

FT-ICR Study of Chemical Reaction of Metal-Carbon Binary Cluster Anions

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Metal-carbon binary clusters generated by the laser vaporization of metal-doped carbon materials used for macroscopic production of endohedral metallofullerene or 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 Transfer Ion Cyclotron Resonance) mass spectrometer. Depending on the metal species, the generated cluster distributions were drastically different. The chemical reaction of these clusters with NO was used as the probe of the structure of clusters. LaC_{2n}^- , ScC_{2n}^- and YC_{2n}^- from La-doped, Sc-doped and Ni/Y-doped carbon samples, respectively, were much less reactive to NO compared with pure carbon clusters. On the other hand, NiC_n^- from Ni/Co-doped and Ni/Y-doped materials was much more reactive than pure carbon clusters. Chemical reaction of LaC_{44}^- with NO compared with bare clusters were shown as an example of the FT-ICR reaction process in Fig.1. Fig.1(a) shows the FT-ICR mass spectrum of the injected and trapped clusters. In order to observe the chemical reaction product on a clean baseline, all clusters except for C_{44}^- , C_{47}^- and LaC_{44}^- were excited away from the ICR cell by the selective RF excitation called “SWIFT” technique. Selected clusters were thermalized to the room temperature by exposures to argon at a pressure of at 1×10^{-5} Torr for 2 seconds after SWIFT. Fig.1(b) shows the mass spectrum measured after this mass selection. Fig.1(c) shows results of after the exposure of C_{44}^- , C_{47}^- and LaC_{44}^- to NO for 1 second. C_{47}^- was most reactive and the signal of C_{47}NO^- was observed. On the other hand, an only small signal of C_{44}NO^- from C_{44}^- and no reaction of LaC_{44}^- were observed. Systematic experiments showed that even-numbered bare carbon clusters were less reactive than odd-numbered clusters and that LaC_{2n}^- ($2n \geq 36$) were much less reactive than bare carbon clusters. Based on a geometrical consideration, “random-cage” structure for C_{2n} , $\text{La}@\text{C}_{2n}$, $\text{Sc}@\text{C}_{2n}$ and $\text{Y}@\text{C}_{2n}$ with all carbon atoms having 3-coordinates bonding was proposed. Furthermore, for Ni/Co and Ni/Y doped samples, the prominent effect of metal atoms during the laser vaporization was speculated to be the enhancement of the closing of this “random-cage” structure.

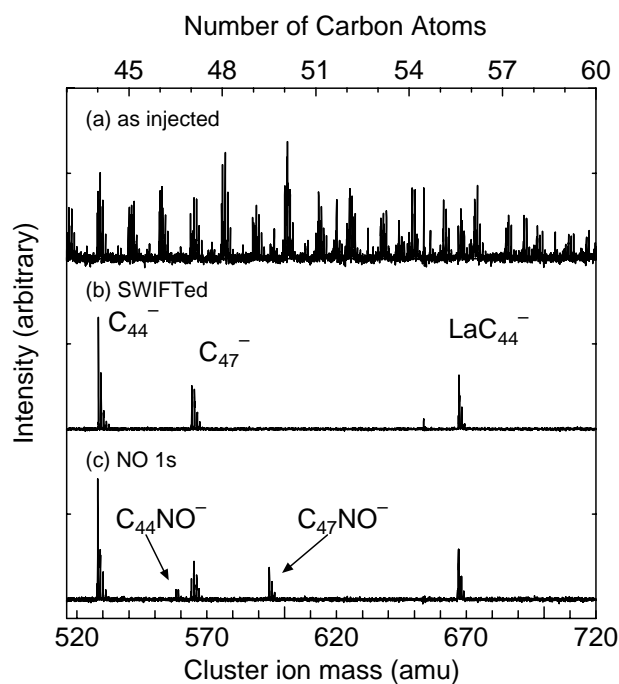


Fig.1 Chemical reaction of LaC_{44}^- with NO compared with bare clusters C_{44}^- and C_{47}^- . (a) As injected, (b) C_{44}^- , C_{47}^- and LaC_{44}^- clusters were selected, (c) after reaction with NO at 10^{-5} Torr.