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Production and mass spectroscopic characterization of metallocarbon clusters incorporating Sc, Y, and Ca atoms

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Abstract

Metallocarbon clusters of the type $Y_mC_n (m = 1–3)$, Sc_mC_n $(m = 1–3)$, and Ca_mC_n $(m = 1,2)$ are produced via the laser-vaporization cluster beam technique. The observed features of the intensity distribution of positive ions in mass spectra suggest that $M@C_n$ (M = Y, Sc, and Ca; $n \geq 44$) and $M_2@C_n$ [M = Y ($n \geq 62$) and Sc ($n \geq 52$)] clusters have endohedral mono- and di-metallofullerene structures, respectively. The mass spectral evidence is also consistent with the idea that Y_2C_n ($29 \leq n \leq 59$) and Sc_2C_n ($29 \leq n \leq 49$) clusters containing an odd number of carbon atoms form "networked" endohedral structures such as $Y@(YC_n)$ and $Sc@(ScC_n)$. (Int J Mass Spectrom 188 (1999) 225–232) © 1999 Elsevier Science B.V.

Keywords: Metallofullerenes; Metallocarbon clusters; Laser vaporization; TOF mass spectrometry; Supersonic cluster beam

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1. Introduction

Over the last several years, endohedral metallofullerenes have attracted much attention, because of their unique structural and electronic properties [1–3]. Metallofullerenes were first generated by the supersonic cluster-beam technique in the gas phase by Smalley and co-workers [4]. So far, various types of metallofullerenes have been produced by the arc-discharge method and subsequently chromatographically isolated. Group III elements (La [5–7], Y [8–10], and Sc [11–13]), group II elements (Ca, Sr, and Ba) [14,15], and most of the lanthanides [16,17] are preferentially encapsulated within fullerene cages. We have verified that a Y atom is located within the carbon cage by a synchrotron x-ray powder diffraction study of $Y@C_{82}$ [18].

The most of the reported solvent-extractable mono-metallofullerenes are of the $M@C_{82}$ type. Wang et al. [19], however, reported the preparation of solvent-extractable $Ca@C_{60}$ by the laser vaporization of a CaO/graphite rod. Kubozono et al. [20] have also reported the extraction of $Ca@C_{60}$ and $Ca@C_{70}$ from the soot produced by the arc-discharge method. Some metal atoms are also encapsulated within fullerene cages as dimers such as $Sc_2@C_{84}$ [11–13], $Y_2@C_{82}$ [9,21], and $La_2@C_{80}$ [6]. Scandium atoms have been found to be encapsulated by C_{82} even as trimer, $Sc_3@C_{82}$, which has been revealed by electron spin resonance (ESR) and mass spectrometry [11,12].

ESR measurements [5,7–12] and UHV scanning tunneling microscopy (STM) [22] of metallofullerenes have indicated the presence of the electron transfer from the encaged metal atoms to the

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carbon cage, although electron density distribution of $Y@C_{82}$ by x-ray diffraction suggests that the encaged Y atom is strongly bound to the carbon cage [13,18]. The observed interaction between the metal atoms and the carbon cage can support the idea that metallocarbon clusters act as an important role in the early formation stage of endohedral metallofullerenes. In fact, Suzuki et al. [23] have reported the presence of a strong correlation between small metallocarbon clusters and the metallofullerenes.

In an effort to obtain information on the structural transformation from small metallocarbon clusters to endohedral metallofullerenes, we have performed a systematic study on the production and mass spectroscopic characterization of the metallocarbon clusters incorporating Sc, Y, and Ca atoms. We have produced various types of metallocarbon clusters (M_mC_n; M = Y, Sc, and Ca) by the laser vaporization of metal/graphite composite rods. The results strongly suggest that the structure of metallocarbon clusters changes dramatically to that of the endohedral metallofullerenes structure above certain cluster sizes. Furthermore, we have also shown the presence of networked di-metallofullerenes for $Y@(YC_n)$ and $Sc@(ScC_n)$ clusters.

2. Experimental

Metallocarbon clusters were produced by a pulsed laser vaporization of various metal/carbon composite rods (Toyo Tanso Co. Ltd.) at 532 nm in a helium buffer gas. The atomic ratios of Y/C, Sc/C, and Ca/C were 0.77, 0.71, and 0.30%, respectively, which are the best doping ratios to produce the endohedral metallofullerenes such as $M@C_{82}$ (M = Y, Sc, and Ca) in the arc-discharge method [9,11,14]. The helium stagnation pressure, which was admitted from a pulsed valve (General Valve 9-279-900) with a pulse length of 500–700 μs, was typically in the range of 5–10 atm. The pulsed laser beam was focused with a lens ($f = 30$ cm) to approximately a 1 mm spot on a target composite rod (4 mm diameter × 20 mm), which was rotating and translating by a stepping motor. The clusters so-produced were expanded into a vacuum source chamber, pumped by a diffusion pump (Anelva CDP-1200), through a 200 mm long nozzle with a 3 mm aperture. The nozzle-skimmer distance was fixed at 25 mm. The cluster ions, after passing a skimmer, proceed into a second chamber pumped by a couple of turbo molecular pumps (Seiko-Seiki STP-200).

The positive and negative clusters formed directly by the laser vaporization (i.e. direct laser vaporization) were mass analyzed by a reflectron time-of-flight (TOF) mass spectrometer with a typical mass resolution of $m/\Delta m \cong 1000$ [24]. The pulsed acceleration of cluster ions was done at 800 V. The TOF ion signals, which were detected by a chevron type microchannel plate (Galileo Electro-Optics 93M0028), were accumulated typically over 200–500 shots and were analyzed by a transient digitizer (LeCroy 9400A). The conversion from time to mass scale and the analysis of the obtained TOF spectra were performed on a personal computer (NEC PC9801-RA).

3. Results and discussion

Fig. 1 shows a typical TOF mass spectrum of Y-doped carbon clusters produced by the laser vaporization of a Y/C composite rod. The binary clusters of the type $Y_mC_n^+$ ($m = 1$–3) as large as $Y_mC_{150}^+$ are readily noticed. The mass peaks that appeared in the spectrum are mostly due to Y-doped carbon clusters. Only very few pure carbon clusters are seen except for the fullerene region ($n \geq 30$). Similarly, we have found that clusters produced by the laser vaporization of the Ca/C and Sc/C composite rods are mostly metallocarbon clusters in the positive ion case (see Figs. 2 and 3), even though the metal doping ratios are only less than 1%.

Fig. 2 shows the TOF mass spectra of (a) yttrium-, (b) scandium-, and (c) calcium-carbon clusters around the cluster size of $M@C_{60}^+$ (M = Y, Sc, and Ca). One of the salient features in the present results is that Ca at C_{60}^+ is particularly enhanced, whereas $Y@C_{60}^+$ and $Sc@C_{60}^+$ are not so prominent. The result might reflect the special stability of $Ca@C_{60}$ [19,20]. The TOF

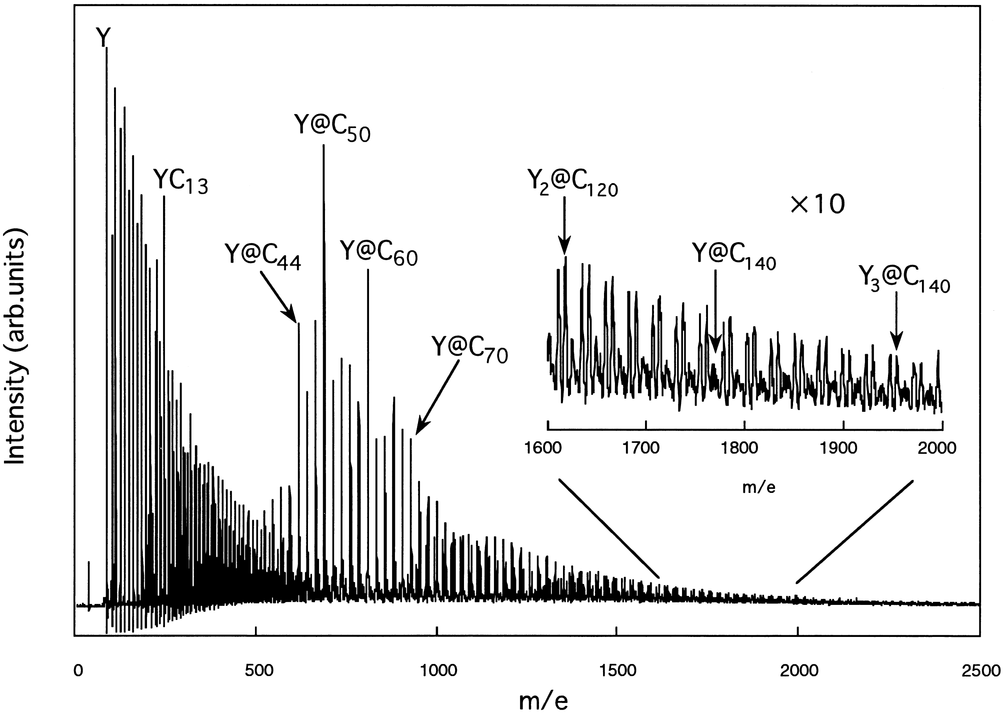

Fig. 1. Laser-vaporization (532 nm) cluster-beam TOF mass spectrum of yttrium-doped carbon clusters. Virtually, all of the mass peaks correspond to Y_mC_n ($2 \leq n \leq 150$, $1 \leq m \leq 3$).

mass spectra in higher fullerene regions are shown in Fig. 3. Interestingly the peaks due to M@ C_{82} are not particularly salient in this laser vaporization work. The primary reason of the high abundance of M@C_{82} in solvent extracts produced by the arc-discharge method does not come from their stability but mainly from their high solubility in various extraction solvents [5].

3.1. Stability of mono-metal MC_n clusters

To analyze these mass spectra quantitatively, we have plotted the intensity of mono- and di-metallo-carbon clusters against their cluster size. Fig. 4 shows the intensity distribution of (a) YC_n^+, (b) ScC_n^+, and (c) CaC_n^+ clusters ($1 \leq n \leq 70$). It is well known that the structure of carbon clusters changes dramatically according to the cluster size [25,26]. Bowers and co-workers [25] have shown the presence of linear ($2 \leq n \leq 10$), ring ($10 \leq n \leq 30$), and the so-called fullerene ($30 \leq n$) structures of the carbon clusters by gas phase ion-chromatography. The presence of an even–odd alternation around the ring structure region ($10 \leq n \leq 30$) for ScC_n^+ and CaC_n^+ clusters is noticeable, where odd-numbered clusters such as MC_{15} and MC_{21} are more enhanced than even numbered. Such intensity features have not been observed in pure carbon clusters C_n^+, which normally exhibit magic peaks at $n = 7$, 11, 15, 19, and 23 [27,28]. This suggests that Sc and Ca atoms are incorporated differently in the even and odd size rings with distinct structures. Jarrold and co-workers [29] have reported that monocyclic ring clusters of LaC_n^+ ($n = 12$–40) with an odd number of carbon atoms are much more enhanced than those with an even numbered. Each even-numbered cluster has structural isomers where the lanthanum atom is inserted into the ring, while odd-numbered clusters have single isomer where the lanthanum atom is attached to the carbon rings. In the case of the ScC_n^+ and CaC_n^+ clusters, Sc

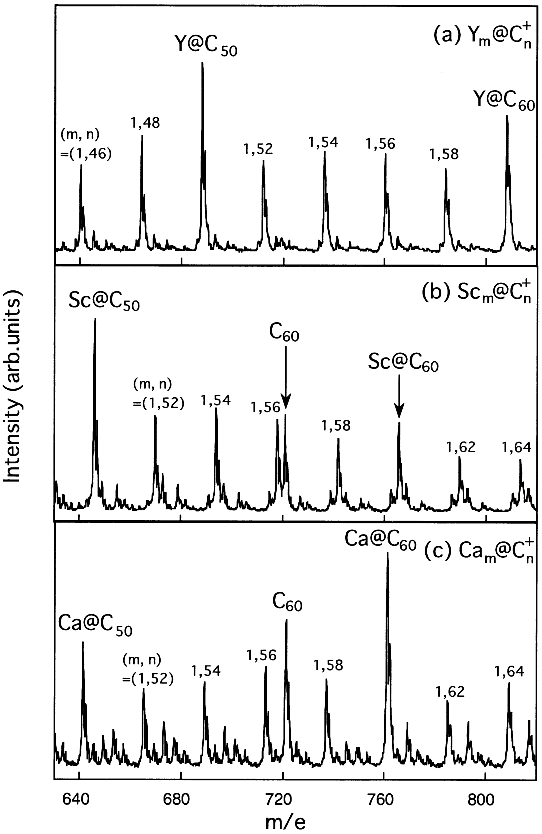

Fig. 2. Laser-vaporization (532 nm) cluster-beam TOF mass spectra of (a) yttrium-doped, (b) scandium-doped, and (c) calcium-doped carbon clusters around the cluster size of M@C$_{60}$(M = Y, Sc, and Ca).

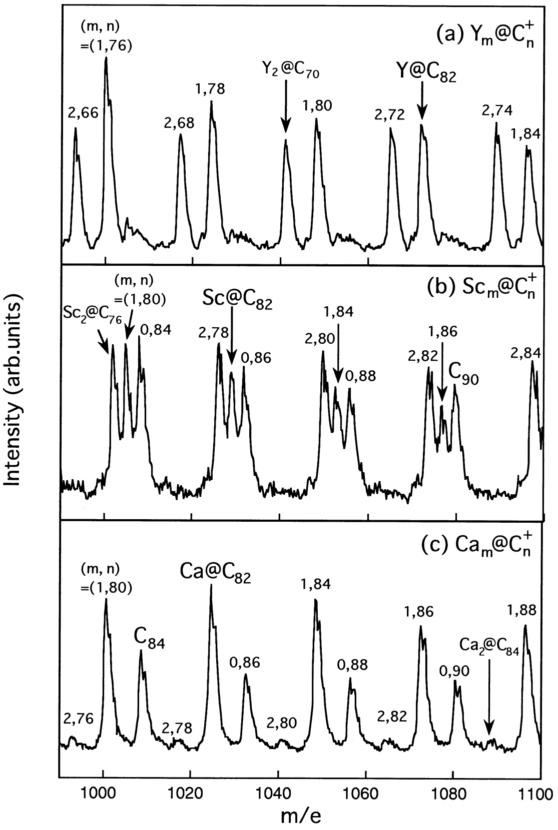

Fig. 3. Laser-vaporization (532 nm) cluster-beam TOF mass spectrum of (a) yttrium-doped, (b) scandium-doped, and (c) calcium-doped carbon clusters around the cluster size of M@C$_{82}$(M = Y, Sc, and Ca).

and Ca atoms may also be bond to the monocyclic carbon rings as proposed in the lanthanum case [29].

Of particular interests in Fig. 4 are the presence of an even–odd alternation above the fullerene size range ($n \geq 30$). As in pure carbon clusters [30], the intensity of the metallocarbon clusters of even cluster size such as M@C$_{50}^+$ and M@C$_{60}^+$ is much more enhanced than that of odd number clusters. This intensity alternation has been considered as an indication of fullerene structure. For the YC$_n^+$ clusters, the even–odd alternation has an onset at $n = 36$. Similar intensity features have been observed in the ScC$_n^+$ clusters, where the even–odd alternation has appeared at $n = 32$. The presence of the onsets implies that Y and Sc atoms start to be incorporated into fullerene cages above $n = 36$ and 32, respectively. We also notice that the alternations increase somewhat drastically at $n = 44$ for both the YC$_n^+$ and ScC$_n^+$ cases. These second onsets may suggest that the fullerene cage ($n \geq 44$) becomes large enough to encapsulate Y or Sc atoms completely and, as a result, it can obtain significant structural stability. For the CaC$_n^+$ case, a similar even–odd alternation clearly starts at $n = 44$, suggesting the endohedral structure becomes the main structure of the Ca fullerenes above $n = 44$.

Based on the above observation, we propose that the smallest size fullerene, which can encapsulate Y, Sc, or Ca atoms completely, is C$_{44}$ as schematically shown in Fig. 5. Smalley and co-workers [5] reported, via the so-called laser "shrink-wrapping" experiments

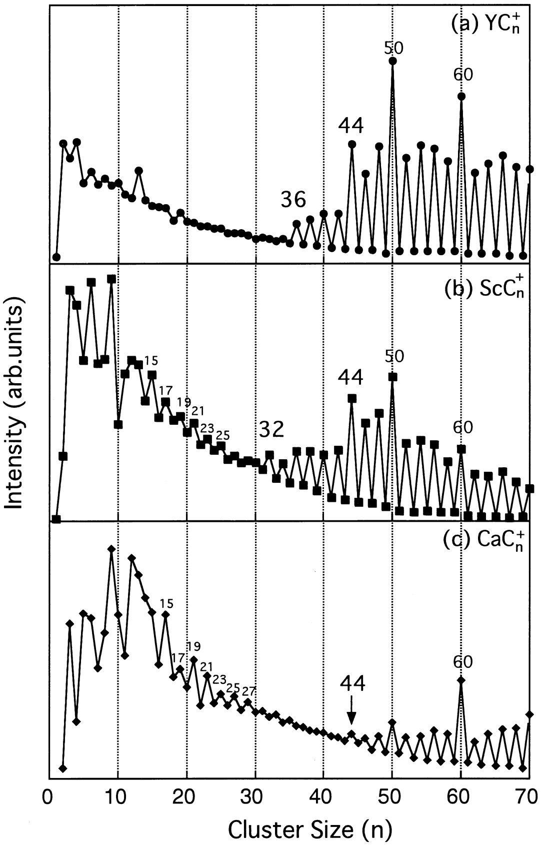

Fig. 4. Intensity distribution of (a) YC_n^+, (b) ScC_n^+, and (c) CaC_n^+ clusters as determined by the corresponding mass spectral peaks.

of La@C_{60}, that the endohedral structure can be retained as small as La@C_{44}. Jarrold and co-workers [31], on the other hand, have reported that La@C_{36} is the smallest endohedral structure as evidenced by the gas-phase ion chromatography experiments. We think that the thresholds at 36 and 44 appeared in the lanthanum case correspond to the first and the second onsets as observed in the present yttrium and scandium cases.

3.2. Metal atom-networked M_2C_n clusters

The intensities of dimetal $Y_2C_n^+$ and $Sc_2C_n^+$ clusters ($1 \leq n \leq 70$) are plotted against their cluster size in Fig. 6. The most intriguing feature in the distributions is that the odd-numbered clusters, $Y_2C_n^+$ ($29 \leq n \leq 59$) and $Sc_2C_n^+$ ($29 \leq n \leq 49$), are more enhanced than those of the even-numbered. This is unexpected, because an even number of carbon atoms is necessary to form an isolated pentagon rule (IPR) satisfying case structures [32]. We have observed a similar intensity distribution for boron- and silicon-

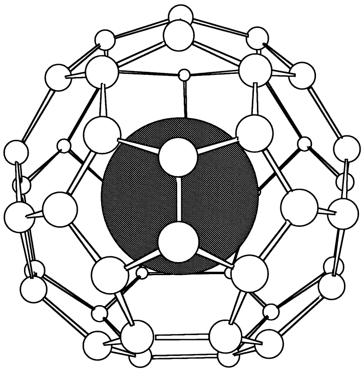

Fig. 5. A structural model of M@C_{44} (M = Y, Sc, Ca): the smallest endohedral metallofullerene.

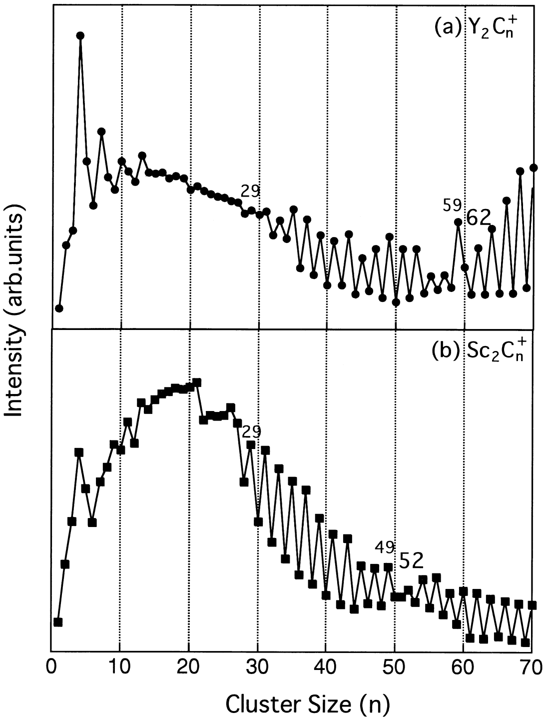

Fig. 6. Intensity distribution of (a) $Y_2C_n^+$ and (b) $Sc_2C_n^+$ clusters as determined by the corresponding mass spectral peaks.

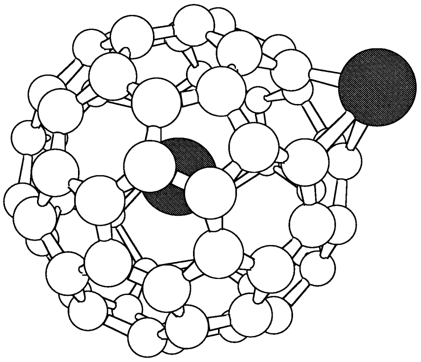

Fig. 7. A structural model of Y@(YC_{59}): a networked endohedral metallofullerene.

networked heterofullerenes, where odd-numbered carbon clusters such as BC_{59} and SiC_{59} are more enhanced than that of the even-number clusters [24].

Jarrold and co-workers [31] have proposed a new type of structure for La fullerenes in a small fullerene size region, where a La atom is incorporated in the fullerene networks. This is mainly because the fullerene cages in this size region are not large enough to encage a La atom. We presume that both the $Y_2C_n^+$ ($29 \le n \le 59$) and $Sc_2C_n^+$ ($29 \le n \le 49$) fullerenes containing odd-numbered carbon atoms form similar networked structures as in the La case. Fig. 7 shows a schematic structural model of Y_2C_{59} [or more precisely Y@(YC_{59})], where one of the Y atoms is encapsulated in the fullerene cage, and the other Y atom is incorporated into the fullerene network. At present, we presume that the networked Y and Sc atoms are covalently bound to three neighboring carbon atoms, in such a way that the Y or Sc atom can cover the defect site of the odd-numbered fullerene cage. The present model is essentially the same as proposed in a dilanthanum metallofullerene model proposed by Jarrold and co-worker [33].

The abundances of the Y_2 and Sc_2 fullerenes of even cluster size increase abruptly at $n = 52$ and 62, respectively. These onsets can be understood as the thresholds of endohedral di-yttrium and di-scundium fullerenes, respectively. A similar onset has been observed for La_2C_{2n} fullerenes by gas-phase ion chromatography experiments [33], which corresponds to C_{64}. Since the ion radii of Y^{3+} (0.93 Å) and Sc^{3+} (0.81 Å) are much smaller than that of La^{3+} (1.15 Å), the observed thresholds at C_{62} and C_{52} are consistent with the La threshold.

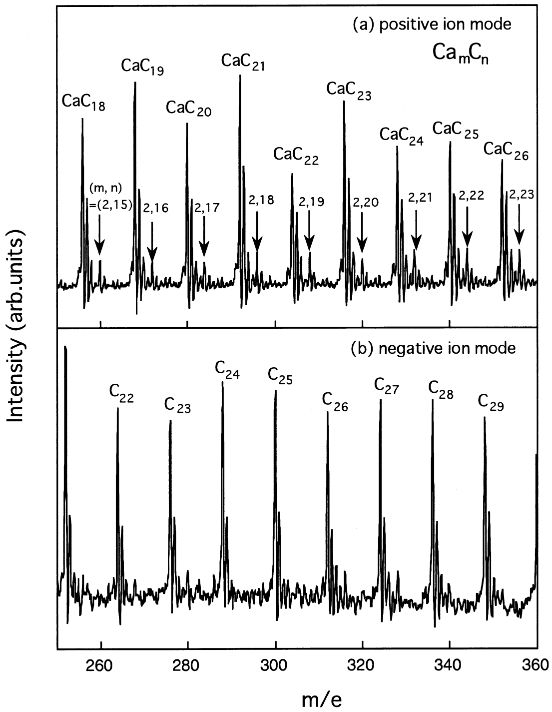

Fig. 8. Laser-vaporization (532 nm) cluster-beam TOF mass spectrum of a calcium-doped carbon clusters: (a) the positive ion mode and (b) the negative ion mode in the cluster size range from CaC_{18} to CaC_{26}.

3.3. Metallocarbon cluster growth via metal ion cores

In contrast to the positive ion case, only a very small amount of negative metallocarbon clusters are observed. Fig. 8(a) and (b) show the TOF mass spectra of positive and negative Ca-doped carbon clusters in the size range from CaC_{18} to CaC_{26}, respectively. The measurements were done under a similar laser-vaporization/nozzle condition. The various types of $Ca_mC_n^+$ ($m = 1$–3) clusters are very much enhanced in the positive ion case, even though the mixing ratio of calcium in the composite rod is only 0.3%. In the negative ion case, however, very few Ca-doped carbon clusters are observed; the clusters appeared in the mass spectrum are mostly due to pure carbon clusters. Similarly for the Y and Sc cases (not shown), the abundance of the corresponding negative metallocarbon clusters are very low. It has been known that the formation mechanism of positive metallocarbon clusters is much different from the corresponding negative cluster ions [23]. Negative ion clusters are generally produced by electron attachment to the neutral clusters, whereas in the positive ion case clustering around a positive metal ion core proceeds to form large metallocarbon clusters. The results obtained here also suggest that a positive metal ion plays a crucial role on the formation of the metallocarbon clusters investigated in the current study.

In a fullerene size region, the negative carbon clusters are again very minor species as already reported [34]. We have, however, observed a similar intensity distribution for the ScC_n^- clusters as observed in ScC_n^+, although the overall feature is relatively weak. This suggests that the mono-metallocarbon clusters, like the corresponding neutral clusters, also begin to form the endohedral structures from the cluster size as indicated in the positive ion cases.

4. Summary

Metallocarbon clusters (M_mC_n; M = Y, Sc, and Ca) are produced by the laser-vaporization cluster-beam technique and are mass analyzed in both positive and negative ion modes in the TOF mass spectrometry. The intensity of negative metallocarbon clusters are much weaker than those of positive clusters, indicating the importance of formation of metal ion cores for the growth of the metallocarbon clusters. The intensity distributions of MC_n clusters (M = Y, Sc, and Ca) suggest that the size of the smallest endohedral mono-metallofullerene is $M@C_{44}$. The intensity distributions of M_2C_n clusters (M = Y and Sc) also suggest that $Y_2@C_{62}$ and $Sc_2@C_{52}$ are the smallest endohedral di-metallofullerenes, respectively. The intensities of Y_2C_n ($29 \leq n \leq 59$) and Sc_2C_n ($29 \leq n \leq 49$) with odd carbon numbers are much more enhanced than the clusters with even-numbered carbon atoms. This might be the fact that $Y_2C_n[\equiv Y@(YC_n)]$ and $Sc_2C_n[\equiv Sc@(ScC_n)]$ with an odd carbon number form networked metallofullerene structures.

Acknowledgements

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References

[1] D.S. Bethune, R.D. Johnson, J.R. Salem, M.S. de Vries, C.S. Yannoni, Nature 366 (1993) 123.
[2] H. Shinohara, Adv. Metal Semicond. Clusters 4 (1998) 205.
[3] H. Shinohara, M. Tanaka, M. Sakata, T. Hashizume, T. Sakurai, Mater. Sci. Forum 232 (1996) 207.
[4] J.R. Heath, S.C. O’Brien, Q. Zhang, Y. Liu, R.F. Curl, H.W. Kroto, F.K. Tittle, R.E. Smalley, J. Am. Chem. Soc. 107 (1985) 7779.
[5] Y. Chai, T. Guo, C. Jin, R.E. Haufler, L.P.F. Chibante, J. Fure, L. Wang, J.M. Alford, R.E. Smalley, J. Phys. Chem. 95 (1991) 7564.
[6] M.M. Alvarez, E.G. Gillan, K. Holczer, R.B. Kaner, K.S. Min, R.L. Whetten, J. Phys. Chem. 95 (1991) 10561.
[7] R.D. Johnson, M.S. de Vries, J. Salem, D.S. Bethune, C.S. Yannoni, Nature 355 (1992) 239.
[8] J.H. Weaver, Y. Chai, G.H. Kroll, C. Jin, T.R. Ohno, R.E. Haufler, T. Guo, J.M. Alford, J. Conceicao, L.P.F. Chibante, A. Jain, G. Palmer R.E. Smalley, Chem. Phys. Lett. 190 (1992) 460.
[9] H. Shinohara, H. Sato, Y. Saito, M. Ohkohchi, Y. Ando, J. Phys. Chem. 95 (1992) 3571.
[10] S. Suzuki, S. Kawata, H. Shiromaru, K. Yamauchi, K. Kikuchi, T. Kato, Y. Achiba, J. Phys. Chem. 96 (1992) 7159.
[11] H. Shinohara, H. Sato, M. Ohkohchi, Y. Ando, T. Kodama, T. Shida, T. Kato, Y. Saito, Nature 357 (1992) 52.
[12] C.S. Yannoni, M. Hoinkis, M.S. de Vries, D.S. Bethune, J.R. Salem, M.S. Crowder, R.D. Johnson, Science 256 (1992) 1191.
[13] M. Tanaka, E. Nishibori, B. Umeda, M. Sakata, E. Yamamoto, H. Shinohara, Phys. Rev. Lett. 78 (1997) 3330.
[14] Z. Xu, T. Nakane, H. Shinohara, J. Am. Chem. Soc. 118 (1996) 11309.
[15] T.J.S. Dennis, H. Shinohara, Appl. Phys. A 66 (1998) 243.

[16] E.G. Gillan, C. Yeretzian, K.S. Min, M.M. Alvarez, R.L. Whetten, R.B.J. Kaner, Phys. Chem. 96 (1992) 6869.

[17] L. Moro, R.S. Ruoff, C.H. Becker, D.C. Lorents, R. Malhotra, J. Phys. Chem. 97 (1993) 6801.

[18] M. Tanaka, B. Umeda, E. Nishibori, M. Sakata, Y. Saito, M. Ohno, H. Shinohara, Nature 377 (1995) 46.

[19] L.S. Wang, J.M. Alford, Y. Chai, M. Diener, J. Zhang, S.M. McClure, T. Guo, G.E. Scuseria, R.E. Smalley, Chem. Phys. Lett. 207 (1993) 354.

[20] Y. Kubozono, T. Ohta, T. Hayashibara, H. Maeda, H. Ishida, S. Kashino, K. Oshima, H. Yamazaki, S. Ukita, T. Sogabe, Chem. Lett. (1995) 457.

[21] J.H. Weaver, Y. Chai, G.H. Kroll, C. Jin, T.R. Ohno, R.E. Haufler, T. Guo, J.M. Alford, J. Conceicao, L.P.F. Chibante, A. Jain, G. Palmer, R.E. Smalley, Chem. Phys. Lett. 190 (1992) 460.

[22] H. Shinohara, M. Inakuma, M. Kishida, S. Yamazaki, T. Hashizume, T. Sakurai, J. Phys. Chem. 99 (1995) 13769.

[23] S. Suzuki, H. Torisu, H. Kubota, T. Wakabayashi, H. Shiromaru, Y. Achiba, Int. J. Mass Spectrom. Ion Processes 138 (1994) 297.

[24] T. Kimura, T. Sugai, H. Shinohara, Chem. Phys. Lett. 256 (1996) 269.

[25] G. von Helden, N.G. Gotts, M.T. Bowers, Nature 363 (1993) 60.

[26] G. von Helden, M.T. Hus, N.G. Gotts, P.R. Kemper, M.T. Bowers, Chem. Phys. Lett. 204 (1993) 15.

[27] E.A. Rohlfing, D.M. Cox, A. Kaldor, J. Chem. Phys. 81 (1984) 3322.

[28] S.B.H. Bach, J.R. Eyler, J. Chem. Phys. 92 (1990) 358.

[29] D.E. Clemmer, K.B. Shelimov, M.F. Jarrold, J. Am. Chem. Soc. 116 (1994) 5971.

[30] H.W. Kroto, J.R. Heath, S.C. O’Brien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162.

[31] K.B. Shelimov, D.E. Clemmer, M.F. Jarrold, J. Phys. Chem. 98 (1994) 12819.

[32] H. Kroto, Nature 329 (1987) 529.

[33] K.B. Shelimov, M.F. Jarrold, J. Am. Chem. Soc. 117 (1995) 6404.

[34] N.G. Gotts, G. von Helden, M.T. Bowers, Int. J. Mass Spectrom. Ion Processes 149 (1995) 217.