

Structures and compositions of group 5 metal oxide cluster ions studied by ion mobility mass spectrometry

著者	WU Jenna Wen Ju
number	82
学位授与機関	Tohoku University
学位授与番号	理博第3162号
URL	http://hdl.handle.net/10097/00123965

論文内容要旨

(NO. 1)

氏名	WU, Jenna Wen Ju	提出年	平成30年
学位論文の 題目	Structures and compositions of group 5 metal oxide cluster ions studied by ion mobility mass spectrometry (イオン移動度質量分析法による5族金属酸化物クラスターイオンの構造と組成に関する研究)		

論文目次

Chapter 1 – Introduction	1
1.1 Gas Phase Clusters	3
1.2 Ion Mobility Analytical Method	4
1.3 Transition Metal Oxides	5
1.4 Group 5 Transition Metal Oxides	6
1.5 This Study	8
1.6 References	9
Chapter 2 – Experimental Principles	13
2.1 Cluster Production	15
2.2 Time of Flight Mass Spectrometry	16
2.3 Wiley-McLaren Type TOF-MS and Space Focusing Condition	18
2.4 Reflectron Type TOF-MS and Energy Focusing Condition	20
2.5 Ion Mobility Spectrometry Analysis	22
2.5.1 Reduced Mobility	24
2.6 References	25
Chapter 3 – Experiment and Calculation Methods	29
3.1 Experimental Apparatus	31
3.1.1 Overview of Experimental Apparatus	31
3.1.2 Overview of Ion Drift Cell	32
3.1.3 Time of Flight Mass Spectrometry	33
3.1.4 Vacuum Devices	34
3.2 Experimental Procedure and Conditions	35
3.2.1 Cluster Ion Production: Details in Cluster Source	35
3.2.2 Arrival Time vs Time of Flight 2D Spectrum	36
3.2.3 Drift Time Estimation and Collision Cross Section	36
3.2.4 Collision Induced Dissociation and Cluster Assignment	37

3.2 Calculation Method	38
3.3.1 Quantum Chemical Calculations	38
3.3.2 MOBCAL program	38
3.3.3 Theoretical Calculation Conditions	39
Chapter 4 – Group 5 Metal Oxides	
4.1 Vanadium Oxide Cluster Ions	45
4.1.1 Mass Spectra under High Injection Energy Condition	46
4.1.2 Mass Spectra under Low Injection Energy Condition	47
4.1.3 Stability of Vanadium Oxide Cluster Ions	48
4.1.4 Arrival Time Distributions from 2D Spectra and Collision Cross Sections	48
4.1.5 Proposed Geometrical Structures	50
4.1.6 Theoretical CCSs and MOBCAL Parameters	52
4.1.7 Structures Assignment and Discussion	53
4.1.8 Stability of Specific Compositions Explained with Theoretical Calculation	55
4.1.9 Vanadium Oxide Cluster Ions Reactions with CO	55
4.1.10 References	57
4.2 Niobium Oxide Cluster Ions	
4.2.1 Mass Spectra under High Injection Energy Condition	83
4.2.2 Mass Spectra under Low Injection Energy Condition	86
4.2.3 Experimental CCSs Estimated with Arrival Time Distribution Plots	87
4.2.4 Proposed Geometrical Structures	89
4.2.5 Theoretical CCSs and MOBCAL Parameters	92
4.2.6 Structure Assignment and Discussion	92
4.2.7 Cluster Species Increase in Number of Oxygen Atoms	93
4.2.8 Similarity and Differenced with Vanadium Oxide Cluster Ions	94
4.2.9 References	95
4.3 Tantalum Oxide Cluster Ions	
4.3.1 Mass Spectra under High Injection Energy Condition	119
4.3.2 Mass Spectra under Low Injection Energy Condition	121
4.3.3 Experimental CCSs Estimated with Arrival Time Distribution Plots	122
4.3.4 Proposed Geometrical Structures	126
4.3.5 Theoretical CCSs and MOBCAL Parameters	128
4.3.6 Structures Assignment and Discussion	129
4.3.7 Similarity and Differenced with Vanadium and Niobium Oxide Cluster Ions	130
Chapter 5 – Conclusion	149
List of Presentations	153
Acknowledgements	161

Introduction

Transition metal oxides, such as the group 5 transition metal oxides, have numerous applications because of their electrical, optical, and magnetic performances. Also, they are of important industrial materials because of their ability to effective oxidation-reduction reactions, and their ability to act as promoters to can enhance catalytic activity, selectivity, and prolong catalyst life. The group 5 metal oxides exist as pentoxides (M_2O_5 , $M = V, Nb, \text{ or } Ta$) in the bulk phase with a formal oxidation state of +5, yet each of its crystalline structure vary largely from one another. Considering the surface structures in the bulk phase as assemblies of clusters of different sizes and isomers, can further support the understanding their catalytic activities and properties. Therefore, exploring the structural differences in the form of gas-phase clusters may give insights the differences in bulk phase properties. Gas-phase clusters provide an ideal and controlled environment to probe their reactivity, or structures as a complementary knowledge to the bulk materials. Especially, there are numerous experimental and theoretical techniques that can be incorporated into the study of gas-phase clusters, an isolated system.

This study intend to unveil the composition and structural information of the group 5 metal oxide cluster ions with ion mobility mass spectrometry (IM-MS). By applying IM-MS and theoretical calculations, detailed cluster structure information such as collision cross section can be evaluated to understand the similarities and differences of the group 5 metal oxide in the cluster phase. These information can be further used to evaluate the difference in their properties as bulk phase materials.

Experiment and calculation method

Experimentally, vanadium, niobium, and tantalum oxide cluster ions ($M_mO_n^\pm$) were first generated by combination of laser ablation and supersonic expansion of O_2/He mixture gas. The generated cluster ions were injected into an ion drift cell with an injection energy of 50 or 250 eV by a pulsed electric field, and collision induced dissociation (CID) occurred along with ion injection. Following the entrance into the ion drift cell, the product ions experience acceleration with an applied electrostatic field and deceleration by collisions with He buffer gas filled inside the cell. The cluster ions reached constant drift velocity depending on their interaction with He buffer gas, and therefore arrived at the cell exit with different arrival times for structure analysis. Arrival time is the time that each cluster ion takes to pass through the cell, and is dependent on its interaction with He buffer gas. Finally, the product ions were delivered through the reflectron-type time-of-flight (TOF) mass spectrometer for mass analysis. The obtained arrival time and TOF were used to analyze the collision cross sections (CCSs) of the size-selected cluster ions by using ion transport theory.

In the theoretical study, geometrical structure candidates were first optimized with Gaussian09 program. The calculation levels were B3LYP/6-311+G(d) for vanadium oxides, B3LYP/DGDZVP for niobium oxides, and B3LYP/cc-pVTZ(O) and cc-pVTZ-pp(Ta) for tantalum oxide cluster ions. Next, theoretical CCSs of the proposed geometrical structures were calculated with the projection approximation method in MOBCAL program.

Results and Discussion

The stable species found upon collision induced dissociation caused by high injection energy at the inlet of the ion-drift cell were $(VO_2)(V_2O_5)_{(m-1)/2}^+$, $(V_2O_4)(V_2O_5)_{(m-2)/2}^+$, $(VO_3)(V_2O_5)_{(m-1)/2}^-$, and $(V_2O_5)_{m/2}^-$ for all

vanadium oxide cluster ions between $m = 2-20$, depending on the odd or even number of vanadium atoms.. As for niobium oxide cluster cations, the most stable species were similarly $(\text{NbO}_2)(\text{Nb}_2\text{O}_5)_{(m-1)/2}^+$, $(\text{NbO}_3)(\text{Nb}_2\text{O}_5)_{(m-1)/2}^-$, and $(\text{Nb}_2\text{O}_5)_{m/2}^\pm$ up to $m = 24$. These compositions for vanadium and niobium oxide cluster ions are of stoichiometric compositions, formed with stoichiometric units or stable building block units. They had an oxygen to metal ratio of approximately $n = 2.5m$. On the other hand, the stable composition of tantalum oxide was found to be $(\text{Ta}_2\text{O}_5)(\text{TaO}_3)_{m-2}^+$ and $(\text{TaO}_3)_m^\pm$ for most species in $m = 1-13$. Relatively oxygen-rich species (in comparison to stoichiometric compositions) were thus stable for tantalum oxide cluster cations, where the oxygen to metal ratio of approximately $n = 3m$.

Next, vanadium oxide cluster ions (V_mO_n^\pm), with $m = \text{even}$, were known to have polyhedral cage structure frameworks, where every vanadium atom forms the vertices of the polyhedron, and are inter-connected by bridging oxygen atoms. The result is proved by comparing the experimental and theoretical collision cross sections of Gaussian09 optimized geometrical structures. Perfect tetrahedron structure is an example of such polyhedron structure. In this tetrahedral structure, vanadium metal atoms bond to a maximum of four oxygen atoms, of which three are bridging oxygen atoms and one is terminal oxygen atom. The geometrical structures of vanadium oxide cluster ions grow smoothly by increasing the size of polyhedron framework.

As for the geometrical structures for niobium oxide cluster ions ($\text{Nb}_m\text{O}_n^\pm$), the same basic framework to vanadium oxide cluster ions was found for $m = 2-7$. From the experimental CCSs observed with IM-MS, a structure transition of Nb_mO_n^+ can be observed at $m = 8-9$, where a decrease in overall CCS growth occurred. Similarly, a transition is found at $m = 7-8$ for Nb_mO_n^- . Such difference in experimental CCS growth suggested a difference in structural formation. At medium to large cluster size, optimized geometrical structures indicated that some Nb atom in the most stable structures of species such as $\text{Nb}_9\text{O}_{22}^+$ were found to have more than 4 oxygen atom coordination, forming NbO_5 or NbO_6 coordination. This is a property greatly different from that of vanadium oxide cluster ions.

Finally, geometrical structures for the oxygen rich tantalum oxide cluster ($\text{Ta}_m\text{O}_n^\pm$) greatly resemble that of vanadium and niobium oxide cluster ions at small m . The optimized geometrical structures of oxygen-rich tantalum oxide clusters shows multiple oxygen atom coordination. For example, the $\text{Ta}_4\text{O}_{11}^+$ structure was a perfect tetrahedral structure with an extra oxygen atom bonded to the terminal metal atom as a superoxide unit. Additionally, the geometrical structures of $\text{Ta}_5\text{O}_{13-16}^+$ resemble that of $\text{V}_5\text{O}_{12}^+$ and $\text{Nb}_5\text{O}_{12}^+$ pyramid framework, and the additional oxygen atoms are found to be on the terminal sites.

In conclusion, though group 5 metal oxides have very similar properties in the bulk phase, they share many similarities and differences in the cluster phase. The main similarity found is the compositions, where all of the group 5 metal oxides are composed of stoichiometric building block units. As cluster size increases, bulk like properties such as number of oxygen atom coordination began to become a dominant property in the gas-phase cluster ions.

別紙

論文審査の結果の要旨

本研究では、5族遷移金属原子酸化物のクラスターの安定組成や構造について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酸化触媒や電池電極材料に利用されており、盛んに研究されている。クラスターの研究は、今後のこれらの酸化物の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、三種類の5族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、飛行時間質量分析、およびイオン移動度分析の実験原理について詳述した。

第三章では、装置構成、実験手順および理論計算の詳細について記述した。

第四章では、バナジウム V、ニオブ Nb、タンタル Ta の酸化物クラスターイオンの安定組成と構造同定の結果を述べている。

まず、 $V_mO_n^{\pm}$ について、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、 $n = 2.5m$ の組成比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。その結果、V 原子 4 個の系では正四面体構造をとる $V_4O_9^+$ が最も強く観測された。これらの多面体型構造では、各 V に 4 個の酸素が配位する構造が得られた。

続いて $Nb_mO_n^{\pm}$ について実験と理論計算の結果を議論した。安定組成では、 $V_mO_n^{\pm}$ と同様に $n = 2.5m$ に近いものが観測され、構造も $V_mO_n^{\pm}$ と同様であった。 $m = 4$ では $Nb_4O_{10}^+$ が最も強く観測され、 $m = 9$ 以上でよりコンパクトな構造に転移する傾向がみられた。この結果、Nb の一部が 5-6 個の酸素原子で配位される構造をとることがわかった。

最後に $Ta_mO_n^{\pm}$ について、上の系と比べて議論した。まず、 $n = 3m$ に近い組成をとることがわかった。また、酸素が過剰となる化学種が観測された。特に $m = 4$ では $Ta_4O_{11}^+$ が最も強く観測され、Ta の四面体骨格の末端に酸素が超酸化物 O_2^- として配位する構造に帰属された。 $Ta_mO_n^{\pm}$ では、各 Ta 原子に 5 個以上の酸素原子が配位する構造をとり、 $V_mO_n^{\pm}$ や $Nb_mO_n^{\pm}$ よりも多くの酸素原子が配位する傾向が見いだされた。

以上の成果は、5族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、WU, Jenna Wen Ju 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。