FLAME-GENERATED CARBON PARTICLES: NEW INSIGHTS ON PARTICLE INCEPTION AND CHARACTERIZATION

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Abstract

Organic carbon and soot particles were produced in premixed ethylene-air flames and characterized with the aim to investigate their possible use as a low-cost solid sorbent for CO2 sequestration.

Surface Enhanced Raman Spectroscopy (SERS) was employed to characterize particle composition, surface functionalities and medium range order of the carbonaceous particles sampled from the flame. SERS results, in addition to the analysis of particle charging processes occurring in flames, allowed inferring new insight on carbonaceous particles in the nucleation mode.

Introduction

Solid particulate formation during rich hydrocarbons combustion is generally considered an unwanted by-product. In the recent years, emerging interest towards the synthesis of advanced materials for innovative applications is driving a good deal of attention towards novel nanostructured carbon material. A leading example of this is the current research progress in graphene-based material, which may soon find wide range of practical applications because of its unusual properties. The nearly-molecular size and unique active surface of carbon nanoparticles produced in rich hydrocarbon flames provide a potential basis for the development of innovative technologies.

In this light, a full knowledge of the inception mechanism as well as the composition and properties of flame-generated nanoparticles is required in order to investigate the potentialities of flame-generated carbon particles as novel and low cost nano-materials for a wide number of applications, spanning from material science and gas separation.

In this work, Surface Enhanced Raman Spectroscopy is employed to characterize particle composition and medium range order of the carbonaceous nanoparticles produced in ethylene/air premixed flames whose temperatures and equivalence ratios are chosen to produce flames across the threshold of soot formation. SERS results, in addition to the analysis of particle charging processes occurring in flames, allow inferring new insight on particle nucleation.

Experimental

Particles were produced in premixed ethylene/air flames with cold gas velocity of 10 cm/s and C/O ratio equal to C/O=0.65 and C/O=0.72. Particles selected by size were sampled from the flame with a dilution probe system-Differential Mobility Analiser (TapCon 3/150).

Ag nanoparticles were used as SERS-active substrate. An Ag colloidal solution was prepared according to the standard procedure described in Ref.[1], and was finally dropped on glass microscope cover-slips, which were dried at atmospheric pressure in a clean chamber.

Electrophoretic deposition on SERS substrates was performed on-line at room temperature downstream of the electrostatic classifier of the DMA by means of an electrostatic precipitator (EP). The electrostatic sample time was calculated to achieve a deposition density of 100 particles on a surface of 1 μ m², assuming 100% collection efficiency. As a consequence, the sampling time ranged from 8 to 30 minutes (depending on flame parameters) and the voltage applied to EP was 8 kV.

SERS spectra were acquired with a μ Raman spectrometer using excitation wavelengh λ_0 =532 nm. Laser energy was reduced to avoid sample photodegradation, the acquisition time was 1-2 s. More detail are reported in Ref. [1]. The charge fraction distribution of flame generated aerosols was measured by a DMA. Earlier works measured equal charge distributions for positively and negatively charged particles sampled from flames at atmospheric pressure [2]. Therefore, we set the operating conditions of the classifier to measure only negatively charged flame species, N₋₁(d_i) replacing the charger with a dummy containing no radioactive source. In all of the analysis presented in this work, we assumed that all charged particles measured were singly charged since, as predicted by Boltzmann theory, the contribution of multiply charged particles at the local flame temperature is negligible. The charge fraction distribution of flame generated aerosols, f₋₁(d_i), was evaluated by dividing, for each size bin of the distribution function, *i*, the number of charged particles by the number of total particles:

$$f_{-1}(d_i) = N_{-1}(d_i)/N(d_i)$$
 (1)

where $N(d_i)$ and $N_{-1}(d_i)$ are the number concentration of total particles and of singly charged species in each size bin. Particle losses in the sampling line have been theoretically estimated and data reported as particle size distributions were corrected for them. To avoid electric fields in the line, all walls in contact with the diluted sample flow were metal, in contact with the outer electrode of the electrostatic classifier of the DMA, and electrically grounded [3].

Results

Figure 1a reports the size distribution of total, N_{tot} , and naturally charged particles, N_{-1} , measured in the flame with C/O=0.65 and C/O=0.72 when the probe orifice is

positioned respectively at 15 and 12mm above the burner. The corresponding charge fraction distribution is reported in bottom of Fig.1a.

In the C/O=0.65 condition the size distribution is bimodal, the first mode comprise particles with sizes of about 2nm and the second one of about 4nm. In the richer flame, C/O=0.72 the distribution extends to about 50nm. An additional difference between the two flames is the amount of charged particles. Specifically, in the flame with C/O=0.65 particle with every size are partially charged, and their charge distribution is close to the curve predicted by the Boltzmann theory at the maximum flame temperature also reported in the figure. In the richer flame, C/O=0.72, the particles in the smaller mode of the size distribution, d<5 nm are not charged.

It is well known that chemi-ionization reactions in the flame front produce small chemi-ions which can charge particles by diffusion charging. If the number of chemi-ions and interaction time are large enough to reach a steady state, particle charge fraction distribution can be described by a Boltzmann distribution at the local flame temperature where the interaction between particles and chemi-ions has occurred. In the post flame zone, where the chemi-ions amount is strongly reduced, particle charge distribution can change because of particle coagulation and persistent nucleation. The charge distribution of a coagulated aerosol again results in a Boltzmann curve at the local gas temperature where the particles had their last coagulation event. Finally, particle nucleation in the post flame zone, where chemiions are drastically reduced, produces uncharged particles.

Considering the above charging processes, the charge fraction of the nucleation mode contains information on the flame location where particles are formed. The results of Fig.1 show that in flames near the particle inception threshold, C/O=0.65, particles are charged near the flame front and remain charged even late, in the post flame zone. A different scenario is observed in richer flames, C/O=0.72, where the smaller particles eventually become uncharged. This evidence strongly indicates that, in these flames, significant amounts of freshly nucleated particles are formed in the post flame zone.

Early particle nucleation, close to the flame front, and persistent nucleation, in the post oxidation zone, occur in significantly different flame conditions in term of temperature, radical and precursor's concentration. It is consequently reasonable to hypothesize that particle composition and formation mechanism pathways may be different in the two cases.

Some clues, useful to shed light at this regard, derive from SERS analysis of inception particles. Raman spectroscopy is a powerful technique widely employed for the characterization of carbonaceous materials. The strong enhancement of Raman signal produced by SERS enabled us to measure the Raman spectrum of nucleation mode size-selected particles and it enabled the investigation of second order 2D Raman bands.

The spectra of amorphous carbon in the region of 2000-2900cm⁻¹ are considered as the superposition of five bands due to second order or combinations of the typical

D and G bands [4] and were fitted by Lorentian lineshape. The band appearing at about 2500-2600cm⁻¹ is attributed to the second order of the D4 band, 2*D4. The 2*D1 band is centered at 2720-2750cm⁻¹ and is the second order of the D1 band; this band is generally the most intense observed in amorphous carbon. The band at about 2920cm⁻¹ is attributed to the combination of the G and D1 band, G+D1. 2*D3 is observed at 3000-3060cm⁻¹. The band centered at 3150-3210cm⁻¹ is finally attributed to the second order of G or D2 band, 2*G, 2*D2. Figure 1b clearly shows that three additional sharp peaks at 2850, 2920 and 3050cm⁻¹ are detected in our SERS spectra due to sp3 CH2 and aromatic CH vibrations. Therefore, we fitted the spectra with the superposition of eight Lorentian curves.

The SERS spectra in the range 2000-3000 cm⁻¹ of size selected particles are reported in Fig.1b. Particles with sizes of d= 2.4 and 4nm were collected from the C/O=0.65 flame and d=2.7 and 40 from the C/O=0.72 flame. W2D₁ is the width of 2D1 band.

The spectra measured for the d=2.7 nm particles present two different shapes, which were averaged and graphed separately in the figure. One spectrum is quite similar to the spectra of particles produced in non-sooting C/O=0.65 flames, while the second one is much more similar to the one for d=40nm particles.

All of the particles in the C/O=0.72 flame present a strong band positioned at 2920 cm^{-1} that is superimposed on a relatively smaller background. The extremely constant position and narrow lineshape of the 2920 cm^{-1} band strengthens the attribution of this peak to vibrations involving H atoms rather than the combination of the G and D1 band since both the G and D1 peaks are much wider and have variable peak positions. Its strong intensity measured in SERS spectra of particles produced above the soot threshold (C/O=0.72 flame) is not completely clear. It may depend on the orientation of the vibrations of H atoms on the particle surface or due to a more efficient charge transfer process. Another possible explanation that cannot be excluded is that the particles coagulate with hydrogenated species in the low temperature flame zone produced by the dilution probe [5].

The second harmonic region of the D and G bands is particularly interesting since it is sensitive to structural changes along the c-axis in crystallite and can be used to obtain information on three-dimensional ordering. Lespade et al. [6] reported a correlation between the wideness of the 2*D1 band at 2700cm⁻¹ and the d₀₀₂ inteplane spacing [6]. This parameter has been found to decrease as the interplane spacing decreases in various amorphous carbon materials, reaching a minimum on the order of 50cm⁻¹ in correspondence with d₀₀₂=3.40Å, and to rise again in highly organized carbon until the band at 2700cm⁻¹ finally splits up in graphitic lattices.

The width of the 2*D1 Lorentian curve, W2D₁, measured for the various particles investigated is reported in Fig. 1. All the particles in C/O= 0.65 flame have a very large width of more than 250 cm-1. Even considering the uncertainty of the data, this value is much higher than the values reported by Lespade et al. [6] who found a maximum of about 100cm⁻¹ in correspondence of d₀₀₂ of about 3.55Å. As a consequence, such particles present a very poor, if any, three-dimensional ordering.

The three-dimensional ordering becomes appreciably higher for particles collected from soot-forming flames, since a lower $W2D_1$ is measured even though particles as large as d=40nm still have $W2D_1>100$ cm⁻¹. This observation suggests that crystallites are present in the particles, but the interlayer d_{002} is still larger than 3.50Å due to the presence of defects in the graphitic planes.

It is interesting to note that in the case of particles with d=2.7 nm sampled in the flame C/O=0.72, the W2D₁ parameter confirms two different particles types. one similar to particles collected in non-sooting flames, with a broader Lorentian band and a second particle type with a higher three-dimensional ordering, similar to the 40 nm particles. The particles with higher 3-D ordering are probably composed of stacking of PAH-like species even though they present lateral sp3 CH₂ bonding.



Figure 1. a) Size distribution of total and charged particles and corresponding charge fraction in C/O=0.65 and 0.72 flames z=15 mm compared with Boltzman curve (B) at the temperature of flame front and sampling point. b) SERS spectra of size selected particles (arrow's tail indicates the size of particles and flame conditions). W_{2D1} is the width of 2D1 band.

Conclusions

Changing flame conditions, two kinds of inception particles have been detected with significantly different structural order. In flames near the particle inception threshold, the analysis of charge distribution indicates that particle formation prevalently occurs close to the flame front, inception particles present the typical bands of amorphous carbon and have a very low, if any, three-dimensional ordering of aromatic islands. In richer flame conditions, persistent particle nucleation becomes relevant and two types of inception particles were observed: one type has Raman feature similar to particles produced in less rich flames; the other type has a clearly higher degree of three dimensional order and possibly presence of aromatic stacks. Interestingly, only in such flames soot particles larger than 10nm are detected and their Raman features are similar to that ones of second type of nucleation particles.

The two different characteristics observed for inception mode particle can be correlated to their formation process. Particles with a low degree of threedimensional order are formed close to the flame front, where the high temperatures and concentrations of radicals and precursor species might favor pathways towards a chemical growth of high molecular mass species. These are probably aromaticaliphatic compounds with a loose nonplanar structure such that steric effects might hinder clustering of aromatic units in parallel planes. The second kind of species are those preferentially formed in the post flame zone, where temperatures are lower, and the concentration and composition of radicals and precursors species are significantly different than near the flame front. These species have a larger threedimensional order since the interplane distance of aromatic islands is significantly lower so that they possibly contain crystallites. In this case, molecular growth likely proceeds mainly through the formation of stabilomer PAHs, which can more easily arrange in parallel planes forming crystallites. It would explain why a threedimensional molecular order in persistent nucleation particles becomes more relevant. In all the particles SERS signals at 2850cm⁻¹ and 2920cm⁻¹ evidence the presence of aliphatic bonds which are not accounted by current models of soot formation.

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