Comparative Cluster Reaction Studies of the V, Nb, and Ta Series

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Reactions of the group 5 transition-metal clusters (Vn, Nb, and Ta clusters) have been investigated in the gas phase by using a fast-flow chemical reactor. Dissociative chemisorption of D2 and N2 is found to be size selective for these bare metal clusters, as well as for the cluster monoxides V2O, Ta2O, and monocarbides V2C. The effect of a single atomic impurity (C or O) on the clusters larger than 10 atoms and becomes negligible for clusters larger than 10–20 atoms. This loss of sensitivity to impurities is consistent with the loss of cluster size selectivity, which occurs in the same size range. Evidence of structural isomerism is found for Nb11, Nb12, and Ta12, which react with N2 with biexponential reaction kinetics. The rate of chemisorption of ethane (C2H6) displays a steady increase with cluster size for V, Nb, and Ta clusters. Finally, the rate of addition of a second ligand to a metal clusters is considered, and examples are analyzed for Nb2N2 + N2.

I. Introduction

Metal clusters constitute a unique class of molecules which interpolate between the two extremes of the isolated metal atom and the bulk metallic surface. In recent years, the chemical and physical properties of the small metal clusters (n = 2–40) and the approach of these properties to bulk values have become a focus of considerable attention. Spectroscopic studies of the smallest clusters (dimers and trimers) have provided electronic and geometrical information for a few systems, although much is yet to be learned. For larger clusters (n = 4–40) spectroscopic data are completely lacking except for a few isolated examples. Chemical reaction studies provide a useful (but indirect) probe into the structural makeup of these novel species and directly probe the approach of chemical behavior to the bulk metallic surface. The earliest reaction studies of iron, cobalt, and niobium clusters reacting with N2 and D2 have shown sharp variations in reactivity as a function of cluster size. Following these early studies considerable theoretical and experimental efforts have concentrated on the effect of cluster size on various properties. Ionization potentials, electron affinities, and magnetic properties have been observed to depend on cluster size, in some cases quite strongly. More recently, reaction studies have been conducted on cluster ions to attempt to discern the effect on the reactivity of a given cluster. In the tradition of surface science, saturation and desorption studies of small iron clusters have provided information concerning binding sites and cluster geometry, much as adsorption isotherm measurements have provided for metal surfaces. At the other end of the spectrum, just as metal atom reactions depend on the orientation of the reacting species, the reactivity of small niobium clusters also shows a stereochemical selectivity which decreases with increasing cluster size. Evidence of cluster structural isomerism, which must occur for sufficiently large metal clusters, has recently been observed for small niobium clusters and cluster cations.

Amid this recent expanse of intriguing and creative experiments, there has not yet been much effort focusing on the possibility of periodic trends in cluster reactivity. Since many chemical and physical properties are similar within a group or family, a comparative study of transition-metal clusters within a given family is warranted. In this paper we present a comparative study of the group 5 transition-metal cluster reactions. These metals, vanadium, niobium, and tantalum, are all highly refractory, share the same bulk metallic crystal structure (bse), and react readily...
with H₂ and N₂ to the point of lattice penetration. In this paper investigations of the reactions of V₄, Nb₄, and Ta₄ with D₂, N₂, and C₂H₆ are reported. Although the reactions of these metal clusters with D₂ and N₂ have been previously studied, it is useful to compare data obtained on the same instrument since results are sensitive to source conditions. In particular, the cluster temperature may well differ from source to source. In addition, we have extended the size range of the clusters investigated to larger species in some cases and have studied the effects of impurity atoms by comparing the reactivity of V₄C, V₄O, and Ta₄O with that of the parent bare metal clusters.

II. Experimental Section

The metal cluster source and fast-flow chemical reactor used in the present study are quite similar to those used in previous investigations. A pulsed supersonic beam of metal clusters is produced by laser vaporization of a metal target within the throat of a pulsed supersonic nozzle. For this investigation niobium (Materials Research Corp., 1/₄-in. diameter), vanadium (Alfa, 1/₄-in. diameter), and tantalum (Aesar, 0.002-in.-thick foil) targets were used. Metal vaporization is achieved by focusing (100-cm focal length lens) the second-harmonic output (532 nm, 40–80 mJ/pulse) of a Q-switched Nd:YAG laser (Quantel Model 580-10) to a 0.5-mm-diameter spot on the metal target rod or disk. Helium, purified by a molecular sieve trap maintained at 77 K and regulated to a pressure of 1.25 psi, is pulsed over the metal target by a magnetically operated double-solenoid valve. The high density of helium in the 2-mm-diameter nozzle throat quenches the metal plasma thereby forming clusters ranging up to 45 atoms in size. The helium carrier gas along with the newly formed clusters then expands into a fast-flow reaction tube (10 cm long, 1-cm i.d.) positioned approximately 5 cm downstream from the point of vaporization. The sudden decrease in density which accompanies expansion into the reaction tube then halts further clustering.

Four equally spaced hypodermic needles protruding into the reaction tube are used to inject either reactant gas diluted in helium or pure helium as a control experiment. These needles are supplied from a common annular reservoir, which is itself supplied with gas from two independently pulsed solenoid valves (General Valve, Series 9) monitored by mass flowmeters (Teledyne Hastings Raydist, Model STSH-50). The average pressure in the reaction tube is estimated to be approximately 100 Torr of a 0.0–2.0% reactant/helium mixture. Alternate pulses of reactant/helium mixtures and pure helium control gas are injected into the flow tube to allow for a comparison between the bare cluster distribution and the product distribution. Following their passage through the reaction tube, the metal clusters expand into vacuum and pass through a skimmer into the ionization region of a reflectron time-of-flight mass spectrometer (TOFMS). Detection of the clusters and their reaction products is accomplished by photoionization time-of-flight mass spectrometry using an excimer laser (Questek, Model 2420) operating on the ArF (6.4 eV) or F₂ (7.9 eV) transitions. The laser fluence is kept low, in the range of 5–50 μJ/cm², to minimize multiphoton absorption and consequent fragmentation of the metal clusters. The resulting ions are then extracted perpendicular to the molecular beam axis, accelerated up a reflecting TOFMS, and collected on a microchannel plate detector (Galileo, Model 3025-B) coupled to a 50-ohm anode assembly. The signal is amplified (Pacific Instruments, Model 2A50), digitized (Transiac, now DSP Technology, Model 2001), and stored as a mass spectrum on a DEC 11/73 microcomputer.

Typically 1000 experimental cycles are averaged for each reagent flow rate, resulting in a reactant mass spectrum and a control mass spectrum. Figure 1 shows a selected portion of the time-of-flight mass spectra for niobium clusters reacting with nitrogen. The figure shows both a control mass spectrum, where

![Figure 1](image-url)
The effective rate constant $k'$, in units of sccm$^{-1}$, displayed as a function of cluster size for D$_2$ chemisorption on V$_9$ and Nb$_9$ clusters. Note the similarity in reaction patterns for V$_9$ and Nb$_9$, yet we have plotted only one point for the corresponding coefficients $c_1$ and $c_2$. Estimated errors for $c_1$ and $c_2$ are ±10–20%; errors in $k'$ and $k_2$ are probably similar except for the slowest rates, which are more difficult to measure. Data obtained using low-intensity ArF (6.42 eV, 193 nm) radiation for photoionization. Data obtained using low-intensity F$_2$ (7.90 eV, 157 nm) radiation for photoionization. $k_1'$ and $k_2'$ are effective rate constants, give in units of sccm$^{-1}$.

In a previous publication$^4$ we reported the existence of two isomers of Nb$_{12}$, corresponding to different structural isomers which do not interconvert on a 100-μs time scale at 300 K. On this basis one expects a biexponential depletion of the form

$$\left[\frac{M_{a1}}{M_{a0}}\right] = c_1 \exp[-k_1'F_R] + c_2 \exp[-k_2'F_R]$$

where $c_1$ and $c_2$ are the fractional concentrations of the two isomeric forms of M$_a$ (weighted by their photoionization cross sections), $k_1'$ and $k_2'$ are the effective rate constants of the two isomeric forms, and F$_R$ is the measured flow rate of the reactant gas (in this case D$_2$). A nonlinear least-squares fit to this functional form provides values of $c_1$, $c_2$, $k_1'$, and $k_2'$. For Nb$_9$ and Nb$_{12}$ reacting with D$_2$ the resulting values of $k_1'$ and $k_2'$ are plotted in Figure 3 as distinct points and are given in Table 1 along with the corresponding coefficients $c_1$ and $c_2$.

In a previous publication$^4$ we reported the existence of two structural forms of Nb$_{11}$, yet we have plotted only one point for Nb$_{11}$ on Figure 3. As shown in Table I, a biexponential fit of Nb$_{11}$ reacting with D$_2$ gives constants indicating the reactive form has nearly a 100% abundance, making it appear that only one structural form is present. When the same cluster is investigated with N$_2$, however, the biexponential reaction kinetics are more obvious and are reproducible by using either an ArF or F$_2$ photoionization laser. Although it is likely that the proportions of the two structural forms of Nb$_{11}$ are sensitive to source conditions, we have attempted to hold these constant as we investigated all of the reactions reported in this paper. In the particular case of Nb$_{12}$, we believe that two isomers are present but have nearly the same reaction rate with D$_2$. On the other hand, these two isomers have very different reaction rates with N$_2$, as indicated in Table 1. Recent observations$^5$ on the reactivity of Nb$_{10}$ with H$_2$ reveal the same effect for Nb$_{10}$: two structural isomers are probably present, based on the observation of two limiting, fully saturated clusters (Nb$_{10}$H$_{12}^+$ and Nb$_{10}$H$_{16}^+$), but both react with nearly the same rate. It is interesting and unexpected that two structural isomers should exist for both Nb$_{11}$ and Nb$_{10}$, and that both should react with hydrogen with comparable rates.

In contrast to niobium, we find no evidence of structural isomerism among vanadium clusters. V$_{2n}$ ranging from $n$ = 3 to 32, in their reactions either with D$_2$ or with N$_2$. Three possibilities exist which could account for this observation. First, isomers could be present, but the isomers of a given cluster size could all react with the same rate. In view of the relatively wide variation of reactivity of small V$_n$ clusters ($n < 15$) with D$_2$ and N$_2$ as functions of cluster size (see Figure 3 and Figure 5), this explanation seems
unlikely. Second, isomers may be present, but interconversion between isomeric forms is proceeding rapidly at the temperature of the flow tube. This would result in the observation of an averaged reaction rate, which would depend on the fractional time spent in each isomeric configuration. Finally, isomers may not be present, because the metal clusters successfully find the lowest potential energy minimum before they are cooled enough to be trapped in a particular configuration. These latter two possibilities seem likely for the vanadium clusters, particularly since vanadium is a much softer and lower melting metal than is niobium. For the larger vanadium clusters \((n > 20)\), however, it is plausible that multiple structural isomers may exist, and these may all react with nearly the same rate because they are likely to have the active site needed to chemisorb efficiently. Other investigators\(^4\) find some evidence of cluster isomerism in \(V_6\), however, based on its approach to two different limiting levels of deuteration \((V_6D_4\) and \(V_6D_{12}\)) at high deuteration concentrations. We have not repeated this experiment at high \(D_2\) flow rates and therefore cannot comment on the presence or absence of two limiting deuterides in our experiments. The presence of two limiting levels of deuteration could result from effects other than cluster isomerism, however, including such possibilities as kinetic bottlenecks or cluster isomerization following addition of one or more \(D_2\) molecules. In any case, we find that \(V_6\) depletes with a single-exponential decay regardless of whether \(D_2\) or \(N_2\) is the reactant.

Figure 3 shows that there are some similarities in reactivity pattern for \(V_n + D_2\) and \(Nb_n + D_2\). The vanadium system shows pronounced even-odd alternations in reaction rate, with \(V_4, V_6, V_{10}\) and \(V_{12}\) significantly less reactive than their odd-numbered neighbors. The niobium system shows a less extreme pattern of even-odd alternation, with \(Nb_8, Nb_{10}\), the less reactive form of \(Nb_{12}\), and \(Nb_{16}\) all relatively inert to \(D_2\). No investigations of the reactivity of tantalum clusters, \(Ta_{n}\), with \(D_2\) were made in the present study due to difficulties in cleanly separating the \(Ta_n\) and \(Ta_{3}D_2\) mass spectral features, particularly for clusters larger than \(Ta_{10}\).

An interesting question in metal cluster reaction studies concerns the effect of a single atomic impurity such as carbon or oxygen on the reactivity of a given metal cluster. For any potential commercial applications of these clusters will have to be supported, perhaps on oxide substrates such as \(Al_2O_3\) or \(SiO_2\) or on graphite. In any case, metal cluster oxides and carbidies are likely to be formed in the course of commercial catalytic processes. For niobium clusters, a qualitative observation has been that for certain clusters such as \(Nb_9\), the oxide in a sense “poisons” the cluster, or makes it less reactive, while an opposite effect is seen with \(Nb_9\) where the oxide enhances the reactivity.\(^{14}\) Figure 4 displays the reactivities of \(V_n, V_{C}, V_{O}\) with \(D_2\), which were obtained with the naturally occurring \(V_{C}\) and \(V_{O}\) impurities that are present in our source. These impurities were found to be most intense immediately after the chamber had been opened to atmosphere and were found to diminish slowly as the metal surface was vaporized. Carbides probably form from laser vaporization/fragmentation of residual diffusion pump oil in the vaporization mount, while oxides (which typically take much longer to clean up) are present in the metal surface itself. For reasons unknown, only vanadium was found to form significant quantities of cluster carbides. For the data displayed in Figure 4 care was taken to exclude high flow rate points where the buildup of \(V_nD_2\) products could obscure the depletion of \(V_{C}\) and \(V_{O}\) and \(V_{CD_2}\) products could obscure the depletion of \(V_{CD_2}\). Since the carbide and oxide impurities were of approximately equal intensity in the mass spectrum, depletion of \(V_{O}\) may be artificially low due to buildup of \(V_{CD_2}\). Both depletion of \(V_{O}\) and buildup of \(V_{CD_2}\) are first-order in \(D_2\), so even constraining ourselves to the low flow rate points will not eliminate this possible artifact. For this reason reaction with \(N_2\) (see section B) provides a more reliable comparison of the relative reactivities of \(V_{C}\) and \(V_{O}\). With high flow rate points omitted by necessity, only the initial depletions could be measured for these impurity-containing clusters, so the reaction rates derived from these studies are based only on the initial slopes of plots similar to those given in Figure 2. Thus, although one might expect isomeric forms of \(V_{C}\) and \(V_{O}\) to be more likely than for \(V_6\), we are sensitive only to the most reactive form of these impurity-containing clusters and therefore cannot observe structural isomerism in these systems.

The presence of an impurity atom such as \(C\) or \(O\) significantly affects the reactivity of the vanadium cluster, as shown in Figure 4. Moreover, the identity of the impurity atom is quite important in determining the nature of the change in reactivity as compared to the pure metal cluster. For example, the addition of carbon to \(V_5\) dramatically decreases its reactivity toward \(D_2\), while the opposite effect is observed for \(V_{C}\) as compared to \(V_6\). On the other hand, the corresponding oxides \(V_{O}\) and \(V_{O}\) show reactivities with \(D_2\) that are quite comparable to those of the parent base metal clusters. Just as has been observed for niobium\(^{14}\) and tantalum\(^{44}\) clusters, the addition of an oxygen atom to \(V_5\) dramatically inhibits its reactivity, while the reactivity of \(V_{O}\) is enhanced relative to \(V_6\). Beyond about 11 metal atoms the effect of the impurity atom begins to subside, as its effects are diluted with increasing cluster size. By \(V_{15}\) there is little difference in \(D_2\) chemisorption rate between \(V_{15}, V_{15}, V_{15}\), and \(V_{15}\).

B. \(N_2\) Chemisorption by \(V_n, V_{C}, V_{O}, Nb_n, Ta_n,\) and \(Ta_O\) Clusters. In previous investigations of the chemisorption of \(N_2\) on \(Nb_n, Co_n,\) and \(Ta_n\) a significant cluster size specificity was observed, contrary to what has been observed for chemisorption of the isoelectronic CO molecule.\(^{13,14}\) It has been suggested\(^{44}\) that molecularly chemisorbed \(CO\) is bound strongly to the metal clusters so that the adduct can survive at the estimated 320 K temperature of the reaction tube, while molecularly bound \(N_2\) desorbs at temperatures much lower than this. Thus, the metal cluster experiments are really probing the rate of dissociative chemisorption of \(N_2\), which has a significant cluster size specificity, presumably due to the severe geometrical or electronic requirements that it places on the metal cluster. Figure 5 displays the effective reaction rate, \(k_i\), for \(V_n, Nb_n,\) and \(Ta_n\) reacting with \(N_2\).

Figure 5. Reactivity patterns for the reactions of V_n, Nb_n, and Ta_n with N_2. While niobium clusters offer the most dramatic display of cluster size specificity, several similarities in the overall reaction patterns of this group of metals are discernible.

The rate of chemisorption on tantalum clusters, Ta_n, for n \leq 11 shown in Figure 5 is very similar to that previously reported.44 We have, however, extended the range of investigation out to n = 30 by propagating the ionization laser down the molecular beam axis, thereby increasing our detection efficiency for the larger clusters, as described in the beginning of this section. Only Ta_{12} shows evidence of a biexponential depletion with N_2. A comparison of the depletion plots of Ta_{12} + N_2 and Nb_{12} + N_2 obtained by fitting depletion plots similar to Figure 2.

The pattern of cluster reactivity for V_n reacting with N_2 is quite similar to that of V_n reacting with D_2. For small clusters (V_4-V_{11}) a pronounced even-odd alternation in rate is observed, followed by a gradual increase in rate up to the largest clusters investigated. Minor dips in reactivity at V_{16} and V_{18} are observed in reactions with either N_2 or D_2. The magnitude of the oscillations in reaction rate is less for N_2 chemisorption than for D_2 chemisorption. No evidence of V_n cluster isomerism was obtained in these studies.

For the niobium clusters reacting with N_2, marked biexponential depletions were observed for Nb_9, Nb_{11}, and Nb_{12}, regardless of whether photoionization was done with ArF (6.42 eV) or F_2 (7.90 eV) radiation.45 Both sets of data have been independently fit to eq 3.1 for Nb_9, Nb_{11}, and Nb_{12}. The resulting values of c_1, c_2, k_1, and k_2 are given in Table I for a given cluster size, the values of all four constants are in reasonable agreement for both sets of photoionization conditions. For these three species the reaction rates of both structural isomers are plotted in Figure 5.

The case of Nb_{12} provides a dramatic example of the effect of structure on reactivity, with the reactivity of the active form at least 100 times larger than that of the inert form. In the context of structural isomerism in Nb_n it should be noted that ionization threshold measurements by the Exxon group33 show all Nb_n clusters to have thresholds defined to within +0.0/−0.10 eV, with the exception of Nb_{12}, for which the reported uncertainty was +0.0/−0.25 eV. Now that structural isomers are known to exist for Nb_{12}, it is perhaps not surprising that the ionization threshold is less well defined in this system, since each isomer may well have a different vertical ionization threshold.

The rate of N_2 chemisorption on tantalum clusters, Ta_n, for n \leq 11 shown in Figure 5 is very similar to that previously reported.44 We have, however, extended the range of investigation out to n = 30 by propagating the ionization laser down the molecular beam axis, thereby increasing our detection efficiency for the larger clusters, as described in the beginning of this section. Only Ta_{12} shows evidence of a biexponential depletion with N_2. A comparison of the depletion plots of Ta_{12} + N_2 and Nb_{12} + N_2 obtained by fitting depletion plots similar to Figure 2.

Figure 6. Logarithmic depletion of the bare metal cluster signals for Nb_{12} and Ta_{12} reacting with N_2 as functions of the N_2 flow rate. In these examples, filled circles indicate data points obtained by using ArF radiation (6.42 eV) for photoionization, while open diamonds designate data points obtained by using F_2 (7.90 eV) photoionization. Both Nb_{12} and Ta_{12} show a strong departure from linear behavior. The fitted curves assume a biexponential reaction process, with two different forms of each cluster. Fitted constants are provided in Table I.

is provided in Figure 6, and the fitted values of c_1, c_2, k_1, and k_2 are given for Ta_{12} + N_2 in Table I.

Comparing the reactions of all three metals with N_2 in Figure 5, it is clear that the reactivity pattern for tantalum clusters reacting with N_2 is intermediate between the relatively weak size dependence seen with vanadium clusters and the much more dramatic pattern observed with niobium. With the exception of Ta_{16} the reactivity patterns for Ta_n and Nb_n are similar for n ranging from 3 to 15, with reactivity minima at n = 8, 10, 12, 14, and 19 in both species and with both species showing structural isomerism for n = 12. Considering that the range of reaction rates k_n is compressed for tantalum relative to niobium, it is possible that structural isomers exist for Ta_n and Ta_{12} as well but are not sufficiently different in reactivity with N_2 for unambiguous detection. Finally, the most glaring discrepancy among the three metals is that the inert nature of Nb_{16} finds no correspondence in either V_{16} or Ta_{16}.

Figure 7 displays the reaction rates, k_n, for V_n, V_{12}, and V_{16} reacting with N_2. As was the case for these species reacting with D_2, the impurity atom is found to significantly alter the chemical reactivity. The reactivity pattern for V_{12} + N_2 shows a striking similarity to that for V_{12} + D_2, as shown in Figure 4. In both cases reactivity minima occur for V_{12}, V_{16}, and V_{18}, with maxima at V_{15} and V_{17}. The reactivity patterns of V_{16} + D_2 and V_{16} + N_2 also show some similarities with minima at V_{14}, V_{16}, and V_{18}, and maxima at V_{15}, V_{16}, and V_{17}. For V_{16} as was found for the V_{12}, V_{16}, and V_{18} clusters reacting with D_2, above n = 15 the effect of the impurity atom is much reduced, as its concentration is increasingly

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(45) It should be noted that both Ta_n and Nb_n show asymmetric broadening in the TOFMS, indicating that a significant contribution for these clusters arises from photofragmentation of larger species.


Reactions of V, Nb, and Ta Clusters

Figure 7. The effect of adatom modification of cluster reactivity is shown here for $V_n$, $V_nC$, and $V_nO$ reacting with $N_2$. The largest effects are seen for small clusters ($n = 3-10$). Note, for example, the large drop in reactivity when a carbon atom is added to $V_5$.

Figure 8. An extended view of the effect of adatom modification of cluster reactivity is developed here for $Ta_n$, and $Ta_nO$ reacting with $N_2$. The effect of the oxygen atom gradually wanes, and the reactivity of $Ta_n$ closely parallels that of $Tan$ for $N_2$ and $N_2O$, the largest effects are seen for $V_5$ and $Nb_5$. In all cases where reaction occurred, weak product features were observed in the mass spectrum, which was obtained by photoionization with low-fluence ($5-50 \mu J/cm^2$) ArF (6.4 eV) radiation. The degree of dehydrogenation of $C_2H_6$ for $V_n$ and $Nb_n$ was not a strong function of cluster size, with all cluster sizes showing $M_nC$, $M_nCH$, $M_nC_2$, $M_nC_2H$, and $M_nC_2H_4$ products. Of these products, the carbide and dicarbide were the most intense in the mass spectrum. Of course, some possibility of thermally induced dehydrogenation resulting from absorption of one or more ionization laser photons exists, and this may partially explain the formation of unexpected products such as $M_nCH$ and $M_nC_2H$. Since $M_nCH_4$ has the same mass as $M_nO$, we cannot determine whether a product of this composition is formed, nor can we determine whether the cluster oxides are reactive.

Figure 9. The chemisorption of ethane on $V_n$ and $Nb_n$ shows no dramatic size dependence but only a gradual increase in reactivity with cluster size. At the highest flow rate of a 95.0% helium mixture tantalum clusters showed only a minimal depletion, so the trend in reactivity with ethane is $V_n > Nb_n > Ta_n$. Ethane was also found to react slowly with $Co_n$ and $Ni_n$ clusters.

In all cases where reaction occurred, weak product features were observed in the mass spectrum, which was obtained by photoionization with low-fluence ($5-50 \mu J/cm^2$) ArF (6.4 eV) radiation. The degree of dehydrogenation of $C_2H_6$ for $V_n$ and $Nb_n$ was not a strong function of cluster size, with all cluster sizes showing $M_nC$, $M_nCH$, $M_nC_2$, $M_nC_2H$, and $M_nC_2H_4$ products. Of these products, the carbide and dicarbide were the most intense in the mass spectrum. Of course, some possibility of thermally induced dehydrogenation resulting from absorption of one or more ionization laser photons exists, and this may partially explain the formation of unexpected products such as $M_nCH$ and $M_nC_2H$. Since $M_nCH_4$ has the same mass as $M_nO$, we cannot determine whether a product of this composition is formed, nor can we determine whether the cluster oxides are reactive.

D. Consecutive Addition Reactions of Metal Clusters. In the mass spectra which provide the raw data for the kinetic measurements discussed here, products are frequently observed which correspond to the addition of a second reactant molecule to the metal cluster. This indicates that consecutive addition reactions, such as

$$M_n + \frac{1}{n_1} M_nN_2 \rightarrow \frac{1}{n_2} M_nN_4$$

occur under the experimental conditions present in the fast-flow reactor. When such consecutive reactions occur, one would expect an initial increase in the observed concentration of $M_nN_2$ followed by an exponential decay. Assuming that the concentration of the reactant gas, $[N_2]$, is constant during the time spent in the reaction tube, one may integrate the rate equations for reactions 3.2 to obtain

$$\frac{[M_nN_2]}{[M_n]} = \frac{k_1}{k_1 - k_2} \left[ e^{-k_2 [N_2] \tau} - e^{-k_1 [N_2] \tau} \right]$$

Converting the rate constants $k_1$ and $k_2$ to effective rate constants $k_1'$ and $k_2'$ by the relationships

$$k_1' [N_2] = k_1' [N_2] \text{ and } k_2' [N_2] = k_2' [N_2]$$

and including the possibility of differing ionization cross sections

For $M_2N_2$ and $M_4$, we obtain the observed ratio of $[M_2N_2]/[M_4]$ as

$$\frac{[M_2N_2]}{[M_4]} = \frac{\sigma(M_2N_2)}{\sigma(M_4)} \frac{k_1'}{k_1' - k_2'} e^{-k_1'F_{N_2}} - e^{-k_1'F_{N_2}} \tag{3.4}$$

where $\sigma(M_2N_2)$ and $\sigma(M_4)$ are the photoionization cross sections of $M_2N_2$ and $M_4$, respectively.

Figure 10 displays the measured ratios $[Nb_5]/[Nb_{10}]$ and $[Nb_{21}]/[Nb_{30}]$ as functions of the $N_2$ flow rate, $F_{N_2}$. The former ratio, $[Nb_5]/[Nb_{10}]$, exhibits a pure exponential decay, as is also shown in the semilog plot of Figure 2. The ratio $[Nb_{21}]/[Nb_{30}]$, on the other hand, shows a rapid rise followed by a slower decay, which is precisely the functional form predicted by eq 3.4. Since $k_1'$ is independently determined by the decay curve of $[Nb_5]/[Nb_{10}]$, it is constrained to that independently determined value, and the values of $k_2'$ and the preexponential factor ($\sigma(M_2N_2)/\sigma(M_4))(k_1' - k_2'$) are obtained by a least-squares fit of $[Nb_{21}]/[Nb_{30}]$ to the functional form of eq 3.4. The resulting fit, given by the solid curve in Figure 10, provides the values of $k_2'$ and the photoionization cross-section ratio ($\sigma(M_2N_2)/\sigma(M_4)$).

We have performed similar analyses for the consecutive addition of $N_2$ molecules to $Nb_3$, $Nb_5$, $Nb_6$, and $Nb_9$. For the first three cases, $Nb_3$, $Nb_5,$ and $Nb_6$, addition of one $N_2$ molecule proceeds quite rapidly, and the second $N_2$ is added at a much slower rate, leading to strong $Nb_5N_2$, $Nb_6N_2$, and $Nb_9N_2$ peaks in the mass spectrum. In the case of $Nb_9$, however, the first addition of an $N_2$ molecule is rate-limiting, and the addition of a second $N_2$ proceeds much more rapidly. As a result, $k_1'/k_1' - k_2'$ is small and negative, and the $Nb_9N_2$ feature is not very intense relative to $Nb_9$ under any conditions. For this case ($k_1' < k_2'$), the exponential rise time for $M_2N_2$ corresponds to the constant $k_2'$, but this is not easily measured since the overall intensity of $M_2N_2$ is small. Fitted rate constants and photoionization cross-section ratios for the $Nb_3$, $Nb_5$, $Nb_6$, and $Nb_9$ clusters reacting with $N_2$ are given in Table II.

IV. Conclusions

A major goal of metal cluster reaction studies has been to characterize the reactivity of various metal cluster–ligand combinations, in the hope that ultimately a model of chemisorption may be constructed that can predict and explain the diverse array of chemical interactions on clusters and metal surfaces. Classifying the unique chemistry of metal clusters in the context of periodic properties is one fragment of information necessary for the construction of this universal model of chemisorption. The focus of this paper has been to delineate the differences and similarities in the reactivity of the clusters of the group 5 transition-metal family.

TABLE II: Sequential Additions of $N_2$ to $Nb$,*

<table>
<thead>
<tr>
<th>System</th>
<th>$k_{1'}$</th>
<th>$k_{2'}$</th>
<th>$k_{2'}/k_{1'}$</th>
<th>$\sigma(Nb_{21}/\sigma(Nb_9))$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$_5$ + $N_2$</td>
<td>0.631</td>
<td>0.134</td>
<td>11.09</td>
<td>1.35</td>
</tr>
<tr>
<td>Nb$_7$ + $N_2$</td>
<td>0.474</td>
<td>0.274</td>
<td>16.54</td>
<td>0.697</td>
</tr>
<tr>
<td>Nb$_9$ + $N_2$</td>
<td>0.565</td>
<td>0.119</td>
<td>11.09</td>
<td>0.274</td>
</tr>
</tbody>
</table>

*As described in the text, $k_2'$ is obtained by fitting the depletion of the bare $Nb_9$ cluster, and this value is used in the fit of the growth and decay of the $Nb_9N_2$ adduct, which is fit to the functional form

$$[Nb_{21}]/[Nb_{30}] = C e^{(k_1'F_{N_2})} - e^{(k_1'F_{N_2})}.$$
Finally, we note that it is possible to kinetically monitor the consecutive addition of ligands to metal clusters. We have investigated the addition of a second $N_2$ molecule to Nb$_3$N$_2$, Nb$_5$N$_2$, Nb$_6$N$_2$, and Nb$_8$N$_2$ and have found that this secondary reaction proceeds much more slowly than the first addition of an $N_2$ for Nb$_3$, Nb$_5$, and Nb$_6$ but proceeds more rapidly for Nb$_8$.

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Registry No. H$_2$, 1333-74-0; N$_2$, 7727-39-9; C$_2$H$_6$, 74-84-0; V$_2$C, 12070-11-0; V$_4$C, 12074-52-0; V$_5$C, 12167-53-1; V$_6$C, 12316-57-3; V$_7$C, 55892-24-5; V$_8$C, 12167-54-2; V$_9$C, 12167-55-3; V$_{10}$C, 12167-56-4; V$_{11}$C, 12167-57-5; V$_{12}$C, 12167-58-6; V$_{13}$C, 12167-59-7; V$_{14}$C, 12167-60-0; V$_{15}$C, 12167-61-1; V$_{16}$C, 12167-62-2; V$_{17}$C, 12167-63-3; V$_{18}$C, 12167-64-4; V$_{19}$C, 12167-65-5; V$_{20}$O, 64764-10-9; V$_{21}$O, 12306-38-6; V$_{22}$O, 12167-40-6; V$_{23}$O, 39350-97-5; V$_{24}$O, 12167-41-7; V$_{25}$O, 54651-68-2; V$_{26}$O, 12509-78-3; V$_{27}$O, 12167-42-8; V$_{28}$O, 12167-43-9; V$_{29}$O, 12167-44-0; V$_{30}$O, 12167-45-1; V$_{31}$O, 12167-46-2; V$_{32}$O, 12167-47-3; V$_{33}$O, 12167-48-4; V$_{34}$O, 12167-49-5; V$_{35}$O, 12167-50-8; V$_{36}$O, 12167-51-9; V$_{37}$O, 121510-43-7; Ta$_{20}$O, 12059-92-6; Ta$_{21}$O, 121510-44-8; Ta$_{22}$O, 12202-05-0; Ta$_{23}$O, 112510-45-9; Ta$_{24}$O, 112510-46-0; Ta$_{25}$O, 112510-47-1; Ta$_{26}$O, 112510-48-2; Ta$_{27}$O, 112510-49-3; Ta$_{28}$O, 71767-52-7; Ta$_{29}$O, 12167-22-4; Ta$_{30}$O, 12167-23-5; Ta$_{31}$O, 12167-24-6; Ta$_{32}$O, 12167-25-7; Ta$_{33}$O, 12167-26-8; Ta$_{34}$O, 12167-27-9; Ta$_{35}$O, 12167-28-0; Ta$_{36}$O, 12167-29-1; Ta$_{37}$O, 12167-30-4; Ta$_{38}$O, 12167-31-5; Ta$_{39}$O, 12167-32-6; Ta$_{40}$O, 12167-33-7; Ta$_{41}$O, 12167-34-8; Ta$_{42}$O, 12167-35-9; Ta$_{43}$O, 12167-36-0; Ta$_{44}$O, 12167-37-1; Ta$_{45}$O, 12167-38-2; Ta$_{46}$O, 12167-39-3.

Genesis and Characterization by Laser Raman Spectroscopy and High-Resolution Electron Microscopy of Supported MoS$_2$ Crystallites

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Sulfidation of Mo/γ-Al$_2$O$_3$ based hydrotreating catalyst is a key step to activate the supported phase. In situ laser Raman spectroscopy (LRS) appears as a suitable technique for identifying intermediate species and characterization of the final state, i.e., MoS$_2$ crystallites supported on Al$_2$O$_3$. A stepwise sulfiding procedure was used in varying different parameters, i.e., hydration state of the oxide precursor, composition of the sulfiding mixture H$_2$/HS or N$_2$/HS, temperature, and time duration. The important role of these experimental conditions in the detection of transient species during sulfidation has been pointed out. Different intermediates such as oxysulfides, sulfido compounds, and MoS$_2$ appear to be the dominant ones, whose existence depends on the previously mentioned parameters. The crystallite size of the MoS$_2$, a function of the Mo loading and determined by HREM, influences the position and width of the 385-cm$^{-1}$ line.

Introduction

The sulfidation of the MoO$_3$/γ-Al$_2$O$_3$ or WO$_3$/γ-Al$_2$O$_3$ hydrotreating catalysts, which are generally associated with a promoter, is the necessary step, usually performed directly in the refinery plant, to get the active working form of the catalysts. This sulfidation step produces supported MoS$_2$ or WS$_2$ particles which have been identified by several techniques. However, a good knowledge of the nature and reactivity of the intermediate species formed during the complex transformation of the oxomolybdate entities into MoS$_2$ on the support surface is of considerable interest in order to optimize the catalytic properties of this active MoS$_2$ phase.

In situ LRS appears a suitable technique for such an investigation as it permits to detect both oxo and sulfido species. To date a large amount of results has been obtained on the oxide precursor whereas sulfidation has been less studied. Schrader and Cheng observed different surface species during the sulfidation of MoO$_3$/γ-Al$_2$O$_3$ catalyst, i.e., oxysulfides, a reduced phase and MoS$_2$. Cobalt present as a promoter favors reduction of the oxomolybate phase but leads to a more difficult sulfidation. Since the work of Arnoldy et al., it appears that water, present in the hydrated precursor, influences the sulfidation rate.

In a previous study we reported LRS observations on WO$_3$ supported catalysts evolution when changing the nature of the sulfiding mixture, temperature, and time of reaction as well as the effect of oxide hydration. The following scheme was proposed: supported oxotungstate $\rightarrow$ oxysulfide $\rightarrow$ WS$_2$. In this work, to complement this previous investigation, the nature of the intermediates formed during the sulfidation steps of molybdate/Al$_2$O$_3$ based catalysts has been investigated by using in situ laser Raman spectroscopy (LRS). Several samples of different Mo loadings have been studied to monitor the effect of this parameter on the size of the MoS$_2$ slabs after sulfidation. Indeed, both LRS and HREM (high-resolution electron microscopy) allow us to observe features of the MoS$_2$ final product.

Experimental Section

Catalysts and Pretreatment. The catalysts studied in this work have been prepared by the pore filling method using γ-Al$_2$O$_3$ extrudate (surface area, 238 m$^2$ g$^{-1}$; pore volume 0.6 cm$^3$ g$^{-1}$) and heptamolybdate solutions. The solid was then dried at 380 K

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