Oxidation of model soot by  $\text{NO}_2$  and  $\text{O}_2$  in the presence of water vapor

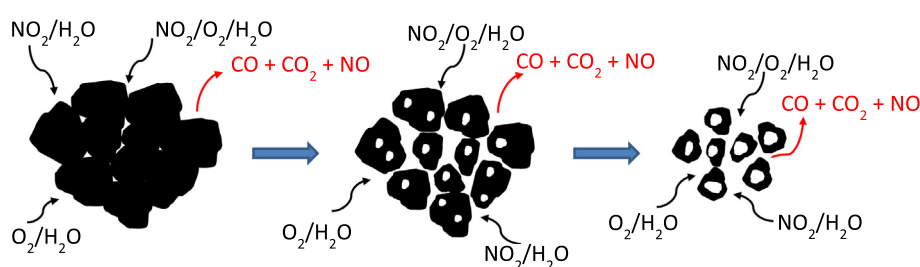
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## HIGHLIGHTS

- Model soot (Printex U) oxidation by  $\text{NO}_2$  and  $\text{O}_2$  in the presence of  $\text{H}_2\text{O}$ .
- Soot oxidation initiated by  $\text{NO}_2$  at low Temperatures.
- Synergistic effect between  $\text{NO}_2$  and  $\text{O}_2$  on soot combustion.
- $\text{H}_2\text{O}$  promotion on soot oxidation.
- Dependence of the kinetic parameters on carbon conversion.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The combustion of model soot (i.e. Printex U) by  $\text{NO}_2$  and  $\text{O}_2$  in the presence of water was investigated in a fixed bed micro reactor under isothermal conditions. A wide range of experimental conditions (e.g. 250–350 °C, 0–5 vol%  $\text{O}_2$ , 0–500 ppmv  $\text{NO}_2$ , 0–5 vol%  $\text{H}_2\text{O}$ ) were considered in order to investigate the role of  $\text{NO}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$  in the combustion process. It was found that the oxidation of soot is initiated by  $\text{NO}_2$  at temperatures where oxygen is unreactive. In addition, a synergistic effect between  $\text{NO}_2$  and  $\text{O}_2$  on soot combustion was observed in the presence of the  $\text{NO}_2$ - $\text{O}_2$  mixture. Both the direct reaction between soot and  $\text{NO}_2$  and also the contribution of gaseous oxygen on the combustion process appeared to rise with the increasing temperature and in the presence of water. Finally, the kinetic analysis of the experimental results showed a non-negligible dependence of the kinetic parameters on carbon conversion and in particular the poor accuracy of the shrinking-core model at low conversion degree.

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## 1. Introduction

$\text{NO}_x$  and particulate matter (PM or soot) emissions from both stationary and mobile diesel engines are widely recognized as an important source of pollution. In particular, diesel engines vehicles are considered as a leading source of PM emissions, which are responsible for serious human health problems, including respiratory diseases (Sydbom et al., 2001). For this reason, remarkable efforts are made by car manufacturers to explore innovative technologies to reduce polluting emissions from diesel engines, and in particular of soot. Although in the past years the development of increasingly sophisticated diesel combustion technologies has

reduced pollutant emissions, nowadays the use of after-treatment technologies is mandatory to fulfil the most recent emissions standards (Twigg, 2011; Johnson and Joshi, 2017). At present, the common after-treatment technology used to reduce soot emissions consists in the employment of diesel particulate filters (DPFs) which trap the soot particles contained in the exhaust stream. In order to prevent pressure drops caused by the collection of particulate, DPFs must be periodically regenerated, generally by the temperature increase (e.g. by combustion on the filter of extra-fuel injected in the exhausts) which leads to the oxidation of the soot particles (active regeneration). More recently, the use of catalytic filters, in which DPFs are coated with a catalytic layer that favors the particulate oxidation at lower temperatures (passive regeneration), has been proposed in order to limit filter overheating and fuel consumption during the regeneration phase (van Setten et al., 2001).

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Aiming at the low-temperature oxidation of soot, the exploitation of  $\text{NO}_2$  as soot oxidizing agent has been considered, being  $\text{NO}_2$  a stronger oxidant than oxygen (Stanmore et al., 2001). This is applied in the CRT (Continuously Regenerating Trap) technology, proposed by Johnson Matthey, which consists of a pre-oxidiser which eliminates the majority of CO and unburned hydrocarbons (UHCs), followed by a filter for the particulate. The pre-oxidiser also converts NO to  $\text{NO}_2$ , which then oxidizes the particulate matter trapped in the wall-flow filter and is back-reduced to NO (Cooper and Thoss, 1989). More recently, an after-treatment system known as DPNR (Diesel Particulate- $\text{NO}_x$  Reduction) has been developed by Toyota (Nakatani et al., 2002; Suzuki and Matsumoto, 2004). This system consists of both a catalytic filter and a specific diesel combustion technology, which has the unique capacity to remove simultaneously both soot and  $\text{NO}_x$ . The new catalytic converter for DPNR is a porous ceramic filter coated with a catalytic layer constituted by a high surface area support (e.g.  $\gamma$ -alumina), a noble metal and an alkaline or alkaline-earth metal oxide, which presents a high  $\text{NO}_x$ -storage capacity. These catalytic systems work under cyclic conditions, alternating a lean phase during which the  $\text{NO}_x$  produced by the engine are adsorbed on the catalyst, with a short rich phase, during which the stored  $\text{NO}_x$  are reduced to nitrogen. Under lean conditions the DPNR system works as a catalyzed soot filter in which soot oxidation occurs thanks to the presence of both  $\text{NO}_x$  and oxygen in the exhausts. In previous works from our group (Castoldi et al., 2006; Matarrese et al., 2014) the activity of model Pt-Ba/ $\text{Al}_2\text{O}_3$  and Pt-K/ $\text{Al}_2\text{O}_3$  catalysts in the removal of soot and  $\text{NO}_x$  according to DPNR concept have been addressed. It has been shown that under cycling conditions, i.e. alternating lean/rich phases according to the typical DPNR operation,  $\text{NO}_x$  are stored onto the catalyst surface and subsequently reduced to nitrogen. In addition, soot oxidation also occurs during the lean phase, and this has been primarily ascribed to the  $\text{NO}_2$  formed upon NO oxidation over Pt sites. Besides, a specific role of the stored  $\text{NO}_x$  in the oxidation of soot has also been demonstrated.

In this respect many studies are available in the literature concerning the oxidation of soot by  $\text{NO}_x$ , with particular reference to  $\text{NO}_2$  (e.g. see the very comprehensive review by Stanmore et al. (2008) and references therein) under conditions relevant to after-treatment technologies. However, a significant interest still persists on the mechanisms and kinetics of the  $\text{NO}_2$ -assisted soot combustion. In particular, despite there is a general consensus on the fact that soot oxidation with  $\text{NO}_2$  is enhanced by the presence of  $\text{O}_2$ , different C- $\text{NO}_2$ - $\text{O}_2$  reaction mechanisms have been proposed so far and the specific role of  $\text{NO}_2$  and  $\text{O}_2$  in the accelerated combustion of soot is still debated. Jacquot et al. (2002) attributed the large increase in the soot oxidation rate, observed when  $\text{O}_2$  is added to the  $\text{NO}_2$ -feed gas, to the reaction between oxygen and the surface intermediates species resulting by the interaction between carbon and  $\text{NO}_2$ . Accordingly, Setiabudi et al. (2004), by correlating flow-reactor experiments with the DRIFT analysis of soot oxidation intermediates, proposed that soot oxidation is initiated by the  $\text{NO}_2$ -soot interaction that creates surface oxygen complexes which are more reactive to oxygen than pristine soot at temperatures where the oxidation with only  $\text{O}_2$  is not significant. In agreement with this hypothesis, Müller et al. (2012) found that initially highly functionalized types of soot are less susceptible to this effect. The C- $\text{NO}_2$ - $\text{O}_2$  oxidation mechanism has been also investigated by Jeguirim et al. (2004, 2005, 2007, 2009a) who suggested the occurrence of two distinct reactions: (i) a direct reaction between  $\text{NO}_2$  and the carbon surface; (ii) a cooperative reaction involving simultaneously  $\text{O}_2$  and  $\text{NO}_2$ . In the latter case,  $\text{NO}_2$  has been indicated to foster the decomposition surface oxygen complexes originated by  $\text{O}_2$ . More recently, Christensen et al. (2017) ascribed the increase of soot oxidation rate, observed in the

presence of  $\text{NO}_2$ , to the weaker O-NO bond in  $\text{NO}_2$  than the O-O bond in  $\text{O}_2$  and to the radical nature of  $\text{NO}_2$  which are expected to favor the oxygen transfer and thus soot combustion.

Based on these considerations the aim of the present work is to further investigate the soot oxidation by  $\text{NO}_2$  and  $\text{O}_2$ . For this purpose, isothermal combustion experiments were carried out at different temperatures and over a wide range of  $\text{NO}_2$  and  $\text{O}_2$  concentrations, both in the absence and in the presence of water, in order to determine the respective contribution to the combustion process in conditions close to automotive exhaust gas after-treatment.

Given that the type and structural characteristics of soot (e.g. elemental composition, surface area, particle size, degree of organization) can affect its oxidation behavior (Leistner et al., 2012; Pahalagedara et al., 2012; Sharma et al., 2012) a commercial soot (Printex U, Evonik-Degussa) was used as model soot, which is widely used as a surrogate for diesel soot laboratory experiments (Fino et al., 2016) and whose properties are well described in the literature (Atribak et al., 2010; Liu et al., 2010; Setiabudi et al., 2004).

## 2. Experimental

Isothermal temperature oxidation (ITO) experiments were used to evaluate the un-catalyzed soot (i.e. Printex U) oxidation characteristics. All reactivity tests were performed in a micro flow-reactor equipment consisting of a quartz tube reactor (7 mm I.D.) connected to a mass spectrometer (ThermoStar 200, Pfeiffer Vacuum) for on-line analysis of  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ; an UV-Analyzer (Limas 11 HV, ABB) for on-line analysis of NO and  $\text{NO}_2$  and a micro GC (Agilent 3000 A) for the on-line analysis of CO and  $\text{CO}_2$ .

The soot oxidation activity was investigated under diluted conditions in order to achieve nearly isothermal conditions thus limiting the temperature rise due to the exothermicity of the reaction. For this purpose in the tests 6 mg of soot (Printex U) were used, diluted with 100 mg of quartz powder. The reactor was inserted into an electric furnace driven by a PID temperature controller/programmer (Eurotherm 2408). The temperature of the sample was measured and controlled by a K-type thermocouple (outer diameter 0.5 mm) directly immersed in the quartz/soot bed. The total gas flow was always set at  $200 \text{ cm}^3/\text{min}$  (at  $0^\circ\text{C}$  and 1 atm).

Before the isothermal oxidation tests, the soot sample was conditioned under helium at  $500^\circ\text{C}$  (heating rate  $15^\circ\text{C}/\text{min}$ ). As suggested e.g. by Yezerets et al. (2005), this procedure removes weakly adsorbed species like adsorbed hydrocarbons (soluble organic fraction, SOF) which could affect the soot oxidation activity and hence the reproducibility of the experiments. Of note, limited mass loss was observed upon heating the soot, generally below 1–3% of the total mass. This is in line with the structure of Printex U mainly consisted of carbon framework with low fraction of volatile material (Atribak et al., 2010; Liu et al., 2010; Setiabudi et al., 2004). After this pre-treatment, the sample was cooled at the desired temperature (in the range  $250$ – $350^\circ\text{C}$ ) and the reactant gas mixture for the oxidation experiment was fed to the reactor.

In the standard run the temperature was set at  $300^\circ\text{C}$  and a flow of He +  $\text{O}_2$  (5% v/v) +  $\text{H}_2\text{O}$  (2% v/v) was fed to the reactor. Then, a rectangular step feed of  $\text{NO}_2$  (300 ppm) was admitted in the gas stream.

To investigate the influence of the individual gas components (i.e.  $\text{H}_2\text{O}$ ,  $\text{NO}_2$  and  $\text{O}_2$ ) on the soot oxidation, their concentrations have been varied while keeping constant the concentration of the other components. The total gas flow rate was kept constant by adjusting the He flow.

In each test, after oxidation of up to 80% of the initial soot carbon mass, the experiment was completed upon increasing the tem-

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