International Journal of Nanoelectronics and Materials
Volume 13, No. 1, Jan 2020 [113-120]

The Adsorption of C_2H_2, C_2H_4, and C_2H_6 on Single Fe Atom Doped SWCNT: A Density Functional Theory Study

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Received 20 June 2019, Revised 15 November 2019, Accepted 31 December 2019

ABSTRACT

The adsorption of certain hydrocarbon gases (C_2H_2, C_2H_4, and C_2H_6) on Fe-doped and Fe-decorated SWCNTs have been researched using Density Functional Theory (DFT) calculations. Three Fe-decorated SWCNT configurations, which are bridge, hollow, and top position of Fe on SWCNT, were calculated to discover the highest energy interaction. The Fe on the hollow configuration was found to be the most stable configuration. The results also show that Fe-decorated SWCNT has stronger adsorption energy than Fe doped SWCNT. Based on geometry structure and adsorption energy, Fe-SWCNT has the best sensitivity for C_2H_2 compared to C_2H_4 and C_2H_6. The adsorption energy order from the highest to the lowest is $C_2H_2 < C_2H_4 < C_2H_6$.

Keywords: C_2H_2, C_2H_4, C_2H_6, DFT, Gas Adsorption.

1. INTRODUCTION

Transformer is a vital and expensive component in electrical power systems. Minor damage to the transformer would lead to huge losses and risks in the system [1]. The quality of the insulation system is one of the main factors that affect the transformer performance. Insulation system degradation forces the transformer to stop working [2]. The degradation of the insulation system due to prolonged operation of the transformer creates thermal stress in the system. This stress leads to the production of certain gases, such as C_2H_2, C_2H_4, and C_2H_6, which may eventually damage the transformer. Therefore, early detection of transformer damage is very crucial.

One of the methods used to identify initial damage in transformer oil is the Dissolved Gas Analysis (DGA). Continuous evaluation of the transformer operating conditions is feasible through the DGA method. This method also allows for possible damage detection. Key gas, IEC ratio, and the graphical representation are three widely used DGA method for diagnosing transformers [3]. Gas concentration is required for the methods used in the DGA application. The needs of the gas sensor are therefore essential.

Researchers around the world have developed various types of gas sensors. Several sensors are based on Solid Oxide Fuel Cell (SOFC) [4], graphene oxide colloid [5], Pd-decorated graphene

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[6], hierarchical structure loaded with Ag ZnO [7], Ni (111) [8], silicene [9], and Single-Walled Carbon Nanotube (SWCNT) [10]. There are also several types of theoretical research on gas sensors, such as CNTs for gas C_2H_2 [11], C_2H_4 [11], and CO [12]. This research focused on C_2H_2, C_2H_4 and C_2H_6 adsorption on SWCNT. The SWCNT armchair (5,5) is chosen as a gas sensor material because it has a zero bandgap [13]. In addition, SWCNTs consists of a single layer of carbon, with all atoms open to the environment, making adsorbing gas molecules relatively straightforward [14]. Group VIII transition metals are suitable catalysts for hydrocarbon involvement reaction [15]. In manufacturing gas sensors, several types of metals were used as catalysts, notably Ni [10], Pt [11], Au, and Ag [16]. According to Zhang (2016) in Tit *et al.* [17], iron (Fe) has the highest sensitivity and selectivity among four metals (Fe, Co, Pd, and Au) when deposited on a ZnO graphite sheet because Fe has the least negative or most electropositive electron. Tit *et al.* (2017) also conducted research using CNT and Fe as catalysts for CO_2 detection, and the results show that Fe added CNTs increased the sensor's sensitivity and selectivity [17]. Hence, the effect of Fe catalyst on gas/SWCNT is elucidated. In this research, the adsorption behaviour of the C_2H_2, C_2H_4, and C_2H_6 molecules on Fe-decorated SWCNT and Fe-doped SWCNT structures is discussed. Based on the analysis, the best option for some gas adsorption should be advised.

2. MODEL AND CALCULATION METHOD

All calculations are carried out using the Vienna Ab initio Simulation Package (VASP) based on Density Functional Theory (DFT) within Kohn-Sham formulation [18-20]. The spin polarization DFT based on Generalized Gradient Approximation (GGA) within the Perdew-Burke-Emzerhof (PBE) functional was used for the geometry optimization [21]. The Brillouin zone was sampled using a 1×7×1 Monkhorst-Pack *k* point grid. The total energies are converged to 0.01 meV and cutoff energy of 520 eV.

Fe-decorated SWCNT and Fe-doped SWCNT are two terms used to distinguish between substituted and deposited atoms. Fe-doped SWCNT (see Figure 1(a)) configuration was made by substituting one of carbon on pristine SWCNT by one of Fe atoms. Therefore, the total number atom in the Fe-doped configuration is 100 atoms (five-unit cells). However, The Fe-decorated configuration (see Figure 1(b)) consists of one Fe atom placed on the top area of pristine SWCNT. The number of carbon atoms of pristine SWCNT is 100 atoms; hence, the total number atom in Fe-decorated configuration is 101 atoms. The hollow position is where Fe is placed in the centre of a hexagon. The top and bridge positions of Fe-decorated SWCNT are also calculated. The top position is where Fe is placed directly above a C atom, and the bridge position is where Fe is placed in the middle of a CC bond [11].

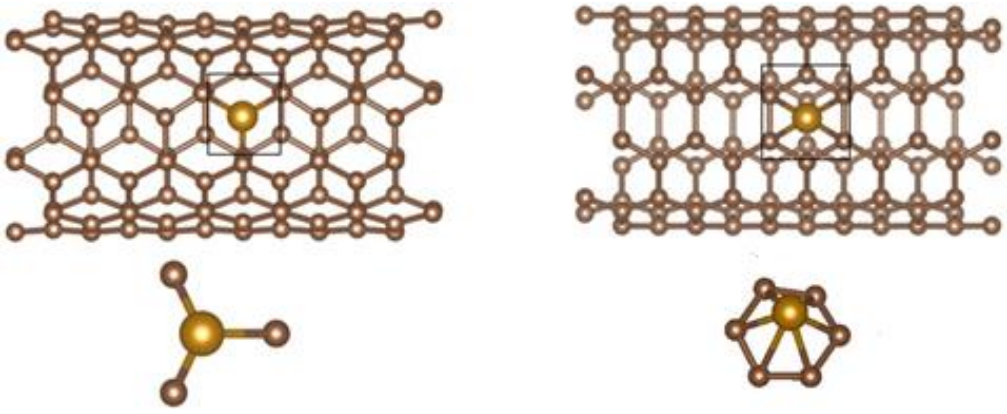


Figure 1. The structure of (a) Fe-doped SWCNT and (b) Fe-decorated SWCNT.

The geometry of the optimized structures and adsorption energies was determined to analyze the interaction between gases and Fe-SWCNT. The adsorption energies were calculated using the following Equation (1) and (2):

$$E_{ads} = E_{adsorbate+FeSWCNT} - E_{adsorbate} - E_{FeSWCNT} \quad (1)$$

$$E_{ads} = E_{adsorbate+SWCNT} - E_{adsorbate} - E_{SWCNT} \quad (2)$$

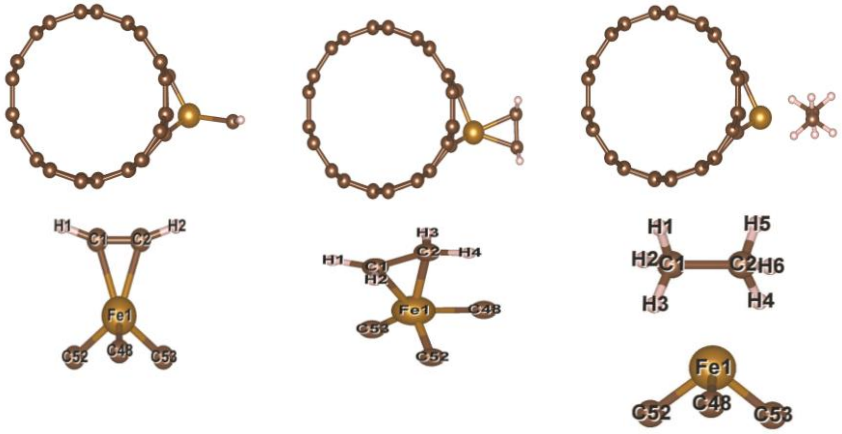
where $E_{adsorbate}$, $E_{FeSWCNT}$, E_{SWCNT} are the total energies of isolated adsorbates, the total energy of Fe-SWCNT, and total energy of SWCNT, respectively. $E_{adsorbate+FeSWCNT}$ and $E_{adsorbate+SWCNT}$ represents the total energies of the Fe-SWCNT–adsorbate and SWCNT–adsorbate systems, respectively. In this paper, the adsorbates are C_2H_2, C_2H_4, and C_2H_6. A negative sign in E_{ads} indicates that that the adsorbate-substrate system is stable and that the adsorption process is exothermic; a positive E_{ads} value suggests that the adsorbate-substrate system is unstable and that the adsorption process is endothermic. The more negative the value of E_{ads}, the more stable the adsorption configuration or the adsorption becomes higher.

3. RESULTS AND DISCUSSION

3.1 Fe-Doped SWCNT Adsorption Energy

As a result of the DFT application, the optimized Fe-doped SWCNT's geometric structure has changed, as summarized in Table 1. As shown in Table 1, Fe-C_1 distance is getting longer as the number of H atoms in each gas increased. A similar trend for C_1-H_1 and C_1-C_2 distance are observed.

Table 1 Comparison of geometrical parameters between the optimized structure of Fe-doped SWCNT and gas

System	C_2H_2	C_2H_4	C_2H_6
Optimized structure			
Distance (Fe-C_1) A	1.97	2.13	2.48
Distance (C_1-H_1) A	1.08	1.09	1.09
Distance (C_1-C_2) A	1.27	1.39	1.53
Angle (C_1-Fe-C_2)	37.84°	38.03°	36.65°
Angle (C_1-C_2-H_2)	152.34°	125.57°	27.45°
Angle (H_1-C_1-C_2)	155.62°	121.18°	109.93°

The adsorption energy of C_2H_2, C_2H_4, C_2H_6 on pristine SWCNT, and Fe-doped SWCNT are summarized in Table 2. It can be seen that the adsorption energy of C_2H_2 is the lowest compared to C_2H_4 and C_2H_6 on the Fe-doped SWCNT. This indicates that C_2H_2 is more strongly attracted to the Fe-doped SWCNT due to the short Fe-C_1 bond, as shown in Table 1.

The adsorption energy of C_2H_2 on the Fe-doped SWCNT is compared with the adsorption energy of C_2H_2 on the pristine SWCNT. The adsorption energy of C_2H_2 on pristine SWCNT, as shown in Table 2 is -0.03 eV, which is lower by 1.47 eV compared to Fe-doped SWCNT. This means that the sensitivity of Fe increased during the C_2H_2 adsorption. This result is consistent with a previous study [17], whereby adding a catalyst would increase the sensitivity in gas adsorption. Table 5 presents the adsorption energy of C_2H_2, C_2H_4, and C_2H_6 in Fe-decorated SWCNT.

Table 2 Energy systems with Fe-doped SWCNT

Structure	Fermi Energy (eV)	Adsorption Energy (eV)
SWCNT	-1.89	-
Fe-doped SWCNT	-3.62	-
C_2H_2/SWCNT	-1.83	-0.03
C_2H_2/Fe-doped SWCNT	-3.52	-1.51
C_2H_4/Fe-doped SWCNT	-3.58	-1.18
C_2H_6/Fe-doped SWCNT	-3.40	-0.22

3.2 Fe-Decorated SWCNT Adsorption Energy

Interaction energy calculation for the top, bridge, and hollow Fe-decorated SWCNT configurations are shown in Table 3. Interaction energy for each position (Table 3) is calculated using Equation (3):

$$E_{int} = E_{SWCNTFe} - E_{SWCNT} - E_{Fe} \quad (3)$$

where E_{SWCNT} and E_{Fe} corresponds to energies of isolated SWCNT and Fe, respectively, while $E_{SWCNTFe}$ is the total energy of Fe-decorated SWCNT. It is found that the hollow configuration has the minimum interaction energy. Hence, it will be used for the next calculation.

Table 3 Configurations of Fe-decorated SWCNT

Site	Distance Fe with nearest C atom (A)	Interaction Energy (eV)
Top	1.84	-2.180
Bridge	1.94	-2.313
Hollow	2.06	-2.945

Table 4 shows the calculation results for each gas's optimized position. The calculation was performed by placing gas molecules on Fe-decorated SWCNT. It shows that Fe-C_1 distance in each gas is getting longer with the increasing number of H atoms. This also applied to Fe-doped SWCNT. It is concluded that the covalent bond of C-H and Fe-C_1 is difficult to be attained as the number of hydrogens in the hydrocarbon grows.

The adsorption energy order from the highest to the lowest is C_2H_2 < C_2H_4 < C_2H_6, which indicates that C_2H_2 has the strongest bond to the Fe-decorated SWCNT. The short length of Fe-C_1 bond of C_2H_2/ Fe-decorated SWCNT (see Table 4) contributes to the binding energy.

Table 4 Comparison of geometrical parameters of optimized structures Fe-decorated SWCNT (hollow position) and gas

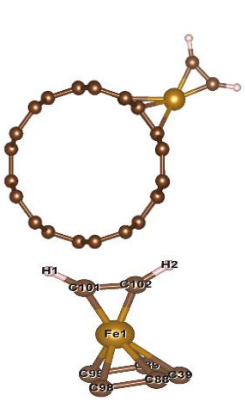
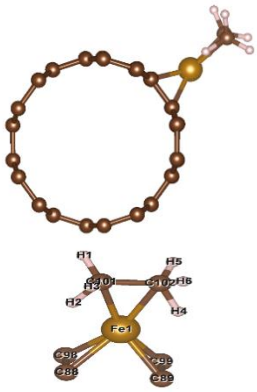
System	C_2H_2	C_2H_4	C_2H_6
Optimized structure			
Distance (Fe -C_1) A	1.83	1.99	2.14
Distance (Fe-H_1) A	2.84	2.57	2.95
Distance (C_1-H_1) A	1.09	1.09	1.09
Distance (C_1-C_2) A	1.32	1.42	1.52
Angle (H_1-C_1-Fe)	149.92^o	108.82^o	128.53^o
Angle (H_1-C_1-C_2)	141.79^o	121.07^o	111.52^o

Table 5 Energy systems with Fe-decorated SWCNT

Structure	Fermi Energy (eV)	Adsorption energy (eV)	References
SWCNT	-1.89	-	
Fe-decorated SWCNT	-1.70	-	
C_2H_2/Fe-decorated SWCNT	-1.81	-3.23	-2.95 on Ni(111) [22]
C_2H_4/Fe-decorated SWCNT	-1.80	-2.29	-2.26 on Pt-decorated graphene[11]
C_2H_6/Fe-decorated SWCNT	-1.51	-1.27	-0.199 on Ni-CNTs[23]

3.3. Discussion

According to the calculation in this paper, all Fe-decorated SWCNT gas adsorption energies are of lower values than Fe-doped SWCNT. This means that Fe-decorated SWCNT is better than Fe-doped SWCNT in terms of C_2H_2, C_2H_4, C_2H_6 gas adsorption. The C_2H_2 gas adsorption energy on Fe-decorated SWCNT (see Table 5) is higher than adsorption energy on Ni (111) [22], whereas the value of the adsorption energy produced for C_2H_4 gas is nearly the same as that Pt-decorated graphene [11]. Calculating the C_2H_6 gas also shows a higher energy adsorption value than that of Ni-CNT adsorption[23].

The ability of Fe-SWCNT detecting gas molecules is attributed to the relatively strong adsorption energy of gas molecules on Fe-SWCNT. Adding Fe to SWCNT through doping and the

decorating mechanism also plays an essential role in assigning the gas's adsorption energy to the SWCNT. To conclude, SWCNT-Fe potential to be used as a gas sensor due to the fact that it reacts well in detecting the gas presence, judging by the powerful values of adsorption energy.

4. CONCLUSION

In summary, the addition of Fe provides significant changes in the adsorption energy compared to pristine SWCNT. It is shown that C_2H_2 gas is more sensitive compared to two other gases (C_2H_4 and C_2H_6), and it is also applied for doped and decorated SWCNT. Besides that, it was also found that the adsorption energy for Fe-decorated SWCNT is stronger than Fe-doped SWCNT.

ACKNOWLEDGMENT

The authors are grateful to the Advanced computational laboratory, Physics Department, ITB that has supported this research and Lembaga Pengelola Dana Pendidikan (LPDP) that has funded this research.

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