FT-ICR Study of Precursor Clusters of Single Wall Carbon Nanotubes (SWNTs)

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ABSTRACT

Metal-carbon binary clusters generated by the laser vaporization of Ni/Co and Ni/Y doped graphite samples used for the macroscopic laser-oven 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 (Fourier Transform Ion Cyclotron Resonance) mass spectrometer. Depending on the metal species, the generation efficiency of metal-carbon binary clusters was drastically different. The chemical reaction of these clusters with NO gas was used as the probe of the geometrical structure of clusters. The reactivity to NO of these binary clusters was completely different. In case of YC_n (n = even, n $\geqq$ 36), chemical reaction of YC_n with NO was not observed while pure carbon clusters were reacted. On the other hand, for MC_n (M = Ni or Co), the reactivity was much higher than pure carbon clusters. It was speculated that a few Ni or Co atoms attached outside of imperfect carbon cage for Ni/Co doped case, and that Y atom was included in the carbon cage for Ni/Y doped case.

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Introduction

The high quality generation of single walled carbon nanotubes (SWNTs) [1,2] 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 [3]. 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 [4] or arc discharge [5] 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.

Experiment

The FT-ICR mass spectrometer and chemical reaction system implemented in this study is based on the design in Smalley's group at Rice University [6]. The FT-ICR is the unique mass spectroscopy based on the ion-cyclotron motion of clusters in a strong magnetic field. In principle, extremely high mass-resolution at high mass-range such as resolution of 1 amu at

10,000 amu range can be obtained. Furthermore, since the ions can be trapped in the vacuum for a few minutes, it is possible to perform the chemical reaction experiments. The schematic drawing of the apparatus is shown in Fig. 1. The cluster beam was generated outside of magnetic field by the laser-vaporization cluster beam. A metal-doped carbon sample disk was vaporized by the focused beam of Nd: YAG laser (2nd Harmonics) while timed pulsed gas was injected to the nozzle. In the atmosphere of helium gas, vaporized atoms condensed to clusters, and then, were carried and cooled by the supersonic expansion of helium gas. The cluster beam was directly injected to the magnetic field through a skimmer with the opening diameter of 2 mm and a deceleration tube. The size range of cluster ions was roughly selected by the deceleration voltage. After deceleration, the cluster ions were trapped in the ICR cell. The kinetic energy of clusters was thermalized with room temperature argon gas at 10^{-5} Torr. Then, nitric oxide (NO) gas was supplied to the cell by a pulsed valve for a fixed period. The pulse value was adjusted so that the pressure at the ICR cell chamber became at 10^{-5} Torr for unreactive clusters and 10^{-7} Torr for reactive clusters. After pumping out, cluster ions were excited to detect the mass distribution.

Results and discussions.

Fig. 2 shows mass spectra of the clusters generated from Ni/Co (0.6 at % Ni and 0.6 at % Co) doped carbon material used for the laser-oven SWNTs generation. Positive (a) and negative (b) mass spectra as injected from the cluster beam source are shown in Fig. 2. There was not a trace of Ni or Co in the positive mass spectrum and C_{60}^{+} and C_{70}^{+} were observed as the magic number. This tendency was almost similar with the case of using pure graphite materials. On the other hand, in the case of negative ions, tiny signals of NiC_n^{-} and CoC_n^{-} were measured in Fig. 3 (expanded view of Fig. 2(b)). Other drastic effect of doping of Ni/Co

was observed in pure carbon cluster distribution. The even-odd alternations were observed from C_{36}^-. When the clusters were generated from the pure graphite materials, this even-odd alternations were not observed. In Fig. 3, the signal of ^{58}Ni with 57.94 amu can be clearly distinguished with no overlap, but ^{59}Co with 58.93 overlaps with Ni-C binary cluster signal. The half of the signal next to NiC_n^- is most likely from CoC_n^-, though the precise decomposition is not easy for this low signal intensity. There was some even-odd difference in the signal intensity of NiC_n^- and CoC_n^-, these peaks were stronger for even-numbered carbon clusters. However, this even-odd difference seems to simply reflect the relative abundance of pure carbon clusters.

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. 4. 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. 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.

The Ni/Y (4.2 % Ni and 1.0 % Y) doped carbon material optimized for the arc-discharge SWNT generation [5] was also studied. The positive mass spectrum shown in Fig. 5(a) was not distinguishable from the Y doped carbon material (0.8 % Y) used for the endohedral metallofullerene generation [7]. Most of clusters had one Y atom and even numbered carbon atoms, and YC_{44}^+, YC_{50}^+, YC_{60}^+ were observed as magic number. On the other hand, only small signals of pure carbon clusters such as C_{60}^+ and C_{70}^+ were observed. In the negative spectrum, however, small pure carbon clusters and Ni attached clusters in addition to YC_{2n}^- were observed. As shown in Fig. 6(a), abundance of Ni attached clusters were sometimes almost the half of odd-numbered pure clusters for around NiC_{40}, but Ni-attachment was not observed for large clusters more than 50 carbon atoms.

Fig. 6 shows the reaction of binary clusters from 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 samples. Even though tiny NiC_n^- clusters such as NiC_{44}^- or NiC_{46}^- were completely reacted away, the reaction of YC_{2n}^- such as YC_{42}^- 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, just like the precursor clusters of endhedral metalfullerenes [7].

Besides the experimental study, molecular dynamics simulations of growth process of binary clusters from randomly distributed carbon and metal atoms were performed [8]. The Y 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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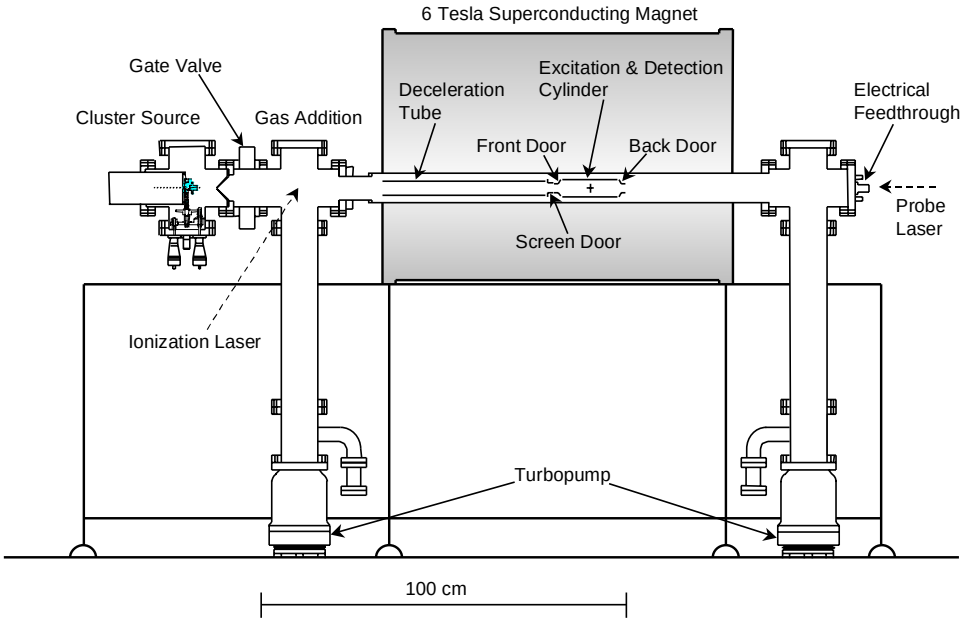

Fig. 1 FT-ICR mass spectrometer directly connected with laser-vaporization cluster beam source.

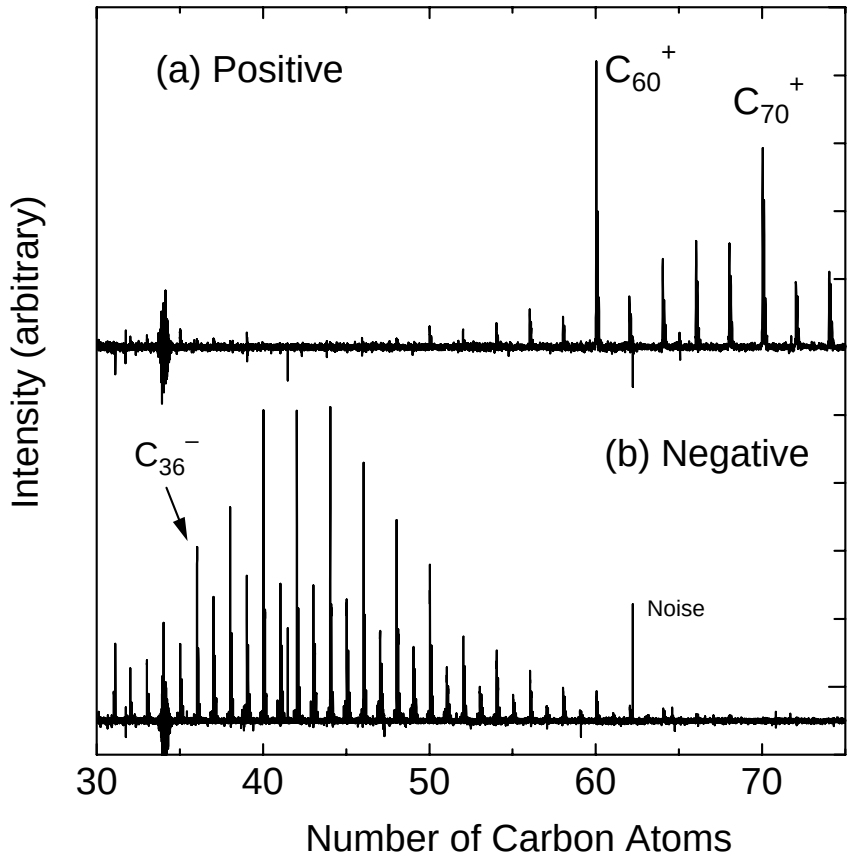

Fig. 2 Positive (a) and negative (b) clusters generated from Ni/Co doped carbon materials.

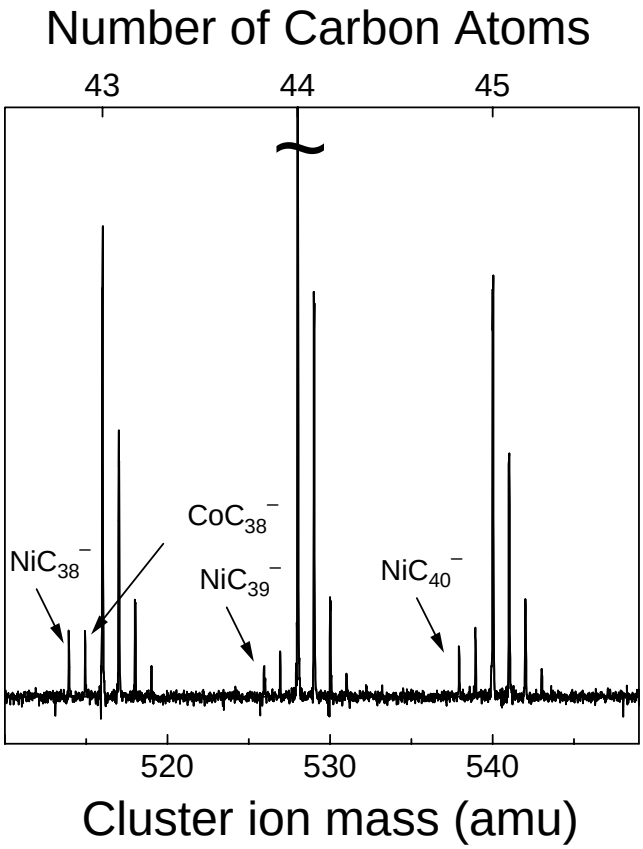

Fig. 3 Expanded view of Fig.2 (b).

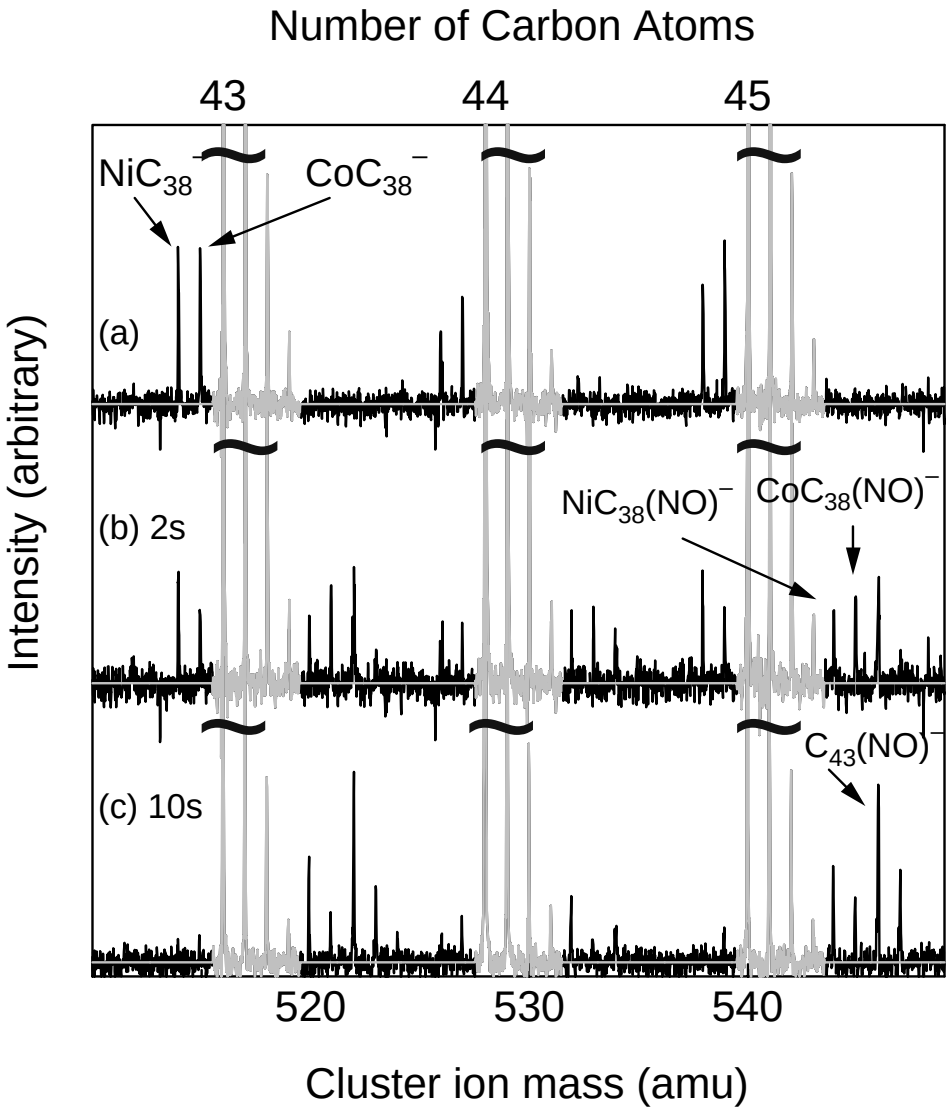

Fig. 4 NO Reaction of NiC_{38}^- and CoC_{38}^- from Ni/Co doped sample.

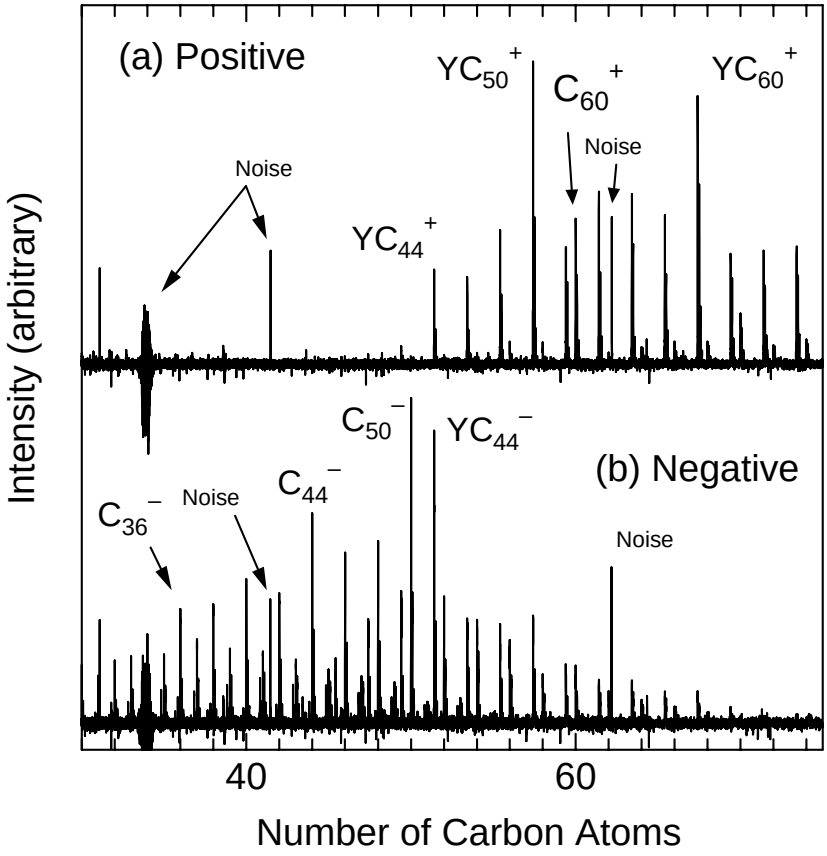

Fig. 5 As injected positive (a) and negative (b) clusters from Ni/Y doped carbon material.

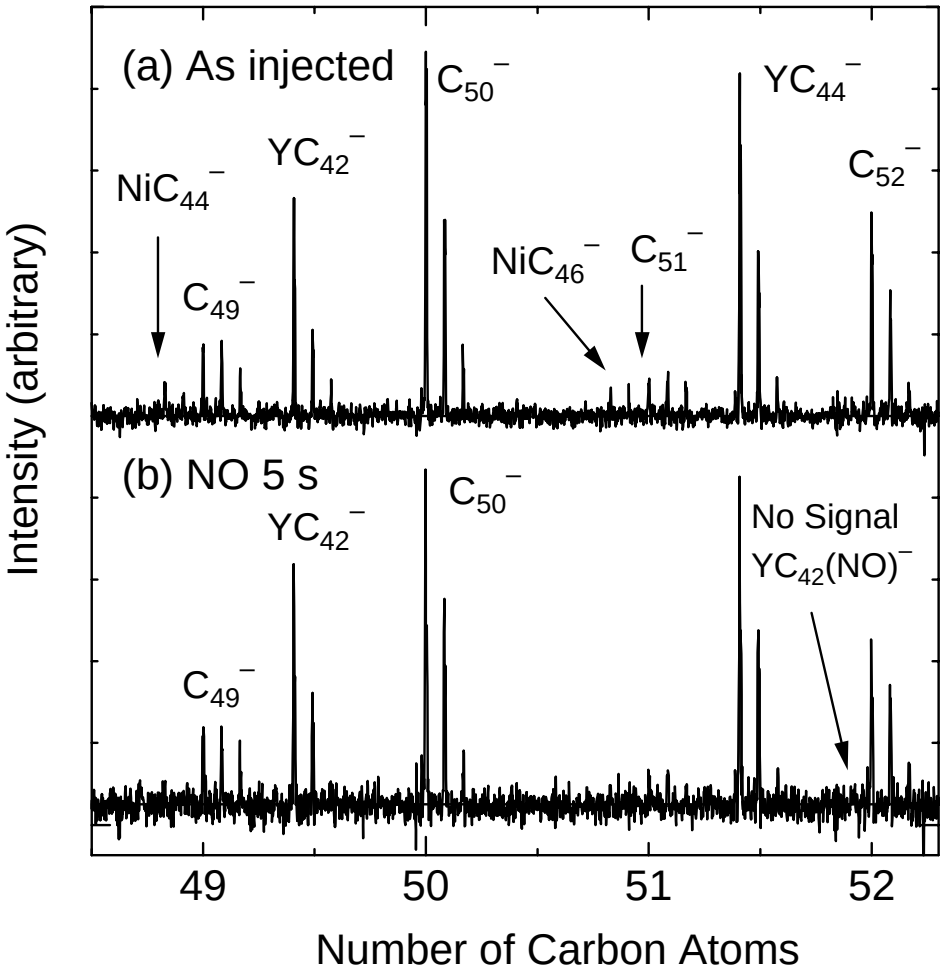

Fig. 6. NO reaction of NiC_n^- and YC_n^- clusters from Ni/Y doped sample.