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A Preparative Scale Synthesis of C_{36} by High-Temperature Laser-Vaporization: Purification and Identification of $C_{36}H_6$ and $C_{36}H_6O$

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Received September 22, 1999

C_{60} has been considered as the smallest fullerene that can be produced, separated, and isolated in macroscopic quantity. This is largely because of the fact that C_{60} is the smallest fullerene which satisfies the so-called isolated pentagon rule (IPR).[1] In fact, it was not until quite recently that the first smaller fullerene than C_{60}, C_{36}, has been produced by the electric arc-discharge method by Zettl and co-workers.[2,3] Their study suggests that a fullerene-like caged C_{36} exists as a covalently bonded cluster-assembled material in the solid state. However, various attempts to reproduce the production of C_{36} by arc-discharge have not so far been successful, probably because the optimum arc discharge conditions on the production of C_{36} are still not known.[4]

Here we report the first successful production of C_{36} hydrides ($C_{36}H_4$ and $C_{36}H_6$) via the high-temperature laser-vaporization of metal-doped graphite rods, which has been commonly used for the production of metallofullerenes[5,6] and single-wall carbon nanotubes (SWNTs).[7] We have found that metal catalysts such as Ni/Co and Ni/Y significantly enhance the production of C_{36} and its hydrides. Furthermore, we have found that purified C_{36} materials exist as a cluster-assembled material in the solid state, not as a molecular form like C_{60}.

Soot containing C_{36} species together with fullerenes (mostly C_{60} and C_{70}) and single-wall carbon nanotubes (SWNTs) was produced by high-temperature (500−1,200 °C) laser-vaporization (Nd:YAG at 532 nm, 7.6 J/cm^2, 10 Hz) of Ni/Co- or Ni/Y-doped graphite rods [Ni(0.6 atomic %)/Co(0.6%) or Ni(4.2%)/Y(1.0%); Toyo Tanso Co. Ltd.] under Ar flow (300 mL/min) at 500 Torr in a furnace. Special precautions were taken to laser-vaporize the fresh graphite surface. The flowing Ar gas swept the soot from the high-temperature vaporization zone to a water-cooled Ni substrate downstream, just outside the furnace. The metal doping into graphite rods, which were optimized originally for the production of SWNTs, significantly enhanced C_{36} generation with respect to pure graphite cases. In situ mass analysis of the soot was performed by a homemade laser-desorption reflectron TOF (LD-TOF) mass spectrometer at 355 nm that was combined with the laser-furnace apparatus, where the trapped soot was anaerobically (in situ) transported to the desorption/ionization region of the TOF mass spectrometer. The separation of C_{36} material from fullerenes was done by high-performance liquid chromatography (HPLC) (330 nm detection, 10 mL/min flow rate)[8] with a 5PPB column (20 × 250 nm, nacalai tesque) with 100% CS_2 eluent.

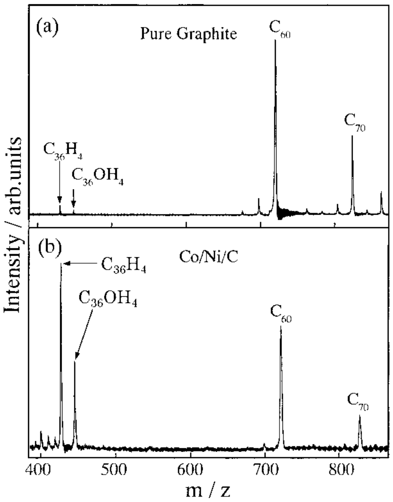

Figure 1. *In situ* laser-desorption TOF mass spectra at 355 nm of as-produced soot produced by high-temperature (1000 °C) laser-vaporization of (a) a pure graphite rod and (b) a Ni/Co-doped composite graphite rod (see text). The enhancement of peaks due to C_{36} species in part b is particularly noticeable.

Figure 1 (parts a and b) shows *in situ* LD-TOF positive mass spectra of the as-produced soot prepared by laser-vaporization of a pure graphite rod and of a Ni/Co-doped composite rod, respectively. The Ni/Co-doping dramatically enhances the peak due to $C_{36}H_4$ together with the oxide, $C_{36}OH_4$. A similar enhancement has been observed for Ni/Y-doping but was not observed for Fe- and Ti-doping. Namely, the formation of C_{36} is efficiently catalyzed by exactly the same metal catalysts as in those for SWNTs. The intact C_{36} is not observed and only the hydrides are detected. C_{36} must be quite reactive so that, immediately after its formation, C_{36} incorporates four hydrogen atoms on the reactive sites even though only a trace amount of hydrogen sources is present in the entire laser-furnace/TOF-MS combined system.

The formation of C_{36} also depends on the furnace temperature as has been reported for fullerenes[5] and SWNTs.[7] C_{36} was not produced at room temperature but efficiently produced above 500 °C; the onset temperature is much lower than those of fullerenes and SWNTs (ca. 800 °C). Of particular interests is the observation that $C_{36}H_4$ (m/z 436) and $C_{36}OH_4$ (m/z 452) converted entirely to $C_{36}H_6$ (m/z 438) and $C_{36}OH_6$ (m/z 454), respectively, upon CS_2 solvent extraction (cf. Figure 2a,b). The mass spectral identification of these species was made by comparing the observed ^{13}C isotope distributions with the calculated distributions (the insert in Figure 2a). The solvent extraction of the $C_{36}H_6$ (m/z 438) species (rather than the intact C_{36} or $C_{36}H_4$) is consistent with a previous report by Piskoti et al.[2] The peak intensity of the oxide species, $C_{36}OH_6$, has decreased after the extraction. The observed transformation from $C_{36}H_4$ to $C_{36}H_6$ on extraction suggests that two reactive sites were newly formed on $C_{36}H_4$, favorable to incorporate two additional hydrogen atoms. This may be due to bond-breaking of the solid composed of $C_{36}H_4$ upon CS_2 extraction, which may lead to the formation of a molecular $C_{36}H_6$ species in solution. The C_{36} species are soluble in CS_2 as reported previously.[2]

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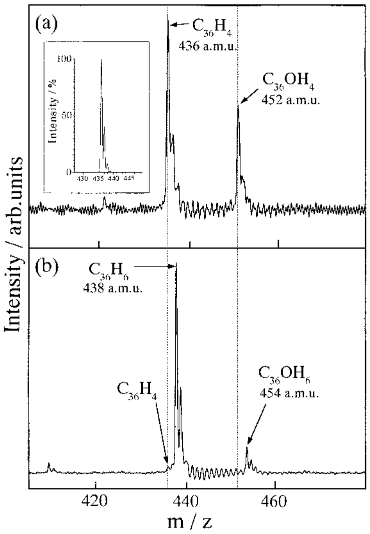

Figure 2. High-resolution LD-TOF mass spectra (355 nm) of C_{36} hydrides of (a) as-produced soot and (b) a CS_2 extract of soot. Mass spectrum (a) was recorded under in situ measurements. The observed ^{13}C isotope distribution of $C_{36}H_4$ is the same as that of the corresponding theoretical distribution as shown in the insert.

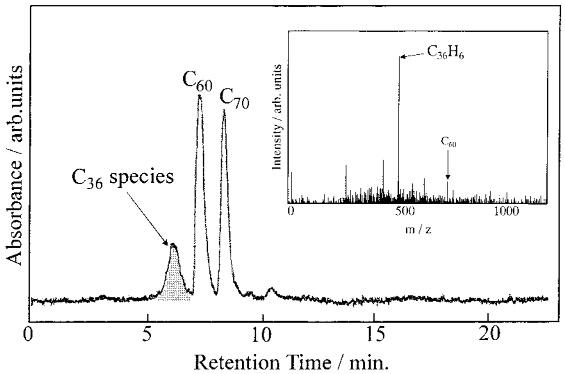

Figure 3. An HPLC chromatogram of a CS_2 extract of soot containing C_{36} species produced by high-temperature (1,000 °C) laser-vaporization (532 nm) of a Ni/Co-doped graphite rod. The peak at 6 min can be identified as due to $C_{36}H_6$. The insert gives a MALDI-TOF mass spectrum of the C_{36} fraction (shaded area) showing an enhanced peak due to $C_{36}H_6$. The small peaks before $C_{36}H_6$ are due to residual hydrocarbons.

Figures 3 shows an HPLC chromatogram of a CS_2 extract of the soot containing C_{36} materials. The peak due to C_{36} species appears at 6 min, earlier than those of C_{60} and C_{70}. The MALDI mass spectral analysis (with a Co ultra-fine powder matrix)[11] of this purified HPLC fraction gives an enhanced peak due to $C_{36}H_6$ (cf. the insert of Figure 3). The UV−vis−NIR absorption spectrum of the purified C_{36} materials in CS_2 (not shown) has the onset at around 2200 nm, suggesting that the C_{36} species has a small band-gap (ca. 0.5 eV). MALDI mass spectra with a higher laser fluence gave a series of peaks due to the oligomers of the C_{36}(i.e., $C_{144}-C_{216}$) species in addition to $C_{36}H_6$. The purified C_{36} forms oligomers (or clusters) immediately after the removal of solvent CS_2 molecules owing to its very high reactivity. Recent theoretical calculations[9,10] also support such an oligomer formation of C_{36}. Further structural characterization of the C_{36} species is now in progress.

Acknowledgment. The authors thank the reviewer of the paper for valuable comments. H.S. also thanks the Japanese Ministry of Education, Science, Sports and Culture for Grants-in-Aid for Scientific Research (B) (2) (No.10554030) and JSPS for Future Programe on New Carbon Nano-Materials for the financial support of the present study.

Supporting Information Available: Details of the experimental setup and further mass spectral characterization of C_{36} species (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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