FT-ICR Studies of Laser Vaporized Clusters from Ni/Co and Ni/Y Loaded Graphite Samples

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ABSTRACT

Metal-carbon binary clusters generated by the laser vaporization of Ni/Co and Ni/Y loaded graphite samples used for the macroscopic production of SWNTs were studied. Positive and negative clusters generated by the laser-vaporization supersonic-expansion cluster beam source were directly injected to the FT-ICR mass spectrometer. The chemical reaction of these clusters with NO was used as the probe of the geometrical structure of clusters. It was speculated that a few Ni or Co atoms attached outside of imperfect carbon cage for Ni/Co loaded case, and that Y atom was included in the carbon cage for Ni/Y loaded case.

Keyword: FT-ICR, Clusters, Chemical Reaction, Mass spectroscopy.

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Introduction

The high quality generation of single walled carbon nanotubes (SWNTs) [1] has demonstrated new possibilities of applications. Despite the expectations of a wide variety of applications, it is still difficult to obtain macroscopic amount of pure SWNTs. In order to find the optimum generation condition of SWNTs, the understanding of the formation mechanism is inevitable. It is well known that the transition metals such as La, Y and Sc can be encapsulated inside the fullerene cage [1]. On the other hand, Ni, Co and/or Fe are required to generate SWNTs. Very strikingly, the generation conditions of endohedral metallofullerene and SWNTs in laser-oven [2] or arc discharge [3] techniques are almost exactly the same except for these metal elements. Here, the effect of these metal atoms on the growth process of carbon clusters leading to endohedral metallofullerene or SWNT is explored through the FT-ICR experiments of metal-carbon binary clusters generated by the laser vaporization of metal-doped carbon materials used for macroscopic production techniques.

Experiments

The FT-ICR mass spectrometer and chemical reaction system [4] used in this study was based on the design in Smalley's group at Rice University [5]. Metal-carbon binary clusters were produced by the laser-vaporization supersonic-expansion cluster beam source. The cluster beam was directly injected to the magnetic field through a skimmer with the opening diameter of 2 mm and a deceleration tube. After deceleration, the cluster ions were trapped in the ICR cell. Then, nitric oxide gas was supplied to the cell by a pulsed valve for a fixed period. After pumping out, cluster ions were excited to detect the mass distribution.

Results and Discussion

Depending on the metal species, the generated cluster distributions were drastically different. In case of a Ni/Co doped sample, there was not a trace of Ni or Co in the positive mass spectrum and tiny signals of NiC_n^- and CoC_n^- were measured for negative spectrum. On the other hand, in the case of Ni/Y doped sample, signals of YC_{2n} with strong magic number clusters YC_{44}, YC_{50} and YC_{60} were observed in positive mass spectrum. This feature was exactly the same as the cluster distribution obtained for Y-doped graphite material used for the macroscopic generation of endohedral metallofullerene [3]. There were small signal of NiC_n clusters in addition to YC_{2n} clusters in negative mass spectrum.

The chemical reaction of these clusters with NO was used as the probe of the structure of clusters. Reaction with 10^{-7} Torr in NO gas for 2 s and 10 s for the case of Ni/Co doped sample are shown in Fig. 1. The chemisorption of NO to NiC_n^- and CoC_n^- were observed much faster rate than pure carbon clusters. After the reaction for 2 s, the product of C_nNO^- gradually appeared. It seems that CoC_n^- reacted a bit faster than NiC_n^-. Since it is expected to be more reactive if a metal atom is exposed to NO, the high reactivity of NiC_n^- and CoC_n^- strongly suggests that Ni or Co atom is outside the carbon cage.

Fig. 2 shows the case of Ni/Y doped sample with 10^{-5} Torr in NO gas for 5 s. It should be noted that the pressure of NO gas was 100 times higher compared with the case of Ni/Co doped experiments. Even though tiny NiC_n^- clusters were completely reacted away, the reaction of YC_{2n}^- with NO was not observed. Comparing signal heights of YC_{2n} and C_{2n}, it can be concluded that YC_{2n} is less reactive than pure carbon clusters. Hence, it is reasonable to assume that Y atom is inside the cage carbon cluster.

Besides the experimental study, molecular dynamics simulations of growth process of binary clusters from randomly distributed carbon and metal atoms were performed [3]. The yttrium containing carbon cage cluster for Y-C system and carbon cage structure with Ni atom staying on a face for Ni-C system were predicted. These simulation results are completely consistent with experimental results.

References

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Captions to Figures

Fig. 1. NO Reaction of NiC_{38}^{-} and CoC_{38}^{-} from Ni/Co loaded sample.

Fig. 2. NO reaction of NiC_n^{-} and YC_n^{-} clusters from Ni/Y loaded sample.

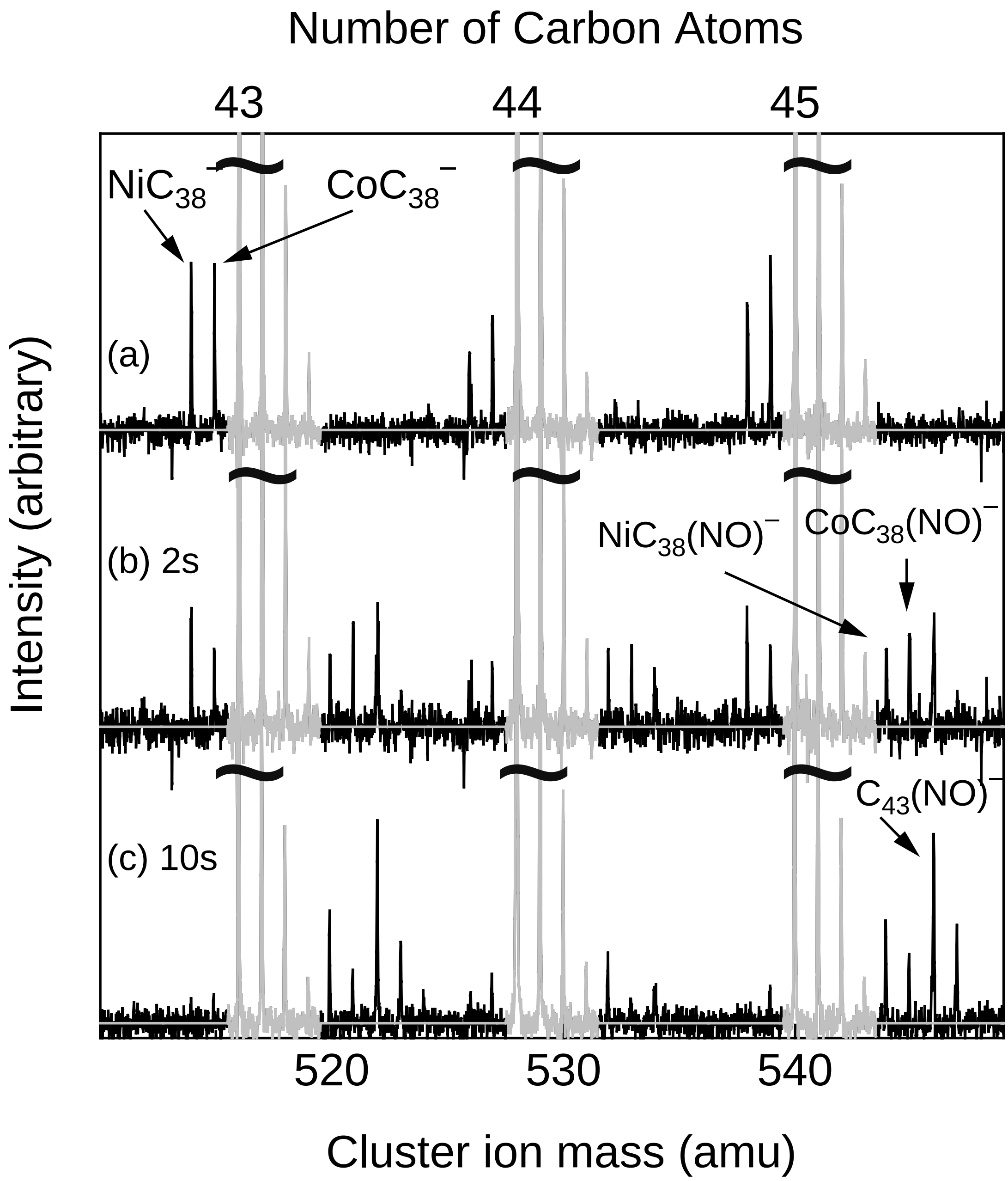

Fig. 1. NO Reaction of NiC_{38}^- and CoC_{38}^- from Ni/Co loaded sample.

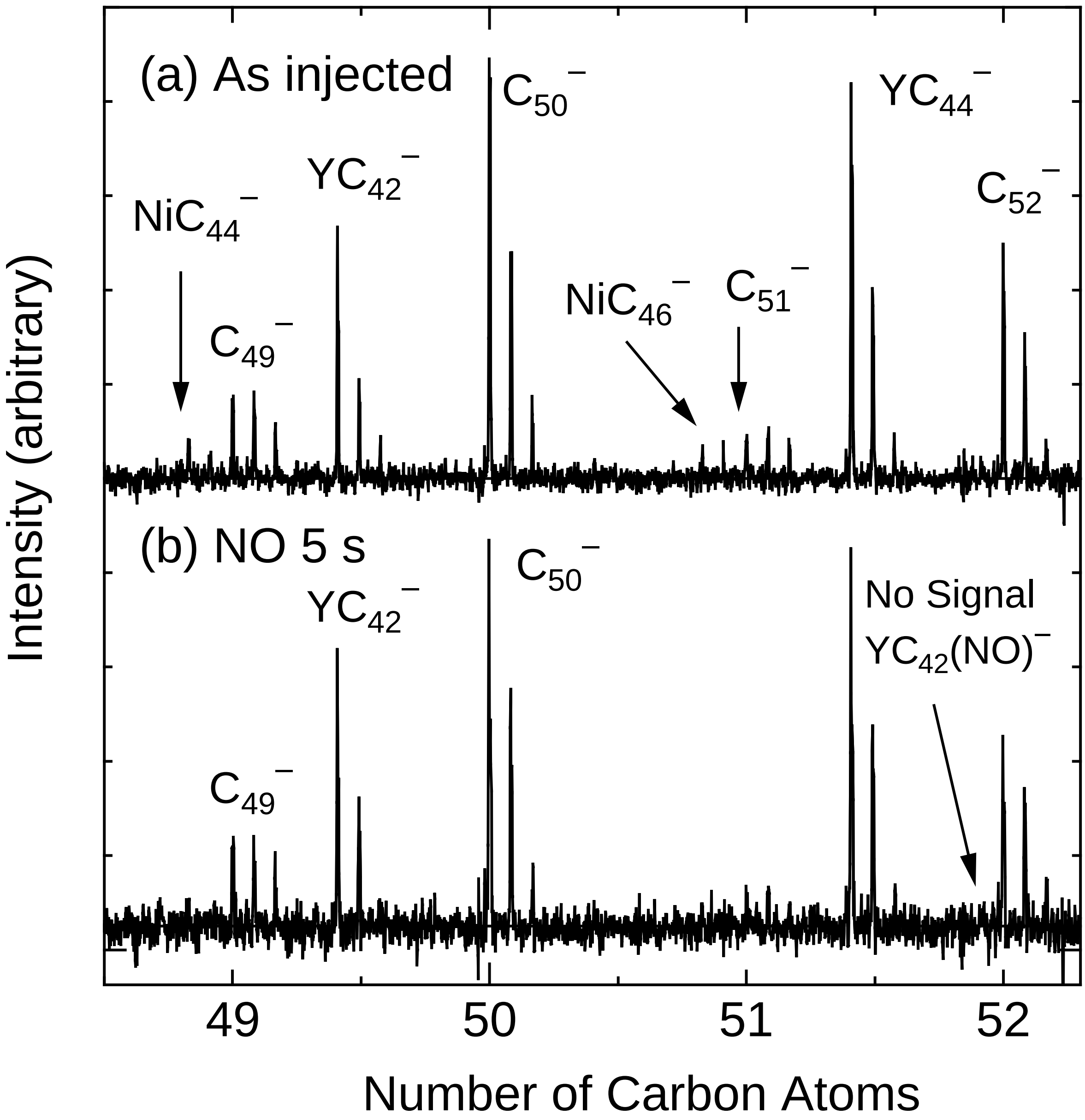

Fig. 2. NO reaction of NiC_n^- and YC_n^- clusters from Ni/Y loaded sample.