Proceedings of the
5th ASME/JSME Joint Thermal Engineering Conference
March 15-19, 1999, San Diego, California

AJTE99-6508

MOLECULAR DYNAMICS SIMULATIONS OF FORMATION OF METAL-CONTAINING FULLERENE

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Keywords: Molecular Dymamics Method, Fullerene, Carbon Cluster, Metal Atom

ABSTRACT

The growth process of metal-containing fullerene was studied using the molecular dynamics method. As for metal-containing fullerene, only the metal atoms such as La, Y or Sc are experimentally assigned to be contained inside the carbon cage. In this paper, the difference of growth process and structures of metal-attached carbon clusters were examined using lanthanum and nickel as the additional metal atoms to clarify the effect of the metal atoms.

In order to model the potential function between carbon and metal atoms appropriate for the classical MD simulation, the binding energy and charge state of various forms of small clusters MC_n (M: La,Ni; n =1-3) were calculated with the density functional theory. A multi-body potential function was constructed as a function of coordinate number of a scandium atom. Here, the Coulomb term and the Morse-type term were separately described considering the large charge transfer from a lanthanum atom to carbon atoms. By using the potential function, the clustering process starting from 500 isolated carbon atoms and 5 metal atoms in a 342 Å cubic cell was simulated under the controlled temperature condition at T_c = 3000 K, and the growth history of metal-attached clusters was studied in detail.

Figure A-1 shows the growth process of La attached clusters obtained in the simulation. The fan-type structure and mono-cyclic or bi-cyclic rings were reproduced around the metal atom for LaC_n (n<20). An open cap structure surrounding the La atom was formed for LaC_n (20<n<50) due to the strong Coulomb interaction, and that resulted in the lanthanum-containing caged cluster.

When Ni atoms were applied as shown in Figure A-2, the structures of small clusters up to NiC_n (n<20) were similar to LaC_n (n<20), while tangled-poly-cyclic structures and random cage were dominant for NiC_n (20<n<50). The nickel atom attached on one face of the caged structure, and could not stay stably inside the carbon cage structure.

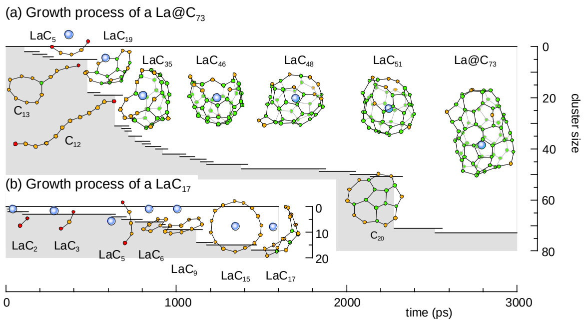

Figure A-1 Growth process of La attached clusters

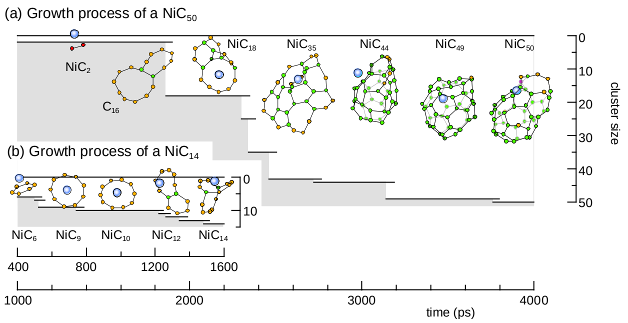

Figure A-2 Growth process of Ni attached clusters

NOMENCLETURE

B^* : normalized bond order function
b : potential parameter
c : atomic charge
D_e: potential well depth
E_b: binding energy
e : electric charge of an electron
f : cut-off function
k_1 : potential parameter
k_2 : potential parameter
N : coordinate number
R_e: equilibrium bond length
r_{ij} : distance between atom i and j
S : potential parameter
T_c : control temperature
t : time
V_A: attractive term
V_C : Coulomb term
V_R: repulsive term

Greek symbols
β : potential parameter
δ : potential parameter

Subscripts
C : carbon atom
M : metal atom

INTRODUCTION

The molecular dynamics method has been developed as a very useful tool for the analysis of micro or molecular-scale heat transfer problems. The next challenging step for the method must be the modification for the application to the problems including the chemical reaction process and the light-matter interaction, such as in micro-material processing in semiconductor industries. Here, we report a possibility of the molecular dynamics simulation of chemical reaction problem in the generation process of an exciting new carbon material, fullerene discovered by Kroto et al. (1985). In addition to the original empty spherical C_{60} and C_{70}, metal containing fullerene [Chai et al. (1991), Shinohara et al. (1992), Kikuchi et al. (1993), Takata et al. (1993)], higher fullerene (Kikuchi et al., 1992) and carbon nanotubes (Iijima, 1991) were successively produced and isolated. Recently, the high quality generation of single-wall nanotubes (SWNTs) [Iijima & Ichihara (1993), Thess et al. (1996)] has demonstrated new possibilities of applications of this material. Although fullerene is now recognized as an attractive new material, the formation mechanism of such symmetric hollow caged structure is still unknown, because the generation techniques of fullerene [Krätschmer et al. (1990), Haufler et al. (1991)] were discovered almost accidentally.

The authors have performed molecular dynamics simulations of the clustering process of carbon atoms to investigate the fullerene formation mechanism, and the temperature dependence of the cluster structures was observed [Yamaguchi & Maruyama (1998), Yamaguchi & Maruyama (1997)]; resulted in graphite-like structures when the control temperature T_c was lower than 2500 K, fullerene-like caged structures for 2500 K < T_c < 3500 K, chaotic 3-dimensional structures for T_c > 3500 K. In addition, the formation of perfect C_{60} structure was demonstrated by giving sufficient collision-free annealing time, and examined the time and temperature scale of the annealing process through the reaction rate of the network transformations. Based on these results, a new formation model of empty fullerene including the temperature effects was presented [Maruyama & Yamaguchi (1998), Maruyama & Yamaguchi (1997)].

In this paper, the formation process of metal-containing fullerenes was studied using the similar molecular dynamics method. According to theoretical studies, the metal-containing fullerene is expected as a more attractive material, however, it is difficult to get macroscopic amount of sample material for experiments due to the low yield of metal-containing fullerene. In order to find the optimum condition of generating metal-containing fullerene, it is inevitable to understand the formation mechanism. According to the experimental studies, only the metal atoms such as Sc, Y or lanthanides can be enclosed inside the carbon cage [Chai et al. (1991), Shinohara et al. (1992), Kikuchi et al. (1993), Takata et al. (1993)]. While on the other hand, the metal atoms such as Ni, Co, or Fe are required to generate the SWNTs [Iijima (1993), Thess et al. (1996)], but the effects of these metal atoms are still unknown. In this paper, the difference of the growth processes between lanthanum-attached clusters and nickel-attached clusters was studied to investigate the effect of metal atoms.

METHOD

The potential function among carbon atoms (Brenner, 1990) was the same as our previous reports [Yamaguchi & Maruyama (1998), Maruyama & Yamaguchi (1998), Yamaguchi & Maruyama (1997), Maruyama & Yamaguchi (1997)]. In order to model the potential function between carbon and metal atoms appropriate for the MD simulation, the binding energy and charge state of various forms of small clusters MC_n (M: La, Ni; n = 1-3) were calculated with the density functional theory based on the Becke's three-parameter exchange functional (Becke, 1993) with the Lee-Yang-Parr correlation (Lee et al., 1988) [B3LYP]. Here, the effective core potentials derived from the LANL2DZ bases in Gaussian 94 (Frish et al., 1995) were used for the metal atoms.

Table 1 Potential Parameters

	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
Ni-C	3.02	1.3	1.8	1.7	2.7	3.0	0.0330	-0.8	-	-

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

$$E_b = f(r_{ij}) \cdot (V_R + V_A + V_C) \tag{1}$$

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

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

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

Here, V_R and V_A denote the Morse-type repulsive and attractive terms, respectively. The Coulomb term V_C is applied only to the La-C interactions which are strongly ionic due to the electron transfer from the lanthanum to carbon atoms. The coordinate number of the metal atom N is defined using the cut-off function $f(r)$, and both the additional term B^*_{ij} and the electric charge value c are expressed as functions of the coordinate number. Here, the effect of the angle among bonds is ignored.

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

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

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

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

Figures 1 and 2 show the binding energy of B3LYP calculation and fitted potential curves for the coordinate number N = 1-3 of La-C and Ni-C systems, respectively. Parameters are shown in Table 1.

The temperature control method is also the same as our previous report [Yamaguchi & Maruyama (1998), Yamaguchi

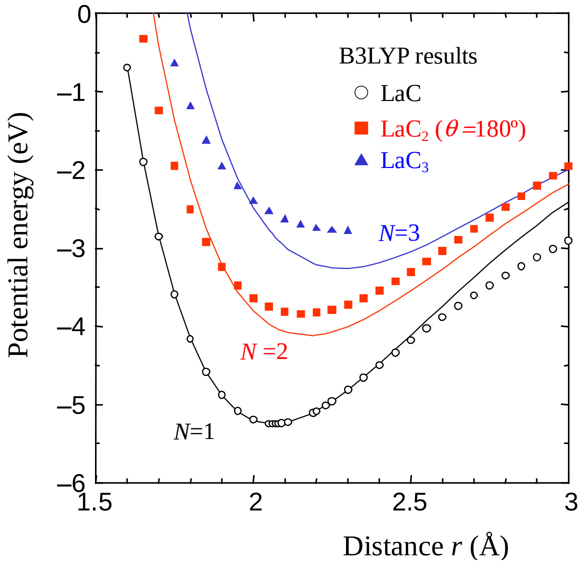

Figure 1 La-C potential function

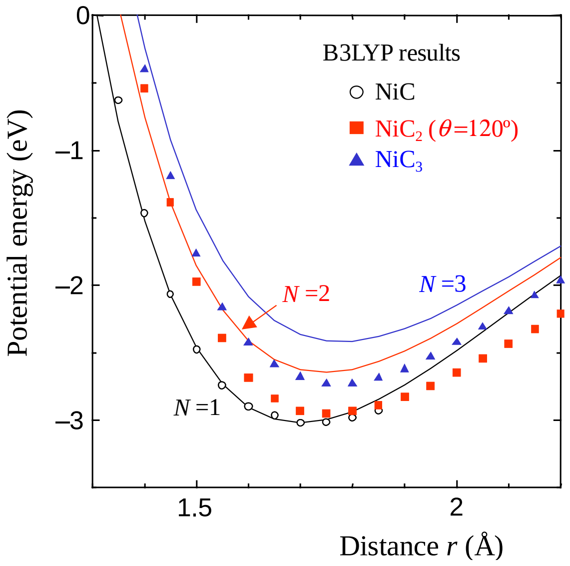

Figure 2 Ni-C potential function

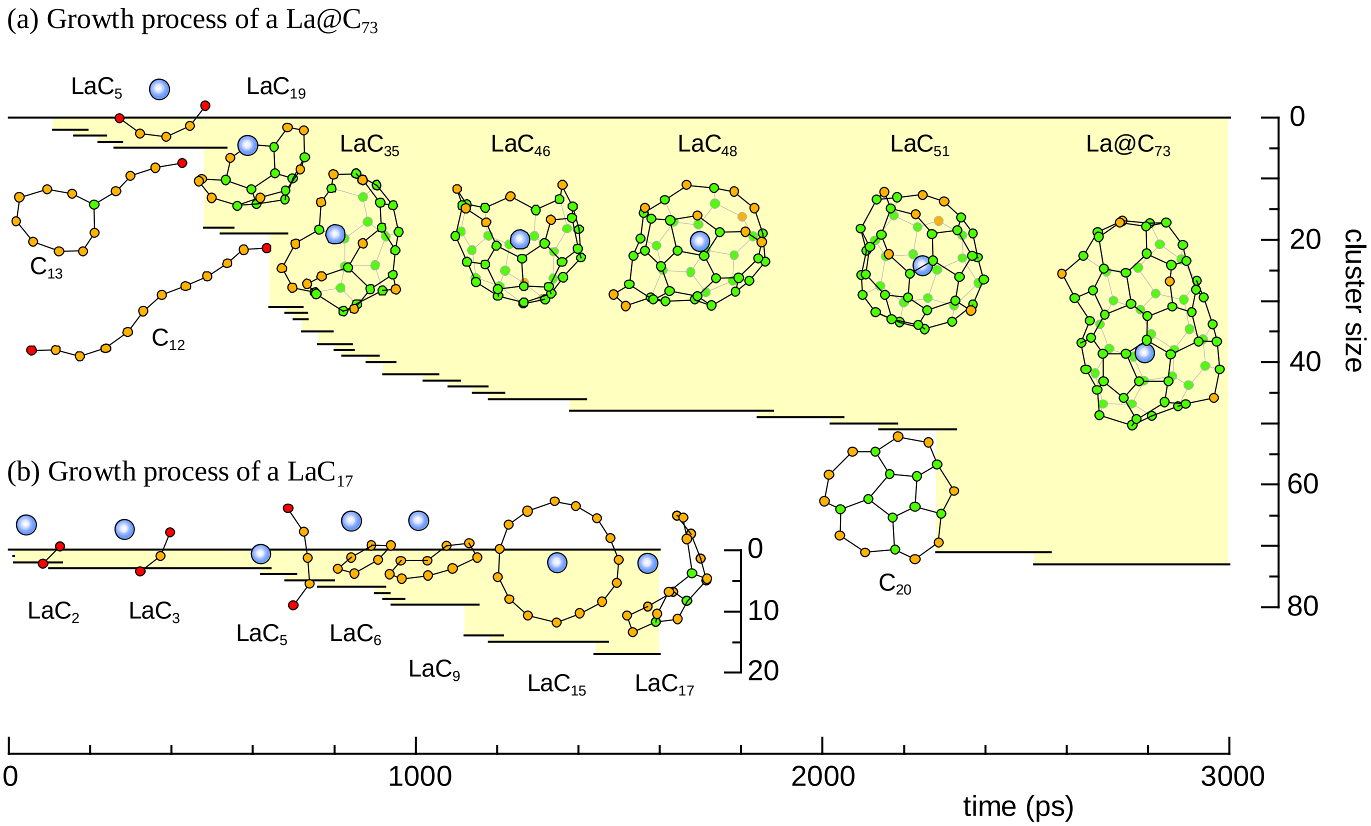

Figure 3 Growth process of La attached clusters

& Maruyama (1997)]. The motion of a cluster was divided into translational, rotational and vibrational motions, and the system temperatures T_T, T_R and T_V were defined as the total average of each motion in the system. Then, simple velocity scaling was independently enforced to each motion every 0.1 ps 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 differential equation of motion.

MOLECULAR DYNAMICS SIMULATIONS

Clustering Process in Lanthanum Containing System

Five hundred carbon atoms and five lanthanum 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 observed in the simulation without metal atoms [Yamaguchi & Maruyama (1998), Maruyama & Yamaguchi (1997)].

Figure 3 shows the growth process of typical lanthanum attached clusters in the simulation; (a) a lanthanum containing caged cluster La@C_{73} observed at t = 3000 ps (the @ denotes the enclosure in the caged structure), and (b) a lanthanum attached cluster LaC_{17} observed at t = 1600 ps. The vertical width and horizontal length denote the cluster size and the existing time of each cluster, respectively. For example, in Figure 3(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. Here, the histories of clusters without lanthanum atom were omitted.

When the cluster was smaller than LaC_5, short carbon chains surrounded the lanthanum atom (fan-type structure) as shown in Figure 3(b). When it grew larger than LaC_6, the lanthanum atom positioned out of the monocyclic carbon ring. Then, the lanthanum atom approached to the center of the monocyclic ring, and all atoms were located in the same plane when the cluster grew as large as LaC_{15}. The host monocyclic ring changed to a poly-cyclic ring and the lanthanum atom was driven out of the plane again around LaC_{17}. The long-range Coulomb attractive force induced curvature to the host poly-cyclic ring. The host annealed to a curved graphitic sheet when it grew as large as LaC_{19} as shown in Figure 3(a), and extended

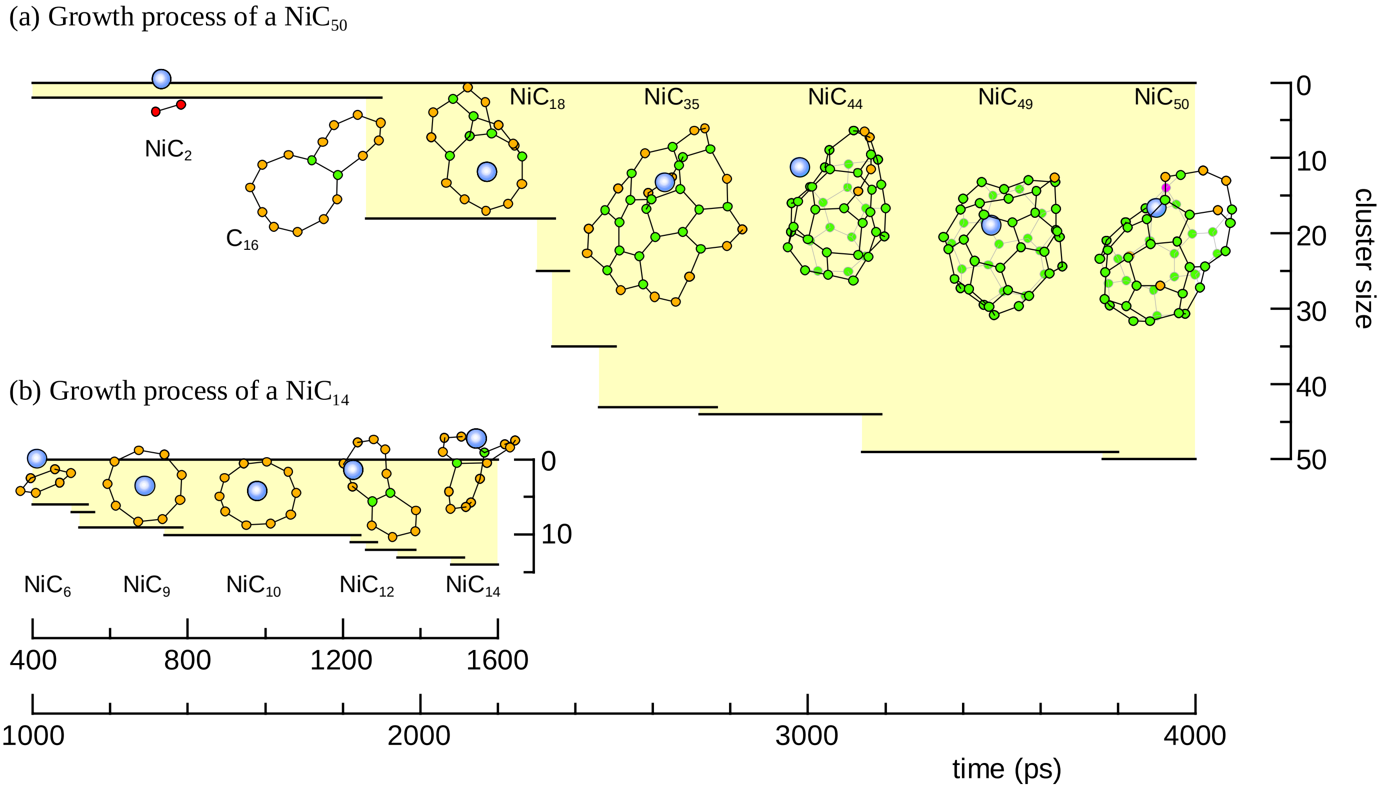

Figure 4 Growth process of Ni attached clusters

the curved graphitic structure until about LaC_{35}, resulted in the formation of an 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 $La@C_{71}$, where the lanthanum atom was almost enclosed in the carbon cage.

Considering the difference of time and temperature scale between the real phenomena and simulation, these hollow caged structures could have sufficient collision free annealing interval to form more sophisticated structures like experimentally isolated metal-containing fullerenes.

Clustering Process in Nickel Containing System

Another clustering process using nickel atoms as the additional metal atoms, which are not experimentally proved to be enclosed in the fullerene cage, was simulated under the same condition as the previous section. Figure 4 shows the growth process of typical nickel attached clusters in the simulation; (a) a nickel attached caged cluster NiC_{50} observed at $t = 4000$ ps, and (b) a nickel attached cluster NiC_{14} observed at $t = 1600$ ps. When the cluster was smaller than NiC_5, the fan-type structure similar to the case of lanthanum attached cluster was reproduced, and when it grew larger than NiC_6, the nickel atom positioned out of the monocyclic carbon ring as shown in Figure 4(b). Then, the nickel atom approached back to the mono-cyclic ring and located almost in the center of the ring when the cluster grew as large as NiC_9. The host mono-cyclic ring changed to a bi-cyclic ring and the nickel atom attached on one face of the ring around NiC_{12}, and then, a poly-cyclic ring appeared around NiC_{14}. Here, a more 3-dimensional structure was preferred due to the interaction of the nickel atom. The host carbon cluster also formed a similar poly-cyclic structure around LaC_{18} as shown in Figure 4(a). When it grew as large as NiC_{35}, the cluster formed both flat graphitic structures and random caged structures, but when it grew as large as $NiC_{44\text{-}50}$, the open caged structure was dominant. At that size, the nickel atom preferred to attach at the large defect of the caged structure such as large rings of more than 7 or 8 membered rings, and frequently moved in and out of the carbon cage. The motion was also observed for the larger caged cluster of NiC_{78} obtained for another nickel atom, and the nickel atom did not stay inside the carbon cage.

Effect of Metal Atoms

The structures of metal attached clusters in the previous two systems, and the clusters in the system without metal atoms [Yamaguchi & Maruyama (1998), Maruyama & Yamaguchi, (1997)] are compared in detail. For (M)C_n ($n<5$), the host carbon cluster itself forms a simple chain structure in all systems, and the fan-type cluster is reproduced by the interaction between the metal atom and all carbon atoms. This fan-type structure corresponds to the energetically most stable structure by the MO calculations [Ayuela et al. (1997), Strout & Hall (1996)]. For (M)C_n ($n<15$), the host carbon cluster forms a monocyclic or bi-cyclic ring in each case, but under the existence of a lanthanum atom, the motion of the host cluster is strongly restricted in a spherical surface around the lanthanum atom. This is caused by the long-range interaction due to the charge transfer from the lanthanum atom to the carbon cluster. On the other hand, the structures of nickel attached clusters are similar to those in the system without metal atoms because the nickel atom induces only short-range interactions with a small number of carbon atoms. The interaction pattern also affects the structures of clusters around (M)C_n ($15<n<50$), where the LaC_n ($15<n<50$) cluster resulted in an open-cap structure in the spherical surface. While the restriction free NiC_n or C_n ($15<n<50$) cluster can anneal to the graphitic flat structure and random caged structure which are comparably stable at that size. For the clusters as large as (M)C_n ($n>50$), the open-cap structured LaC_n ($n>50$) manages to close the structure at a certain size. On the other hand, the host of the NiC_n ($n>50$) prefers to form a caged structure. However, the nickel atom attaches at the large defect of the carbon cage and frequently moves in and out of the cage due to the local short-range interaction, and that prevents the host cage from closing the structure. The C_n ($n>50$) cluster manages to form a closed cage and anneal to a more stable structure.

Compared to the final cage structure of the empty fullerene which depends on the annealing process from an imperfect caged structures [Maruyama & Yamaguchi (1998), Maruyama & Yamaguchi, (1997)], the final structure of the lanthanum containing fullerene seems to depend much on the early stage of the growth process. The open-cap structures of small clusters are kept for a long time due to the strong spherical restriction. Therefore, from the initial fixed small open-cap, the cluster grows through open-cap structures to the final lanthanum containing fullerene. The nickel atom helps to stabilize the defect of the caged structure and prevents the host from annealing to the closed cage.

CONCLUSIONS

Multi-body potential functions of metal-carbon system were constructed based on the MO calculations of small MC_n (M: La, Ni) using the density functional theory. By applying the potential function to the molecular dynamics method, the clustering processes starting from randomly distributed carbon and metal atoms were simulated and the formation process of metal attached caged carbon clusters were observed. When lanthanum atoms were applied, the open-cap structure surrounding the lanthanum atom resulted in the lanthanum containing caged cluster. On the other hand, when nickel atoms were applied, the nickel atom prevented the carbon cage from closing the structure. The difference of fullerene-cage was also discussed compared with the empty fullerene.

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.

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