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Journal of Alloys and Compounds 344 (2002) 347–351

Journal of ALLOYS AND COMPOUNDS

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Influence of the noble metal on the properties as oxygen exchanger of Rh/LnO$_x$ systems (Ln: Ce,Tb): Application of the oxygen buffering capacity (OBC) technique

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Abstract

Ceria-based mixed oxides are being used as key components in TWC formulations, especially to widen the temperature range where ceria can be an effective oxygen exchanger. In TWC formulations, supported noble metals can modify the redox properties of the oxide acting as support. In this work, oxygen exchange properties of a set of oxides and mixed oxides have been studied with and without noble metal. The temperature range where the samples are effective has been studied by OBC (oxygen buffering capacity) measurements. This technique allows us to study the ability of a sample to buffer fast oscillations in the composition of the environment, and thus, to evaluate in a wide range of temperatures its ability as fast oxygen exchanger. Some interesting synergic effects can be found for noble metal-supported oxides.

Keywords: Rare-earth oxides; Supported noble metals; Oxygen buffering capacity

1. Introduction

Redox properties are important qualities in ceria and related materials used as TWC components [1–5]. Amongst these properties, oxygen storage capacity (OSC) and high speed to exchange oxygen are necessary to effectively buffer oxygen partial pressure oscillations [6], and thus widen the window of air-to-fuel ratios in which the exhaust catalysts are effective. OBC technique has been revealed as an excellent way to check the properties of a material to buffer the oxygen oscillations [7–9]. Different ceria-related materials, at present or potentially used in TWC formulations, have been reported in the literature as being good oxygen exchangers [3,4,10,11]. TWC are complex catalysts, so not only the intrinsic properties of these materials are of interest. In this work the influence of supported noble metal on ceria, terbia and Ce–Tb mixed oxide on the OBC property of these materials has been investigated.

2. Experimental

The properties as oxygen exchangers of a set of lanthanide oxides have been investigated in this work. The study of the ceria-based systems was performed on a pure ceria sample with a specific surface area of 147 $m^2 g^{-1}$. Rh/CeO$_2$ was prepared by impregnating the preceding cerium oxide with an aqueous solution of Rh(NO$_3$)$_3$, being the metal loading 2.78%. As a reference, a 3.7% Rh/SiO$_2$ catalyst was also prepared, being the metallic dispersion very close to that of Rh/CeO$_2$. Terbium and cerium–terbium oxides were prepared by precipitation with concentrated ammonia of 1 M solutions of the corresponding nitrates, being the wet precipitates dried and calcined at 600 and 900 °C, respectively. Terbium content of the Ce/Tb mixed oxide was 20 mol%. As for Rh/CeO$_2$ sample, rhodium supported on the terbium and cerium–terbium oxides were prepared by impregnation, with metal loadings of 4% for Rh/TbO$_x$ and 2.5% for Rh/CeTbO$_x$.

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PII: S0925-8388(02)00383-3

The structure of all the samples (except Rh/SiO_2) was confirmed to be fluorite-like by X-ray diffraction. The fluorite structure was kept by the samples during all the experiments performed in this paper. The only exceptions were for terbium oxide samples, which changed their structure to the fluorite-related cubic sesquioxide, when it was reduced to Tb_2O_3.

Before all the experiments performed, the samples were always pretreated 'in situ' at 600 °C for 1 h in a flow of O_2(5%)/He (60 $cm^3\ min^{-1}$), and cooled slowly under the oxidizing mixture up to 125 °C. At this temperature, the gas flow was switched to He, the oxides being further cooled to 25 °C under flowing inert gas. This standard pretreatment guarantees a common well-defined starting redox state throughout our whole study.

TPD experiments were performed by using a VG Sensorlab 200D mass spectrometer as analytical device. The gas flow-rate of He was always 60 $cm^3\ min^{-1}$, and the heating rate 10 °C min^{-1}. We have also run TPO-like experiments in a flow (60 $cm^3\ min^{-1}$) of O_2(5%)/He. In this latter case, the analytical tool consisted of a TCD detector; the heating rate was 10 °C min^{-1}.

Oxygen storage capacity (OBC) technique has been applied as described in Ref. [7]. Both isothermal and temperature-programmed experiments were performed for OBC measurements, with the heating rate of the latter being 20 °C min^{-1}.

3. Results and discussion

3.1. Oxygen buffering capacity of ceria-based samples

Fig. 1a reports on oxygen buffering capacity (OBC) experiments performed on ceria at 400, 500 and 600 °C. This property is negligible for this oxide over all the temperature range studied. This is a remarkable observation taking into account the traditional applications of this material as an oxygen exchanger in three-way catalyst compositions [1,3,5,12]. Fig. 1b and c account for the OBC measurements performed on Rh/SiO_2 and Rh/CeO_2. The percentages of OBC for all of these samples are listed in Table 1. As it is unlikely that SiO_2 could be involved in redox processes, OBC for Rh/SiO_2 would be attributed to the supported metal. When Rh is supported on ceria, which is a reducible oxide, OBC is greatly enhanced. Thus, the OBC values on Rh/CeO_2 are higher (Table 1), and the amplitude of oxygen pressure oscillations is lower (Fig.

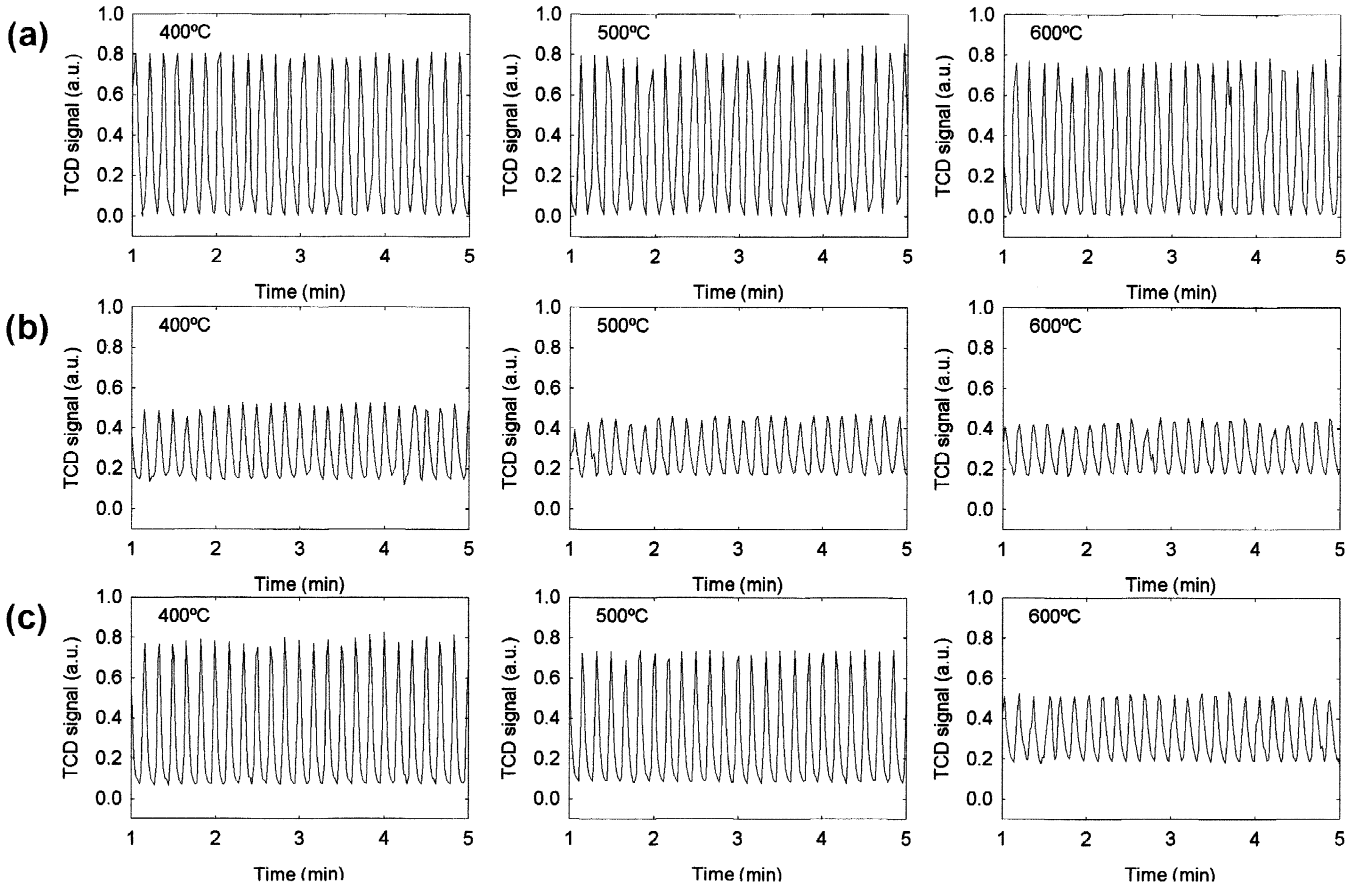

Fig. 1. Isothermal OBC experiments performed on CeO_2 (a), Rh/CeO_2 (b) and Rh/SiO_2 (c), at three different temperatures. The OBC percentages corresponding to each experiment are listed in Table 1.

Table 1
Attenuation of the oscillations during OBC experiments at constant temperature of the samples plotted in Fig. 1

	Temperature (°C)		
	400	500	600
CeO_2	0	0	0
Rh/CeO_2	66	70	77
Rh/SiO_2	3	10	54

Data expressed as: $\%OBC = \frac{A_{non-buffered} - A_{buffered}}{A_{non-buffered}} \cdot 100.$

1c) in all the temperature range studied, being 66% of the unbuffered oscillations at temperatures as low as 400 °C. At this temperature, the capacity of ceria to buffer pO_2 oscillations is zero and nearly negligible in Rh/SiO_2. Therefore, we can conclude that OBC on Rh/CeO_2 is not simply the result of the overlap of rhodium and ceria buffering capacities, so some kind of synergetic effect must be taken into account.

3.2. Oxygen buffering capacity of terbia-based samples

Fig. 2 shows the profiles of the evolution of OBC when the temperature is increased for TbO_x and Rh/TbO_x samples. It can be seen in Fig. 3 that TbO_x can be reduced in both inert gas flow (Fig. 3a) and O_2(5%)/He flow (Fig. 3b). Fig. 3c shows how TbO_x can be readily reoxidised when cooled under O_2/He. Both reduction and reoxidation processes occur as two well-defined peaks. For the TPD experiment (Fig. 3a), those peaks appear centred at 450 and 740 °C, respectively, being shifted to 487 and 855 °C when the reduction is performed under O_2/He (Fig. 3b). For the reoxidation (Fig. 3c), the peaks are centred at 433 and 780 °C. The quantity of oxygen evolved or consumed during those peaks is always the same, independently of the treatment that the sample is being submitted. Thus, the composition of the terbium oxide after the low temperature peak is known to be Tb_4O_7, being Tb_2O_3 after the high temperature reduction peak [13,14]. There is a temperature range, from about 490 to 540 °C, where the phase Tb_4O_7 seems to be stable both under He and under O_2/He.

Fig. 2a and b show the overlap of the evolution of OBC over the two peaks of reduction of TbO_x when the temperature is increased. It should be noticed that TbO_x begins to buffer slightly the oscillations of oxygen partial pressure from temperatures around 300 °C. The increase of the buffering capacity is not very significant up to 600 °C. After that temperature, there is an abrupt increase in the OBC of the sample, reaching its maximum value at 700 °C, and keeping its good properties as an oxygen buffer until 900 °C (Fig. 2b). In that temperature range, it can be observed that the oxide is reduced under He, as well as oxidised under O_2/He, so it is possible to uptake oxygen when the pressure is raised, and release that oxygen when the pressure is lowered, thus buffering the oscillations.

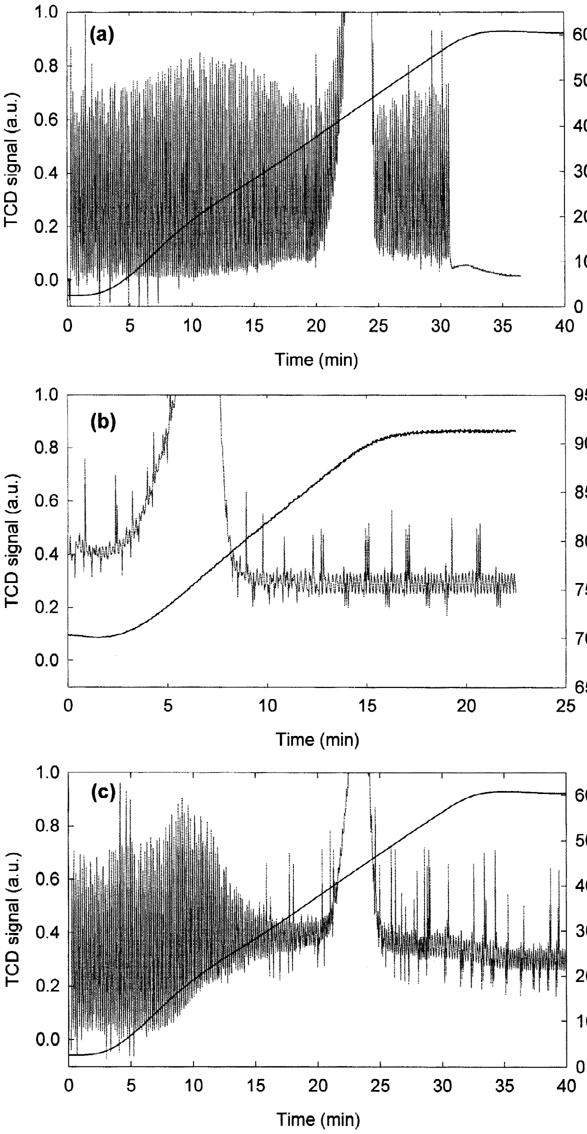

Fig. 2. Evolution of OBC versus temperature for TbO_x (a and b), and Rh/TbO_x (c). (a) and (b) show the evolution of OBC for TbO_x at two different temperature ranges.

The evolution of OBC versus temperature for Rh/TbO_x is shown in Fig. 2c, where a peak can also be observed attributable to terbia reduction centred at about 400 °C. It is clear from this figure that this sample begins to buffer at a lower temperature (≈200 °C) than terbia without metal supported. Especially remarkable is that at 300 °C, before the evolution of the first reduction peak, OBC reaches a value of 89%, maintaining this value until the end of the experiment, at 600 °C. It should be noticed that the position of the reduction peaks for Rh/TbO_x is not significantly changed with respect to that of the TbO_x without noble metal [15]. Again, as in the case of ceria-based systems, it can be seen the positive effect on the properties as an oxygen buffer, when rhodium is supported on a reducible oxide.

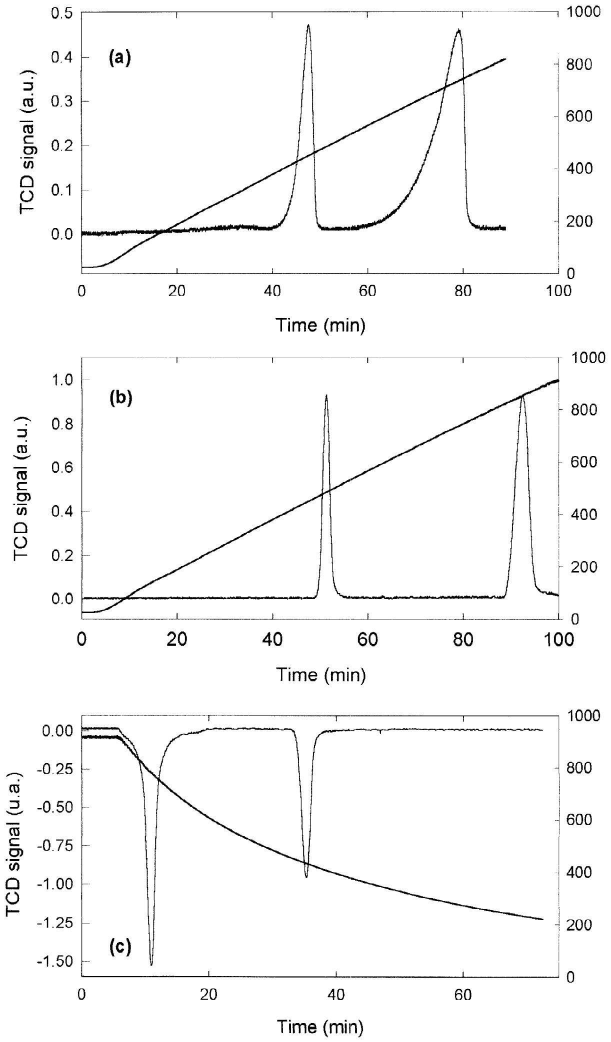

Fig. 3. (a) TPD experiment performed on TbO_x. TPO-like experiment under flowing O_2(5%)/He for the same oxide: (b) heating, and (c) cooling.

3.3. Oxygen buffering capacity of cerium–terbium mixed oxides

The reduction profile of this mixed oxide under an inert gas flow (Fig. 4) shows a peak for oxygen desorption centred at 400 °C. A broad profile after this first peak shows the maintenance of the reduction process while the temperature is increasing. The reduction process stops when the temperature reaches a constant value at the end of the experiment.

During the temperature-programmed OBC experiment, the reduction process of the Ce/Tb mixed oxide, overlaps the OBC phenomena, and produces the effect shown in the left side of Fig. 5a. Once the reduction corresponding to the first peak of the TPD is over, a great increase in the ability of the sample to buffer the oscillations can be observed, reaching an OBC of 96% just below 600 °C. It is worth noting that the amplitude of the oscillations remains constant (the %OBC does not change) when the experiment reaches the highest temperature, 600 °C, but the average value of oxygen partial pressure decreases. This is in good agreement with the TPD experiment shown in Fig. 4.

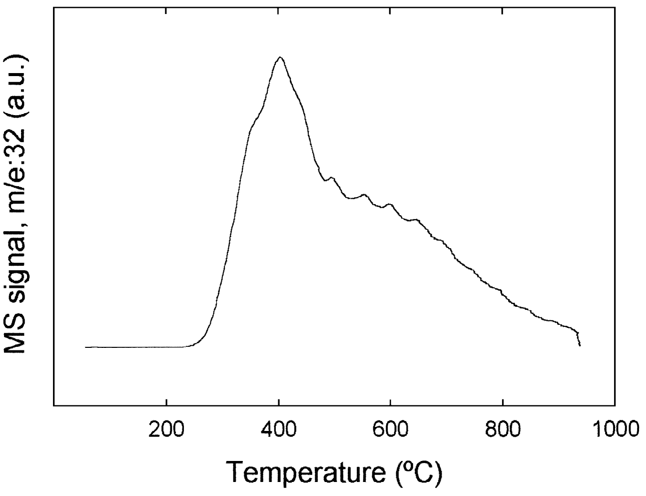

Fig. 4. TPD experiment performed on the cerium–terbium mixed oxide ($Ce_{0.8}Tb_{0.2}O_x$).

The OBC experiment on Rh/$CeTbO_x$ (Fig. 5b) shows a similar profile, with a significant increase in the average value of oxygen partial pressure corresponding to a reduction feature at about 200 °C. As in the OBC experiments for the mixed oxide, the average value for the oscillations decreases when the temperature reaches a

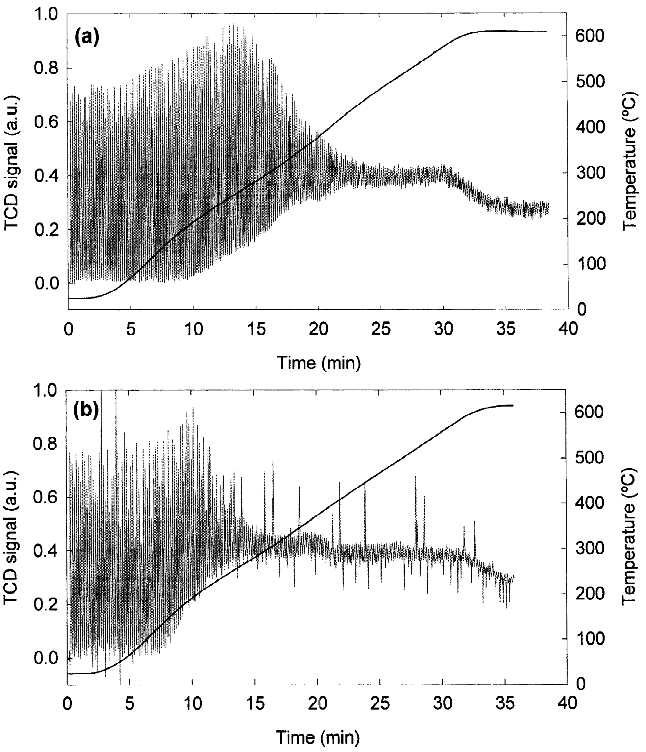

Fig. 5. Evolution of OBC versus temperature for $Ce_{0.8}Tb_{0.2}O_x$ (a) and Rh/$Ce_{0.8}Tb_{0.2}O_x$ (b).

constant value. At the end of the experiments, the OBC value is quite similar in both metal supported and metal-free mixed oxide. The main difference arises from the temperature at which the OBC phenomena begin to be effective, being much lower on Rh/CeTbO$_x$. In this case, the efficiency to buffer the oxygen partial pressure oscillations is very high, 97%, just after the reduction feature at 200 °C.

4. Conclusions

Supporting noble metals on the oxides investigated in this work does not seem to induce significant changes of reducibility, neither on inert gas or under O_2(5%)/He flow. Nevertheless, a significant increase on the OBC values at low temperatures is observed in the rhodium-containing oxides with respect to the oxides alone. This increase is only appreciable when the temperature is not high enough to produce an important buffer effect on the oxide without metal. Otherwise, when the temperature is high enough, and the oxide has a high buffering capacity, supported noble metal do not produce any further enhancement on the OBC. In those cases, the highest OBC value observed for the oxide with and without noble metal is almost the same. The only exception to this rule is Rh/CeO_2. In this latter case, the noble metal supported on ceria enhances the OBC in all the range of temperature investigated compared to pure ceria. It has to be taken into account, however, that metal-free ceria has a very low buffering capacity in all the range of temperatures investigated.

Acknowledgements

This work has been supported by the CICYT (Project No. MAT99-0570) and the Junta de Andalucía.

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