

Oxygen buffering capacity of mixed cerium terbium oxide: a new material with potential applications in three-way catalysts

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A new method to compare the oxygen buffering capacity (OBC) of catalysts shows that Ce–Tb mixed oxide presents an exceptional capability for attenuating fast oscillations of oxygen partial pressure.

Ceria has been for years one of the components of catalytic automobile exhaust converters (TWC). The capacity and the rate of response to buffer the oscillations of the oxygen partial pressure in the waste gases are recognised among its key properties.¹ However, improvements in such features are currently demanded for designing better catalytic cartridges for cleaner cars.^{2,3}

The present paper reports on a simple technique to compare the oxygen buffering capacity (OBC) of catalysts. We illustrate the working principle of this new method with results given by four samples: CeO₂, Rh (3 mass%)/CeO₂, Rh (3 mass%)/SiO₂, and a Ce–Tb mixed oxide (20 mol% Tb), hereafter referred to as CT-80/20.

The results reported here show that the performance of CT-80/20 is much better than that of the other studied systems. We highlight the overlying properties of CT-80/20 in the following conditions: (a) at low temperature, with the catalyst starting to work effectively from 473 K, (b) over a very broad range, including temperatures higher than 873 K, (c) in the absence of noble metal, CT-80/20 being superior to the two Rh-containing tested catalysts, and (d) following severe ageing and sintering treatments. The new method described herein was useful to reveal and discriminate the advantages of CT-80/20, giving in a single test valuable information both of the capacity and rate of response of the samples as oxygen buffers.

The ceria and silica supports were high surface area samples, with 100 and 180 m² g⁻¹ BET surface area, respectively. Rhodium was dispersed in both cases by conventional impregnation from aqueous nitrate solutions. The metal dispersion obtained in both cases by HREM is higher than 70%. The Ce–Tb mixed oxide was prepared by precipitation with ammonia from a solution of the nitrates. The terbium-modified ceria was obtained by calcination at 873 K, showing fluorite-like structure and a BET surface area of 45 m² g⁻¹. The pretreatment for CeO₂ and CT-80/20 samples consisted of oxidation at 873 K in a flow of O₂(5%)–He, followed by slow cooling to 293 K. The rhodium-containing samples were first reduced in hydrogen at 623 K, flowed with helium from 623 up to 673 K, cooled in helium to 293 K, and reoxidized in a flow of O₂(5%)–He up to 373 K. After these pretreatments, the gas flow, in each case, is turned to He, and the temperature is tuned to the value selected for carrying out the test.

The experimental method consists of injecting 0.25 ml O₂(5%)–He pulses, at 10 s intervals, over the 60 ml min⁻¹ inert gas stream. The O₂ content at the outlet of the reactor is measured with a thermal conductivity (TC) detector. The O₂ content is the result of the balance of the oxygen injected, consumed and released by the sample.

The amount of catalyst used in the experiments was 200 mg. We focus the comparative study of the four catalyst samples at

673 K, this rather low value being relevant because of the particular interest of improving the TWC efficiency during the cold start period of operation of motor vehicles.^{2,3}

If the sample does not have any oxygen buffer capacity at the selected operating conditions, we detect oscillations in the TC signal with a maximum height of 0.75 mV. This is found for pure ceria, as shown in Fig. 1(a). A blank test without sample leads to a pattern of oscillations coincident with that shown in Fig. 1(a).

Conversely, Fig. 1(b) clearly illustrates how the Rh/CeO₂ catalyst attenuates the oscillations of the oxygen partial pressure induced by the pulses. Those injected during the first minute of the sample and making it active for buffering; after this the catalyst reaches a steady response to the oxygen pressure oscillations. When the injections cease after 8 min the sample gradually returns to its initial equilibrium state in the flowing He carrier. The efficiency of a sample as an oxygen buffer can be accounted by the attenuation factor, defined as the ratios of the steady-state amplitude of the oscillations in the absence of sample (0.75 mV) and in its presence. For Rh/CeO₂ the attenuation factor is 2.1.

The Rh/SiO₂ sample is tested as a representative case of a catalyst in which it is assumed that the support does not have the

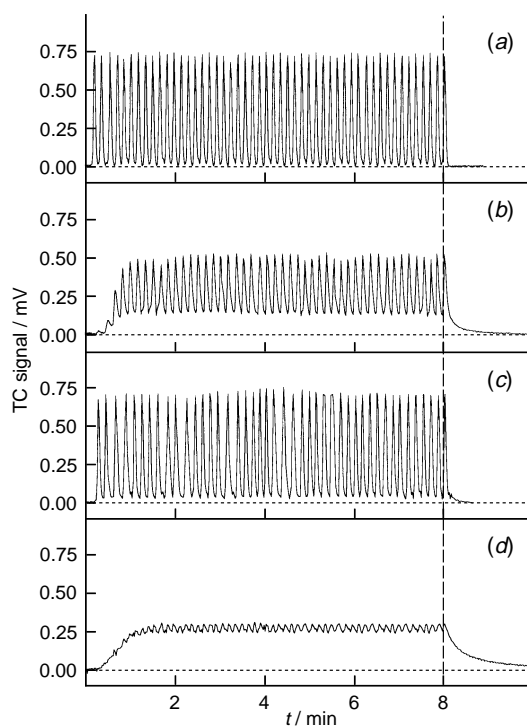


Fig. 1 TC signals for OBC experiments carried out at 673 K on: (a) CeO₂, (b) Rh/CeO₂, (c) Rh/SiO₂ and (d) CT-80/20. The dotted vertical line corresponds to the time at which we stopped the injection of pulses.

ability to contribute to the OBC. In this case, Fig. 1(c), the oxygen signal oscillations show only a tiny level of attenuation, with an attenuation factor of 1.06. Such an effect must be attributed to the influence of the oxygen partial pressure on its chemisorption-desorption on the oxidised rhodium.

The above experiments [Fig. 1(a)–(c)] allow one to conclude that the OBC of the Rh/CeO₂ catalyst is not the result of the simple overlap of Rh and CeO₂ buffering capacities, and that a synergetic effect must be invoked to understand its behaviour. This observation is in agreement with the well known existence of singular metal-support interactions for noble metals supported on ceria,^{1,4–8} thus giving credence to the reliability of the experimental technique.

Fig. 1(d) shows the behaviour of the Ce–Tb mixed oxide, CT-80/20. This catalyst gradually varies its oxidation level retaining part of the oxygen injected in the starting pulses. After this, the CT-80/20 oxide reaches a state in which its oxygen buffering ability is extremely high. The attenuation factor of the oxygen pressure oscillations in this case is 10.8. This behaviour is related to the ability of the mixed oxide to rapidly change its composition in response to the pulses. It is through these changes that CT-80/20 can attenuate the O₂ pressure oscillations, undergoing oxidation when the atmosphere is rich in oxygen and reduction when the O₂ partial pressure in the flowing gas is low.

The performance of CT-80/20 was also outstanding when the temperature was changed within very broad limits. This can be checked by analysing the results of a similar pulse experiment carried out at a linear heating rate of 20 K min⁻¹, from 323 up to 873 K. In this way rapid collection of OBC data was possible. Fig. 2 shows the temperature range in which the catalyst does not have the ability to attenuate pulses ($T < 473$ K). From 473 to 573 K the attenuation of the pulses rapidly increases while from 573 to 873 K the attenuation factor remains high and almost constant.

The very high rate of response of the CT-80/20 mixed oxide in the whole temperature range in which the oxygen pressure oscillations attenuation is effective is remarkable. Because of

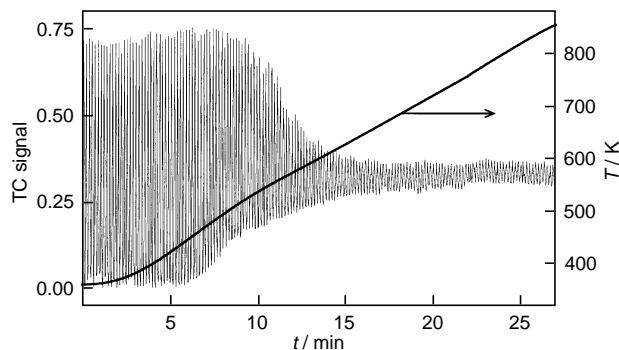


Fig. 2 TC signal for an OBC experiment on CT-80/20, at a heating rate of 20 K min⁻¹

experimental constraints the frequency of the pulses, 0.1 Hz, could not be increased; however, it is not far from the typical frequency of such oscillations in real TWC converters, of the order of 1 Hz.^{2,3}

Some other available results show that the performance of CT-80/20 is maintained for low surface area samples (8 m² g⁻¹), obtained by ageing the starting mixed oxide for 2 h at 1123 K in a flow of He. In this case the attenuation factor of the oxygen pulses remains >8. This result suggests the participation of oxygen from the bulk in the buffering mechanism. The lack of a proportional dependence between the OBC of CT-80/20 and the surface area of the sample is a very valuable feature for catalysts like TWCs which must operate under high temperature conditions for prolonged periods, thus potentially contributing to extension of its useful lifetime.⁸

One additional comment is that, like pure ceria, the buffering abilities of pure terbia are very different from those for the terbia modified cerium oxide, CT-80/20. The mixed oxide presents a much better performance than those of its individual components.

The details of the experimental conditions used in these tests have been adapted to obtain a good discrimination among the essayed samples. However, it would be possible to change some of the experimental settings, such as loop volume, amount of sample, inert gas flow rate, *etc.*, to obtain a good level of discrimination for other catalysts or temperature testing conditions.

In conclusion, we have proposed a new method to compare, in a fast and simple way, the OBCs of catalysts. Using this method we find that the modification of pure ceria by addition of 20 mol% of terbia increases dramatically its capability for attenuating fast oscillations of the oxygen partial pressure. This makes the terbia-modified cerium oxide CT-80/20, which shows superior properties over Rh/CeO₂, a potential candidate for inclusion in improved TWC formulations.

Footnote and References

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- 1 B. T. Kilbourn, *Cerium. A Guide to its Role in Chemical Technology*, Molycorp Inc., 1992.
- 2 P. Degobert, *Automobiles and Pollution*, Society of Automotive Engineers, Inc., 1995.
- 3 A. Trovarelli, *Catal. Rev. Sci. Eng.*, 1996, **38**, 439.
- 4 T. Bunluesin, E. S. Putna and R. J. Gorte, *Catal. Lett.*, 1996, **41**, 1.
- 5 J. Soria, A. Martínez-Arias and J. C. Conesa, *Vacuum*, 1992, **43**, 437.
- 6 S. Bernal, J. J. Calvino, G. A. Cifredo, J. M. Rodríguez-Izquierdo, V. Perrichon and A. Laachir, *J. Chem. Soc., Chem. Commun.*, 1992, 460.
- 7 S. Bernal, F. J. Botana, J. J. Calvino, M. A. Cauqui, G. A. Cifredo, A. Jobacho, J. M. Pintado and J. M. Rodríguez-Izquierdo, *J. Phys. Chem.*, 1993, **97**, 4118.
- 8 B. Engler, E. Koberstein and P. Schubert, *Appl. Catal.*, 1989, **48**, 71.

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