Reactions of $V_4O_{10}^+$ cluster ions with simple inorganic and organic molecules

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ABSTRACT

The reactivity of mass-selected $V_4O_{10}^+$ cluster ions toward hydrocarbon molecules including CH_4, C_2H_4, and C_2H_6 was explored in the references case by case. Herein, further systematic studies on the reactions of $V_4O_{10}^+$ with simple inorganic and organic molecules (H_2, CO, CH_4, C_2H_2, C_2H_4, and C_2H_6) are presented. The vanadium oxide cluster ions are prepared by laser ablation and the $V_4O_{10}^+$ clusters are selected by a quadrupole mass filter and interacted with the simple molecules in a hexapole reaction cell. The reactant and product ions are detected by a reflectron time-of-flight mass spectrometer. Hydrogen and oxygen atom transfer reactions are observed. Density functional theory calculations are carried out for the reaction mechanism of $V_4O_{10}^+ + H_2$. The oxygen atom transfer (OAT) channel $V_4O_{10}^+ + H_2 \rightarrow V_4O_9^+ + H_2O$ is much more exothermic than the hydrogen atom transfer (HAT) channel $V_4O_{10}^+ + H_2 \rightarrow V_4O_{10}H^+ + H$ whereas the former is less favorable than the later in terms of the reaction kinetics. The computational result is in good agreement with the experiment that the HAT (H_2 splitting) rather than the OAT (water formation) is observed for $V_4O_{10}^+ + H_2$.

1. Introduction

Vanadium oxide clusters are being actively studied [1–16] in order to discover molecular level mechanisms for chemical processes over the surfaces of vanadium oxide based catalysts that are widely used in laboratory and industry [17–19]. Among various vanadium oxide clusters, the tetranuclear $V_4O_{10}^+$ cluster cation is probably the most actively studied [12,20–27] because this cluster system possesses an oxygen-centered radical ($O^{\bullet-}$) that is highly reactive with small molecules under thermal collision conditions. Castleman, Bonačić-Koutecký, and their co-workers are among the first to identify oxygen atom transfer (OAT) reaction with ethylene: $V_4O_{10}^+ + C_2H_4 \rightarrow V_4O_9^+ + C_2H_4O$ [25,27]. Soon after, Schröder, Sauer, Schwarz, and co-workers identified the hydrogen atom transfer (HAT) reaction with the very stable molecule methane: $V_4O_{10}^+ + CH_4 \rightarrow V_4O_{10}H^+ + CH_3$ [23]. In the reactions of $V_4O_{10}^+$ with the C_2–C_4 alkanes, both of the OAT (observation of $V_4O_9^+$) and HAT (observations of $V_4O_{10}H^+$ and $V_4O_{10}H_2^+$) channels could usually be identified [24]. Meanwhile, the reactivity of $V_4O_{10}^+$ toward C_2H_4 and CH_4 has been often compared with that of other cluster ions

such as $V_{4-x}P_xO_{10}^+$ ($x = 1$–2) [28,29], $V_{4-x}Y_xO_{10-x}^+$ ($x = 1$–3) [30], $V_2O_5(SiO_2)_x^+$ ($x = 1$–4) [31], $VAl_3O_7^+$ [32], and $P_4O_{10}^+$ [33,34].

The above reactivity studies involved with $V_4O_{10}^+$ and related systems [35,36] have provided molecular level insights into the chemistry of $O^{\bullet-}$ species that were proposed to react with organic molecules over bulk V_2O_5 based catalysts [37–42]. The $O^{\bullet-}$ species were also reported to react with simple inorganic molecules such as H_2 and CO over the V_2O_5/SiO_2 catalysts [41,42]. It is thus interesting to study how the $O^{\bullet-}$ radical centers may react with these simple molecules over the $V_4O_{10}^+$ cluster ions. For example, both the OAT and HAT can be thermodynamically possible for $V_4O_{10}^+ + H_2$ on the basis of the density functional theory (DFT) calculated structures and energies of $V_4O_9^+$, $V_4O_{10}^+$, and $V_4O_{10}H^+$ [23,25] as well as those of the related main group species:

$$V_4O_{10}^+ + H_2 \rightarrow V_4O_{10}H^+ + H, \quad \Delta H_{0K} = -0.82\,\text{eV} \quad (1)$$

$$V_4O_{10}^+ + H_2 \rightarrow V_4O_9^+ + H_2O, \quad \Delta H_{0K} = -2.06\,\text{eV} \quad (2)$$

It is noteworthy that condensed phase study suggested that surface reactions of H_2 with $O^{\bullet-}$ probably generate the surface adsorbed OH^- ions: $O^{\bullet-} + H_2 \rightarrow OH^- + H$ and then $O^{2-} + H \rightarrow OH^- + e^-$ in which the electron becomes trapped at a vacancy [41,43].

In this work, a quadrupole (Q) mass filter and a hexapole (H) reaction cell are constructed and attached to a reflectron time-of-flight mass spectrometer (TOF-MS) equipped with a laser ablation cluster source. The reactions of $V_4O_{10}^+$ with simple inorganic

molecules H_2 and CO are studied with the QH-TOF method. The reaction channels and rate constants for the interactions of $V_4O_{10}^+$ with the C_1 and C_2 hydrocarbons CH_4, C_2H_2, C_2H_4, and C_2H_6 are also measured for comparisons.

2. Experimental and theoretical methods

2.1. Experimental details

A schematic diagram of the experimental apparatus is shown in Fig. 1. The TOF-MS that is labeled as 12 (L12) in the figure and the cluster source (L1–L5) are the same as the ones used in previous studies [44,45]. The quadrupole mass filter (L7) and the hexapole reaction cell (L10) are homemade in this study and some of the dimensions are listed. A brief introduction of the experiment is given below. The vanadium oxide clusters are generated by pulsed laser ablation of a rotating and translating V disk (L3) in the presence of 0.5% O_2 seeded in a He carrier gas (99.999%) with a backing pressure of 5 atm. A 532 nm (second harmonic of Nd^{3+}: yttrium aluminum garnet-YAG) laser with an energy of 5–8 mJ/pulse and a repetition rate of 10 Hz is used. The gas is controlled by a pulsed valve (L1: General Valve, Series 9; the same for L9). The clusters formed in a gas channel (L4: 2 mm diameter × 25 mm length) are expanded with a supersonic jet (L5) into the quadrupole mass filter (L7) through a 4 mm diameter hole in an electric shielding plate (L6, use of this plate increases cluster signal very significantly). In order to mass-select the $V_4O_{10}^+$ ions, the DC (direct current) and RF (radio frequency) potentials applied to the quadrupole rods are ± 68.1 V (U) and 887 V (V_{pp}, $f = 1.150$ MHz), respectively. The calculated a and q values for the Mathieu equation are 0.22 ($a = 8eU/(mr_0^2(2\pi f)^2)$, $r_0 = 3.50$ mm) and 0.73 ($q = 2eV_{pp}/(mr_0^2(2\pi f)^2)$), respectively. The selected $V_4O_{10}^+$ ions pass through an ion focusing assembly (L8) and a 4 mm diameter hole (indicated by d6), enter into the hexapole reaction cell (L10: 80 mm length), and are reacted therein with the reactant gas molecules (H_2, CH_4, and others) that are controlled with a second pulsed valve (L9). The RF potentials applied to the hexapole rods are around 150 V (V_{pp}, 0.892 MHz). Both of the RF powers (for Q and H) are delivered through handmade air-core transformers that are driven by commercially available RF solid state amplifiers (75A250A from AR USA and XST021050100W from Shenzhen Xingshengtong China) connected with an RF signal generator (DG1022 from Qingdao Kechuang China). The reactant and product ions pass through a 4 mm diameter hole in the electric shielding plate L11 and are then detected with a homemade reflectron TOF-MS that was described previously [44]. The DC potentials applied to the cluster source and hexapole rods are both set to be zero (grounded) in this work.

In our experiments, the reactant gases are delivered in the pulsed rather than the continuous mode. This design can save reactant gases and keep a good vacuum for the TOF-MS. However, it becomes difficult to measure the instantaneous reactant gas pressures inside the reaction cell (L10) [46]. The following equation is used to estimate the reactant gas pressure (P) at the time (t) the cluster ions enter into the cell (the center region of L10)

$$P = P_0\, e^{-(t-t_0)/\tau} \tag{3}$$

in which P_0 is the instantaneous gas pressure of the reactant molecules in the cell at the time (t_0) the pulsed valve (L9 in Fig. 1) is closed and τ is the decay time for the flowing of the reactant gas from the cell to the vacuum. The τ value can be calculated as:

$$\tau = \frac{V}{2CS} \tag{4}$$

in which V is the volume of the cell (3.22×10^4 mm^3 in our design), S (12.56 mm^2) is the cross-sectional area defined by the aperture (diameter indicated as d6 in Fig. 1) through which the cluster ions enter into and come out of the cell, and C is the speed of sound and it can be calculated under the approximation of ideal gas as $C = \sqrt{\gamma kT/m}$, in which γ is the adiabatic index, k is the Boltzmann constant, T is the temperature of the cell (298 K), and m is the mass of the reactant molecule. Assuming that (1) each gas pulse delivers N reactant molecules into the cell within period of δt at a constant flow rate ($N/\delta t$) and (2) it takes the gas molecules very short time (with respect to δt and τ) to reach equilibrium pressure within the cell, the P_0 value in Eq. (3) can be derived as:

$$P_0 = \frac{NkT}{V}\frac{\tau}{\delta t}(1 - e^{-\delta t/\tau}) \tag{5}$$

The N value in Eq. (5) can be well determined by calculating (with ideal gas law) the total number of molecules injected (through L9 in Fig. 1) within a high number of gas pulses (M):

$$N = \frac{\delta P}{M} \times \frac{V'}{kT} \tag{6}$$

in which V' is the volume of the handling system that contains the reactant gas and δP is the pressure change in the gas handling system after the reactant gases are pulsed into the reaction cell for a period of time (for example, 3′0″, then $M = 3 \times 60 \times 10 = 1800$). Using Eq. (4), the τ values (decay time in μs) can then be determined to be about 970 (H_2, $\gamma = 1.40$), 3640 (CO, $\gamma = 1.40$), 2830 (CH_4, $\gamma = 1.32$), 3860 (C_2H_4, $\gamma = 1.24$), and so on. The δt value (width of the reactant gas pulse ≈200–400 μs) in our experiment is set to be much shorter than the τ values for most reactant gases so that the P_0 can be almost independent on δt because the term $(\tau/\delta t)(1 - e^{-\delta t/\tau})$ in Eq. (5) is close to 1 in this case. For the H_2 gas that has a relatively small τ value, the $(\tau/\delta t)(1 - e^{-\delta t/\tau})$ factor is about 0.86 if the δt is set to be 300 μs. The time delay $t - t_0$ (≈2000 μs) in Eq. (3) is adjusted
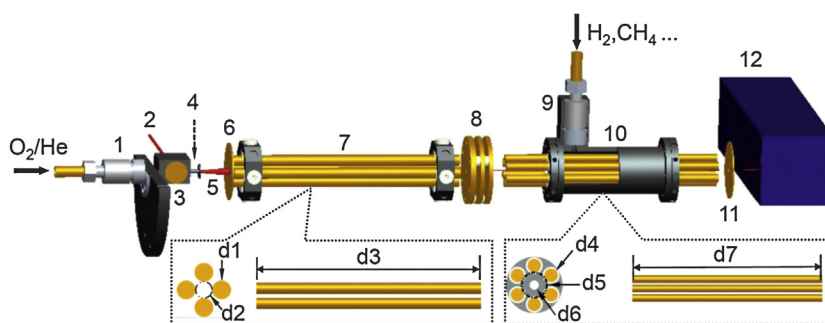

Fig. 1. A schematic diagram of the experimental apparatus. Labels 1–12: 1 and 9 (pulsed valves), 2 (ablation laser), 3 (sample disk), 4 (cluster formation channel), 5 (supersonic jet), 6 and 11 (electric shielding plates), 7 (quadrupole mass filter), 8 (ion focusing assembly), 10 (hexapole reaction cell), and 12 (reflectron time-of-flight mass spectrometer). Dimensions in mm: $d1 = 8.00$, $d2 = 7.00$, $d3 = 160.0$, $d4 = 6.00$, $d5 = 11.16$, $d6 = 4.0$, $d7 = 150.0$, $d(2-8) = 203$, and $d(2-12) = 422$, in which $d(2-8)$ and $d(2-12)$ are the distances between the laser spot on 3 and the centers of 8 and 12 (ion extraction region), respectively.