Experimental Investigation of Carbon Oxidization

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The oxidation of carbon samples: C_{60}, $C_{60}(OH)_n$, $C_{60}(O)_n$, $C_{60}(H)_n$, C_{70}, diesel particulate matter (PM), activated carbon, and graphite was carried out using a thermogravimetry equipped with a mass spectrometer. It was found that incorporation of O, OH, and H onto C_{60} surfaces promotes oxidation at a temperature lower than that without incorporation. This finding is helpful to understand the mechanism of PM removal in plasma discharges. A simple oxidation mechanism of C_{60} and its derivatives is given.

Recent literature shows that the oxidation of particulate matter (PM) emitted from diesel engines occurs in reactive gases containing oxygen species generated by plasma discharges at a gas temperature far lower than that for PM combustion.[1] Plasma discharges can promote formation of O–C=O and C–O bonds on PM surfaces.[2] A report given by Li et al. suggested that O atoms can be incorporated between C–C or C=C bonds to form epoxy groups,[3,4] where O atoms can be generated by plasma discharges. The presence of epoxy groups promotes the further oxidation of carbon skeleton. However, there is no experimental evidence to complement the suggestion of the promotion of carbon oxidation by incorporating O on its surfaces.

PM contains mainly soot.[5] Soot is formed from agglomeration and growth of carbon precursors and of a basic structure element graphene. Therefore, the oxidation of soot originates from the oxidation of graphene. Graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. As graphene is the basic structural element of all carbon allotropes including graphite, carbon nanotubes, and fullerenes, the oxidation of fullerene and their derivatives is helpful to understand the promotion of carbon oxidation by incorporating O atoms on surfaces and to understand PM oxidation in plasma discharges. Table 1 summaries the typical carbon bonds including oxygen and hydrogen within various carbon samples. In this study, the oxidation of C_{60}, $C_{60}(H)_n$, $C_{60}(OH)_n$, $C_{60}(O)_n$, graphite, activated carbon (AC), and PM has been characterized using thermogravimetry (TG, TG-8120, Rigaku) to investigate the influence on oxidation of the O-atom incorporated carbon samples.

The experiments were carried out by loading carbon samples (2–3 mg) into an alumina pan within the TG and heating the pan at a scanning rate of 5 or 10 °C/min in 10% oxygen atmosphere (100 mL/min). Fullerene C_{60} (99.5% purity, Cat. No. 08226-95), $C_{60}(H)_n$ (hydro[60]fullerene, $n \approx 30$), $C_{60}(OH)_n$ (hydroxyl[60]fullerene, Cat. No. 181710-95, $n = 6$–12), $C_{60}(O)_n$ (oxo[60]fullerene, mainly $C_{60}(O)_1$ and $C_{60}(O)_2$ with C_{60} and $C_{60}(O)_n$, $n \geqq 3$) were purchased from Kanto Chemical Co. (Tokyo). Graphite (Cat. No. 072-03845, 98% purity) was from Wako Pure Chemical Industries Ltd. (Tokyo). AC (Cat. No. 3001-17280) was obtained from GL Science Inc. (Tokyo). PM was collected from the exhaust gas of a diesel engine. Due to heating, the weight of carbon sample decreases. The weight decrease in percentage of each carbon sample at various temperatures was defined using eq 1.

Table 1. Typical carbon bonds within carbon samples[6,7]

Carbon samples	Typical carbon bonds
C_{60}	C–C, C=C
$C_{60}(H)_n$	C–C, C=C, C–H
$C_{60}(O)_n$	C–C, C=C, C–O–C
$C_{60}(OH)_n$	C–C, C=C, C–O–H
Graphite	C=C
Activated carbon	C=C, O=C–OH, C=O, C–H, C–OH
PM	C–C, C=C, C=O, O–C=O, O=C–OH

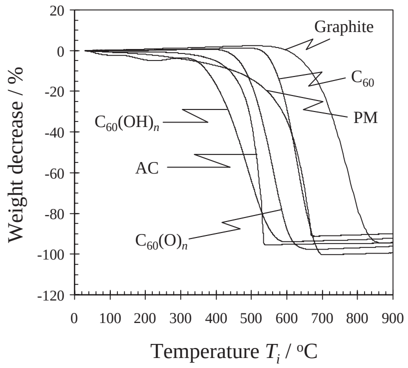

Figure 1. Weight decreases of carbon samples.

$$\text{Weight decrease} = -\frac{m_i}{m_0} \times 100\% \tag{1}$$

Where, m_0 and m_i are the weights of the carbon sample before heating and after heating to a temperature of T_i °C, respectively. T_i is up to 900 °C.

The oxidation products were monitored using a mass spectrometer (MS, M-200QA, Anelva).

Figure 1 shows typical weight decreases of carbon samples from 25 to 900 °C in 10% oxygen (He balanced). The weight of each sample decreased in a wide temperature range. The weight decrease of C_{60} did not change below 530 °C and decreased rapidly above 530 °C. The weight of PM and $C_{60}(OH)_n$ decreased gradually above 50 °C.

Figure 2 shows the temperatures at which the weight decrease of each sample is 10%, 50%, or 90%. $C_{60}(OH)_n$ has the lowest temperatures of T_{10} and T_{50}. Graphite has the highest temperatures of T_{10}, T_{50}, and T_{90}. The orders of each temperature are as follows.

$$T_{10}\text{: } C_{60}(OH)_n < C_{60}(H)_n < C_{60}(O)_n < \text{PM} < \text{AC} < C_{60} < \text{Graphite} \tag{2}$$

$$T_{50}\text{: } C_{60}(OH)_n < C_{60}(H)_n \approx \text{AC} < C_{60}(O)_n < \text{PM} < C_{60} < \text{Graphite} \tag{3}$$

$$T_{90}\text{: } \text{AC} < C_{60}(OH)_n \approx C_{60}(H)_n < C_{60}(O)_n < \text{PM} \approx C_{60} < \text{Graphite} \tag{4}$$

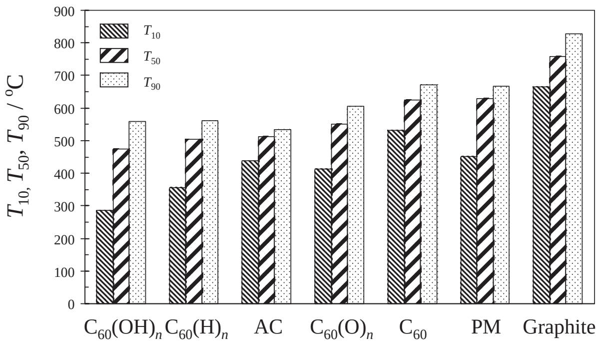

Figure 2. T_{10}, T_{50}, and T_{90} of each sample.

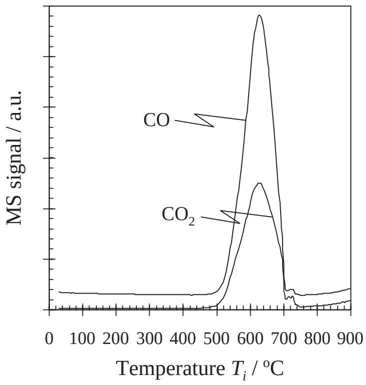

Figure 3. Mass spectra of CO and CO_2 during C_{60} oxidation at various temperatures.

In comparison with C_{60}, the temperatures (T_{10}) of $C_{60}(OH)_n$, $C_{60}(O)_n$, and $C_{60}(H)_n$ are reduced by 247, 118, and 177 K, respectively; the temperatures (T_{50}) of which are reduced by 149, 73, and 119 K, respectively. These facts implied that C_{60} after incorporating OH, O, or H bonds on its surfaces becomes more easily oxidized by oxygen. As there are many C=O, COO, and C–H bonds in PM, the temperature T_{50} of PM is lower than that of graphite although soot in PM and graphite have the same graphene element structure.

The temperature T_{90} denotes the temperatures of carbon samples near complete combustion. The T_{90} values of C_{60} with OH, O, and H bonds are less than that of C_{60}, indicating that the carbons in C_{60} continue to be oxidized after the oxidation of C–OH, C–O and C–H already present before its oxidation.

Therefore, the presence of OH, O, and H in C_{60} can ignite combustion at a lower temperature than C_{60} only.

The main products of carbon sample oxidation are CO and CO_2. Figure 3 shows their signals from mass spectral measurements during C_{60} and $C_{60}(O)_n$ oxidation. The peak signal ratios of CO to CO_2 are C_{60}: 2.2, $C_{60}(O)_n$: 2.1, $C_{60}(OH)_n$: 1.2, $C_{60}(H)_n$: 1.6, PM: 0.6, AC: 0.3, graphite: 0.2. The peak signal ratio of C_{60} is close to that of $C_{60}(O)_n$; this fact suggested that C_{60} and $C_{60}(O)_n$ oxidation may have the same mechanism as shown in Reactions 5 and 6. A further study on this oxidation mechanism is required.

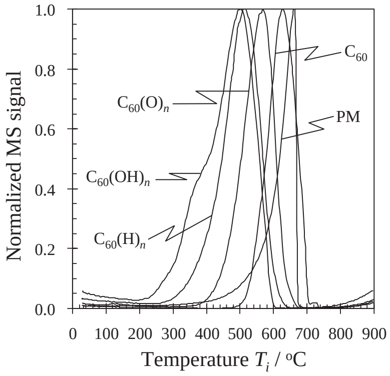

Figure 4. Mass spectra of CO at various temperatures.

$$-C{=}C\bullet + O_2 \rightarrow -C{=}C{-}O \qquad (5)$$

$$-C{=}C{-}O \rightarrow -C\bullet + CO \qquad (6)$$

As the peak signal ratios of $C_{60}(OH)_n$, $C_{60}(H)_n$, and PM are different from those of C_{60} and $C_{60}(O)_n$. The presence of H may play an important role in gaseous phase oxidation of CO and in CO_2 formation directly from C_{60}.

Figure 4 illustrates CO signals in the mass spectra during oxidation of C_{60}, $C_{60}(H)_n$, $C_{60}(OH)_n$, $C_{60}(O)_n$, and PM. The positions and shapes of each spectrum are different, indicating the oxidation of those carbon samples occurs through different oxidation mechanisms that require further study.

The oxidation of C_{60}, $C_{60}(H)_n$, $C_{60}(OH)_n$, $C_{60}(O)_n$, graphite, activated carbon (AC), and PM has been characterized. It was found that C_{60} after incorporating OH, O, or H bonds becomes more easily oxidized by oxygen. This finding is profitable to show direct evidence helpful to understand the mechanism of PM oxidative removal in plasma discharges at a temperature far lower than that for combustion.

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