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Reactivity of the interior surface of (5,5) single-walled carbon nanotubes with and without a Stone–Wales defect

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ABSTRACT

The adsorption of hydrogen and fluorine atoms on the interior surface of defect-free and Stone–Wales defect armchair (5,5) single-walled carbon nanotubes were investigated using density functional theory. The reaction energy values for the hydrogenation and fluorination at all the possible unique sites were obtained at the UB3LYP/6-31G* level. The calculated reaction energy values were used to corroborate the reactivities of different sites on the interior surface of SWCNTs. The results indicate that for defect-free nanotube, endohedral adsorption is rather unfavorable both for hydrogen and fluorine. The computed exothermicities range from 4.8 to 13.4 kcal/mol for hydrogenation and from 16.6 to 23.2 kcal/mol for fluorination. However, the introduction of a SW defect on the (5,5) SWCNT improves the chemical reactivity of the interior surface of the defected tube. The computed exothermicities for the endohedral hydrogen and fluorine atoms are within the ranges of 7.0–33.4 and 18.5–41.8 kcal/mol, respectively. The most exothermic and reactive site on the interior surface of SW defective (5,5) SWCNT is the C2 site shared by two seven-membered rings and one five-membered ring. This is different from the results reported on the reactivity of the exterior surface of SW defective nanotubes. The electronic and vibrational properties of the (5,5) SWCNTs with adsorption of hydrogen and fluorine atoms on the interior surface were also explored.

1. Introduction

Since their discovery in 1991 [1], single-walled carbon nanotubes (SWCNTs) have received a great deal of attention. This extraordinary interest is due to their unique structural, mechanical, and electrical properties [2] and various promising applications, including hydrogen storage [3], chemical sensors [4], and nanobioelectronics [5], etc. Many synthetic methods have been developed for the controlled design of carbon nanotubes (CNTs), such as arc discharge [6], laser ablation [7], and catalytic chemical vapor deposition (CVD) techniques [8,9]. However, the experimentally available SWCNTs are not defect-free. Various kinds of defects are known to be present in actual carbon nanotubes, such as vacancies, pentagons, heptagons, dopants, and Stone–Wales (SW) defects [10–13]. The presence of these defects can significantly influence the physical and chemical properties of SWCNTs [14–17].

A very important topological defect in CNTs is the SW defect [10]. It is obtained by rotating a C—C bond by 90° in the hexagonal network, leading to the formation of two pairs of five-membered and seven-membered rings. The exterior surface of defect-free SWCNTs is less reactive compared to fullerenes, due to their only moderately curved regions [18]. In contrast, defect-containing nanotubes lead to a local deformation of the graphitic sidewall and thereby introduce an increased curvature. As a result, the nanotube containing SW defects might be more favorable for subsequent chemical reactions. Much has been studied on the reactivity of the exterior surface of SW defective nanotubes [19–23]. For instance, Lu et al. [22] studied the surface reactivity based on the armchair (5,5) CNT model in reacting with O, CH_2, and O_3 species and demonstrated that the central C—C bond of SW defects in CNT is less reactive chemically than the C—C bonds at perfect sites. As for the reactivity of the interior surface of SW defective nanotubes, however, little theoretical studies have been reported to our best knowledge.

Covalent functionalization of CNTs can effectively modify their physical and chemical properties; hydrogenation and fluorination are among the most widely investigated functionalizations. For example, metallic SWCNTs were transformed to semiconducting ones by functionalizing the sidewalls of SWCNTs using fluorine and hydrogen atoms [24,25]. Chemisorption of hydrogen and fluorine atoms on the exterior surface of defect-free SWCNTs has been extensively investigated, both experimentally [26–29] and theoretically [30–35]. However, there is limited information on the defect-containing SWCNTs [36,37]. Recently, using density functional theory, Dinadayalane et al. [36] examined the chemisorption of

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hydrogen and fluorine atoms on the defect of armchair (5,5) SWCNT and investigated the surface reactivity of SW defects in SWCNTs (but only the exterior surface of (5,5) SWCNTs was considered). We studied the chemisorption of hydrogen atoms on the SW defective armchair (n,n) (n = 4–8) SWCNTs (but endohedral adsorption only the central 7–7 ring fusion was considered) [37]. Considering that the interior surface of defect-free SWCNTs is chemically inert, it becomes very important to know the reactivity of the interior surface of SW defective SWCNTs. In the present study, the reactivity of the interior surface of (5,5) SWCNTs with and without SW defects to hydrogen and fluorine atoms were studied through density functional theory method.

2. Calculation methods

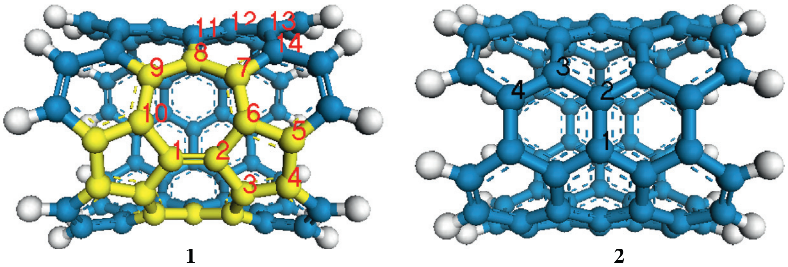
Following the previous researcher [36], a finite-length cluster, $C_{70}H_{20}$, was considered to represent the defect-free armchair (5,5) SWCNT. Both ends of the finite-length tube were saturated by hydrogen atoms to avoid dangling bonds. A SW defect in SWCNTs was formed by rotating one of the C—C bonds by 90°. The geometries of (5,5) armchair SWCNTs with and without SW defects were fully optimized with hybrid density functional theory (DFT) at the B3LYP/6-31G* level [38,39]. For the (5,5) SWCNTs with hydrogen and fluorine atoms adsorbed at different sites, geometries were optimized and reaction energies determined with the UB3LYP/6-31G* method. To ensure the optimized geometries are indeed minima, vibrational frequencies at the UB3LYP/6-31G* level were computed for the hydrogenated and fluorinated structures. All geometry optimizations and frequency calculations were carried out using the Gaussian 03 program system [40].

The reaction energies of a single hydrogen/fluorine atom adsorbed on the interior surface of (5,5) SWCNTs were calculated according to the expression $E_r = E_{(CNT+H/F)} - E_{(CNT)} - E_{(H/F)}$, where $E_{(CNT+H/F)}$ denotes the total energy of nanotube plus the H/F atom; $E_{(CNT)}$ and $E_{(H/F)}$ correspond to the total energies of the bare nanotube and the single H/F atom, respectively. In order to compare our results with previous DFT calculations by Dinadayalane et al., the zero point vibrational energies have not been included in the reaction energies, E_r. In addition, the basis set superposition error (BSSE) corrections for the reaction energies were also estimated using the Boys–Bernardi counterpoise technique [41] at the same level of theory.

3. Results and discussion

Defect-free and SW defective nanotubes were first optimized. The optimized geometrical structures of (5,5) armchair SWCNTs with and without SW defect (denoted as **1** and **2** for simplicity hereafter) that were calculated by B3LYP/6-31G* are shown in Fig. 1. The calculated C1—C2 bond length at the 7–7 ring fusion of the SW defect $C_{70}H_{20}$ is 1.345 Å, suggesting the formation of a double C═C bond (whose typical bond length in small hydrocarbons is about 1.33 Å). The results agree with the previous ones [22]. To study the reactivity of the interior surface of (5,5) armchair SWCNTs, endohedral adsorptions of hydrogen and fluorine atoms at the different carbon sites (C_2, C_3, C_4, C_7, C_8, C_{11}, C_{12}, C_{13}, and C_{14} in **1**, and C_2, C_3, and C_4 in **2**, respectively; Fig. 1) were considered. All the investigated hydrogenated and fluorinated structures were fully optimized at the UB3LYP/6-31G* level. The selected C—H and C—F bond lengths and the reaction energies (E_r) for the chemisorptions of hydrogen and fluorine atoms at different carbon sites on the interior surface of **1** and **2** are presented in Table 1. After passivation by hydrogen or fluorine atoms, the newly formed C—H bond length is about 1.11 Å in all cases, which is consistent with earlier studies [30,37] and close to the C—H distance in methane (1.09 Å). The C—F bond distances are more variable; they range from 1.450 to 1.527 Å and are slightly longer than the typical C—F single bond (1.39 Å in CH_3F). The shortest C—H and C—F bonds are at C2 of **1**. Atom C2 is shared by two seven-membered rings and one five-membered ring.

The reaction energies (the BSSE corrected and uncorrected energies) of the endohedral hydrogen and fluorine atoms at different carbon sites are all negative value. This implies that the absorption reactions are exothermic. As far as the BSSE-corrected reaction energies are concerned, the values BSSE of hydrogenated structures are very small with the range from 1.1 to 1.2 kcal/mol. Consequently, there is no significant difference between the corrected and uncorrected energies. In contrast, the BSSE values become large for fluorinated structures with the range from 6.5 to 6.9 kcal/mol. Thus, BSSE correction is significant for obtaining reliable adsorption energies. Since the orders of the BSSE and no BSSE reaction energies are similar. Here, our discussion will be based mainly on the uncorrected energies unless otherwise specified. For the defect-free (5,5) armchair SWCNT, the endohedral hydrogen atom reaction energies of the C2, C3, and C4 adsorption sites are −6.0, −4.8, and −13.4 kcal/mol, respectively, while the endohedral fluorine atom reaction energies of the C2, C3, and C4 adsorption sites are −17.9, −16.6, and −23.2 kcal/mol, respectively. The fluorine atom chemisorption is more exothermic (by 10–12 kcal/mol) than the corresponding hydrogen atom chemisorption. Dinadayalane et al. [36] used the UB3LYP/6-31G* level of theory to study the reaction energies of the exohedral hydrogen and fluorine atoms at various carbon sites on the exterior surface of the defect-free (5,5) SWCNT. They obtained the exohedral hydrogen atom reaction energies of the C2, C3, and C4 adsorption sites are −34.3, −35.0, and −42.8 kcal/mol, respectively; the exohedral fluorine atom reaction energies of the C2, C3, and C4 adsorption sites are −45.3, −46.5, and −54.6 kcal/mol, respectively. Compared to the above results, it is clear that exohedral nanotube adsorption is energetically more favorable (by 28–30 kcal/mol) than the corresponding endohedral adsorption, which is consistent with the



1 **2**

Fig. 1. Fully DFT optimized (at the level of theory B3LYP/6-31G*) structures for Stone–Wales defect (**1**) and defect-free (**2**) armchair (5,5) SWCNTs, $C_{70}H_{20}$. The carbon atoms of the Stone–Wales defect region of **1** are shown in yellow. Atom numberings are according to Ref. [36]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)