

Difference in composition and structure growth observed in group 5 metal oxide cluster ions studied by ion mobility mass spectrometry

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[Abstract] Geometrical structures of vanadium, niobium, and tantalum oxide cluster ions ($M_mO_n^\pm$, $M = V, Nb, \text{ and } Ta$) were studied with ion mobility mass spectrometry (IM-MS). The clusters were observed to grow in size by increasing the number of M_2O_5 units for $V_mO_n^\pm$ and $Nb_mO_n^\pm$, yet $Ta_mO_n^+$ grows by increasing TaO_3 units. The structures of $V_4O_{10}^\pm$ were perfect tetrahedral structures. With $V=O$ unit on vertices and O atoms on edges, following this pattern, cluster size increases with additional V_2O_5 units forming a larger polyhedron framework structure up to at least $m = 12$. Furthermore, while having similar geometrical structures, structure growth by adding additional Nb_2O_5 units to each $Nb_mO_n^\pm$ cluster was also observed up to approximately $m = 7$. On the other hand, for $Nb_mO_n^\pm$ ($m > 7$) and oxygen rich $Ta_mO_n^+$, structures with Nb or Ta atom bonding to at least four O atoms were favored.

[Introduction] Group 5 metal oxides are important in the field of catalysis, and there are numbers of industrial processes which are either catalyzed by vanadium oxides, or use niobium oxides and tantalum oxides as promoters because of their reducible nature. 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. Gas phase clusters can be considered to be the simplest model to understand the surface structure and active sites of oxide catalysts. Numerous experimental and theoretical techniques have been incorporated into the study of gas-phase clusters, such as mass spectrometry, photodissociation, IR spectroscopy, and density functional theory calculation. In this study, 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.

[Methods] Experimentally, vanadium, niobium, and tantalum oxide cluster ions were first generated by combination of laser ablation and supersonic expansion of O_2/He mixture gas (concentration dependent on the oxides). The generated cluster ions were injected into an ion drift cell with an injection energy of 50 or 250 eV applied by a pulsed electric field, and collision induced dissociation occurred along with ion injection. Following the entrance into the ion drift cell, the product ions experienced 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 cluster ions by using ion transport theory.

In the theoretical study, geometrical structure candidates were first optimized with Gaussian09 program, and the calculation level 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 projection approximation methods in MOBCAL program.

[Results and Discussion] Structure comparison on $V_mO_n^\pm$ and $Nb_mO_n^\pm$, and the difference in structural assignment due to structure transition found in $Nb_mO_n^\pm$ were discussed in the past reports [1,2]. Here, discussion on the composition and the structural assignment will be expanded to three group 5 transition metal oxide cluster ions including $Ta_mO_n^\pm$.

First on the discussion of compositions: the stable species found upon collision induced dissociation caused by high injection energy at the inlet of the ion-drift cell were $(VO_2)(V_2O_5)_{(m-1)/2}^+$ and $(V_2O_4)(V_2O_5)_{(m-2)/2}^+$ for all vanadium oxide cluster cations between $m = 2-60$. As for niobium oxide cluster cations, the most stable species were similarly $(NbO_2)(Nb_2O_5)_{(m-1)/2}^+$ and $(Nb_2O_5)_{m/2}^+$ up to $m = 24$. These compositions, formed with the stoichiometric units or stable building block units, have an oxygen to metal ratio of approximately $n = 2.5m$. On the other hand, the stable composition of tantalum oxide was found to be $(Ta_2O_5)(TaO_3)_{m-2}^+$ and $(TaO_3)_m^+$ for $m = 2-13$. Relatively oxygen-rich species were thus stable for tantalum oxide cluster cations, where the oxygen to metal ratio of approximately $n = 3m$. Clearly, tantalum oxide cluster cations were built based on TaO_3 units.

Next, the geometrical structures discussed in the past reports stated that vanadium oxide cluster ions have polyhedral cage structure frameworks, where every vanadium atom forms the vertices of the polyhedron, and are inter-connected by bridging oxygen atoms. The structure for the most abundant composition among the V_4 series, $V_4O_9^+$, is shown in Figure 1. In this tetrahedral structure, vanadium metal atoms

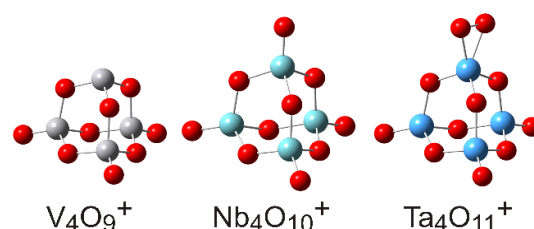


Figure 1. Optimized geometrical structure of $M_mO_n^+$, where $M = V, Nb$ and Ta , and $m = 4$.

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 cations ($Nb_mO_n^+$), the same basic framework to vanadium oxide cluster ions was found for $m = 2-7$. For example, the structures of most stable species of Nb_4 series, $Nb_4O_{10}^+$ is also shown in Figure 1. It was reported from the previous report that a structure transition of $Nb_mO_n^+$ observed at $m = 8-9$ causes a decrease in overall CCS growth, and different structural formation: some Nb atom bonds to more than 4 oxygen atoms, forming NbO_5 or NbO_6 coordination [1].

Finally, geometrical structures for the oxygen rich tantalum oxide cluster ($Ta_mO_n^+$) greatly resemble that of vanadium and niobium oxide cluster ions at small m . The $Ta_4O_{11}^+$ structure in Figure 1 shows that the extra oxygen atom is bonded to the terminal site of

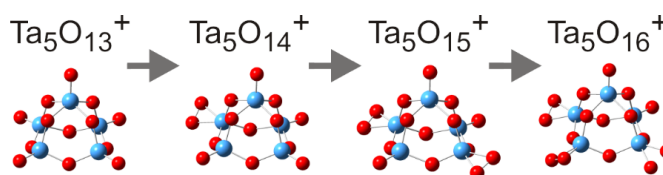


Figure 2. Optimized geometrical structure of $Ta_5O_{13-16}^+$.

the tetrahedral framework structure 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 could be found on the terminal sites as shown in Figure 2.

It is concluded from the above discussion that the number of oxygen atoms increases with increasing mass of the constituent metals for $M_4O_n^+$, from 9 oxygen atoms in vanadium oxide to 10 oxygen atoms in niobium oxides to 11 oxygen atoms in tantalum oxides. This difference comes from their difference in the number of available coordination sites.

[Reference]

- [1] J. W. J. Wu, R. Moriyama, M. Nakano, K. Ohshimo, F. Misaizu, *Phys. Chem. Chem. Phys.* **19**, 24903 (2017).
 [2] Wu, Moriyama, Nakano, Ohshimo, Misaizu, The 11th Molecular Science Symposium, 1P053 (2017).