

Running headline: Cerium oxide-catalysed DPF regeneration.

Evidences of the cerium oxide-catalysed DPF regeneration in a real diesel engine exhaust.

M. Valencia¹, E. López¹, S. Andrade¹, Iris M. L.¹, N. Guillén Hurtado², V. Rico Pérez², A. García García², C. Salinas Martínez de Lecea², A. Bueno López^{2,*}.

¹ Galician Automotive Technology Center, Testing Labs. Pol. Industrial A Granxa P.O. 36400 Parcela 249-250. Porriño-Pontevedra (Spain).

² Inorganic Chemistry Department. University of Alicante. Ap. 99 E03080. Alicante (Spain)

*agus@ua.es

Abstract

The active phase $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_2$ has been loaded on commercial substrates (SiC DPF and cordierite honeycomb monolith) to perform DPF regeneration experiments in the exhaust of a diesel engine. Also, a powder sample has been prepared to carry out soot combustion experiments at laboratory. Experiments performed in the real diesel exhaust demonstrated the catalytic activity of the Ce-Pr mixed oxide for the combustion of soot, lowering the DPF regeneration temperature with regard to a counterpart catalyst-free DPF. The temperature for active regeneration of the $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_2$ -containing DPF when the soot content is low is in the range of 500-550 °C. When the $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_2$ -containing DPF is saturated with a high amount of soot, pressure drop and soot load at the filter reach equilibrium at around 360 °C under steady state engine operation due to passive regeneration. The uncoated DPF reached this equilibrium at around 440 °C. Comparing results at real exhaust with those at laboratory allow concluding that the $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_2$ -catalysed soot combustion in the real exhaust is not based on the NO_2 -assisted mechanism but is most likely occurring by the active oxygen-based mechanism.

Keywords: DPF regeneration; soot; ceria; doped-ceria; diesel engine contamination.

1.- Introduction

The commercially available CRT (Continuously Regenerating Trap) system is suitable for soot removal in diesel exhausts [1, 2]. This system consists of a DPF (Diesel Particulate Filter) located downstream a Pt-containing DOC (Diesel Oxidation Catalyst). Both CO and the unburned hydrocarbons are oxidised to CO₂ and H₂O in the DOC, where NO is also oxidised to NO₂. Soot particles are filtered in the DPF, where the NO₂-assisted combustion takes place. Intense research effort has been carried out during the last decade in order to replace Pt by cheaper active phases, cerium oxide being one of the most promising options [3-5]. Advances in the preparation of both pure and doped cerium oxides, including zirconium, praseodymium, lanthanum or yttrium, among other dopants in the parent oxide, have been reported for this application [3-8]. Until now, the most promising ceria-based formulations we have studied at laboratory scale are those with cerium and praseodymium, combining high activity with thermal stability. Scaling up this study to a real diesel exhaust is not obvious because the poor soot-catalyst contact in a real filter is not equal to that simulated in laboratory experiments. As far as we know, the ceria-catalysed regeneration of DPFs in real diesel exhausts has not been reported, this being the main goal of the current study.

2.- Materials and Methods

According to previous results [6], Ce_{0.5}Pr_{0.5}O₂ is the best ceria-based active phase for soot combustion. This mixed oxide has been prepared both as powder and supported on a commercial cordierite honeycomb monolith (by Corning; 400 cpsi; length 140 mm; diameter 144 mm) and on a commercial SiC DPF (by CTI; 300 cpi; length 254 mm; diameter 144 mm). The powder catalyst was prepared by air calcination at 500 °C of an intimate mixture of cerium and praseodymium nitrates. The mixed oxide was loaded both on the DPF and on the cordierite honeycomb monolith by impregnation

of the substrate with a water solution of the metal nitrates, which were decomposed by 500 °C air calcinations. The concentrations of the nitrate solutions were those required to achieve 0.7 and 10 w/w % loading of $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_2$ on the DPF and honeycomb monolith, respectively.

Engine test bench experiments were performed with the catalyst-containing honeycomb monolith and with two DPFs, with and without catalyst respectively, in the exhaust of a HDI turbo charged diesel engine 1.6 L, equipped with exhaust gas recirculation system (EGR) (maximum power 110 CV at 4000 rpm; maximum torque 240 Nm at 1750 rpm), running with commercial diesel fuel at different loading. The engine test bench used is from SCHENCK, model TITAN S190, with a STARS automation software platform (power: 190 kW; maximum torque: 600 Nm; maximum speed: 10000 rpm). Specific gas analysers (Horiba Mexa 7170D) were used for gas composition monitoring (CO and CO₂: non-dispersive infrared analysers (NDIR); NO/NO_x: chemi-luminescence detector (CLD); total hydrocarbons (THC): flame ionization detector (FID); O₂: magneto-pneumatic detector (MPD)) and the amount of solids in the gas stream was monitored with an opacimeter (AVL 415S; measurement principle: measurement of filter paper blackening). The pressure drop in the DPFs was monitored during the tests with two pressure indicators connected just before and after the filter.

Soot combustion experiments were also performed at laboratory with two gas mixtures (30000h⁻¹; 5% O₂/N₂ or 500 ppm NO_x/5% O₂/N₂) by heating a loose contact mixture of 20 mg soot (Printex U) + 80 mg powder catalyst from 25 to 750 °C at 10 °C/min. Fisher-Rosemount specific gas analysers were used for CO, CO₂, O₂, NO and NO₂ monitoring (Models BINOS 100, 1001 and 1004). The soot conversion was determined from CO and CO₂ evolved. Commercial model soot has been selected for

these experiments, instead of real soot collected in the exhaust pipe, because the non-homogeneity of real soot is a handicap to obtain reproducible combustion results at laboratory.

3.- Results and Discussion

First set of experiments consisted of measuring the emissions of the engine running at 2000 rpm with different dynamometer torques, and the results obtained are compiled in Figure 1a. The soot concentration decreases and the NO_x release increases by increasing the dynamometer torque from 80 to 172 N·m, while the opposite occurs above 172 N·m, where high CO emission is also detected. This behaviour is related to the air to fuel ratio used to reach each dynamometer torque (see Figure 1b). The dynamometer torque is increased from 80 to 172 N·m by feeding more air to the air-fuel mixture, and therefore the formation of oxidised species (NO_x) is progressively promoted, while high excess fuel is required to overcome 172 N·m (the engine was calibrated for optimum behaviour at 172 N·m / 2000 rpm), and therefore the formation of reduced species (soot and CO) is favoured.

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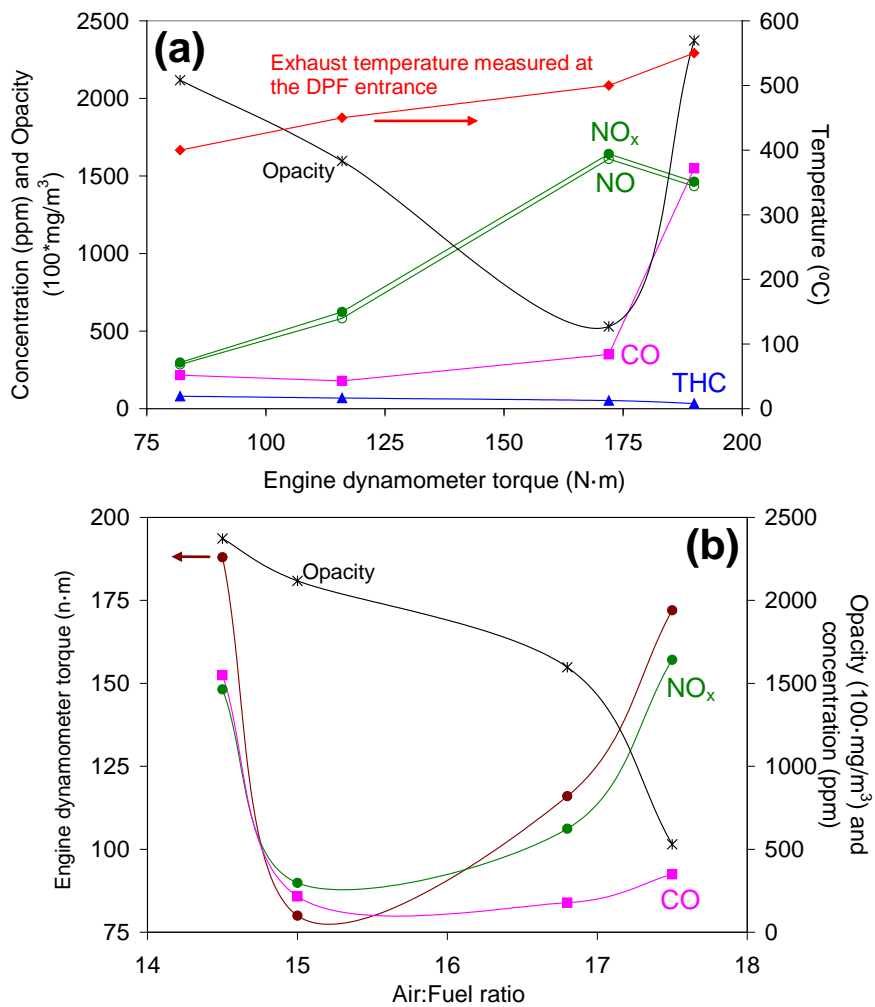


Figure 1. (a) Emissions for different dynamometer torque and (b) effect of the air to fuel ratio in pollutants production (engine running at 2000 rpm).

The exhaust temperature (Figure 1a) increased with the engine loading, as expected, and temperatures equal or lower than 550 $^{\circ}\text{C}$ were selected for further soot combustion experiments. This leads us to place the DPFs just at the entrance of the exhaust pipe (see Figure 2), fitted to the engine itself, otherwise the temperature is not high enough for soot combustion.



Figure 2. Picture of the DPF holder fitted to the diesel engine exit.

Experiments were performed in the engine test bench, with the engine running in several conditions, with the commercial DPF (without active phase) and with the as-prepared $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_2$ catalyst-containing DPF. Virtually complete soot removal was achieved in all experiments performed, both with the catalyst-free and catalyst-containing filter. On the contrary, CO and hydrocarbons were almost not

oxidised on the DPFs (conversion were always lower than 15%) and the oxidation of NO to NO_2 was null on both DPFs. Hence, the study was focused on the DPFs regeneration by soot combustion, and such regeneration is followed by measuring the pressure drop in the filters.

As shown in Figure 3, the pressure drop in the catalyst-containing filter was higher in most running conditions tested compared to the catalyst-free DPF, because the $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_2$ active phase partially blocks the SiC porosity. As a general trend, the pressure drop in the filters increased with time because the engine loading was progressively increased in consecutive steps. A detailed analysis shows a slight increase of the pressure drop for some particular running conditions, which is attributed to the accumulation of soot in the filters. Once the engine loading was high enough to reach $550\text{ }^\circ\text{C}$ in the gas stream (measured at the entrance of the DPFs), the pressure drop in the catalyst-containing DPF decreases with regard to the previous running conditions, while this did not occur in the catalyst-free DPF. This pressure drop decrease was attributed to the catalytic combustion of the soot collected in the filter, demonstrating that the $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_2$ catalyst promotes filter regeneration.

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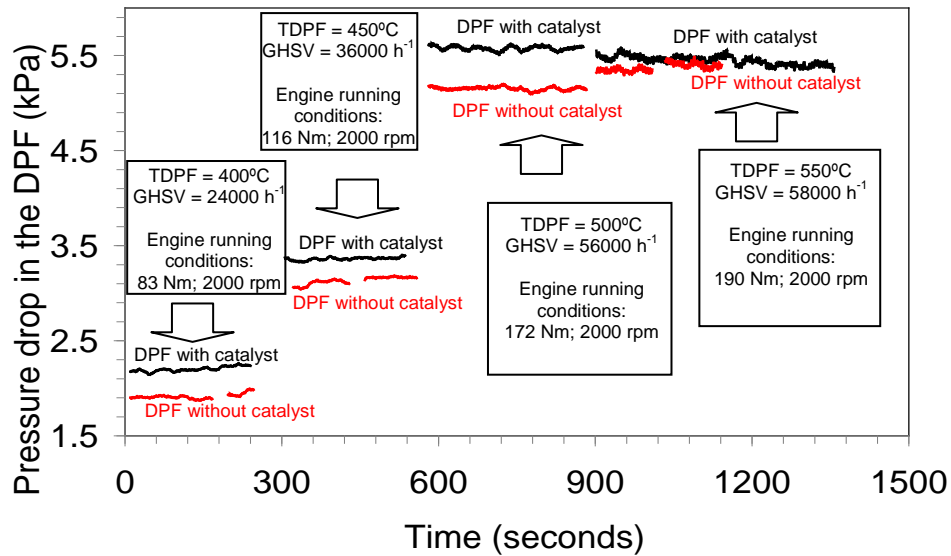


Figure 3. Pressure drop in two DPFs, loaded with $Ce_{0.5}Pr_{0.5}O_2$ catalyst and without active phase respectively, under different engine running conditions.

Additional soot combustion experiments were performed with the DPFs after collecting soot for 3 hours, with the engine running at idle conditions. After this time the dynamometer torque is progressively increased, while keeping the dynamometer rate at 1000 rpm, until the selected temperature of the exhaust gas is stable and the running conditions are maintained for few minutes before the dynamometer torque is raised to a higher loading. As observed in the Y axis of Figure 4, the pressure drop in the filters is roughly 10-20 times higher in these experiments than in those previously performed with the empty filters (see Figure 3), since a high amount of soot is already loaded on the filter at the beginning of the measurements of Figure 4.

The qualitative behaviour of both filters in the experiments of Figure 4 is similar. Below a certain temperature the pressure drop increases with time, due to the progressive accumulation of soot on an already loaded filter, while the pressure drop remains constant once the temperature is high enough to combust soot, that is, once the soot accumulation and combustion rates are equal. As deduced from Figure 4 the

temperature required to combust soot is lower in the catalyst-containing filter than in the catalyst-free one, supporting that the $Ce_{0.5}Pr_{0.5}O_2$ mixed oxide promotes regeneration. It was expected that ceria-based catalysts accelerate soot combustion because this has been observed at laboratory, but to our knowledge this is the first time it has been reported at real scale.

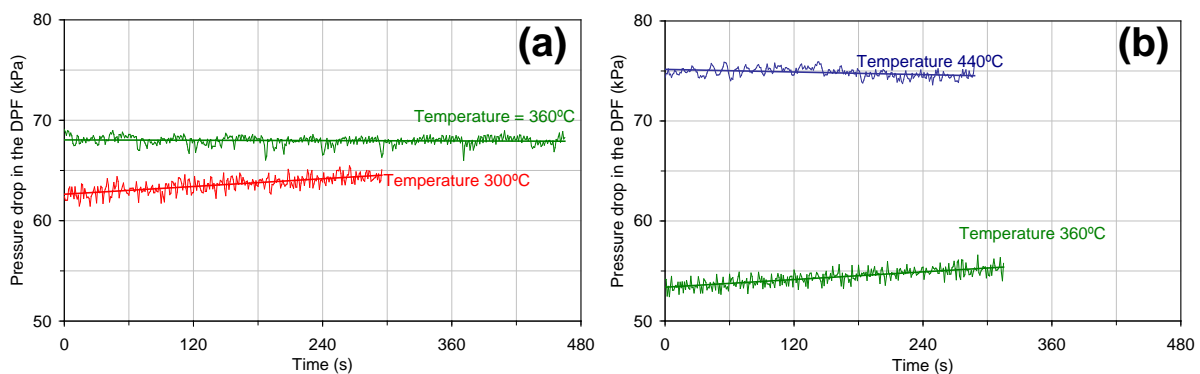


Figure 4. Pressure drop in the DPF (a) loaded with $Ce_{0.5}Pr_{0.5}O_2$ catalyst and (b) without active phase, in both cases after collecting soot for 3 hours with the engine running at idle conditions.

In order to analyse the soot combustion mechanism in the $Ce_{0.5}Pr_{0.5}O_2$ -containing DPF, a cordierite honeycomb monolith was loaded with $Ce_{0.5}Pr_{0.5}O_2$ and tested in the engine test bench. The aim of these experiments is to analyse if the $Ce_{0.5}Pr_{0.5}O_2$ mixed oxide is able to oxidise NO to NO_2 in the real diesel exhaust, and therefore, if the NO_2 -assisted soot combustion mechanism could occur. The potential catalytic oxidation of NO to NO_2 cannot be directly deduced from experiments performed with DPF filters because the NO_x -soot reactions affect the NO/ NO_2 ratio and would mask the potential catalytic NO_2 production.

The CO, THC, NO_x and soot removals achieved with the $Ce_{0.5}Pr_{0.5}O_2$ -loaded honeycomb monolith are plotted in Figure 5 together with the percentage of NO oxidised to NO_2 . All removal percentages are low (lower than 20 %) or null, and the

NO oxidation to NO₂ was also almost null (Figure 5). This is in contradiction to the general belief that ceria is able to oxidize NO to NO₂, because this is the behaviour observed in most laboratory experiments that have been published.

These experiments allowed concluding that the Ce_{0.5}Pr_{0.5}O₂-catalysed soot combustion in the real exhaust is not based on the NO₂-assisted mechanism [9] but is most likely occurring by the active oxygen-based mechanism [3].

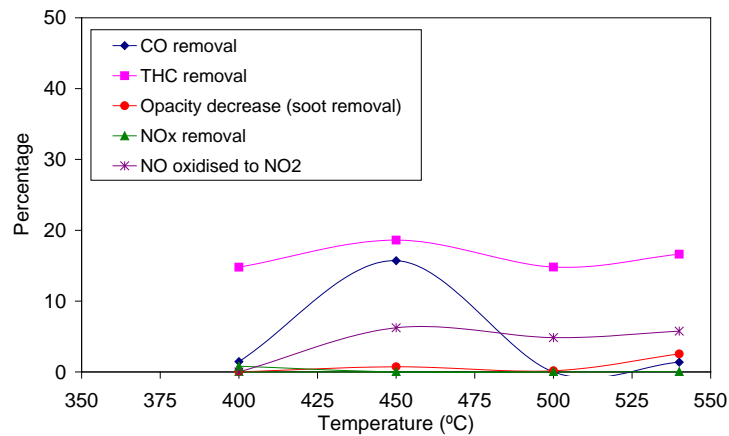


Figure 5. Performance of a Ce_{0.5}Pr_{0.5}O₂-loaded honeycomb monolith in the engine test bench (engine running conditions included in Figure 1).

The “active oxygen” soot combustion mechanism has been described to occur at laboratory scale with some metal oxide catalysts, like those of ceria, which are able to capture gas phase O₂ molecules and yield highly reactive oxygen species to soot [3]. This mechanism is usually assumed to have a minor contribution to soot combustion in real DPFs because it was expected that the loose contact between soot and catalyst particles hinder the active oxygen transfer. However, the current study suggests that the contact in a real DPF is good enough and/or the production of active oxygen by Ce_{0.5}Pr_{0.5}O₂ is high enough to allow the active oxygen mechanism to have a major relevance in real filters.

Finally, in order to identify the two potential soot combustion mechanisms (the NO_2 -assisted mechanism and the “active oxygen” mechanism) soot combustion experiments were performed at laboratory with the $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_2$ powder active phase. Figure 6a compiles soot combustion profiles obtained with two O_2 containing gas mixtures, with and without NO_x respectively, and Figure 6b shows the NO_2 production profiles in soot-free experiments performed with NO_x/O_2 .

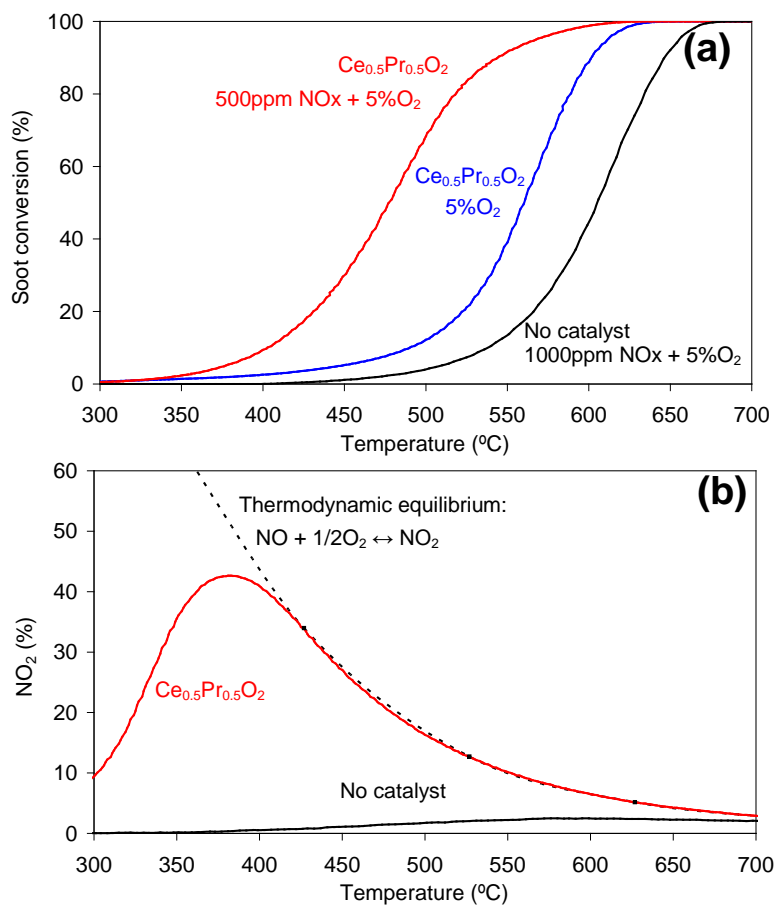


Figure 6. (a) Soot combustion and (b) NO_2 production in laboratory experiments.

Opposite to that observed in the engine test bench, the $\text{Ce}_{0.5}\text{Pr}_{0.5}\text{O}_2$ catalyst is able to oxidise NO to NO_2 at laboratory conditions, with maximum production at around 400 $^{\circ}\text{C}$. The inhibition of the catalytic oxidation of NO to NO_2 in the real diesel exhaust is tentatively attributed to the presence of inhibitors (mainly H_2O and/or CO_2). In correspondence with the NO_2 production, the catalytic combustion of soot takes

place at laboratory above 350 °C in the NO_x/O₂ gas mixture while it occurs at around 550 °C in the O₂-only gas stream (see Figure 6a), that is, the NO₂-assisted mechanism takes place in the experimental condition of the laboratory experiments. In the absence of NO₂, the active oxygen-based mechanism may occur and this temperature is consistent with that of DPF regeneration in the engine test bench experiments included in Figure 3. In conclusion, the Ce_{0.5}Pr_{0.5}O₂-containing DPF regeneration temperature, in the conditions of the experiments included in Figure 3, matches better with the soot combustion temperature at laboratory with O₂ rather than with NO_x/O₂ (note that Figure 4 experiments take place at high pressure, and therefore, the regeneration temperature decreases with regard to that of Figure 3).

4.- Conclusions.

The active phase Ce_{0.5}Pr_{0.5}O₂ has been loaded on a commercial SiC DPF, improving filter regeneration by catalysed soot combustion in experiments performed in a real diesel exhaust. The temperature for active regeneration of the Ce_{0.5}Pr_{0.5}O₂-containing DPF when the soot content is low is in the range of 500-550 °C. When the Ce_{0.5}Pr_{0.5}O₂-containing DPF is saturated with a high amount of soot, pressure drop and soot load at the filter reach equilibrium at around 360 °C under steady state engine operation due to passive regeneration. The uncoated DPF reached this equilibrium at around 440 °C. The Ce_{0.5}Pr_{0.5}O₂-catalysed soot combustion in the real exhaust is not based on the NO₂-assisted mechanism but is most likely occurring by the active oxygen-based mechanism.

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