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On the hydrophilic/hydrophobic character of carbonaceous nanoparticles formed in laminar premixed flames

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ABSTRACT

Carbon nanoparticles in laminar premixed flames are broadly divided into two classes based on the bimodal shape of the particle size distribution and on the different chemical and physical properties that these particles present depending on the combustion conditions, such as residence time, equivalence ratio, and fuel chemical composition. The chemical and structural characteristics of carbon nanoparticles have been the subject of numerous works because these properties might be of relevance for particle reactivity and optical properties. Few information are available on their hydrophilic properties although these are of relevance for the human health, the climate change, in addition to the technological implementation of condensation nuclei particle counters in aerosol science, water scrubbers and electrostatic precipitators. The aim of this work is to investigate the hydrophilic/hydrophobic behavior of carbon nanoparticles formed in different flame conditions. Static contact angle measurements in addition to chemical and physical characterization of the carbon nanoparticles have been implemented. Results show that nanoparticles formed in richer flame conditions, are the most hydrophobic, whereas nanoparticles of organic carbon, formed in relatively leaner flame condition, appeared to be the most hydrophilic.

The reason for a different water affinity of particles, and especially of the smaller organic carbon nanoparticles, has been discussed by analyzing the different material in terms of their chemical/structural composition and in terms of surface functionalities. While no significant differences have been found by Raman spectroscopy in terms of their carbon structure, the different hydrophilicity is explained in terms of the different amount of surface oxygen detected by X-ray photoelectron spectroscopy (XPS). Combustion conditions are therefore very important in outlining the hydrophilic/hydrophobic tendency of the carbon particles.

1. Introduction

Mitigation and control of the formation and emission of fine and ultrafine particles from both stationary and automotive combustion sources have been a technological goal for many decades and important progresses have been made over the years [1]. Nevertheless, combustion still represents a major source of particulate matter in industrialized areas [2]. The incomplete combustion of fossil or bio-derived fuels leads to the formation of an extremely large and complex variety of carbonaceous species. These species may be emitted from the combustion system as gas-phase molecules, e.g. polycyclic aromatic hydrocarbons (PAHs), condensed phases, e.g. organic macromolecules or molecular clusters/nanoparticles, and solid particles, e.g. soot. All these compounds undergo further chemical and physical transformations either within the exhaust manifolds or in the atmosphere as a result of reactions with other pollutants under the effect of sunlight radiation.

The emission of combustion generated particles in the atmosphere is of concern because of their negative effects on both human health and climate changes [3,4]. Indeed, several toxicological and epidemiological studies have associated combustion aerosols with increased morbidity and mortality [5]. Moreover, combustion aerosol released in the atmosphere may have important implications on the Earth's radiation balance, and so on global warming and climate change, by both directly absorbing solar radiation and/or indirectly by acting as condensation nuclei for water and ice cloud formation [6].

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Nomenclature

PAHs	polycyclic aromatic hydrocarbons	d_p	particle diameter, nm
OC-PM	organic carbon particulate matter	θ	static contact angle, radians (°)
OC-NPs	organic carbon nanoparticles	γ_{LV}	liquid vapor surface interfacial tension, N/m
soot-NPs	soot nanoparticles	γ_{SV}	solid vapor surface interfacial tension, N/m
SMPS	Scanning Mobility Particle Sizer	γ_{SL}	solid liquid surface interfacial tension, N/m
PSD	particle size distribution function	R_a	average surface roughness, nm
AFM	Atomic Force Microscopy	$I(D)/I(G)$	ratio between the absolute intensity of the D peak and the G peak, dimensionless
XPS	X-ray photoemission spectroscopy	L_a	average size of the graphitic domain, nm
HAB	height above the burner, mm	O/C	oxygen to carbon atoms ratio, dimensionless
λ	radiation wavelength, nm		

This last point focuses on the relevance of the interaction of combustion aerosols with water that also affects how the particles may translocate, be stored in and/or excreted from biological systems and how they may affect ecosystems. From a technological point of view particulate matter (PM)-water affinity is relevant for the correct design of wet scrubber and wet electrostatic precipitator in addition to the development of condensation nuclei counter in aerosol science.

How combustion particles interact with water is still mostly unknown and one of the largest uncertainties of models in predicting climate change concerns on how the anthropogenic aerosols affect cloud characteristics [7]. Several studies have investigated cloud formation in presence of various kind of aerosol emission, like those produced by industrial sources, fires, or ships and airplanes, and have found that clouds formed in the presence of combustion emissions have a significantly higher number concentration of the small droplets than clouds in pristine air [8–11]. Nevertheless, among the anthropogenic aerosol the ability of organic carbon particulate matter (OC-PM) to act as cloud condensation nuclei is not well-understood and OC-PM might be as important as sulfates in acting as cloud condensation nuclei [12].

This study is focused on the properties of different classes of carbon nanoparticles formed in premixed flames with different combustion conditions (C/O ratio and residence time) with particular emphasis on their hydrophilic/hydrophobic properties. Fuel-rich laminar premixed flames mainly generate two types of carbon nanoparticles [1]: nanoparticles with sizes between 2 and 3 nm and larger particles with sizes of the order of tens of nanometers [13–15]. These two classes of particles differ not only by their size but also in terms of their chemical/structural properties [16,17], so that the first class has been referred to as OC-NPs, and the second as primary soot nanoparticles (soot-NPs). As a consequence, these two classes of carbon particles present different optical and electronic properties, i.e. different spectral light absorption and emission, refractive index, optical band gap [1]. Our aim is to correlate the chemical and morphological properties of the particles with their ability to interact with water.

2. Experimental apparatus

Two atmospheric pressure laminar premixed ethylene–air flames were stabilized on a water cooled sintered bronze McKenna burner with a diameter of 6 cm. For both flames the cold gas velocity was kept constant at 10 cm/s while C/O ratio was set to 0.63 ($\Phi = 1.91$) and 0.67 ($\Phi = 2.03$) in order to produce both monomodal and bimodal particle size distributions (PSDs) in flame [18].

Combustion products were extracted from the flame centerline at different heights above the burner (HABs) moving the entire burner vertically with respect to the dilution probe by means of a translation stage that gave an accuracy of ±0.1 mm for HAB. The collected particles were analyzed for the determination of the PSDs in number, their chemical and morphological characteristics, surface properties and their hydrophilic/hydrophobic behaviors.

Flame products were sampled by a turbulent flow dilution probe made of a circular tube with 1 cm outer diameter with a sampling orifice (ID = 0.3 mm, thickness = 0.5 mm). The probe was positioned horizontally, and N_2 was used as diluent, ensuring a dilution ratio larger than the critical value below which particles start to coagulate [13–15]. Particle size distributions were measured on-line by a Scanning Mobility Particle Sizer (SMPS) [13–15]. Basically, the sampled particles, suspended in the N_2 flow, were first passed through a radioactive (Am-241) bipolar diffusion charger, to attain the Fuchs' steady-state charge distribution, and then selected with a cylindrical electrostatic classifier, model TapCon 3/150, and counted using a Faraday cup electrometer.

Off-line analyses were performed on the particles sampled with a tubular probe as that used for PSD measurements with an orifice diameter of 0.8 mm which provides a dilution ratio of the order of 10^2. The particles were collected on-line by diffusion and impact on Silver and Teflon filters (Merk Millipore, pore size 0.45 μm), by placing the filter holder in the sampling line.

The hydrophilic/hydrophobic properties of the flame-formed carbon nanoparticles were investigated by static contact angle measurements. The contact angle, θ, is the angle formed by a liquid at the three-phase contact line where the liquid, the gas and the solid intersect. For our measurements, 6 μl of distilled water were directly dropped on the filters previously covered by particles and a picture of the spreading water drop was taken by means of an optical microscope 800×.

Particles collected on filters were also analyzed by Atomic Force Microscopy (AFM) to determine the average roughness of the coated filter surface, by Raman spectroscopy to gain chemical/structural information, and by X-ray photoemission spectroscopy (XPS) for surface analysis.

The analysis of surface roughness was performed with a Scanning Probe Microscope (SPM) NTEGRA Prima from NT-MDT at room temperature and 30% relative humidity. The instrument was operated in semi-contact mode in air, using NANOSENSORS™ SSS-NCHR super-sharp silicon probes with nominal tip radius of 2 nm, in order to perform topographic imaging of samples with a scan rate of 0.3–0.5 kHz over selected areas of 10 μm × 10 μm (1024 × 1024 pixel resolution). The acquired images were then analyzed by means of the Roughness Analysis mode of Nova SPM software, which furnishes the values of the Average Roughness, R_a, defined as the arithmetic average of the absolute values of the roughness profile ordinates.

Raman spectra were measured using a Horiba XploRA Raman microscope system equipped with a 100× objective (NA 0.9, Olympus). The laser source was a frequency doubled Nd:YAG laser ($\lambda = 532$ nm, 12 mW maximum laser power at the sample).