

Similarities and Differences in Structural Growth between Niobium Oxide and Vanadium Oxide Cluster Ions Studied with Ion Mobility Mass Spectrometry

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[Abstract] Geometrical structures of niobium and vanadium oxide cluster ions ($M_mO_n^\pm$, $M = \text{Nb}$ or V) were studied with ion mobility mass spectrometry. The clusters grew in size by increasing the number of M_2O_5 building blocks. $V_4O_{10}^\pm$, which contained two V_2O_5 building blocks, had tetrahedral structures with V atoms on vertices and O atoms on bridging and terminal sites. Addition of V_2O_5 units increases the size of the polyhedron framework structures. However, this was not the case for niobium oxide cluster ions. While having similar structures with vanadium oxides at small cluster sizes up to approximately $m = 7$, niobium oxide cluster ions favor compact structure formation as m increases. Some Nb atoms bond to more than four O atoms, and forms structure more compact than the polyhedron frameworks.

[Introduction] Group V metal oxides are important in the field of catalysis, and there are numeral industrial processes which are either catalyzed by vanadium oxide or niobium oxide, or which use these oxides as support for catalysts because of their reducible nature. Both of them exists as pentoxides (M_2O_5 , $M = \text{V}, \text{Nb}$) in the bulk phase with a formal oxidation state of +5. Gas-phase clusters can be considered as the simplest model to understand the surface structure and active sites of oxide catalysts. Many 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 calculations.

[Methods] Niobium and vanadium oxide cluster ions were generated by combination of laser ablation and supersonic expansion of mixture gas (10% O_2/He for $Nb_mO_n^\pm$, and 5% O_2/He for $V_mO_n^\pm$). The generated cluster ions were injected into an ion drift cell with an injection energy of 50 eV or 250 eV by a pulsed electric field, and collision induced dissociation occurred around the cell entrance. 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 eventually reached constant drift velocity depending on their interaction with He buffer gas, and therefore arrive at the exit with different arrival times. Arrival time is the time a cluster ion spent to pass through the cell, and depends on its interactions with the 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.

In theoretical study, geometrical structure candidates were first optimized with Gaussian09 program, and the calculation level were B3LYP/6-311+G(d) for vanadium oxides and B3LYP/DGDZVP for niobium oxides. Next, theoretical CCSs of the proposed geometrical structures were calculated with projection approximation method in MOBCAL program.

[Results and Discussion] Structure comparison on Nb_mO_n^+ and V_mO_n^+ , which have compositions of $(\text{M}_2\text{O}_5)_{m/2}^+$ (for m ; even) and $(\text{MO}_2)(\text{M}_2\text{O}_5)_{(m-1)/2}^+$ (for m ; odd), was discussed in the last report for $m = 2-10$ [1]. We will further discuss the result not only for $m = 2-10$ of the cations, but also up to at least $m = 12$ for both cluster cations and cluster anions.

Experimental CCSs of each cluster ion calculated from the arrival time vs. TOF 2D plot were plotted in Figure 1a and 1b, for both vanadium oxide and niobium oxide cluster cations between $m = 2-12$. From the last report, we discussed that (a) vanadium oxide cluster cations had a very smooth growth in experimental CCS and (b) structural transition was found in niobium oxide cluster cations between $m = 8$ and 9 [1]. We were able to prove this structural transition with optimized geometrical structures, which was apparent with change in experimental and theoretical CCSs less than 5 \AA^2 . Additional stable geometrical structures were also found since last report to show this trend. On the other hand for cluster anions, structural transition was found between $m = 11$ and 12 for vanadium oxides, and $m = 7$ and 8 for niobium oxides.

What can be observed in structure transition found in both vanadium oxide cluster anion and niobium oxide cluster ions is the target of our current discussion. As shown in Figure 1, by an addition of NbO_2 , the theoretical CCS increased from $m = 8$ to 9 by less than 2 \AA^2 (whereas 7 \AA^2 increase after adding VO_2 for vanadium oxide). A possible explanation to this small change in CCS is the bonding arrangement of the geometrical structure of $\text{Nb}_9\text{O}_{22}^+$. For example, structure of $\text{Nb}_8\text{O}_{20}^+$ has a cube like framework, where each Nb atom connects to three bridging O atoms and one terminal O atom. Following this rule, as m increases, the cavity within the structure framework also increases. However, $\text{Nb}_9\text{O}_{22}^+$ does not have a cavity like $m = 8$, and several Nb atoms bonded to more than four O atoms. As a result, a decrease in structural growth can be observed. As for vanadium oxide cluster cation, no structure transition was observed, thus we concluded that almost all structures grow by increasing the polyhedron framework structure.

[Reference]

[1] Wu, Moriyama, Nakano, Ohshimo, Misaizu, The abstract of 10th Molecular Science Symposium, 1E07 (2016).

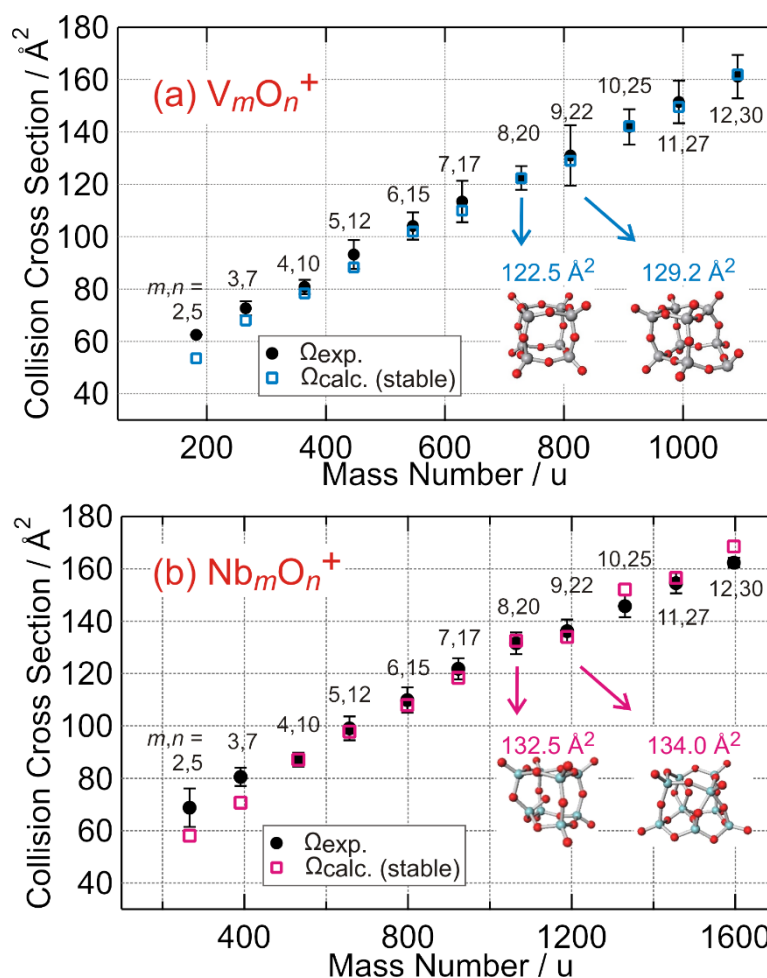


Fig. 1. Experimental and theoretical CCSs of (a) V_mO_n^+ and (b) Nb_mO_n^+ . The possible structures of $m, n = 8,20$ and $9,22$ are also shown.