Gas Phase Reaction of Ni/Co/C Mixed Clusters

OMasamichi Kohno, Shuhei Inoue and Shigeo Maruyama

Engineering Research Institute and Department of Mechanical Engineering, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan

Metal-carbon binary clusters generated by the laser vaporization of Ni/Co (0.6 at % Ni and 0.6 % Co) doped or Ni/Y (4.2 at % Ni and 1.0 % Y) doped carbon materials used for 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 (Fourier Transfer Ion Cyclotron Resonance) mass spectrometer. In case of a Ni/Co doped carbon material, there was not a trace of Ni or Co in the positive mass spectrum and tiny signals of NiC_n and probably CoC_n were measured for negative spectrum as in Fig.1(a). The chemical reaction of these clusters with NO was used as the probe of the structure of clusters. The reaction experiments with NO were done without the selection of clusters because the signal level was so low. The reaction results with 10^{-7} Torr NO for 2 s and 10 s are shown in Fig.1. The chemisorption of NO to NiC_n and CoC_n were observed in much faster rate than pure carbon clusters. It seems that CoC_n reacted a bit faster than NiC_n. After the reaction for 10 s, the product of C_nNO gradually appeared. In general, 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 results of a Ni/Y doped carbon material will be also discussed at the presentation. More drastic effect of doping of Ni/Co was observed in pure carbon cluster distribution as follows. The even-odd alternation was observed and this even-odd feature starts from C₃₆. Considering that even-numbered clusters were favored to generate, these features are recognized as the tendency toward closing the random-cage structures, though it is not clear how metal atoms change these pure-carbon cluster distributions. One possible explanation may be that Ni or Co atoms interact with small carbon clusters to help the cage closure but are thrown away when the carbon size grows as large as 40 to 50 atoms where it can form stable random cage structure itself.



Fig.1. Reaction of NiC_{38} and CoC_{38} with NO.