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The role of heteroatoms in carbon nanotubes for hydrogen storage

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Abstract

Carbon materials should have specific centers for hydrogen adsorption/absorption. The Universal Force Field and Density Functional Theory have been used to find the role of heteroatom substitution in carbon nanotubes as an activator. The effect of various heteroatoms like nitrogen, phosphorus, sulphur and boron for hydrogen activation and their geometrical positions has been identified for easy hydrogenation. This will be one of the possible centers where hydrogen adsorption/absorption is initiated.

Keywords: Carbon nanotubes; Adsorption; Absorption; Gas storage; Surface properties

1. Introduction

An efficient hydrogen storage medium is an inevitable component for the adoption of hydrogen as an energy carrier. Hydrogen storage in the solid matrices like metals, intermetallics, porous solids and carbon materials appears to be appropriate option. In the case of metals and intermetallics, the factors adverse to storage purpose are either limitation in storage capacity or the reversibility of stored hydrogen under favourable experimental conditions [1–3]. After the report by Rodriguez et al. that the carbon nanomaterials can store up to nearly 67 wt.% of hydrogen, the research in this area took a dramatic turn with a variety of investigations dealing with modification of carbon materials like metal loading, preparing carbon materials in different geometrical forms with phase purity and addition of metal oxides. However, none of these have unambiguously established that carbon nanomaterials can store hydrogen to the extent required by the Department of Energy (DOE) of United States (US) standards [4–12]. Different methods and various levels of computational studies have also been carried out in resolving these contradictory reports on the quantity of hydrogen uptake by carbon nanomaterials. Unfortunately, the results have not yet converged. Essentially, all the theoretical calculations so far reported in literature address one or the other aspects of the problem as follows. 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 has an influence on the hydrogen adsorption [13,14]. The reports dealing with adsorption of hydrogen inside the tubes consider various types of carbon nanotubes (CNTs) like, zigzag, armchair and chiral by their geometrical arrangements. However, the hydrogen adsorption is favoured only on some specific sites [15,16]. The reports which deal with tube diameter and tube geometry like (5, 5), (10, 10) arrangements show that the adsorption is not only dependent on tube diameter, but also on the structural arrangements of the carbon nanotubes [17,18]. They are unable to unequivocally point out whether hydrogen adsorption is preferred inside the nanotube or adsorption in the interstices between the tubes. Above all, these studies have been somewhat silent on the

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sites on which hydrogen activation takes place before they are adsorbed on the carbon atoms in the nanotubes.

Recently, inelastic neutron scattering experiments have been carried out to find the site and strength of hydrogen binding in carbon materials at low temperatures. The results show that binding strength of hydrogen molecule is almost the same for all kinds of carbon materials and the magnitude of interaction is around 5 kJ/mol [19,20]. These studies lead to the conclusion that condensing the hydrogen molecule does not lead to any interaction with the carbon surface. It is generally believed that, carbon sites are unable to activate the hydrogen molecule. There must be strong interaction between the hydrogen and carbon surface (chemisorption) to give rise to high storage capacity. For chemisorption, the hydrogen molecule should be activated. Thus, the need for an activator for hydrogenation in carbon materials is realized and the activator should be easily hydridable than carbon and facilitate the migration of the dissociated hydrogen to equipotential carbon surface. While considering these aspects, heteroatoms such as N, P, S and B seem to be promising activators in heteroatom containing carbon materials for hydrogen storage application.

The aim of this work is to examine the effect of substitution of heteroatom in carbon nanotube (CNT) network for hydrogen activation and the mechanism of hydrogen migration. To study the activation of hydrogen by the heteroatoms, we apply a combined Universal Force Field (UFF) and Density Functional Theory (DFT) methods. In the later stage, DFT method has been utilized to study the reaction mechanism by using simple clusters chosen from the reactive part of the CNT for accurate results.

2. Model design and methodology

In our present study, typically three Single Walled Carbon nanotubes (SWNTs) of armchair type (4,4) with each tube having 32 carbon atoms making tube diameter of 5.56 Å have been considered. First, we have carried out full geometry optimization of one SWNT with DFT by using Becke's three parameter hybrid functional with LYP correlation functional (B3LYP) and 6-31G (d,p) basis set [21,22]. The terminal sites of the CNT cluster are saturated with hydrogen atoms in order to avoid the edge effect [23]. This optimized SWNT has been utilized to construct an interface with three nanotubes of interstitial site 3.64 Å (the distance between two tubes) as shown in Fig. 1a. The valency of each element is taken into consideration for the calculations. It is reported in literature that the hydrogen molecule has preferential interaction at the interface of the carbon nanotubes [24]. The model describes the interface of the three carbon nanotubes that has been optimized with Universal Force Field parameter (UFF 1.02) [25] in Cerius^2 software.

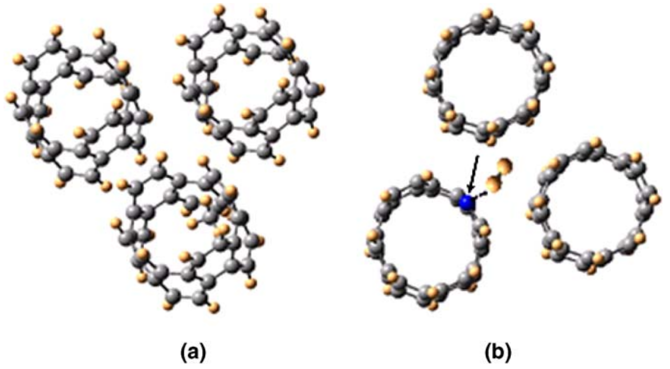

Fig. 1. (a) The side view of the UFF optimized CNT (4,4) cluster taken for the study, where the terminal positions are saturated with hydrogen. (b) Top view of the heteroatom (arrow indicated ball) containing CNT cluster with the hydrogen molecule interaction.

The geometric parameters of the cluster models minimized by force field method (Table 1) coincide well with the normal bond length values. The intermolecular torsions are all zero indicating that the cluster model minimized by Force Field method can be reliable. The hydrogen molecule is allowed to interact at the top of cluster as shown in Fig. 1b. The interactions are found to be effective on the top of carbon atoms rather than on the top of carbon hexagon cluster [16]. Computations using DFT have been carried out on optimized configuration obtained using UFF. The single point energy and bond population analysis were carried out by DFT on the optimized configurations by using B3LYP/6-31G (p,d) basis set. To reduce the computational cost combined UFF/DFT method has been utilized to find the effect of heteroatom on hydrogen activation as this combined method have been effectively utilized for such large systems [16]. The substitutional positions for heteroatoms in the CNT cluster model have been chosen based on the fact that the interstitial position offers

Table 1
The geometric parameters of the CNT cluster optimized by employing Universal Force Field (UFF 1.02) method

Cluster model	Average bond length (Å)			Average bond angles (°)			
	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-substituted CNT	1.409	1.336	1.359	117.4	122.1	121.0	121.6
P-substituted CNT	1.417	1.768	1.710	104.6	103.0	119.2	122.4
S-substituted CNT	1.416	1.790	1.736	99.6	103.2	118.8	122.4
B-substituted CNT	1.420	1.486	1.431	106.6	109.6	120.5	120.8

minimum potential energy for the cluster and our calculations also show the same. The stability of the substituted CNT plays a crucial role in hydrogenation reaction and they seem to be stable by showing the minimum energy difference between pure CNT and the substituted CNT.

To study the reaction mechanism a simple cluster model with 14 carbon atoms has been taken, which is the terminal and reactive part in the SWNT for the hydrogen interaction and hydrogenation as shown in Fig. 1a. The ends of the cluster are saturated with hydrogen in order to avoid the boundary effect [23]. The cluster was fully optimized with density functional B3LYP method with 6-31G (p,d) basis set. The geometrical parameter of the simple cluster shows planar in nature. Here we have considered this simple cluster only to study the reaction of hydrogen with the carbon surface and the structural effect like tube curvature are not taken into the consideration. The nature of stationary points thus obtained was characterized by frequency calculations. All the transition states corresponding to hydrogen migration were located and characterized as saddle points using the frequency calculations. It was found to possess one imaginary frequency at the same levels of theory. The geometric parameters and the nature of the imaginary frequencies were examined using the graphical interface program, Gauss View 03. All the DFT calculations were performed using Gaussian 03 in a cluster of IBM Linux machine [26].

3. Results and discussion

The total energy, H–H bond distance and the dissociation energy of hydrogen molecule obtained are given in Table 2. The points that emerge out of the results are, (i) Hydrogen activation has been favoured by a decrease in the hydrogen dissociation energy in the case of substitution of heteroatoms like N, P and S. The dissociation energy of hydrogen in its free state is 4.76 eV, and remains unaltered when it is placed in between the pure carbon nanotubes (4.51 eV). Whereas it is altered to 0.13, 0.22 and 2.33 eV for S, N, and P substituted CNTs, respectively. Though the calculated dissociation energy values are unrealistically small, they definitely indicate that the dissociation of hydrogen molecule is a facile process on heteroatom substituted carbon nanotubes. Even though the calculated dissociation energy is small, the process of hydrogen storage may involve other barriers including mass transport and hence could not be achieved at such low energies.

The lowering of this dissociation energy of hydrogen molecule can be explained on the basis of redox potential values of the respective redox 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 vs SHE). 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 CNT compared to that of pure CNT, indicating that there is considerable amount of activation of hydrogen molecule in heteroatom containing CNTs. (ii) Substitution of boron atom in the CNT shows interesting results. Single boron substitution cannot activate the hydrogen molecule. Two boron atoms are essential for the hydrogen activation. The dissociation energy of hydrogen for single boron substitution is 5.95 eV where as when two boron atoms are substituted in adjacent positions, the dissociation energy is reduced to 3.88 eV. It is further decreased to 0.28 eV when two boron atoms are substituted in the alternate positions. This implies substitution of boron at alternate positions is more favourable for hydrogen activation rather than substitution at adjacent positions. It can be substantiated that B–B bond length is a key factor for H–H bond activation. An alternate position of B substitution seems to be favourable for the activation of hydrogen, where in bonding appears to be similar to that of diborane [27,28].

The orbital contributions have been analyzed by taking the HOMO level of CNT cluster. In the case of

Table 2

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

Substitution	Total energy (Hartrees)	Bond length H_1–H_2 (Å)	Dissociation energy (eV)
Hydrogen	−1.175	0.708	4.76
Unsubstituted CNT	−3686.5502	–	–
Unsubstituted CNT + H_2	−3687.7161	0.776	4.51
Nitrogen substituted CNT	−3702.5908	–	–
Nitrogen substituted CNT + H_2	−3703.5989	0.835	0.22
Phosphorus substituted CNT	−3989.1694	–	–
Phosphorus substituted CNT + H_2	−3990.2550	0.815	2.33
Sulphur substituted CNT	−4046.0020	–	–
Sulphur substituted CNT + H_2	−4047.0067	0.817	0.13
Boron substituted CNT	−3671.7254	–	–
Boron substituted CNT + H_2	−3672.9440	0.818	5.95
Two boron substituted CNT (adjacent)	−3658.6666	–	–
Two boron substituted CNT (adjacent) + H_2	−3659.8092	0.913	3.88
Two boron substituted CNT (alternate)	−3659.3491	–	–
Two boron substituted CNT (alternate) + H_2	−3660.3594	0.928	0.28

Table 3
The percentage orbital contribution of the HOMO level of the pure CNT and heteroatom substituted CNT before and after hydrogen interaction

% of orbital contribution from HOMO level (energy in Hartrees)	Carbon		Heteroatom		Hydrogen	
					b[a]	t[a]
Contribution	s	p	s	p	s	s
Unsubstituted CNT (−0.1612)	0	100	–	–	–	–
Unsubstituted CNT + H_2 (−0.1613)	0	100	–	–	0	0
Nitrogen substituted CNT (−0.1617)	1	98.30	0	0.18	–	0.56
Nitrogen substituted CNT + H_2 (−0.1371)	0.52	37.39	1.37	31.91	26.66	2.15
Phosphorus substituted CNT (−0.1611)	1	96.85	0	1.71	–	0.53
Phosphorus substituted CNT + H_2 (−0.1516)	1	85.62	0.04	8.06	4.83	0.49
Sulphur substituted CNT (−0.1375)	1	76.87	0	21.17	–	1.16
Sulphur substituted CNT + H_2 (−0.1207)	0.45	41.80	0.35	41.65	14.87	0.88
Boron substituted CNT (−0.1576)	1	94.87	0	3.59	–	0.5
Boron substituted CNT + H_2 (−0.1534)	1	96.26	0.10	1.12	1	0.54
Two boron substituted CNT (adjacent) (−0.1568)	1.01	96.98	0	1.53	–	0.5
Two boron substituted CNT (adjacent) + H_2 (−0.1564)	6.26	88.34	0.10	4.67	0.28	0.4
Two boron substituted CNT (alternate) (−0.1540)	12.56	80.41	0.60	5.49	–	1
Two boron substituted CNT (alternate) + H_2 (−0.1572)	14.67	73.93	0.73	4.48	5.32	0.86

[a] Where b—bonded hydrogen to heteroatom and t—terminal hydrogen in the cluster.

unsubstituted CNT, the main contribution to the HOMO level is from 2p orbital of carbon (Table 3). There is no contribution from the terminal hydrogen present in the cluster, which clearly shows that terminal hydrogen used to saturate the valency will not affect the results obtained.

On interacting with the hydrogen molecule with CNT cluster, there is no contribution of H 1s orbital to HOMO values. This indicates that there is no bond formation between the CNT and hydrogen molecule. In the case of heteroatom substituted CNT, the HOMO level contribution is from 2p orbital of the carbon. Upon interaction with hydrogen molecule, the contribution to HOMO level comes from both H 1s orbital and the p orbitals of heteroatom, which unambiguously shows that there exists bond

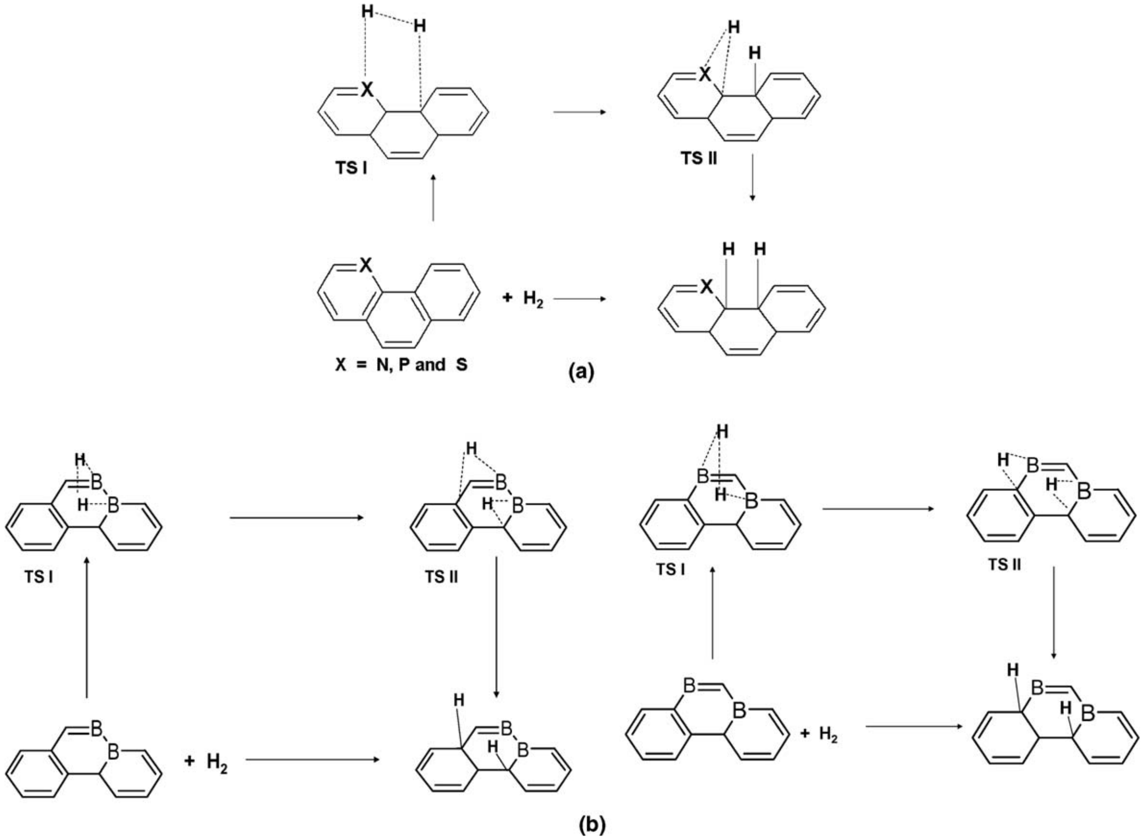

Fig. 2. (a) The proposed mechanistic path way for hydrogenation of heteroatom substituted CNTs. (b) The mechanistic pathway for the hydrogenation of boron substituted CNTs in the adjacent and alternate positions.

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

Substitution	E_a I (eV)	E_a II (eV)	H_1–H_2 (Å)	X–H (Å)	C–H_1[a] (Å)	C–H_2[a] (Å)
Unsubstituted CNT cluster	10.02	–	0.71	–	–	–
Nitrogen substituted CNT cluster	3.84	4.58	1.45	1.11	1.70	1.94
Phosphorus substituted CNT cluster	3.81	3.99	1.51	1.61	1.27	2.33
Sulphur substituted CNT cluster	3.65	4.85	1.50	1.75	1.24	2.40
Two boron substituted CNT cluster (adjacent)	2.22	2.98	1.95	1.31	2.59	2.72
Two boron substituted CNT cluster (alternate)	1.5	2.33	2.95	1.47	1.47	2.34

Where E_a = TE (transition state) − TE (reactant).
[a] Shortest C–H bond distance.

formation between the heteroatom and hydrogen molecule. The valuable information obtained is that the incoming hydrogen molecule is activated at the heteroatom sites and further gets transferred to the carbon sites, as in the case of spill over mechanism which is due to the fact that the existence of equipotential sites favours such a facilitating situation. It is deduced from the bond length, bond energies and wave function values that the presence of heteroatoms in carbon nanotubes activates hydrogen and leads to adsorption of hydrogen.

The calculation of transition state parameters show that the reaction proceeds from one minimum to another minimum via an intermediate maximum. The movement of hydrogen from the heteroatom can be conceived by the transition state theory calculation as shown in Fig. 2. The activation energy (ΔE_a) for this process has been obtained using the calculated parameters. The results are tabulated in Table 4 and the energy profile diagram of the mechanistic path way for the substitution of heteroatoms like N, P and S are given in Fig. 3.

From the results, it is clear that the energy for the activation of hydrogen in the first transition state is lower for the heteroatom containing CNT compared to pure CNT. In addition, the subsequent transfer of hydrogen to carbon is a facile process in presence of heteroatom. Boron containing CNT with boron atom located at alternate positions shows considerable reduction in the overall activation barrier compared to boron located at the adjacent positions. The proposed mechanism is given in Fig. 2b. These results support the contention that heteroatoms are the appropriate sites for hydrogen activation. On our earlier experimental results [29] related to ammonia evolution are ascertained by hydriding the nitrogen containing CNTs compared to the unsubstituted CNTs. In recent results it has been shown that high hydrogen adsorption is possible by the substitution of heteroatom like nitrogen in the carbon frame work [30]. These results further support the results of the present theoretical calculations.

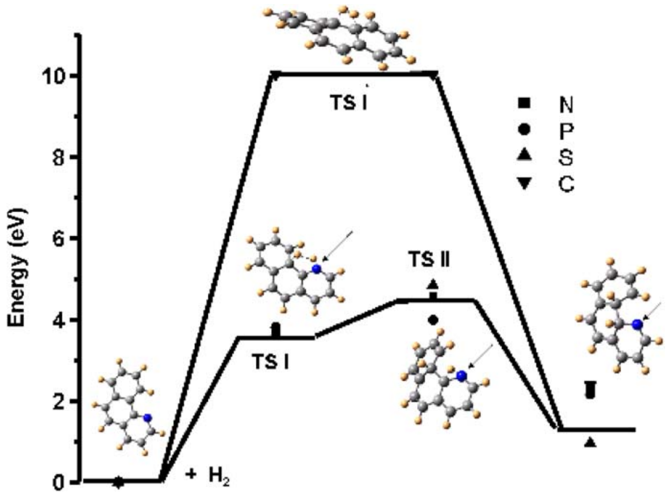

Fig. 3. The transition state energy profile of the heteroatom substituted CNTs cluster calculated by DFT method (B3LYP) with 6-31G (p,d) basis set (the arrow indicated balls are heteroatoms like N, P and S).

4. Summary

The present studies thus have shown that hydrogenation of CNTs requires activation centers and the heteroatom containing CNTs are able to activate the hydrogen in a facile manner compared to pure CNTs. For effective hydrogenation and hydrogen storage these heteroatoms should be incorporated geometrically and chemically into the carbon network.

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