

Thermal reactivity of fullerene

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Abstract

Fullerene is a typical nano-carbon material with interesting properties. Though a great deal of research has been performed on the basic properties of fullerene to the present, little thermal research has been reported. This study examined the physical and chemical properties, thermal reactivity, and combustion reactivity of fullerene. The results obtained were as follows.

Fullerene is a carbon material with high crystallinity which has higher carbon content compared to the other carbon materials. Fullerene C₆₀ and Mixed fullerene(MF) caused sublimation and suffered oxidation in air at lower temperature compared standard carbon black. And C₆₀ was more thermally stable than MF, which contained higher fullerenes including C₇₀, according to the oxidation reaction in air.

Fullerenes burn, while the carbon black does not burn. However, in the burning rate test by the U N ,fullerenes are not a flammable materials.

Keywords: Fullerene, Nano-carbon, TG-DTA, Burning test, Inflammability

1. Introduction

Fullerene consists only of carbon atoms, and it is a nano-sized “carbon molecule” with a hollow structure. C₆₀ is one example of a fullerene. Its structure is shown in Fig. 1.

As a representative nano-carbon material, fullerene is expected to find applications in various fields. The existence of carbon molecules such as fullerene was antici-

pated in 1970¹⁾, and it was experimentally confirmed for the first time in research on the interstellar molecule in 1985²⁾. Since its successful artificial creation in 1990³⁾, energetic research has been carried out in Japan, the U.S. and Europe, and the characteristic properties of globular carbon molecules have been successively clarified. Fullerenes have various carbon numbers, including C₆₀, and many research reports have been published on their properties, but research on its thermal stability has not been carried out to a large extent. This study examined the physical and chemical properties, thermal reactivity, and combustion reactivity of fullerene.

2. Experimental

2.1 Samples

The species of fullerene used in this study were fullerene C₆₀ (1), mixed fullerene (2), and fullerene-similar carbon powder (3) produced under a reduced atmosphere using the combustion method by the Frontier Carbon Co.(FCC). In order to examine the effect of particle size on reactivity, the samples were pulverized and abbreviated as samples (4)-(6). Standard carbon black (7) made by the Sid Richardson Carbon Company was used for comparison.

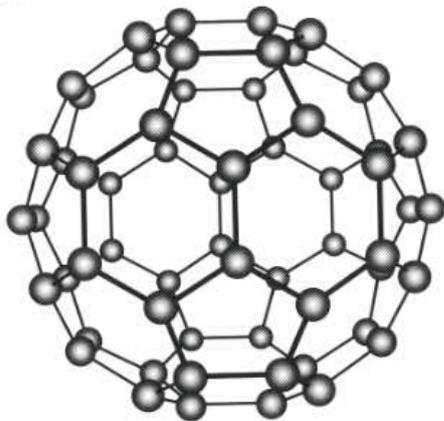


Fig. 1 Carbon structure of fullerene (C₆₀).

- (1) Fullerene C60 (abbreviation: C60, trade name: Nanom puple ST, C₆₀: over 96 %)
- (2) Mixed fullerene (abbreviation: MF, trade name: Nanom mix ST, C₆₀: about 60 %, C₇₀: about 20 %. In addition, mixed fullerene included the higher fullerenes.)
- (3) Fullerene-similar carbon (abbreviation: FB, trade name: Nanom black ST, the solvent insoluble of soot including the fullerene)
- (4) Fullerene C60 fine powder (abbreviation: C60-F, resulting from grinding (1))
- (5) Mixed fullerene fine powder (abbreviation: MF-F, trade name, Nanom mix ST-F, resulting from grinding (2))
- (6) Fullerene-similar carbon fine powder (abbreviation: FB-F, trade name: Nanom black ST-F, resulting from grinding (3))
- (7) Standard carbon black (abbreviation: IRB#7)

2.2 Experimental

2.2.1 Purity analysis

Fullerene content was determined using high-pressure liquid chromatography (HPLC)⁴⁾. For the HPLC separation of fullerenes, a YMC-Pack ODS-AM (3 μ m, 75 \times 4.6 mmID, YMC Co.Ltd., Kyoto, Japan) was used. The mobile phase was toluen/methanol = 48 / 52(vol %) and the elution rate was 0.8 ml \cdot min⁻¹.

Calibration curves were obtained using pure fullerenes C60 and C70, which were refined separately using the sublimation method on the MF raw material made by the FCC.

Elemental analysis was carried out by measuring nitrogen, hydrogen, and carbon using the CHNS/O Analyzer2400 made by the PERKIN ELMER Co., and oxygen using an oxygen nitrogen simultaneous analysis device TC-436 made by the LECO Co.

Water content was determined by the coulometric titration method using an aquameter CA-200 and a moisture vaporization device VA-200 made by the Dia Instrument Co.

Ash content was determined following by JIS K1474 after heating for 2 hours at 815 $^{\circ}$ C in air.

2.2.2 Physical property measurement

IR spectra were obtained using FT-IR and IRA-2, made by the Japan Spectral Diffraction Industry Co., and qualitative analysis was carried out using the KBr tablet molding method.

SEM images were measured using a fully automatic microanalysis device JCXA-733 made by the JEOL Co.

X-ray powder diffraction analysis was carried out using a particular status environmental X-ray diffraction device DX-3500K made by the JEOL Co. The measurement was carried out using the powder method.

The particle size distribution was measured using a laser diffraction/scattering-style particle size distribution measurement device LA-920 made by the HORIBA Co.

The specific surface area was measured using an automatic specific surface measuring device Gemini 2360 made by the Micrometrics Co.

2.2.3 Thermal analysis

Thermal analysis was carried out using the thermal analyzer Thermo Plus 2 made by the Rigakudenki Co. under heating up to 1000 $^{\circ}$ C in air. The measurement process consisted of weighting about 2 mg of the sample in an open container made of alumina with a heating rate of 20 $^{\circ}$ C min⁻¹. Thermal analysis in a nitrogen atmosphere was carried out under heating up to 1000 $^{\circ}$ C using a thermal analysis device Exstar 6000 made by the SII nanotechnology Co. A 5-mg sample was weighted in an open platinum container and heated at a rate of 20 $^{\circ}$ C min⁻¹.

The isothermal oxidation reaction was carried out in air using the thermal analyser Thermo Plus 2 made by the Rigakudenki Co. An approximately 2-mg sample was placed in an alumina container. The oxidation temperatures at 4 points ranged from 365-400 $^{\circ}$ C for MF and C60, 350-425 $^{\circ}$ C for FB ,and 450-510 $^{\circ}$ C for IRB#7.

2.2.4 Combustion test

The small gas flame test was followed by the “the small gas flame test” on dangerous object 2 (the combustible solid) based on Japanese fire protection law, and it was carried out 10 times⁵⁾.

The burning rate test was carried out twice for every sample, correspondent to the United Nations' hazardous materials transportation advice on “burning rate testing method⁶⁾”.

3. Results and discussion

3.1 Physical and chemical properties of fullerene

3.1.1 Purity

Fullerene is the only carbon material which is soluble in aromatic solvents such as toluene and xylene. A chromatogram of C60 is shown in Fig. 2-1, 2. The purity of C60 was confirmed to be 99.6 % by the lack of other peaks in the HPLC when toluene / methanol was used as an eluate. A chromatogram of MF is shown in Fig. 2-3, 4. C₆₀ and C₇₀ were the main components of MF, and the total amount of fullerene composed of C₆₀, C₇₀, and higher fullerenes was 97 %.

The results of fullerene purity and elemental analysis for each sample are shown in Table 1. IRB#7 was used as the standard carbon black in this experiment, and its carbon content was 96.75 %. The carbon content of C60 is 99.6 %. The hydrogen, nitrogen, and oxygen contents were about 0.3 % or less, less than in standard carbon black. C60 is also a high-purity carbon material with an ash content of 0.1 % or less.

MF showed a high carbon content of 99.3 %, but its carbon content was still lower than that of C60. Additionally, hydrogen, nitrogen, and oxygen each had a value under 0.3 %, less than that of the standard carbon black, and MF is also a high-purity carbon material with an ash content of 0.1 % or less.

However, FB which is insoluble in all solvents and contains slight amounts of fullerene, has a low carbon content compared to those of the fullerenes.

C60 and MF together adhered 0.1 % or less with water. The water adhesion value of FB is about 0.1 %. Thus, C60 and MF are materials with lower hygroscopicities than the standard carbon black, which has a water adhesion value of 1.3 %.

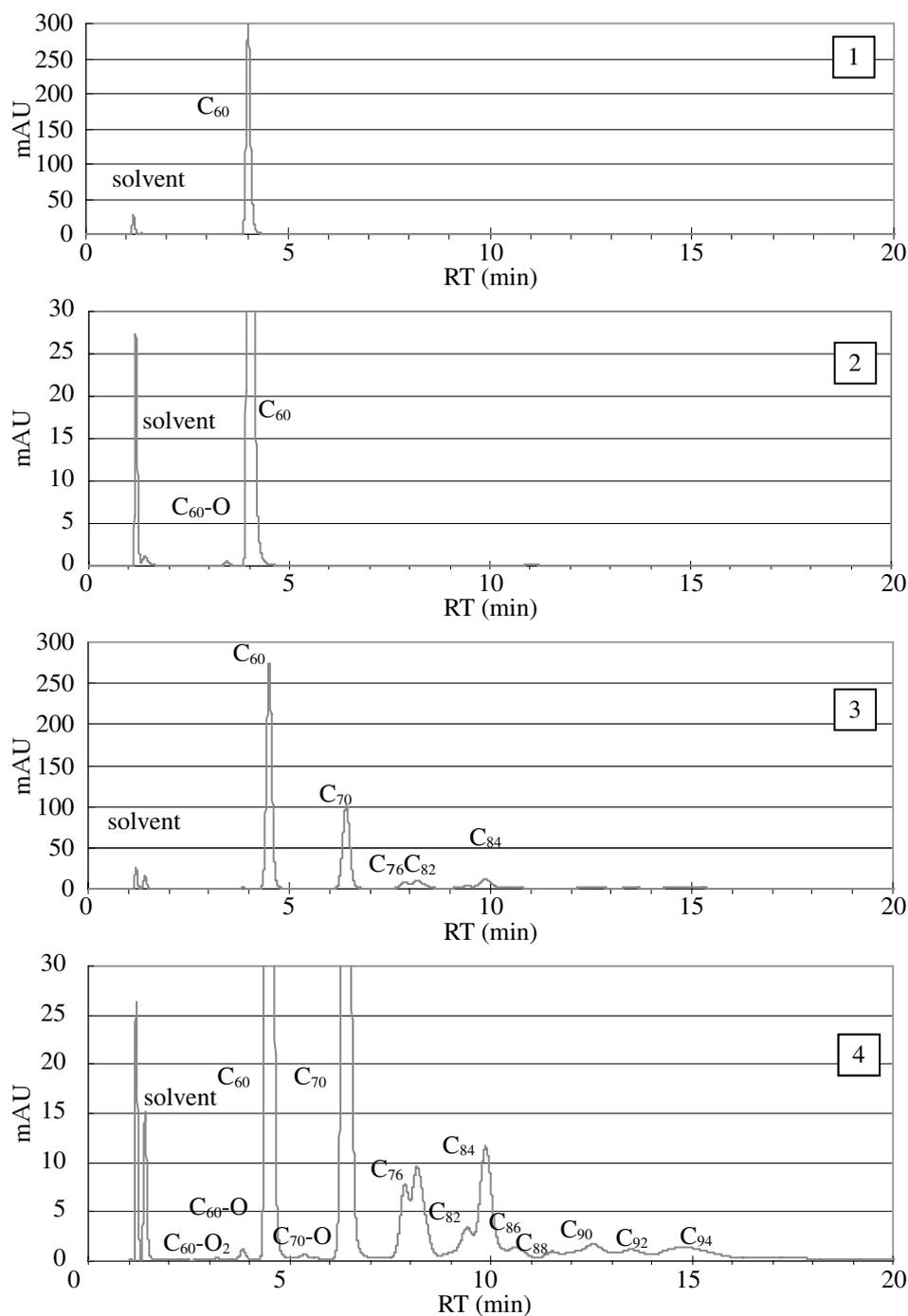


Fig. 2 HPLC of fullerene (C₆₀) and mixed fullerene (MF).

1: C₆₀ 2: The scale of the vertical line is expanded at 10 times of C₆₀

3: MF 4: The scale of the vertical line is expanded at 10 times of MF

The condition of HPLC, eluant: 48 vol % toluene/methanol 0.8 ml·min⁻¹, column: YMC-Pack

ODS-AM, S-3 μm, 75*4.6 mm I.D. column temp.: 40 °C wave length: 308 nm, injection volume: 5 μl

Table 1 Purity and elementary analysis.

	Purity (%)			Element (%)					
	C ₆₀	C ₇₀	HF*	C	H	N	O	H ₂ O	Ash
C ₆₀	99.59	<0.1	0.17	99.6	<0.3	<0.3	0.10	0.034	0
MF	58.47	23.81	14.64	99.3	<0.3	<0.3	0.28	0.032	0
FB	0.36	0.23	0.14	97.9	<0.3	<0.3	1.51	0.122	0
IRB#7	—	—	—	96.2	<0.3	<0.3	2.43	1.30	0.22

*HF: higher fullerene.

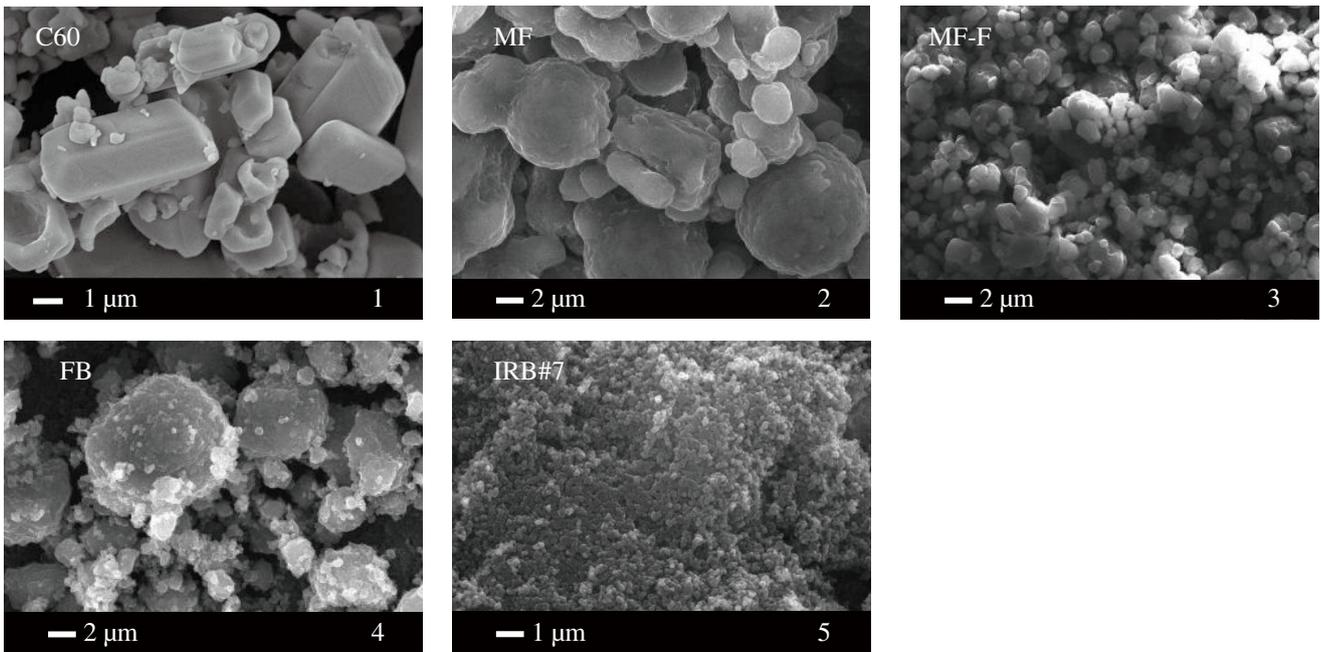


Fig. 3 SEM images of fullerene and carbon materials. 1: C60 2: MF 3: MF-F 4: FB 5: IRB#7

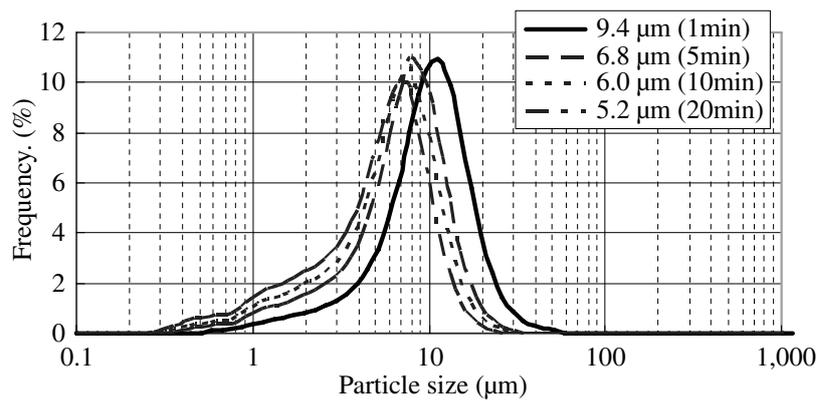


Fig. 4 Particle size distribution curves of fullerene (C60).

Table 2 Particle size, Specific surface area, and Burning rate of fullerene and carbon materials.

	C60	C60-F	MF	MF-F	FB	FB-F	IRB#7
Particle size (μ)	9.4	1.14	10.6	2.16	385	0.71	0.25
Specific surface area (m ² g ⁻¹)*	3.9	—	1.8	—	95.7	—	72.9
Burning rate (mm·min ⁻¹)	1.2	1.8	1.4	3.2	2.6	7.7	Buning is not continued.

*By multipoint B.E.T. nitrogen adsorption.

3.1.2 Properties of the fullerene particle

Figure 3 shows the SEM images of fullerene. C60 had a columnar crystalline form, around 10 μm in size. MF had a globular shape, in which crystals aggregated to form secondary crystallites several μm to over ten μm in size, similar in size to C60. The MF-F (ground MF) had a spherical shape 0.5-2 μm in size. FB and IRB#7 were also almost globular.

Figure 4 shows the particle size distribution curves for C60. Measurements were carried out using ethanol and an 1 % aqueous surfactant DBS solution (dodecyl benzene-sulfonic acid) to add to the water as a dispersion medium.

Particle size decreased in proportion to dispersion time of the ultrasonic wave. The particle size of each sample after 1 minute are shown in Table 2. The particle size of C60 and MF were almost 10 μm. Though IRB#7 was pelletized into millimeter-sized pieces, it cracked in proportion to time spent under an ultrasonic wave, with a median diameter of 0.25 μm after 15 minutes. However, both C60 and MF were transformed into pieces of around 1 μm in size by fine grinding, and their sizes did not diminish into the submicron region. Particle size coincided almost exactly with the results of SEM observation.

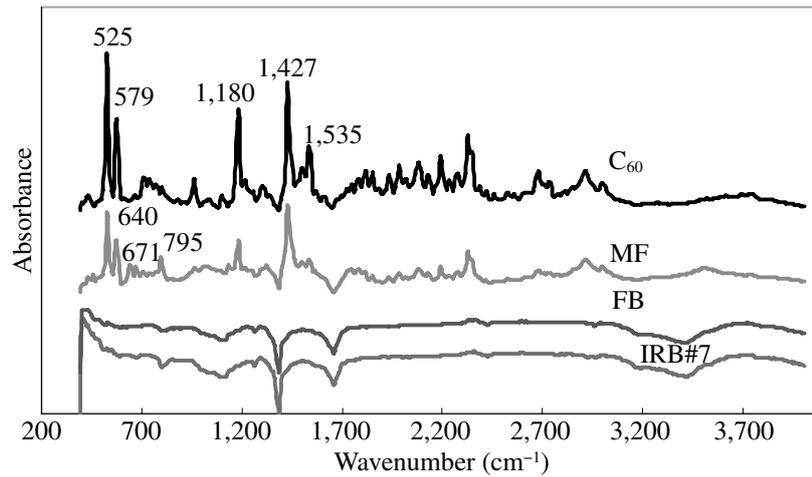


Fig. 5 FT-IR spectra of fullerene and carbon materials.

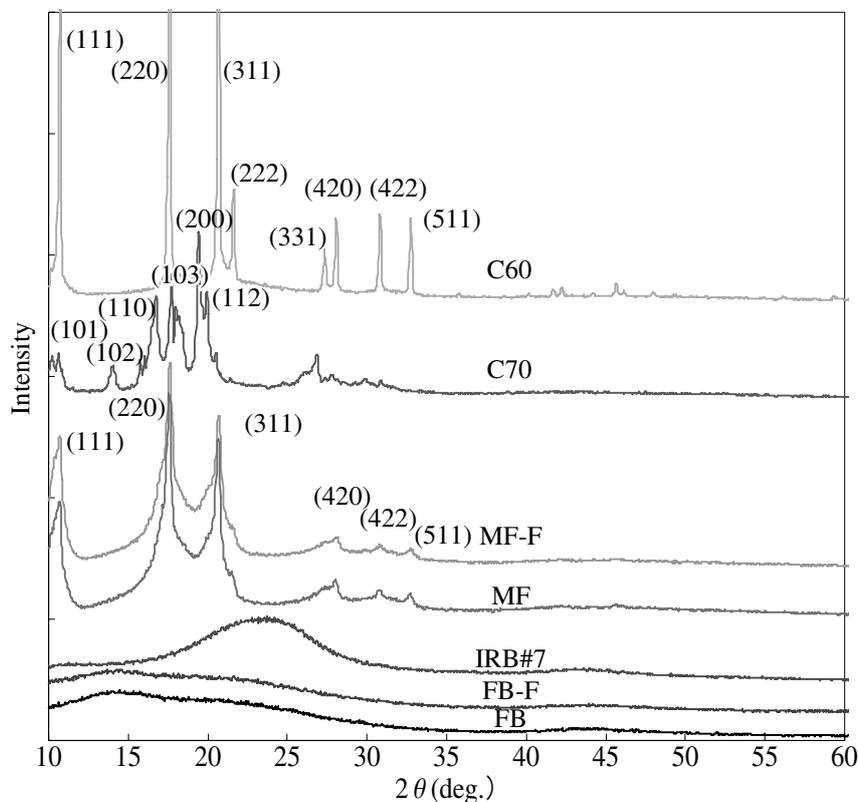


Fig. 6 XRD patterns of fullerene and carbon materials.

The results of specific surface area measurements determined by applying the multipoint B.E.T. method to each sample are shown in Table 2. The specific surface area of C₆₀ and MF had values of about 3.9 m²g⁻¹ and 1.9 m²g⁻¹, respectively, low in comparison with those of FB and IRB#7.

3.1.3 Chemical properties of the fullerene particle

FT-IR spectra are shown in Fig. 5. C₆₀ exhibited absorption at 1535, 1427, 1180, 579, and 525 cm⁻¹. MF exhibited absorption at 795, 671, and 640 cm⁻¹, in addition to the C₆₀'s peaks. The characteristic peaks reported in literature⁷⁻⁹ for C₇₀ (795, 671 and 640 cm⁻¹) have been observed. These results allow MF to be distinguished from C₆₀. However, neither FB nor standard carbon black

IRB#7 show any of the characteristic IR spectra absorption.

Figure 6 shows the powder X-ray diffraction patterns. C₆₀ showed characteristic peaks ascribed to the (511), (422), (420), (331), (222) (311), (220) and (111) lattice from the wide-angle side. The C₇₀ made by FCC was used as a reference, and showed peaks at (112), (200), (103), (110), (102) and (101). In MF, peaks at (511), (422), (420), (311), (220) and (111) were recognized and ascribed to C₆₀, and the characteristic peaks of C₇₀ were almost unrecognizable. Fullerene had sharper peaks than standard carbon black, which had a broad peak over 20-30 degrees. FB had lower crystallinity than IRB#7, and was estimated to be nearly amorphous carbon. Moreover, grinding did not have any recognizable effect on the shape of the crystal for MF.

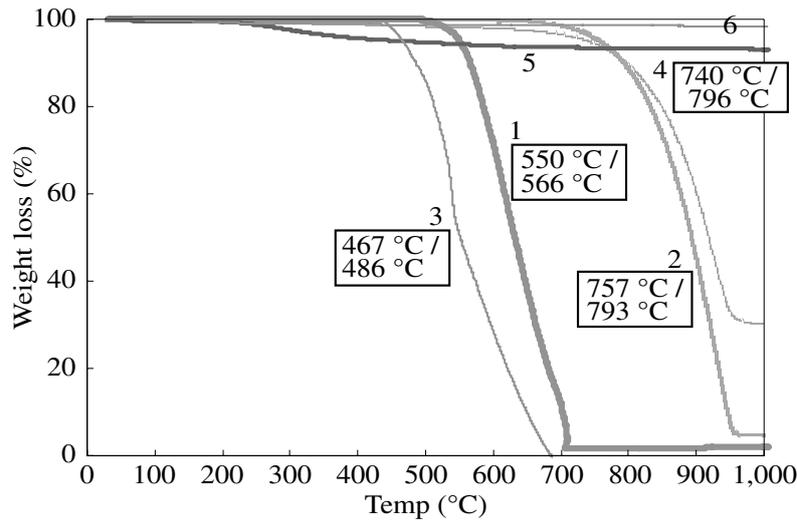


Fig. 7 TG curves of fullerene and carbon materials in air or N₂.
 1: C60 in air 2: C60 in N₂ 3: MF in air 4: MF in N₂ 5: FB in N₂ 6: IRB#7 in N₂
 The numeral in the graph shows the temperature of the weight loss of 5% and 10%.

3.2 Thermal reactivity of fullerene

3.2.1 Sublimation of fullerene

Figure 7 shows the thermogravimetric(TG) curves of fullerene in nitrogen and in air. When C60 was heated in nitrogen, sublimation began just past 600 °C, and the entire quantity had almost sublimed near 1000 °C. Along with the results of research by Chen H.S. *et al.*¹⁰⁾, the sublimation of C60 was successfully confirmed.

The thermal behavior of MF in air and nitrogen is also shown in Fig.7-3,4. Though MF sublimation also began just past 500 °C, it had not entirely sublimed even at 1000 °C, at which temperature about 30 % of initial carbon remained unsublimed and carbonized. It is deduced that this result was caused by the competition between the polymerization and the sublimation, though this conclusion was not experimentally examined. That is, the higher fullerenes was easily polymerized rather than sublimed and fixed by the carbonization before complete sublimation.

The temperature at which 5-10 % sublimation had occurred was determined in order to compare the degrees of fullerene sublimation. These temperatures were 757-793 °C for C60 and 740-796 °C for MF. These results show that C60 has a greater tendency than MF to sublimate. This fact was ascribed to the fact that MF is a mixture of C₆₀, C₇₀ and higher fullerenes with high sublimation temperatures^{11, 12)}. The behaviors of FB and IRB#7 in nitrogen are shown in Fig. 7. Sublimation of the standard carbon black IRB#7 was not observed. FB sublimated a small amount, seemingly as an effect of the presence of fullerene which was slightly included.

3.2.2 Oxidation reaction of fullerene under heating in air

Figure 8 shows the thermal analysis of fullerene oxidation in air. The oxidation reaction in air started at 483 °C for C60, which was rapidly oxidized from 558 °C (peak temperature) and completely eliminated by 640 °C. The oxidation initiation temperature for MF was lower than

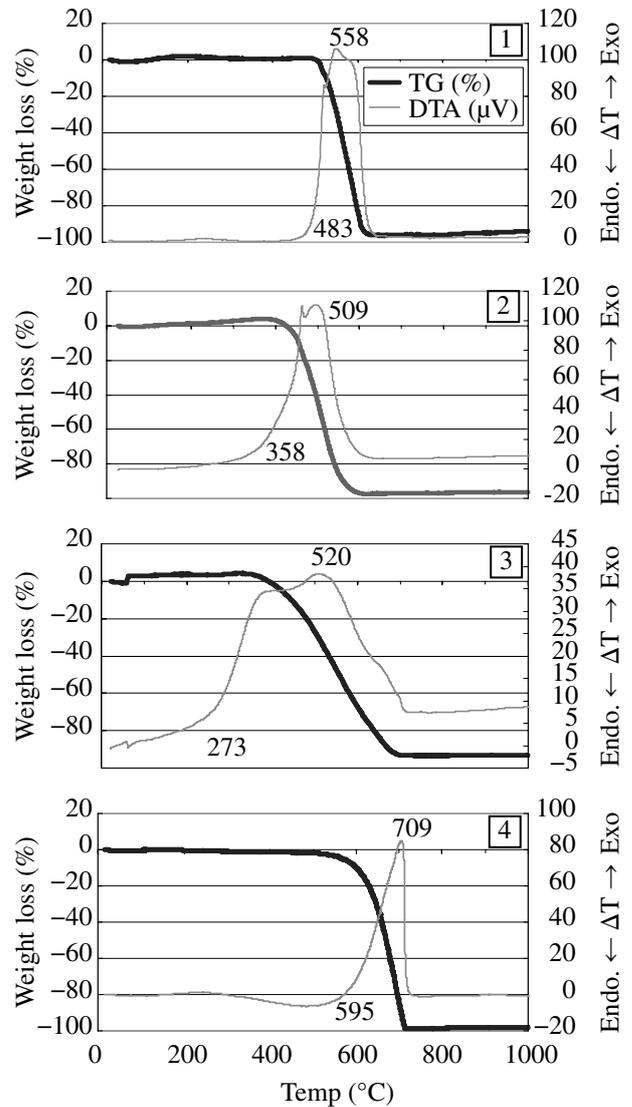


Fig. 8 TG / DTA curves of fullerene and carbon materials in air.
 1: C60 2: MF 3: FB 4: IRB#7

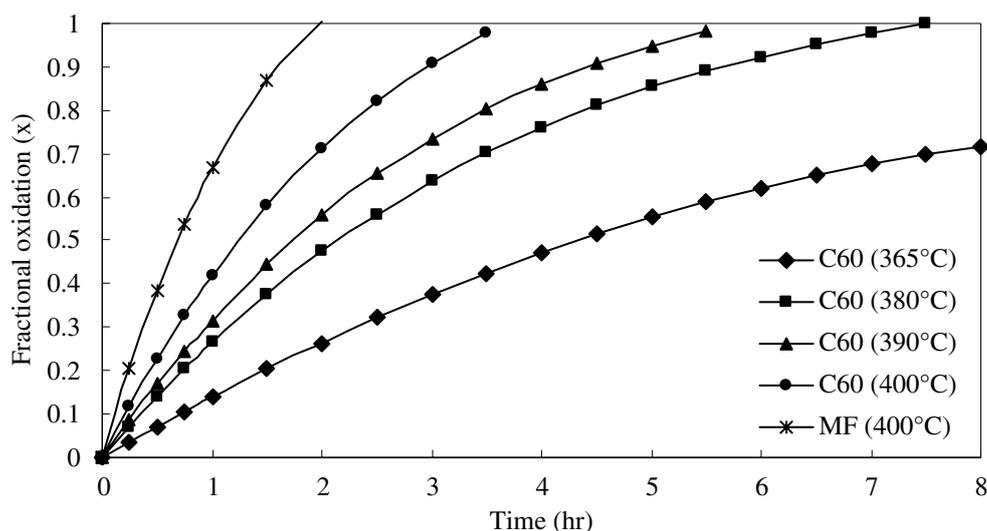


Fig. 9 Isothermal oxidation reaction of fullerene (C60) and mixed fullerene (MF).

Table 3 Kinetic parameters of fullerene and carbon materials.

	N60	MF	FB	IRB#7
Exothermic reaction start temp. (°C)	483	358	273	595
Exothermic peak temp (°C)	558	509	520	709
Rate equation	Surface reaction-controlled shrinking unreacted-core model $k't = 1 - (1-x)^{1/3}$	Diffusion-controlled shrinking unreacted-core model $k't = 1 - 3(1-x)^{2/3} + 2(1-x)$	Diffusion-controlled shrinking unreacted-core model $k't = 1 - 3(1-x)^{2/3} + 2(1-x)$	Gas-phase mass transfer controlled model $k't = x$
Frequency factor (1/h)	23.4	27.2	7.7	18.9
Activation energy (kJ/mol)	141	162	66	132

Sample weight; 2mg, Heating rate; 20 °C·min⁻¹.

that for C60, and MF was rapidly oxidized from 509 °C (peak temperature) and eliminated completely by 610 °C. The oxidation initiation temperature for FB was 273 °C, the lowest among the remaining samples. The complete oxidation temperature was higher than those of C60 and MF. The standard carbon black IRB#7 had the highest oxidation initiation temperature of 595 °C, and the temperature at which its oxidation was completed was also the highest. From these results, it can be concluded that C60 is more stable for oxidation than both MF and FB, though oxidation began at a lower temperature for C60 than it did for IRB#7.

3.2.3 Isothermal oxidation reaction

Figure 9 shows the fractional oxidation vs. time curves for C60 or MF obtained by isothermal TG in air.

The isothermal oxidation of C60 was measured within a temperature range of 365–400 °C, and C60 had been completely oxidized within about 4 hours of heating at 400 °C. MF showed thermal behavior resembling that of C60,

and it was rapidly oxidized at 400 °C. The oxidation rate of FB was smaller than that of C60 and MF. In addition, it had not disappeared completely at 425 °C, even after 6 hours had passed. Oxidation was not very active for IRB#7 below 450 °C, and the oxidation rate increased at 500 °C.

Although fullerene and other samples had columnar or spherical shapes in the SEM photograph, the solid globular model was applied to the analysis of the oxidation reaction as a first approximation. In this model, fullerene oxidation was initiated on the surface of the solid and a product layer was formed in the core of the reaction. Next, vapor-phase oxygen diffused through the product layer and reacted to as yet unreacted species at the surface, with the reactive interface moving to the interior, unreacted part of the particle. Thus, oxidation was supposed to proceed according to following three processes: (1) the mass transfer in the gas laminar film, (2) the diffusion through the product layer, and (3) the reaction at the unreacting nucleus surface¹³. Constructed from the pseudo-steady state approximation, the following equations represent these processes:

- (1) Gas-phase mass transfer is the rate-determining step:
 $kt = x$
- (2) Diffusion through the reacted layer is the rate-determining step:
 $kt = 1 - 3(1 - x)^{2/3} + 2(1 - x)$
- (3) A chemical reaction at the interface between the reacted and unreacted zones is the rate-determining step:
 $kt = 1 - (1 - x)^{1/3}$

where, x is fractional oxidation, t is reaction time, k is constant depending upon the temperature and the characteristics of the reaction system.

C60 shows good applicability to Eq. (3). A constant k depending only on temperature was obtained from the decline of plotting $(1 - (1 - x)^{1/3})$ vs. time. An Arrhenius plot of constant k at each temperature provided the apparent activation energy (temperature dependency of k) for C60 oxidation.

The oxidation of MF and FB in air proceeded according to the equation of diffusion control in the product layer (Eq. (2)), and that of standard carbon black IRB#7 proceeded according to the equation of the gas laminar film diffusion control rate (Eq. (1)). The rate equation and kinetic parameters thus obtained are shown in Table 3. FB showed a low exothermic reaction initiation temperature and a small apparent activation energy for oxidation. Therefore, FB had a low thermal stability, which was ascribed to its large specific surface area.

3.3 Combustion reactivity of fullerene.

3.3.1 Small gas flame test.

Though MF ignited within 10 seconds, it did not continue combustion for 10 seconds. Similarly, FB ignited within 3 seconds but did not sustain combustion for 10 seconds. However, MF-F and FB-F, which were prepared from MF and MB by pulverization, ignited within 10 seconds and sustained combustion for 10 seconds.

3.3.2 Burning rate test.

Though MF and FB are both burnt in red heat, they are not therefore flammable materials, since their burning rates are small. Similarly, MF-F and FB-F are both burnt in red heat, but they are not therefore flammable materials, since their burning rates are small. When C60 and MF were burnt, they emitted red heat with no flame. FB also burnt emitting a small amount of red heat with no flame. There was no difference between C60 and MF in burning rate, and the burning rate of FB was two times larger than that of C60 and MF. Though IRB#7 took on a red color in places where flame was applied, it did not ignite.

The effect of particle size on burning rate was examined, and the results are shown in Table 2. Pulverized C60 had a burning rate 1.5 times greater than that without pulverization, MF 2 times and FB about 3 times.

4. Conclusion

The following conclusions were obtained from the physical and chemical analysis, thermal reactivity test and combustion reactivity test performed on fullerene.

- 1) C60 and MF had lower ash contents and higher carbon contents than the other carbon materials, and can thus be designated as high-purity carbon materials. C60 showed high crystallinity, and MF was an aggregation of crystallites.
- 2) Though standard carbon black scarcely sublimed, fullerenes caused sublimation above 500 °C in N₂. C60 completely sublimed at lower temperature compared to MF, which partially remained without subliming. C60 was more thermally stable than MF, which contained higher fullerenes including C₇₀, according to the oxidation reaction in air.
 The oxidation of C60 in air proceeds via a surface reaction-controlled shrinking unreacted-core model, and the oxidation of MF in air via a diffusion-controlled shrinking unreacted-core model.
- 3) In the burning rate test by the United Nations' hazardous materials transportation advice, fullerenes burn, while the carbon black does not burn. And its burning rate is inversely proportional to its particle size. But fullerene is not a flammable material at any particle size.

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フラーレンの熱反応性

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フラーレンは炭素原子のみからなり、中空構造をもったナノサイズの「炭素分子」である。フラーレンには代表的なC₆₀を含め、さまざまな炭素数を持つものが存在し、基礎的な性質についての研究は、現在まで数多くなされているが、熱的な研究報告は少ない。従って、本研究ではフラーレンの物理的、化学的性質と熱反応性及び燃焼反応性について検討した。

その結果、フラーレンは結晶性の高い炭素材で、標準カーボンブラックに比べて、酸化開始温度が低く、燃焼速度も速く、熱的な反応性が高い。

また、燃焼速度は粒子径に反比例し速くなるが、粒子径によらず可燃性物質には該当しないことが判った。

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