ARE CARBON MATERIALS APPROPRIATE FOR SOLID STATE HYDROGEN STORAGE?

Ph.D Seminar II

M. Sankaran
CYD01012

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Options available for hydrogen storage

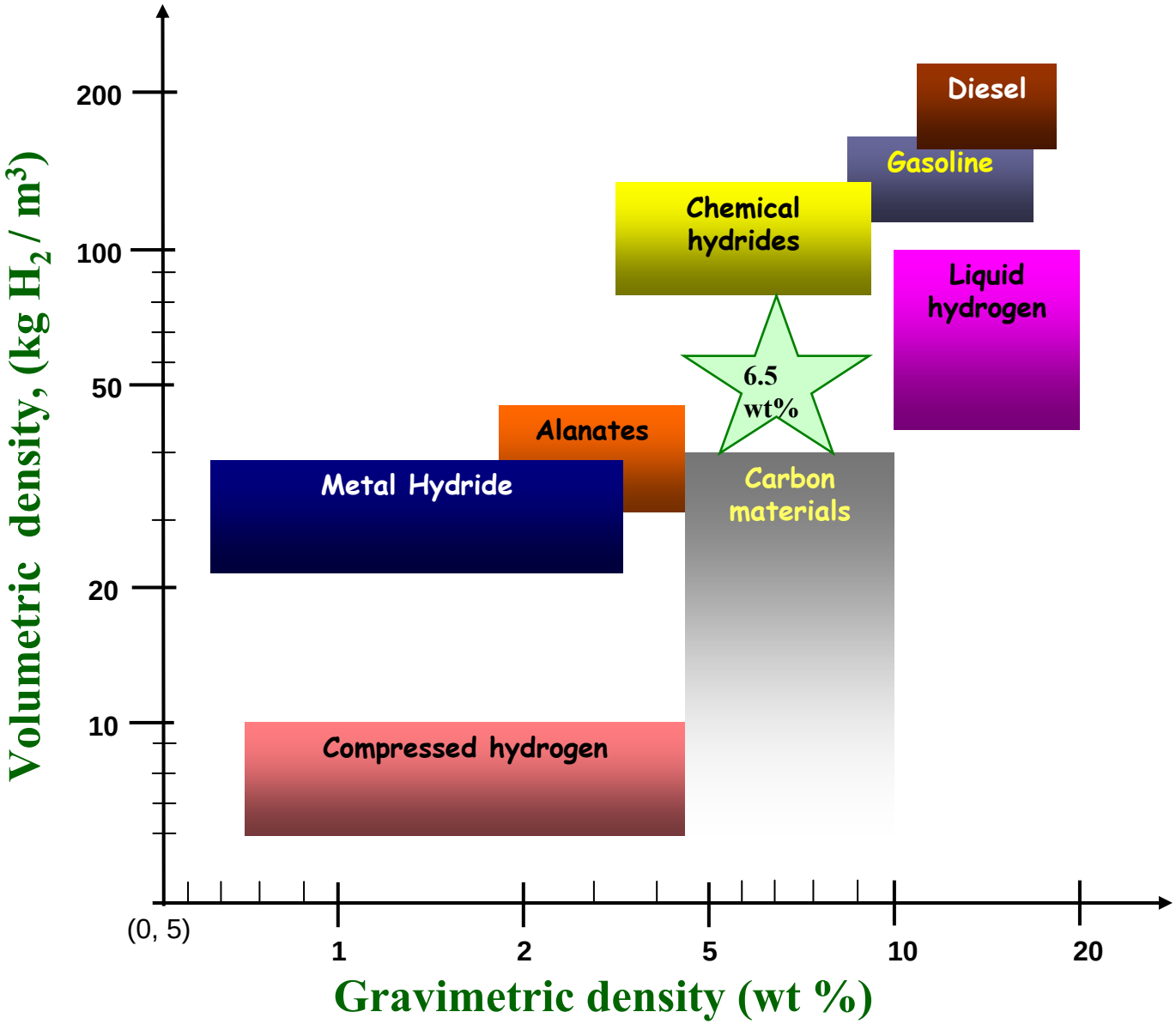
- High pressure gas cylinders
- Liquid hydrogen in cryogenic tanks

Hydrogen storage by solid state materials appears better option

Requisites for a solid state hydrogen storage medium

- ✓ Favourable thermodynamics
- ✓ Fast kinetics (quick uptake and release)
- ✓ Large storage capacity (gravimetric and volumetric density)
- ✓ Effective heat transfer
- ✓ Higher cycle number for hydrogen sorption/desorption
- ✓ Desirable mechanical strength and durability
- ✓ Safe under normal use

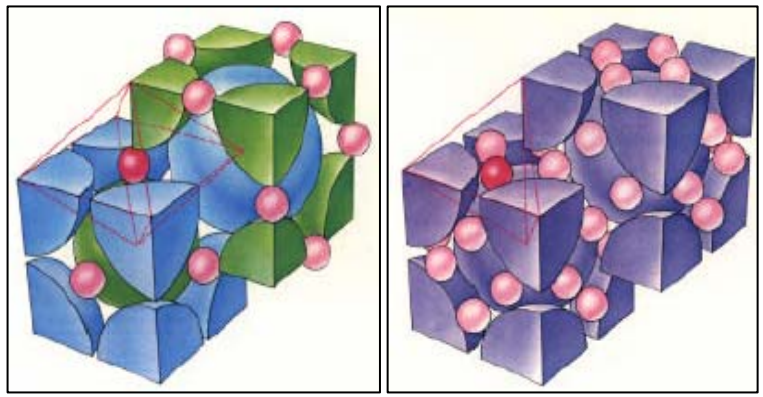
Hydrogen storage capacity



Solid state materials for hydrogen storage

Metal hydrides (MgH_2, BeH_2, TiH_2)
Decomposition temperature

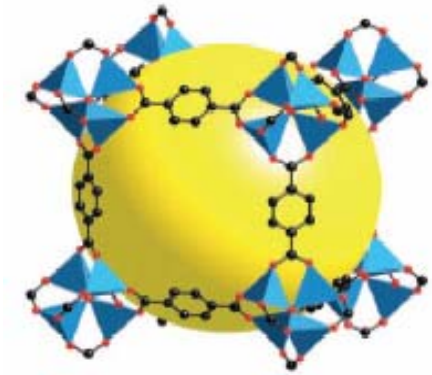
Intermetallics (AB (FeTi), A_2B (Mg_2Ni, ZrV_2), AB_5 ($LaNi_5$))
Maximum storage capacity <3 wt%



Intermetallics

Complex metal hydrides (Alanates, Borohydrides)
Catalytic, multi step decomposition, poor kinetics

Porous materials (MOF, Oxides, glass microspheres)
Experimental parameters not favourable



MOF

Zeolite -Y

Carbon materials ..!

Louis Schlapbach and Andreas Züttel, *Nature* 414 **(2001)** 353

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.

Hydrogen storage capacity reported in carbon nanostructures

Material	Temp (K)	Pressure (bar)	Wt%	Group
GNF (Herring bone)	RT	113.5	67.6	Chambers *et al.*, (1998)
Graphitic Nano Fibers	RT	101	10	Fan *et al* ., (1999)
Graphitic Nano Fibers	RT	80-120	10	Gupta *et al.*, (2000)
SWNTs (low purity)	273	0.4	5-10	Dillon *et al.*, (1997)
SWNTs (high purity)	80	70-180	8.25	Ye *et al.*, (1999)
SWNTs (50% purity)	RT	101	4.2	Liu *et al* ., (1999)
SWNTs (high purity + Ti alloy)	300-600	0.7	3.5-4.5	Dillon *et al.*, (1999)
Li-MWNTs	473-673	1	20	Chen *et al.*, (1999)
Li-MWNTs (K-MWNTs)	473-673	1	2.5 (1.8)	Yang *et al.*, (2000)
MWNTs	RT	Ele.chem	<1	Beguin *et al.*, (2000)
CNF	RT	1-100	0.1-0.7	Poirier *et al.*, (2001)
SWNTs	300-520	1	0.1	Hirscher *et al.*, (2000)
Various CNM	RT	35	<0.1	Tibbets *et al.*, (2001)
SWNTs (+ Ti alloy)	RT	0.8	0	Hirscher *et al.*, (2001)

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?

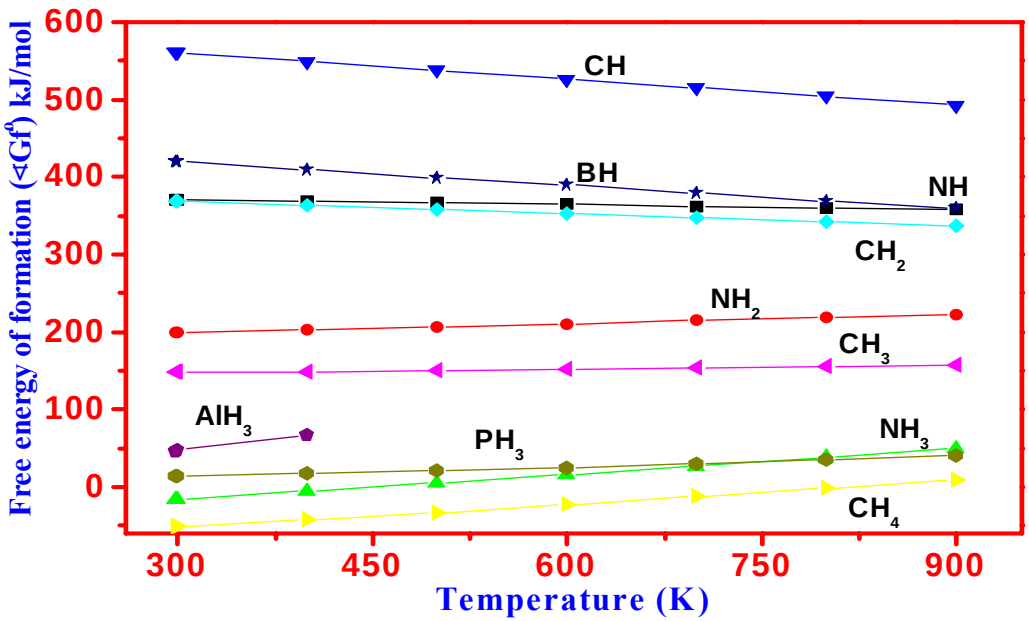
(iv) Where does the lacuna lie? Is it in our theoretical foundation of the postulate or is it in our inability to experimentally realize the desired levels of storage?

Alternate postulates

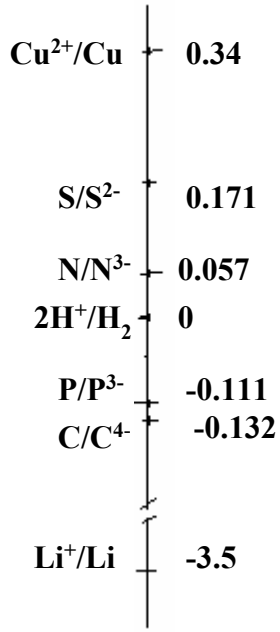
- Necessity of active sites
- Heteroatom containing carbon materials - appropriate candidates?
- Gradation of the carbon materials containing various heteroatoms
- Geometrical positions of the heteroatoms

Heteroatom in carbon materials

- Equipotential sites
- Sites themselves hydridable



Ellingham diagram for various species



Standard redox potential (V) for various couples

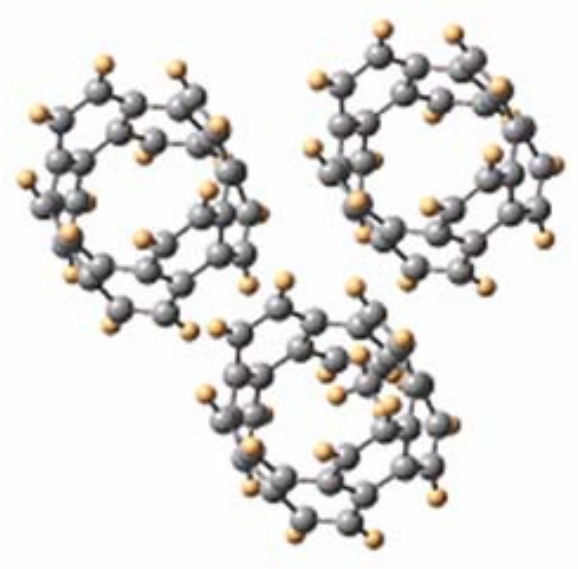
- Catalytic or Stoichiometric? & Possible combinations

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

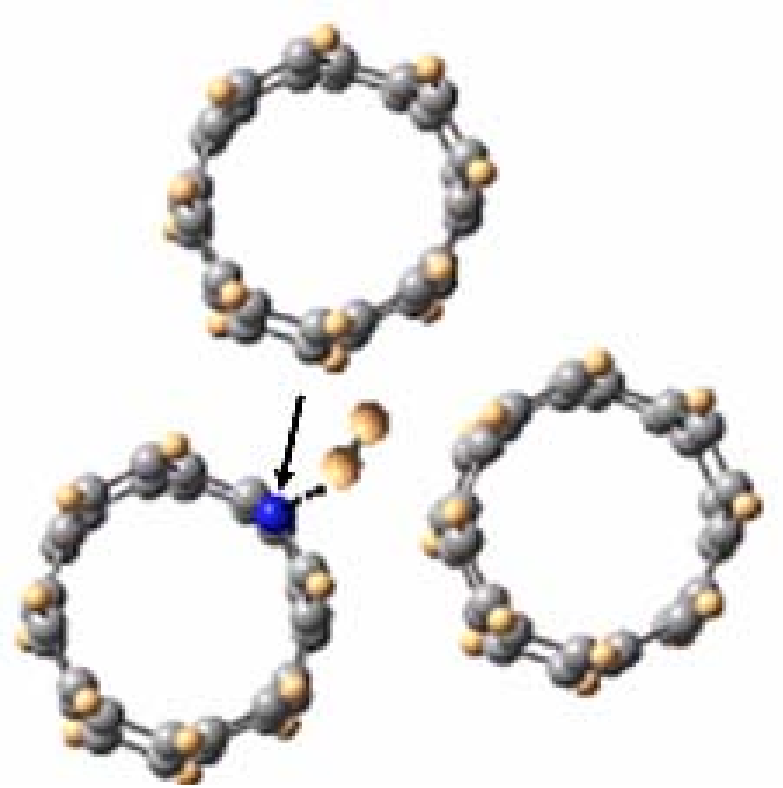
Model

- Three Single Walled Carbon nanotubes (SWNTs) of armchair type (4, 4)



- Each tube having 32 carbon atoms
- Tube diameter - 5.56 Å

Methodology



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*)

The geometric parameters of the optimized clusters

Cluster	Average bond length (Å)			Average bond angles (deg)			
	C-C	X-C		<C-X-C		<X-C-C	<C-C-C
		Reported	Observed	Reported	Observed		
CNT	1.416	1.385	1.396	120.0	120.9	123.0	123.0
N CNT	1.409	1.336	1.359	117.4	122.1	121.0	121.6
P CNT	1.417	1.768	1.710	104.6	103.0	119.2	122.4
S CNT	1.416	1.790	1.736	99.6	103.2	118.8	122.4
B CNT	1.420	1.486	1.431	106.6	109.6	120.5	120.8

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	-3686.5502	-	-
CNT + H_2	-3687.7161	0.776	4.51
NCNT	-3702.5908	-	-
NCNT + H_2	-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 H_2 on SCNT

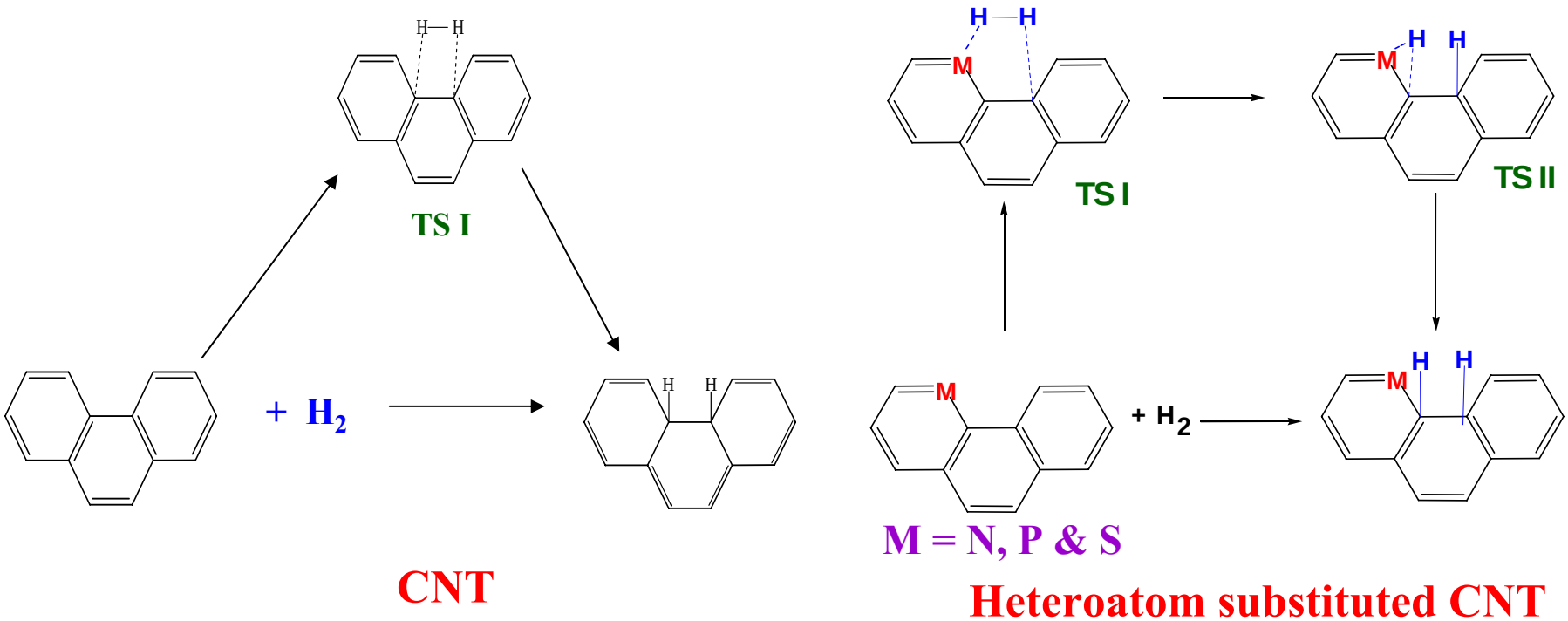
Substitution	Total Energy (Hartrees)	H_1-H_2 (Å)	Dissociation Energy (eV)
H_2	-1.175	0.708	4.76
CNT	-3686.5502	-	-
CNT + H_2	-3687.7161	0.776	4.51
SCNT	-4046.0020	-	-
SCNT + H_2	-4047.0067	0.817	0.13

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

The mechanistic pathway for hydrogenation of heteroatom substituted CNTs.

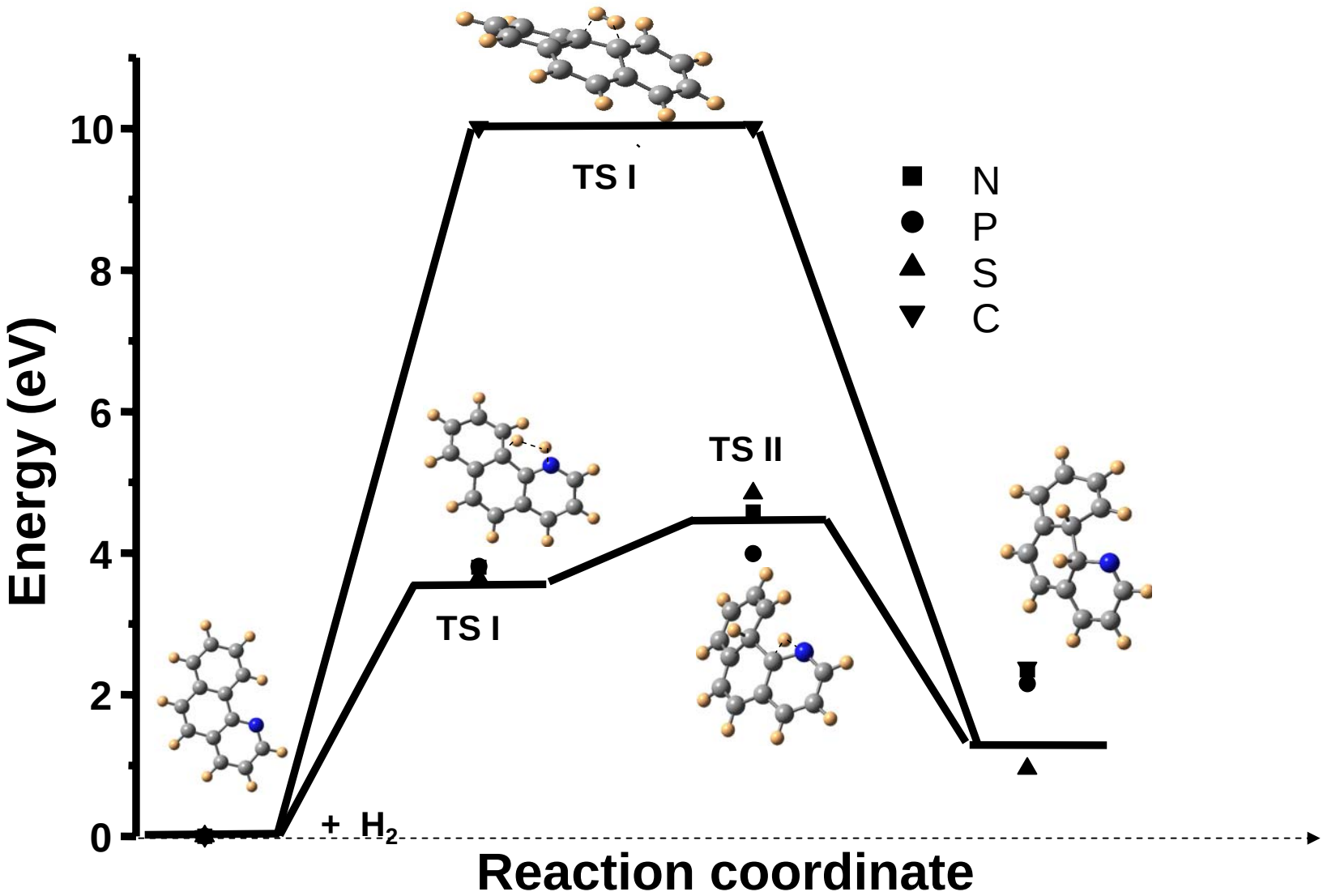


★ TRANSITION STATE OPTIMIZATION USING DFT

★ B3LYP/6-31G*

B.Viswanathan, M.Sankaran and R.Ganesan, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 48 **(2003)** 943

Energy profile for hydrogen interaction with heteroatom substituted CNT clusters



Transition state optimized parameters of the cluster and values of activation energy

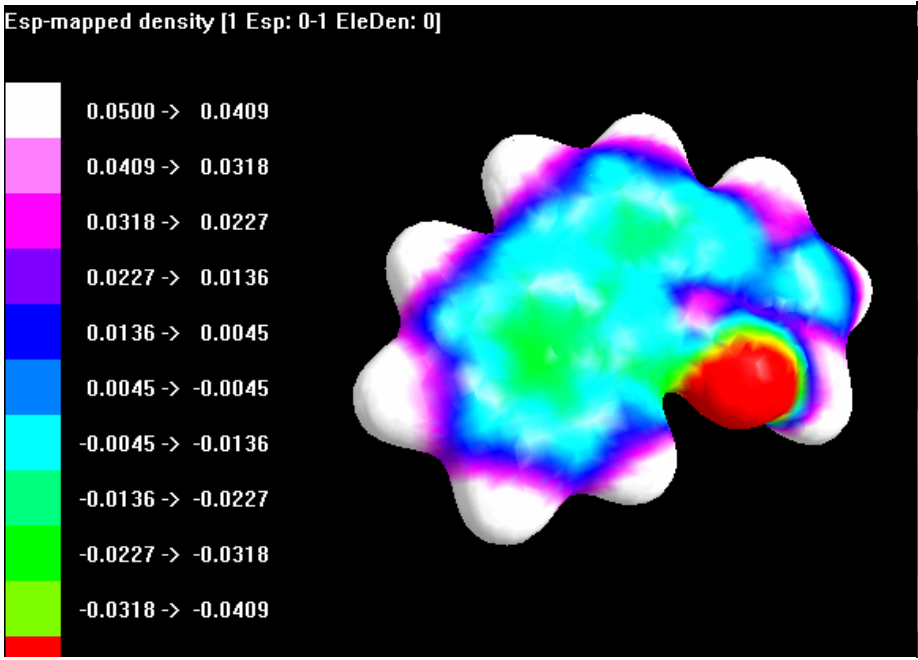
Substitution	E_a I (eV)	E_a II (eV)	H_1-H_2 (Å)	X-H (Å)	C-H_1 * (Å)	C-H_2 * (Å)
CNT	10.02	-	0.71	-	-	-
N CNT	3.84	4.58	1.45	1.11	1.70	1.94
P CNT	3.81	3.99	1.51	1.61	1.27	2.33
S CNT	3.65	4.85	1.50	1.75	1.24	2.40

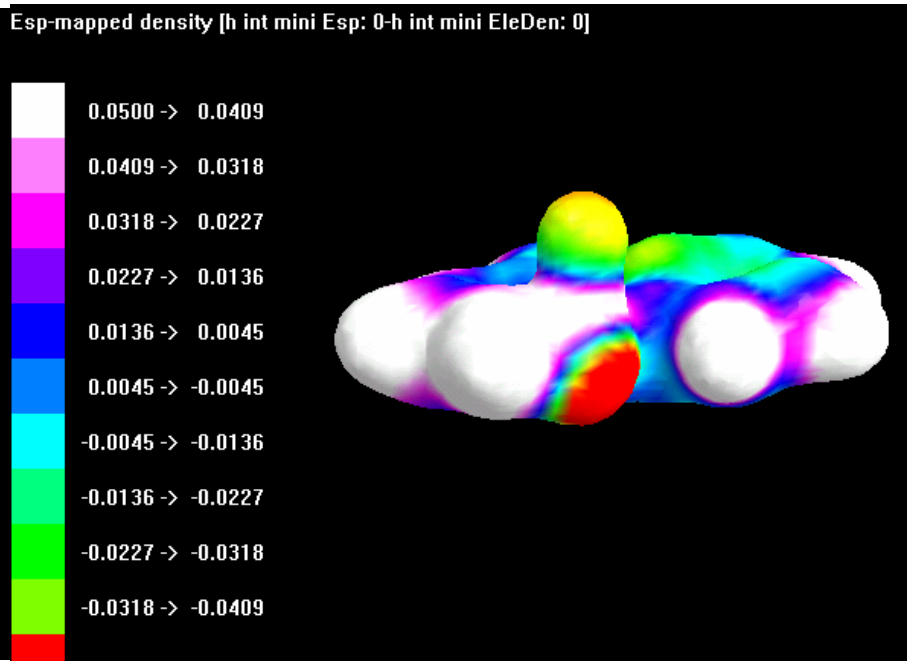
E_a = E (transition state) – E (reactant)

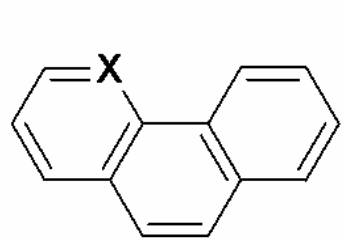
* Shortest C-H bond distance

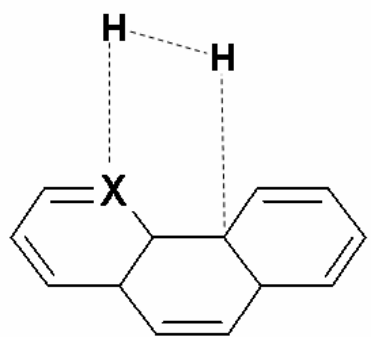
M. Sankaran, and B. Viswanathan, *Carbon* (in press) (doi:10.1016/j.carbon.2006.03.025)

Electron density contour of heteroatom containing cluster before and after hydrogen interaction









Bond length and dissociation energy of H_2 on BCNT

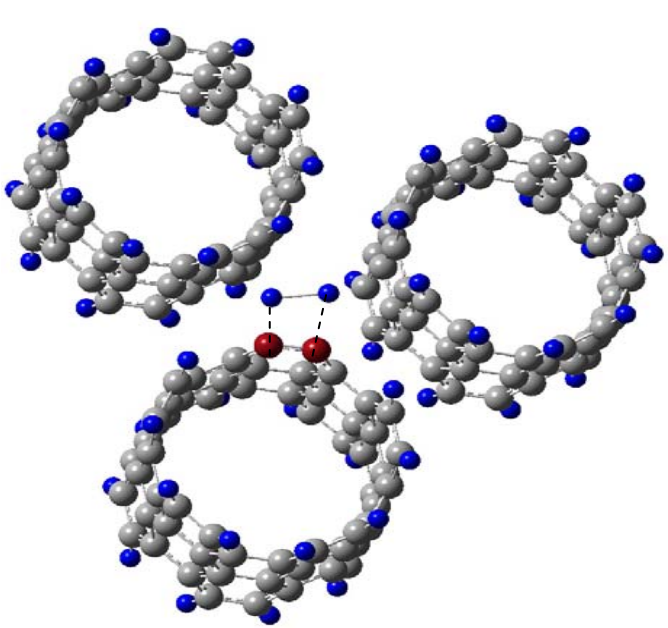
Substitution	Total energy (Hartrees)	H_1-H_2 (Å)	Dissociation energy (eV)
H_2	-1.175	0.708	4.76
CNT	-3686.5502	-	-
CNT + H_2	-3687.7161	0.776	4.51
B CNT	-3671.7254	-	-
B CNT + H_2	-3672.9440	0.818	5.95

Character of HOMO

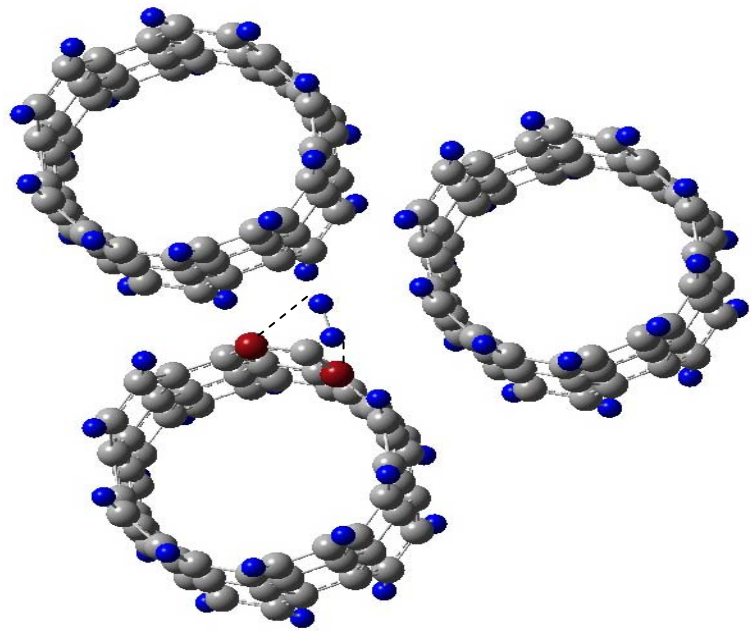
HOMO level (Hartrees)	% of orbital contribution					
	C		B		H	
Contribution	s	p	s	p	s_b	s_t
CNT (-0.1612)	0	100	-	-	-	-
CNT + H_2 (–0.1613)	0	100	-	-	0	0
BCNT (–0.1576)	1	94.87	0	3.59	-	0.5
BCNT + H_2 (– 0.1534)	1	96.26	0.10	1.12	1	0.54

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

Boron substitution in adjacent and alternate positions in carbon nanotubes



Adjacent position



Alternative position

Bond length and dissociation energy of H_2 on BCNTs

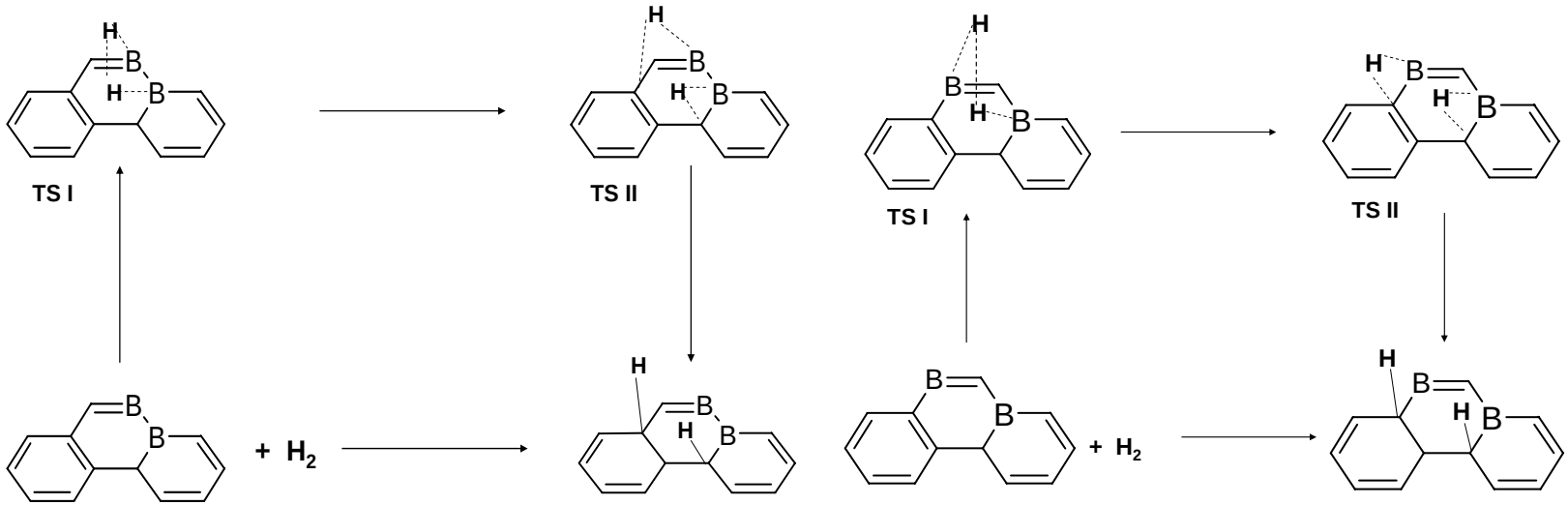
Substitution	Total energy (Hartrees)	H_1-H_2 (Å)	Dissociation energy (eV)
H_2	-1.175	0.708	4.76
CNT	-3686.5502	-	-
CNT + H_2	-3687.7161	0.776	4.51
2B CNT (adjacent)	-3658.6666	-	-
2B CNT (adjacent)+ H_2	-3659.8092	0.913	3.88
2B CNT (alternate)	-3659.3491	-	-
2B CNT (alternate)+ H_2	-3660.3594	0.928	0.28

Character of HOMO

HOMO level (Hartrees)	% of orbital contribution					
	C		B		H	
	s	p	s	p	s_b	s_t
CNT (-0.1612)	0	100	-	-	-	-
CNT + H_2 (–0.1613)	0	100	-	-	0	0
2B CNT (adjacent) (– 0.1568)	1.01	96.98	0	1.53	-	0.5
2B CNT (adjacent) + H_2 (– 0.1564)	6.26	88.34	0.10	4.67	0.28	0.4
2B CNT (alternate) (– 0.1540)	12.56	80.41	0.60	5.49	-	1
2B CNT (alternate) + H_2 (– 0.1572)	14.67	73.93	0.73	4.48	5.32	0.86

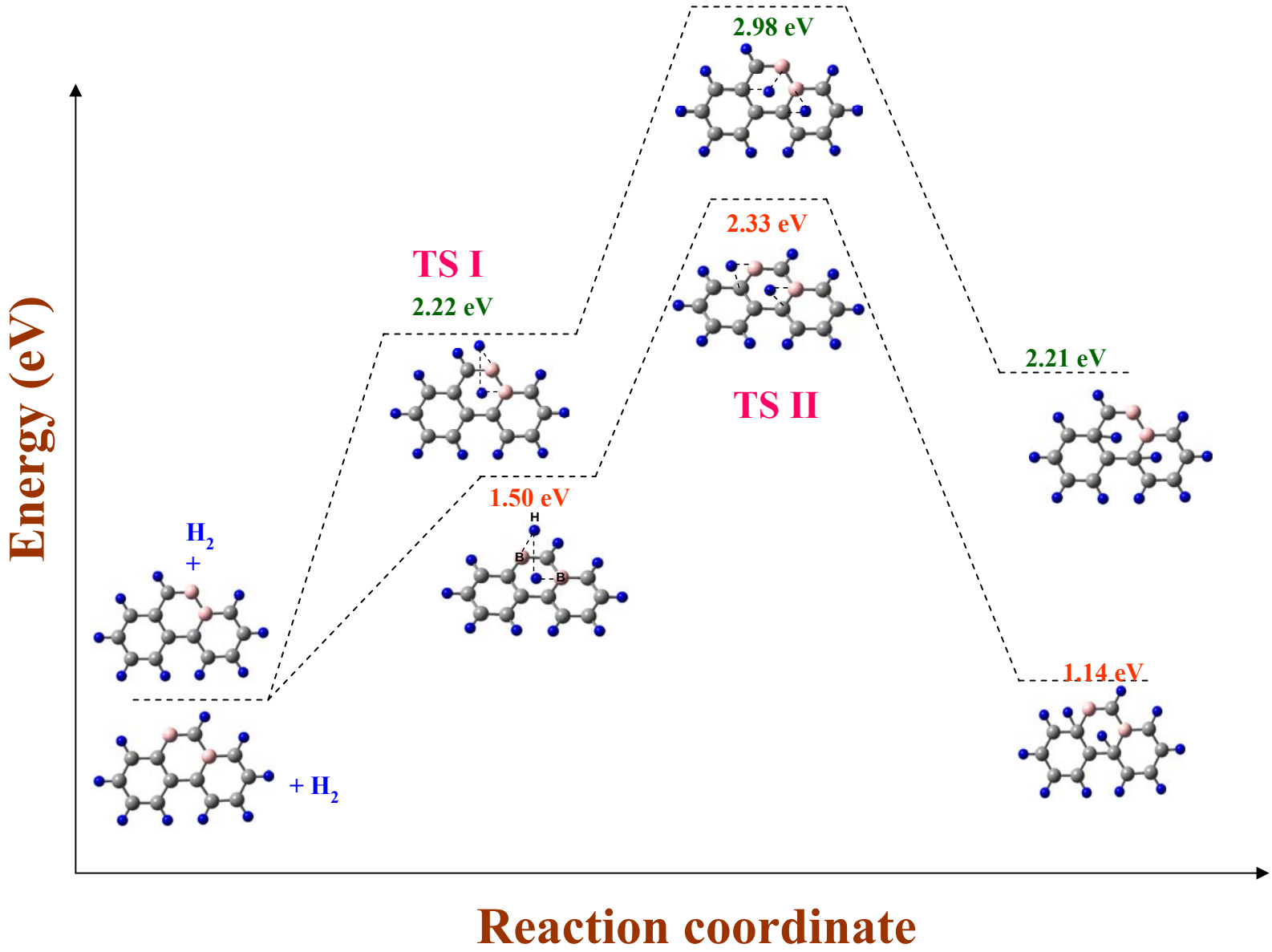
* b- bonded hydrogen to boron and t- terminal hydrogen in the cluster

Mechanistic pathway for hydrogenation of boron substituted CNT in adjacent and alternate positions



- ★ TRANSITION STATE OPTIMIZATION USING DFT
- ★ B3LYP/6-31G*

Energy profile of boron substituted CNT clusters



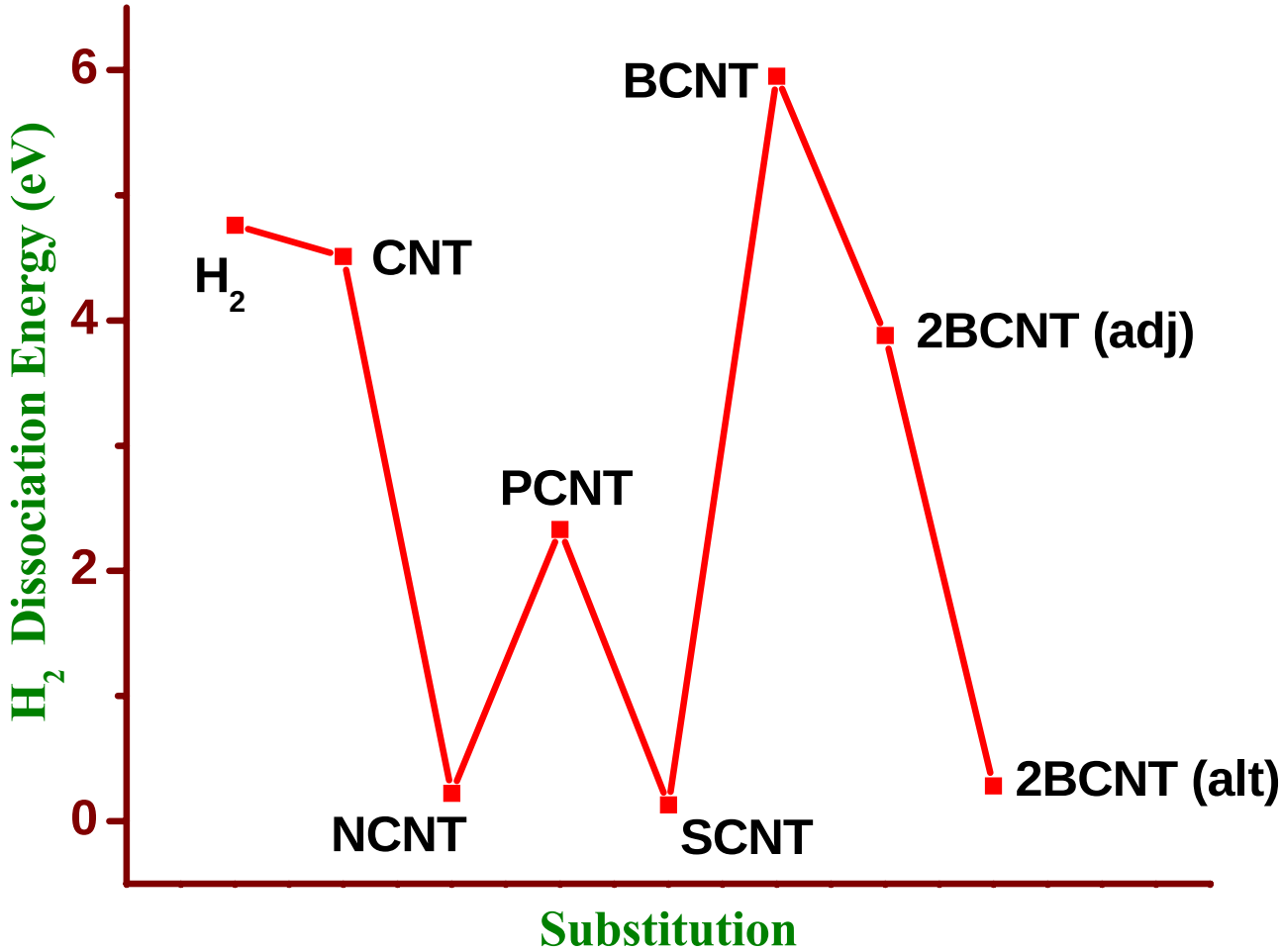
The transition state optimized parameters of the cluster and the values of the activation energy

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	-	-	-
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

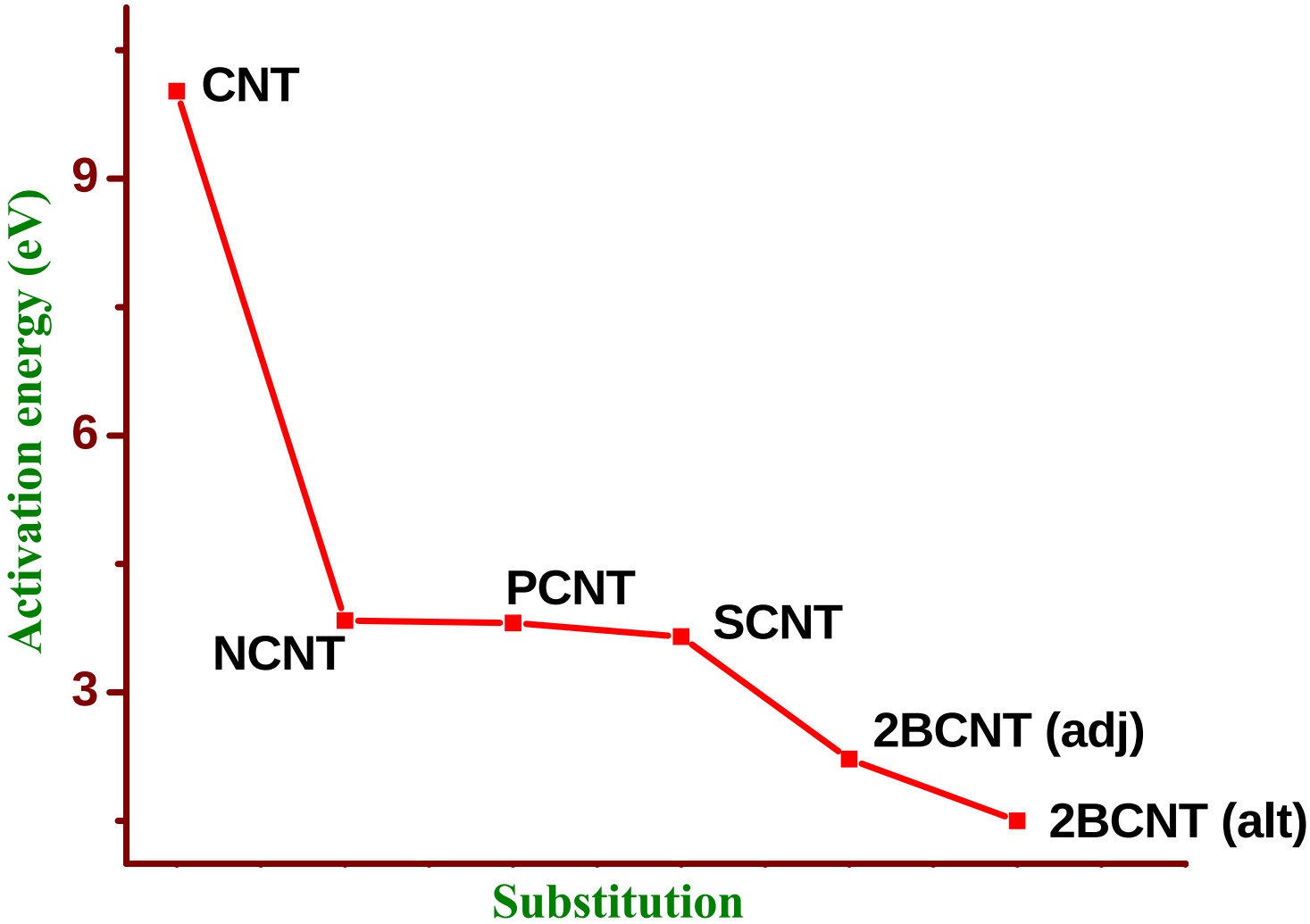
E_a = E (transition state) – E (reactant)

* Shortest C-H bond distance

The dissociation energy of the H_2 with heteroatom substitution



Variation of activation energy for the TS I

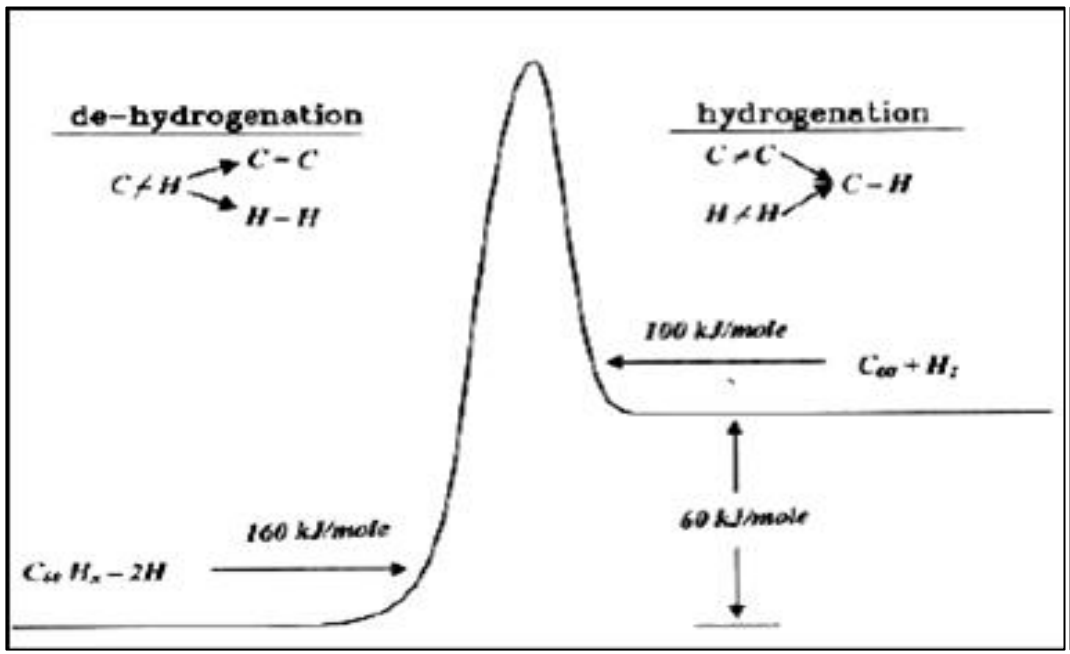


Fullerenes

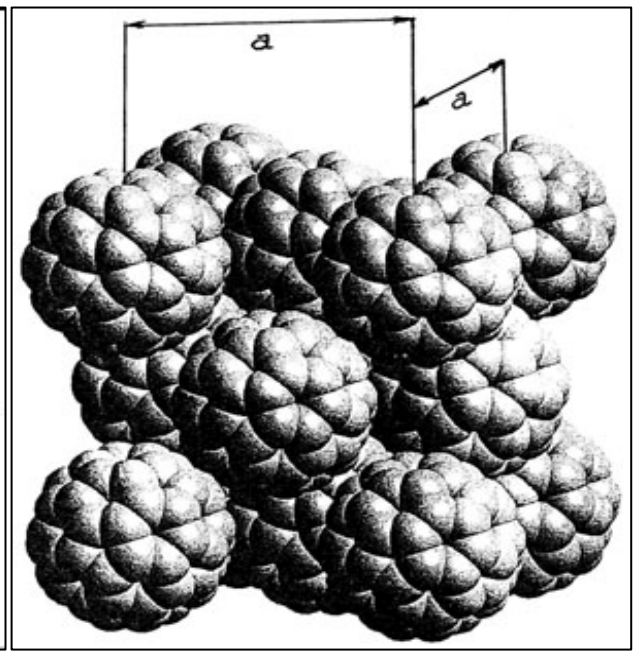
Theoretical storage capacity 7.7 wt% ($C_{60}H_{60}$)

$$C_x + x/2\ H_2 \leftrightarrow C_xH_x$$

High temperature (400 – 450 °C) & Pressure (60 – 80 MPa)



E_a of hydrogenation and dehydrogenation



Fullerite

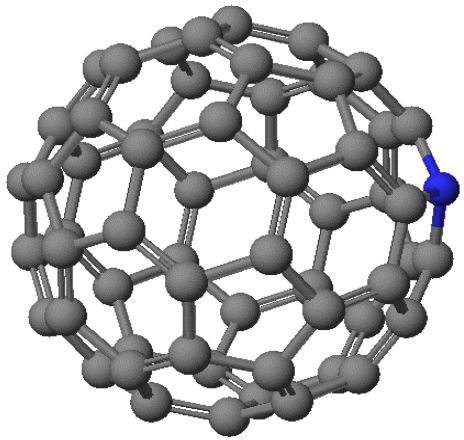
Research in hydrogen – Sorption properties of fullerites

Method	Chemical reaction	Conditions: pressure p temperature T
Direct non-catalytic hydrogenation	$C_{60} + H_2 \Rightarrow C_{60}H_{2-18}$ (2.4 Wt%)	pH_2= 50–85 MPa, T = 573–623 K
Reaction of gaseous hydrogen with $C_{60}Pd_{4.9}$	$C_{60}Pd_{4.9} + H_2 \Rightarrow C_{60}H_{2-26}$ (3.48 Wt%)	pH_2= 2.0 MPa, T= 473–623 K
Catalytic hydrogenation in toluene solution in the presence of Ru/ C	$C_{60} + H_2 \Rightarrow C_{60}H_{36-48}$ (6.3 Wt%)	pH_2= 2-12 MPa, T= 383–553 K
Radical hydrogenation with promoter, C_2H_5I	$C_{60} + H_2 \Rightarrow C_{60}H_{\sim 36}$ (4.8 Wt%)	pH_2= 6.9 MPa, T= 723 K
Reduction with lithium in ammonia in the presence of t-BuOH	$C_{60} + H_2 \Rightarrow C_{60}H_{18-36}$ (4.8 Wt%)	T = 78 K
Reduction in toluene solution through hydro borating or hydrozirconating	$C_{60} + H_2 \Rightarrow C_{60}H_{2-4}$ (0.6 Wt%)	T = 278 K
Hydrogen transfer on the fullerene from the dihydroanthracene	$C_{60} + H_2 \Rightarrow C_{60}H_{18-36}$ (4.8 Wt%)	T = 623 K
Fullerene hydrogenation in the Zn–conc. HCl–toluene system	$C_{60} + H_2 \Rightarrow C_{60}H_{18-36}$ (4.8 Wt%)	T = 293 K
Electrochemical hydrogenation the 30% KOH solution	$C_{60} + x\,H_2 + xe \Leftrightarrow C_{60}H_{\sim x} + xOH$	Under normal conditions

Hydrogen activation in heteroatom substituted fullerene molecule

Model

Fullerene (C_{60}) cluster and heteroatom substituted C_{60}



METHODOLOGY

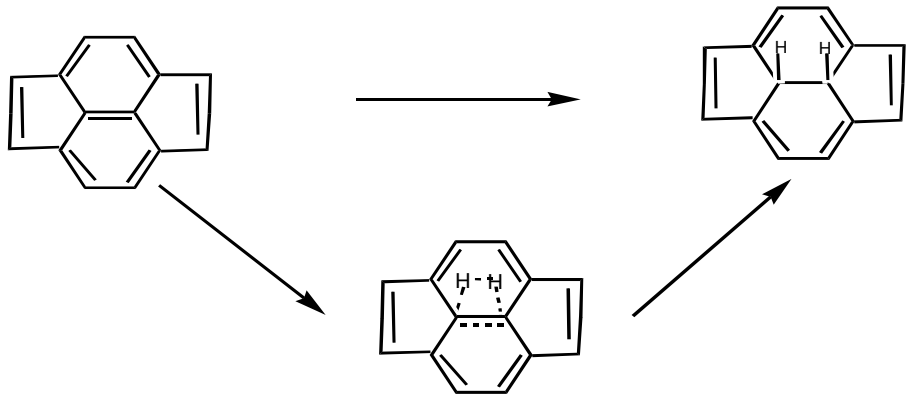
Energy minimization – UFF 1.02 (Cerius2 Software)

Single point energy – DFT (B3LYP/6-31G*)

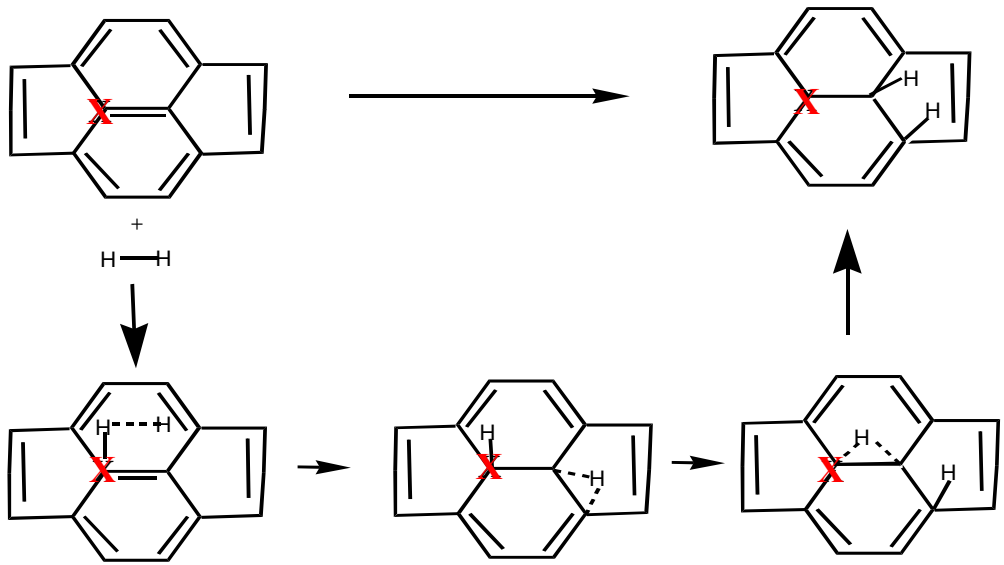
Bond length and dissociation energy of H_2 on the fullerene

	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

Transition state path ways for hydrogen interaction



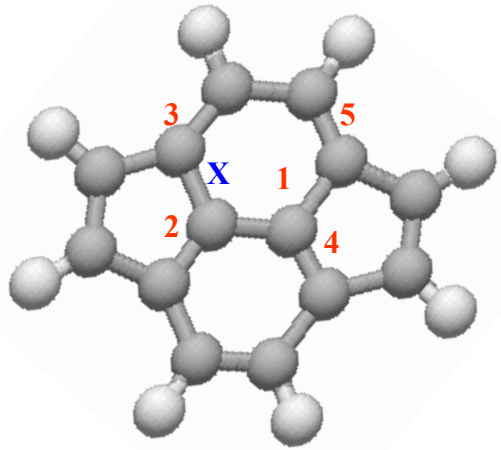
Unsubstituted fullerenes



X= N, P & S

Substituted fullerenes

Optimized geometrical parameters of the simple cluster



- ✶ Transition state optimization using DFT
- ✶ B3LYP/6-31G*

Cluster	$X-C_1$ Å	$X-C_2$ Å	$X-C_3$ Å	C_4-C_1-X deg	C_2-X-C_1 deg	$C_4-C_1-X-C_2$ deg	$C_5-C_1-X-C_3$ deg
UNSUB	1.35	1.43	1.43	122.63	122.63	0.00	0.00
N-SUB	1.35	1.42	1.40	124.54	120.31	-8.83	9.28
P-SUB	1.60	1.68	1.69	124.90	101.48	-32.59	34.25
S-SUB	1.58	1.70	1.70	124.38	101.49	31.73	-31.73

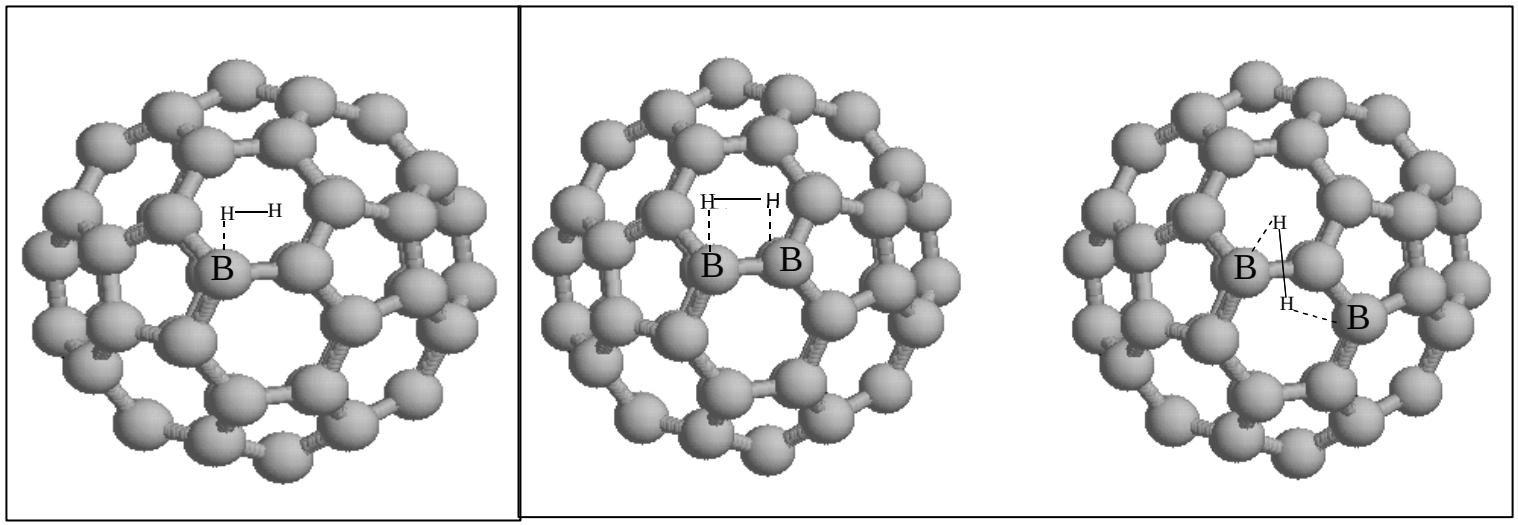
The transition state optimized parameters for various clusters and E_a for each pathway

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)

K. Muthukumar, M. Sankaran and B. Viswanathan, Eurasian. Chem. Tech. Journal 6 (**2004**) 139

Boron substituted fullerene



METHODOLOGY

Energy minimization – UFF 1.02 (Cerius2 Software)

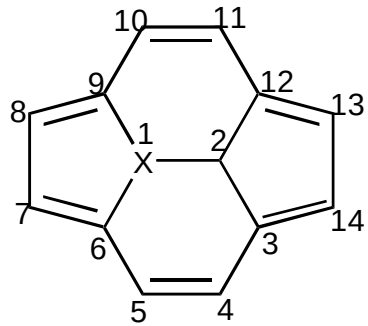
Single point energy – DFT (B3LYP/6-31G*)

Geometrical parameters of the boron substituted fullerene (C_{60}) molecule employing UFF 1.02

X - Single boron substitution

X, 2 - Boron substituted at adjacent positions

X, 3 - Boron substituted at alternate positions

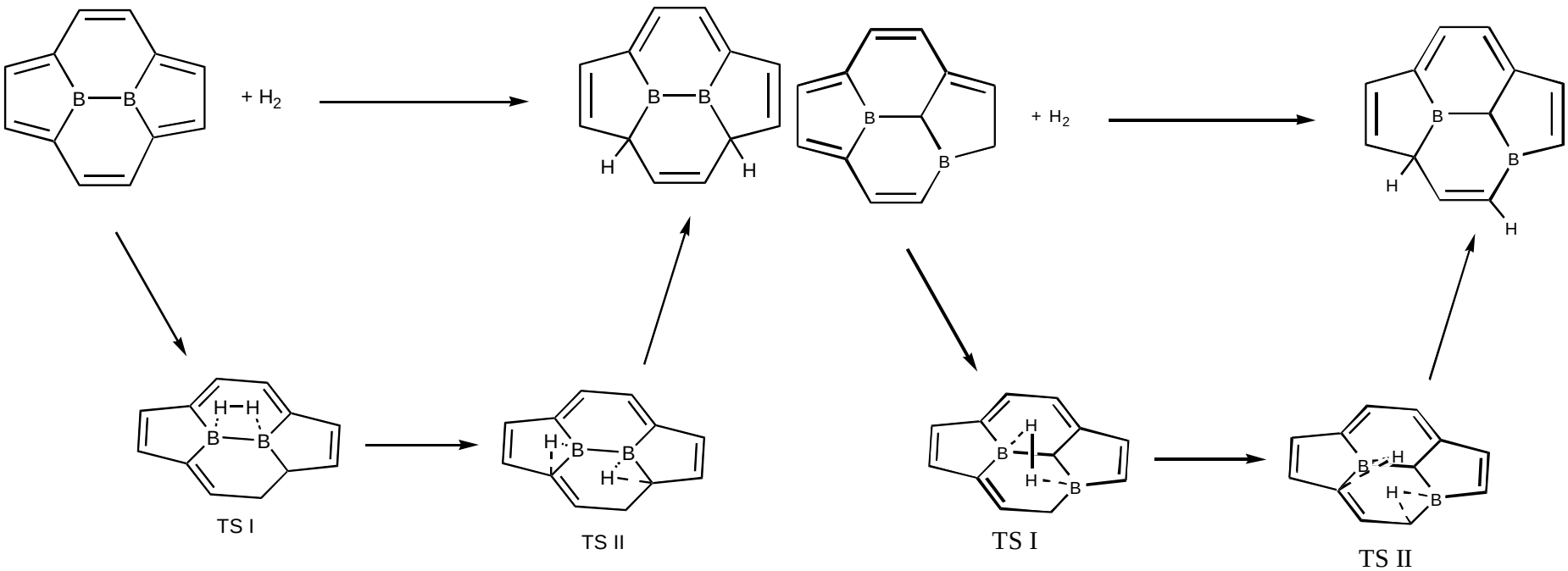


Substitution	X-2 Å	X-6 Å	X-9 Å	2-3 Å	2-12 Å	3-4 Å	<X-2-3 deg	< 9-x-2-3 deg	<6-x-2-3 deg
C_{60}	1.400	1.400	1.420	-	-	-	108.1	0.0	0.0
Single (X)	1.656	1.589	1.580	-	-	-	116.4	7.1	-7.3
2 'B' (adj) (X, 2)	1.516	1.580	1.569	1.569	1.581	-	78.1	1.7	1.7
2 'B" (alt) (X, 3)	1.486	1.591	1.637	1.472	1.313	1.620	111.4	30.0	-59.8

Bond length and dissociation energy of hydrogen on fullerenes

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

Proposed mechanistic pathways for hydrogenation

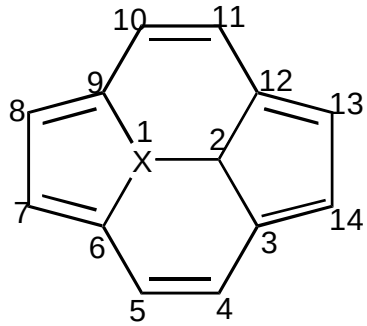


Adjacent substitution

Alternate substitution

- **TRANSITION STATE OPTIMIZATION USING DFT**
- **B3LYP/6-31G***

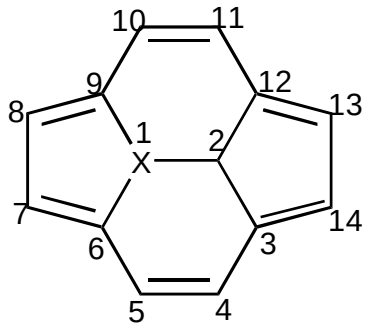
Geometrical parameters of the simple cluster



Cluster	X-2 Å	X-6 Å	X-9 Å	2-3 Å	2-12 Å	3-4 Å	<X-2-3 deg	< 9-x-2-3 deg	<6-x-2-3 deg
C_{60}	1.400	1.400	1.420	-	-	-	120.0	0.0	0.0
cluster	1.352	1.431	1.431	-	-	-	122.6	0.0	0.0
2 'B' (adj)	1.568	1.509	1.509	1.509	1.509	1.483	121.4	0.0	0.0
2 'B" (alt)	1.453	1.571	1.527	1.527	1.395	1.566	113.7	-16.1	-15.4

* where X = boron atom

Transition state optimized parameters and the E_a for the proposed pathway



Substitution	E_aI (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

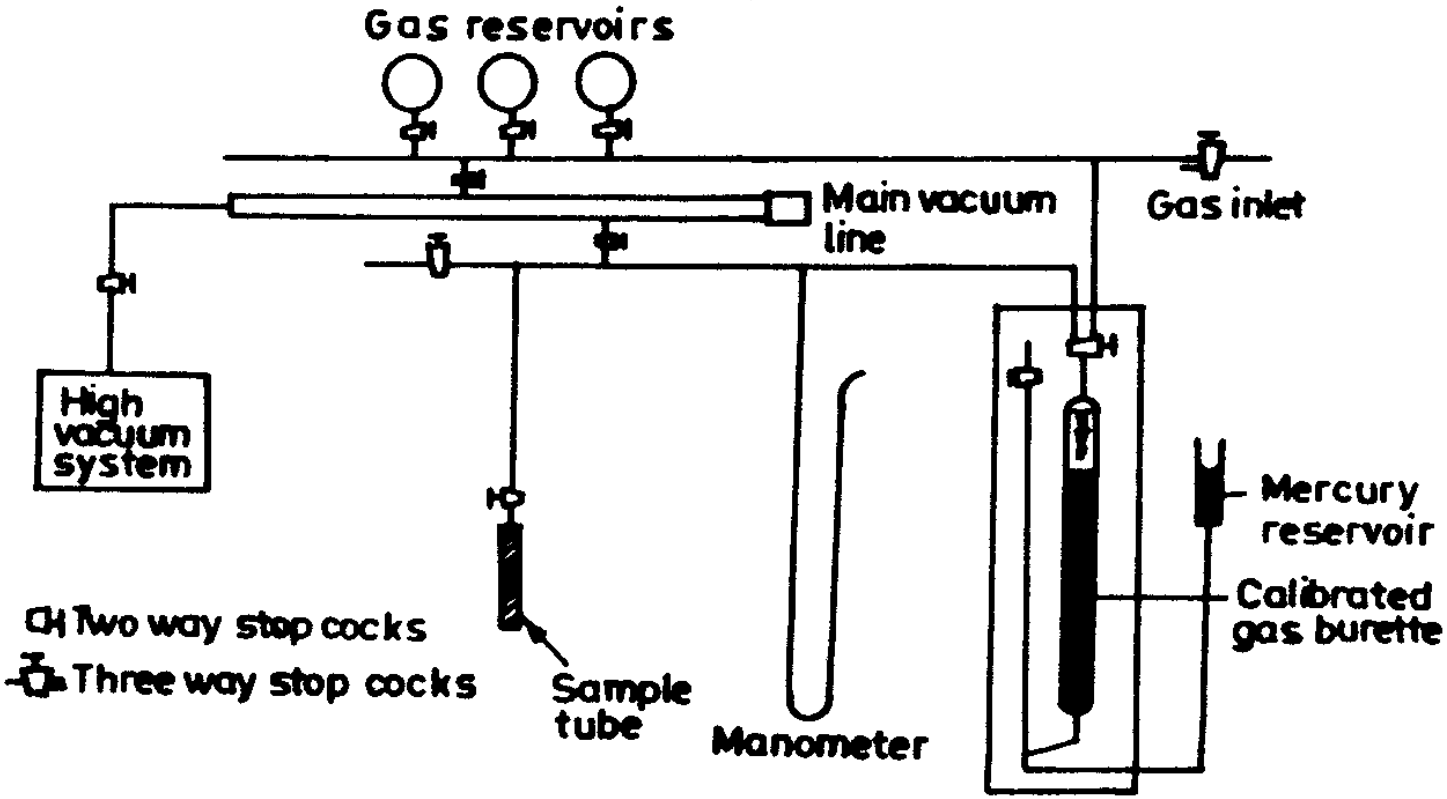
Outcome

- 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

Experimental studies
Effect of heteroatom on hydrogen interaction

- Experimental setup ----- Low Pressure & High Pressure
- Hydrogen adsorption studies on activated carbon and modified activated carbon
- Preparation of nitrogen containing carbon nanomaterials by different methods - Hydrogen storage capacity
- Synthesis, characterization and hydrogen storage capacity of boron containing carbon nanomaterials

Hydrogen adsorption study by volumetric method

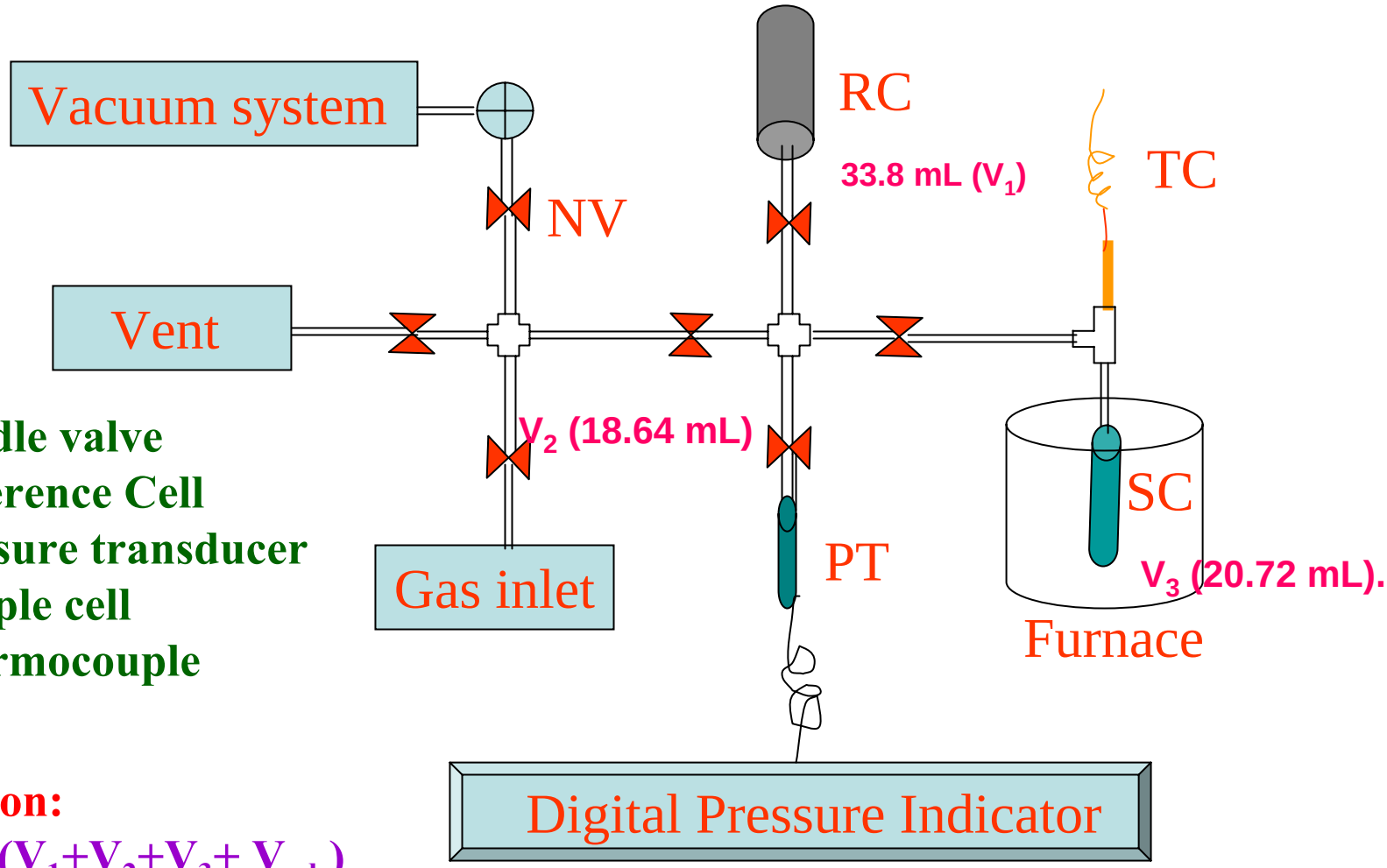


Low pressure hydrogen adsorption (glass)

Experimental procedures

- Sample evacuated (10^{-5} Torr) at 300°C for 6h
- Pressure change monitored with respect to volume of gas adsorbed
- Dead space calculated using He gas
- H_2 adsorbed at various temperatures - thermodynamic data
- Surface area – N_2 adsorption at 77 K - BET equation

High pressure adsorption apparatus



NV- Needle valve
RC- Reference Cell
PT- Pressure transducer
SC- Sample cell
TC- Thermocouple

Calculation:

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

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

where Z = Compressibility factor

Activated carbon and modifications

1. Activated carbon (CALGON & CDX-975)
2. Metal supported CALGON
3. Chemical treatments on CDX-975

Determination of surface area by BET method

- CDX- 975 – 500 mg taken - dried in oven at 100 °C
- Catalyst dead space calculations done at 77 K (He gas)
- Nitrogen adsorption carried out at 77 K

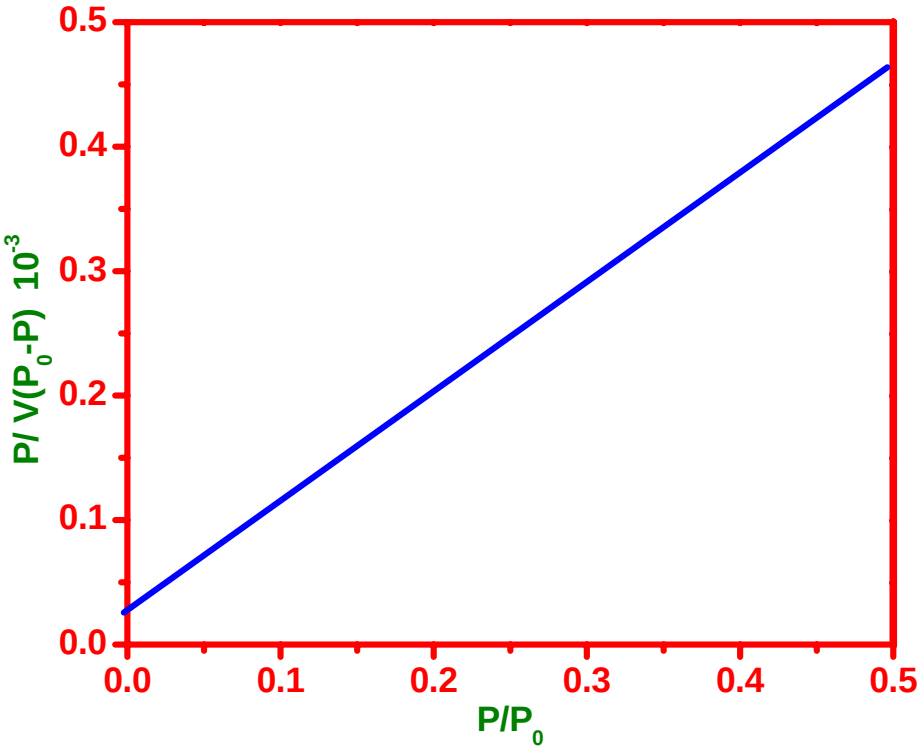
Adsorption data:

Equilibrium pressure (mm Hg)	Volume adsorbed (cm^3/g)	P/P_o	$P/V(P_o-P) \times 10^{-3}$
98	78.25	0.13	1.89
137	85.55	0.180	2.57
187	95.11	0.246	3.43
244	105.85	0.321	4.46
288	114.53	0.379	5.32
335	122.78	0.462	6.42

$P/V(P_o-P)$ Vs P/P_o
linear plot (in range of 0.05-0.30)

Surface area:

$SSA_{BET} = V_m \times N_o \times \sigma \times 10^{-20} m^2 / M$



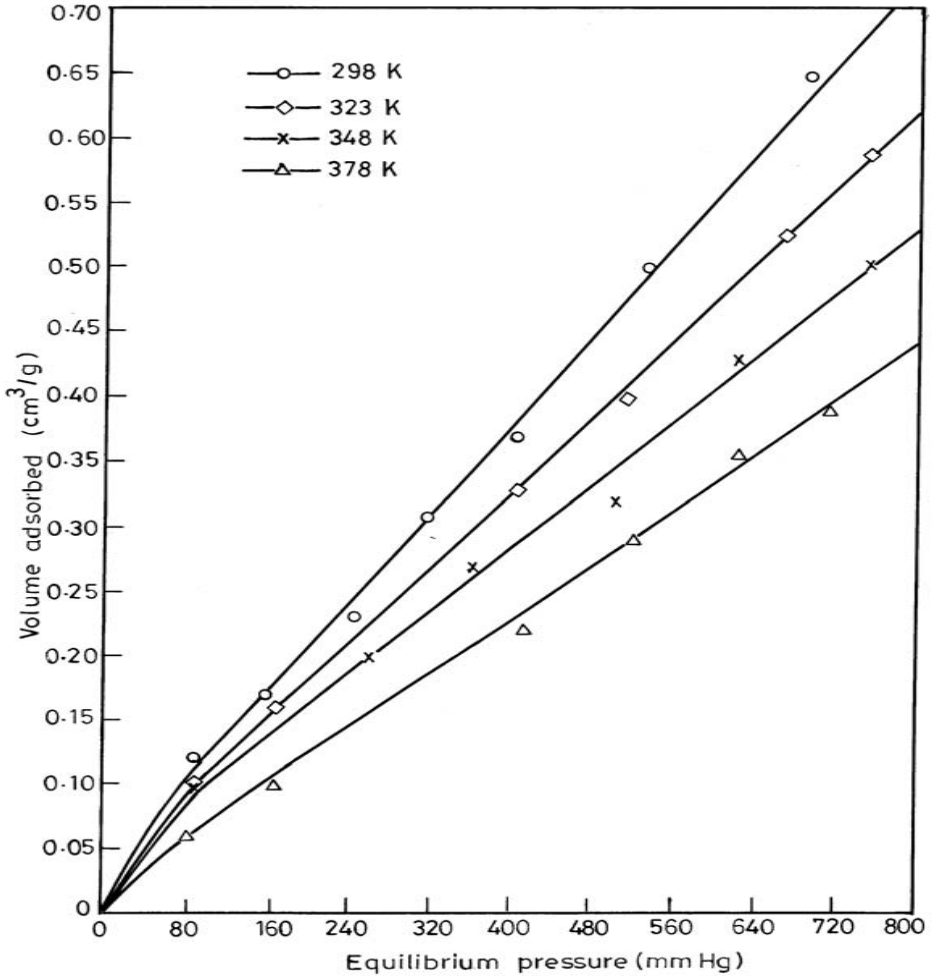
From Graph :

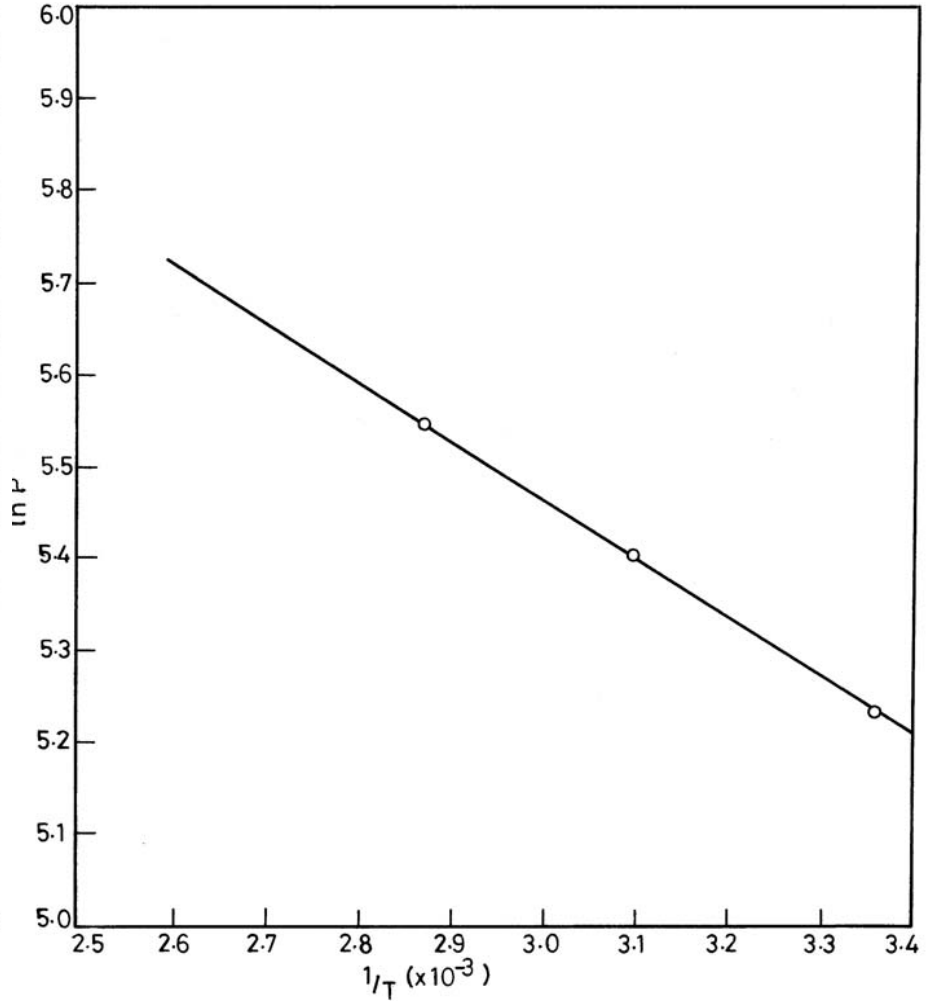
Intercept = 1.8×10^{-4}
Slope = 0.0132
Slope + intercept = 0.0134
V_m = 1/slope + intercept = 74.80

$S = 6.023 \times 10^{23} \times 16.2 \times 10^{-20} \times 74.80\ m^2 / 22414 \times 1\ g$

Surface area = 326 m^2/ g

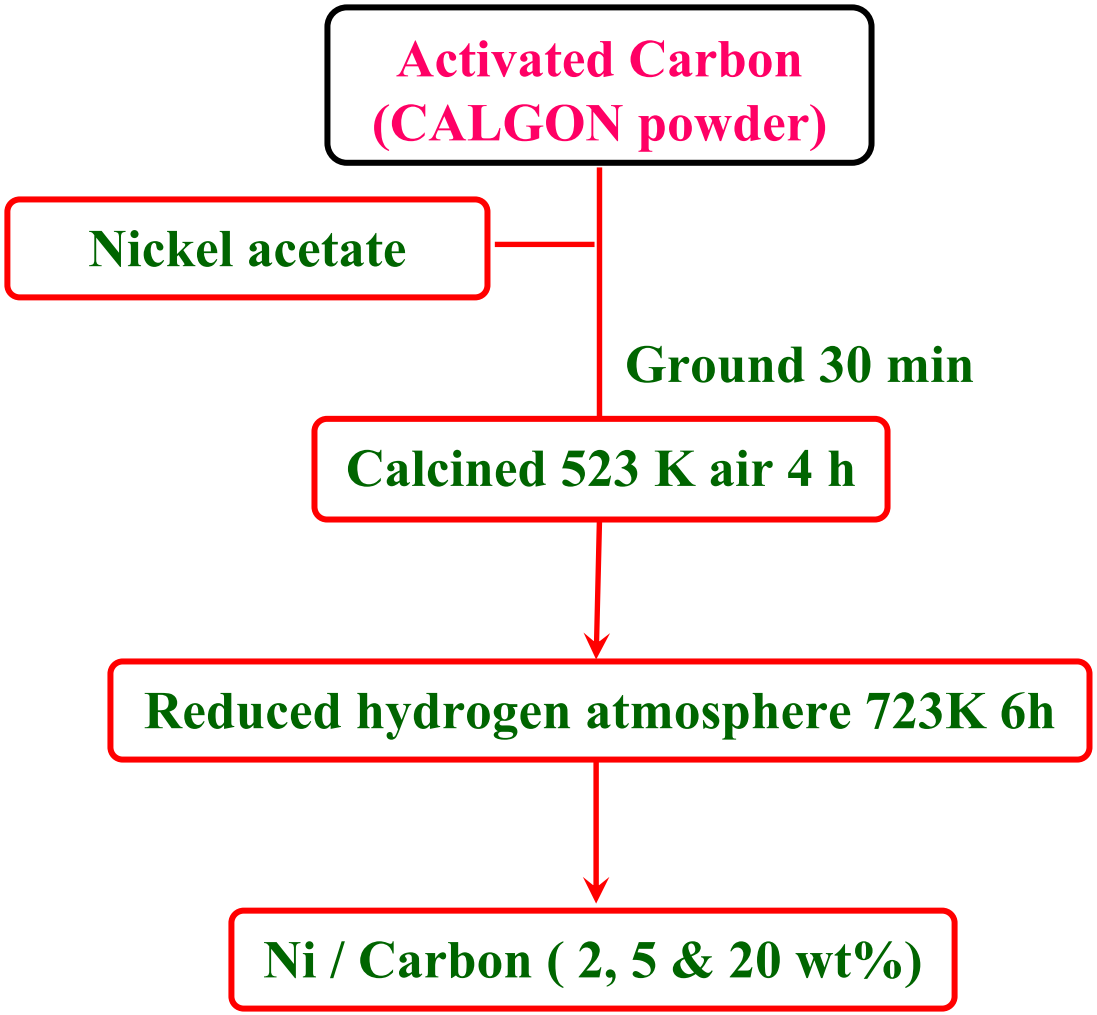
Hydrogen adsorption activity of activated carbon (CALGON granules) at various temperatures



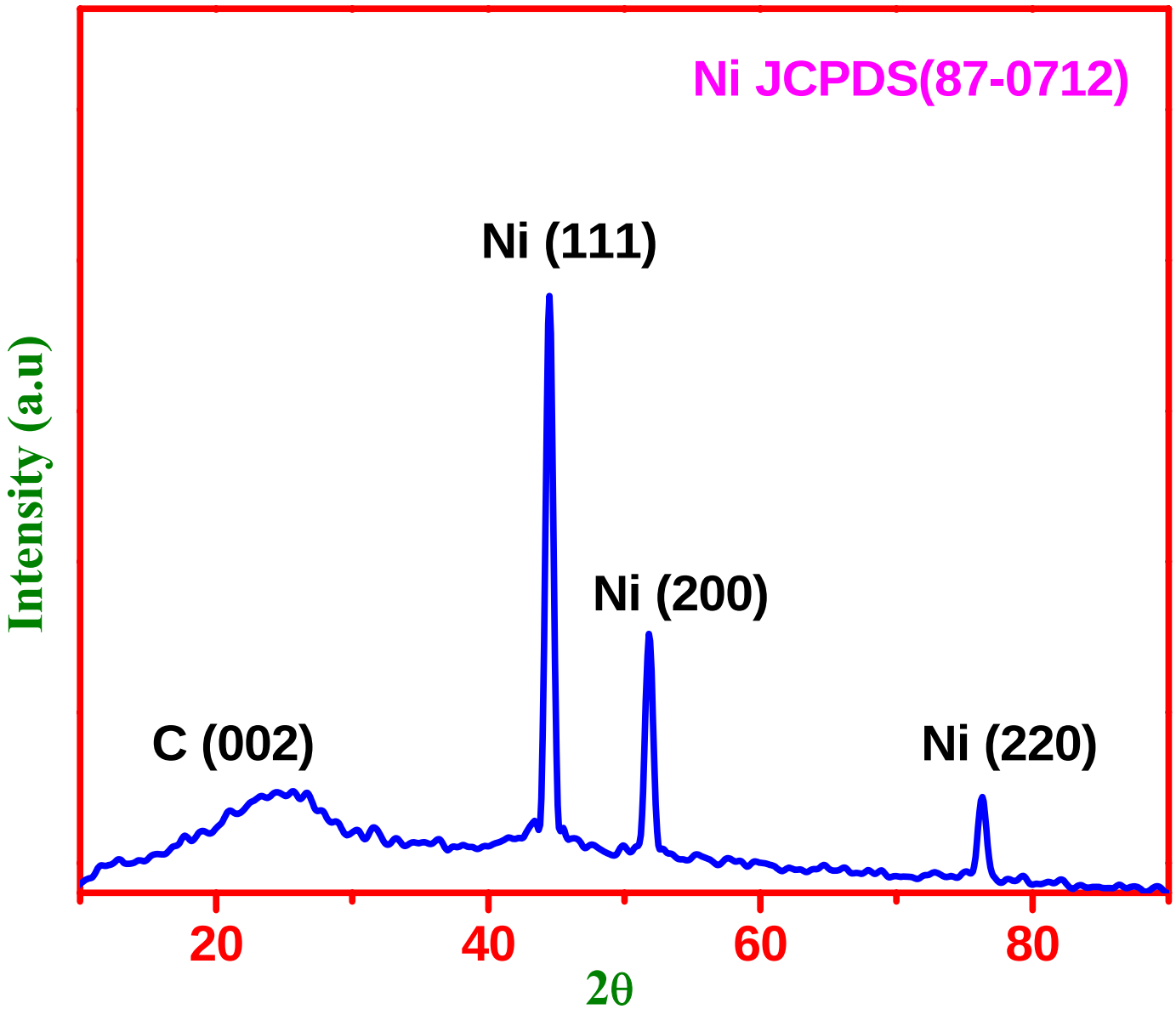


Heat of adsorption -6 kJ / mol

Nickel supported on carbon

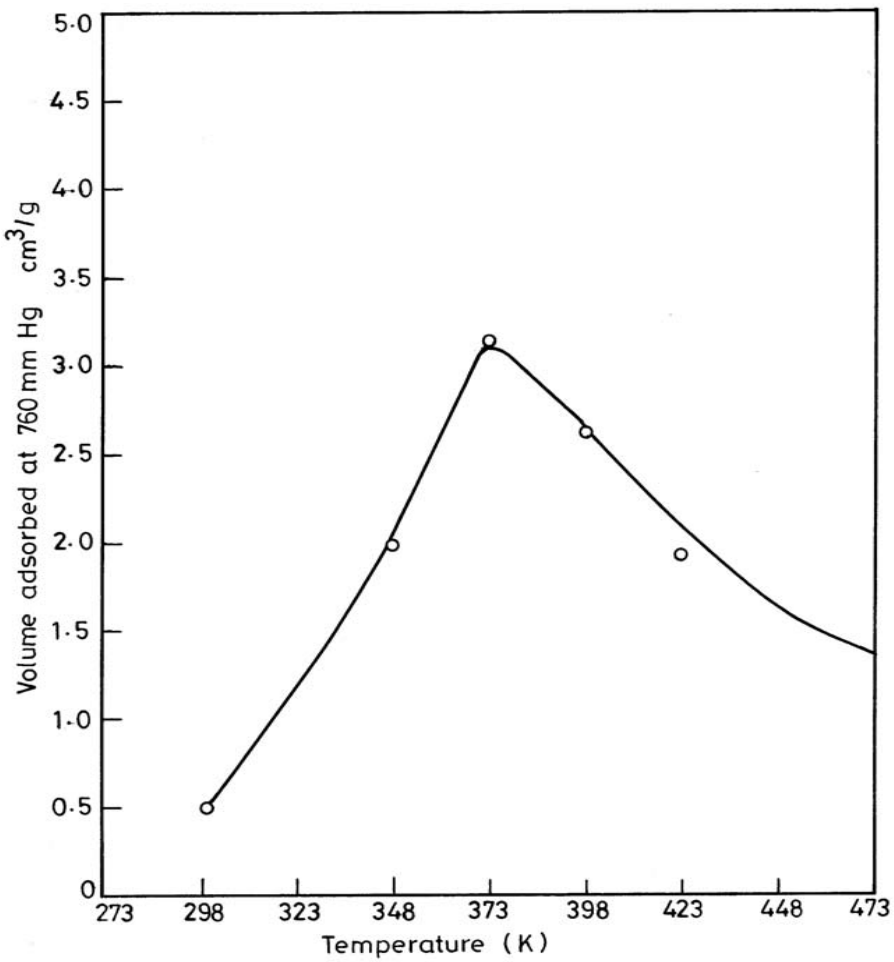


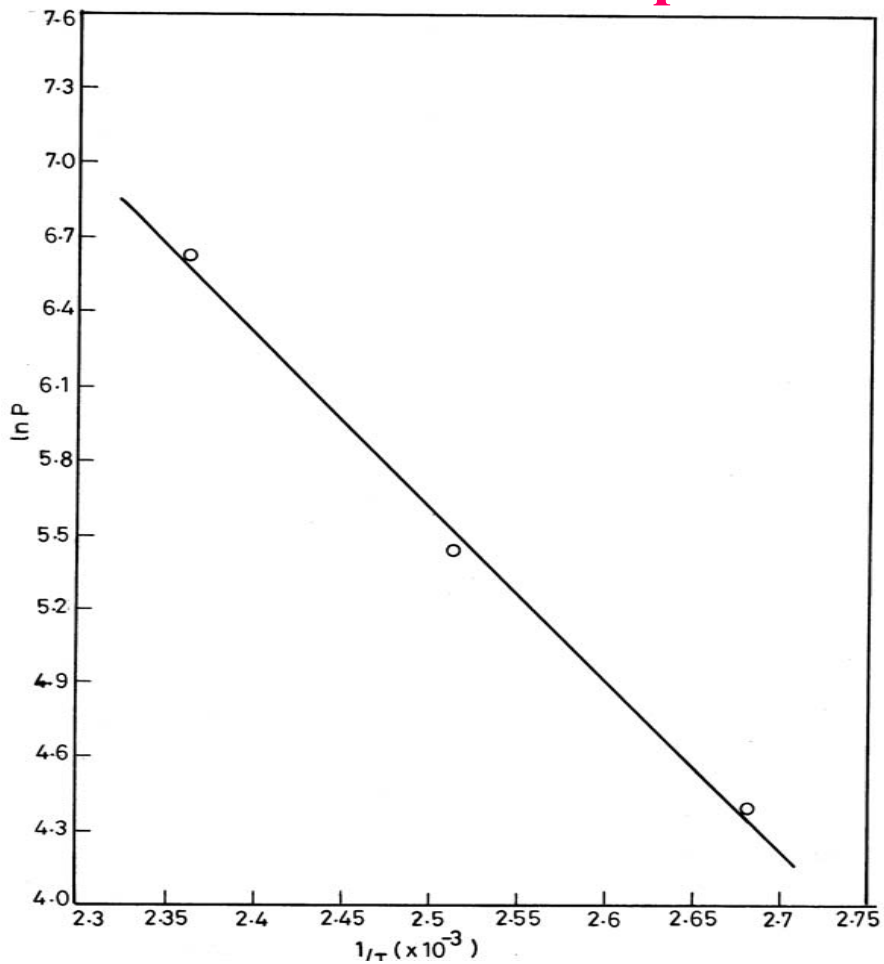
XRD pattern of Ni supported on carbon



Hydrogen adsorption activity of 20 wt% Ni/C at various temperatures

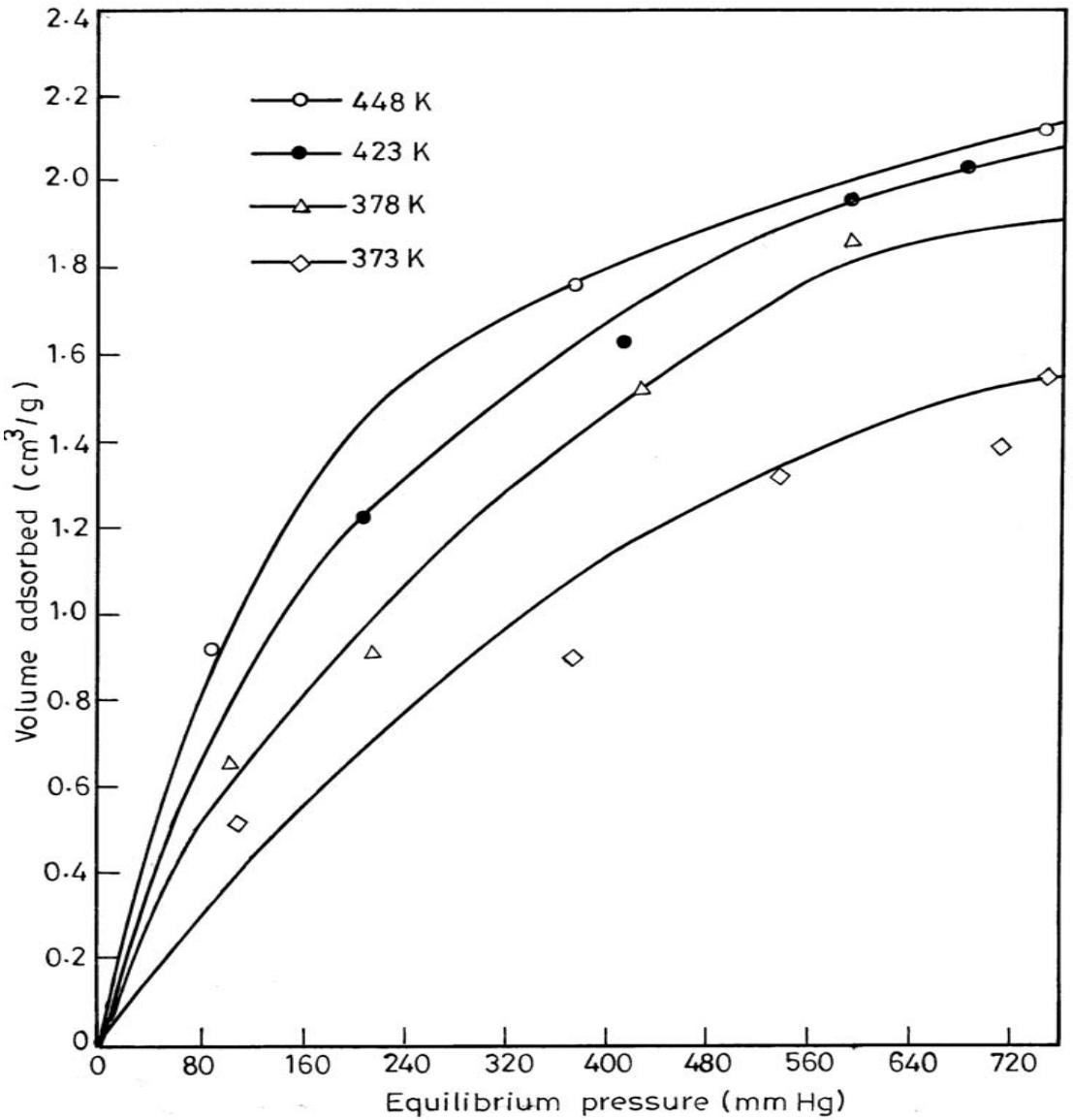
Van't Hoff `s plot



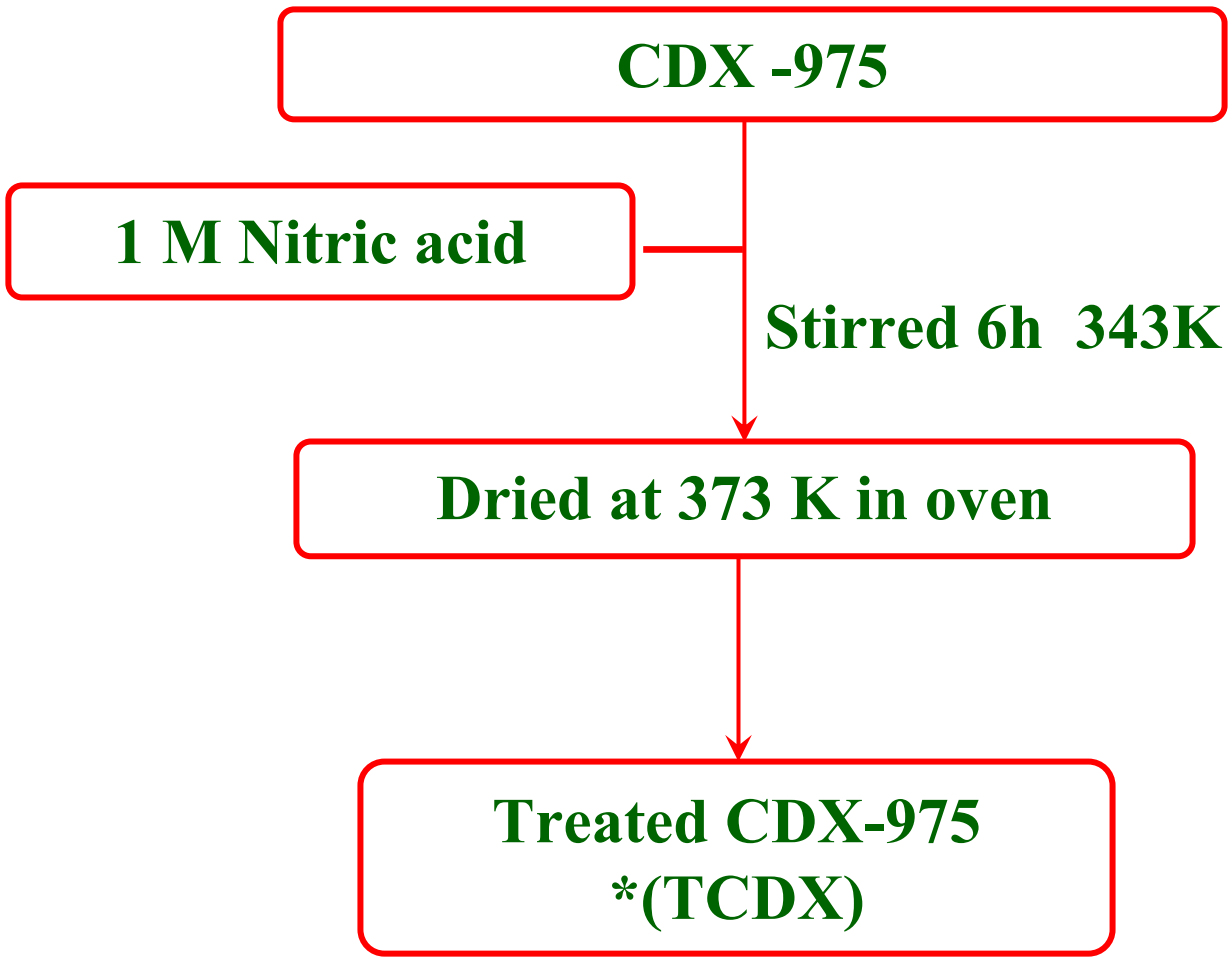


Heat of adsorption of 20 wt% Ni/C -59 kJ / mol

Hydrogen adsorption activity of 2 wt% Ni/C at various temperatures



Treatment of CDX-975



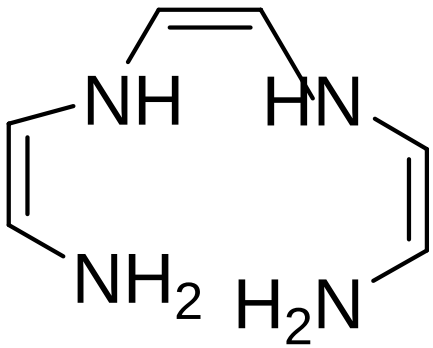
Amine treatment of CDX-975

CDX -975

Tri ethylene tetra amine

Refluxed 473 K 6h

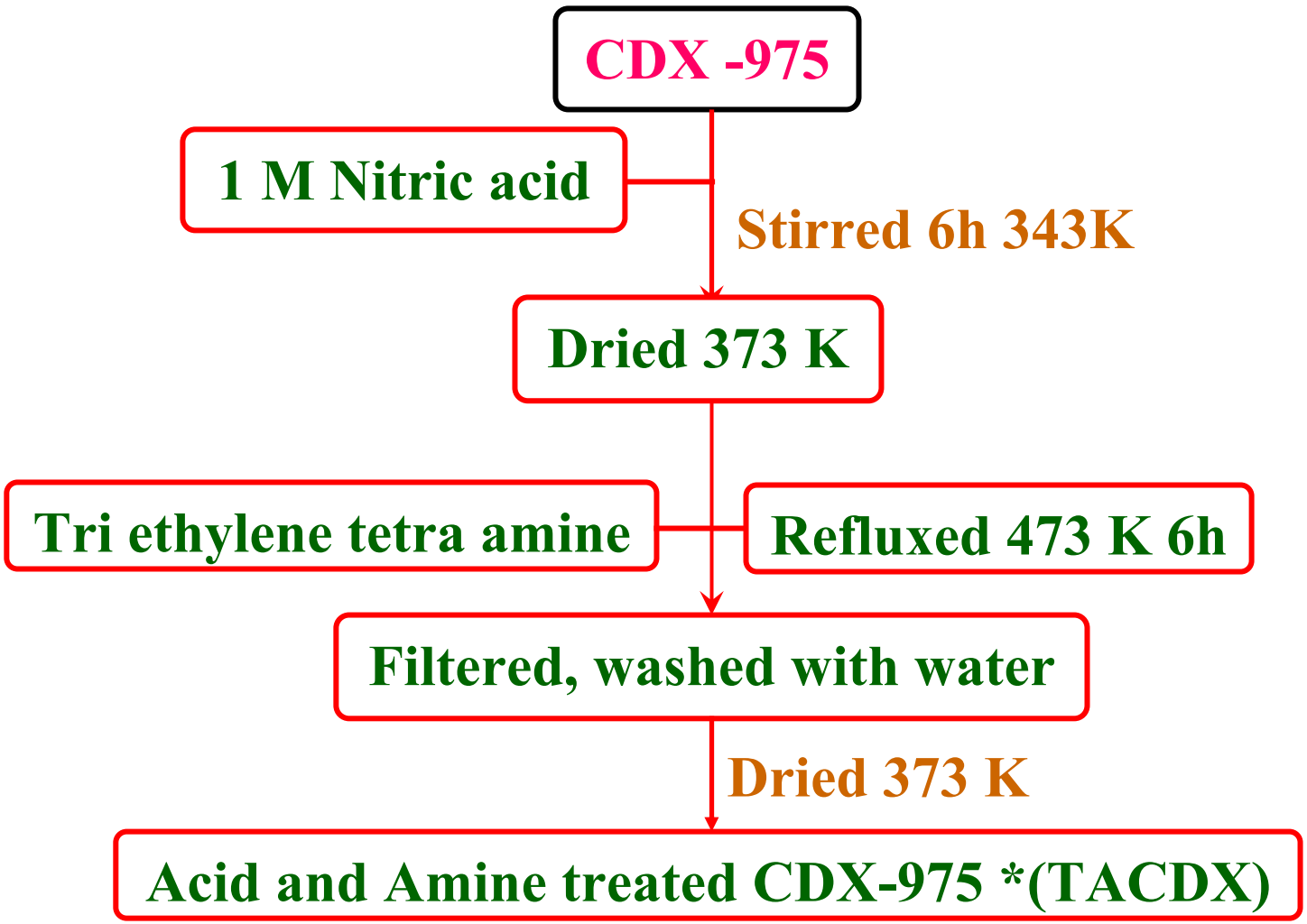
Filtered, washed with water



Dried 373 K

Amine treated CDX-975 *(ACDX)

Acid and amine treatment of CDX-975



Hydrogen adsorption 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 adsorption 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		

Preparation of nitrogen containing carbon nanomaterials and their hydrogen storage capacity

Preparation of nitrogen containing carbon nanomaterial

PVP dissolved in 2M HCl

TEOS

Stirred 45°C 20h

Precipitate filtered washed

Dried air 110°C

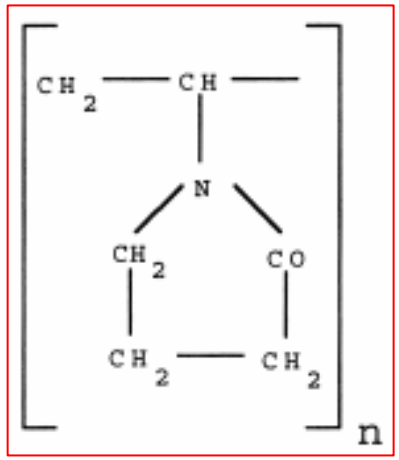
Mesoporous materials

Carbonized Ar atm 900°C 6h

Carbon /silica composite

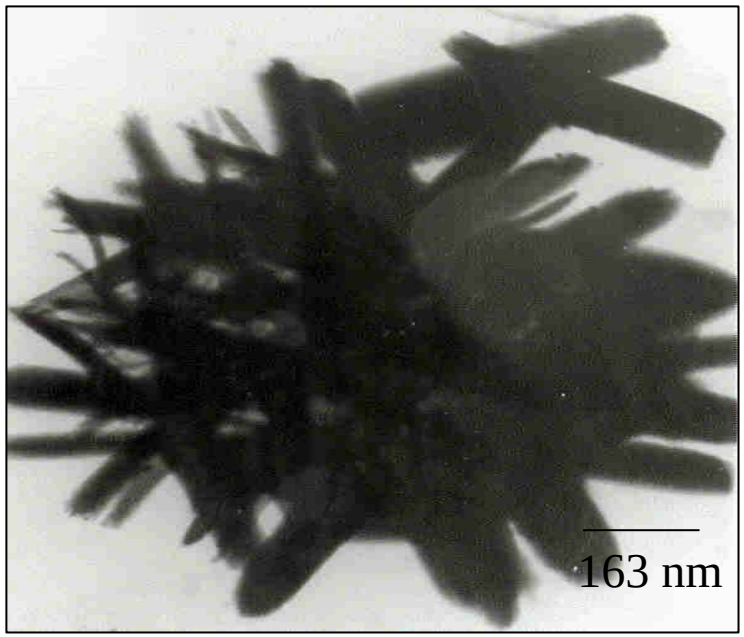
HF treatment

Carbon nanomaterial

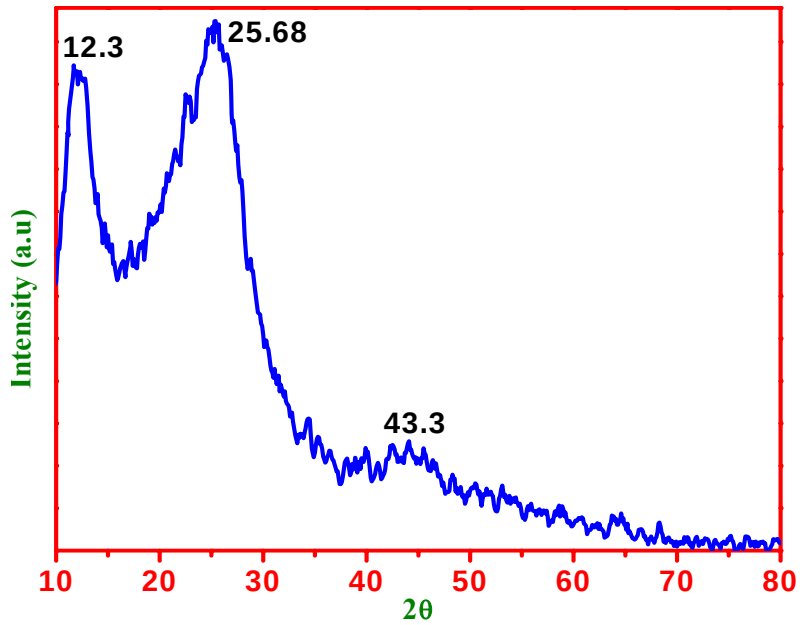


PVP

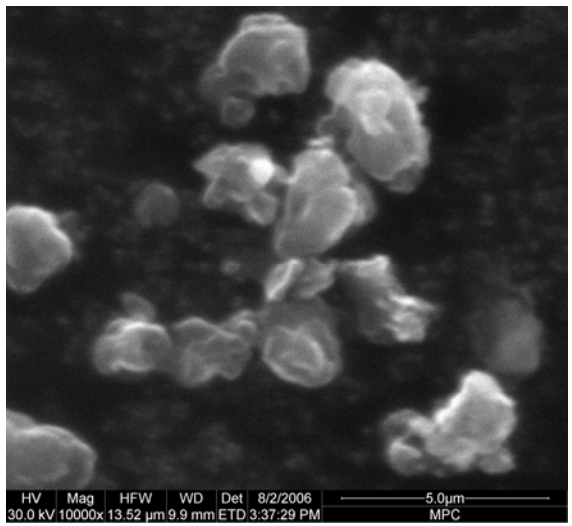
XRD, SEM and TEM images

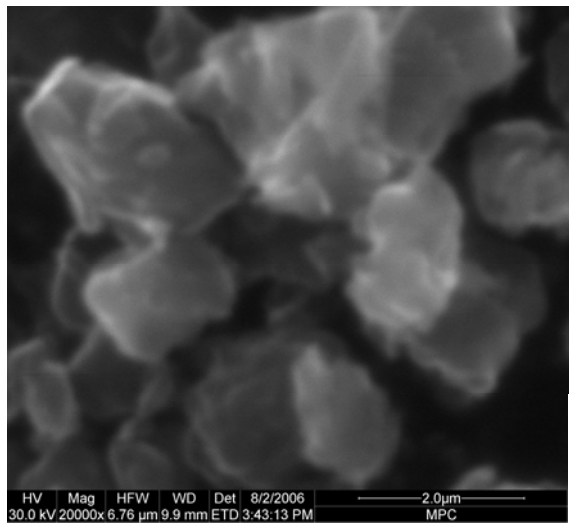


TEM image



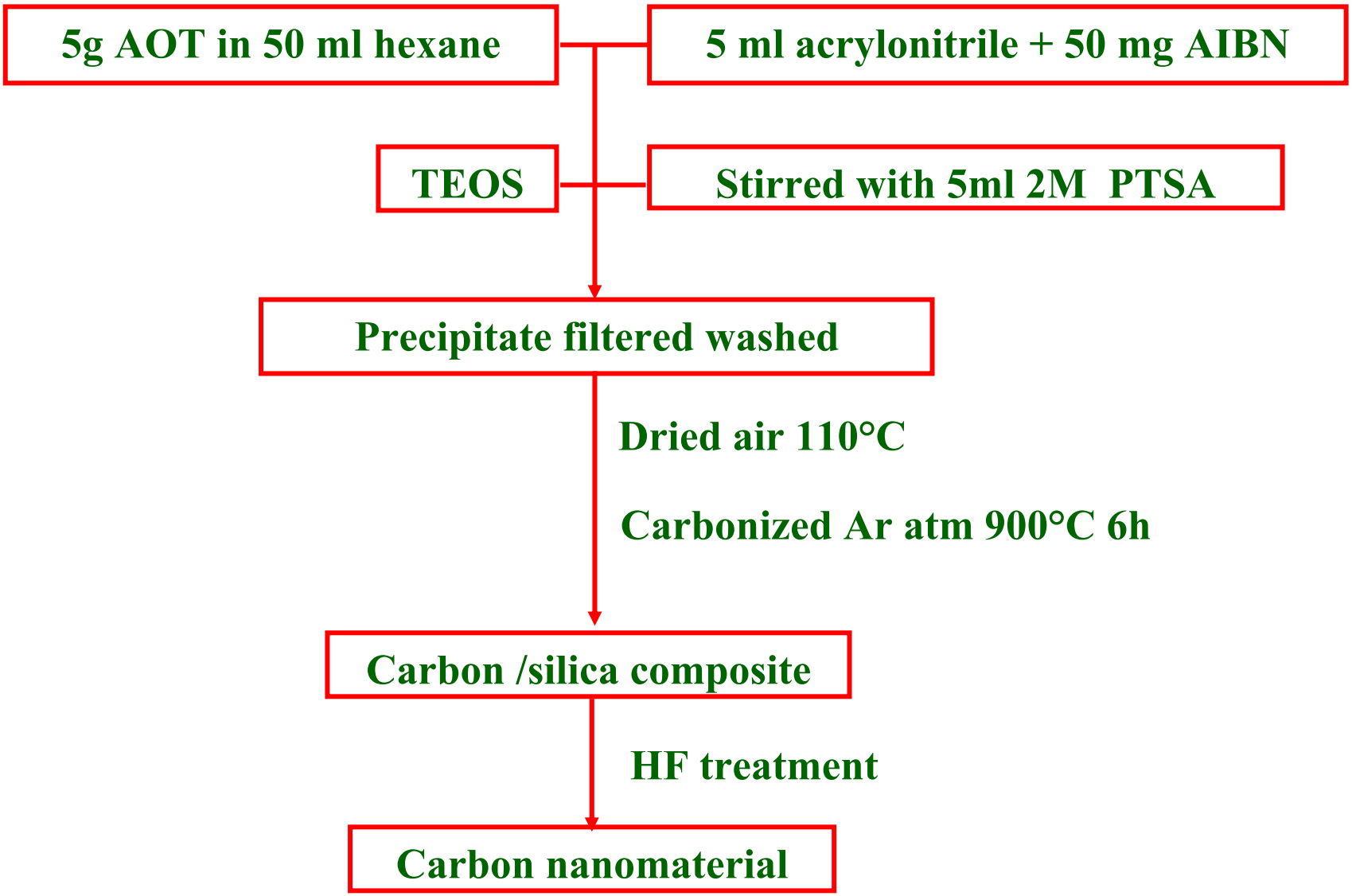
Nitrogen content 7.7%
by CHN analysis



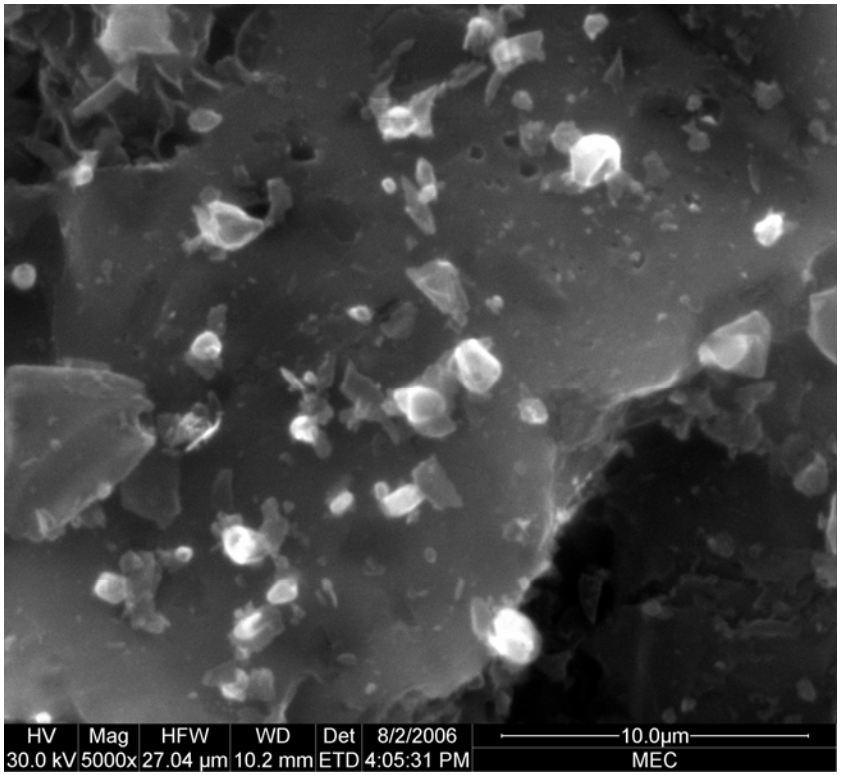


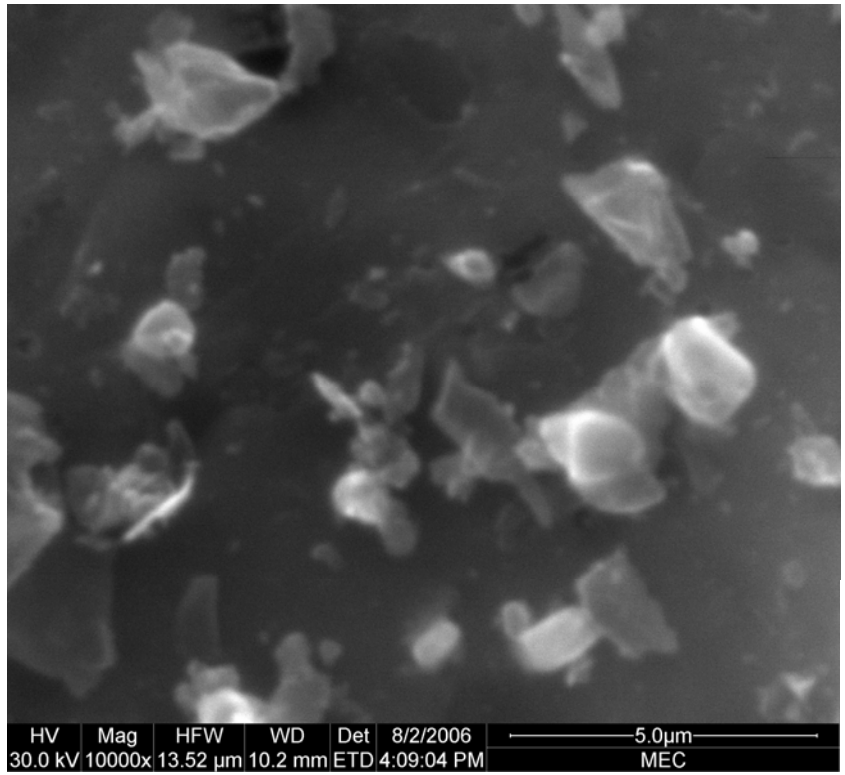
SEM images

Carbon prepared by microemulsion polymerization method



SEM images



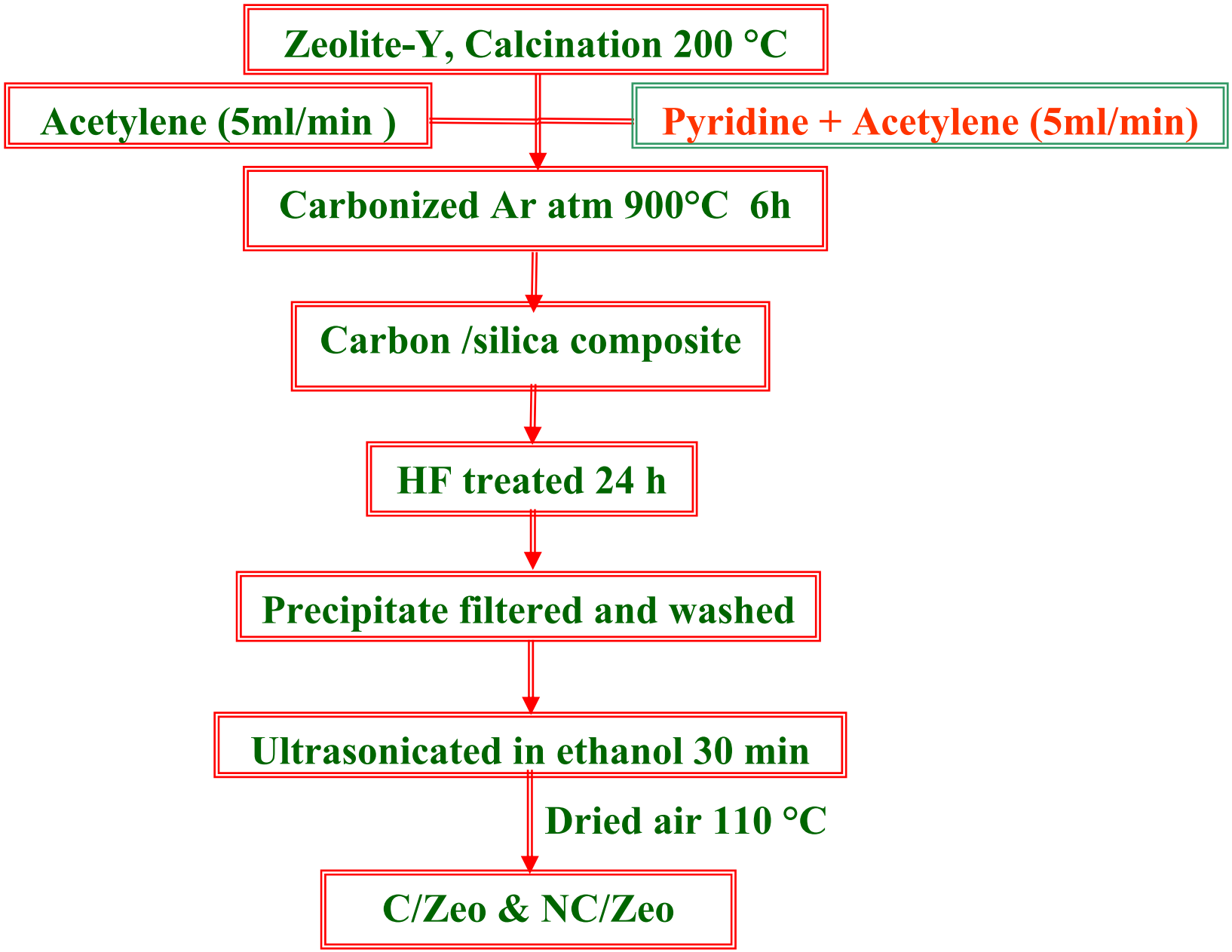


Nitrogen content 4.6% by CHN analysis

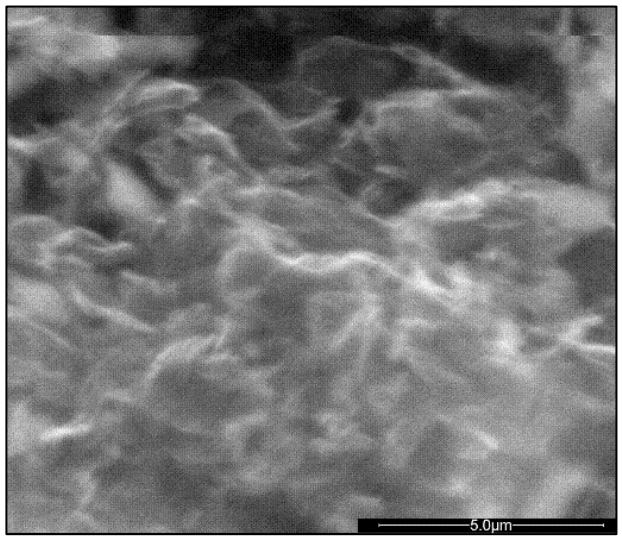
Preparation of carbon nanomaterials - various templates

- Zeolite - Y
- Pillared clay
- Alumina membranes

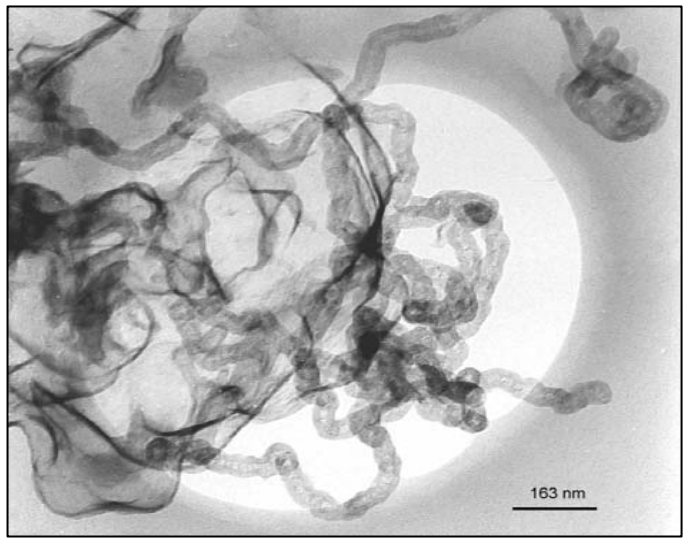
1. Carbon prepared using Zeolite –Y



SEM and TEM images of carbon nanomaterials prepared using zeolite as template



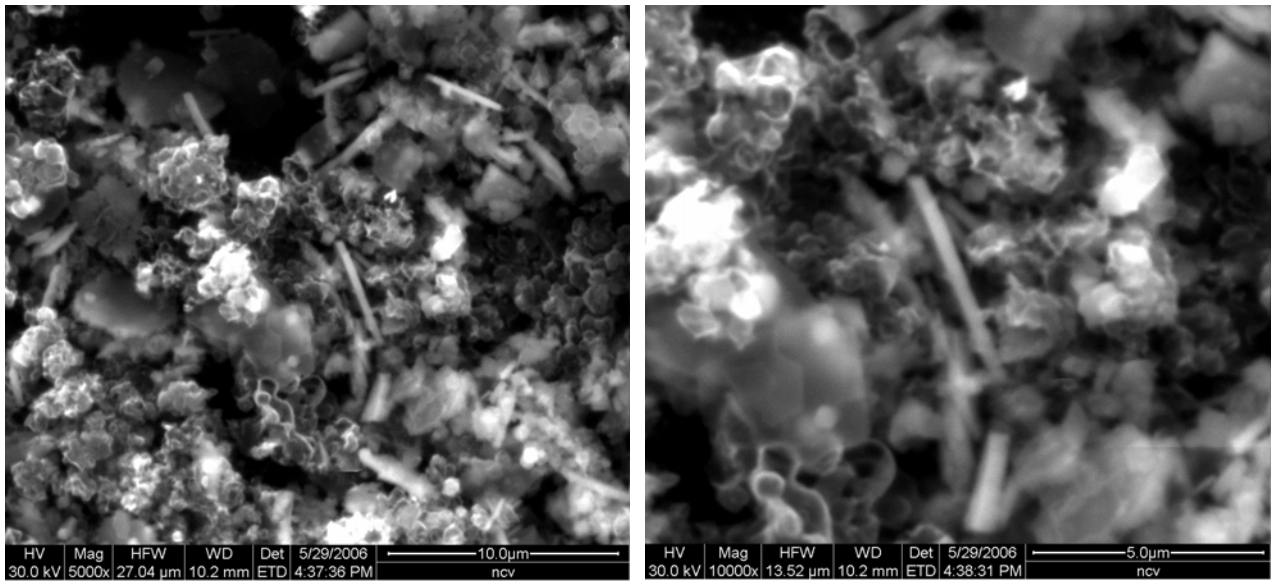
SEM image



TEM image

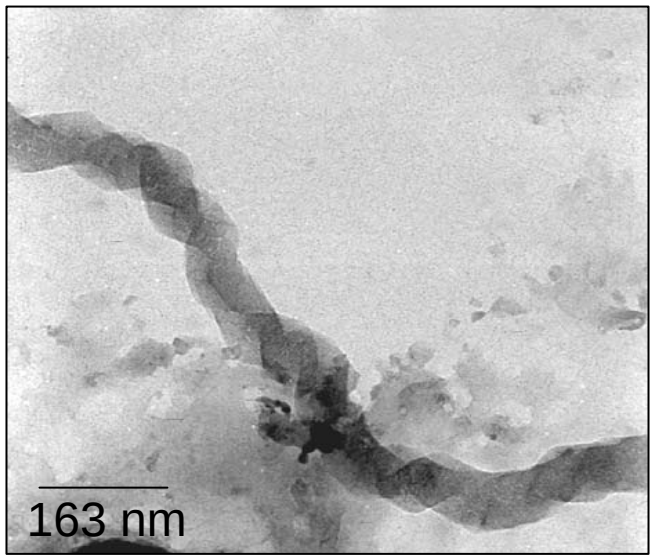
C/Zeolite

SEM and TEM images of nitrogen containing carbon nanomaterials



SEM images

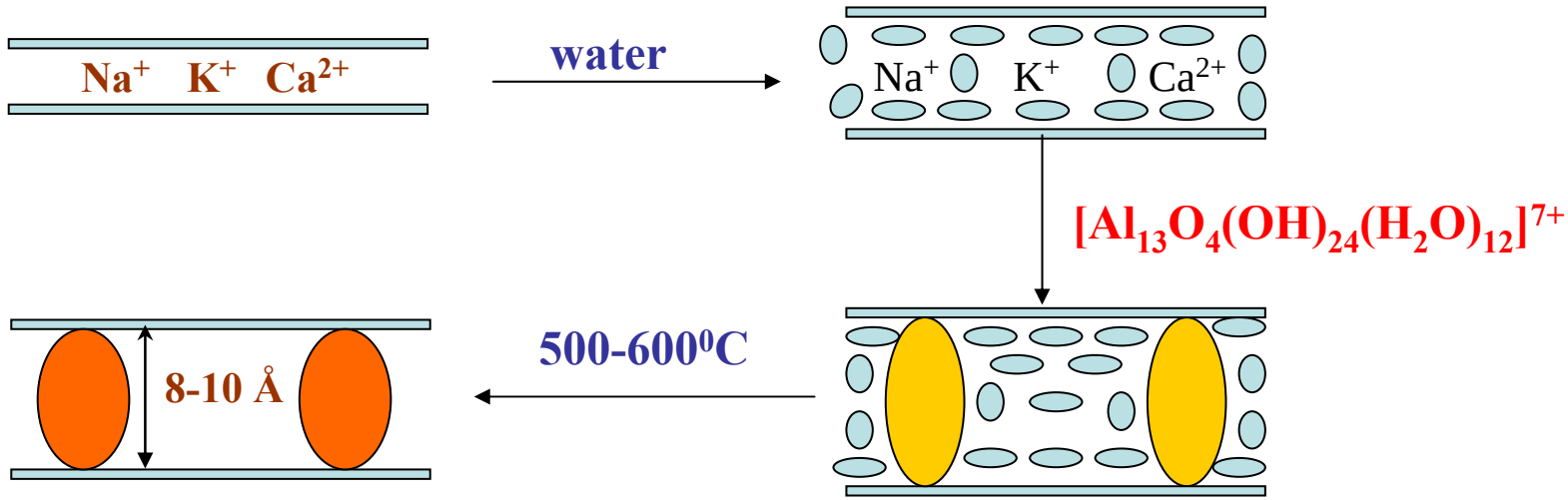
NC/zeolite



TEM image

2. Preparation of carbon nanomaterials using clay

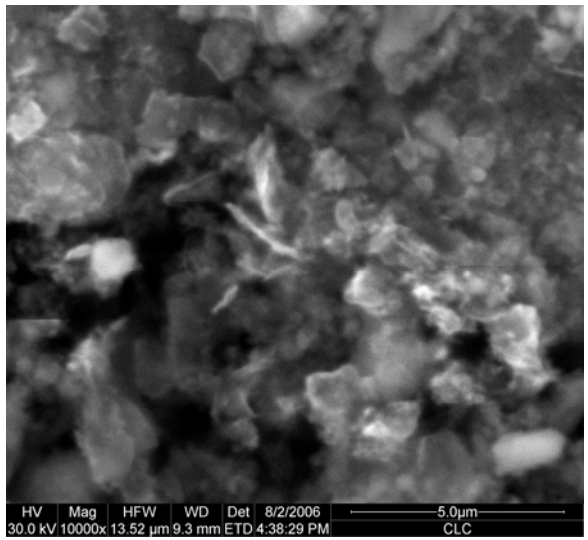
Pillared Clay: Process of pillaring

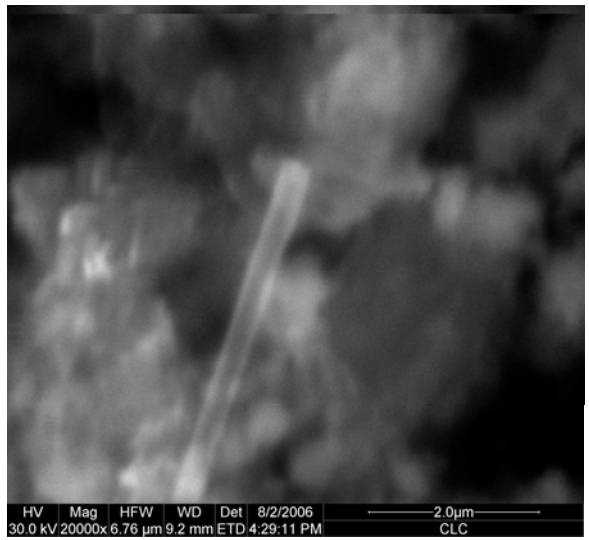


- Acetylene gas (carbon source) - 5 ml/min flow rate (C/Clay)
- Acetylene + pyridine (nitrogen containing material) (NC/Clay)
- Carbonized 900 °C Ar atmosphere
- Treated with 48% HF for 24h washed with distilled water.

A. Gil *et al.*, *Catal. Rev-Sci. Engg.* 42 **(2000)** 145.

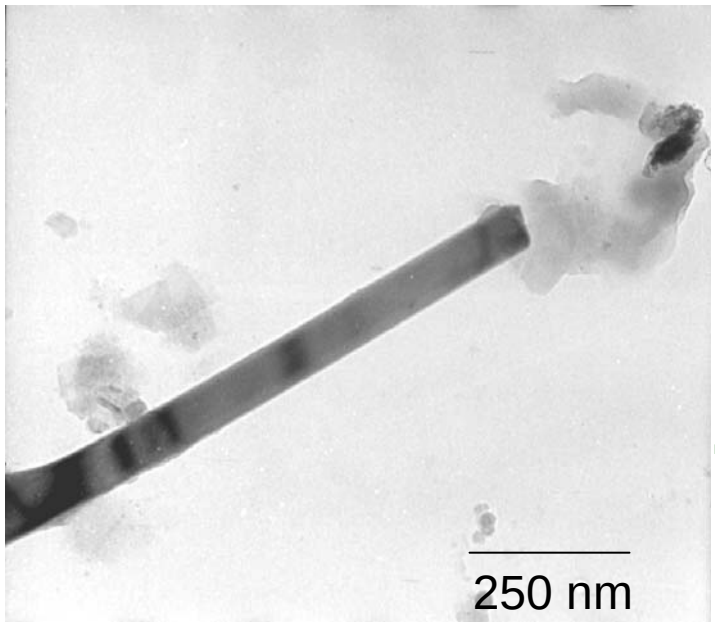
SEM and TEM images of carbon nanomaterials prepared using clay as template





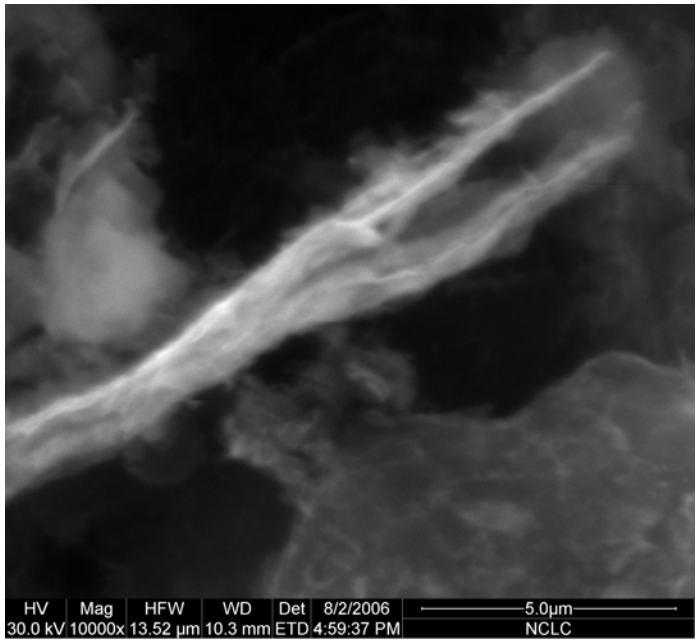
SEM images

C/clay

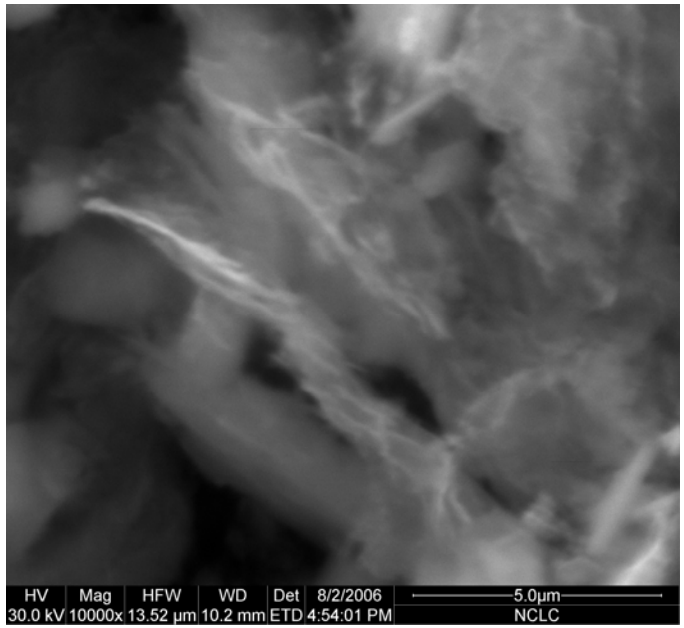


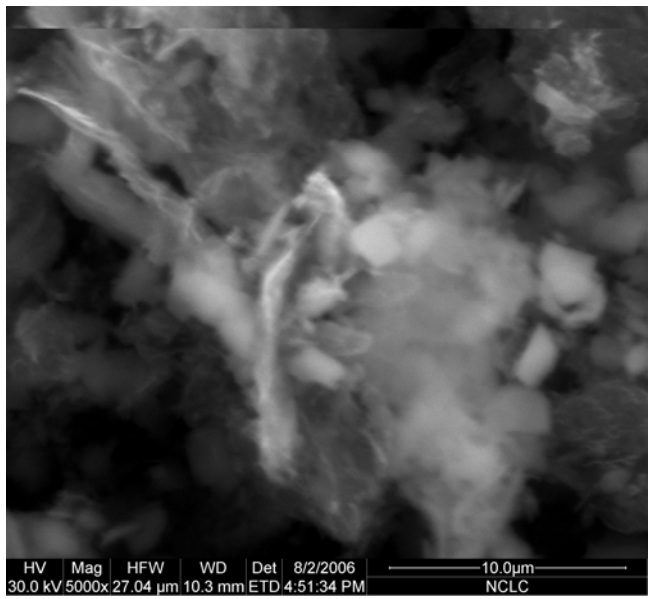
TEM image

Nitrogen containing carbon material (NC/ clay)

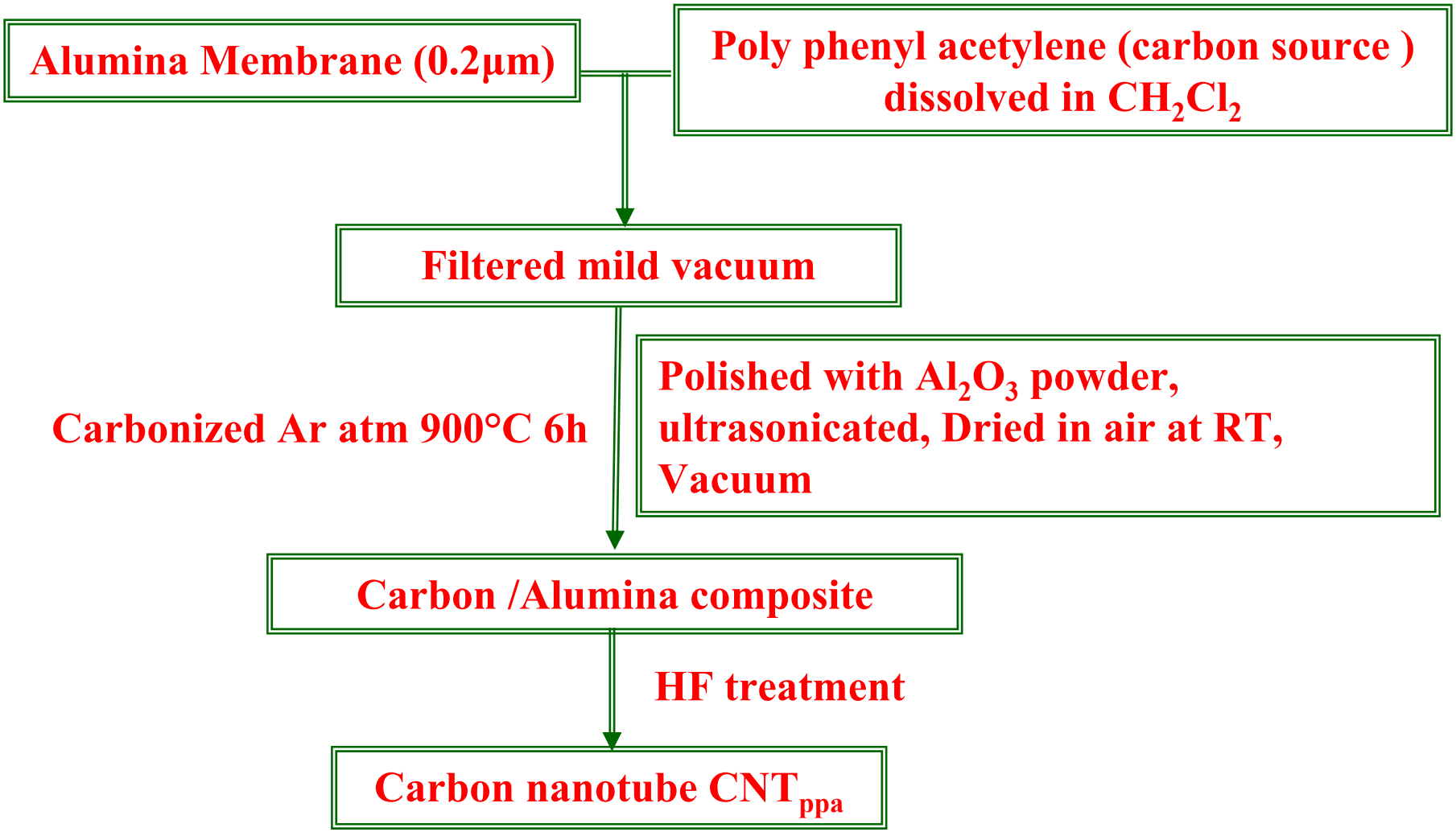


SEM images

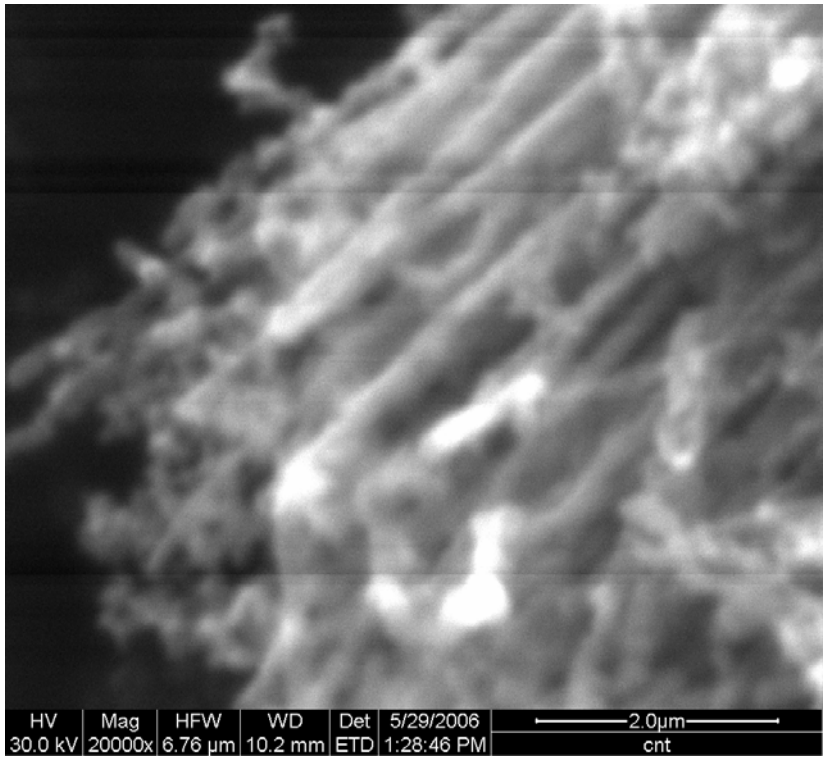




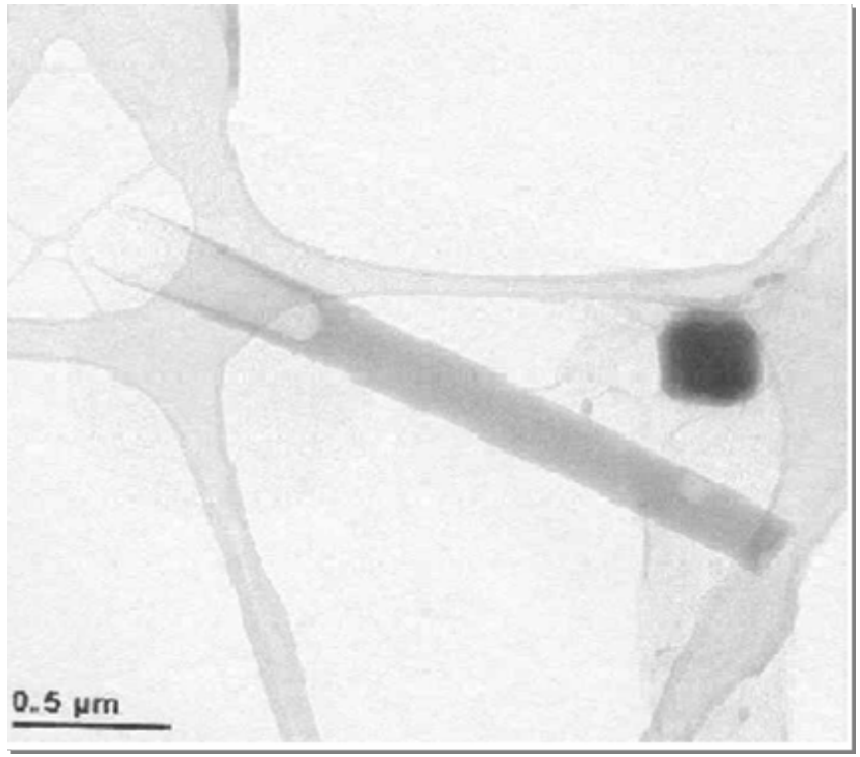
3. Preparation of carbon nanomaterials using alumina membrane as template



SEM and TEM images of carbon nanotube (CNT) prepared from Poly phenyl acetylene



SEM image



TEM image

Preparation of nitrogen containing carbon nanotubes (NCNT)

Alumina Membrane

Pyrrole (0.1M)

PTSA (0.2M)

$FeCl_3.6H_2O$ (0.2M)

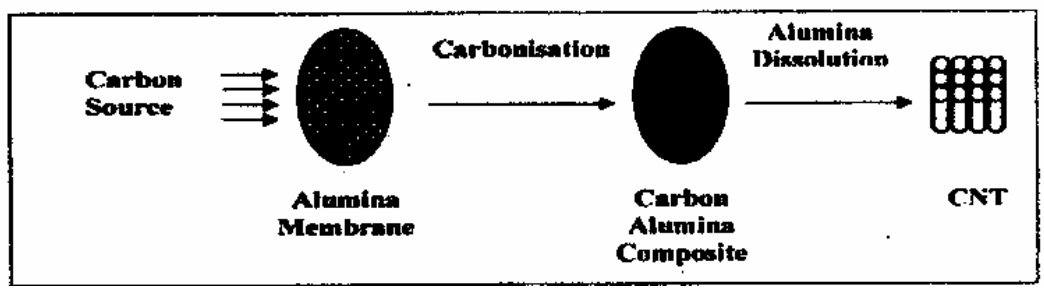
Polymerization at RT for 3h

PPY/Alumina

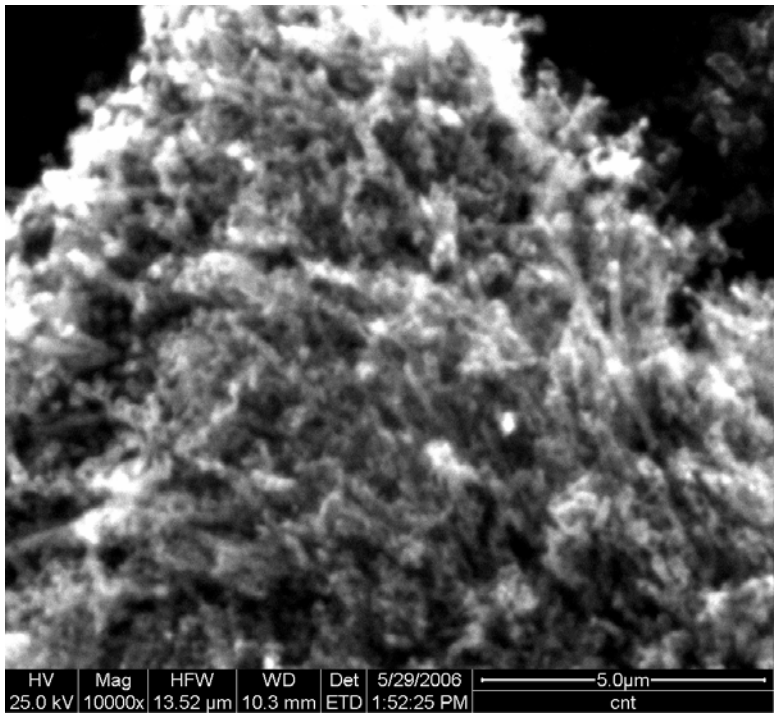
Carbonization 1173K Ar,4h

Carbon / Alumina

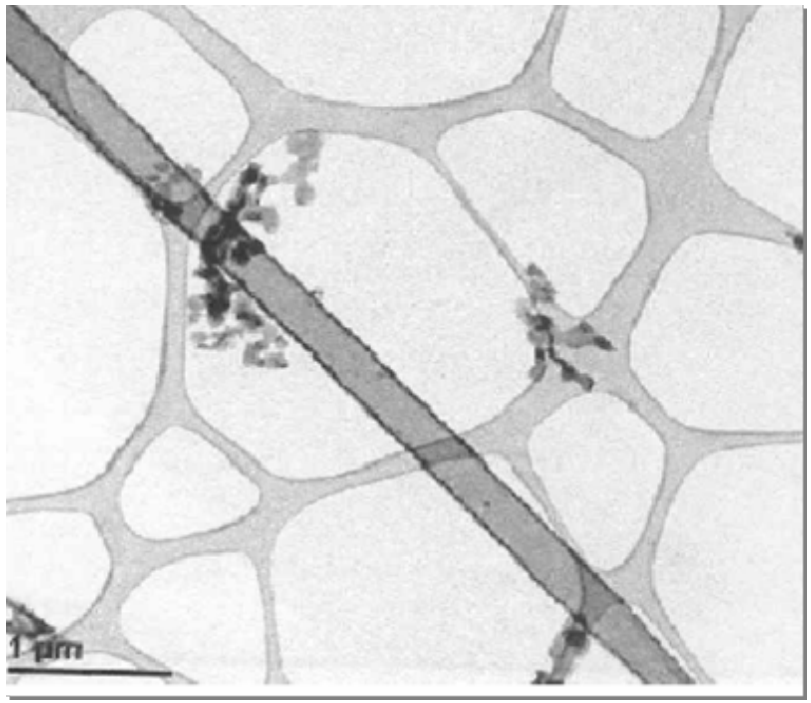
48% HF 24h



SEM and TEM images of nitrogen containing carbon nanotube (NCNT) prepared from polypyrrole



SEM image



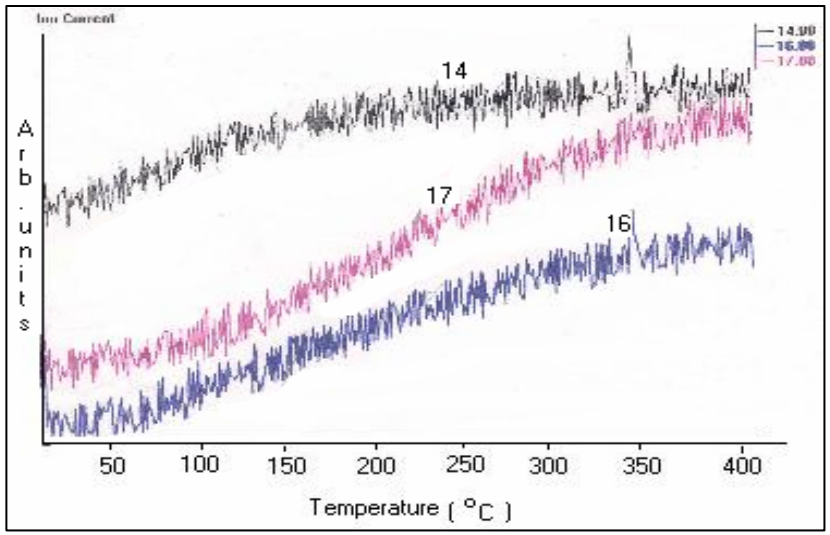
TEM image

Nitrogen content 6.5% by CHN analysis

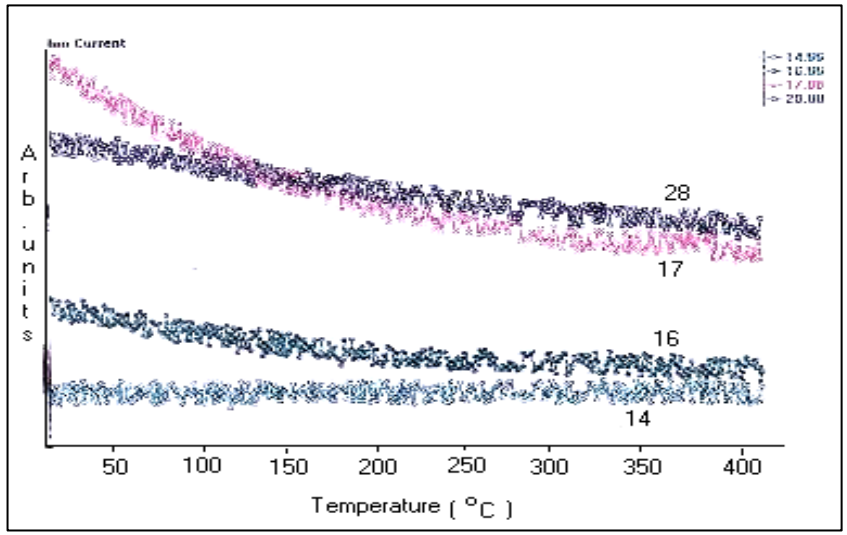
Hydrogen interaction study

- **METHODS**
  - ❖ **Hydrogen storage capacity of CNTs - Measured by Evolved Gas Analysis (EGA)**
  - ❖ **Desorbed gases - quadruple mass spectrum**
- **EXPERIMENTAL CONDITIONS FOR EGA**
  - ❖ **Adsorption 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

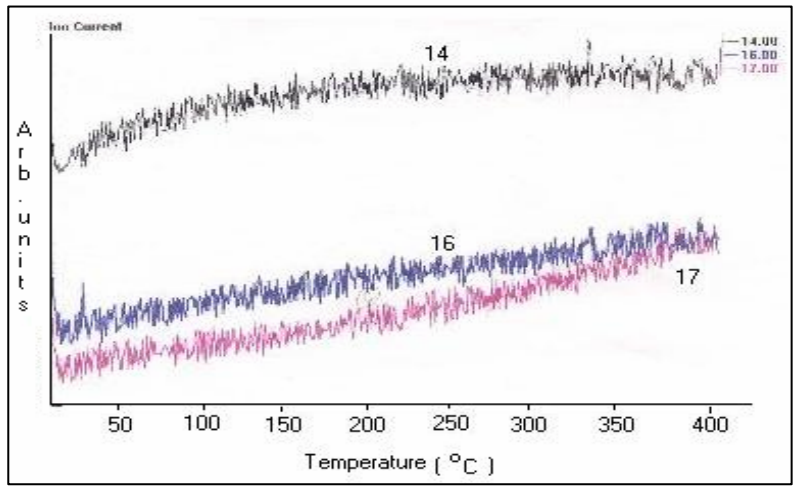


NCNT



CNT

- Formation of ammonia observed from EGA
- Interaction of Nitrogen with Hydrogen - Formation of Ammonia
- Recycling of catalyst-decrease of Ammonia participation of Nitrogen.



NCNT recycled

M.Sankaran and B.Viswanathan, *Bull. Catal. Soc (India)*, 2 (**2003**) 9

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)

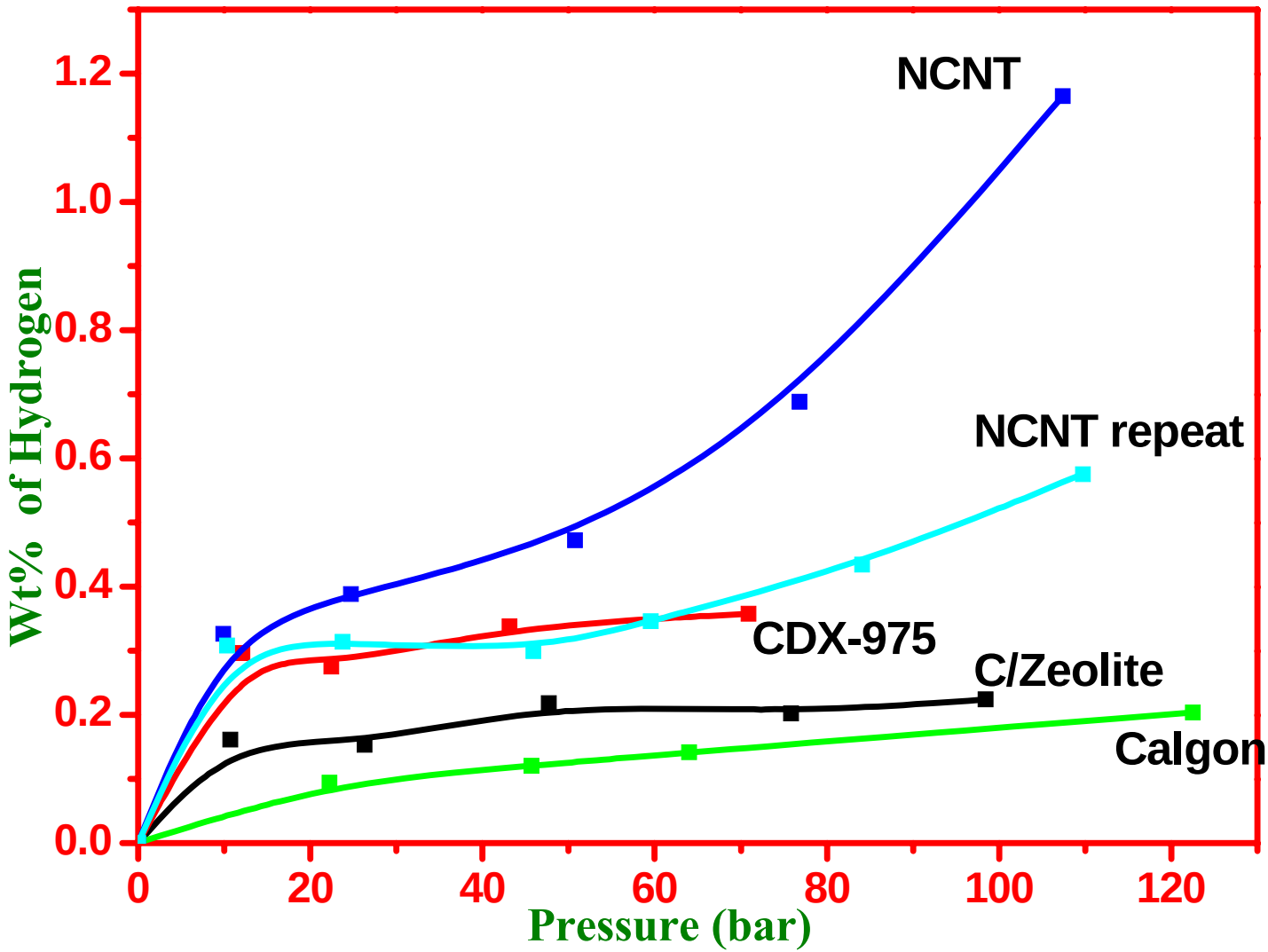
  Nitrogen content 4.3 % by CHN analysis

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

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

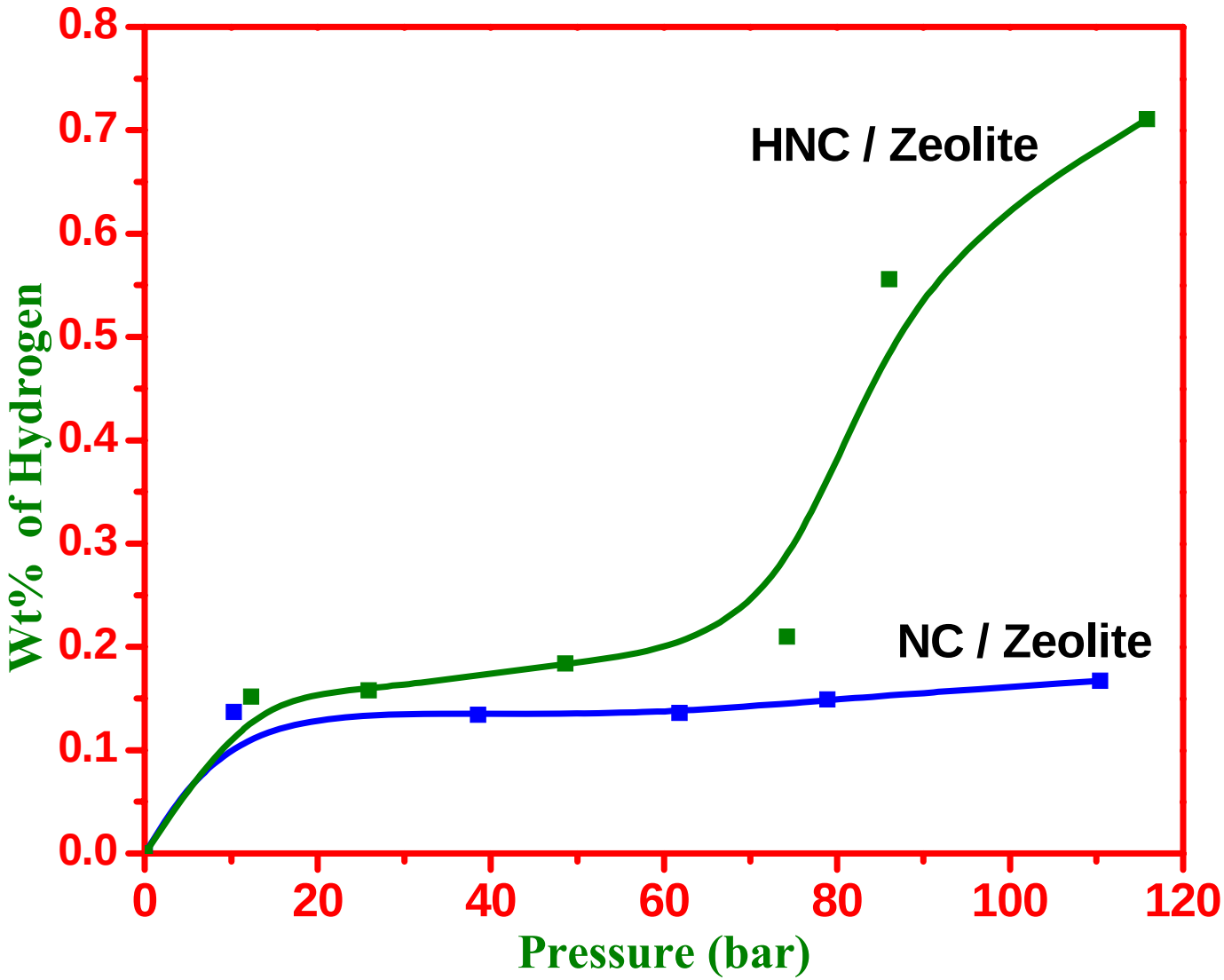
	Surface area (m^2/g)	Hydrogen adsorption (cm^3/g) at 1 atm and at various temperatures (°C)				
		-196	25	100	150	200
NC (mesoporous)	93.0	20.2	0.34	0.90	-	-
NC (emulsion)	182	64.4	-	2.78	-	-
C/Zeolite	633	28.0	-	3.42	4.23	-
NC/Zeolite	646.5	-	-	-	-	-
C/ Clay	48.8	-	-	3.0	3.22	-
N/ Clay	66.4	7.45	-	2.4	-	-
NCNT/Membrane	246	47.5	-	6.11	-	9.5

Hydrogen storage capacity at various pressures

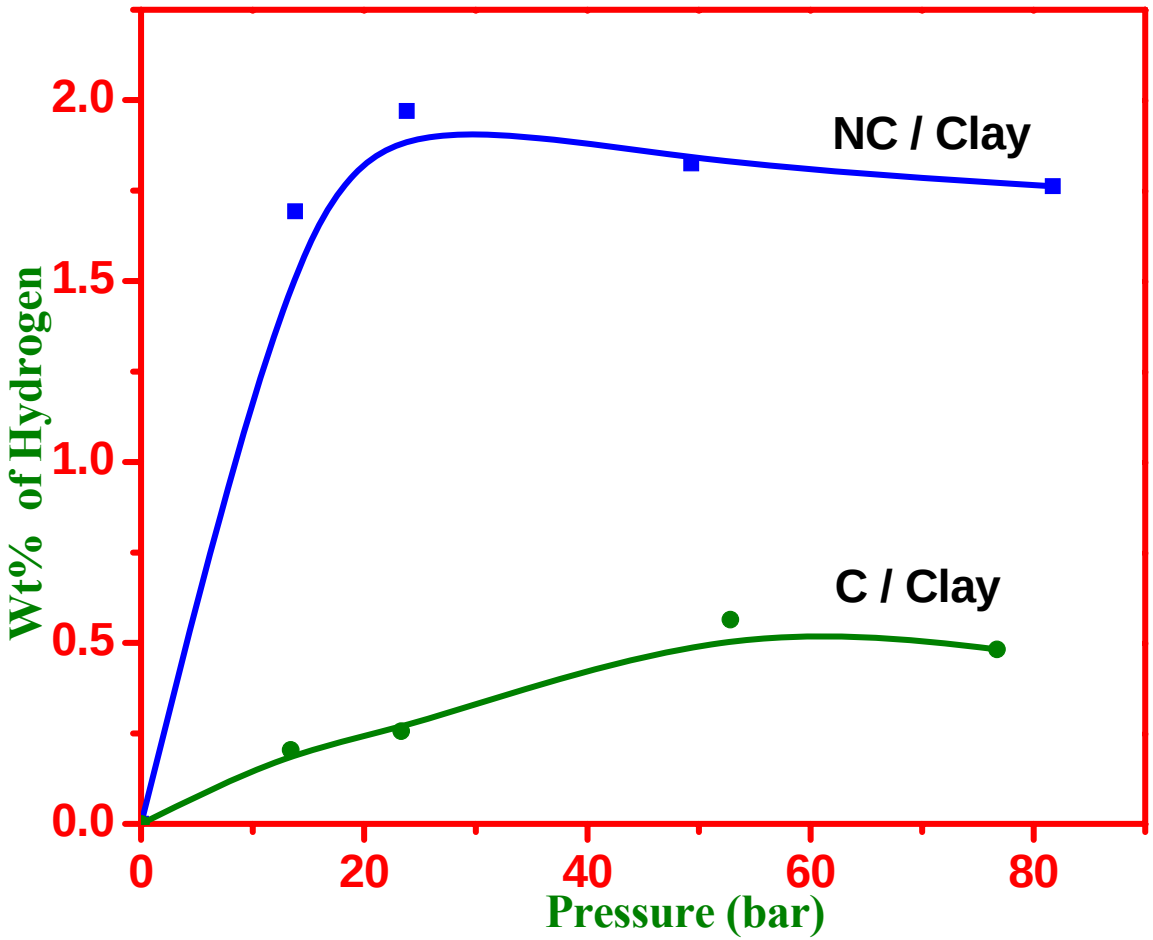


M.Sankaran and B.Viswanathan, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 51 **(2006)** (accepted)

Effect of heat treatment at 800 °C in Ar atm



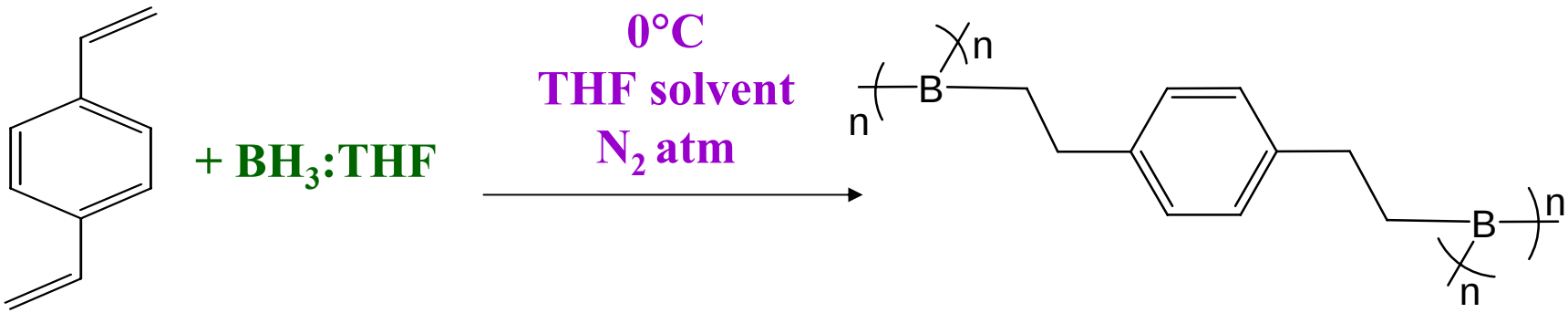
High pressure adsorption study on carbon nanomaterials prepared using clay as template (C& NC/ Clay)



Synthesis, characterization and hydrogen storage capacity of boron containing carbon nanomaterials

Using hydroborane polymers

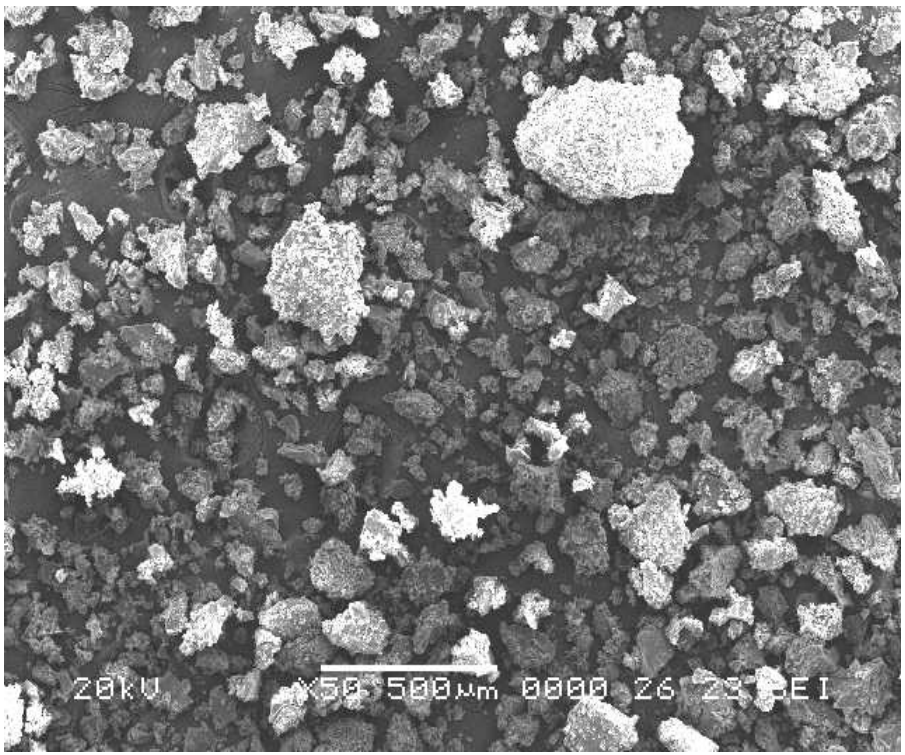
Preparation :

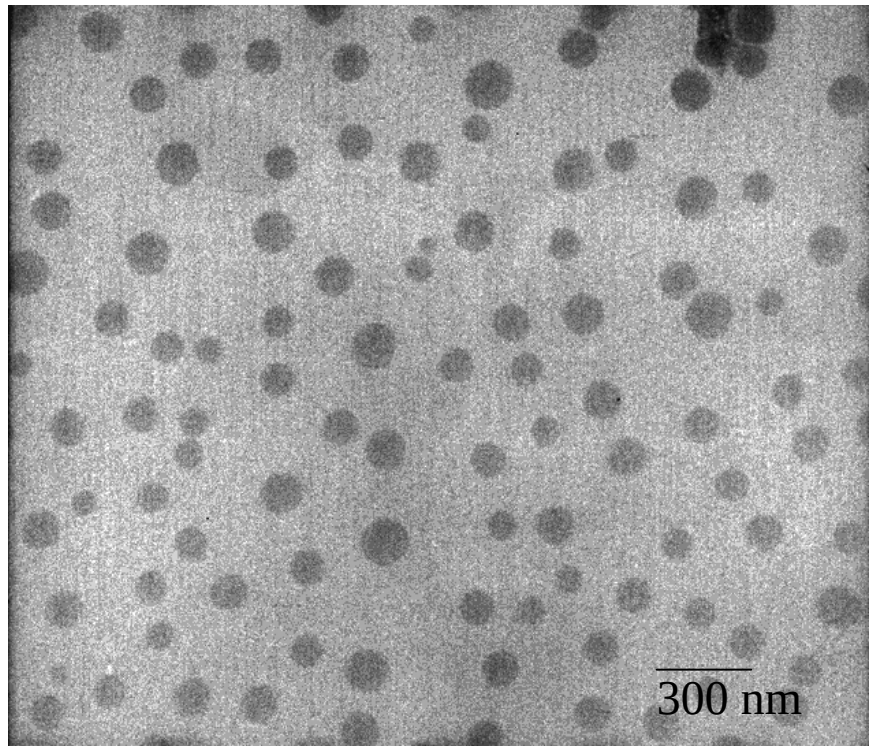


$$3NaBH_4 + 4\,BF_3 \xrightarrow[N_2\ atm]{0^\circ C,\ THF\ solvent} 4BH_3{:}THF_{(l)} + 3NaBF_4 \downarrow$$

The percentage of boron present in the carbon is 4.12%
(after the carbonization of the polymer estimated by colorimetric method).

Micrographic images of boron containing carbon

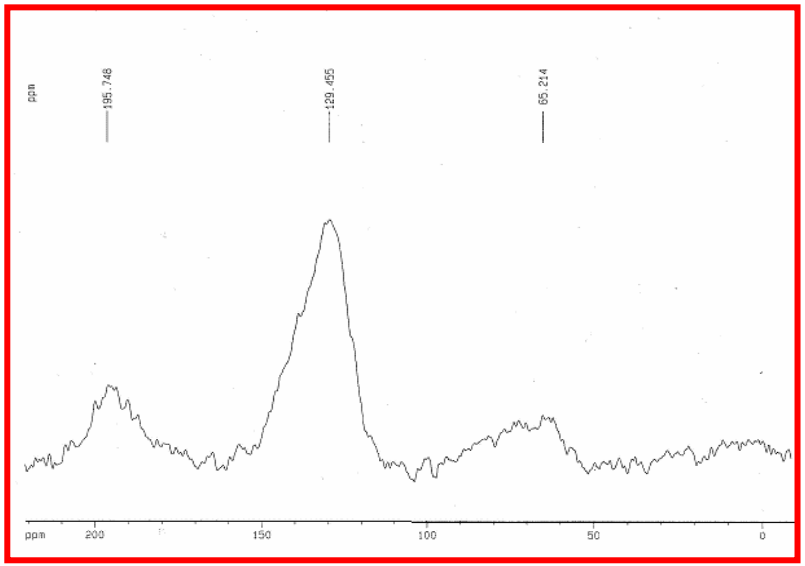




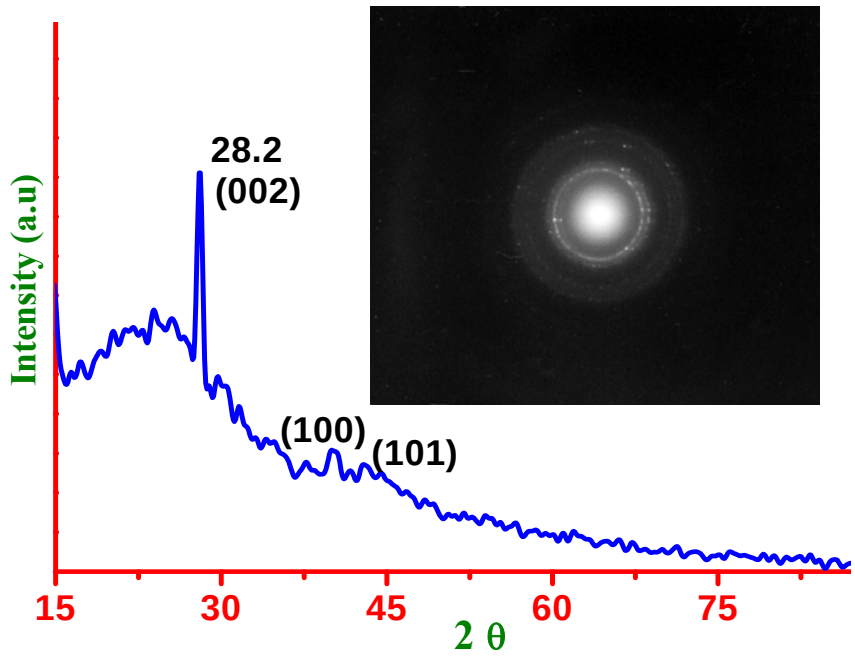
SEM image **TEM image**

Shows spherical morphology with particle size of 100 nm

^{13}C NMR, SAED and XRD pattern of boron containing carbon



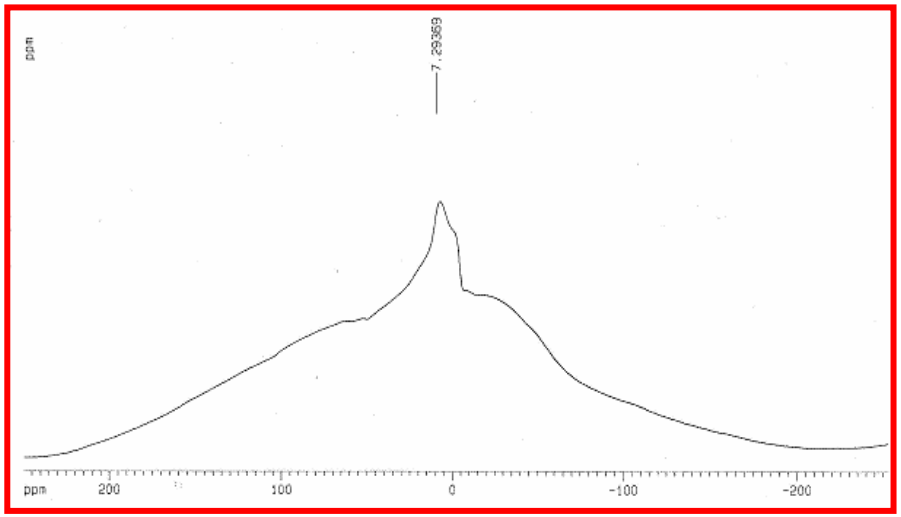
CP MAS ^{13}C NMR

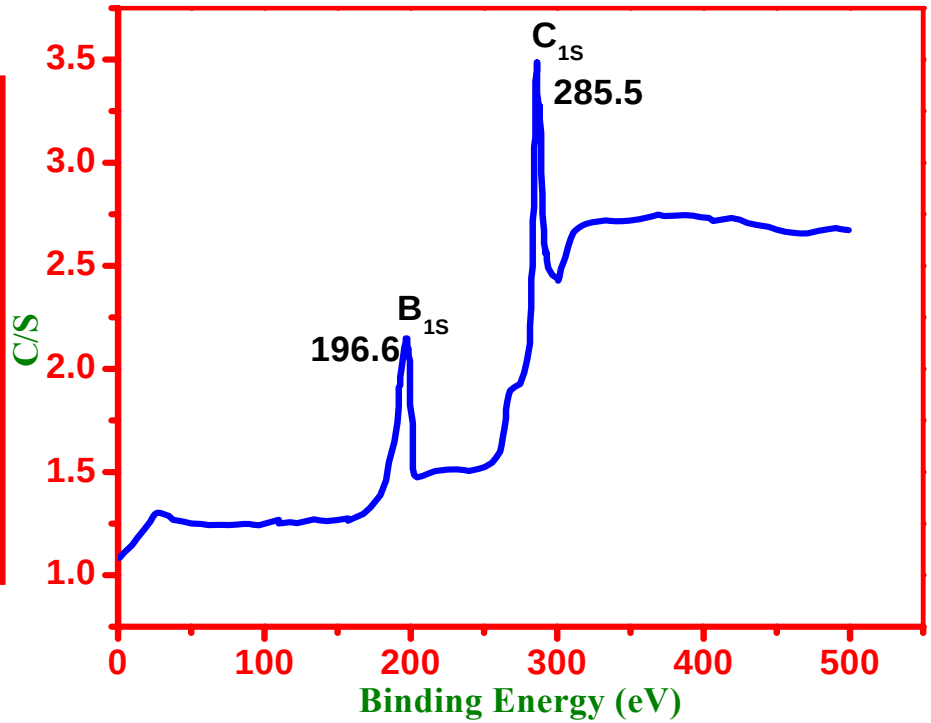


XRD - d = 3.16 (calculated from 2Θ value)

SAED - d = 3.2 (from the diameter of the ring pattern)

^{11}B NMR & XP Spectrum of boron containing carbon

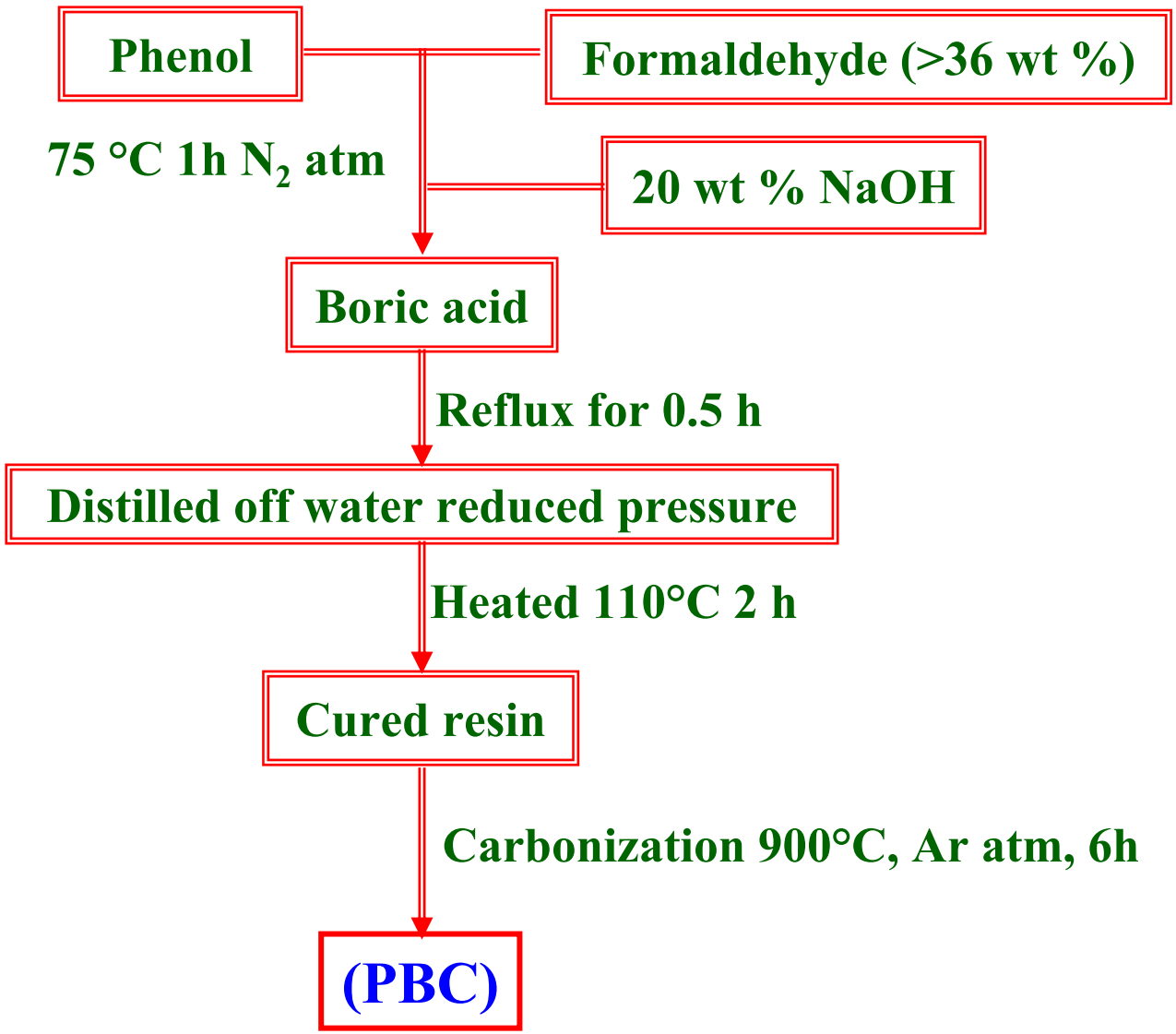




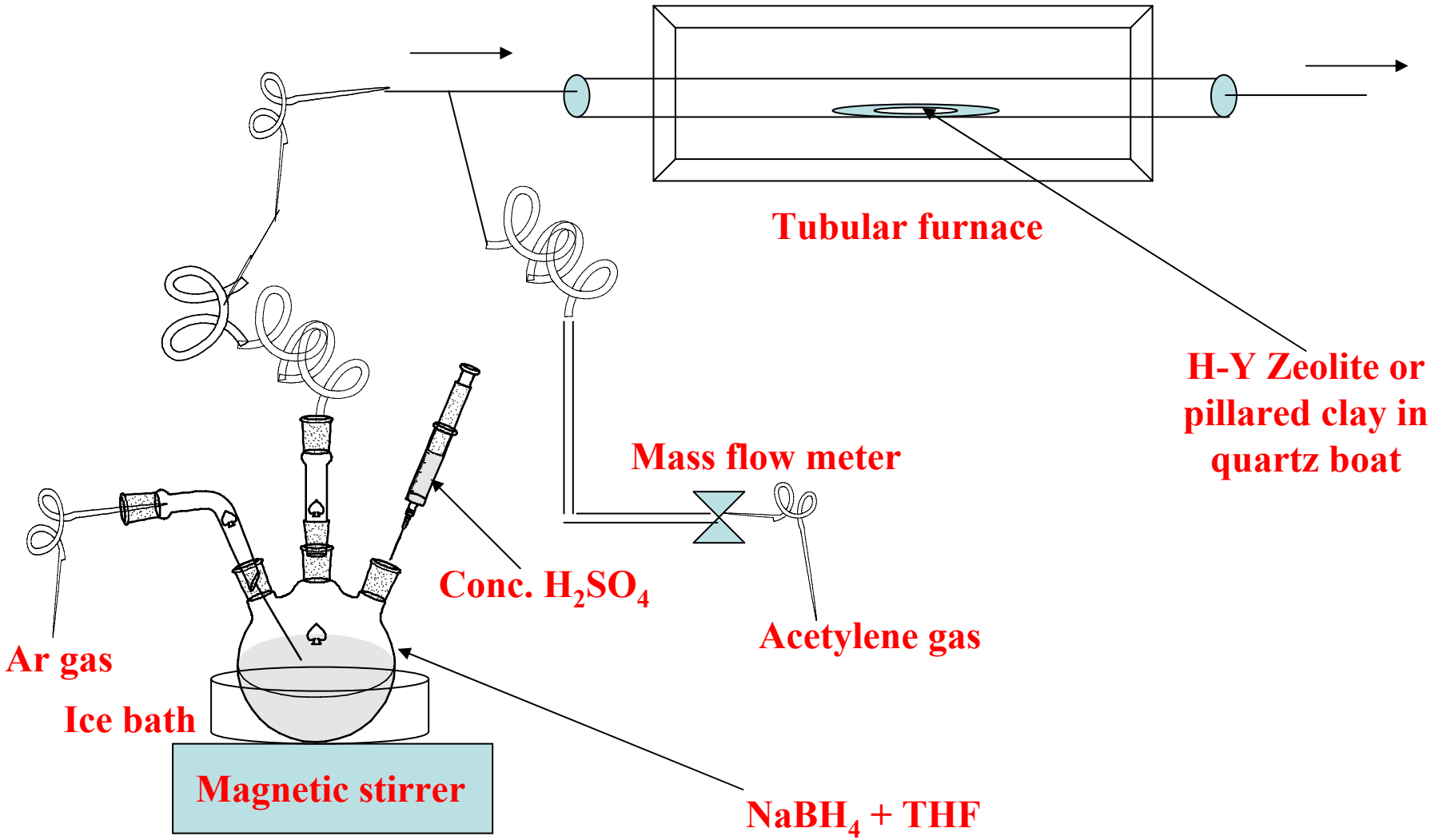
CP MAS ^{11}B NMR SPRECTRA

presence of boron in carbon

Preparation of boron containing carbon material by crosslinking phenol polymers (PBC)

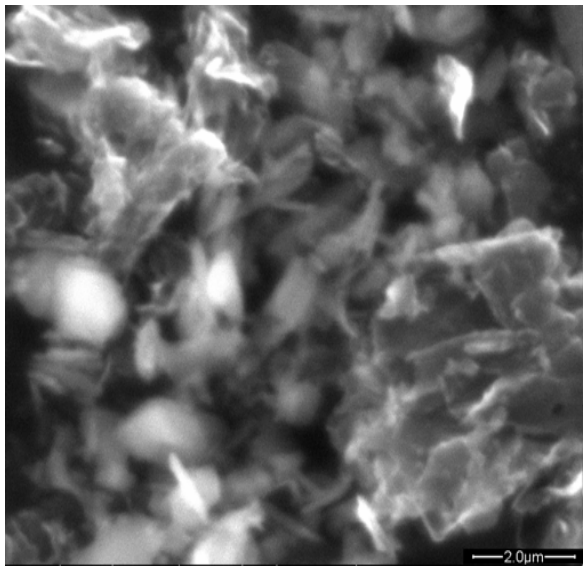


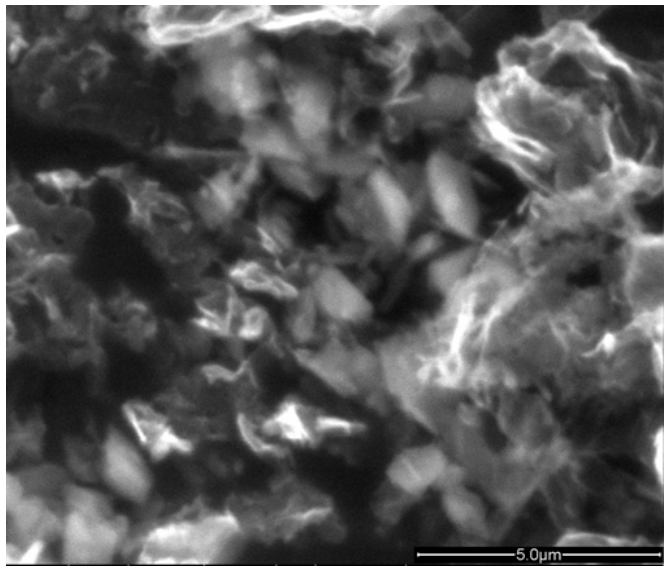
Preparation of boron containing carbon nanomaterials using zeolite and pillared clay



Chemical vapor deposition of borane gas + acetylene mixture over template

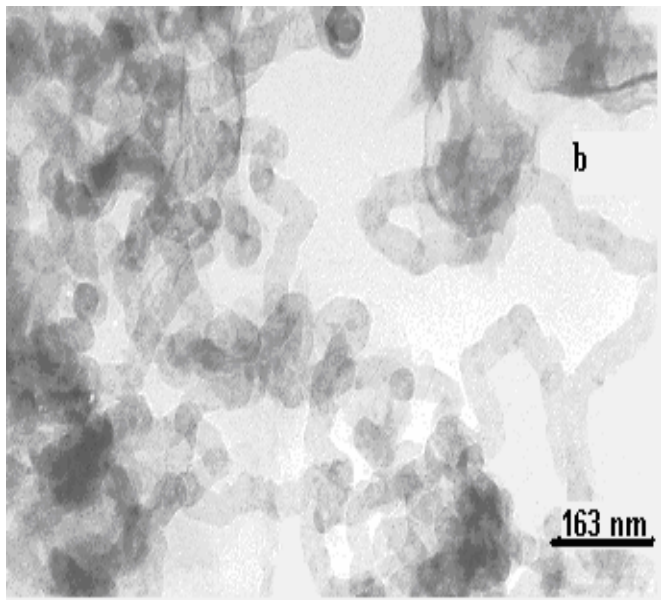
SEM and TEM images of boron containing carbon materials





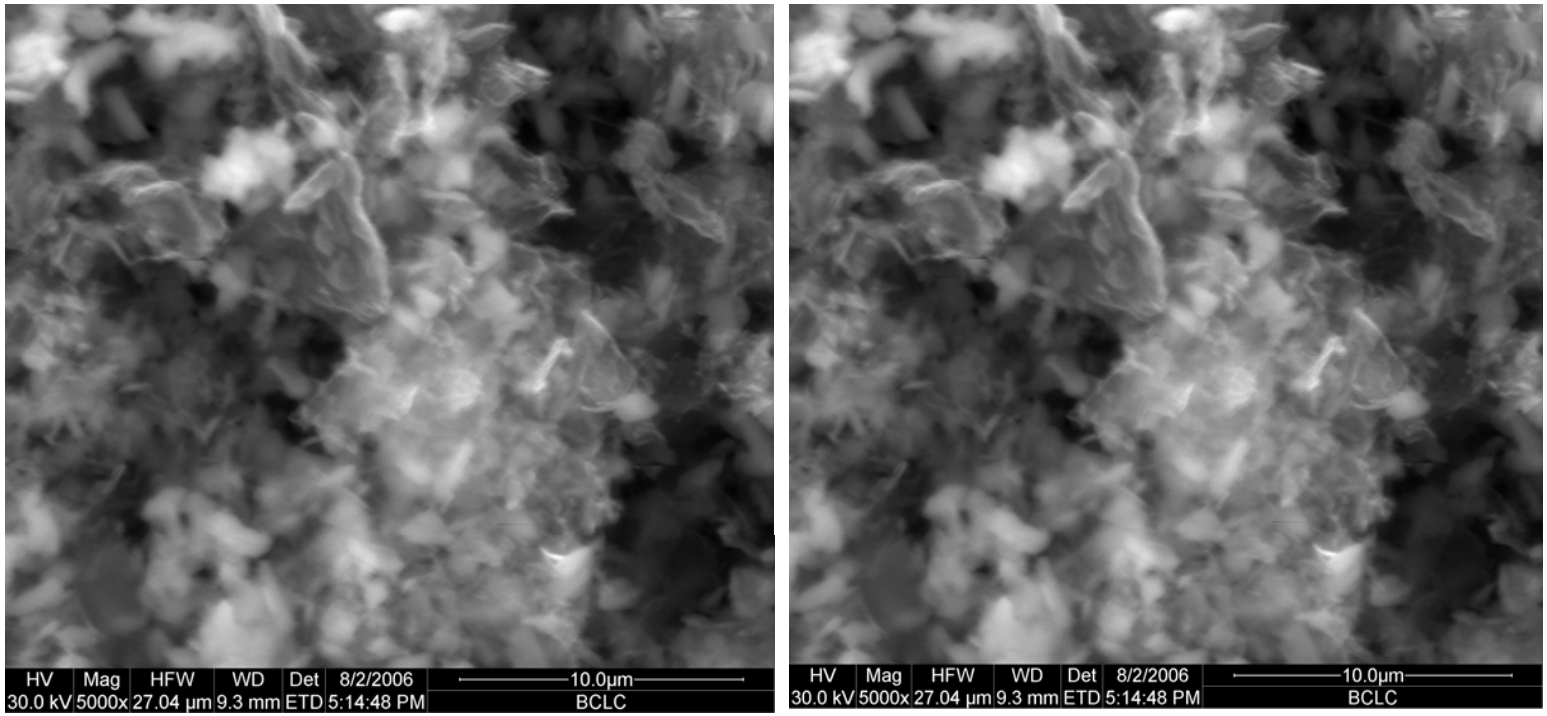
SEM images

BC / Zeolite



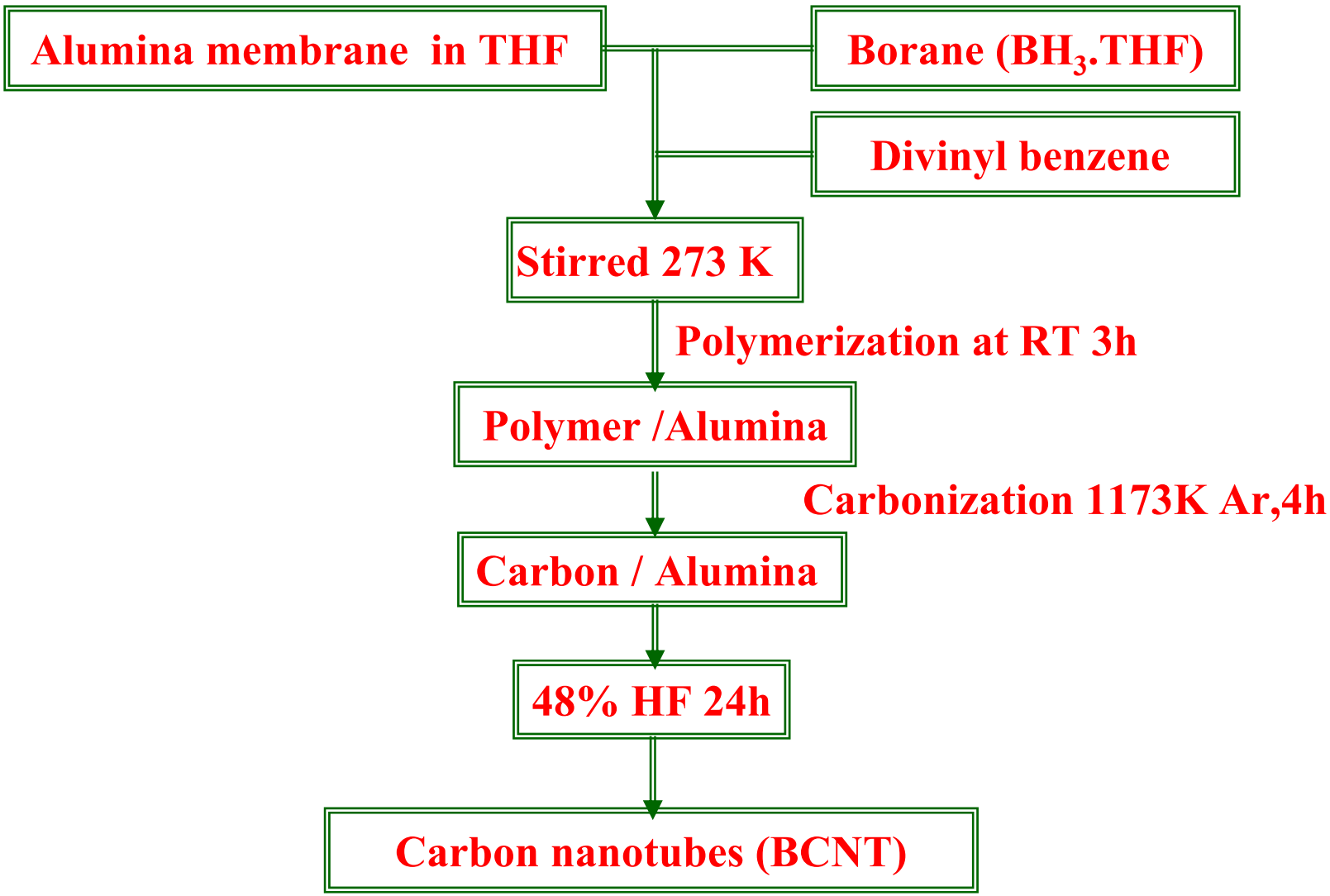
TEM image

SEM images of boron containing carbon materials

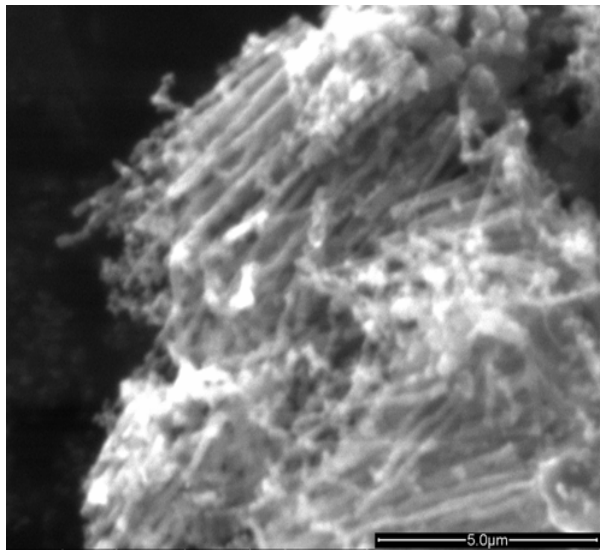


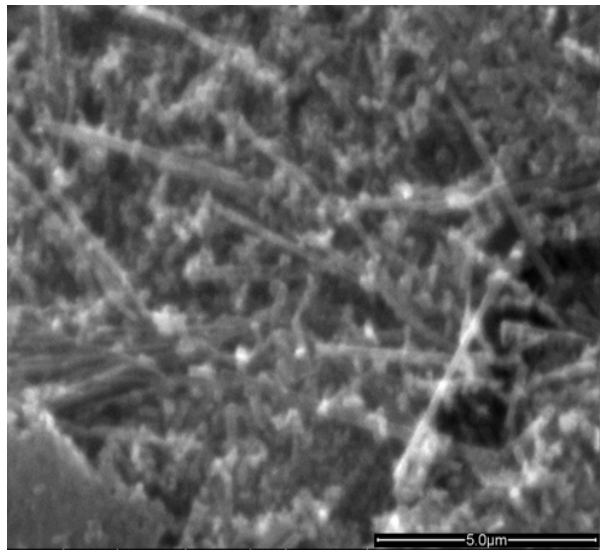
BC / Clay

Boron containing carbon nanotubes prepared using alumina membrane

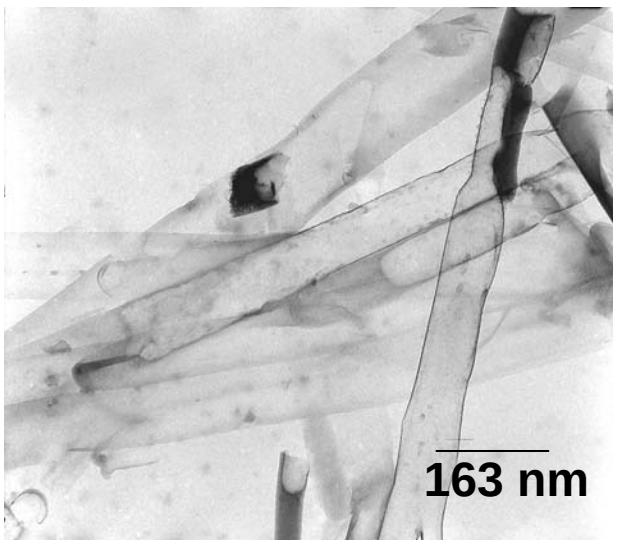


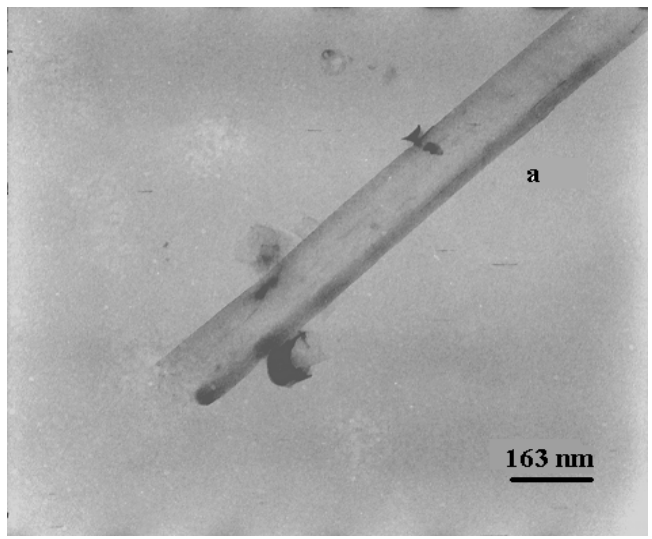
SEM and TEM images of boron containing carbon nanotubes





SEM images

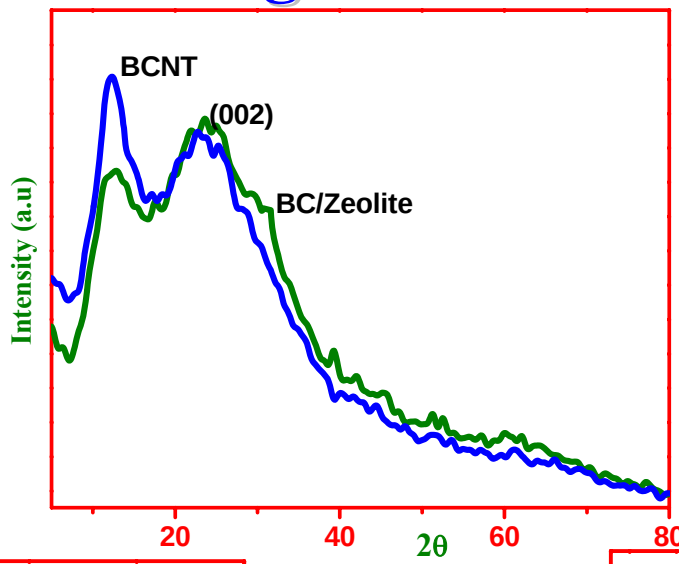




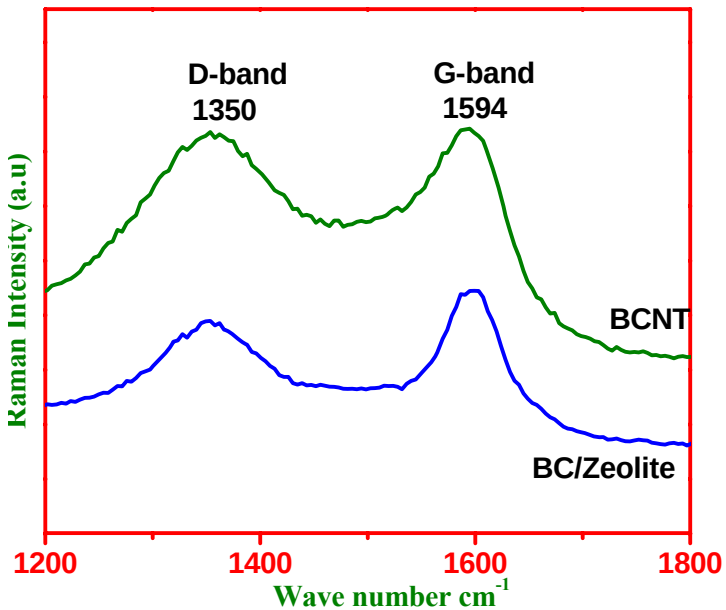
TEM images

BCNT/ Membrane

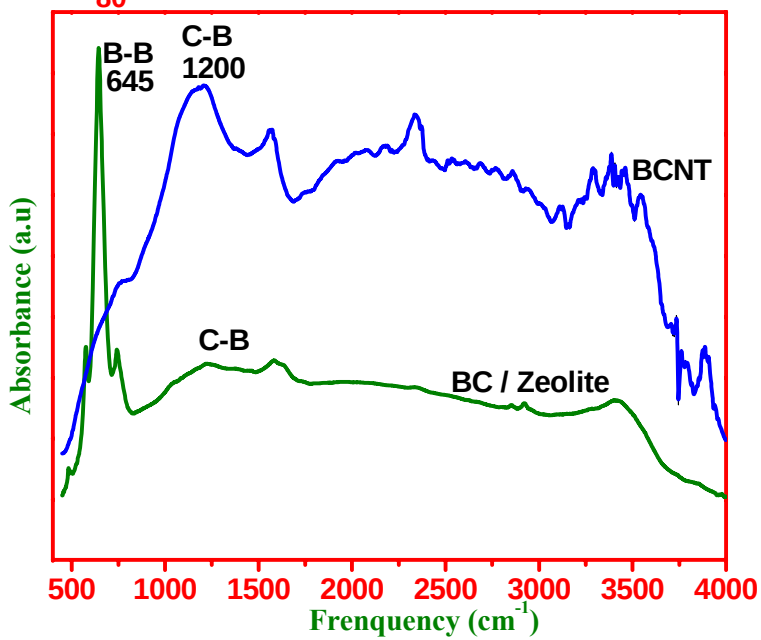
XRD, IR and Raman spectrum of boron containing carbon nanomaterials



XRD pattern

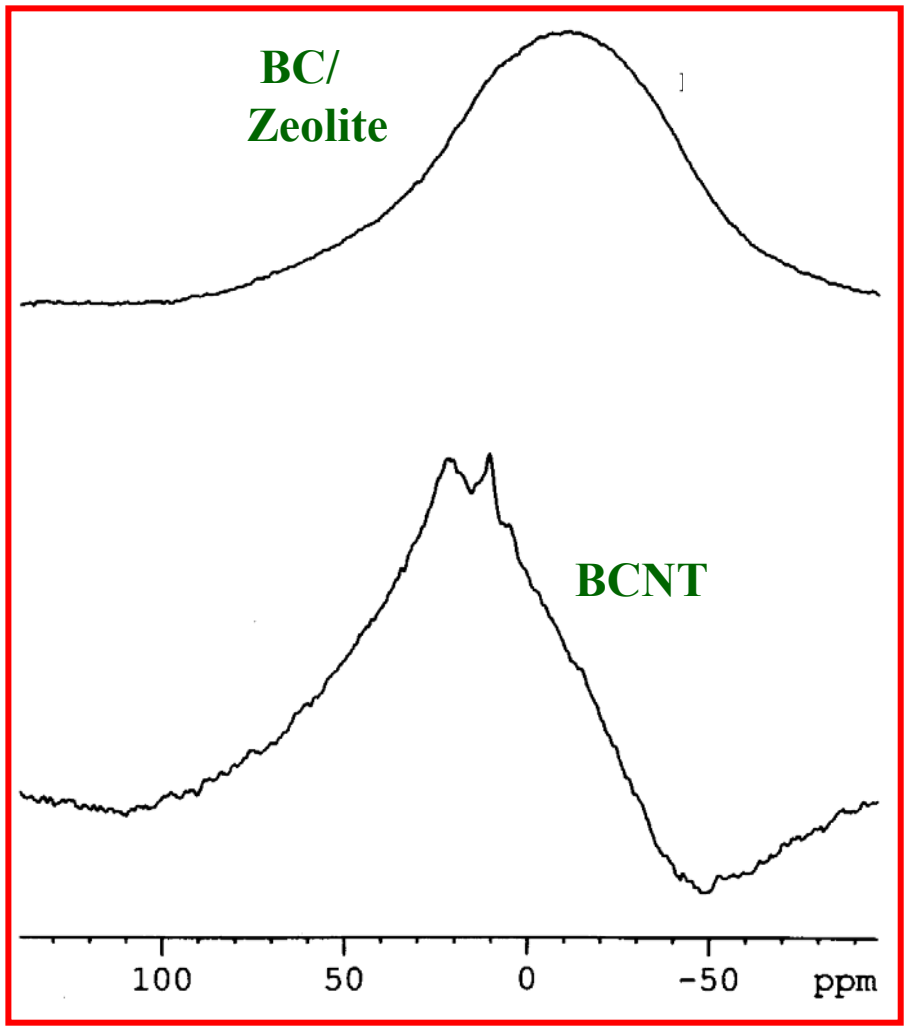


Raman spectrum



IR spectrum

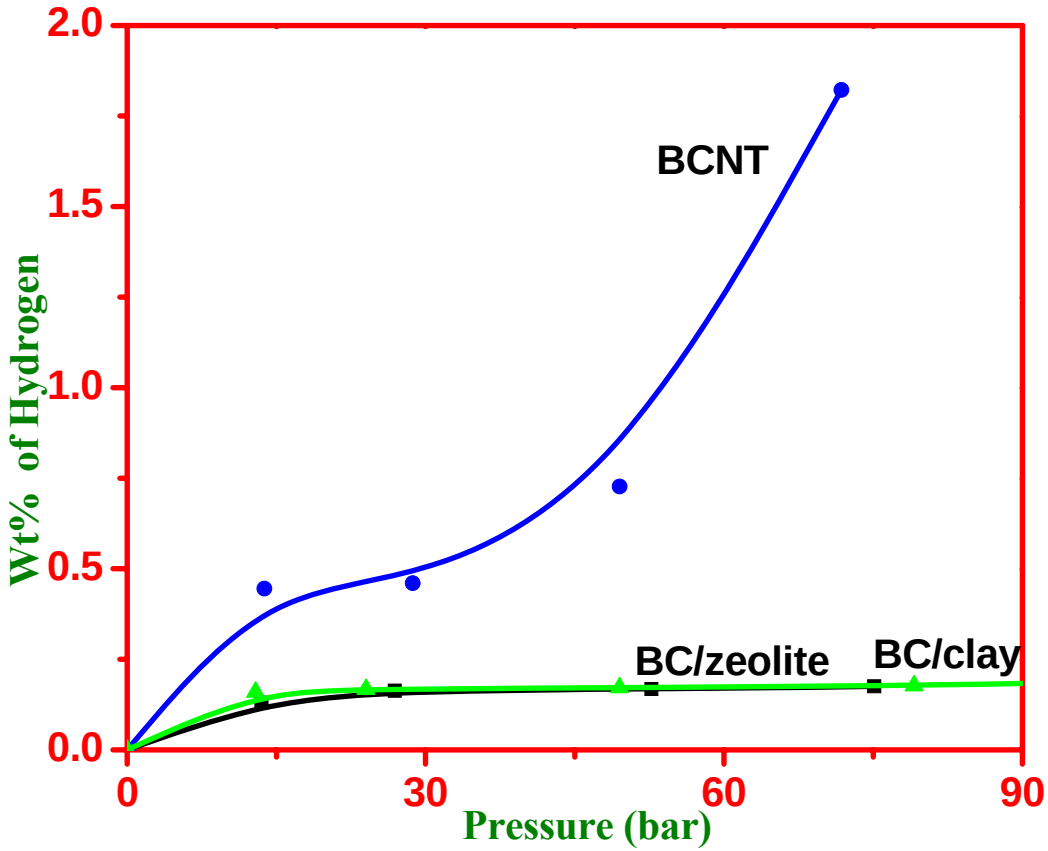
CP MAS ^{11}B NMR spectra of boron containing carbon nanomaterials



Hydrogen adsorption activity of boron containing carbon nanomaterials at 1 atm

Carbon nanomaterial	Surface area (m^2/g)	Amount of hydrogen adsorbed (cm^3/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
BC/Clay	32.7	1.09		1.7	
BC/Zeolite	62.3	3.22	-	2.38	4.73

Hydrogen storage capacity of boron containing carbon materials



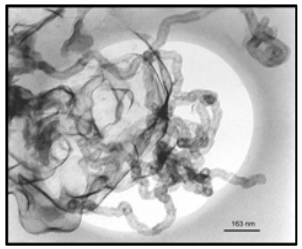
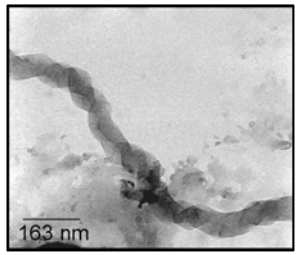
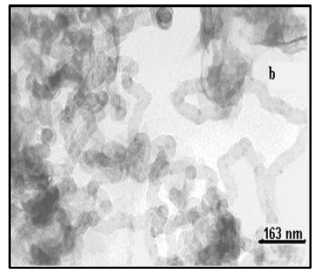
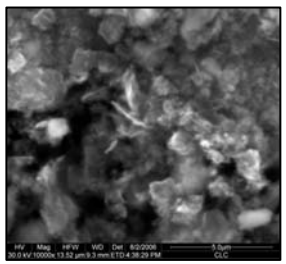
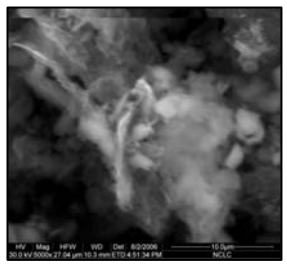
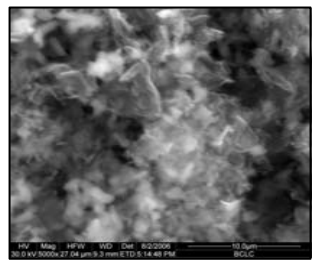
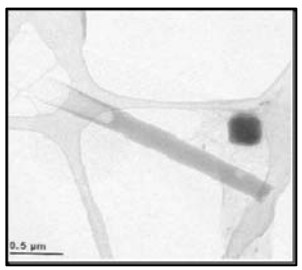
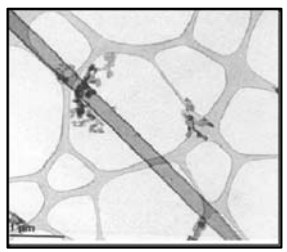
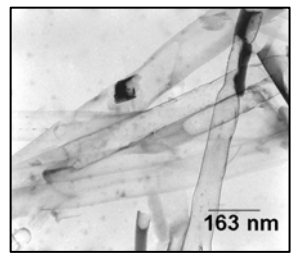
Boron containing carbon nanotubes prepared with polymer precursor, show different boron chemical environments and structural morphology. This configuration has a bearing on hydrogen sorption characteristics.

M.Sankaran, B.Viswanathan and S. Srinivasa Murthy, *Bull. Catal. Soc (India)*, 5 (**2006**) 56

Hydrogen storage capacity of heteroatom substituted carbon nanomaterials

Carbon Materials	Surface area (m^2/g)	Hydrogen storage capacity at room temperature	
		Pressure (bar)	Wt%
Calgon	931	100	0.18
CDX-975	325	80	0.35
C/Zeolite	*633*	*100*	*0.2*
NC/Zeolite	*647*	*100*	*0.17*
HNC/Zeolite	-	*100*	*0.72*
BC/Zeolite	*62*	*80*	*0.18*
C/Clay	49	80	0.48
NC/Clay	66	80	1.75
BC/Clay	33	100	0.2
NCNT/Membrane	246	100	1.2 (0.6)
BCNT/Membrane	-	80	2.03

Morphology and the hydrogen storage capacity

C/Zeolite  0.2 Wt %	**NC/ Zeolite**  0.17 (0.72) Wt%	**BC/ Zeolite**  0.18 Wt%
C/ Clay  0.48 Wt %	**NC/ Clay**  1.75 Wt %	**BC/ Clay**  0.2 Wt %
CNT/ Membrane  0.61 Wt%	**NCNT/ Membrane**  1.2 (0.6) Wt %	**BCNT/ Membrane**  2.03 Wt %

EPILOGUE

- The anxiety of Scientists to achieve the required hydrogen storage in solid state for commercial exploitation appears to be a far cry.

- However, the hope and possibility are favourable and it is only a matter of time before one can achieve the desired levels of storage.

- It is unfortunate that at this stage, a more positive feasibility could NOT be realized.

- The scientific journey for this goal has to continue till further for some more time…… ….

Acknowledgement

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