Preparation and Extraction of Ca@C_{60}

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Endohedral metallofullerene Ca@C_{60} has been prepared by arc-heating of graphite rod containing calcium oxide, CaO, and extracted by pyridine under the oxygen-free condition. The laser desorption time-of-flight (LD-TOF) mass spectrum of the pyridine solution exhibits five main peaks due to C_{60}^+, Ca@C_{60}^+, C_{70}^+, Ca@C_{70}^+, and C_{74}^+. It has been found that Ca@C_{60} can be extracted only under the atmosphere of degassed pyridine owing to its high oxygen-sensitivity.

Ca@C_{60} is one of the fundamental compounds among the endohedral metallofullerenes, and it is meaningful to study the physical and chemical properties caused by its high symmetry. In 1993, Wang et al. reported the preparation of Ca@C_{60} by laser vaporization of CaO/graphite rod and its extraction by using carbon disulfide (CS_2);[1,2] they also showed that Ca@C_{60} is soluble in pyridine. The laser desorption Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrum of a CS_2 solution containing Ca-endohedral fullerenes shows three peaks due to C_{60}^+, Ca@C_{60}^+ and C_{70}^+.[1,2] On the other hand, it is predicted by ab-initio SCF Hartree-Fock calculations that the Ca ion in C_{60} cage is not located at the center of C_{60} but at the off-center displaced by 0.7 Å from the center, and that the electronic charge of Ca ion is +2.[1,3] However, no progress in the experimental work has been achieved owing to no establishment of the extraction-procedure for Ca@C_{60}. In the present letter, the extraction-procedure of Ca@C_{60} is reported in detail. Key guidelines on obtaining a large amount of Ca@C_{60} required to the elucidation of the physical and chemical properties has been established.

The soot containing Ca-endohedral fullerenes was prepared by arc-heating of CaO/graphite rod (Toyo Tanso; CaO concentration of 1.0 mass %) at 25 V and 80 A under 200 Torr (1 Torr = 133.322 Pa) He atmosphere. The extraction of Ca@C_{60} was tried for several solvents under the air atmosphere or under the oxygen-free condition. Aniline, CS_2, 2,6-lutidine and toluene (Wako Pure Chemicals; GR), benzonitlile, chlorobenzene and pyridine (Ishidzu Seiyaku; GR), and *t*-butylbenzene (Tokyo Kasei; GR) were tried to use as the extraction-solvents. Water in each solvent was removed according to the procedure shown by Perrin and Armarego.[4]

Mass spectra were measured by use of laser desorption time-of-flight (LD-TOF) mass spectrometer (Finnigan Vision 2000); laser desorption and ionization were done at 337 nm.

Figure 1(a) shows the LD-TOF mass spectrum of the soot containing Ca-endohedral fullerenes. The peaks in the mass spectrum can be attributed to C_{60}^+, Ca@C_{60}^+, C_{70}^+, C_{72}^+, Ca@C_{70}^+, C_{74}^+, C_{76}^+, Ca@C_{74}^+, C_{78}^+ Ca@C_{76}^+, C_{80}^+, Ca@C_{78}^+, C_{82}^+, C_{84}^+ and Ca@C_{82}^+. This is the first observation of the metallofullerenes such as Ca@C_{74}^+, Ca@C_{76}^+ and Ca@C_{78}^+. Since the hollow fullerenes C_{76} and C_{78} have been isolated,[5,6] the presence of Ca-endohedral fullerenes, Ca@C_{76} and Ca@C_{78}, are reasonable. Formation of C_{74} has not yet been confirmed, but Sc_2@C_{74} has been isolated.[7] Therefore, the presence of Ca@C_{74} is also reasonable. The peaks due to C_{60}^+, Ca@C_{60}^+ and C_{70}^+ are observed as reported by Wang et al.[1,2] The peak due to Ca@C_{70}^+ is clearly observed in Figure 1(a), although the peak was markedly small in the mass spectrum reported by Wang et al.[1,2] The peak due to Ca@C_{82}^+ is small in comparison with that due to Ca@C_{60}^+.

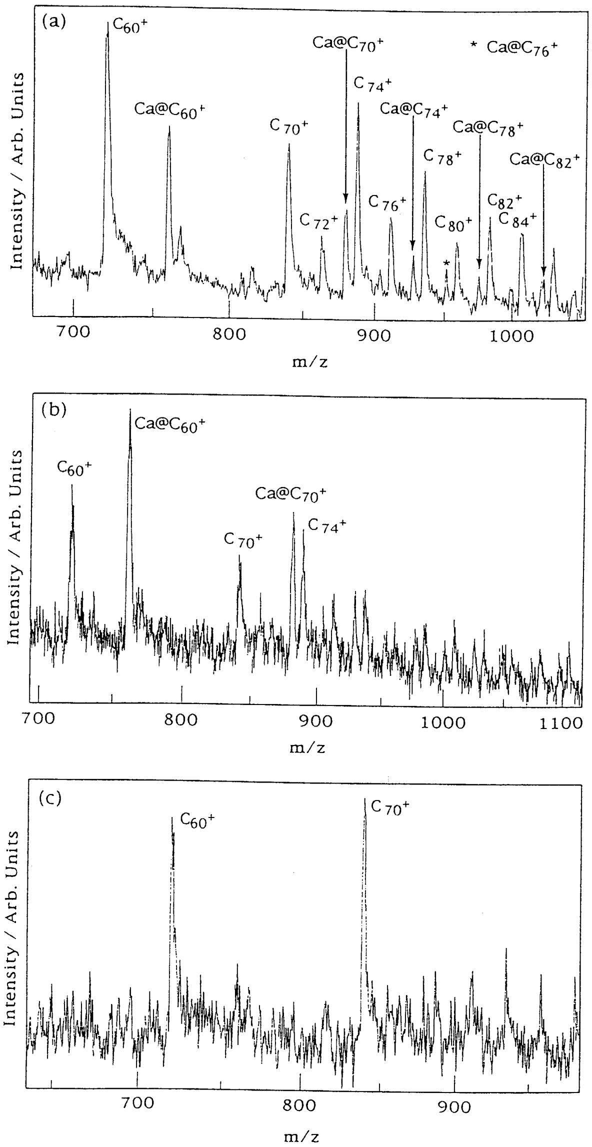

Figure 1. LD-TOF mass spectra of (a) the soot, (b) the pyridine extracted solution and (c) the residue after extraction.

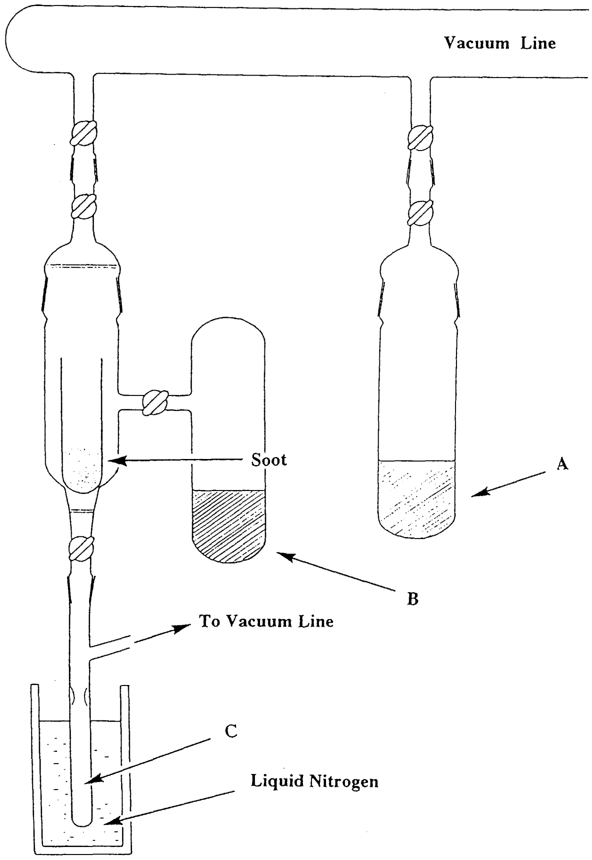

Figure 2. Apparatus employed for extraction under the condition of oxygen-free.

This feature is different from the mass spectrum of the soot generated by laser vaporization of LaO_3/graphite rod, in a sence that the intensity of the peak due to $La@C_{82}^+$ is almost comparable to that of $La@C_{60}^+$.[8] As can be seen from Figure 1(a), the amount of $Ca@C_{60}$ generated by arc-heating is comparable to that of C_{70}. The present results clearly shows that the Ca-endohedral fullerenes such as $Ca@C_{60}$ and $Ca@C_{70}$ can be prepared efficiently by arc-heating.

Under the air atmosphere $Ca@C_{60}$ could not be extracted from the soot by any of the solvents tried, probably because of the high oxygen-sensitivity of $Ca@C_{60}$. As the second trial, we have examined the extraction under the oxygen-free condition by using the apparatus as shown schematically in Figure 2.[9] A solvent was degassed by the freeze-pump-thaw method and distilled from a vessel A to B. The soot was extracted by a distilled solvent in the apparatus. The extracted solution was introduced into a vessel C under the oxygen-free condition and stored. The LD-TOF mass spectrum of the solution extracted with pyridine is shown in Figure 1 (b). The five main peaks in the spectrum are attributable to C_{60}^+, $Ca@C_{60}^+$, C_{70}^+, $Ca@C_{70}^+$ and C_{74}^+. The peak due to $Ca@C_{82}^+$ could not clearly be observed. The result indicates the low stability of $Ca@C_{82}$ in contrast to the fairly high stability of $La@C_{82}$.[8] No peaks due to $Ca@C_{60}^+$ and $Ca@C_{70}^+$ are detected for the solutions extracted by using the other solvents. Figure 1 (c) shows the LD-TOF mass spectrum of the residue after the extraction. No peaks due to $Ca@C_{60}^+$ and $Ca@C_{70}^+$ are observed, while the peaks due to C_{60}^+ and C_{70}^+ are observed. It can be concluded that the Ca-endohedral fullerenes have successfully been extracted by using pyridine as a solvent under the oxygen-free condition.

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9 The extraction was performed by immersing ca. 100 mg of soot in 50 ml of pyridine for 18 h at room temperature.