Raman microscopic analysis of changes in structure and reactivity of soot undergoing oxidation and gasification by oxygen

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Soot particles from diesel engines have become recently an important subject in environmental, scientific, and political discussions. Soot particles are hazardous environmental pollutants and account for a major fraction of fine air particulate matter in urban areas. They can cause and enhance respiratory, cardiovascular, and allergic diseases, and they influence atmospheric chemistry, physics, and climate (Oberdörster, et al., 2005).

Efforts in reduction of soot particulate from diesel engine exhaust can be achieved by use of after-treatment systems. These technologies generally require a regeneration method, which efficiently oxidises and gasifies soot deposits in the filter or catalyst structures. A prerequisite for further technical improvement of soot particulate after-treatment systems is comprehensive information about the microstructure, and oxidative behaviour of soot originating from diesel engines. Usually high resolution electron microscopy (HRTEM), thermal gravimetry (Su et al., 2004) and kinetic experiments (Messerer et al., 2005) are used to investigate the microstructure and oxidation behaviour of the soot particles. These investigations have shown that differences in the oxidation behaviour of different types of soot are associated with the different microstructures.

Our recent study has demonstrated that Raman microscopy (RM) can be applied to investigate changes in the structure and reactivity of soot upon oxidation and gasification by nitrogen oxides and oxygen in a diesel exhaust after-treatment model system at 523 and 573 K (Ivleva et al., 2006). RM provides fingerprint spectra, which allow the distinction of a wide range of chemical substances with the spatial resolution of an optical microscope. The first-order Raman spectra of soot are generally characterized by two broad and strongly overlapping peaks with intensity maxima near 1580 (G or “Graphite” peak) and 1350 cm$^{-1}$ (D or “Defect” peak). Based on experimental observations and theoretical calculations, up to five bands corresponding to different vibration modes in the sample have been suggested to account for the observed spectra (Sadezky et al., 2005).

We have applied RM to follow structural changes in spark discharge (GfG) soot and light duty diesel vehicle (LDV) soot upon oxidation and gasification by oxygen (5% O$_2$ in N$_2$) at 473 – 773 K with a heating rate of 5 K/min. Raman spectra have been recorded before and during the oxidation process, and spectral parameters have been determined by curve fitting (Sadezky et al., 2005) with five bands (G, D1-D4). Figure 1 shows the evolution (narrowing of peaks) in the spectra of GfG soot in the oxidation process (473 – 773 K with 50 K step). Analysis of spectral parameters showed pronounced decrease of the relative intensity of the D3 band for GfG soot, which suggests rapid preferential oxidation of a highly reactive amorphous carbon fraction. Moreover width of D1 band exhibited a pronounced decrease with increasing temperature, indicating an increase of structural order and decrease of chemical heterogeneity in GfG soot undergoing oxidation. In our future work we plan to combine RM, kinetic experiments, and HRTEM to obtain precise information about structure-reactivity-relationship for different soot samples.