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Formation of Met-Cars and Face-Centered Cubic Structures: Thermodynamically or Kinetically Controlled?

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On the basis of a series of experimental studies[1-5] from our laboratory, it is well established that metallocarbohedrenes, or Met-Cars for short, are a stable class of cluster materials. The first member[1] of the Met-Cars family was discovered about two years ago in the system of $Ti_8C_{12}^+$, which displays a very prominent magic number in the cluster distribution. Soon afterward, similar molecular clusters were observed in the systems[2] of V_8C_{12}, Zr_8C_{12}, and Hf_8C_{12}. Very recently, the chromium, molybdenum, and iron analogues have become newly observed members of the Met-Car family.[6]

To account for their exceptional stability, we initially proposed a pentagonal dodecahedron structure.[1] This cage-like structure is consistent with all the experimental findings.[1-10] It is also supported by numerous theoretical calculations, although distortion from the idealized pentagonal dodecahedron has been suggested.[11-21] Considering the fact that the bulk structures of TiC, VC, and ZrC, etc. all show face-centered cubic (fcc) crystal patterns, our experimental findings that Met-Cars are the dominant species formed through gas-phase plasma reactions are somewhat surprising. For the similar metal–carbon cluster systems of Ta_mC_n and Nb_mC_n, however, fcc nanocrystal structures have been observed. Therefore, in general, there are two possible structures that can be developed in these metal–carbon systems, i.e., Met-Cars and cubes. Since only one structural pattern is generally observed for one particular cluster system, it has been suggested that their thermodynamical stabilities might be responsible for the selective formation of specific structures, e.g., Met-Cars or fcc structures.

However, Pilgrim and Duncan have reported[7] that, under their experimental conditions, both cubic structures and Met-Cars are seen in systems of $Ti_mC_n^+$ and $V_mC_n^+$. Moreover, they have suggested that the cubic species dominate over the Met-Cars at low laser power. An important question that immediately follows is whether or not these two structures are developed independently, and whether or not other systems which display only one of these structures can be forced to adopt the other growth pattern. Since the reaction intermediates were absent under Pilgrim and Duncan's conditions, it has been impossible to provide a definite answer to this critical question, especially to sort out the mechanisms for the formation of Met-Cars and cubic structures. Interestingly, the theoretical calculations by Reddy and Khanna[19] suggest that the formation of Met-Cars or fcc clusters is governed by the relative concentrations of Ti and C atoms. Herein, we present new experimental results on the system of Nb_mC_n under various conditions. It is shown that the experimental conditions are extremely critical for the formation of either Met-Cars or cubic structures, as predicted by Reddy and Khanna. Moreover, the new data show that the cubic structures do not develop on top of Met-Cars, but rather, they grow independently.

The experiments were performed by using both time-of-flight and quadrupole mass spectrometer techniques coupled with a laser vaporization source; details are given elsewhere.[22,23] A rotating metal rod is vaporized by the second harmonic output of a Nd:YAG laser at 532 nm. The typical laser power is around 10 mJ/pulse, and the laser beam is tightly focused by a 20 cm focal length lens. Both neutral and ionic metal–carbon clusters are produced by plasma reactions between the vaporized metal and the hydrocarbons such as methane and ethylene. Under the present plasma reaction conditions, the reacting hydrocarbons lose all their hydrogens and both neutral and ionic metal–carbon clusters are generated. To probe the cationic distributions of the metal–carbon clusters, either a pulsed electric field is applied to the acceleration grids of the TOF apparatus or a quadrupole mass analyzer is employed without an ionizer. Alternatively, in the studies of the neutral metal–carbon clusters a second Nd:YAG laser is used to ionize the plasma reaction products, either with the third harmonic output at 355 nm or with the second harmonic output at 532 nm. Typically, the ionizing laser is operated in an unfocused condition at a laser power of 50 mJ/pulse and a 5-mm diameter. In this case, the resulting ionic metal–carbon clusters are analyzed by a time-of-flight mass spectrometer. The ions are detected by a micro channel plate detector and the signal is then fed into a digital oscilloscope (2-GHz digitizing speed).

Figure 1a displays a typical mass spectrum of $Nb_mC_n^+$ when the ionic clusters in the plasma reaction source are detected directly by a quadrupole mass spectrometer. It is evident that the cluster ion $Nb_8C_{12}^+$ is the predominant species in the mass spectrum. However, when the neutral Nb_mC_n clusters are photoionized by a 532-nm laser beam, the mass spectrum is seen to display a distinctly different pattern as shown in Figure 1b. The clusters grow at a 1:1 metal:carbon ratio, and a different magic number, $Nb_{14}C_{13}^+$, is observed; likewise species corresponding to other cubic sizes are readily seen, i.e., (4,4...2×2×2), (6,6...2×2×3), and (18,18...3×3×4). Since there is an intrinsic difference between these two spectra, i.e., one is for a direct ion distribution while the other is for a neutral one, a series of systematic studies were carried out to focus on the ionic clusters and examine whether the distributions can be influenced by the experimental conditions (e.g., hydrocarbon concentration, laser power, and timing between the laser pulse and the addition of the hydrocarbon reactants). Figure 1c displays a mass spectrum obtained when the reactant concentration and the laser power are reduced as compared to

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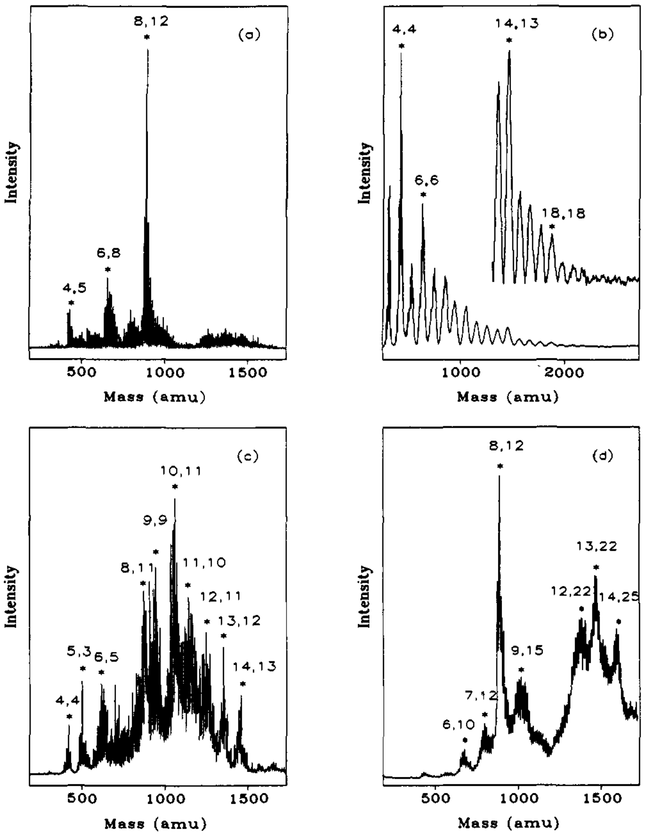

Figure 1. (a) A typical mass spectrum of ionic $Nb_mC_n^+$ clusters formed in the plasma reaction source and detected by a quadrupole mass spectrometer. The source conditions were as follows: 8% CH_4 seeded in He at a total backing pressure of 4000 Torr was used as the reactant gas, and a laser power of 15 mJ/pulse at 532 nm was used to vaporize the Nb metal rod. (b) A typical mass spectrum of neutral Nb_mC_n clusters photoionized by a 532-nm laser at 50 mJ/pulse and detected by a time-of-flight mass spectrometer. The source conditions were as follows: pure C_2H_4 at a backing pressure of 3000 Torr was used as the reaction gas, and a laser power of 15 mJ/puse was used to vaporize the Nb metal rod. (c) A typical mass spectrum of ionic $Nb_mC_n^+$ clusters formed in the plasma reaction source detected by a quadrupole mass spectrometer. The source conditions were as follows: 4% CH_4 seeded in He at a total backing pressure of 5000 Torr was used as the reactant gas, and a laser power of 10 mJ/pulse at 532 nm was used to vaporize the Nb metal rod. (d) A typical mass spectrum of ionic $Nb_mC_n^+$ clusters formed in the plasma reaction source detected by a quadrupole mass spectrometer. The source conditions were as follows: 20% CH_4 seeded in He at a total backing pressure of 5000 Torr was used as the reactant gas, and a laser power of 15 mJ/pulse at 532 nm was used to vaporize the Nb metal rod.

the conditions employed in the experiments shown in Figure 1a. Interestingly, the distribution is thereupon drastically different from the one shown in Figure 1a. The Met-Car species becomes a minor feature in the distribution, and the dominant peaks are the clusters with a metal:carbon ratio around 1:1. At the same time, the intensity truncation at $Nb_{14}C_{13}^+$ is evident, indicating that the cubic structures are formed.

When the hydrocarbon concentration is increased, the clusters grow to larger size with yet a distinctly different pattern as seen in Figure 1d. High laser power usually facilitates dehydrogenation of the hydrocarbon and the formation of higher carbon and metal dicarbide concentrations. The main cubic structures disappear, and no prominent cluster peaks are seen with a metal:carbon ratio around 1:1; under these conditions no magic number at $Nb_{14}C_{13}^+$ is observed. Instead, the Met-Car species are the dominant cluster ions in the distribution, and other prominent peaks corresponding to $Nb_{11}C_{21}^+$, $Nb_{13}C_{22}^+$, and $Nb_{14}C_{25}^+$ are readily seen. It is worth noting that a similar growth mechanism is also found in the system of Zr_mC_n clusters, where magic numbers at $Zr_{13}C_{22}$ and $Zr_{14}C_{23}$ are indicative of formation of double cage structures. The present observation of intense peaks at $Nb_{13}C_{22}^+$ and $Nb_{14}C_{25}^+$ can be explained in a similar fashion. But, it should be noted that due to the unique double-cage structure of $Nb_{14}C_{21}^+$ (there are four metal atoms in two adjacent faces; see ref 4 for details), it is found that under the present carbon-rich conditions four additional carbon atoms are attached to the base unit of $Nb_{14}C_{21}^+$ and bridge the four adjacent metal atoms.

The central question that we would like to address is, Why are different distributions present for the same cluster system of Nb_mC_n under various experimental conditions? Since Figure 1a represents the ionic cluster while Figure 1b depicts the neutral species, the different cluster distributions imply differences in reactivities. In the neutral clusters, the formation mechanism is dominated by the 1:1 metal:carbon ratio, the major small species in the reactor which provides the feed material for the cluster growth process. It is not very surprising that no magic number at Nb_8C_{12} is observed because this growth mechanism does not provide sufficient numbers of carbon atoms required for the formation of Met-Cars. On the other hand, under the conditions employed in the case of the ionic cluster experiments, the clusters develop through additions of NbC_2 besides NbC units. Hence, the Met-Car $Nb_8C_{12}^+$ is formed predominantly as shown in Figure 1a. Strikingly, the ionic cluster distributions are observed to change under various experimental conditions, which provides the critical evidence that different growth mechanisms are indeed involved. In general, at low carbon concentration, the ionic clusters grow predominantly through a 1:1 metal:carbon ratio and cubic structures are formed. However, at high carbon concentration, the Met-Cars are formed predominantly and multicage structures begin to develop. Most importantly, no prominent peaks corresponding to cubic structures and no magic number at $Nb_{14}C_{13}^+$ are seen in the mass spectrum under carbon-rich conditions. The present finding that one structure is formed preferentially over the other clearly indicates that these two structures are developed independently, in agreement with the theoretical predictions by Reddy and Khanna.[19]

The photodissociation studies[7] by Pilgrim and Duncan suggest that the cubic structures dissociate into Met-Cars. One question arises as to whether the Met-Cars are mainly formed through photodissociation of cubic structures by the vaporization laser pulses. Our present studies clearly indicate that different growth mechanisms are responsible for the formation of either Met-Cars or cubes. Indeed, the multicage structures, which are never photodissociation products, are developed at high laser power and high hydrocarbon concentrations. The fact that Met-Cars can be formed[7] through photodissociation of cubic $M_{14}C_{13}^+$ implies that Met-Cars are extremely stable; otherwise the smaller cubic fragments would be produced instead of Met-Cars.

In summary, the present results, which show that either cubes or Met-Cars are formed selectively by varying the experimental conditions, establish that the thermodynamics of the reactions is not the only factor for the formation of certain cluster structures. Clearly, our experimental observations imply that kinetic factors do play a major role in the formation of either structure.

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