

Raman Study of Nanostructure Evolution of Diesel Soot During Oxidation

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During the last decades there has been a major worldwide concern for the protection of the environment that led to the development of numerous associated technologies. In the area of air pollution reduction, serious efforts have been made for the control of automotive emissions, such as soot particulates from diesel engines, which are hazardous environmental pollutants. These particles can be effectively removed from the exhaust by means of a Diesel Particulate Filter (DPF), which has to be regenerated periodically (soot oxidation) in order to avoid undesirable backpressure in the engine (Konstandopoulos *et al.*, 2005). In the present work we perform a microstructural analysis during the oxidation of soot particles to clarify the mechanism of soot oxidation.

Several studies have been conducted on the chemical structure and reactivity of different types of soot and related carbonaceous materials employing Raman spectroscopy (Ivleva *et al.*, 2007; Fang *et al.*, 2004; Sadesky *et al.*, 2005). This method provides fingerprint spectra which allow distinction of a wide range of chemical substances and of order-disorder effects on carbonaceous materials.

The Raman spectra of soot can be divided into areas of first-order ($<1800\text{ cm}^{-1}$) and second-order ($2200\text{--}3400\text{ cm}^{-1}$) peaks. The bands that appear at the first region are the G ("Graphite") band at around 1580 cm^{-1} which is attributed to the natural vibration mode of the six-member ring planes in the graphite structure, as well as the bands around 1150 , 1350 , 1500 and 1620 cm^{-1} , known as D_4 , D_1 , D_3 and D_2 , respectively (figure 1).

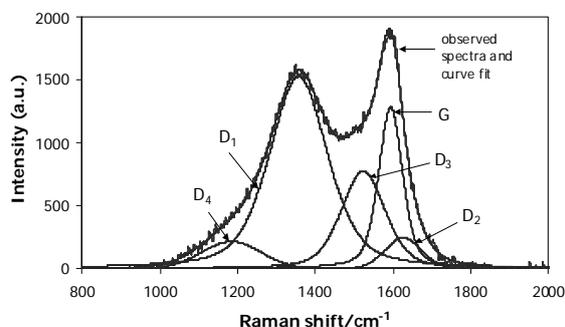


Figure 1. Curve fit for the first-order Raman spectra of soot.

The 1350 cm^{-1} band (D_1 band), commonly called the defect band, is attributed to a graphitic

lattice vibration mode with A_{1g} symmetry and is known to be characteristic for disordered graphite. The 1500 cm^{-1} band (D_3) appears between the two maxima peaks and originates from the amorphous carbon fraction of soot.

In the current work, we investigated the use of Raman microspectroscopy in following structural changes in several engine soot samples upon oxidation. The soot particles were acquired from filters exposed in diesel engine exhaust. The effect of the engine type (common rail versus rotary pump engine), the engine operating conditions (varying engine speed and load) and the combustion mode (conventional versus Homogeneous Charge Compression Ignition, HCCI) were studied. For comparison purposes, the structural evolution of a carbon black (synthetic soot) sample was also studied. The soot oxidation experiments were performed under a flow of air (100 ml/min) with a temperature increase from 25 to 600°C at a rate of 3°C/min .

The soot samples were morphologically characterized by Transition Electron Microscopy (TEM), while their oxidation rate was determined by Thermogravimetric analysis (TGA). Raman spectra have been recorded before and during the oxidation process with a Raman microscope system using a 514.5 nm laser line as an excitation source (delivering $\sim 7.5\text{ mW}$). The spectral parameters have been determined by curve fitting with five bands (G, D_1 - D_4) as proposed by Sadesky *et al.* (2005). The integrated intensity ratio I_{D_1}/I_{G_a} and the band width values of D_1 and D_3 were used to investigate the degree of graphitization of soot samples. The synthetic soot indicated higher degree of structural order than the engine soot. Among the different types of engine soot analyzed the more significant differences were noticed among soot particles acquired under different engine combustion modes.

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