論文の内容の要旨

Experimental and theoretical study
on initial stage of oxidation of metal clusters
（金属クラスターの酸化反応初期過程に関する
実験的・理論的研究）

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1. Introduction

Metal clusters, defined as assemblies of a few to hundreds of metal atoms, have gained current attention as promising candidates for novel catalysts because they exhibit unique chemical properties owing to specific geometric and electronic structures.[1] Another attractive feature of metal clusters as catalytic material is that their chemical properties can be tuned over a wide range by changing the size and composition of the clusters.

Interaction between oxygen molecules and metal clusters is very important because it is a key step for aerobic oxidation catalyzed by metal clusters[2] and it is related to the stability of the clusters under ambient conditions. In my doctoral study, I focused on oxidation processes of clusters of cobalt and iridium in the gas phase and studied stability and structures of the metal oxide clusters by means of mass spectrometry, photoelectron spectroscopy and ion mobility mass spectrometry with a help of density functional theory (DFT) calculations. The aim of this work is to attain molecular level understanding on the interaction between metal clusters and oxygen molecules and to gain an insight into rational development of atomically precise metal oxide clusters as novel catalysts in the real world.

2. Oxidation of cobalt cluster anions

Although stable compositions and geometric structures of cobalt oxide clusters have been reported,[3] there is no report on how the oxidation of cobalt clusters is initiated to finally form stable oxide clusters. I conducted experimental and theoretical studies on the early stage of the oxidation reaction of cobalt cluster anions Co_n^- and geometric and electronic structures of the products $Co_nO_m^-$.

Experiments were conducted by using a home-made time-of-flight mass spectrometer (TOF-MS) coupled with a magnetic bottle photoelectron spectrometer (MB-PES).[4] Cobalt cluster anions Co_n^- were generated by the irradiation of a focused output of the second harmonic of a Nd:YAG laser onto a cobalt rod under pulsed helium carrier gas. Cobalt cluster anions were subsequently introduced into a reaction cell filled with oxygen whose partial pressure was adjusted by changing the valve opening time t_{PV}. Finally the anionic species were extracted into the TOF-MS by applying a pulsed high voltage. The photoelectron was detached from $Co_nO_m^-$ by irradiating the fourth harmonic of a Nd:YAG laser and were detected by MB-PES. DFT calculations were performed at B3LYP/6-31+G(d) level.

Fig. 1 Schematic image of experimental apparatus.

Figure 2 shows the typical mass spectra of $Co_nO_m^-$ recorded by changing t_{PV}. The intensity distributions of $Co_nO_m^-$ did not show even-odd alternation with respect to m, indicating that $Co_nO_m^-$ are produced via dissociative adsorption of O_2. The distributions of $Co_nO_m^-$ were gradually shifted to larger m values with increase in the O_2 pressure and reached those expected from the bulk composition (Co_3O_4) at a high O_2 pressure. At relatively low O_2 pressures, two types of magic compositions were observed; intensities of mass peaks indicted by triangles and circles (Figures 2c and 2d) dropped abruptly by removing or adding one O atom, respectively. In order to shed light on the origin of their magic behaviors, adiabatic electron affinities (AEAs) of $Co_nO_m^-$ were determined from the onset of the photoelectron spectra. The AEAs increased monotonically with m, but increased abruptly at the magic compositions indicated by triangles. These results suggest the origin of the former magic clusters is high stability against thermionic emission. Structural change upon sequential oxidation was theoretically studied using $Co_7O_m^-$ ($m \leq 6$) as an example. The optimized structures shown in Figure 3 demonstrated that O atoms are attached sequentially to the facets or edges of Co_7^- while retaining the Co_7 core structure. On
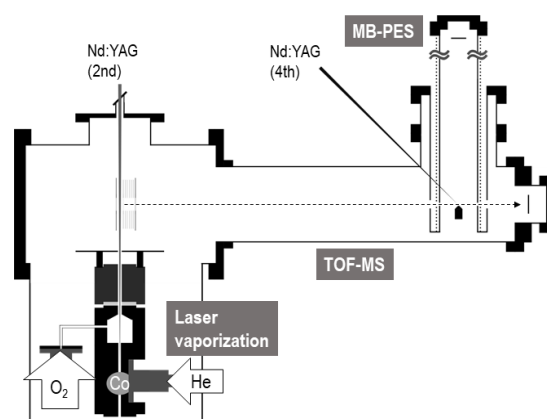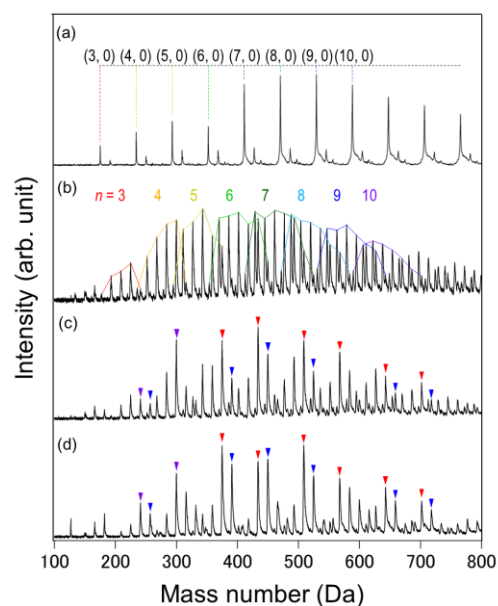

Fig. 2 Typical mass spectrum of $Co_nO_m^-$ obtained at t_{PV} = (a) 0, (b) 140, (c) 150, and (d) 200 μs. The notation (n, m) represents the chemical compositions of $Co_nO_m^-$.

the basis of these results, we propose that the latter magic $Co_nO_m^-$ clusters correspond to stable intermediates of the oxidation reaction whose surfaces are fully covered by O atoms. The sudden drop of peak intensity by the addtion of a single O atom is associated with sudden decrease in the binding energy of O atom.
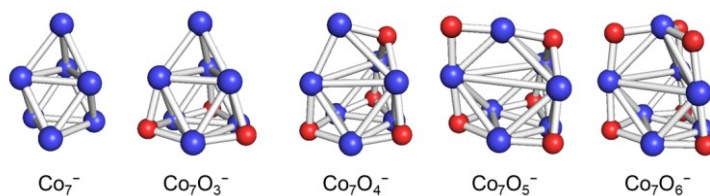

Fig. 3 Calculated structure of $Co_7O_m^-$.

3. Iridium oxide clusters

It was reported that iridium cluster had a partially oxidized area on the surface in the aerobic condition and showed a higher selectivity in hydrogenation of the NO_2 group. The selective hydrogenation was ascribed to preferential adsorption of the NO_2 group onto the oxidized area and activation of the hydrogen on the nonoxidized area.[5] However, there is no experimental research on the atomic packing structure of isolated iridium oxide clusters although theoretical calculation predicted planar structural motifs for $Ir_5O_m^-$ ($m \geq 6$).[6] Formation of planar motifs in iridium oxide clusters is in contrast to three dimensional motifs in cobalt oxide clusters although iridium and cobalt belong to the same group in the periodic table. Here, I conducted the ion mobility-mass spectrometry and DFT calculation on iridium oxide cluster anions $Ir_nO_m^-$ in order to unravel the structural evolution as a function of m.

Experiments were conducted by using an ion mobility TOF-MS apparatus installed at Tohoku University.[7] Iridium oxide clusters were generated by irradiating a focused output of the second harmonic of a Nd:YAG laser onto an iridium rod under the O_2-seeded helium carrier gas. Iridium oxide cluster anions were introduced into a drift cell filled with helium by pulsed voltage. Collision cross sections (CCSs) were determined from the arrival time in the cell. After drift cell, the target ions were analyzed by TOF-MS. DFT calculations for structural calculation were performed at B3LYP/def-SV(P) level. Theoretical CCSs were calculated by using projection approximation method in MOBCAL.[8]

Figure 5 shows experimental CCS values of $Ir_nO_m^-$ ($n = 4$–8) plotted as a function of m in the range of 0–14. The CCSs values for $n = 4$–6 increase monotonically with m as expected. The
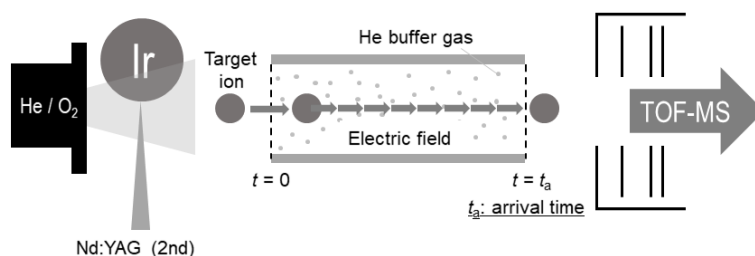

Fig. 4. Schematic image of ion mobility measurement.
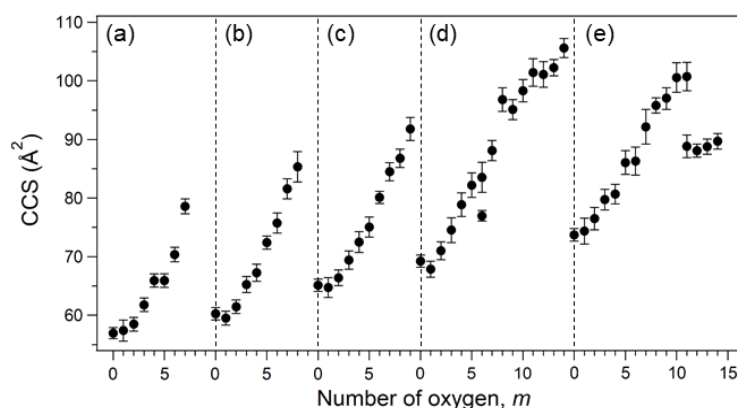

Fig. 5. Experimental CCS values of $Ir_nO_m^-$ with (a) $n = 4$, (b) 5, (c) 6, (d) 7, and (e) 8 as a function of m.

CCS values for $n = 7$ grow gradually with size as in the case for $n = 4$–6, but also take an irregularly smaller value than neighbors at $m = 6$. The CCS values for $n = 8$ increase monotonically in the range of $m = 0$–11, decrease suddenly at $m = 11$, and increase again in the range of $m = 11$–14. These results suggest the coexistence of structure isomers for $Ir_7O_6^-$ and $Ir_8O_{11}^-$. Theoretical calculations on $Ir_8O_m^-$ indicates that oxide structure with on-top oxygen atoms have larger CCS values than that with bridging (μ_2-bonded) oxygen atoms (Figure 6). Based on the theoretical calculation results, I proposed that oxygen-deficient ($m \leq 11$) and oxygen-rich ($m \geq 11$) clusters have on-top and bridging oxygen motifs, respectively. Oxygen atoms were bonded to the cubic Ir_8^- core as on-top motif sequentially as the core structure was distorted in $m \geq 7$, which is in sharp contrast to the case of Co_n^- where oxygen atoms were bonded as μ_2 or μ_3 motifs (Figure 3). Then all oxygen atoms were bonded as bridging motif in $m > 11$ and Ir-Ir bonds of the core no longer existed in this region.
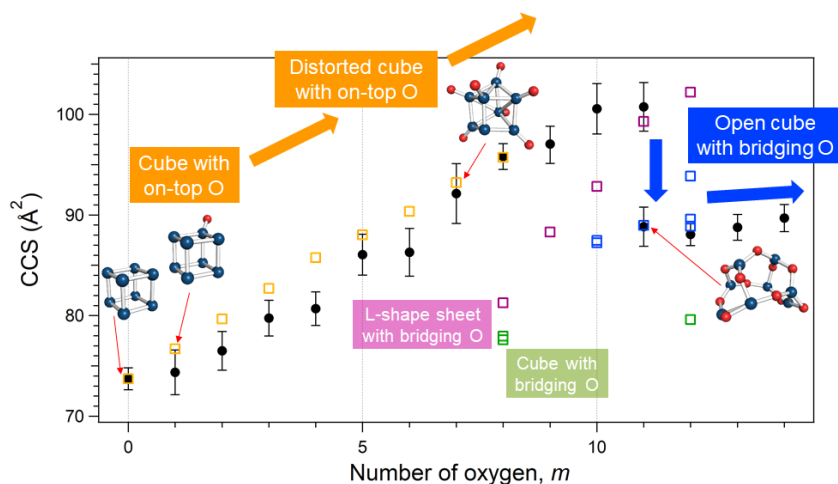

Fig. 6. CCSs of $Ir_8O_m^-$ ($m = 0$–14). Black circles indicate the experimental value. Orange, blue, green and purple squares indicate the calculated CCS values of isomers 1–4, respectively. The structures were derived from DFT calculation.

4. Conclusion

In this study, initial stages of oxidation process of cobalt and iridium cluster anions were investigated experimentally and theoretically. Oxygen atoms are bonded sequentially to the surface of cobalt cluster anions while retaining the core structure. In contrast, oxygen atoms are bonded sequentially to the terminal site of iridium cluster anions and on-top bonding motif suddenly underwent transformation into bridging μ_2 bonding motif at a later stage of the oxidation. These contrasted behaviors may reflect the difference in the electron orbitals involved in the bonding.

Reference

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