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Preparation and Characterization of CeO_2 under an Oxidizing Atmosphere. Thermal Analysis, XPS, and EPR Study

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Cerium hydroxide samples prepared with different precipitating agents (NaOH, KOH, NH_4OH) have been studied by thermogravimetry, X-ray photoelectron spectroscopy (XPS), and electron paramagnetic resonance (EPR). The untreated samples are a mixture of CeO_2 and $Ce(OH)_4$ with a small quantity of $Ce(OH)_3$ present in the bulk of the solid. A part of the Ce^{3+} species remains stable even after calcination at high temperatures (1073 K) under air. The residual alkali elements issuing from the precipitating agents induce variations on the final state of the solid.

Introduction

Similar to alumina, titania, and silica, ceria is widely used as support in catalysis.[1–4] In fact, cerium, which is the most abundant of the lanthanides, is the only one which can have compounds with two oxidation states, Ce(III) and Ce(IV).[5] When heated to high temperatures or treated under reducing atmospheres or even doped with trivalent cations,[6] ceria, which has a fluorite structure,[7,8] is known to show large deviations from its CeO_2 stoichiometric composition.[4,6,9–11] The nonstoichiometric cerium dioxide CeO_{2-x} has been the subject of several investigations.[6–8,12–14] This defect structure of the oxide makes it a powerful solid electrolyte for fuel cells.[6,15,16] Moreover, it is known that ceria has a great affinity for hydrogen atoms as it is able to form a hydride[17] or a bronze.[4] 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 such as Pt, Pd, Cu, ..., having cerium oxide as support, points out ceria as a promising support candidate in the synthesis gas ($CO + H_2$) conversion catalysts and selective hydrogenation of unsaturated compounds.[2–4]

Generally, ceria is prepared by the dehydration of the cerium hydroxide. The $Ce(OH)_3$ prepared from a salt of Ce(III) and an alkaline solution will be oxidized at room temperature by the oxygen of the air into $Ce(OH)_4$.[5] This last product gives the cerium dioxide by dehydration.

In this work, thermal analysis, and electron paramagnetic resonance (EPR) and X-ray photoelectron spectroscopy (XPS) have been largely exploited to study the influence of the precipitating agents (NaOH, KOH, NH_4OH) on the cerium hydroxide, freshly prepared and after calcination at high temperatures.

Experimental Section

Solid Preparation. All solids were prepared by precipitation of cerium hydroxide with alkali solution (NaOH, KOH, NH_4OH) from cerium(III) nitrate hexahydrate, $Ce(NO_3)_3{,}6H_2O$ (Rhône-Poulenc) in aqueous medium at pH = 11. The resulting hydroxide was filtered, washed and dried for about 20 h in a drying oven ($\sim$373 K). The calcination of the hydroxides was done under a flow of dried air (50 mL min^{-1}). The temperature was raised at a rate of 200 K h^{-1} from room temperature to 1073 K. The microflow reactor used for this treatment was assembled with an EPR quartz tube permitting the introduction of the sample into the resonance cavity of the EPR spectrometer without exposure to the atmosphere.

Thermogravimetry (TG). The thermal decomposition of the solid was studied by thermogravimetry using a microbalance type SARTORIUS 4433 MP 8. Untreated samples (40–50 mg) were heated in a quartz crucible under a flow of 4 L h^{-1} of dry pure air. The temperature was raised at a rate of 1 K min^{-1} from room temperature to 1173 K. The loss of weight were determined using quartz as reference.

XPS Measurements. XPS spectra were recorded on a Kratos AEI ES 200 B spectrometer with an Al Kα anticathode ($h\nu$ = 1486.6 eV). The samples were crushed into a fine powder and pressed on an indium support. The spectra were recorded at room temperature and under high vacuum (10^{-8} Torr). The

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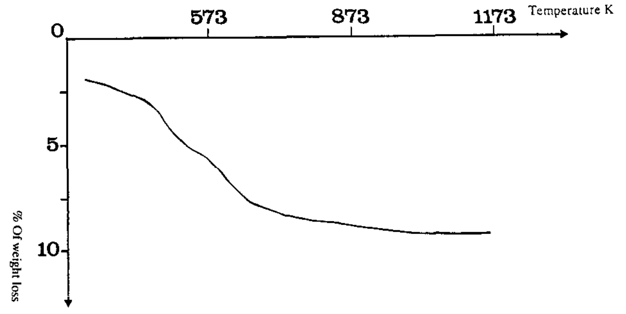

Figure 1. Thermal decomposition under dried air of cerium hydroxide prepared with NH_4OH. Heating rate 1 K min^{-1}.

binding energies were determined using the C 1s peak at 285.0 eV as a standard.

The surface atomic composition n_A/n_B was calculated using the formula

$$\frac{I_A}{I_B} = \frac{n_A}{n_B}\frac{\sigma_A}{\sigma_B}\frac{\lambda_A}{\lambda_B}\frac{T_A}{T_B}$$

where σ represents the photoelectron cross section taken from Scofield tables;[18] λ is the escape depth of the photoelectron, proportional to the kinetic energy $(E_k)^{0.8}$ (ref 19), and T is the transmission factor of the spectrometer, proportional in our case to the kinetic energy. Atomic ratios were calculated for Na 2s and K 2p versus Ce 4d.

EPR Measurements. The EPR measurements were carried out on a VARIAN E9 spectrometer. A dual-purpose cavity operating with a frequency of *ca.* 9.3 GHz (X band) was used. The magnetic field was modulated at 100 kHz. All spectra were recorded at a microwave power sufficiently small to avoid saturation effects. Precise **g** values were obtained by comparison with a sample of reference "strong pitch" $g = 2.0028$. All measurements were performed at 77 and 293 K.

Results and Discussion

Thermogravimetry. Figure 1 presents the percentage of weight loss for the cerium hydroxide prepared with NH_4OH after the calcination of the solid, under a dry air flow, from room temperature to 1173 K. A 5.31% loss in weight was recorded from 293 to 478 K and another one of 3.89% from 478 to 1173 K. The total loss is then 9.20%. Similar results have been obtained when the solid was prepared with NaOH or KOH.

The cerium hydroxide has been prepared from a Ce(III) salt [$Ce(NO_3)_3$]. Then, we can suppose that the hydroxide exists in the form of $Ce(OH)_3$, the theoretical loss of the solid dehydration:

$$2Ce(OH)_3 + {}^1/_2O_2 \rightarrow 2CeO_2 + 3H_2O \qquad (I)$$

should be 9.94%. This value is close to the total loss obtained experimentally. But, since under a flow of dried argon we have demonstrated that the total loss, after the calcination of the solid, does not change compared to that obtained under air, it is then evident to suppose that reaction I is not responsible of the above loss. In fact, it is already shown[5] that $Ce(OH)_3$ changes, during its preparation under air and at room temperature, into $Ce(OH)_4$ which gives the yellow color to the cerium hydroxide. In our case, the solid obtained after drying in the oven (~373 K) is yellowish; thus, the $Ce(OH)_4$ hydroxide ought to be present in the solid and the amount of $Ce(OH)_3$ must be negligible.

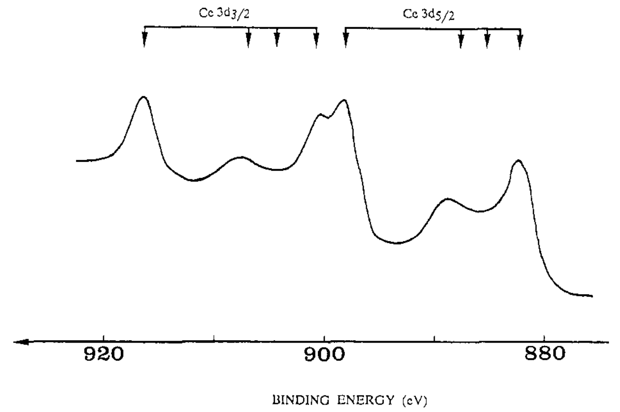

Figure 2. Ce 3d XPS spectrum for the untreated sample prepared with NaOH.

If we consider now that the totality of the untreated sample is in the form of $Ce(OH)_4$. Contrarily to $Ce(OH)_3$, the transformation of $Ce(OH)_4$ into CeO_2 occurs without oxygen following the reaction

$$Ce(OH)_4 \rightarrow CeO_2 + 2H_2O \qquad (II)$$

The theoretical loss of reaction II must be 17.29%. This value is considerably higher than the experimental one (9.20%). The difference between these two values can be explained by the partial dehydration of the hydroxide into CeO_2 during its drying in oven. Consequently, from the beginning the untreated sample is a mixture of $Ce(OH)_4$ and CeO_2 with a small quantity of $Ce(OH)_3$. This assumption will be confirmed by the XPS and EPR studies.

Considering that $Ce(OH)_4$ and CeO_2 are the major constituents of the solid, and that the experimental loss effectively due to the dehydration is 3.89%,[1] the percentage of each phase, according to the calculations using reaction II, must be about 22.5% for $Ce(OH)_4$ and 77.5% for CeO_2.

XPS Results. Figure 2 shows the Ce $3d_{3/2}$ and Ce $3d_{5/2}$ XPS spectrum measured on the untreated sample prepared with NaOH. All the Ce 3d XPS spectra of the untreated and calcined samples prepared with different alkali solutions (KOH, NH_4OH) have the same shape as the spectrum given in Figure 2 with six peaks at BEs 882.5, 888.7, 898.2, 900.7, 907.6, and 916.5 (±0.2) eV. Similar spectra have been observed by other authors for pure CeO_2.[2,20-22]

Cerium compounds are known to exhibit rather complex features due to hybridization with ligand orbitals and fractional occupancy of the valence 4f orbitals. Although many theoretical and experimental studies[20-29] have been elaborated since the initial work of Burroughs *et al.*,[30] absolute assignment of the features has not been made

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Table I. Intensities Ratios of the Ce 3d and Ce 4d XPS Spectra

	sample NH_4OH		sample KOH		sample NaOH	
XPS intensity ratio	untreated	calcined	untreated	calcined	untreated	calcined
I Ce $3d_{sat}$/I Ce $3d_{tot}$	0.135	0.134	0.137	0.136	0.141	0.135
I Ce 3d/I Ce 4d	1.45	1.45	1.22	1.21	1.44	1.02

and controversy still exists. It has been demonstrated that the Ce 3d XPS spectrum of a Ce^{4+} compound can be resolved into six structures and if some Ce^{3+} species are also present, four more structures are added.[22-23] Furthermore, CeO_2 and Ce_2O_3 always show peaks at ~882.5 and ~916.5 eV, as well as at ~885 and ~903.7 eV, which are considered as being fingerprints characterizing Ce^{4+} and Ce^{3+} oxides, respectively.[31] The origins of all these peaks are discussed in the work of Kotani *et al.*,[22] where a filled valence band of the impurity Anderson model was used for this issue.

All the observed peaks on our spectra could be assigned to Ce^{4+} species by comparison with data reported in the literature[2,22,23] and no signal relative to Ce^{3+} species is analysed on the spectra. Moreover, Harrison *et al.*[32] confirm that the Ce(III)/Ce(IV) ratio variation, observed at the surface of the analyzed sample, strongly affects the absolute binding energy positions of the Ce 3d features. Notice that no shift is observed on our Ce 3d XPS spectra after calcination of the samples at 1073 K for 2 h, and consequently Ce(IV) is the only oxidation state of the analyzed surfaces. This result will be confirmed by the study of the O 1s lines.

Owing to the complexity of the Ce 3d spectrum, some authors prefer not to use it for quantitative measurements,[31] whereas others[20,21,23] have elaborated different relations to quantify the Ce(III) and Ce(IV) concentrations in a given sample. The results obtained from the analysis of a pure CeO_2 powder show that the satellite peak (~916.5 eV) contribution represents 13.4% of the total Ce 3d signal intensity.[20] In fact, these results are in good agreement with our data reported in Table I.

Quantitative analysis was elaborated for each sample in term to study the thermal treatment effect on the surface composition. For the sample prepared with NaOH and washed with hot water the surface analysis does not reveal the presence of sodium in both cases, untreated or calcined sample. Moreover, the ratio I Ce 3d/I Ce 4d remains unchanged before and after calcination. However, the atomic ratio n_{Na}/n_{Ce} changes from zero for the untreated sample to 1.36 after calcination at 1073 K for two hours under dry air, and the intensity ratio I Ce 3d/I Ce 4d decreases from 1.44 to 1.02 (Table I) in the case of the sample washed with cold water. These latter results can be explained by the migration of the sodium to the solid surface which suppresses the ejection of Ce 3d electrons.

For the sample prepared with KOH and washed with cold water the intensity ratio I Ce 3d/I Ce 4d remains approximately the same before and after calcination (Table I). This behavior can be explained by the weak presence of potassium on the solid surface after calcination (n_K/n_{Ce} = 0.17) compared with sodium concentration. Then, it is necessary to wash the prepared sample with hot water in order to remove all residue of the alkali elements issuing from the precipitating agents (NaOH and KOH). Whatever the proceeding of the cerium hydroxide preparation with NH_4OH was, no variation is noticed for the ratio I Ce 3d/I Ce 4d before and after calcination (Table I). Furthermore, the surface analysis does not reveal the presence of any intruding elements.

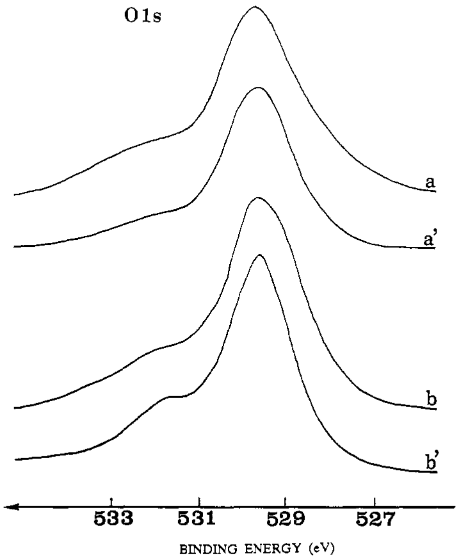

Figure 3. O 1s XPS spectra for samples prepared with (a) NH_4OH and (b) KOH. (a, b) untreated samples (a', b') calcined at 1073 K for 2 h under dry air.

More information can be also obtained by comparison of the O 1s XPS spectra. Indeed, the O 1s peak of the cerium compounds was the subject of many investigations.[28,29,33] In our case, and for the samples prepared with KOH and NH_4OH (Figure 3) these spectra show two components. The low-BE component in the range of 529.3 ± 0.2 eV is ascribable to oxidic species, whereas high-BE components (531.7 ± 0.2 eV) are due to hydroxidic species and/or ambient moisture. The oxygen peak at the high BE is always less intense than the oxidic one. For the sample prepared with NaOH and washed with hot water, the same results as above are obtained (Figure 4a,a') whereas, the intensity of the peak at ~531.7 eV increases significantly after thermal treatment at 1073 K (Figure 4b,b') in the case of the sample prepared with NaOH and washed with cold water. This behavior can be related to the migration of sodium after calcination, which probably promotes the presence of hydroxides on the solid surface. Finally, it is interesting to notice that the O 1s peak at BE = 529.3 ± 0.2 eV, attributed to oxidic species, is characteristic of CeO_2 according to Praline *et al.*,[29] who assigned the O 1s peaks at BEs 529.6 and 530.3 eV to CeO_2 and Ce_2O_3, respectively. These results confirm the only presence of Ce^{4+} species on solids surface.

EPR Results. Figure 5a shows the EPR spectrum observed at 77 K for the untreated cerium hydroxide prepared with NH_4OH. This spectrum is characteristic of Ce^{3+} ions [f^1 ions; $g_e > g_\perp > g_\parallel$] since similar spectra

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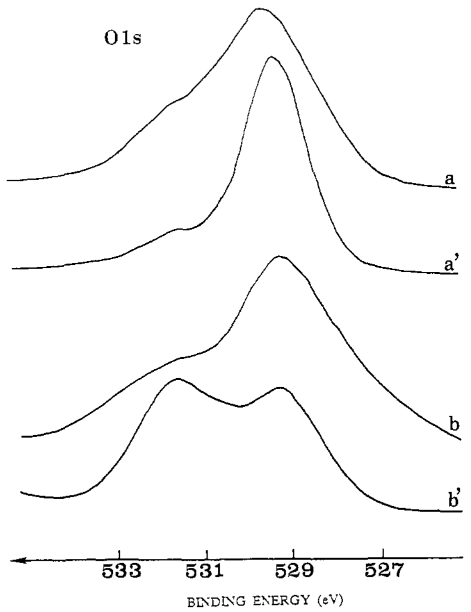

Figure 4. O 1s XPS spectra for samples prepared with NaOH and washed with (a) hot (b) cold water. (a, b) untreated samples (a', b') calcined at 1073 K for 2 h under dry air.

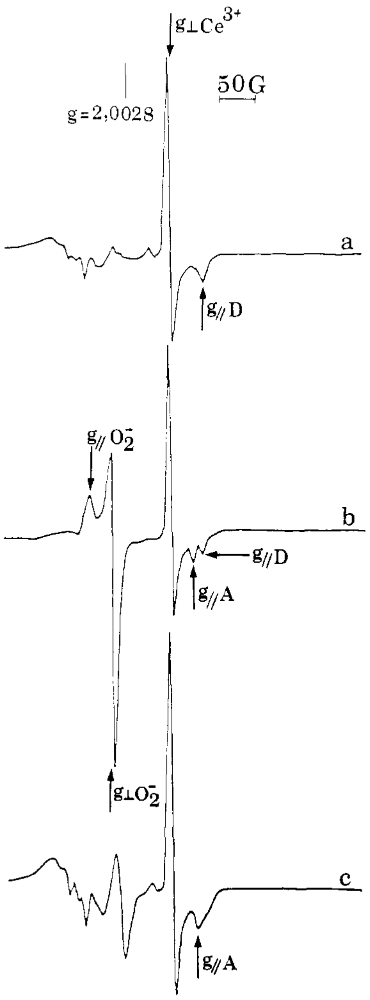

Figure 5. EPR spectra recorded at 77 K for cerium hydroxide prepared with NH_4OH and treated under dry air at different temperatures: (a) untreated, (b) 673 K, and (c) 1073 K.

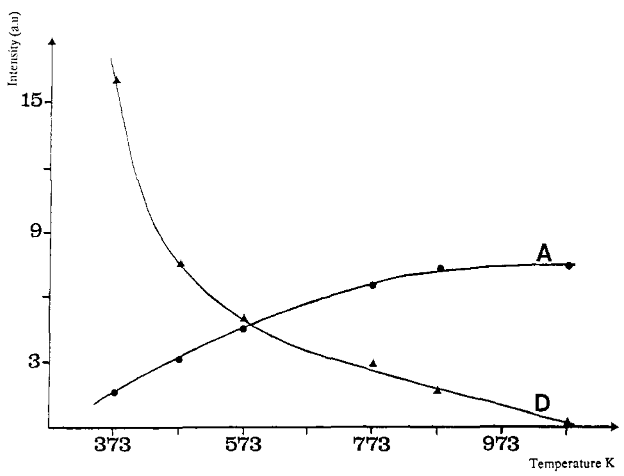

Figure 6. Intensities of the two signals Ce^{3+} (A) and Ce^{3+} (D) versus the calcination temperature for the sample prepared with NH_4OH.

were obtained by other authors for reduced CeO_2[1,4] and have been assigned to above species. Apparently, the spectrum is formed by the superposition of two signals: A ($g_{\perp} = 1.967$; $g_{\parallel} = 1.947$) and D ($g_{\perp} = 1.967$; $g_{\parallel} = 1.940$). The intensity of signal A is insignificant compared to that of signal D. The D intensity decreases progressively with the increase of the calcination temperature from 293 until 1073 K and finally disappears (Figures 5b,c and 6). On the contrary, the A intensity increases slowly to attain at 1073 K a value remaining inferior to the initial intensity of signal D.

For the cerium hydroxide prepared with KOH or NaOH, the two signals A and D remain observable as previously. However, the intensity of Ce^{3+} (A) becomes equal to zero in the case of the sample prepared with NaOH and calcined at 1073 K. When the sample is prepared with NaOH and washed with hot water, as described in the XPS part, the Ce^{3+} (A) signal does not disappear at high temperatures (1073 K).

The observed signals A and D can be attributed to the presence of two different Ce^{3+} sites in the solid. Since $\Delta g_A > \Delta g_D$ ($\Delta g = g_{\perp} - g_{\parallel}$) the coordination number of Ce^{3+} (A) is less than that of Ce^{3+} (D).[34,35] In fact, from the A and D intensity variations with the dehydration of the solid (Figure 6), it can be deduced that the D species are surrounded by more H_2O molecules than the A species. Furthermore, it is known that the calcination of oxides at high temperatures induces oxygen vacancies in the solid.[1] Consequently, signal A is probably due to Ce^{3+} ions in the bulk of the solid, stabilized by some lattice defects whereas signal D corresponds to Ce^{3+} ions with easily removable ligands.

If we suppose that the totality of the untreated sample exists in the form of CeO_2 and $Ce(OH)_4$ with a small quantity of $Ce(OH)_3$, the latter entity will be responsible of the signal D observed in the cases of the untreated samples. During the calcination under dry air, the first fraction of $Ce(OH)_3$ changes into CeO_2 (inactive in EPR) and the second one into Ce_2O_3 responsible of signal A. To illustrate the intensity variation of the two signals A and D, the following reaction is proposed:

$$4Ce(OH)_3 + {}^1/_2O_2 \rightarrow 2CeO_2 + Ce_2O_3 + 6H_2O \quad \text{(III)}$$

The sites Ce^{3+} (A) and Ce^{3+} (D) are related to the presence

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of Ce_2O_3 and $Ce(OH)_3$ entities, respectively. Effectively, at 1073 K Ce^{3+} (D) disappears and the A intensity is approximately half of the D initial intensity (Figure 6), which verifies the stoichiometry of the above reaction.

The disappearance of the Ce^{3+} signal in the case of the calcined sample prepared with NaOH and washed with cold water could be due to the presence of sodium. In fact, as demonstrated in the XPS study, increasing the calcination temperature favors sodium migration to the solid surface. Apparently, this migration makes easier the access of oxygen to the bulk of the solid to oxidize all residue of Ce(III) species into Ce(IV).

In addition to the signals A and D observed on the spectra of the preceding samples, a new signal ($g_{\parallel} = 2.034$ and $g_{\perp} = 2.011$) appears with the augmentation of calcination temperature (Figure 5b,c). The parameters of this signal are similar to those assigned by other authors to O_2^- species bounded to Ce^{4+} ions and exhibited an EPR spectrum characteristic of an axial symmetry.[36,37] The large positive shifts of the *g* values from the values expected, considering the ionic model of O_2^-,[37] may be due to some coupling of the molecular ion orbitals with the 4f orbital electrons in the cerium ions.[36] The appearance of strong signals of O_2^- bounded to Ce^{4+} ions points to the availability of an important number of electrons, probably arising from Ce^{3+} ions in lattice positions,[4] capable of being transferred to O_2 molecules. Furthermore, Zhang and Klabunde[38] have detected three different ways of O_2^- adsorption according to the surface sites. By comparison with their results,[38] we can assigned two ways of adsorption for our O_2^- species. One, O_2^- located on surface Ce^{4+} ions with both oxygen nuclei equidistant from the surface. The other one is very similar, but the local field is slightly different. This assumption is in harmony with the variation of the O_2^- signal intensity versus the calcination temperature (Figure 7). The line shape of this variation exhibits two maxima at 673 and 873 K probably in relation with the presence of the two sites of Ce^{3+} ions in the ceria.

To study the stability of the Ce^{3+} signal in the presence of other elements, samples of CuCe oxide with different copper contents have been prepared using the coprecipitation method with NH_4OH as alkaline solution.

The EPR spectra of the freshly prepared and untreated samples show a decrease in the intensity of the Ce^{3+} signal when the copper content is increased in the solid. This Ce^{3+} signal disappears for copper concentrations higher than $Cu/Ce = 5 \times 10^{-2}$. Moreover, it should be pointed out that, even at low copper content ($Cu/Ce < 5 \times 10^{-2}$), the EPR Ce^{3+} signal disappears with increasing calcination temperature. This behavior can be related to the presence of the redox couple Cu^{2+}/Cu^+ which appearently promotes the oxidation of the residual Ce^{3+} ions into Ce^{4+}, especially at high temperatures. Furthermore, when the calcined samples (CuCe–O) are treated under a reducing atmosphere, the Ce^{3+} signal is regenerated and can be observed on the EPR spectra.[1]

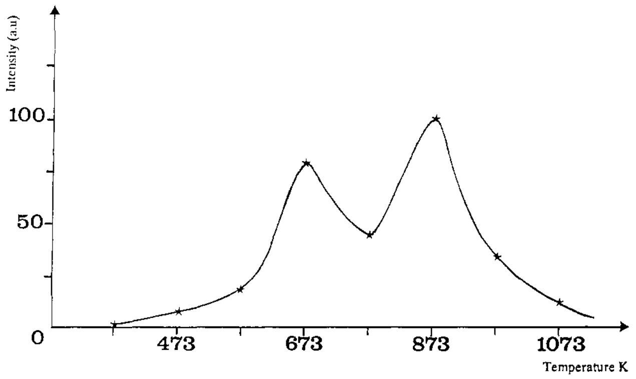

Figure 7. Intensity of O_2^- signal versus the calcination temperature for the sample prepared with NH_4OH.

Conclusion

In this work, many samples of cerium hydroxides, prepared with different alkali solutions (NaOH, KOH, and NH_4OH), have been studied. The untreated samples were always constituted by a mixture of CeO_2 and $Ce(OH)_4$ with a small quantity of $Ce(OH)_3$ probably present in the bulk of the solid. The XPS study reveals the presence of Ce(IV) species on the solids surface and no traces of Ce(III) species were analyzed. A part of the Ce^{3+} ions remains stable under the form of Ce_2O_3 even after calcination at high temperatures (1073 K). Apparently the presence of sodium, in the case of the sample prepared with NaOH and washed with cold water, promotes the oxidation of the residual Ce^{3+} species into Ce^{4+} at high temperatures. Moreover, this study has detected the presence of O_2^- species bounded to Ce^{4+} ions.

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