ELSEVIER

Journal of Alloys and Compounds 250 (1997) 449–454

Journal of
ALLOYS
AND COMPOUNDS

Reducibility of ceria–lanthana mixed oxides under temperature programmed hydrogen and inert gas flow conditions

S. Bernal, G. Blanco, G. Cifredo, J.A. Pérez-Omil, J.M. Pintado, J.M. Rodríguez-Izquierdo*

Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, Puerto Real 11510, Cádiz, Spain

Abstract

The present paper deals with the preparation and characterization of La/Ce mixed oxides, with La molar contents of 20, 40 and 57%. We carry out the study of the structural, textural and redox properties of the mixed oxides, comparing our results with those for pure ceria. For this aim we use temperature programmed reduction (TPR), temperature programmed desorption (TPD), nitrogen physisorption at 77 K, X-ray diffraction and high resolution electron microscopy. The mixed oxides are more easy to reduce in a flow of hydrogen than ceria. Moreover, in an inert gas flow they release oxygen in higher amounts and at lower temperatures than pure CeO_2. The textural stability of the mixed oxides is also improved by incorporation of lanthana. All these properties make the ceria–lanthana mixed oxides interesting alternative candidates to substitute ceria in three-way catalyst formulations.

Keywords: Ceria; Lanthana; Mixed oxides; Three-way catalysts; TWC; Reducibility; TPR; TPD; Oxygen exchange

1. Introduction

Ceria is nowadays one of the key components of three-way automotive catalysts (TWC) [1–3]. The roles attributed to CeO_2 in these systems are very diverse. They include the textural stabilization of the alumina support, the increase of the level of noble metals dispersion, the promotion of the activity for the water gas shift reaction and the ability to exchange oxygen with the environment [2–6]. The last property is of crucial importance to favor the redox reactions characteristic of the exhaust gas cleaning process.

Many academic and industrial laboratories work at present with the aim of improving the current performance of TWC to be able to accomplish with foresight more restrictive emissions regulations. On this line, a strategy followed by several authors is to add trivalent rare earth ions, Ln^{3+}, in any of the preparation steps. The formation, to some extent, of Ce/Ln mixed oxides generates extrinsic oxygen vacancies and, according to previous reports, promotes an increase in the rate and of the total amounts of oxygen exchange with definite atmospheres [7–10]. Whereas, the presence of other components in the TWC makes it difficult to conclude the true benefits of the formation of mixed oxides, and those rather related with the occurrence of alumina–rare earth or noble metal–rare earth interactions. These interaction effects can prevent even the possibility of knowing the actual composition of the Ce/Ln mixed phases which are present in the catalysts.

This paper is focused on the study of the behavior of Ce/La mixed oxides. In our approach we pursue the aim of getting fundamental information on the structural, textural and redox properties of several of these oxides with different La content. The absence of alumina or noble metals will help to make a realistic evaluation of some aspects of the true contribution of the mixed oxides to the potential improvements of oxygen exchange in TWC.

2. Experimental

Three La/Ce mixed oxides, with La molar contents of 20, 40 and 57%, have been prepared starting from appropriate mixtures of 1 M solutions of the corresponding nitrates. These nitrates, 99% pure, were 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 further washed five times with distilled water, and calcined in air at 873 K for 2 h. The names of the samples are L20C, L40C and L57C. A pure ceria sample, also prepared in our lab, is useful as a reference for the study of the ceria–lanthana samples.

---

*Corresponding author. Fax: (34-56) 834-924; Tel: (34-56) 834-924; e-mail: josemaria.izquierdo@uca.es

0925-8388/97/$17.00
PII S0925-8388(96)02825-3

A Philips, PW 1820, diffractometer allowed the recording of the X-ray diffraction patterns of the samples. The PC version of the diffraction profiles analysis software package, Fullproof, kindly provided by J. Rodriguez Carvajal [11], was used for preliminary studies of the X-ray patterns, and for a precise determination of the lattice parameters. The BET specific surface areas of the as-prepared and thermally treated oxides were obtained from N_2 adsorption isotherms at 77 K.

Temperature programmed desorption (TPD), and temperature programmed reduction (TPR), were used to characterize the mixed oxides. In both cases the analytical device was a mass spectrometer, VG Sensorlab 200D. Gas flow-rates, for inert gas in TPD, and for H_2 in the case of TPR, were always 60 ml/min. The heating rate was 10 K/min in all the experiments. The furnace and reactors available for these measurements enable us to work in a temperature range between 298 and 1223 K. Further details of the experimental device used for TPD and TPR and its calibration procedures are reported elsewhere [12].

The gases used in this work, Oxygen N50 grade, Helium N60 grade and Hydrogen N55 grade, were supplied by Air Liquide, being further purified by passing through zeolite 4A and, in the cases of helium and hydrogen, through oxytraps from Alltech.

A Jeol JEM-2000-EX electron microscope, with a structural resolution of 0.21 nm, was used to obtain images of severely reduced mixed oxides.

3. Results and discussion

After calcination in air at 873 K the ceria and ceria–lanthana samples present X-ray diffraction patterns characteristic of a fluorite type structure [13]. The lattice parameters obtained from the diagrams reveal how the unit cell dimensions gradually increase with the lanthanum content [14,15], Table 1. This result, and the analysis of the shape of the diffraction peaks, allows us to be confident of the formation of true homogeneous solid solutions. In this sense, for the studied range of compositions our results are in agreement with pioneering reports on the behavior of CeO_2–La_2O_3 and CeO_2–Y_2O_3 systems [14,16].

In order to clean the surface of the oxides and to reach a better reference state for all the samples, before running the TPD and TPR experiments, they were pretreated with flowing oxygen, for 1 h, at 873 K, slowly cooled down to 473 K also in oxygen, and further cooled down to ambient temperature in a flow of helium.

Table 1
Lattice parameters and quantitative TPR data for the La/Ce mixed oxides

	L20C	L40C	L57C
a	0.548	0.554	0.561
b	46.66	33.79	23.51
c	42.30	32.14	23.18

a: Lattice parameters (nm) of the La/Ce mixed oxide samples. $a_0(CeO_2)=0.5411$ nm.
b: Amounts of water (mg g^{-1} oxide) evolved in the TPR experiments.
c: Theoretical amounts of water (mg g^{-1} oxide) corresponding to the reduction of the La/Ce mixed oxides.

Fig. 1 shows TPR traces for *m/e* ratio 18, recorded with the mass spectrometer, for pure ceria and for the mixed oxides L20C, L40C and L57C. The samples were maintained at 1223 K for the time necessary to return to the signal baseline. That time is different for ceria (about 5 h) than for the mixed oxides (1–3 h). These signals can be unequivocally assigned to water produced by the reduction of Ce^{4+} to Ce^{3+}, with the subsequent elimination of the stoichiometric amount of oxygen.

The total amounts of water evolved from each sample can be calculated by integration of the signal vs. time plots. They are shown in Table 1, jointly with the theoretical amounts of water that would correspond with reduction of all the cerium ions, present as Ce^{4+} in the pretreated samples, to Ce^{3+} in the reduced samples. The good agreement of both values for each mixed oxide, within the limits of the experimental error for the TPR measurements, supports the assumption that the oxygen pretreated samples can be formulated as $La_{0.20}Ce_{0.80}O_{1.90}$, $La_{0.4}Ce_{0.6}O_{1.8}$ and $La_{0.57}Ce_{0.43}O_{1.715}$. Thus, the samples

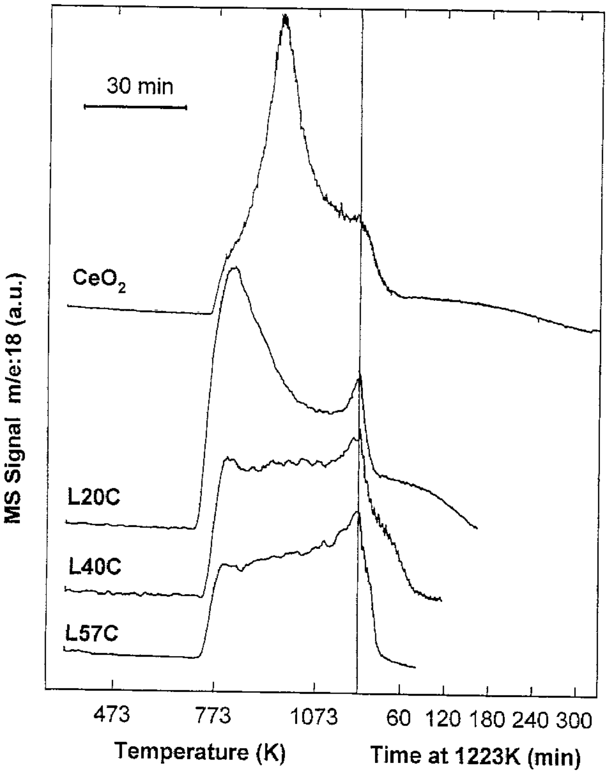

Fig. 1. Temperature programmed reduction H_2O traces (*m/e* 18) corresponding to ceria and lanthana–ceria mixed oxide catalyst samples. On the left hand side we represent the results obtained during the programmed increase in temperature. On the right hand side we show the water signal evolution with time at a constant temperature of 1223 K.

present 5, 10 and 14.25% of anion vacancies, in good agreement with the nominal values selected in the preparation step.

The TPR results (Fig. 1) deserve further analysis. The reduction of the mixed oxides, tracked through the water evolution signals, are quite similar for the three samples. The main difference refers to the intensity of the first peak, centered at 823 K. Thus, the amounts of water evolved, and the levels of reduction associated to that peak, follow the trend L20C>L40C>L57C. After the first peak the TPR traces for the mixed oxides show a continuous reduction signal up to 1073 K, and a second neat peak with leads in each case, after 1–3 h at 1223 K, to the complete reduction of the cerium to Ce^{3+}. If we compare the behavior of TPR signals of ceria with those of the mixed oxides we can highlight two differences. First, for the case of ceria there is a weak reduction effect in the range 600–800 K. Such effect has been attributed by several authors to the surface reduction of ceria [17–20]. Second, the trace corresponding to ceria from 800 to 1223 K is quite similar to the traces of the mixed oxides, although shifted 150 K to higher temperatures. It can suggest that the mechanisms involved in the bulk reduction of ceria and of the Ce/La mixed oxides are similar.

The TPD traces in inert gas confirm the different behavior of ceria and Ce/La mixed oxides, see Fig. 2. In these experiments the trends for the *m*/*e* ratio 32 resume the relevant information, taking account of oxygen evolution from the samples. It is observed that the progressive release of a very small amount of oxygen with the increase in temperature is the only effect shown by the pure ceria. Such effect, starting from 773 K, leads to a tiny separation of the signal from the baseline, without featuring any definite peak up to 1223 K. On the contrary, the mixed oxides release significant amounts of oxygen starting from 423 K. The TPD traces show in each case three definite peaks. From the integration of the oxygen signals it is possible to calculate the loss for each sample, as well as the global level of reduction corresponding to such losses. If we define the level of reduction as the percentage of Ce^{3+} with respect to the total cerium content of the sample, we obtain 1.3, 4.2 and 4.9% for the L20C, L40C and L57C samples, respectively. The reduction levels reached in the TPD experiments are of course lower, though significant, when compared to the TPR reductions in the flow of hydrogen.

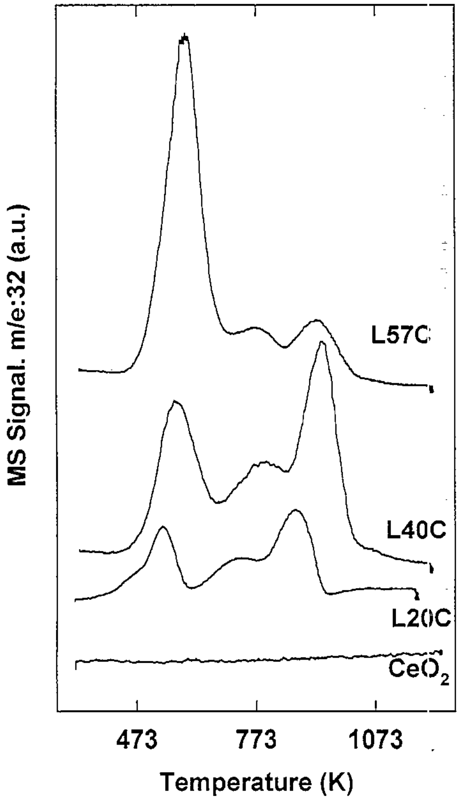

Fig. 2. Temperature programmed desorption O_2 traces (*m*/*e* 32) corresponding to ceria and lanthana–ceria mixed oxide catalyst samples.

One point which deserves comment is that the onset of oxygen loss under inert gas appears at lower temperature, 423 K, than in hydrogen, 740 K. This presumably striking fact could be understood assuming two different explanations.

The first one emphasizes that the oxygen loss takes place in each case by different mechanisms [21]. Thus, ceria and La/Ce mixed oxides adsorb hydrogen at 423 K, in such a way that a significant fraction of the exposed oxide ions transform into OH groups. The formation of vacancies would require in such case the recombination of neighboring hydroxyl groups to form water. However, in an inert atmosphere the formation of anion vacancies takes place through the direct elimination of oxygen along with the formation of surface oxygen vacancies which can eventually migrate to the bulk. The opposite trends in reducibility of the mixed oxides in the TPR (L20C> L40C>L57C) and in the TPD experiments (L57C> L40C>L57C) gives also additional support to the proposition of two neatly different mechanisms of oxygen loss depending on the surrounding atmosphere.

Previous studies on the diffusivity of oxygen in Ce/La mixed oxides prepared at high temperatures suggest that the bulk diffusivity of oxygen vacancies at temperatures below 573 K is low [22]. In that case the first step of the reduction in inert gas, Fig. 2, would essentially consist of a selective surface process. The reduction grade reached by the mixed oxides in inert gas flow after completion of the first TPD peaks are compatible with such a surface type process. This conclusion can be reached if, following the discussion on the surface oxygen concentration of ceria reported elsewhere [23,24], we assume the presence of about 10 O^{2-} ions (or oxygen vacancies) per square nm in the surface of the fluorite structured Ce/La mixed oxides.

A second alternative explanation allowing the understanding of the low temperature of oxygen desorption in the mixed oxides is to consider that, at least, the first TPD peak corresponds to desorption of superoxide species formed during the pretreatment with oxygen previous to the temperature programmed desorption experiments. In this respect it should be said that the oxygen desorbed amounts calculated from the first TPD peaks can be compatible with the existence of superoxide, O_2^- ions, nested in surface oxygen vacancies present in the mixed oxides. The lack of these oxygen peaks in the TPD spectra of ceria is consistent with its very low surface oxygen vacancy concentration. On the contrary, the mixed oxides have a vacancies content growing in parallel with the La concentration. From this point of view it would be easy to understand why the intensity of the first TPD peak runs in parallel with the addition of lanthana to the mixed oxide formulation.

Some literature reports can give support to the proposal of superoxide ions as responsible for the low temperature TPD oxygen peaks. In [25] the authors report on the superoxide species formed on evacuated ceria samples: they consider three different O_2^- types, the more stable being that nesting in surface oxygen vacancies. Also noteworthy of comment, such a type of superoxide is the only one whose concentration increases with that of the surface vacancies. Whereas, in the case of this pure ceria sample, the thermal stability of the superoxide ions is relatively low, being completely evacuated after 1 h of treatment at 373 K. In [26] the authors have established the formation of superoxide species on a rare earth sesquioxide: lanthana. Such O_2^- species are stable under 120 torr of oxygen at 473 K, requiring 30 min evacuation at that temperature for its complete elimination. In conclusion, these reports suggest the feasibility of formation of the superoxide species in the surface of the mixed oxides at the pretreatment conditions.

The textural stability of the ceria and/or mixed oxides is another interesting aspect for catalytic applications. It is well known that high or medium surface area ceria sinters at temperatures in excess of 773 K. This effect is particularly severe under reducing atmospheres. The lack of the ability to retain well developed surface areas under reaction conditions can restrict the oxygen exchange capacity of these oxides. In this sense it is worth while to observe the fact that the TWC must work effectively under a broad range of temperature–atmosphere settings. For some of these settings, particularly for those corresponding to low temperatures and mild reducing agents, the oxygen exchange processes will be restricted to the surface of the samples.

With this in mind we have measured the BET surface areas of the ceria and mixed oxide samples following four different reduction treatments in flow of hydrogen, for 1 h, at 773, 873, 973 and 1173 K. The results show that, in this respect, the mixed oxides are also overlying in properties to pure ceria, Table 2. Despite the fact that the Ce/La mixed oxides also experience significant losses in surface area, they always remain higher than those corresponding to ceria. To highlight as an example one of these results, the L40C sample retains 20 m^2 g^{-1} of active surface after reduction at 973 h, in comparison with pure ceria that retains only 5.3 m^2 g^{-1}, 10% of its initial surface area.

Table 2
Evolution of the BET surface areas (m^2 g^{-1}) of the ceria and La/Ce mixed oxide samples

	CeO_2	L20C	L40C	L57C
Fresh samples	51	68	46	27
Reduced at 773 K	51	57	46	29
Reduced at 873 K	13	25	35	20
Reduced at 973 K	5.3	7	20	12
Reduced at 1173 K	2.5	5	6.0	3.3

One more aspect to be considered in relation to the application of mixed oxides in TWC is the structural evolution of the samples exposed to prolonged high temperature treatments. The information recorded in this respect is interesting in relation with the deactivation of TWC catalysts.

The TPR results, shown in Table 1, point to the formation of $Ce_xLa_{1-x}O_{1.5}$ as a limit composition after the completion of such treatments. X-Ray diffraction and HREM data are currently available to this respect. To obtain these data we first treated the samples in a flow of hydrogen for 5 h at 1223 K. After evacuation in flowing helium at the same temperature, the samples were cooled at 191 K, and then treated with a mixture of diluted oxygen (5%) in helium. This treatment tries to avoid the abrupt exposition of the reduced oxides to the room atmosphere. In spite of that, the so treated samples make, for a moment, contact with the air. The X-ray diffraction diagrams of these reduced samples were immediately recorded, Fig. 3. Other portions of the same prepared samples were studied by HREM, Fig. 4.

The X-ray diagrams, Fig. 3, show the coexistence of two different phases. The more intense diffraction peaks correspond with the pattern of A-type hexagonal sesquioxides. In an experiment performed with strongly reduced ceria the only observed lines were also those of the A-type sesquioxide. In the case of the mixed oxides, lines corresponding to a C-fluorite type structure are also observed, although with weak intensities relative to those of the A variety. In an inset in Fig. 3 it is possible to notice two significant details. On the one hand, the fluorite lines are shifted with regards to the ideal CeO_2 structure in a sense which allows the taking into account of the existence of La^{3+}, or alternatively Ce^{3+}, in these crystallites. On the other hand, the broadening of the peaks associated to the C-type structure is indicative of the existence of smaller crystallites for this phase than for the A-type sesquioxide structure. This observation can be confirmed by HREM studies. The HR electron micrographs of the severely reduced Ce/La mixed oxides show a fraction of small particles with fluorite structure, and a major part of the

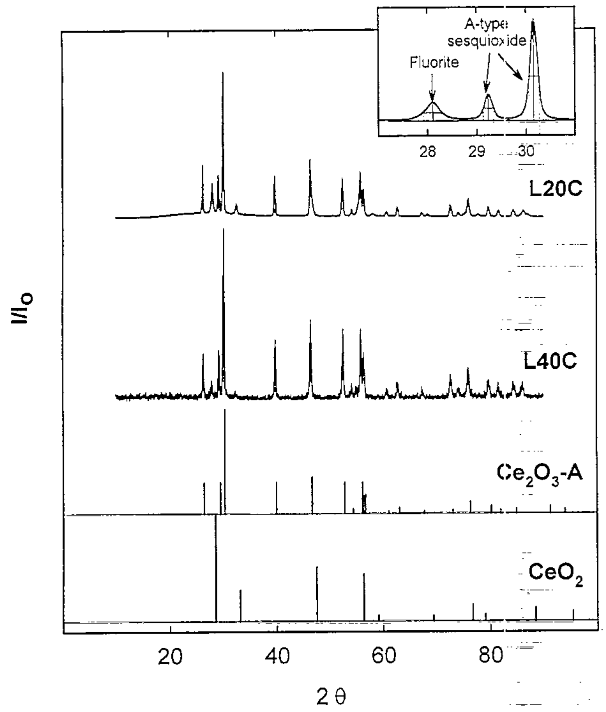

Fig. 3. Reference difraction patterns for cubic CeO_2 and hexagonal Ce_2O_3, and its comparison with the X-ray diffraction patterns of severely reduced L20C and L40C mixed oxides. The inset in the upper part of this figure corresponds to the pattern of the L20C sample.

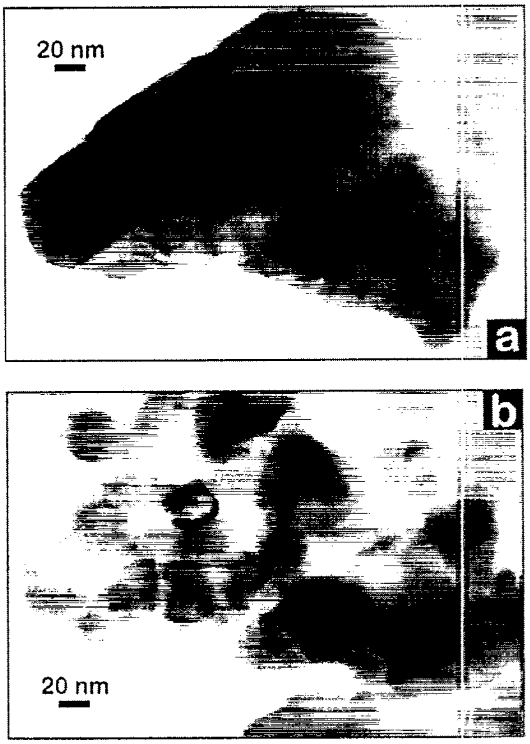

Fig. 4. High resolution electron micrographs representative of the heavily reduced L40C sample. (a) Large hexagonal sesquioxide particle and (b) small fluorite type crystallites.

sample as large particles with SAED patterns characteristic of the A-type structure. Moreover, the surface of the A-type reduced ceria shows clear evidence of being covered by a layer of amorphous material [24]. This behavior is less evident, though suspected, for the sesquioxide phase resulting from mixed oxide reduction.

These observations can be related with other previously discussed facts. Thus, the presence of small crystallites in the severely reduced mixed oxide samples, and its lack for pure ceria, are facts consistent with the higher residual BET surface areas shown by the mixed oxides following a high temperature reduction treatment. Consequently, such small crystallites are not observed for reduced ceria. According to the TPR results, we assume that following a severe reduction treatment in flow of hydrogen, all the ceria or Ce/La mixed oxide samples are in the sesquioxide state. Whereas, small crystallites, like those remaining in the mixed oxides, can be readily reoxidized when the sample contacts with air. Conversely, the A-type sesquioxide particles seem to undergo a surface reoxidation, leading to the formation of an amorphous crust which prevents the further reoxidation of the ceria or the reduced mixed oxide.

4. Concluding remarks

When treated under flow of hydrogen or inert gas, the Ce/La mixed oxides here studied present features of behavior which make them good candidates as potential components of TWC catalysts. Most of the results presented and discussed in this paper have been obtained at temperature programmed dynamic conditions, and further completed with isothermal treatments at high temperatures. The studies under dynamic conditions are of particular interest in the frame of TWC applications, because of the fast response required in these catalysts to any change in the composition of the gas feed. Moreover, these results have been obtained for samples with surface area values in the range useful for catalytic applications. In this way, we could detect the occurrence of effects linked to surface processes.

We can highlight several favorable aspects of the Ce/La mixed oxides with regard to pure ceria: (a) The mixed oxides are more easy to reduce in flow of pure hydrogen than ceria, (b) the mixed oxides, in a helium flow, desorb oxygen at much lower temperatures and in higher amounts than pure ceria and (c) the textural stability of the mixed oxides is higher than that of CeO_2, particularly under reducing environments.

Concerning the optimun La content of the mixed oxides to promote high oxygen exchange capacities, it seems to depend on the type of environment in which the sample is at work. Thus the observed trends for oxygen release under inert gas and oxygen atmospheres have been shown to be opposite.

Acknowledgments

This work have received financial support from DGICYT, under Projects PB94-1305 and PB95-1257, and from CICYT, under project MAT96-0931.

References

[1] K.C. Taylor, *Catal. Rev. Sci. Eng., 35* (1993) 456.

[2] B. Harrison, A.F. Diwel and C. Hallet, *Platinum Met. Rev., 32* (1988) 73.

[3] D. Kalakkad, A.K. Datye and H.J. Robota, *J. Catal., 148* (1994) 729.

[4] J.G. Kim, *Ind. Eng. Chem. Prod. Res. Dev., 21* (1982) 267.

[5] J. Summers and S.A. Ausen, *J. Catal., 58* (1979) 131.

[6] D.D. Beck and C.J. Carr, *J. Catal., 144* (1993) 296.

[7] B.K. Cho, *J. Catal., 131* (1991) 74.

[8] T. Miki, T. Ogawa, M. Haneda, N. Kakuta, A. Ueno, S. Tateishi, S. Matsuura and M. Sato, *J. Phys. Chem., 94* (1990) 6464.

[9] G.R. Rao, J. Kaspar, S. Meriani, R. di Monte and M. Graziani, *Catal. Lett., 24* (1994) 107.

[10] A.D. Logan and M. Shelef, *J. Mater. Res., 9* (1994) 468.

[11] J. Rodríguez-Carvajal, *Proceedings of the Satellite Meeting on Powder Diffraction of the XV Congress of the International Union of Crystallography, Toulouse, France 1990,* p. 127.

[12] S. Bernal, R. García and J.M. Rodríguez-Izquierdo, *Termochim. Acta, 70* (1983) 249.

[13] N. Minkova and S. Aslanian, *Cryst. Res. Technol., 24* (1989) 351.

[14] E. Zintl and U. Croatto, *Z. Anorg. Allg. Chem., 242* (1939) 79.

[15] S.J. Hong and A.V. Virkar, *J. Am. Ceram. Soc., 78* (1995) 433.

[16] D.J.M. Bevan, W.W. Barker, T.C. Parks and R.L. Martin, in L. Eyring (ed.), *Rare Earth Research*, Gordon and Breach, New York, 1965, p. 441.

[17] H.C. Yao and Y.F.Y. Yao, *J. Catal., 86* (1984) 254.

[18] P. Fornasiero, R. di Monte, G.R. Rao, J. Kaspar, S. Meriani, A. Trovarelli and M. Graziani, *J. Catal., 151* (1995) 168.

[19] G. Balducci, P. Fornasiero, R. di Monte, J. Kaspar, S. Meriani and M. Graziani, *Catal. Lett., 33* (1995) 193.

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

[21] H.H. Kung, Transition Metal Oxides: Surface Chemistry and Catalysis, Elsevier, 1989.

[22] H.L. Tuller and A.S. Nowick, *J. Electrochem. Soc., 122* (1975) 255.

[23] S. Bernal, J.J. Calvino, G.A. Cifredo, J.M. Gatica, J.A. Pérez-Omil and J.M. Pintado, *J. Chem. Soc. Faraday Trans., 89* (1993) 3499.

[24] J.M. Pintado, *Doctoral Thesis*, University of Cadiz, 1996.

[25] X. Zhang and K.J. Klaubunde, *Inorg. Chem., 31* (1992) 1706.

[26] J.X. Wang and J.H. Lunsford, *J. Phys. Chem., 90* (1986) 3891.