THE EFFECT OF ETHANOL ON SOOT PRECURSORS NANOPARTICLES BY PHOTOIONIZATION-DMA

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Abstract
The effect of ethanol addition in ethylene laminar premixed flames, on the characteristics of soot's precursor nanoparticles, was investigated by aerosol photoionization technique. Indeed photoelectric charging of particles is a powerful tool for online characterization of fine and ultrafine aerosol particles because of its high sensitivity and chemical selectivity. Photoionization charging efficiency, i.e. the ratio between the generated positive ions and the corresponding neutral ones, was measured for flame-generated carbonaceous nanoparticles.
Nucleation mode nanoparticles were sampled by means of a dilution probe, to prevent particle coagulation, size-selected and analyzed on-line. The fifth harmonic of a Nd:YAG laser, 213 nm (5.82 eV), was used as an ionization source, whereas a differential mobility analyzer (DMA) coupled to a Faraday cup electrometer was used for particle classification and detection. Carbonaceous nanoparticles in the nucleation mode, i.e. with sizes ranging from 1 to 10 nm, show a photoionization charging efficiency clearly dependent on the percentage of ethanol used as dopant in the ethylene flame. In particular, we observed that the more ethanol was added as fuel, the lower the particle photo-charging efficiency was. This result clearly indicates a modification in the nanoparticle chemical structure as the amount of ethanol is increased. These experimental evidences may be explained by the decrease of aromaticity of the particles and/or by the presence of oxygen bonds within the nanoparticles. Further work is necessary to confirm the validity of these two hypotheses with the use of complementary techniques. However, the results reported herein confirm particle photoionization as a powerful analytical diagnostic tool, providing fingerprints and characterization of combustion aerosol.

Introduction
The mechanism underlying the phenomenon of particle inception and growth in flames is extremely complex, involving gas-phase free radical reactions, particle nucleation through polymerization and/or clustering reactions, particle growth by heterogeneous gas-to-solid reactions as well as physical coagulation and/or

coalescence processes, particles annealing, and oxidation [1]. Fuel composition strongly affects the kinetics of nanoparticles formation. However, most of the works aimed at investigating particle inception and growth in flame typically deal with model conventional hydrocarbon fuels such as: ethylene, acetylene, methane, and benzene [1]. In this regard, the growing interest in the use of alternative renewable biofuels as substitute of conventional petroleum-based liquid fuels has rapidly prompted the research focus towards the understanding of their effects on pollution emission and on particles chemical composition and morphology. For instance, it is widely demonstrated that biofuels can change both the combustion dynamics and the formation of pollutants such as soot particles or nitrogen oxides [2, 3].

In the present study we investigated the effect of ethanol addition in laminar premixed ethylene flame on particle inception by measuring the UV laser photoionization of particles selected in size by means of a differential mobility analyzer (DMA). Photoelectric charging of particles is a powerful tool for the online characterization of submicrometer aerosol particles [4], since this technique has high sensitivity and chemical selectivity. In a our recent study [5] we implemented an experimental method based on aerosol photoionization of size-selected flame-formed nanoparticles, by means of an UV laser source (5.82 eV photon energy), by and an electrostatic classifier-electrometer (DMA). The method showed to be successful in differentiating particles as small as only few nanometer when collected from ethylene flames at different equivalent ratio.

Experimental

Laminar premixed ethylene/ethanol-air flames were stabilized on a capillary burner, d = 5.6 cm, with a cold gas velocity of the unburned premixed gases set at V=5.5 cm/s (TPS). The fuel mixture was changed by the addition of an increasing amount of vaporized ethanol keeping constant the equivalent ratio at Φ=1.82 (C/O=0.60). Air was preheated and mixed with the ethanol supplied by a HPLC syringe pump, which furnished a stable and constant flow rate, then, the mixture was sent to the burner. The ethanol added was varied from 15% to 30% of the total carbon fed. The experimental setup for the online particle sampling and photoionization measurements is reported in Figure 1. Particles were sampled by means of a stainless steel probe made of a tube, with wall thickness of 0.5 mm, having a pinhole with diameter of 0.2 mm, which was placed horizontally above the burner at different heights above the burner. The sampling gas entered in the probe through the orifice, where it was immediately diluted by a nitrogen flow to obtain a dilution ratio on the order of 10^4, required to prevent particle from artificial coagulation phenomena. The particle size distribution was measured on line with a DMA. Changes in ethanol addition caused the flame luminosity to move from slightly yellow (pure ethylene flame) to blue (30% ethanol addition flame) because of its impact on particle formation. Details on experimental and procedures are reported elsewhere [5].

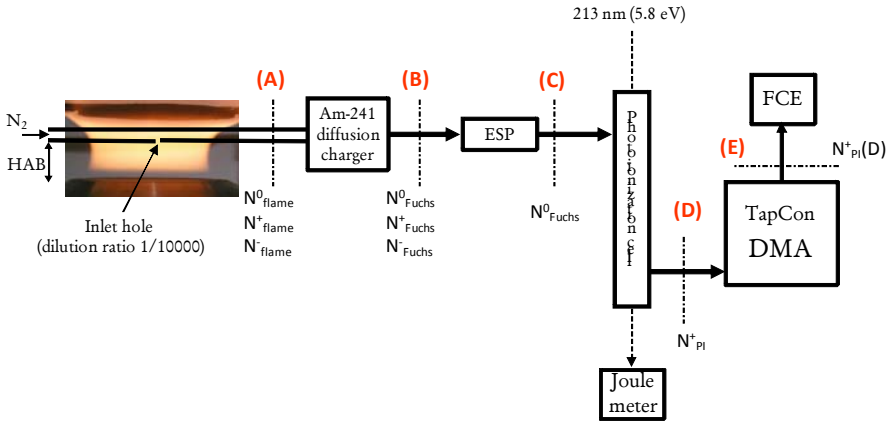

Figure 1 Experimental lay-out for flame formed carbonaceous nanoparticles photoionization measurements.

After passing the photoionization chamber, the positively charged particles in the aerosol (point D in Figure 1) were classified based on their electrical mobility by means of a differential mobility analyzer (DMA). The DMA detector was a Faraday cup electrometer, with sensitivity as low as 1 fA. Once the number of both neutral (N^0) and photoionized particles (N^+_{PI}) were measured, the photoionization charging efficiency (CE) was obtained by the following equation:

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

Results and discussion

Particle size distributions (PSDs) for all the investigated laminar premixed flames, are shown in Figure 2. In all the flames, the PSD is mono-modal at low HAB, with the maximum particle number concentration at about 2−2.5 nm. When the HAB increases, the PSD becomes bimodal, with a first mode still located at the diameter of 2−2.5 nm and a second mode that firstly appear near 4 - 8 nm. In the pure ethylene flame, particles strongly increased in size by increasing the residence time, and the appearance of a bimodal size distribution was already evident at 10-11 mm above the burner. The effect of ethanol addition on particle size and number concentration can be easily gathered by comparing the four charts in Figure 2. The addition of 15% of ethanol produced changes in PSDs as clearly seen in the figure: bimodality appear only at 12–14 mm above the burner and even at HAB=16 mm particles are not larger than 20 nm. A similar trend was produced when 20% of ethanol was added to the fuel, whereas bimodality of PSDF is not observed at 30% of ethanol addition. Salamanca et al [6] pointed out the importance of comparing PSD collected from flames with different amounts of ethanol addition at different residence time. For instance, from the data showed in Figure 2, we may compare

the PSD of the pure ethylene flame at HAB=13 mm with that one measured at HAB=16 mm in the flame with 15% of ethanol addition. The two PDSs present the same bi-modality with a similar number of particles and size of both modes that are centered respectively at a mobility diameter of 2-2.5 nm and at 10-12 nm.

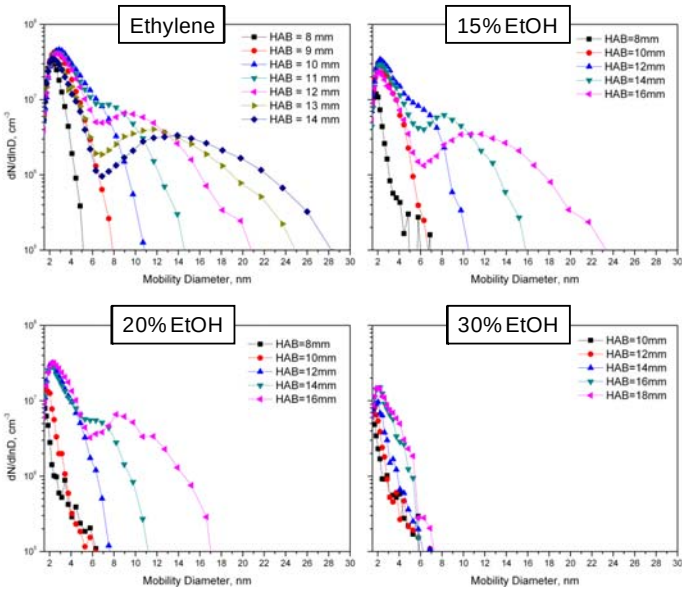

Figure 2 Particle size distributions obtained for all flames with constant equivalence ratio (ϕ = 2.01) at different HAB. The HAB of each curve is reported in the legend.

This experimental observation was attributed to an overall slowdown in the formation process of soot and soot precursor particles due to the addition of ethanol. In order to analyze the effect of ethanol on particle inception, for each flame the ionization efficiency of particles belonging to the first mode of the PSD were compared. For each flame we selected the appropriate HAB leading to similar conditions in terms of particle inception, namely producing a mono-modal size distributions with a similar shape. Figure 3 shows the PSDs of the four investigated flame conditions, with and without ethanol addition. These were selected because representative of the flame condition just before nanoparticles starts to coagulate leading to the formation of larger particles. Particles with a fixed diameter, i.e. 2.4 nm, were therefore selected by the classifier of the DMA and the fraction of particles photoionized by the light beam was measured as function of the laser power density, *I*. Photoionization charging efficiency (CE) as function of laser power density are reported in Figure 3. For laser power density usually below 0.5−0.6 MW/cm2, a linear trend is observed, which is indicative of the proportionality between number of photoionized particles and number of incident photons. This result allows to conclude that the investigated carbonaceous nanoparticles photo-ionize by means of a single photon process when the photon

energy is $h\nu$=5.82 eV. Based on this it is possible to conclude that all of the analyzed flame-formed nanoparticles have a photothreshold, or ionization potential, lower or at most equal to the energy of the employed photon; thus, IP ≤ 5.82 eV. Further details can be found elsewhere [5].

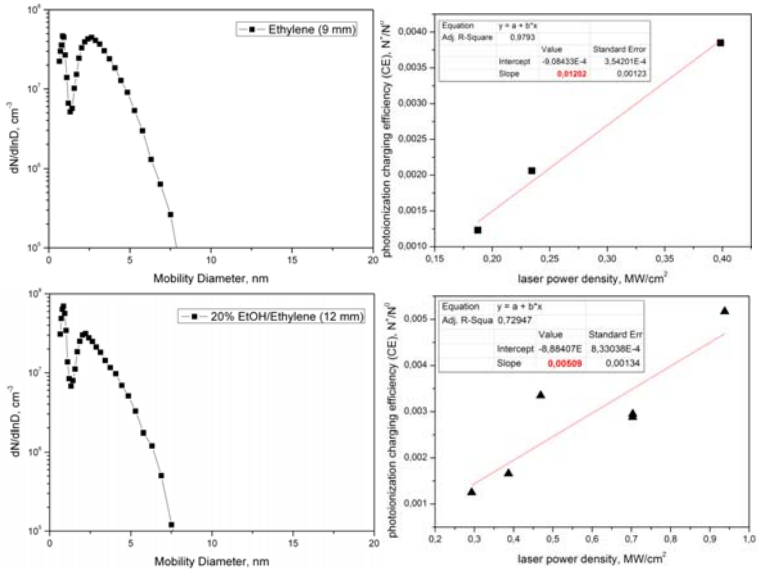

Figure 3 On the left: Mono-modal particle size distributions for two of the different flames investigated. Note, data refers to different HABs depending of the level of ethanol addition. On the right: Photoionization charging efficiency of D = 2.4 nm nanoparticles as function of laser power below the occurrence of photo-fragmentation and/or saturation.

Beside the order and threshold of the photoionization process, the photoionization yield is a very powerful parameter which may be used as an analytical method to provide a chemical characterization of particles. Photoelectric yield, is defined as the probability of electron emission per incident photon per unit surface area, [4]. However, in aerosol based experiments particle photoelectric yield, $y_{particle}$, can be also considered [5]. This is the probability of electron mission per incident photon per particle and is therefore proportional to the charging efficiency CE divided by the light beam power density. Thus, the slope of the linear plots in the Figure 5, i.e. CE/*I*, allows comparing changes in the $y_{particle}$ of different particles in the different flames. In Figure 4, CE/*I*, for all the investigated particles, is plotted for comparison. Particle photoelectric yield decreases as function of the percentage of ethanol addition. These particles, belonging to the first mode in the size distribution, can be reasonably considered as inception nuclei which are the result of chemical and physical reactions involving gas-phase compounds such as polycyclic aromatic hydrocarbons. Two effects could explain the decrease in ionization efficiency of particles: a decrease in the extent of aromatic moiety or an

increase in particle polarity due to the presence of oxygen bonding in the particles. Further work is necessary verify if they effectively occur in our flame conditions and currently we can only limit to a speculative discussion. Photoionization efficiency increases the larger is the extent of the aromatic moieties forming the nanostructures is [5]. However, in a previous study aimed at investigating ethanol influence on soot and soot precursors in flame by laser induced fluorescence it was showed little or no effect in the aromaticity of the compound formed in flames with different percentage of ethanol addition as evidenced by negligible differences in the fluorescence spectra [7]. On this base it seems dubious that a change in particle aromaticity could explain the ionization results. Nevertheless, given the complexity of the chemical composition of the involved species, neither for photoionization or fluorescence the sensitivity of the measurements to the decrease of aromatic moiety is actually known so that additional investigations are required to shed light on this hypothesis. The second hypothesis relies on the presence of oxygen functional groups in the nanoparticles and the increase of their concentration for a larger percentage of ethanol in the fuel. Many works have reported that ethanol addition to flames affect both the nature of aromatic cluster as well as the oxygen content in the particles even though the effect may depends on fuel and flame conditions [8, 9]. Further work is necessary to confirm the validity of these two hypotheses with the use of complementary techniques such as Raman spectroscopy and FTIR for instance.

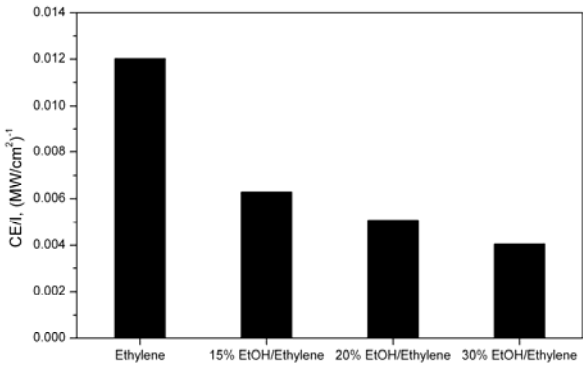

Figure 4 Photoionization charging efficiency/laser power density (CE/I) for 2.4 nm particle mobility diameter as function of the different flame conditions.

Conclusions

An aerosol based experiment has been designed to measure photoionization properties of size-selected inception particles formed in ethylene/ethanol/air premixed flames. Particle formation and growth in flames with an increased percentage of ethanol has been characterized by measuring size distribution profiles along the flame. For each flame, the appropriate HAB has been chosen as representative of the flame condition just before inception nanoparticles starts to

coagulate leading to the formation of larger particles. A decrease of the particle photoelectric yield, or CE/I, with increasing the ethanol percentage in the fuel ratio was observed. This effect indicate a change in the chemical composition of the inception nanoparticles, which may be explained by the decrease of aromaticity of the particles and/or by the presence of oxygen bonds within the nanoparticles. Further work is necessary to confirm the validity of these two hypotheses with the use of complementary techniques.

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