Influence of reduction treatment on the structural and redox behaviour of ceria, La/Ce and Y/Ce mixed oxides

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A methodology based on reoxidation at 298 K with O_2(5%)/He pulses followed by quantitative TPO runs allowed us to study the redox state reached by CeO_2 and Ln^{3+}-containing ceria-based mixed oxide samples (Ln^{3+}: La^{3+} or Y^{3+}) after their reduction in a flow of hydrogen. The temperature range covered in the reduction treatments was from 623 up to 1223 K. During the severe reduction treatments hexagonal sesquioxide phases segregate from all the samples. The reduction temperature at which segregation occurs follows the trend La/Ce $<$ Y/Ce $<$ CeO_2. The TPO and H_2-TPD traces of reduced samples which showed evidence of segregation in XRD exhibit characteristic features which can also be used as an indication of this effect. The discussion is focussed on the overall and detailed understanding of the reoxidation process and on the analysis of the H_2-TPD profiles.

Keywords: ceria, lanthanum, yttrium, mixed oxides, three-way catalysts, TWC, reducibility, reoxidation, structural transformation

1. Introduction

Ceria-based mixed oxides containing trivalent rare earth cations (Ln^{3+}) are interesting materials as oxide anion conductors [1]. The vacancies created in the anion sublattice by the presence of Ln^{3+} favour the reduction of Ce^{4+} cations [2,3], offering the possibility to use such materials as components for improved exhaust catalysts for cars [4,5]. In other words, the presence of the trivalent cations in the formulation of these oxides should be helpful in promoting the redox cycling of the cerium cations ($Ce^{4+} \rightleftharpoons Ce^{3+}$) that must take place as a function of the composition of the exhaust gases leaving the engine. The increased ability for its reduction under milder conditions [2,3] makes these materials interesting as candidates for relieving emission problems during cold start operation of vehicles [6], in which the performance of conventional formulations incorporating pure CeO_2 as an additive is not satisfactory.

One of the possible drawbacks of this application of ceria-based Ln^{3+}-containing oxides is that under severe reducing treatments they can undergo a partial transformation from the initial fluorite-like cubic structure to the hexagonal sesquioxide structure. These transformations induce a loss of their capacity for effective oxygen exchange with the reaction environment [7]. Such structural change involves a rearrangement of the cation sublattice, which is the argument used to explain why the reoxidation conditions required for restoring the fluorite-like cubic structure must be more severe. This problem has been mentioned previously by Perrichon et al. [8,9] in studies focussed on the characterisation of high-surface-area cerium dioxides. In this work we present new data for ceria and we compare its behaviour with that of La/Ce and Y/Ce mixed oxides. In the case of La^{3+} we deal with a cation very similar in size to that of the reduced cerium, Ce^{3+}; whereas Y^{3+} is significantly smaller than Ce^{3+} and Ce^{4+} [10]. These new results, as well as those reported in [8,9], shed light from a catalytic perspective on the large amount of information accumulated in previous studies of the phase diagrams of cerium oxide and other reducible rare earth higher oxides [11–14].

2. Experimental

The La/Ce and Y/Ce mixed oxides, with La molar contents of 20 and 40%, and Y content of 20%, were prepared starting from appropriate mixtures of 1 M solutions of the corresponding nitrates, 99% pure, supplied by Fluka. An excess of concentrated ammonia (5 : 1 ratio), p.a. quality from Merck, was used to precipitate the mixed oxide precursors, which were washed five times with distilled water and calcined in air at 873 K for 2 h before storage. These samples are labeled as L20C, L40C, and Y20C. Induced coupled plasma (ICP) analysis allowed us to confirm that the experimental and nominal compositions are in good agreement. A pure ceria sample was also prepared following the same procedure. All these samples appeared by X-ray diffraction (XRD) and high-resolution electron microscopy (HREM) to be fluorite-like homogeneous materi-

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als. The initial specific surface areas of the oxides were all in the range from 25 to 70 $m^2\,g^{-1}$, falling with the reduction treatments as described in [2]. The surface areas of the mixed oxides remained higher than that of CeO_2 during the reduction treatments.

The gases used in this work, H_2, O_2, O_2(5%)/He and He – all of them graded as N55 or better – were supplied by Air Liquide and were further purified by passing them through 4A-type zeolite, and for the cases of the H_2 and He, also through oxygen traps from Alltech.

Before each experiment, 200 mg aliquots of the samples were pretreated *in situ* in a quartz U-shaped reactor, in order to clean their surfaces and to reach reproducible reference states. The standard pretreatment consisted of calcination in 60 $ml\,min^{-1}$ of flowing O_2 at a heating rate of 10 $K\,min^{-1}$ up to 873 K (1 h) followed by a slow cooling down to 473 K in O_2 and further cooling to room temperature in a flow of helium. Quantitative temperature-programmed reduction (TPR) data reveal that these standard pretreatments lead to clean samples, in which the cerium cations are fully oxidised [7].

The reduction treatments applied to the oxides consisted of exposing the samples to a flow of 60 $ml\,min^{-1}$ of H_2 and increasing the temperature at a linear heating rate (10 $K\,min^{-1}$) up to the selected maximum. Unless otherwise specified, the duration of the reduction treatment at the maximum temperature selected was 1 h. For the study of the levels of reduction reached by ceria and the mixed oxides, it was necessary to follow the procedure previously established in [15] for Rh/CeO_2 catalysts. The reoxidation is carried out in two different stages. In the first, the sample in flowing He is allowed to react with 0.5 ml O_2(5%)/He pulses. Thus, we can avoid its fast reoxidation, preventing its eventual overheating due to the evolved heat of reaction. After reaching saturation with diluted oxygen pulses, a temperature-programmed oxidation (TPO) experiment is run in each case. Both the integrated oxygen consumption and the shape of the TPO traces will be useful in each case as sources of information. Temperature-programmed desorption (TPD) of H_2 was also carried out following the selected reduction treatments, further cooling in a flow of hydrogen down to 295 K and switching to a flow of helium of 60 $ml\,min^{-1}$. Both the TPO and H_2-TPD experiments were run at a heating rate of 10 $K\,min^{-1}$. A thermal conductivity detector (TCD) was used to follow the oxygen pulses and TPO traces, and a mass spectrometer was used as the detector in H_2-TPD experiments.

A Philips PW 1820 diffractometer, operating with Cu Kα radiation, allowed the recording of the XRD diffraction patterns of the samples. To study previously reduced samples, a careful protocol was followed to avoid fast reoxidations by sudden contact with air. This protocol consisted of cooling the sample to 200 K in inert gas, switching to O_2(5%)/He, and slowly allowing the temperature to increase to 295 K.

3. Results

3.1. Characteristics of the redox behaviour

The first objective was the characterisation of the level of reduction reached by the samples following each of the selected reduction treatments under hydrogen flow. As described in section 2, this must be done in two stages: the first one is a mild treatment with diluted oxygen pulses at 295 K and, after reaching saturation with pulses, the samples are oxidised in a second stage with diluted oxygen in a TPO experiment. Thus, the total level of reduction in each case is determined from the addition of the oxygen consumption in pulses and in the TPO [15].

Figure 1 shows the results for CeO_2 and for the mixed oxides L20C, L40C and Y20C, expressed as percentages of cerium reduced to Ce^{3+}. A first observation is that, for the lowest reduction temperatures, i.e., 773 K, the oxygen consumption is clearly higher for the mixed oxides. This is in good agreement with previously reported TPR experiments and with the oxygen evolution observed in TPD experiments, thus confirming that these mixed oxides are easier to reduce than ceria under relatively mild conditions [2].

It can also be seen in figure 1 that, for each sample, the plots accounting for the contribution of the oxygen pulses go through a maximum, decreasing for more severe reduction treatments. In parallel, the oxygen consumption associated with the TPO experiments increases smoothly for the milder reduction treatments and shows a sharp increase

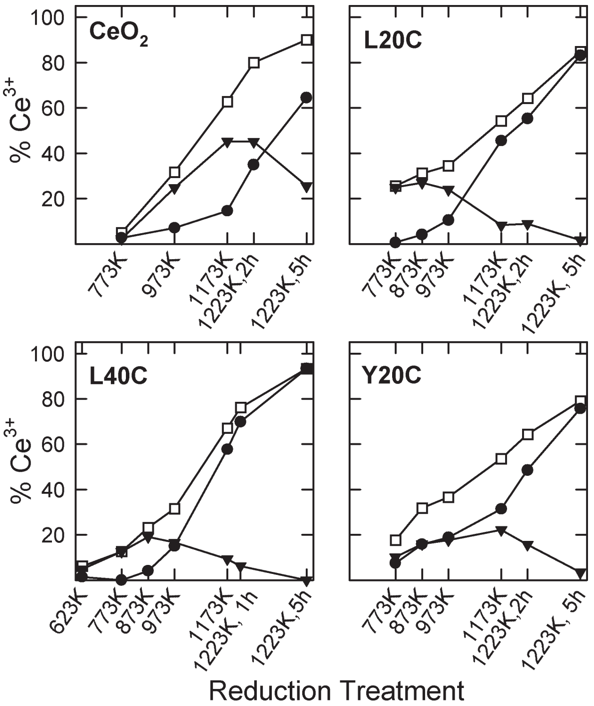

Figure 1. Results of reoxidation experiments following reduction treatments in a flow of hydrogen for pure ceria, L20C, L40C and Y20C. Temperatures and times of treatment in hydrogen as indicated in the figure. (▼) Reoxidation with pulses, (●) reoxidation by TPO, (☐) addition of pulse and TPO oxygen consumption.

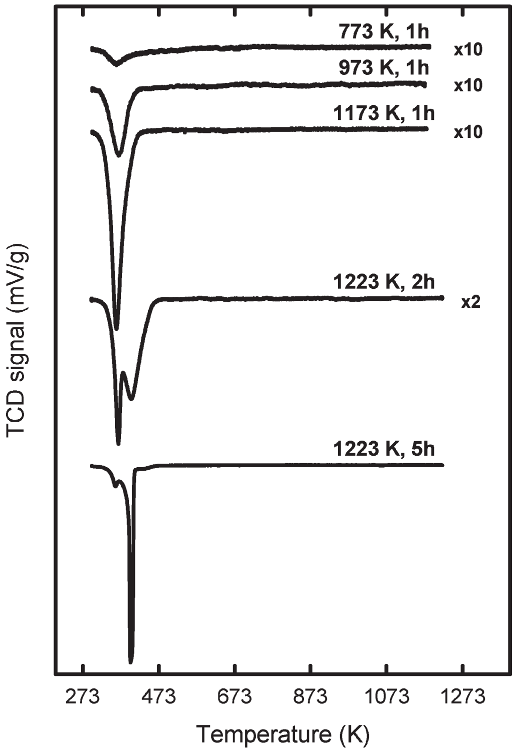

Figure 2. TPO traces recorded for CeO_2 after reduction at the temperatures indicated.

in coincidence with the reduction conditions at which a decreasing trend of pulse consumption starts to be observed. As deduced from figure 1, such behaviour is a common feature for all four oxides. However, the temperature at which the trace of pulse consumption declines differs between the oxides compared. The resolution of the plots is limited by the number of available experimental data points; nevertheless, the observed trends clearly reveal that the onset temperatures, T_h, at which the inflexions in behaviour would appear follow the trend La/Ce $<$ Y/Ce $<$ CeO_2. As described below, such temperature values also define the onset of change for other chemical features of the samples; we will interpret these changes as related to the segregation of hexagonal sesquioxide phase.

Figures 2 and 3 show the TPO traces recorded for CeO_2 and for the L40C sample reduced at increasing temperatures. It is observed that when the reduction temperature is higher than T_h (1223 K for CeO_2 and 973 K for L40C) these traces can be deconvoluted into several peaks. Conversely, below T_h the TPO profiles are characterised by a single peak or by the lack of well defined peaks with significant intensity. These trends are also observed for L20C and Y20C.

In addition, the H_2-TPD traces give interesting information about the reduction process for ceria and for the mixed oxides. In figure 4 it is observed that after reduction at 973 K the H_2-TPD trace of L40C splits into two peaks. As a second example, figure 5 shows a similar pattern for the Y20C mixed oxide, giving two hydrogen features when reduced at 1223 K.

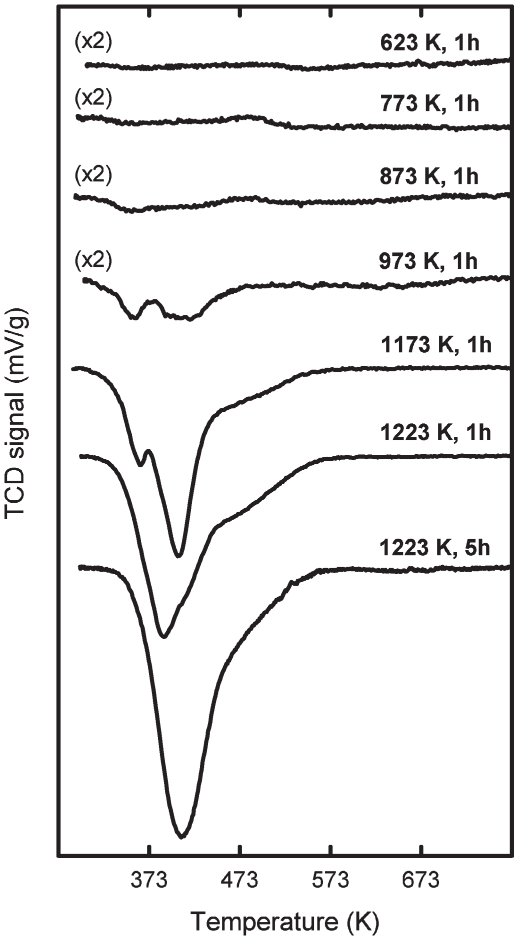

Figure 3. TPO traces recorded for the L40C mixed oxide after reduction at the temperatures indicated.

The XRD diagrams for CeO_2 (figure 6) show segregation after reduction at 1223 K, in fairly good coincidence with the results discussed above. In the case of the L40C mixed oxide, the segregation is detected at a lower reduction temperature (973 K) (figure 7), also in good agreement with the observed splittings of the TPO and H_2-TPD traces (figures 3 and 4). This allows us to confirm the existence of a correlation between the reduction conditions at which the segregation of the hexagonal phase takes place, as defined in each case by means of T_h, and some characteristic features of the chemical behaviour of the samples.

The XRD pattern of a severely reduced Y20C mixed oxide (figure 8) is rather complex and deserves a special comment. It can be interpreted by taking as references other mixed oxide diffraction studies reported in the literature. Wallenberg et al. [16,17] studied a sample with the same composition as Y20C and observed that the electron diffraction patterns show some diffuse reflections coincident with those of a cubic sesquioxide, although not all the expected spots for a C sesquioxide structure are present. The authors interpret such an observation as suggesting the formation of what they call a “modulated fluorite” structure, for which the long-range ordering of the vacancies in definite directions allows the observation of some of the characteristic

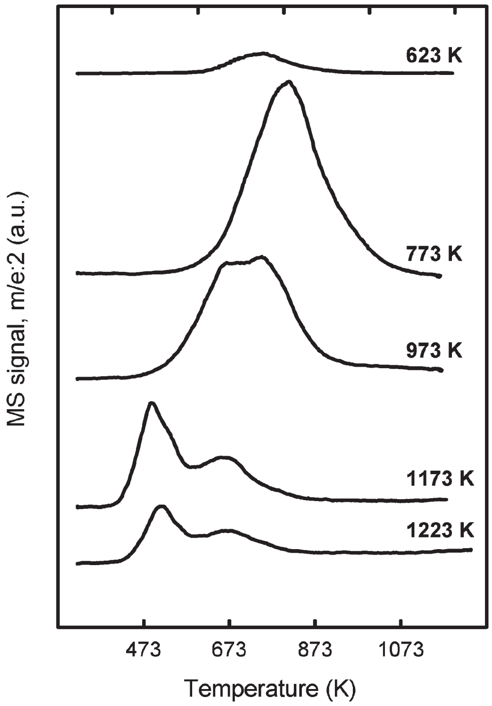

Figure 4. H_2-TPD traces of the L40C mixed oxide reduced in a flow of hydrogen for 1 h at the indicated temperatures and cooled down in hydrogen atmosphere.

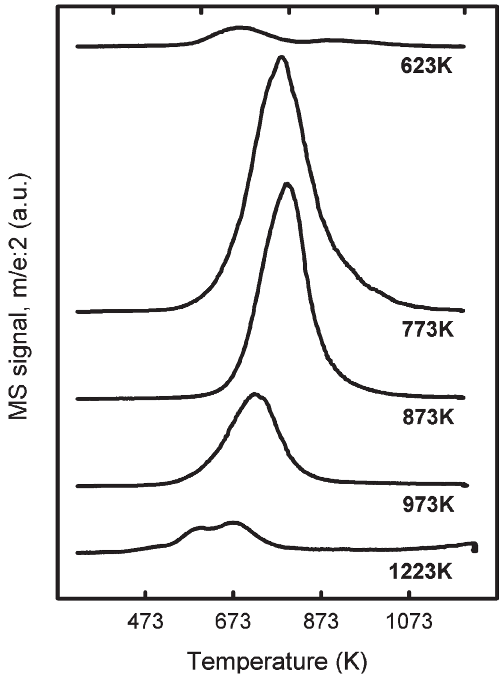

Figure 5. H_2-TPD traces of the Y20C mixed oxide reduced in a flow of hydrogen for 1 h at the indicated temperatures and cooled down in a hydrogen atmosphere.

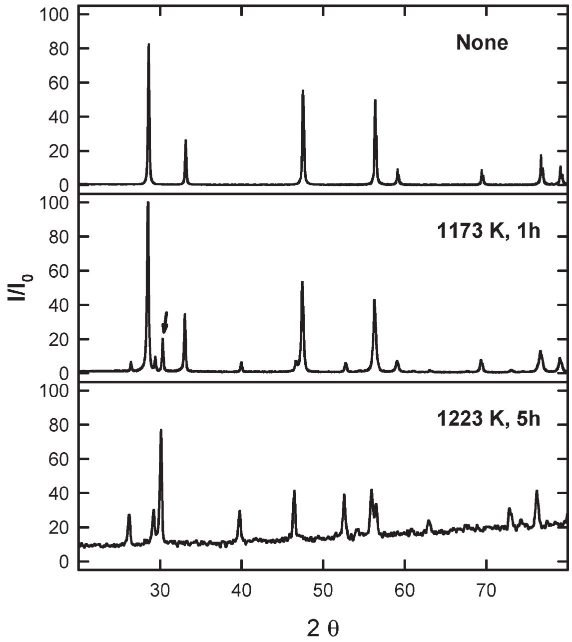

Figure 6. XRD patterns of CeO_2 after the indicated reduction treatments.

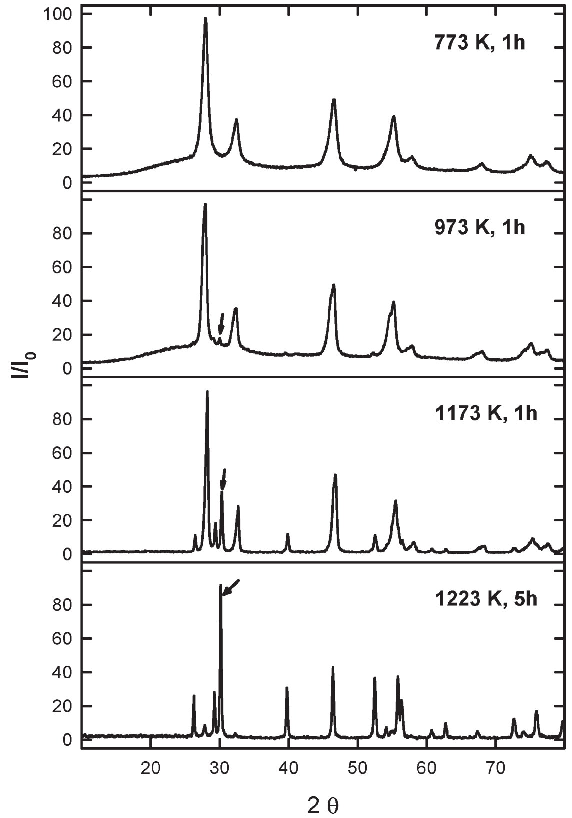

Figure 7. XRD patterns of the L40C mixed oxide after the indicated reduction treatments.

features of the C sesquioxide. Such diffraction features become apparent in the XRD pattern of yttria–ceria mixed oxides with 50 mol% of yttria [18,19], and grow in relative intensity with the content of yttria. A similar observation has also been reported by El Houte et al. [20] for the case of a Gd/Ce mixed oxide with 49 mol% of gadolinia. These authors did not observe, either, the complete set of lines expected for the C-type sesquioxide. In the pattern of figure 8, the lines labelled as F can be attributed to a fluorite phase, which is related to the appearance of lines asso-

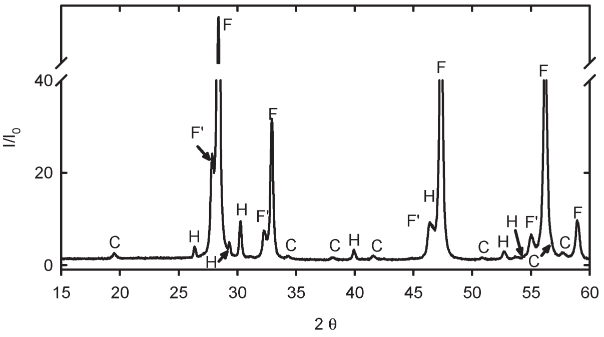

Figure 8. XRD pattern of the Y20C mixed oxide after 5 h reduction in a flow of hydrogen at 1223 K.

ciated to vacancy ordering labelled as C. All the F lines show splitting towards lower diffraction angles, indicating the formation of another fluorite phase, F′. In the case of this F′ phase, because of the low intensity of its main peaks, it is not possible to observe the existence of satellite peaks, which would provide evidence for the long-range ordering of its vacancies. Finally, as expected from the above-mentioned reoxidation and H_2-TPD studies, the lines labelled as H show clear evidence for the segregation of hexagonal sesquioxide.

3.2. Stoichiometric limits for the segregation of hexagonal sesquioxide phases

The detailed reoxidation studies – pulses followed by TPO – allowed us to quantify the vacancy concentration created following each of the reduction treatments. In addition, the composition of the samples allows the estimation of the initial vacancy concentration, assuming that the substitution of two Ce atoms by La generates one oxygen vacancy. Thus, on the grounds of the results described in section 3.1 one can calculate by a simple addition the vacancy concentration compatible with the absence of segregation and the content for which hexagonal sesquioxide segregation is detected (table 1).

The results shown in table 1 suggest that, contrary to the large differences observed when comparing the temperatures at which segregations are detected, the stoichiometries at which they occur are very similar for ceria and for the L20C and L40C samples. Consistent with this observation, the ionic radii of the Ce^{3+} cation is very similar to that of La^{3+} [10]. This means that the distortion introduced by the substitution of cerium by lanthanum in the lattice resembles the instability introduced in the structure by the reduction of an equivalent amount of Ce^{4+} ions to Ce^{3+}. In this way we find a basis to understand why, from the viewpoint of the stoichiometric limits for phase segregation, the behaviours of CeO_2, L20C and L40C are very similar.

In the phase diagram for pure ceria there is a region, with x ranging from 1.5 to 1.714, in which the hexagonal sesquioxide, Ce_2O_3, and the fluorite-related iota phase, $CeO_{1.714}$ [11,12], coexist. In accordance with this, once the composition of the iota phase is reached, further reduction would lead to hexagonal phase segregation. It can be observed in table 1 that the composition $x = 1.714$ is within the limits for which the phase segregation for CeO_2, L20C and L40C was detected. We should mention at this point that some metastable reduced phases with $x < 1.714$ have also been tentatively proposed in detailed phase diagram studies of the higher rare earth oxides [12,13]. Nevertheless, even the authors that proposed the formation of such metastable phases failed to isolate them when using pure hydrogen as the reducing agent [13]. Some other authors working in less aggressive reducing atmospheres also were not able to identify such intermediate strongly reduced phases [14].

It is also evident from the data in table 1 that, from a stoichiometric viewpoint, the structure of the Y20C mixed oxide is more stable towards segregation of the hexagonal sesquioxide than those of the other samples. Thus, when compared with L20C, L40C or even with CeO_2, it becomes clear that the introduction of a smaller guest cation, Y^{3+}, leads to fluorite-type structures which tolerate without segregation a higher content of oxygen vacancies.

4. Discussion

In section 3 we have focussed on the observation of chemical features which can be used to detect structural transformations taking place when pure ceria or La/Ce and Y/Ce mixed oxides are severely reduced. In this discussion we shall comment on some key chemical arguments that can help to understand why those features appear.

First, regarding the chemistry of the reoxidation processes, it should be mentioned that, even for those reduction treatments which did not yet lead to segregation of the hexagonal phase, the pulse treatment did not cause the

Table 1
Stoichiometric limits within which segregation of the hexagonal sesquioxide phase occurs.

Sample	Composition		Hexagonal sesquioxide segregation	
	After pretreatment [a]	After reduction	Not detected	Detected
CeO_2	CeO_2	CeO_x	$x \geqslant 1.742$	$x \leqslant 1.687$
L20C	$Ce_{0.8}La_{0.2}O_{1.9}$	$Ce_{0.8}La_{0.2}O_x$	$x \geqslant 1.762$	$x \leqslant 1.685$
L40C	$Ce_{0.6}La_{0.4}O_{1.8}$	$Ce_{0.6}La_{0.4}O_x$	$x \geqslant 1.753$	$x \leqslant 1.694$
Y20C	$Ce_{0.8}Y_{0.2}O_{1.9}$	$Ce_{0.8}Y_{0.2}O_x$	$x \geqslant 1.679$	$x \leqslant 1.638$

[a] Confirmed from ICP analysis and by integration of the TPR signal reported in [2].

complete reoxidation of the sample (figure 1). Thus, the amounts of oxygen determined from the TPO experiments are not negligible. This may suggest that the pulse reoxidation at room temperature leads to the formation of an oxidised crust, which prevents further migration of oxygen to the core of the mixed oxide particles. This assumption would be consistent with the known data on the thermal dependence of ionic conductivity for ceria-doped mixed oxides [1]. When the TPO proceeds and oxygen diffusion is activated by elevated temperatures, it would be reasonable to detect a single oxygen consumption peak, as seen in the traces recorded after reduction treatments at 773, 973 and 1173 K in figure 2.

If the reduction treatment of the sample is carried out at temperatures higher than T_h, TPO traces showing several peaks might be expected. The reoxidation of the hexagonal phase would require not only the activation of oxygen diffusion to the core of the particles, but also the rearrangement of the cation sublattice. As the cubic phase content decreases with the reduction temperature and the specific surface area of the samples decreases through sintering [2], the oxygen consumption in the pulse reoxidation treatment also decreases.

Further elements of complexity such as: (i) possible segregation of components during the reduction, (ii) bi- or multimodal crystallite size distribution, as noted in [2], or (iii) eventual overheating of the sample due to very fast reoxidation [7], can make the TPO traces more complex than would be expected for the simple two-phase model considered in the above paragraph. Nonetheless, in accordance with these comments, for those situations in which a single fluorite-like phase is formed during the reduction treatments, we have never observed TPO traces with more than one peak.

However, it must be pointed out that, even for the case of the strongest reduction treatments, leading to near complete transformation of the cubic fluorite-like phase into the hexagonal sesquioxide, the pulse treatment at room temperature leads to a non-negligible level of reoxidation. In the case of ceria this effect is particularly apparent, becoming less important as the Ln^{3+} content increases (figure 1). These observations can be correlated with high-resolution electron microscopy (HREM) studies reported elsewhere [2,21]. Thus, in [2] it was observed how pure ceria reduced for 5 h at 1223 K, showing an XRD pattern without any indication of characteristic fluorite features, gave HREM micrographs in which an amorphous layer covers the Ce_2O_3 sesquioxide particles. This suggests that this amorphous layer, likely fully oxidised ceria, prevents the further reoxidation of the sample, which, in principle, is known to be extremely reactive towards oxidation.

Very recently [21], we have also observed by HREM that micrographs of a heavily reduced La/Ce mixed oxide sample, exposed to air, showed indications of epitaxial growth of dioxide layers on a reduced hexagonal sesquioxide structure. The technique used for this interpretation, developed in our laboratory, is based on the digital processing of Moiré fringe patterns, which are apparent in those micrographs [22,23]. The difference with the case of ceria can be understood assuming that, in its case, the higher reactivity induces the very fast formation of an amorphous protective layer, while the lower heat of reaction for the mixed oxide allows the formation of an ordered epitaxial thin protective film.

Taking account of the formation of protective layers on the reduced phases, the points mentioned above increase confidence in the protocol described in section 2 to detect by XRD the formation of sesquioxide segregation for reduced samples. This is further supported by the good correlation shown between the detection of XRD peaks of very low relative intensity, showing the incipient formation of hexagonal sesquioxide, as seen in figure 7 (973 K, 1 h), and the chemical phenomena which have been identified as fingerprint indications of the segregation of the sesquioxide phases.

Regarding the H_2-TPD results, for reduction temperatures lower than those at which segregation occurs, the traces are characterised by the presence of a single peak. For reduction temperatures at which segregations are observed, a second feature, peaking at lower temperatures, is seen in the H_2-TPD traces (figures 4 and 5). This new peak increases in relative intensity with respect to the former as the reduction temperature increases. The most feasible interpretation of this behaviour would be to assume that this new peak corresponds to hydrogen desorption from the surface of the hexagonal sesquioxide. The higher the reduction temperature, the higher would be the fraction of hexagonal phase and the lower the content of fluorite-like phase, in agreement with the above reasoning.

The total amounts of desorbed hydrogen, obtained by integration of the H_2-TPD traces, decrease with the reduction temperature. This suggests a surface nature for the desorbed hydrogen, in agreement with previous reports from our laboratory on the characterisation of reduced ceria samples [24]. The estimated surface hydrogen concentration, determined from the specific surface areas of the reduced samples, are compatible with this proposal of surface adsorbed hydrogen forms.

There are two more arguments to be addressed as conclusions. The first one is to highlight the interest of these tests for the *in situ* detection of sesquioxide segregation. Both the TPO and H_2-TPD traces give useful and very sensitive tests to detect if a fluorite-like mixed oxide sample has undergone sesquioxide segregation. The tests can be performed using equipment usually available in catalysis laboratories, so avoiding contact with air, and also skipping the inconvenience of the fast and careful recording of XRD patterns. We must highlight that, when only very tiny sesquioxide diffraction peaks are observed, the TPO or H_2-TPD traces already showed clear indications of the occurrence of segregation.

The second argument concerns the pertinence of the severity of the reduction treatments carried out in this work in relation to the actual conditions which the TWC catalysts experience. Although we must recognise that some of the treatments given to these samples are much more severe than those at which TWC catalysts are conventionally exposed, it should be remembered that one of the most attractive goals now pursued is to extend the life of the TWC catalysts, in order to obtain the best fitting between the duration of the catalyst and that of the vehicle itself in the future. Thus, when dealing with the development of new formulations, it is usual in industrial practice to expose the catalysts to testing conditions far more severe than those occurring in the ordinary working regime. In this sense, the tests reported here would allow the classification of new ceria-based mixed oxide formulations according to their resistance to the formation of sesquioxide segregations. It would be expected that high temperature excursions or prolonged use of the catalyst cartridges would eventually lead to this deleterious effect, following similar trends to those determined in our tests.

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References

[1] H. Inaba and H. Tagawa, Solid State Ionics 83 (1996) 1.

[2] S. Bernal, G. Blanco, G. Cifredo, J.A. Pérez Omil, J.M. Pintado and J.M. Rodríguez-Izquierdo, J. Alloys Comp. 250 (1997) 449.

[3] M. Ozawa, M. Kimura and A. Isogai, J. Mater. Sci. 26 (1991) 4818.

[4] N. Miyoshi, S. Matsumoto, M. Ozawa and M. Kimura, SAE paper no. 891870, Society of Automotive Engineers, Dearborn, MI (1989).

[5] S. Matsumoto, N. Miyoshi, T. Kanazawa, M. Kimura and M. Ozawa, *Catalytic Science and Technology*, Vol. 1, eds. S. Yoshida, N. Tabezawa and T. Ono (Kodansha/VCH, Tokyo/New York, 1991) p. 335.

[6] T. Kirchner, A. Dounerstag, A. König and G. Eigenberger, Preprints of CAPOC4, Brussels, April 9–11, 1997, Stud. Surf. Sci. Catal., to be published.

[7] G. Blanco, Dr. thesis, University of Cadiz (1997).

[8] V. Perrichon, A. Laachir, G. Bergeret, R. Fréty, L. Tournayan and O. Touret, J. Chem. Soc. Faraday Trans. 90 (1994) 773.

[9] A. Laachir, V. Perrichon, A. Badri, J. Lamotte, E. Catherine, J.C. Lavalley, J. El Fallah, L. Hilaire, F. Le Normand, E. Quéméré, G.N. Sauvion and O. Touret, J. Chem. Soc. Faraday Trans. 87 (1991) 1601.

[10] R.D. Shannon, Acta Crystal. A 32 (1976) 751.

[11] B.G. Hyde, D.J.M. Bevan and L. Eyring, Proc. Roy. Soc. A 259 (1966) 70.

[12] L. Eyring, in: *Handbook on the Physics and Chemistry of the Rare Earths*, eds. K.A. Gschneidner and L. Eyring (North-Holland, Amsterdam, 1979) chapter 27, p. 337.

[13] R.P. Turcotte, J.M. Warmkessel, R.J.D. Tilley and L. Eyring, J. Solid State Chem. 3 (1971) 265.

[14] U. Lott, H. Rickert and C. Keller, J. Inorg. Nucl. Chem. 31 (1969) 3427.

[15] S. Bernal, G. Blanco, J.J. Calvino, G.A. Cifredo, J.A. Pérez-Omil, J.M. Pintado and A. Varo, Stud. Surf. Sci. Catal. 82 (1994) 507.

[16] R. Wallenberg, R. Withers, D.J.M. Bevan, J.G. Thompson, P. Barlow and B.G. Hyde, J. Less. Comm. Met. 156 (1989) 1.

[17] R.L. Withers, R. Wallenberg, D.J.M. Bevan, J.G. Thompson and B.G. Hyde, J. Less Comm. Met. 156 (1989) 17.

[18] D.J.M. Bevan, W.W. Baker, T.C. Parks and R.L. Martin, in: *Rare Earth Research III*, ed. L. Eyring (Gordon and Breach, London, 1965) p. 441.

[19] N. Gabbitas, J.G. Thompson, R.L. Withers and A.D. Rae, J. Solid State Chem. 115 (1995) 23.

[20] S. El Houte and O.T. Sörensen, Internal Report Riso-M-2495, Risö National Laboratory, Roskilde, Denmark (1985).

[21] G. Blanco, J.J. Calvino, C. López-Cartes, J.A. Pérez-Omil, J.M. Pintado and J.M. Rodríguez-Izquierdo, Inst. Phys. Conf. Ser. 153 (1997) 387.

[22] S. Bernal, F.J. Botana, J.J. Calvino, G.A. Cifredo, J.A. Pérez-Omil and J.M. Pintado, Catal. Today 23 (1995) 219.

[23] J.A. Pérez-Omil, Dr. thesis, University of Cadiz (1994).

[24] S. Bernal, J.J. Calvino, G.A. Cifredo, J.M. Rodríguez-Izquierdo, V. Perrichon and A. Laachir, J. Catal. 137 (1992) 1.