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Illuminating the earliest stages of the soot formation by photoemission and Raman spectroscopy

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ABSTRACT

In spite of advances in recent years, the current understanding of the nucleation and initial growth of soot in flames is still rather limited. The chemico-physical properties of just-nucleated particles and particles at the early stage of growth are here investigated by X-ray and ultraviolet photoemission spectroscopy, UV–visible and Raman spectroscopy. Both classes of particles are produced and selectively analyzed by opportunely selecting both flame and sampling conditions.

The complementarity of the methods and the consistency of the results allowed us to evidence the differences in the carbon structure of the two particles. Both kind of particles are predominantly composed by sp^2 carbon and contain a few percent of oxygen mainly as ether-like bonds. A few percent of sp^3 carbon has been observed in grown particles, and it coexists with a more developed graphitic structure with moderately larger aromatic islands, a lower band gap and higher density of states. The results of this work help to clarify the physicochemical transformation experienced by the just nucleated particles with sizes of 2–3 nm during the early steps of the growth process, which is fundamental for the improvement of current models of soot inception and growth.

1. Introduction

Soot formation in flames has long been an object of experimental, numerical and theoretical investigation [1-3] mostly aimed at developing more efficient and less polluting combustion technologies. Indeed, carbonaceous soot nanoparticles produced by combustion of fossil and bio-derived fuels are known to have negative implications on human health, climate change, and energy conversion efficiency [4-8]. Many earlier studies have been focused on particle morphology and nanostructure and on the dependence of these characteristics on their oxidation reactivity as fundamental prerequisite for low-emission technologies [9,10]. By contrast, flames have been long and widely used also for the synthesis of nanomaterials [11]. Among the several reasons that make the flame synthesis an attractive route for the production of nanomaterials there are the easy scalability for massive production and the low cost of the process. Titania and silica nanoparticles, as well as many others materials, are commonly produced by flame route [11]. Additionally, carbon nanomaterials such as carbon fullerenes and nanotubes have been historically produced by combustion processes [12–14], and more recently also graphene [15] and graphene-like materials [16] have been produced in flames. In this contest, carbon particles, like those formed in flames especially in the nanometer size range, may also have optical and electronic properties potentially interesting for new applications, as in the field of the organic electronic [17-22]. This perspective renews the scientific interest for the formation of carbon particles in flames.

Investigation of premixed flat laboratory flames is definitely the most common and reliable way to retrieve kinetic information on the soot particle formation and growth processes as well as to gain information on the particle physicochemical properties. Indeed, in these flames kinetic information can be retrieved by the analysis of flame evolution with the height above the burner which is proportional to the flame residence time. When hydrocarbon fuels are burned under fuel-rich conditions, the hydrocarbon molecules

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undergo pyrolytic reactions which initiate a series of complex chemical and physical pathways first leading to the formation of radical species. These, in turn, react and undergo cyclization reactions resulting in the formation of the first aromatic ring, i.e., the benzene molecule. The following step consists in the transition from benzene molecules to larger aromatic compounds, which is mainly described by means of a sequence of hydrogen abstraction followed by acetylene addition reactions, i.e., the HACA mechanism, or by recombination of resonantly stabilized radicals [23]. The subsequent transition from the gas-phase or molecular compounds to soot particles represents the most critical step of the entire process and in recent years a great deal of work has been devoted to this latter point [24-27].

Several mechanisms have been proposed and currently debated for particle inception. A more exhaustive discussion on this topic can be found in recent review papers [24-27]. We can here mention the physical clustering through i) van der Waals' forces of pericondensed aromatic hydrocarbons, with or without aliphatic chains, or oligomers of aromatic hydrocarbons, i.e., high molecular mass compounds characterized by aromatic functionalities linked by aliphatic bonds; ii) the radical recombination of large molecules or iii) the formation of curved fullerenic-like structures [28-32]; to highlight that different mechanisms are likely to produce particles with distinct chemical and structural composition. In order to fully understand the inception mechanism there is a stringent need to precisely assess the presence of aliphatic components and/or heteroatoms, sp^3/sp^2 bonding and H/C content, size of the aromatic islands and degree of disorder in the structure.

Several experimental evidences show that at the early stages of particle formation in various flame configurations the particle size distribution (PSD) is bimodal, with a first mode typically centered at few nanometers (2–3 nm), and a second mode composed by larger particles [33-39]. The bimodality is generally ascribed to the competition between particle inception and coagulation [34]. However, the strong increase of total particle volume concentration in flame, which is observed in correspondence to the formation of the second mode [40,41], leaves open the question on the relevance of surface growth reaction at the initial steps of particle growth. Earlier studies pointed out that in addition to their different size, these two classes of particles also differ in terms of their chemical/structural characteristics, physical state, optical and spectroscopic properties, and coagulation efficiency [40-47], which might denote an important discontinuity in the overall soot physicochemical/graphitization evolution in flames. Even so, the mechanisms involved in the transition between just nucleated and grown particle are still under debate and a general consensus on the particle chemico-physical properties is far to be reached [27]. Accordingly, the importance of physical factors, like temperature-time history and coagulation, versus chemical surface reactions with gas phase compounds in affecting particle evolution needs to be more thoroughly assessed.

This work extends the findings of a series of recent studies, performed by of our group, aimed at investigating the chemico-physical changes between the two classes of soot nanoparticles [40-42]. To this aim, the two classes of particles have been selectively collected by sampling in two appropriate flame regions and analyzed by means of X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) that are quantitatively sensitive to all kind of carbon and heteroatoms, to complement the information obtained by Raman spectroscopy and UV–vis spectroscopy, being these latter more sensitive to the sp^2 carbon content.

A variety of powerful X-ray techniques, including XPS, have been used in the recent years to investigate soot particles [36, 48-53]. This is the first attempt to use it to study the two classes of particles formed at the early stages of nucleation and initial particle growth, and to exploit the combination with other techniques to obtain chemical and physical information on the evolution of soot nanoparticles in flames.

2. Experimental system

A flat laminar premixed ethylene–air flame was stabilized on a water cooled synthesized bronze McKenna burner. The cold gas stream velocity was set at 10 cm/s and the carbon to oxygen (C/O) atomic ratio was 0.67, corresponding to a flame equivalence ratio Φ of 2.03. In this configuration the flame is low-sooting as demonstrates its slightly yellow color. A low-sooting flame was selected to improve the spatial resolution in the analysis of soot inception. Soot nanoparticles measurements were performed by changing the distance from the burner surface.

Combustion products were withdrawn from the flame centerline by means of a tubular dilution probe as also described in previous studies [34-42]. These works also pointed out the flame boundary conditions are sensibly affected by the presence of the probe. This is clearly evidenced by the temperature profiles measured along the flame for each of the probe position in flame, which are reported in Fig. 1 in ref. [41]. Indeed, the presence of the probe produces a steep decrease of the flame temperature in a region of about 3 mm below the probe. This has the effect of increasing the particle residence time and it is therefore necessary to use the same flame-conditions/probe-effect when comparing results from different experiments and models. In this work this has been achieved by using the same probe to collect particles for each of the characterization technique. To collect samples at different height positions in the flame, the burner was moved vertically with respect to the fixed dilution probe using a translation stage that gave an accuracy of ± 0.1 mm on HAB.

Particle size distribution was measured on line by differential mobility analysis (DMA). A sketch of the experimental apparatus is reported in Fig. 1. Flame products were sampled through an orifice (ID = 0.2 mm, thickness = 0.5 mm) of the tubular probe (with 1 cm outer diameter) positioned horizontally, and mixed with the N_2 turbulent flow, used as diluent with a dilution ratio (DR) of $3\cdot10^3$ [34-42] to quench chemical reactions as described in earlier works [34]. The sampled particles, suspended in the N_2 flow, were first passed through a radioactive (Am-241) bipolar diffusion charger to be subsequently selected through a cylindrical electrostatic classifier, differential mobility analyzer (DMA model TapCon 3/150), and finally counted by a Faraday cup electrometer.

Off-line analyses were performed on soot particles sampled with a tubular probe similar to that used for the online DMA measurements, and collected on Teflon filters (Merk Millipore Fluoropore PTFE, pore size 0.45 µm) for the UV–vis light absorption analysis and on silver filters (Merk Millipore, pore size 0.45 µm) for Raman and Photoemission Spectroscopy. Silver filters were specifically used for XPS and UPS measurements for which an electrically conductive substrate is required. The probe used for filter sampling had a larger orifice diameter than that used for DMA measurements, 0.8 mm instead of 0.2 mm, to collect a larger sample flow and to reduce the sampling time necessary to collect enough material for the analysis. Even so, the dilution ratio in this latter case was enough to quench flame reactions, DR = $1\cdot10^2$.

Particles collected on the Teflon filters were suspended in dichloromethane (DCM), following a sonication-assisted solvent extraction, for the UV–visible absorption spectroscopy. The UV–visible absorption spectra were recorded by an Agilent UV–vis 8453 spectrophotometer. Following earlier studies [54-57], the optical band gap, i.e., the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), of the combustion-formed soot nanoparticles was