X-ray study of freshly emitted carbonaceous nano-aerosols by synchrotron radiation.

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Over the last few decades, much research has been conducted on the toxicological and global warming influences of combustion generated aerosols. Due to their complex composition and morphology, their reactivity and more especially their hygroscopicity are not well understood. Beyond the question of soot reactivity, pioneering work has been devoted in the last decades to the surface analysis of soot particles by XPS (Toosi et al., 1992; Kirchner et al., 2003) and to the identification of chemical entities attached to the soot surface, which could improve our understanding on soot hydrophilicity (Vander Wal et al., 2011). Nevertheless, in all these studies, measurements have been performed on particles deposited on substrates and, even if high-resolution soft X-ray photoelectron spectroscopy is a powerful characterization tool, hydrophilicity can only be examined using isolated nanoparticles, with no interaction with a substrate. The major aim of this study is to demonstrate the potential of XANES/XPS analysis of airborne carbonaceous aggregates above the C (1s) and O (1s) thresholds, and to compare these results with those obtained from conventional bulk analysis.

These experiments have been carried out with soft X-rays at the PLEIADES beamline of the SOLEIL synchrotron in France. The aerosol source is an industrial propane diffusion flame apparatus (combustion aerosol standard mini-CAST Jing Ltd). Particles were injected through a diffusion dryer prior to entering an aerodynamic lens. Alignment of the aerodynamic lens with the X-ray synchrotron beam was carried out by using SiO_2 nanoparticles generated by atomization, and the particle concentration in the interaction chamber was monitored with a Faraday Cup/electrometer.

Due to the demonstrative aspect of this first attempt of XPS/XANES of airborne soot particles, several technical issues have been considered during the experiment but we were successful in acquiring some photoemission and absorption spectra. Four different fuel-to-oxygen ratios were investigated for XANES and two for XPS, corresponding to a contribution of organic carbon (OC) components to the total mass of carbon ranging from 8 % to 35 %. Only XANES spectrum will be discussed in this abstract and examples of spectra are presented in Figure 1.

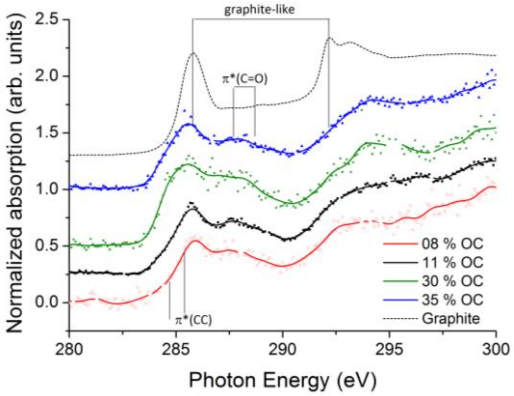

Figure 1. XANES spectrum as a function of OC

Beyond the proof of feasibility, XANES spectra obtained here for different operating conditions of the CAST burner are promising. One interesting point is the drift to lower energy of the C=C region as the OC content increases, together with a slight decrease in intensity around 292 eV. If one compares this to spectra for graphite, this shows that the graphite-like contribution of the nanoparticle decreases to the benefit of aliphatic-like carbon of the OC phase, including double and triple CC moieties. For each sample, we also observe a significant contribution of π* (C=O) resonances at 287.5-288.5 eV; further assignment is still in progress.

A discussion, concerning the technical difficulties encountered during the alignment of the carbonaceous nanoparticles beam and the less effective focusing power of the aerodynamic lens for this type of nanoparticles, will be done. Beyond these experimental difficulties, leading to a limited resolution of the obtained spectra, the feasibility of XPS and XANES analysis of freshly emitted airborne carbonaceous aggregates is demonstrated and opens the way to further investigation on the surface chemistry and reactivity of soot particles.

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