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# Active oxygen from $CeO_2$ and its role in catalysed soot oxidation

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An advanced TAP reactor is used for the first time to study $CeO_2$ catalysed soot oxidation using labelled oxygen. In the absence of catalyst, oxidation takes place above 500 °C and mainly labelled oxidation species (CO and $CO_2$) were observed. In the presence of catalyst, it is shown that the gas-phase labelled oxygen replaces non-labelled lattice oxygen of $CeO_2$ creating highly active oxygen. This highly active non-labelled oxygen reacts with soot giving CO and $CO_2$. The creation of such active oxygen species starts from 400 °C and it will decrease the soot oxidation temperature. The rate of gas-phase oxygen exchange by the $CeO_2$ lattice oxygen and the rate of this very active lattice oxygen with soot are much faster than the reaction rate of $^{18}O_2$ reacting with soot directly. Similarly the rate of active oxygen reaction with soot is much faster than the rate of its combination giving gas-phase $O_2$.

**KEY WORDS:** active oxygen; ceria; oxidation; oxygen exchange; soot; temporal analysis of products.

## Introduction

The major problem during soot (small-size carbon particles) elimination in diesel engine exhaust gases is the too high onset temperature for soot combustion to create a spontaneous and self-propagating regeneration of the soot filters. Therefore, the development of appropriate catalyst to decrease this temperature is an issue of ongoing investigation of the automotive industry, catalyst manufacturers, and universities [1,2]. Despite $CeO_2$ and $CeO_2$-based solid solutions containing different rare-earth metals were thoroughly studied for three-way catalyst (TWC) application [3], only a few reports analyse the utilization of these materials for soot oxidation and its mechanism. Soot oxidation experiments carried out recently in our laboratory [4], however, pointed out that $CeO_2$ and $CeO_2$-based solid solutions have the potential to increase the soot oxidation rate by involving the participation of "active oxygen" and thereby lowering the on-set temperature of the soot oxidation.

In this communication, a more detailed role of $CeO_2$ in the soot–$O_2$ reaction that is studied in an advanced TAP reactor for the first time using labelled oxygen ($^{18}O_2$) is presented.

## Experimental

The $CeO_2$ catalyst was prepared by $Ce(NO_3)_3{\cdot}6H_2O$ (Aldrich, 99%) thermal decomposition in air at 1000 °C for 90 min. The BET surface area of the calcined catalyst is 3 $m^2/g$, Raman and XRD characterisation confirmed the typical Fluorite-type structure. The average $CeO_2$ crystallite size determined using the Scherrer equation is about 100 nm. The model soot used in this study is a carbon black from Degussa S.A. (Printex-U) whose characterisation was reported elsewhere [5].

The interactions between gas-phase $O_2$ and $CeO_2$ was studied at different temperatures between 200 and 600 °C in an advanced TAP-reactor system (described elsewhere [6]) using labelled and non-labelled oxygen. A small cylindrical reactor (7 mm i.d.) containing the catalyst is connected to an ultra-high vacuum system ($10^{-6}$ Pa). Small gas pulses, typically consisting of $\sim 10^{16}$ molecules of pure oxygen, were feed to the catalyst using high-speed gas pulsing valves. The reactor is coupled to three mass spectrometers that are able to measure the components of the gas leaving the reactor with a maximum sampling frequency of 1 MHz. In a separate experiment Ar gas was pulsed through the catalyst bed at different temperatures and it can be considered that it does not interact chemically with the catalyst. Ar response profile is reference for non-interacting gas. Comparison of the Ar and $O_2$ response will show the extent of the interaction. The oxygen pulse experiments were carried out with 100 mg of catalyst (around $10^{20}$ molecules of $CeO_2$) and this amount is much higher than the amount of gas pulsed. At least $10^4$ $O_2$ pulses are necessary to reach similar molecular amounts of catalyst. Therefore, it is assumed that the small number of labelled oxygen pulses used in studying its interaction at each temperature do not change the nature of the catalyst.

The first step of experiment consisted of stabilisation of the catalyst at 200 °C in vacuum by pulsing non-labelled $O_2$ until oxygen uptake by the catalyst was not observed any more. The steady state was reached within

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about 125 pulses. Subsequently, the temperature was increased to 300, 400, 500, and 600 °C and non-labelled $O_2$ was pulsed at each temperature. Above 200 °C, oxygen up-take was not observed after 25 pulses as the catalyst was already saturated. Once the above sequences of experiments were performed, temperature was decreased to 200 °C and stabilised and the same set of experiment were carried out using labelled $O_2$ ($^{18}O_2$).

Similar experiments described above were carried out with soot (10 mg) and soot (10 mg) mixed with $CeO_2$ (100 mg) catalyst in tight contact. In these experiments, only labelled $O_2$ was pulsed.

## Results and discussion

Figure 1 shows the responses of the different $O_2$ species evolved after injecting the pulses of labelled oxygen ($^{18}O$–$^{18}O$) to the $CeO_2$ catalyst. The responses shown in figure 1 were normalised at all the temperatures. The total amounts of oxygen obtained by integrating and adding the areas corresponding to the different oxygen species evolved are similar, indicating good mass balance of the system studied (95–100%). The Ar response profiles were superimposed for comparison.

The oxygen response profiles shown in figure 1 from 200–500 °C were similar to that of Ar response profiles. Only the oxygen response profile at 600 °C is somewhat different from that of Ar response profile. The shapes of the oxygen response profiles at different temperatures between 200–500 °C were also similar which demonstrate that there is no appreciable interaction between $^{18}O$–$^{18}O$ and $CeO_2$ in the above temperature range. However, at 600 °C; part of the pulse ($^{18}O$–$^{18}O$) was absorbed and non-labelled oxygen ($^{16}O$–$^{16}O$) and scrambled molecules ($^{16}O$–$^{18}O$) were evolved. The source of $^{16}O$ is the lattice oxygen atoms of $CeO_2$ and, therefore, this finding demonstrates that oxygen exchange between gas-phase molecular oxygen and the oxygen on the lattice occurred above 500 °C. He *et al.* [7] also observed oxygen exchange in solid solutions containing Zr, Y, and Ce in experiments performed in a flow microreactor.

The mass balance from figure 1 indicated that, at 600 °C, about 40% of the $^{18}O$–$^{18}O$ pulsed sticks on the catalyst and mainly $^{16}O$–$^{16}O$ is evolved. This $^{16}O$–$^{16}O$ has to be formed only by recombination of two oxygen atoms from the lattice. A small amount of scrambled $O_2$ (about 3%) is also observed. Though it is hardly seen in figure 1, the detailed analysis of responses at 500 °C pointed out that, about 5% of the labelled oxygen sticks on the catalyst and the corresponding amount of non-labelled $O_2$ is evolved.

It is important to mention that pulses of non-labelled $O_2$ (not shown) did not show difference between the shapes of peak profiles at all the temperatures studied including 600 °C. This means that the oxygen exchange occurs very fast and this exchange is only detectable using labelled $O_2$.

Figure 2 shows the profiles corresponding to the pulses of labelled $O_2$ to the soot–$CeO_2$ mixture. In these experiments, $O_2$, CO, and $CO_2$ were monitored. Table 1 summarises the monitored mass numbers and the corresponding species for these numbers. This table also compiles the percentage of each gas evolved at the respective temperature. Data corresponding to experiments performed with only soot, without any catalyst, is also included in the table 1.

In labelled $O_2$ pulse experiments performed with the soot–$CeO_2$ mixture at 200 and 300 °C, no oxidation products were detected, and shapes of the $O_2$ responses are similar to Ar response profile. 100% of labelled $O_2$ was measured at the reactor outlet, which also indicates that there was no soot oxidation at these temperatures. However, above 400 °C, part or all of the labelled $O_2$ pulsed to the soot–$CeO_2$ mixture was consumed and CO and $CO_2$ were detected as reaction products of soot oxidation. For example, at 600 °C, the $O_2$ pulsed was completely consumed and 27 and 73% of the gas evolved was CO and $CO_2$, respectively. As expected, the increase of temperature increased CO formation, still

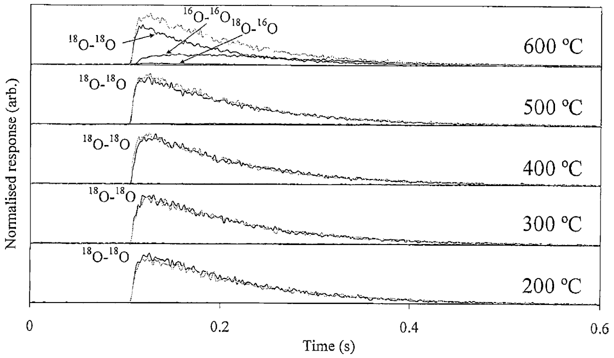

Figure 1. TAP experiments with $CeO_2$ and labelled $O_2$ pulses. (Grey lines: Ar reference; black lines: $O_2$ species).

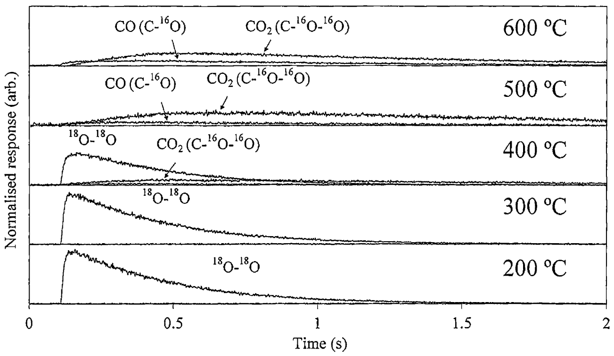

Figure 2. TAP experiments with soot mixed with $CeO_2$ and labelled $O_2$ pulses.

Table 1
Percentage of gasses evolved in TAP experiments with pulses of labelled oxygen

| Mass | Species | Soot | | | | | Soot + $CeO_2$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Catalyst temperature (°C) | | | | | | | | | |
| | | 200 | 300 | 400 | 500 | 600 | 200 | 300 | 400 | 500 | 600 |
| 48 | $CO_2(C\text{–}^{18}O\text{–}^{18}O)$ | – | – | – | 1 | 4 | – | – | – | – | – |
| 46 | $CO_2(C\text{–}^{16}O\text{–}^{18}O)$ | – | – | – | 2 | 5 | – | – | – | – | – |
| 44 | $CO_2(C\text{–}^{16}O\text{–}^{16}O)$ | – | – | – | 1 | 2 | – | – | 32 | 85 | 73 |
| 36 | $O_2(^{18}O\text{–}^{18}O)$ | 100 | 100 | 100 | 89 | 71 | 100 | 10 | 63 | – | – |
| 34 | $O_2(^{16}O\text{–}^{18}O)$ | – | – | – | – | – | – | – | – | – | – |
| 32 | $O_2(^{16}O\text{–}^{16}O)$ | – | – | – | – | – | – | – | – | – | – |
| 30 | $CO(C\text{–}^{18}O)$ | – | – | – | 2 | 13 | – | – | – | – | – |
| 28 | $CO(C\text{–}^{16}O)$ | – | – | – | 5 | 5 | – | – | 5 | 15 | 27 |

"–" not evolved

$CO_2$ being the main carbon-containing product. Note that both CO and $CO_2$ contained non-labelled oxygen. This indicates that the labelled $O_2$ pulsed sticks on the catalyst and the non-labelled oxygen on the lattice reacts with soot. It seems that the catalyst is acting as a pump, which provides its lattice oxygen to the soot when labelled $O_2$ is pulsed.

The non-catalysed soot and labelled $O_2$ reaction showed different behaviour. Data in table 1 indicate that there is no reaction below 400 °C, and at 500 and 600 °C, part of the labelled $O_2$ is consumed. CO and $CO_2$ evolved at both temperatures. CO and $CO_2$ containing non-labelled oxygen have to be attributed to surface oxygen complexes on the carbon before reaction. However, $^{18}O$-containing CO and $CO_2$ evolve from the reaction of soot with labelled $O_2$.

All the above results indicate that the $CeO_2$ performance in the soot–$O_2$ reaction is related to the well-known oxygen storage capacity of this material. $CeO_2$ lattice oxygen oxidises soot and the gas-phase $O_2$ fills the vacant sites created by the soot–$CeO_2$ reaction. This indicates that a redox cycle is taking place during the soot oxidation process. Considering the formation of $CO_2$ as main product of soot oxidation, the mechanism could be described as follows:

$$nCe^{16}O_2 + C \rightarrow nCe^{16}O_{2-2/n} + C^{16}O_2 \qquad (1)$$

$$nCe^{16}O_{2-2/n} + {}^{18}O_2 \rightarrow nCe^{16}O_{2-2/n}{}^{18}O_{2/n} \qquad (2)$$

In the first step (equation 1), soot (C) is oxidised by lattice oxygen, and in the next step (equation 2), gas-phase $O_2$ is chemisorbed on the catalyst. According to the well-known behaviour of $CeO_2$ in TWC [3,6] it is expected that the labelled oxygen stick on vacant sites, generally defects related to the presence of $Ce^{3+}$ atoms of the $CeO_2$ lattice. This chemisorption induces the formation of new highly reactive "active oxygen" species that comes from the lattice and not from gas-phase molecules. In the absence of reductants (like carbon in this study or CO and hydrocarbons in TWC), these highly reactive species are recombined and evolves again as $O_2$, as it can be deduced from the figure 1. In the presence of soot, however, the highly reactive oxygen atoms generated by the catalyst will not recombine to yield $O_2$, but reacts with soot to give CO and $CO_2$. The selectivities of different species indicate that the rate of $^{18}O_2$ exchange with $CeO_2$ and the creation of active oxygen is much faster than the rate of $^{18}O_2$ reacting with soot directly. Similarly the rate of active oxygen reaction with soot should be much faster than the rate of its combination giving gas-phase $O_2$.

The above finding opens up a new route for the development of soot oxidation catalysts based on "active oxygen" species and future work should be focussed on the generation and feasible utilisation of highly reactive "active oxygen".

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