Effect of Chemical Composition of Real PM on Combustion Temperature

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Abstract: The controlling factor for combustion temperature of particulate matter (PM) was investigated using PM collected from diesel engine and gasoline direct injection engine exhausts. The combustion temperature was not well correlated with crystallinity and particle size of PM, while dependent on the chemical composition, i.e., the oxygen content in PM determined by XPS, EELS, and elemental analysis. The result suggests that the presence of oxygen-containing functional groups of COOH, OH, and C=O at defect sites promotes PM combustion.
Keywords: PM combustion, Surface functional groups, Crystallinity.

1. Introduction

Particulate matter (PM) in atmosphere is responsible for harmful effects on lung diseases. Automobile exhaust is one of the major sources of PM. Therefore, PM is removed in automotive catalytic systems by collecting with ceramic filter and combustion into CO_2. For an effective combustion of PM, the correlation between nature of PM and its flammability should be clarified. Several papers have reported the relation between flammability of PM and structural factors, such as particle size and crystallinity [1-3]. In the present study, using PM generated from real diesel and gasoline engines, the structure-reactivity correlation in PM was clarified.

2. Experimental

Samples of PM are collected by ceramic filter mounted after real diesel and gasoline engines. Commercially available carbon black (#4000B) supplied from Mitsubishi Chemical Co. Ltd. was also used. These were characterized by TEM images (JEOL JEM-2100-F), Raman spectra (JASCO RMP-330), XRD patterns (Rigaku MiniFlex II/AP), XPS spectra (JEOL JPS-9000MC), EELS (JEOL EM-10000 BU), and elemental analyzer (Perkin-Elmer 240II CHNS/O). The reactivity of PM was evaluated by TG-DTA (Rigaku Thermo plus EVO 2) in a flow of 6.5 % O_2/N_2 at 100 mL/min. A sample was heated at 110 ºC for 60 min to remove adsorbed water and other impurities, and then a TG-DTA profile was measured with temperature ramp rate of 5 ºC/min to 800 ºC.

3. Results and discussion

Figure 1 shows TG-DTA profiles of PM combustion. The temperatures at which the PM conversion attained to 50% (T_{50}) were used as an indicator of reactivity. The values of T_{50} were 794 ºC for #4000B, 633 ºC for PM1, 603 ºC for PM2, 534 ºC for PM3, 560 ºC for PM4, 566 ºC for PM5, and 559 ºC for PM6, respectively. The combustion temperatures of real PM were more than 100 ºC lower than a commercial carbon black having good crystallinity. The combustion temperatures were compared with crystallinity, particle size (surface area) and chemical compositions of PM in order to find structure-reactivity correlation. TEM images showed that only #4000B carbon black showed good crystallinity, i.e., thick and long-range graphite lamellae were observed on outer particle, while a fingerprint like structure with thin and short-range graphite lamellae were observed in the PM samples. There was no significant difference in the morphology among the PM samples. In Raman spectra two characteristic bands are observed at 1580 cm^{-1} assigned to G band (stands for "graphitic") and 1350 cm^{-1} is assigned to D band (stands for "defected") were observed. Although #4000B showed very strong G band, G/D ratio for the PM samples are almost unity and there is not much difference among the PM samples. The values of T_{50} were not correlated with surface areas of PM.

The combustion temperatures of PM were significantly affected by chemical compositions of PM. Figure 2 shows the compositions of PM determined by C K-edge EELS spectra. The spectra were mainly composed of a sharp π* peak at lower energy and a broad σ* peak at higher energy, and can be separated into four Gaussians, assignable to graphite C=C, aromatic C=C, C-OH or C=O, and COOH, respectively [4]. Figure 3 shows the dependence of T_{50} on the O/C ratio of PM determined by EELS. As increase in oxygen content of PM, the combustion temperature gradually decreased. Good correlations between T_{50} and O/C ratio determined by XPS and elemental analysis were also observed. The results indicate that the oxygen content is a major controlling factor for PM combustion.

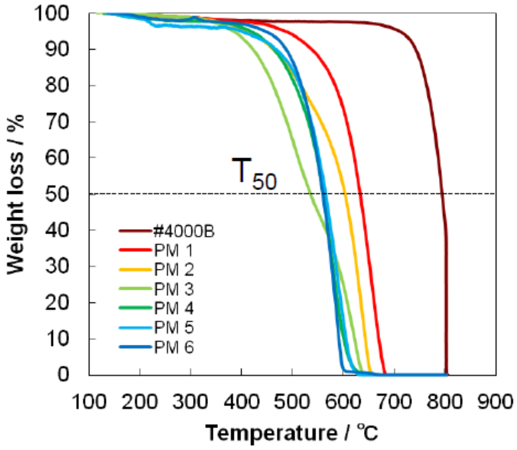

Figure 1. Profiles of weight loss for PM combustion under a flow of 6.5 % O_2/N_2 at 100 mL/min

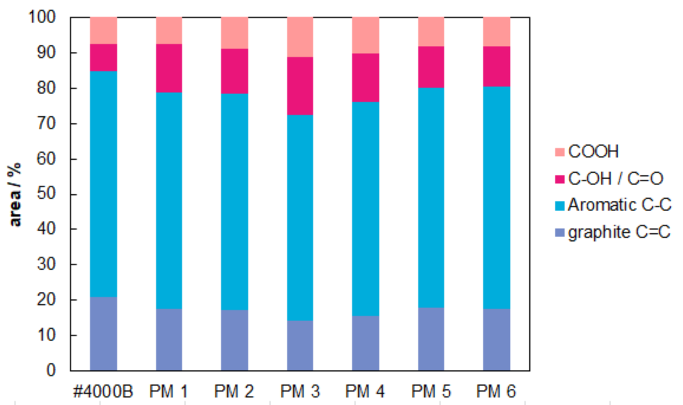

Figure 2. Chemical compositions of PM determined by EELS.

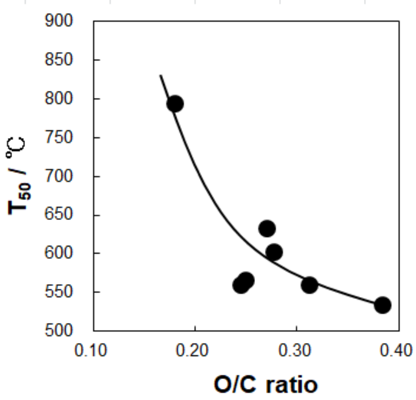

Figure 3. Dependence of T50 on O/C ration of PM.

4. Conclusions

It was found that the oxygen content in PM strongly contributes the combustion temperature of PM, which suggests promotion of PM combustion by oxygenated functional groups of COOH, OH, and C=O.

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