

Comparison of soot reactivity in the presence of O₂ or NO₂

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Abstract

Soot reactivity in the presence of NO₂ was studied and compared to that in the presence of oxygen. At 500°C, in the presence of 1000 ppm of O₂ or NO₂, NO₂ is the better oxidant. The NO₂ reaction is significant at and above 300°C. The rate of soot combustion in the presence of NO₂ is increased by the presence of O₂ (5%) and is catalysed by the presence of water. This rate is high enough to ensure an equilibrium in the particulate filter between the soot production and the soot consumption.

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The respect of the very strict regulations regarding emissions from automobiles necessitates to design new aftertreatment systems. To decrease the particulate emissions from Diesel engines, it appears necessary to proceed with a filtration system. Such a system has already appeared in the exhaust line of the Peugeot 607. A Diesel particulate filter is fitted in the exhaust line and a system based on additional hydrocarbon injection allows the periodical trap regeneration when this latter is filled with soot. In this device, the key parameter is the Diesel soot reactivity in the presence of oxygen (5-15%) at temperatures above 550°C. Another solution is the use of the Continuously Regenerating Trap (CRT), based on the continuous oxidation of soot by NO₂ in the temperature range 200-500°C. In that case, NO₂ is produced by catalytic oxidation of NO in a converter situated upstream. The typical NO₂ concentration is close to 500 ppm. Very little is known about the reactivity of soot in the presence of NO₂. The goal of this paper is to give some key results regarding this reactivity and to compare it to the reaction soot-oxygen.

Experiments were performed with a fixed bed of carbon black (around 100 mg) submitted to a synthetic gas flow containing oxygen and/or NO₂ in helium at a given temperature. The effect of the presence of water was also investigated. The rate of carbon black oxidation was computed from the measurement of outlet CO, CO₂ concentrations. The outlet NO and NO₂ concentrations were also monitored. Commercial carbon black (Cabot Vulcan 6) was used as a reference material representative of the Diesel soot material.

Results

Typical results are presented in Figure 1 which describes carbon black oxidation by NO₂ at 300°C under a gas flow rate of 100 NI h⁻¹.

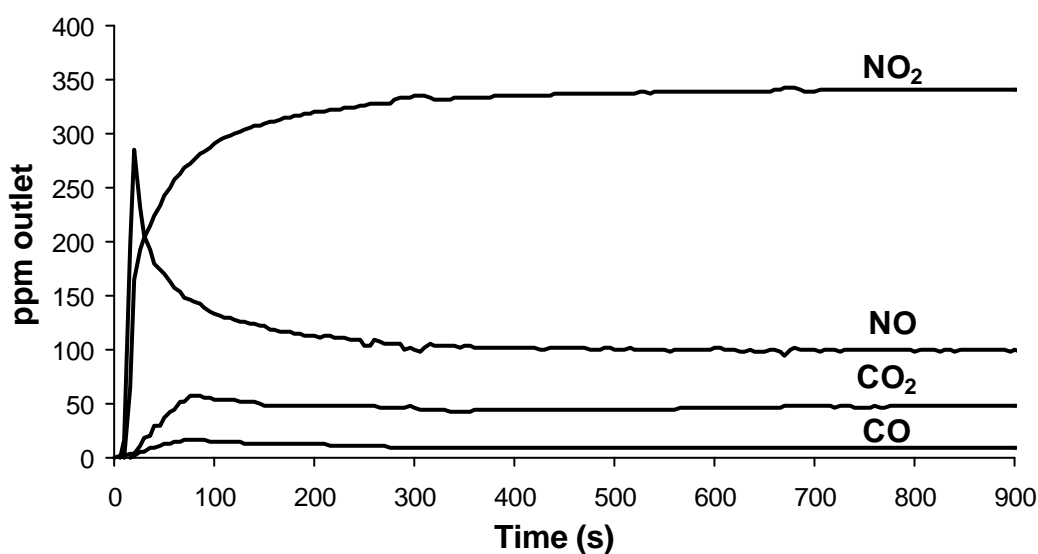
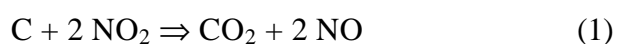


Figure 1: Emissions at 300°C (437 ppm NO₂ inlet, 100 mg of carbon black, 100 NI h⁻¹).

After a transient regime, steady state is obtained with CO, CO₂ NO and NO₂ emissions in agreement with the two following global reactions:



The rate of carbon consumption was very small, leading to a sample mass almost constant during the 900s of experiment and explaining the existence of a steady state regime of oxidation. The rate of carbon oxidation increases when the inlet mole fraction of NO_2 increases or when the temperature goes up in the range 300-450°C, as indicated by Figure 2. The rate of CO_2 production is higher than that of CO , meaning that reaction 1 prevails.

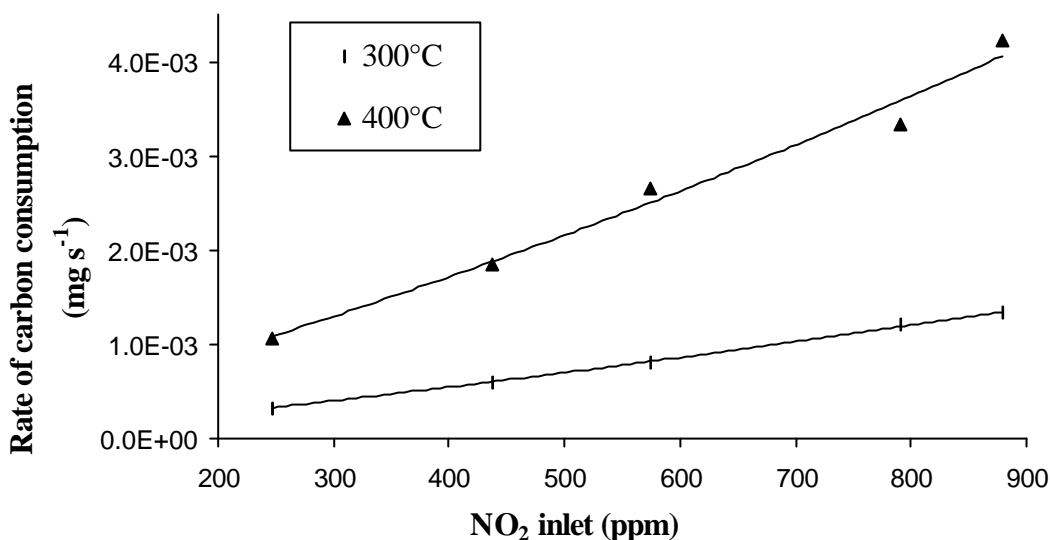


Figure 2: Effect on the inlet mole fraction of NO_2 and temperature on the rate of carbon consumption at steady state (100 mg of carbon black).

Effect of the presence of oxygen and water in the inlet gas mixture

Oxidation of carbon black was performed in the presence of NO_2 alone, $\text{NO}_2 + \text{O}_2$, $\text{NO}_2 + \text{H}_2\text{O}$ (5 %), or $\text{NO}_2 + \text{O}_2$ (5%) + H_2O (5%) at 300°C. The emissions of CO and CO_2 corresponding to these different situations are given in Figure 3.

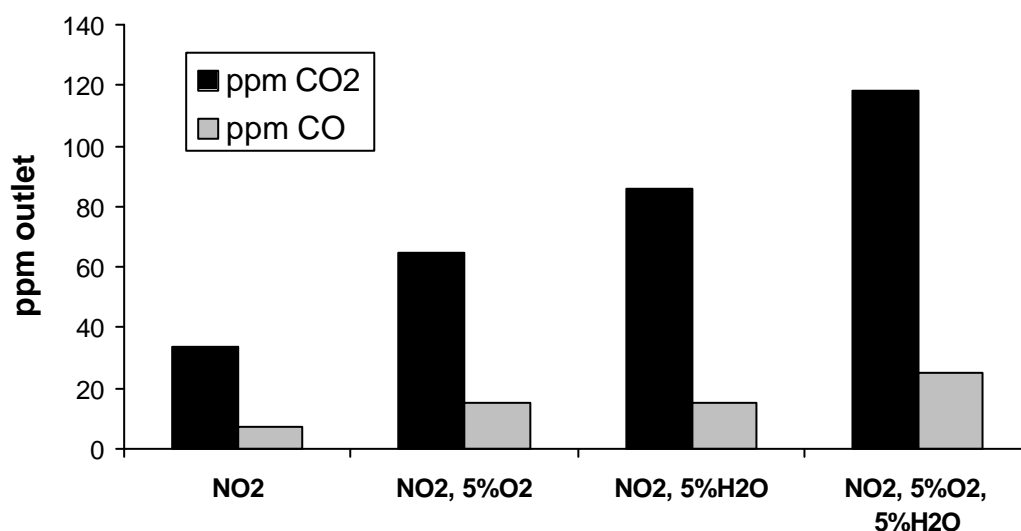


Figure 3 Effect of the presence of oxygen and/or water on the emissions of CO_2 and CO at 300°C (inlet NO_2 concentration: 437 ppm).

The rate of carbon consumption increases when oxygen is injected together with NO₂. It must be emphasised that oxygen alone does not oxidise carbon black at this temperature (nor at 400°C). The rate of carbon consumption also increases in the presence of water. When both oxygen and water are injected together with NO₂, there is a significant cumulative effect. The rate of carbon consumption is then 91% higher than with NO₂ alone. From a comparison between the number of oxygen atoms present in the reacting NO₂ molecules and the number of oxygen atoms present in the products NO, CO and CO₂, we can demonstrate that the oxygen atoms present in the water molecules are not consumed to give products. This means that water acts as a catalyst in the soot/NO₂ reaction.

These results are in agreement with a mechanism in which an intermediate forms between soot and NO₂, eventually also if oxygen is present. This intermediate further reacts with oxygen and/or NO₂ in a catalysed reaction if water is present to give the products CO, CO₂ and NO.

Comparison between carbon black reactivity in the presence of O₂ or NO₂.

This comparison was made under the same experimental conditions, relevant for both reactions. The concentration of NO₂ and O₂ were 0.1% and the temperature 500°C. Under these conditions both oxidation reactions occur significantly. Results are presented in Figure 4, showing that NO₂ is a better oxidant than oxygen for carbon black.

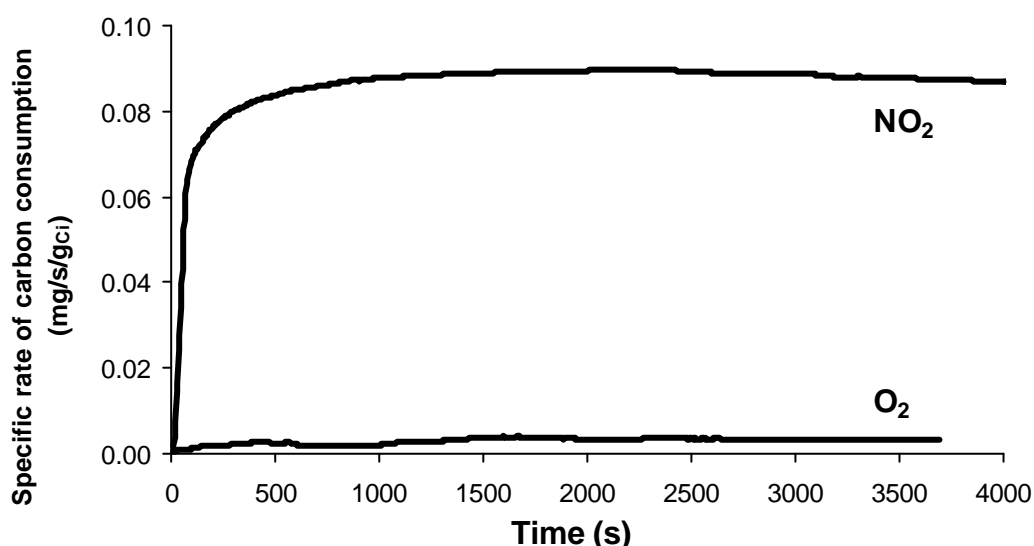


Figure 4: Carbon black oxidation in the presence of NO₂ (0.1%) or O₂ (0.1%) at 500°C.

Carbon black oxidation occurs at a temperature as low as 300°C at a very low rate in the presence of 500 ppm of NO₂. This low rate of oxidation is enough to ensure, within the particulate trap, an equilibrium between the soot production and the soot consumption. This makes feasible the use of such a principle to remove Diesel soot from exhausts of Diesel vehicles.

References

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