A molecular dynamics study on the formation of metallofullerene

Yasutaka YAMAGUCHI & Shigeo MARUYAMA
Department of Mechanical Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

The growth process of metal-containing fullerenes is studied by using the molecular dynamics method similar to our simulations of prefect C_{60} and C_{70} formation [1,2]. In order to model the metal-carbon potential function appropriate for the MD simulation, the binding energy and charge state of various forms of small clusters MC_n (M: La, Sc, Ni) were calculated with the density functional theory based on the Becke's three-parameter exchange functional with the Lee-Yang-Parr correlation (B3LYP). A multi-body potential function was constructed as a function of coordinate number of a metal atom, where the Coulomb and the Morse terms were separately described considering the charge transfer from a metal atom to carbon atoms. The differences of the La-C, Sc-C and Ni-C interactions are qualitatively expressed as strongly ionic, weakly ionic and non-ionic, respectively.

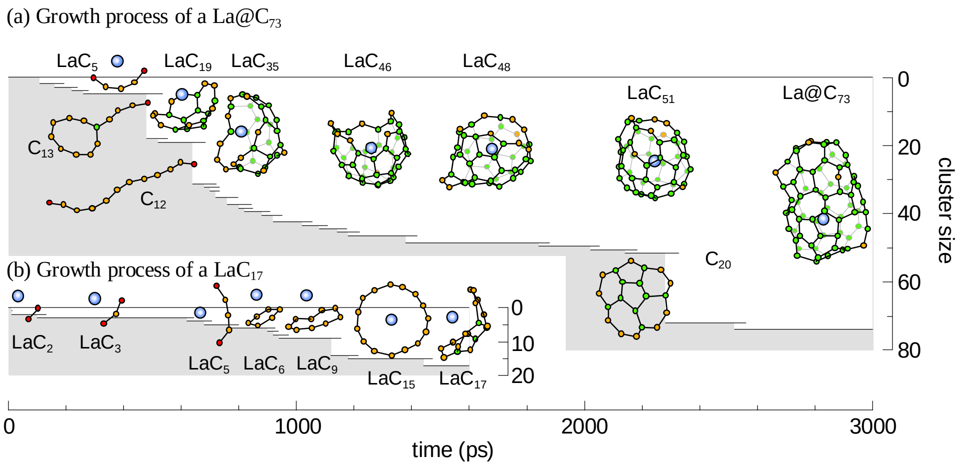
The clustering processes starting from randomly distributed 500 carbon and 5 metal atoms in a 342Å cubic cell were simulated under the controlled temperature condition, where the translational, rotational and vibrational temperatures of clusters were kept nearly equilibrium at T_c=3000K. Fig. 1 and 2 show the growth processes of typical metal attached carbon clusters, where the vertical position and horizontal length denote the size and the existing time of clusters, respectively.

When La atoms were applied as the additional metal, short carbon chains surrounded the La atom for the cluster smaller than LaC_5, and the La atom attached on the monocyclic carbon ring for LaC_{6-15} as shown in Fig. 1. The host monocyclic ring changed to a poly-cyclic ring and the La atom attached on it around LaC_{17}, where the Coulomb attractive force induced curvature to the host poly-cyclic ring. The host annealed to a curved graphite-like sheet when it grew as large as LaC_{19}, and extended the structure until about LaC_{35}, resulted in the formation of a stable open-cap structure, and kept growing with closing the open-cap structure.

Another clustering process using Sc atoms was simulated under the same condition. The structures of the host carbon clusters were not affected a lot compared to those in La-C system because of the weaker Coulomb force. The cluster annealed to the 3-dimensional open cage structure around ScC_{40}, where the Sc atom moved around open edge, and finally, the Sc atom slipped into the caged structure just before closing at around $Sc@C_{54}$ and stably encapsulated inside the cage.

Nickel atoms, which is not experimentally assigned to be encapsulated in the fullerene cage so far, were also applied as shown in Fig. 2. The growth process is very similar to that for Sc attached cluster. Although, even at the final stage, the Ni atom preferred to attach at the large defect of the caged structure such as large rings of more than 7 or 8 membered, and frequently moved in and out of the carbon cage.

1. Y. Yamaguchi and S. Maruyama, *Chem. Phys. Lett.*, **286**, 336 (1998)
2. S. Maruyama and Y. Yamaguchi, *Chem. Phys. Lett.*, **286**, 343 (1998).


(a) Growth process of a $La@C_{73}$

(b) Growth process of a LaC_{17}

Fig. 1. Growth process of La attached clusters: (a) $La@C_{73}$ and (b) $La@C_{17}$.

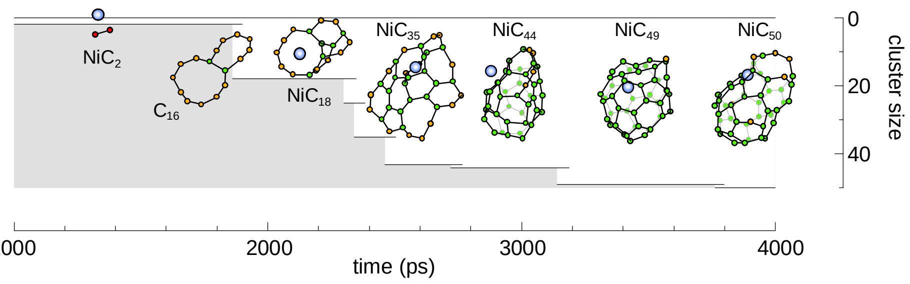


Fig. 2. Growth process of a Ni attached cluster NiC_{50}.

A MOLECULAR DYNAMICS STUDY ON THE FORMATION OF METALLOFULLERENE

Yasutaka Yamaguchi & Shigeo Maruyama
Department of Mechanical Engineering
The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

The growth process of metal-containing fullerene was studied by using the molecular dynamics method. Based on DFT calculations of small clusters MC_n (M: La, Sc, Ni) and M_n (M = La, Sc, Ni), a multi-body potential functions for M-C and M-M interactions were constructed with Morse-type and Coulomb terms. The clustering process starting from isolated 500 carbon and 5 metal atoms was simulated under the controlled temperature condition at 3000 K. When La atoms were applied, the stable open-cap structure surrounding the La atom resulted in the La-containing caged cluster. For Sc-C and Ni-C systems, structures of host carbon clusters were not largely affected by metal atoms. The Sc atom was completely encapsulated in the caged structure at the final stage of the growth process, while the Ni atom stayed at the open edge of the cage.

INTRODUCTION

After the discovery of C_{60} by Kroto *et al.* (1) in 1985, macroscopic amount of empty fullerene (2,3), metallofullerenes (4-7), higher fullerenes (8) and carbon nanotubes (9) were successively produced and isolated. Recently, the high quality generation of single walled nanotubes (SWNTs) (10,11) has demonstrated new possibilities of applications, Though fullerene is now recognized as a new attractive material, the formation mechanism of these symmetric hollow caged structures is still unknown.

We have performed molecular dynamics simulations of the clustering process of carbon atoms to investigate the fullerene formation mechanism (12,13), and the temperature dependence of the cluster structures was observed (12). In addition, the formation of perfect C_{60} structure was demonstrated by giving sufficient annealing time, and the time and temperature scale of the annealing process was examined considering the reaction rate of the network rearrangements. Based on these results, a new formation model of empty fullerene was proposed (13).

The formation process of metallofullerene was studied using the similar molecular dynamics simulations in this paper. Despite the expectations of applications, it is still difficult to obtain macroscopic amount of metallofullerene due to the extremely low yield of generation. In order to find the optimum generation condition, the understanding of the formation mechanism is inevitable. According to experimental studies, the transition metals such as Ca, Sr, Va, Sc, Y and lanthanides can be encapsulated inside the fullerene cage. On the other hand, Ni, Co, or Fe are required to generate the SWNTs (10,11), although they are not assigned to be encapsulated in the fullerene cage. Here, the effects of these metal atoms on the growth process of carbon clusters are still unknown. The difference of the growth processes among La, Sc and Ni containing systems were studied to investigate the effect of metal atoms in this paper.

METHOD

The potential function among carbon atoms was the same as in our previous reports (12-14). For the purpose of modeling the metal-carbon and metal-metal potential functions applicable for the MD simulation, the binding energy and charge state of various forms of small clusters MC_n and M_n (M: La, Sc, Ni) were calculated. Here the density functional theory based on the Becke's three-parameter exchange functional (15) with the Lee-Yang-Parr correlation (16) (B3LYP) was applied with the effective core potentials included in LANL2DZ basis of Gaussian 94 (17). The semi-empirical calculation results (18) were also referred for the Ni-Ni interaction.

Metal-carbon multi-body potential functions were constructed as functions of carbon coordinate number of a metal atom. The total potential energy was expressed as the sum of binding energy E_b as follows.

$$E_b = V_R + V_A + V_C \tag{1}$$

$$V_R = f(r_{ij}) \frac{D_e}{S-1} \exp\left\{-\beta\sqrt{2S}(r_{ij} - R_e)\right\} \tag{2}$$

$$V_A = -f(r_{ij}) \cdot B^* \frac{D_e S}{S-1} \exp\left\{-\beta\sqrt{2/S}(r_{ij} - R_e)\right\} \tag{3}$$

$$V_C = -f(r_{ij}) \frac{e^2}{4\pi\varepsilon_0} \frac{c_\mathrm{C} c_\mathrm{M}}{r_{ij}} \tag{4}$$

Here, r_{ij}, V_R and V_A denote the distance between metal i and carbon j, Morse-type repulsive and attractive terms, respectively. The Coulomb term V_C is applied only to the La-C and Sc-C interactions that were calculated to be strongly ionic due to the charge transfer from the metal to carbon atoms.

The coordinate number of the metal atom N^C is defined using the cut-off function $f(r)$, and both the additional term B^*_{ij} and the electric charge c are expressed as functions of the coordinate number. The effect of the angle among bonds is ignored here.

$$f(r) = \begin{cases} 1 & (r < R_1) \\ 1 + \cos\dfrac{r - R_1}{R_2 - R_1} \;/\, 2 & (R_1 < r < R_2) \\ 0 & (r > R_2) \end{cases} \tag{5}$$

$$N^\mathrm{C} = 1 + \sum_{\text{carbon } k(\neq j)} f(r_{ik}) \tag{6}$$

$$B^* = \left\{1 + b(N^\mathrm{C} - 1)\right\}^\delta \tag{7}$$

$$c_\mathrm{M} = 3 - \exp(-k_1 N^\mathrm{C} + k_2), \quad c_\mathrm{C} = c_\mathrm{M} / N^\mathrm{C} \tag{8}$$

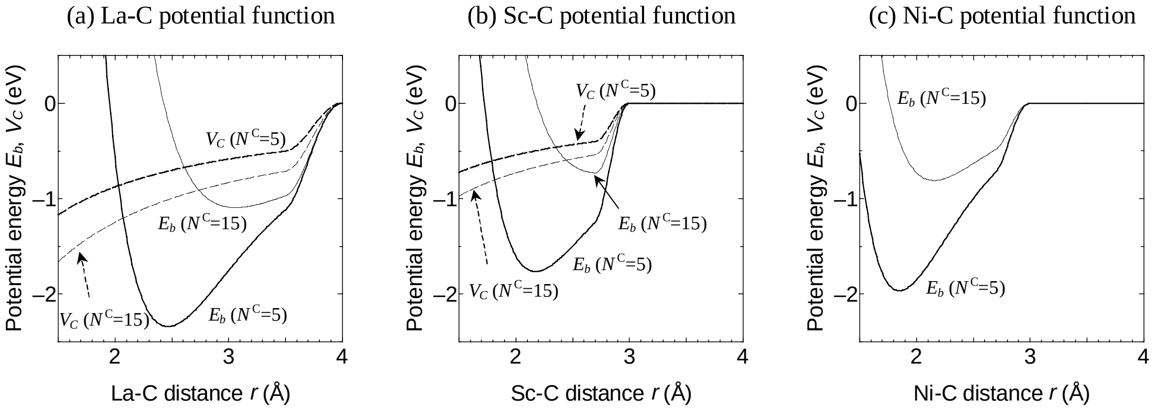
The potential parameters are shown in Table 1, and the total potential E_b and Coulomb term V_C of La, Sc and Ni for N^C=5 and N^C=15 are demonstrated in Fig. 1. The Coulomb interaction of La-C is much stronger than that for Sc-C.

Table 1 Potential parameters for metal-carbon interactions.

	D_e (eV)	S	β (1/Å)	R_e (Å)	R_1 (Å)	R_2 (Å)	b	δ	k_1	k_2
La-C	4.53	1.3	1.5	2.08	3.2	3.5	0.0854	-0.8	0.0469	1.032
Sc-C	3.82	1.3	1.7	1.80	2.7	3.0	0.0936	-0.8	0.0300	1.020
Ni-C	3.02	1.3	1.8	1.70	2.7	3.0	0.0330	-0.8	-	-

Table 2 Potential parameters for metal-metal interactions.

	S	β (1/Å)	D_{e1} (eV)	D_{e2} (eV)	C_D	R_{e1} (Å)	R_{e2} (Å)	C_R	R_1 (Å)	R_2 (Å)
La-La	1.3	1.05	0.740	2.64	0.570	3.735	0.777	0.459	4.0	4.5
Sc-Sc	1.3	1.4	0.645	1.77	0.534	3.251	0.919	0.620	3.5	4.0
Ni-Ni	1.3	1.55	0.74	1.423	0.365	2.520	0.304	0.200	2.7	3.2


(a) La-C potential function

(b) Sc-C potential function

(c) Ni-C potential function

Fig. 1 Metal-carbon potential function E_b ,Coulomb term V_C and potential function of M_2 for: (a) La-C, (b)Sc-C and (c) Ni-C.

Metal-metal interactions were defined in the same formula as in eq. (1). In this case, the equilibrium binding energy D_e and the bond length R_e are expressed as direct functions of the metal coordinate number N_{ij} instead of using the term B^* in eq. (3).

$$N^{\mathrm{M}}{}_{i} = 1 + \underset{\text{metal } k(\neq j)}{\quad} f(r_{ik}), \quad N_{ij} = (N^{\mathrm{M}}{}_{i} + N^{\mathrm{M}}{}_{j})/2 \tag{9}$$

$$D_e(N_{ij}) = D_{e1} + D_{e2} \exp\{-C_D(N_{ij} - 1)\} \tag{10}$$

$$R_e(N_{ij}) = R_{e1} - R_{e2} \exp\{-C_R(N_{ij} - 1)\} \tag{11}$$

The potential parameters are shown in Table 2, and the potential shapes for metal dimers are shown in Fig. 1.

The temperature control method is also the same as our previous report (12), where the translational, rotational and vibrational temperatures of the system were independently controlled every 0.1 ps by simple velocity scaling so that the difference between the control temperature T_c and each temperature was reduced to 60 %. Verlet's method was adopted to integrate the difference equation of motion.

RESULTS AND DISCUSSIONS

Lanthanum Containing System

Five hundred carbon atoms and 5 La atoms in gas phase with random positions and velocities were distributed in a 342 Å cubic box with full periodic boundary condition. The system was controlled toward a control temperature T_c of 3000 K. These parameters correspond to the condition in which C_{60} and C_{70} caged clusters were obtained in the simulation without including metal atoms (12).

Fig. 2 shows the growth process of typical La attached clusters in the simulation; (a) a La containing caged cluster La@C_{73} observed at t = 3000 ps, and (b) a La attached cluster LaC_{17} observed at t = 1600 ps. The vertical width and horizontal length denote the cluster size and time, respectively. For example, in Fig. 2(a), the LaC_5 and C_{13} cluster independently existed each other, coalesced at about 530 ps, and the LaC_{19} was formed after the addition of a carbon atom at about 550 ps.

When the cluster was smaller than LaC_5, short carbon chains surrounded the La atom [fan-type structure (19,20)] as shown in Fig. 2(b). When it grew larger than LaC_6, the La atom attached on the monocyclic carbon ring, and positioned in the center of the monocyclic ring at LaC_{15}. The host monocyclic ring changed to a polycyclic ring and the La atom attached on it around LaC_{17}, where the Coulomb attractive force induced curvature to the host polycyclic ring. The host annealed to a curved graphitic sheet when

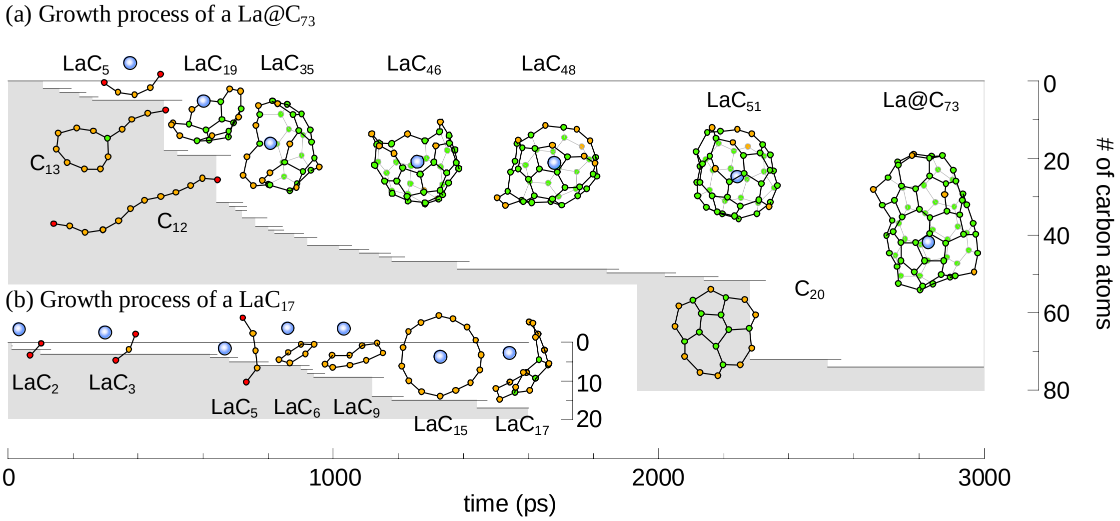


Fig. 2 Growth process of La attached clusters: (a) La@C_{73} and (b) La@C_{17}.

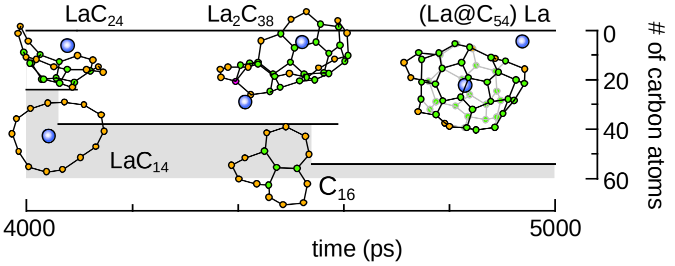


Fig. 3 Collision of La attached clusters.

it grew as large as LaC_{19} as shown in Fig. 2(a), and extended the structure until about LaC_{35}, resulted in the formation of a stable open-cap structure. The cluster grew larger with closing the open-cap structure, however, the number of carbon atoms was not enough to close the open-cap at about LaC_{50}. In this case, a collision with a large cluster of C_{20} prevented gradual growth and resulted in the formation of a caged cluster larger than $La@C_{71}$, and the La atom was almost encapsulated in the carbon cage.

Considering the difference of time and temperature scale between the real phenomena and simulation (13), these hollow caged structures could have sufficient collision free annealing interval to form more sophisticated structures.

Fig. 3 shows the collision process of other two La attached clusters. In this case, two La atoms could not attach on the same face of the flat structure during the coalescence process due to the Coulomb repulsion, and that resulted in the encapsulation of only one La atom.

Scandium containing system

Another clustering process using Sc atoms was simulated under the same condition as the previous section. Fig. 4 shows the growth process of a ScC_{55} observed at t = 4000 ps. A first remarkable difference of the process from La-C system is apparent for the structures of MC_n ($20<n<40$) because of the weaker Coulomb force. The cluster annealed to the 3-dimensional open cage structure around ScC_{43}, where the Sc atom moved around open edge. The Sc atom slipped into the caged structure just before closing at around $Sc@C_{54}$.

In addition to this final stage of encapsulation, the flat structures around ScC_{35} maybe related to the possibility of catching another Sc atom, which is in good agreement with experimentally observed prominence of di-metallofullerene for Sc-C system.

Nickel containing system

Nickel atom, which is not experimentally assigned to be contained in the fullerene cage so far, was also examined. As shown in Fig. 5, the growth process is very similar to that for Sc attached cluster. However, at the final stage, the Ni atom preferred to attach at the large defect of the caged structure such as large rings of more than 7 or 8 membered, and frequently moved in and out of the carbon cage. Fig. 6 shows the similar motion also observed for the larger caged cluster of NiC_{78} obtained for another Ni atom.

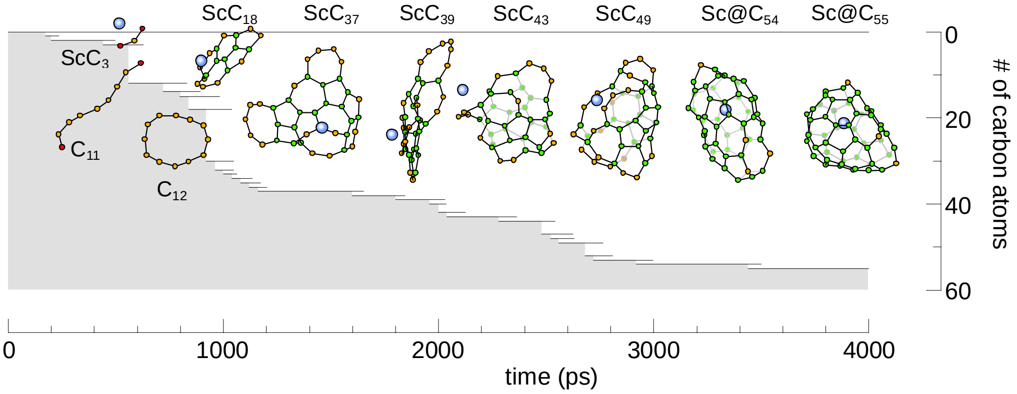


Fig. 4 Growth process of a Sc attached cluster $Sc@C_{55}$.

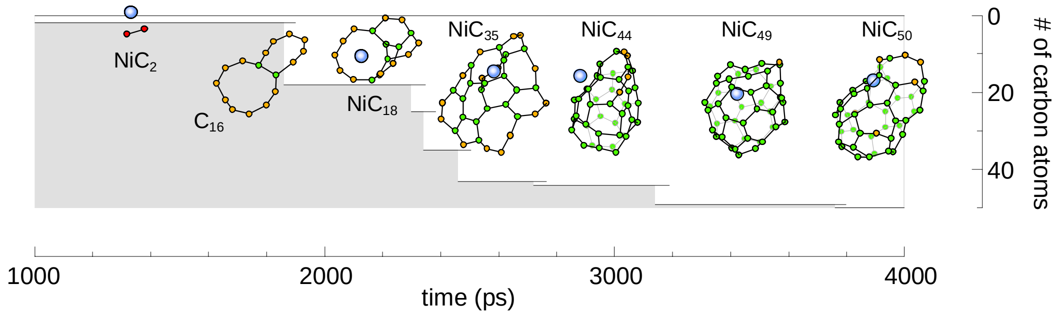


Fig. 5 Growth process of a Ni attached cluster NiC$_{50}$.

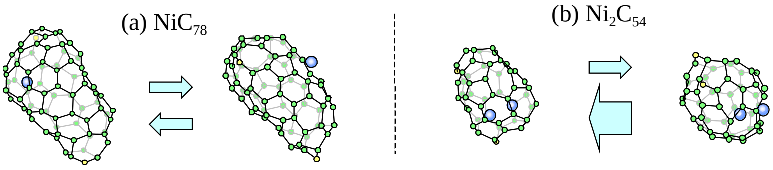


Fig. 6 Structures of Ni attached cage clusters: (a) NiC$_{78}$ and (b) Ni$_2$C$_{54}$.

Moreover, when two Ni atoms were enclosed in the host cage as shown in Fig. 6 (b), the Ni atoms remained inside the cage more stably than the case of single Ni atom, and that can be a hint of a new endohedral metallofullerene.

CONCLUSIONS

Multi-body potential functions of metal-carbon and metal-metal system were constructed based on the MO calculations of small MC$_n$ and M$_n$ (M: La, Sc, Ni) using the density functional theory. By applying the potential function to the molecular dynamics simulation, the clustering processes starting from randomly distributed carbon and metal atoms were simulated and the formation process of metal attached caged carbon clusters were examined. When La atoms were applied, the stable open-cap structure surrounding the La atom resulted in the La-containing caged cluster. For Sc-C system, the Sc atom was encapsulated in the host cage at the final stage of the growth process. For Ni-C system, the Ni atom finally stayed on a face of large ring of the caged structure.

ACKNOWLEDGEMENTS

This work was supported by Grant-in-Aid for JSPS Fellows (No. 08004746) and Grant-in-Aid for Scientific Research (No. 09450085) from the Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES

1. H. W. Kroto, et al., *Nature*, **318**, 162 (1985).
2. W. Krätschmer, et al., *Nature*, **347**, 354 (1990).

3. R. E. Haufler, et al., *Proc. Mat. Res. Soc. Symp.*, **206**, 627 (1991).
4. Y. Chai, et al., *J. Phys. Chem.*, **95**, 7564 (1991).
5. H. Shinohara, et. al., *J. Phys. Chem.*, **96**, 3571 (1992).
6. K. Kikuchi, et al., *Chem. Phys. Lett.*, **216**, 23 (1993).
7. M. Takata, et al., *Nature*, **377**, 46 (1995).
8. K. Kikuchi, et al., *Chem. Phys. Lett.*, **188**, 177 (1992).
9. S. Iijima, *Nature*, **354**, 56 (1991).
10. S. Iijima, T. Ichihara, *Nature*, **363**, 603 (1993).
11. A. Thess, et al., *Science*, **273**, 483 (1996).
12. Y. Yamaguchi and S. Maruyama, *Chem. Phys. Lett.*, **286**, 336 (1998).
13. S. Maruyama and Y. Yamaguchi, *Chem. Phys. Lett.*, **286**, 343 (1998).
14. D. W. Brenner, *Phys. Rev. B*, **42**, 9458 (1990).
15. A. D. Becke, *J. Chem. Phys.*, **98**, 5648 (1993).
16. C. Lee, et al., *Phys. Rev. B*, **37**, 785 (1988).
17. M. J. Frisch, et al., *Gaussian 94 Revision E.1*, Gaussian, Inc., Pittsburgh PA (1995).
18. E. Curotto, et al., *J. Chem. Phys.*, **108**, 729 (1998).
19. A. Ayuela, et al., *Z. Phys. D*, **41**, 69 (1997).
20. D. L. Strout, B. M. Hall, *J. Phys. Chem.*, **100**, 18007 (1996).