Can Heteroatoms be the activators for hydrogen storage in carbon nanotubes?

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Introduction

The studies on the storage of hydrogen took a dramatic turn in 1998-99, when 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) of the most hydrogenated carbon compound namely CH_4 where the hydrogen to carbon weight ratio is 0.25 g H_2/g C. Subsequently there have been various reports in literature to substantiate these observations [3-7] and none of them in any way could realize the expected (DOE standards) 6.5 weight percent leave alone repeating the original adsorption capacity claimed.

The present investigation has therefore been undertaken with the following objectives and postulates (i) 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 and (ii) If heteroatom containing carbon nanotubes were to be one of the materials appropriate for hydrogen storage, then the questions to be addressed are: (a) what is the gradation of materials containing various heteroatoms? (b) 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). From the analysis of the reports in literature, 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).

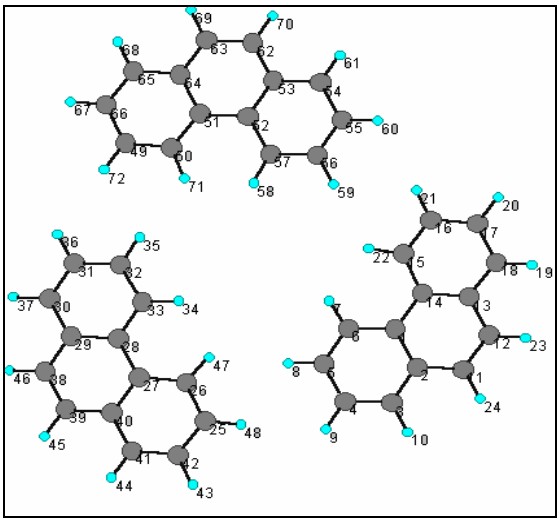

Figure 1. The Cluster model (the heteroatoms are substituted in positions (26,33,50,57,15 and 6)

Theoretical methods

The terminal sites of the cluster are saturated with hydrogen in order to avoid the edge effect [8]. 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. Similar procedure was adopted for heteroatom substituted cluster models.

Results and discussions

The hydrogen molecule is allowed to interact with the carbon atoms of the unsubstituted nanotube and the dissociation energy of hydrogen was calculated (Table 1). The dissociation energy of hydrogen in its free state is 4.74 eV, and remains unaltered when it is placed 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 (26,33,50,57,15,6) are chosen based on the fact that these interstitial positions offer minimum potential energy for the cluster. 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 1. 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). 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 nanotubes, indicating that there is considerable activation of hydrogen molecule in heteroatom containing carbon nanotubes.

In order to understand the role of hetero atoms in hydrogen activation in carbon nanotubes the calculations have been carried out to estimate the value of activation energy value of each of the steps of hydrogen activation and migration (Fig 2) within the framework of Transition state theory and the essential results are given in Table 2. These results also support our contention that heteroatoms may be appropriate for activation of hydrogen on carbon nanotubes.

Conclusions

Heteroatom containing carbon nanotubes are able to activate the hydrogen compared to pure carbon nanotubes. This activated hydrogen can migrate to other sites and opens up another avenue in the search of material for the hydrogen storage.

Table 1. The 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

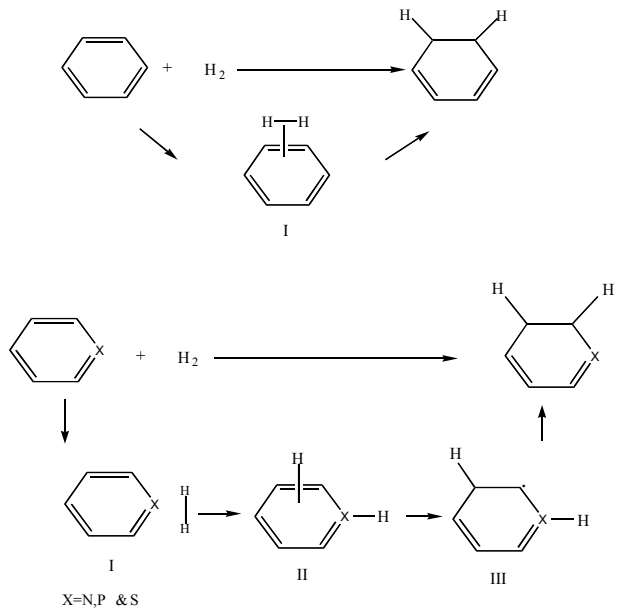

Figure 2. Proposed transition state path ways for hydrogen storage in carbon nanotubes and hetroatom (N,Pand S) containing carbon nanotubes.

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Table 2. The transition state optimized parameters for various clusters and energy of activation for each pathway.

Substitution	Ea[c] I (eV)	Ea II (eV)	Ea III (eV)	H-H (Å)	X-H (Å)	C_2-H[b] (Å)	C_2-H[a] (Å)	C_3-H (Å)
Carbon	15.08	-	-	0.65	-	-	-	-
Nitrogen	3.91	8.50	1.30	1.69	1.19	1.39	1.16	1.13
Phosphorus	3.15	8.84	2.24	2.11	1.62	1.74	1.12	1.26
Sulphur	4.27	9.30	3.58	2.18	1.51	2.32	1.58	1.67

a - after migration, b - before migration, c - Ea=TE (each transition state) – TE (reactant)