Stable Compositions and Structures of Oxide Cluster Ions of Copper and Palladium Studied by Ion Mobility Mass Spectrometry

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(イオン移動度質量分析法を用いた
銅及びパラジウムの金属酸化物クラスターイオンの安定組成と構造の研究)

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論　文　内　容　要　旨

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Introduction

Transition metal oxides are always important for the researchers because of their diverse use such as catalysts for various industrial processes. The chemical nature of the active oxygen species of the oxidation catalysts is considered as a governing factor for the specific catalytic activities along with other factors, e.g., particle size, compositions, and structures. In particular, the arrangement of oxygen species on the metal surface and their stability are important for evaluating the catalytic activity for different purposes in the molecular level. Study of gas-phase clusters of metal oxide (Cu and Pd) is an important approach for understanding the microscopic properties of the active sites in copper and palladium oxides. Especially, the geometrical arrangement of different types of oxygen species on the metal-surface and their stability are important to evaluate catalytic activity of the nano-sized models. Moreover, the structural changes with cluster size are also important for applied science, because the functions of nanomaterials are expected to depend on their structures. In the gas-phase, a number of experimental and theoretical investigations have been carried out so far on copper oxide, $Cu_nO_m^+$, and palladium oxide, $Pd_nO_m^{+/-}$ cluster ions. Most of the previous study concerned structural assignments based on theoretical calculations, and limited to a several compositions for small copper and palladium oxide cluster ions. Experimental studies on stable compositions and structures along with theoretical investigations have not been revealed comprehensively yet. Therefore, in the present study, stoichiometric compositions and size-dependent structures of copper and palladium oxide cluster ions have been investigated by ion mobility mass spectrometry (IMMS) in order to gain insight into the nature of the oxygen-metal interaction, geometry, and stability. For these purpose, geometrical structures of the proposed compositions are optimized by quantum chemical calculations and structural assignment can be done by comparing experimentally observed collision cross section (CCS) with theoretically calculated CCS. So this paper attempts to integrate this study into different chapters.

In chapter 2, the details of the experimental principles and background of the experimental techniques, mainly ion mobility, are presented. Here details of cluster production, and principle about precise assignment of mass and mobility are discussed. Chapter 3 mainly deals with experimental set up including ion drift cell, and vacuum devices are discussed here. In chapter 4, experimental procedure and calculation methods to determine the collision cross section of each cluster species are discussed. The results of copper oxide and palladium oxide cluster ions are summarized in chapter 5. Details on stable compositions, and structure determination results of individual cluster species, e.g., copper oxide cluster cations, palladium oxide cluster cations and palladium oxide cluster anions based on mobility analysis and theoretical calculation are discussed here. In this section, stable compositions are discussed on the basis of collision induced dissociation under high energy conditions, estimation of experimental CCSs, optimization of imaginary structures by quantum chemical calculations (DFT), and calculation of theoretical CCSs are mentioned. Finally, geometrical structures of targeted cluster species are determined by evaluating experimental and theoretical CCSs, and interpretation about similarities and dissimilarities among the different clusters are discussed.

Experiment and calculation method

The experiments were performed by using a home-made IMMS vacuum apparatus consisting of ion source, an ion drift cell for IMS and a reflectron-type time-of-flight (TOF) mass spectrometer. Metal oxide cluster ions, ($M_nO_m^{\pm}$, M = Cu, and Pd) were generated by a combination of laser vaporization and supersonic expansion of 5% O_2/He carrier gas. Generated cluster ions were injected into the ion-drift cell with kinetic energies (E_{inj}) of 50−250 eV by a pulsed electric field at a given time. Inside the ion drift cell, cluster ions get acceleration with an applied electrostatic fields and next deceleration is caused by the collision with He-buffer gas filled inside the cell. The cluster ions finally reached a constant drift velocity depending on their interaction with He buffer gas toward the end of drift region. The time sends in the drift cell depends on the collision cross sections between cluster ions and He atoms in the cell. Therefore, cluster ions with different size and structures were detected at different arrival times. TOF mass spectra of cluster ions were obtained by summing up all the ion signals at every arrival time existing in the ion drift cell with spatial distributions depending on their mobilities. 2D plot of TOF vs arrival time was also observed from the measurement where TOF and arrival time corresponds to mass and CCSs, respectively. Arrival time distributions (ATDs) were also obtained from the 2D plot for the estimation of Ω_{exp}. From these ATDs, experimental CCSs were estimated by applying kinetic theory of ion transport. On the other hand, for theoretical calculations, structures were optimized by B3LYP/cc-pVDZ (Cu), SDD (Pd), aug-cc-pVDZ (O) basis sets in Gaussian 09. Theoretical CCSs (Ω_{calc}) for the optimized structures were calculated by either trajectory method (TM) or projection approximation (PA) method in MOBCAL program. By comparing Ω_{exp} and $\Omega_{\mathrm{calc,}}$ geometrical structures of a specific composition were determined.

Results and Discussion

Stable compositions of $M_nO_m^{\pm}$ cluster ions were obtained from the IMMS measurements mainly from the injection energy (E_{inj}) dependence. Cluster ions have tendencies to be populated to specific compositions with increasing injection energy from 50 eV to 250 eV, because of CID just after injection into the ion drift cell before thermalization. As for copper oxide cluster cations, the most stable species were obtained $Cu_nO_m^+$ (n:m) ~ (2:1) as a characteristics features, whereas for $Pd_nO_m^+$, pure metallic cluster (m = 0), and oxygen-deficient, ($n > m$) were obtained with respect to CID at higher injection energy condition (250 eV), although $Pd_nO_m^-$ was given no metallic clusters. At the lower injection energy of 50 eV, a variety of cluster species were commonly observed for these cluster ions, where the stoichiometries were found to have much oxygen rich in comparison with higher injection energy counterpart.

Next, the structural assignment concentrated on the cluster ions containing more oxygen were assigned for the compositions of $Cu_nO_m^+$ (n = 2-8), $Pd_nO_m^+$ (n = 3-5), and $Pd_nO_m^-$ (n = 2−7, $n \leq m$).   In the case of $Cu_nO_m^+$ cluster cation, the stable compositions of $Cu_nO_{\sim n/2}^+$, the experimental CCSs increase smoothly up to n = 6 and then reach a plateau as mass increases. Therefore, systematic structural growth was observed for n = 2-6, in which structure can be made by adding simply either one copper atom or coper oxide monomer, and then started to form complex shapes at n = 7 and 8. Both 2D and 3D compact structures were assigned for $Cu_nO_n^+$. For $Cu_nO_{n-1}^+$ cluster ion, stepwise structural growth was observed from 2D→3D for sizes $Cu_3O_2^+$ to $Cu_4O_3^+$, $Cu_5O_4^+$ to $Cu_6O_5^+$, and $Cu_7O_6^+$ to $Cu_8O_7^+$. Additionally, 2D sheet and 3D compact isomers were found coexisting in the $Cu_5O_4^+$ and $Cu_7O_4^+$ cluster ions.

As for the $Pd_nO_m^+$ clusters, structural assignments for the cluster size, n = 3−5 were done based on the wide range of compositions with the increment of number of oxygen. In the present IMMS study, structures containing metal-core configuration were suggested commonly for the various number of O atoms, m, as a characteristic feature. For example, $Pd_3O_m^+$ cluster cations, structural transition was observed from one-dimensional (1D) chain to 2D branched / 2D sheet and finally to 3D compact structures with increasing m. These 2D and 3D isomers were found to retain their triangular metal-core configuration. Also for the $Pd_4O_m^+$ cluster ions, 2D sheet and 3D compact isomers were assigned; as for the 3D isomers, structures maintain tetrahedral metal-core configuration. Two structural isomers were assigned for $Pd_5O_m^+$, one with 3D square pyramidal metal-core configuration and another one was 3D distorted pentagonal. Furthermore, the structures of oxygen-deficient cluster ions include atomic oxygen preferentially, whereas structures with molecular oxygen were commonly assigned for oxygen-rich ($m > n$) cluster ions.

Finally, for the structures of $Pd_nO_{n-1}^-$ cluster anions were found to be preferentially constructed by consecutive Pd–O–Pd bonds. On the other hand, structures with molecular oxygen (–O–O–) appeared at $n \geq 4$ along with atomic oxygen for $Pd_nO_n^-$ clusters. Moreover, bulky and compact isomers were found to coexist for $Pd_4O_4^-$, $Pd_5O_{4,5}^-$, and $Pd_6O_{5,6}^-$ cluster ions. These findings showed marked contrast with the corresponding cationic clusters, suggesting a charge effect.