

1E07

Comparative study on compositions and structures of niobium oxide and vanadium oxide cluster ions by ion mobility mass spectrometry

(Tohoku Univ.) ○ J. W. J. Wu, R. Moriyama, M. Nakano, K. Ohshimo, and F. Misaizu

INTRODUCTION

The group V metal oxides, both as bulk metal oxides and supported metal oxides, had great potential for catalytic purposes. Both of them exist as pentoxides (M_2O_5 , $M = V, Nb$) in the bulk phase as catalyst with a formal oxidation state of +5. Studies on gas-phase clusters provided means to model catalytic sites and reaction mechanisms of these metal oxides. Experimental studies such as photodissociation and IR spectroscopy, along with theoretical calculations based on density functional theory, were utilized to find out the structural and electronic properties of these oxide cluster ions ($M_mO_n^{0/+/-}$, $M = V, Nb$).^{1,2} The neutral Nb_4O_{10} cluster was reported to possess a T_d symmetry of tetrahedral structure, which is similar to the neutral V_4O_{10} cluster.¹ The corresponding cluster cations and anions should also obtain similar structures with slightly lower symmetry. It was also known from past studies of vanadium oxides cluster cations that an elongated terminal oxygen was observed in the tetrahedral structure of $V_4O_{10}^+$.³ This elongation can act as a reactive center toward chemical reactions, which plays an important role in catalysts.

In the present study, ion mobility mass spectrometry (IM-MS) was utilized to study both vanadium oxide and niobium oxide cluster ions. The obtained structural information (collision cross sections, CCSs) is therefore compared with theoretical study to further confirm the structures of the two oxide cluster ions.

METHODS

Both niobium and vanadium oxide cluster ions were generated by a combination of laser vaporization and supersonic expansion of mixture gas (5% O_2/He for $V_mO_n^{+/-}$, 10% O_2/He for $Nb_mO_n^{+/-}$). The generated cluster ions were injected into an ion drift cell with an injection energy of 50 or 250 eV by a pulse electric field, and collision induced dissociation (CID) occurred around the cell entrance. Following the entrance of product ions into the ion drift cell, they experience acceleration with an applied electrostatic field and deceleration by collisions with He buffer gas filled inside the cell. The cluster ions therefore arrive the exit of ion drift cell with different arrival times. Arrival time is the time a cluster ion spent to pass through the cell, and is dependent 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 data of arrival time and TOF can be used to analyze the CCSs of the cluster ions.

For theoretical study, structural candidates were first optimized with Gaussian 09, and the calculation levels were B3LYP/6-311+G(d) for vanadium oxides and B3LYP/DGDZVP for niobium oxides. Next, the theoretical CCSs of the proposed structures were calculated with projection approximation method in MOBCAL program.

RESULTS AND DISCUSSION

First, relatively stable compositions with respect to CID were determined for vanadium and niobium oxide cluster ions ($M_mO_n^{+/-}$, $M = V, Nb$) with the mass spectra taken from high injection energy condition (250 eV), as shown in Table 1. The stable compositions of the

vanadium oxides were already discussed in our past study,^{3,4} in which they had clear parity dependences as shown in the table. Both of the vanadium and niobium oxide cluster ions were formed with the building blocks MO₂, MO₃, and M₂O₅,

Table 1. Stable compositions of vanadium and niobium oxide cluster ions.

$V_mO_n^{+/-}$	m ; even	m ; odd
Cations	$(V_2O_4)(V_2O_5)_{(m-2)/2}^+$	$(VO_2)(V_2O_5)_{(m-1)/2}^+$
Anions	$(V_2O_5)_{m/2}^-$	$(VO_3)(V_2O_5)_{(m-1)/2}^-$
$Nb_mO_n^{+/-}$	m ; even	m ; odd
Cations	$(Nb_2O_5)_{m/2}^+$	$(NbO_2)(Nb_2O_5)_{(m-1)/2}^+$
Anions	$(Nb_2O_6)(V_2O_5)_{(m-2)/2}^-$	$(NbO_3)(Nb_2O_5)_{(m-1)/2}^-$

as reported in past CID studies. The main difference of the stable species found is the number of oxygen for the cluster with even sized clusters, where the niobium oxides always has one more oxygen than that of vanadium oxide cluster ions.

Next, after determination of the stable compositions of the two oxides, the CCS of each cluster ion was calculated from the arrival time vs. time-of-flight 2D plot. CCSs of the two cluster cations are shown in Figure 1. The vanadium oxide cluster cations generally have smaller CCSs compared to niobium oxide cluster cations. The growing trends of the two oxide cluster cations are very similar up to $m = 8$, with an average difference of 7 Å². However, the CCS difference decreases to less than 4 Å² for $m = 9$ and 10, indicating a decrease in structural growth of niobium oxide cluster cations in comparison to those of vanadium oxide cluster cations.

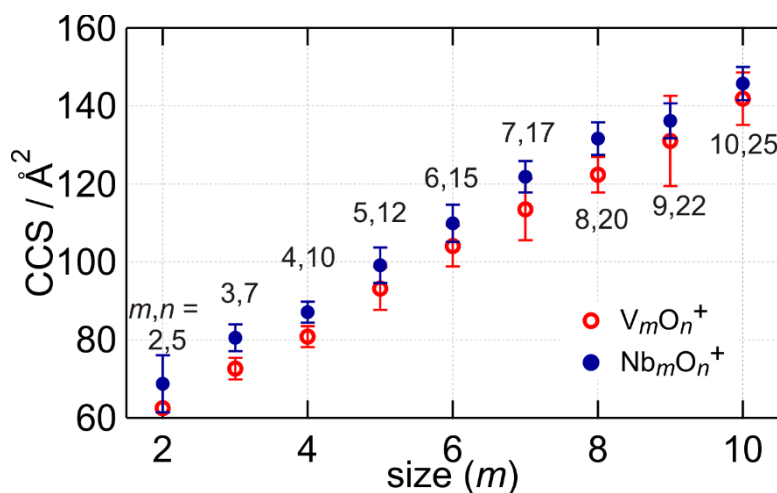


Figure 1. Collision cross sections of vanadium oxide cluster cations and niobium oxide cluster cations.

From the theoretical calculation of several proposed geometrical structures, the two oxides were proved to have similar structures as shown in Figure 2 by comparing the experimental and theoretical CCSs up to $m = 8$. The highly symmetric and stable tetrahedral cage structures of V₄O₁₀⁺ and Nb₄O₁₀⁺, which were both reported in past studies,^{5,6} are clearly proved here. The two odd numbered metal oxide ions were shown to have the same bridged and pyramid structures. As discussed above, a possible structural change should occur for Nb_mO_n⁺ around $m = 9$ to 10, where the experimental CCS growth decreases relative to the vanadium oxides as shown in Figure 1.

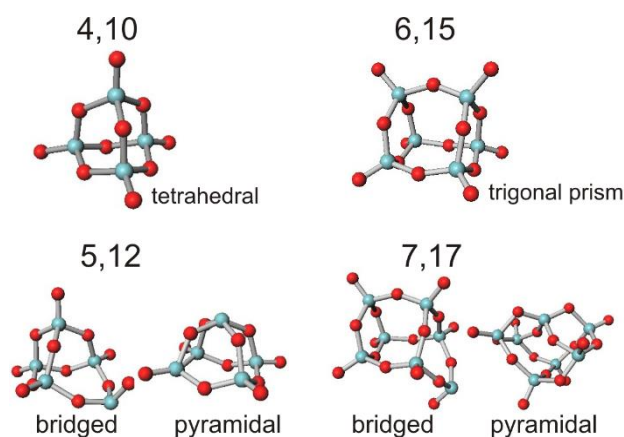


Figure 2. Stable geometrical structures of both vanadium and niobium oxide cluster cations for $m = 4-7$.

- [1] K. S. Molek et al., *J. Chem. Phys.*, **123**, 144313 (2005). [2] H.-J. Zhai et al., *J. Am. Chem. Soc.*, **129**, 13270 (2007). [3] J. W. J. Wu et al., *J. Phys. Chem. A*, **120**, 3788 (2016). [4] R. Moriyama et al., *Bull. Chem. Soc. Jpn.*, in press (2016). [5] X. Zhang, and H. Schwarz, *Chem. Eur. J.*, **16**, 1163 (2010). [6] A. Fielicke et al., *J. Am. Chem. Soc.*, **125**, 3659 (2003).