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Photofragmentation of Vanadium Oxide Cations

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Laser-induced fragmentation of mass-selected vanadium oxide cluster cations at 532 nm is investigated in a time-of-flight mass spectrometer. The major species observed in the initial mass distribution can be described as having a stoichiometry similar to bulk vanadium oxides, with some species possessing additional O_2 units bonded to the cluster. At low laser fluence, the major photofragmentation channel observed is the loss of O_2 or consecutive O_2 units from clusters that are oxygen rich. When the laser fluence is increased, additional fragmentation channels are observed. The majority of the clusters investigated, from $V_2O_8^+$ to $V_6O_{16}^+$, ultimately lose the necessary neutral fragments to form the product ions VO_2^+ and VO^+. The results suggest that VO_2 and VO have lower ionization potentials than larger vanadium oxide clusters.

Introduction

Photofragmentation studies of gas-phase cluster ions can be utilized to provide information on stability, possible structures, and bonding. Photofragmentation techniques[1] have been used to study pure metal,[2−6] carbon,[7,8] fullerene,[9,10] and Met-Car[11−16] cluster systems, among many others. To simplify identification of the fragments, typically, a specific cluster is mass selected from a distribution of cluster sizes, prior to photofragmentation. After mass selection and photofragmentation, the products are identified by a variety of energy analysis techniques. Photofragmentation/photodissociation techniques have been employed to determine photodestruction cross sections, relative stability, dissociation energies, and product branching ratios. These techniques have been utilized in the cluster field to investigate size-dependent properties of many different cluster systems.

The collision-induced dissociation and reactivity of vanadium oxide cluster cations[17] have been investigated in our research group in order to gain insight into the structure and properties of these species which are potentially important in catalysis. Supported vanadium oxides have been investigated for use, and employed commercially, as catalysts[18,19] in selective organic oxidation reactions,[20] the reduction[21,22] of NO with NH_3, and to control the emissions of electric power plants. These supported and nonsupported vanadium oxide catalysts are typically inexpensive and relatively environmentally friendly. Even though these catalysts find widespread use, the reasons behind their unique properties remain a topic of debate. It is widely accepted now that the substrate plays a critical role in the catalyst's activity. Gas-phase studies of vanadium oxide clusters are limited, but can be employed to learn more about the structure and reactivity of these species and hence their potential role in various catalytic mechanisms. The present investigation provides additional information on the dissociation behavior and properties of vanadium oxide clusters.

Experiment

The time-of-flight (TOF) mass spectrometer used in the present investigation has been described previously[11] and only the major features and modifications are discussed herein. The vanadium oxide clusters are produced in a laser vaporization source. The surface of a rotating and translating vanadium rod is vaporized with the second harmonic of a Nd:YAG laser at 532 nm at an adjustable time delay after a pulsed valve is actuated. Typically, pure oxygen is used as both the reactant and backing gas at a backing pressure of ∼4.8 atm. Different dilutions of oxygen in helium were investigated; however, no significant variation in the initial cation distribution was observed. The initially hot clusters are cooled as they expand through a nozzle, from the high-pressure region of the source into the low-pressure region of a vacuum chamber.

Vanadium oxide cations, anions, and neutrals are produced in the laser vaporization source. In the present experiment, only the cations are investigated. The cations are extracted into the TOF mass spectrometer using two fast high-voltage transistor switches[23] to pulse the repeller and extractor grids simultaneously to predetermined voltages. The voltages are chosen to set the first-order space focus[24] at the position where the cluster ion packet is overlapped with the photofragmentation laser. One difficulty encountered when extracting cations directly from the source, rather than using photoionization to form cations from neutral clusters, is the initial energy distribution of the clusters. The cations fill a larger volume in the extraction region and therefore have a larger initial energy distribution, which leads to a decrease in mass resolution. This increase in the initial energy distribution is partially compensated by the use of a reflectron,[25] which helps to limit peak broadening.

After the ions are accelerated, they pass through a set of ion-focusing optics, then travel ∼80 cm in a field-free region before reaching a pulsed mass gate. The mass gate consists of two parallel plates, one that is kept near ground potential and the other that is maintained at several hundred volts. When an ion encounters the mass gate, its trajectory is altered and the ion no longer reaches the detector. When the species of interest arrives at the mass gate, the high-voltage plate is pulsed to near ground potential and the chosen mass passes through the mass gate. Thereafter, the high-voltage plate of the mass gate is again pulsed to high voltage in order to deflect the higher-mass species off axis of the spectrometer.

Photofragmentation of the mass-selected cations is induced with the second harmonic, 532 nm, of a second Nd:YAG laser which intercepts the cluster packet approximately 10 cm after

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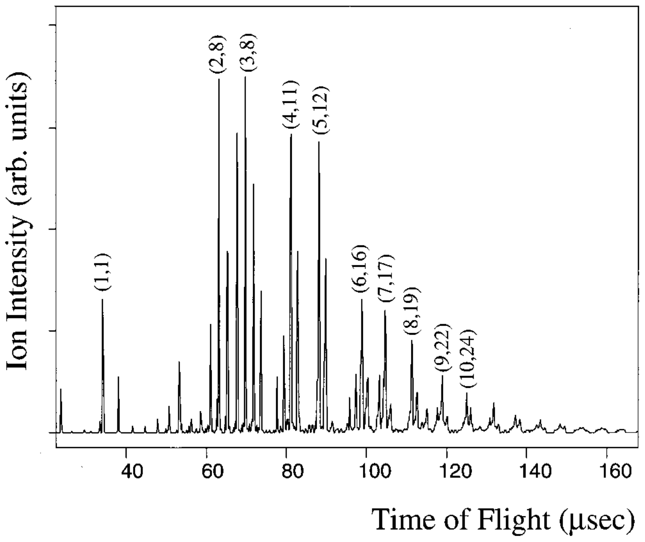

Figure 1. Mass spectrum of vanadium oxide cations generated in the laser vaporization source. The numbers (*x*,*y*) above selected peaks represent the number of vanadium and oxygen atoms, respectively, in each $V_xO_y^+$ cluster. The spectrum was obtained while operating the reflectron in hard reflection mode; therefore the initial energy spread of the ions in the extraction region is not compensated.

the mass gate. The photofragmentation is carried out in a field-free region of the spectrometer. After fragmentation, the fragment or daughter ions and the remaining intact parent ions travel another 100 cm to a reflectron. The reflectron can be operated in either hard reflection mode, which effectively only increases the flight length of the spectrometer and hides any fragmentation because the parent and fragments do not separate (photofragmentation is performed in a field free region). Alternatively, the reflectron can be operated in soft reflection mode, which allows for energy analysis and fragment identification.[26] After being turned around in the reflectron, the ions travel another 100 cm where they are detected at a dual microchannel plate detector (Galileo Corporation). The ion current is recorded as a function of time and averaged on a digital oscilloscope (LeCroy 9304A). Thereafter, the data is transferred and analyzed on a personal computer.

Results

A mass spectrum illustrating a typical vanadium oxide cation distribution is shown in Figure 1. The most intense peak in each metal grouping is labeled. As noted in an earlier publication by Bell et al.[17] the major peaks can be described as having stoichiometries of $(VO_2)_n(V_2O_5)_m(O_2)_{0-2}^+$ or equivalently as $(VO_2)_x(VO_3)_y(O_2)_{0-3}^+$. These stoichiometries are consistent with bulk vanadium oxide, which is found to be constructed of VO_2 and V_2O_5 building blocks,[27] except for the possible addition of excess O_2 units. These earlier collision-induced dissociation (CID) experiments, performed in a triple quadruple mass spectrometer, have demonstrated that there are several very stable species, namely $V_2O_4^+$, $V_3O_{6,7}^+$, $V_4O_{8,9}^+$, $V_5O_{11,12}^+$, $V_6O_{13,14}^+$, and $V_7O_{16,17}^+$, that require approximately 3−5 eV (center-of-mass reference frame) of energy to induce fragmentation. The major CID product ion observed was VO^+ for the parent ions $V_3O_6^+$, $V_4O_8^+$, and $V_5O_{11}^+$; and VO_2^+ for the parent ions $V_2O_4^+$, $V_3O_7^+$, $V_4O_9^+$, and $V_5O_{12}^+$. It was suggested that the clusters with higher oxygen content were composed of the noted exceptionally stable clusters, but with additional O_2 units attached. The oxygen-rich clusters $V_2O_6^+$, $V_3O_{8,9}^+$, $V_4O_{10}^+$, $V_5O_{13}^+$, $V_6O_{15}^+$, and $V_7O_{18}^+$ all were observed to lose an O_2 unit under single-collision conditions at near thermal energies. In the study described herein, the photofragmentation of the oxygen-rich vanadium oxide cations is investigated and further evidence is provided for the weak association of additional O_2 units on the aforementioned stable clusters. Additional fragmentation channels are observed at higher laser fluences.

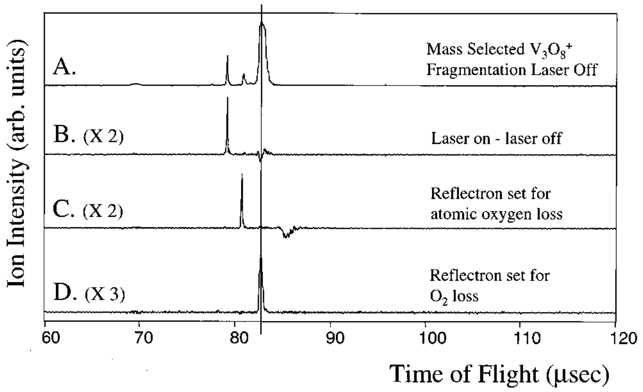

Figure 2. Photofragmentation products for $V_3O_8^+$. The trace labeled "A" shows the mass-selected parent ion $V_3O_8^+$, the less intense peaks to the left of the parent peak are due to metastable dissociation of the parent ion and a small amount of collision-induced dissociation of the parent ion as it is accelerated in the TOF extraction region. Both the product ion contribution due to metastable dissociation and collision-induced dissociation are subtracted out when the fragmentation laser-off trace is subtracted from the fragmentation laser-on trace, as shown in "B". The parent ion depletion is shown by the dip in trace "B". Trace "C" is an example of a loss channel that is not observed, while trace "D" confirms the loss of an O_2 unit from the parent ion. Fragmentation products are identified when they align with the vertical line drawn through the parent peak.

Photofragmentation of Vanadium Oxide Cations. After mass selection of each species of interest and photofragmentation with a collimated second harmonic of a Nd:YAG laser (532 nm = 2.33 eV), the fragment ions are identified using an energy analysis technique in a reflectron. The laser has a one-centimeter beam diameter at the point where the laser beam intersects the ion packet. The experimental apparatus measures the parent ions and the daughter or fragment ions; the neutral fragments lost during dissociation are not directly observed, but can be inferred from the parent and daughter compositions.

The fragment ions are identified by appropriately adjusting the voltage on the reflectron in soft reflection mode, determined by the relationship

$$m_f = m_p \times \frac{U_f}{U_p}$$

where m_f and m_p are the masses of the fragment and parent ions and U_f and U_p are the fragment and parent ion energies, respectively. In practice, the fragment ions are identified by first recording the time of arrival of the parent ion at a set reflectron potential corresponding to the parent ion energy U_p. Then, an appropriate voltage, U_f, is calculated for every possible loss channel and the reflectron is sequentially set to each determined voltage to search for the possible appearance of the daughter ions. For every daughter ion present, a peak will appear in the mass spectrum at the same time of arrival as the parent when the voltage is appropriately adjusted. This is due to the fact that at the determined voltage the daughter ion will follow the original trajectory in the reflectron as the parent. See Figure 2 for an example of this technique. Each fragment identification spectrum consists of a photofragmentation laser-on spectrum minus a photofragmentation laser-off spectrum. The subtraction

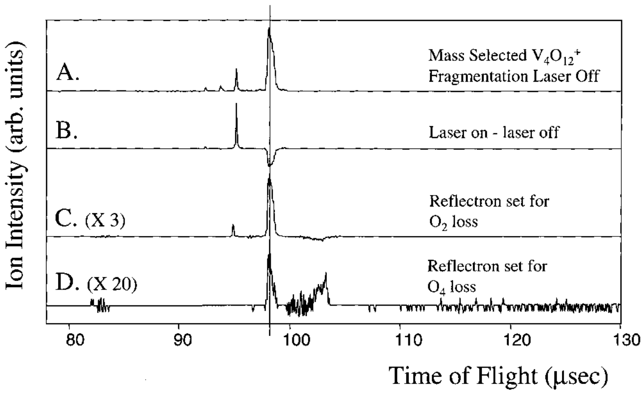

Figure 3. Photofragmentation products for $V_4O_{12}^+$. Both O_2 and O_4, most likely two O_2 units, are observed. The magnification factors for traces "C" and "D" are shown.

TABLE 1: Summary of the Neutral Loss Channels Observed under Low Fluence Conditions and the Resulting Photofragmentation Products

$V_xO_y^+$ parent ion	proposed stoichiometry	neutral loss	photodissociation product $V_xO_y^+$
2,7	$VO_2VO_3(O_2)$	O_2	2,5
2,8	$(VO_2)_2(O_2)_2$	O_2, O_2	2,4
3,7	$(VO_2)_2VO_3$	none	3,7
3,8	$(VO_2)_3(O_2)$	O_2	3,6
4,10	$(VO_2)_4(O_2)$	O_2	4,8
4,11	$(VO_2)_3(VO_3)(O_2)$	O_2	4,9
4,12	$(VO_2)_4(O_2)_2$	O_2, O_2	4,8
5,13	$(VO_2)_4(VO_3)(O_2)$	O_2	5,11
6,16	$(VO_2)_6(O_2)_2$	O_2, O_2	6,12

excludes fragmentation channels that might arise due to other non-photoinduced dissociation processes such as metastable and collision-induced dissociation. While this process is time-consuming, it is found to be a very sensitive technique that allows the unambiguous determination of all possible photofragmentation products.[11]

Photofragmentation at Low Laser Fluence. When the photofragmentation laser fluence is kept at a low enough level (10−20 mJ/cm^2), only the oxygen-rich vanadium oxide cluster cations are observed to dissociate. All clusters with the stoichiometry $(VO_2)_n(V_2O_5)_m(O_2)_{0-2}^+$ or equivalently $(VO_2)_x(VO_3)_y(O_2)_{0-3}^+$ are observed to lose any attached O_2, apparently as intact O_2 units. For example $V_2O_8^+$, which can be thought of as having the stoichiometry $(VO_2)_2(O_2)_2^+$, is observed to lose two intact O_2 units. No other dissociation channels are observed. The results are summarized in Table 1. These observations support the earlier conclusions from the study by Bell et al.[17,34] that the oxygen-rich vanadium oxide cations contain weakly bound O_2 units on a stable ion core. The loss of the excess O_2 unit was observed at near thermal energy collisions; this suggests that at low laser fluence, on average only one 532 nm photon is absorbed by the clusters. The 532 nm photon used to induce the dissociation can be thought of as heating the parent cluster, causing the weakly bound excess O_2 units to evaporate from a stable, strongly bound species. Figure 3 shows the loss of O_2 and O_4 from $V_4O_{12}^+$. The loss of O_4 is most likely the consecutive loss of two intact O_2 units, but the current experimental technique does not allow for positive identification of the probable nonconcerted nature of the mechanism.

TABLE 2: Photoinduced Dissociation Channels Observed at High Fluence at 532 nm

$V_xO_y^+$ parent ion	neutral loss	photodissociation product $V_xO_y^+$
2,7	O_2	2,5
	O_3	2,4
	O_4[a]	2,3
	VO_6	1,1
2,8	O_2	2,6
	O_4[a]	2,4
	VO_6	1,2
	VO_7	1,1
	VO_8	1,0
3,7	V_2O_5	1,2
	V_2O_6	1,1
3,8	O_2	3,6
	VO_4	2,4
	V_2O_6	1,2
	V_2O_7	1,1
4,10	O_2	4,8
	V_3O_8	1,2
	V_3O_9	1,1
4,11	O_2	4,9
	V_3O_9	1,2
	V_3O_{10}	1,1
	V_3O_{11}	1,0
4,12	O_2	4,10
	O_4[a]	4,8
	V_3O_{10}	1,2
	V_3O_{11}	1,1
5,13	O_2	5,11
	V_3O_9	2,4
	V_4O_{11}	1,2
	V_4O_{12}	1,1
6,16	O_2	6,14
	V_3O_{10}	3,6
	V_4O_{12}	2,4
	V_5O_{14}	1,2
	V_5O_{15}	1,1

[a] The observed loss of a mass corresponding to O_4 is most likely the loss of two intact oxygen molecules.

Photofragmentation at High Laser Fluence. When the photofragmentation laser fluence is raised (50 to 75 mJ/cm^2) by loosely focusing the laser beam and raising the energy per pulse, additional fragmentation channels are observed. Although the dominant dissociation channel remains as the loss of the excess O_2 units, two additional major dissociation channels are observed which typically lead to the production of VO_2^+ and VO^+. A small number of other fragmentation channels are observed for a few of the investigated clusters; all of the results are presented in Table 2. For example, at high laser fluence, $V_4O_{12}^+$ loses two O_2 units, V_3O_{10}, and V_3O_{11} to yield $V_4O_{10}^+$, $V_4O_8^+$, VO_2^+, and VO^+. Figure 4 illustrates the loss channels observed, at high fluence, for $V_5O_{13}^+$. These loss channels match the losses observed by Bell et al.[17] at higher collision energies of between 3 and 5 eV. These collision energies correspond to the absorption of at least two photons of 532 nm light.

Typically, in non-state selective photofragmentation processes in cationic clusters, it is expected that during fragmentation the species with a higher ionization potential (IP) will be lost as a neutral fragment, while the species with a lower IP will keep the positive charge. O_2 has an ionization potential[28] of 12.07 eV, while none of the vanadium oxides are expected to have IP's of that magnitude, so O_2 is expected to leave the clusters as a neutral molecule. It is at first surprising to observe the fragmentation products VO_2^+ and VO^+, resulting from the loss of a large V_xO_y neutral fragment from the original parent cluster ion. For pure transition metal clusters, a general trend of a reduction in IP as the cluster size increases is typically observed[29,30] and can be generally described by several models including the conducting sphere droplet model (CSD)[31,32] and the effective coordination number model (ECN).[33] The IP's of pure vanadium clusters decrease continuously from the monomer (6.74 eV) to larger clusters and the value begins to become

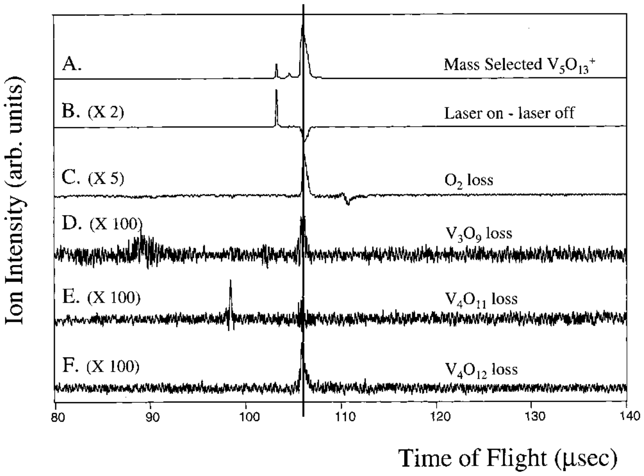

Figure 4. Photofragmentation products for $V_5O_{13}^+$. The loss of neutral fragments O_2, V_3O_9, V_4O_{11}, and V_4O_{12} are observed. The sensitivity of using a reflectron for product identification is demonstrated; the loss of V_4O_{12} from $V_5O_{13}^+$ corresponds to a loss of 86% of the initial mass of the parent ion. The product ions are easily identified.

almost constant at ∼5 eV for clusters containing eleven or more atoms.[30] However, the presence of oxygen can greatly alter the IP of the clusters, causing the IP to increase with an increase in oxygen content. The results of a recent collision-induced dissociation experiment[34] suggest that the IP's of VO_2^+ and VO^+ are among the lowest of the vanadium oxide clusters. This was determined by observing which fragment retained the charge in a collision-induced dissociation, assuming that the fragment with the lower IP would preferentially retain the charge. The adiabatic ionization potential of VO has recently been measured by Harrington and co-workers to be 7.2386 ± 0.0004 eV. However, the ionization potentials of the larger vanadium oxide clusters have not yet been directly measured.

Conclusions

The photofragmentation of mass-selected vanadium oxide cluster cations was investigated over a range of cluster sizes from $V_2O_7^+$ to $V_6O_{16}^+$. At low photofragmentation laser fluence, the oxygen-rich clusters were found to lose excess O_2 units until the stoichiometry of the cluster corresponded to a bulklike composition, $(VO_2)_n(V_2O_5)_m^+$ or equivalently as $(VO_2)_x(VO_3)_y^+$. The parent cluster ions that start with a bulklike stoichiometry were not observed to dissociate. As the laser fluence was increased, additional fragmentation channels were observed, corresponding to neutral losses resulting in the production of VO_2^+ and VO^+, some clusters also exhibit loss channels resulting in $V_2O_4^+$ and $V_3O_6^+$. During a photofragmentation event, the charge is expected to remain with the species of lower ionization potential, so it is concluded that VO_2 and VO have lower ionization potentials than most of the larger vanadium oxide clusters.

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