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The heterogeneous reaction between soot and NO_2 at elevated temperatures

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Diesel engines emit a high number of harmful particles. In order to reduce the soot load in the atmosphere the European Union and the US Environmental Protection Agency have set stringent limit values. To keep them the soot particles emitted by the engine are collected in a *wall flow Diesel particulate filter (DPF)*. This DPF is fully loaded with soot after a short time, and thus the exhaust system will be blocked. Therefore the DPF has to be regenerated. Two strategies are applicable. 1) *Active regeneration* is working on the basis of a Cerium-catalyst. 2) With *Passive regeneration* the oxidants are the exhaust gas components alone. Oxygen is comprised with a concentration of 5-10%. However, in many engines the conditions for the burn-off of soot with oxygen, but without a catalyst (Temperature $> 550^{\circ}$C), aren't met. For nitrogen dioxide (NO_2) about 250˚C-300˚C are sufficiently high. The problem with NO_2 is its low concentration in the exhaust gas. Therefore a pre-catalyst has to be used which oxidises NO to NO_2.

The reaction between soot and NO_2 has been object of research in many studies. However insights into reaction mechanisms at elevated temperatures ($>100^{\circ}$C) are not available. Therefore, we did a temperature dependent study on the reaction between soot and NO_2 using *Temperature-Programmed-Desorption-Mass-Spectroscopy (TPD-MS)* and *Diffuse-Reflectance-Infrared-Fourier-Transform-Spectroscopy (DRIFTS)* as research methods. *Diesel-engine-soots* and *model-soots* were investigated. Furthermore *Hexabenzocoronene* was used as a model substance, supplying a well-known molecular structure. The following questions have been dealt with:

- The reaction mechanism for the reaction between soot and NO_2 above 100˚C

- Influence of the physico-chemical properties of the soot on the reaction with NO_2
- The reactive sites for the reaction between soot and NO_2
- Definition of a model substance to put the research so far on a common base

Under consideration of all the experimental results two feasible reaction mechanisms for the reaction between soot and NO_2 have been established:

$$1)\ C + NO_2 \rightarrow C\text{-}O\text{-}NO \rightarrow C{=}O + NO \quad (T > 150^{\circ}C)$$

$$C{=}O + C\text{-}NO_2 \rightarrow [COONO]^* \rightarrow CO_2 + NO$$

$$2)\ C + 2\ NO_2 \rightarrow C(ONO)_2 \rightarrow CO_2 + 2\ NO \quad (T > 150^{\circ}C)$$

1) NO_2 is bound to the surface via the oxygen atom. While the temperature increases NO splits of. The remaining C=O group is oxidized by another NO_2-molecule. Acetyl-nitrite is formed as an intermediate (*), which decomposes thermally into CO_2 and NO.

2) Two NO_2 molecules are bound to the soot surface. The generated functional group decomposes at a temperature above 150˚C into CO_2 and NO.

These two reaction mechanisms will be discussed. Furthermore, detailed answers on the questions above, especially on the possibility of the use of a model substance will be given.