Preparation of intense multi-element metal cluster ions with single composition

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Abstract. A source of composition-selected multi-element cluster ions has been developed toward investigation of chemical reactivity of the clusters supported on a solid surface. The cluster ions are produced in a gas aggregation cell equipped with several magnetron sputtering devices, and their composition is selected by a quadrupole mass filter. The translational and internal kinetic energies of the single-composition cluster ions are reduced by collision with cold helium to achieve cluster-impact deposition onto the surface at a low collision energy. It has been succeeded to obtain single-composition silver-copper bimetal cluster ions more intense than several tens pA. A typical translational energy width is 0.5 eV per cluster.

1. Introduction

Chemical and physical properties of clusters change significantly and characteristically with a number of constituent atoms of the cluster (cluster size) due to specific changes of the geometric and electronic structures of the clusters. In this extension, it is straightforward to see that multi-element clusters have larger variety and novelties in their properties because of inhomogeneous electronic interaction between atoms of different elements as well as many possible geometric isomers even at a given composition. Furthermore, multi-element clusters can be a model system of cocatalysis to understand effects of the second (and third, …) element(s) on the catalytic activity. In these relations, several studies on bi-element clusters have been reported [1-6]. However, these studies do not show production of single-composition clusters with practical intensities. Furthermore, no report has been made on tri- or more-element metal clusters. In this report, preparation of intense multi-element metal cluster ions with a single-composition is described, aiming at investigation of chemical reactivities of multi-element clusters supported on a solid surface. Therefore, the cluster ions are required to be as intense as several tens pA in order for the preparation of the supported clusters by cluster impact [7-9] in a reasonable time. In addition, the translational kinetic-energy width of the cluster ions should be narrower than ~1 eV in order not only to achieve a low-energy impact for avoiding the cluster dissociation at the cluster impact but to obtain a uniform geometry of the clusters on the surface, as the geometry is determined by the impact energy as well as the cluster-surface interaction.

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2. Experimental apparatus

Figure 1 shows a sectional top plan of the apparatus developed. The machine consists of a multi-element cluster-ion source, octopole ion guides, a quadrupole deflector, a quadrupole mass filter for the cluster ions, a gas-collision cell, a cluster-deposition equipment and a quadrupole mass filter for the reaction products desorbed from the supported clusters. In this report, the description is concentrated on the production and the cooling of the cluster ions.

![Diagram of the apparatus](image)

The multi-element cluster ions are produced in a gas-aggregation cell equipped with magnetron sputtering sources [8] having a target of a different element for each placed in a parallel and off-centered arrangement; five magnetrons are attachable in this source. In simultaneous operation of the magnetrons at the powers of 20-100 W, atoms and ions of different elements are ejected from the targets by argon-ion impact, and they are allowed to aggregate into cluster ions in collision with helium and argon in the aggregation cell cooled by liquid nitrogen filled in a jacket surrounding the cell. The flow rates of the argon supplied to each magnetron and the helium are regulated independently with mass-flow controllers; typical flow rates are 15 and 60 cm$^3$ min$^{-1}$ (sccm) for the argon and the helium, respectively, so that the pressure of the aggregation cell is ~10 Pa. The distance between each magnetron and an exit nozzle (7 mm of inner diameter and 10-mm long) of the aggregation cell is optimized externally and independently (typically 120 mm).

The cluster ions thus produced are admitted into the first ion guide (290-mm long) placed in a jacket filled with liquid nitrogen, in which the diameter of the ion beam is reduced by collision with helium so as to increase ion transmittances of the ion optics placed downstream. The ion-guide is supplied with an rf voltage (500 KHz, 300 V$_{p-p}$) from a home-built RF oscillator driven by a FET. The rf frequency was optimized by adjusting an inductance and a capacitance placed in parallel to the ion guide. In the quadrupole deflector, only cations are deflected by 90 degrees toward the quadrupole mass filter so as to keep the mass filter from contamination with intense neutral species. Simultaneously, this deflector acts as an energy filter so as to obtain a narrow translational energy width of the cluster ions for a high ion-transmittance and resolution through the mass filter. The ions are injected into the mass filter (Extrel MEXM-9000, mass range of 25-9000 amu) through two cylindrical electrostatic lenses in order for the composition selection of the cluster ions.

The composition-selected cluster ions are admitted into the collision cell filled with helium leaked through a needle valve. The collision cell and then the helium are cooled by liquid nitrogen filled in a jacket, where the helium is pre-cooled by passing through a copper tube (~10 m) wound around the outer wall of the jacket. The cluster ions are guided by an octopole ion-guide (1-m long, 1 MHz, 300 V$_{p-p}$) equipped in the collision cell in order to prevent the ions from being scattered out during the collisional cooling.

The intensity of the cluster ions is measured as an ion current, $I$, hitting on a metal plate at any place (e.g. rods of the ion guide, the electrostatic lenses, etc.) through a home-built current-voltage converter having a conversion factor of 10$^8$ V A$^{-1}$ and a serial home-built passive low-pass filter with cut-off frequencies of 3 and 8 Hz. The translational energy distribution of the cluster ions is measured...
by a retarding-potential method, i.e. a numerical difference of $I$ with respect to a bias voltage, $V_{bias}$, applied to the detector plotted as a function of $V_{bias}$.

3. Results and Discussion

3.1. Production of multi-element cluster ions

Figure 2 shows a typical mass spectrum of bimetal cluster cations of silver and copper, $\text{Ag}_N\text{Cu}_M^+$, detected at the third ion-guide rods; $\text{Ag}_N\text{Cu}_M^+$ are also discernible as shoulders of $\text{Ag}_N^+$ at their heavier sides. We have succeeded in producing the bimetal cluster ions in a wide size range with intensities more than several tens pA. The numbers of the Ag and Cu atoms in a cluster ion are controllable coarsely by the electric powers supplied to the magnetrons. It is easily expected to produce tri- or more-element cluster ions by operating more magnetrons in a similar manner.

3.2. Cooling of cluster ions

Figure 3 shows a translational energy distribution of $\text{Ag}_{44}^+$ without and with introducing helium in the collision cell, the pressure of which increased from $10^{-5}$ to $10^{-1}$ Pa ranges by the helium introduction. The best-fit curves give FWHM of 5 and 0.5 eV without and with the cooling, respectively. Therefore, one can decrease the collision energy as low as 0.5 eV, which is one order of magnitude lower than the...
dissociation energy of Ag\textsubscript{44}\textsuperscript{+}, so that the cluster is hardly dissociated by the impact on the surface. Furthermore, one can make the cluster impact at precisely-controlled collision energy to achieve a uniform geometry of the clusters on the surface. It was confirmed by mass analysis of the ions passed through the collision cell that the ions are not dissociated after the experience of the collision with the helium.

3.3. Optimization of frequency of rf voltage applied to ion guide

Figure 4 shows the transmittance of Ag\textsubscript{N}\textsuperscript{+} through the first ion guide at various frequencies of the rf voltage applied to the first ion guide. These results indicate that the heavier cluster ions have the higher transmittance through the ion guide with the higher frequency. In this manner, the optimized frequencies were applied to the three ion guides depending on the mass of the cluster ions of interest.

![Figure 4. Transmittance, \( T_{IG1} \), of silver cluster cations, Ag\textsubscript{N}\textsuperscript{+}, through the first ion guide as a function of \( N \) at various rf frequencies applied to the ion guide. The relative transmittance is shown with respect to \( T_{IG1} \) at 1.2 MHz.](image)

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