Reactions of Neutral Vanadium Oxide Clusters with Methanol

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Reactions of neutral vanadium oxide clusters with methanol and ethanol in a fast-flow reactor are investigated by time-of-flight mass spectrometry. Single-photon ionization through soft X-ray (46.9 nm, 26.5 eV) and vacuum ultraviolet (VUV, 118 nm, 10.5 eV) lasers is employed to detect both neutral cluster distributions and reaction products. In order to distinguish isomeric products generated in the reactions V₅O₃ⁿ⁺ + CH₃OH, partially deuterated methanol (CD₃OH) is also used as a reactant in the experiments. Association products are observed for most vanadium oxide clusters in reaction with methanol. Products VOD, V₂O₃D, V₃O₆D, and V₄O₈D are observed for oxygen-deficient vanadium oxide clusters reacting with methanol, while oxygen-rich and the most stable clusters can extract more than one hydrogen atom (H/D) from CD₃OH to form products VO₂DHₐ, V₂O₃DHₐ, V₃O₆DHₐ, V₄O₈DHₐ, and V₅O₉DHₐ. Species VO₂(CH₃)₂, VO₃(CH₃)₂, V₂O₅(CH₃)₂, V₃O₇(CH₃)₂, and V₅O₉(CH₃)₂ are identified as some of the main products generated from a dehydration reaction for V₅O₅ + CH₃OH. A minor reaction channel that generates VOCH₂O (VOCD₂O) can also be identified. An obviously different behavior appears in the reaction V₅O₅ + CH₃OH and VO + CH₃OH reaction systems. The calculation results are in good agreement with the experimental observations.

I. Introduction

Transition metal oxides are important heterogeneous catalysts, and their properties and reactions have been the subject of numerous studies. The oxidation of methanol is interesting because of its importance in catalytic processes; for example, oxidative reforming of methanol is an important catalytic process in fuel cells. Selective oxidation of methanol on supported vanadium oxide catalysts has been considered as a simple probe reaction for a number of other selective oxidation reactions. The major product of methanol oxidation over V₂O₅ is found to be formaldehyde, with minor products of dimethyl ether, etc. The mechanism for oxidation of methanol on supported vanadium oxide is suggested to be methanol oxidation by the catalyst, and not by gas-phase molecular O₂. In this case, O₂ molecules are used to oxidize the reduced V⁴⁺ or V⁵⁺ sites back to active V⁵⁺ sites. In situ Raman and UV-visible measurements reveal that the catalytically active sites are fully oxidized surface VO₄ sites. Three different V=O functionalities, terminal V=O, bridging V=O−V, and bridging V=O-support bonds, are identified for the surface of supported vanadium oxide in the catalytic methanol oxidation process. In some studies, terminal V=O are considered to be the active sites, and in others, bridging V=O−V are considered to be the active sites. Recently, Wachs et al. suggested that the bridging V=O-support bond contributes to methanol oxidation. Although an extensive research effort over the past two decades to explore the process of methanol oxidation in the condensed phase has been undertaken, a fundamental understanding of these catalytic reactions at an atomic and molecular level is still lacking. The complicated catalytic surface process is still difficult to interpret fully.

Gas-phase metal/metal oxide clusters and their reactions with small molecules are considered to be a model system for active sites of condensed/surface phase chemistry. Clusters generated in gas phase have relatively well-defined structures and size-dependent properties, and they are relatively accessible by theoretical calculations. A full understanding of reaction behavior of gas-phase clusters can, in principle, provide insight into the mechanism of practical catalyst systems. The reactivity of vanadium/nioibium/tantalum/zirconium oxide cluster ions toward methanol has been studied in the gas phase using mass spectrometric techniques. The reactions of mass-selected M⁺ and M⁰⁺ (M = V, Nb, and Ta) with CH₃OH have been studied by Tang and co-workers using Fourier transform ion-cyclotron resonance (FT-ICR) mass spectrometry coupled with a laser ablation ion source. In their experiments, VO₂CH₄⁺, VO₂CH₂O⁺, and VO₂⁺ are detected as the main products of the reaction VO⁺ + CH₃OH; some secondary reaction products V(OCH₃)₃⁺ and V(OH)₃⁺ are also observed. Employing a guided ion beam mass spectrometer, Castleman et al. studied the reactions of methanol with V₅O₅⁺ and Nb₂O₅⁺ cluster ions. The products observed in their experiments are H₂, CH₃, CH₂OH, and CH₃O attached to mass-selected cluster ions. Recently, Schwarz’s group published a comprehensive study of V₅O₅⁺ and V₅O₅⁻(OH)⁺ (m = 1−4, n = 1−10) cluster ion reactivity toward methanol using a mass spectrometric technique coupled with an electrospray ion source. Several reaction channels are identified in their experiments: abstraction of a hydrogen atom, a methyl radical or a hydroxymethyl radical, elimination of methane, and adduct formation. Formaldehyde is produced via four different pathways. In another experiment,
they\textsuperscript{23} studied reactions of methanol with mass-selected V\textsuperscript{+}, VOH\textsuperscript{+}, VO\textsuperscript{+}, and VO\textsuperscript{2+} cations by FT-ICR mass spectrometry with an ablation ion source. Oxidation state of the metal is a key factor that determines cluster reactivity. Waters and co-workers investigated the metavanadate anion [VO\textsubscript{3}\textsuperscript{−}]\textsuperscript{−} ionizing toward methanol and ethanol through a combination of ion–molecule reactions and isotope labeling experiments in a quadrupole ion trap mass spectrometer. They found that VO\textsubscript{3}\textsuperscript{−} reacts with methanol to form VO\textsubscript{3}(\textsuperscript{17}O\textsubscript{2}CH\textsubscript{3}) through the elimination of water.\textsuperscript{25} Most gas-phase cluster reactivity studies exploit the reactivity of metal oxide clusters with various small molecules, including methanol. Additionally, theoretical studies are employed to elucidate the mechanisms of ion–molecule reactions between metal/metal oxide cluster ions and small molecules, including methanol.\textsuperscript{21,23,25–27} Partial charge transfer between metal oxide clusters and support materials (either bulk or surface) may play an important role in catalytically active processes in the condensed phase. On the other hand, gas-phase studies of neutral clusters can provide useful information that can assist one in the analysis of condensed phase catalysis systems. Neutral clusters generally exhibit significantly different reactivity than ionic clusters in some reactions.\textsuperscript{25–31}

Recently, our group has employed a new desktop, 26.5 eV/photon (46.9 nm), soft X-ray laser coupled with time of flight mass spectrometer (TOFMS) to study gas-phase van de Waals clusters\textsuperscript{22} and neutral metal oxide clusters and their reactions.\textsuperscript{33} With this ionization source, all neutral cluster species and their reaction products can be ionized and detected. In the study of vanadium oxide clusters reacting with C\textsubscript{2} hydrocarbons, we found that the double bond of C\textsubscript{2}H\textsubscript{4} can be broken by neutral oxygen-rich vanadium oxide clusters.

In the present work, reactions of neutral vanadium oxide clusters with methanol and ethanol are studied. Many reaction products are observed, and four kinds of reactions are identified by employing CH\textsubscript{3}OH and deuterated (CD\textsubscript{3}OH) methanol. DFT calculations are performed to study the reaction pathways of VO\textsubscript{2} + CH\textsubscript{3}OH and VO + CH\textsubscript{3}OH reaction systems. The mechanisms of V\textsubscript{n}O\textsubscript{m} + CH\textsubscript{3}OH reactions are discussed in detail and potential catalytic cycles for condensed-phase processes are suggested.

II. Procedures

A. Experiment. The reactions of neutral vanadium oxide clusters with methanol/ethanol are investigated using a time-of-flight mass spectrometer (TOFMS) coupled with single-photon ionization by a desktop 26.5 eV soft X-ray laser. Since the experimental apparatus has been described in detail elsewhere,\textsuperscript{33} only a general outline of the experimental scheme will be presented in this report. Briefly, neutral vanadium oxide clusters are generated in a conventional laser vaporization/supersonic expansion source. A focused 532 nm laser (second harmonic of a Nd:YAG laser, 1064 nm) is employed to ablate a target of vanadium metal foil (99.7\%, Aldrich) at about 20 mJ/pulse. A mixture of 0.5\% O\textsubscript{2} and He is used as expansion gas at 80 psig for the generation of V\textsubscript{n}O\textsubscript{m} neutral species. The reactant gas, formed by flowing He (99.9\%, 15 psi) through a reservoir containing methanol/ethanol (CH\textsubscript{3}OH and C\textsubscript{2}H\textsubscript{5}OH are spectroscopic grade, deuterated CD\textsubscript{3}OH is 99.8 atom % D, Aldrich) at room temperature, is pulsed into the reactor tube located at about 20 mm downstream from the exit of the expansion channel. The instantaneous reactant gas mixture pressure in the reactor cell is about 1–2 torr in this setup. In this design, the fast flow reactor (70 mm length, \(\varnothing\) 6 mm) is coupled directly to the cluster formation channel (40 mm length, \(\varnothing\) 1.8 mm).

After the fast flow reactor, the ions created in the ablation source and fast flow reactor are removed by an electric field. Vanadium oxide clusters generated from the ablation source react with reactant gases in the fast flow reactor. The design of fast-flow reactor is similar to the one adopted by Smallley et al.\textsuperscript{34} This method is commonly used in the study of elementary reactions of ions and neutral metal clusters. The possibility of charge exchange between the ions and the much more abundant neutral species can be neglected based on the study of Kaldor et al.\textsuperscript{34,c} Additionally, we have demonstrated that ion–molecule reactions do not occur in our studies of V\textsubscript{n}O\textsubscript{m} clusters reacting with small hydrocarbons.\textsuperscript{35} Neutral clusters and reaction products pass through a 4 mm skimmer into the ionization region of a TOFMS (Wiley–McLauran design, R.M. Jordan Co.), where these neutral species are ionized by the slightly focused soft X-ray laser. The resolution of the mass spectrometer (\(\Delta m/m\)) is about 1/1000. The calibration of mass spectrum in the experiments is based on the distribution of vanadium oxide clusters. If reactant (CH\textsubscript{3}OH, CD\textsubscript{3}OH, or C\textsubscript{2}H\textsubscript{5}OH) is added into fast flow cell reactor to collide with metal oxide clusters, mass resolution will be somewhat degenerated, but it is still better than 1/500. In the present experiments, mass spectra are accumulated about 250 laser pulses.

The rotational and vibrational temperatures of VO\textsubscript{2} clusters have been measured to be about 50 and 700 K, respectively.\textsuperscript{35a} The temperatures of larger clusters should be higher than smaller clusters since more formation energy is released during larger cluster formation. In our experiments, the reactant gas mixture, CH\textsubscript{3}OH/He or CH\textsubscript{2}CH\textsubscript{2}OH/He, is pulsed into a fast flow cell reactor at 15 psi backing pressure. The instantaneous gas pressure in the fast flow reactor is approximately 1–2 torr when the metal oxide clusters pass through. The clusters carried by the molecular beam stay in the cell for about 50 \(\mu\)s (velocity of molecular beam is about 1.5 km/s, and reactor length is 70 mm). In the fast flow cell, more than one thousand collisions occur between the clusters and bath gas at a rate about 10\%s. Therefore, most of the metal oxide clusters are cooled to room in these reactivity experiments. The concentration of alcohol is about 15\% in He (backing pressure of He is 15 psi, and vapor pressure of CH\textsubscript{3}OH is about 125 torr at 298 K). The collisions between CH\textsubscript{3}OH and clusters are estimated at about 100 in the fast flow cell.

The soft X-ray laser (26.5 eV/photon energy) emits pulses of about 1 ns duration with an energy/pulse of 10 \(\mu\)J at a repetition rate of up to 12 Hz.\textsuperscript{36} A pair of gold-coated mirrors, a toroidal and a plane mirror, is placed in a grazing incidence Z-fold configuration just before the ionization region of the TOFMS to provide alignment and focusing capabilities for the laser with respect to the molecular beam in the ionization region. The transmissivity of the Z-fold mirror system is about 40\%. A large number of He\textsuperscript{+} ions can be produced by 26.5 eV ionization of He in the molecular beam, and these could broaden the V\textsubscript{n}O\textsubscript{m}, etc. mass spectral features. The soft X-ray laser radiation is not tightly focused in the ionization region to avoid multiphoton ionization and a space charge Coulomb effect due to He\textsuperscript{+} ions.

Since a 26.5 eV photon from the EUV laser is able to ionize the He carrier gas employed in the expansion, the microchannel plate (MCP) ion detector voltage is gated to reduce the MCP gain when He\textsuperscript{+} arrives at the mass meter, in order to prevent detector circuit overload and saturation. 118 nm laser light is generated by focusing the third harmonic (355 nm, \(~30 \text{mJ/pulse}\)) of a Nd:YAG laser in a tripling cell that contains about a 250 torr argon/xenon (10/1) gas mixture. To separate the
generated 118 nm laser beam from the 355 nm fundamental beam, a magnesium fluoride prism (apex angle = 6°), which was not employed in our previous studies, is inserted into the laser path. In this case, one is quite sure that mass signals are generated by ionization purely through the VUV laser radiation at low power (∼1 µJ/pulse, pulse duration ∼5 ns).

B. Theoretical Calculations. DFT calculations are carried out using the Gaussian 03 program. The B3LYP functional and TZVP basis set are used. Vyboishchikov et al. employed DFT calculations to study vanadium oxide clusters at the B3LYP/TZVP level for the first time, and then more thorough tests of this method were performed by Sauer and co-workers. More recent studies of the reactivity of vanadium oxides using the B3LYP functional can be found in ref. 41. The calculations are performed on two reaction systems, VO + CH3OH and VO + CH2OH. For each reaction channel, the calculation involves geometry optimization of various reaction intermediates and transition states. Intrinsic reaction coordinate (IRC) calculations are also performed to confirm that a transition state connects two appropriate local minima on the reaction potential energy surface. The reaction potential surfaces (PES) plotted in the terms of zero-point-energy-corrected ΔE are thus used to explain experimental results.

III. Results

A. VnOₙ Clusters. Figure 1 displays mass spectra, generated by 26.5 eV single-photon ionization of reactants and products for the reactions of VnOₙ clusters with CH₃OH. Neutral vanadium oxide clusters are generated at low oxygen concentration conditions (0.5% O₂/He expansion). In the present paper, the formula VnOₙ is used to represent general vanadium oxide clusters. The predominant species are identified as reactants VO₂, VO₃, VO₄, VO₅, VO₆, VO₇, VO₈, VO₁₀, VO₁₂, etc., as shown in the lower spectra of Figure 1, a, b, and c, for different cluster size regions. These vanadium oxide clusters have the most stable stoichiometric structures as demonstrated experimentally and theoretically. A number of oxygen-deficient vanadium oxide clusters (VO, VO₂, VO₃, VO₄, VO₅, VO₆, VO₇, VO₈, VO₁₀, VO₁₁, and VO₁₂) are observed in the cluster distribution. They are missing one or two oxygen atoms compared to the most stable clusters, and present a tendency to become the most stable clusters by reacting with O or O₂. Some oxygen-rich clusters (VO₃, VO₄, etc.) are also observed in the mass spectra. They have one or more oxygen atoms compared to the most stable clusters and present a tendency to lose O or O₂ and become the most stable clusters. Additionally, one can find that these oxygen-rich neutral vanadium oxide clusters are always present with one or more attached hydrogen atoms, such as VO₂H₂, VO₃H₂, VO₄H₂, etc. The TOFMS signals are often more intense than their pure VnOₙ counterpart signals. For the most stable vanadium oxide clusters (except VO₂), the hydrogen-containing cluster signals are smaller than 5% of the metal oxide cluster signals; and for oxygen-deficient clusters, no hydrogen-containing cluster signals are observed in the VnOₙ cluster distribution.

B. Reactions of VnOₙ Clusters with CH₃OH. To study the reactions of neutral VnOₙ clusters with methanol, mixed CH₃OH/He gas is pulsed into the reactor at a pressure of 15 psi. When the neutral vanadium oxide clusters generated from the ablation/expansion source pass through the reactor cell, collisions will occur between neutral VnOₙ clusters and CH₃OH molecules. Reaction products and the remnant neutral VnOₙ clusters are detected by a 26.5 eV laser ionization. As shown in Figure 1, several kinds of main products are identified for the reactions VnOₙ + CH₃OH.

First, association products, VO(CH₃OH)₁₋₂, VO₂(CH₃OH)₁₋₂, VO₃(CH₃OH)₁₋₂, VO₄(CH₃OH)₁₋₂, and VO₅(CH₃OH)₂, are observed and they are generated from association reactions. Hydrogen transfer may occur between VnOₙ and CH₃OH in these association complexes. Second, a series of products VOH,
VO₂H₂, VO₂H, VO₂H₂, V₂O₃H₂, V₂O₃H, V₂O₄H, and V₂O₃H₀₁₂ are identified in the mass spectra. They can be distinguished in the mass spectra of Figure 1. V₅O₃H₀₁₂, VO₂H₁₂, V₂O₃H₁₂, and V₂O₄H₁₂ are identified for the clusters with the most stable stoichiometry (VO₂, VO₂O, VO₂O₂, and VO₂O₂). Oxygen-rich vanadium oxide clusters (VO₂, VO₂O, VO₂O₂, etc.) can extract more than one hydrogen atom from methanol to form clusters, such as VO₂H₂, VO₂O₂H₂, and VO₂O₂H₂, (Figure 1). Any trace of H₂O, hydrocarbons, H₂, etc., absorbed in or on the metal, or surface OH in the experimental system can be a hydrogen source due to the high reactivity of oxygen-rich clusters, in general. The mechanisms for these reactions and the number of involved methanol molecules required for product generation are discussed below.

The third variety of products observed in V₅O₃ + CH₃OH reactions is V₅O₃(CH₃OH)₀₁₂ for example, V₂O₃CH₃O, V₂O₃(CH₃OH)CH₂O, V₂O₃CH₃O, VO₂(CH₃OH)CH₂O, VO₂(CH₃OH)CH₂O, etc. These species can be generated from dehydrogenation or dehydration reactions. The product V₅O₃CH₃O can also be formulated as the isobaric cluster V₅O₃(CH₃)₂ for example, VO₂CH₃O has the same mass number as VO₂(CH₃)₂, and similar isobaric pairs can be noted for VO₂CH₃O/VO₂CH₃O, VO₂CH₃O/VO₂CH₃O, VO₂CH₃O/VO₂CH₃O, etc. (shown in Figure 1). They are considered to be the fourth type of product in V₅O₃ + CH₃OH reactions. V₅O₃(CH₃)₂ is generated from a dehydrogenation reaction between V₅O₃ and two CH₃OH. Additionally, some minor products VO₂CH₃O, VO₂(CH₃OH)CH₂O, VO₂O₂CH₃O, and VO₂O₂CH₃O are detected in the mass spectrum of Figure 1. We will discuss reaction mechanisms in detail in the Discussion section for these reaction products.

Methanol clusters are easily formed in the molecular beam, so a weak signal of the (CH₃OH)₂ dimer relative to CH₃OH signal is detected (Figure 1) when the gas mixture CH₃OH/He is pulsed into the reactor tube. The huge signal for CH₃OH is truncated by adjusting the timing of the MCP detector turn on to prevent detector circuit overload and saturation. One knows that the (CH₃OH)₂⁺⁺ signal is always observed after the ionization of the neutral trimer (CH₃OH)₁₂ so no observation of protonated (CH₃OH)₂⁺⁺ (n ≥ 2) in the mass spectrum indicates that methanol clusters are not prevalent under these experimental conditions. Therefore, reactions between V₅O₃ and methanol clusters can be neglected in our experiments.

The reaction of V₅O₃ + CH₃OH is also studied using 118 nm laser ionization. As shown in Figure 2, most of the products observed are similar to those detected by 26.5 eV soft X-ray laser ionization shown in Figure 1b. Distinguishing the mass spectra of Figure 1: V₅O₃CH₃O have the same mass number as V₅O₃(CH₃)₂, and VO(CH₃OH)₂ has the same mass number as VO(CH₃OH)₂ since the mass number of CH₃OH is equal to molecular O₂. Therefore, the reaction channels for V₅O₃ + CH₃OH reactions cannot be completely resolved in the mass spectra of Figure 1. In order to distinguish the isomers produced in the reactions of V₅O₃ + CH₃OH, deuterated methanol (CD₃OH) is employed in the reaction mixture instead of CH₃OH. Figure 3, a, b, and c, presents the mass spectra obtained under the same experimental conditions as described above except CD₃OH is substituted for CH₃OH. Products VOCOD₃OH, V₂OCOD₃OH, V₂OCOD₃OH, V₂OCOD₃OH, and VOCOD₃OH are assigned to association products between V₅O₃ and CD₃OH. In the experiments with CD₃OH, no significant peaks at V₅O₃H, V₅O₃H, V₅O₃H, and VO₃H are observed (see Figure 3c). VOH is, however, observed. These VO₃H signals can be distinguished from their neighbor VO₂O, VO₂O, and VO₂O signals even though they partly overlap each other. One mass unit can readily be resolved between V₂O₃D and V₂O₃D, V₂O₃D, and V₂O₃D, and V₂O₃D are identified as the major products of hydrogen-abstraction reactions for oxygen-deficient vanadium oxide clusters reacting with CD₃OH, while V₂O₃D and V₂O₃D and V₂O₃D are identified as the major products of hydrogen-abstraction reactions for oxygen-deficient vanadium oxide clusters reacting with CD₃OH. In addition, isotopic scrambling for reaction products can be neglected in our experiments because only products of one D attached to oxygen-deficient vanadium oxide clusters (V₂O₃D) are observed in the reaction V₅O₃ + CD₃OH; otherwise, one should observe the products of both D and H atom attached to oxygen-deficient clusters just as reaction products observed for the most stable vanadium oxide clusters (V₂O₃H, V₂O₃D, and V₂O₃HD).

In the reactions of V₅O₃ + CH₃OH, isobaric products V₂O₃CH₃O and V₂O₃CH₃O have the same mass number (in Figure 1); however, they can be distinguished as two separated products V₅O₃CD₃D and V₅O₃CD₃D with different mass numbers for V₅O₃ and CD₃OH reactions. Both VOCD₃D and VOD(CD₃)D are observed, while only VO₂D(CD₃)D, VO₂D(CD₃)D, V₂O₃D(CD₃)D, V₅O₃D(CD₃)D, and V₅O₃D(CD₃)D are observed (see...
Figure 3). Products VO$_2$(CH$_3$)$_2$, VO$_3$(CH$_3$)$_2$, V$_2$O$_5$(CH$_3$)$_2$, V$_3$O$_7$(CH$_3$)$_2$, and V$_3$O$_8$(CH$_3$)$_2$ rather than VO$_2$CH$_2$O, VO$_2$CH$_2$O, V$_2$O$_5$CH$_2$O, V$_3$O$_7$CH$_2$O, and V$_3$O$_7$CH$_2$O are thus confirmed for the reactions $V_mO_n$ + CH$_3$OH. $V_mO_n$(CH$_3$)$_2$ can be generated from multiple alcohol molecules reactions with $V_mO_n$ clusters.

Assigned vanadium oxide clusters and their reaction products with CH$_3$OH and CD$_3$OH are listed in Table 1.

D. Reactions of $V_mO_n$ Clusters with C$_2$H$_5$OH. Another alcohol compound, ethanol C$_2$H$_5$OH, is also used as a reactant with $V_mO_n$ clusters. When C$_2$H$_5$OH/He gas is added to the reactor, many new product signals are observed in the mass spectra associated with reactions between $V_mO_n$ and C$_2$H$_5$OH. As shown in Figure 4, the major products observed are association adducts $V_mO_n$(C$_2$H$_5$OH)$_n$, implying that different reaction mechanisms must be responsible for $V_mO_n$ cluster reacting with CH$_3$OH and reacting with C$_2$H$_5$OH.

E. DFT Calculations of VO$_2$ + CH$_3$OH and VO + CH$_3$OH Reactions. In order to explore the reaction mechanisms for the above described chemistry, we perform DFT calculation for the reaction of VO$_2$ + CH$_3$OH. Several possible reaction pathways are considered as follows:

\[
\begin{align*}
\text{VO}_2 + \text{CH}_3\text{OH} &\rightarrow \text{HVO}_2\text{H} + \text{CH}_3\text{O} & \Delta H_{298} = -0.69 \text{ eV} \\
&\rightarrow \text{HOVOH} + \text{CH}_2\text{O} & \Delta H_{298} = -0.60 \text{ eV} \\
&\rightarrow \text{OVOCH}_2 + \text{H}_2\text{O} & \Delta H_{298} = -0.32 \text{ eV} \\
&\rightarrow \text{VO}_2\text{CH}_2 + \text{H}_2\text{O} & \Delta H_{298} = +0.6 \text{ eV} \\
&\rightarrow \text{VO}_2\text{CH}_2\text{O} + \text{H}_2 & \Delta H_{298} = -0.51 \text{ eV}
\end{align*}
\]

Figure 5 displays the potential surface for reaction 1 and optimized geometries of reaction intermediates and transition states. Two possible channels are found for dehydrogenation reaction to generate products CH$_2$O + HVO$_2$H (P1):

\[
\begin{align*}
R1 &\rightarrow \text{IM1} \rightarrow \text{ts1/2} \rightarrow \text{IM2} \rightarrow \text{ts2/3} \rightarrow \text{IM3} \rightarrow \text{P1} & \text{(channel Ia)} \\
R1 &\rightarrow \text{IM1} \rightarrow \text{ts1/4} \rightarrow \text{IM4}_1 \rightarrow \text{ts4} \rightarrow \text{IM4}_2 \rightarrow \text{ts4/3} \rightarrow \text{IM3} \rightarrow \text{P1} & \text{(channel Ib)}
\end{align*}
\]

The reactions of VO$_2$ with CH$_3$OH start with the formation of adduct complex IM1, in which O atom of CH$_3$OH connect to V atom of VO$_2$. In channel Ia, first H atom transfers from OH to an O atom of VO$_2$ to form IM2, which is the most stable structure on this potential surface. The second H atom transfer from the CH$_3$ moiety to the VO$_2$ occurs to form IM3 via transition state ts2/3. In structure IM3, the length of the C−V bond is increased, leading to generation of final products P1 (CH$_2$O + HVO$_2$H), in which the two H atoms connect with V and O atoms. In channel Ib, the first H atom transfers from the CH$_3$ group to an O atom of VO$_2$ to form intermediate IM4$_1$, and then the structure changes to isomeric IM4$_2$. The second H atom transfers from the OH moiety to the V atom of the VO$_2$ cluster to form IM3 through transition state ts4/3 with a small positive barrier of about 0.05 eV. Comparison of these two reaction channels, evidence that channel Ia, in which the first H atom transfers from the OH moiety to the VO$_2$, is more favorable than channel Ib, in which the first H atom transfers from the CH$_3$ moiety to the VO$_2$. In addition, the final product CH$_2$O can also dissociate to CO + H$_2$ because the energy of CO + H$_2$ is close to CH$_2$O; however, the dissociation barrier for the

Figure 3. Reactions of $V_mO_n$ clusters with CD$_3$OH studied by 26.5 eV soft X-ray laser ionization. The mass spectrum is obtained under the same experimental conditions as given in Figure 1 except that CD$_3$OH is substituted for CH$_3$OH. Expanded mass regions around different size clusters are shown in (a), (b), and (c).
reaction \( \text{CH}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \) is high, ca. 90 kcal/mol (~4 eV). Therefore, the reaction \( \text{VO}_2 + \text{CH}_3\text{OH} \rightarrow \text{HVO}_2\text{H} + \text{CO} + \text{H}_2 \) cannot occur at room temperature.

Different reaction products, \( \text{P}_2 \) (HOVOH + CH\(_2\)O), can be generated in channel II as follows,

\[
\text{IM}_1 \rightarrow \text{IM}_2/\text{IM}_3 \rightarrow \text{IM}_4/\text{IM}_5 \rightarrow \text{IM}_6 \rightarrow \text{IM}_7 (\text{channel II})
\]

In this reaction channel, first an H atom transfers from the CH\(_3\) to an O atom of VO\(_2\) just as described above for channel Ib; but the second H atom transfers from the OH to another O atom of VO\(_2\) to form \( \text{IM}_5 \). To form the reaction product \( \text{P}_2 \), two H atoms bond to different two O atoms. This channel is also thermodynamically available overall barrierless at room temperature.

![Figure 4](image-url)  
**Figure 4.** Reactions of \( \text{V}_{n}\text{O}_n \) clusters with \( \text{C}_2\text{H}_5\text{OH} \) studied by 26.5 eV soft X-ray laser ionization. The lower spectrum displays the \( \text{V}_{n}\text{O}_n \) cluster distribution; the upper spectrum displays the new cluster distribution and products for the reaction \( \text{V}_{n}\text{O}_n + \text{C}_2\text{H}_5\text{OH} \) after \( \text{C}_2\text{H}_5\text{OH}/\text{He} \) is added to the fast flow reactor.

![Figure 5](image-url)  
**Figure 5.** DFT calculated potential energy surface for the reaction \( \text{VO}_2 + \text{CH}_3\text{OH} \) at the theory level B3LYP/TZVP. Structures are the optimized geometries of the reaction intermediates and transition states. Relative energies are in eV.

<table>
<thead>
<tr>
<th>( \text{V}_{n}\text{O}_n )</th>
<th>( \text{V}_{n}\text{O}_n + \text{CH}_3\text{OH(M)} )</th>
<th>( \text{V}_{n}\text{O}_n + \text{CD}_3\text{OH(M)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{VO} )</td>
<td>( \text{VOH} )</td>
<td>( \text{VOH, VOD} )</td>
</tr>
<tr>
<td>( \text{VOC}\text{H}_2\text{O(VOC}\text{H}_2\text{O}) )</td>
<td>( \text{VOC}\text{D}_2\text{O} )</td>
<td>( \text{VOC}\text{D}_2\text{O} )</td>
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<td>( \text{VO}_2 )</td>
<td>( \text{VO}_2\text{H, VO}_2\text{H}_2 )</td>
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<td>( \text{VOC}\text{H}_2\text{O(VOC}\text{H}_2\text{O}) )</td>
<td>( \text{VOC}\text{D}_2\text{O} )</td>
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<td>( \text{VO}_2\text{H, VO}_2\text{H}_2 )</td>
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<td>( \text{VO}_2\text{H, VO}_2\text{H}_2 )</td>
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**TABLE 1:** Observed Primary Neutral Vanadium Oxide Clusters and Their Reaction Products with \( \text{CH}_3\text{OH} \) and \( \text{CD}_3\text{OH} \) Based on Figures 1 and 3
Reactions of Neutral VₙOₙ Clusters with CH₃OH

In the potential surface for VO₂ + CH₃OH reactions (Figure 5), two dehydration reaction channels can be calculated as follows:

R1 → IM1 → ts1/4 → IM4_1 → ts4 → IM4_2 → ts4/7 → IM7 → P3 (channel III)

R1 → IM1 → ts1/2 → IM2 → ts2/3 → IM3 → ts3/8 → IM8 → P4 (channel IV)

In channel III, the H atom of the CH₃ moiety transfers to an O atom of VO₂ for the first step. After a structural rearrangement (IM4_1 → ts4 → IM4_2), the second H atom transfers from the OH moiety to the same O atom to form intermediate IM7, in which the H₂O moiety is weakly bonded to the remainder of the cluster, finally leading to form products H₂O and OVOCH₂ (P3). In product OVOCH₂, an O atom is a bridge bond between V and C atoms. In channel IV, the first H atom transfers from the OH to an O atom of VO₂ without a barrier. The second H (CH₃) atom transfer has a barrier of about 0.15 eV, and the potential energy of P4 (VO₂CH₂ + H₂O) is higher than that of initial reactants by 0.64 eV. Therefore, channel IV is a high-temperature reaction channel.

On the VO₂ cluster, a dehydrogenation reaction with CH₃OH is also overall barrierless and thermodynamically available at a room temperature as channel V in Figure 5:

R1 → IM1 → ts1/2 → IM2 → ts2/3 → IM3 → ts3/9 → IM9 → P5 (channel V)

on this pathway, the hydrogen atoms transfer from the CH₃ and OH moieties to the V atom of the VO₂ cluster, leading to form H₂ + VO₂CH₂ (P5) products.

The calculation for VO₂ may not be a perfect demonstration of reaction mechanisms for all the vanadium oxide clusters; however, this does indicate that the same reaction may occur on other larger stable clusters, in which VO₂ is considered a building block; such clusters include V₂O₄, V₂O₅, V₃O₇, etc. Analogous reaction products are observed in the mass spectra for these larger stable vanadium oxide clusters as well.

Calculational results indicate that hydrogen abstraction (channel I and channel II), dehydration (channel III), and hydrogen elimination (channel V) reactions are thermodynamically favorable and overall barrierless for the VO₂ + CH₃OH reaction. All these reaction products, such as VO₂H₂, OVOCH₂, and VO₂CH₂O, are detected in the experiments: thus, calculational results are in good agreement with experimental observations.

The potential surface on the dehydrogenation reaction between VO and CH₃OH

\[
\text{VO} + \text{CH}_3\text{OH} \rightarrow \text{VOCH}_2\text{O} + \text{H}_2 \quad \Delta H_{298} = -2.07 \text{ eV} \tag{2}
\]

is explored and displayed in Figure 6. Two possible reaction channels are found as follows:

R2 → IM10 → ts10/13 → IM13 → ts13/14 → IM14 → ts14/12 → IM12 → P6 (channel VI)

In channel VI, VO bonds with CH₃OH by a C–V bond to form association complex IM10, and then first an H atom transfers from OH to the V atom of VO to form IM11, which is the most stable intermediate structure on the potential surface. Second, an H atom transfers from the CH₃ moiety to the V atom again leading to IM12 formation. Finally, H₂ leaves the complex species to generate reaction product P6 (VOCH₂ + H₂). In channel VII, the first H transfers from CH₃ moiety to the VO to form IM13, and then the H atom of OH transfers to the V atom. Both channel VI and channel VII can occur overall barrierlessly at room temperature. Based on DFT calculations, the hydrogen elimination reaction between VO and CH₃OH is thermodynamically available and overall barrierless: this is consistent the experimental observation of product OVOCH₂ in the mass spectrum (Figures 1a and 2a).

IV. Discussion

A. Comparison between 26.5 and 10.5 eV Ionization. In the present work, a 26.5 eV (46.9 nm) soft X-ray laser is employed to ionize vanadium oxide clusters and their reaction products with methanol and ethanol. The high single-photon energy might possibly fragment/photodissociate neutral clusters or their reaction products during the ionization process and thereby confuse the identification of ground-state neutral species chemistry. In order to clarify this issue, a comparison experiment is done in which both a 10.5 and a 26.5 eV laser are used for ionization in the study of VₙOₙ cluster reactions with CH₃OH.

![Figure 6. DFT calculated potential energy surface for the reaction VO + CH₃OH → OVOCH₂ + H₂ at the theory level B3LYP/TZVP. Structures are the optimized geometries of the reaction intermediates and transition states. Relative energies are in eV.](image-url)
Near threshold single-photon ionization using a 10.5 eV laser photon does not leave enough excess energy in the clusters to fragment any vanadium oxide cluster or break any chemical bonds of the reaction products following ionization of the neutral species. Comparing Figure 1b (26.5 eV ionization) and Figure 2 (10.5 eV ionization), one notes that the reaction products present are almost the same. Our conclusion is that the fragmentation or photodissociation of neutral vanadium oxide clusters and their reaction products caused by a single 26.5 eV photon is virtually not present in these experiments, as is well documented in ref 32a for Nb, Ta, and V samples at both 26.5 and 10.5 eV ionization energies. In our previous work, we have found that the distribution of neutral V4O9 is nearly the same using either method for ionization, with the exception that some oxygen-rich clusters with high ionization energies (>10.5 eV) cannot be detected by 10.5 eV photon ionization. The reason we prefer to use 26.5 eV laser as the ionization source is that it can ionize all the metal oxide clusters generated in the expansion/ablation source and all reaction products generated in the reactor. For example, V2O2H2 is detected by a 26.5 eV laser as shown in Figure 1b but cannot be detected by a 10.5 eV laser (see Figure 2). Additionally, the signal intensity of metal oxide clusters and their reaction product detected by a 26.5 eV laser as shown in Figure 1b but cannot be detected by a 10.5 eV laser. 26.5 eV ionization offers more opportunities to explore large and oxygen-rich clusters and their reactions so that a general mechanism for the reactions of total cluster distribution can be explored.

B. Rate Constants for VmOx Clusters Reacting with CH3OH. As shown in Figure 1, the decay fractions (I0 – I)n/I0 of the VmOx signals in the reactions with CH3OH are 0.3 (VO), 0.56 (VO2), 0.66 (VO3), 0.5 (V2O4), 0.56 (V2O5), 0.81 (V3O6), 0.38 (V3O7), and 0.86 (V4O10), respectively. I0 and I are the intensities of VmOx signal before and after reaction with CH3OH, respectively. The decrease of the signals caused by collisions with He and reactant CH3OH is estimated as 50% based on the signal changes of V2O5, V3O clusters etc. (see Figure 1), which have almost no reactions with CH3OH molecules. Under the experimental conditions, such as estimated CH3OH partial gas pressure (~0.15 torr) and reaction time (~50 µs), the pseudo-first-order rate constants k (ln(I/I0) = –kt) are the concentrations of reactant in the reactor 22b,33b of VmOx + CH3OH reactions are calculated as 1.3 × 10−12 (VO), 3.1 × 10−12 (VO2), 4.1 × 10−12 (VO3), 2.6 × 10−12 (V2O4), 3.1 × 10−12 (V2O5), 6.3 × 10−12 (V3O6), 1.8 × 10−12 (V3O7), and 7.4 × 10−12 (V4O10) cm3 s−1. These data indicate that the stable neutral clusters V2O5, V3O7, and V4O10 are more active with CH3OH than are the oxygen-deficient clusters VO, V2O3, and V4O10. Bell and co-workers 5 experimentally and theoretically studied selective oxidation of methanol to formaldehyde on silica supported vanadium oxide. They find that the apparent activation energies for formaldehyde formation are 24.3 kcal/mol (theoretical calculation) and 23 kcal/mol (experimental measurement). The pre-exponential factors for the apparent first-order rate coefficients are 4.0 × 107 atm−1 s−1 (1.5 × 10−12 cm3 s−1) by theoretical calculation and 1.9 × 107 atm−1 s−1 (0.7 × 10−12 cm3 s−1) by experimental measurement. If one suppresses the barrier (∆E = 0) for the reaction in the condensed phase, the apparent rate constant is equal to the pre-exponential factor, yielding limiting rate constant for the reaction (k = k0 exp(−∆E/RT); if ∆E = 0, k = k0). Note that for neutral VmOx clusters reacting with CH3OH obtained in the gas phase, the rate constants are also ~10−12 cm3 s−1 and are similar to those found for the condensed phase.

C. Reactions of VmOx + CH3OH/CD3OH. Reactions of neutral vanadium oxide clusters with methanol in a fast-flow reactor are investigated by time-of-flight mass spectrometry coupled with single photon ionization at 26.5 eV. Several kinds of reaction channels can be identified for VmOx + CH3OH/CD3OH reactions. The details of these mechanisms are discussed for each type of reaction.

Association Reactions. Association reactions are found to be one of the main reaction channels for vanadium oxide clusters reacting with methanol. Association products VmOxCH3OH are detected for most of the vanadium oxide clusters. These association reactions are surely stabilized by collisions in the reactor, most likely with He gas, but also other species. On the basis of our calculations as shown in Figure 5, the most stable structure for the association complex VO2CH3OH is the structure of intermediate IM2, in which one H atom transfers from the CH3 moiety to an O atom of VO2. For the VOCH3OH complex, the H atom transfers from the OH moiety to the V atom to form the most stable structure IM11 (Figure 6). For the larger clusters, the structure of association products will be more complicated, so we simply use VmOxCH3OH to represent the association reaction products.

As shown in Figure 1, complexes VOCH3OH, VO2CH3OH, V2O4CH3OH, V3O6CH3OH, V4O10CH3OH, etc. are observed as products of the reaction of VmOx + CH3OH. In the reaction with unlabeled methanol CH3OH, the mass difference ∆m = 32 can correspond to CH3OH or O2 in the mass spectrum. For example, V2O4CH3OH can also be assigned to VO2; however, these isobars can be distinguished in the reaction of V6O10 with deuterium-labeled methanol CD3OH. Under the present experimental conditions, almost all VmOx clusters can associate with methanol to form VmOxCH3OH. In addition, we also find that methanol molecules do not associate with neutral Zr6O10 oxide clusters. Moreover, methanol molecules only tend to associate with the most stable and oxygen-rich Nb6O10 and Ta6O10 clusters, unlike for the present case in which almost all VmOx clusters tend to associate with CH3OH. These experimental results suggest that methanol molecules can be readily adsorbed on neutral vanadium oxide clusters. These experimental results imply that, in the condensed phase, methanol molecules will be readily adsorbed onto the surface of a vanadium oxide catalyst and that this behavior is not necessarily universal with respect to all surfaces and/or molecules.

Hydrogen Abstraction Reactions. The abstraction of hydro- gen atoms from CH3OH to form VmOxH1,2, occurs for almost all neutral vanadium oxide clusters as shown in Figure 1. Note that products with only one H atom (VOH, V2O3H, V3O6H, and V4O10H1) are observed for oxygen-deficient clusters (VO, V2O3, V3O6, and V4O10), while products with one or two H atoms (V2O3H1,2, V3O6H1,2, V3O6H1,2, and V4O10H1,2) are observed for the most stable clusters (VO2, V3O7, V4O10, and V4O10).

Abstraction of two H atoms from CH3OH will lead to a CH2O (formaldehyde) product. Unfortunately, we cannot detect the neutral CH2O product in our experiments since a strong CH2O− signal appears in the mass spectrum due to photodissociation of CH3OH by the 26.5 eV photons. Hydrogen abstraction reactions involve C−H and/or O−H cleavage of CH3OH. The reaction mechanisms can be revealed in labeling experiments with CD3OH since the cleavage of C−D or O−H will yield distinguishable products through mass spectrometry. For the reaction products V2O3H2, two hydrogen atoms may be abstracted from one or two methanol molecules. Of course, the same issues arise for mass-selected cluster ion reactions in a
Reactions of Neutral $V_{n}O_{m}$ Clusters with CH$_3$OH

fast-flow reactor. Based on DFT calculations, the reaction for $VO_2$ abstracting two hydrogen atoms from two methanol molecules is not thermodynamically favorable,

$$VO_2 + 2CH_3OH \rightarrow VO_2H_2 + 2CH_3OH/OCH_3 \Delta H_{298} = +2.6 \text{ eV}/2.9 \text{ eV} \quad (3)$$

Therefore, for $V_{n}O_{m}$ clusters, the abstraction of two hydrogen atoms from two methanol molecules should not be a major concern for the present study.

Figure 5 displays the mechanism for a hydrogen abstraction reaction between $VO_2$ and CH$_3$OH (reaction 1) generated through DFT calculations. Calculational results indicate that, for the stable cluster $VO_2$, abstraction of two H atoms from CH$_3$OH is a thermodynamically favorable reaction that is overall barrierless as shown in channel I. Hydrogen-transfer processes have no barrier no matter which H atom of CH$_3$ or OH moiety transfers first. For the oxygen-deficient cluster $V_{2}O_{3}$, abstraction of two H atoms from the CH$_3$OH molecule (reaction 4) is not a thermodynamic available reaction at room temperature:

$$V_{2}O_{3} + CH_3OH \rightarrow V_{2}O_{3}H_2 + CH_3O \Delta H_{298} = +0.44 \text{ eV} \quad (4)$$

Therefore, the reaction products $VO_2$H, $V_2O_3$D, etc. are observed for stable vanadium oxide clusters (VO$_2$, V$_2$O$_5$, V$_3$O$_7$, etc.), but no products $V_2O_3$D, $V_3O_7$HD etc. are observed for oxygen-deficient clusters (V$_2$O$_5$, V$_3$O$_7$, etc.).

As shown in Figure 3 for oxygen-deficient clusters, observed products of hydrogen abstraction reactions are dominated by $VOD$, $V_2O_3D$, and $V_2O_5D$ etc., employing CD$_3$OH in labeling experiments. This indicates that the abstracted hydrogen is derived from the CH$_3$ moiety of CD$_3$OH, and the concomitant product is CD$_2$OH. For the most stable vanadium oxide clusters, the products $VO_2H$, $VO_2D$, $VO_3H$, $VO_3D$, $V_2O_5H$, $V_2O_5D$, $V_3O_7H$, etc. are observed in labeling experiments, revealing that abstracted hydrogen atoms come from both CD$_3$ and OH units of methanol even though the O–H bond (104.4 kcal/mol$^{45}$) is stronger than the C–H bond (94 kcal/mol$^{45}$). Note that the signal intensities for $VO_2H$, $V_2O_3H$, and $V_3O_7H$ are close to those for $VO_2D$, $V_2O_5D$, and $V_3O_7D$, while only $V_2O_5D$ and $V_2O_3D$ signals are observed (Figure 3, CD$_3$OH experiment). This implies that these hydrogen abstraction reactions are controlled by a dynamic mechanism on the reaction potential energy surface and not by a kinetic or statistical process, governed by the concentration ratio of D to H in CD$_3$OH.

Based on our calculations, abstracting one H atom from the CH$_3$OH molecule is not a thermodynamically available reaction for VO$_2$ or $V_2O_3$ clusters at room temperature,

$$VO_2 + CH_3OH \rightarrow VO_2H + OCH_3 \quad \Delta H_{298} = +1.47 \text{ eV} \quad (5a)$$

$$V_2O_3 + CH_3OH \rightarrow V_2O_3H + OCH_3 \quad \Delta H_{298} = +1.35 \text{ eV} \quad (5b)$$

Note that some $V_{n}O_{m}$CH$_3$ products are observed in the mass spectra, for example, VO$_2$CH$_3$ ($V_2O_3CD_3$), $V_2$O$_3$CH$_3$ ($V_3O_7CD_3$), $V_2$O$_5$CH$_3$ ($V_2O_5CD_3$), and $V_3$O$_7$CH$_3$ ($V_3O_7CD_3$). These products may be generated from the reactions of

$$2V_{m}O_{n} + CH_3OH \rightarrow V_{m}O_{n+1}H + V_{m}O_{n}CH_3 \quad (6a)$$

$$2V_{m}O_{n} + CH_3OH \rightarrow V_{m}O_{n+1}H + V_{m}O_{n}CH_3 \quad (6b)$$

Therefore, these $V_{n}O_{m}$H/$V_{n}O_{m}$D reaction products must be generated from multiple molecular reactions between $V_{n}O_{m}$ clusters and methanol molecules. We estimate that about 100 collisions occur between a $V_{n}O_{m}$ cluster and methanol molecules in the fast flow cell reactor. Additionally, in the studies of $V_{n}O_{m}$ clusters reacting with methanol, we find that oxygen-deficient Nb$_2$O$_6$, and Ta$_2$O$_6$ clusters are not able to abstract H atom from CH$_3$OH to generate Nb$_2$O$_6$H$_{1,2}$ or Ta$_2$O$_6$H$_{1,2}$ products.

Oxygen-rich vanadium oxide clusters are documented to be very active in attaching H atoms from any hydrogen source (H$_2$O, hydrocarbons, etc.) in a high-vacuum system. Consequently, hydrogen-attached oxygen-rich vanadium oxide clusters ($V_2O_6H_{1,2}$, $V_3O_8H_{1,2}$, etc.) are always observed in the distribution of neutral vanadium oxide clusters; however, this is not true for all metal oxide clusters we have studied.$^{33c}$ The results of the present study indicate that generation of CH$_2$O (formaldehyde) through the abstraction of two H atoms (dehydrogenation) from one CH$_3$OH molecule can only occur on oxygen-rich and stable vanadium oxide clusters, and not on oxygen-deficient clusters.

The study of gas-phase cluster reactions can generate significant insight into condensed-phase elementary reaction steps (mechanisms and potential energy surfaces) for catalytic processes because clusters have relatively well-defined structures and size-dependent properties, and are readily accessible by theory. In the present study of neutral vanadium oxide cluster reactions with methanol, one finds: (1) the oxygen-deficient $V_{n}O_{m}$ clusters ($VO_2$, $V_2O_5$, $V_3O_7$, etc.) can abstract only one hydrogen atom from CH$_3$OH molecules to form $V_{n}O_{m}$H (VOH, $V_2O_5H$, $V_3O_7H$, etc.) products; (2) the stable $V_{n}O_{m}$ clusters ($VO_2$, $V_2O_4$, $V_2O_5$, $V_3O_7$) abstract more than one hydrogen atom from CH$_3$OH to form $V_{n}O_{m}$H$_{1,2}$ products; and (3) oxygen-rich $V_{n}O_{m}$ clusters ($VO_3$, $V_2O_6$, $V_3O_8$, etc.) can abstract more than one H atom from any hydrogen source in a high-vacuum system. DFT calculations show that for the VO$_2$ cluster, abstraction of two H atoms from CH$_3$OH to generate the formaldehyde product is thermodynamically favorable and overall barrierless; nonetheless, such a reaction is not thermodynamically available for the oxygen-deficient cluster $V_2O_5$ (reaction 4). Experimental and theoretical results suggest that, in the condensed phase, an oxygen-rich surface of a vanadium oxide catalyst will be able to generate a formaldehyde (H$_2$CO) product.

Methanol is one of the most important chemical intermediates used in industrial chemistry. Formaldehyde (H$_2$CO) is the major product in selective oxidation of methanol on supported vanadium oxide catalysts.$^{5,6}$ A catalytic cycle of CH$_3$OH oxidation to H$_2$CO and H$_2$O on VO$_2$ can be suggested based on our experiments and theoretical calculations. Thus, even though these gas-phase results are not necessarily specific to a complete reaction cycle, one can still suggest a mechanism for a catalytic condensed-phase process, as presented in Scheme 1.

In this catalytic cycle, the first step is the abstraction of two H atoms from CH$_3$OH by a VO$_2$ cluster or site to form products H$_2$CO (formaldehyde) and HVO$_2$H (reaction 1a). On the basis of our calculations, this process is a thermodynamically favorable and without a barrier (channel I and channel II, Figure 5). The reaction product HVO$_2$H is observed in mass spectrum
obtained for the $V_nO_m + CH_3OH$ reaction (see Figures 1 and 3). In the second step of this cycle, the regeneration part of the cycle, the intermediate $HVO_2H$ is oxidized by $O_2$ to generate products $H_2O$ and $VO_2$ as given in the exothermic reaction

$$HVO_2H + \frac{1}{2}O_2 \rightarrow VO_2 + H_2O \quad \Delta H_{298} = -1.3 \text{ eV}$$

(7)

The overall reaction of methanol oxidation by $O_2$ is thermodynamically available at room temperature:

$$CH_3OH + O_2 \rightarrow H_2O + CH_2O \quad \Delta H_{298} = -1.6 \text{ eV}$$

(8)

In this catalytic cycle, methanol is selectively oxidized to formaldehyde by a $VO_2$ cluster. Since the same reaction products $V_nO_m H_2$ are detected for other large, stable vanadium oxide clusters such as $V_2O_4$, $V_2O_5$, $V_3O_7$, etc., we deduce that the catalytic cycle for $VO_2$ will be available for all large, stable vanadium oxide clusters, and thus for the condensed phase for which such sites or surfaces may exist.

As pointed out above, the $VO_2 + CH_3OH$ reaction is thermodynamically favorable and overall barrierless based on our DFT calculations and experimental observations. Nonetheless, a significant barrier exits for selective oxidation of methanol on the supported vanadium oxide catalysts.\(^5\) Generation of formaldehyde through methanol oxidation on a vanadium oxide surface is a high-temperature reaction ($>600$ K). One can consider two reasons for this difference between the behavior of gas-phase clusters and condensed phase surfaces: (1) the metal oxide clusters generated in the gas phase can be considered more active radicals than condensed-phase surface species; (2) at high temperature, interaction between metal oxide molecules and the metal oxide and support materials results in more active sites in terms of oxygen-deficient and oxygen-rich sites and species. Additionally, the condensed-phase studies suggest that $V^{3+}$ and $V^{5+}$ sites are more active than $V^{3+}$ sites on the surface.\(^3\) Thus, both gas-phase clusters and condensed-phase surface studies suggest that an oxygen-rich rather than an oxygen-deficient surface of a vanadium oxide catalyst will be favorable for generation of a formaldehyde ($H_2CO$) product.

**Dehydration and Dehydrogenation Reactions.** As displayed in Figure 1, a series of new products is observed in the reactions between vanadium oxide clusters with $CH_3OH$. Each specific mass channel corresponds to two possible isobaric products: $VO_2CH_2O/VO_2(CH_3)OH$, $VO_3CH_2O/VO_3(CH_3)OH$, and $V_2O_5CH_2O/V_2O_5(CH_3)OH$, etc. These products are distinguished by isotopic labeling experiments ($CD_3 \leftrightarrow CH_3$). As shown in Figure 3, $VOCD_3$, $VOCD_2$, $VOC(CH_3)CD_2$, $VOC(CH_3)(CD_3)$, etc. are assigned as the dominant products, while only $OVD(OCD)$ and $O_2VCD_{2O}$ are observed at the low-mass region. These products can be generated from dehydration or dehydrogenation reactions through multiple molecular reactions; for example

$V_mO_n + 2CD_3OH \rightarrow V_mO_n(CD_3OH)_2 \rightarrow V_mO_{n+1}(CD_3)_2 + H_2O \ (9a)$

$V_mO_{n-1} + 2CD_3OH \rightarrow V_mO_{n-1}(CD_3OH)_2 \rightarrow V_mO_{n+1}(CD_3)_2 + H_2 \ (9b)$

The results of the labeling experiments demonstrate that eliminated $H_2O$ or $H_2$ in reactions 9a and 9b are taken from OH units of two $CD_3OH$ molecules, suggesting that two $CD_3OH$ molecules are first adsorbed on the appropriate vanadium oxide clusters, and then a dehydration (reaction 9a) or dehydrogenation (reaction 9b) reaction occurs involving two $CD_3OH$ molecules. Product $H_2O$ is obtained from the OH moieties of two $CH_3OH$ molecules, since all deuterium atoms are left on the clusters to generate $V_mO_{n}(CD_3)_2$. In the study of mass-selected $V_nO_m^{+}$ clusters,\(^22,23\) products $V_nO_{m-1}(CD_3O)_2$ are observed for $V_nO_m^{+}$ clusters.

Dehydration of $CH_3OH$ on vanadium oxide clusters must be very fast because almost no association products with two $CH_3OH/CD_3OH$ molecules are observed in the mass spectrum, even though dehydration products $V_nO_m(CD_3)_2$ are detected for most clusters reacting with $CD_3OH$. The structure of $VO_2(CH_3)_2$ is calculated as shown in Figure 7. In structure 1, two $CH_3$ moieties are connected to two $O$ atoms, respectively. This is more stable than structure 2, in which two $CH_3$ moieties are connected to one $O$ atom. For large $V_mO_n(CD_3)_2$, the structures are more complicated; however, we suggest that the structure with two $CH_3$ moieties is connected to two $O$ atoms of $V_nO_m$ will be the lowest-energy structure. Additionally, a secondary reaction, $V_nO_mCH_2O + CD_3OH \rightarrow V_nO_mCH_2O(CH_3OH)$, occurs so that products $VO_2CH_2O(CH_3OH)$ and $V_2O_5CH_2O(CH_3OH)$ are observed in the experiments.

In order to explore the mechanism of dehydration and dehydrogenation reactions of methanol on $V_mO_n$ clusters, DFT calculations are performed to study the reactions of $VO$ and $VO_2$ clusters with $CH_3OH$. Products $OVOCH_3$ ($OVOCD_2$) and $O_2VOCH_2$ ($O_2VOCD_2$) are observed in the reactions of $V_mO_n$ clusters with methanol as shown in Figures 1a and 3a. Product $OVOCH_2$ can be generated from two possible reactions: dehydration (1c) and/or dehydrogenation (2). Based on DFT calculations, both dehydration on the $VO_2$ cluster (reaction 1c) and dehydrogenation on the VO cluster (reaction 2) are thermodynamically available and overall barrierless (see Figures 5 and 6). The structure of $OVOCH_2$ can be found in P3 and P6. The dehydrogenation reaction of $CH_3OH$ is also favorable on $VO_2$ clusters as channel V. We suggest that dehydrogenation reactions of $CH_3OH$ on $V_nO_m$ clusters are thermodynamically favorable and overall barrierless. Note that $CH_3OH$ dissociation...
to generate CH₃O and H₂ is an endothermic reaction with a barrier of 3.9 eV.⁴⁶

**Comparison between V₊Oₙ Neutral and Ionic Cluster Reactions with CH₃OH.** A comprehensive investigation of V₊Oₙ⁺ cluster ion reactivity toward methanol has recently been reported by the Schwarz group.²³ Association reactions, dehydration reactions to generate formaldehyde, elimination reactions to form water and hydrogen, etc. are identified based on observation of reaction products. All these reactions and products for the V₊Oₙ⁺ cluster ions are also observed for the neutral V₊Oₙ cluster reactions with methanol in the present study. In the cluster ion studies, ref 23a reports that high-valent V₉O₁₂⁺, V₈O₁₀⁺, V₇O₈⁺, V₆O₆⁺, V₅O₄⁺⁺ clusters are more reactive with respect to formaldehyde formation than are the lower valent cluster ions (VO⁺, V₂O₅⁺, V₃O₄⁺⁺, V₄O₃⁺⁺, V₅O₂⁺⁺, V₆O₁⁺⁺). Similar behavior is also observed for neutral V₊Oₙ cluster reactions with CH₃OH: abstraction of two H atoms from CH₃OH to form formaldehyde only occurs on the clusters VO₂, V₂O₄, V₃O₆, V₄O₈, and V₅O₁₀, but does not occur on the clusters VO, V₂O₃, V₃O₅, etc. In addition, ref 23a finds that H₂ elimination reactions to generate V₊Oₙ(CH₃O)₂⁺ products only occur for small V₊Oₙ⁺ cluster ions (VO⁺, VO₂⁺⁺, etc.), similar to the present study findings that the reaction products VO₂CD₂O and VOCD₂O are the only detected ones for the V₊OₙCD₂O product generation. Some other products detected for the neutral V₊Oₙ clusters reacting with CH₃OH are different from the V₊Oₙ⁺ cluster ion reactions, such as VO₂H, V₉O₉(CH₃)₂, etc., which are generated from multiple molecular reactions between neutral V₊Oₙ clusters and methanol molecules in the fast flow reactor. Specific neutral clusters cannot be selected to react with chosen reactants, as done for cluster ion studies. Rate constants for V₊Oₙ⁺ cluster reactions with methanol are measured to be of the order of 10⁻¹² cm³ s⁻¹ which is about 10² times faster than those for neutral V₊Oₙ cluster reactions (~10⁻¹² cm³ s⁻¹) in the present study. Based on the DFT calculations, Sauer et al. conclude that V₊Oₙ⁺ cluster ions are much more reactive toward methanol than are neutral clusters.²⁷

**D. Reactions of V₊Oₙ + CH₃CH₂OH.** Ethanol (CH₃CH₂OH) is also used as a reactant to study the reactivity of V₊Oₙ clusters toward alcohols in general. As shown in Figure 3, association complexes V₉O₉(CH₃CH₂OH and V₈O₈(CH₃CH₂OH)H are the major products of V₈O₈ + CH₃CH₂OH reactions. V₈O₈⁺⁺ (CH₃CH₂OH)H product may be generated from hydrogen atom transfer reactions between two ethanol molecules following their association with a V₈O₈ cluster. Hydrogen abstraction products, such as VOH, VO²H, V₂O₃H, V₃O₄H, etc., observed in V₈O₈ + CH₃OH reactions are not observed for V₈O₈ + CH₃CH₂OH reactions. Moreover, no obvious product is generated from dehydration or dehydrogenation for V₈O₈ and CH₃CH₂OH reactions. A significant difference between CH₃OH and CH₃CH₂OH chemistry in reactions with V₈O₈ clusters is apparent. One plausible reason for failure to observe anything but adduct formation with ethanol is that larger molecule leads to a longer lifetime of the intermediates formed, thereby allowing more efficient collisional stabilization, so that dissociation products are not observed for vanadium oxide clusters reacting with ethanol.

**V. Conclusions**

The reactions of neutral vanadium oxide clusters with methanol and ethanol are investigated employing 26.5 eV soft X-ray laser and 10.5 eV nm laser ionization coupled with TOFMS. In the experiments, nearly identical reaction products are detected using 26.5 and 10.5 eV laser ionizations. We conclude that neutral vanadium oxide clusters and their reaction products are not fragmented or photodissociated by 26.5 eV photons. Three major reactions are identified for V₊Oₙ + CH₃OH/CD₃OH:

1. **Association reactions:** Association products V₈O₈CH₃OH are observed for most of vanadium oxide clusters in the experiments, indicating that methanol molecules are easily adsorbed on neutral vanadium oxide clusters. In the condensed phase, the surface of a vanadium oxide catalyst should easily absorb methanol molecules.

2. **Hydrogen abstraction reactions:** Oxygen-deficient vanadium oxide clusters (VO, V₂O₅, V₃O₇, etc.) can abstract only one hydrogen atom from a CH₃ unit of CH₃OH to form VOH, V₂O₅H, etc. products. The most stable vanadium oxide clusters (VO₂, V₂O₅, V₃O₇, etc.) can abstract more than one hydrogen atom from CH₃ and/or OH moiety of CH₃OH to form V₈O₉H₂ products. Oxygen-rich vanadium oxide clusters (V₈O₉, V₉O₁₀, etc.) can abstract more than one H atom from any kind of hydrogen source in a high-vacuum system. The experimental results indicate that abstraction of two H atoms from CH₃OH to generate a CH₂O (formaldehyde) product takes place on oxygen-rich and stable vanadium oxide clusters but not on oxygen-deficient vanadium oxide clusters. DFT calculational results support experimental observations that the reaction of VO₂ + CH₃OH → HOVOH/HVO₂H + H₂CO is thermodynamically favorable and overall barrierless; however, VO₂ + CH₃OH → V₂O₃H₂ + CH₂O is not a thermodynamically available reaction. Experimental and theoretical results suggest that, in the condensed phase, an oxygen-rich surface of a vanadium oxide catalyst will be able to generate a formaldehyde (H₂CO) product.

3. **Dehydration reactions:** Intense signals of VO₂(CD₃)₂, VO₂(CD₃)₂⁺, V₂O₅(CD₃)₂, V₂O₅(CD₃)₂⁺, and VO₃(CD₃)₂ are observed in the experiments, indicating that the dehydration reaction, V₈O₉ + 2CD₃OH → VO₂(CD₃)₂OH → V₈O₉(CD₃)₂H + H₂O, is one of the major reaction channels for the V₈O₉ reactions. A concomitant product H₂O is derived from the OH moieties of two methanol molecules. Dehydration of CH₃OH on vanadium oxide clusters must be very fast because almost no association products V₈O₉(CH₃OH)₂ are detected in the experiments. Additionally, products VOCH₃O (VOCD₂O) and VO₂CH₃O (VO₂CD₂O) are observed in the reaction of V₈O₉ clusters with CH₃OH (CD₃OH). They can be generated from reaction channels of dehydrogenation or dehydration. Based on the basis of our calculations, both of dehydrogenation and dehydration for VO + CH₃OH and VO₂ + CH₂OH reactions are thermodynamically available and without barriers at room temperature. An obviously different behavior is observed for V₈O₉ reactions with CH₃CH₂OH compared to CH₃OH. Association reactions are identified as the only major channel for the reaction of V₈O₉ with CH₃CH₂OH.

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**References and Notes**
