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C=C Bond Cleavage on Neutral $VO_3(V_2O_5)_n$ Clusters

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Abstract: The reactions of neutral vanadium oxide clusters with alkenes (ethylene, propylene, 1-butene, and 1,3-butadiene) are investigated by experiments and density function theory (DFT) calculations. Single photon ionization through extreme ultraviolet radiation (EUV, 46.9 nm, 26.5 eV) is used to detect neutral cluster distributions and reaction products. In the experiments, we observe products $(V_2O_5)_nVO_2CH_2$, $(V_2O_5)_nVO_2C_2H_4$, $(V_2O_5)_nVO_2C_3H_4$, and $(V_2O_5)_nVO_2C_3H_6$, for neural V_mO_n clusters in reactions with C_2H_4, C_3H_6, C_4H_6, and C_4H_8, respectively. The observation of these products indicates that the C=C bonds of alkenes can be broken on neutral oxygen rich vanadium oxide clusters with the general structure $VO_3(V_2O_5)_{n=0,1,2...}$. DFT calculations demonstrate that the reaction $VO_3 + C_3H_6 \rightarrow VO_2C_2H_4 + H_2CO$ is thermodynamically favorable and overall barrierless at room temperature. They also provide a mechanistic explanation for the general reaction in which the C=C double bond of alkenes is broken on $VO_3(V_2O_5)_{n=0,1,2...}$ clusters. A catalytic cycle for alkene oxidation on vanadium oxide is suggested based on our experimental and theoretical investigations. The reactions of V_mO_n with C_6H_6 and C_2F_4 are also investigated by experiments. The products $VO_2(V_2O_5)_nC_6H_4$ are observed for dehydration reactions between V_mO_n clusters and C_6H_6. No product is detected for V_mO_n clusters reacting with C_2F_4. The mechanisms of the reactions between VO_3 and C_2F_4/C_6H_6 are also investigated by calculations at the B3LYP/TZVP level.

I. Introduction

The oxidation of alkenes over supported metal oxide catalysts is a very important catalytic process in the chemical industry. For example, catalytic partial oxidation of propylene ($CH_2{=}CHCH_3$) produces acrolein (CH_2CHCHO), one of the more employed industrial chemical intermediates.[1−3] A number of bulk metal oxide catalysts have been used for these reactions.[3,4] Since processes on metal oxide catalytic surfaces are so complex, a fundamental understanding of these catalytic processes is still not available, and thus a rational approach to effective catalyst synthesis is difficult. Gas phase studies of metal oxide clusters and their reaction behavior can help to understand the mechanism of elementary reactions in catalytic processes under isolated, controlled, and reproducible conditions.[5−10]

Great efforts have been made to understand the mechanism of alkene oxidation on condensed phase catalytic surfaces through both experimental[11−21] and theoretical studies of

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transition metal oxide clusters.[22−27] Using a tandem mass spectrometer equipped with an electrospray ionization (ESI) source, Feyel and co-workers[26] studied the oxidation of 1-butene (C_4H_8) with mass selected $V_3O_7^+$ cluster ions. Oxidative dehydrogenation (ODH) of hydrocarbons is identified as a major reaction channel, accompanied by a minor channel involving C−C single bond cleavage to generate a product $V_3O_7(C_2H_4)^+$. The reactions of mass selected $V_mO_n^+$ with ethylene (C_2H_4) were investigated by Castleman and co-workers.[16,17] Oxygen transfer reactions are observed in their experiments and are determined to be the most energetically favorable channel for $V_2O_5^+/V_4O_{10}^+ + C_2H_4$ reactions based on theoretical calculations.[16] In the studies of $V_mO_n^+$ reactions, they found that the clusters $V_2O_{4,5}^+$, $V_3O_7^+$, and $V_5O_{12}^+$ are able to break the C2−C3 (single bond) of 1-butene (C_4H_8) to produce $V_mO_nC_2H_4^+$. In the reaction of $V_mO_n^+$ with 1,3-butadiene (C_4H_6), major association products are identified in addition to some minor reactions, such as oxygen abstraction, dehydration, etc.[18,19] No significant reactivity for anionic clusters $V_mO_n^-$ toward 1-butene or 1,3-butadiene is reported in their experiments.[19] While the reactions of metal oxide cluster ions with alkenes have been widely investigated in the gas phase, very few studies have been carried out for neutral metal oxide clusters and their reactions, since one must find a valid method to ionize neutral species without fragmentation. Additionally, some highly oxidized (e.g., VO_3, etc.) metal oxide clusters have high ionization energies (IE).[28] We believe that the study of neutral metal oxide clusters and their reactions can provide valuable information about active sites of metal oxides employed for catalytic processes.

Recently, we studied the reactions of neutral vanadium oxide clusters with ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2) employing a new desk-top, 26.5 eV/photon (46.9 nm), soft X-ray laser for ionization.[22] Using this ionization source, all the species of neutral metal oxide clusters and their reaction products can be detected. We found that oxygen rich clusters $VO_3(V_2O_5)_{n=0,1,2...}$ (e.g., VO_3, V_3O_8, and V_5O_{13}) can lead to a cleavage of the C=C bond of C_2H_4 to produce $(V_2O_5)_nVO_2CH_2$ clusters, while association products are observed for reactions $V_mO_n + C_2H_6/C_2H_2$. Neutral V_mO_n clusters present a significantly different reactivity than $V_mO_n^\pm$ cluster ions in reactions with C_2H_4. Since cleavage of C=C/C−C bonds in hydrocarbons is the key step in the decomposition of large hydrocarbons into small molecules, investigation of C=C bond breaking on neutral oxygen rich $VO_3(V_2O_5)_{n=0,1,2...}$ clusters takes on special importance.

In the present studies, the reactivity of neutral vanadium oxide clusters toward alkenes C_2H_4 (ethylene), C_3H_6 (propylene), C_4H_8 (1-butene), C_4H_6 (1,3-butadiene), and C_2F_4 (tetrafluoroethylene) and C_6H_6 (benzene) is investigated employing single photon ionization at 26.5 eV (46.9 nm) to analyze reactants and products in a time-of-flight mass spectrometer (TOFMS). Products generated through C=C bond cleavage of the alkenes are detected in all cases for $V_mO_n + C_2H_4/C_3H_6/C_4H_8/C_4H_6$. Oxygen rich vanadium oxide clusters with structure $VO_3(V_2O_5)_{n=0,1,2...}$ exhibit a specific activity with regard to the C=C bond cleavage of alkenes. In the studies of V_mO_n reacting with C_2F_4 and C_6H_6, reactions different than those observed for alkenes are identified due to the effects of F replacement of H and ring formation. DFT calculations are performed to explore the mechanisms for the reaction of VO_3 with C_3H_6, C_2F_4, and C_6H_6 and aid in the interpretation and explanation of our experimental observations.

II. Experimental and Theoretical Methods

Experiments performed for this study of neutral cluster reactions involve a time-of-flight mass spectrometer coupled with single photon ionization of reactants and products by a desk-top 26.5 eV EUV laser. The experimental apparatus has been described in detail elsewhere.[22,29] Briefly, the neutral vanadium oxide clusters are generated in a conventional laser vaporization/supersonic expansion cluster source by laser ablation (focused 532 nm laser, 10−20 mJ/pulse) of vanadium foil into a carrier gas of ∼0.5% O_2/He at 80 psi. The reactant gases (15 psi), pure C_2H_4, C_3H_6, C_3H_8, C_4H_6, C_4H_8, C_4H_{10}, C_6H_6/He, and C_2F_4, are pulsed into the fast flow reactor that is similar to the equipment designed by Smalley et al.[30] The instantaneous reactant gas pressure in the reactor cell is about 1∼2 Torr so that good cooling is achieved for the neutral metal oxide clusters generated in the ablation source. In this design, a fast flow reactor (70 mm length, ∅ 6 mm) is coupled directly to the cluster formation channel (40 mm length, ∅ 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. This method is commonly used in the study of elementary reactions of neutral and ionic metal clusters.[30−34] The possibility of charge exchange between the ions and much more abundant neutral species can be neglected based on the study of Kaldor et al.[32] Additionally, the products observed in our neutral vanadium oxide cluster reactions with alkenes[22] are not observed in mass selected vanadium oxide cluster ion reactions.[15−17,26] So we are confident that the products observed in our experiments are generated from neutral vanadium oxide clusters reacting with C_xH_y and not from cluster ions. Additionally, in the studies of neutral V_mO_n clusters reacting with C_2H_2, C_2H_4, and C_2H_6, cluster distributions and identified reaction products obtained by using 26.5 eV laser and 10.5 eV (118 nm) laser for ionization are nearly identical except for signal intensities.[22] Cluster fragmentation cannot occur during near threshold single photon ionization with a 10.5 eV laser.[28] Therefore, we assume that fragmentation during the 26.5 eV ionization process can be neglected in the present studies, as well. Since the 26.5 eV laser can ionize He and O_2 as well as alkenes, C_2F_4, and C_6H_6 reactants, which have high concentrations in the expansion/reaction cell system, we must gate the microchannel plate (MCP) detector voltage to protect it from overload and saturation.

The soft X-ray laser (26.5 eV/photon energy) emits pulses of about 1 ns duration with an energy/pulse of 10 μJ that is reduced to 3∼5 μJ after transversing a *z*-fold mirror system and is not tightly focused in the ionization region to avoid multiphoton ionization

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and a space charge Coulomb effect due to He^+ ions produced by 26.5 eV ionization of He in the molecular beam.

DFT calculations are carried out using the Gaussian 03 program.[35] The B3LYP functional[36−38] and TZVP basis set[39] are used to study the reactions of VO_3 with C_3H_6, C_2F_4, and C_6H_6. Vyboishchikov et al.[40a] 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 coworkers.[40] This method was also adopted by Justes and co-workers[16a] to compare the O dissociation energies of VO^+ and VO_2^+ with their experimental results. More recent studies of the reactivity of vanadium oxides using the B3LYP functional can be found in ref 41. The enthalpies of formation for C_2 hydrocarbons are also calculated very well at this level of theory. This method was shown previously to describe the $VO_3 + C_2H_4$ reaction system in good agreement with experimental results.[22] For each reaction channel, the calculation involves geometry optimization of various reaction intermediates and transition states through which the intermediates evolve into one another. Intrinsic reaction coordinate (IRC) calculations[42,43] are performed so that a transition state connects two appropriate local minima on the reaction pathways. The relaxed potential energy surface (PES) scan implemented in Gaussian 03 is extensively used to get good initial structures for the stable and transition states determined. In this method, once a stable state is found, several relaxed potential energy surfaces (PESs) can be scanned for possible internal reaction coordinates. The maximum and new minimum on a relaxed PES correspond to good guesses for transition and new stable states, respectively. Reaction barriers calculated employing the B3LYP function can be underestimated by as much as 50 kJ/mol.[40c] The electronic configuration of VO_3 is $^2A''$ (C_s point group). Only reaction potential energy surfaces for species in doublet states are considered, as quartet states are considerably higher in energy for reactants, products, and most of the reaction intermediates and transition states. Since the reaction may not happen at thermal equilibrium in the fast flow reactor due to the low pressure (1∼2 Torr) used in the experiment, some of the species will react before they undergo full collisional stabilization and thermalization by the carrier gas. Thermal equilibrium may not be achieved in the present experiments. The reaction potential surfaces (PES) plotted in the terms of zero-point energy corrected ΔE are thus used to explain experimental results.

III. Results

In the present experiments, a 26.5 eV laser is employed to ionize neutral clusters and their reaction products. The V_mO_n cluster distribution, generated under low oxygen concentration (0.5% O_2/He expansion gas at 80 psi), is displayed in the mass spectrum of Figure 1a. Three categories of vanadium oxide clusters can be identified. Vanadium oxide clusters VO_2, V_2O_4, V_2O_5, V_3O_7, V_4V_{10}, V_5O_{12}, V_6O_{15}, etc. can be expressed as stoichiometries of the form $(VO_2)_{0,1}(V_2O_5)_n$. These clusters are the most stable clusters (highest intensities for V_mO_n within a given V_m cluster family) in the neutral V_mO_n cluster distribution based on both experiments[29a] and calculations.[44,45] Oxygen rich clusters VO_3, V_2O_6, V_3O_8, V_5O_{13}, etc. have one more oxygen atom compared to the most stable clusters. They can be expressed as $(V_2O_5)_nO$ and $VO_3(V_2O_5)_n$ for the clusters containing even and odd number of V atoms, respectively. These oxygen rich clusters are found to associate one or two hydrogen atoms to make more stable structures. These clusters cannot be ionized by 10.5 eV laser due to high ionization energy. Oxygen deficient clusters VO, V_2O_3, $V_3O_{5,6}$, $V_4O_{8,9}$, etc. can also be observed; they have one or more oxygen atoms fewer than the most stable clusters (see Figure 1a).

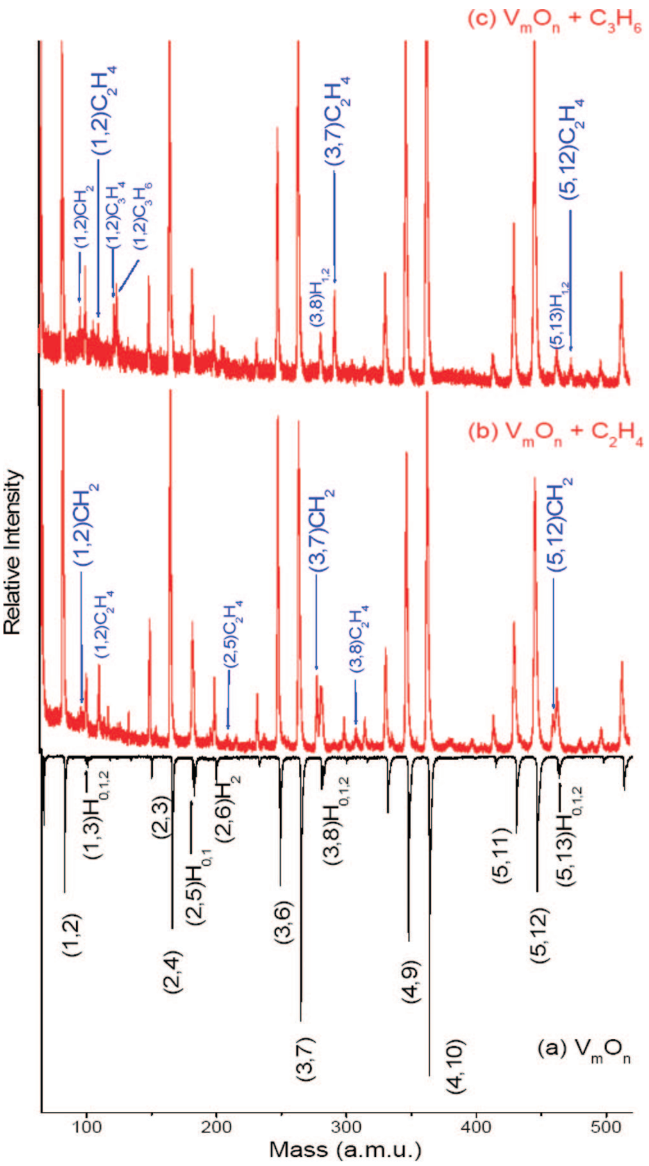

Figure 1. Reactions of V_mO_n clusters with pure ethylene (C_2H_4) and propylene (C_3H_6) studied by 26.5 eV soft X-ray laser ionization. (a) V_mO_n cluster distribution generated with 0.5% O_2/He expansion gas at 80 psi. Reactant gases (15 psi), (b) pure C_2H_4 and (c) pure C_3H_6, are added to the fast flow reactor. New products of the reactions are detected.

a. V_mO_n + C_2H_4/C_3H_6/C_4H_8/C_4H_6 Reactions. To study neutral V_mO_n cluster reactions with alkenes, reactant gases (pure C_2H_4,

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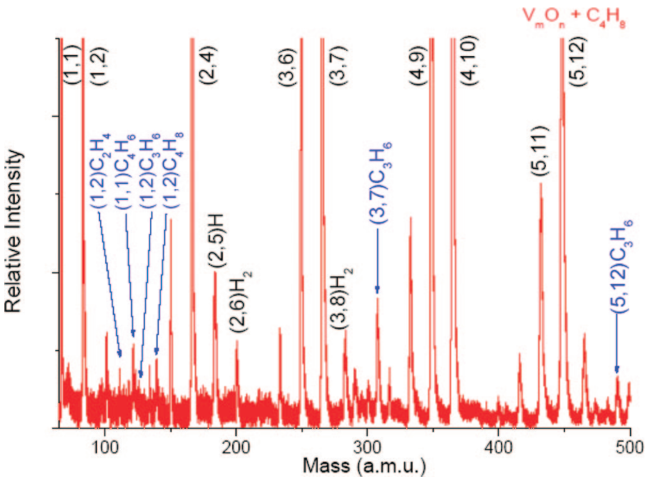

Figure 2. Reactions of V_mO_n clusters with pure 1-butene (C_4H_8). Reactant gas pure C_4H_8 (15 psi backing pressure) is added to the fast flow reactor. New reaction products and remaining clusters are detected by 26.5 eV soft X-ray laser ionization.

C_3H_6, C_4H_8, and C_4H_6) are individually and separately pulsed into the fast flow reactor to interact with neutral vanadium oxide clusters generated from the ablation/expansion source. As shown in Figure 1b, when C_2H_4 ($H_2C{=}CH_2$) is added to the reactor, the products VO_2CH_2, $V_3O_7CH_2$, and $V_5O_{12}CH_2$, generated from $V_mO_n + C_2H_4$ reactions, can be identified as the main products; several other association products, $VO_2C_2H_4$, $V_2O_5C_2H_4$, and $V_3O_8C_2H_4$, are also observed. In previous studies, we have demonstrated that the V_mO_n cluster distribution and reaction products of $V_mO_n + C_2H_4$ are almost the same detected through 26.5 eV (46.9 nm) and 10.5 eV (118 nm) laser ionizations, except that some vanadium oxide clusters with high ionization energies are only detected by 26.5 eV laser.[22] This observation indicates that no significant fragmentation occurs during the ionization process employing 26.5 eV radiation.

As shown in Figure 1c, if the reactant propylene ($H_2C{=}CHCH_3$) is added into the fast flow reactor, a series of new signals is assigned to products $VO_2C_2H_4$, $V_3O_7C_2H_4$, and $V_5O_{12}C_2H_4$ for the reactions $V_mO_n + C_3H_6$. Additionally, some products (VO_2CH_2, $VO_2C_3H_4$, and $VO_2C_3H_6$) are only detected for small vanadium oxide clusters.

Figure 2 displays the mass spectra generated from reactions between V_mO_n and 1-butene (C_4H_8, $H_2C{=}CHCH_2CH_3$). The complexes $VO_2C_3H_6$, $V_3O_7C_3H_6$, and $V_5O_{12}C_3H_6$, are identified as the major products, while several small signals corresponding to VOC_4H_6, $VO_2C_2H_4$, and $VO_2C_4H_8$ are also observed. 1,3-Butadiene (C_4H_6, $H_2C{=}CH{-}CH{=}CH_2$) is another alkene with two C=C double bonds used as a reactant. For neutral clusters V_mO_n reacting with 1,3-butadiene, products $VO_2C_3H_4$, $V_3O_7C_3H_4$, and $V_5O_{12}C_3H_4$ are detected along with a few association products, $VO_2C_4H_6$ and $V_2O_4C_4H_6$, as shown in Figure 3. Additionally, signals of oxygen rich V_mO_n clusters VO_3, V_3O_8, V_5O_{13} disappear in the reactions of V_mO_n clusters with alkenes (C_3H_6, C_4H_8, and C_4H_6), as shown in Figures 1, 2, and 3.

The observed products in the mass spectra, such as $(V_2O_5)_n$-VO_2CH_2, $(V_2O_5)_nVO_2C_2H_4$, $(V_2O_5)_nVO_2C_3H_4$, and $(V_2O_5)_nVO_2C_3H_6$, are generated from neural V_mO_n cluster reactions with C_2H_4, C_3H_6, C_4H_6, and C_4H_8, and not from fragmentation caused by a 26.5 eV laser photon. In previous studies,[22,29a] we compared experimental results for 26.5 and 10.5 eV ionization and found that the neutral vanadium oxide cluster distribution and their reaction products detected by the two ionization methods are almost the same. The only caveat here is that oxygen rich clusters, such as VO_3, V_2O_6, V_3O_8, etc., can only be detected by 26.5 eV ionization, but not by 10.5 eV ionization, due to their high ionization energy. For the V_mO_n + C_2H_4 reaction, reaction products VO_2CH_2, $V_3O_7CH_2$, and $V_5O_{12}CH_2$ are observed in the mass spectra employing both 10.5 and 26.5 eV laser ionization.[22] Moreover, 10.5 eV single photon energy is not large enough to rupture a C=C bond following ionization. The distribution of fragmentations produced from photodissociation of alkenes at 26.5 eV is totally different from the observed products for the V_mO_n + alkenes reactions. For example, photodissociation products of the C_2H_4 molecule are measured as $C_2H_4^+$ (30%), $C_2H_3^+$ (35%), $C_2H_2^+$ (28%), C_2H^+ (3%), and CH_2^+ (3%) using 26.5 eV laser ionization. The observed products for the $V_mO_n + C_2H_4$ reaction are $(V_2O_5)_n$-VO_2CH_2 (VO_2CH_2, $V_3O_7CH_2$, etc.) and the association products $V_mO_nC_2H_4$. Products such as $VO_2C_2H_3$ or $V_3O_7C_2H_3$ for the $V_mO_n + C_2H_4$ reaction are not observed. Thus the observed products in these experiments employing 26.5 eV ionization are most probably generated from reaction between neutral vanadium oxide clusters and alkenes rather than from fragmentation caused by 26.5 eV single photon ionization.

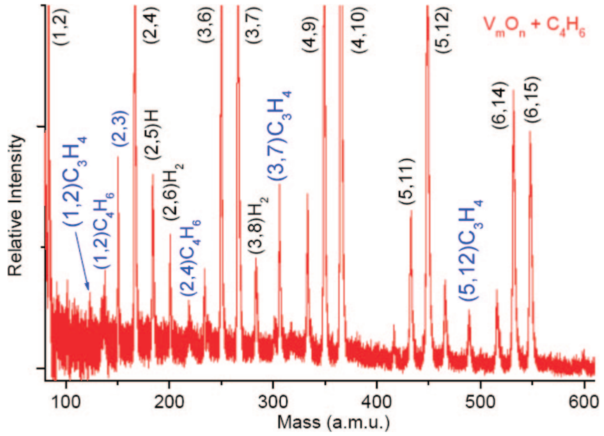

Figure 3. Reactions of V_mO_n clusters with 1,3-butadiene (C_4H_6). Reactant gas pure C_4H_6 (15 psi) is added to the fast flow reactor. New reaction products and remain clusters are detected by 26.5 eV soft X-ray laser ionization.

On the basis of our experimental observations and theoretical calculations, formaldehyde (H_2CO) is the expected product for the vanadium oxide clusters $VO_3(V_2O_5)_n$ reacting with alkenes; unfortunately, the product H_2CO is not detected in these experiments with 26.5 eV ionization. Signals of reactant molecules (C_2H_4, C_3H_6, C_4H_6, and C_4H_8) and of photodissociation products of these reactants are too intense and overload the MCP detector when the 26.5 eV laser is used for ionization. We must gate the MCP detector voltage to cut off these large signals to protect the MCP detector from overload and saturation. Unfortunately, the H_2CO signal is covered by these features, even with the implementation of a mass gate for our reflectron TOFMS. Additionally, the ionization cross section for H_2CO is small at 26.5 eV, and the concentration of the H_2CO product is probably too low to detect under these unfavorable conditions.

b. V_mO_n + C_6H_6/C_2F_4. As displayed in Figure 4, products $VO_2C_6H_4$, $V_2O_4C_6H_4$, $V_3O_7C_6H_4$, and $V_5O_{12}C_6H_4$ are observed for reactions of $V_mO_n + C_6H_6$. These products are different than those generated by the reactions V_mO_n + C_2H_4/C_3H_6/C_4H_6/C_4H_8. Note that no product of the form $V_4O_{10}C_6H_4$ or $V_6O_{15}C_6H_4$ is

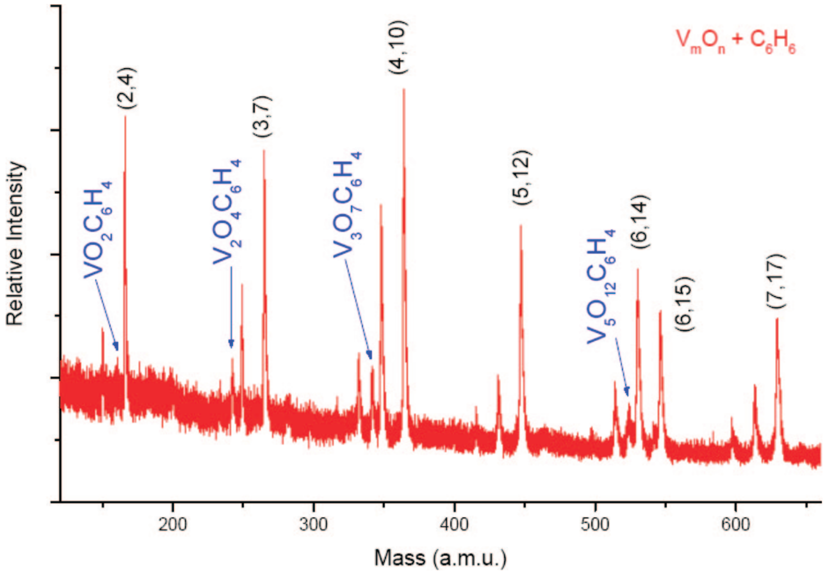

Figure 4. Reactions of V_mO_n clusters with benzene (C_6H_6). Reactant gas C_6H_6/He (15 psi) is added to the fast flow reactor. New reaction products and remaining clusters are detected by 26.5 eV soft X-ray laser ionization.

observed in the spectrum, indicating that dehydration reactions occur between $VO_3(V_2O_5)_n$ and C_6H_6 with the only exception for the reaction $V_2O_5 + C_6H_6 \rightarrow V_2O_4C_6H_4 + H_2O$. Reactions between V_mO_n and tetrafluoroethylene ($CF_2{=}CF_2$) are also investigated; however, no significant product is detected in the experiments, not even association complexes, using 26.5 eV X-ray laser ionization. The mechanisms for V_mO_n clusters (VO_3) reacting with C_2F_4 and C_6H_6 are studied by DFT calculations and are discussed in the following section.

IV. Discussion

a. V_mO_n + Alkenes (C_2H_4, C_3H_6, C_4H_8, C_4H_6). As shown in Figure 1b, products VO_2CH_2, $V_3O_7CH_2$, and $V_5O_{12}CH_2$ are identified as the main products for the reactions of V_mO_n + C_2H_4, implying that the following reactions occur:

$$(V_2O_5)_nVO_3 + H_2C{=}CH_2 \rightarrow (V_2O_5)_nVO_2CH_2 + H_2CO \tag{1}$$

In reaction 1, the C═C bond of ethylene (C_2H_4) is broken on specific vanadium oxide clusters, $VO_3(V_2O_5)_n$. On the basis of DFT calculations,[22] the reaction $VO_3 + C_2H_4 \rightarrow VO_2CH_2 + H_2CO$ is thermodynamically favorable by 0.3 eV and is an overall barrierless reaction at room temperature; therefore, one can deduce that the general reaction (1) can also occur to generate products VO_2CH_2, $V_3O_7CH_2$, and $V_5O_{12}CH_2$ expressed as $(V_2O_5)_nVO_2CH_2$. One notes that products, such as $V_2O_5CH_2$ and $V_4O_{10}CH_2$, etc., are not observed in the experiments, indicating that C═C bond breaking for C_2H_4 only occurs on oxygen rich vanadium oxide clusters with $VO_3(V_2O_5)_n$ stoichiometries. Another possible reaction, $VO_2 + C_2H_4 \rightarrow VO_2CH_2 + CH_2$ ($\Delta H_{298} = +3.5$ eV), corresponding to the observation of product VO_2CH_2, is also considered; however, it is not a thermodynamically available reaction at room temperature. Thus, products $(V_2O_5)_nVO_2CH_2$ do not arise from reaction $(V_2O_5)_nVO_2 + C_2H_4 \rightarrow (V_2O_5)_nVO_2CH_2 + CH_2$, and one can conclude that C═C bond cleavage is not favorable for the most stable neutral vanadium oxide clusters (VO_2, V_2O_4, V_2O_5, V_3O_7, ...).

We have documented that the products VO_2CH_2 and $V_3O_7CH_2$ detected by the 26.5 eV laser are definitely generated from the neutral vanadium oxide cluster reacting with C_2H_4 and are not generated from fragmentation during the ionization processes since such reaction products are also detected by using 10.5 eV laser ionization. One knows that, in this latter instance, insufficient excess energy exists in the clusters to break any bonds during the ionization processes by 118 nm single photon, near threshold ionization. Therefore, it is reasonable to consider that analogous products detected in the studies of V_mO_n + alkene reactions are not associated with fragmentation due to high photon energy at 26.5 eV.

The above results of $V_mO_n + C_2H_4$ reactions suggest that all C═C bonds of alkenes might be cleaved on vanadium oxide clusters with stoichiometries and structures $VO_3(V_2O_5)_n$. To explore this possibility, other alkene molecules are used instead of ethylene to react with neutral V_mO_n clusters. As shown in Figure 1c, if reactant propylene ($H_2C{=}CHCH_3$) is added into the reactor, a series of new signals is assigned to products $VO_2C_2H_4$, $V_3O_7C_2H_4$, and $V_5O_{12}C_2H_4$ for the reactions V_mO_n + C_3H_6. These products can be generated from the following reactions:

$$(V_2O_5)_nVO_3 + H_2C{=}CHCH_3 \rightarrow (V_2O_5)_nVO_2C_2H_4 + H_2CO \tag{2}$$

In this reaction, C═C bonds of propylene are broken as in the reactions of V_mO_n with ethylene. This chemistry can be considered driven by the formation of the stable product formaldehyde (CH_2O).

Several reaction products identified as $VO_2C_3H_6$, $V_3O_7C_3H_6$, and $V_5O_{12}C_3H_6$ are also observed for the reactions between V_mO_n and 1-butene (C_4H_8, $H_2C{=}CHCH_2CH_3$) as displayed in the mass spectrum of Figure 2. These products can be generated from C═C bond cleavage reactions as follows:

$$(V_2O_5)_nVO_3 + H_2C{=}CHCH_2CH_3 \rightarrow (V_2O_5)_nVO_2C_3H_6 + H_2CO \tag{3}$$

1,3-Butadiene (C_4H_6, $H_2C{=}CH{-}CH{=}CH_2$) is an alkene with two C═C double bonds used as a reactant. For neutral clusters V_mO_n reacting with 1,3-butadiene, products $VO_2C_3H_4$, $V_3O_7C_3H_4$, and $V_5O_{12}C_3H_4$ are detected along with a few association products $VO_2C_4H_6$ and $V_2O_4C_4H_6$ (shown in Figure

3). A C═C bond of C_4H_6 can be cleaved on V_mO_n clusters as in the reaction,

$$(V_2O_5)_nVO_3 + H_2C{=}CHCH{=}CH_2 \rightarrow (V_2O_5)_nVO_2C_3H_4 + H_2CO \quad (4)$$

Note that in reactions 1−4, the C═C bonds of the alkenes are cleaved in reactions with $(V_2O_5)_nVO_3$ clusters, and H_2CO (formaldehyde) molecules are formed as an additional separated product. Oxygen rich clusters VO_3, V_3O_8, and V_5O_{13} detected in the pure vanadium oxide cluster distribution disappear when alkenes (C_2H_4, C_3H_6, C_4H_8, and C_4H_6) are added to the reactor as shown in Figures 1, 2, and 3, indicating the high reactivity of these clusters. Therefore, we conclude that C═C bonds of alkenes are broken in reactions with neutral vanadium oxide clusters (VO_3, V_3O_8, and V_5O_{13}) of the general form $(V_2O_5)_nVO_3$ via reactions 1−4.

The mechanism of C═C bond breaking on $(V_2O_5)_nVO_3$ clusters to generate a H_2CO (formaldehyde) product can be explored through DFT calculations. On the basis of the calculation results for the reaction $VO_3 + C_2H_4$,[22] the reaction starts with the O atom of VO_3 attacking a C atom of the $CH_2{=}CH_2$ molecule to form an association intermediate releasing about 0.67 eV energy, in which the C═C double bond in $CH_2{=}CH_2$ is significantly weakened to become a single C−C bond. A stable five-membered ring intermediate is then formed via [3 + 2] cycloaddtion. A large amount of energy (2.12 eV) is then released, leading to C−C bond breaking to generate VO_2CH_2 and H_2CO products. The channel $VO_3 + C_2H_4 \rightarrow VO_2CH_2 + H_2CO$ is an overall barrierless reaction pathway and can occur at room temperature.

To understand the reaction mechanisms between V_mO_n with larger alkenes, we apply DFT calculations to $VO_3 + C_3H_6$ reaction at the B3LYP/TZVP level:

$$VO_3 + H_2C{=}CHCH_3 \rightarrow VO_2C_2H_4 + H_2CO \qquad \Delta H = -0.29\ \text{eV} \quad (5)$$

As shown in Figure 5, the reaction starts with VO_3 attacking the C═C bond of the C_3H_6 molecule to form intermediate **1**, in which the C═C double bond in $CH_3CH{=}CH_2$ (bond length = 1.33 Å) is significantly weakened to become a single C−C bond 1.48 Å in intermediate **1** (C−C single bond length = 1.5 Å in C_3H_6). Via transition state **1/2**, a lowest energy intermediate **2** with a five-membered ring is formed and releases a large amount of energy about 2.68 eV. Through transition state **2/3**, the C−C bond of intermediate **2** ruptures and yields intermediate **3**, in which CH_2 and C_2H_4 radicals connect with two O atoms of VO_3 by C−O bonds. In intermediate **5**, the formation of a V−O−C three-membered ring weakens and stretches the V−O bond between the H_2CO moiety and the $VO_2C_2H_4$ moiety and finally results in generating products **P2** ($VO_2C_2H_4 + H_2CO$) with the release of 0.29 eV energy. The pathway is thermodynamically favorable and barrierless for reaction 5. Another reaction pathway, **3** → **3/4** → **4** → **P1** ($VO_2CH_2 + CH_3CHO$), is also thermodynamically available. The reaction products $VO_2CH_2H_4$ and VO_2CH_2 are observed in Figure 1c. The mechanism of C═C breaking for $V_mO_n + C_3H_6$ is the same as for the $V_mO_n + C_2H_4$ reaction. The formation of the most stable structures with five-membered rings in both reactions are the key steps for C═C bond cleavages. We believe that the same mechanism will be found for VO_3 reacting with other alkenes, such as C_4H_8 and C_4H_6, since similar reaction products generated from C═C bond cleavage are observed in these experiments. A complete potential surface for the $VO_3 + C_3H_6$ reaction can be found in ref 27.

For the reactions of vanadium oxide clusters with C_3H_6/C_4H_8/C_4H_6, another possible reaction pathway for C═C bond cleavage is to generate products $(V_2O_5)_nVO_2CH_2$ and C_2H_4O/C_3H_6O/C_3H_4O product—with the exception of $VO_2C_2H_4$ for $VO_3 + C_3H_6$ reaction; however, these products are not observed in the mass spectra presented Figures 1c, 2, and 3. Further computation on large vanadium oxide clusters are required to explore more detailed reaction mechanisms for these reactions.

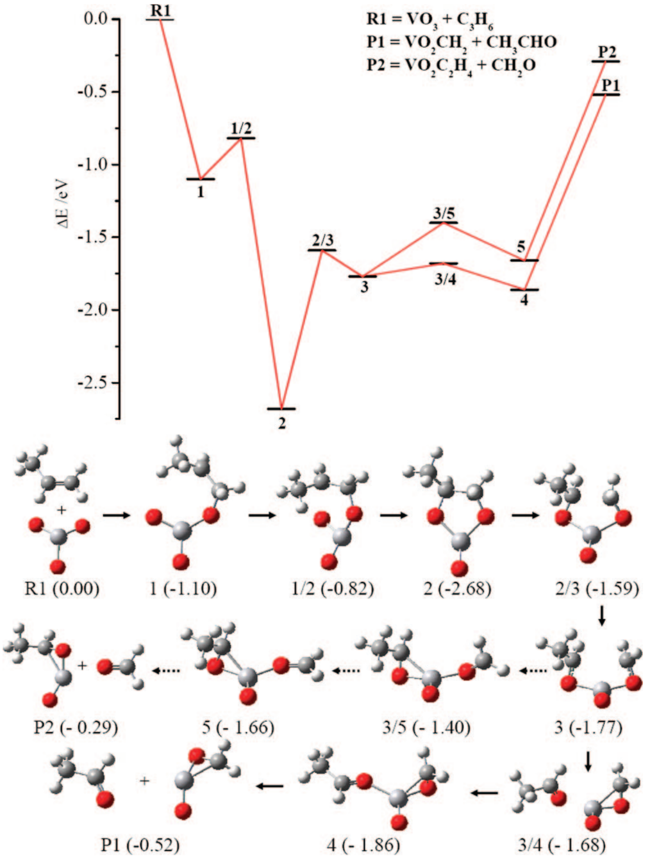

Figure 5. DFT calculated potential energy surface for the $VO_3 + C_3H_6 \rightarrow VO_2C_2H_4 + H_2CO$ reaction at the theory level B3LYP/TZVP. Structures are the optimized geometries of the reaction intermediates and transition states. The profiles are plotted for zero-point vibration corrected energies. Relative energies are in eV. A complete potential surface of $VO_3 + C_3H_6$ reaction can be found in ref 27.

VO_3 has one more oxygen atom compared to the stable vanadium oxide VO_2, so it can be considered as an oxygen centered radical. The oxygen rich vanadium oxide clusters VO_3, V_3O_8, V_5O_{13}, etc. can be expressed as $VO_3(V_2O_5)_{n=0,1,2,...}$. As shown in Figure 6, the V_3O_8 structure can be generated from V_2O_5 bonded to VO_3 and expressed as $(V_2O_5)(VO_3)$. For the $V_3O_8 + C_2H_4$ reaction, a five-membered ring structure is also found for the stable complex species $V_3O_8C_2H_4$ (Figure 6c); this structure is similar to those found for the $VO_3 + C_2H_4$/C_3H_6 reaction (Figure 5, intermediate **2**). The double bond of $H_2C{=}CH_2$ is weakened to a single bond in the five-membered ring structure, eventually leading to a broken C−C bond. Recently, Santambrogio et al. studied the structures of $V_mO_n^-$ anion clusters by experimental IRMPD spectra and DFT calculations.[15] Closed shell clusters $V_3O_8^-$, $V_5O_{13}^-$, and $V_7O_{18}^-$ can be identified as a $(V_2O_5)_{n=1,2,3}(VO_3)^-$ structure, in which VO_3 and (V_2O_5) moieties are clearly found, similar to that of the neutral cluster V_3O_8, shown in Figure 6.

The present gas phase studies of neutral vanadium oxide cluster reactions with alkenes can suggest a possible catalytic model for oxidative cleavage of alkenes on condensed phase

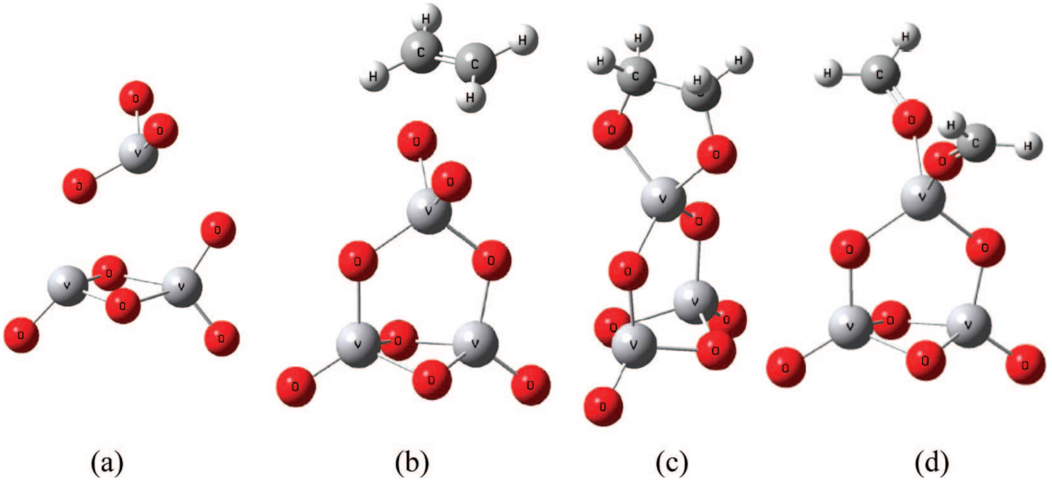

Figure 6. DFT calculations (B3LYP/LANL2DZ) of structures: (a) VO_3 and V_2O_5; (b)V_3O_8 and C_2H_4; (c) $V_3O_8C_2H_4$; (d) C═C cleavage on V_3O_8.

surfaces. On the basis of our present studies, we can offer a catalytic model for aldehyde formation through oxidation of alkenes on VO_3. On the basis of our calculations (B3LYP/TZVP), the reaction $VO_2C_2H_4 + O_2 \rightarrow VO_3 + CH_3CHO$ is also thermodynamically available without a barrier. A thermodynamically feasible catalytic cycle can be suggested as follows: In reaction 7, C_3H_6 (propylene) is cleaved at the C═C bond

$$\begin{array}{ll} VO_3 + H_2C{=}CHCH_3 \rightarrow VO_2C_2H_4 + H_2CO & \Delta H = -0.25\text{ eV} \\ VO_2C_2H_4 + O_2 \rightarrow VO_3 + CH_3CHO & \Delta H = -2.66\text{ eV} \\ \hline H_2C{=}CHCH_3 + O_2 \rightarrow CH_3CHO + H_2CO & \Delta H = -2.91\text{ eV} \end{array} \quad (6)$$

and is oxidized to H_2CO (formaldehyde) and $VO_2C_2H_4$ products. If these reactions take place in an oxygen rich environment, $VO_2C_2H_4$ can be oxidized by O_2 molecules in a second step to generate VO_3 and CH_3CHO. Both steps in this cycle are exothermic and overall barrierless. DFT calculations indicate that the VO_3 moiety can be considered as an active site for neutral vanadium oxide clusters:[22] V_3O_8, V_5O_{13}, etc. clusters can be considered as $(V_2O_5)_{1,2...}$ bonded to VO_3, as shown in the general formula $VO_3(V_2O_5)_n$. Therefore, a general catalytic oxidation reaction of alkenes on vanadium oxide clusters is suggested as

$$R{-}HC{=}CH_2 + O_2 \xrightarrow{VO_3(V_2O_5)_n} R{-}CHO + H_2CO \qquad (7)$$

In this reaction, alkenes are oxidized by O_2 to produce aldyhydes on vanadium oxide with a structure $VO_3(V_2O_5)_{n=0,1,2}$. In practical catalysis, the selective oxidative cleavage of alkenes is very important. Our study provides useful information for designing catalysts to aid in the oxidation of alkenes.

The study of gas phase cluster reactions can generate significant insight to the understanding of condensed phase elementary reaction steps (mechanisms and potential energy surfaces) for catalytic processes. In particular, V_mO_n radical clusters may serve as models of oxygen rich or oxygen poor defect sites and intermediate reactive centers on catalytically active surfaces during the catalytic processes. In the present studies of vanadium oxide clusters reacting with alkenes (C_2H_4, C_3H_6, C_4H_6, and C_4H_8), we find that oxygen rich clusters $VO_3(V_2O_5)_{n=0,1,2...}$ are very oxidative toward breaking C═C bonds. On the basis of our calculations, the open-shell radical cluster VO_3 is the active center for neutral vanadium oxide clusters and is identified as a building block for the larger oxygen rich clusters $VO_3(V_2O_5)_n$, in which the $(V_2O_5)_n$ moiety can be considered as a model for the stable metal oxide surface: the VO_3 moiety can be thought of as the active site on a $(V_2O_5)_n$ surface, as shown in Figure 6.

Selective oxidation of propylene to acetaldehyde over a V_2O_5/SiO_2 catalyst has been studied by Ruszel et al.:[2b] the mechanism for this heterogeneous catalytic reaction is suggested to be associated with electrophilic addition of surface oxygen species, O_2^- or O^-, to the C═C double bond of propylene to form peroxo or oxo intermediates that can decompose with cleavage of the C−C bond.[2b] This catalytic reaction mechanism is similar to the proposed [3 + 2] cycloaddition reaction mechanism for the VO_3 cluster reacting with C_3H_6 in the present gas phase study. Additionally, the selective oxidation of methanol on supported vanadium oxide catalysts is considered as a probe or test reaction for a number of selective oxidation reactions. The catalytically active sites for this system are identified as VO_4 sites on a fully oxidized surface,[46] and in this catalytic reaction O_2 molecules are employed to oxidize the reduced V^{+4} or V^{+3} sites back to active V^{+5} sites. Note that a similar oxidation reaction mechanism is found for the VO_3 cluster reaction with alkenes, as suggested in reaction 7. These oxygen rich active sites or high oxidation state sites of metal oxides in condensed phase systems can be generated in a high oxygen environment or formed through oxidation−reduction reactions between catalysts and supporting metal oxides.

b. Mechanism of V_mO_n + C_2F_4 Reactions. Substitution of the hydrogen atoms in small hydrocarbons by fluorine has a marked effect on many of their physical and chemical properties. Asymmetric replacement of hydrogen by fluorine can result in a significant increase in the molecular dipole moment, and a C−F bond is also stronger than a C−H bond.[47,48] We detect no reaction products when C_2F_4 gas is used as a reactant added into the fast flow reactor. To explore the effect of fluorine replacement in reactions of V_mO_n + alkenes, we investigate the mechanism of $VO_3 + C_2F_4$ by DFT calculations at the theory level B3LYP/TZVP. As shown in Figure 7, the potential surface for the $VO_3 + C_2F_4$ reaction is similar to that of $VO_3 + C_2H_4$/C_3H_6 reactions (Figure 5). The O atom of VO_3 attacks C_2F_4 to

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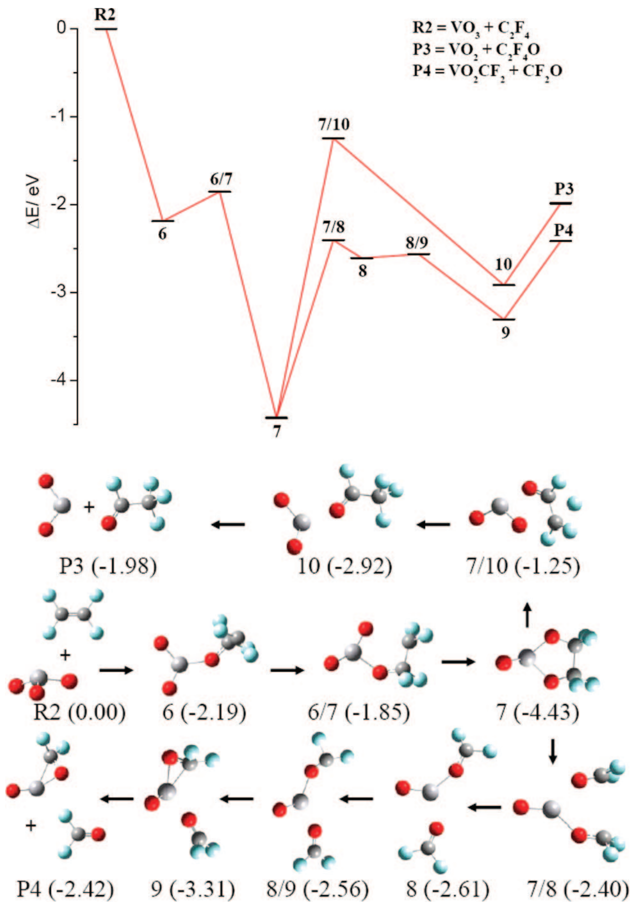

Figure 7. DFT calculated potential energy surface for the VO_3 + C_2F_4 reaction at the theory level B3LYP/TZVP. Structures are the optimized geometries of the reaction intermediates and transition states. The profiles are plotted for zero-point vibration corrected energies. Relative energies are in eV.

form intermediate **6**, and then form a lowest energy intermediate **7** with a five-membered ring via transition state **6/7**. About 4.43 eV is released in this step. Two reaction pathways, (1) an oxygen transfer reaction to produce VO_2 + C_2F_4O and (2) a C═C cleavage reaction to produce VO_2CF_2 + CF_2O, are thermodynamically available without barriers at room temperature. Note that the reaction potential surface for the VO_2 + C_2F_4 reaction is similar to that of the VO_2 + C_2H_4/C_3H_6 reactions; however, no significant reaction product is detected in the experiments. The theoretical result is then in disagreement with experimental observations.

The effects of fluorine on alkenes, most notably for tetrafluoroethylene, have been investigated by others under different circumstances.[48−50] Experimental and theoretical studies of the reaction O + C_2F_4 → CF_2 + OCF_2 are undertaken by Nguyen et al.[48] They find that the O + C_2F_4 reaction is initiated by a chain-addition to the C═C double bond of C_2F_4 to form an intermediate OC_2F_4 without a transition state, at the B3LYP/6−311+G(3df) level of theory. Their calculational results are in conflict with experimental studies; the overall rate constant for the O + C_2F_4 reaction depends positively on temperature with an Arrhenius activation energy of 0.6 ± 0.2 kcal/mol.[51] To explore this issue, they employ a combination method using B3LYP, G2M(UCC, MP2), CBS-QB3, and G3, and find a transition state for O + C_2F_4 with a barrier of 0.4 kcal/mol. Comparison of the potential surface for the O + C_2F_4 reaction[48] with that of the VO_3 + C_2F_4 reaction (Figure 7) suggests a very similar reaction mechanism: the O atom, or O atom of VO_3, attacks C_2F_4 to form OC_2F_4/$VO_3C_2F_4$ without a barrier. Breaking of the C═C double bond then leads to generation of the products, F_2CO + CF_2/VO_2CF_2 + F_2CO. Structure of the intermediate OC_2F_4 is similar to that of $VO_3C_2F_4$ if VO_3 is considered to be an oxygen centered radical. Therefore, if we consider a steric effect for VO_3 in place of the O atom reacting with C_2F_4, one can suggest that a transition state with a higher barrier for the VO_3 + C_2F_4 reaction than that found for the O + C_2F_4 reaction exists. This barrier cannot be calculated at B3LYP/TZVP level, however. The barrier may impede the reaction between VO_3 and C_2F_4, resulting in no product detected on the time scale of the present experiment.

c. Mechanism of V_mO_n + C_6H_6 Reactions. Benzene has a delocalized π double bond system with no particular localized single or double bonds; the delocalization of electrons makes benzene more stable typically than alkenes. As displayed in Figure 4, products $VO_2C_6H_4$, $V_2O_4C_6H_4$, $V_3O_7C_6H_4$, and $V_5O_{12}C_6H_4$ are observed for reactions V_mO_n + C_6H_6. The products may be generated from possible dehydration reactions:

$$V_mO_{n+1} + C_6H_6 \rightarrow V_mO_nC_6H_4 + H_2O \qquad (8)$$

Reaction products generated from the reactions V_mO_n + C_6H_6 are different from those generated by V_mO_n + alkene reactions. The potential surface for the reaction,

$$VO_3 + C_6H_6 \rightarrow VO_2C_6H_4 + H_2O \qquad \Delta H = -0.79 \text{ eV} \qquad (9)$$

is calculated at the B3LYP/TZVP level as shown in Figure 8. As a first step, the O atom of VO_3 bonds to one C atom of the C_6H_6 molecule to form the structure of intermediate **11**. Through transition state **11/12**, one H atom transfers from a C atom to an O atom of VO_3. Following structural adjustment via transition state **12/13**, intermediate state **13** is formed, and then another H atom is transferred to the same O atom of VO_3 as a second step. In the structure of intermediate **14**, a H_2O moiety is connected to $VO_2C_4H_6$ by a weak bond. Step three yields final products H_2O and $VO_2C_4H_6$ while releasing energy of 0.79 eV. On the basis of this calculation, a dehydration reaction between VO_3 and C_6H_6 is thermodynamically favorable and overall barrierless. This calculated process is in agreement with our experimental observation of a $VO_2C_4H_6$ product in the mass spectrum as displayed in Figure 4. Note that these dehydration reactions occur only on oxygen rich vanadium oxide clusters $VO_3(V_2O_5)_n$ except for V_2O_5.

For the reaction of VO_3 + C_6H_6, the potential energy barrier for the transition state **11/12** is 0.06 eV lower than the potential energy of reactants (see Figure 8); however, the Gibbs energy barrier for **11/12** is 0.49 eV higher than the energy of reactants (see Supporting Information). This indicates that the reaction intermediates are not fully at thermal equilibrium due to the relatively low pressure (1∼2 Torr) of these gas phase experiments. The reaction potential surfaces in terms of the Gibbs free energies (ΔG_{298}) for VO_3 + C_3H_6/C_2F_4/C_6H_6 reactions can be found in the Supporting Information.

d. Specificity of C═C Bond Cleavage Reactions. C═C bond cleavage of alkenes on neutral V_mO_n clusters is a unique reaction. First, this reaction only occurs on neutral $(V_2O_5)_nVO_3$ clusters. No product is detected with regard to C═C bond scission for reactions of alkenes with the most stable V_mO_n

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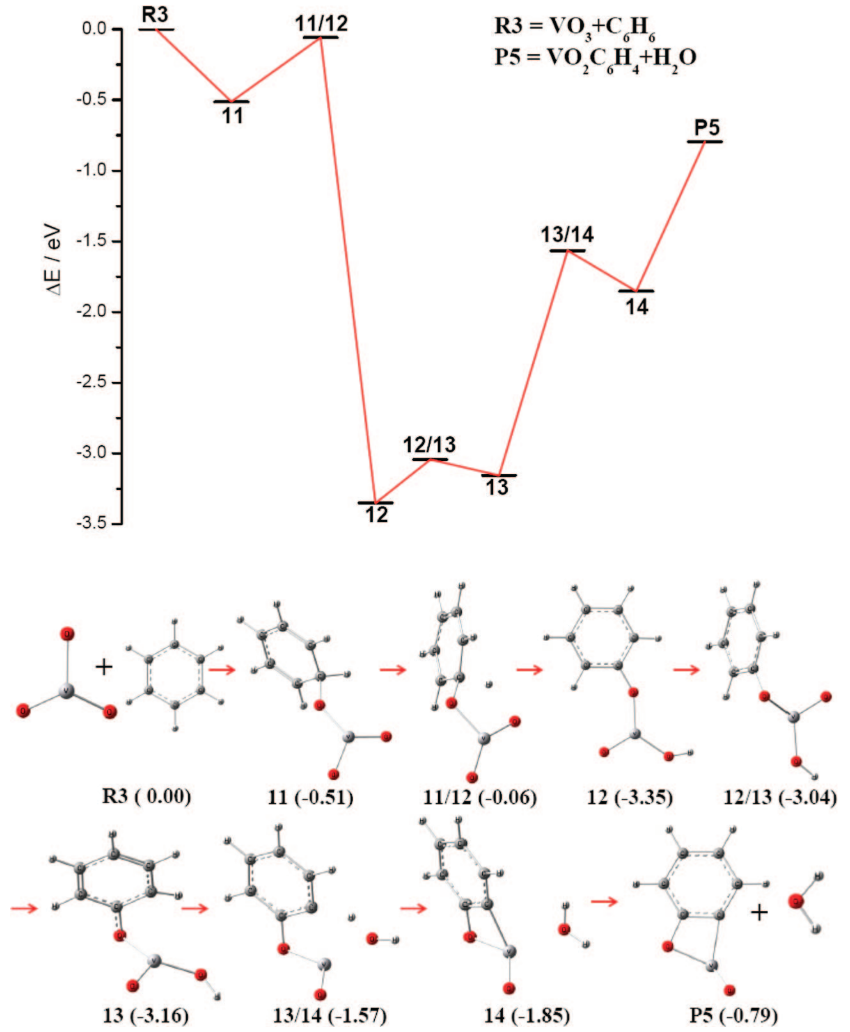

Figure 8. DFT calculated potential energy surface for $VO_3 + C_6H_6$ reaction at the theory level B3LYP/TZVP. Structures are the optimized geometries of the reaction intermediates and transition states. The profiles are plotted for zero-point vibration corrected energies Relative energies are in eV.

clusters (VO_2, V_2O_5, V_3O_7, V_4O_{10}...), oxygen deficient clusters (VO, V_2O_3, V_3O_6...), or oxygen rich clusters with an even number of V atoms (V_2O_6, V_4O_{11}...). Second, only $C{=}C$ double bonds of alkenes cleave on neutral vanadium oxide clusters. The single $C{-}C$ bond of alkanes and triple $C{\equiv}C$ bond of alkynes are not broken on neutral vanadium oxide clusters. In our studies of neutral V_mO_n cluster reactions with saturated hydrocarbons C_2H_6, C_3H_8, and C_4H_{10}, the intensities of V_mO_n cluster signals decrease roughly in the same proportion (no unique reactions occur) expect for a few association products. The reactivity of saturated hydrocarbons is lower than that of unsaturated species in reactions with neutral V_mO_n clusters. We also investigate reactions between V_mO_n and tetrafluoroethylene ($CF_2{=}CF_2$) and find that $C{=}C$ bond cleavage does not occur in this case. Third, these reactions only occur on vanadium oxide clusters: reactions of other neutral metal oxide clusters, such as Nb_mO_n, Ta_mO_n, Ti_mO_n, Co_mO_n, Si_mO_n, Fe_mO_n, Hf_mO_n, and Zr_mO_n, with alkenes do not generate products corresponding to $C{=}C$ bond cleavage. Experimental and theoretical results indicate that the activity of metal oxide clusters is dependent on many issues—bond energies, reaction barriers, reaction rates, etc.—and not only on the oxygen content of M_mO_n clusters. Fourth, these reactions only occur on neutral clusters. Neutral vanadium oxide clusters behave differently than do the comparable cluster ions in reactions with alkenes. Oxygen transfer reactions are observed as a major reaction channel for $V_mO_n^+$ cluster ions reacting with C_2H_4;[16] for $V_mO_n^+ + C_4H_8$ reactions, $V_mO_nC_2H_4^+$ products are observed for clusters $V_2O_{4,5}^+$, $V_3O_7^+$, and $V_5O_{12}^+$ due to single bond C2−C3 cleavage.[18,19] $V_3O_7^+$ is especially efficient in the dehydrogenation of 1,3-butadiene and in the cracking of 1-butene;[18,19,26] however, the products that correspond to double bond breaking are not observed in any $V_mO_n^+$ cluster reaction with alkenes. A calculation for the reaction system $VO_3^+ + C_2H_4$ indicates that the reactivity of VO_3^+ is quite different from that of VO_3. VO_3 [generally $VO_3(V_2O_5)_n$] is quite reactive due to its oxygen radical (O•) center character. In contrast, a peroxo (−O−O−) moiety exists for the ground state of VO_3^+, which leads to lower reactivity for VO_3^+ than for VO_3 in the reaction with C_2H_4. This indicates that a net charge can change the electronic and geometrical structures of a cluster and influence its reactivity significantly. A detail study of $V_mO_n^+ + C_2H_4$ reaction will be published in the future.

V. Conclusions

An experimental and theoretical study of the reactions of neutral V_mO_n clusters with the alkenes (ethylene, propylene, 1-butene, and 1,3-butadiene, and tetrafluoroethylene) and benzene is conducted. We find that the $C{=}C$ bonds of the alkenes

C_2H_4, C_3H_6, C_4H_6, and C_4H_8 are cleaved on vanadium oxide oxygen rich clusters of the form $VO_3(V_2O_5)_{n=0,1,2...}$, generating products $(V_2O_5)_nVO_2CH_2$, $(V_2O_5)_nVO_2C_2H_4$, $(V_2O_5)_nVO_2C_3H_4$, and $(V_2O_5)_nVO_2C_3H_6$ for reactions $V_mO_n + C_2H_4/C_3H_6/C_4H_6/C_4H_8$, respectively. Formaldehyde (H_2CO) molecules are formed as another product of these reactions. The cleavage of C═C bonds of alkenes on neutral V_mO_n clusters is a unique reaction. These reactions do not occur for (1) the most stable V_mO_n clusters, (2) oxygen rich V_mO_n clusters with an even number of V atoms, (3) other metal oxide clusters, such as Nb_mO_n, Ta_mO_n, Ti_mO_n, Co_mO_n, Si_mO_n, Fe_mO_n, Hf_mO_n, Zr_mO_n, (4) vanadium oxide cluster ions ($V_mO_n^{\pm}$), and (5) $V_mO_n + C_2F_4$ or C_6H_6. No reaction products are detected for $V_mO_n + C_2F_4$ reactions. For the reactions of $V_mO_n + C_6H_6$ only the dehydration products $VO_2C_6H_4$, $V_2O_4C_6H_4$, $V_3O_7C_6H_4$, and $V_5O_{12}C_6H_4$ are detected. DFT calculations indicate that the reaction $VO_3+C_3H_6 \rightarrow VO_2C_2H_4 + H_2CO$ is thermodynamically favorable and overall barrierless at room temperature and that a VO_3 moiety may be considered as an active site for $VO_3(V_2O_5)_{n=0,1,2...}$ structures. On the basis of experimental data and DFT calculations, a catalytic cycle for oxidation of alkenes to produce formaldehyde and aldehydes on vanadium oxide is suggested. The experimental and theoretical studies of $VO_3 + C_2F_4/C_6H_6$ reactions indicate that C═C bond cleavage does not occur for these two reactions due to fluorine replacement and delocalized π double bond effects.

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Supporting Information Available: The complete author list of ref 35 and the reaction potential surfaces in terms of the Gibbs free energies (ΔG_{298}) for $VO_3 + C_3H_6/C_2F_4/C_6H_6$ reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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