FT-ICR Study of Chemical Reaction of Acetonitrile Molecules on Cobalt Clusters

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The chemical vapor deposition (CVD) method is the most common technique for production of single walled carbon nanotubes (SWNTs). During the CVD process, an SWNT grows from decomposed carbon atoms on a catalytic metal particle fed by molecules such as CO, CH_4 or ethanol at high temperature. Therefore, understanding surface chemical reaction is critically important, however, little is known due to the complexity of these nanoparticles. Recently, Thurakitseree et al. [1] reported that changing the carbon feedstock from pure ethanol to a few % mixture of acetonitrile (CH_3CN) in ethanol during CVD drastically reduces the average diameter of the SWNTs, and this change is reversible and repeatable. It is suggested that the nitrogen atoms in acetonitrile molecules impeded the formation of larger diameter SWNT on the surface of catalytic particles. However, the detailed mechanism of the reaction is also still not clear.

In this study, the chemical reactions of cobalt cluster cation with acetonitrile was observed by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with direct injection laser vaporization cluster beam source [2]. Cobalt clusters were trapped within the FT-ICR cell, subsequently acetonitrile was introduced. Figure 1 shows the typical mass spectrum of the reaction products from Co_{11}^+ clusters. Dotted lines indicate the simple chemisorption of acetonitrile such as $+CH_3CN$ or $+(CH_3CN)_2$. We can also observe the dehydrogenated chemisorption such as $+(CCN)_2$ or $+(CCN)_2(HCCN)$. Figure 2 shows the schematic diagram of the $Co_{11}(CCN)_2^+$ cluster. The drastic cluster size dependence of these reaction such as the change of simple /dehydrogenate chemisorption ratio was observed. The difference of reactivity compared with the ethanol (C_2H_5OH), nitrogen-free molecules, and the cluster size dependence of these reactions will also be discussed.

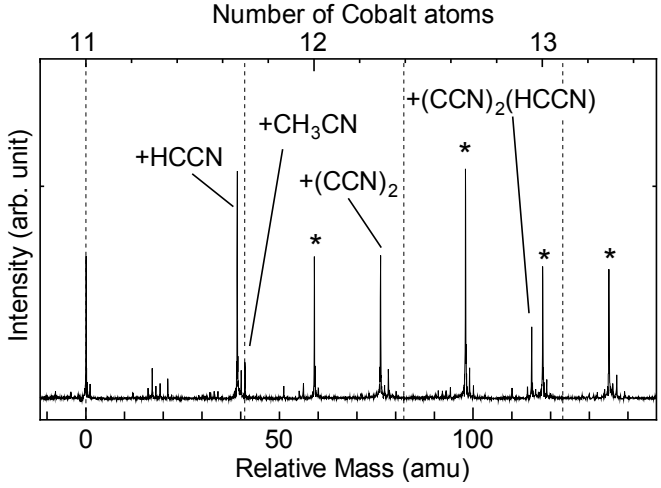

Fig.1 Chemisorption on Co_{11}^+ clusters; * indicates peaks originated from Co_{12}^+ or Co_{13}^+.

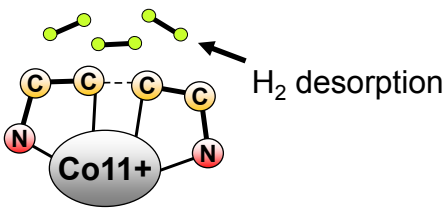

Fig.2 Schematic diagram of $Co_{11}(CCN)_2^+$ cluster.

[1] T. Thurakitseree, et al., ACS Nano, 7 (2013) 2205.
[2] S. Maruyama, et al., Rev. Sci. Instrum., 61 (1990) 3686.