

Active oxygen from CeO₂ and its role in catalysed soot oxidation

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Received 15 September 2004; accepted 7 October 2004

An advanced TAP reactor is used for the first time to study CeO₂ catalysed soot oxidation using labelled oxygen. In the absence of catalyst, oxidation takes place above 500 °C and mainly labelled oxidation species (CO and CO₂) were observed. In the presence of catalyst, it is shown that the gas-phase labelled oxygen replaces non-labelled lattice oxygen of CeO₂ creating highly active oxygen. This highly active non-labelled oxygen reacts with soot giving CO and CO₂. 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 CeO₂ lattice oxygen and the rate of this very active lattice oxygen with soot are much faster than the reaction rate of ¹⁸O₂ 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 O₂.

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 CeO₂ and CeO₂-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 CeO₂ and CeO₂-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 CeO₂ in the soot–O₂ reaction that is studied in an advanced TAP reactor for the first time using labelled oxygen (¹⁸O₂) is presented.

Experimental

The CeO₂ catalyst was prepared by Ce(NO₃)₃·6H₂O (Aldrich, 99%) thermal decomposition in air at 1000 °C for 90 min. The BET surface area of the calcined catalyst is 3 m²/g, Raman and XRD characterisation confirmed

the typical Fluorite-type structure. The average CeO₂ 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 O₂ and CeO₂ 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 ~10¹⁶ 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 O₂ response will show the extent of the interaction. The oxygen pulse experiments were carried out with 100 mg of catalyst (around 10²⁰ molecules of CeO₂) and this amount is much higher than the amount of gas pulsed. At least 10⁴ O₂ 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 O₂ 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 O₂ 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 O₂ (¹⁸O₂).

Similar experiments described above were carried out with soot (10 mg) and soot (10 mg) mixed with CeO₂ (100 mg) catalyst in tight contact. In these experiments, only labelled O₂ was pulsed.

Results and discussion

Figure 1 shows the responses of the different O₂ species evolved after injecting the pulses of labelled oxygen (¹⁸O–¹⁸O) to the CeO₂ 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 ¹⁸O–¹⁸O and CeO₂ in the above temperature range. However, at 600 °C; part of the pulse (¹⁸O–¹⁸O) was absorbed and non-labelled oxygen (¹⁶O–¹⁶O) and scrambled molecules (¹⁶O–¹⁸O) were evolved. The source of ¹⁶O is the lattice oxygen atoms of CeO₂ 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 ¹⁸O–¹⁸O pulsed sticks on the catalyst and mainly ¹⁶O–¹⁶O is evolved. This ¹⁶O–¹⁶O has to be formed only by recombination of two oxygen atoms from the lattice. A small amount of scrambled O₂ (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 O₂ is evolved.

It is important to mention that pulses of non-labelled O₂ (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 O₂.

Figure 2 shows the profiles corresponding to the pulses of labelled O₂ to the soot–CeO₂ mixture. In these experiments, O₂, CO, and CO₂ 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 O₂ pulse experiments performed with the soot–CeO₂ mixture at 200 and 300 °C, no oxidation products were detected, and shapes of the O₂ responses are similar to Ar response profile. 100% of labelled O₂ 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 O₂ pulsed to the soot–CeO₂ mixture was consumed and CO and CO₂ were detected as reaction products of soot oxidation. For example, at 600 °C, the O₂ pulsed was completely consumed and 27 and 73% of the gas evolved was CO and CO₂, respectively. As expected, the increase of temperature increased CO formation, still

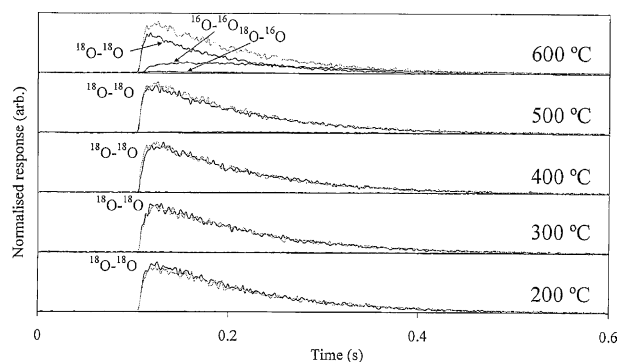


Figure 1. TAP experiments with CeO₂ and labelled O₂ pulses. (Grey lines: Ar reference; black lines: O₂ species).

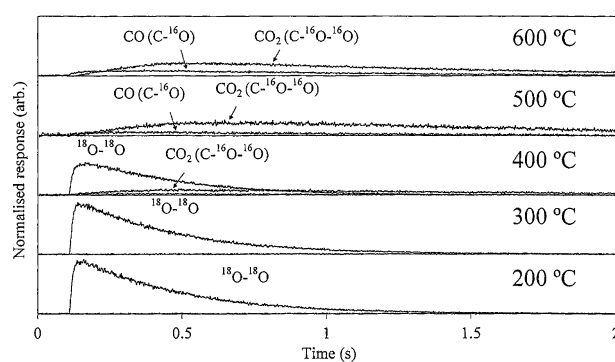


Figure 2. TAP experiments with soot mixed with CeO₂ and labelled O₂ pulses.

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

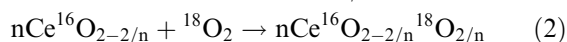
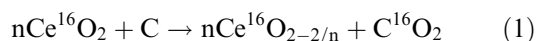
Mass	Species	Soot					Soot + CeO ₂				
		Catalyst temperature (°C)									
		200	300	400	500	600	200	300	400	500	600
48	CO ₂ (C- ¹⁸ O- ¹⁸ O)	–	–	–	1	4	–	–	–	–	–
46	CO ₂ (C- ¹⁶ O- ¹⁸ O)	–	–	–	2	5	–	–	–	–	–
44	CO ₂ (C- ¹⁶ O- ¹⁶ O)	–	–	–	1	2	–	–	32	85	73
36	O ₂ (¹⁸ O- ¹⁸ O)	100	100	100	89	71	100	10	63	–	–
34	O ₂ (¹⁶ O- ¹⁸ O)	–	–	–	–	–	–	–	–	–	–
32	O ₂ (¹⁶ O- ¹⁶ O)	–	–	–	–	–	–	–	–	–	–
30	CO(C- ¹⁸ O)	–	–	–	2	13	–	–	–	–	–
28	CO(C- ¹⁶ O)	–	–	–	5	5	–	–	5	15	27

“–” not evolved

CO₂ being the main carbon-containing product. Note that both CO and CO₂ contained non-labelled oxygen. This indicates that the labelled O₂ 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 O₂ is pulsed.

The non-catalysed soot and labelled O₂ 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 O₂ is consumed. CO and CO₂ evolved at both temperatures. CO and CO₂ containing non-labelled oxygen have to be attributed to surface oxygen complexes on the carbon before reaction. However, ¹⁸O-containing CO and CO₂ evolve from the reaction of soot with labelled O₂.

All the above results indicate that the CeO₂ performance in the soot–O₂ reaction is related to the well-known oxygen storage capacity of this material. CeO₂ lattice oxygen oxidises soot and the gas-phase O₂ fills the vacant sites created by the soot–CeO₂ reaction. This indicates that a redox cycle is taking place during the soot oxidation process. Considering the formation of CO₂ as main product of soot oxidation, the mechanism could be described as follows:



In the first step (equation 1), soot (C) is oxidised by lattice oxygen, and in the next step (equation 2), gas-phase O₂ is chemisorbed on the catalyst. According to the well-known behaviour of CeO₂ in TWC [3,6] it is expected that the labelled oxygen stick on vacant sites, generally defects related to the presence of Ce³⁺ atoms of the CeO₂ 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 O₂, 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 O₂, but reacts with soot to give CO and CO₂. The selectivities of different species indicate that the rate of ¹⁸O₂ exchange with CeO₂ and the creation of active oxygen is much faster than the rate of ¹⁸O₂ 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 O₂.

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”.

Acknowledgments

The authors want to thank the Spanish MEC for the fellowship to ABL and Engelhard Corporation for their financial support.

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