

Investigation by Means of H₂ Adsorption, Diffraction, and Electron Microscopy Techniques of a Cerium/Terbium Mixed Oxide Supported on a Lanthana-Modified Alumina

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N₂ adsorption at 77 K, temperature-programmed desorption (TPD), X-ray and neutron diffraction, and high-resolution electron microscopy (HREM) were used to characterize a Ce_{0.8}Tb_{0.2}O_{2-x}/La₂O₃-Al₂O₃ oxide. This research shows that the supported cerium/terbium mixed oxide has good thermal stability up to 700 °C under H₂ (5%)/Ar and above this temperature in air or inert atmosphere. A combination of HREM and hydrogen chemisorption is shown to be a good method for estimating the dispersion of the supported cerium/terbium mixed oxide. The parallel study of its structural evolution also provides some interesting data on the deactivation of the supported Ce_{0.8}Tb_{0.2}O_{2-x} by reaction with the supporting alumina at 900 °C under H₂ (5%)/Ar and the formation of a LnAlO₃ perovskite phase.

1. Introduction

The latest generation of three-way catalysts (TWCs) requires new redox materials with an enhanced oxygen storage capacity and a wider temperature range for effective operation.¹ Although most of the recent literature concerning alternative materials for TWC applications deals with Ce/Zr-based systems,^{2–5} various studies performed in our laboratory have shown that both redox properties (OSC, oxygen storage capacity, and OBC, oxygen buffering capacity) and thermal stability can also be improved, in comparison with pure ceria, by incorporation into the CeO₂ lattice of other dopants such as La, Y, and particularly Tb.^{6–8}

Deactivation due to the high temperature and oscillating chemical environment under which they operate

is known to be one of the most challenging problems in ceria-based TWC catalysts. The reaction of reduced CeO₂ with the Al₂O₃ support leading to the perovskite CeAlO₃ phase is generally acknowledged as a major cause of this deactivation.^{9–12}

According to the literature,^{13,14} one way of preventing this undesirable deactivation mechanism consists of modifying the alumina support by surface deposition of lanthana. It is well-known¹⁵ that La³⁺ and Ce³⁺ have very similar ionic radii. Likewise, both La and Ce sesquioxides exhibit the hexagonal A-type structure of Ln₂O₃. Accordingly, doping the alumina with lanthana might allow for the formation of a mixed surface phase, which might act as a barrier preventing the reaction of Ce³⁺ (or Tb³⁺) with the Al₂O₃ support.

In ref 16, we report on a study of the influence of the pH of the impregnating solution on the microstructural nature of a La-modified alumina as a key parameter to be determined before its future application as the support for pure CeO₂ or a cerium/terbium mixed oxide.

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In a preliminary study,¹⁷ the La₂O₃/Al₂O₃-supported cerium/terbium mixed oxide was characterized using several complementary techniques such as TPD, XRD, HREM, FTIR spectroscopy and XPS analysis. Among several other results, such investigation allowed the microstructure of the supported mixed oxide prepared in this way to be characterized and the incorporation of La³⁺ species into the cerium/terbium mixed oxide lattice to be detected, thus revealing the complexity of this multicomponent system. In this paper, we are mainly concerned with the evolution of the structural and some of the chemical properties of the Ce_{0.8}-Tb_{0.2}O_{2-x}/La₂O₃-Al₂O₃ system when submitted to different aging treatments.

2. Experimental Section

2.1. Sample Preparation. The support used in this work consists of a transition Al₂O₃^{18,19} kindly supplied by Condea. Its BET surface area, as determined by N₂ adsorption at 77 K, was 140 m²g⁻¹. The alumina sample was then doped with lanthana (20 g per 100 g of alumina). As previously reported,¹⁷ lanthana-modified alumina was prepared using an incipient wetness technique from an aqueous solution of La(NO₃)₃·6H₂O. After a single impregnation stage, the sample was dried at 80 °C for 10 h and finally calcined at 900 °C for 4 h. Before impregnation, the pH of the precursor solution was adjusted to pH = 6 to avoid any undesirable acid attack on the alumina support.¹⁶ Following an analogous method, a solution of cerium(III) and terbium(III) nitrates in a 4:1 molar ratio was deposited onto the La-modified alumina support using a weight ratio of 20 g of mixed oxide per 100 g of La-modified alumina. Finally, the sample was submitted to calcination at 700 °C for 4 h to obtain the mixed oxide (fresh sample). The chemical composition of the supported mixed oxide was selected as the more suitable for TWC application in accordance with our previous studies on the massive cerium/terbium mixed oxide system.^{7,8} The resulting weight composition of the catalyst prepared in this way is 16.7% cerium/terbium mixed oxide, 13.9% lanthana, and 69.4% alumina.

After preparation, and before experimentation, the sample was submitted to an "in situ" cleaning pretreatment consisting of heating in a flow of O₂ (5%)/He for 1 h at 550 °C, followed by cooling under a flow of O₂ (5%)/He to 150 °C, and finally, cooling to ambient temperature in a flow of He. In this way, a reproducible starting redox state for the supported cerium/terbium mixed oxide was obtained.

The reduction protocols consisted of heating the sample under a flow of H₂ (5%)/Ar (60 mL min⁻¹) from 25 °C to the selected final temperature (*T*_{redn}) at a rate of 10 °C min⁻¹. The sample was kept at *T*_{redn} for 1 h, was then switched to a flow of Ar (60 mL min⁻¹) for 1 h, and finally was cooled to room temperature, again under a flow of Ar.

2.2. Characterization Techniques. After selection of the reduction temperatures by means of the temperature-programmed reduction of the prepared sample, the chemical behavior of the reduced mixed oxide was investigated by temperature-programmed desorption (TPD-H₂). Parallel evolution of the specific surface area was studied by means of N₂ adsorption at 77 K. The N₂ adsorption measurements were performed in a high-vacuum glass system in which a residual pressure of 10⁻⁶ Torr could be routinely achieved. The device was equipped with a capacitance gauge (MKS model BHS 1000), which enables measurements to be made in the range 0–1000 Torr to an accuracy of 0.1 Torr.

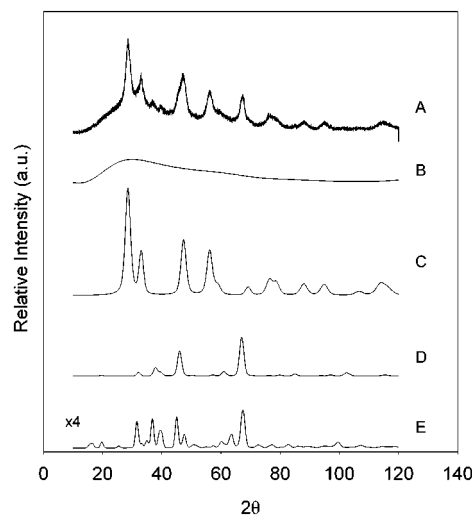


Figure 1. X-ray diagram obtained for the supported cerium/terbium mixed oxide calcined in air at 700 °C for 4 h (A) and the phases present, as deduced from Rietveld analysis: (B) background, (C) Ce_{0.8}Tb_{0.2}O_{2-x}, (D) η-Al₂O₃, and (E) θ-Al₂O₃.

The parameters of TPD experiments (sample weight of 200 mg, He flow of 60 mL min⁻¹, and heating rate of 10 °C min⁻¹) were selected as used for the unsupported mixed oxide studied previously.⁷

For the study of the structural evolution, the experimental techniques employed were X-ray diffraction (XRD), neutron diffraction (ND), and high-resolution electron microscopy (HREM). X-ray diffraction was performed at room temperature using a powder Philips PW1820 diffractometer, operating with Cu Kα radiation ($\lambda = 1.54$ nm). The 2θ angle ranged from 10° to 130°, and the counting step was 0.02°. In the case of the sample reduced at 900 °C, a room-temperature neutron diffraction diagram was obtained at the Berlin Neutron Scattering Center of the Hanh–Meitner Institut, with the E2 powder diffractometer. This apparatus is equipped with a multidetector covering a 2θ range of 80°, starting at 3°. The wavelength of the neutrons was 0.12175 nm. For the neutron data and some of the X-ray diagrams, Rietveld analysis was performed using the Fullprof program.²⁰ Finally, HREM images were recorded on a JEOL 2000 EX microscope equipped with a top-entry specimen holder and an ion pump. Its structural resolution is 0.21 nm.

3. Results and Discussion

3.1. X-ray Diffraction. In the case of the so-called fresh sample, i.e., calcined in air at 700 °C, a Rietveld analysis was carried out, the experimental multiphase spectra being decomposed into three single spectra corresponding to (1) a fluorite-type mixed oxide of cerium and terbium, (2) θ-Al₂O₃, and (3) a transition alumina designated as η-Al₂O₃ (to simplify calculations η-Al₂O₃ and the more ordered and related structure δ-Al₂O₃ were refined as a single phase). In addition, there was a significant amount of a spectra of an amorphous phase (see Figure 1), previously detected in the bare La-modified support (results not shown) but not present in the nonmodified transition alumina; this contribution can thus be interpreted as arising from a lanthanum-containing surface phase. No crystalline phases that could be attributed to either La₂O₃ phases resulting from its aging in air²¹ or LaAlO₃ could be

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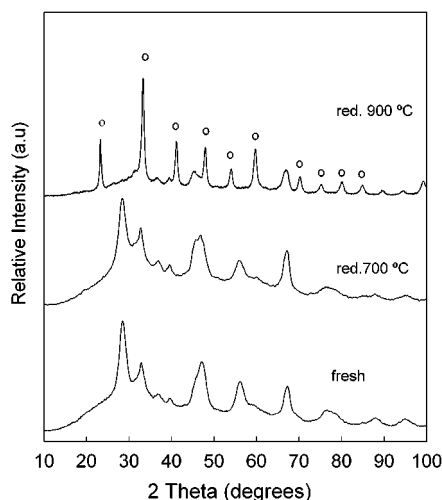


Figure 2. X-ray diagrams obtained for the supported cerium/terbium mixed oxide reduced at the indicated temperatures and only calcined at 700 °C. Aluminate phase (LnAlO_3) labeled as O.

identified. The percentages by weight of the crystalline phases deduced by Rietveld analysis were $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-x} = 15\%$, $\theta\text{-Al}_2\text{O}_3 = 14\%$, and $\eta\text{-Al}_2\text{O}_3 = 71\%$ (these figures are approximate because the Brindley coefficient was considered to be 1²²). These results are in good agreement with the nominal values. Also worth noting is the refined lattice parameter of $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-x}$, 0.5441 nm, a value significantly larger than expected for the fully oxidized $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_2$ (0.5294 nm). This finding indicates the presence of Ln^{3+} ions, either Tb^{3+} , La^{3+} , or both. XPS data reported in ref 17 support the view that the latter option is more likely. A significant amount of Tb^{3+} in the initial sample would explain this longer lattice parameter.

X-ray diffractograms obtained for the supported cerium/terbium oxide after different treatments are presented in Figure 2. As observed, the catalyst reduced at 700 °C shows only the characteristic peaks of the mixed oxide and those corresponding to alumina, in the same way as the calcined sample. There are no significant indications of the presence of any other phase. This is not the case with the $\text{CeO}_2/\text{Al}_2\text{O}_3$ system,¹¹ which, after the same treatment, shows the characteristic CeAlO_3 peaks. This means that lanthana deposited over the support in the case of the mixed oxide¹⁶ performs its function, at least at temperatures up to 700 °C, by hindering LnAlO_3 formation, whereas in the case of ceria supported on bare alumina, this does not occur. For the supported cerium/terbium mixed oxide reduced at 900 °C, the lanthanum-containing barrier is not effective, and the disappearance of the characteristic mixed oxide peaks and the appearance instead of the above-mentioned perovskite can be observed.

We also studied by Rietveld analysis the sample reduced at 700 °C, paying special attention to the width of the cerium/terbium mixed oxide peaks to quantify the average crystal size (see Table 1). A comparison with the value obtained for the fresh sample reveals that this parameter, like that of the lattice, does not change significantly upon reduction at temperatures up to 700 °C.

Table 1. Parameters Obtained by Rietveld Analysis of the X-ray Diagrams Recorded for the $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-x}/\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ Catalyst

treatment	<i>a</i> (nm)	average crystal size (nm)	Rwp ^a (%)	χ^2 ^b
calcination at 700 °C	0.5441	7.72	8.01	2.17
reduction at 700 °C	0.5445	7.73	8.03	2.02

^a Rwp = experimental data fit. ^b χ^2 = goodness of fit.

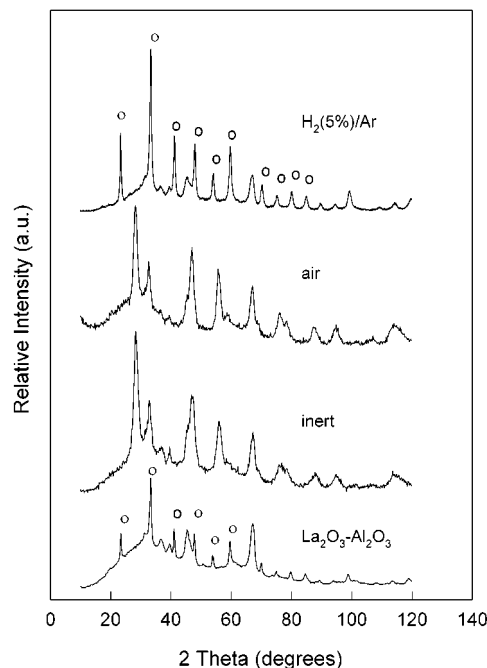


Figure 3. X-ray diagrams obtained for the supported cerium/terbium mixed oxide subjected to 900 °C for 1 h under the indicated atmospheres. For comparison, the diagram corresponding to the bare La-modified alumina support calcined in air at 900 °C is also included. (O) LnAlO_3 ($\text{Ln} = \text{Ce}, \text{La}, \text{Tb}$)

Regarding the stability of the supported cerium/terbium mixed oxide, the influence of different environments other than a flow of H_2/Ar was also studied. In particular, we investigated the effect of heating the sample to 900 °C in a flow of Ar (60 mL min^{-1}) and under static atmosphere of air. Figure 3 shows X-ray diagrams recorded after 1 h of treatment in both cases. As can be seen, the aluminate phase detected under H_2/Ar is not formed upon heating of the sample either in a flow of Ar or in static air. Only peaks that can be attributed to the mixed oxide and the support are observed. Also remarkable are the observations resulting from a comparison of the results commented on above with the X-ray diffractogram corresponding to lanthana-modified alumina calcined in air at 900 °C (also included in Figure 3). As can be seen, peaks corresponding to a LaAlO_3 phase appear in the latter case, whereas under analogous treatment conditions, such a phase is not detected for the supported mixed oxide.

The latter observation is consistent with the XPS data reported previously for this system.¹⁷ In accordance with these data, part of the lanthanum is incorporated into the cerium/terbium oxide lattice during the preparation of the sample, either during impregnation with the cerium/terbium mixed nitrate or, more likely, during the subsequent calcination step. Hence, the depletion of La^{3+} close to Al_2O_3 and the oxidizing atmosphere, which

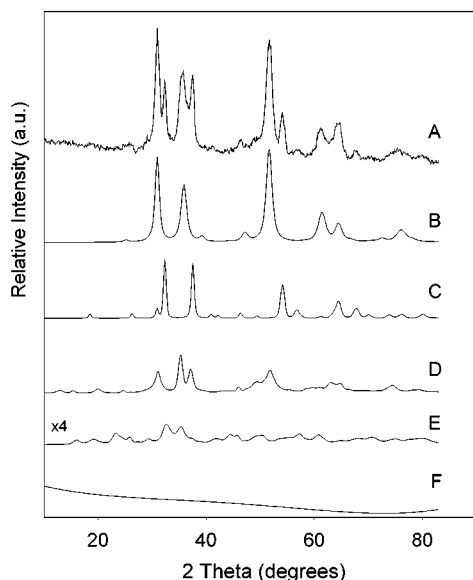


Figure 4. Neutron diffraction pattern obtained for the supported mixed oxide reduced at 900 °C in H₂ (5%)/Ar (A) and phases present as deduced by Rietveld analysis: (B) LnAlO₃, (C) θ -Al₂O₃, (D) η -Al₂O₃, (E) monoclinic Ln₂O₃, and (F) background.

prevents the formation of Ce³⁺ and Tb³⁺, would explain the absence of LnAlO₃ in the sample containing the cerium/terbium mixed oxide.

3.2. Neutron Diffraction. This technique was applied to characterize the supported cerium/terbium mixed oxide after reduction in H₂ (5%)/Ar at 900 °C. The Rietveld analysis ($\chi^2 = 1.03$ as defined in ref 20; see Figures 4 and 5) allows us to identify three different

crystalline phases, namely, a perovskite LnAlO₃, η -alumina, and θ -alumina, as well as a very minor amount of monoclinic Ln₂O₃ (perhaps due to a small impurity of another rare earth element). The same comments made above for the X-ray analysis are applicable here. It is worth noting that there were no traces of a cerium/terbium mixed oxide, which suggests, as already noted, that it reacted with part of the alumina until completely depleted to form a LnAlO₃ phase. Likewise, the amorphous phase that is present in the fresh sample could not be observed either (Figure 4), which also suggests that La³⁺ ions could have been incorporated into the perovskite LnAlO₃.

In the case of LnAlO₃, also detected by XRD, it was even possible to quantify the occupation degree of the Ln positions, because of the different neutron scattering factors of La, Tb, and Ce. The results were 74.3% for Ce, 18.4% for Tb, and 7.3% for La. This means that almost the entire Ln content in this phase is obtained from the supported mixed oxide. In the case of monoclinic Ln₂O₃, it was not possible to identify the lanthanide element, because of the small quantity of this phase (ca. 6 wt %).

3.3. High-Resolution Electron Microscopy. Figure 6 shows HREM images corresponding to the sample (a) only calcined and (b) reduced at 700 °C. This study revealed that, after the initial deposition and further calcination of the cerium/terbium nitrate precursors, the mixed oxide is actually present in the form of microcrystals with a fluorite-type structure, the size of which ranges from 4 to 16 nm.

After reduction at 700 °C, no significant changes were observed, the cerium/terbium mixed oxide remaining

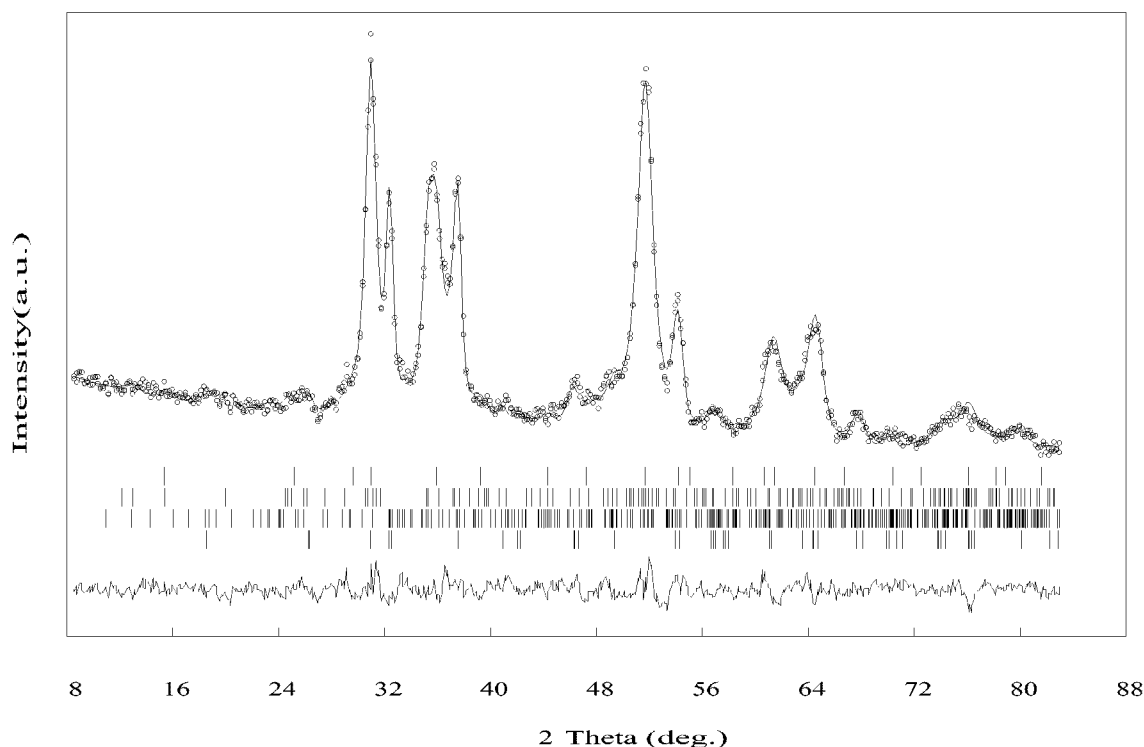


Figure 5. Neutron diffraction experimental diagram obtained for the supported mixed oxide reduced at 900 °C in a flow of H₂ (5%)/Ar (dots) and simulated spectrum obtained by Rietveld analysis. The spectrum obtained by subtracting the experimental and adjusted data is also represented (lowest trace). Vertical ticks indicate Bragg positions. There are vertical ticks at four heights, corresponding to the Bragg positions of the four phases, which are (from the highest to the lowest) η -Al₂O₃, θ -Al₂O₃, monoclinic Ln₂O₃, and LnAlO₃.

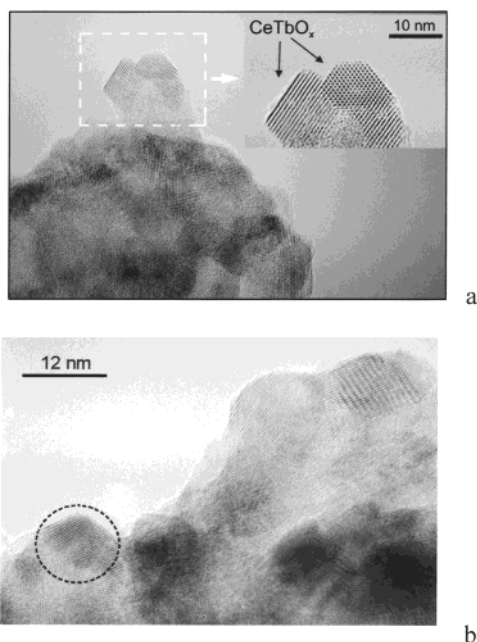


Figure 6. HREM images obtained for a $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-x}/\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst (a) calcined in air at 700 °C and (b) reduced in a flow of H_2 (5%)/Ar at 700 °C, where some cerium/terbium mixed oxide microcrystals can be observed.

present as microcrystals with an average size similar to that of the microcrystals detected for the fresh sample. This observation, which agrees with that from the X-ray diffraction as commented above, was confirmed by performing a study of the cerium/terbium mixed oxide crystal size distribution for both samples, which yielded mean crystal sizes of 7.6 and 8.4 nm for the fresh and reduced samples, respectively. The correspondence between the results obtained by XRD and HREM shows the consistency in this study.

3.4. TPD of Preadsorbed H_2 . For these experiments, the sample, after being submitted to the previously mentioned cleaning and oxidizing pretreatment, was heated under a flow of H_2 (5%)/Ar (60 mL min^{-1}) at the selected reduction temperature for 1 h and then cooled to 25 °C under the same atmosphere. Figure 7 shows the evolution undergone by the trace for m/e 2 as a function of T_{redn} . The signal of the catalyst reduced at 350 °C exhibits a single very low-intensity peak of H_2 centered at around 560 °C. In parallel, a significant amount of H_2O (m/e 18) could also be observed. This suggests that, during the reduction treatment at 350 °C, only a partial reduction of the mixed oxide occurs, some further reduction taking place during the TPD experiment. The latter process would result from the desorption as H_2O of a very significant part of the hydrogen chemisorbed on the sample when it is cooled to 25 °C under the flow of H_2 /Ar. Similar effects have previously been reported for pure ceria samples.²³

As in the case of earlier studies on ceria²³ and several ceria-based mixed oxides,⁶ the intensity of the hydrogen desorption peak reaches a maximum after reduction at 500 °C. As the reduction temperature is increased to 600, 700, and 900 °C, the TPD signal becomes progres-

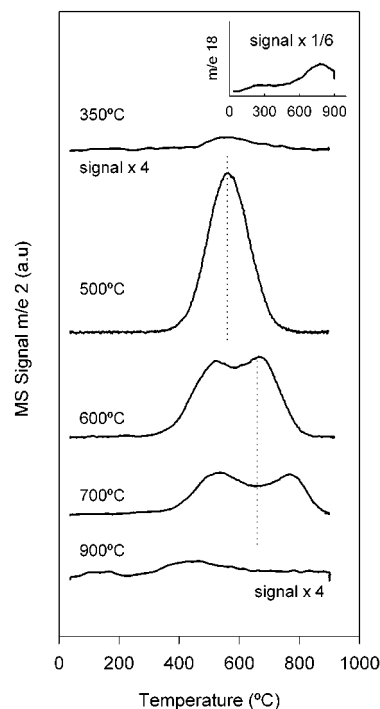


Figure 7. Signal of m/e 2 recorded by mass spectrometry during the TPD experiments of the supported cerium/terbium mixed oxide after treatment with H_2 (5%)/Ar for 1 h at the indicated temperatures.

Table 2. Study by Mass Spectrometry of H_2 Chemisorption on Supported Cerium/Terbium Mixed Oxide Treated under H_2 (5%)/Ar at the Indicated Temperatures for 1 h

reduction temperature (°C)	μmol of H_2 /g of mixed oxide
350 ^a	7.7
500	411.8
600	360.8
700	221.8/274 ^b
900	44.1

^a Together with the H_2 desorption, a strong desorption of H_2O takes place. ^b Sample reduced and evacuated at 700 °C, further reoxidized in O_2 (5%)/He at 550 °C, and finally treated with H_2 (5%)/Ar at 500 °C.

sively less intense and splits into two peaks. A parallel series of experiments performed on the bare support ($\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$) showed that, under the reduction conditions followed here, no significant H_2 chemisorption takes place. In accordance with these observations, the TPD- H_2 diagram might well be interpreted in terms of hydrogen desorption from the supported cerium/terbium mixed oxide. The spillover of some hydrogen from the mixed oxide onto the alumina support is another possibility to be considered. However, the similarity between the TPD- H_2 diagrams recorded for the pure^{6,24} and supported cerium/terbium mixed oxides with the same Ce/Tb molar ratio strongly suggests the interpretation proposed.

To quantify the hydrogen chemisorbed, we integrated the TPD traces in Figure 7, obtaining the results included in Table 2. Two main observations can be made: First, the amount of hydrogen adsorbed per gram of mixed oxide diminishes gradually as the reduction

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temperature increases. A similar trend was reported earlier for ceria²³ and ceria-containing mixed oxides.⁶ Second, it is confirmed that, as seen qualitatively in Figure 7, the treatment under H₂ (5%)/Ar at 500 °C leads to the maximum amount of chemisorbed hydrogen (411.8 μmol of H₂/g of Ce_{0.8}Tb_{0.2}O_{2-x}). Therefore, this treatment was selected to estimate the dispersion of the mixed oxide, i.e., the amount of exposed surface area of the mixed oxide per gram of cerium/terbium mixed oxide. Using the value corresponding to the limit of the capacity to adsorb hydrogen (4.5 atoms of H/nm²) previously determined for a pure cerium/terbium mixed oxide treated in the same way,²⁵ and considering that the process is limited to the surface, the dispersion was found to be 110 m² of Ce_{0.8}Tb_{0.2}O_{2-x} per gram of mixed oxide. This value is very close to that deduced from the crystal size distribution obtained using the HREM technique on the sample subjected only to calcination, which was 83 m²/g of the mixed oxide, which can be estimated by assuming a spherical geometry for Ce_{0.8}Tb_{0.2}O_{2-x} crystallites and a density of 7.132 g cm⁻³ of pure ceria. This good agreement confirms the usefulness of hydrogen chemisorption as a simple technique for evaluating the active surface area of the supported mixed oxide.

The data presented point to the deactivation of the supported mixed oxide for interaction with hydrogen as a consequence of reduction treatments at high temperature. In principle, this chemical behavior might be interpreted as the consequence of one or more different effects: (1) a loss of mixed oxide dispersion by a sintering process, (2) a loss of mixed oxide by transformation into a different phase, or (3) a change in the redox state of the mixed oxide. As already discussed, both XRD and HREM indicated that neither a significant change in the cerium/terbium mixed oxide dispersion nor other structural transformation occurs at least after reduction at temperatures up to 700 °C. Similarly, both X-ray and neutron diffraction studies indicate that, upon reduction at 900 °C, the mixed oxide disappears as a result of reaction with the support to form a new/different aluminate phase. Therefore, we conclude that the latter must clearly be responsible for the lowest value observed in Table 2, while changes in the redox state must account for the deactivation effect found in the lower reduction temperature range. To gain a better understanding of the influence of the redox state of the cerium/terbium mixed oxide on its hydrogen chemisorption capacity, an additional experiment was performed on the sample reduced at 700 °C. Following a subsequent evacuation with inert gas, the sample was reoxidized at 550 °C in a flow of O₂ (5%)/He, the treatment needed to attain the redox state presented by the supported cerium/terbium mixed oxide before the reduction, as described in the Experimental Section. After the reoxidation, the sample was reduced in H₂ (5%)/Ar at 500 °C for 1 h and was then cooled slowly in a flow of H₂ (5%)/Ar. The objective was to determine the degree of reversibility of the deactivation phenomenon, comparing the result with that obtained after reduction of the sample at 500 °C, the signal from which was taken as our reference.

As seen in Table 2, after the above treatment, the chemisorptive capacity was not fully recovered, as the value obtained by integration of the signal recorded (274 μmol of H₂ per gram of mixed oxide) was lower than that obtained for the sample reduced at 500 °C. This could be interpreted as indicating some irreversible loss of the mixed oxide by interaction with the support. Although, after reduction at 700 °C, the XRD analysis did not show formation of LnAlO₃ crystalline phase, the interaction of a proportion of the cerium/terbium mixed oxide with the alumina to form an incipient amorphous aluminate that crystallizes at a higher temperature, as was, in fact, detected after reduction at 900 °C, cannot be excluded.

As a final test, we tried to discount the possible influence of the textural evolution on the above-mentioned deactivation. For this purpose, the specific surface areas of the supported cerium/terbium mixed oxide following only calcination and following reduction at 700 and 900 °C were measured, and values of 92, 79, and 61 m²/g, respectively, were obtained. According to these results, a reduction of surface area does take place, but it is not large enough to explain by itself the deactivation effect observed. It should be noted that, after reduction at 700 °C, only 14% of the specific surface area of the fresh sample is lost, whereas almost 50% of the H₂ chemisorption is depleted merely by an increase in the reduction temperature from 500 to 700 °C (Table 2). The discrepancy in the evolution of chemisorption with respect to texture appears even more pronounced when the values obtained for the 700 and 900 °C reduction temperatures are compared: the surface area is reduced by 23% with increasing T_{redn} , whereas the H₂ adsorption is reduced by a factor of 5.

4. Conclusions

In the present paper, we have focused our studies on the stability of the supported cerium/terbium mixed oxide and on some aspects of its chemical behavior, thus continuing our previous work on this system.¹⁷ It should be noted that the study performed is the first involving these kinds of ceria-based mixed oxides that we can find in the literature concerning environmental catalysis. Moreover, from the results obtained in this study, the Ce_{0.8}Tb_{0.2}O_{2-x}/La₂O₃-Al₂O₃ oxide investigated appears to be a promising material with potential applications as a support for TWCs. The main contributions from this research can be summarized as follows:

(1) Analysis by XRD and HREM reveals that, upon reduction at 700 °C, no CeAlO₃ can yet be detected; it can, however, be detected with systems based on CeO₂ supported on bare alumina.¹¹ This demonstrates the effectiveness of doping with lanthana in the case of the cerium/terbium mixed oxide as a promoter for preventing Ce and Tb loss by reaction with alumina. Also worthy of note is our finding that the cerium/terbium mixed oxide is stable under thermal treatment in both static air and inert atmosphere, even at 900 °C.

(2) After reduction in H₂ (5%)/Ar at 900 °C, aluminate phase formation is detected by both X-ray and neutron diffraction. Rietveld analysis of the neutron diffraction pattern enabled the determination of the lanthanide composition of LnAlO₃, which is Ce/Tb-rich, although a minor fraction of La was also detected, as was previously

(25) Finol, D. Ph.D. Thesis, University of Cádiz, Cádiz, Spain, 1999.

found in the mixed oxide,¹⁷ thus confirming the complex character of the system.

(3) TPD-H₂ experiments indicate strong deactivation of the sample when the reduction temperature is increased. The XRD, ND, and HREM studies indicate that no significant changes in the cerium/terbium mixed oxide occur upon reduction at less than 700 °C, whereas reduction at 900 °C leads to the disappearance of the Ce_{0.8}Tb_{0.2}O_{2-x} active phase through its reaction with the support to form a new LnAlO₃ phase. These observations, together with the results from TPD experiments after reoxidation treatments and measurements of N₂ adsorption at 77 K, suggest that the observed deactivation effect is mainly related to the change of the redox state with reduction treatments below 700 °C and to the loss of the cerium/terbium mixed oxide above that temperature and that it is not significantly due to sintering phenomena.

(4) Finally, the study performed shows that a combination of HREM and hydrogen chemisorption after reduction at 500 °C can successfully be used to determine the dispersion of the supported cerium/terbium mixed oxide. It should be noted that the supported cerium/terbium mixed oxide will be more convenient for catalytic purposes than the bulk oxide, given the improved dispersion.^{7,22}

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