Reactions of Vanadium and Niobium Oxides with Methanol

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Received: October 10, 2003

As part of an ongoing study in our laboratory to elucidate the reactivities of the group V metal oxide clusters, reactions between vanadium and niobium oxide cations and methanol were conducted using a guided ion beam mass spectrometer coupled to a laser vaporization source. Size-specific cluster reactions were identified, with some indicated products being the same as those formed in methanol reactions over condensed phase niobia and vanadia catalysts, namely, H_2CO and C_2H_6O. The effects of the properties of the clusters, among them size, stoichiometry, oxidation state, and composition on their reactivity toward methanol, are discussed.

Introduction

Transition-metal oxides have proven to be effective catalysts for a variety of industrial reactions. Methanol, in particular, has extraordinary potential as a possible alternative fuel source;[1] consequently, it is widely investigated over condensed phase catalysts[2] as well as in fuel cell reactors.[3−5] To that end, some research efforts have been focused on the conversion of liquid fuel to supply a fuel cell. In particular, consideration is being given to using an integrated fuel processor to release the hydrogen from liquid methanol.[3]

Methanol oxidation has been investigated on supported vanadia catalysts. As an example, Vohs et al. studied the oxidation of methanol to formaldehyde on titania-supported vanadia catalysts. They found formaldehyde production to occur above 600 K and the reactivity of the reaction to be structure sensitive with the activation energy decreasing with increasing vanadia coverage.[6] Schlögl et al. have used UV−vis diffuse reflectance spectroscopy to investigate the oxidation of methanol by heteropoly compounds.[7] They found that the Keggin anions were precursors to catalytic activity; however, the structure for the catalytically active form changed on the surface leaving the actual structure of the active site unknown.

In addition to the interest in its catalytic conversion, investigations into mechanisms of methanol oxidation over metal oxide surfaces have been used as a method of characterization for the surface under investigation.[8] For example, dimethyl ether is formed when strong acid is present on the surface, whereas carbon oxides are produced when the surface is strongly basic.[9] Wachs et al. have performed experiments on the oxidation of methanol over supported V_2O_5[10] and MoO_3[11] catalysts. By studying surface methoxy species and comparing turnover frequencies for various surfaces, they were able to establish that VO_x species are more active than MoO_x species.[12]

Current surface-sensitive techniques often lack the ability to definitively determine the exact nature of the active site responsible for the catalytic activity. The use of gas phase clusters to study industrially significant reactions, such as the oxidation of methanol, is gaining acceptance as a valuable complementary method for probing the active sites responsible

for selected classes of reactions. By viewing a metal oxide surface as a collection of clusters as suggested by Muetterties and Witko et al., one can see the potential value this technique has.[13,14] In addition, Somorjai has stated that surface chemical bonds have cluster-like properties.[15] Information on the active sites can be gained from the gas phase studies of cluster ions and neutrals[16] as well as the studies performed in the condensed phase. This information may aid researchers in uncovering the mechanism governing certain catalytic processes, allowing for the development of more selective and efficient catalysts.[17]

In the context of unraveling mechanisms related to catalytic reactions, several research groups have devoted efforts to studying the reactions of gas phase clusters[18−24] through experimental means as well as theoretical calculations.[25] It is becoming increasingly recognized that electron density and even charge state can be a significant factor to consider in unraveling the mechanisms of certain catalytic reactions, and gas phase cluster studies are especially amenable to investigating these. For example, in considering active sites, it has been suggested that OH^- and O^{2-} groups exist on γ-Al_2O_3 surfaces and that these sites are responsible for the nucleophilic behavior present in many catalytic oxidation processes.[26] Ionic active sites also have been proposed by Kung et al.[27] and Kiely et al.[28] in the CO oxidation on supported gold catalysts. Therefore, if charge is a characteristic of the active site, using cluster ions as models for the sites may provide insight, which neutral studies are unable to produce.

The nature of the active site responsible for a given catalytic process is a point of concern on an industrial level as well as being of interest in fundamental research. Somorjai et al. have studied the active sites in heterogeneous catalysis and have made progress with single reaction channels.[29] However, the active sites responsible for multichannel processes still remain a catalytic puzzle. Schlögl et al. have investigated the active sites of silver as a catalyst for the oxidation of methanol.[30] They were able to determine that one of three types of adsorbed oxygen on the silver surface was involved in the formation of formaldehyde from methanol. Freund et al. have studied the oxidation of CO on alumina-supported vanadia systems.[31] They found the bridging V−O species to most likely be responsible for the conversion of CO to CO_2 due to the high incidence of

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oxidation occurring over higher coverages, characterized by the increased presence of bridging V−O bonds. The nature of the active site for the oxidation of methanol on metal oxide surfaces has also been addressed theoretically.[32] Weber used extended Hückel caculations to study the rate-limiting step for the oxidative dehydrogenation of methanol over primarily vanadium oxide based clusters. His results showed that the hydrogen atoms seem to favor attaching to the metal rather than to an oxygen ligand; however, he was unable to determine whether the terminal or bridging oxygens played more of a role in the process.

The study of gas-phase cluster ions as active-site models on catalytic surfaces has provided useful information on the possible mechanisms responsible for the process. Zamaraev et al. have shown that reactions of $Mo_xO_y^+$ clusters with methanol are similar to those occurring over molybdenum- and oxygen-containing surfaces in the condensed phase.[33] Using a multistage mass spectrometer, O'Hair et al. investigated the catalytic oxidation of methanol using molybdenum oxide anions. Cycle 1 proposed in their paper shows formation of formaldehyde as a collisionally activated process of $Mo_2O_6(OCH_3)^-$ and all the steps of the cycle are the essential steps proposed over industrial catalysts.[34] In our own laboratory during an investigation of group V metal oxide cluster ions and ethylene, we found an oxygen-transfer reaction pathway to be a dominant channel for certain $(V_2O_5)_n^+$ clusters.[35] On the basis of mass changes observed experimentally and with theoretical calculations, neutral acetaldehyde is the most likely product, also in agreement with results from condensed phase catalytic experiments.[36]

Gas phase investigations of methanol reactions have been made using a variety of metal-based clusters. The reactivity of methanol toward $M_xO_y^-$ [M = Mn, Fe, Co, Ni, Cu][37] and $Nb_xO_y^-$ [38] clusters has been studied using Fourier transform ion cyclotron resonance. In addition, the photodissociation of $Au_n^+(CH_3OH)_m$ clusters has been investigated by Dietrich et al.[39] While the mechanism over Pt is not completely known, formate has been proposed as the active intermediate in the direct oxidation over a Pt electrode using surface-enhanced IR absorption spectroscopy.[40] Theoretical means have also been implemented to investigate the interaction of methanol with surfaces. Thomas et al. conducted a theoretical study on the oxidation of methanol on V_2O_5 using extended Hückel theory. Their results showed that the way methanol adsorbs to the surface affects the oxidative mechanism. Of the three pathways studied, the formation of formaldehyde was favored.[41]

The present study aims to analyze the reactivity of vanadium and niobium oxide cluster cations toward methanol in an attempt to possibly divulge some mechanistic information on the reactions between these metal oxide surfaces. The insight gained also adds to the wealth of knowledge already acquired on the group V metal oxides. The factors that may affect the reactivity including size, stoichiometry, oxidation state, and composition are also addressed herein.

Experimental Section

The experiments discussed herein were performed on a guided ion beam mass spectrometer coupled to a laser vaporization source described in detail previously.[42] Briefly, the metal oxide cluster ions are generated by ablation of a rotating and translating metal rod using a Nd:YAG laser. At a predetermined time, oxygen seeded in helium (∼8%) is passed over the rod using a pulsed valve. The clusters are formed through plasma reactions, cooled via supersonic expansion, and focused into a quadrupole, first through a skimmer followed by a set of electrostatic lenses

and deflectors. The ion of interest is mass selected in the first quadrupole and guided into the octopole, which functions as a reaction cell, through a second set of electrostatic lenses. The reactions conducted in the octopole are performed at near-thermal energies and the pressure of the methanol (Sigma Aldrich, St. Louis, MO) introduced into the system ranges from 0 to approximately 0.6 mTorr, effecting single- as well as multiple-collision conditions. Experiments were also performed with deuterated methanol, CD_3OD, (Cambridge Isotopes, Andover, MA) to ensure correct mass assignments, particularly with regard to the association of H_2. The products generated from the reaction cell are focused through a third set of electrostatic lenses, mass analyzed using a second quadrupole, and detected using a channeltron electron multiplier.

Results

The results of the reactions between vanadium and niobium oxide cluster cations and methanol are shown in Table 1. The products are listed according to increasing mass as some of the relative intensities of the products change depending on the pressure of the reaction cell as will be discussed later.

Vanadium. The vanadium oxide cluster cations studied included $VO_{1,2}^+$, $V_2O_{4-6}^+$, $V_3O_{6-8}^+$, $V_4O_{9-11}^+$, and $V_5O_{12,13}^+$. All of the clusters studied with the exception of $V_4O_{11}^+$ showed the association of CH_3 and CH_3OH to the mass selected parent ion. All the clusters studied except VO^+ also exhibited association of C_2H_6O to the selected ion. The attachment of H_2 to the selected ion occurred for VO_2^+, $V_2O_4^+$, and $V_3O_{7,8}^+$. In addition, reactions of methanol with $V_2O_5^+$ and $V_2O_6^+$ produced a species corresponding to H_2 association to $V_2O_4^+$. These studies were confirmed using deuterated methanol. Beginning studies using light methanol showed a shoulder on the clusters, as can be seen in the lower mass spectrum in Figure 1. The deuterated studies were performed to ascertain if the shoulder was the result of H_2 association. The upper mass spectrum in Figure 1 of $V_2O_4^+$ shows the separation of the shoulder resulting from the association of D_2 with deuterated methanol.

A few clusters showed reactivities toward more oxygen deficient analogues. For example, consider $V_2O_6^+$. In addition to the associations onto the $V_2O_6^+$, in reactions the parent ion also displayed O_2 loss leaving $V_2O_4^+$; also observed were H_2 and CH_3 associations onto $V_2O_4^+$. Also, $V_4O_{11}^+$ showed $V_4O_9^+$ as a product, commonly observed with several reactant gases,[43] as well as CH_3, CH_3OH, and C_2H_6O association onto $V_4O_{10}^+$. V_2O_6 loses O_2 easily as does $V_4O_{11}^+$ and is termed an oxygen-rich cluster because it loses oxygen at near-thermal energies during collision-induced dissociation experiments conducted previously in our laboratory.[44]

Niobium. The niobium oxide cluster cations studied for this investigation include NbO_2^+, $Nb_2O_{4-6}^+$, $Nb_3O_{7,8}^+$, $Nb_4O_{9-11}^+$, and $Nb_5O_{12,13}^+$. All the clusters studied show the association of methanol to the selected ion without exception. The association of CH_3 was observed with all the niobium-based clusters except NbO_2^+, $Nb_2O_6^+$, and $Nb_5O_{12}^+$. The C_2H_6O adduct was seen with all the clusters studied with the exception of $Nb_3O_8^+$ and $Nb_4O_{9,10}^+$. The H_2 adduct was observed with the following parent ions, NbO_2^+, $Nb_2O_{4,5}^+$, $Nb_3O_{7,8}^+$, $Nb_4O_{11}^+$, and $Nb_5O_{12}^+$. These products were confirmed using deuterated methanol as was done with the vanadium oxide clusters. In addition to the association products on the mass-selected ion, $Nb_2O_6^+$ also showed atomic oxygen loss, leaving $Nb_2O_5^+$ and addition of H_2 onto $Nb_2O_5^+$. $Nb_3O_8^+$ showed analogous products to $Nb_2O_6^+$, leaving $Nb_3O_7^+$ and $Nb_3O_7H_2^+$ as two of the products observed.

Vanadium and Niobium Oxides

J. Phys. Chem. B, Vol. 108, No. 12, 2004 **3857**

TABLE 1: List of the Products Observed for the Reactions between $V_xO_y^+$ and $Nb_xO_y^+$ with Methanol

cluster	$V_xO_y^+$	$Nb_xO_y^+$
(1,1)	$VOCH_3^+$	
	$VOCH_3OH^+$	
(1,2)	$VO_2H_2^{+\ a}$	$NbO_2H_2^{+\ a}$
	$VO_2CH_3^+$	$NbO_2CH_3OH^+$
	$VO_2CH_3OH^+$	$NbO_2C_2H_6O^+$
	$VO_2C_2H_6O^+$	
(2,4)	$V_2O_4H_2^{+\ a}$	$Nb_2O_4H_2^{+\ a}$
	$V_2O_4CH_3^+$	$Nb_2O_4CH_3^+$
	$V_2O_4CH_3OH^+$	$Nb_2O_4CH_3OH^+$
	$V_2O_4C_2H_6O^+$	$Nb_2O_4C_2H_6O^+$
		$Nb_2O_4C_2H_6O_2^+$
(2,5)	$V_2O_4^+$	$Nb_2O_5H_2^{+\ a}$
	$V_2O_4H_2^{+\ a}$	$Nb_2O_5CH_3^+$
	$V_2O_5CH_3^+$	$Nb_2O_5CH_3OH^+$
	$V_2O_5CH_3OH^+$	$Nb_2O_5C_2H_6O^+$
	$V_2O_5C_2H_6O^+$	
(2,6)	$V_2O_4^+$	$Nb_2O_5^+$
	$V_2O_4H_2^{+\ a}$	$Nb_2O_5H_2^{+\ a}$
	$V_2O_4CH_3^+$	$Nb_2O_6CH_3OH^+$
	$V_2O_6CH_3^+$	$Nb_2O_6C_2H_6O^+$
	$V_2O_6CH_3OH^+$	
	$V_2O_6C_2H_6O^+$	
(3,6)	$V_3O_6CH_3^+$	
	$V_3O_6CH_3OH^+$	
	$V_3O_6C_2H_6O^+$	
(3,7)	$V_3O_7H_2^{+\ a}$	$Nb_3O_7H_2^{+\ a}$
	$V_3O_7CH_3^+$	$Nb_3O_7CH_3^+$
	$V_3O_7CH_3OH^+$	$Nb_3O_7CH_3OH^+$
	$V_3O_7C_2H_6O^+$	$Nb_3O_7C_2H_6O^+$
(3,8)	$V_3O_8H_2^{+\ a}$	$Nb_3O_7^+$
	$V_3O_8CH_3^+$	$Nb_3O_7H_2^{+\ a}$
	$V_3O_8CH_3OH^+$	$Nb_3O_8H_2^{+\ a}$
	$V_3O_8C_2H_6O^+$	$Nb_3O_8CH_3^+$
		$Nb_3O_8CH_3OH^+$
(4,9)	$V_4O_8^+$	$Nb_4O_9CH_3^+$
	$V_4O_9CH_3^+$	$Nb_4O_9CH_3OH^+$
	$V_4O_9CH_3OH^+$	
	$V_4O_9C_2H_6O^+$	
(4,10)	$V_4O_9^+$	$Nb_4O_{10}CH_3^+$
	$V_4O_{10}CH_3^+$	$Nb_4O_{10}CH_3OH^+$
	$V_4O_{10}CH_3OH^+$	
	$V_4O_{10}C_2H_6O^+$	
(4,11)	$V_4O_9^+$	$Nb_4O_{11}H_2^{+\ a}$
	$V_4O_{10}CH_3^+$	$Nb_4O_{11}CH_3^+$
	$V_4O_{10}CH_3OH^+$	$Nb_4O_{11}CH_3OH^+$
	$V_4O_{10}C_2H_6O^+$	$Nb_4O_{11}C_2H_6O^+$
(5,12)	$V_5O_{12}CH_3^+$	$Nb_5O_{12}H_2^{+\ a}$
	$V_5O_{12}CH_3OH^+$	$Nb_5O_{12}CH_3OH^+$
	$V_5O_{12}C_2H_6O^+$	$Nb_5O_{12}C_2H_6O^+$
(5,13)	$V_5O_{12}^+$	$Nb_5O_{13}CH_3^+$
	$V_5O_{13}CH_3^+$	$Nb_5O_{13}CH_3OH^+$
	$V_5O_{13}CH_3OH^+$	$Nb_5O_{13}C_2H_6O^+$
	$V_5O_{13}C_2H_6O^+$	

Discussion

This particular study is part of an ongoing investigation in our laboratory into the reactivities of the group V metal oxide cluster ions toward a variety of reactant gases.[17] These studies have shown that a variety of factors affect the reactivity of the metal oxide ion including size, stoichiometry, oxidation and charge state, degree of coordinative saturation, and composition. These factors were also found to influence the reactivities of vanadium and niobium oxide cluster ions toward methanol. In the following, certain examples that epitomize these effects are discussed.

As mentioned above, Figure 1 shows the mass spectra of $V_2O_4^+$ with deuterated and light methanol. The identity of the shoulder on the $V_2O_4^+$ cluster in the lower spectrum is elucidated using CD_3OD to be association of H_2 to the selected
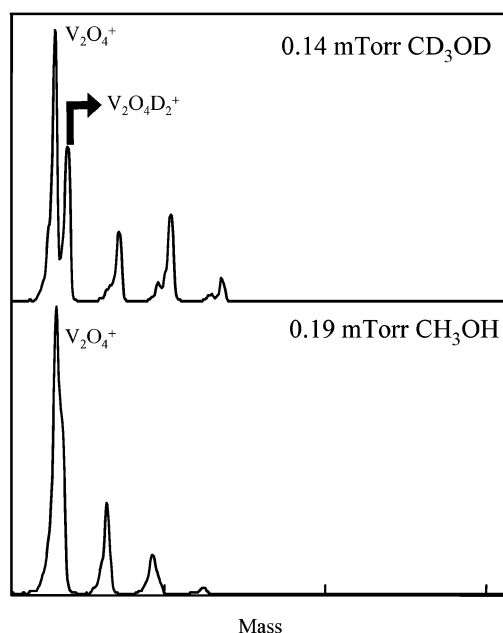
Figure 1. Mass spectra for $V_2O_4^+$ with (a) 0.14 mTorr CD_3OD and (b) 0.19 mTorr CH_3OH.

ion. Since we are unable to detect neutral species in our mass spectrometer, there are a few possible structures for the neutral species. One possibility is the formation of formaldehyde shown in the equation below

$$V_2O_4^+ + CH_3OH \rightarrow V_2O_4^+H_2 + CH_2O \qquad (1)$$

This is a common product observed over condensed-phase vanadia catalysts.[45] The pressure at which this is observed in the upper spectrum in Figure 1 is 0.14 mTorr CD_3OD and effects the transition between single- and multiple-collision conditions. However, small amounts of D_2 have been observed to attach with the pressure less than 0.1 mTorr, which effects single-collision conditions. Therefore, there is a strong possibility that reaction 1 is occurring. The association of D_2 is also noted at pressures greater than 0.1, and therefore, it is possible there is more than one collision occurring in the reaction cell; hence, there are other possible neutral products at elevated pressures. The reaction below shows the interaction between $V_2O_4^+$ and two methanol molecules, each losing a single hydrogen atom

$$V_2O_4^+ + 2CH_3OH \rightarrow V_2O_4^+H_2 + 2CH_3O \qquad (2)$$
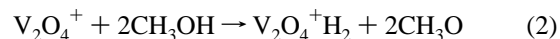
This would yield two possible radical species, the methoxy radical ($^•OCH_3$) and the hydroxymethyl radical ($^•CH_2OH$). Being reactive in nature, the likelihood of the radicals existing as such is very small. However, a primitive analysis, i.e., ignoring the presence of $V_2O_4^+$, of the enthalpy of this process shows the production of either radical species is highly endothermic, 437.8 and 384.2 kJ/mol for the methoxy and hydroxymethyl radicals, respectively. If by some chance, the radicals were formed, they could potentially recombine to form ethanediol, dimethyl peroxide, or ethyl hydroperoxide, each having the formula $C_2H_6O_2$. If this is indeed occurring even to a small extent, using our current experimental set up, it is not possible to say definitively which neutral species would be produced during this reaction. The likelihood of these species being produced, however, is relatively insignificant. The implementation of theoretical methods would greatly aid the uncertainty of which pathway has the highest probability of occurring given the experimental conditions.
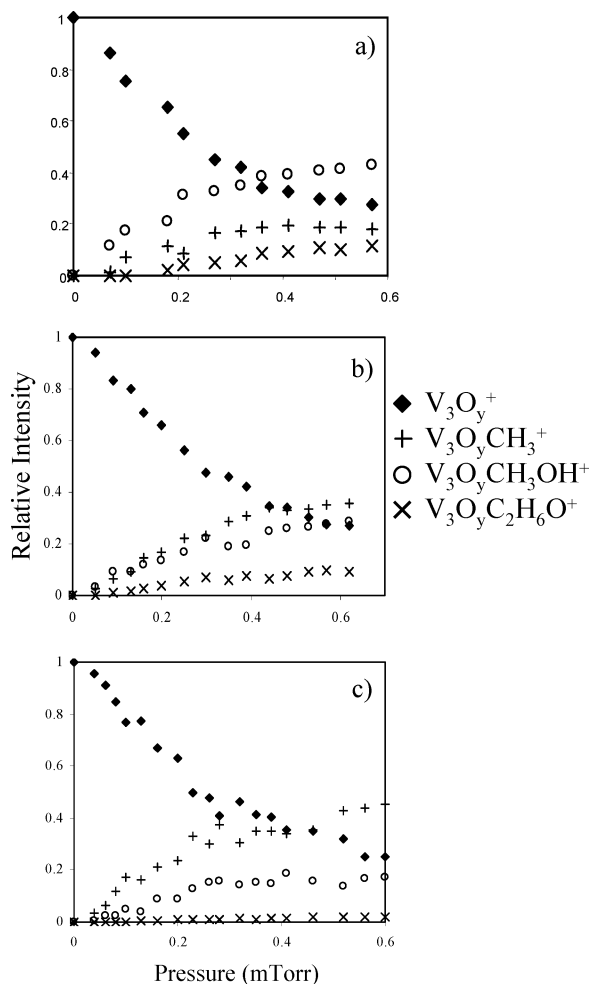
Figure 2. Branching ratios for (a) $V_3O_6^+$, (b) $V_3O_7^+$, and (c) $V_3O_8^+$ with methanol.

Figure 2 shows the branching ratios for $V_3O_{6-8}^+$ with methanol. Each of the clusters shows the same products, association of CH_3, CH_3OH, and C_2H_6O; however, the dominant product changes when $V_3O_6^+$ is compared with $V_3O_7^+$ and $V_3O_8^+$. The formation of C_2H_6O may arise from the reaction of two methanol molecules forming the adduct and water as shown below in reaction 3

$$V_3O_6^+ + 2CH_3OH \rightarrow V_3O_6^+C_2H_6O + H_2O \qquad (3)$$
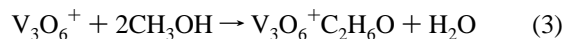
$V_3O_6^+$ shows molecular association as the most intense of the three products at every energy studied. For $V_3O_7^+$ and $V_3O_8^+$, the association of CH_3 shows a stronger presence than methanol association. Even for this small range of clusters, it can be seen that the stoichiometry of these metal oxides affects the preferred moiety to associate during the reactions with methanol.

A second example of the effect that stoichiometry has on the reactivity is with the $Nb_4O_{9-11}^+$ clusters shown in Figure 3. $Nb_4O_9^+$ and $Nb_4O_{10}^+$ both yield the association of CH_3 and CH_3OH; however, the preference for these products is drastically different. The CH_3 adduct is dominant at lower pressures and then decreases under multiple-collision conditions for $Nb_4O_9^+$. $Nb_4O_{10}^+$, however, shows a steady increase of $Nb_4O_{10}CH_3^+$, which continues through the entire pressure range, and CH_3-OH association is only a minor product. $Nb_4O_{11}^+$ shows the CH_3 and CH_3OH product as was observed with $Nb_4O_9^+$ and $Nb_4O_{10}^+$ and the C_2H_6O adduct. $Nb_4O_{11}^+$ does not have a particularly dominant product at any of the pressures studied,
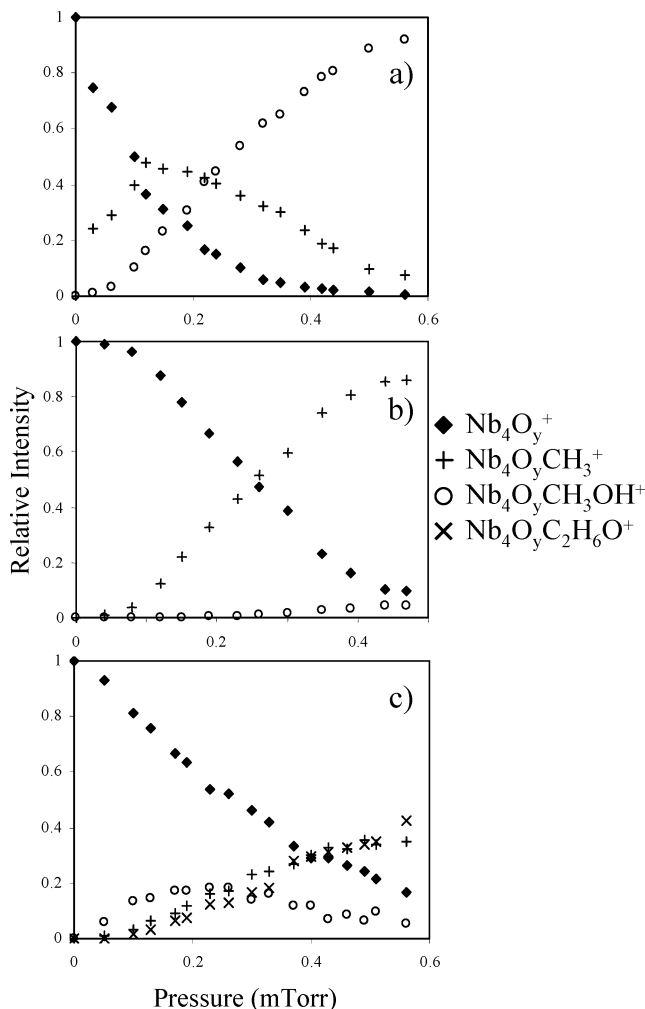

Figure 3. Branching ratios for (a) $Nb_4O_9^+$, (b) $Nb_4O_{10}^+$, and (c) $Nb_4O_{11}^+$ with methanol.

unlike both $Nb_4O_9^+$ and $Nb_4O_{10}^+$. At elevated pressures, the CH_3 and C_2H_6O adducts are of similar intensities. Given the similar size and composition of the clusters in this series, this group shows the dramatic effect the number of oxygen atoms has on the reactivity of the cluster.

It should be noted here that the structure of the C_2H_6O adduct is unknown at this time. There are a few possibilities to be considered. One possibility is dimethyl ether, CH_3OCH_3. This product is observed when methanol is reacted over a vanadium oxide condensed-phase surface and is therefore a feasible outcome in the course of these reactions.[45,46] It is also conceivable the adduct is ethanol, CH_3CH_2OH. Ethanol is not reported as a product of methanol oxidation over condensed-phase vanadium- and niobium-based catalysts; hence, it is not as likely to be the structure for C_2H_6O as dimethyl ether. A third possibility for C_2H_6O is dissociative adsorption. This would probably result from a methyl and a methoxy group adsorbed on two different sites on the cluster. We have previously observed multiple associations with other systems; hence, this is a possibility that deserves consideration.[47] At present the configuration is unknown; however, further structural investigation of the C_2H_6O products may provide some insight. Theoretical calculations would be particularly useful to address these possible reaction products.

Oxidation state is another factor which can greatly affect the reactivity of a particular cluster. The oxidation state of the vanadium in VO_2^+, $V_3O_7^+$, and $V_5O_{12}^+$ is +5. Figure 4 shows
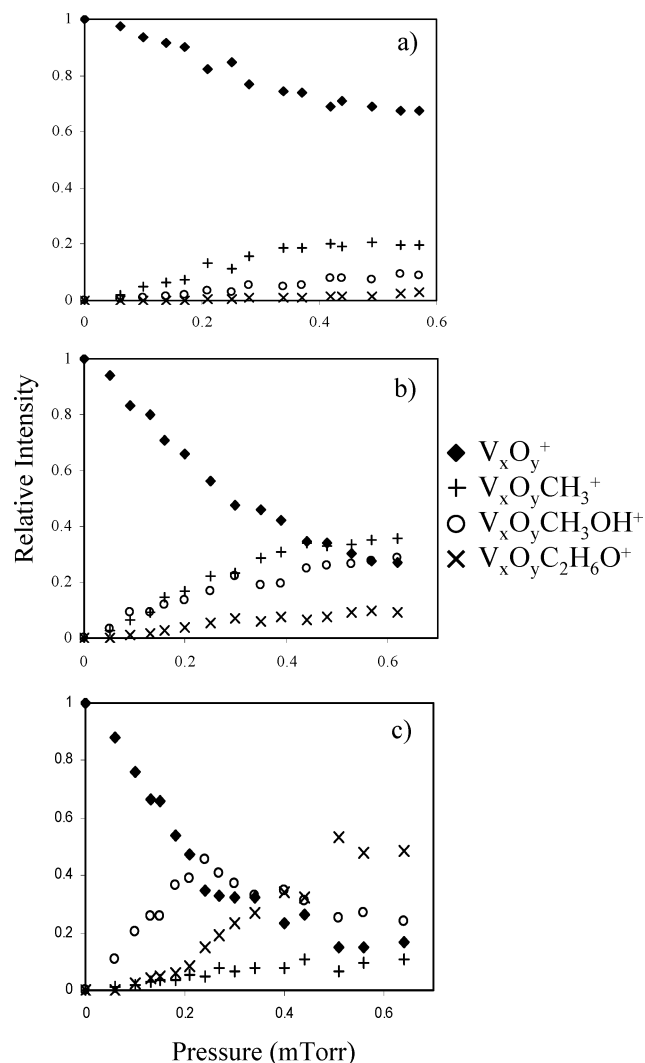
Vanadium and Niobium Oxides

J. Phys. Chem. B, Vol. 108, No. 12, 2004 **3859**

Figure 4. Branching ratios for (a) VO_2^+, (b) $V_3O_7^+$, and (c) $V_5O_{12}^+$ with methanol.

Figure 5. Branching ratios for (a) NbO_2^+, (b) $Nb_3O_7^+$, and (c) $Nb_5O_{12}^+$ with methanol.

the branching ratios for these three clusters with methanol. The products observed with each cluster are association of CH_3, CH_3-OH, and C_2H_6O. In the case of $V_5O_{12}^+$, there is an initial increase in molecular association followed by a decrease and subsequent increase in the association of C_2H_6O at elevated pressure, effecting multiple-collision conditions. The decrease in the methanol association product suggests this product was consumed during the formation of the C_2H_6O association product. For VO_2^+ and $V_3O_7^+$, each of the three adducts increases incrementally with an increase in methanol pressure with the VO_2^+ cluster slightly less reactive than $V_3O_7^+$. These two species display a remarkably different reactivity pattern than $V_5O_{12}^+$, showing that, in this case, the oxidation state of the metal is not the decisive factor in the reactivity toward methanol.

The differences and similarities in the reactivities for NbO_2^+, $Nb_3O_7^+$, and $Nb_5O_{12}^+$ are illustrated by their branching ratios shown in Figure 5. All three clusters yield molecular association and the C_2H_6O adduct; only the NbO_2^+ lacks the addition of CH_3. Their patterns in reactivity vary as the pressure of methanol increases. Similar to $V_5O_{12}^+$ discussed above, $Nb_3O_7^+$ and $Nb_5O_{12}^+$ show similar reactivities with CH_3OH and C_2H_6O associations predominant at low and high reactant gas pressures, respectively. This striking similarity is believed to be due primarily to the oxidation state of the niobium, since the size and structure of the clusters differ. However, when compared
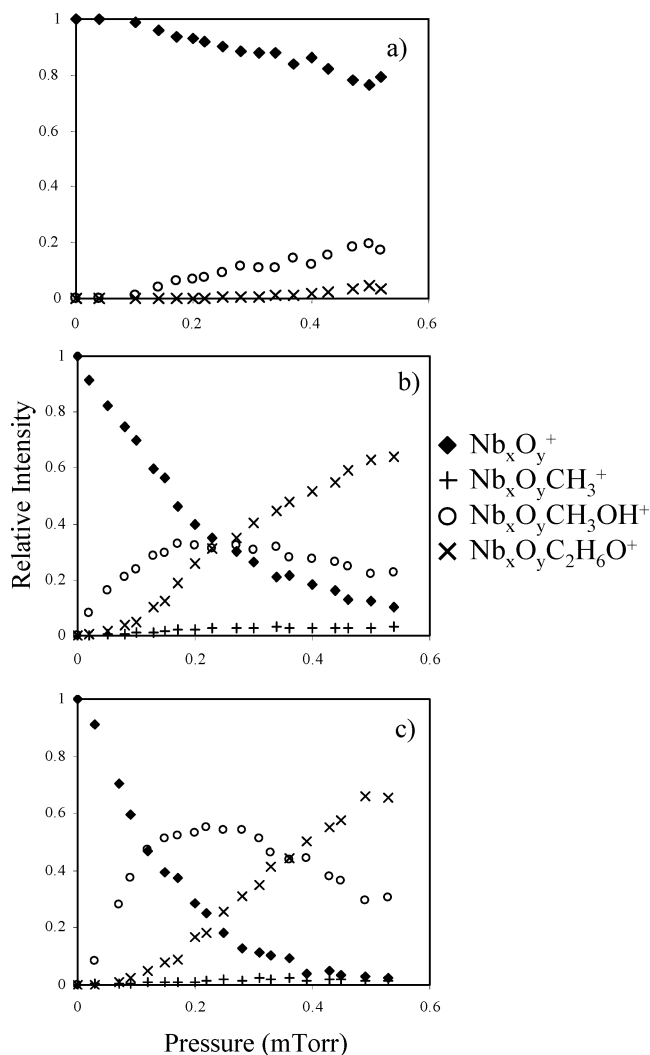
to NbO_2^+, the pattern of reactivity is remarkably different, neither the association of CH_3OH nor C_2H_6O can be considered a dominant product. NbO_2^+ has the same oxidation state as $Nb_3O_7^+$ and $Nb_5O_{12}^+$. Therefore, it must be a combination of qualities that need to be present for particular reactivity patterns to emerge. For example, in this case, the oxidation state may be one required element, although the presence of more than one metal center in the niobium oxide clusters may also be necessary to show the dominant association of CH_3OH at low pressures and C_2H_6O at higher pressures.

Figures 4 and 5 show that the branching ratios of VO_2^+, $V_3O_7^+$, and $V_5O_{12}^+$ and NbO_2^+, $Nb_3O_7^+$, and $Nb_5O_{12}^+$, respectively, can be compared and evaluated in terms of cluster composition, namely, the identity of the metal. As discussed above for VO_2^+, $V_3O_7^+$, and $V_5O_{12}^+$, the oxidation state of the vanadium remains the same, +5; however, the reactivity differs. The oxidation state of niobium in NbO_2^+, $Nb_3O_7^+$, and $Nb_5O_{12}^+$ is also +5, and in this case, the reactivity is more similar to the various species. There is an initial increase in the association of CH_3OH, followed by a decrease and subsequent introduction of C_2H_6O association. Although the initial increase of methanol association is lower for $Nb_3O_7^+$ than for $Nb_5O_{12}^+$, the similarities in reactivity cannot be denied. The reactivities of both $Nb_3O_7^+$ and $Nb_5O_{12}^+$ are similar to that of $V_5O_{12}^+$. In the case of the larger niobium oxides, the oxidation state of the metal is

an important but not the sole factor leading to similar reactivity toward methanol. In Figure 5, the branching ratio for NbO_2^+ is also shown. While NbO_2^+ has the same oxidation state as $Nb_3O_7^+$ and $Nb_5O_{12}^+$, it has quite a different reactivity pattern. Also, for the analogous vanadium oxides, the oxidation state of the metal does not necessarily determine the reactivity. For $V_3O_7^+$, the three products observed grow in gradually as the pressure of the methanol increases. This example shows that the composition and oxidation state of the metal oxide does affect the reactivity of a given cluster; however, there are other factors which also must be taken into consideration. $V_3O_7^+$ and $Nb_3O_7^+$ exhibit markedly different reactive patterns, while $V_5O_{12}^+$ and $Nb_5O_{12}^+$ are very similar.

Size is also a factor affecting the reactivity of the cluster toward methanol. Here, the relative reactivities of MO_2^+, $M_3O_7^+$, and $M_5O_{12}^+$, shown in Figures 4 and 5, are a good example. In each of these clusters, the oxidation state of the metal is +5. Looking first at the vanadium oxide cluster cations in Figure 4, it can be seen that the reactivity changes. The smaller clusters exhibit incremental increases in their product intensities whereas the $V_5O_{12}^+$ cluster shows a decrease in the formation of CH_3OH association. While the oxidation state of the vanadium and the composition remain the same, the size and the structure differ and therefore are the reason for the discrepancy. As the size of the cluster increases, it is intuitively obvious that the structures must also change. Therefore, it is difficult to discuss the effect of size without also addressing structure, considering they are so intimately connected. This size effect is also evident with the niobium oxide cluster cations shown in Figure 5. In this case, NbO_2^+ is the cluster with differing reactivity. Only the smallest cluster in the series, NbO_2^+, shows the incremental increase in product formation while the $Nb_3O_7^+$ and $Nb_5O_{12}^+$ show the growth and decay of methanol association. Other researchers have studied the effect of cluster size on reactivity. For example, Gates et al. have investigated the effect of size on the reactivity of supported iridium catalysts.[48] They found the Ir_4 cluster to be several times more reactive than the Ir_6 cluster in the hydrogenation of ethene. Irion et al. has also studied the size and energy effect of various Cu_n^+ clusters during reactions with oxygen.[49] In addition, Bondybey et al. found differing reactivities toward the dehydrogenation of p-xylene on Nb_n^+ ($n = 2-26$).[50]

As briefly mentioned above, as the size of the cluster increases, the structure must also change to conform to the lowest energy configuration for a given set of experimental conditions. The structures of several group V metal oxide clusters have been investigated both experimentally and theoretically.[51−55] The lowest energy structures for the anionic[52,53] and cationic[35,54] $V_{2}O_{4−6}^+$ clusters are double oxygen bridging structures. This was also found to be stable for the $Nb_2O_6^+$ cluster.[55] As the size increases further, the structures take on a cage arrangement.[53−55] It is also possible for the structure to change while still maintaining a certain reactive moiety as was found with an oxygen-centered radical in the $V_2O_5^+$ and $V_4O_{10}^+$ clusters.[35] This could explain the similarities between the $Nb_3O_7^+$ and $Nb_5O_{12}^+$ clusters and their reactions with methanol. If a similar characteristic does not exist for both $V_3O_7^+$ and $V_5O_{12}^+$, this might also explain the differences in their respective reactivity patterns. However, additional calculations need to be performed to compare the structures of the clusters within the range discussed in this study to compare and contrast the variety of structural components that may react with the methanol and explain the reaction patterns observed under our experimental conditions.
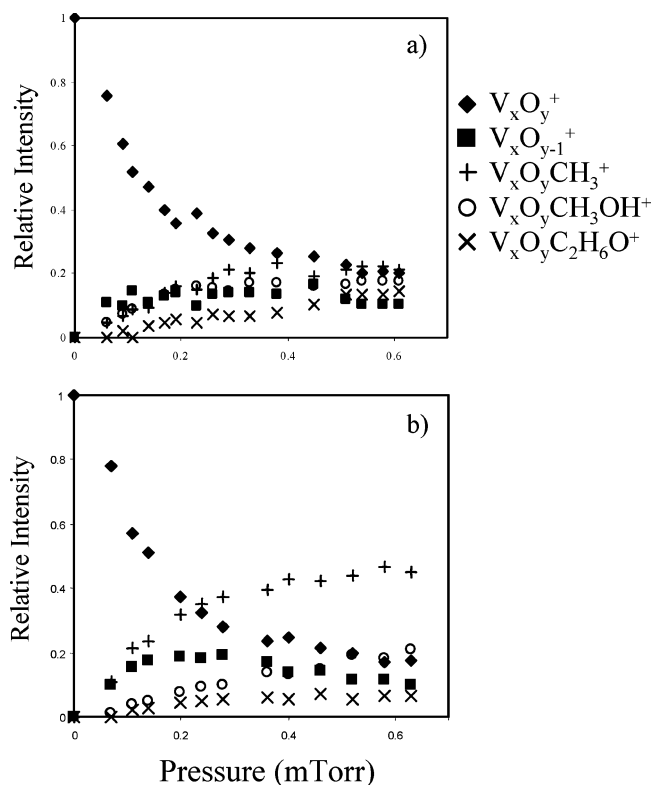

Figure 6. Branching ratios for (a) $V_2O_5^+$ and (b) $V_4O_{10}^+$ with methanol.

As discussed above, the structures of $V_2O_5^+$ and $V_4O_{10}^+$ both possess an oxygen-centered radical species determined by density functional theory.[35] This moiety is believed to be responsible for the oxygen transfer by the $V_2O_5^+$ and $V_4O_{10}^+$ clusters to ethane and ethylene. It is therefore worth noting whether the oxygen-centered radical is responsible for an oxygen-transfer reaction pathway or any other specific reactivities. Figure 6 shows the branching ratios for $V_2O_5^+$ and $V_4O_{10}^+$ with methanol. Nominally, the reaction products are the same, association of CH_3, CH_3OH, and C_2H_6O and also the loss of an oxygen atom yielding $V_2O_4^+$ and $V_4O_9^+$ for $V_2O_5^+$ and $V_4O_{10}^+$, respectively. The $V_2O_5^+$ cluster does not show any particularly dominant product; however, $V_4O_{10}^+$ does show a significant association of CH_3 onto the selected ion. While the oxygen-centered radical is most likely responsible for the formation of $V_2O_4^+$ and $V_4O_9^+$, it is probably not the active species that leads to a notable appearance of the CH_3 association in the branching ratio for $V_4O_{10}^+$ and only a minor showing for the $V_2O_5^+$ cluster.

Comparisons between the gas phase reaction studies, such as the ones described herein, and condensed phase reactions provide continual validation for the work conducted in our laboratory. The dehydrogenation of methanol to yield formaldehyde results in the loss of H_2 from methanol. As discussed above, one possible pathway for the formation of the observed $V_2O_4^+H_2$ product yields formaldehyde as a neutral product. This product was observed over supported vanadia catalysts by Wachs et al.[56] Using IR, Raman, UV−vis, and diffuse reflectance spectroscopies, they found formaldehyde formation with 90−99% selectivity over titania-, zirconia-, niobia-, and ceria-supported vanadia catalysts. As discussed herein, dimethyl ether is one of the possible conformations of the C_2H_6O adduct observed with several of the clusters analyzed for this study. Busca et al. have also studied methanol oxidation over vanadia-based catalysts and found the range of products obtained

Vanadium and Niobium Oxides

J. Phys. Chem. B, Vol. 108, No. 12, 2004 **3861**

depends on the redox properties and the acidity of the catalyst.[57] Among the products they listed is dimethyl ether.

Other products over condensed phase catalysts include CO_2, CO, dimethoxymethane $(CH_3O)_2CH_2$, and methyl formate CH_3-OCHO.[8] These products are not observed during the reaction between the metal oxide clusters and methanol discussed here. These products may require more than one active site to form from methanol, an environment which may not be accessible on the surface of the cluster. Also, if any of these products are formed and remained unattached to the cluster, we would be unable to detect them through the mass analysis. For instance, conceivably if CO_2 were formed from two methanol molecules, the other potential products could be CH_4, $2 H_2$ molecules, and the mass-selected ion seemingly unaffected, all of which are undetectable in our mass spectrometer.

Conclusions

Employing a guided ion beam mass spectrometer, we have been able to individually analyze a variety of vanadium and niobium oxide cluster cations and their behavior when exposed to methanol at increasing pressure. The products consisted of associating H_2, CH_3, CH_3OH, and C_2H_6O to the mass-selected cluster. The reactivity of each cluster depended on a variety of factors including size, stoichiometry, oxidation state, structure, and composition. In many cases, it is obvious that not a single characteristic of the cluster is responsible for the displayed reactivity. For example, the oxidation state and the composition were both factors in the reactivity of the MO_2^+, $M_3O_7^+$, and $M_5O_{12}^+$ clusters. The MO_2^+ and $M_5O_{12}^+$ displayed similar reactivities, but the $M_3O_7^+$ clusters differed.

The experimental setup allows us to investigate different clusters and their response to a given reactant gas under nearly identical experimental conditions. The information gained here may be applied to the knowledge already gathered about the group V metal oxide reactivities in the gas phase and also possibly to divulge information on possible active sites on catalytic surfaces. We are unable to perform a complete catalytic cycle; however, the data acquired has shown remarkable consistency with catalytic processes conducted in the condensed phase. It is this analogy from the gas to condensed phase that shows the potential for gas phase cluster studies to be taken seriously in the realm of catalysis, by providing information on potential catalytically active sites and hence the mechanisms for certain processes which still remain elusive.

The unanswered questions remaining from this study, such as the structure of the C_2H_6O adduct and the neutral product from the H_2 association onto selected clusters, still need to be addressed. Theoretical calculations may provide insight into the C_2H_6O structure and the likelihood of the neutral dehydrogenation product being formaldehyde. Also, experimental studies on the structure of the C_2H_6O adduct are planned with slight modification to our current setup.

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