt %	1.75 Wt %	0.2 Wt %
CNT/ Membrane	NCNT/ Membrane	BCNT/ Membrane
Not measured	1.2 (0.6) Wt %	2.03 Wt %

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 heteroatom 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.**

Acknowledgement

Grateful thanks are due to

- **Prof. B. Viswanathan**
- **Prof. S. Srinivasa Murthy**
- **The Heads of Department of Chemistry and Deans**
- **The Doctoral committee members and faculty of the Department of Chemistry**
- **The authorities for providing the various facilities**
- **The supporting staff, fellow research scholars and friends**

LIST OF PUBLICATIONS BASED ON RESEARCH WORK

1. Sankaran, M., A. Kalaiselvan, R. Ganesan, P. Venuvanalingam and   B. Viswanathan, (2002) Heteroatom substituted carbon nanotubes: can they be the activating centers for hydrogen absorption, *Bull.Catal.Soc.India*, 1(6), 167-17.

2. Sankaran, M. and B. Viswanathan, (2003) Hydriding of nitrogen containing carbon nanotubes, *Bull.Catal.Soc.India*, 2(1&2), 9-11.

3. Viswanathan, B., M. Sankaran and M. Aulice Scibioh, (2003) Carbon nanomaterials -are they appropriate candidates for hydrogen storage?   *Bull.Catal.Soc.India*, 2(1&2), 13-26.

4. Viswanathan, B., M. Sankaran and R. Ganesan (2003) Can heteroatoms be the activators for hydrogen storage in carbon nanotubes, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*. 48 (2), 943-944.

5. Muthukumar, K., M. Sankaran and B. Viswanathan, (2004) Hydrogenation of substituted Fullerenes – A DFT study, *Eurasian. Chem. Tech. Journal*. 6, 139-143.

6. Sankaran, M., K. Muthukumar and B. Viswanathan (2005) Boron Substituted Fullerene – Can they be one of the Option for Hydrogen Storage? *Fullerene, Nanotubes and Carbon Nanostructures*, 13(1), 43-52.

7. Sankaran, M. and B. Viswanathan (2006) The role of heteroatoms in carbon nanotubes for hydrogen storage. *Carbon*, 44 (13), 2816-2821.

8. Sankaran, M. and B. Viswanathan (2006) Heteroatom substituted carbon nanotubes as candidate for hydrogen storage, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*. 51(2), 803-804.

9. Sankaran, M., B. Viswanathan and S. Srinivasa Murthy, (2006) Possibility of Hydrogen Storage by Boron Substituted Carbon nanotubes, *Bull.Catal.Soc.India*, 5, 56-61.

10. Sankaran, M. and B. Viswanathan (2007) Hydrogen storage in boron substituted carbon nanotubes, *Carbon*. 45, 1628-1635.

11. M. Sankaran, B. Viswanathan and S. Srinivasa Murthy (2007) Boron substituted carbon nanotubes - How appropriate are they for hydrogen storage? *International Journal of Hydrogen Energy* (in press)

12. M. Sankaran and B. Viswanathan (2007) Nitrogen Containing Carbon Nanotubes as a Possible Hydrogen Storage Medium (communicated)

In National/International Conference

1. Viswanathan, B., M. Sankaran and R. Ganesan, Can hetroatoms be the activators for hydrogen in carbon nanotubes? (Oral presentation) Presented in Fuel Cell Systems and Fuel Processing for Fuel Cell Applications- 226th American Chemical Society (ACS) National Meeting Co-sponsored by the ACS Fuel & Petroleum Chemistry Divisions held at New York City, NY September 7-11, 2003.

2. Viswanathan, B., M. Sankaran and S. Srinivasa Murthy, Carbon Nanomaterials for Hydrogen Storage, Indo-Belarus workshop on 'Advances in sorption based thermal devices' held at Minsk, Belarus, 2-3 Nov 2004.

3. Sankaran, M. and B. Viswanathan, Hydrogen storage by carbon materials – Heteroatoms as activating centers (Oral presentation) presented in International Conference on SOLID STATE HYDROGEN STORAGE – Materials and Applications held at Hyderabad, India, Jan 31 - Feb1 2005.

4. Sankaran, M. and B. Viswanathan, Heteroatom substituted carbon nanotubes as candidate for hydrogen storage. (Oral presentation) accepted for presentation in Chemistry and Applications of carbon nanotubes and nanoparticles in Fuel Chemistry division – 232nd American Chemical Society (ACS) National Meeting held in September 10 - 14, 2006, San Francisco, CA, USA.

5. Sankaran, M., B. Viswanathan and S. Srinivasa Murthy, Hydrogen storage in boron substituted carbon nanotubes (Oral presentation) presented in International Workshop on Hydrogen Energy (Production, Storage and Application) held in November 5-9, 2006, Jaipur, India.

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

Answers to the examiners questions

1. In the introductory chapter (p. 36) and also in chapters 5(p. 116) and 6 (p. 135) it has been mentioned explicitly that Iijima has discovered carbon nanotubes in 1991, which is not really true. Although a large percentage of academic and popular literature attributes the discovery of hollow, nanometer sized tubes composed of graphitic carbon to Sumio liiima of NEC in 1991, many others have produced and observed CNTs much earlier including Radushkevich and Lukyanovich (Russian J. Phys. Chem.1952), Oberlin, Endo, and Koyama (J. Cryst. Growth, 1976, 32, 335) etc. Please see the 2006 editorial written by Marc Montl1ioux and Vladimir Kuznetsov in the journal *Carbon* for the interesting and often misstated origin of CNT.

   The Russian scientist found the carbon nanotubes in early stage but they just reported formation and their properties are not well established for exploitation. However Iijima was the first who presented the possibilities of these materials. After the discovery by Iijima in 1991, carbon nanotubes have been prepared by various methods and exploited its application in all field. The current research interest in CNT is due to the report of Iijima and in that sense, it is appropriate to give the credit to this author.

2. What are the limitations of the DFT calculations (p.89) on both CNT and fullerenes for extracting hydrogen adsorption energetics? It may be better to discriminate between Hydrogenation and hydrogen storage, at least for some systems like lithiated CNT, since we know that physisorption is primarily responsible for the latter. How does the calculation of transition state parameters fit with the experimental data? (p. 89 & 96)

DFT calculations for system of molecules with larger number of atoms are rather difficult since it is computationally expensive and time consuming process. However, among all the available theoretical methods to determine the energietics, DFT remains the better option. For the condensed state systems this remains to be the better option. For comparison purposes, DFT provides reliable estimates.

In the process of hydrogen storage, the activation of hydrogen is the first step and then the hydrogen interaction. The interaction should be higher than the physisorption energy of 5 kJ/mol of Hydrogen. Even recent reports by neutron inelastic scattering experiments came to the conclusion that there should be strong interaction for effective hydrogen storage in carbon materials. Transition state parameters calculated show that the energy of activation of hydrogen molecule and the subsequent hydrogen movement to carbon surface are important.

3. What is the basis of selecting Ni (why not Pd?) support to carbon for activating hydrogen adsorption, apart from the obvious reason of a good hydrogenation catalyst? (p.102) If volumetric, gravimetric and TPD data give conflicting values for hydrogen adsorption capacity, what can be done to estimate this independently?

Nickel seems to be the better option to choose as a model system to substainate the spillover property of metal as similar to the heteroatom containing carbon nanotubes. When compared with Pd and Ni, Pd easily absorbs hydrogen. Nickel is known to act as an activator in dissociating hydrogen. In order to compare the effect of heteroatom with that of the metal containing system, nickel has been used.

4. Considering both the preparation of N containing CNTs in chapter 5, and also the results of theoretical studies in chapter 3, nothing is mentioned on the maximum amount of heteroatom substitution possible with out breaking the structure. How does the 1D/IG ratio in Fig. 5.1 (p.118) vary with the nitrogen content? What does the change in FWHM in this figure signify?

It is projected that a maximum of 20% of nitrogen can be substituted in the carbon nanotubes structure without breaking, essentially these substituted nitrogen should be stable enough even after the hydrogen cycling. This point has been well established in thesis and minimal amount of nitrogen is sufficient to activate hydrogen.

The ID/IG ratio in Raman spectra represents the significant disorder in the structure which is due to incorporation of nitrogen atom in the carbon structure. With increase in nitrogen content the ratio of ID/IG increases. Due to the increased disorderness of the graphitic structure the D-band shows an increase in the FWHM. This represents clearly the increase in the disorder and the substitution of nitrogen in the carbon lattice.

5. Since hydroborane polymer completely decomposes at 773 K, what is the need for going to 1173K for 6 h for preparing the sample (p. 143)? Similarly how do we know that leaching with *48%* HF for 6 h completely removes the template? Is this better than template removal by leaching in alkali? What is the meaning of "order of disordeness" (p. 147)? NMR proof for the presence of two different environments of boron in BCNTI is very interesting and calls for a plausible schematic representation of this. Also considering the unique merits of some of these materials developed in this study, like 2 wt. % hydrogen storage (p.156), has any statistical estimate of reproducibility been made?

Polymer shows complete decomposition at 773 K, but higher temperature of 1173 K has been used in the synthesis procedure for complete carbonization of all the precursor in short time and make carbon materials leading to graphitization, leading to formation of meta stable carbon materials like tubes at this temperature.

Leaching of template with HF seems to be the better option compared to treatment with alkali, because alkali forms salt with the carbon materials and also there is possibility some alkali metal to adhere to the carbon surface. HF forms volatile products and experimental procedures are simple to purify the carbon nanotubes after the removal of template.

The D- band represents the disorder induced in the graphitic structure of carbon nanotubes. The variation of the intensity of D-band shows the extant of disorder, since three different materials have been compared with different amounts of substitutional level.

The reproducibility of hydrogen absorption activity of boron containing carbon nanotubes have been done for three cycles and it shows there is no decrease in the hydrogen storage capacity.

6. How does the heteroatom substitution results in the tuning of the electronic properties of CNT? (p. 157). What is the effect on band structure? Similarly is it possible to illustrate quantitatively the higher redox potential of N, P, S, B than that of carbon for consideration as promising activators Although Fig. 7.1 gives an elegant comparison, the limitations of template aided synthesis (p. 159-161) should be kept in mind when we compare these for hydrogen storage with other types of CNT. What are the factors controlling the hydrogen storage capability? Also was there any attempt to compare their response times?

By the substitution of heteroatom the electronic property is varied with respect to the nature of substitution like electron donating nature of nitrogen and electron withdrawing nature of boron will affect the band structure.

These are other interesting aspects like variation of redox potential and change in electronic properties. These aspects are not considered in the present thesis as the objective was to develop a material for hydrogen storage.

The studies have been carried out to compare and show how the heteroatom facilitates the hydrogen storage capacity. Templates and different carbon source will have effect in carbon nanotubes for hydrogen storage. However, it is realized that other preparation conditions can affect the hydrogen absorption characteristics and these aspect have been brought out in the thesis. We have not yet compared the response time since the thesis focused on equilibrium measurements.

Thank you