The Carbonization Behavior of Fullerenes

Isao Mochida, Minato Egashira, Kaori Dakeshita, Seong-Ho Yoon and Yozo Korai
Institute of Advanced Material Study, Kyushu University
Kasuga, Fukuoka, 816, Japan

1. Introduction

The arc-discharge preparation procedure produces C_{60} at the yield of ca. 10% at present regardless of the laboratories. Although higher yield of C_{60} is strongly wanted, any preparation procedures give so called "soot" as the major product that looks like carbon black and is basically insoluble in any solvent[1]. It is an intriguing question whether C_{60} is an intermediate for the soot in the reaction initiated by the arc discharge.

In this study, C_{60}, C_{70}, and the toluene soluble component of fullerene soot was carbonized. Such a study can clarify the consecutive natures of a series of reactions to form first C_{60} and then soot[2].

2. Experimental

The fullerene soot was produced by arc discharge method using a graphite electrode. The produced soot(Fs) was separated into two fractions by Soxhlet extraction with toluene. About 10% of Fs is soluble in toluene. The toluene-soluble fraction(Fs-TS) was then isolated by evaporating solvent to be recrystalized, and heated in vacuum at 110°C to remove the residual solvent. The Fs-TS fraction was analyzed by HPLC (inverse phase octadecylsilica as the column packing, n-hexane as the mobile phase, UV-visible absorption spectrometry(detecting light : 280nm) as the detector). Thus obtained Fs-TS powder was used for the carbonization in the present study. Pure C_{60} (purity 99.9%) and C_{70} (purity 99.5%) were obtained from Shinku Yakin Co.

Fs-TS powder was carbonized in tube furnace under Ar flow (flow rate: 200ml/min) at the heating rate of 4°C/min to the prescribed temperature, and hold for 1 to 2 h at the temperature. The temperatures were 200,400,500,800, and 1000°C. The behaviors during heating were also probed by TGA in flowing N_2. Carbonaceous product at 1000°C was further calcined and graphitized to 2500°C.

The heated material was extracted by toluene. The toluene-soluble fraction was also analyzed by HPLC. The whole product was characterized by X-ray diffraction and TEM.

3. Results and Discussion

Fig.1 shows the TG curves of Fs-TS, pure C_{60} and C_{70} in N_2 atmosphere. As reported[3], they showed the remarkable weight loss at 800°C(Fs-TS,C_{60}) and 900°C(C_{70}), respectively. However some residue was obtained in the cases of Fs-TS and C_{70}. The residual weight was more from Fs-TS than from C_{70}, and increased twice when the flow rate was reduced to a half, thus C_{70} is more readily carbonized to the residue than C_{60}. Their change to the residue competes to their sublimation.

Table 1 summarizes the compositions of Fs-TS and its heated products. The toluene-insoluble fraction was produced at 250°C and increased as the rise of heating temperature to 1000°C. In the toluene-soluble fraction, other components than C_{60} and C_{70}(probably higher fullerenes) increased as the rise of heating temperature. It suggests the transformation of C_{60} and C_{70} to the toluene-insoluble fraction which contains the intermediates of higher fullerenes.

Fig.2 shows the X-ray diffraction patterns of Fs-TS and its heated products. Though Fs-TS showed the fcc pattern which is characteristic of C_{60}[1], the carbonized product lost, suggesting its amorphous nature. Graphitized material showed the characteristic pattern of glass-like carbon, which is the combination of the sharp peak of 26° and the broad peak near 26°. It is notable that the sharp peak of 26.0° carried a shoulder peak of 26.3°.

The comparison of carbonized Fs-TS with fullerene soot(quinoline-insoluble, QI) was also carried out. **Fig.3** shows the TEM images of both materials and their graphitized derivatives. Both raw and graphitized materials showed grain-assemble forms of amorphous structure and thin graphite(3~4 layers, 1nm thick) walls, respectively. The similarity of two materials suggests that C_{60} and C_{70} can be intermediates for the soot during the arc-discharge. Therefore the yields of C_{60} and C_{70} can be increased by the rapid run-away of new-born fullerenes from the hot zone in the discharge.

References

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Table 1. Compositions of Fs-TS and its Heated Products

Heat Treatment 1)	Compositions(%)				
	C60	C70	Other TS	Toluene-Insoluble	Loss 2)
non-treated	76	22	2	-	-
250 ℃,2hrs	69	17	10	2	2
400 ℃,2hrs	64	14	6	9	5
500 ℃,2hrs	63	17	3	15	4
500 ℃,5hrs	63	16	2	14	5
800 ℃,2hrs	-	-	-	21	79
1000 ℃,1hr	-	-	-	24	76

1) Amount of Fs-TS : 0.10 g
Heating in an alumina boat, under the Ar flow rate of 200 ml/min.
Heating rate : 4℃/min
2) Sublimed

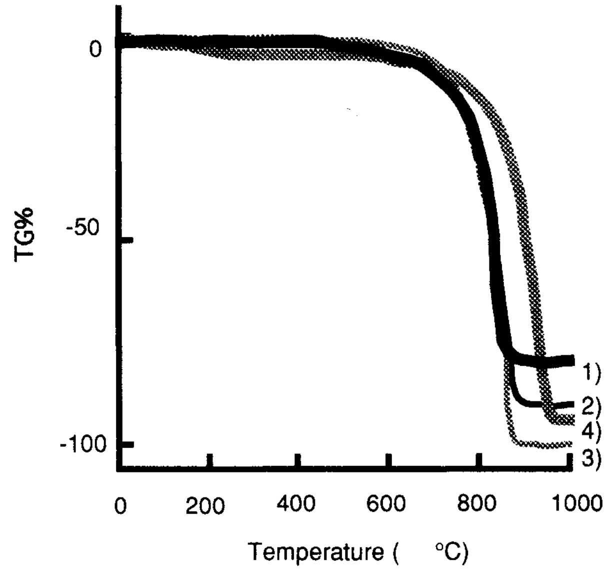

Fig.1. TG Profiles of Fullerenes in N_2 Flow
1) Fs-TS under the N_2 flow rate of 100 ml/min.
2) Fs-TS under the N_2 flow rate of 200 ml/min.
3) C_{60} under the N_2 flow rate of 200 ml/min.
4) C_{70} under the N_2 flow rate of 200 ml/min.

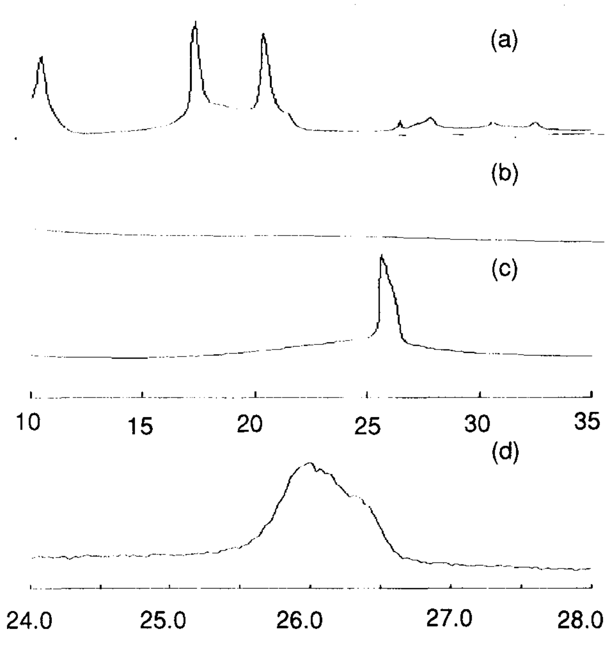

Fig.2. X-Ray Diffraction Profiles of Fs-TS and its Heated Products (Target : Cu)
(a) Fs-TS (b) 1000℃ heated (c) 2500℃ heated
(d) More detailed profile of (c), 24.0° to 28.0° of 2 θ .

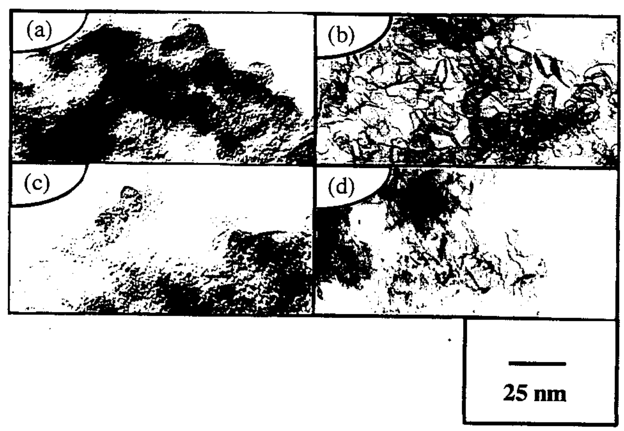

Fig.3. TEM Images of Carbonized Fs-TS, Fs-QI and Their Graphitized Products (Bright Field)
(a) 1000℃ heated Fs-TS
(b) Graphitized Fs-TS
(c) Fs-QI
(d) Graphitized Fs-QI