All-Electron DFT Modeling of SWCNT Growth Initiation by Iron Catalyst

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Abstract. Electronic and geometrical structures of $\text{Fe}_4\text{C}_n(\text{CO})_m$ ($n+m \leq 6$) and Fe_4C_n ($n=7-16$) clusters along with their singly negatively and positively charged ions are computed using density functional theory with generalized gradient approximation (DFT-GGA). Isomers with CO bonded directly to the iron atoms and bonded to a carbon atom chemisorbed on the cluster surface are optimized for the $\text{Fe}_4\text{C}_2\text{CO}$, $\text{Fe}_4\text{C}_2(\text{CO})_2$, $\text{Fe}_4\text{C}_3\text{CO}$, and $\text{Fe}_4\text{C}_4\text{CO}$ series. The computed total energies are used to estimate the energetics of the Boudouard disproportionation reactions $\text{Fe}_4\text{C}_n(\text{CO})_m + \text{CO} \rightarrow \text{Fe}_4\text{C}_{n+1}(\text{CO})_{m-1} + \text{CO}_2$. Optimizations of the Fe_4C_4 – Fe_4C_{16} clusters have shown that dimers C_2 are formed in the lowest energy states of Fe_4C_4 , trimers C_3 – in Fe_4C_5 and Fe_4C_6 , tetramers C_4 – in Fe_4C_7 and Fe_4C_8 , a pentamer C_5 – in Fe_4C_9 , and a hexamer C_6 – in Fe_4C_{10} . C_n rings attached to a Fe_3 face are formed in the lowest energy states of Fe_4C_n beginning with $n=11$.

1 Introduction

Single-walled carbon nanotubes (SWCNT) are expected to have a huge impact on various technological areas related to fabrication of sensors, composite materials, hydrogen storages, and computer memories. They can be grown using different methods typically from hydrocarbons [1], alcohol [2], and graphite [3]. The method of catalytic chemical vapor deposition [4] (CCVD) makes use high temperatures to produce carbon and a supported catalyst [5] to initiate the carbon nanotube growth. Carbon nanotubes grown using this method are often multi-walled while probably more advantageous for technology are single-walled. This process is cyclic and involves restoration of catalyst after each production cycle.

The high-pressure high-temperature HiPco [6] method is continuous and its floating or gas-phase catalyst is formed *in situ* from iron pentacarbonyl $\text{Fe}(\text{CO})_5$. Using carbon monoxide as feedstock is rather intriguing, because CO is one of the most stable diatomics with the experimental bond strength of 11.09 eV. Carbon nanotubes produced in this process are always single-walled and are believed [7] to nucleate and grow via the Boudouard disproportionation reaction $\text{CO} + \text{CO} \rightarrow \text{C}_{\text{SWCNT}} + \text{CO}_2$.

The mechanism of carbon nanotube growth is not well understood. Recent experiments [8] using epitaxial precipitation of carbon on catalyst surfaces provided evidence that open tubes drive the carbon nanotube growth. However, Jost et al. [9]

discovered that in the CCVD approach both cap and circumference growth occur. An empirical model of nucleation [10] in a CCVD process assumes that carbon supersaturates melted catalyst particles and a curved graphene sheet begins to form, which evolves into a SWCNT cap and subsequently lifts off the catalyst surface. The results of molecular dynamics simulations [2,11,12] of carbon nanotube growth from carbon dissolved in a catalyst particle are in agreement with this model. Other theoretical studies [13,14] dealt with the SWCNT growth from different carbon species including carbon flakes composed of hexagons and pentagons over Ni catalyst. These computations were performed using pseudopotentials and the plane-wave formalism.

2 DFT-GGA Simulations of HiPco

In order to gain insight into carbon nucleation in the HiPco process, we have performed all-electron density functional theory calculations with a generalized gradient approximation (DFT-GGA) on Fe_nC [15], Fe_nCO ($n \leq 6$) [16], and $\text{Fe}_4\text{C}_n(\text{CO})_m$ ($n+m \leq 3$, both C and CO are attached to Fe_4) [17] clusters, and estimated the energies of Boudouard CO disproportionation reactions $\text{Fe}_4\text{C}_n(\text{CO})_m + \text{CO} \rightarrow \text{Fe}_4\text{C}_{n+1}(\text{CO})_{m-1} + \text{CO}_2$. The energies found are relatively small and are in the range from -0.26 eV [$\text{Fe}_4\text{C}(\text{CO})^+$] to $+0.74$ eV [$\text{Fe}_4(\text{CO})_3$]. While most of the nanotube growth experiments to date most likely involve neutral systems, we consider cations and anions in addition to the neutrals. If the reactivity of the cation or anion appears to be much higher than that of the neutral, it would be advisable to alter the experimental conditions to enhance the number of cations or anions.

Next, we explored [18] the energetics of CO attachment to a carbon atom that had already precipitated on an iron cluster due to a preceding Boudouard reaction and evaluated the energetics of CO disproportionation reactions $\text{Fe}_4\text{C}_n(\text{CO})_m + \text{CO} \rightarrow \text{Fe}_4\text{C}_{n+1}(\text{CO})_{m-1} + \text{CO}_2$ for higher coverage ($n+m \leq 5$). We chose Fe_4^- , Fe_4 , and Fe_4^+ clusters since the Fe_4^+ cluster is known [19] to catalyze the growth of benzene from ethylene and cyclopropane in a low-pressure gas-phase process. The number of iron atoms in clusters formed in the HiPco process ranges from ~ 10 to ~ 300 and it is not clear if smaller iron clusters Fe_3 to Fe_{10} can technologically be effective for the SWCNT growth because of different restrictions such as coalescence of small clusters. Our computations show that the binding ability of clusters Fe_4 , Fe_5 , and Fe_6 is nearly the same. Therefore, one can anticipate that our computations on using computationally manageable Fe_4 clusters are capable of reproducing the essentials in initiating the SWCNT growth.

Our computations [18] arrived at several conclusions: (i). CO prefers attachment to a C atom precipitated on the Fe_4 surface in the ground state $\text{Fe}_4\text{C}_2(\text{CO})^+$ and $\text{Fe}_4\text{C}_3(\text{CO})^+$ cations while CO is attached directly to iron atoms in the neutral ground states of the $\text{Fe}_4\text{C}_2(\text{CO})$ and $\text{Fe}_4\text{C}_3(\text{CO})$ clusters; (ii). Dimerization of carbon atoms is preferable in Fe_4C_4 , Fe_4C_5 and its ions, while C_3 trimers form in the ground states of Fe_4C_6 and its ions; (iii). Formation of a C_6 ring catalyzed by Fe_4 is energetically unfavorable and it is unlikely that this ring will initiate growth of an SWCNT at least for an iron cluster of this size; (iv). Antiferromagnetic (AF) states corresponding to small spin multiplicities may closely approach ferromagnetic states with larger spin multiplicities. For example, the AF states of Fe_4C_6 with $2S+1=5$ and $2S+1=1$ are above its

ferromagnetic (FM) $2S+1=13$ ground state by +0.38 eV and +0.74 eV, respectively. This is in contrast with Fe_4 , where AF states were found at energies exceeding 1 eV.

3 Geometry Patterns in Fe_4C_n

Since attachment of COs followed by subsequent Boudouard reaction leads to formation of carbon atoms, we consider next the trends in rearrangement of carbon atoms in the lowest energy isomers of clusters Fe_4C_n , $n=7-15$. As before, computations are performed at the BPW91 level of DFT-GGA theory where B means the Becke's exchange [20] and PW91 stands for the Perdew-Wang's correlation [21] functionals. We use the 6-311+G* basis set [22]. We have optimized neutral as well as singly charged negative and positive ions of Fe_4C_n for $n=7-16$ and found that the lowest energy isomers possess the same geometrical shape independent of the charge state.

Figure 1 shows isomers of Fe_4C_7 , Fe_4C_7^- , and Fe_4C_7^+ . As is seen, the lowest energy isomers are nonplanar and contain a ring formed by C_3 , C_4 , and two iron atoms. The corresponding AF isomers have similar geometrical structures and are placed in total energy by ~ 0.5 eV higher, while an isomer of Fe_4C_7 in which C_4 is replaced by a C_3 triangle and a C atom is significantly higher. The ground-state spin multiplicities [23, 24] of bare clusters Fe_4 , Fe_4^- , Fe_4^+ are 15, 16, and 12, respectively. Attachment of two carbon chains decreases the spin multiplicity of Fe_4 , Fe_4^- , and does not change the spin multiplicity of Fe_4^+ . Similar behavior of the spin multiplicities is found for carbon attachments in Fe_4C_n for $n>7$.

The ground states of Fe_4C_8 and its ions have similar rings as in the ground states of the Fe_4C_7 series, where the C_3 ring is replaced by a C_4 ring. The spin multiplicity of Fe_4C_8 and Fe_4C_8^- are the same as in Fe_4C_7 and Fe_4C_7^- , respectively, while the ground state of the Fe_4C_8^+ cation is AF and has $2S+1=5$. This trend continues in the Fe_4C_9 series. The ground-state Fe_4C_9 neutral is presented in Fig. 2 and possesses a chair-type geometrical structure.

In order to form the ground-state Fe_4C_{10} neutral, an additional carbon atom attaches to the C_5 unit and attaches to Fe_4 from below. In Fe_4C_{11} , a C_{11} ring attached to a Fe_3 face corresponds to the lowest energy isomer. Let us note, that a C_{10} ring attached to a Fe_3 face forms an isomer of Fe_4C_{10} that is +1.86 eV higher in total energy than the isomer shown in Fig. 2. In the lowest energy isomer of Fe_4C_{16} , a carbon C_{16} ring attaches to a Fe_3 face (see Fig. 2). This trend continues in Fe_4C_{17} , and is expected to stop at C_{20} where bowl, cage, and ring isomers are found [25] to be energetically indistinguishable.

The dependence of total energies of Fe_4C_n on the spin multiplicities, or, in other words on excess spin densities at iron sites, shows no clear pattern. Thus, the difference in total energies of Fe_4C_7 when moving from the lowest $2S+1=13$ state to the lowest $2S+1=1$ state is 1.00 eV, that is, the same as in the bare iron cluster Fe_4 , while for Fe_4C_6 and Fe_4C_{12} small differences of 0.38 and 0.50 eV are found, respectively.

Figure 2 shows also the ground state of the corresponding neutral C_n species optimized at the same BPW91/6-311+G* level of theory. In agreement with experiment [26], we found that ground-state C_n and C_n^- are linear for $n=3-9$ and have ring forms of C_{2v} , C_{2h} , or C_s symmetry for $n=10-20$. In the cation series, the ring configurations are the most stable ones beginning with $n=8$.

Fig. 1. Bond lengths are in Å, excess spin densities at iron atoms are in electrons, and M is the spin multiplicity $2S+1$. AF means state where excess spin densities at iron sites are coupled antiferromagnetically.

In accord with this geometrical shape change in C_n , the carbon atoms forms dimers, trimers, tetramers and pentamers in Fe_4C_n for $n=4-9$, a tetramer and an hexamer in intermediate Fe_4C_{10} , and rings beginning with $n=11$.

Since the ring structures of C_n are only preferable up to $n=20$, one expects that further carbon attachment would lead to carbon sheets, which is next step toward the growth of a carbon nanotube. The computations of Fe_4C_n for $n>16$ are currently under way.

Let us consider briefly the thermodynamic stability of Fe_4C_n and C_n taking first Fe_4C_7 as an example:

Fig. 2. Ground states of neutral Fe_4C_9 , Fe_4C_{10} , Fe_4C_{12} , Fe_4C_{16} together with ground states of C_9 , C_{10} , C_{12} , and C_{16} . Bond lengths are in Å, excess spin densities at iron atoms are in electrons, and M is the spin multiplicity $2S+1$. Note that pure C_n are 0.8 scaled in order to fit the figure.

Complimentary channels show a similar trend of a larger binding energy for C_4 than C_3 .

The channel $C_3 + C_4 \rightarrow C_7$ produces 6.18 eV, which results in the energy of the $Fe_4C_7 \rightarrow Fe_4 + C_7$ channel of 5.58 eV. Of course, the same energy is obtained in the direct computation $E_{tot}(Fe_4C_7) - E_{tot}(Fe_4) - E_{tot}(C_7)$. One sees that the binding energies of C_n to Fe_4 or Fe_4C_m ($n, m = 3$ or 4) are rather similar to the energy gained from $C_3 + C_4 \rightarrow C_7$.

Beginning with $n=11$, the carbons form a ring and the additional C—C bonds may influence thermodynamic patterns. Let us consider, as an example, the decay channels of Fe_4C_{16} .

That is, the detachment of C_8 from the ring in Fe_4C_{16} is less costly than the detachment of C_8 from the iron cluster in Fe_4C_8 and the C_{16} ring is less bound to Fe_4 than are the two C_4 chains in the Fe_4C_8 cluster. The ring formation becomes favorable due to the high energy of dimerization $C_8 + C_8 \rightarrow C_{16}$, which is 8.11 eV according to our computations at the same level of theory, and not from a stronger bonding of the ring to the cluster.

4 Conclusion

The results of our computations using density functional theory on Fe_4C_n , $n=7-16$, revealed that

- (i) The carbon atoms forms two chains attached in such a way as to form a ring containing two iron atoms for $n=7, 8$ and 9 .
- (ii) Carbon atoms form rings on the top of a Fe_3 face for $n=11-16$.
- (iii) Fe_4C_{10} presents an intermediate state between these (i) and (ii) where C_4 and C_6 do not form a ring.
- (iv) The trend in preferable deposition of carbon atoms on the Fe_4 cluster is similar to the trend in geometrical shape of free C_n species, where the linear—ring transition occurs at $n=10$.
- (v) The iron catalyst in the HiPco process reduces significantly the barrier for the Boudouard reaction which releases carbon atoms followed by their reconstruction into rings at the catalyst surface. After the ring template is created on the catalyst, it is likely that all subsequent carbon atom production on the catalyst leads to growth of the SWNT. However, there could well be a tradeoff between growth rate and the number of defects.

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References

1. Su, M., Liu, J.: A scalable CVD method for the synthesis of single-walled carbon nanotubes with high catalyst productivity, *Chem. Phys. Lett.* 322 (2000) 321-326.
2. Maruyama, S., Murakami, Y., Shibuta, Y., Miyauchi, Y., Chiashi, S.: Generation of Single-Walled Carbon Nanotubes from Alcohol and Generation Mechanism by Molecular Dynamics Simulations, *J. Nanosci. Nanotech.* 4 (2004) 360-367.
3. Arepalli, S.: Laser Ablation Process for Single-Walled Carbon Nanotube Production, *J. Nanosci. Nanotech.* 4 (2004). 317-325.
4. Dai, H., Rinzler, A.G., Nikolaev, P., Thess, A., Golbert, D.T., Smalley, R.E.: Single-wall nanotubes produced by metal-catalyzed disproportionation of carbon monoxide, *Chem. Phys. Lett.* 260 (1996) 471-475.
5. Kong, J., Cassel, A.M., Dai, H.: Chemical vapor deposition of methane for single-walled carbon nanotubes. *Chem. Phys. Lett.* 292 (1998) 567-574.
6. Nikolaev, P., Bronikowski, M.J., Bradley, R.K., Rohmund, F., Colbert, D.T., Smith, K.A., Smalley, R.E.: Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide, *Chem. Phys. Lett.* 313 (1999) 91-97.
7. Nikolaev, P.: Gas-Phase Production of Single-Walled Carbon Nanotubes from Carbon Monoxide: A Review of the HiPco Process, *J. Nanosci. Nanotech.* 4 (2004) 307-316.
8. Tsui, F., Ryan, P.A.: Self-Organization of Carbide Superlattice and Nucleation of Carbon Nanotubes, *J. Nanosci. Nanotech.* 4 (2004) 408-413.
9. Jost, O., Gorbunov, A., Liu, X., Pompe, W., Fink, J.: Single-Walled Carbon Nanotube Diameter, *J. Nanosci. Nanotech.* 4 (2004) 433-440.
10. Gavillet, J., Thibault, J., Stéphan, O., Amara, H., Loiseau, A., Bichara, C., Gaspard, J.-P., Ducastelle, F.: Nucleation and Growth of Single-Walled Nanotubes: The Role of Metallic Catalysts, *J. Nanosci. Nanotech.* 4 (2004) 346-359.
11. Zhao, J., Martinez-Limia, A., Balbuena, P. B. Understanding Catalysed Growth of Single-Wall Carbon Nanotubes, *Nanotechnology*, 16, (2005). S575-S581.
12. Ding, F., Rosén, A., Bolton, K.: Molecular dynamics study of the catalyst particle size dependence on carbon nanotube growth, *J. Chem. Phys.* 121 (2004) 2775-2779.
13. Fan, X., Buczko, R., Puzos, A.A., Geohegan, D.B., Howe, J.Y., Pantelides, S.T., Pennycook, S.J.: Nucleation of Single-Walled Carbon Nanotubes, *Phys. Rev. Lett.* 90 (2003) 145501-145504.
14. Wells, J.C., Noid, D.W., Sumpter, B.G., Wood, R.F., Zhang, Q.: Multiscale simulations of carbon nanotube nucleation and growth: Electronic structure calculations: *J. Nanosci. Nanotech.* 4 (2004) 414-422.
15. Gutsev, G.L., Bauschlicher, Jr., C.W. : Structure of neutral and charged Fe_nCO clusters ($n = 1-6$) and energetics of the $\text{Fe}_n\text{CO} + \text{CO} \rightarrow \text{Fe}_n\text{C} + \text{CO}_2$ reaction, *J. Chem. Phys.* 119 (2003) 368-3690.
16. Gutsev, G.L., Bauschlicher, C.W., Jr.: Interaction of carbon atoms with Fe_n , Fe_n^- , and Fe_n^+ clusters ($n=1-6$), *Chem. Phys.* 291 (2003) 27-40.
17. Gutsev, G.L., Mochena, M.D., Bauschlicher, C.W., Jr.: Structure and properties of Fe_4 with different coverage by C and CO, *J. Phys. Chem.* 108 (2004) 11409-11418.

18. Gutsev, G.L., Mochena, M.D., Bauschlicher, C.W., Jr.: All-electron DFT modeling of SWCNT growth on iron catalysts from carbon monoxide feedstock, *J. Nanosci. Nanotech.*, in press.
19. Schnabel, P., Irion, M.P., Weil, K.G.: Evidence for low-pressure catalysis in the gas phase by a naked metal cluster: the growth of benzene precursors on iron (Fe_4^+), *J. Phys. Chem.* 95 (1991) 9688-9694.
20. Becke, A.D.: Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A* 38 (1988) 3098-3100.
21. Perdew, J.P., Wang, Y.: Accurate and simple analytic representation of the electron-gas correlation energy, *Phys. Rev. B* 45 (1992) 13244-13249.
22. Raghavachari, K., Trucks, G.W.: Highly correlated systems: Excitation energies of first row transition metals Sc–Cu, *J. Chem. Phys.* 91 (1989) 1062-1065.
23. Chrétien, S., Salahub, D.R.: Kohn-Sham density-functional study of low-lying states of the iron clusters $\text{Fe}_n^+/\text{Fe}_n/\text{Fe}_n^-$, *Phys. Rev. B* 66 (2002) 155425-155437.
24. Gutsev, G.L., Bauschlicher, C.W., Jr.: Electron affinities, ionization energies, and fragmentation energies of Fe_n clusters ($n = 2-6$): A Density Functional Theory study, *J. Phys. Chem. A* 107 (2003) 7013-7023.
25. An, W., Bulusu, S., Zeng, X.C.: Ab initio calculation of bowl, cage, and ring isomers of C_{20} and C_{20}^- , *J. Chem. Phys.* 122 (2005) 1-8.
26. Yang, S., Taylor, K.J., Craycraft, M.J., Conceicao, J., Pettiette, C.L., Cheshnovsky, O., Smalley, R.E.: UPS of 2–30-atom carbon clusters: Chains and rings, *Chem. Phys. Lett.* 144 (1988) 431-436.