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Hydrogen dissociation on diene-functionalized carbon nanotubes

Javad Beheshtian · Ali Ahmadi Peyghan · Zargham Bagheri

Abstract Chemical functionalization of a zigzag carbon nanotube (CNT) with 1, 3-cyclohexadiene (CHD), previously reported by experimentalists, has been investigated in the present study using density functional theory in terms of energetic, geometric, and electronic properties. Then, the thermodynamic and kinetic feasibility of H_2 dissociation on the pristine and functionalized CNTs have been compared. The dissociation energy of the H_2 molecule on the pristine and functionalized CNT has been calculated to be about −1.00 and −1.55 eV, while the barrier energy is found to be about 3.70 and 3.51 eV, respectively. Therefore, H_2 dissociation is thermodynamically more favorable on the CNT-CHD system than on the pristine tube, while the favorability of the dissociation on the pristine tube is higher in term of kinetics.

Keywords Carbon nanotubes · DFT · Functionalization · Hydrogen

Introduction

Molecular hydrogen adsorption and dissociation on catalysts are of great industrial importance in hydrogenation

J. Beheshtian
Department of Chemistry,
Shahid Rajaee Teacher Training University,
P.O. Box: 16875-163, Tehran, Iran

A. Ahmadi Peyghan (✉)
Young Researchers Club, Islamic Azad University,
Islamshahr Branch,
Tehran, Iran
e-mail: ahmadi.iau@gmail.com

Z. Bagheri
Physics Group, Science Department, Islamic Azad University,
Islamshahr Branch, P.O. Box: 33135-369, Islamshahr, Tehran, Iran

and dehydrogenation processes [1–3]. In these reactions, H_2 is dissociated into active hydrogen atoms, adsorbed on the catalyst surface. Understanding the elementary processes of the H_2 dissociation is crucial in design and development of novel high efficiency catalysts and also in hydrogen storage materials. Hydrogen sorbent materials can be divided into two main categories, including those which the hydrogen molecule is dissociated and chemically bonded to their surface as hydrides; and those that the hydrogen molecules are physisorbed on their surface [4]. In recent years, considerable research efforts have been devoted to investigation of metals (e.g., Mg, Cr, Mn, etc.) and their alloys for hydrogen dissociation due to their high hydrogen storage capacities by weight and low cost [5–8]. One of the main disadvantages of metal-based hydrogen dissociating alloys is the ease of formation of a closed oxide layer on their surface which impedes hydrogen adsorption [9]. This phenomenon is underlined by the observation that adsorption kinetics of any metal hydride system strongly depends on sample pretreatment and residual gaseous contaminations such as O_2, H_2O, or CO [10].

Carbon nanotubes (CNTs) have attracted great attention since their discovery in 1991 [11] because of their marvelous structure, nanometer dimensions, high stability, and excellent conductivity or semiconductivity [12]. Recent reports have shown that the hydrogen adsorption potential of CNTs falls short of the requirements of practical applications. However, physisorption on crude CNTs may not be suitable for hydrogen dissociation [13, 14].

Now, chemically modified (i.e., functionalized) nanotubes are being extensively promoted as one of the solutions to overcome these problems. Chemical functionalization is a commonly used method to tailor the physical and chemical properties of the nanotubes. It has been reported that covalent functionalizations using adatoms, organic molecules,

and functional groups can effectively change the electronic structures, hydrogen adsorption behavior, magnetic properties, and solubility of the nanotubes [15–18]. The hydrogen storage capacity of boron-substituted CNTs has been investigated by Sankaran et al. [19], observing a maximum of 2 wt% hydrogen storage capacity. Also, hydrogen storage properties of the purified CNT and nanocrystalline platinum-dispersed CNT have been investigated in the pressure range of 1–100 bar, at 298 and 125 K. Based on the obtained results, the platinum-dispersed CNT showed a hydrogen uptake up to 3.03 wt% at 125 K and 78 bar [20]. Lee et al. [21] have activated the CNTs using CO_2 in the temperature range of 723–1323 K and found that the hydrogen storage capacity has been enhanced to 0.78 wt% by increasing the temperature to 1123 K.

CNT can behave as an electron-deficient dienophile in the Diels-Alder reactions with numerous electron-rich dienes. Electron-rich dienes are also reagents of choice for [2+4] cycloaddition. Interactions between CNTs and a series of diene molecules such as 1, 3-cyclohexadiene (CHD) have been experimentally investigated by Sumanasekera et al. [22]. In the present work, [2+4] Diels-Alder reactions of one CHD with CNT will be theoretically investigated

based on analyses of structure, energies, HOMO–LUMO gaps (E_g), stability, etc. using density functional theory (DFT). Our results are likely to be useful for further studies related to CNT functionalization and construction of CNT-based materials.

Computational methods

Geometry optimizations, natural bond orbital (NBO), and density of states (DOS) analyses were performed on a (6, 0) zigzag CNT (constructed of 84 carbon atoms), and different F-CNTs (functionalized CNTs) at B3LYP/6-31G* level of theory as implemented in GAMESS suite of program [23]. This level of theory is a popular approach which has been commonly used for nanotube structures [24–28]. In order to avoid boundary effects, atoms at the open ends of the tube have been saturated by hydrogen atoms. The dissociation energy (E_{dis}) of the H_2 molecule has been defined as follows:

$$E_{dis} = E(H_2/CNT - CHD) - E(CNT - CHD) - E(H_2), \quad (1)$$

where $E(H_2/CNT\text{-}CHD)$ is the total energy of the adsorbed H_2 molecule on the functionalized CNT sur-

Fig. 1 Partial structure of CNT and its DOS. Distances are in Å
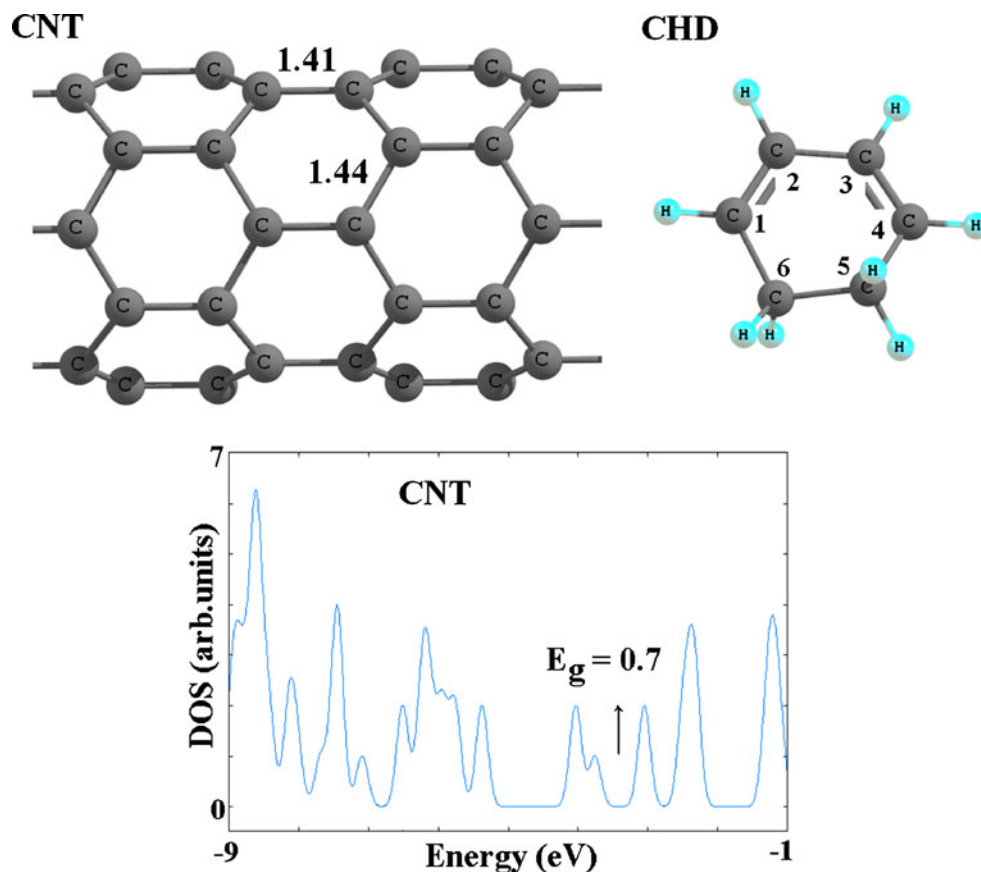
face, and E(CNT-CHD) and $E(H_2)$ are total energies of the CNT-CHD and the H_2 molecule, respectively. Negative value of E_{dis} indicates the exothermic character of the dissociation. Quantum- mechanical descriptors such as electron affinities, ionization potentials, and global hardness have been calculated and compared for the optimized structure.

Results and discussion

Functionalization of CNT

Figure 1 shows the optimized geometries of the pristine CNT and CHD molecule. Two types of C-C bonds can be identified in CNT, one with the bond length of 1.41 Å and in parallel with the tube axis, and another with the bond length of 1.44 Å, diagonal to the tube axis. The length and diameter of the optimized bare CNT have been computed to be about 15.7 and 4.8 Å. From the DOS plot of the bare CNT (Fig. 1), it can be concluded that it is a semi-metallic material with an E_g of 0.70 eV.

In order to investigate chemical functionalization of the exterior surface of the CNT by CHD molecule, we have put C1 and C4 carbon atoms of the molecule (Fig. 1) atop the parallel and diagonal C-C bonds of the CNT, and then it has been assumed that the [4+2] cycloaddition has occurred. The main purpose is to study the thermodynamic feasibility of the reaction which has been previously reported in experimental works [22]. We have defined the energy of reaction, E_r, in the usual way as follows:

$$E_r = E(CNT - CHD) - E(CNT) - E(CHD), \qquad (2)$$

where E(CNT-CHD) corresponds to the energy of the CNT functionalized by CHD, E(CNT) is the energy of the isolated CNT, and E(CHD) is the energy of the single CHD molecule. The E_r values corresponding to the functionalization of CHD are calculated to be +0.68 and −0.41 eV for diagonal and parallel bond addition,
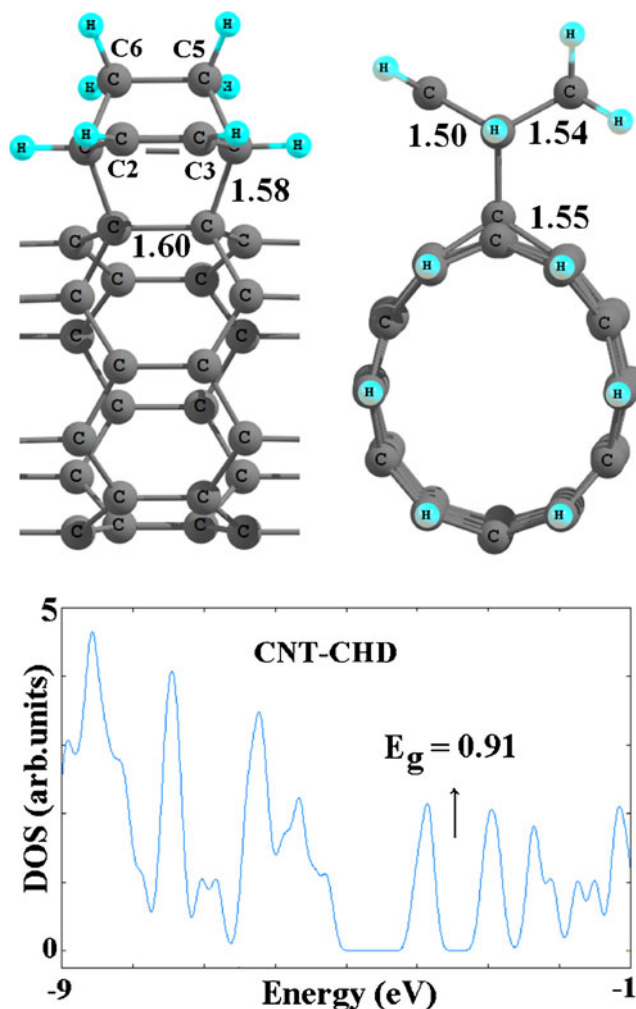
Fig. 2 Side and top views of optimized configuration of CHD-functionalized CNT and its DOS. Distances are in Å

respectively, indicating the exothermicity of the functionalization in the case of parallel bond addition. More detailed information including values of E_g and the charge transfer (Q_T) has been listed in Table 1. As shown in Fig. 2, two carbon atoms of CHD are bonded to the carbon atoms of the parallel bond so that the length of the newly formed C-C bonds are about

Table 1 Reaction energy of CHD with CNT (E_r, eV), Mulliken charge on the adsorbed molecule (Q_T), the HOMO, LUMO and gap (E_g) in between energies (eV) and energy of Fermi level (E_{FL}, eV) for CHD/CNT complex

*Complex	E_r	Q_T (e)	E_{HOMO}	E_{FL}	E_{LUMO}	E_g	ΔE_g(%)	**η
CNT	–	–	−3.75	−3.40	−3.05	0.70	–	0.35
Parallel	−0.41	0.046	−3.96	−3.50	−3.05	0.91	30.0	0.45

*See Figs. 1 and 2.

** Hardness calculated as ($0.5 \times E_g$)

1.58 Å, with a charge transfer of 0.046 e from the adsorbate to the tube.

Furthermore, the reaction induces a locally structural deformation to the CNT. For example, one of the angles in hexagonal ring is significantly decreased from 113.7° to 98.8°, and the adsorbing parallel bond is pulled outward from the tube surface with the bond length increasing from 1.41 Å to 1.60 Å. The natural bond orbitals (NBO) analysis has indicated that such structural deformation is attributed to the rehybridization of the adsorbing C atoms from sp^2 to nearly sp^3. As shown in Fig. 1, isolated CHD molecule has almost planar geometry. When the CHD is attached to the CNT, significant out-of-place displacement of the C atoms is observed, where C3–C4–C5 angle is reduced from 120.4° to 109.2°, thus the plane of the CHD is bent due to the intramolecular steric repulsion.

DOS plot of the stable configuration of the CNT-CHD (Fig. 2) shows a considerable change, indicating that the electronic properties of the CNT are very sensitive toward the CHD adsorption. Further inspection of the DOS plot reveals that the conduction levels in the functionalized CNT is approximately similar to that of the pristine form, while the valence levels significantly shift upward so that the E_g value of the tube is dramatically increased from 0.70 to 0.91 eV (by about 30 % change) after the functionalization. Also, as it can be seen in Table 1, the side functionalization increases the global hardness (η) from 0.35 in the pristine CNT to 0.45. Therefore, our computational results demonstrate that the CHD addition to the CNTs provides a promising way for altering their properties and structure. It has also been found that further chemical functionalization of the CNTs results in apparent disturbance to their electronic properties.

Hydrogen dissociation on the pristine and functionalized CNTs

In the next step, we have investigated the dissociation of H_2 molecule on the pristine and functionalized CNTs, exploring how the CNT functionalization with CHD influences the hydrogen dissociation. To this end, two different dissociation sites for the pristine CNT (top of

Fig. 3 Optimized **a** diagonal and **b** parallel configurations of H_2 dissociation on pristine CNT and their DOS. Distances are in Å
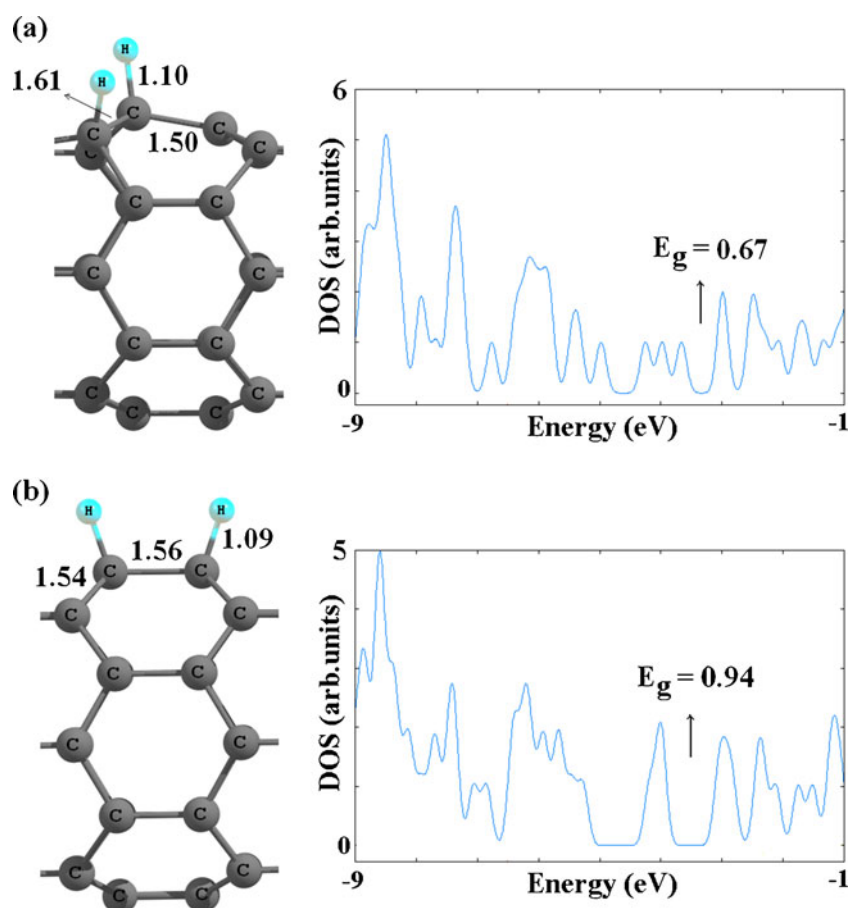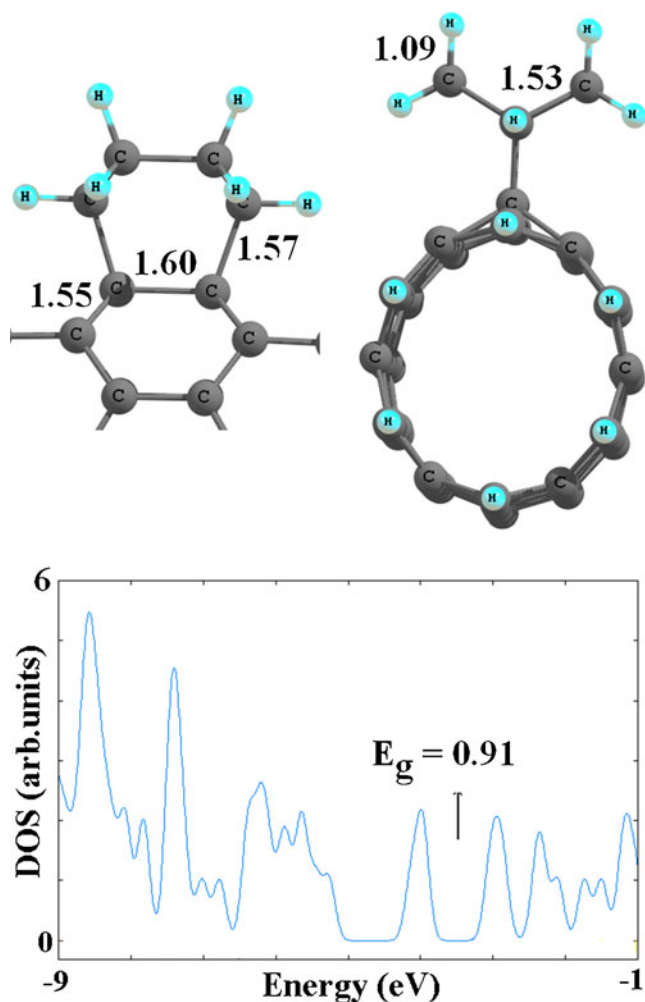
Fig. 4 Side and top views of optimized configuration of H₂ dissociation on CHD-CNT and its DOS. Distances are in Å

different bonds, Fig. 3a and b) and one for the functionalized CNT (top of C2-C3 double bond in adsorbed CHD, Fig. 4) have been considered. The E_g, E_{dis}, and Mulliken charge analysis are summarized in Table 2. The results show that the adsorption is site selective and the H₂ prefers to be dissociated on the top of the

parallel bond of the pristine CNT with E_{dis} of −1.00 eV. In this configuration (Fig. 3b), the length of newly formed H-C is about 1.09 Å, indicating that the interaction is very strong and a new covalent bond has been formed. This E_{dis} is significantly higher than that of the diagonal site (−0.25 eV). However, we have found that the H₂ dissociation on C2-C3 double bond (in the adsorbed CHD) is the most favorable dissociation site (−1.55 eV) with rather a significant Mulliken charge transfer of 0.255 e from the H₂ to the C2-C3 bond. This phenomenon can be rationalized by the fact that there is delocalized π electron in the surface of the pristine CNT and H₂ dissociation can locally disrupted the aromaticity. Based on the NBO analysis, C2-C3 bond is elongated after the adsorption process from 1.33 to 1.55 Å. It suggests that this bond may be activated using the substrate of CNT-CHD as a catalyst for helping the conversion of H₂ to H atoms.

Based on the calculated DOS, our results also indicate that dissociation of the hydrogen on walls of the CNT-CHD does not make significant changes in the electronic properties of the nanotube (Fig. 4). Therefore, it can be concluded that the dissociation of H₂ molecule cannot essentially change the electrical conductance of the CNT-CHD, suggesting that CNT-CHD has no capability of generating an effective response to the H₂ molecule. In other words, this reaction is electronically *harmless*.

Subsequently, kinetic favorability of the H₂ dissociation on the parallel bond of the CNT and also on the functionalized one has been explored. As shown in Fig. 5, it is necessary for the H₂ molecule to overcome the energy barrier so that the reaction can progress. In both cases, the H-H bond becomes so weak in TS structure so that the bond length increases from 0.74 to 1.31 Å (for the pristine CNT) and 1.43 Å (for the CNT-CHD) and two new C-H bonds are formed. The activation energies of the H₂ dissociation for the pristine CNT and CNT-CHD are about 3.51 and 3.70 eV (Fig. 5), respectively. Based on the calculated results,

Table 2 Dissociation energy of H₂ on pristine CNT and CHD/CNT (E_{dis}, eV), Mulliken charge on the adsorbed molecule (Q_T), the HOMO, LUMO and gap (E_g) in between energies (eV) and energy of Fermi level (E_{FL}, eV) for different H₂ dissociation

*Complex	E_{dis}	E_{HOMO}	E_{FL}	E_{LUMO}	E_g	$\Delta E_g(\%)$	η
Parallel CNT	−1.00	−3.99	−3.52	−3.05	0.94	34.2	0.47
Diagonal CNT	−0.25	−3.66	−3.32	−2.99	0.67	4.2	0.33
CHD/CNT	−1.55	−3.95	−3.49	−3.04	0.91	0.0	0.45

*See Figs. 3 and 4

Fig. 5 Structure and energy diagram for H_2 dissociation on **a** pristine CNT and **b** CNT-CHD. Energies are in eV. The energies of reactants have been taken as the reference point with energy equal to zero
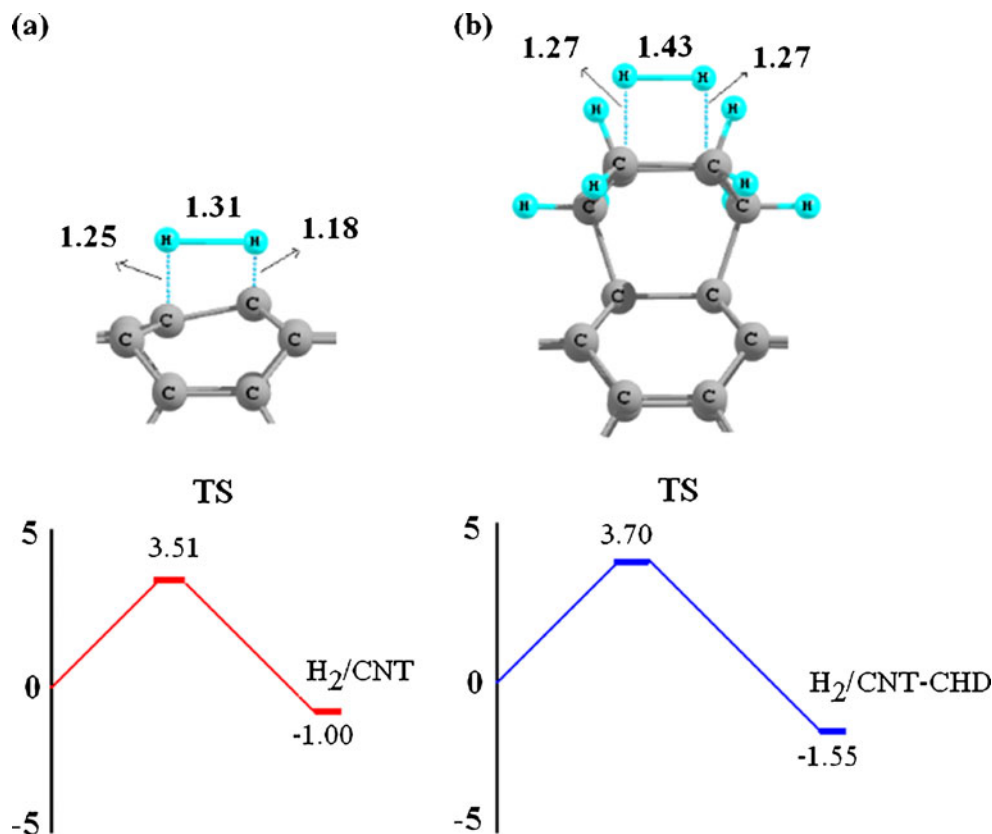
H_2 dissociation on the pristine CNT is kinetically more favorable than that on the CNT-CHD. It can be inferred that the activation energies for CNT-CHD are larger due to the repulsion between the H atoms in the CHD with the H_2 molecule, which can impede the dissociation process. However, H_2 dissociation on the CNT-CHD system is thermodynamically more favorable than on the CNT while it is less favorable in terms of kinetics.

Conclusions

We have performed a DFT study on the chemical functionalization of a zigzag CNT with CHD in terms of energetic, geometric, and electronic properties which has been previously reported by experimentalists. Based on the obtained results, the H_2 dissociation on CNT-CHD is thermodynamically more favorable than that on the pristine CNT, but this process needs somewhat more activation energy to progress. The dissociation energy for the H_2 molecule on the pristine and CHD-functionalized CNT were calculated to be about −1.00 and −1.55 eV and its barrier energies were found to be about 3.70 and 3.51 eV, respectively.

References

1. Tripodi P, Armanet N, Asarisi V, Avveduto A (2009) Phys Lett A 373:3101–3108
2. Dittmeyer R, Höllein V, Daub K (2001) J Mol Catal A Chem 173:135–184
3. Pallassana V, Neurock M (2000) J Catal 191:301–317
4. Park SJ, Lee SY (2010) Int J Hydrog Energy 35:13048–13054
5. Wu G, Zhang J, Wu Y, Li Q, Chou K, Bao X (2009) J Alloys Compd 480:788–793
6. Wu E, Li W, Li J (2012) Int J Hydrog Energy 37:1509–1517
7. Abraham A, Padama B, Kasai H, Kawai H (2012) Surf Sci 606:62–68
8. Pozzo M, Alfé D (2009) Int J Hydrog Energy 2009:1922–1930
9. Barkhordarian G, Klassen T, Bormann R (2004) J Alloys Compd 364:242–246
10. Fromm E, Uchida H (1987) J Less-Common Met 131:1–12
11. Iijima S (1991) Nature 354:56–58
12. Chelmecka E, Pasterny K, Kupka T, Stobiński L (2012) J Mol Model 18:1463–1472
13. Lawrence J, Xu G (2004) Appl Phys Lett 84:918–920
14. Han SS, Kang JK, Lee HM, Duin ACT, Goddard WA (2005) Appl Phys Lett 86:203108–203111
15. Rajarajeswari M, Iyakutti K, Kawazoe Y (2012) J Mol Model 18:771–781
16. Chełmecka E, Pasterny K, Kupka T, Stobiński L (2012) J Mol Model 18:2241–2246
17. Liu S, Shen Q, Cao Y, Gan L, Wang Z, Steigerwald ML, Guo X (2010) Coord Chem Rev 254:1101–1116

18. Wang X, Li S, Xu Y, Wan L, You H, Li Q, Wang S (2007) Appl Surf Sci 253:7435–7437
19. Sankaran M, Viswanathan B (2007) Carbon 45:1628–1635
20. Reddy ALM, Ramaprabhu S (2008) Int J Hydrog Energy 33:1028–1034
21. Lee SY, Park SJ (2010) Int J Hydrog Energy 35:6757–6762
22. Sumanasekera GU, Pradhan BK, Romero HE, Adu KW, Eklund PC (2002) Phys Rev Lett 89:166801–166804
23. Schmidt M et al (1993) J Comput Chem 14:1347–1363
24. Beheshtian J, Baei MT, Peyghan AA (2012) Surf Sci 606:981–985
25. Ahmadi A, Hadipour NL, Kamfiroozi M, Bagheri Z (2012) Sensors Actuators B Chem 161:1025–1029
26. Dinadayalane TC, Murray JS, Concha MC, Politzer P, Leszczynski J (2010) J Chem Theory Comput 6:1351–1357
27. Beheshtian J, Bagheri Z, Kamfiroozi M, Ahmadi A (2012) J Mol Model 18:2653–2658
28. Beheshtian J, Soleymanabadi H, Kamfiroozi M, Ahmadi A (2012) J Mol Model 18:2343–2348