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New insights into the performance of ceria–zirconia mixed oxides as soot combustion catalysts. Identification of the role of “active oxygen” production

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ABSTRACT

Soot combustion experiments with O_2 and with O_2 + NOx mixtures were performed with model and real soot samples and with a Pt-catalyst and several Ce–Zr catalysts. It was demonstrated that all the Ce–Zr catalysts tested are more effective for soot combustion (due to the important production of active oxygen), than the Pt-catalyst is, even though the noble metal yielded the highest NO_2 production level. A synergetic effect was observed between the NO_2-assisted and active oxygen-assisted soot combustion for the Ce–Zr catalysts studied. The contribution of the active oxygen generated by these mixed oxides to soot combustion, with regard to the NO_2-assisted combustion, becomes more important as soot combustion temperature increases (because of the decrease of soot reactivity). The properties of the Ce–Zr catalysts affect significantly their active oxygen production capacities.

1. Introduction

Diesel particulate filter (DPF) technology is in a state of optimisation and cost reduction and new catalyst formulations that oxidise soot at the catalyst–soot surface, thus promoting regeneration, are emerging. On the other hand, DPF technology is moving towards more passive and safe regeneration, and therefore, new future needs and challenges are imposing [1]. One of the current technologies, the so-called continuously regenerated trap (CRT), is based on the NO_2-assisted soot combustion, since NO_2 is much more oxidising than O_2 and NO. This reaction pathway solves the problem of poor contact between soot and catalyst. However, the successful CRT application demands sufficient NO_2 production capacity and an optimal usage of NO_2. The exhaust temperature has also to be high enough for the reaction to take place at the required rate [2–5].

One alternative option would consist of developing catalysts which produce highly reactive oxygen species from O_2 molecules [6]. This approach will become of special interest for the last generation diesel engines, since modern engine combustion modes hardly emit NOx, and therefore, the current NO_2-assisted CRT systems will not be so efficient. Among this kind of catalysts, some advances were pursued in CeO_2-based formulations during the last years [6,7], but unfortunately, the useful utilization of such active oxygen species seems to be also limited by the contact between soot and catalyst.

In order to make feasible the soot combustion process promoted by these active oxygen species, two challenges must be faced: i) to improve the physical contact between soot particles and catalyst, which is an issue difficult to achieve under loose contact mode (very similar to that contact existing in a real filter [8]) and ii) to produce an amount of active oxygen high enough to assure that, at least, a few proportion reaches the soot particles surface. The second challenge could be approached by raising the temperature, so leading to high temperature soot combustion strategies, which are being currently investigated [9,10], and using catalysts with high active oxygen production capacity such as very active Ce–Zr mixed oxides.

The goal of this study is to explore the potential of active oxygen generated by ceria–zirconia catalysts to accomplish soot combustion, and in particular, to identify the conditions under which this active oxygen-assisted mechanism contributes/prevails with regard to the NO_2-assisted combustion. In order to achieve this goal, soot combustion experiments with O_2 or with O_2 + NOx mixtures were performed with several models and real soot samples of very different reactivities. Different catalysts were compared, including ceria–zirconia mixed oxides with similar composition but very different BET surface area, bulk oxygen mobility and surface properties, that is, with very different active oxygen production capacity, and a Pt catalyst with high NO_2 production capacity.

2. Materials and methods

Catalytic tests with soot:catalyst mixtures of 1:4 weight ratio, under loose contact as defined by Neeft et al. [11], were performed in a thermobalance (TA Instruments, model SDT 2960). The temper-

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Table 1
Characterisation of the ceria–zirconia catalysts.

Catalyst	Nominal composition	BET surface area (m^2/g)	Ce/Zr surface atomic ratio	Oxygen mobility[a]
COP	$Ce_{0.76}Zr_{0.24}O_2$	67	5.0(3.2)[b]	Medium (two reduction peaks)
RME	$Ce_{0.76}Zr_{0.24}O_2$	128	1.2(3.2)	High (one reduction peak)
RH (commercial)	$Ce_{0.75}Zr_{0.25}O_2$	113	3.1(3.0)	High (one reduction peak)

[a] Obtained from H2-TPR experiments.
[b] Nominal ratio in parentheses.

ature was raised at 10 °C/min from room temperature until 800 °C in 100 ml/min flow of 5% O_2/He.

Catalytic tests were also performed with a NOx + O_2 mixture in a tubular reactor coupled to specific NDIR/UV gas analysers, using the same soot:catalyst ratio and also under loose contact mode. The temperature was increased from room temperature until 750 °C at 10 °C/min in 500 ml/min flow of 500 ppm NOx + 5% O_2/N_2 (GHSV of 30.000 h^{-1}). Details of this experimental setup were published elsewhere [4]. Blank experiments (without soot) were also carried out in order to analyse the NO_2 production capacity of the catalysts.

Three soot samples were tested in this study: a carbon black from Cabot (Vulcan XC-72R), a carbon black from Degussa (Printex-U), which is widely used in the literature as model diesel soot for laboratory experiments, and a diesel soot collected in a power bench after an oxidation catalyst placed in the exhaust of a 1.9 cm^3 diesel engine running at 2000 rpm. A complete physico-chemical characterisation of these soot samples was reported elsewhere [12].

Three different ceria–zirconia catalysts were selected for this study. Two home-made $Ce_{0.76}Zr_{0.24}O_2$ catalysts prepared by means of (i) a straightforward coprecipitation route and (ii) a reversed microemulsion method, which are referred to as COP and RME, respectively. A commercial catalyst from Rhodia ($Ce_{0.75}Zr_{0.25}O_2$) was also tested, which is denoted by RH. Some characterisation data of these mixed oxides are presented in Table 1. The details of the two synthesis routes employed and the whole information of the characterization procedures were conveniently explained elsewhere [13,14].

A home-made 1% Pt/γ-Al_2O_3 catalyst was also used, which was prepared by volume-excess impregnation of γ-Al_2O_3 (Alfa-Aesar, 88 m^2/g) with $[Pt(NH_3)_4](NO_3)_2$ (Sigma–Aldrich, 99.995%) and calcination at 700 °C.

3. Results and discussion

3.1. Catalytic soot combustion with O_2

Fig. 1(a)–(c) presents the soot conversion profiles for diesel soot, Printex-U and Vulcan XC-72R, respectively, mixed under loose contact mode with the Ce–Zr catalysts and combusted under 5% O_2/He, and for the counterpart uncatalysed reactions. From the uncatalysed reactions, it is deduced that the real diesel soot (Fig. 1(a)) is the most reactive soot sample, presenting a combustion onset temperature and a T50% temperature as low as 350 °C and 511 °C, respectively. The model soot Vulcan XC-72R is the least reactive one (Fig. 1(c)), the Printex-U reactivity (Fig. 1(b)) lying in between those of the real diesel soot and Vulcan XC-72R. A detailed analysis of the reactivity of these three soot samples is out of the scope of the current study, since a specific study was previously reported dealing with this particular aspect [12].

The effect of the Ce–Zr catalysts in the real diesel soot combustion (Fig. 1(a)) is negligible, in other words, the contribution of the active oxygen transfer (from catalyst to soot surface) to the soot combustion reaction is not substantial with regard to the O_2 direct attack (uncatalysed reaction). On the contrary, the Ce–Zr catalysts accelerate the Printex-U and Vulcan XC-72R combustion, in a different extent depending both on the catalyst and on the soot sample. The role of the Ce–Zr catalyst is more important as the soot reactivity decreases, and the differences among the soot conversion profiles obtained with Vulcan XC-72R are higher than those observed for Printex-U. These results indicate that the role of Ce–Zr active oxygen for soot combustion becomes more relevant as the soot combustion temperature increases.

In spite of the detailed analysis of the Ce–Zr catalysts reactivity is not the main aim of this study, it is interesting to pay certain attention to the different catalytic behaviour of the three Ce–Zr mixed

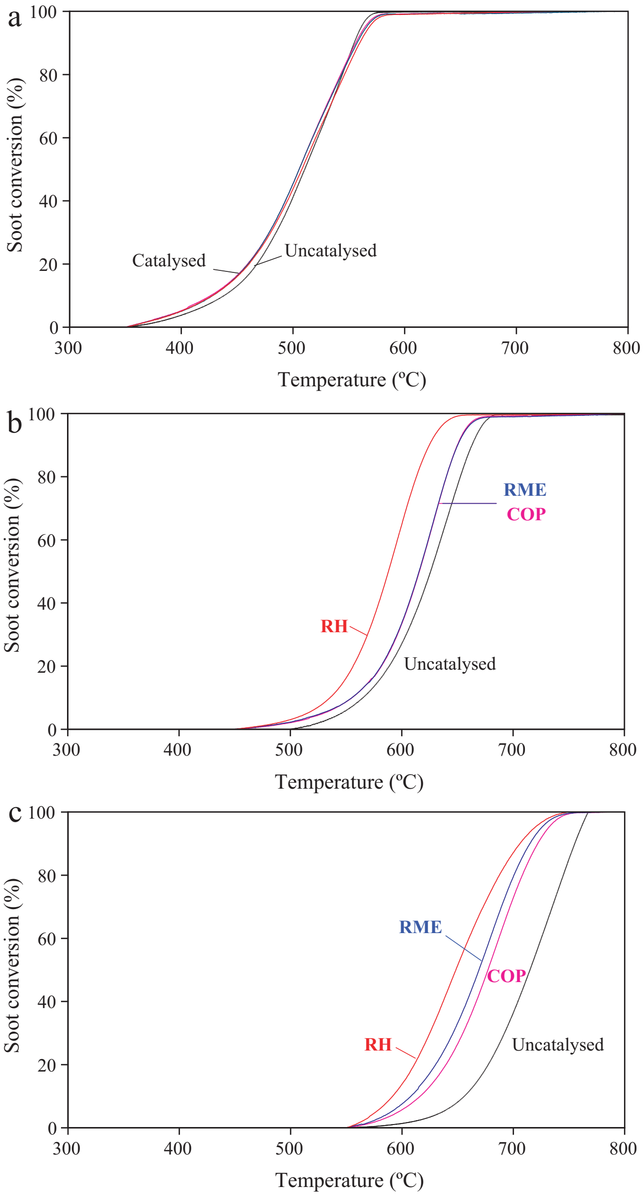

Fig. 1. Soot combustion by O_2 in TGA under loose-contact: (a) diesel soot, (b) Printex-U and (c) Vulcan XC-72 R.

oxides used, since this analysis will be useful to interpret properly further results. From Fig. 1(c), it is deduced that the catalytic activity of the Ce–Zr catalysts follows the order:

RH > RME > CO

This trend can be ascribed to the catalyts' ability to produce and transfer oxygen, under loose contact mode, to the soot particles, which is governed not only by the BET surface area of the catalyst but also by its chemical properties. For instance, the RME sample has a higher BET surface area than the RH sample (see Table 1) while the catalytic activity is opposite to this trend. Taking into account our previous background about the properties of the Ce–Zr materials selected for this study [13,14], the trend in activity could be tentatively ascribed to a best mobility of the lattice oxygen from both the surface and sub-surface layers, joined to a better exchange with gas phase-O_2 for Rhodia sample, because this commercial catalyst presents the most homogeneous atomic distribution among the three catalysts tested (see Table 1).

As a main conclusion of the soot combustion experiments with O_2, it can be underlined that the effect of Ce–Zr mixed oxides on soot combustion depends on their capacity for active oxygen production on the range of temperature where soot combustion takes place. This catalytic effect becomes more important as the soot intrinsic reactivity decreases.

3.2. *Catalytic soot combustion with NOx/O_2*

The role of active oxygen in the soot combustion under NOx + O_2 was also analysed. Under these experimental conditions two main catalytic pathways must be considered, namely, the catalytic oxidation of NO to the highly oxidising NO_2, which further reacts with soot, and the direct reaction between active oxygen species and soot, the only allowed catalytic pathway in the absence of NOx (see Section 3.1). Authors' previous publications reported the important role of the catalytic NO_2 production in soot combustion for catalysts of different chemical nature, such as a Cu/Al_2O_3 series [15], several perovskites [16] and ceria–zirconia mixed oxides calcined at different temperatures [17], among others. Generally speaking, these catalysts presented a very poor capacity to produce/deliver active oxygen under loose contact mode, and therefore, a linear relationship between NO_2 production and soot combustion was found because the NO_2-assisted combustion mechanism clearly prevailed.

In an attempt to separate the contribution of the active oxygen and the NO_2-assisted combustion, a 1% Pt/γ-Al_2O_3 catalyst was tested in the current study for soot combustion under NOx + O_2, in addition to the Ce–Zr catalysts, since Pt catalysts are very active for NO oxidation to NO_2 while this noble metal does not present catalytic activity to increase the rate of soot combustion under O_2 alone as reported by Setiabudi et al. [18].

First of all, the NO_2 production capacity of the different catalysts was evaluated in blank experiments, that is, without soot in the reactor, and Fig. 2 compiles the NO_2 profiles obtained. The Ce–Zr catalysts are less efficient as NO_2 producers than the noble metal catalyst is, as expected. Setiabudi et al. also found that platinum was much more active than ceria for NO oxidation to NO_2 [18].

The soot combustion profiles obtained under NOx/O_2 are plotted in Fig. 3. Even though the Pt catalyst generates a much higher amount of NO_2 (Fig. 2) than the Ce–Zr mixed oxides, this noble metal catalyst is less efficient for soot combustion compared with whatever ceria–zirconia catalyst selected for this study. In addition, a relationship between NO_2 production (Fig. 2) and soot combustion (Fig. 3) is not observed for the Ce–Zr catalysts. It has to be also mentioned that NO_2 slip occurred during all the Ce–Zr-catalysed soot combustion experiments, that is, the NO_2 availability does not limit soot combustion. All these experimental facts demonstrate that, in some cases, the NO_2-assisted soot combustion is not the main soot combustion pathway for the Ce–Zr catalysts selected in this study, but the active oxygen-promoted combustion contributes/prevails under some experimental situations. For

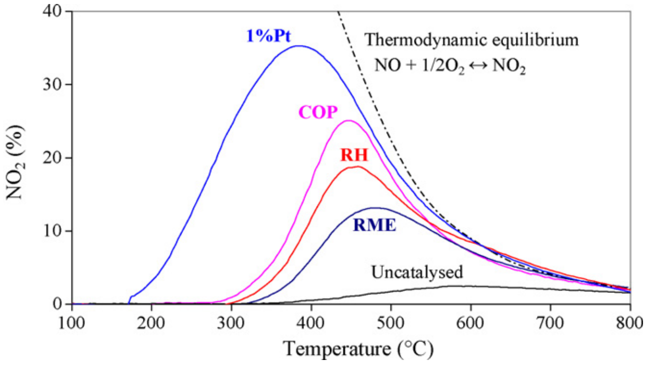

Fig. 2. NO_2 production profiles obtained in blank experiments (without soot).

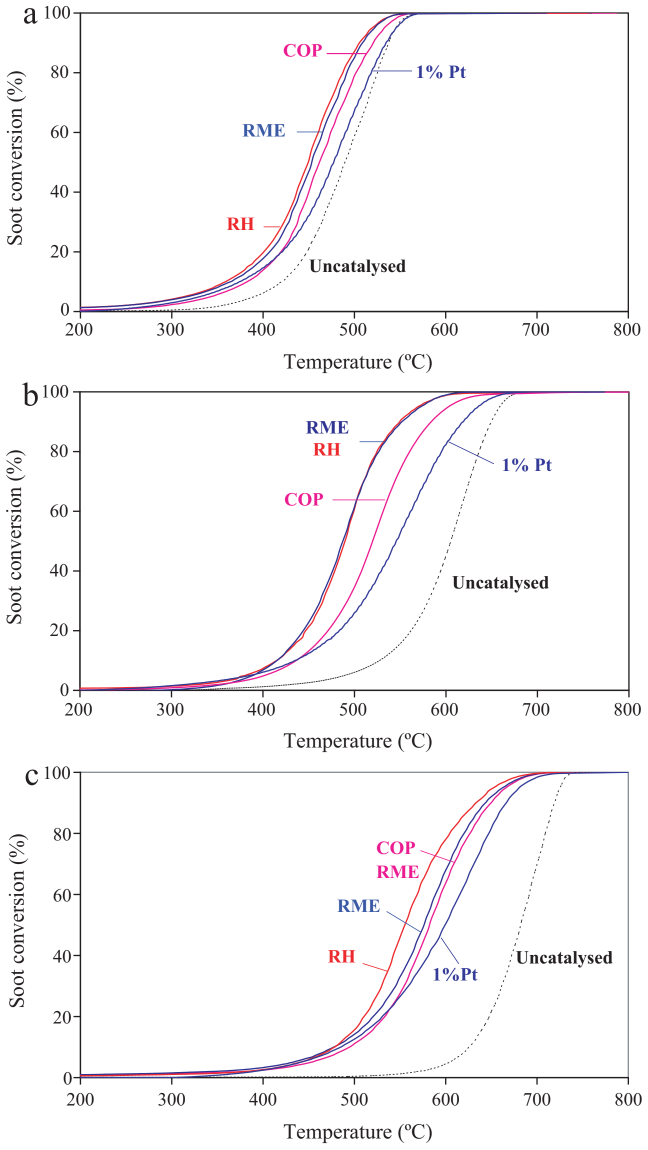

Fig. 3. Soot combustion by NOx + O_2, in the tubular reactor coupled to gas analysers under loose-contact: (a) diesel soot, (b) Printex-U and (c) Vulcan XC-72 R.

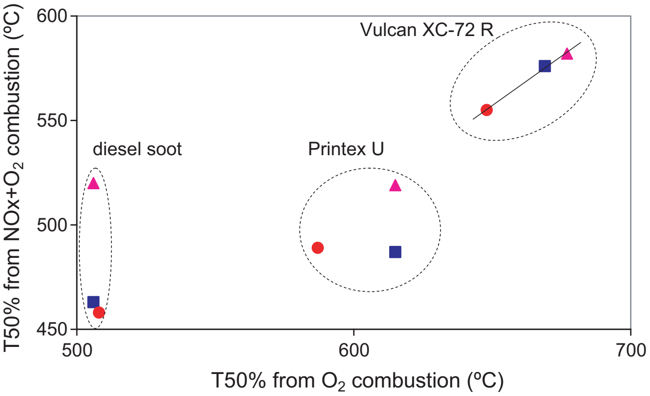

Fig. 4. Relationship between soot combustion under NOx + O_2 and under O_2 for Ce–Zr catalysed reactions (■ : RME; ● : RH; ▲ : COP).

this reason, some of the conclusions about the Ce–Zr performance during O_2 combustion (see Section 3.1) remain valid in the presence of NOx. Under NOx + O_2, the differences between the uncatalysed and the Ce–Zr catalysed reaction, and also the differences among Ce–Zr catalysts, become more important as the soot is less reactive. In other words, the participation of the active oxygen, even in the presence of NOx, is progressively more relevant as the soot combustion temperature increases.

It has to be remarked that the important contribution of the active oxygen mechanism to soot combustion for the Ce–Zr catalysts studied does not rule out, *a priori*, the contribution of some other mechanisms, mainly the NO_2-assisted combustion in combination with the uncatalysed O_2-combustion. In addition to active oxygen species, the NO_2 yielded by the catalysts will also react with soot, and the direct attack of O_2 molecules to the soot surface is also expected to occur once the soot surface is partially oxidised by NO_2. These synergisms were reported previously in carbon gasification studies [19,20].

In addition, synergisms among the different soot combustion mechanisms (catalytic pathways) are also expected. For instance, it is reasonable to think that the Ce–Zr mixed oxide's active oxygen is transferred not only to soot but also to NO (to yield NO_2) and, in the other way around, Setiabudi et al. [18] proposed that the formation of ceria's active oxygen is initiated by NO_2 in the gas phase, which was supported by the fact that active oxygen was desorbed from the ceria surface as a consequence of previous interaction with NO_2.

Taking into account all these premises and in order to analyse in more detail the contribution of the active oxygen mechanism to the ceria–zirconia-catalysed soot combustion under NOx + O_2, the T50% temperatures (required for 50% soot combustion in a particular experiment) obtained with NOx + O_2 were plotted (in Fig. 4) against the counterpart values obtained in O_2-combustion experiments. Clear differences for the three soot samples studied were observed.

For the least reactive soot sample (Vulcan-XC 72R), whose combustion proceeds in the highest range of temperatures, a linear correlation is obtained between the results obtained in the absence and presence of NOx. This relationship suggests the relevance of the ceria–zirconia's active oxygen-assisted combustion against other contributions. On the contrary, for the most reactive soot sample (diesel soot), the T50% values for NOx + O_2 experiments are independent on those obtained in the absence of NOx. In fact, no clear evidences of catalytic activity were noted under O_2 (see Fig. 1(a)). This indicates that the active oxygen mechanism does not clearly prevail for diesel soot, even though an interesting synergism between NO_2-assisted and active oxygen-assisted soot combustion is shown, which can be noted when Pt-catalysed soot combustion is compared with ceria–zirconia mixed oxides-catalysed soot combustion curves (Fig. 3(a)). Besides, the results depicted on this latter figure reflect that the well-known NO_2 + O_2 synergism is not the cause accounting for the trends, because if it was, Pt would be the most active catalyst for soot combustion under NOx + O_2.

Considering the trend exhibited for Printex-U, represented in Fig. 4, an intermediate situation can be seen with regard to Vulcan XC-72 R and diesel soot. There is not a linear correlation for this soot. The participation of different mechanisms (NO_2-assisted and active oxygen-assisted combustion) can be proposed. Taking into account that Pt/Al_2O_3 is the least active catalyst, also for this soot, the synergism among NO_2 + O_2 direct oxidation should also play a minor role.

Therefore, it can be concluded that the effect of the ceria–zirconia catalysts selected for this study, which present high active oxygen production capacity for soot combustion with NOx + O_2, is mainly twofold: (i) NO_2 production in an adequate range of temperature to initiate and/or continue the soot combustion reaction and (ii) high ability to produce and deliver active oxygen species to the soot surface in order to continue the soot combustion. This second aspect is interesting to combust low reactivity soots, as the next generation diesel's soot will be more graphitic in nature and more difficult to be oxidised, as suggested by some authors [21]. Besides, some Ce–Zr catalysts could be interesting for high temperature soot combustion in the case of low or free NOx exhausts, as they showed catalytic activity under O_2 alone. This aspect is novel since the feasibility to produce and transfer active oxygen from ceria–zirconia catalyst to soot surface, under the loose-contact mode, had not been previously demonstrated.

4. Conclusions

As a summary, the main conclusions of the current study are:

- Highly active oxygen species produced by Ce–Zr catalysts in the presence of O_2 can be transferred to the soot surface under the loose-contact mode, which is especially evident for low-reactivity soot samples whose combustion takes place at high temperatures.
- Contribution of active oxygen from Ce–Zr mixed oxides to soot combustion is relevant even in the presence of NOx.
- Contribution of active oxygen from Ce–Zr mixed oxides to soot combustion with regard to the NO_2-assisted mechanism, becomes more important as soot combustion temperature increases.
- All the Ce–Zr catalysts tested are more effective for soot combustion than a reference Pt-catalyst, due to the important contribution of the active oxygen-assisted mechanism.

A synergetic effect was observed between the NO_2-assisted and the active oxygen promoted soot combustion for the Ce–Zr catalysts studied.

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