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Oxygen buffering capacity (OBC) of praseodymium-modified CeO_2: influence of the Pr distribution in the ceria host lattice

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This work reports on the redox behaviour of different ceria–praseodymia mixed oxides with two different chemical compositions (Ce/Pr molar ratios of 4 : 1 and 9 : 1). The samples consist of bulk oxides and ceria-supported samples with varying mixed oxide loading (equivalent to 7 or 12 mixed oxide layers). As revealed by x-ray diffraction and high-resolution electron microscopy, the samples consist of homogeneous fluorite-like mixed oxides. Their redox properties were characterized by means of the oxygen buffering capacity (OBC) technique, which quantitatively evaluates the capacity of the samples for attenuating fast oscillations of the oxygen partial pressure in the He stream flowing through the sample. These oscillations are induced by injecting with a high frequency pulses of oxygen into the inert gas stream. Although the XPS analyses performed on both a bulk and a supported sample showed Ce/Pr molar ratios very close to each other, the bulk mixed oxide exhibits significantly better OBC values. Also remarkable is that an ageing treatment at 1223 K improves the OBC response of the supported mixed oxides. In accordance with the XPS data, the enhancement of their redox properties runs parallel to an increase in the Ce/Pr surface ratio. These results are discussed in terms of the role played by the depth profile distribution of Pr in the different oxide samples.

KEYWORDS: oxygen buffering capacity; three-way catalysts; Ce/Pr mixed oxides; XPS

INTRODUCTION

In recent years, the necessary improvement in the properties and duration of the automotive catalysts has driven a wide effort in this field of research.[1–5] One desirable improvement is to obtain a better oxygen exchange efficiency at low temperatures, which is related to the exhaust problem during the cold-start period.[6] For such a purpose, some mixed oxides have been studied as an alternative to pure cerium dioxide,[3–5,7–9] which is a main component in three-way catalysts (TWCs). Ceria–praseodymia mixed oxides have shown excellent properties in this respect.[3,4] Worth noting are the excellent redox properties exhibited by Ce–Pr mixed oxides, and the efficiency for oxygen exchange applications should be outlined. In order to gain more insight into the superficial or bulk nature of the mechanism involved in the oxygen exchange process, different characterization techniques have been used on both bulk and supported Ce–Pr samples. This paper reports a study using techniques like such as oxygen buffering capacity (OBC)[10] and XPS as an alternative to the other usual techniques in catalytic studies.

EXPERIMENTAL

Sample preparation

Following the procedure described in Ref. 9, two different Ce–Pr mixed oxides with 10 and 20 mol.% Pr were prepared. The samples will be labelled CP-90/10 and CP-80/20, respectively.

Supported mixed oxides were prepared by impregnating a cerium oxide support (8 $m^2\ g^{-1}$) with an aqueous solution of praseodymium and cerium nitrates in the appropriate proportions. The nitrate concentrated solutions were kindly provided by Rhône-Poulenc and diluted to a concentration of 0.1 M. The incipient wetness impregnation technique was followed. After each impregnation step, the samples were calcined at 873 K in air for 1 h. Three ceria-supported mixed oxides were prepared by using this procedure. Those labelled CSCP-80/20 and CSCP-90/10 have the same mixed oxide loading (equivalent to seven monolayers), but different Pr molar contents of 20% and

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10%, respectively. The third supported oxide was prepared with a Pr content of 20%, but the mixed oxide loading was equivalent to 12 monolayers. This sample will be referred to as CSCP-80/20(12).

Structural characterization techniques

The structural characterization of the samples was performed by x-ray diffraction (XRD) and high-resolution electron microscopy (HREM). The XRD powder diffraction patterns were collected on a Phillips PW 1820 diffractometer by using Cu Kα radiation and an Ni filter. A Jeol JEM-2000-EX electron microscope with a structural resolution of 0.21 nm was used to obtain the HREM images.

Oxygen buffering capacity (OBC)

Oxygen buffering capacity has been applied as described in Ref. 10. Simultaneous to the OBC experiments, the samples were heated at a rate of 10 K min^{-1} from room temperature to 873 K. Prior to all the OBC measurements the samples were submitted to a cleaning treatment consisting of heating at 873 K in a flow of O_2(5%)/He for 1 h, followed by slow cooling to 293 K, always in a flow of the oxidizing mixture.

X-ray photoelectron spectroscopy

The XPS spectra were recorded using the spectrometer ESCA-300 (Scienta, Uppsala, Sweden) at LISE FUNDP in Namur. The base pressure in the system was 3×10^{-10} Torr. The photoemission was excited by a monochromatized Al Kα x-ray beam ($h\nu = 1486.6$ eV). The energy resolution of the analyser was better than 0.35 eV. The powder samples were pressed onto double-sided adhesive tape and analysed without further treatment. Because charging effects were observed during the photoemission measurements, an electron flood-gun was used to restore the charge balance on the surface, seeking the settings at which the highest count rate was achieved; the peak position was stabilized and the broadening of the most intense core levels was limited. Binding energy correction was done using the C 1s core level at 284.9 eV as an internal reference.

RESULTS

Structural characterization

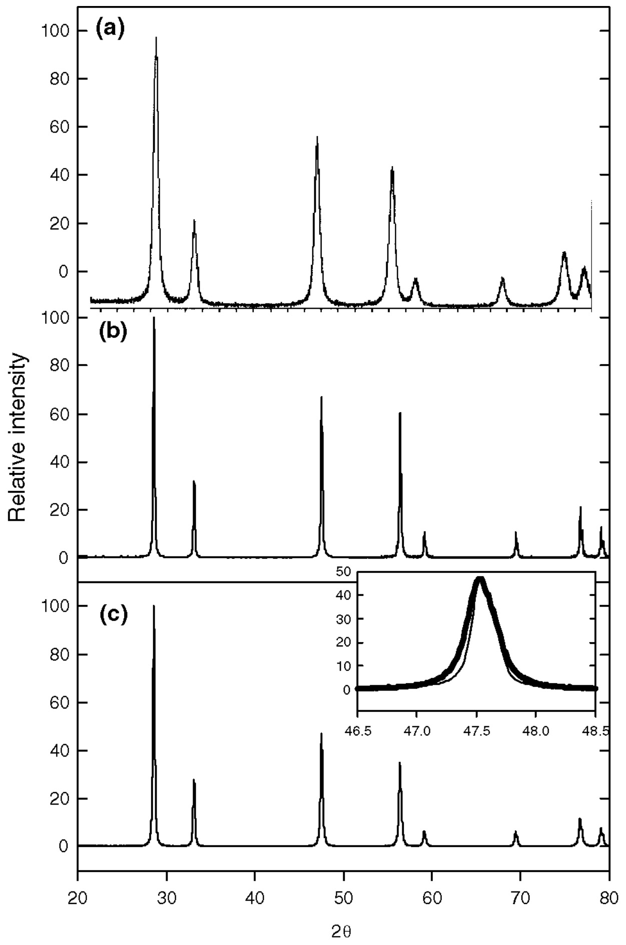

Figure 1. X-ray diffraction patterns corresponding to: (a) bulk ceria-supported mixed oxide CP-80/20; (b) pure ceria; (c) supported CSCP-80/20 mixed oxide. The inset shows the comparison between the ceria support shown in (b) (thin line) and the supported mixed oxide of (c) (thick line).

A structural characterization of both bulk and supported Ce–Pr mixed oxides was carried out by XRD. Results for bulk mixed oxides showed that the structure for both 10 and 20 mol.% Pr oxides is fluorite-like. As an example, Fig. 1(a) accounts for the XRD pattern of the CP-80/20 sample. If we compare the pattern for the mixed oxide with that corresponding to the pure ceria sample used as support [Fig. 1(b)], apart from the difference in the width of the diffraction peaks due to different crystal size it is apparent that both patterns are very close to each other. This is reasonable because the Ce^{4+} ionic radius (97 pm) is very similar to that of Pr^{4+} (96 pm). There is just a slight shift of the diffraction peaks of the CP-80/20 pattern towards lower angles. This corresponds to a slight increase of the lattice parameter, which can be attributed to the presence of some Pr^{3+} (112.6 pm) in the oxide lattice. Thus, the shift of the angles is almost negligible for the (111) diffraction peak (28.6°) and only 0.02° for the (220) planes at ~47.5°.

Supported mixed oxides also show XRD patterns typical of a fluorite-like structure, corresponding to both the ceria support and the mixed oxide. The XRD pattern of the supported CSCP-80/20 sample is presented in Fig. 1(c). Despite the fact that the pattern seems to correspond to only one fluorite phase, from the asymmetry observed in the shape of the diffraction peaks the presence of a second fluorite phase can be inferred. As can be seen in the inset of Fig. 1, which represents the corresponding peaks for the (220) planes, the pattern for the pure ceria support (thin line) is narrower than that for the supported system. In the inset, it is evident that the asymmetry commented on above can be located mainly in the low angle part of the peak, corresponding to the presence of a mixed oxide phase with a bigger lattice parameter. Also, a misfit in the base of the peaks can be observed, and this can be indicative of a smaller crystal size for the mixed oxide phase.

High-resolution electron microscopy was also applied to the characterization of the supported mixed oxides.

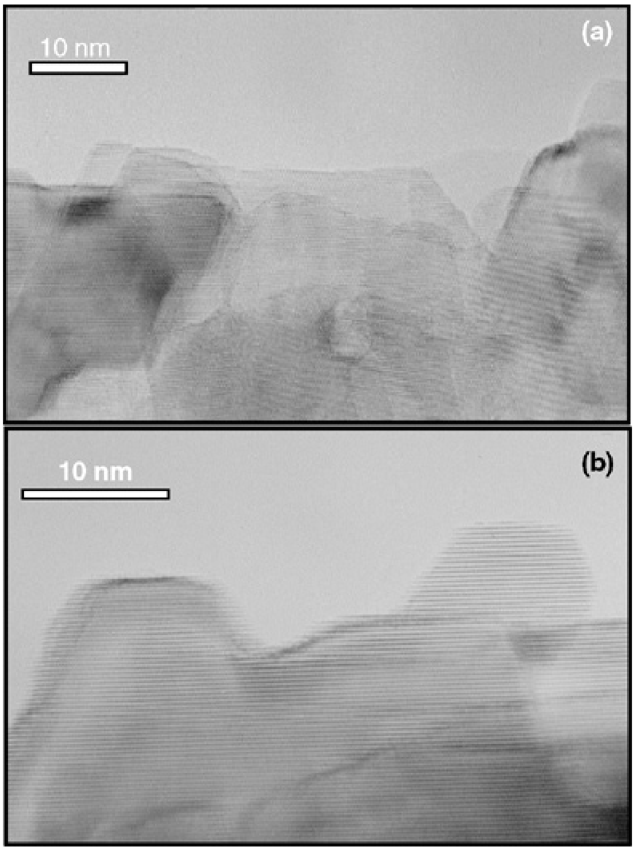

Figure 2. High-resolution electron micrographs of the ceria-supported mixed oxide CSCP-80/20 taken at different magnifications: (a) 400 K; (b) 600 K.

Figure 2 shows two HREM micrographs of the supported mixed oxide CSCP-80/20 at two different magnifications. As the nature of both the ceria support and the supported mixed oxide is very similar, it is a complicated task to distinguish them by HREM. Nevertheless, as revealed by the HREM study, the supported system consists of a great extension on a set of big crystallites (diameter >50 nm) accompanied by smaller ones (diameters of 10 nm on average). The larger microcrystals may tentatively be assigned to the ceria support, whereas the smaller ones might correspond to the mixed oxide particles.

Oxygen buffering capacity

The OBC of the bulk and supported Ce–Pr mixed oxides was studied along a range of temperatures as described in Ref. 10. An oxygen buffer produces a decrease of the amplitude of the fast oscillations (0.1 Hz) in the oxygen pressure, keeping them in a more narrow range. The OBC properties of different samples can be quantified by using the following equation:

$$\%OBC = \frac{A_{NB} - A_B}{A_{NB}} \times 100$$

where A_{NB} and A_B are, respectively, the amplitudes of the oscillations before and after passing through an active sample.

A temperature-programmed OBC experiment, following a linear heating ramp, can relate the buffering capacity to the temperature of the sample. Thus, the OBC of the samples was studied from room temperature to 873 K. The composition, BET surface areas and OBC values measured at 823 K for all the bulk and supported oxides studied in this paper are listed in Table 1.

Figure 3(a–c) shows the temperature-programmed OBC experiments performed on the bulk Ce–Pr mixed oxides with 20 and 10 mol.% Pr, with pure ceria included for comparison. It can be observed that in the case of the mixed oxides the OBC gradually increases as the temperature rises, whereas it is almost negligible in all the experiments for the ceria reference. It is evident from Fig. 2 and the data collected in Table 1 that Ce–Pr mixed oxides are excellent buffer systems, much better than pure ceria. In effect, for the mixed oxides the redox activity starts to be measurable at a very low temperature ($\sim$473 K), reaching OBC values as high as 95% at 573 K in the case of CP-80/20, or 673 K in CP-90/10.

As observed in Table 1, all ceria-supported mixed oxides show oxygen buffering capacities significantly lower than the corresponding bulk mixed oxides. Figure 3(d,e) shows the temperature-programmed OBC experiments run for some fresh supported oxides. The sample with the lower Pr content has the lowest OBC values in the entire temperature range (max. 15%). For the samples with 20% Pr, the 12-layer supported oxide CSCP-80/20(12) exhibits the higher OBC values, significantly higher than that determined for the seven-layer CSCP-80/20 sample.

Table 1. Quantitative results obtained from the OBC measurements performed on a series of Ce–Pr mixed oxides

Sample	Composition of the mixed oxide (% Pr)	BET surface area (m^2 g^{-1})	% OBC		Amount of interchanged O_2 at 873 K (mmol O_2 mol^{-1} sample)	Surface reduction (mmol O_2 mol^{-1})
			673 K	873 K		
CeO_2	0	8	0	0	—	—
CP-90/10	10	37	69	96	0.22	14.3
CP-80/20	20	40	82	98	0.23	13.2
CSCP-90/10						
Fresh	10	10	7	15	0.04	3.6
Aged	10	5	14	34	0.08	1.8
CSCP-80/20						
Fresh	20	10	17	26	0.06	3.6
Aged	20	5	14	53	0.12	1.8
CSCP-80/20(12)						
Fresh	20	12	57	63	0.15	4.3
Aged	20	7	35	75	0.17	2.5

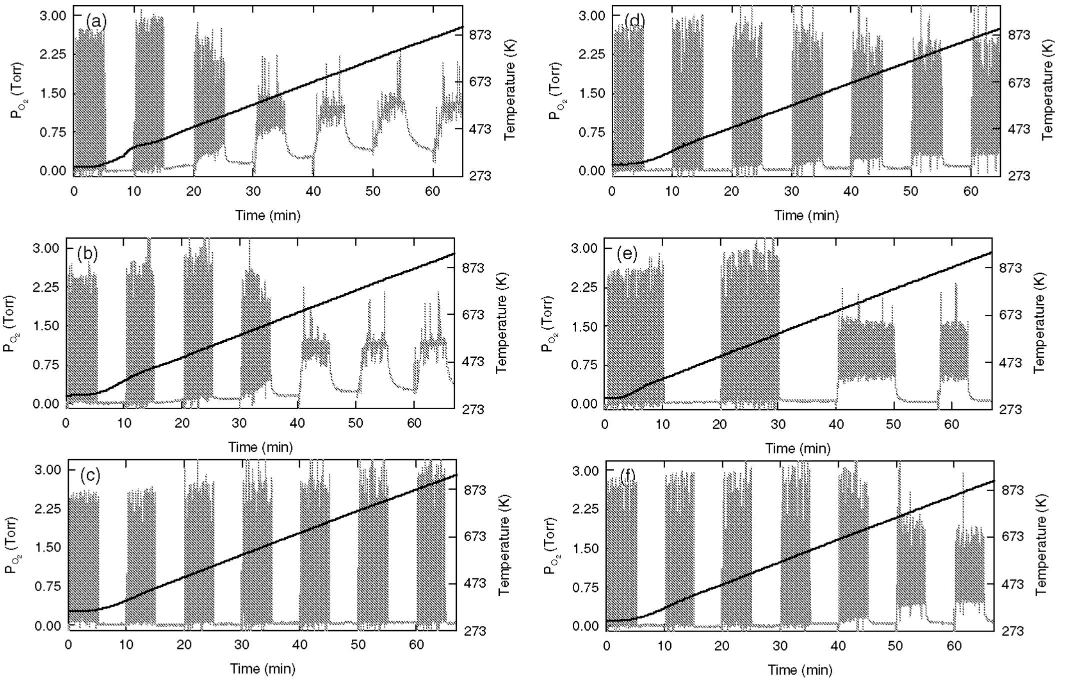

Figure 3. Temperature-programmed OBC experiments performed on: (a) CP-80/20; (b) CP-90/10; (c) pure CeO_2; (d) CSCP-80/20; (e) CSCP-80/20(12); (f) aged CSCP-80/20.

When those mixed oxides were submitted to a thermal treatment consisting of heating under flowing helium at 1223 K for 3 h, the OBC values of the resulting samples were significantly higher [Fig. 3(f)]. In spite of this improvement in their redox efficiency, however, the OBC values determined for the aged supported oxides are still under those determined for the bulk mixed oxide samples. This surprising result will be discussed later.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was applied for determining the surface composition of both the fresh and aged CSCP-80/20 mixed oxide. The XPS spectra were collected for both Ce 3d and Pr 3d core levels, which were used to estimate the surface Ce/Pr ratio for both samples. The Pr molar percentage for the fresh CSCP-80/20 sample was ~25%, whereas it was decreased to 14% in the aged sample. This apparent loss of Pr during the ageing treatment can be explained easily by a migration of Pr ions into the bulk of the ceria support, induced by the thermal treatment.

DISCUSSION

The results reported above (Table 1) show the excellent oxygen buffer properties of the bulk Ce–Pr mixed oxides. Supported mixed oxides were initially prepared in order to have samples with high performance with the lowest Pr content. The results reported here, however, show that the performance of those supported oxides is not as good as expected, in all samples being lower than those of the corresponding bulk mixed oxides. Taking this into account, and in order to establish adequate parameters governing the oxygen storage behaviour in this kind of sample, it is important to study the superficial or massive nature of the oxygen involved in the OBC. During the buffering process, the amounts of oxygen consumed by the samples when the pressure is high and later released when the pressure decreases must be equal. This quantity of oxygen that is alternately consumed and released can be determined directly from the OBC experiments. The quantities of oxygen involved in the buffering process at 873 K are listed in Table 1. Knowing the BET surface area of the samples and assuming that the fully oxidized surfaces contain 10.1 oxygen atoms per square nanometre on average,[11] we have calculated the quantities of oxygen corresponding to a purely surface reduction (listed in Table 1 for all the studied oxides). For bulk mixed oxides, it can be noted that the amount of oxygen corresponding to surface reduction is more than 60 times higher than the quantity of oxygen actually involved in the buffering process. Data listed in Table 1 for the supported mixed oxides were calculated on the assumption that all the exposed surfaces of the samples correspond to mixed oxide. Again, for these samples the exchanged amounts are significantly smaller than those corresponding to surface reduction.

In spite of the fact that the amounts of oxygen measured in these experiments could account for reduction and oxidation processes involving only the surface of the oxides, there is not a direct relationship between the surface area and the amount of oxygen exchanged. In this sense it is particularly worth noting the behaviour of the supported samples. In effect, if the buffering process consisted of a purely surface process, it might be expected that both bulk and supported mixed oxides would exhibit rather similar behaviour. This buffering capacity should decrease when the samples are submitted to the ageing treatment, because the surface area of the samples also decreases. On the contrary, however, what is observed is an increase of the OBC for all the aged samples. The structural characterization that has been carried out on the samples does not give enough information concerning the distribution of the mixed oxide on the ceria surface. For this reason, XPS was used to provide additional information, in this case on the outermost layers of the samples.

The measured OBC values also rise when the mixed oxide loading is increased from the equivalent of seven layers in CSCP-80/20 to 12 layers in CSCP-80/20(12). This is in good agreement with the above observations, in the sense that it is evident that any change induced on the supported oxides that leads to a bigger mass of mixed oxide improves the OBC performance.

To summarize, there are two main factors that produce an improved oxygen buffering capacity: the Pr molar content of the mixed oxide phase and the amount of bulk mixed oxide present in the sample. In conclusion, in spite of the small quantities of oxygen involved in the process, which could be justified initially by using only the surface of the samples, evidence of the bulk nature of OBC has arisen from this study, the key parameter accounting for the OBC performance of the systems studied in this paper being the bulk nature of the mixed oxide phase.

CONCLUSIONS

A set of bulk and supported Ce–Pr mixed oxides has been investigated in this paper. Oxygen buffering capacity, a technique developed in our laboratory, was first applied to bulk mixed oxides. These oxides showed an excellent ability to buffer fast oscillations in the oxygen partial pressure, such as those occurring during the working conditions of automotive exhaust catalysts. As deduced from our results, the buffering capacity of both massive and supported mixed oxides is increased with the Pr content. When studying the OBC of the supported mixed oxides, the results showed lower performance than in the bulk mixed oxide samples.

The quantities of oxygen involved in the buffering process were lower than those estimated for a purely surface process. Nevertheless, OBC experiments show that supported samples have a very limited ability in the oxygen uptake/release fast process. An ageing treatment leading to an increase of the thickness of mixed oxide, and consequently to a decrease in its Pr proportion, improves strongly the OBC of the supported samples. Thus, the thicker the layer of supported oxide, the larger the OBC value. Likewise, on ageing, the thinner the layer, the larger the enhancement of the OBC. This leads to a worthwhile goal for the practical use of such mixed oxides to prepare supported Ce–Pr mixed oxides, with the best properties obtained by using a minimum amount of Pr.

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