Interaction between Fe and single-walled carbon nanotube near the entrance

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Abstract.
We have investigated the interaction between an Fe atom and a single-walled carbon nanotube near the entrance, by means of the first principles total energy calculation. (10,0) carbon nanotube composed of 80 atoms is used for the calculation. We determined the most stable position of the Fe atom near the entrance of the nanotube.

1. Introduction
Since the discovery of fullerenes [1], multi-walled carbon nanotubes [2] and single-walled carbon nanotubes [3], nano carbon materials have been attracted much current interest. In particular, carbon nanotubes are expected to be applied to a variety of nano-devices. Recently, some first-principles study inserting foreign atoms and molecules to the single-walled carbon nanotube has been performed. One is a first-principles molecular dynamics simulation to insert sodium or potassium atom into single-walled carbon nanotube through the surface of cage clarifying that encapsulation is possible [4]. The other is the electronic structure calculation of carbon peapod, C₆₀ encapsulated single-walled carbon nanotubes [5]. Concerned with carbon peapod, fullerenes inside the peapod coalescing each other and forming stable zeppelinlike carbon molecules are observed experimentally at suitable high kinetic energy [6]. One way to synthesize single-walled carbon nanotubes is the arc discharge method which is to evaporate the mixture of metal and carbon in an inert gas atmosphere. In this way, Fe is used for a metal catalyst [7]. By this method, the cage or tube structures are made up with carbon atoms and single-walled carbon nanotubes are created. For this fact, it is interesting to investigating the relationship between single-walled carbon nanotubes and an Fe atom. Concerning single-walled carbon nanotube and Fe atom, some theoretical calculations have been performed quite recently. One is a study to investigate an Fe atom interacting with the surface of single-wall carbon nanotubes [8]. The other is a calculation of single-walled armchair carbon nanotubes doped with 3d transition metals [9]. However, the behavior of an Fe atom around the entrance of single-walled carbon nanotube has not been theoretically investigated yet. In the present study, we analyze the most stable position and the potential curve of an Fe atom in a single-walled carbon nanotube by using a first-principles method.
2. Methodology
In the present study, we consider (10,0) single-walled carbon nanotube composed of 80 carbon atoms. We choose points $A \sim G$ near the entrance of the single-walled carbon nanotube as shown in Fig.1. From these points, we draw the perpendicular lines to the central axis of optimized single-walled carbon nanotube. We put an Fe atom on the perpendicular lines from points $A \sim D$ and from points $E \sim G$ to the central axis as shown in Fig.2 and Fig.3, respectively. We also choose points $H \sim K$ on the central axis shown in Fig.4 and put an Fe atom at one of these points. At each position, we calculate the total energy of the system to find the most stable position of Fe.

For the first-principles calculation, we adopt the Materials Studio (MS) Modeling DMol3[10,11,12]. This is an all-electron method which uses numerical basis functions, each of which is a localized atomic orbital (AO). Since we use localized basis only in this calculation, the cell is non periodic. We use the double numerical plus d-function (DND), which provides reasonable accuracy for modest computational cost. We use the PWC (Perdew-Wang correlation) [13] based on the local density approximation (LDA) of density functional theory (DFT). In the calculation, we use smearing of electron occupancy to get good convergence. We gradually change the value of the smearing parameter smaller and calculate again. We repeat this procedure until a value of the smearing parameter becomes equal to zero. Then, we analyze the behavior of the potential curve for an Fe atom.

3. Results and Discussion
The results of the calculated total energy are shown as follows. Here the energies given are all relative values.

The result calculated on the perpendicular lines from points $A \sim D$ to central axis shown in Fig.2 is plotted in Fig.5. In Fig.6, the abscissa is the distance from the surface of the single-walled carbon nanotube cage. We calculate from the position where an Fe atom is not too close to C atoms.

This result suggests that the total energy of the system becomes higher from points $A \sim D$. Therefore the potential energy that an Fe atom feels becomes higher and an Fe atom becomes unstable when it enters in the tube deeper. This suggests that an Fe atom is difficult to enter inside the single-walled carbon nanotube. Furthermore, except for the position near the cage surface of single-walled carbon nanotube, when an Fe atom gets near the central axis, it tends to be unstable.

The result calculated on the perpendicular lines from points $E \sim G$ to the central axis shown in Fig.3 is plotted in Fig.6.

The total energy of the system becomes higher from $E \sim G$ to the central axis, its becomes unstable. This tendency is common to points $A \sim D$. Therefore the potential energy that an Fe atom feels becomes higher and an Fe atom becomes unstable when it enters in the tube deeper. The result of the total energy at points $H \sim K$ on the central axis shown in Fig.4 is plotted in Fig.7.

According to this result, we find that when an Fe atom moves apart from the entrance of single-walled carbon nanotube, an Fe atom becomes unstable. We can see that the differences in points $I \sim K$ are smaller than the differences in the $A \sim D$ lines and in the $E \sim G$ lines. So this result suggests that there is a stable point near the entrance of nanotube.

These calculations tell us that Fig.8 is the most stable position for Fe atom. During these calculations, we have fixed the structure of the single walled carbon nanotube. So Fig.8 may not be the true optimized structure. To see the most stable structure, we apply geometric optimization starting from the system shown in Fig.8. After this optimization, we find that the most stable structure of the system which consist of an Fe atom and single-walled carbon
nanotube is given by Fig.9. Although the entrance of the carbon nanotube is slightly deformed, the overall structure is essentially the same as that given in Fig.8.

4. Summary
In this paper, we have calculated the total energy of (10,0) carbon nanotube incorporated with an Fe atom by using the *ab initio* program DMol³. Just under the surface of the nanotube cage, the total energy becomes higher as an Fe atom enters deeper, while on the central axis, the change in the total energy is small. The difference in the energy between inside and outside of nanotube gets smaller and smaller when the Fe atom gets closer to the central axis. Collecting all the results, we find that the most stable position is at the point shown in Fig.8 or, after optimization, at the point shown in Fig.9.

According to these results, we find that an Fe atom does not enter the nanotube automatically. Without any external energy, the Fe atom will settle at the position shown in Fig.9. This result goes well with the actual behavior. On the way of composing nanotubes, though Fe atoms exist around nanocages and fullerenes, they do not enter the single-walled carbon nanotubes. This result, that the most stable point is near the entrance of nanotube, seems to be related to the fact that the Fe atom acts as a catalyst to grow single-walled carbon nanotubes.

5. References
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**Figure 1.** The starting locations of the perpendicular lines on which total energy is calculated.

**Figure 2.** The perpendicular lines starting from points *A* ~ *D* directing to the central axis
Figure 3. The perpendicular lines starting from points $E \sim G$ directing to the central axis.

Figure 4. Points $H \sim K$ on the central axis.

Figure 5. Calculated total energy on the perpendicular lines starting from points $A \sim D$.

Figure 6. Calculated total energy on the perpendicular lines starting from points $E \sim G$.

Figure 7. Result of the total energy at points $H \sim K$ on the central axis.

Figure 8. The most stable position of an Fe atom.
Figure 9. The most stable structure of the system which consist of an Fe atom and single-walled carbon nanotube.