Electronic structures of Pt clusters adsorbed on (5,5) single wall carbon nanotube

Dam Hieu Chi [a,d,*], Nguyen Thanh Cuong [a], Nguyen Anh Tuan [a,d], Yong-Tae Kim [a],
Ho Tu Bao [a], Tadaoki Mitani [a], Taisuke Ozaki [b], Hidemi Nagao [c]

[a] *Japan Advanced Institute of Science and Technology, School of Materials Science, 1-1 Asahidai, Nomi, Tatsunokuchi, Ishikawa 923-1292, Japan*
[b] *National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan*
[c] *Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan*
[d] *Faculty of Physics, Hanoi University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Viet Nam*

Abstract

We present a DFT study for the adsorption of single Pt atom and Pt clusters on graphene surface and carbon nanotube. Adsorption of a Pt atom shows a heavy dependence of binding energy on the graphene curvature. The adsorbed Pt atoms tend to form clusters, than to disperse on the graphene surface. The Pt–Pt bond length and the charge transfer from Pt clusters to the nanotube vary as a function of cluster size. A simulation of oxygen adsorption suggests higher performance for catalytic activities of Pt clusters adsorbed on the nanotube, in comparison with free Pt clusters.
© 2006 Elsevier B.V. All rights reserved.

1. Introduction

Catalysis plays an innovative role in developing new technologies. Therefore, catalyst design (a key factor for enhancing technological performance) has become a big issue in industrialization. Nanotechnology is believed to be important in heterogeneous catalysis due to its peculiar properties and potential applications. Because of their potential applications as building blocks for functional nanostructured materials, electronic devices, and nanocatalysts, interest in metal nanoclusters has been growing recently [1].

On the other hand, it is believed that cluster size strongly affects the properties of the clusters [1], promoting the requirement for a proper method to synthesize clusters of a certain size. The carbon nanotube [2,3] with its beautiful

tubular structure and large effective surface, which can facilitate the adsorption of small catalyst particles, is strongly proposed as a solution for the cluster size control problem.

Recently we succeeded in establishing a new concept, based on a fundamental bottom-up approach, for synthesizing highly dispersed and size-controlled Pt clusters on carbon nanotube supports, which is called the single-atom-to-cluster (SAC) approach [4]. An extreme single atom dispersion, and size control of clusters made from these dispersed single atoms, was achieved by the method.

In this Letter, we report our theoretical study on Pt atoms and clusters adsorbed on graphene surface and carbon nanotube. Our calculations demonstrate that the cluster state is more stable than the single atom dispersed state for Pt on a graphene surface. The study of the adsorption of Pt_n ($n = 3, 5, 7$) clusters on metallic (5,5) single wall carbon nanotube (Pt_n/SWNT) suggests a mixing between electron states of the nanotube and the adsorbed clusters. The adsorption derived strong Pt–C bondings and charge transfers from Pt single atoms and Pt clusters toward the tube.

* Corresponding author. Address: Japan Advanced Institute of Science and Technology, School of Materials Science, 1-1 Asahidai, Nomi, Tatsunokuchi, Ishikawa 923-1292, Japan. Fax: +81 761511535.
E-mail address: dam@jaist.ac.jp (D.H. Chi).

An investigation of the adsorption of O_2 on the Pt_n/SWNT theoretically confirms the influence of the transition in the electronic structure on the catalytic performance of the systems.

2. Simulation details

We performed calculations based on density functional theory (DFT) [5,6] using DMol³ [7] and OpenMX [8] codes, with the electronic wave functions expanded in double valence plus d-functions. For the exchange and correlation terms, the generalized gradient approximation (GGA) PBE functional [9] is used. The Density Functional Semi-core Pseudo Potentials [10] (DMol³) and Troullier–Martine PseudoPotentials [11] (OpenMX) are used to describe the interaction between the core and the valence electrons. The cluster calculations were carried out for the adsorption of one Pt atom on graphene and the bent graphene surfaces with difference curvatures. The bent graphene surfaces were built by using parts of the (n,n) SWNTs with hydrogen adjustment (containing 84 carbon atoms and 26 hydrogen atoms). All of the carbon atoms at the boundary were fixed in the optimization.

For calculations of Pt clusters adsorbed on the (5,5) single wall carbon nanotube, we applied the periodic supercells with edge lengths of a and b lattices of 25.0 Å and 16.0 Å, which are large enough for us to be able to ignore the interaction between the Pt_n-nanotube and its periodic images. The c lattice (17 Å) aligned with the axis is tuned to match the periodic condition. The irreducible Brillouin zone is sampled by eight k-points generated by the Monkhorst–Pack technique [12]. Binding energies for adsorption were computed using the expression

$$E_{bind} = E_{Pt_n} + E_{SWNT,Graphene} - E_{Pt_n/SWNT,Graphene} \qquad (1)$$

where E_{Pt_n} and $E_{SWNT,Graphene}$ are the total energies of a freestanding Pt atom/cluster and a bare carbon nanotube/graphene surface, respectively, and $E_{Pt_n/SWNT,Graphene}$ is the total energy for the optimized configuration with Pt atom and clusters adsorbed on the nanotube/graphene surface.

3. Results and discussion

3.1. Adsorption of Pt single atom on graphene surface and (5,5) single wall carbon nanotube

We investigated the adsorption of a Pt single atom on the graphene surface in the preliminary stage of our study. The adsorption of a Pt atom on the bridge sites is found to have the highest binding energy (1.45 eV), consistent with previous study [13]. As a comparison, we examined the adsorption of Pt atom on the bent graphene surfaces with different curvatures. The obtained binding energies (Fig. 1a) clearly show that the curvature of the graphene surface increases the binding energies with Pt atoms. The large adsorption energy suggests substantial hybridization in electron orbitals of Pt atoms and metal-adjacent C atoms. Indeed, we found that the d electron states of Pt exhibit hybridized characteristics with s and p electron states of C, and these electrons are distributed not only in the region of the Pt atom, but also on the graphene surface to some extent (Fig. 1b), confirming the $sp^2 \rightarrow sp^3$ transition of metal-adjacent C atoms. Consideration of the energy reveals that the cluster state is more stable than the single atom dispersed state for Pt, despite the large adsorption energy of Pt atom on the graphene surface, in accordance with our experimental observations [4]. We also performed the calculation for the adsorption of a Pt atom on the (5,5) SWNT. We again observed substantial hybridization in the electron orbitals of the Pt atom and the metal-adjacent C atoms in the SWNT (Fig. 1c), consistent with previous predictions [14,15].

3.2. Adsorption of Pt clusters on (5,5) single wall carbon nanotube

First principles studies on the adsorption of Pt_n ($n = 3, 7, 13$) clusters on a (5,5) SWNT were performed for the next step. We chose the clusters with highest stability: the triangle structure, CTP structure [16], and I_h structure [17] for Pt_3, Pt_7, and Pt_{13} clusters, respectively. The adsorption configurations were optimized carefully, after considering several initial structures.
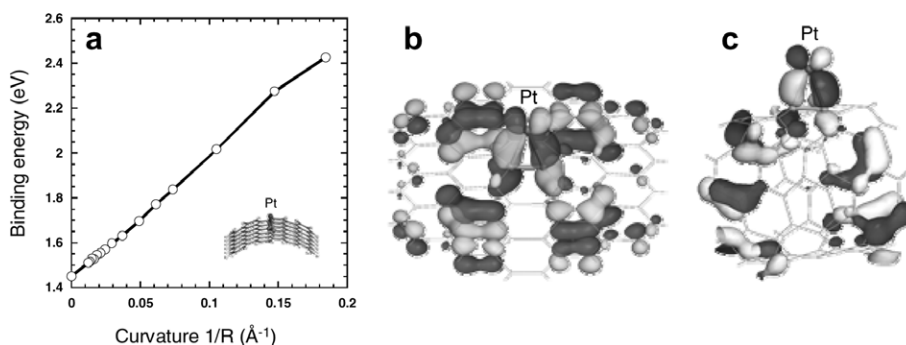

Fig. 1. Curvature dependence of binding energy of single Pt atoms on bent graphene surfaces and the adsorption configurations on graphene surface and (5,5) SWNT. (a) Curvature dependence of binding energy of Pt atoms on bent graphene surfaces. The molecular orbitals (with spd hybridized character) of the adsorbed Pt atom systems are shown in (b) on graphene surface (at $E = -7.055$ eV) and in (c) on a (5,5) SWNT (at $E = -8.168$ eV).
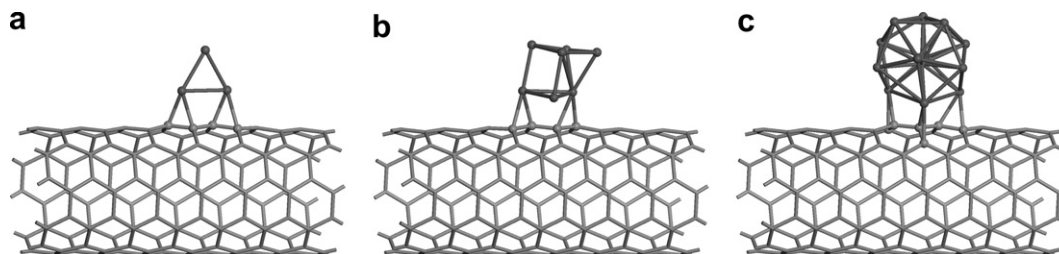
Fig. 2. Adsorption configurations of Pt$_3$ (a), Pt$_7$ (b), and Pt$_{13}$ (c) clusters on (5,5) SWNTs. The light gray cylinders indicate C atoms and C–C bonds, and the dark balls and cylinders indicate Pt atoms and Pt–Pt bonds.

For the adsorption of Pt$_3$ cluster, surprisingly only two Pt atoms have contact with the outer wall of the SWNT, these two atoms are located on top of the bridge sites of the tube (Fig. 2a). A similar calculation was performed by using CASTEP code with plane wave basis set, resulting in a similar adsorption configuration for Pt$_3$ cluster on the carbon nanotube. For the adsorption of Pt$_7$ cluster, similar to the case with Pt$_3$, our calculation reveals that it also adsorbed on the SWNT with two SWNT-adjacent Pt atoms (Fig. 2b). The adsorbed configuration shows an obvious deformation of the Pt$_{13}$ cluster with three SWNT-adjacent Pt atoms (Fig. 2c). The average Pt–Pt bond length in Pt$_3$, Pt$_7$, and Pt$_{13}$ are 2.57 Å, 2.72 Å, and 2.83 Å, respectively, suggesting the highest rebound between Pt atoms in the adsorbed Pt$_{13}$ clusters. For comparison, our obtained average Pt–Pt bond length in the free Pt$_3$, Pt$_7$, and Pt$_{13}$ clusters are 2.52 Å, 2.63 Å, and 2.76 Å, respectively. The binding energies of the three clusters adsorbed on the SWNT are summarized in Table 1, showing an obvious dependence of binding energy on the num-

ber of SWNT-adjacent Pt atoms. Calculations of the density of state (DOS) for the free and the adsorbed Pt clusters (Pt$_3$, Pt$_7$, and Pt$_{13}$) were performed. However, in this study, we are most interested in the adsorption on the SWNT of the Pt$_{13}$ cluster with I_h symmetry and a size of ca. 1 nm [17], because from previous experimental studies [4], we have learned that Pt clusters with a size of nearly 1 nm have the best catalytic performance. Therefore, in the discussion below, we focus on the adsorption of this cluster, due to its special interest.

Fig. 3c and 3e show the DOS of the adsorbed Pt$_{13}$ cluster (a-Pt$_{13}$) and free I_h Pt$_{13}$ cluster (f-Pt$_{13}$). At a glance, a deformation can be recognized in the DOS of a-Pt$_{13}$, including a change in shape and a shift by about 0.47 eV toward the lower energy region, compared with of the DOS of the f-Pt$_{13}$ cluster. The DOS for the geometrically deformed Pt$_{13}$ (d-Pt$_{13}$) cluster in isolation from the (5,5) SWNT (Fig. 3d) was calculated for comparison. The DOS of the d-Pt$_{13}$ cluster is found to be more similar to that of the a-Pt$_{13}$ cluster than to that of the f-Pt$_{13}$ cluster, suggesting that the deformation in the shape of the DOS of the adsorbed cluster is mainly derived from its geometric deformation. However, an obvious contribution from the hybridization between electron states of the nanotube and the metal cluster can be identified.

Table 1
Binding energy for adsorptions of the Pt$_n$ ($n = 3, 7, 13$) on the SWNT

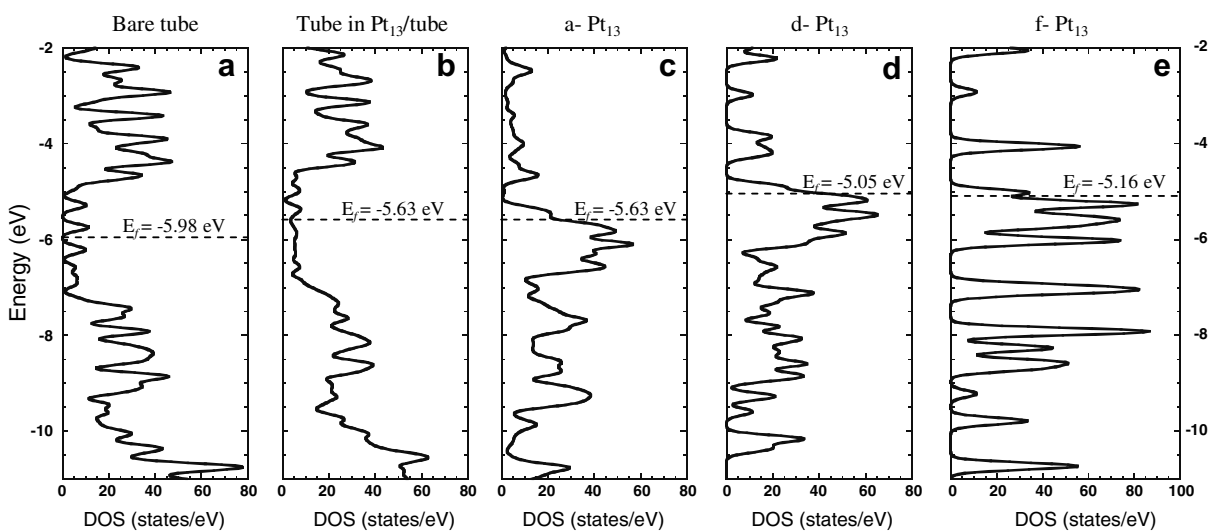|	Pt$_3$	Pt$_7$	Pt$_{13}$
E_b (eV)	2.94	2.99	4.81

Fig. 3. Projected density of states of (a) a bare (5,5) SWNT, (b) the SWNT where Pt$_{13}$ is adsorbed on, (c) the Pt$_{13}$ adsorbed on the SWNT (a-Pt$_{13}$), (d) the geometrically deformed and free-standing Pt$_{13}$ (d-Pt$_{13}$), and (e) the free-standing I_h Pt$_{13}$. The horizontal dotted lines denote the Fermi levels.
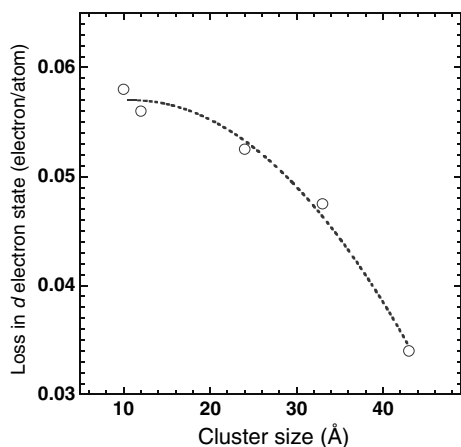
Fig. 4. Cluster size dependence of the loss in d-electron state of Pt atoms in Pt_n/CNT systems (compared with that of Pt in foil).

The difference in the Fermi level of the a-Pt_{13} cluster and the d-Pt_{13} cluster clearly shows a charge transfer from the Pt clusters into the carbon nanotube in the adsorption process. On the other hand, the DOS of the SWNT where the Pt_{13} cluster is adsorbed (Fig. 3b) shifts up by about 0.35 eV in comparison with a bare (5, 5) SWNT (Fig. 3d). This substantial shift can be explained by the reduction in effective Coulomb potential due to the charge transfer.

From the X-ray absorption experiment, we measured the number of unoccupied d-electron states of Pt atoms in the clusters adsorbed on the carbon nanotube. Fig. 4 shows the cluster size dependence of the loss of d-electron state of Pt atoms in cluster (compared with that of Pt in foil). We found that a Pt atom in clusters with a radius of about 1 nm, adsorbed on a carbon nanotube, has an occupied state of less than 0.06 electrons with d character than a Pt atom in foil.

For comparison, we performed Mulliken charge analyses to evaluate the amount of electron transfers from the Pt clusters to the SWNT (Table 2). The charge transfer amount (per Pt atom) is found to decrease with the size of the adsorbed cluster, qualitatively in agreement with our experimental observation. This result suggests a hypothesis for the origin of the loss of the d-electron state of Pt atoms, in which the charge transfer is the main contributor.

The above-mentioned charge transfer behavior, together with the transition in the electronic state of both Pt and metal-adjacent C atoms, is expected to affect the electronic structure and therefore the performance of the catalytic activities of the system.

3.3. Adsorption of O_2 on Pt_{13}/SWNT

To gain insight into the performance of catalytic activities of the Pt clusters adsorbed on carbon nanotubes, we carried out a study of the adsorption of O_2 on the Pt_{13} adsorbed on the (5, 5) SWNT. We considered several configurations for the adsorption of O_2 and calculated their electronic structures. We also conducted similar calculations for the adsorption of O_2 on the free Pt_{13} for comparison. All of our calculations demonstrated that electron states of O_2 hybridize more easily with the electron state of the Pt cluster adsorbed on the SWNT, than with that of the free Pt cluster, due to the lower Fermi level. These results preliminarily confirm our above-mentioned expectation that the adsorption of the Pt cluster on the SWNT affects catalytic activities. Further investigation of the catalytic activities of Pt clusters adsorbed on carbon nanotubes is promising.

4. Conclusions

We performed first principles studies on the adsorption of a single Pt atom on a graphene surface and on a (5, 5) single wall carbon nanotube, the adsorption of Pt_n ($n = 3, 7, 13$) clusters on a (5, 5) single wall carbon nanotube. The best adsorption sites for single Pt atoms are the bridge-type sites on graphene surfaces and outer wall of the SWNT, and the curvature of the surface does heavily affect the adsorption. Consideration of energy reveals that the cluster state is more stable than the single atom dispersed state for Pt on a graphene surface. The study of the electronic structure suggests a mixing between electron states of the nanotube and the metal clusters in adsorption. The adsorption resulted in strong Pt–C bondings and charge transfers from Pt single atoms and Pt clusters toward the SWNT. An investigation of the adsorption of O_2 on the Pt cluster adsorbed on the SWNT theoretically confirms the influence of the transition in the electronic structure on the performance of catalytic activities of the systems. The present results clearly demonstrate that the electron exchange nature in the metal clusters adsorbed on carbon nanotube systems brings about a new aspect of heterogeneous catalyses.

Acknowledgements

References

[1] G. Schmid, Adv. Eng. Mater. 3 (2001) 737.
[2] E. Frackowiak, G. Lota, T. Cacciaguerra, F. Beguin, Electrochem. Commun. 8 (2005) 129.

Table 2
Charge transfer from the Pt clusters to the carbon nanotube in the adsorption process

	Pt_3	Pt_7	Pt_{13}
Total charge transfer (e)	0.81	1.23	1.86

[3] R. Yuge, T. Ichihashi, Y. Shimakawa, Y. Kubo, M. Yudasaka, S. Iijima, Adv. Mater. 16 (2004) 1420.

[4] Yong Tae Kim et al., Angew. Chem. Int. Ed. 45 (2006) 407.

[5] P. Hohenberg, W. Kohn, Phys. Rev. B 136 (1964) 864.

[6] W. Kohn, L.J. Sham, Phys. Rev. A 140 (1965) 1133.

[7] B. Delley, J. Chem. Phys. 92 (1990) 508.

[8] T. Ozaki, Phys. Rev. B 67 (2003) 155108.

[9] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.

[10] B. Delley, J. Chem. Phys. 113 (2000) 7756.

[11] N. Troullier, J.L. Martine, Phys. Rev. B 43 (1991) 1993.

[12] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 12 (1976) 5188.

[13] A. Maiti, A. Ricca, Chem. Phys. Lett. 395 (2004) 7.

[14] E. Durgun, S. Dag, V.M.K. Bagci, O. Gulseren, T. Yildirim, S. Ciraci, Phys. Rev. B 67 (2003) 201401.

[15] G. Chen, Y. Kawazoe, Phys. Rev. B 73 (2006) 125410.

[16] Wei Quan Tian, Maofo Ge, B.R. Sahu, Dianxun Wang, Toshiki Yamada, Shinro Mashiko, J. Phys. Chem. A 108 (2004) 3806.

[17] E. Apra, A. Fortunelli, J. Phys. Chem. A 107 (2003) 2934.