

## Induced Changes in Ceria by Thermal Treatments under Vacuum or Hydrogen

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The reduction of CeO<sub>2</sub> either under vacuum or hydrogen at temperatures between 295 and 773 K has been investigated by gravimetric methods and IR, <sup>1</sup>H-NMR, and ESR spectroscopies. Thermal treatments of the samples under vacuum produce mainly the progressive dehydroxylation of the samples and a weak surface reduction. However, treatments under hydrogen modify substantially this behavior. The gravimetric results show two well-differentiated processes: a fast weight gain due to incorporation of H<sub>2</sub> in the oxide bulk, followed by an important weight loss due to lattice oxygen extraction. Infrared data indicate that H<sub>2</sub>-treatments at temperatures below 673 K do not significantly change the surface concentration of hydroxyl groups, but they induce an important decrease above that temperature. The magnetic resonance spectra confirm the hydrogen incorporation in the oxide, mainly in the bulk, when the sample is heated under H<sub>2</sub> in the 373-773 K range. © 1987 Academic Press, Inc.

### Introduction

Ceria (CeO<sub>2</sub>) has the same fluorite structure as thoria and zirconia, but is different in that pure CeO<sub>2</sub> undergoes large departures from stoichiometry at elevated temperatures in a reducing atmosphere. Non-stoichiometric cerium dioxide CeO<sub>2-x</sub> has been the subject of several investigations (1-5). In some cases the investigation was focused on the study of the bulk properties, because its defect structure makes this oxide a powerful solid electrolyte for fuel cells (6-7).

Another interesting feature of cerium oxide, from the standpoint of catalytic behavior, is its basicity. This functionality when combined with the hydrogenation property of a metal in ceria-supported group VIII metals points out ceria as a promising support candidate in the synthesis gas (CO + H<sub>2</sub>) conversion catalysts. Recently, Meriaudeau *et al.* (8) have investigated the *n*-hexane hydrogenolysis reaction on several alumina-, titania-, and ceria-supported Pt catalysts, and concluded that the strong metal support interaction (SMSI) is present in both reduced Pt/CeO<sub>2</sub> and Pt/TiO<sub>2</sub> catalysts, although their reactivities are significantly different. Different explanations can be ventured but "anomalous" electronic ef-

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fects due to large departures from stoichiometry of a partially reduced ceria could explain these differences.

In this paper, we have used gravimetric methods, magnetic resonances ( $^1\text{H-NMR}$  and ESR), and infrared spectroscopy to show that following reduction under hydrogen, a large amount of hydrogen is rapidly incorporated into the oxide, which subsequently produces lattice oxygen ion extraction and modifies the oxide properties.

### Experimental

Cerium nitrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , Rhône Progil S.A.) 99.6% purity with Si, Pb, Mn, and Na as the main impurities was used as precursor. The cerium hydroxide was prepared by adding dropwise a 0.1 M  $\text{NH}_4\text{OH}$  solution to a 0.32 M cerium nitrate solution with constant stirring until complete precipitation at pH close to 6.2. The resulting precipitate was repeatedly washed, followed by drying *in vacuo* at room temperature for 12 hr. The sample so obtained was thermally decomposed in constant rate decomposition (CRD) equipment which operates at a constant and very low water vapor pressure of 10 N m $^{-2}$  (133.3 N m $^{-2}$  = 1 Torr). Temperatures were increased slowly and not linearly with time; for instance, about 350 hr were needed to reach 500 K (mainly removal of physically adsorbed water) while the overall time required to reach 673 K was 535 hr. After this treatment the sample was exposed to air. The specific surface area determined by the BET method was 58.3 m $^2$  g $^{-1}$ .

Reduction experiments were carried out gravimetrically in a Cahn microbalance connected to a high vacuum line and gas-handling system. A sample of 80 mg was isothermally reduced at temperatures between 473 and 773 K in a flow (9 dm $^3$  hr $^{-1}$ ) of  $\text{H}_2$ , obtained through a Ag-Pd thimble of a commercial  $\text{H}_2$  diffuser. Equilibrium of

reduction was considered when the weight variation per hour was lower than 0.2% of the overall weight change.

The  $^1\text{H-NMR}$  spectra were obtained with a pulse spectrometer SXP 4/100 (Bruker) with a Fourier transform unit Aspect 2000. The NMR frequency of proton was 70 MHz. All spectra were recorded at room temperature and the number of accumulations in each experiment was chosen in such a way that the signal-to-noise ratio was higher than 30. Dehydroxylation treatment of the samples was carried out in a special vacuum cell, capable of maintaining dynamic vacuum of ca.  $1 \times 10^{-3}$  N m $^{-2}$ , between 295 and 773 K for 2 hr. Subsequent reduction of this sample was carried out in the same cell between 373 and 773 K for 2 hr in  $\text{H}_2$  (13.3 kN m $^2$ ). After this treatment, the sample was outgassed at room temperature and then spectra were recorded. The extent of hydrogen incorporated was quantified by reference to a mica standard. ESR spectra were obtained with a Bruker ER 200 D spectrometer, operating in the X-band. The spectra were recorded at 77 K. A Mn:MgO standard ( $g = 2.0066$ ) was used to calibrate the magnetic field. Samples of 50 mg placed inside a quartz-probe cell were pretreated *in vacuo* or in  $\text{H}_2$  following the same procedure as stated above for the NMR experiments.

For the infrared experiments, the  $\text{CeO}_2$  samples were ground to a fine powder and pressed to  $1.3 \times 10^4$  kN m $^{-2}$  into 1.2-cm-diameter wafers. These wafers were placed in a special vacuum cell assembled with greaseless stopcocks and NaCl windows. Pretreatment of the samples consisted either of heating at 773 K for 2 hr under vacuum or of reduction in  $\text{H}_2$  at temperatures between 473 and 773 K for 2 hr followed by outgassing at 473 K for 2 hr. Infrared spectra were obtained with a Perkin-Elmer 680 B spectrophotometer, interfaced to a data system. All spectra were recorded in the absorbance mode.

## Results

### Thermogravimetric Measurements

The microgravimetric results show noticeable weight changes of the  $\text{CeO}_2$  sample when in contact with  $\text{H}_2$  ( $9.3 \text{ kN m}^{-2}$ ) at different temperatures (Fig. 1). The adsorption isobar (amount of  $\text{H}_2$  incorporated at equilibrium as a function of temperature) of  $\text{H}_2$  in the 195–500 K range indicates that  $\text{H}_2$  chemisorption is an activated process, i.e., the extent of  $\text{H}_2$  adsorption increases with temperature. The only exception below 200 K must be due to some participation of the physical adsorption of  $\text{H}_2$ . Above 500 K, a slower weight loss process takes place due to the removal of lattice oxygen. This second process will be referred to hereafter as a reduction step. The extent and rate of  $\text{H}_2$  reduction are strongly dependent on the temperature of reduction ( $T_R$ ), as can be concluded from the kinetic reduction curves and the extent of  $\text{H}_2$  reduction (amount of  $\text{H}_2$  consumption obtained when the sample weight varied less than  $0.2\%/hr$  of the overall  $\text{H}_2$  already consumed) at 573

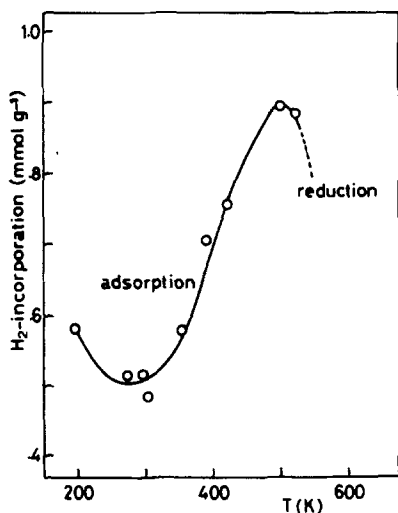


FIG. 1. Isobar of hydrogen ( $9.3 \text{ kN m}^{-2}$ ) on ceria samples. Dashed line indicates the appearance of a process which involves lattice oxygen removal (weight loss).

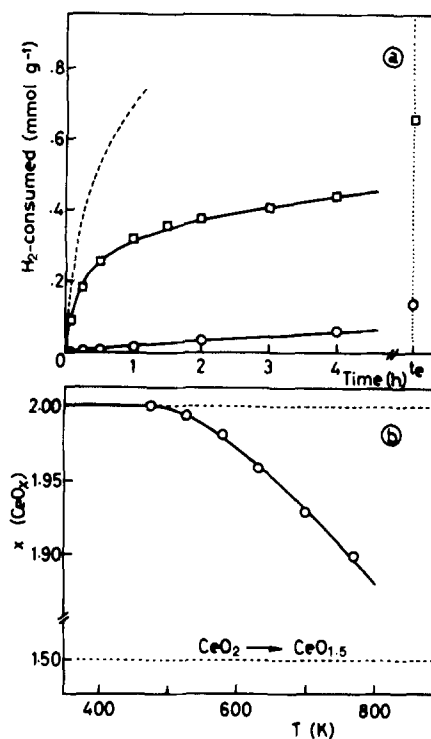


FIG. 2. (a) Kinetic reduction curves of hydrogen ( $9.3 \text{ kN m}^{-2}$ ) at 573 K ( $\circ$ ) and 773 K ( $\square$ ).  $t_e$  was the time required to attain equilibrium reduction. Dashed line represents Otsuka *et al.*'s data taken from Ref. (9). (b) Reduction degree at equilibrium as a function of the temperature of reduction.

and 773 K presented in Fig. 2b. For comparative purposes, the same figure includes Otsuka *et al.*'s data for  $\text{H}_2$  reduction of  $\text{CeO}_2$  at 873 K under an initial  $\text{H}_2$  pressure of  $13.6 \text{ kN m}^{-2}$ . Since the reduction is an activated process, which implies a higher reduction rate with increasing  $T_R$ , the higher reduction rate found by Otsuka *et al.* (9) at 873 K is in good agreement with our results. The apparent activation energy of the reduction by  $\text{H}_2$  obtained from the Arrhenius plot of the initial reduction rate ( $r_0$ ) (calculated from the slopes of the kinetic curves at zero time) at 573 and 773 K was  $139.2 \text{ kJ mole}^{-1}$ , even considering that the relative ease of the  $\text{CeO}_2$  reduction remains low, i.e.,  $\text{CeO}_{1.90}$  at 773 K (Fig. 2b).

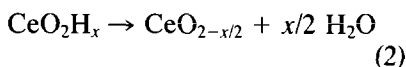
These observations may be explained by

the following reactions:

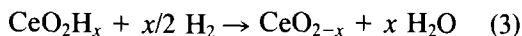
#### Chemisorption



#### Reduction



or



Reaction (1) describes the weight gain of ceria samples after  $\text{H}_2$  treatments up to about 500 K, whereas Reactions (2) or (3) account for the weight loss as due to the lattice oxygen removal at  $T_R > 500$  K.

#### Nuclear Magnetic Resonance

The  $^1\text{H}$ -NMR spectra of the sample, after outgassing at different temperatures ( $T_e$ ) between 295 and 773 K, are presented in Fig. 3a. The intensity of the signal decreases with  $T_e$  from 1.8 to 0.1 a.u. (arbitrary units) in the studied temperature range (Fig. 3b). The full width at half maximum (FWHM) is almost constant, but a broadening of the wings of the signal is observed between 573

and 773 K. The variation of the second moment of the signal ( $S_2$ ) with  $T_e$  is shown in Fig. 3c. The value of  $S_2$  decreases with  $T_e$  up to 573 K, but it increases above that temperature.

The sample, previously outgassed at 773 K, was studied after reduction with  $\text{H}_2$  at different temperatures ( $T_R$ ); the spectra are presented in Fig. 4a. The intensity of the signal increases from the initial value of 0.1 to 0.8 a.u. at 673 K (Fig. 4b), showing an important broadening ( $S_2$  increases from 5.5 to 12  $\text{G}^2$ ) in the same range of  $T_R$  (Fig. 4c). The intensity and width of the signal decrease at  $T_R > 673$  K. The NMR spectra of the sample reduced at 673 and 773 K present two components (Fig. 4a): a narrow signal of low intensity which is centered at the resonance magnetic field, and a broader component showing larger intensity which is shifted with respect to the resonance magnetic field.

#### Infrared

The IR spectra of  $\text{H}_2$ -reduced ceria samples at temperatures 473–773 K in the

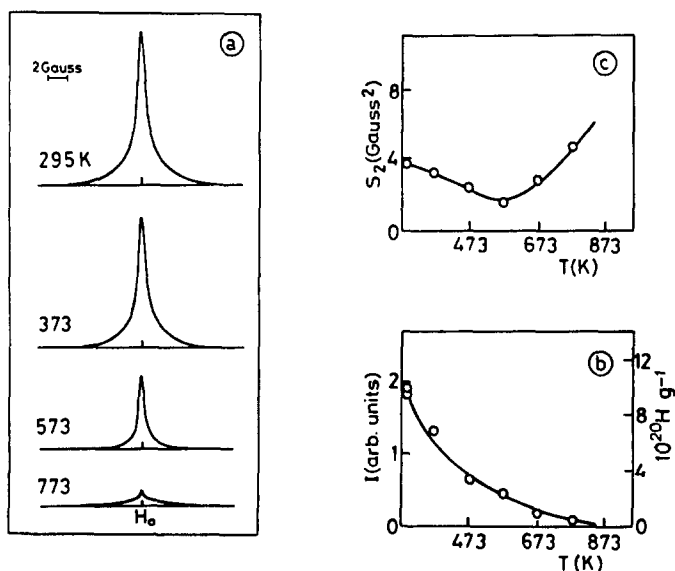


FIG. 3. (a)  $^1\text{H}$ -NMR spectra of  $\text{CeO}_2$  sample outgassed for 2 hr at different temperatures. Influence of the temperature of treatment on the integrated intensity (b) and second moment (c) of the signal.

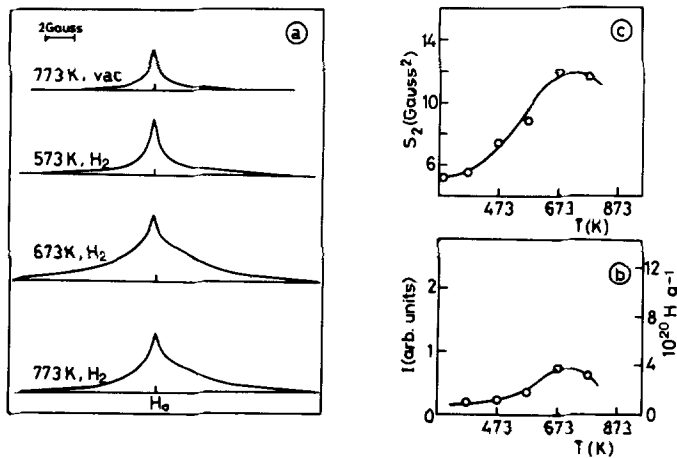


FIG. 4. (a)  $^1\text{H-NMR}$  spectra of  $\text{CeO}_2$  sample outgassed at 773 K, reduced in  $\text{H}_2$  ( $13.3 \text{ kN m}^{-2}$ ) for 2 hr at different temperatures and outgassed at 295 K. Influence of the reduction temperature on the integrated intensity (b) and second moment (c) of the signal.

stretching vibration region of OH groups are given in Fig. 5a. As can be seen, the background spectrum (Fig. 5a) of the  $\text{CeO}_2$  sample outgassed under high vacuum at 773 K shows bands at 3640, 3615, and 3515  $\text{cm}^{-1}$  indicating the existence of different environments for OH groups at the ceria

surface (10). The relative abundance of these OH groups was studied after exposing the sample to  $\text{H}_2$  for 2 hr at temperatures between 473 and 773 K. Molecular water formed during reduction was removed by outgassing under high vacuum of ca.  $1 \times 10^{-3} \text{ N m}^{-2}$  at 473 K for 2 hr. At  $T_R$

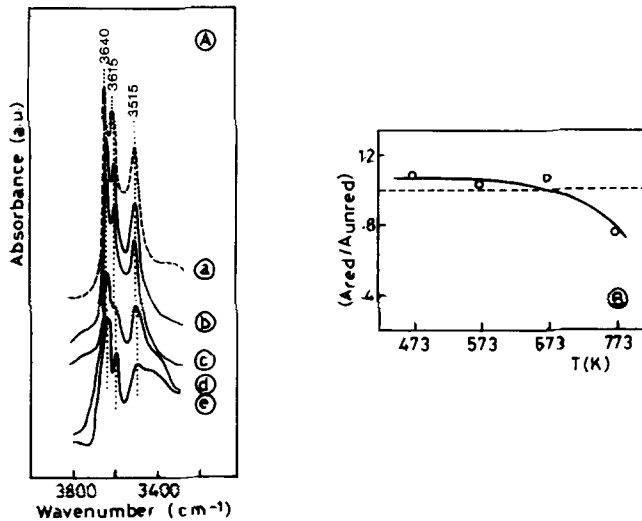


FIG. 5. (A) Infrared spectra in the stretching vibration region of OH groups of different  $\text{CeO}_2$  samples: (a) background after outgassing at 772 K; (b), (c), (d), and (e), after  $\text{H}_2$  treatment at 473, 573, 673, and 773 K, respectively.  $\text{H}_2$ -treated samples were always outgassed at 473 K to remove the molecular water formed during reduction. (B) Absorbance of the OH groups relative to that of the unreduced samples as a function of the reduction temperature.

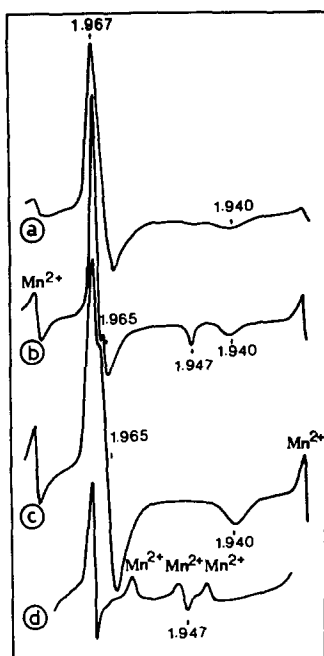


FIG. 6. ESR spectra of the unheated sample (a), outgassed at 373 K (b), and after reduction in  $H_2$  at 573 K for 24 hr and outgassing at 773 K for 4 hr (d). A different sample prepared at 473 K and outgassed at 373 K (c).

below 573 K the spectra do not essentially differ from the cerium oxide background. However, noticeable changes in both intensity and linewidth of the spectra appeared at the highest reduction temperatures (Figs. 5d and e). These effects are better viewed in a representation of the normalized absorbance of the band near  $3640\text{ cm}^{-1}$  in relation to that of the unreduced sample,  $(A_{\text{red}}/A_{\text{unred}})_{3640}$ , as a function of the reduction temperature (Fig. 5b). This ratio remains unchanged, and near 1, up to 673 K but falls above this temperature. It suggests that dehydroxylation is favored by the hydrogen treatments at temperatures above 673 K.

#### Electron Spin Resonance

The spectrum of the untreated sample is composed of two signals with resolved  $g$  values at high field,  $g = 1.940$  (signal A) and  $g = 1.947$  (signal B), and the other  $g$  com-

ponents overlap at  $g = 1.967$ . Signal A displays a larger intensity than B (Fig. 6a). An additional signal due to  $Mn^{2+}$  ions is also shown by all spectra. The spectrum linewidth becomes narrower after outgassing at 373 K in vacuum ( $\sim 1.3 \times 10^{-2}\text{ N m}^{-2}$ ), particularly in the region where signals A and B are overlapping, and a new component at  $g = 1.965$  is resolved (Fig. 6b). By comparison with the spectrum obtained for another sample outgassed at 373 K, prepared by the CRD procedure at 473 K, where only one signal is observed (Fig. 6c), signal A can be described by  $g_1 = 1.967$ ,  $g_2 = 1.965$ ,  $g_3 = 1.940$ , and signal B by  $g_{\perp} = 1.967$ ,  $g_{\parallel} = 1.947$ . If the sample outgassed at 373 K is in contact with oxygen ( $133\text{ N m}^{-2}$ ), the spectrum intensity is only slightly affected, but an important signal with  $g_1 = 2.030$ ,  $g_2 = 2.016$ ,  $g_3 = 2.011$  is observed. The parameters of this signal are similar to those assigned by other authors to  $O_2^-$  species bound to  $Ce^{4+}$  ions (11, 12). The large positive shifts of the  $g_2$  and  $g_3$  values from the values expected, considering the ionic model of  $O_2^-$  (12), may be due to some coupling of the ion orbitals with the  $4f$  orbital electrons in the cerium ions (11). With increasing  $T_e$ , the spectrum lineshape does not change significantly and the intensity increases slowly due, particularly, to the contribution of signal B, which is larger than A for  $T_e > 473\text{ K}$ .

When the sample outgassed at 773 K is in contact with hydrogen ( $\sim 4\text{ kN m}^{-2}$ ) the shape of the spectrum does not change, but all the signals show an increase in intensity. No variations are observed after heating under  $H_2$  up to 473, but at  $T_R = 573\text{ K}$  signals A and B decrease slowly with heating time, disappearing after several hours. For  $T_R > 573\text{ K}$  both signals are absent from the spectrum. However, if the sample heated 24 hr at 573 K, with obliterated signals A and B, is outgassed for 4 hr at 773 K, both signals reappear, starting with signal B (Fig. 6d). The recovery of the signals is eas-

ier if the sample has previously been in contact with oxygen at room or higher temperature. If the sample has been reduced at 773 K, the signals are not recovered by outgassing and thermal treatments under oxygen are necessary. The  $\text{Mn}^{2+}$  signal increases only slightly after outgassing at 773 K, and increases much more when the sample is subsequently in contact with  $\text{H}_2$  at 295 K. A small intensity drop is observed after thermal treatments under  $\text{H}_2$  at  $T > 573$  K and a larger one is observed by pumping out hydrogen. Oxygen adsorption produces an increase of the  $\text{Mn}^{2+}$  signal. The increase of the  $\text{Mn}^{2+}$  signal with reducing treatments indicates that the manganese impurities present in the  $\text{CeO}_2$  were in part in a higher oxidation state and have been reduced, probably with the simultaneous formation of oxygen vacancies.

## Discussion

### *Reduction under Vacuum*

The intensity drop of the  $^1\text{H-NMR}$  signal by outgassing in the 295–773 K range is explained by the progressive elimination of hydroxyl groups. The narrowing of the signal with thermal treatment ( $T_e < 573$  K) points to an increase of the mean distance between the surface hydroxyl groups. However, the increase of the second moment of the spectra observed for  $T_e > 573$  K indicates the influence of a new effect, probably the formation of paramagnetic centers on the surface as a consequence of the elimination of lattice oxygen ions. These paramagnetic centers broaden the  $^1\text{H-NMR}$  line through dipolar interactions. Consequently the value of  $S_2$  is affected in a different way by  $T_e$  through two mechanisms:  $S_2$  decreases because of surface dehydroxylation and increases due to the generation of paramagnetic centers. The minimum of the  $S_2$ – $T_e$  curve at 573 K indicates that above that temperature the influ-

ence of paramagnetic centers on the protons contributes to the  $S_2$  value more than the effect due to dehydroxylation.

In  $\text{CeO}_2$ , ESR signals with  $g$  values in the range of those of A and B have been assigned by other authors to trapped electrons in cerium ions (13) or to defects (14). Our results are not conclusive but the observation of two signals and the changes of their relative intensity with the treatments can be better explained by assuming that they arise from  $\text{Ce}^{3+}$  ions in two different environments than from trapped electrons in oxygen vacancies. The narrowness of the signal and their detection at 295 K would indicate, in that case, that  $\text{Ce}^{3+}$  ions have a large relaxation time, as should be expected for interstitial cations in a surrounding of low symmetry. Signal A, which is affected by the dehydroxylation treatment, is probably due to  $\text{Ce}^{3+}$  ions with easily removable ligands. This signal corresponds to species either on the surface, affected by the outgassing treatments, or in the bulk, and not affected. Signal B, which grows by outgassing at higher temperatures, is also probably due to  $\text{Ce}^{3+}$  ions in the bulk stabilized by some lattice defects. The appearance of strong signals of  $\text{O}_2^-$  bound to  $\text{Ce}^{4+}$ , when the outgassed sample is in contact with oxygen, points to the availability of an important number of electrons capable of being transferred to  $\text{O}_2$  molecules. The minor modifications of A, B, and  $\text{Mn}^{2+}$  signal intensities indicate that most of them are not detected by ESR. Considering the NMR results, indicating the formation of paramagnetic centers and that the  $\text{O}_2^-$  ions are bound to  $\text{Ce}^{4+}$  ions, the donor sites are probably  $\text{Ce}^{3+}$  ions in lattice positions, which are not observed because of the large broadening of the signal due to the short relaxation time of these ions in symmetric environments. The formation of these lattice  $\text{Ce}^{3+}$  ions must be a consequence of the formation of oxygen vacancies during the reduction process, which is, in turn, the

most accepted mechanism for reduction of near-stoichiometric  $\text{CeO}_2$  (15). Although some interstitial  $\text{Ce}^{3+}$  ions are also probably formed, their abundance in relation to the oxygen vacancies must remain small.

### Reduction by $\text{H}_2$

Although the gravimetric results indicate that reduction above 573 K causes a weight loss in the sample (Fig. 2b), the  $^1\text{H-NMR}$  spectra show an increase of the signal intensity under similar conditions. The value of the maximum increase, observed at  $T_R = 673$  K, corresponds to  $3.4 \times 10^{20} \text{ H g}^{-1}$ . This incorporation of hydrogen, described by mechanism (1), can take place with the formation of hydroxyl groups or hydride species. A better understanding of these results may be obtained by analysis of the evolution the IR spectra with the thermal reduction. As observed in Fig. 5b, the absorbance of the OH groups (band near  $3640 \text{ cm}^{-1}$ ) relative to the absorbance of those groups of the unreduced sample remains virtually unchanged, and close to 1, up to 673 K and then decreases markedly. These results indicate that  $\text{H}_2$  incorporation below 673 K takes place without formation of surface OH groups during  $\text{H}_2$  treatment. This finding, therefore, could be taken as indirect evidence that the incorporation of  $\text{H}_2$  into ceria is a bulk phenomenon. The stabilization of water molecules on the sample at that temperature is not significant because it is not supported by the  $^1\text{H-NMR}$  spectra. The free water molecules or the water bound to cations would produce a narrow line or two split lines (doublet), respectively, which are not observed.

The intensity of the  $^1\text{H-NMR}$  spectra decreases when the sample is heated under  $\text{H}_2$  at  $T_R > 673$  K, which can be explained either by condensation of the initial OH groups or by the extraction of lattice oxygen ions by chemical reaction with the previously stabilized hydrogen. At  $T_R = 773$  K the reduction reached an equilibrium corre-

sponding to  $\text{CeO}_{1.90}$  which indicates a deeper reduction than that found by Breyse *et al.* (16), who have reported that  $\text{CeO}_2$  changes its composition from  $\text{CeO}_{1.985}$ , outgassed at 773 K, to  $\text{CeO}_{1.945}$  after reduction under  $\text{H}_2$  at the same temperature. Therefore, during the reduction process two mechanisms, incorporation of hydrogen and oxygen removal from the lattice, affect in different ways the weight of the sample.

The obliteration of the bulk ESR signals by heating under hydrogen at 573 K, when the  $^1\text{H-NMR}$  spectra show incorporation of hydrogen into the sample, indicates that hydrogen diffuses into the bulk of  $\text{CeO}_2$ , where it affects the paramagnetic centers. The broad and shifted  $^1\text{H-NMR}$  line indicates the interaction of hydrogen nuclei with unlocalized electrons. The  $^1\text{H-NMR}$  spectrum observed in the sample reduced at 673 K is similar to that observed by Ancion *et al.* (17) in a mixed molybdenum vanadium bronze. Preliminary XRD data on  $\text{H}_2$ -treated  $\text{CeO}_2$  samples above 673 K indicated an increase of the lattice cell parameters (18), which also support bronze formation.

The fact that the small signals A and B, absent in the ESR spectrum of the sample reduced at  $T_R = 573$  K, can be recovered by outgassing treatments with or without the help of oxygen adsorption, points also to the existence of a small amount of diamagnetic hydride-like species that can diffuse easily toward the bulk or the surface of the sample depending on the treatments. A similar situation was observed in  $\text{H}_2$ -reduced Rh/TiO<sub>2</sub> catalysts above 573 K (19).

In conclusion, the experimental results indicate that by heating under  $\text{H}_2$  above 473 K an important amount of hydrogen is incorporated into bulk  $\text{CeO}_2$ , which produces bronze-like species (mechanism 1). At the same time, these activated hydrogen species can react with the lattice oxygen ions. Taking into account the low activation en-



ergy for the reduction ( $139.2 \text{ kJ mole}^{-1}$ ), it seems that the reduction process could be located at the surface, forming anion vacancies. The oxygen ion extraction, following mechanism (2) or (3), will form water molecules that will condense away from the sample, causing the observed weight loss. The presence of the stabilized hydrogen must affect the adsorption and catalytic properties of the sample and could explain the differences observed between  $\text{CeO}_2$  samples outgassed and reduced at high temperatures (14) and other less reducible oxides such as  $\text{TiO}_2$  when used as support of group VIII metals (8).

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