

EFFECT OF “COLD” ZONE ON PARTICLE FEATURES IN BURNER-STABILIZED STAGNATION (BSS) PREMIXED ETHYLENE FLAMES

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Abstract

In burner-stabilized stagnation (BSS) flames the probe used to sample particles is embedded in a disk. This allows to have well defined boundary conditions; however, particles pass through a “cold zone” (temperature below 1000K). This zone can significantly modify the features of the particles due to condensation of material from gas phase onto the particles. In order to investigate the effect of this zone, particulate collected from ethylene burner-stabilized stagnation flames was chemically characterized. Several diagnostic tools were used to shed light on the effect of temperature on soot properties in this peculiar flame configuration. Particles were thermophoretically sampled on the stagnation plate and analyzed by Raman and UV–visible spectroscopy, techniques sensitive to particle internal structure. Complementary information on the functional groups located at the edge of the polyaromatic system constituting soot nanostructure was obtained by FTIR analysis. The experimental conditions chosen provide a broad range of sooting conditions to understand the temperature effect on soot properties in ethylene BSS flames.

Introduction

Combustion processes under fuel-rich conditions lead to the formation and consequent emission of a wide class of carbon-based byproducts, ranging from gas-phase polycyclic aromatic hydrocarbons (PAH) to solid particles/aggregates passing through high molecular weight aromatic compounds. Combustion-formed particulate properties are important for determining its value for practical applications as well as its impact on the environment, air quality and human health [1, 2]. A great variety of diagnostic techniques has been proposed for studying soot and its precursor formation [3, 4]. Among them in-situ optical diagnostic techniques are usually preferred since the measurements do not perturb the combustion process and present a high sensitivity, however they can only give fewer details about sizes and morphology/nanostructure of the particles.

The sampling of soot particles in laminar premixed flames is a common method for studying soot formation. However, probe intrusiveness into the flame can introduce a significant perturbation of the flame configuration and a subsequent uncertainty in the interpretation of experimental data. To partially overcome this problem a burner-stabilized stagnation (BSS) flame has been proposed by Wang and coworkers as experimental approach for soot sampling [5]. In this flame configuration, the sampling probe is embedded in a water-cooled circular plate positioned above the flame, which acts as flow stagnation surface. If from one side this experimental configuration guarantees a defined boundary condition downstream of the flame for a more accurate description of the perturbation of the flame due to the sampling system, on the other side it induces a significant perturbation of the flame temperature profiles. This experimental set-up is widely diffuse in the combustion community, mainly to study particle size distribution of premixed flames. However, very few studies have been devoted to the chemical characterization of soot formed in BSS flame. Thus, it appears of great importance the knowledge of the properties of particles formed in these peculiar systems and how the collected material is related to the particles formed in practical combustion systems. To this aim in this work we have chemically characterized the particulate collected from ethylene BSS flames with the same feed of the premixed flames previously studied by Abid et al. [6]. By changing the inlet cold gas velocity, different maximum flame temperatures were obtained. An array of diagnostic tools was used to shed light on the effect of temperature in this peculiar flame configuration on soot properties.

Experimental

Experimental set-up

The experimental set-up is the same described by Abid et al. [5] and the flame feeds are the same reported by Abid et al. [6]. Thus just for simplicity even if we have use a BSS system, in the following the flames will be labeled C3, C4, C5 and C6 as done by Abid et al. [6]. We have examined the composition and nanostructure of particulate sampled from a set of ethylene-argon-oxygen flames previously characterized [6], all with an equivalence ratio $\Phi=2.07$ but varying in maximum flame temperatures. The maximum flame temperature is nearly the same of the flames studied by Abid et al. [6] since the perturbation of the stagnation plate lowers only the temperature of the post-flame region keeping unchanged the temperature of the oxidation region [5]. The distance of the stabilization plate from the burner was set at 12.5mm. A brief summary of the operating conditions of the flames is reported in Table 1. Carbonaceous samples were collected mechanically removing the deposited material from the stabilization plate. In order to standardize the procedure, the flame was light on whilst a metal cover was positioned onto the plate, preventing particle from being deposited onto the stabilization plate during the initial transient regime of the flames. After removing the cover, the material deposited drives by thermophoretic force onto the plate. A total deposition time of

300s was used. Successively the flame was rapidly turned off and particles were mechanically removed from a 2.5x2.5 cm² spot in the middle of the burner. The procedure was repeated several times in order to obtain enough material to perform the analysis.

Table 1. Summary of flame studied ([6])

Flame no.	Cold gas velocity ^a , cm*s ⁻¹	Maximum flame temperature, K
C3	8.00	1736±50
C4	6.53	1710±50
C5	5.50	1660±50
C6	4.50	1610±50

^a STP conditions

Carbon particulate characterization

Raman spectra were measured by means of a Horiba XploRA Raman microscope system (Horiba Jobin Yvon, Japan) with an excitation wavelength of $\lambda = 532$ nm. FTIR spectra in the 3400–600 cm⁻¹ range were acquired in the transmittance mode using a Nicolet iS10 spectrophotometer. Analyses were performed on the sample dispersions prepared by mixing and grinding the carbon particulate matter samples in KBr pellets (0.2–0.3 wt%). Carbon particulate was suspended in N-methyl-2-pyrrolidinone (NMP) and analyzed in a 1-cm path length quartz cuvette using an Agilent UV–vis 8453 spectrophotometer.

Results

The Raman spectra of soot sampled in C3-C6 flame are reported in Fig. 1. The two typical peaks of carbon materials, near 1600 cm⁻¹ (G or “graphite” peak) and 1350 cm⁻¹ (D or “defect” peak), can be observed in the first order spectral Raman region, between 1000-1800 cm⁻¹. The peak broadness underlies the highly disordered structure of soot. The G band has been assigned to the C=C stretching of all pairs of sp² atoms, whereas the D peak is due to the breathing modes of sp² atoms in rings [7]. Tuinstra and Koenig [7] showed that the D mode intensity increases linearly with decreasing size of graphite crystals L_a. However, increasing the defects and reducing L_a below 2 nm, this relationship is no longer valid. Thus, in highly disordered carbons the development of a D peak indicates ordering, exactly opposite to the case of graphite [7]. As can be observed in Fig. 1 the intensity of the D peak increases in respect to the G peak, going from C6 to C3, indicating the progressive aromatization of soot as the flame temperature rises.

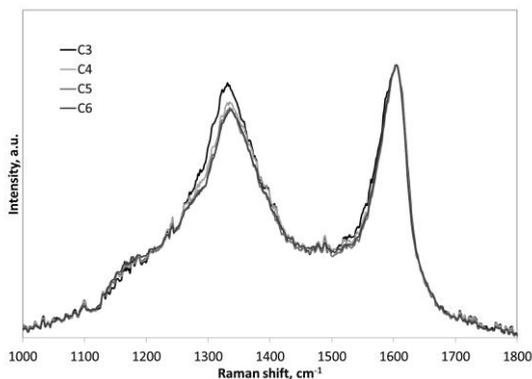


Figure 1. Raman spectra of particulate collected from C3, C4, C5 and C6 flames.

The particulate collected from the C3 flame was found to be partially soluble in NMP. The spectrum of the C3 particulate soluble in NMP along with the UV-Visible spectra of particulate collected in the C4, C5 and C6 flames is reported in the Tauc domain, i.e. $(A \cdot E)^{0.5}$ vs the energy of the radiation, E , expressed in electron Volt, and normalized at 4 eV ($\sim 300\text{nm}$) in Fig. 2.

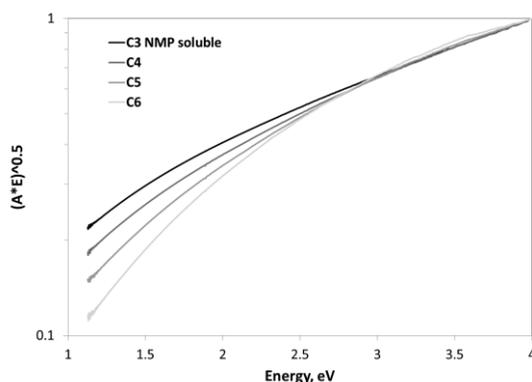


Figure 2. UV-Visible spectra normalized at 4 eV and reported in the Tauc domain of carbon particulate collected from C3, C4, C5 and C6 flames.

Reporting the UV-Visible spectra in the Tauc domain, allows the visualization of the different absorption properties of carbons also retrieving the optical band gap widely used as optical parameter significant of soot properties [8]. It is remarkable that the optical band gap, calculated in the 400-1100nm (3.1-1.13eV) range, decreases with the flame temperature rise, moving from 0.66 eV for the C6 flame to 0.2 eV for the C3 flame. This inference hints to a higher electronic delocalization, i.e. a greater aromatization in agreement with the Raman results. FT-IR spectroscopy has been performed to analyse particle functional groups [9]. Consistently, the infrared mass absorption coefficients reported in Fig.3 show that C6 and C5 samples are the less light-absorbing soot. The qualitative analysis of the

aliphatic C-H stretching region, in the 3000–2800 cm^{-1} wavenumber range, reveals that aliphatic hydrogen is present mainly in form of methylene groups being the most intense peak at 2925 cm^{-1} attributed to asymmetric CH_2 stretching. Aromatic hydrogen presents strong signals between 900 cm^{-1} and 700 cm^{-1} , where the hydrogen bending out-of-plane (OPLA) of aromatic systems occurs, whereas the aromatic C-H stretching signal, occurring at about 3050 cm^{-1} , is generally characterized by a lower absorption strength, and can be clearly seen only in the C5 and C6 soot.

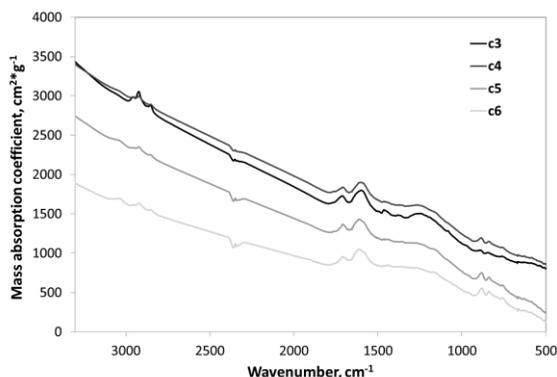


Figure 3. Infrared mass absorption coefficient of particulate collected from C3, C4, C5 and C6 flames.

As expected as the flame temperature rises, i.e. moving from C6 to C3 flames, the aromatic hydrogen lowers [10,11]. The opposite was found for aliphatic hydrogen, showing very high signals for C3 soot. This result is quite surprising and apparently in contrast with what shown so far. Actually, the band gap analysis of the NMP-soluble fraction and the Raman spectroscopy analysis of the total particulate put in evidence the stronger aromatic character of C3. These results were consistent with the higher temperature of the C3 flame, as soot in a hotter chemical environment should experience stronger aromatization and also dehydrogenation processes [10,11]. The higher mass absorption coefficient measured by FT-IR spectroscopy was in agreement with the other spectroscopic techniques, thus the nature of the superimposed spectral features due to aliphatic hydrogen remains unclear. However, just this high aliphatic content could be the reason for the partial solubility of the C3 particulate in NMP. A possible explanation is that the flame environment is affected by probe perturbation: when the probe cools down the flame, gas-phase compounds condensate onto soot particles matter changing their superficial functionalities without changing their bulk properties in terms of carbon network. To this regard, it is worth to note that the mean particle size significantly decreases with increasing flame temperature from flames C6 to C3 [12]. Hence, surface phenomena are expected to be more intense for the small particles produced by the C3 flame and along with the higher

temperature can justify a higher tendency toward aliphatic addition on soot particles edges.

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