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Reactivity of Niobium−Carbon Cluster Ions with Hydrogen Molecules in Relation to Formation Mechanism of Met−Car Cluster Ions

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It is known that a niobium−carbon Met−Car cluster ion ($Nb_8C_{12}^+$) and its intermediates ($Nb_4C_4^+$, $Nb_6C_7^+$, etc.) are selectively formed by the aggregation of the Nb atoms in the presence of hydrocarbons. To elucidate the formation mechanism, we prepared $Nb_nC_m^+$ with every combination of n and m in the gas phase by the laser vaporization technique. The reactivity of $Nb_nC_m^+$ with H_2 was examined under the multiple collision condition, finding that $Nb_nC_m^+$ between $Nb_2C_3^+$ and $Nb_8C_{12}^+$ are not reactive with H_2. On the basis of the H_2 affinity of $Nb_nC_m^+$ experimentally obtained, we propose a dehydrogenation-controlled formation mechanism of niobium−carbon Met−Car cluster ions.

Introduction

Since the first report of metallocarbohedrene, Ti_8C_{12}, in 1992, a variety of types of metal carbon clusters have been investigated.[1–6] For niobium carbon clusters, Nb_nC_m, two types of stoichiometries have been studied intensively: those corresponding to cubic crystallites (e.g., Nb_4C_4, $Nb_{14}C_{13}$) and metallocarbohedrenes (Nb_8C_{12}, $Nb_{13}C_{22}$).[6–12] These clusters were generated in pulsed laser vaporization sources, in which Nb atoms aggregate in the presence of hydrocarbons. Several groups have found that $Nb_4C_4^+$, $Nb_6C_7^+$, $Nb_8C_{12}^+$, and $Nb_{14}C_{13}^+$ dominantly and selectively formed in the gas phase. Because these cluster ions range in $1 \leq m/n \leq 1.5$, it was believed that building blocks, NbC and NbC_2, generated in the laser vaporization sources aggregate to form cluster ions with different stoichiometries. However, the formation mechanism of $Nb_nC_m^+$ is not known well.[13,14]

The purpose of the present study is to propose the formation mechanism based on experimental studies. In this relation, $Nb_nC_m^+$ were prepared in the gas phase by a different method: We used two separate pulsed lasers to generate niobium atoms from a niobium metal rod and carbon atoms from a bulk graphite rod in the gas phase by laser vaporization in a manner similar to Kaya and co-workers.[15] It was found that $Nb_nC_m^+$ with $1 \leq m/n \leq 1.5$ are not necessarily "magic stoichiometries" (see Figure 1). Hence, we supposed that the dehydrogenation reaction from hydrocarbons must be a bottleneck process in the selective formation of $Nb_nC_m^+$ with $1 \leq m/n \leq 1.5$. To reveal the dehydrogenation processes, we examined the counter reaction of dehydrogenation, that is, hydrogenation of $Nb_nC_m^+$, elucidating the specific behavior of $Nb_nC_m^+$ with $1 \leq m/n \leq 1.5$.

Experimental Section

A niobium metal rod (99.9%) and a graphite rod (99.99%) were set downstream of the supersonic source from a solenoid pulsed valve (General Valve). The rods were irradiated with tightly focused laser pulses (~10 mJ/pulse) at a wavelength of 532 nm from a Quanta Ray GCR-170 and from a Continuum Surelite II Nd:YAG laser for generating the plasma. The evaporated niobium atoms and carbon atoms were cooled in the gas phase by the He gas (>99.99995%; 9 atm) from the valve, forming $Nb_nC_m^+$ clusters. The clusters then entered into the collision cell filled with H_2 gas (>99.99999%; 4 atm) from another General valve. After the multiple collisions of He and H_2 in the collision cell, the cluster ions entered the vacuum chamber (typically $\sim 8 \times 10^{-4}$ Torr) and were introduced into the differentially pumped chamber through a skimmer, where the cluster ions were accelerated orthogonally by a pulsed electric field for the time-of-flight mass analysis. The resolution of the mass spectrometer exceeds 1000, which allows observing the attachment of a light hydrogen atom to $Nb_nC_m^+$.

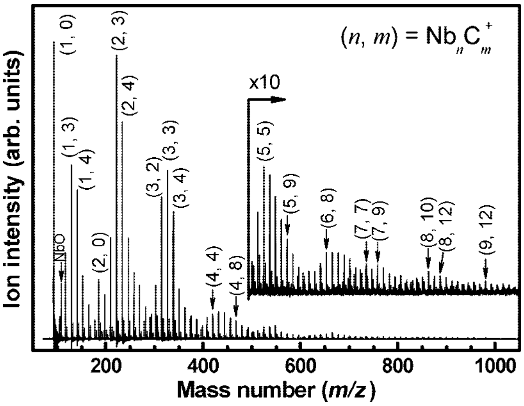

Figure 1. Mass spectrum of $Nb_nC_m^+$ produced by laser vaporization using two separate pulsed lasers to generate niobium atoms and carbon atoms in the gas phase.

Results and Discussion

Figure 1 shows a mass spectrum when the collision cell was filled with no H_2 gas. There are ion peaks assigned to

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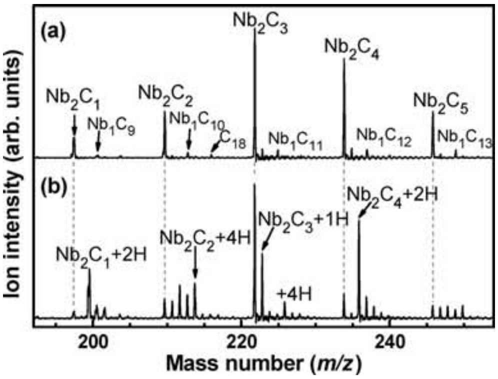

Figure 2. Mass spectra of ions before and after the reaction with H_2 in the gas cell are shown in a and b, respectively.

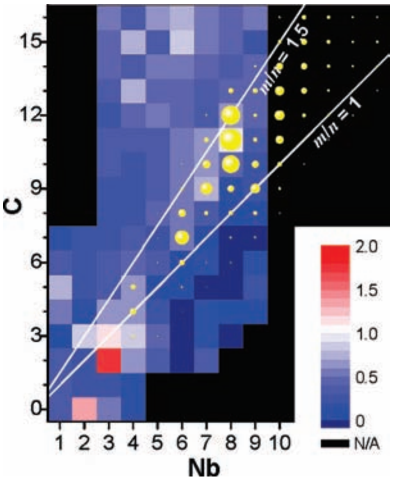

Figure 3. Ratio of ion intensity of $Nb_nC_m^+$ after the reaction with H_2 to the ion intensity before the reaction. The higher value indicates the lower reactivity of $Nb_nC_m^+$ with H_2. Superimposed yellow bubbles display the ion abundances observed by Duncan's group using a 532 nm laser for vaporization.[7] Solid lines indicate the carbon-to-metal ratio for cage structures and cubic structures.

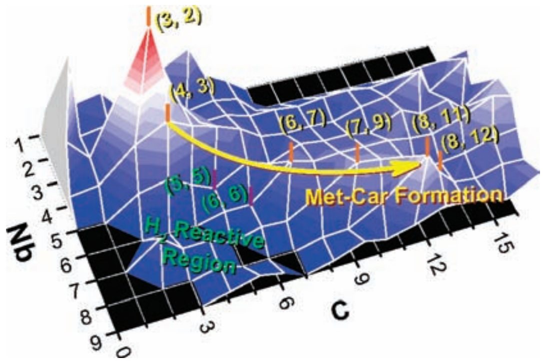

Figure 4. 3D map showing the ratio of the intensity of $Nb_nC_m^+$ after the reaction with H_2 to the ion intensity before the reaction. A ridge between $Nb_2C_3^+$ and $Nb_8C_{12}^+$ indicates that these clusters have lower reactivities with H_2.

$Nb_nC_m^+$with every combination of n and m in the size range $1 \leq n \leq 9$, $0 \leq m \leq 16$ in a mass spectrum, except for NbO^+. Figure 2a and b shows mass spectra before and after $Nb_nC_m^+$ were subjected to reaction with H_2 in the gas cell, respectively. In Figure 2b, ion peaks assignable to $Nb_nC_mH_k^+$ ($k = 1, 2, 3, ...$) were observed in addition to the parent ions $Nb_nC_m^+$. There appear cluster ions containing odd numbers of hydrogen atoms in the mass spectrum, suggesting that hydrogen molecules adsorb onto the cluster ions as atoms after dissociating the chemical bond of the hydrogen molecules. Hence, we are able to assert that hydrogen molecules adsorb onto the cluster ions not by weak physical forces, but by strong chemical bonds (chemisorption).

When $Nb_nC_m^+$ reacts with the hydrogen molecules, the peak intensities of $Nb_nC_m^+$ decrease. For instance, the intensity of $Nb_2C_4^+$ was reduced significantly, whereas $Nb_2C_4H_k^+$ ($k = 1-5$) begin to appear in the mass spectrum. From the decrease of $Nb_2C_4^+$, we can suggest that $Nb_2C_4^+$ is reactive with the H_2 molecules. On the other hand, the intensity of $Nb_2C_3^+$ after the multiple collisions with H_2 is almost the same as the intensity of $Nb_2C_3^+$ before the collisions, inferring that $Nb_2C_3^+$ is not reactive with the H_2 molecules. By examining the mass distribution closely, we found that collisional hydrogenation accompanies dissociation of the cluster ions, releasing Nb, C, and H atoms. Hence, we cannot determine uniquely the parent of the product ion, as far as the reactions of the size-selected cluster ions were examined. However, what we should emphasize here is that at least $Nb_2C_3^+$ survives the multiple collisions by the H_2 molecules, and hence, it hardly reacts with H_2.

Figure 3 exhibits as a map the ratio of the ion intensity of $Nb_nC_m^+$ after the reaction with H_2 to the ion intensities before the reaction. Evidently, there are cluster ions which exhibit lower ratios (close to zero) and higher ratios (more than 0.5). Taking the collisional dissociation of $Nb_nC_m^+$ into account, we are able to consider that the cluster ions showing the higher ratios have essentially no reactivity with H_2. In fact, Freiser and co-workers observed that $Nb_6C_7^+$, whose ratio of ion intensity is 0.6 in Figure 3, does not react with H_2 when it is trapped in the H_2 gas at 2×10^{-7} Torr for up to 10 s.[11] The plot depicts the general tendency that Nb-rich cluster ions are more reactive than the C-rich cluster ions. More importantly, in Figure 4, $Nb_nC_m^+$ located between $Nb_2C_3^+$ and $Nb_8C_{12}^+$ form a ridge in the plot, indicating that these cluster ions are not reactive with H_2. In addition, there is a gap at $Nb_5C_5^+$ in the ridge.

The nonreactivity of $Nb_nC_m^+$ with H_2 indicates that the energy barrier for the H_2 attachment is high enough or the H_2 attachment is energetically unfavorable (or both), meaning that $Nb_nC_m^+$ has a negative H_2 affinity. Under these conditions, the counter reaction, that is, dehydrogenation of $Nb_nC_mH_k^+$, should proceed readily because the reaction is energetically favorable. This conjecture is supported by the fact that in the aggregation of the Nb atoms in the presence of hydrocarbons, $Nb_3C_2^+$ and $Nb_3C_3^+$ having a negative H_2 affinity were produced as the dehydrogenated cluster ions, whereas $Nb_3C_{m\geq4}^+$ having a positive H_2 affinity were generated together with their hydrogenated ones (see ref. 10 Figure 1).[10] Hence, we assume that the formation of hydrogenated or the dehydrogenated cluster ions is determined by the H_2 affinity, although the reactivity depends not only on the H_2 affinity, but also on the energy barriers and the prefactors of individual reactions, in general.

Now we can propose the growth processes of $Nb_nC_m^+$ using methane as an example. The growth of $Nb_{n-1}C_{m-1}^+$ to $Nb_nC_{m-1}^+$ is caused by the attachment of the Nb atom (reaction 1), whereas the growth of $Nb_nC_{m-1}^+$ to $Nb_nC_m^+$ proceeds by two steps: attachment of CH_4 (reaction 2) and subsequent dehydrogenation (reaction 3).

$$Nb_{n-1}C_{m-1}{}^+ + Nb \rightarrow Nb_nC_{m-1}{}^+ \quad (1)$$

$$Nb_nC_{m-1}{}^+ + CH_4 \rightarrow Nb_nC_mH_4^+ \quad (2)$$

$$Nb_nC_mH_4{}^+ \rightarrow Nb_nC_m{}^+ + 2H_2 \quad (3)$$

Reactions 1–3 proceed repetitively, and the cluster ions grow until stable $Nb_8C_{12}^+$ or larger cluster ions are formed. If dehydrogenation reaction 3 does not proceed, the cluster ions remain hydrogenated. It is expected that the hydrogenated cluster ions will not grow further. As shown in Figure 4, $Nb_nC_m^+$ between $Nb_2C_3^+$ and $Nb_8C_{12}^+$ has the negative H_2 affinity. Hence, $Nb_nC_m^+$ is considered to grow along the ridge until $Nb_8C_{12}^+$ under the condition that Nb atoms are continuously supplied. Beyond $Nb_8C_{12}^+$, the nearest cluster ion that has a negative affinity is $Nb_9C_{16}^+$.[5] The large gap between $Nb_8C_{12}^+$ and $Nb_9C_{16}^+$ may decelerate the growth, resulting in abundant formation of $Nb_8C_{12}^+$ in the gas phase. In fact, $Nb_nC_m^+$ observed by Duncan and co-workers are situated along the ridge (see Figure 3), and the abundances of them are higher, especially at $n = 4, 6, 7$, and 8, when $Nb_nC_m^+$ has a negative affinity.[7]

The H_2 affinity of $Nb_nC_m^+$ depending upon the stoichiometry relates to the electronic structures. Dance and co-workers calculated the geometrical and electronic structures of Nb_nC_m and $Nb_nC_m^+$ ($m/n \sim 1$) by the density functional method.[16] The calculated values of the HOMO−LUMO gap of $Nb_nC_m^+$ correlate well with the reactivities of $Nb_nC_m^+$ with H_2, suggesting that the negative H_2 affinity of the cluster ions is due to the larger HOMO−LUMO gap.

In summary, we prepared $Nb_nC_m^+$ with every combination of n and m in the gas phase by the laser vaporization technique. The reactivity of $Nb_nC_m^+$ with H_2 was examined under the multiple collision condition. We found that $Nb_nC_m^+$ between $Nb_2C_3^+$ and $Nb_8C_{12}^+$ have a negative H_2 affinity. This finding is consistent with the selective growth of $Nb_nC_m^+$ ($1 \leq m/n \leq 1.5$) by the dehydrogenation reaction of hydrocarbons.

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