

Formation Process of Empty and Metal-Containing Fullerene --Molecular Dynamics and FT-ICR Studies--

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The formation mechanism of empty and metal-containing fullerene was studied through molecular dynamics simulations and FT-ICR mass spectroscopy of laser vaporized carbon cluster. With classical molecular dynamics simulations using modified Brenner potential, the clustering process starting from 500 isolated carbon atoms in gas phase was simulated under the controlled temperature condition. When the control temperature was at $T_c = 3000$ K, imperfect caged clusters like C_{60} and C_{70} were obtained. Additional annealing simulations to compensate the short time-scale of the simulation resulted the perfect I_h-C_{60} structure through Stone-Wales transformations. A fullerene formation model featuring the random caged structure and annealing at the size range of C_{40} to C_{60} was proposed through the detailed study of the precursor structures in simulations.

In order to incorporate metal atoms in the simulation, multi-body classical potential functions for metal-carbon and metal-metal interactions were constructed based on DFT (density functional theory) calculations of various forms of small clusters MC_n and M_n ($M = La, Sc, Ni$). The classical potential was expressed with the Morse term and the Coulomb term as function of coordinate number of a metal atom. The simulated clustering process with addition of 1 % of metal atoms was compared with the pure carbon simulation. 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 host carbon clusters were not affected so much as the La-C case due to the weaker Coulomb interaction, and the Sc atom was encapsulated in the host cage at the final stage of the growth process. Ni-C system was also simulated to explore the possible role of metal atoms in the generation of SWNT. The precursor clusters were similar to those in Sc-C system, although the Ni atom finally stayed on a face of 7 or 8 member-ring of the caged structure.

Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer directly connected to the laser vaporization cluster beam source was implemented to study the clustering process. With increase of cluster nozzle pressure, three different types of positive mass spectra were obtained for pure carbon clusters: smaller than about C_{60} with odd numbered clusters up to C_{40} ; almost only C_{60} and a trace of C_{70} ; well-known even atom mass with intense peaks at C_{60} and C_{70} . Qualitatively the lower pressure condition of the cluster source corresponded to the earlier stage of the MD simulation. Through these comparisons, we speculated that the even-numbered clusters corresponded to the annealed random caged clusters. The FT-ICR mass spectra of metal-carbon binary clusters were studied for sample materials normally used for generation of metal-containing fullerene and SWNT; La: 0.8%, Y: 0.8%, Sc: 0.8%, Gd: 0.8%, Ce: 0.8%, Ca: 0.3%, and Ni:4.2% - Y: 1%. Positive La-C, Y-C, Sc-C, Gd-C, Ce-C binary clusters commonly showed strong MC_{2n}^+ signal in the range of $36 < 2n < 76$ with intense magic numbers at MC_{44}^+ , MC_{50}^+ and MC_{60}^+ . Characteristics of these small clusters were compared with results of molecular dynamics simulations.