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Computational Chemistry

Elixir Comp. Chem. 50 (2012) 10539-10540

ISSN: 2229-712X

Hydrogen adsorption on transition element-doped SWCNT

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ARTICLE INFO

Article history:

Received: 1 August 2012;

Received in revised form:

31 August 2012;

Accepted: 20 September 2012;

Keywords

Density Functional Theory;

Transition element;

Adsorption;

Binding energy;

Density of states.

ABSTRACT

Density functional theory (DFT) studies H_2 adsorption on transition element (TE) doped single walled carbon nanotubes (SWCNTs) using Dmol^3 software. We consider transition element as Ti doped various sites on the surface of armchair (5,5) SWCNT. The simulation results shows that binding energy of H_2 adsorption on Ti doped SWCNT is much higher than pure SWCNT. We calculate the density of states for doped and pure SWCNTs, which is a show dramatic change in their structure on adsorption of H_2 molecules. This study shows that the transition element doped SWCNTs can be used as a good H_2 storage at various sites.

Introduction

Hydrogen is one of the alternate, clean and safe energy, for main reasons are due to energy demand to lack of fossil fuels and unable to control the environmental pollution by CO emission in atmosphere [1]. The main problem is that hydrogen storage has to be developed as portable applications. There are various methods for adsorption hydrogen storage such as metal hydrides, complex hydrides, metal organic frameworks, activated carbon and carbon nanotubes . These methods are evaluated in terms of the 6.5% wt gravimetric density and of the 65 kgm^{-3} volumetric density are announced by US Department of Energy (DOE) [2].

Recently, Carbon nanotubes (CNTs) much research interest outstanding properties like mechanical, electrical, optical and magnetic respectively. Since 1991, Ijima discovered nanostructure materials named carbon nanotubes (CNTs) [1-5]. CNTs are one of the carbon families that have hardness equivalent to diamond and also act as a conductor like graphene. The single or multi layer graphene sheets, rolled in a concentric way, give rise to Single-Walled Carbon Nanotube (SWCNT) or Multi-Walled Carbon Nanotubes (MWCNTs). CNTs posses high surface area and porous structures which is tailored for energy storage [6-13].

The transition metal Ti absorbed on CNT high capacity of H_2 adsorption which can revealed by Early Yildrium et al [14 -16]. Transition elements (Pd, Pt, Rh, and V etc.) doped with SWCNTs can be adsorbed gaseous molecules like carbon monoxide, methane and hydrogen, although pure SWCNTs have no response to these gaseous molecules [17]. Transition metal -doped SWCNTs for the detection of gas molecules such as H_2, CH_4, CO, H_2S at different sites has shown by Zhao et. al [18].

In this paper we investigate the electronic structure and geometric structure of adsorption H_2 molecules on the Ti on different sites doped SWCNT (5,5) using density functional theory (DFT) calculations.

Computational methods

We carry out the Density Functional Theory (DFT) calculations using Dmol^3 package [19] embodied in Materials Studio. We have chosen armchair (5, 5) SWCNT as the model system. For calculations all electrons were performed with the double numerical basis sets plus polarization functional (DNP). Additionally exchange-correlation functional the generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof (PBE) [20] and Spin-unrestricted DFT is used to obtain all the results reported below. In transition element such as Ti, atom, scalar relativistic effect is taken into account when dealing with its core electrons. In this structure 40 carbon atoms single Ti atom and H_2 molecules. The Brillouin zone is sampled by 1×1×3 along the tube axis using the Monkhorst–Pack scheme [21],

We have considered three possible sites, that H_2 adsorption on the transition elements doped SWCNT. The sites can be consider in single aromatic ring as (i) H site, the center of the hexagon C-C , (ii) A site, the parallel C-C bond and (iii) Z site, zigzag C-C bond. The electronic structures, geometrical structures and a total energy calculation is performed for each stable configuration. Transition element adsorbed on the top of the SWCNT the binding energy E_b is defined as

$$E_b = E_T(TE) + E_T(SWCNT) - E_T(TE+SWCNT)$$

where $E_T(TE)$,$E_T(SWCNT)$,$E_T(TE+SWCNT)$ are the total energies of a free transition element atom, the pure SWCNT and the Ti doped SWCNT system, respectively.

Results and Discussion

Structures

The optimized structure of pure SWCNT, the bond length of C-C bond is 1.41 Å , also Ti doped SWCNT for three different sites are exposed in Figure1(Pure CNT,A site , H site and Z site). For the study of H_2 adsorption, H_2 molecule was placed at the top of the doped Ti atom at a distance of 1.7 Å. After the geometry optimization, the bond lengths get increased. The calculated binding energies range from 1.31 to 1.42 eV for the three stable configurations. The optimized structures show these

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systems are stable. We found that H and Z sites are more stable compare to A site.

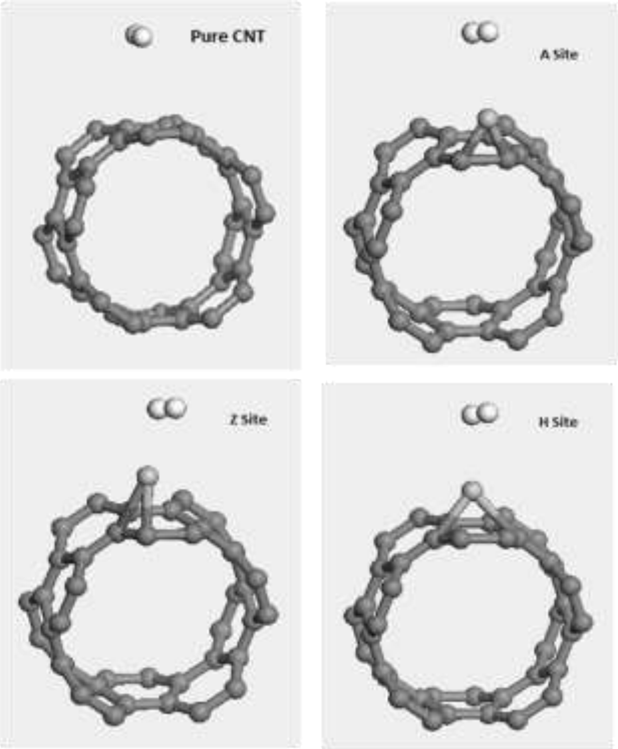

Figure 1: Structure for Pure CNT, Ti doped A, Z and H site CNT

Density of States

The calculated density of states (DOS) for pure SWCNT, TE doped SWCNT and adsorption of H_2 molecules on TE doped SWCNT are shown in Figure 2. Fascinatingly, from the DOS plots it is observed that the density of states of TE doped SWCNT and H_2 adsorbed TE doped SWCNT shows changes in their peaks. For pure SWCNT, dominate peaks are observed at -0.43eV,-0.10 eV, 0.03eV, 0.20eV, 0.28eV, 0.30 eV which are below the Fermi energy level. The peaks above Fermi level appears at, -0.10 eV, 0.03eVand 0.20eV, DOS of Ti doped SWCNT show peaks (DOS for A site in Figure 2) between -0.18 eV to -0.025 eV.

These changes are due to the 3d states of TE. In the case of H_2 adsorbed Ti doped SWCNT (DOS for Z site in Figure 2) between the range -0.15 eV to -0.027 eV , In the case of H_2 adsorbed Ti doped SWCNT (DOS for H site in Figure 2) the peaks appear between the energies of -0.16 eV to -0.027 eV . This change occurs by the overlap of atomic orbital between -0.43 eV to 0.35eV.

On comparing the DOS of pure SWCNT, H_2 adsorbed Ti doped SWCNT shows much change. The bottom of conduction band moves up by 0.27 eV, and then the top of valence band moves down by - 0.16 eV. The binding gap is less than 0.5 eV in all case, which supports the fact that the adsorption of gas molecules on Ti doped SWCNT is physisorption. These results show that the Ti doped SWCNTs stands as a promising candidate for the hydrogen storage applications.

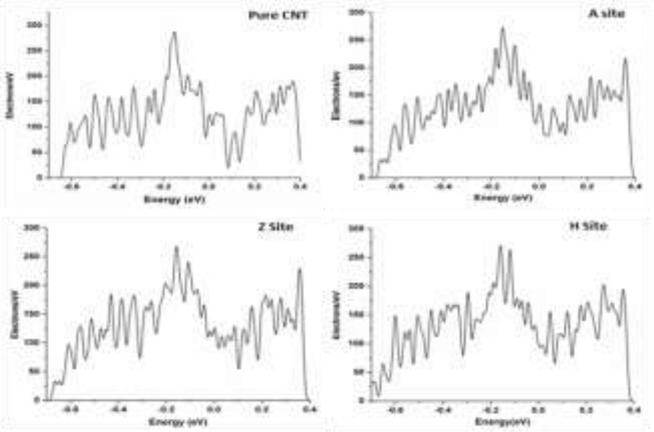

Figure 2: Density of states for Pure CNT, Ti doped A, Z and H site CNT

Conclusion

In this work we have studied the doping of transition-metal atoms on the (5,5) arm chair SWCNT and pure SWCNT using density functional theory (DFT) with PBE and DNP basis set. We found that transition element such as Ti doped SWCNTs adsorb H_2 molecules effectively compares to pure SWCNT. Above and beyond both Ti doped on SWCNTs Z and H sites are activated sites, in addition that H_2 can be effectively adsorbed H_2 on the Ti doped SWCNTs.

Acknowledgements

The Department of Science and Technology (DST), New Delhi, is greatly acknowledged for providing Dmol3 code.

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