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Reaction of Cationic Vanadium Oxide Clusters with Ethylene in a Flow Tube Reactor[†]

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A time of flight mass spectrometer coupled with a cluster formation and reaction source is employed to study the reactivity of cationic vanadium oxide clusters ($V_mO_n^+$) toward ethylene (C_2H_4) in the gas phase. The cationic vanadium oxide clusters with $m=1-10$ and $n=1-26$ (depending on m) are generated by reaction of laser ablation created vanadium plasma with O_2 in a supersonic expansion and then reacted with the ethylene in a flow tube reactor. Hydrogen atoms are attached in most of the oxygen saturated clusters ($2n \geq 5m$) in our experimental condition. The reactivity of $V_mO_n^+$ toward C_2H_4 is usually higher than that of hydrogen containing clusters, $V_mO_nH_{2x}^+$. Larger clusters show less reactivity than smaller ones. Most of the observed products are in the forms of $V_mO_nC_2H_4^+$ and $V_mO_nH_{2x}C_2H_4^+$ due to direct association. C_2H_4 clustering products ($(C_2H_4)_n^+$, $n=2-6$) are also observed.

Key words: Time of flight mass spectrometer, Vanadium oxide clusters, Flow tube reactor, Reactivity

I. INTRODUCTION

Transition metal oxides (TMOs) are important group of industrial heterogeneous catalysts [1-5]. However, molecular level mechanisms of many processes catalyzed by TMOs are unclear. Considering the localization of electron motion in most metal oxides and thus validity of the concept that a catalytic reaction happens on catalytic active sites [6,7], gas phase metal oxide clusters composed of limited number of atoms that are fully accessible by both experiment and theory are excellent model systems to investigate for understanding the intrinsic reaction mechanisms in the condensed phase catalytic processes [8,9]. On the other hand, discovery and understanding of oxide cluster chemistry will finally shed light on design, synthesis, and more effective use of the TMO catalysts.

Among TMOs, vanadium oxides are extensively used as heterogeneous catalysts [4,5,10]. Vanadium oxide based catalysts are used in many important industrial processes, such as the oxidation of SO_2 to SO_3 for the production of sulfuric acid, the selective oxidation of hydrocarbons, and the selective reduction of NO_x with NH_3 [1,11,12]. To explore molecular level mechanisms in the condensed phase catalysis involving vanadium oxides, the reactivity of vanadium oxide cluster ions with small hydrocarbon compounds has been studied in the gas phase using mass spectrometric techniques

as well as quantum chemistry calculations [13-29]. In all the experimental studies, in which quadrupole based or ion cyclotron mass spectrometers are usually used, vanadium oxide cluster ions react with gas molecules (such as A) in low pressure (1.33 μPa -133 mPa) [16,18]. This reaction condition can be considered as single collision condition: $V_mO_n^+ + A \rightarrow (V_mO_nA^+)^* \rightarrow \text{products}$. In the low pressure reaction, there is no bath gas (or not enough collision) to take away energy from the initial collision complex $(V_mO_nA^+)^*$ that bears association energy, center of mass kinetic energy, and cluster initial vibrational energy [30]. The association energy between a cation and a neutral molecule is high (typically around 2-4 eV for $V_mO_n^+$ with C_2H_4) [23]. Once this energy is relaxed in the collisional complex by intra-cluster vibrational redistribution, the complex can be vibrationally very hot ($\Delta T_{\text{vib}} \approx 1560$ K for $V_2O_5^+$ association with C_2H_4) [23,31]. The hot $(V_mO_nA^+)^*$ complex either falls apart to initial reactants ($V_mO_n^+ + A$) or transfers to reaction products easily. In a real condensed phase catalytic process, surface phonons and collisions through high pressure gas molecules will take away association energy between reactants and the active sites and the reactions proceed under conditions with well defined temperature. This energy dissipation process cannot be well described in the low pressure gas phase study although the low pressure study is of importance for the investigation of intrinsic properties of TMO catalysts.

With the above considerations, we discard to use these low pressure (quadrupole based or ion cyclotron) mass spectrometric techniques to study TMO cluster reactivity although there are many advantages, for example, individual cluster can be isolated for detailed study. We built a high pressure reaction apparatus (flow-tube

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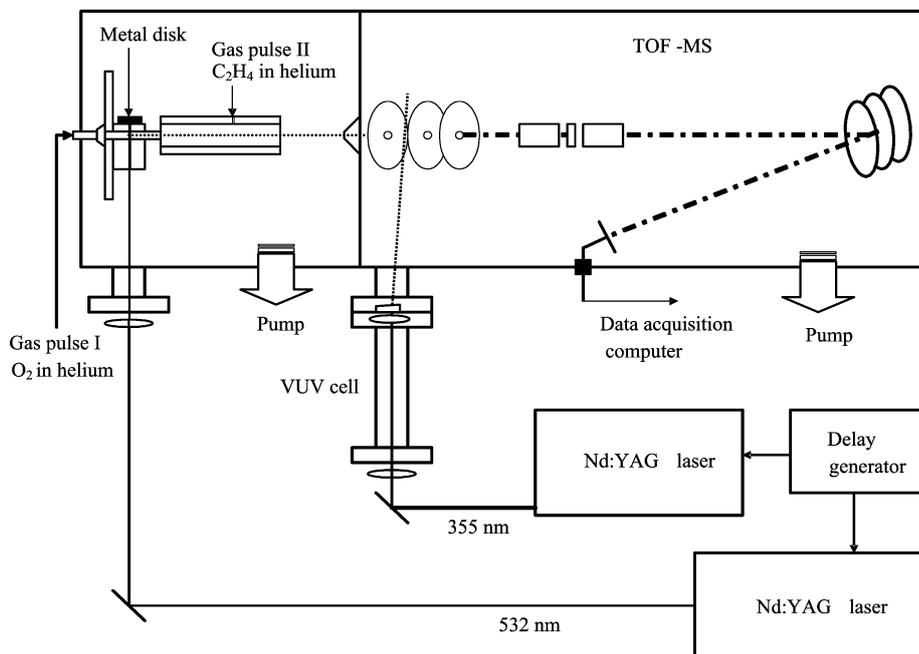


FIG. 1 A schematic diagram of the experimental setup for studying the reactivity of ionic and neutral transition metal oxide clusters in the gas phase.

reactor) [32,33] to study reactivity of TMO clusters. In this case, pre-formed clusters react with reactant(s) seeded in inert carrier gas (such as He). The instant total gas pressure for cluster reacting with gas molecules is typically around 1.33–13.3 kPa. Due to large number of collisions between He bath gas and the reaction complex $((V_mO_nA^+)^* + He \rightarrow V_mO_nA^+ + He)$, the reaction temperature can be considered as near room temperature if the reactor is not temperature-controlled. This will certainly provide new reactivity information that reflects molecular level reaction mechanisms in real catalysis. The same apparatus can be used to study neutral TMO cluster reactivity as long as an effective method is used to detect neutral clusters and reaction products [34–39]. In this work, the reaction of $V_mO_n^+$ clusters with C_2H_4 is investigated in the high pressure flow tube reactor. New phenomena that were not observed in previous low pressure studies are found.

II. EXPERIMENTS

A flow tube reactor for study of TMO cluster reactivity was constructed. Its design is similar to the one adopted by Smalley and his coworkers [32]. The experimental setup is schematically shown in Fig.1.

The vacuum system includes two vacuum chambers. One is for the cluster generation and reaction, and the other is for reactant and product detection. $V_mO_n^+$ clusters are generated by a focused 532 nm laser (Nd:YAG, 10 Hz, 5–8 mJ/pulse, 8 ns duration) onto a 15 mm diameter vanadium foil (0.13 mm thick, 99.7%, Sigma-

Aldrich) in the presence of 1% O_2 seeded in 506 kPa He carrier gas. The vanadium foil is glued on a spring loaded aluminum metal disk. A translational and rotational (spiral) motion of the disk is managed by a single motor (Maxon) that is powered by a commercial controller (University of Science and Technology of China) with wide range of speed adjustment. The gas is controlled by a pulsed valve (General Valve, series 9) with a commercial controller (University of Science and Technology of China). The clusters are formed in a dimension adjustable gas channel with a “waiting room” [33]. Typical dimensions used in this study are 3.2 mm in diameter by 3 mm in length for the waiting room and 2.5 mm in diameter by 25 mm in length for the rest of the channel. The gas channel is coupled directly to a tube/reactor (stainless steel, 6.3 mm inner diameter by 76 mm in length). The reactant gas, C_2H_4 (DaLianDaTe, 99.96%, without further purification) seeded in helium is injected into the reactor by a second pulsed valve (General Valve, series 9). The delay time between the two valve openings can be adjusted so that the $V_mO_n^+$ clusters are pre-generated in the narrow cluster formation channel and then react with downstream C_2H_4 in the flow tube reactor. Pressure in the reactor is estimated to be about 2.7 kPa in the presence of reactant gas pulse.

After reaction of $V_mO_n^+$ with C_2H_4 in the reactor, reactants, products, and the buffer gases are expanded into the first chamber (~ 13.3 mPa) to form a molecular beam. The beam enters the vacuum of the second detection mass spectrometer chamber (~ 133 μ Pa) through a 3-mm-diameter skimmer. Ionic species in the molec-

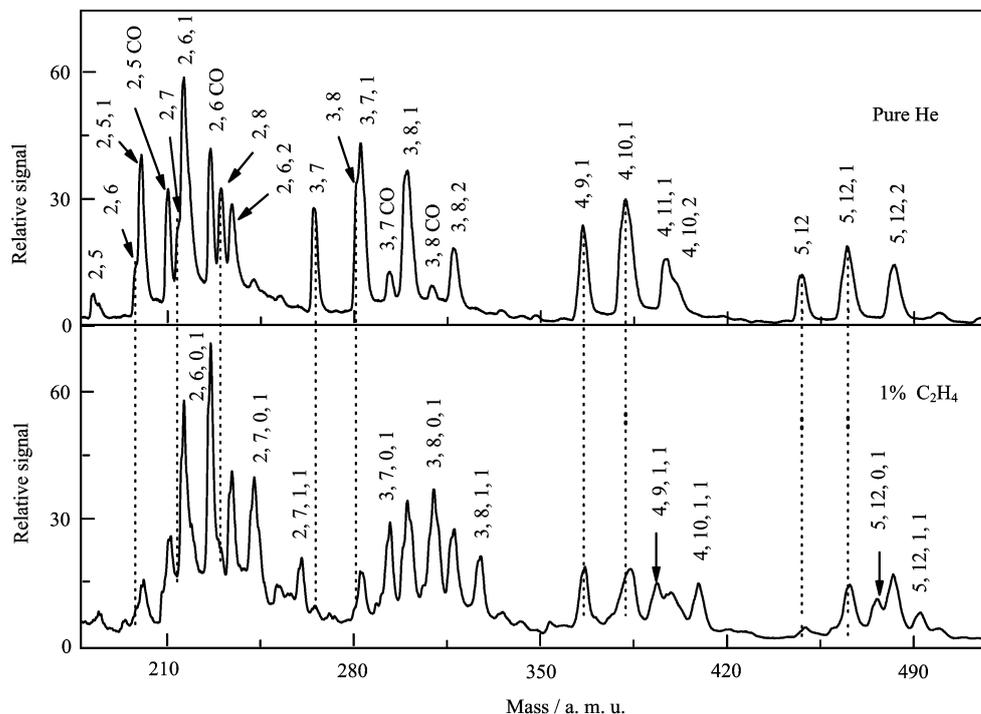


FIG. 2 TOF spectra for reaction of $V_m O_n H_{2x}^+$ ($m=2-5$) with C_2H_4 seeded in helium. Label m, n ; m, n, x ; m, n, x, y ; and m, n, CO denote mass spectrometer detected species $V_m O_n^+$; $V_m O_n(H_2O)_x^+$; $V_m O_n(H_2O)_x(C_2H_4)_y^+$; and $V_m O_n CO^+$; respectively.

ular beam are directly detected by a reflectron time of flight mass spectrometer (TOF-MS) equipped with pulsed power supplies. The TOF signals are recorded and averaged typically for 500 laser shots by a fast digitizing card managed by a LABVIEW program. The instrument is also designed to adopt a vacuum ultraviolet (VUV) laser source to single-photon ionize the neutral TMO clusters without fragmentation [34-39], so that the reactivity of neutral oxide clusters can be investigated.

III. RESULTS

The TOF spectra for reactions of the $V_m O_n^+$ clusters with 1% C_2H_4 in $V_2 O_x^+$ - $V_5 O_x^+$, $V_6 O_x^+$ - $V_{10} O_x^+$, and VO_x^+ mass regions are plotted in Figs.2-4, respectively. Reference spectra for cluster collision with pure helium are also provided for comparison. Because the molecular beam in the current experimental setup is perpendicular to the ion source plates, the mass resolution of the instrument is low (Fig.1). The full width at half maximum of mass peak $V_3 O_7^+$ is 2.2 a.m.u. which determines a mass resolution of 120 in this region. Figure 2 shows that $V_3 O_8^+$ (281 a.m.u.) and $V_3 O_7 H_2 O^+$ (283 a.m.u.) are nearly overlapped. The width and shape of this overlapped mass peak is quite different from that of isolated mass peak such as $V_3 O_7^+$. This makes $V_3 O_8^+$ be differentiated from $V_3 O_7 H_2 O^+$.

The masses are carefully calibrated by using narrow and symmetric mass peaks (VO^+ , $V_3 O_7^+$, $V_4 O_9 H_2^+$, $V_5 O_{12}^+$, $V_7 O_{16}^+$). The distribution of the pre-formed clusters (reference spectra, Pure He) is quite regular for clusters containing three or more vanadium atoms. Figures 2 and 3 show that pure vanadium oxide clusters are generated for $V_2 O_{5-8}^+$, $V_3 O_8^+$, $(V_2 O_5)_n VO_2^+$ with $n=1-2$, and $(V_2 O_5)_n VO^+$ with $n=3-4$. Hydrogen atoms are attached to almost all other clusters that can be interpreted as complex in the form of $V_m O_n(H_2O)_x^+$ due to H_2O impurities in the system. Mass peaks that matches carbon impurities are present in V_2 and V_3 clusters ($V_2 O_5 CO^+$, $V_2 O_6 CO^+$, $V_3 O_7 CO^+$, and $V_3 O_8 CO^+$, as shown in Fig.2). In the experiment, different concentrations of O_2 (0-20%) are also tested for generating the cationic vanadium oxide clusters. It is generally found that large clusters are relatively more abundant if higher concentrations of O_2 are used. In this work, a typical mass distribution which covers both small and large clusters generated with 1% O_2 is present.

After reacting with 1% C_2H_4 , the signal of all the pure vanadium oxide clusters in Fig.2 ($V_2 O_{5-8}^+$, $V_3 O_{7-8}^+$, and $V_5 O_{12}^+$) disappears almost completely, while the signal of the hydrogen containing clusters does not decrease much. The rate of signal depletion of the clusters in the high mass region (Fig.3) is relatively smaller than that in the low mass region (Fig.2). Direct association products, corresponding to the depletion of pre-formed $V_m O_n(H_2O)_x^+$ ($x=0$ and 1) are ob-

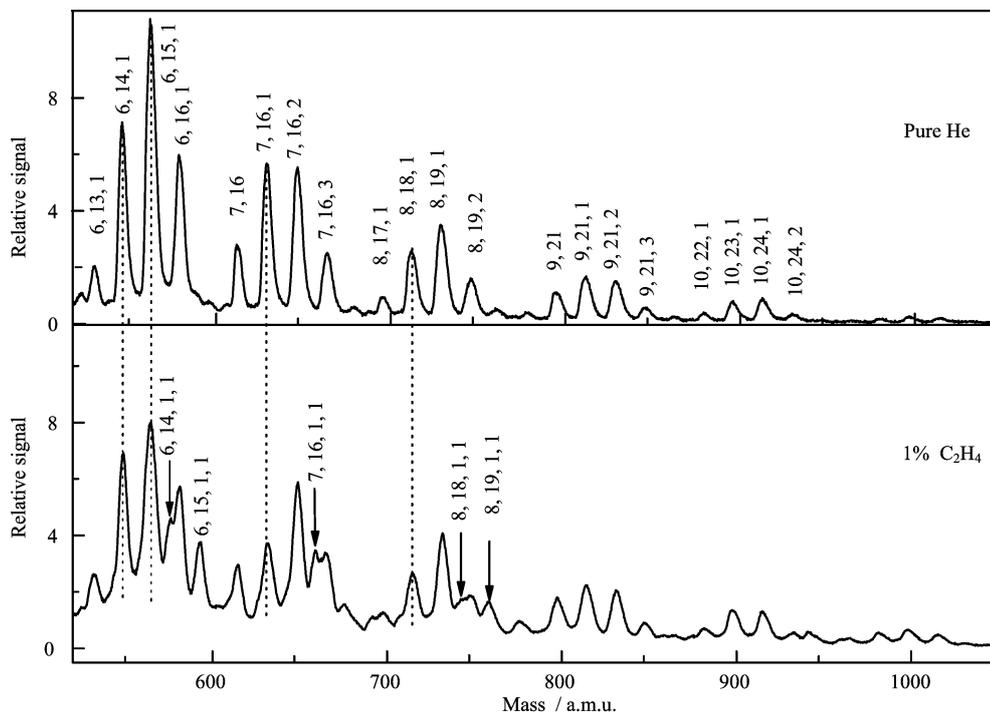


FIG. 3 TOF spectra for reaction of $V_m O_n H_{2x}^+$ ($m=6-10$) with C_2H_4 seeded in helium. See caption of Fig.2 for explanation of the label.

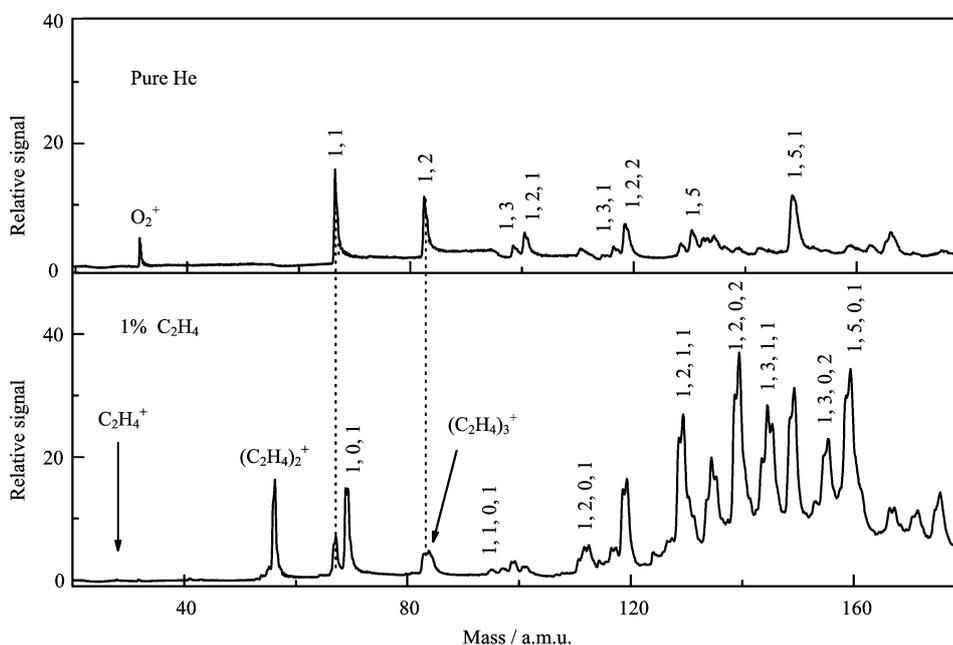


FIG. 4 TOF spectra for reaction of $VO_n H_{2x}^+$ with C_2H_4 seeded in helium. See caption of Fig.2 for explanation of the label.

served, $V_5 O_{12} (H_2O)_{0-1} C_2H_4^+$, $V_6 O_{14-15} H_2 O C_2H_4^+$, $V_3 O_{7-8} C_2H_4^+$, $V_3 O_8 H_2 O C_2H_4^+$, $V_7 O_{16} H_2 O C_2H_4^+$, $V_4 O_{9-10} H_2 O C_2H_4^+$, and $V_8 O_{18-19} H_2 O C_2H_4^+$. In this study, the TOF experimental method can not answer whether C_2H_4 molecule is dissociatively absorbed in the observed products or not. It would be interesting to

use other methods such as theoretical calculations to answer this question. The product analysis for V_2 clusters are interfered by carbon impurity peaks (Fig.2). $V_2 O_6 C_2H_4^+$ and $V_2 O_7 C_2H_4^+$ that correspond to depletion of $V_2 O_6^+$ and $V_2 O_7^+$ are observed. Depletion of $V_2 O_8^+$ is clearly present but there is no apparent

corresponding product. After the reaction, the signal increase at 226 a.m.u ($V_2O_6CO^+$ or $V_2O_6C_2H_4^+$) is higher than the signal decrease at 198 a.m.u ($V_2O_6^+$). This suggests that $V_2O_8^+ + C_2H_4 \rightarrow V_2O_6C_2H_4^+ + O_2$ is happening in the flow tube reactor. A weak peak at 260 a.m.u is assigned to $V_2O_7H_2OC_2H_4^+$ with no corresponding pre-formed clusters.

The TOF spectra in VO_x region (Fig.4) are confusing and interesting as well. After the reaction with 1% C_2H_4 , the signal decrease of pre-formed clusters such as VO^+ and VO_2^+ is observed, while the signal increase of some products such as $VO_2(C_2H_4)_2^+$ and $VO_5C_2H_4^+$ is too much compared to the signal of the pre-formed clusters. This discrepancy may be due to un-stability for VO_x cluster formation found in the experiment. Mass peaks that can be assigned to $(C_2H_4)_2^+$ and $(C_2H_4)_3^+$ are observed.

IV. DISCUSSION

The reaction of $V_mO_n^+$ with low pressure (<133 mPa) C_2H_4 gas was studied by a guided ion beam spectrometer in Ref.[18], where most of the observed products ($V_mO_n^+C_2H_4$) are due to direct association. This is in agreement with the result in this study by using flow tube reactor setup. Because the reaction temperature is very high in the guided ion beam experiment, products due to O transfer ($V_mO_n^+ + C_2H_4 \rightarrow V_mO_{n-1}^+ + C_2H_4O$) or O_2 loss ($V_mO_n^+ + C_2H_4 \rightarrow V_mO_{n-2}C_2H_4^+ + O_2$ or $V_mO_{n-2}^+ + C_2H_4O_2$) were observed for $(V_2O_5)_n^+$ with $n=1-3$, $V_2O_6^+$, and $V_3O_8^+$. There is no evidence that these reactions are present in the flow tube reactor; for example, for $V_3O_8^+$ reacting with C_2H_4 , only association product $V_3O_8C_2H_4^+$ is observed (Fig.2). Two products ($V_3O_6^+$ and $V_3O_6C_2H_4^+$) were observed in the guided ion beam study for $V_3O_8^+$ reacting with C_2H_4 . This is strong evidence that the He bath gas with high pressure (~2.7 kPa) in the flow tube reactor stabilizes/cool the initial collision complex $(V_3O_8C_2H_4^+)^*$ through collisions. The collisions are not present in the guided ion beam experiment due to a requirement of low pressure to run the instrument. This suggests that the reactivity study by high pressure/low temperature flow tube reactor provides better chance to understand molecular level reaction mechanism for low temperature heterogeneous catalysis.

One of the interesting findings in this work is that for clusters with three or more vanadium atoms, no pure oxide clusters are present for cluster with even number of vanadium atoms, such as $(V_2O_5)_n^+$ with $n \geq 2$ are not observed in our experimental conditions. This suggests that these cationic radicals with open shell electronic structure are very reactive with water to form hydrogen containing clusters. In contrast, species with possible close shell electronic structure, such as $(V_2O_5)_nVO_2^+$

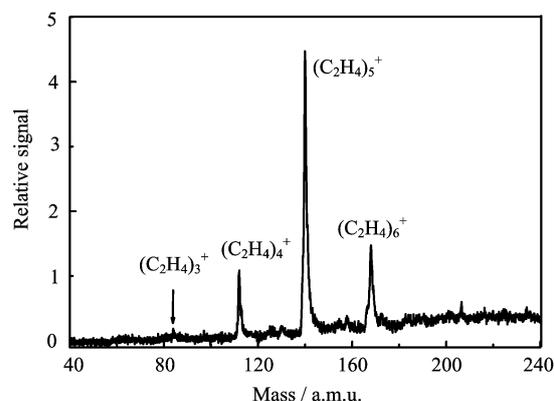
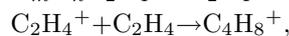
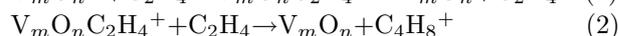


FIG. 5 TOF spectra for reaction of $V_mO_nH_{2x}^+$ with 10% C_2H_4 seeded in helium. The two gas pulses (Fig.1) are much more strongly mixed in this experiment than in the experiments to get spectra in Figs.2-4.

and $(V_2O_5)_nVO^+$ are relatively less-reactive with water so that $V_3O_7^+$, $V_5O_{12}^+$, $V_7O_{16}^+$, $V_9O_{21}^+$ are observed. It is interesting to note that $V_3O_7^+$, $V_5O_{12}^+$, and $V_7O_{16}^+$ is very stable toward 532 or 355 nm multiphotons [40]. In Figs.2-4, most of the pre-formed clusters are hydrogen or water containing. Because water vapor pressure in the gas and vacuum systems should be very low, the generation of so many $V_mO_n(H_2O)_x^+$ clusters suggests that supported vanadium oxide catalysts prepared at high-temperature and dry inert gas are most probably still hydrogen containing or will be hydrogen containing during use. This suggests that active site of the catalysts owns $O=V(OH)_2-O$ -support rather than $O=V(O_2)-O$ -support structure if there is no other choices [41-43].

The second interesting finding in this work is that $(C_2H_4)_n^+$ clusters are observed (Fig.4). The TOF spectrum for reaction of generated $V_mO_nH_{2x}^+$ with 10% C_2H_4 in the flow tube reactor is plotted in Fig.5. The time delay between the two gas pulse openings (Fig.1) is adjusted so that very strong mixing of the two pulses is achieved. In this case, the signal of all the $V_mO_n^+$ clusters depletes and only C_2H_4 clustering signal ($(C_2H_4)_n^+$, $n=3-6$) is present. One reasonable explanation for the result in Fig.5 is that too much collisions in the flow tube reactor cause complete charge transfer from $V_mO_nH_{2x}^+$ to C_2H_4 . The following three processes, termed as (1), (2), and (3), respectively, may be involved in the flow tube reactor to cause C_2H_4 charging and clustering:



Because monomer species $C_2H_4^+$ is not observed while $(C_2H_4)_2^+$ is strongly observed in the condition to get the spectra in Fig.4, it suggests that the direct charge transfer through process (1) may not

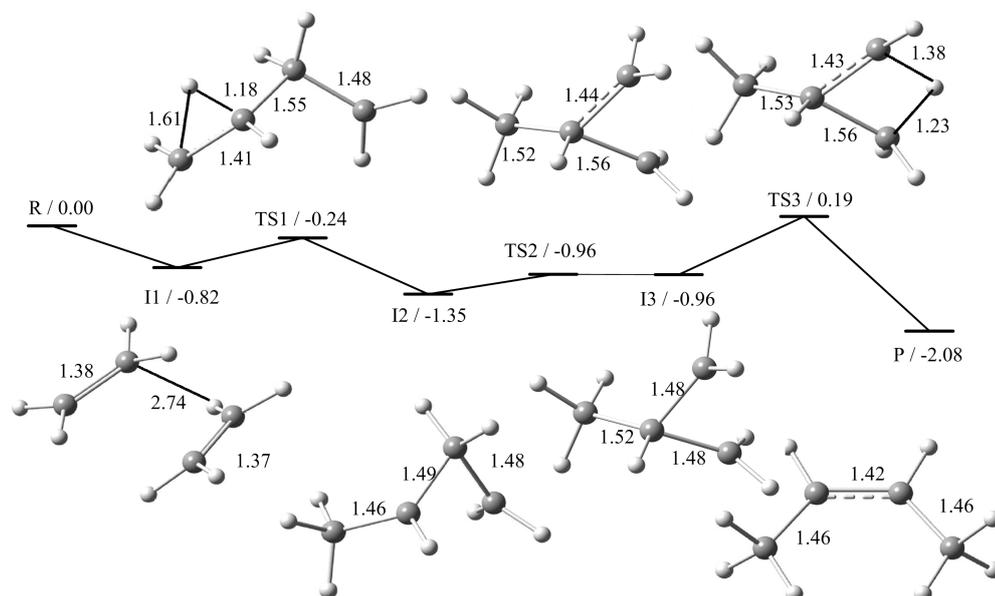


FIG. 6 Reaction path for $C_2H_4^+ + C_2H_4 \rightarrow C_4H_8^+$ calculated at B3LYP/6-311++G(d,p) level of theory by using Gaussian 03 program. In the figure, reaction intermediates (I1, I2, I3) and transition states (TS1, TS2, TS3) with relative free energies (ΔG in eV) at 298 K are denoted as $I_n/\Delta G$ and $TS_n/\Delta G$, respectively. $R/\Delta G$ and $P/\Delta G$ denote reactant ($C_2H_4^+ + C_2H_4$) and product (2-butene cation) with relative free energies, respectively. Structure of each reaction complex is also shown with C–C bond lengths and some C–H distances giving in Å.

be possible. Process (2) makes sense with the following considerations: $V_mO_nC_2H_4^+$ products are observed in Figs.2-4; ionization energy (IE) of C_4H_8 (such as 2-butene) is 9.1 eV which is lower than the IE of some V_mO_n clusters, such as VO_3 and V_4O_{10} [36], this makes process (2) thermodynamically favorable; and no evidence of secondary association products [$V_mO_n(C_2H_4)_2^+$] are strongly observed in this study and previous studies [18]. After dimer species $C_4H_8^+$ is formed through process (2), self-growth (process (3)) may be present to form larger polymer clusters in the flow tube reactor. The absent observation of $C_2H_4^+$ in Fig.4 discards the possibility that electrons from the laser ablation play a role in the C_2H_4 charging and clustering processes. To explore self-polymerization process (3) in the gas phase, first principle calculation at B3LYP/6-311++G(d,p) level is applied for the simplest reaction $C_2H_4^+ + C_2H_4 \rightarrow C_4H_8^+$. The result is shown in Fig.6. $C_2H_4^+$ approaches C_2H_4 overall barrierlessly to form valence bonded species I2 and I3. 2-butene cation (P) formation is subject to a small barrier (0.19 eV) in the room temperature. This calculation supports and is supported by the results in a previous study [44], where after multiphoton ionization of Van der Waals ethylene clusters ($(C_2H_4)_{m+n} + xh\nu \rightarrow (C_2H_4)_m^+ + e + (C_2H_4)_n$) in a supersonic molecular beam, carbon-carbon valence bond formation is present in $(C_2H_4)_m^+$.

V. CONCLUSION

A flow tube reactor apparatus coupled with TOF-MS was built to study the reactivity of transition metal oxide clusters toward gas molecules under high pressure (1.33-13.3 kPa) and low temperature (~ 300 K) conditions. The reaction of cationic vanadium oxide clusters with ethylene is investigated in this study. New chemistries such as collision stabilization, charge transfer, and ethylene gas phase polymerization not presented in previous low pressure (1.33 μ Pa-133 mPa)/high temperature studies are observed. Vanadium oxide clusters solvated with and without water show low and high reactivity toward ethylene, respectively. Such property may be considered in design and use of vanadium oxide catalysts for specific condensed phase reactions. Molecule level mechanisms for ethylene polymerization over condensed phase metal oxides such as CrO_3 and V_2O_5 may be discovered by further experimental and theoretical studies of the cluster reactivity in the flow tube reactor conditions.

VI. ACKNOWLEDGMENTS

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