

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

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URL	http://hdl.handle.net/10097/00126104

論文内容要旨

(NO. 1)

氏名	LATIF, Mohammad Abdul	提出年	令和元年
学位論文の 題目	Stable Compositions and Structures of Oxide Cluster Ions of Copper and Palladium Studied by Ion Mobility Mass Spectrometry (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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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, $\text{Pd}_n\text{O}_m^{+/-}$ 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, ($M_nO_m^\pm$, $M = \text{Cu}$, 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 Ω_{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^+ ($n:m$) \sim (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 $\text{Cu}_n\text{O}_{\sim n/2}^+$, 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 copper 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 $\text{Cu}_n\text{O}_{n-1}^+$ 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 $\text{Pd}_n\text{O}_{n-1}^-$ 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^- , $\text{Pd}_5\text{O}_{4,5}^-$, and $\text{Pd}_6\text{O}_{5,6}^-$ cluster ions. These findings showed marked contrast with the corresponding cationic clusters, suggesting a charge effect.

論文審査の結果の要旨

本研究では、銅とパラジウムの酸化物のクラスターの安定組成や構造を、イオン移動度質量分析法を用いて調査することを目的とした。これらの遷移金属酸化物は触媒などの機能性材料として利用され、盛んに研究されている。クラスターの研究は、今後の酸化物ナノ材料としての利用への貢献が期待できる。本研究では、これらの遷移金属酸化物のクラスターの正負イオンについて、安定組成とその構造同定を行った。

第一章では、本研究の学術的背景や、本研究の目的について記述した。

第二章では、クラスター生成、イオン移動度分析、および飛行時間質量分析の実験原理について詳述した。

第三章では、実験装置の構成について記述した。

第四章では、実験手順および理論計算の詳細について記述した。

第五章では、銅酸化物クラスター正イオン Cu_nO_m^+ 、パラジウム酸化物クラスター正負イオン Pd_nO_m^+ 、 Pd_nO_m^- の安定組成と構造同定について、得られた結果を述べている。

まず、 Cu_nO_m^+ で、衝突誘起解離反応条件下での質量分析から安定化学種を決定した。その結果、 $n:m \approx 2:1$ に近い化学種の形成を見出した。また移動度分析から得られる衝突断面積と理論計算との比較から、その構造を議論した。

続いて Pd_nO_m^+ について実験と理論計算の結果を議論した。この系では、特定の安定組成が観測されず、衝突誘起解離反応で酸素原子を脱離する傾向がみられた。そこで Pd_3O_m^+ 、 Pd_4O_m^+ 、 Pd_5O_m^+ の系列で酸素原子数の変化に伴う構造変化を観測したところ、金属クラスターを核として酸素が原子または分子状に配位していくことがわかった。

最後に Pd_nO_m^- について議論した。まず、金属原子と酸素原子がほぼ同数の Pd_nO_n^- や $\text{Pd}_n\text{O}_{n-1}^-$ といった組成をとることがわかった。このうち $\text{Pd}_n\text{O}_{n-1}^-$ ($n = 2-7$) では酸素原子はすべて Pd-O-Pd のように原子状で架橋している構造が得られた。一方、 Pd_nO_n^- では、 $n \geq 4$ で分子状酸素が架橋する構造が見出された。

以上の成果は、銅およびパラジウムの気相金属酸化物クラスターイオンに関する系統的な研究に新たな知見を与えるものである。また同時に、本人が自立して研究活動を行うために必要な高度の研究能力と学識を有することを示している。ゆえに、LATIF, Mohammad Abdul 提出の博士論文は博士(理学)の学位論文として合格と認める。