Carbon nanomaterials – are they appropriate candidates for hydrogen storage?

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Abstract
The purpose of this communication is to address the issue of hydrogen storage by carbon nano materials from various standpoints. Hydrogen storage materials appear to have at least two components, one of them being the hydrogen activator and the other is the hydrogen acceptor**.** The logic involved in selecting an activator in carbon materials for hydrogen storage applications has been postulated. The validity of this logic is tested both theoretically as well as by preliminary experiments.

1. General Introduction

The concept of hydrogen economy is based on three important aspects of using hydrogen as the fuel for our energy needs, namely production, storage and distribution. However, today all the three aspects have not yet reached any mature status to be adopted and placed in position to be exploited by the society. This situation is mainly for the reason that the available technologies for production and storage are not economical and the distribution infrastructure is yet to be built up.

The storage of hydrogen took a dramatic turn with the report in 1998-99, Rodriguez et al [1,2] reported exotic values of hydrogen absorption by carbon nano structures up to 10-12 hydrogen molecules per carbon atom, though in a sequent communication they have reduced this up to 4 molecules per atom of carbon. This is nearly twice (0.4 g H_2/g C) which is higher than the most hydrogenated carbon compound namely CH_4 where the hydrogen to carbon weight ratio is 0.25 g H_2/g C. Thus the claims for hydrogen absorption so far reported exceeds all the possible valence theories which can to the maximum account for 2 molecules of hydrogen per carbon atom. Since any form of carbon nano material cannot have all its four valences not saturated, it may not be possible to achieve this limit of two hydrogen molecules per carbon atom. In order to overcome this argument for the high absorption capacity, Rodriguez et al [1,2] explained the anomalously high values of hydrogen sorption reported by them in terms of intercalation of hydrogen in the molecular form by weak van der Walls forces between the graphene layers. This argument is proposed since the kinetic molecular diameter of hydrogen is smaller (0.289 nm) than the interlayer spacing in graphite materials (0.335-0.350 nm). If such an intercalation were to occur, then the lattice of the graphite material should expand but intercalation has also to be associated with electron exchange and sharing in order to give rise to bonding. Most of the graphite intercalation compounds are classified in terms of either donor or acceptor systems depending on the electro negativity differences. Since the electro negativity difference between carbon and hydrogen is very small activation of hydrogen at the intercalation sites may be difficult. Even if the defect sites are present they may not be

functioning as the activation centres for hydrogen.

The next postulate which has been repeatedly attempted and reported in literature is activation by metals. A variety of metals like nickel, copper, iron, lithium and potassium have been supported on carbon. The basic idea in this is that the metal sites will activate hydrogen (either in molecular or atomic form) and these species then can migrate on to the carbon surface. This concept stems from the spill over postulate normally invoked to explain the unusual catalytic behaviour or low temperature reduction of metal oxides by the addition of some group VIII metals to oxide surfaces like alumina, iron oxide and molybdenum oxide. In this case the dissociated hydrogen on the group VIII metal spills over to the oxide surface through some ad lineation layer of water or other transporting agents. The driving force for this transfer of hydrogen atoms or molecules to sites which are not capable of directly activating hydrogen is the potential of the sites to take up hydrogen in the activated state from other sources. This driving force may arise from various factors like the electro negativity difference between hydrogen and the oxide ions, the unsaturated valences of the oxide surface or the geometrical arrangement of ionic species in the spilt over surface, or the inherent heterogeneity of the surface potential of the sites. However, this type of transport is feasible if the accepting site possess greater affinity for the spilt over species than the surface where the species is generated for subsequent spill-over. But in the case of metal supported on carbon surfaces, the metal sites are capable of activating hydrogen, but the transport to the carbon surface is not a facile process since the electro negativity difference between carbon and hydrogen is not high enough and the carbon surface by nature is not heterogeneous so as to promote the migration of hydrogen species from the metallic sites [3, 4]. Secondly, the group VIII metals have their own affinity for hydrogen and most of these metals have been used as components of intermetallic systems which are examined for hydrogen storage purposes. There are a variety of intermetallics that have been examined for hydrogen storage purposes [5-8]. There are three generic intermtallic systems namely AB, AB_2, and AB_5 which have been examined for hydrogen storage applications in a variety of compositions and the essential results are given in Table 1. There are some important deductions that one has to take note of. These include:

(i) Most of the known and available metallic systems except magnesium based systems show absorption capacity in the range to 2-4 weight percent only.

(ii) Magnesium based systems show higher absorption capacity up to 7 weight percent.

(iii) The absorption and desorption process of metal hydrides are seriously subject to thermodynamic and kinetic limitations so that their commercial exploitation is very limited at present.

As an extension of this, Bogdanovic et al [9] reported that the sodium alanates that are non-reversible could be made reversible by doping with Ti, the practical possibility of the following two –stage reaction was shown

$$NaAlH_4 \leftrightarrow 1/3\ Na_3AlH_6 + 2/3\ Al + H_2 \leftrightarrow NaH + Al + 3/2H_2$$

Stoichiometrically, the first step accounts for 3.7 weight percent H_2 release and the second step 1.9 weight % for a total net release of 5.6 weight %.The temperatures for desorption at one atmosphere are around 305 K for the first step ($NaAlH_4$ decomposition) and about 405 K for the second step (for Na_3AlH_6 decomposition) [8-13]. The major drawbacks associated with lightweight alanates are (i) formation

of alanates are associated with byproducts that are difficult to remove and consequently hamper hydrogen storage capacity (ii) These substances are sensitive to moisture or air (iii) There are no suitable catalysts at present that can facilitate reversible adsorption (iv) In addition, the multiple step decomposition is not suitable for mobile applications.

The US department of Energy (DOE) Hydrogen Plan has set a standard for a possible realization by providing a commercially significant benchmark for the amount of reversible hydrogen absorption. The benchmark requires a system weight efficiency (the ratio of stored hydrogen weight to system weight) of 6.5 weight percent hydrogen and a volumetric density of 62 kg H_2 since a vehicle powered by a fuel cell would require more than 3.1 kg of hydrogen for a distance travel of about 500 km. No storage technology is capable of meeting these goals to date [4].

2. Hydrogen sorption by Carbon materials

Carbon materials are attractive candidates for hydrogen storage, because of a combination of adsorption ability, high specific surface, pore microstructure and low mass density. Hydrogen sorption by carbon nano-materials has assumed considerable importance in recent times especially from the contexts of

1. Adsorption capacities ranging from 0 to 67 weight percent have been claimed. The essential data on this aspect are assembled in **Table 2** for ready reference.
2. There are possibilities of using these materials for hydrogen storage and subsequently use them in fuel cells and automobiles.
3. It is also necessary to understand the geometric and electronic features required for activation of hydrogen molecule on these surfaces.

This situation has given rise to a need for rationalizing the available data and to propose a reasonably acceptable and realizable adsorption capacity by these materials.

2.1. Conventional Carbon

For *conventional porous carbon* the hydrogen uptake is proportional to its surface area and pore volume, while, regretfully, a high hydrogen adsorption capacity (4-6 wt %) can be obtained only at low temperatures such as cryogenic conditions [15]. Rzepka et al [16] reported 0.7wt% storage in activated carbon with a specific surface of 2600 m^2/g at T=300K and p=6MPa. This poor limit is attributed to lack of availability ideal slit pores. Since any ideal solid for hydrogen storage should posses texture consisting of slit shaped layers having a width anywhere higher than the kinetic diameter of hydrogen namely 2.89 Å. It is difficult to obtain high –surface –area activated carbon adsorbent with small pore sizes with narrow pore size distributions.

2.2. Engineered carbon

Engineered carbon material such as graphitic nanofibers (GNFs) are taken for advantage at this stage, which can be produced by decomposition of mixtures of ethylene, hydrogen and carbon monoxide on selective metal and alloy catalyst, with three distinct structures such as tubular (90°), platelet (~0°) and herringbone (45°) in which the angle indicates the direction of the fiber axis relative to the vector normal to the graphene sheets. The spacing between each layer is the same as in conventional carbon, ~3.4 Å with diameter 5 - 500 nm. The hydrogen storage capacities reported are 0-50 wt% for platelet and herringbone at 12Mpa/ 300K condition and ~ 10 wt% for tubular structures [1].

To visualize the results of Chambers et al., [1] one has to assume that the number of layers of H_2 between planes of graphite

Table 1. Hydrogen Stoage capacity of metallic and intermetallic systems.

Material	P_{des}(atm)	T(K)	H-atoms/ cm^3($x10^{22}$)	Weight % of hydrogen
MgH_2	~10^{-6}	552	6.5	7.6
Mg_2NiH_4	~10^{-5}	528	5.9	3.6
$FeTiH_2$	4.1	265	6.0	1.89
$LaNi_{5H}6$	1.8	285	5.5	1.37

Table 2.Summary of reported hydrogen storage torage capacities in carbon nanostructures storage capacities in carbon nanostructures

Adsorbent	**Hydrogen Storage (wt%)**	**Conditions**	**References**
		Temperature (K) / Pressure (MPa)	
SWNT(low purity)	5-10	273/0.04	22
SWNT(high purity)	3.5-4.5	298/0.04	
SWNT(high purity)	8	80/8	24
SWNT(50% purity)	4	300/12	25
SWNT	2	80/10	43
SWNT	11	80/10	27
SWNTs	~0.1	300-520/0.1	21
SWNT	6.5	300/16	65
SWNT	10	300/0.04	23
Li doped MWNT	20	200-400/0.1	28
K doped MWNT	14	300/0.1	
Li doped MWNT	2.5	200-400/0.1	29
K doped MWNT	1.8	<313/0.1	
MWNT	5	300/10	26
K doped MWNT	1.8	300/0.1	30
GNFs (tubular)	11.26	298/11.35	1
GNFs (herring bone)	67.55	298/11.35	
CNFs	~10	300/10.1	19
CNFs	~5	300/10.1	20
GNFs	10	300/8-12	29
Nano-structured graphite	7.4	~300/1.0	42
SWNT-Fe	<0.005	300/0.08	33
SWNT-Ti-6Al-4V	1.47	300/0.08	33
SWNT-$TiAl_{0.1}V_{0.04}$	~7	300/0.067	32

could somehow as large as five and would require a nearest neighbor distance, within one of these five monolayers, of only 0.98 Å or one H_2 per 0.82 $Å^2$. However, since the kinetic diameter of H_2 is 2.89 Å, it is difficult to realize this situation. Though several groups have succeeded in fabricating GNFs, subsequent measurements could not confirm the high hydrogen storage capacity and the examples include:

- Ahn et al. [17] found in GNFs by volumetric method at 8 MPa / 77 K and at 18 MPa /300 K only less than 0.01 wt. % hydrogen storage.
- Ströbel et al. [18] measured the hydrogen adsorption on different carbon materials using a microbalance at 12.5 MPa/296 K and observed a maximum weight increase corresponding to a hydrogen uptake of 1.6 wt.%.
- A group from the Chinese Academy of Science [19] reported a hydrogen uptake of 10–13 wt.% at 11 MPa /300K after boiling the GNFs in HCl. In a further publication [20] the same group reduces the values for the hydrogen storage capacity of GNFs by a factor of two. Up to now none of these experiments could be repeated or confirmed by other groups.
- Hirscher et al [21] measured hydrogen storage capacity as 0.5 wt % for GNFs ball milled under D_2 atmosphere at 0.08 MPa /300K by thermal desorption studies (TDS).

Among nanostructures, tubular materials are especially interesting because their morphology is assisted with an intrinsic multi functionality that arises from four different contact regions, as tube opening, outer surface, inner surface and interstitial region. These properties render nanotubes as promising candidates for the realization of highly functional, effective and resource saving nanodevices for storage and release purpose. In addition, pores of molecular dimensions can adsorb large quantities of gases; hydrogen can probably condense with high-density inside narrow single walled nanotubes even at room temperature. For conventional physical adsorption, the gas adsorption in a porous substance is maximized, when the pores are not larger than a few molecular diameters and under these conditions the potential fields from the walls of the macropore overlap to produce a stronger interaction than would be possible for on semi-infinite plane. If the escaping tendency of the gases is less than the adsorption potential, entire micro pore may be filled with a condensed adsorbate phase.

2.3 Studies on single walled carbon nanotubes (SWCNTs)

Since carbon nanomaterials have been claimed as stated earlier, as the materials of future for hydrogen storage applications, it is essential that the reported data in literature are analyzed with a view to evolve appropriate conditions for optimal storage of hydrogen in carbon materials.

- Dillon *et al.,*[22,23] by using TDS, reported hydrogen storage capacity of non-purified bundles of single walled nanotubes for the total sample as 0.01wt% and for pure single walled nanotubes ~ 5-10 wt% at < 0.1 MPa/RT. The improvement in the later case is attributed to the opening and filling of nanotubes.

- Ye et al [24] carried out measurements at two different experimental conditions such as 300K at a pressure of 160 atm and at low temperature of 80 K at a range of pressures such as 0.5, 4.5, 70 and 130 atm. Prior to the measurement, some of the material

was sonicated for 10h in DMF then vacuum degassed for 10h at about 500 K, with the aim of cutting the tubes and disrupting the rope structure. A high value of 8 wt% of uptake capacity was obtained at 80 K with a hydrogen pressure of 12 MPa. However, in these measurements certain corrections on thermal effects resulting from the compression/decompression of the gas and from the adsorption/desorption have not been taken into account.

- Liu et al. [25] reported for SWNTs (dia = 1.85 nm) a reproducible storage capacity of 4.2 wt.% at 10 MPa/ RT. The SWNTs were soaked in hydrochloric acid and then heat-treated in vacuum. The stored hydrogen could be released under ambient pressure at room temperature.

- Hirscher et al [21] measured hydrogen storage capacity as 1.0 wt % for SWNTs ball-milled under D_2 atmosphere at 0.08 MPa at RT by TDS.

However, it should be specified that none of these experiments could be repeated or confirmed independently in other laboratories up to now.

2.4 Studies on Multi walled carbon nanotubes (MWCNTs):

Another type of carbon nano-tubes are multi-walled nano-tubes (MWCNT). These systems provide additional possibilities and sites for the activation and adsorption of hydrogen in between the walls of the nano tubes. The spacing between the two concentric walls of the tubes can be considered to be ideal sites for hydrogen adsorption since the hydrogen molecule is present in the force field exerted by the walls on both sides of the molecule. This could give rise to activation and adsorption of hydrogen in a different manner. In this context it is essential one carefully analyses the existing data on hydrogen sorption by multi-wall CNTs.

- Zhu et al.,[26] reported the hydrogen adsorption at 100 atm /RT to the extent of ~ 2.5-5.08 wt% in MWNCTs subjected to surface treatment with the aim of removing contamination and to form micropores or etch grooves. These surface irregularities increase the quantity of adsorbed hydrogen as hydrogen molecules diffuse into the nanotube layers as a consequence of strong interaction with delocalized π-electrons of graphitic plane.
- Wu et al. [27] have obtained multi-walled carbon nanotubes from the catalytic decomposition of CO and CH_4 on powder Co/La_2O_3 catalyst and found that the size of the nanotubes was controllable by adjusting the composition of the catalysts, and by annealing the crystallinity could be improved. They concluded that their nanotubes are "able to uptake a certain amount of H_2 under ambient conditions".

2.5 Studies on modified carbon nanomaterials

Attempts have been made in the past using doped/modified CNTs for hydrogen storage purpose. Chen et al. [28] reported a large hydrogen uptake in GNFs, carbon nanotubes and graphite doped with alkali metals. These samples were initially heated in situ at 873 K in a flow of purified hydrogen to remove adsorbed water and contaminants. The doped nanotubes exhibited storage capacities ~ 20 wt% (473-673K) and 14 wt% for hydrogen at RT and 1 atm for lithium and for potassium doping respectively at room temperature.

Yang [29] revisited these data by preparing the doped nanotubes following the same procedure as Chen et al [28] and measured the adsorption-desorption capacities using a comparable thermogravimetric analyzer. Special caution needs to be taken to remove any moisture contamination of the hydrogen while measuring the adsorption capacity. Since moisture drastically increased the weight gain and leads to erroneous results. So, in dry hydrogen the adsorption was found to be ~ 2.5 wt% for lithium-doped nanotubes and 1.8 wt% for potassium-doped nanotubes, and these results were independently confirmed by Pinkerton et al. [30].

The inconsistency in these reports are attributed to the fact that, Chen et al. [28] performed the alkali metal doping by – as they call it – a solid state reaction using nitrate and carbonate salts of the alkali metals. Heating the mixture of carbon materials with $LiNO_3$, and Li_2CO_3 under hydrogen flow result in the formation of LiO_2.

Yang confirmed the occurrence of following chemical reactions

$$2LiNO_3 + C + H_2 \rightarrow Li_2CO_3 + H_2O + 2\,NO$$

and then

$$Li_2CO_3 + H_2 \rightarrow Li_2O + H_2O + CO$$

LiO_2 is highly hygroscopic and hence sensitive to moisture in the thermo-gravimetric experiment. This interpretation is confirmed further by the investigation of Hirscher et al [18] as they did not find any hydrogen desorption in graphite doped with Li or K.

In all these hydrogen uptake studies, three common features exist: slow uptake, partial irreversibility of adsorbed species, and the use of transition metals in synthesis (Fe, CO, or Ni) that may not be completely removed by purification. Hydrogen spillover from metal to carbon surface is well discussed in literature [3, 4].

Yang and Lueking [31] experimentally showed that hydrogen storage on multiwalled nanotubes (MWNTs) was dependent on the degree of catalyst removal. At atmospheric pressure, removal of the catalyst decreased the uptake from 0.6% to below detection limits.

In 2000, Dillon et al [32] incorporated a metal alloy $TiAl_{0.1}V_{0.04}$ to a purified laser-generated SWNT employing a high-power ultrasonic cutting procedure and found the maximum adsorption capacity 7.0 wt %. The hydrogen adsorption occurs in two different sites approximately 2.5 wt % of hydrogen evolved at 300 K and the remainder desorbed between 475 to 850 K. However the uptake is not solely attributed to the presence of alloy but also to the process associated electron transfer that is responsible for hydrogen storage. Hirscher et al [33] reported 1.5 wt% storage capacity for SWNTs doped with alloy of Ti-6Al-4V by sonicating in 5M HNO_3. However the hydrogen uptake was explained with the assumption that the hydrogen is stored in Ti alloy particles only.

From Table 2 it can be seen that, except for the results of Chambers et al. [1] at room temperature, the hydrogen uptake is of the order of a few percent, a value also obtained by Ye et al. [24] at 80 K. The latter experimental value is comparable to the one computed by Darkrim et al. [34] by molecular simulations with comparable thermodynamic conditions and for nearly the same SWNT configurations. The results summarized are correspond to a range of pressures between 0.04 and 12 MPa. In addition there exists relative difference in the nature and of

composition of samples used and also the measurements were performed with small amount of sample material on very sensitive apparatuses for long durations. During such a long time of measurement, care must be exercised to retain the physical condition and stability to avoid drifts of device.

The tabulated results also include few experiments were carried out at high temperatures as well, in such cases the contact of samples with hydrogen and in desorption, the magnitude of physisorption and chemisorption must be quantified. An interrogation about the accessibility of nanotubes to hydrogen molecules exist for two reasons: (i) when they are open, their diameters are of the order of molecular size and their length is of three orders higher; (ii) the space between tubes in the bundles has the same, high length/diameter ratio. It is known that different factors can influence the gas adsorption such as specific area of the materials [15], methods used to open the tubes [22, 24], the intercalation of metals [29, 30] in order to increase the gas uptake and the purification of the adsorbent [35] before any adsorption measurements.

3. Mode of adsorption of hydrogen

In spite of extensive results available on hydrogen uptake by carbonaceous materials the actual mechanism of storage still remains a mystery. The interaction may either based on van der Walls attractive forces (Physisorption) or on the overlap of the highest occupied molecular orbitals of carbon with occupied electronic wave function of hydrogen electron, overcoming the activation energy barrier for hydrogen dissociation (Chemisorption). The physisorption of hydrogen limits the hydrogen to carbon ratio to less than one hydrogen atom per two carbon atoms (i.e., 4.2 mass %), while in chemisorption the ratio of two hydrogen atom per one carbon atom is realized similar to the case of polyethylene. Physisorbed hydrogen has a binding energy normally of the order of 0.1 eV, while chemisorbed hydrogen has C-H covalent bonding, with a binding energy of more than 2-3 eV.

3.1 Molecular adsorption

Several reports, both experimental [16, 22, 24, 25] and theoretical [36, 37, 38] studies attribute the uptake of hydrogen atom to physisorption of hydrogen on carbon. However one has to keep in mind that (i) No evidence was found for an influence of the geometric structures of the nanostructured carbon on the amount of hydrogen adsorbed. (ii) Further, all attempts to open the nanotube and adsorb hydrogen inside the tube did not result in increase adsorption of hydrogen molecule, a conclusion drawn by Zuttel and Orimo [39]. (iii) Theoretical studies beyond well known physisorption lead to a large set of various maximum hydrogen – adsorption capacities. Most of the results were obtained under special conditions such as at 0 K or with high energy hydrogen atom implantation. No evidence was found for a higher density of hydrogen in and on carbon nanostructures, as compared with liquid hydrogen at ambient conditions.

3.2 Atomic adsorption

Various theoretical [38, 40, 41] and experimental studies [21, 22, 24, 33] deal with the chemisorption of hydrogen on carbon materials. Dillon et al., [22] and Orimo et al [42] in their studies observed two different peaks at two different temperatures during the desorption by TDS, and the temperature regions correspond to the existence of both physisorbed and chemisorbed states of hydrogen.

The existence of hydrogen in an intermediate state between physisorption and chemisorption is scientifically unclear in the literature till date. In this context, it is essential to take a careful view on significant gravimetric storage benchmarks and analyze them.

(i) 0.7 wt% experimental value of adsorption by activated also carbon and calculated for ideal slit pores with a specific surface of 2600 m^2/g at T=300 K and p=6 MPa [12], correspond to the atomic ratio H/C=0.085 means that 1 hydrogen atom is assigned to 11.8 atoms of carbon on average.

(ii) 6.5 wt% is the Department of Energy (DOE) benchmark of a system with necessary weight efficiency [14, 15]. The atomic ratio H/C is 0.83; this means that 1 H atom is assigned to 1.2 C atoms. The DOE benchmark requires almost one hydrogen atom per each carbon atom. This is similar to the C_2H_2 molecule, which has strong covalent bonding. Such a ratio for H_2 gas and available pore pattern of carbon nanotubes donot fit into the frame work for capillary forces built on van der Waals' interactions.

(iii) 67.5 wt% is the maximum value for storage in herringbone fibers [1]. The atomic ratio H/C is 25. This means that 25 H atoms are assigned to 1 C atom. Carbon is diluted in hydrogen, a reversal of what one would expect.

In the literature, the concept of interaction of atomic hydrogen is not clearly dealt with and if it becomes a facile process, one can achieve higher storage capacities. In order to achieve atomic hydrogen adsorption an activator is essential to dissociate the incoming hydrogen molecule and the dissociated hydrogen atoms can move on to carbon surfaces (spill over route). Therefore it is clear that carbon material cannot activate hydrogen in catalytic manner in its pure form. Metal or metal oxide doped carbon material offer high sorption capacities than their pure counterparts may fit into this concept.

Though the metal and metal oxide doped carbon nanotubes offer higher sorption capacities (~ 5-6 wt %), the desorption process occurs in two steps as mentioned earlier, consequently leading to lower usable capacity. This is due to the fact that M-H bonds are stronger than C-H bonds. In order to increase the user capacity ratio of carbon nanomaterials one has to find suitable activator that could split the incoming hydrogen gas molecules and transfer them to carbon sites. The essential criteria for such an activator can be listed as (i) the activator must possess equi-potential sites with that of carbon. Sites (ii) the sites in this activator should be easily hydridable and (iii) they should act as *catalytic sites* rather than mere *reactive sites* that lead to stiochemetric reaction

Heteroatoms such as N, P, S and B are identified as activators fulfilling these desirable attributes.

3.3 Theoretical Models

Experimental observations so far reported in literature claim uptakes anywhere between 0-68 wt percent. There are a number of theoretical studies probably aimed at resolving these contradictory reports on the quantity of hydrogen uptake by carbon nanotubes. In spite of various model calculations that have been carried out using a variety of computational techniques, the results are not yet converged. Essentially all the theoretical calculations so far reported in literature address one or the other aspects of the problem as follows:

1. Physisorption [43-49] or Chemisorption [50, 51] or Complex chemical pathway, though have been mentioned but not fully explained [52].
2.The *sites* at which adsorption occurs have not bet been identified. Whether hydrogen adsorption takes place inside the tube or outside the tube? The calculations seem to favour adsorption in between the tubes rather than inside the tubes. There are also indications that the arrangement of the tube also has an influence on the hydrogen adsorption. [24,43,53-55]
3.Influence of *geometrical* arrangements of carbon sites in the nanotubes has also been addressed. The reports dealing with adsorption of hydrogen inside the tubes consider various types of sites like, zigzag, armchair, chiral and show that hydrogen adsorption is favoured only in some specific sites [56-58].
4.There are also reports which deal with tube diameter, tube geometry like (5,5), (10,10) arrangements and show that adsorption is not only dependent on tube diameter, but also the structural arrangements of the carbon nanotubes. [54,59-62]
5.There are a few studies on the evaluation of interaction potential, which show that the adsorption strength is not adequate to account for any substantive chemisorption on carbon nanotubes. [44,48,63]
6.There are a few studies relating to effect of experimental variables like pressure and temperature as well as inclusion of hydrogen in the carbon frame work and the resultant effect of alteration of the carbon nanotube geometries [64,65]
7.Influence of additives on the carbon nanotubes towards sorption properties has also been addressed [52].
The current status of these attempts can be summarized as follows:

1. None of these studies could establish whether carbon nanotubes could adsorb hydrogen up to the extent DOE standards of 6.5wt% or 62% in terms of volumetric density.
2. None of these studies are able to unequivocally state whether hydrogen adsorption is preferred inside the nanotube or in the interstices between the tubes.
3. Above all, these studies have been somewhat silent on the sites on which hydrogen activation takes place before they are adsorbed by the carbon atoms of the nanotube. It is generally believed that the carbon sites present are unable to activate the hydrogen molecule [66].

4. Heteroatom containing CNTS – their relevance

The present investigation has therefore been undertaken with the following objectives and postulates.

- Hydrogen adsorption on carbon materials especially nanotubes, is possible only when it contains some sites wherein hydrogen molecule can be activated. Taking the clue from nature, it is postulated that the presence of heteroatoms in the carbon nanotubes may be the appropriate sites for activation of hydrogen.
- If heteroatom containing carbon nanotubes were to be one of the materials appropriate for hydrogen storage, then the questions to be addressed are: (i) what is the *gradation* of materials containing various heteroatoms? (ii) What are the geometrical *positions* in the nanotubes that are active?

In order to understand the interaction of hydrogen molecule in pure carbon nanotubes and heteroatoms (N, P, S and B) substituted carbon nanotubes, cluster model calculations have been carried out using Density Functional Theory (DFT).

5. DFT calculations on hydrogen sorption by heteroatom CNTS

From the analysis of the literature reports, it is clear that the hydrogen molecule is interacting at the interstitial positions of the carbon nanotubes than inside the nanotubes. The cluster model, which describes the interface of the three tubes, is considered in these studies (Fig.1). The terminal sites of the cluster are saturated with hydrogen in order to avoid the edge effect [58]. The geometry of the cluster is optimized using Universal Force Field (UFF 1.02) approach. The hydrogen molecule is allowed to interact with optimized cluster and the geometry of the system is optimized. Cerius2 software was used for force field calculations. Using force field optimized parameters, DFT single point energy and bond population calculations were done by Becke's three parameter hybrid functional with LYP correlation functional (B3LYP) and 6-31G(d) basis set using Gaussian98W for more accurate result [67]. Similar procedure was adopted for heteroatom substituted cluster models. The spin multiplicity of each calculation was selected to give reasonable chemical structure [68].

Though the geometry of graphite structure, consists of basal plane with C-C distance of 1.42 Å and valence angle of 120°, for embedding hydrogen atom C-H = 1.1 Å and valence angle of ∠HCC 120°, analysis of geometric parameters for each individual bond is not meaningful in our model since it is finite, the geometric parameters are not uniform for different bonds in the model. The intermolecular torsional angles are kept zero. The average values of all the C-C bond length and bond angles are given in Table 3. From this table, one can see that the cluster model optimized by force Field method is a reliable one.

The hydrogen molecule is allowed to interact with the carbon atoms of the unsubstituted nanotube and the dissociation energy of hydrogen was calculated (Table 4). The dissociation energy of hydrogen in its free state is 4.74 eV, and remains unaltered when inserted in between the pure carbon nanotubes (4.76 eV).

In order to study the influence of heteroatoms toward the activation of hydrogen, various heteroatoms (N, P and S) are substituted at different positions of the cluster as shown in Fig 1. The substitutional positions for heteroatoms as given in brackets (26,33,50,57,15,16) are chosen based on the fact that these interstitial positions offer minimum potential energy for the cluster as can be seen from the inlet diagram of potential energy curve. In the presence of heteroatoms, the dissociation energy of hydrogen molecule is considerably decreased compared to that of pure carbon nanotubes as can be seen from the values presented in Table 4. This indicates that heteroatom can activate the hydrogen molecule and its presence favors the dissociation of hydrogen.

This conclusion can also be arrived from the redox potential values of the couples involved. For instance, redox potentials of heteroatoms are higher than that of carbon (S/S^{2-}, N/N^{3-}, P/P^{3-}, C/C^{4-} are respectively, 0.171, 0.057, -0.111 and -0.132 V).These redox potential values shows that the reducing property of hetero atom is more than that of carbon. This explains why pure carbon is not able to activate hydrogen to the extent of decreasing its dissociation energy.

The same fact can be further independently supported by the Ellingham diagram which indicates that free energy of formation for N-H bond is more favourable than that of C-H bond. The bond length of the hydrogen molecule is elongated in heteroatom substituted carbon nanotube compared to that of pure carbon

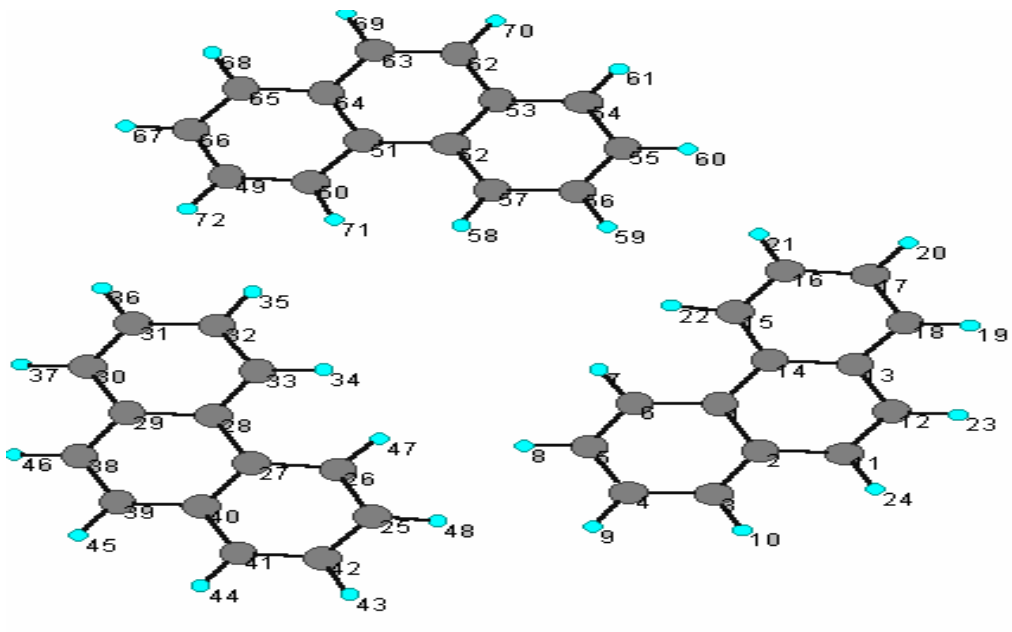

Fig 1. Cluster model (the hetero atoms are substituted in positions (26,33,50,57,15 and 6)

Table3. Geometric parameters of the minimized cluster

Cluster Model	Bond length (Å)					Bond angles (deg)			
	C_{25}-X^*_{26}	X_{26}-C_{27}	C_{27}-C_{28}	C_{28}-C_{33}	C_{33}-C_{32}	<C_{25}-X_{26}-C_{27}	<X_{26}-C_{27}-C_{28}	<C_{27}-C_{28}-C_{33}	<C_{28}-C_{33}-C_{32}
Unsubstituted	1.396	1.417	1.429	1.416	1.397	120.9	123.0	123.0	120.9
N-substituted	1.359	1.364	1.413	1.409	1.398	122.1	121.0	121.6	120.4
P-substituted	1.736	1.762	1.428	1.417	1.395	103.0	119.2	122.4	121.0
S-substituted	1.710	1.732	1.428	1.416	1.397	103.2	118.8	122.4	120.9

C-X* Bond length (Å)	Reported	Observed	<C-X-C Bond angle (deg)	Reported	Observed
Unsubstituted	1.385	1.396	<C-C-C	120.0	120.9
N-substituted	1.336	1.359	<C-N-C	117.4	122.1
P-substituted	1.768	1.710	<C-P-C	104.6	103.0
S-substituted	1.790	1.736	<C-S-C	99.6	103.2

*X= C, N, P and S

Table 4. Bond length and dissociation energy of hydrogen on the clusters.

Heteroatom	Mode of substitution	Bond length (H-H) (Å)	H_2 dissociation energy (eV)
Hydrogen	-	0.708	4.74
Un substituted CNT	-	0.708	4.76
Nitrogen substituted CNT			
	1 N + 1 H_2	0.84	0.31
(Each ring 1N)	3 N + 1 H_2	0.84	0.32
	3 N + 3 H_2	0.84	0.33
(Each ring 2N)	6 N + 1 H_2	1.08	0.56
	6 N + 3 H_2	1.08	0.50
Phosphorus substituted CNT			
	1 P + 1 H_2	0.81	2.06
(Each ring 1P)	3 P + 1 H_2	0.82	1.36
	3 P + 3 H_2	0.82	1.51
Sulphur substituted CNT			
	1 S + 1 H_2	0.81	0.27
(Each ring 1S)	3 S + 1 H_2	0.81	1.03
	3 S + 3 H_2	0.81	0.25

Table 5. Percentage Orbital contribution of atomic orbitals to HOMO level.(a Bonded hydrogen and b is terminal hydrogen)

Contribution		% of orbital contribution from HOMO							
		CNT – 0.2083 (eV)	CNT + $1H_2$ –0.1877 (eV)	Nitrogen substituted CNT (1N) -0.2062 (eV)	Nitrogen substituted CNT ($1N+1H_2$) -0.1396 (eV)	Phosphorous substituted CNT (1P) -0.2038 (eV)	Phosphorous substituted CNT ($1P+1H_2$) -0.1746 (eV)	Sulphur substituted CNT (1S) -0.1439 (eV)	Sulphur substituted CNT ($1S+1H_2$) -0.1305 (eV)
Carbon	s	0	0	0	3.09	0.01	0.69	0.01	1.67
	p	100	100	100	27.12	99.95	47.69	70.80	39.80
Heteroatom	s	-	-	0	19.06	0	11.06	0	0.25
	p	-	-	0	17.18	0.04	23.82	29.17	39.48
Hydrogen[a]	s	0	0	-	31.28	-	16.49	-	17.86
Hydrogen[b]	s	0	0	0	2.27	0	0.25	0.02	0.94

nanotubes, indicating that there is considerable activation of hydrogen molecule in heteroatom containing carbon nanotubes.

In order to determine the percentage orbital contribution, the wave function of the HOMO level of each cluster is analyzed. In the case of unsubstituted carbon nanotube, main contribution to the HOMO level is from 2p orbital of carbon (Table 5). On interacting with the hydrogen molecule, there is no contribution from H 1s orbital of hydrogen molecule to HOMO levels of cluster. This indicates that there is no bond formation between pure carbon nanotube and hydrogen molecule. While in the case of heteroatom-substituted nanotubes, the HOMO level consists of 2p orbital of carbon. On interaction with hydrogen molecule, the contribution comes from both H 1s orbital and p orbital of heteroatom, which unambiguously indicates that there exists bond formation between the heteroatom and hydrogen.
Even though the contribution comes from heteroatoms and hydrogen of substituted carbon nanotubes, the major percentage of contribution comes from carbon orbitals only. This elucidation provides us with the valuable clue that the incoming hydrogen molecule is activated at the heteroatom sites and further transfer to carbon sites as in the case of spill over mechanism, attributing to the fact that the existence of equi-potential sites favors such a facilitating situation. From the values of bond lengths, bond energies and wave functions, it is deduced that the presence of heteroatoms in carbon nanotubes activates hydrogen [69].

At this juncture, it is worthwhile to compare the yet another heteroatom, boron, substituted carbon nanotubes for hydrogen sorption studies. The reason for this separate treatment offered to boron substitution in CNT is not due to its acceptor capacity (since, other heteroatoms such as N, P, and S are potential electron donors) but the kind of mechanism by which the dissociation of hydrogen molecule take place as it is different from other heteroatom substituted CNTs.

Similar type of cluster model calculations were carried out for boron substituted carbon nanotubes and the results are presented in Table 6. As can be seen from the table, it is obvious that the presence of single boron atom substitution in carbon nanotube can not activate hydrogen molecule unlike the other heteroatoms considered. A minimum of two boron atoms are essential to activate the hydrogen molecule. In addition, the geometric position of the second boron atom is also a critical one in deciding the activation. While considering adjacent and alternative substitutional positions for boron atoms, the alternative substitution facilitates hydrogen activation to a greater magnitude. It can be substantiated that the B-B bond length is a key factor in the H-H bond activation. In the alternate positions for B atoms seems to favour for the activation of hydrogen as the bonding appears to be similar to what is obtainable in diborane.

6. Experimental evidence for activation of hydrogen by heteroatoms in CNT

Against this theoretical back ground and the proposed speculation regarding the capacity of heteroatoms as activator towards hydrogen molecule, the hydrogen adsorption process in heteroatom containing carbon nanotubes and pure carbon nanotubes has been examined. These preliminary experiments deal with nitrogen as the heteroatom for substitution in CNTs. Details of the methods of generating nitrogen containing carbon nano tubes can be seen elsewhere [70, 71].Hydrogen absorption characteristics

were evaluated by evolved gas analysis technique (EGA). In a typical experiment, the sample was loaded in the EGA chamber and was evacuated to10^{-6} Torr by heating the sample to 400K. Hydrogen was then admitted into the chamber while the sample was heated at a rate of 20 K /min to 693 K. The chamber was then cooled to room temperature and the chamber was again evacuated to 10^{-6} Torr. The sample was then heated at the same heating rate up to 693 K while simultaneously monitoring the gas evolved by mass spectrometer. It was seen that the carbon nanotube containing nitrogen gave a trace corresponding to mass number 17, indicating ammonia formation. The evolution of ammonia was pronounced above 473 K. However, in the case of carbon nanotubes obtained from polyphenyl acetylene gave only back ground signal corresponding to mass number 17. In order to ascertain this observation, a second hydriding of the nanotube prepared from polypyrrole was carried out in EGA unit and it was observed that the amount of ammonia evolved considerably decreased. By independent method, the evolution of ammonia was ascertained by spectrophotometry using Nessler's reagent. From the amount of ammonia evolved it has been estimated that CNTs containing 20 wt% of nitrogen is capable of taking up about 1 wt % of hydrogen. These studies gave clear indication that hydrogen activation is taking place on the heteroatoms of the carbon nanotubes. If this hydrogen could be transported to the carbon skeleton by spill over processes, it may be possible to achieve DOE standards of (6.5 wt %) hydrogen storage capacity in heteroatom containing CNTs[72]. This leads us to the devise methods for the surface transport of the hydrogen species on the carbon surface and also generates the necessary driving force for this migration on the carbon nanotube frame work. This possibility as well as the effect of nature of the hetero-atoms on the reactivity of carbon nanotubes is to be exploited in future.

7. Perceptions

The analysis and the results presented in this communication lead to the following perceptions for hydrogen sorption by carbon nanomaterials.

- At the present time materials known for hydrogen storage applications including metal hydrides, intermatallics, and alanates cannot be used for vehicular applications for the well known limitations in these systems. Carbon materials are considered as appropriate candidates due to their low mass density and their reversible storage ability at ambient conditions.
- Among the nanostructures of the carbon tubular geometry is attractive
- Though tubular structure with idealized slit pore size is preferred, carbon materials can only uptake the hydrogen molecule but it cannot activate the hydrogen molecule.
- Though chemical modifications of CNTs were attempted with metal/metal oxides. reversibility at ambient conditions cannot be realized.
- A rationale has been evolved to identify an activator with the desirable characteristics and heteroatoms such as (N, P, S and B) were identified as suitable candidates. A minimum of single atom substitution in the carbon skeleton is showing a notable adsorption capacity in the case of heteroatoms such as N, P and S. While, a minimum of two boron atom substitution at alternative positions is essential to achieve the significant activation.
    - However, optimization is required in gradation of activator and their geometrical positions on carbon skeleton.

- The heteroatoms can participate in the activation reactions either in a stiochiometric or catalytic way. It is obvious that only catalytic sites way is appealing for cyclability of the process.
- An estimate on the basis of residual valency leads to a possible realizable storage capacity of about 8 weight percent which probably is the experimentally realizable in the near future with appropriate activator and suitable modification of the surface properties of carbon.

Table 6. Dissociation energy of hydrogen in boron substituted carbon nanotubes

Heteroatom	**Mode of substitution**	**Bond length (H-H) (Å)**	**H_2 dissociation energy (eV)**
Hydrogen	-	0.708	**4.74**
Un substituted CNT	-	0.708	**4.76**
Boron substituted CNT			
	1 B + 1 H_2	0.82	**5.95**
	6 B + 1 H_2	0.79	**2.99**
2B Adjacent	2 B + 1 H_2	0.74	**2.59**
2B Alternate	2 B + 1 H_2	0.72	**1.26**

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