Carbon Hybridization Determination in Soot and Carbon Black

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Solid pollutants, especially Diesel Engine soot are a growing research topic both in industrial and environmental research. Studies on atmosphere impact, effect on human health and on structure and reactivity correlations are undertaken. We demonstrate a possibility to use EELS in order to deduce predominant carbon hybridization in various forms of carbon materials. The results allow a correlation of reactivity of the materials with the possibility to deduce chemical reactivity of the carbons directly from TEM/EELS investigations.

We investigate soot and carbon black samples. Industrial carbon black samples being Furnace soot (FW 1) and Lamp Black (FR 101) are obtained from Degussa. Soot aerosol (GfG) is collected from a spark discharge soot generator (Palas). These substances are compared with heavy duty diesel engine soot collected from a low emission engine (set up to fulfill the Euro IV conditions), as well as black smoke (BS) soot. Highly ordered pyrolytic graphite (HOPG) is used as a carbon reference.

A Phillips TEM/STEM CM 200 FEG transmission electron microscope equipped with a field-emission gun is used to study the morphology and microstructure of the carbonaceous materials. EELS spectra are recorded with the Gatan Imaging Filter GIF 100.

HRTEM investigations reveal differences in microstructure of the different soot and carbon black materials [1]. The corresponding carbon-K-ionization edges are shown in in Fig. 1a. In order to avoid the possible influence of anisotropy of the samples all measurements are carried out under the so called "magic-angle-condition"[2, 3]. The correct settings are verified with a HOPG crystal where no changes in the carbon-K-ionization edge are found when tilting the sample out of the (002) orientation (Fig. 1b). The spectra are processed with a background removal and deconvoluted. The presence of the π^* peak at 285 eV in all the carbon samples is characteristic for π bonds in sp^2-coordinated carbon. The σ^* feature ($\Delta E > 292$ eV) stems mainly from directional σ bonds. The comparison of the spectra of the different soot and carbon black materials with the spectrum of HOPG reveals (Fig. 1a) that all samples exhibit a predominant sp^2-rich form. The main trend in all spectra is the loss of fine structure at $\Delta E > 296$ eV and a fluctuation of the relative intensities of the π^* and σ^* peaks. An additional feature in the spectra is the variation of the intensity between the at $\Delta E = (287 \pm 1)$ eV. This feature is usually assigned to C–H bonds.

Assuming that the intensity distribution in the carbon-K-ionization edge represents the density of anti-bonding states located within the electron probe volume it is possible to determine the relative amounts of π- and σ-bonds in the carbons from the relative intensities of the π^* and σ^* features in the near-edge structure (Fig. 1c). To estimate the relative amounts, it is assumed that the ratio of integrated areas under the π^* peak and the σ^* peak is proportional to Nsp^2/Nsp^3, the ratio of the density of π and σ states. This ratio is normalized with respect to the value determined for HOPG [4, 5]. Table 1 shows the calculated quantification of the sp^2/sp^3 hybridization ratio from the respective spectra. The Nsp^2 amount ranges from 54% in the case of the GfG soot to 77% in the the Lamp Black, indicating the comparatively high graphitization of the latter. The recorded diverseness in microstructure and electronic structure influence the overall chemical behavior of the material. A difference in reactivity towards oxygen is already reported [1, 6].

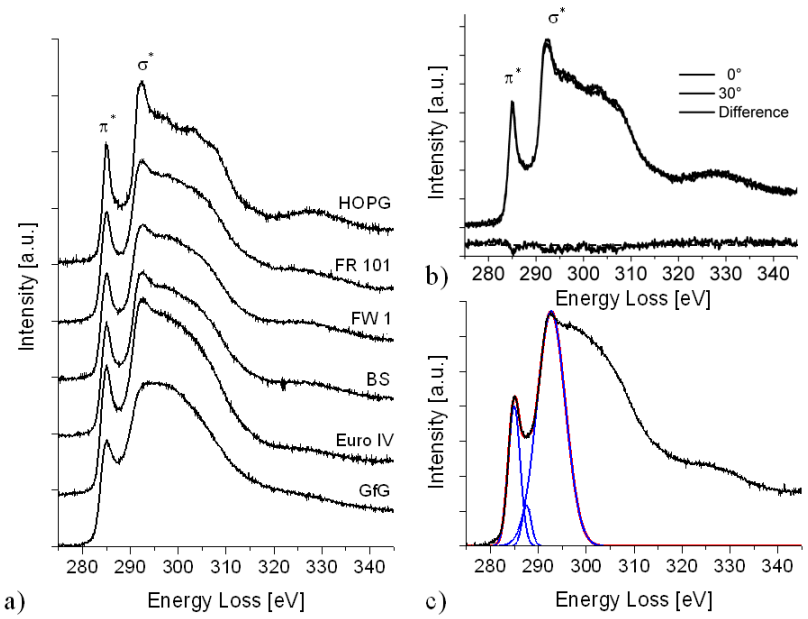

Fig. 1 a) EELS measurements on the soot and carbon black materials, b) verification of magic angle conditions, c) fitting procedure to determine the sp^2/sp^3 hybridization ratio

Table 1 Quantification of the sp^2/sp^3 hybridization ratio from the EELS experiments.

	Nsp^2 %	Nsp^3 %
GfG Soot	54	46
Euro IV Soot	66	34
BS Soot	76	24
Furnace Soot	77	23
Lamp Black	77	23
Graphite	100	0

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