

Behaviour of different soot combustion catalysts under NO_x/O₂.

Importance of the catalyst-soot contact.

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Abstract

Four different catalysts (Pt/Al₂O₃, Ce_{0.8}Zr_{0.2}O₂, PrO_{2-x} and SrTiCuO₃) have been investigated in a laboratory scale to evaluate its potential as diesel soot catalysts under different experimental conditions, which simulate the situation found in a Continuously Regeneration Technology trap (dual-bed configuration of catalyst and soot) or a Catalyst-Coated Filter system, (single-bed configuration, both catalyst and soot particles mixed under loose-contact mode). Under dual-bed configuration, the catalysts' behaviours towards soot combustion are very similar, despite of the differences observed in the NO₂ production profiles. However, under single-bed configuration, there are important differences in the soot combustion activities and in the NO₂ slip profiles. The configurations chosen have an enormous impact on CO/(CO+CO₂) ratios of combustion products as well. The most active catalyst under NO_x+O₂ is PrO_{2-x} combining high contribution of active oxygen-assisted soot combustion as well as high NO₂ production activity along the catalytic bed.

Keywords: Soot combustion; NO_x+O₂; Ce_{0.8}Zr_{0.2}O₂; PrO_{2-x}; SrTiCuO₃; Pt-catalyst.

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Introduction

Diesel engine emissions, particularly soot and NO_x, have gained considerable attention due to their health risk and environmental concern [1]. The different legislations dedicated to diesel particulate matter (denoted as PM and composed of aggregated carbonaceous soot and adsorbed hydrocarbons) emissions of vehicles (i.e. for passenger cars in Europe, 0.005 g of PM/km since 2009) [2] have led to the development of different aftertreatment technologies mainly based on the use of a filter (a wall-flow filter constituting a monolith of either silicon carbide or cordierite) [3, 4]. The accumulation of the diesel soot in the filter occurs due to the fact that the temperature of the filter is lower than that of the non-catalytic oxidation of the soot during different driving conditions. To limit the pressure drop in the exhaust line to an acceptable level, a periodic regeneration of the filter must be performed. The ignition temperature of the soot particles can be effectively lowered with the aid of catalysts which promote their combustion.

In this sense, the study of the catalysed combustion of soot can be approached from different perspectives according to the possible strategies implemented (or to be implemented in a near future) in the gas exhaust. One option is the regeneration of the soot collected in the DPF by using an oxidation catalyst located upstream (Continuously Regenerating Trap technology). This catalyst should exhibit a very high activity towards the NO oxidation to NO₂. Pt-containing catalysts are the most common systems, (which also function as a catalyst for CO and HC oxidation) even though other inorganic oxides are very effective as NO₂ producers as well and have been investigated in the last years [5,6]. Other options include the deposition of a catalytic coating onto the filter surface (denoted as CCF) which is a candidate for application in the near future [4, 7]. A crucial issue in this context is the contact between catalyst and soot which can be improved by the use of catalysts mobile under practical

conditions [8] or multifunctional catalysts, enabling both soot direct combustion (*via* contact points, i.e. “active oxygen” production and effective transfer to the soot surface) and indirect combustion (*via* NO₂ formation) on the coated filter. The ability of ceria-based mixed oxides to promote NO₂-assisted combustion and “active oxygen”-assisted soot combustion has already been reported [9]. The goal of this work is to compare the effectiveness of a ceria-zirconia mixed oxide, a pure praseodymium oxide, a Pt/Al₂O₃ catalyst and a SrTiCuO₃ perovskite as soot combustion catalysts under different experimental conditions which simulate the situation found in a CRT or a CCF system, respectively. The catalysts were selected based on their different activity for NO₂ formation.

Materials and methods

Catalyst preparation

Ce_{0.8}Zr_{0.2}O₂ mixed oxide was synthesised by the coprecipitation route [10]. The required amounts of ZrO(NO₃)₂·xH₂O (supplied by Aldrich, tech. grade) and (NH₄)₂Ce(NO₃)₆, (supplied by Panreac, 99.0% of purity) were dissolved in water and the hydroxides were precipitated by dropping an ammonia solution to keep the pH about 9 and subsequent filtering. After drying the precipitate at 110°C in air overnight, the powder was calcined in air for 1 h at 500°C. This straightforward method was also adopted to synthesise the praseodymium oxide (PrO_{2-x}) using Pr(NO₃)₃·6H₂O (supplied by Sigma Aldrich, 99.9%) as precursor and the same drying and calcination conditions.

The sol-gel method was employed to synthesise the perovskite by using citric acid, hydrogen peroxide, titanium (IV) isopropoxide, isopropyl alcohol (Ti precursor:citric acid

ratio of 1:2.5), followed by the addition of strontium nitrate and copper (II) nitrate trihydrated. The amounts of nitrate precursors used were those to obtain a mixed oxide with formulae $\text{SrTi}_{0.89}\text{Cu}_{0.11}\text{O}_3$. The detailed procedure is reported elsewhere [11]. Finally, a home-made Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyst (with nominal composition of 1%) was prepared by volume-excess impregnation of $\gamma\text{-Al}_2\text{O}_3$ (Alfa-Aesar, $88\text{m}^2/\text{g}$) with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ (Sigma-Aldrich, 99.995%) and calcination at 700°C in air for 5 h. The final Pt content of the catalyst was 0.5% determined by ICP-AES.

Catalyst characterisation.

The catalysts were characterized by N_2 physisorption at -196°C in an automatic volumetric system (Autosorb-6B from Quantachrome) after degassing the samples at 250°C for 4 h.

X-ray diffractograms were measured on a Seifert powder diffractometer using the $\text{CuK}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$). Diffractograms were recorded between 10° and 60° (2θ) with a step size of 0.05° and a time per step of 3 s.

XPS characterization was carried out in a VG-Microtech Multilab electron spectrometer using Mg-K α (1253.6 eV) radiation source. To obtain the XPS spectra, the pressure of the analysis chamber was maintained at 5×10^{-10} mbar. The binding energy (BE) scale was adjusted by setting the C1s transition at 284.6 eV.

The real platinum content on the Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyst was determined by extraction of the metal with aqua regia (IUPAC name nitric acid hydrochloride), using the aqua regia/catalyst ratio of 100/1 (w/w), and stirring this mixture for 48 h. at room temperature. After that, the mixture was carefully filtered using a nylon membrane filter (average pore diameter of 400 nm) to remove the alumina support. The resulting metal solution was diluted

using a volumetric flask and analysed by ICP-OES, in a Perkin Elmer Optima 4300DV system.

Catalytic activity tests.

Catalytic tests were carried out at atmospheric pressure in a cylindrical fixed-bed reactor coupled to specific NDIR-UV gas analysers for CO, CO₂, NO, NO₂ and O₂ monitoring (Fisher-Rosemount, models BINOS 1004, 100 and 1001), performing two different kinds of tests: soot combustion experiments and blank experiments without soot.

In soot combustion experiments a carbon black from Evonik Degussa S.A. (Printex-U) was used as model soot. The soot-catalyst mixture was heated (with 1:4 ratio of both components) from 25 to 750°C at 10°C/min in 500 ml/min flow of 500 ppm NO_x + 5% O₂/N₂ (GHSV ≈ 30000 h⁻¹). Two different soot-catalyst configurations were tested under this atmosphere: i) the dual-bed configuration consisted of a catalyst bed (80 mg of catalyst + 100 mg of SiC) located upstream the soot bed (20 mg of soot + 200 mg of SiC), being separated both particle beds by quartz-wool in an attempt to simulate the CRT situation, and ii) the single-bed configuration consisted of 80 mg of catalyst + 20 mg of soot + 300 mg of SiC mixed with a spatula following the so-called “loose contact” procedure [12], simulating the CCF situation. Under this single-bed configuration, additional soot combustion experiments were performed under 500 ml/min flow of 5% O₂/N₂ (without NO_x), to obtain complementary results.

Blank experiments (without soot), based also on temperature programmed reaction under 500 ml/min flow of 500 ppm NO_x + 5% O₂/N₂, were conducted with catalysts (80 mg of catalyst + 300 mg of SiC) to analyse their NO₂ production activity.

Results and discussion

Activity results.

Textural, structural and surface characterisation of the four catalysts studied in this work was reported in previous publications [9-11, 13]. A summary of some physico-chemical properties is compiled on Table 1. The average crystal size of the samples was also compiled with the exception of that of perovskite. The diffractogram corresponding to SrTiCuO₃ showed perovskite-like structure, with some segregation of TiO₂ (rutile) and SrCO₃ and full incorporation of copper within the mixed oxide framework. Comparison of nominal and real Sr/Ti and Sr/Cu surface atomic ratios, obtained from XPS, reported Sr-enrichment on the particle surface [11].

Ce_{0.8}Zr_{0.2}O₂ analysis confirmed good insertion of Zr into the ceria lattice with a value of the average lattice parameter, obtained from XRD, close to the theoretical value obtained from Vegard's law [10]. On the other hand, PrO_{2-x} showed asymmetric XRD peaks, suggesting the presence of more than one praseodymium oxide (PrO_{1.83} or Pr₆O₁₁ and PrO₂ as well).

The catalysts represent very different kind of catalytic systems, ranging from supported-noble metal to single oxide phase, or, even, mixed oxides and, therefore, it is expected that they exhibit different catalytic behaviours. Actually, these four catalysts were chosen according to their specificities and peculiarities for the reaction of NO oxidation to NO₂ -NO₂ generation under NO+O₂- due to the different mechanisms according to which the catalysts are active for this reaction. For this reason, they are able to produce high amounts of NO₂ in different ranges of temperatures.

The NO to NO₂ oxidation activity of the selected catalysts was evaluated in blank experiments and Figure 1a compiles the NO₂ profiles obtained in terms of temperature. It is

important to note that the uncatalysed NO oxidation reaction occurred at very low extent under the same experimental conditions (with only SiC in the reactor). The predicted NO₂ level considering the thermodynamic equilibrium of the NO oxidation reaction to NO₂ is also represented in Figure 1a as a dotted line, showing that this reaction is thermodynamically favoured at low temperature but not at high temperature.

The catalysts selected show very different profiles of NO oxidation to NO₂, according to their different mechanisms of performance, thus allowing us to analyse its implication on the soot combustion reaction. The maximum production of NO₂ was achieved with the oxide PrO_{2-x}, reaching 48% of NO₂ generation at 375°C. This solid presents a NO₂ production profile with two peaks, the first one at low temperatures (from 100°C to 250°C) and the second one at mild temperatures (from 250°C) in which the amount of NO₂ increases with temperature until the thermodynamic equilibrium is reached. This relevant ability of praseodymium-based oxides for NO₂ production was reported previously [14].

On the other hand, Pt/Al₂O₃ shows a lower maximum of NO₂ production than PrO_{2-x}, and displays a relevant production of NO₂ at low and mild temperatures.

The NO₂ production profile of Ce_{0.8}Zr_{0.2}O₂ mixed oxide takes place at mild temperature with a peak similar to the second peak shown by PrO_{2-x} but broader in shape.

Finally, the perovskite (SrTiCuO₃) produces NO₂ at mild and high temperatures (peak beyond the thermodynamic equilibrium). Note that this catalyst effectively stores nitrites/nitrates and most of NO₂ is not evolved up to the corresponding decomposition temperature is reached as will be explained below.

The different degree of interaction between the reactive gas mixture (NO_x+O₂) and the different oxides has been studied by blank experiments as well. The corresponding NO_x removal profiles are included in Figure 1b for PrO_{2-x}, Ce_{0.8}Zr_{0.2}O₂ and SrTiCuO₃ oxides. As commented above, SrTiCuO₃ is an excellent catalyst for NO_x storage/release, chemisorbing a

high amount of NO_x during the experiment (490 μmol NO_x retained/g_{catalyst} which eventually was reversibly released (530 μmol/g_{catalyst}) in a pronounced peak between 440 and 550°C (see Figure 1b). The species retained are nitrites/nitrates as reported in a previous publication [6] and most of them are released as NO₂ (even showing a peak beyond the curve of the thermodynamic equilibrium in Figure 1a).

The decomposition temperature range of the NO_x species stored on the perovskite is equal to that reported by Kustov et al. [15] for alumina-supported strontium nitrate. This fact joined to the relevant Sr-enrichment on the particles and the detection of SrCO₃ as a crystallographic phase by XRD reveals that formation-decomposition of SrNO₃-like species is taking place.

Lower amount of ad-NO_x species, compared with the perovskite, is being generated on PrO_{2-x}. There is a first step of NO_x removal at around 100°C, followed by desorption at 150°C. These ranges of temperatures are congruent with the NO₂ generation profile and could be explained by NO_x physical adsorption on the oxide followed by oxidation of ad-NO_x species at low temperatures and NO₂ desorption. This peak at low temperature, absent in the NO₂ production profile of Ce_{0.8}Zr_{0.2}O₂, could be ascribed to a loss of O₂ by heating the sample which reacts fastly with the ad-NO_x species yielding NO₂. Logan et al. [16] reported thermal desorption of O₂ (not observed on pure ceria samples) linked to praseodymium-containing samples. The higher the praseodymium content in the mixed oxides, the higher the released amount of oxygen detected.

The second peak could be assigned to more stable praseodymium-nitrite/nitrate species generation, which eventually decompose from 250°C (maximum value at 375°C). By comparing PrO_{2-x} and Ce_{0.8}Zr_{0.2}O₂, it can be suggested that less amount of ad-NO_x species and with higher stability are formed on ceria-zirconia, thus explaining the lower NO₂ desorption peak in Figure 1a.

Figure 2 depicts the soot combustion profiles using the selected catalysts under the two configurations studied. There are not significant differences among catalysts in the dual-bed configuration (represented by triangles in Figure 2). This situation would be that obtained by the direct effect of NO₂ production of the catalysts in a blank experiment (Figure 1a). It is deduced that even though the Pt-catalyst presents a superior activity to oxidise NO to NO₂, mainly at low temperatures, all the NO₂ produced cannot be effectively used to oxidise soot at these low temperatures (as it will be commented later, in the context of NO₂ slip under the different situations). The same comments could be valid for PrO_{2-x}, exhibiting NO₂ generation activity at very low and mild temperatures. Conversely, under the single-bed configuration, the soot conversion curves are importantly shifted towards lower temperature, suggesting that other reaction pathways are taken place due to the poor but allowed soot-catalyst contact. Besides, there are important differences in catalytic activity among the catalysts, and Ce_{0.8}Zr_{0.2}O₂ together with PrO_{2-x}, resulted to be the most active catalysts for soot combustion.

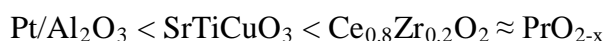
In an attempt to gain more insight into the reasons of these differences of performance, the soot combustion reactions were also conducted under 5% O₂/N₂ for the single-bed configuration, and the corresponding soot conversion profiles were plotted in Figure 3. The results obtained clarify the information compiled in Figure 2, since the Ce_{0.8}Zr_{0.2}O₂ mixed oxide exhibits a large capacity to oxidise soot under O₂, (due to its important ability to produce and transfer “active oxygen” to the soot surface) [9] as well as PrO_{2-x}, thus explaining their superior activity under NO_x/O₂. However, it is important to distinguish the two rare-earth oxides different behaviour. Meanwhile PrO_{2-x} is even more active than Ce_{0.8}Zr_{0.2}O₂ under NO_x/O₂ (single-bed configuration), it is similar under O₂.

Under O₂, PrO_{2-x} provides good response at low temperatures, probably because of the ease of reducibility of Pr⁴⁺ cations on surface compared with Ce⁴⁺, (even though the BET surface area is lower than that of Ce_{0.8}Zr_{0.2}O₂), and the higher proportion of reducible cations

(PrO_{2-x} is the pure oxide). However, at high temperature, the trend is the opposite. It could suggest that when bulk (or sub-surface) oxygen is involved the ceria-zirconia's behaviour is better.

It is worth mentioning the results reported by Sinev et al [17], who concluded that reduced Pr³⁺ cations were responsible for activation of oxygen on the surface, but Pr³⁺/Pr⁴⁺ and perhaps Ce³⁺/Ce⁴⁺ could participate in other processes, such as charge transfer in the bulk of the oxide.

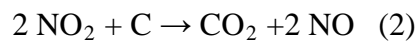
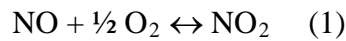
On the other hand, the perovskite presents lower catalytic activity for soot oxidation under O₂, but some activity is shown at high temperatures. Actually, it is known that oxygen vacancies can be created on this type of mixed oxide, mainly after proper doping with foreign cations [18-20] and re-filled with O₂-gas phase, contributing to facilitate oxidation reactions. The Cu-catalytic role in terms of oxidation reactions should also be taken into account. On the contrary, the Pt-catalyst is the least active for soot combustion under O₂ and its activity in NO_x/O₂ must be explained by its capacity to produce NO₂. Interestingly, at high temperatures the order in activity under NO_x/O₂ is the same than that under O₂, suggesting the relevance of the "active oxygen"-assisted soot combustion which seems to prevail with regard to the NO₂-assisted soot combustion.



However, the loose contact existing between Pt/Al₂O₃ and soot also promotes importantly the soot combustion process from 350°C under NO_x/O₂, accelerating the reaction with regard to the dual-bed configuration (Figure 2, in blue lines).

To investigate more deeply how NO₂ is specifically used for the soot combustion reaction in both configurations, Figure 4 represents the NO₂ slip percentage in terms of temperature for the two situations studied using Pt. For the sake of clarity, the Pt-catalyst will be discussed

first and separately. Even though under single-bed configuration soot combustion is seen accelerated for Pt-catalyst (with regard to dual-bed), more NO₂ slips. A reasonable explanation for that is the platinum's ability to recycle the NO molecules (arisen from the NO₂-soot reaction) again to NO₂, acting as a source of NO₂ along the catalytic bed, thus providing continuously NO₂ molecules at a temperature relevant to be used for soot combustion. NO can have a catalytic role, as well, according to this global scheme of reactions:



It is clear that the difference between the NO₂ produced in a blank experiment (1.82 mmol NO₂/g_{catalyst}) and the NO₂ slip in the soot-catalyst single-bed configuration (0.53 mmol/g_{catalyst}) is insufficient for soot combustion, therefore NO is used multiple times. This explains the significantly higher combustion rate for the single-bed configuration than that of the dual-bed configuration. Similar results were found by Setiabudi et al. at laboratory scale testing Pt-impregnated ceramic foam [21,22].

Considering the rest of the catalysts, the discussion involving the oxides was conducted jointly. Figure 5 represents the NO₂ slip during the soot combustion experiments under dual bed configuration using the perovskite, the ceria-zirconia and the praseodymia samples. Similarly to the profile monitored for Pt-catalyst, NO₂ does not slip from 450-550°C, indicating that all the compound emitted is being effectively used for soot combustion. It is interesting to comment the perovskite's curve, because this sample hardly emits NO₂, in other words, their amounts and ranges of temperatures for NO₂ generation indicate an optimal usage

in the case of a dual bed configuration, since this catalyst yields the same profile of soot conversion with regard to the other catalysts, but it is the solid producing less NO₂ slip.

It is observed that the lower the NO₂ amount generated during a blank experiment, the lower the amount of NO₂ slip. For the case of praseodymia, with a double-peak profile, it can be said that the low-temperature peak is not seen modified if Figure 1a is compared with Figure 5. Under these very low oxidation temperatures, NO₂ does not seem to interact with the model soot by creating Surface Oxygen Complexes (SOC). On the contrary, the second peak is seen diminished, as occurs for the rest of catalysts.

Figure 6 compiles the NO₂ slip profiles during the soot combustion experiments under single-bed configuration and, now, more NO₂ slips whatever the oxide considered; even though, the single-bed configuration promotes soot combustion in a higher extent than the dual-bed configuration does, the catalysts promote soot combustion with respect to the dual-bed configuration. For ceria-zirconia and perovskite a type of recycle reaction mode of NO-NO₂ seems to take place here, likely involving the ad-NO_x species created during the NO_x/O₂ reaction and/or affecting the formation/decomposition equilibriums. For pure praseodymia, the NO₂ slip amount monitored during soot combustion under single-bed configuration is the highest one, even higher than that of Pt-catalyst. This leads to understand the shift of PrO_{2-x}'s soot conversion curve compared with that obtained with ceria-zirconia. The very high praseodymia's capacity to produce NO₂ along the single-bed configuration (compared with ceria-zirconia), could be due, besides to a higher degree of NO_x interaction with corresponding formation of ad-NO_x species and subsequent oxidation, as seen on Figures 1a and 1b, to a lower thermostability of the corresponding praseodymium nitrites/nitrates created on surface compared with those of ceria-zirconia. From 350-525°C, PrO_{2-x} provides enough NO₂ amounts (compared to ceria-zirconia) thus accelerating the soot combustion reaction. From 525°C on, due to the $\text{NO} + 1/2\text{O}_2 \leftrightarrow \text{NO}_2$ equilibrium is shifted back, both curves overlap.

Conversely, both catalysts show similar behaviours (even slightly better for $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$) for soot combustion in the absence of NO_x , suggesting that when sub-surface/bulk oxygen is taking part in the catalytic process, the mixed oxide is preferred. In fact, Sinev et al [17] demonstrated that solid-gas oxygen transfer was faster for a Ce-Pr mixed oxide than for a pure praseodymia.

Impact on combustion product emission and mechanistic implications derived.

The impact of these configurations (dual-bed versus single-bed situation) on the emitted products (CO/CO_2) during soot combustion was also evaluated. Table 2 illustrates these estimations. The NO_2 amounts effectively used in soot combustion for the experiments under dual-bed configurations are compiled on Table 2 as well (column 3). They were estimated by subtracting the NO_2 emitted during the dual-bed experiment (column 2) from the NO_2 produced during a blank experiment (column 1). These calculated amounts are clearly insufficient to achieve the combustion of the Printex-U sample (theoretical amount of ≈ 19 mmol $\text{CO}_x/\text{g cat}$). Therefore, in general, the O_2 -soot combustion is also taking place in a large extent, with high selectivities to CO as reaction product compared to CO_2 (column 4).

For the case of the uncatalysed reaction, it can be considered that only O_2 -carbon reaction is occurring, since the activity of NO in carbon oxidation in the absence of NO_2 is low compared to that of O_2 [23,24]. The mechanism of soot oxidation is well-accepted as initiated by the formation of surface oxygen complexes (SOCs) acting as intermediates, according to Mul et al [25] and Tabor et al [26] and then leading to CO and CO_2 , which can be formed from either the thermal decomposition of SOCs or from the reaction of SOCs with oxygen. At our experimental conditions, significant soot oxidation only takes place at relatively high temperature ($>450^\circ\text{C}$), yielding a $\text{CO}/(\text{CO}+\text{CO}_2)$ % qualitatively high (64%).

By using the dual-bed configuration under NO_x/O_2 , the catalysts function only as NO_2 generators. The amounts of NO_2 produced by the four different catalysts enter the soot bed and then the NO_2/O_2 -soot reaction takes place. This situation can be considered as a non-catalytic reaction. Under these magnitudes of NO_2 production generated by the four catalysts, there are not significant differences in soot conversion profiles as shown on Figure 2. But interestingly, there are some discrepancies concerning the values of mmol NO_2 consumed/ $\text{g}_{\text{catalyst}}$ corresponding to the Pt-catalyst with regard to the rest of mixed oxides. This highest amount should be connected to the enhanced NO_2 production from low temperatures (150°C), which seems to produce more SOCs on soot surface which eventually will lead to a higher CO_2 production (which means lower $\text{CO}/(\text{CO}+\text{CO}_2)$ ratio) for Pt/ Al_2O_3 under dual-bed configuration. This is in agreement with previous results reported by Azambre et al. [27]. These authors found associative and dissociative chemisorption occurring around 200°C and yielding nitrogenated and oxygenated adsorbed intermediates because of NO_2 -soot reaction. Subsequent TPD analyses showed NO_2 , NO and CO_2 as main products detected, when enough intermediates' coverage was achieved [27]. Therefore, significant CO productions under our experimental conditions suggest relevant contribution of O_2 -combustion pathway, with the oxidation rate being controlled by the concentration of O_2 in the gas phase and its diffusion throughout the soot bed, in agreement with literature [28], thus yielding similar soot conversion curves. The level of NO_2 production seems to have more impact on the ratio of emitted product for the specific case of platinum.

Conversely, by using the single-bed configuration, soot particles are in loose-contact with the catalyst and there is random distribution of soot and catalyst particles along the catalytic bed. For Pt/ Al_2O_3 , the higher NO_2 -slip amount accompanied by a shift of the soot

conversion profile toward lower temperatures (with regard to the dual-bed configuration) as well as low activity under O_2 strongly suggest that NO released from NO_2 -soot reaction is easily recycled to NO_2 by the catalyst to accelerate the combustion process under these experimental conditions. Therefore, the recycle reaction of NO to NO_2 and the soot combustion under NO_2 (and O_2) are coupled. These findings are in close agreement with results reported in the literature [21,22, 28].

The utilisation of Pt under single-bed configuration has a large impact on the emitted combustion products, since no CO emissions were detected (both under NO_x+O_2 and O_2). This is due to effective CO to CO_2 oxidation catalysed by the platinum active sites distributed along the catalytic bed. Same results under laboratory scale were published by Setiabudi et al. [22].

Considering the rest of the catalysts, CO productions are considerably lower here compared to the dual-bed configuration but not zero as measured for Pt/ Al_2O_3 . A combination of reasons is operating here: i) lower reaction temperatures, which lead, in general to lower CO/ CO_x ratios, according to general thermodynamics in carbon oxidation reactions [29]; ii) potential catalysts' performance towards CO to CO_2 oxidation and iii) possible influence of active oxygen-assisted soot combustion.

It is important to point out that CO/(CO+ CO_2) ratios, for the rest of the catalysts, under single-bed configuration are strongly influenced by ad- CO_2 species creation (carbonation) favoured at high temperatures under NO_x+O_2 and O_2 . This was confirmed by imbalance of CO_x emission/ $g_{catalyst}$, (not yielding the theoretical amount expected by burning-off the soot amount). This was mainly observed for the ceria-zirconia sample (the lowest CO_2 emissions, compared with the rest of catalysts, quantified both under NO_x+O_2 and under O_2), but also in a lower extent for pure praseodymia and perovskite. Therefore, the real

CO/(CO+CO₂) ratios would be even lower for these catalysts but not zero as for the Pt-catalyst.

Conclusions

Based on our findings in the current study, the following conclusions can be summarised concerning the use of the four different catalysts selected (Pt/Al₂O₃, Ce_{0.8}Zr_{0.2}O₂, PrO_{2-x} and SrTiCuO₃) for the purpose of soot combustion under different configurations:

- The utilisation of these four catalysts under dual-bed configurations, in other words, as NO₂ generators, does not lead to significant differences in soot combustion under NO_x+O₂, despite of the differences shown by the catalysts in terms of ranges of temperatures and amounts of NO₂ production.

- Conversely, the poor but allowed contact achieved under loose-contact mode of soot and catalyst (single-bed configuration) always leads to decrease of soot combustion temperatures. All the catalysts produce higher amounts of NO₂ slip under single-bed configuration than under dual-bed configuration.

- Concerning the Pt catalyst, the improvement of the catalytic activity under loose-contact with regard to the dual-bed situation can be accounted for the influence of the NO-NO₂ recycle reaction, yielding an optimal utilisation of NO₂, thus providing this compound continuously along the catalytic bed. This explains that at low temperatures of combustion, Pt is the most active catalyst (together with PrO_{2-x}). On the contrary, Pt is the least active catalyst for soot combustion, (among those tested), under O₂ alone.

- The most active catalysts under O₂ are PrO_{2-x} and, (even slightly better), Ce_{0.8}Zr_{0.2}O₂, probing that they take part actively in the active oxygen-assisted soot combustion. However, the fact that PrO_{2-x} generates the largest amount of NO₂ slip under loose-contact, accounts for the best behaviour of praseodymia compared to ceria-zirconia for soot combustion under NO_x+O₂.

- Single-bed against dual bed-configuration has an enormous impact on the $\text{CO}/(\text{CO}+\text{CO}_2)$ ratio of combustion product, always leading to lower CO production. For the specific case of Pt, CO emissions under NO_x+O_2 and O_2 are always zero, due to the influence of the CO to CO_2 oxidation reaction catalysed by the platinum active sites distributed along the catalytic bed.

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List of Tables

Table 1. Data concerning the four catalysts used.

Sample	S_{BET} (m²/g)	Average crystal size* (nm)
Ce _{0.8} Zr _{0.2} O ₂	57	7
PrO _{2-x}	32	12
SrTiCuO ₃	6	---
1%Pt/Al ₂ O ₃	88	16

*SrTiCuO₃ exhibits phase segregation

Table 2. Data estimated from catalytic reactions under the different situations studied.

Situation	Blank experiment	Dual-bed (NO_x+O₂)	Dual-bed (NO_x+O₂)	Dual-bed (NO_x+O₂)	Single-bed (NO_x+O₂)	Single-bed (O₂)
Catalyst	mmol NO ₂ emitted/g catalyst	mmol NO ₂ emitted/g catalyst	mmol NO ₂ consumed/g catalyst	CO/(CO+CO ₂) (%)	CO/(CO+CO ₂) (%)	CO/(CO+CO ₂) (%)
Uncatalysed	--	--	--	64	64	60
Pt/Al ₂ O ₃	1.82	0.40	1.42	36	0	0
SrTiCuO ₃	0.78	0.10	0.68	57	4	2
Ce _{0.8} Zr _{0.2} O ₂	0.99	0.20	0.79	54	12	5
PrO _{2-x}	1.58	0.63	0.95	57	9	1

Figure captions

Fig. 1a. NO₂ production profiles during blank experiments for the catalysts selected (500 ppm NO/5%O₂/N₂; 500ml/min).

Fig. 1b. NO_x chemisorption profiles during blank experiments for the oxides-based catalysts (500 ppm NO/5%O₂/N₂; 500ml/min).

Fig. 2. Soot conversion curves obtained under different experimental conditions (500 ppm NO/5%O₂/N₂; 500ml/min); triangles: dual-bed configuration; solid lines: single-bed configuration.

Fig. 3. Soot conversion curves obtained under single-bed configuration (5%O₂/N₂; 500ml/min).

Fig. 4. NO₂ slip production, in soot combustion experiments under NO_x+O₂ (500 ppm NO/5%O₂/N₂; 500ml/min), obtained for the Pt-catalyst; triangles: dual-bed configuration; solid lines: single-bed configuration.

Fig. 5. NO₂ slip production, in soot combustion experiments under NO_x+O₂ (500 ppm NO/5%O₂/N₂; 500ml/min), obtained for the oxides-based catalysts under dual-bed configuration.

Fig. 6. NO₂ slip production, in soot combustion experiments under NO_x+O₂ (500 ppm NO/5%O₂/N₂; 500ml/min), obtained for the oxides-based catalysts under single-bed configuration.

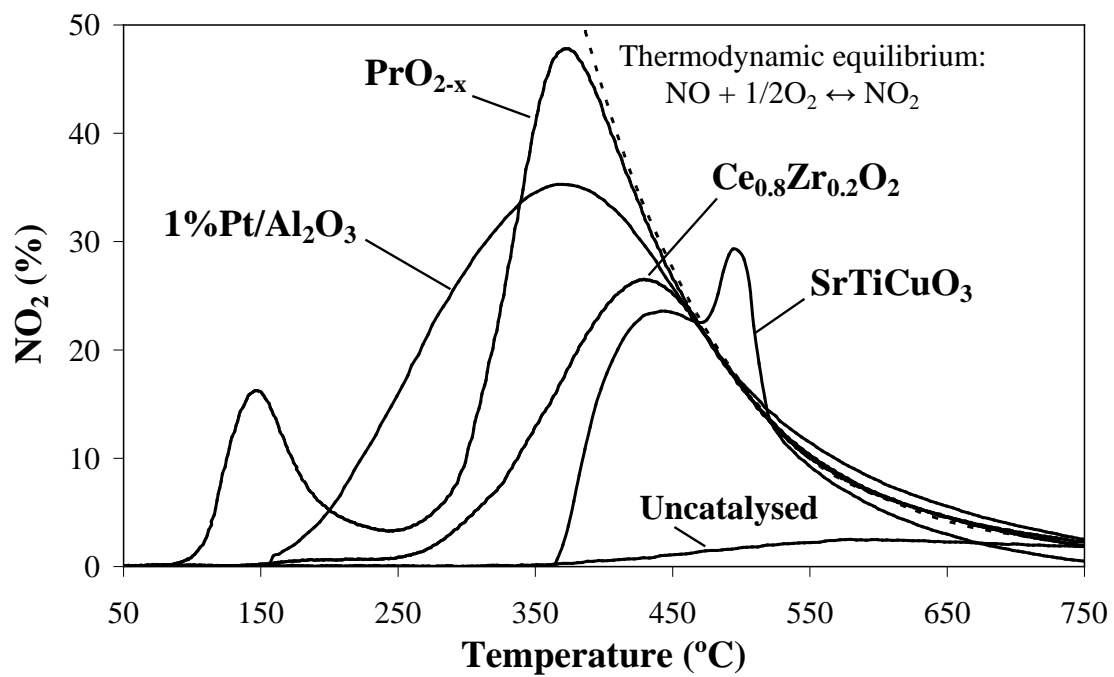


Figure 1.a.

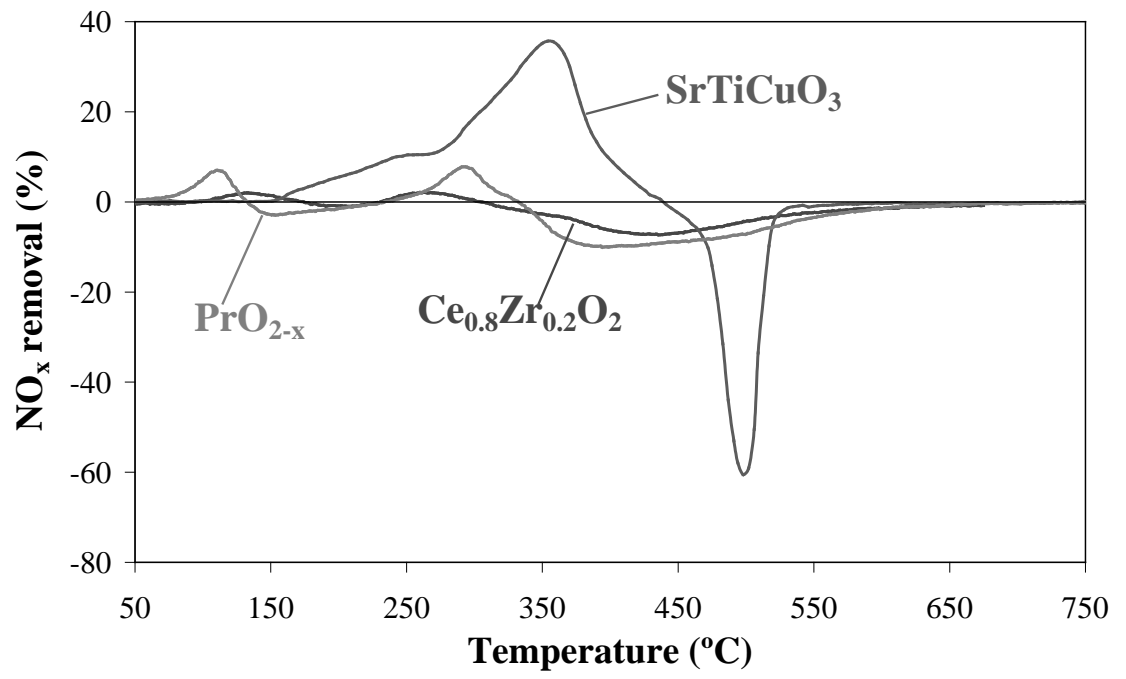


Figure 1.b.

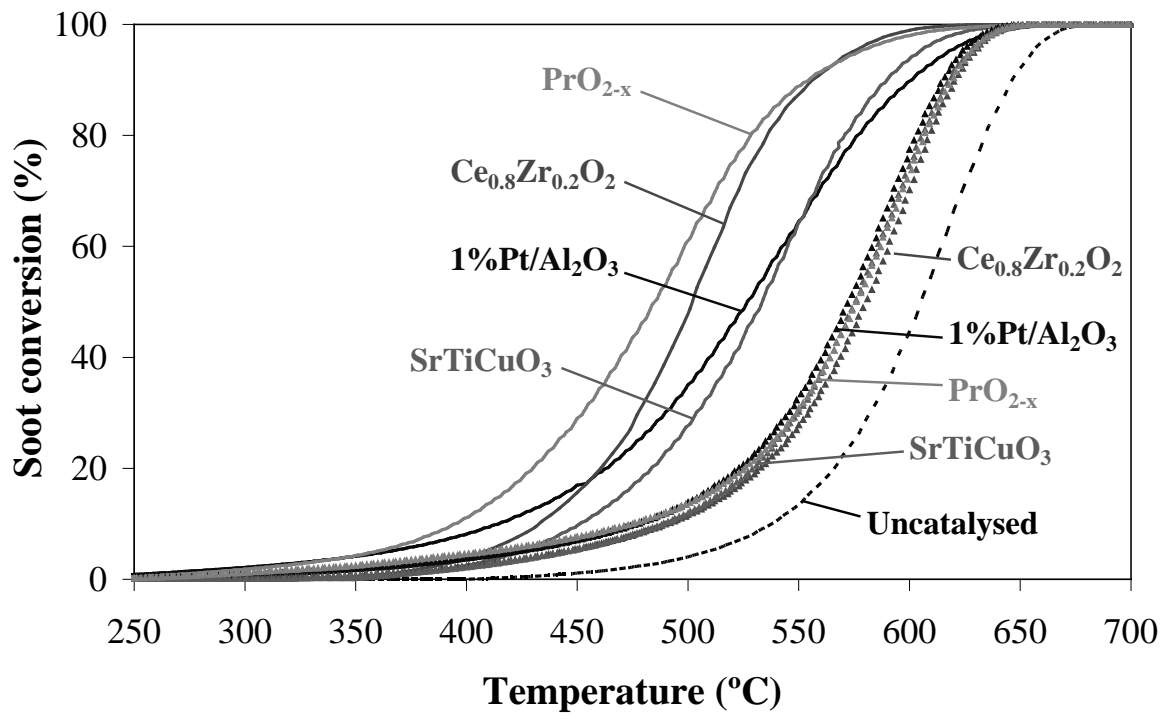


Figure 2.

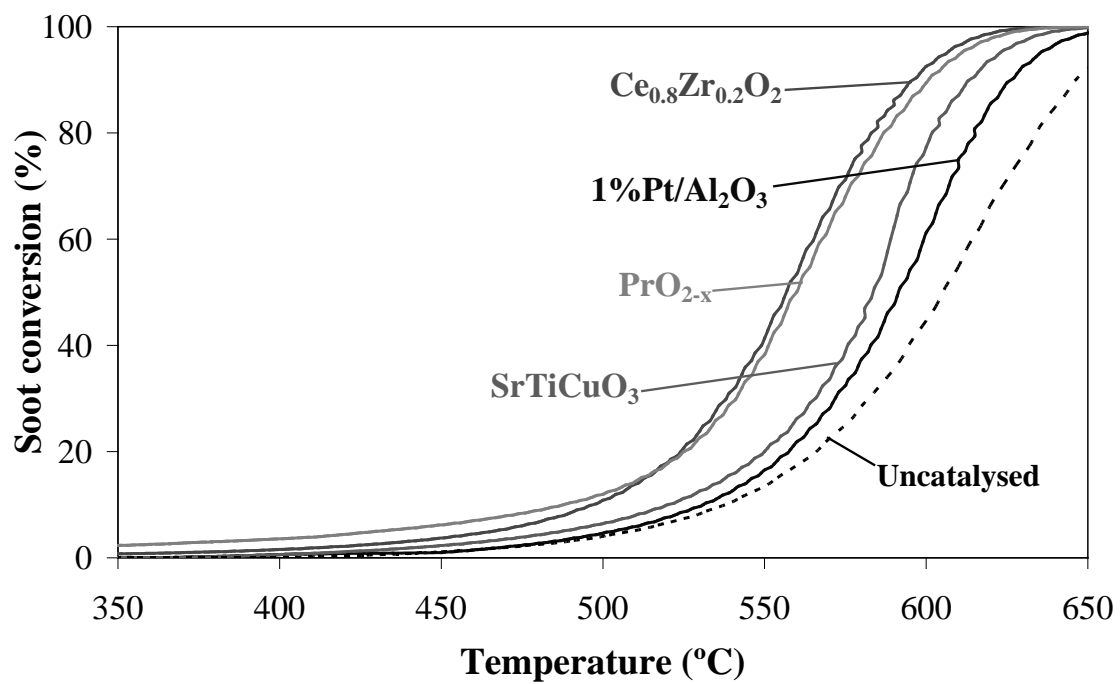


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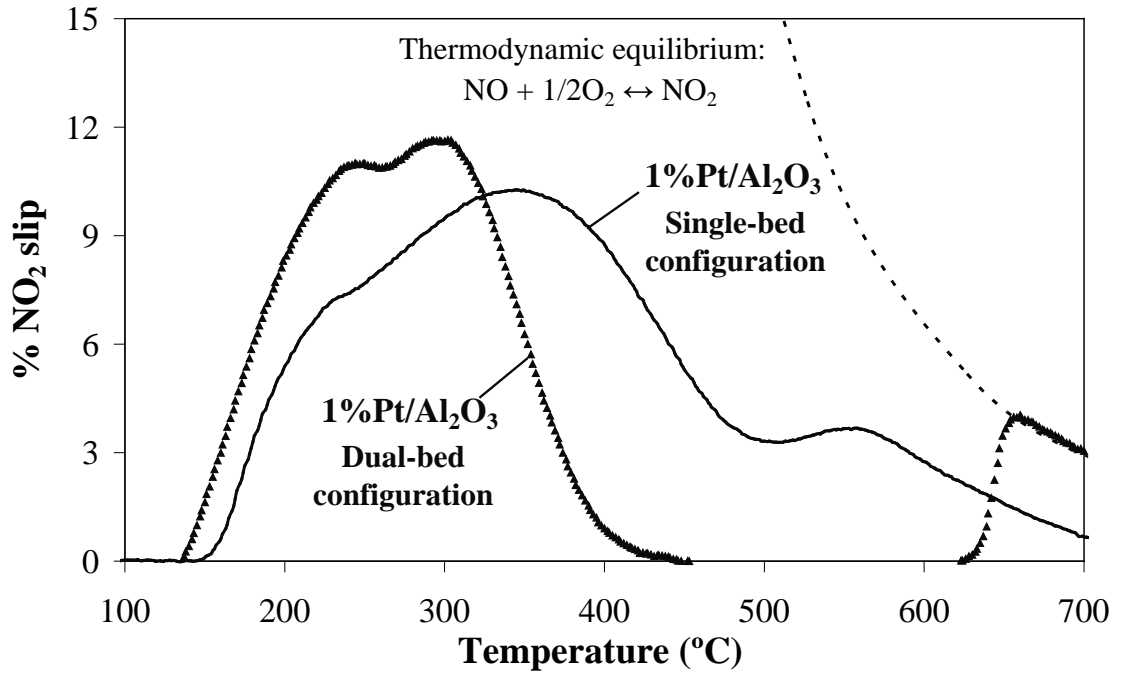


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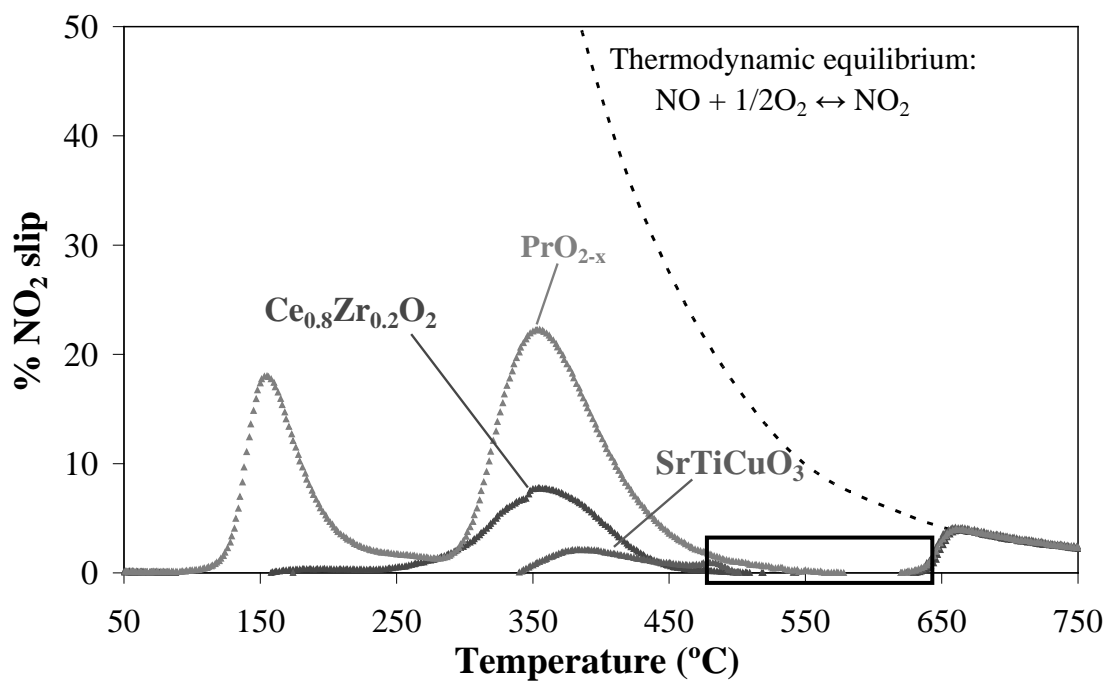


Figure 5.

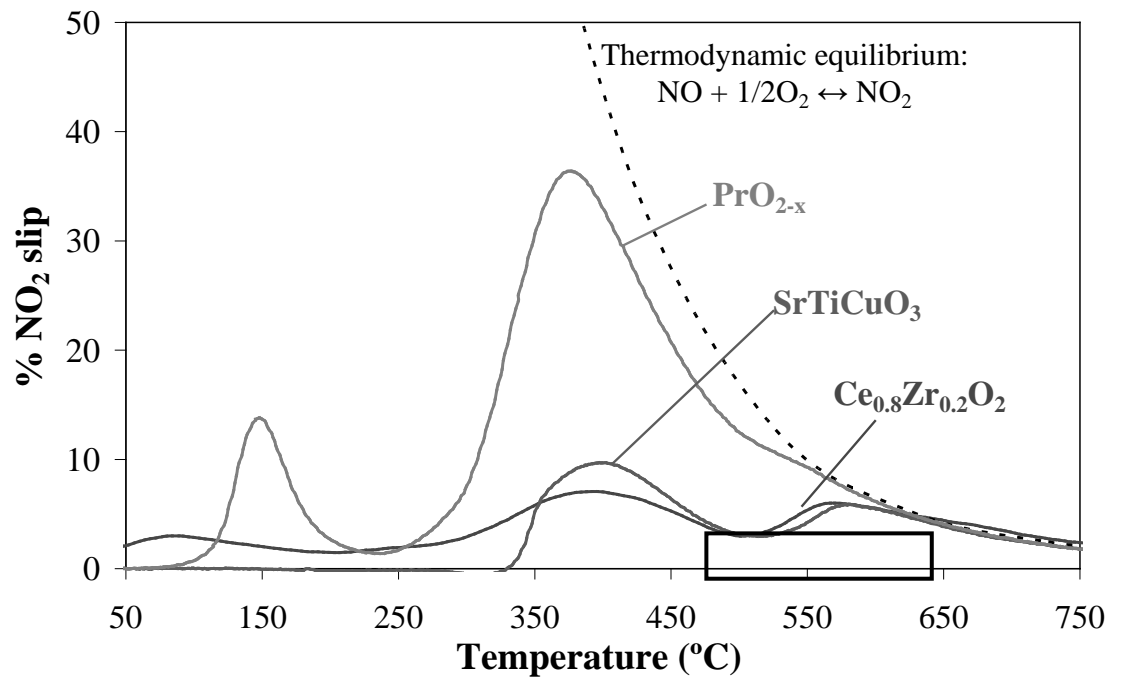


Figure 6.