The evolution of soot particles in premixed and diffusion flames by thermophoretic particle densitometry

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Abstract

In this study, an improved version of the thermophoretic particle densitometry (TPD) method, introduced by McEnally et al. (1997) has been used for quantitative and qualitative characterization of soot particles generated in both premixed and diffusion flames. To this aim, the dependence of thermocouple temperature response on particle concentration and properties of collected material has been exploited. A variety of values for the thermal emissivity of flame-formed carbonaceous particles are measured, ranging from $\varepsilon \approx 0.4$–0.5 for freshly nucleated particles up to the value of $\varepsilon = 0.95$, typical of a mature soot. The data demonstrate that a correct determination of ε is necessary to accurately evaluate the particle volume fraction at the early stage of the soot formation, where particle concentration measurement is indeed particularly challenging.

Raman spectroscopy analysis of the carbon particles has been conducted with the aim to better understand and to support the observed variation in the thermal emissivity of the carbon particles. In particular, the variation of thermal emissivity is showed to take up with a variation of hydrogen percentage and optical bandgap.

Data also evidence that oxidation has a severe role in affecting both the determination by TPD of soot emissivity and soot concentration. In flame regions where soot oxidation occurs, the present formulation of TPD technique severely underestimate soot concentration.
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Keywords: Soot; Thermal emissivity; Carbonization; Raman spectroscopy

1. Introduction

Soot formation in combustion is subject to on-going researches in response of increasingly stringent regulation, due to concerns about human health and environment, as well as the need of more efficient energy conversion. Flame-generated carbon nanoparticles, however, consist of a very broad set of compounds which can differ in size, nanostructure and chemical composition, thus exhibiting a wide spectrum of optical and physical properties [1,2]. The difficulty in describing

the soot formation/evolution originates from the complexity of the flame environment and by the large variety of parameters affecting the soot mechanism. Among the many aspects involved in the soot formation process, the transition from the gas-phase to the solid soot particles, i.e., the nucleation, is still under debate [3]. Once nucleated, however, carbonaceous nanoparticles further transform in flame. Early nucleated nanoparticles can, indeed, coagulate and/or coalesce, can be subject of surface growth and, in addition, they can undergo carbonization and oxidation. Hence, the chemical and physical properties of soot nanoparticles can be significantly different in relation to their different thermal histories within the flame. Each of these processes is effective in modifying the overall chemical/structural characteristics of the soot particles and in turn their optical/physical properties. Recent studies on soot particle physicochemical evolution in premixed flames pointed out that coagulation co-occur with a sensible variation of the particle optical properties [4]. Also, carbonization and oxidation have been already demonstrated to have significant impact on the soot particle overall makeup [5,6]. Oxidation affects both the amorphous carbon content of the particles and the characteristics of the basic structure units which describe the carbon nano-graphitic domains constituting the soot particles [1,7].

From a diagnostic point of view the possibility to follow both qualitatively and quantitatively the entire soot formation process is particularly valuable. Relevant is the development of simple and reliable methods sensitive to both particle concentration and composition suitable to monitoring diffusion flames. Indeed in such flames the use of most of the on-line and off-line methods is particularly challenging and in situ line-of-site techniques require sophisticated data inversion procedures.

TPD is an attractive method to measure soot volume fraction in flame first developed by McEnally et al. [8] based on previous investigations by Eisner and Rosner [9]. A similar investigation was then the object of an our work, where changes in particle emissivity were reported as due to particle carbonization in premixed flames [10].

The objective of this work is to implement and expand the TPD technique by in-depth analyzing correlations between thermal emissivity and physicochemical properties of the particles. To this aim, we first investigated a premixed flame whose particle physical/chemical evolution was the object of a recent work [4]. The results constitute the basis for implementing the TPD experiment in a diffusion flame. The core of the work is the investigation of the physicochemical evolution of soot in a non-smoking, co-flow laminar diffusion flame from the early stages of carbon nanoparticle formation to the oxidation occurring at the flame tip. The results herein presented demonstrate the ability of TPD to simultaneously probe the soot volume fraction and structure during the soot graphitization process.

2. Experimental

An atmospheric pressure co-flow laminar diffusion flame was investigated. The burner was similar to that of McEnally et al. [11] and consists of a 1.18 cm I.D. uncooled vertical tube for the fuel mixture and a 10.8 cm I.D. concentric tube for the air. The air annulus is reduced at the burner exit by a ring with I.D. 5.5 cm to stabilize the flame [11]. The fuel mixture was composed by ethylene and nitrogen with flowrates respectively of 220 cm^3/min and 500 cm^3/min. Air was provided at a flow rate of 44,000 cm^3/min. This non-smoking diffusion flame was the subject of several experimental [11,12] and numerical [13,14] investigations and it was identified as one of the target flames (ISF-3 Co-flow2, Condition a) [15] at the Third International Sooting Flame (ISF) Workshop.

Experiments were also carried out on an ethylene/air laminar premixed flame stabilized on a McKenna burner with cold gas velocity of 9.8 cm/s and C/O = 0.67.

TPD was used to measure soot particle volume fraction by means of the procedure thoroughly described by McEnally et al. [8]. This method has been further implemented in order to measure the hemispherical thermal emissivity, ε, of the carbon layer deposited by thermophoresis on the thermocouple junction, thus achieving both quantitative and qualitative information of the flame-generated soot particles. An uncoated type-R (Pt/Pt-13%Rh) thermocouple was used for TPD measurements. The thermocouple bead diameter, measured by an optical microscope, was 235 μm.

We have evaluated the surface roughness of the carbon deposit on the thermocouple since surface roughness also affects the emissivity of a surface, its effect depending on the ratio of the square root mean roughness, R_q, to the light wavelength, λ [16]. Surface analysis of the deposits on the thermocouple has been carried out with a Scanning Probe Microscope NTEGRA Prima from NT-MDT, obtaining the square root mean roughness, R_q. The instrument was operated in semicontact mode in air using NANOSENSORS™ SSS-NCHR supersharp silicon-probes. In our flame conditions, soot deposits have a R_q in the order of 20–50 nm. so that $R_q/\lambda < 0.2$ in the visible-infrared spectral region, and can be described as a smooth specular reflector by the diffraction theory [16]. From this theory, it results that in our flame conditions the increase of emissivity respect to the smooth surface is of the order of few percent ($\varepsilon_{rough}/\varepsilon_{smooth} = 6\%$ at Z/HT = 0.6, $\varepsilon_{rough}/\varepsilon_{smooth} = 20\%$ at Z/HT = 0.78 in the diffusion flame and even less relevant in the premixed flame), well within the experimental