PARTICLE INCEPTION STUDY IN FUEL RICH LAMINAR PREMIXED FLAMES BY PHOTOIONIZATION MEASUREMENTS

M. Commodo*, L.A. Sgro*, A. D'Anna, P. Minutolo***
commodo@irc.cnr.it
* Istituto di Ricerche sulla Combustione, CNR, P.leTecchio 80, 80125, Napoli, Italy
** Dip. Ingegneria Chimica, Università Federico II, P.leTecchio 80, 80125, Napoli, Italy

Abstract
Photoelectric charging of particles is a powerful tool for on-line characterization of submicron aerosol particles. Photoionization based techniques have high sensitivity and chemical selectivity, they yield information on electronic properties of the material and are sensitive to the state of the surface. In the present study the photoionization charging efficiency, i.e. the ratio between the generated positive ions and the corresponding neutral ones, of flame formed carbonaceous nanoparticles is measured. The fifth harmonics of a Nd:YAG laser, 213 nm (5.82eV), is used as ionization source for the collected nanoparticle, a differential mobility analyzer (DMA) and a electrometer (Faraday cup) are then used for particles classification and detection. Carbonaceous nanoparticles in the nucleation mode, i.e. D=1-10 nm, show a photoionization charging efficiency clearly dependent on the flame conditions. In particular,we observed that the richer is the flame, i.e. higher equivalent ratio, the higher is the photon charging efficiency. These results clearly show that photoionization is a powerful diagnostic tool for the physical-chemical characterization of combustion aerosol, and it may lead further insights into the soot formation mechanism.

Introduction

Soot formation in combustion is a very complex topic which involves: gas-phase free radical reactions, particle nucleation through polymerization/clustering pathways, particle growth by heterogeneous gas-to-solid reactions and by physical coagulation/coalescence processes, soot annealing and oxidation. Furthermore, such a complexity is amplified by the fact that all the mentioned phenomena are strongly dependent on the fuel chemical structure and physical status (gas, liquid or solid), burning configuration, temperature, and pressure [1, 2].

In the present work we use an UV laser-induced photoionization system coupled to a differential mobility analyzer (DMA) with the aim to gain further insight into the mechanism of soot formation in flames. Specifically, the lower sizes of the so called ultrafine particles with diameter smaller than 10 nm, are sampled from laminar premixed flame and investigated in terms of their propensity to be ionized by interaction with UV light.

Photoelectric charging of particles is a powerful tool for on-line characterization of

submicron aerosol particles [3]. Photoionization based techniques have high sensitivity and chemical selectivity, they yield information on electronic properties of the material and are sensitive to the of the surface composition.
In the framework of the chemistry of combustion by-products, vacuum ultraviolet (VUV) single-photon photoemission spectroscopy has recently attracted a good deal of interest for its potential in discriminating among different molecular isomers [4].
Photoemission from small particles suspended in gas was developed by Burtscher and Schmidth-Ott and co-workers to investigate small particles and to characterize and monitor combustion aerosols [5]. The aerosol photoemission phenomena was described as a four steps process which can be resumed in: 1) excitation of an electron by photon absorption, 2) escape of the photoexcited electron from the surface barrier potential, escape of the electron from the image and Coulomb potential, 4) back diffusion and electron recapture [5]. The authors also found an increased photo-activity of the combustion aerosol when PAHs of three or more rings were adsorbed on the surface [6, 7]. Similar results were also obtained by Niessner and co-authors [8, 9].
Recent development of flame synthesis-sampling methods to produce organic and metal nanoparticles or of on-line methods to measure size distribution of particles formed in flames are triggering the interest of combustion community towards the characterization of particles produced in burner stabilized-stagnation configuration. As a consequence of the flame cooling and stagnation operated by the probe, particle coagulation as well as inception or surface growth mechanisms might be significantly different from those in burner stabilized-free flames. This might affect the particle composition and in particular the surface properties. In light of this it is particularly relevant to develop methods to characterize on-line particle composition and surface.

Experimental and procedures

The experimental set-up is reported in Fig. 1. Combustion generated particles are sampled in atmospheric pressure laminar premixed ethylene/air flames by a high dilution sampling probe and sent on-line,in the following order, to (see):

1) an Am-241 radioactive diffusion charger to attain thewell knowFuchs' steady-state ions distribution [10];
2) an electrostatic precipitator to remove any ions in the gas stream before the interaction with the light source;
3) an ionization cell where particles are irradiated by an UV laser beam, the fifth harmonic of a Nd:YAG laser λ_0=213 nm (5.82 eV).
4) a differential mobility analyzer (DMA) operated in negative mode, i.e. the central electrode as negative pole, to separate and select the positive ion particles;
5) a Faraday cup electrometer, with sensitivityof1 fA, to measure the electricalchargeof positive ion particles produced by photoemission.

Once the number of positive ions formed as a consequence of the photoionization process is estimated, the photoionization charging efficiency (CE) can be simply expressed by the following equation:

$$CE = \frac{N_{PI}^{+}}{N^{0}} \quad (1)$$

where N_{PI}^{+} is the number of the positive particle ions formed by photoionization, and N^{0} is number of neutral particles measured by using the diffusion charger and adopting the Fucks'model for steady-state ions distribution.
The photoionization CE measured for carbonaceous nanoparticles produced in various flames are then compared as function of different equivalence ratio.

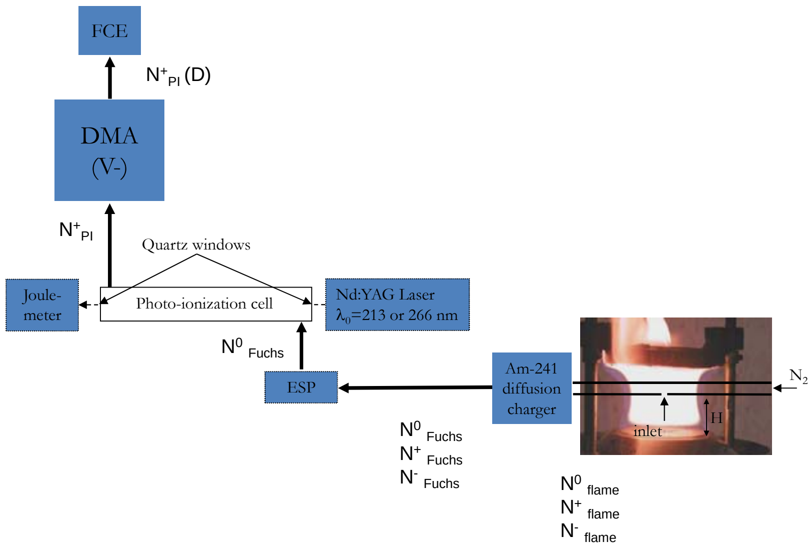

Figure 1. Experimental lay-out for flame formed carbonaceous nanoparticles photoionization measurements.

Results and discussion

Particle size distributions (PSDs) were preliminary measured in the laminar premixed flames of ethylene/air with C/O ratio ranging from 0.57 (blue colored flame) up to 0.69 (fairly yellow flame) by positioning the sampling probe at 15 mm for all of them. The PSDs, are mono-modal for the C/O=0.57 with a maximum number concentration at about 2.5 nm, and bi-modal for the richer flame conditions with a first mode still located at 2.5 nm and a second mode with a maximum ranging from 4 to 12 nm depending on the flame C/O ratio, see Fig. 2. Positive ion particles generated by photoionization are then measured. The number of ion particles with a defined diameter is measured keeping constant the voltage applied to the classifier of the DMA. The number of positive ion particles generated by photoionization are plotted as a function of the laser power in Fig. 3. The linearity between particle ions and laser power (number of incident photons) clearly shows that the photoionization phenomena occurs as a single photon process and so the selected UV wavelength of 213 nm has a photon energy which exceed the ionization threshold, i.e. ionization potential, of the investigated particles.

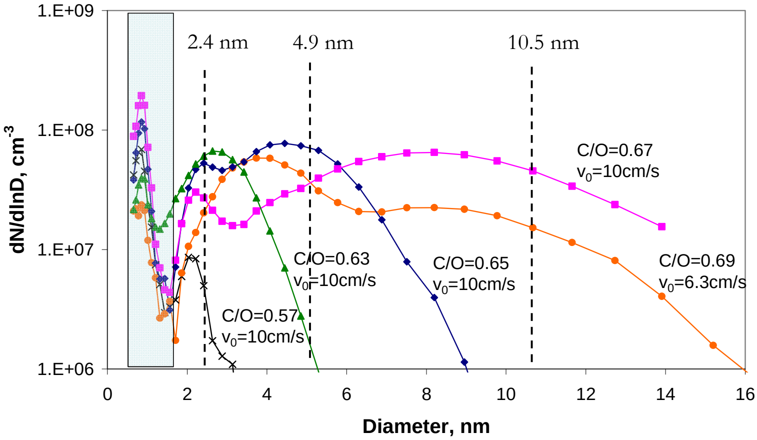

Figure 2. Particles size distribution in the investigated laminar premixed ethylene/air flames.

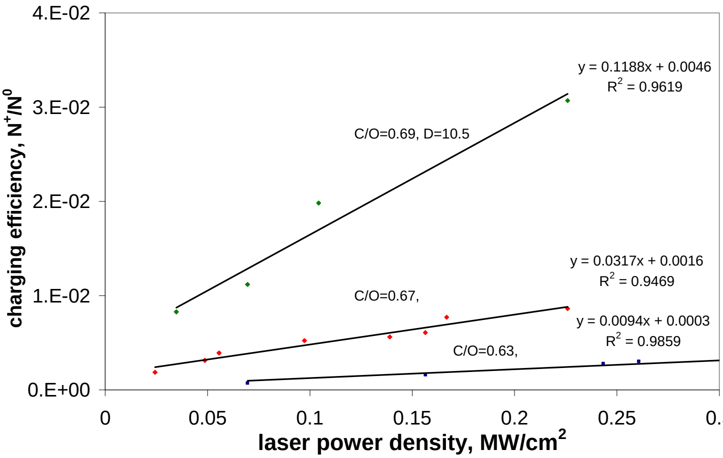

Figure 3. The linear correlation of the photoionization charging efficiency and the laser power as a proof of the single-photon process.

In Figure 4, the CE measured for all investigated conditions are plotted together for comparison. A direct comparison of the photoionization CE for nanoparticles with sizes ranging from 2 – 10 nm is very complex and challenging for several reasons. Aerosol photoemission is, in fact, the results of several phenomena including: photon absorption, ionization threshold of the material, electron ejection, particle sfericity

and possible effect of surface absorbed compound [1]. As a consequence, comparing nanoparticles with different sizes from the very small with a molecular-like composition to the larger ones with a solid structure is a very difficult task.
In the present study we limited the investigatonto the comparison of particle with the same size collected from different flames. As shown in the Fig. 4, increasing in the C/O ratio results in a evident increase of the photoionization CE for all of the three classes of particles, D=10.58 nm, 4.94 nm, and 2.42 nm. As a general rule, higher aromatic structures lead to a lower photoionization potential. The data showed in the Figure 4 are consistent with the assumption that in richer flame conditions, the higher fuel concentration allows the building-up of macromolecular structures,nucleation mode particles, with more extended aromatic functional groups . The technique results to be very sensitive to the changes in the chemical-physical properties of the flame formed nanoparticles.However, dividing the measured CE values by the geometrical particle cross section, i.e. by D^2it turns out that larger particles (D=4.94 nm, and D=10.58 nm) have a lower photoionization yield per unit area than inception particles (D=2.42 nm). This rather counterintuitive results suggest that other phenomena then the simply chemical structure of the particle, i.e. photothreshold of the bulk material, must be taken in account when comparing particle with different sizes.

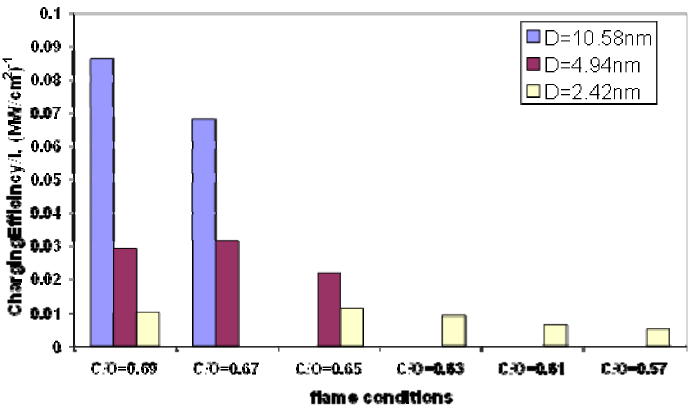

Figure 4. Photoionization charging efficiency for three different particles size as a function of the different flame conditions.

Conclusion

An aerosol based experiment has been designed to measure photoionization properties of size-selected inception and grown particles formed in ethylene/air premixed flame.
Particle photoionization yield increases with particle size. Preliminary results show an increase of photoelectric yield per unit surface with increasing C/O ratio for particles with the same size. This is an indication of a change in the chemical composition and might indicate a larger extension of the aromatic island [6] in the particles formed in richer flame conditions.

Larger particles (D=4.94 nm, and D=10.58 nm) have a lower photoionization yield per unit area than inception particles (D=2.42 nm). The following effects may be considered: 1) different absorption cross section of the small particles as compared to larger ones; 2) deviation from the spherical approximation for the smaller particles; 3) larger compounds may have larger internal energy dissipation; 4) the increase of electron recapture for larger particles; 5) polarization effects due to surface functionalities.

Future work is certainly needed to better understand photoemission of combustion formed nanoparticles. However, the reported results seems to reveal photoionization as very powerful mean to gain information on ultrafine combustion aerosol. Other possible applications may be related to the possibility to investigate surface properties of inorganic metal nanoparticles suspended in a gas which is crucial in terms of knowledge of their reactivity and solubility and toxicological effects.

Acknowledgment

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