FT-ICR Reaction Experiments and Molecular Dynamics Simulations of Precursor Clusters for SWNTs

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The formation mechanism of single walled carbon nanotubes (SWNTs) is investigated through experimental and molecular dynamics simulation studies of interaction of metal atoms and carbon clusters. Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer directly connected to the laser-vaporization cluster beam source (1,2) was used for the chemical reaction experiments of metal-carbon binary clusters generated by the laser-vaporization of Ni/Co or Ni/Y loaded carbon materials used for the macroscopic production of SWNTs. Positive mass spectra of clusters vaporized from Ni/Co (0.6 at % Ni and 0.6 % Co) loaded graphite sample showed no apparent mass signal due to the clusters with Ni or Co atoms. However, enhanced production of C_{60}^{+} and C_{70}^{+} and larger even-numbered pure carbon clusters in the size range up to 200 carbon atoms were observed. On the other hand, tiny signals of NiC_n and CoC_n were observed for the negative cluster ions. The chemical reaction experiments of these clusters with NO in the FT-ICR spectrometer strongly suggested that metal atom was outside of the carbon cage. The more drastic effect of doping of Ni/Co was the observation of large pure carbon clusters in the negative spectrum up to about C_{200}^{-}. Here, clusters with even numbers of carbon atoms were much more enhanced. Since such large carbon clusters had never been observed as intrinsic negative ions from pure graphite vaporization, these clusters clearly demonstrate the very efficient formation of large caged carbon clusters in relatively low temperature atmosphere. Similar chemical reaction experiments for the Ni-Y loaded sample showed that Ni atom was again outside the carbon cage but Y atom was inside the carbon cage just-like the precursor clusters to the endohedral metallofullerene (1,2).

The formation process of metal-carbon binary clusters was also studied using the molecular dynamics simulations. The Brenner potential between carbon atoms and our classical potential between carbon clusters and metal atoms were employed (3,4). The growth process of carbon clusters from completely random vapor phase was simulated with and without 1 % of metal atoms. Inclusion of La atoms enhanced the clustering process to the random caged carbon clusters with a La atom inside the cage (4). It seemed that Ni atoms also somewhat enhanced the clustering process to the random-cage structure. However, a Ni atom on the face of the random cage prohibited the complete anneal of the cage structure. Collisions of such imperfect random-cage clusters lead to the large aggregate with some bulges due to the original random cage clusters. It is expected that these bulges should be the initial seed of SWNTs.

References

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