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Thermal desorption of oxygen from near-stoichiometric cationic vanadium oxide clusters

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ABSTRACT

Oxygen desorption from cationic vanadium oxide clusters, $V_nO_m^+$ ($n = 2$–10), composed of a near-stoichiometric (n:m = 2:5) frame with excess oxygen attached was investigated in a thermal energy region by time-of-flight mass spectrometry and thermal desorption spectrometry. Oxygen molecules were observed to desorb from the clusters during heating. The activation energy for desorption was estimated from the temperature dependence of different clusters and exhibited an even–odd alternation with respect to the cluster size, n. This alternation can be explained in terms of oxidation states of the vanadium atoms.

1. Introduction

Vanadium oxide has been used in the chemical industry as a catalyst for the oxidation of SO_2 and selective oxidation of hydrocarbons, and as a result, its catalytic activities have been thoroughly investigated [1]. Because surfaces play important roles in the catalytic properties of vanadium oxide [2,3], gas-phase clusters are considered to constitute an ideal model for real catalysts and have, thus, attracted broad attention [4–6]. Collision-induced dissociation (CID) has been employed to study the structures and reactivities of vanadium oxide clusters, $V_nO_m^+$, in combination with density functional theory (DFT) calculations [7,8]. The CID experiments revealed that $V_nO_m^+$ are composed of near-stoichiometric (n:m = 2:5) frames with weakly adsorbed oxygen [1]. Stoichiometric or slightly oxygen-rich species have been found to be reactive in hydrocarbon cracking. For instance, Bell et al. revealed that the size-selective reactivity of $V_nO_m^+$ is correlated with the oxidation states of vanadium [9]. Dong et al. reported that slightly oxygen-rich clusters, such as VO_3, V_3O_8, and V_5O_{13}, can cleave the C=C bond of C_2H_4 [7]. Hence, the V—O bond of these near-stoichiometric clusters is worthy of further study. However, although most practical chemical reactions occur in a thermal energy region, the detailed bonding character of oxygen, which is released at near thermal energy, remains unknown. Therefore, in the present study, oxygen desorption from $V_nO_m^+$ ($n = 2$–10) in a thermal energy region was investigated using time-of-flight mass spectrometry (TOF-MS) and temperature-programmed desorption (TPD). An even–odd alternation of the activation energy, which was not revealed in the CID experiments, was observed. This even–odd alternation was interpreted in terms of the oxidation states of vanadium.

2. Materials and methods

Oxygen desorption from $V_nO_m^+$ in a thermal energy region was investigated using TPD and TOF-MS [10]. In a cluster source, a vanadium rod was vaporized by a Nd:YAG pulsed laser (532 nm) in the presence of 0.1–0.3% oxygen diluted in helium (0.7 MPa), as shown in Figure 1. The generated $V_nO_m^+$ ($n = 2$–10) was placed in an extension tube whose temperature was controllable in a range of 300–1000 K. Subsequently, the $V_nO_m^+$ clusters expanded into the vacuum and gained a kinetic energy of 3.5 keV in the acceleration region for mass analysis. The clusters traveled in a 1-m field-free region and were reversed by a dual-stage reflectron. Then, they were detected with a Hamamatsu double-micro-channel plate detector. Signals from the detector were amplified with a 350-MHz preamplifier and digitized using an oscilloscope. Averaged TOF spectra (typically averaged over 500 sweeps collected in 50 s) were analyzed using a computer.

The TPD curves were obtained by measuring the intensities of the cluster ions as a function of the extension tube temperature [10], which was continuously increased or decreased at 7 K/min. In the extension tube, $V_nO_m^+$ clusters gained thermal energy through multiple collisions with helium atoms. The residence time of the cluster ions in the extension tube was more than 100 μs, and the number density of the helium atoms exceeded 10^{18} cm^{-3}. Hence, the $V_nO_m^+$ clusters were estimated to undergo more than 10 000

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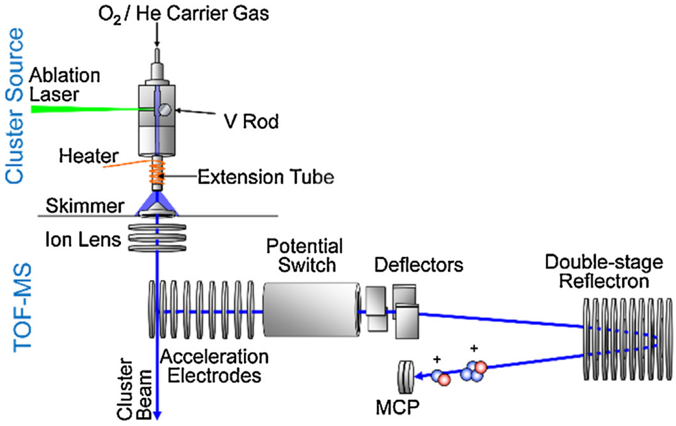

Figure 1. Schematic diagram of the apparatus used in the present study.

collisions with helium, ensuring that thermal equilibrium was achieved in the extension tube.

The temperature fell gradually at 0.1–1 K/min near room temperature because the extension tube did not have a cooling system. However, this slow cooling rate did not seriously affect the TPD curves. Normalization of the intensities was necessary because heating the cluster ions expanded their spatial distribution in the gas phase, and as a result, the detection efficiency decreased as the temperature increased, regardless of the masses of the cluster ions. The intensity ratios obtained were also averaged every 10 K to reduce the intensity fluctuations. The resulting TPD curves contain an uncertainty of 20–30 K because of the non-uniform temperature in the tube.

As oxygen in helium also entered the extension tube, it could be taken up by $V_nO_m{}^+$ clusters. This adsorption could be observed by monitoring the shift in the TPD curve as the oxygen concentration changed [11]. However, no appreciable change was noted in the range of 0.1–0.3%. Hence, we conclude that the oxygen concentration in the extension tube was so low that the adsorption in the extension tube was negligible. Thus, TPD was conducted in the presence of 0.15% oxygen.

3. Results and discussion

A mass spectrum of $V_nO_m{}^+$ ($n = 2$–10) clusters prepared at room temperature with 0.15% oxygen is shown in Figure 2a. Each set of peaks can be assigned to the clusters, which have the same number of vanadium atoms and different numbers of oxygen atoms. Considering that oxidation states of vanadium and oxygen atoms are +5 and −2, respectively, we define $V_nO_m{}^+$ with n:m = 2:5 as the stoichiometric composition. Stoichiometric and oxygen-rich clusters dominated the mass spectrum. Smaller clusters were likely to adsorb more oxygen than larger clusters because of their localized charges [5]. Because $V_nO_m{}^+$ tends to associate with H_2O or extract hydrogen atoms from H_2O [12], several peaks assignable to $V_nO_mH_k{}^+$ were also observed near the peaks of $V_nO_m{}^+$ because of the H_2O remaining in the vacuum chamber as an impurity.

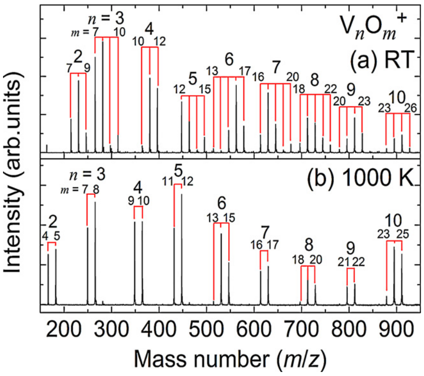

Figure 2. (a) Mass spectrum of $V_nO_m{}^+$ ($n = 2$–10) produced in 0.15% oxygen diluted in helium at room temperature. (b) Mass spectrum of $V_nO_m{}^+$ after heating in the extension tube to 1000 K.

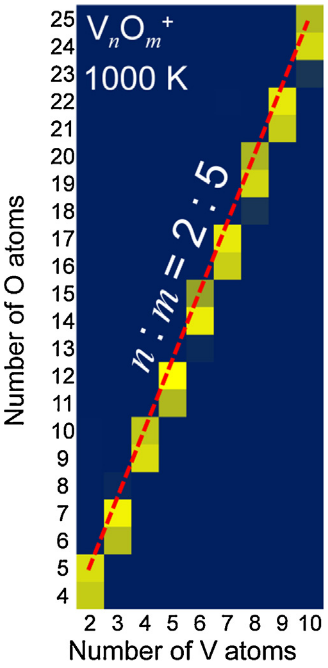

Figure 3. Map of the abundances of $V_nO_m{}^+$ after heating the extension tube heated to 1000 K. The brighter yellow indicates that the cluster is more abundant. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Figure 2b shows a mass spectrum of $V_nO_m{}^+$ after the extension tube was heated to 1000 K; thus, the $V_nO_m{}^+$ clusters prepared in the cluster source were heated and released oxygen. As a result, only near-stoichiometric clusters, expressed as $(VO_2)_n(V_2O_5)_m{}^+$ and $(VO_3)_n(V_2O_5)_m{}^+$ ($n, m = 0, 1, 2, 3, \ldots$), considered to be the most stable species in a thermal energy region, were observed. Indeed, the vanadium:oxygen ratio of these clusters was approximately 2:5, as indicated in Figure 3.

The present results are consistent with those of Bell et al. [1]. According to their study, near-stoichiometric VO_2, VO_3, and V_2O_5 units were considered to be the main building blocks of $V_nO_m{}^+$ based on CID experiments, where more than thermal energy (typically >2 eV) was supplied via single collisions to isolated clusters in vacuum. They suggested that the oxygen-rich species were composed of a stable stoichiometric frame with additional oxygen molecules physically or chemically adsorbed onto the clusters. They also showed that further oxygen release from $(VO_2)_n(V_2O_5)_m{}^+$ does not occur because of the stability of the building blocks. Indeed, supplying excess energy to the clusters via CID fragmented the building blocks.

To facilitate discussing oxygen desorption in greater detail, TPD curves are displayed in Figures 4 and 5 for $V_nO_m{}^+$ with odd and even numbers of vanadium atoms, respectively. The $V_nO_m{}^+$ intensity was normalized so that the total intensity of $V_nO_mH_l{}^+$ is equal to 1 for each n as the dissociation of VO_2, VO_3, and V_2O_5 does not occur. Indeed, 3–5 eV is required to cause stable species to dissociate [1]. In each plot, concomitant changes of the intensity ratios were observed. For instance, the intensities of $V_4O_9{}^+$ increased and $V_4O_{11}{}^+$ decreased as the temperature rose, as shown in Figure 4b.