Studies on chemical reactions of transition metal clusters with oxygen by using FT-ICR mass spectrometer

Yuta Tobari,[1] Kazuki Ogasawara,[2] Shohei Chiashi,[2] Shigeo Maruyama,[2] and Toshiki Sugai[1]

[1] *Department of Chemistry, Toho University, Funabashi, Japan*

[2] *Department of Mechanical Engineering, The University of Tokyo, Tokyo, Japan*

Transition metal oxide clusters have been used as industrial catalysts with their unique size effects. However, their size dependence and oxidation reactivity are not well known. Here we present studies on reactions of transition metal clusters with O_2 by using FT-ICR.

Details of experimental apparatus and techniques have been described elsewhere [1]. Metal clusters were produced by a laser vaporization cluster source and were injected and trapped in a cell under a magnetic field of 6 T. The trapped clusters were thermalized in several seconds and were then exposed to oxygen for 100-1000 ms. The pressure of O_2 of the cell were approximately 5×10^{-7} Torr.

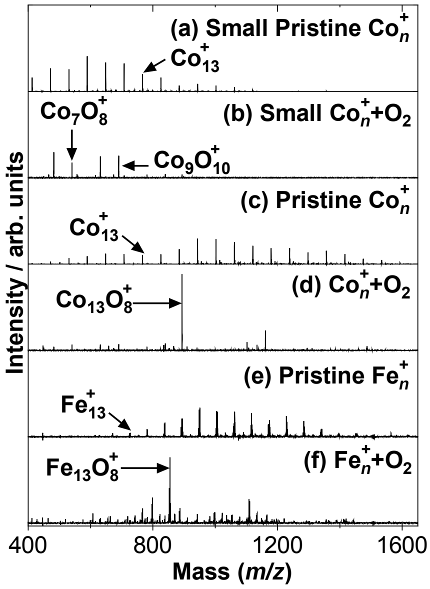

Fig. 1 Mass spectra of metal and metal oxide clusters.

Figure 1 shows mass spectra of pristine metal (M_n^+: M = Co or Fe) clusters and product metal oxide clusters ($M_nO_{2m}^+$) with/without O_2, respectively. When the pristine cluster (Co_n^+) size distribution was smaller (n = 6-18) in Fig. 1a, the products were $Co_nO_{2m}^+$ (n = 5-11, $2m$ = 6-12) without any magic numbers (Fig. 1b). The ratio of $2m/n$ were 1.1-1.3. When the cluster size was larger (n = 8-28) as shown in Fig. 1c, we can observe a salient magic number of $Co_{13}O_8^+$ [2] with the much lower ratio of $2m/n$ = 0.6. The production condition of $Co_{13}O_8^+$ clarifies that it is derived from larger parent pristine clusters (Co_n: n >13) through dissociative oxidation processes [3]. The intensity analyses also support the production processes with the fact that $Co_{13}O_8^+$ is much more abundant than the pristine Co_{13}^+. Figures of 1e and 1f show almost identical cluster distributions of Fe_n and Fe_nO_{2m} to those of Co_n and Co_nO_{2m} in Figs. 1c and 1d. The results together with their intensity analyses reveal universal dissociative oxidation processes of transition metal clusters.

Our preliminary reaction rate analyses reveal that the obtained rate constants of Co_n and Fe_n (n = 7-26) are similar to the Langevin ion-molecule collision rate constant ($k_L \sim 5.3\times10^{-10}$ cm^3 s^{-1}), which is consistent to the studies on $Ni_n + O_2$ (n = 2-15) reported by Sugawara and Koga [4].

References

[1] S. Inoue and S. Maruyama, Jpn. J. Appl. Phys. 47 (2008) 1931.
[2] Q. Sun, et al., Phys. Rev. B 62 (2000) 8500.
[3] F. Liu, F. X. Li, and P. B. Armentrout, J. Chem. Phys. 123 (2005) 064304.
[4] K. Sugawara and K. Koga, Chem. Phys. Lett. 409 (2005) 197.