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RAMAN SPECTROSCOPY OF SOOT WITH VARIOUS FRACTIONS OF ORGANIC COMPOUNDS: STRUCTURAL CHARACTERIZATION DURING HEATING TREATMENT FROM 25 ^{O}C TO 1000 ^{O}C

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Introduction

Soot formation in combustion is a complex process involving gas phase chemical kinetics, heterogeneous reactions on the particle surface and particle dynamics [1–3]. Hence size, morphology, internal structure, and optical properties of soot depend on various parameters in the combustion process such as the fuel, type of combustion process as well as the reaction time and temperature history. In previous studies, we focused on investigations of composition, morphology and nanostructure of soot produced by a mini-CAST 5201C soot generator, and their relations to the absorption coefficient using online soot particle aerosol mass spectrometry (SP-AMS), thermal-optical analysis, HRTEM, and multi-wavelength extinction [4,5]. Yet, there is missing information on the internal bonding structures of soot and chemical properties of OC as well as their possible connection with graphenic structures. These features will be emphasized in this work via Raman spectroscopy. The heat treatment at stepwise higher temperatures (up to around 1000 ^{o}C) leads to structural changes for the soot, and as the measurements are performed in an inert N_2 atmosphere, oxidation processes are avoided. The heating process also leads to an interesting thermal effect on the Raman band intensities.

Materials and Methods

The mini-CAST soot with various characteristics were achieved by changing the flame operating conditions (OP) detailed in Table 1, from small soot particles with high organic fraction (OP7) to larger aggregated soot particles with low organic fraction (OP1) [4,5]. These thin soot films were heated in N_2 by a LINKAM (TL1200) heating stage. Raman spectra of the heat-treated soot at each heated temperature were recorded by our homebuilt Raman spectrometer with an excitation wavelength at 532 nm.

Table 1. Burning conditions and characteristics of soot at different operating points.

OP	Propane (Lmin^{-1})/oxidation air (Lmin^{-1})/N_2 mixing gas (Lmin^{-1})	N_2 quenching gas (Lmin^{-1})	Dilution flow (Lmin^{-1})	OC/TC [4]	(OC+PC)/TC [4]	PAH/TC [4]	Fringe length (nm) [5]	Fringe tortuosity (nm) [5]	GMD (nm) [5]
1	0.06/1.55/0	7	0	9%	9%	0.009%	~ 0.61 ± 0.02	~1.18 ± 0.01	310
5	0.06/1.47/0.2	7	0	12%	18%	0.6%	0.56 ± 0.01	1.20 ± 0.02	200
6	0.06/1.42/0.25	7	0	32%	59%	3.9%	0.54 ± 0.02	1.21 ± 0.01	130
7	0.06/1.36/0.3	7	0	53%	87%	5.5%	0.499 ± 0.01	1.23 ± 0.01	80

OC, Organic Carbon; PC, Pyrolytic Carbon; TC, Total Carbon; PAH, Polycyclic Aromatic Hydrocarbon; GMD,

geometric mean diameter of the aggregate size distributions.

Results and Discussion

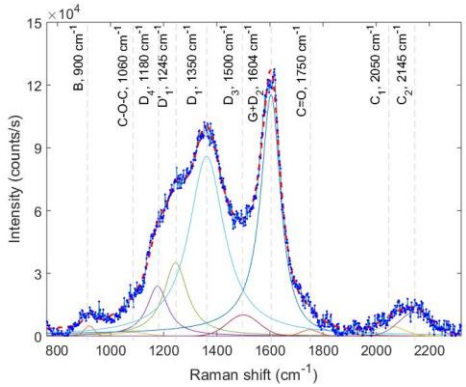

Fig. 1: Raman spectral deconvolutions of non-heat treated OP6 soot

Beside well-known peaks such as D_1, D_3, D_4, and G [6], the stretch vibrations in oxygen involving C-O-C ether bonds and carbonyl C=O as well as sp hybridized bonds are also observed in Raman spectra of rich organic soot OP6 and OP7. In addition, C-H "out-of-plane" mode also appears at ~ 870 – 900 cm^{-1}.

The Raman spectroscopic method has been compared with HRTEM image to determine information on polyaromatic unit size of these soot particles. The heat treatment in N_2 gas of the soot allows us to study soot structural changes and volatility of organic compounds without oxidation processes. All details of this study will be presented in the talk.

Conclusions

We present a spectral analysis of Raman and photoluminescence signals from various soot types produced by a mini-CAST soot generator, and also how these characteristic features changes as a result of heating in an inert nitrogen atmosphere. The study includes four different soot types from black aggregated soot with low organic fraction (OP1) to brownish smaller soot particles with high organic fraction (OP7). The main contributions from the present Raman spectroscopic study are:

- During heat treatment of the soot to elevated temperatures, we observe a strong decrease of the broadband photoluminescence as well as of the characteristic Raman peaks related to the organic compounds.
- The appearance of peaks related to C-H "out-of-plane" bending motions and sp hybridization showing thermal instability has been discussed for the first time for deposited soot. They show up clearly rich soot and can be associated to species formed during the early soot formation processes.
- Contribution of ether and carbonyl oxygenated bonds could be detected, thereby providing a chemical speciation of the oxygenated groups in the organic compounds.

Raman band intensity dependence on the OC content was discussed, and it was found to increase for the OP cases with higher OC content.

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