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

著者	WU Jenna Wen Ju
学位授与機関	Tohoku University
学位授与番号	11301甲第18269号
URL	http://hdl.handle.net/10097/00124053

Doctoral Thesis

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

Jenna W. J. WU

2018

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Chapter 1 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 promotors to can enhance catalytic activity, selectivity, and prolong catalyst life. The group 5 metal oxides exist as pentoxides (M_2O_5, M = V, Nb, 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.

Chapter 2 – 3 Experimental Principle and Method

Ion mobility mass spectrometry is an analytical method that separates ions in the gas phase under the influence of an electric field in the presence of an inert gas as collision gas in an ion drift cell. Gas-phase ions can be separated according to their size and shape, which is on the basis of their mobilities measured in the ion drift cell. A common technique for ion mobility spectrometry is the combination with mass spectrometry. Coupling with mass spectrometry allows the determination of molecular weight, or mass,

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.

Chapter 4 Group 5 Transition Metal Oxides

Vanadium Oxide Cluster Ions

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. These compositions for vanadium 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 $n = 2.5m$.

Next, vanadium oxide cluster ions ($V_mO_n^{\pm}$), with m = 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 of $V_4O_9^+$ or $V_4O_{10}^-$, 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.

Niobium Oxide Cluster Ions

First, the stable compositions found for niobium oxide cluster ions, Nb_mO_n, up to $m = 24$ were slightly different from vanadium oxide counterpart: $(NbO_2)(Nb_2O_5)_{(m-1)/2}^+$ and $(Nb_2O_5)_{m/2}^+$. Similarly, these compositions are formed with stoichiometric units or stable building block units.

As for the geometrical structures for niobium oxide cluster ions ($Nb_mO_n^{\pm}$), the same basic framework to vanadium oxide cluster ions was found for m = 2-7. $Nb_4O_{10}^+$ is intensively found for cluster cations, which also have the same tetrahedral framework as the vanadium oxide counterpart. 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 $Nb_9O_{22}^+$ 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.

Tantalum Oxide Cluster Ions

Finally, different from vanadium and niobium oxide cluster ions, On the other hand, the stable composition of tantalum oxide was found to be $(Ta_2O_5)(TaO_3)_{m-2}^+$ and $(TaO_3)_m^{\pm}$ 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 $n = 3m$.

Geometrical structures for the oxygen rich tantalum oxide cluster ($Ta_mO_n^{\pm}$) 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 $m = 4$, $Ta_4O_{11}^+$ was also found to have a perfect tetrahedral structure, yet it contains an extra oxygen atom bonded to the terminal metal atom as a superoxide unit. Additionally, the geometrical structures of $Ta_5O_{13-16}^+$ resemble that of $V_5O_{12}^+$ and $Nb_5O_{12}^+$ pyramid framework, and the additional oxygen atoms are found to be on the terminal sites. From here, tantalum atoms bond to excess oxygen atoms with more than 4 oxygen coordination, which is a similar property found in the bulk materials.

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.