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HPLC analysis for fullerenes up to C_{96} and the use of the laser furnace technique to study fullerene formation process

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Abstract. The ambient temperature dependence of the yield of fullerenes was systematically investigated toward furthering the understanding of the fullerene formation mechanism. The change in yield of fullerenes from C_{60} to C_{96} was quantitatively examined as a function of fullerene size, temperature, and position of target in the gradient of temperature. As a result, it was found that the formation of higher fullerenes requires higher furnace temperature, presumably because of the presence of higher reaction barriers prior to the accomplishment of the fullerene cage. In connection with such a thermal effect on the yield of fullerenes, we have also carried out an experiment to deduce the spatial distribution of such an endothermic reaction area in which the external heating is effectively active. Furthermore, in order to establish the presence of such a particular area for the fullerene formation, we used a high-speed video camera to directly detect emission from hot particles, which was found to be closely related to fullerene formation.

PACS. 36.40.-c Atomic and molecular clusters – 81.05.Tp Fullerenes and related materials; diamonds, graphite

1 Introduction

The fullerene formation process has been one of the most intriguing subjects in the field of carbon clusters since the discovery of C_{60} by Kroto *et al.* [1], particularly after the establishment of macroscopic preparation of fullerenes [2]. However, the formation mechanism has not been established yet, and a lot of hypothetical formation mechanisms (for example, pentagon road [3], fullerene road [4], ring stacking [5–7], ring coalescence, and annealing [8–12]) have been proposed. The ion chromatography technique suggested that the isomerization process of carbon clusters from polycyclic rings into more compact fullerene-like isomers might be important for bulk fullerene formation [9]. These gas-phase experiments indicate that high internal energy is necessary for isomerization of carbon clusters.

On the other hand, Haufler *et al.* used a laser furnace technique for the first time to prepare macroscopic amounts of C_{60}. They reported that C_{60} is effectively generated only when the fullerene-forming zone was heated above 1000 °C [13]. This experimental result indicated that one of the important physical parameters for the fullerene formation is the temperature in the fullerene-forming zone. They also suggested that a kind of annealing process is essential for the formation of closed cages.

In the present work, we used a laser furnace technique, as well as an HPLC analysis, to perform a systematic investigation on the temperature effect, in order to clarify how the furnace-controlled temperature affects the size distribution of fullerenes, including C_{60}, C_{70}, and other higher fullerenes up to C_{96}. Furthermore, on the basis of such a temperature effect, we present here evidence indicating the extent of the spatial distribution of the reaction zone for fullerene formation following laser ablation of graphite.

2 Experiment

We used a laser furnace technique for producing soot-containing fullerenes [13–16]. The rotating graphite rod, surrounded by a 1-meter-long quartz or a ceramic tube (16 or 18 mm in diameter, respectively) was irradiated to generate fullerene soot by loosely focused fundamental ($\lambda = 1064$ nm) or second harmonic ($\lambda = 532$ nm) of Nd: YAG laser light (fundamental: Spectra-Physics GCR-3, second harmonic: Spectra-Physics GCR-290, operated at 10 Hz). The fluence of the laser light was 600 mJ/cm^2 in the present work. The tube temperature was varied by an electric furnace from room temperature to 1500 °C. Ar was used as a foreign gas, and the pressure inside the tube was kept at 200 Torr. Ar was flowed very slowly during the laser irradiation so that the fullerene soot efficiently deposited at the downstream exit of the furnace.

After collection of the soot, toluene was used for extraction of soluble materials such as C_{60} and other higher

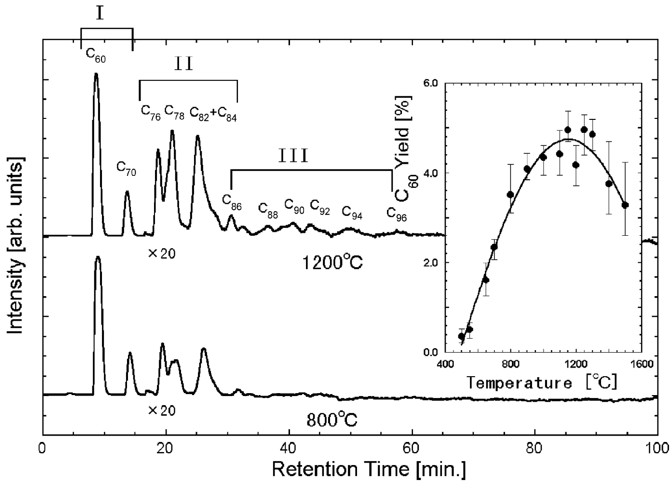

Fig. 1. The HPLC chromatograms of the fullerenes prepared at different temperature (800 °C and 1200 °C). The inserted figure is the temperature dependence of the absolute yield of C_{60}.

fullerenes. In order to determine the yield of fullerenes, first, a UV–VIS spectrum of the extract in toluene solution was measured. Using the available absorption coefficient of C_{60} at 335 nm, the absolute yield of C_{60} was deduced (the weight of C_{60} was divided by the weight loss of graphite rod). Finally, the yields of the higher fullerenes up to C_{96} were determined by an HPLC analysis.

3 Results and discussion

Figure 1 shows two typical examples of the HPLC analysis of the fullerenes prepared at different furnace temperatures, demonstrating how the temperature influences the relative yields of higher fullerenes up to C_{96}. The insert is a plot of C_{60} absolute yield as a function of temperature. The yield of C_{60} sharply increases at around 500 °C to 1000 °C, then tends to saturate, and finally, at around 1300 °C, starts to decrease. The general trends suggested from Fig. 1 are the following: From the viewpoint of the fullerene yield at a fixed temperature, we can rougly classify fullerenes with different sizes into three groups, I, II, and III, as shown in Fig. 1. Here, C_{60} and C_{70} fullerenes, showing the highest yields, are classified as group I, C_{76} to C_{84} as group II, and C_{86} to C_{96}, which show the lowest yield, as group III. The relative yields within each group are almost the same, but from group to group, there are considerable differences in yield, for example, the yield of fullerenes associated with group III is lower by almost one order of magnitude than those associated with group II.

Figure 2 shows plots of absolute yields of each fullerene as a function of temperature. Generally, the yield of all fullerenes examined here rapidly increases between 500 °C and 1000 °C, and tends to saturate above 1000 °C. However, it is noteworthy that the degree of increase of yield with increasing temperature is greatest for the fullerenes in group III, and is second largest for those in group II. It

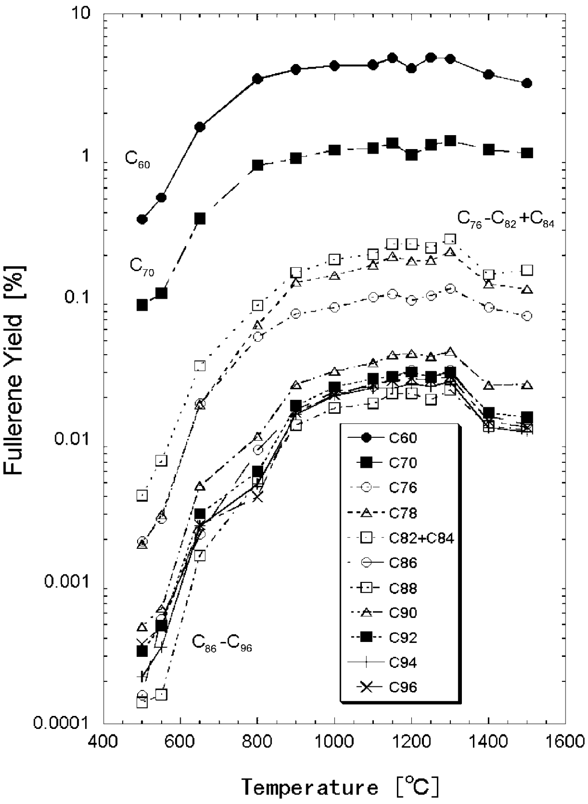

Fig. 2. The temperature dependence of the absolute yields of C_{60}–C_{96}.

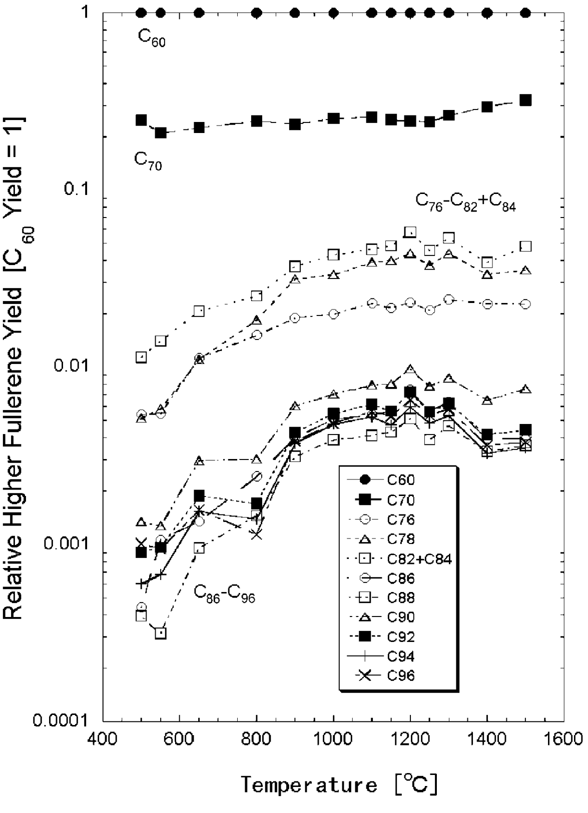

Fig. 3. The temperature dependence of the yields of C_{70}–C_{96} relative to C_{60}.

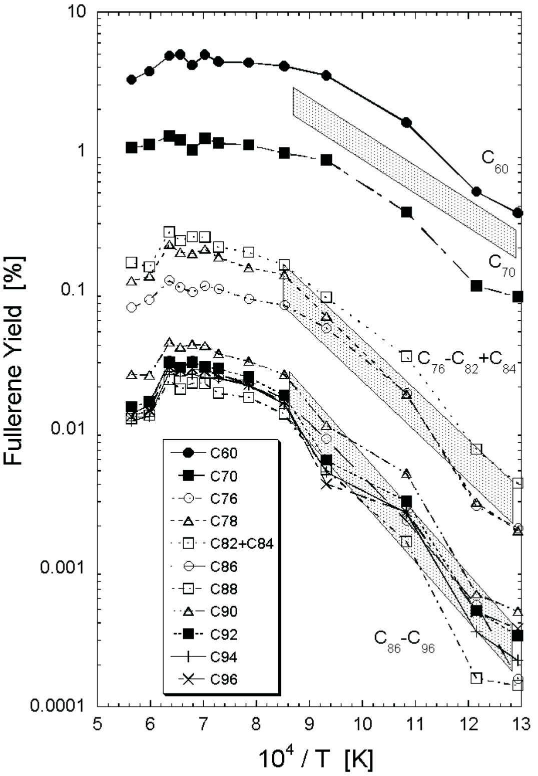

Fig. 4. The temperature dependence of the absolute yields of C_{60}–C_{96}, plotted as a function of 1/T.

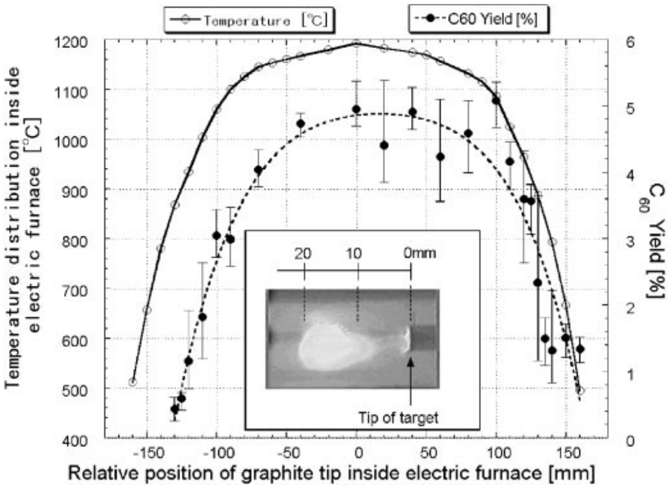

Fig. 5. The temperature distribution inside electric furnace (○) and the absolute yield of C_{60} (●), plotted as the relative position of graphite tip inside electric furnace. The inserted figure is a picture of the flame caused by laser irradiation of a graphite rod at 1150 °C in 200 Torr Ar gas, as observed by a high-speed video camera.

is also noteworthy, for groups II and III, that even above 1000 °C there still remains a tendency for the yields to increase slightly, whereas the yields of C_{60} and C_{70} are already saturated at this level. In order to demonstrate such a tendency more clearly, in Fig. 3, the yields of the fullerenes are replotted by normalizing them to C_{60}. Here the size dependence for the yields under different temperatures are more clearly seen, and the general trends characterizing group I–III are much more pronounced.

According to our previous temperature-dependence experiment (the temperature was varied up to 1200 °C, and the size of fullerene was examined up to C_{84}) [15], we suggested that there is an apparent activation-energy-involved process prior to accomplishment of fullerene formation [15]. From the analysis of the 1/T plot against the yield, for instance, C_{60} and C_{70} were seen to have almost the same Arrhenius' activation energy (about 0.8 eV), and the higher fullerenes, such as C_{76}–C_{84}, much larger activation energy. Using the present data, we also carried out 1/T plots for the fullerenes from C_{60} to C_{96}, as shown in Fig. 4. As can be seen from Fig. 4, each 1/T plot cannot be simply described by a straight line. However, if we assume a straight line in the region observed at the temperature less than 1000 °C, then very roughly speaking, the fullerenes of group I appear to have the smallest activation energy, and those of group III have the largest one. Therefore, here we can tentatively conclude that at least in some parts of the whole reaction path, there might exist a reaction channel with a barrier leading to an activation energy that is strongly dependent on fullerene size. The smaller fullerenes require the smaller activation energy; the larger ones, the larger activation energy. However, it should also be pointed out here that total process of fullerene formation must be exothermic, as has been demonstrated by many theoretical investigations. Therefore, it is likely that the endothermic process mentioned above would play a key role in the fullerene formation itself, as well as in the size selection of higher fullerenes at a certain stage in the overall reaction scheme.

Finally, we present here some experimental evidence on the question of how large the reaction zone is expanded around the graphite target for the fullerene formation. For this purpose, the position of the graphite rod was varied in the electric furnace so that a temperature gradient appears around the tip of the target. The degree of the gradient greatly depends on the position inside the furnace. The furnace used in the present work is 200 mm in length, and actual temperature distribution inside the furnace was experimentally determined, as is shown in Fig. 5. There is a significant temperature gradient particularly around the entrance and exit regions (−100 mm and +100 mm position in Fig. 5, respectively). The laser light is introduced from the left side in this figure so that the laser ablated carbon vapor travels from the right to the left side. Under such circumstance, if we put the graphite rod at the entrance (−100 mm point in Fig. 5), the tip of the target is kept at 1050 °C, while the free space, 20 mm away from the tip of the rod, is 920 °C. Therefore, if the key reaction takes place very close to the tip of the target, the resulting fullerene yield should reflect the one which would occur at 1050 °C, like those described in the previous section. On the other hand, if the reaction essentially occurs in the foreside, far from the tip of the target, the yield should decrease, reflecting rather lower ambient temperature.

The yields of C_{60}, obtained when the position of the graphite rod is changed, are shown in Fig. 5. The overall feature about the yield of C_{60} can be well described by the temperature distribution inside the furnace. However, it should be pointed out that the C_{60} yield curve shifts to the right side (to the direction of the exit), in comparison with the actual temperature distribution. The degree of the shift is, roughly speaking, about 20 mm to the right side. This can be reasonably explained only by the following. As mentioned already, when the target is put at a −100 mm point in the furnace, for example, the actual temperature of the tip is 1050 °C, while the region 20 mm away from the tip of the rod is 920 °C. Therefore, there appears to be a 130 °C difference in temperature between two positions. The experimental result clearly indicates that the yield of C_{60} obtained by putting the rod at the −100 mm position does reflect the ambient temperature at around 900 °C, and not at 1050 °C. In other words, the overall feature of the 20 mm shift appearing in the C_{60} yield curve would suggest that the actual reaction zone is distributed in the region about 20 mm away from the tip of the rod of the target on average.

Finally, we briefly describe another experimental observation related to the fullerene formation zone. Recently, we found that there appears to be a strong emission of the black-body type followed by laser ablating phenomenon. The emission intensity was found to decay with a time scale of several milliseconds. This long time-scale emission was strongly associated with high yields of fullerenes. An image of the emission as recorded by a high-speed video camera is shown as in insert in Fig. 5. It is interesting to note that the position mainly observed for the long-lived emission is quite consistent with the one estimated by the position-sensitive yield curve of C_{60} mentioned above.

4 Conclusion

In the present study, the temperature dependence of the yields for the fullerenes from C_{60} to C_{96} has systematically and quantitatively been investigated. It was confirmed that the relative yields for higher fullerenes of C_{70}–C_{96} to C_{60} drastically change when the ambient temperature of fullerene-forming zone, controlled by an electric furnace, is changed. The results strongly suggest that the fullerenes with the sizes up to C_{96} can be roughly be classified into three groups, and the larger fullerenes require the larger activation energy. It is also strongly indicated from the present work that the fullerene formation essentially takes place at a certain area, possibly 10–30 mm from the graphite surface.

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