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Characterization of cerium oxides prepared in water and sodium hydroxide mixtures

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Abstract

Non-stoichiometric cerium oxides were prepared in NaOH–H_2O mixtures of various compositions at room temperature from hydrated cerium(III) nitrate and cerium(IV) sulphate as precursors. The resulting products were characterized by their compositions (chemical, thermogravimetric and energy-dispersive spectrometry analysis) and by their morphology (X-ray diffraction, granulometry and electron microscopy). The compounds obtained by bubbling oxygen in cerium(III) nitrate solutions are amorphous. Their oxidation states are close to 3.8 and their average grain size is 7.6 μm. In contrast, those obtained from cerium(IV) sulphate solutions are better crystallized and have lower oxidation states. These compounds are formed of grains of about 9.2 μm.

1. Introduction

Among the lanthanides, cerium is the element which has the largest field of application, *e.g.* in metallurgy, nuclear technology and in the silicates industry. Cerium oxides are usually used in the glass industry, and for the manufacture of acetic acid and synthetic fibres. In the ceramic industry, cerium oxide is used as an opaque-making agent for enamels.

Various routes for the synthesis of cerium oxides and hydroxides are given in the literature: (i) calcination of cerium(III) salts leading to the formation of CeO_2, which has to be reduced at 1250 °C by hydrogen to give Ce_2O_3 [1], (ii) NH_4OH precipitation of aqueous nitrate solutions [2].

Obtaining cerium oxides using highly concentrated sodium hydroxide and water mixtures has not yet been systematically studied. Water and alkaline hydroxide mixtures are frequently used for the synthesis of various metallic oxides and hydroxides. In previous works [3–5] we have studied the equilibria

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which exist both in these pure media and in the same media containing metallic cations. In particular, such investigations enabled us to construct equilibrium potential–composition diagrams which gave the areas of stability of (hydr)oxide compounds. Nevertheless, these diagrams only take into account compounds whose Gibbs energy is known. Besides, only energetic information is available from this type of diagram and they give no indication of the compounds' physical properties. So, one of our aims is to set up a correlation between the composition of the preparation media and the chemical and physical properties of the product prepared in water and alkaline hydroxide mixtures. Such an investigation was recently reported for manganese oxides [6]. The products obtained using this synthetic route were subsequently studied in order to determine their chemical composition and particle size [6, 7].

The purpose of this paper is (i) to study the chemical behaviour of cerium in NaOH–H_2O mixtures, (ii) to apply the results in the preparation of cerium oxides from nitrate or sulphate salts as precursors, and (iii) to characterize them. Moreover, we have tried to find evidence of a correlation between the preparation method used and the chemical composition and morphology of the products obtained.

2. Thermochemical behaviour of cerium in NaOH–H_2O mixtures

In order to determine the chemical conditions required to prepare our products, we set up the potential–composition diagram of cerium at 25 °C to reveal the predominant areas of Ce–O–H compounds at room temperature.

The method of producing this diagram has been described previously [4]. The Gibbs energies of the compounds involved in chemical equilibria are needed.

A great deal of thermochemical data are available in the literature. The data needed to establish the potential–composition diagrams were chosen from the most recent literature available and that which fit best the experimental observations. These values [8–11] are collected in Table 1.

TABLE 1

Gibbs free energies of species needed to establish the potential–composition diagram of Cerium in water and sodium hydroxide mixtures at 298 K

	Species						
	CeO_2	Ce_2O_3	$Ce(OH)_3$	Na_2CeO_3	$H_2O(g)$	OH^-	NaOH
$\Delta G^\circ_{f\,198}$ (kJ mol^{-1})	−1026.67	−1733.51	−1323.49	−919.00	−228.582	−157.41	−381.95
Reference	8	8	9	See text	8	11	8

2.1. *Existence of $Ce(OH)_3$*

Considering the equilibrium:

$Ce_2O_3 + 3H_2O = 2Ce(OH)_3$

It is possible to show that $Ce(OH)_3$ is stable in the whole composition range of concentrated H_2O–NaOH mixtures. This is due to the fact that the water pressure calculated from the Gibbs energy variation for the reaction cannot be attained by any suitable mixture since it is lower than the lowest water pressure corresponding to the saturated sodium hydroxide medium. We therefore decided that Ce_2O_3 was not suitable for setting up the potential–composition diagram.

2.2. *Estimation of thermochemical data for sodium cerates*

No thermochemical data for cerates are available in the literature. Nevertheless, it is possible to estimate these values using the computing methods suggested by Kubaschevski and Evans [12]. These methods are based on the fact that, for compounds with identical stoichiometric proportions, the formation enthalpies of metallic oxides can be correlated empirically with the atomic number of the metal. The standard molar formation enthalpies ΔH°_{f298} at 25 °C of some homologous species [10] such as Na_2SiO_3 (-1563.27 kJ mol^{-1}), Na_2TiO_3 (-1591.18 kJ mol^{-1}) and Na_2SnO_3 (-1154.78 kJ mol^{-1}) are plotted *vs.* the atomic number Z of the metallic atom in Fig. 1. The values for sodium cerate Na_2CeO_3 (-1020.90 kJ mol^{-1}) was obtained by extrapolation.

The standard entropy S°_{298} of Na_2CeO_3 may be obtained from the sum of the entropies of the oxides Na_2O (75.06 J mol^{-1} K^{-1} [8] and CeO_2 (62.34 J mol^{-1} K^{-1} [8]). This estimation assumes that the entropy variation of the following reaction

$Na_2O + CeO_2 = Na_2CeO_3$

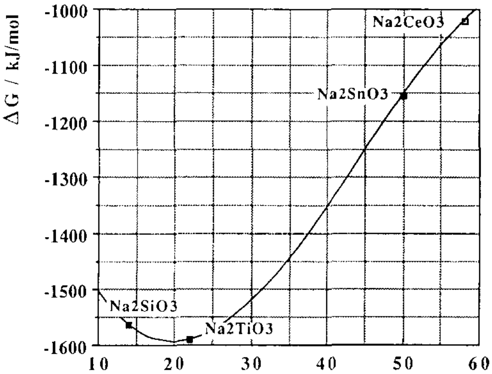


Fig. 1. Variation of the standard molar formation enthalpy of Na_2MO_3 compounds with respect to the atomic number Z of the metallic atom M.

is zero, *i.e.*

$$S°(Na_2CeO_3) = S°(Na_2O) + S°(CeO_2) = 137.40 \text{ J mol}^{-1} \text{ K}^{-1}$$

The variation $\Delta S°$ of the standard formation entropy of Na_2CeO_3 is obtained from the standard entropies of the elements which are taken from ref. 8 (sodium 51.17 J mol^{-1} K^{-1}, O_2 205.02 J mol^{-1} K^{-1} and cerium 69.45 J mol^{-1} K^{-1}).

$$\Delta S°(Na_2CeO_3) = S°(Na_2CeO_3) - 2S°(Na) - \tfrac{3}{2}S°(O_2) - S°(Ce)$$
$$= -341.92 \text{ J K}^{-1}$$

Thus, it is possible to calculate $\Delta G°(Na_2CeO_3)$ applying Helmholtz's simplified equation:

$$\Delta G° = \Delta H° - T\Delta S° = -919.02 \text{ kJ}$$

In order to find out whether Na_2CeO_3 exists in the water and sodium hydroxide mixtures, the following acid–base equilibrium:

$$CeO_2 + 2NaOH = Na_2CeO_3 + H_2O(g)$$

is considered. The variation of the Gibb's energy for this reaction is +643 kJ which indicates that the equilibrium lies strongly to the left, and that Na_2CeO_3 cannot exist in any appreciable amount in these media.

2.3. *Equilibrium potential–composition diagram*

Water and alkaline hydroxide mixtures have previously been studied with regard to their thermochemical characteristics; this led to the determination of ionic and molecular species activities in water and sodium hydroxide, water and potassium hydroxide [3] and water and lithium hydroxide [5] mixtures.

This information allowed us to analyse the acid–base and redox reactions which may occur in these media. This was done by setting up the potential–composition diagrams of various elements in which the potential is given with respect to the reference system M^+/M ($M \equiv Na$, K or Li) and the composition is represented by the logarithm of the alkaline hydroxide activity [log a(MOH)] [4]. Similarly, the potential–log a(NaOH) diagram for cerium, accounting for the various stable species of cerium in the water and sodium hydroxide mixtures at 25 °C, has been set up (Fig. 2). This diagram, obtained from literature data only, allows us to see that the two extreme stable oxidation states of cerium in these media are III and IV. Thus, we can expect to prepare cerium oxides with oxidation states ranging between III and IV.

3. Experimental procedures

3.1. *Materials*

The starting materials used to prepare cerium oxides were cerium(IV) sulphate [$Ce(SO_4)_2 \cdot 4H_2O$] and cerium(III) nitrate [$Ce(NO_3)_3 \cdot 6H_2O$], both

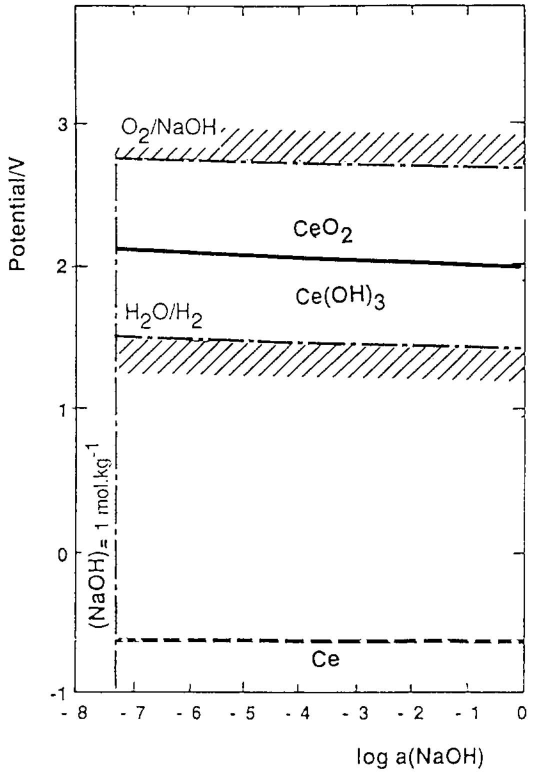


Fig. 2. Equilibrium potential–log[a(NaOH)] diagram of cerium in NaOH–H_2O mixtures at 25 °C.

supplied by Merck. Three concentrations of sodium hydroxide (Prolabo) were used: 2, 12.5 and 25 mol kg^{-1} (respective mole fractions 0.0347, 0.1837, 0.3103).

6.0 g of cerium salt were introduced in a beaker containing 75 ml of NaOH–H_2O mixture and saturated with oxygen. Oxygen bubbling was then maintained throughout the duration for the oxide precipitation, *i.e.* to at least 40 min (longer times do not produce any modification of the nature of the products).

Extraction of the product was accomplished by centrifugation. The solid oxide was then separated from the liquor by filtration and washed several times (from 4 to 16 washings) with 5 ml of absolute alcohol. Finally, the precipitate was dried at 80 °C for 24 h.

It should be noted that washing with water is prohibited because, according to our observations, this leads to the same product which can be obtained in dilute NaOH–H_2O mixture.

By comparing the amount of oxide produced with the theoretical amount, we can determine an oxide yield. Depending on the experiments, the yield ranges from 60% to 80%.

3.2. *Chemical analysis*

Acidimetric titration of Na_2CO_3 inserted in the products, iodometric titration and thermogravimetric analysis with an ADAMEL apparatus type 59, mod. II. for the determination of the oxidation state and amount of water of the prepared oxides were used for the chemical characterization of the cerium oxides. The procedures are explained with the results.

3.3. *Electron microscopy and energy-dispersive spectrometry analysis*

The scanning and transmission electron microscopy (SEM and TEM) was performed on a Jeol JEM 100 CX II which operates with an accelerating voltage of 100 kV. Quantitative analysis of the cerium oxides was obtained in STEM mode thanks to the scanning device (ASID 4D) of the microscope and X-ray energy-dispersive spectrometry (EDS): Link AN 10000 with an ultrathin window.

Generally for TEM observations, the specimen powders are ground with a mortar, suspended by ultrasonic dispersion in a liquid and deposited onto a holey carbon film supported over a copper grid. Operating in this way we observed damage of the crystallites. So afterwards the specimens were only suspended by ultrasonic dispersion in ethanol for the TEM observations and X-ray microanalysis.

For the SEM observations, the samples were prepared by spreading a thin layer of the cerium oxide powder onto a support covered with carbon glue. Then the surface was coated with a thin layer of gold.

3.4. *X-ray diffraction*

The X-ray diffraction patterns were obtained with a Théta 60 CGR apparatus using the $K\alpha_1$ ray of cobalt (1.789 Å).

3.5. *Granulometry*

The particle sizes were measured by means of a Coulter® Multisizer connected to a Bull Micral 35F computer. The samples were suspended in a methanol and 5 wt.% LiCl mixture and ultrasonically dispersed (for 40 s) before each measurement.

4. Characterization of the prepared cerium oxides

4.1. *Chemical compositions*

4.1.1. *Determination of the pollutant sodium-to-cerium ratio*

Acidimetric titrations. Knowing that concentrated $NaOH–H_2O$ mixtures strongly absorb atmospheric carbon dioxide, the precipitated compounds could contain a small amount of coprecipitated Na_2CO_3. A part of the Na_2CO_3 is eliminated by washing with alcohol and the remaining amount is determined by acidimetric titration.

100 mg of a precipitate sample are mixed with 20 ml of water and titrated with HCl 0.1035 mol l^{-1} using methyl red as an acid–base indicator. At the first trace of pink, the solution is boiled for 2 min to eliminate the

carbon dioxide. The titration is then continued until the appearance of a persistent pink color.

The results shown in Fig. 3(a) represent the plot of the [Na]/[Ce] ratio *vs.* the number of washings, whatever the nature of the precursor (nitrate or sulphate) used and the concentration of NaOH. Thus, it appears that nearly 10 washings with 5 ml of absolute alcohol are necessary to obtain samples of cerium oxides practically free of Na_2CO_3.

X-ray energy dispersive spectrometry analysis. We also performed an EDS analysis (see *e.g.* Fig. 3(b)) to determine the pollutant [Na]/[Ce] ratio. In Fig. 3(a), we can observe that this ratio is always small and decreases with the number of washings. Moreover, for samples practically free of any Na_2CO_3, this ratio is very close to zero. Although EDS analysis is performed on a very small volume compared with acidimetric titrations, we obtained coherent results for these two techniques. This fact proves that Na_2CO_3 is linked homogeneously together with cerium oxide.

4.1.2. Oxidation state and amount of water

This result, in addition to the fact that the oxides produced may contain a certain amount of water, leads to the formulation of these oxides as follows:

$CeO_{1.5+x}\cdot zH_2O$

with $0<x<0.5$, the cerium oxidation state being equal to $2(1.5+x)$. The values of x and z were determined from iodometric titrations and thermogravimetric experiments because the EDS analysis is not applicable for oxygen and hydrogen quantitative analysis.

Iodometric titrations. Nearly 100 mg of a prepared precipitate sample are introduced into a solution containing 3 ml of 6 mol l^{-1} HCl and 5 ml of 20% KI and heated slightly until complete dissolution. 5 ml of a sodium acetate solution (3.55 mol l^{-1}) are added to avoid the oxidation of iodide by the dissolved oxygen. Iodine produced by the reaction

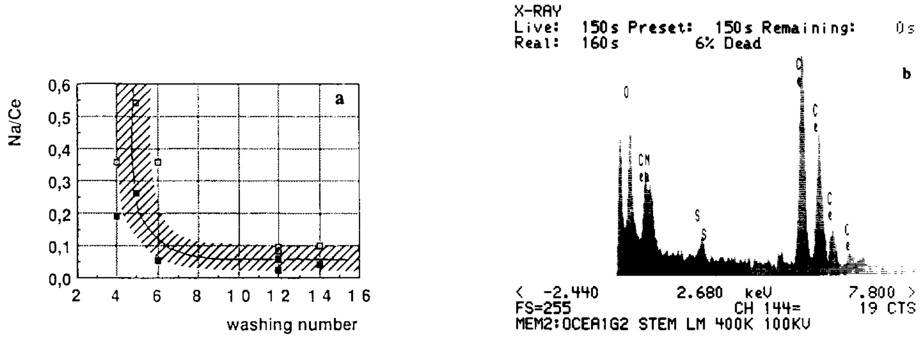


Fig. 3. (a) Plot of the [Na]/[Ce] ratios obtained from chemical analysis (□) and from EDS analysis (■) *vs.* the number of alcohol washings. (b) Typical EDS spectrum of a cerium oxide obtained from cerium(IV) sulphate precursor.

$$CeO_{1.5+x}\cdot zH_2O+2xI^-+(3-2x)H^+=Ce^{3+}+xI_2+(1.5+x+z)H_2O$$

was titrated with a sodium thiosulphate solution (0.1 mol l^{-1}).

The added thiosulphate volume V_i (ml), the concentration C (mol l^{-1}) and the sample mass m_i (mg), are related according to the following expression:

$$(2m_i-16CV_i)x-(18CV_i)z=164.15CV_i \qquad (1)$$

Values are collected in Table 2.

Thermogravimetric analysis. Preliminary studies showed that no weight loss occurs beyond 600 °C. The weight loss Δm_t for each sample (weight m_t) was thus measured at this temperature and is given in Table 2.

The compound $CeO_{1.5+x}\cdot zH_2O$ loses water according to the reaction

$$CeO_{1.5+z}\cdot zH_2O=CeO_{1.5+x}+zH_2O$$

which shows that the relative weight variation ($\Delta m_t/m_t$) is related to the parameters x and z by the expression:

$$\Delta m_t/m_t=18z/[140.15+16(1.5+x)+18z]$$

which may be rewritten:

$$16x\Delta m_t/m_t+18(\Delta m_t/m_t-1)z=-164.15\Delta m_t/m_t \qquad (2)$$

Determination of the parameters x and z and discussion. The values of x and z are determined from the results obtained by iodometric and thermogravimetric analysis. This is done by resolving the system of eqns. (1) and (2). The values are given in Table 2.

TABLE 2

Results from thermogravimetric and volumetric analysis of cerium oxide samples of general formula $CeO_{1.5+x}\cdot zH_2O$, yNa_2CO_3

	Precursor					
	$Ce(SO_4)_2$	$Ce(SO_4)_2$	$Ce(SO_4)_2$	$Ce(NO_3)_3$	$Ce(NO_3)_3$	$Ce(NO_3)_3$
NaOH (mol kg^{-1})	25.0	12.5	2.0	25.0	12.5	2.0
Numbers of washes	4	12	6	12	5	14
m_t (mg)	279.9	195.8	196.4	294.6	195.5	198.9
Δm_t (mg)	29.6	22.1	27.8	25.6	18.8	26.7
m_i (mg)	103.3	99.94	106.6	104.6	115.9	104.4
V_i (ml)	4.35	4.35	4.40	4.85	5.15	4.70
$1.5+x$	1.66	1.76	1.89	1.93	1.91	1.91
z	0.23	0.55	0.86	1.20	0.89	0.70
y	0.18	0.047	0.18	0.041	0.27	0.05

The plot of the NaOH mole fraction dependence of *z* is given in Fig. 4. It appears that the amount of water in the cerium oxides depends on the nature of the precursor. Also, whatever the precursor, the amount of water decreases quite linearly with the mole fraction of sodium hydroxide.

Concerning the oxidation state of the cerium oxides, we observe in Fig. 5 a surprising effect of the mole fraction of NaOH. In fact, starting from a cerium(IV) salt, we obtained oxides whose cerium oxidation state decreased with the mole fraction of sodium hydroxide until it reached a value close to III. In contrast, the products obtained from cerium(III) nitrate have a cerium oxidation state which remains close to IV, regardless of the NaOH mole fraction.

Our interpretation of this observation is based upon our proposal of two reaction mechanisms (marked I and II, Fig. 6) described hereafter.

In the first case, the oxidation states of the products showed that a reduction reaction of the cerium(IV) precursor has occurred. The lack of

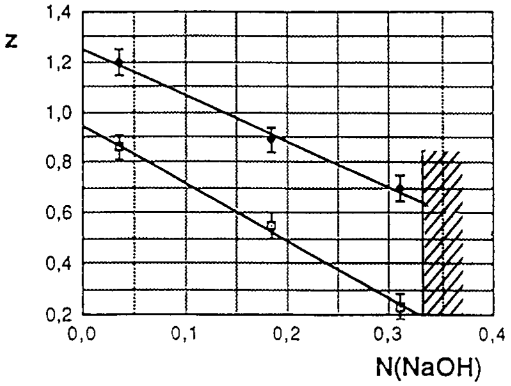


Fig. 4. Plot of the amount of water *z* of the cerium oxides *vs.* the NaOH mole fraction of the medium for ◆ nitrate and ⊡ sulphate precursors.

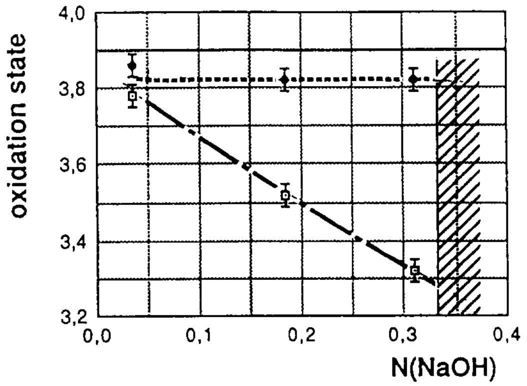


Fig. 5. Plot of the oxidation state of the cerium oxides *vs.* the NaOH mole fraction of the medium for ◆ nitrate and ⊡ sulphate precursors.

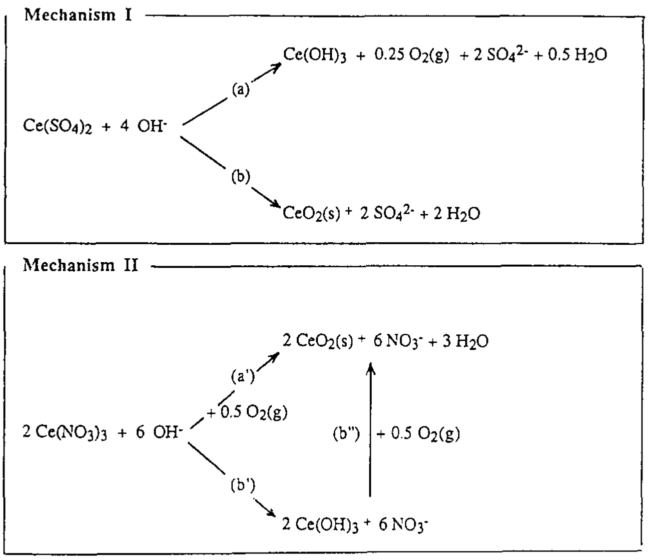


Fig. 6. Schematic representation of the possible reaction pathways for the production of cerium oxides from ceric sulphate or cerous nitrate.

any reducing agent in the solution implies that the cerium(IV), which is less complexed with sulphate anions than with oxide anions, has been reduced by the medium, the latter being oxidized with oxygen evolution (pathway (a)). Simultaneously, an acid–base reaction must occur leading to the formation of cerium dioxide (pathway (b)), accounting for the oxidation states higher than 3.

If cerium(III) nitrate is used as a precursor, however, we notice that the oxidation states of the products are only slightly lower than 4 (Fig. 5). This indicates a stronger oxidation by oxygen (mechanism II, Fig. 6) either directly (pathway (a′) or through the transient acid–base reaction of hydroxide $Ce(OH)_3$ formation (pathway (b′)).

The transformation reactions of the cerium(III) and cerium(IV) salts into cerium oxides do not depend on the activity of Na^+ cations but rather on that of OH^- anions (Fig. 6). Yet, we have previously demonstrated that OH^- activity is quite constant whatever the concentration of sodium hydroxide [3]. These remarks suggest that physical factors, such as viscosity, should have a predominant effect on the mechanism. Indeed, a high viscosity of the medium, corresponding to a high NaOH concentration, slows down the anion exchange reaction (sulphate → oxide or nitrate → hydroxide). In the case of the cerium(IV) precursor, this favours reaction (a) in Fig. 6, which is evidenced by EDS analysis in determining the [S]/[Ce] ratio (Fig. 7). The plot of the [S]/[Ce] ratio *v* the NaOH mole fraction of the medium shows in fact an increasing amount of sulphur in the resulting compounds with the NaOH mole fraction. The sulphate is trapped in the prepared cerium oxide when the viscosity of the medium increases. However, if we use cerous nitrate as a precursor for the oxide, mechanism II shows that viscosity

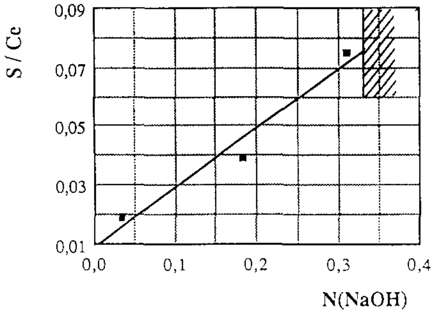
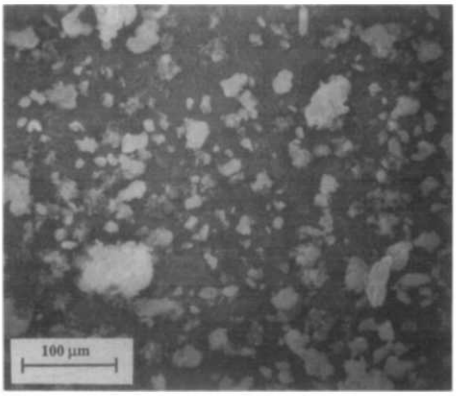


Fig. 7. Plot of the [S]/[Ce] ratios obtained from EDS analysis *vs.* the NaOH mole fraction of the medium.



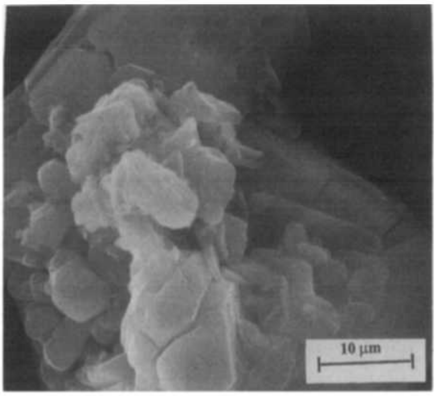


Fig. 8. SEM image of a typical cerium oxide prepared from tetrahydrated cerium(IV) sulphate in 12.5 mol kg^{-1} NaOH.

Fig. 9. SEM image of a typical cerium oxide prepared from tetrahydrated cerium(IV) sulphate in 12.5 mol kg^{-1} NaOH.

(related to the NaOH mole fraction) has practically no influence on the nature of the oxides produced.

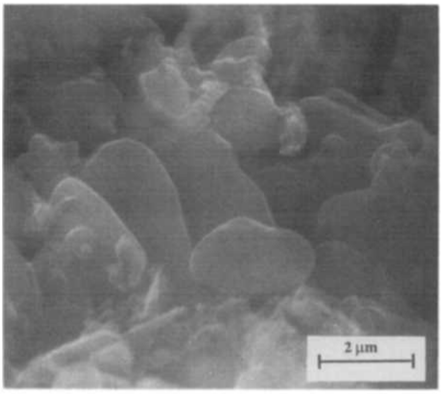
4.2. Morphology of the oxides

4.2.1. Scanning electron microscopy

With a large field of view, we noted that all the powders tend to agglomerate into lumps (Fig. 8). At larger magnifications the morphology of these packs differs with the nature of the precursor but seems independent of the NaOH mole fraction. In the case of the cerium(IV) sulphate precursor the sample crystallized in rounded plates (Fig. 9 and (10). With the cerium(III) nitrate precursor, the prepared oxide cerium is porous (Fig. 11).

4.2.2. Transmission electron microscopy

Using TEM we studied the structure of the prepared powders. First, we noticed that the structure of the oxides seems to be independent of the



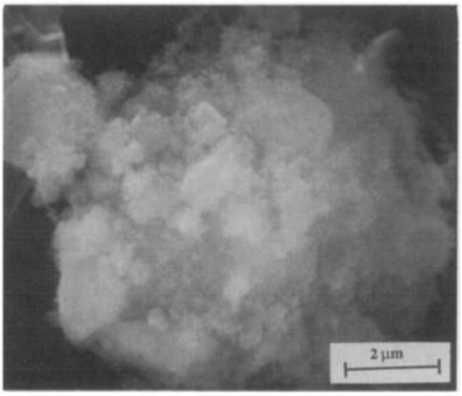


Fig. 10. SEM image of a typical cerium oxide prepared from tetrahydrated cerium(IV) sulphate in 25 mol kg^{-1} NaOH.

Fig. 11. SEM image of a typical cerium oxide prepared from hexahydrated cerium(III) nitrate in 25 mol kg^{-1} NaOH.

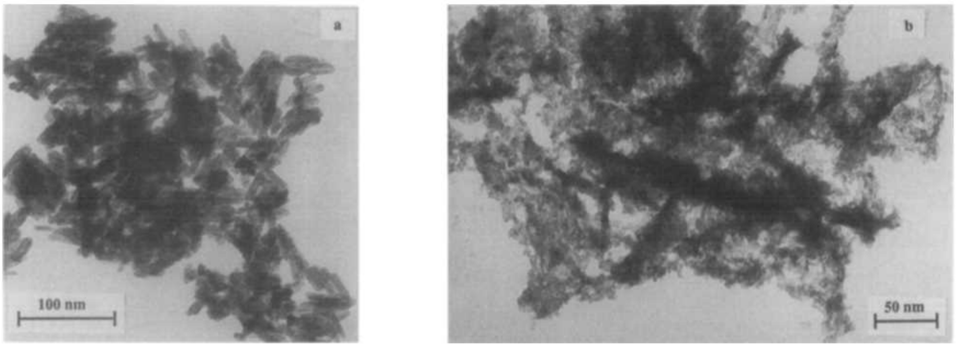


Fig. 12. TEM images of typical cerium oxides prepared in 25 mol kg^{-1} NaOH: (a) with hexahydrated cerium(III) nitrate precursor, and (b) with tetrahydrated cerium(IV) sulphate precursor.

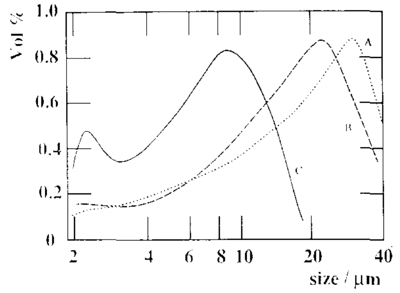
sodium hydroxide concentration of the mixture (within the 2–25 mol kg^{-1} range) in which they were prepared.

In contrast, we again found the effect of the precursor. Indeed, the oxide powders obtained from cerium(III) nitrate consist of small homodispersed particles which have the shape of grains of rice. For example, Fig. 12(a) shows particles corresponding to an oxide powder prepared in a 25 mol kg^{-1} sodium hydroxide solution. Their dimension is 34 nm by 10 nm.

When cerium(IV) sulphate was used as a precursor, we obtained very small homodispersed spherical particles ($\phi = 4$ nm) laid side by side (Fig. 12(b)).

4.2.3. Granulometry

The characteristic feature of these products is the wide grain size distribution they present (Fig. 13 and 14). Moreover, we observe smaller



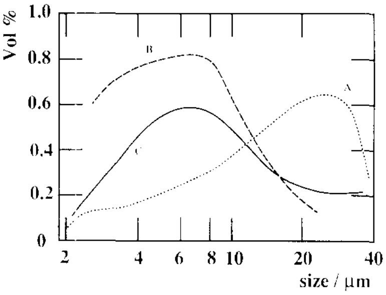
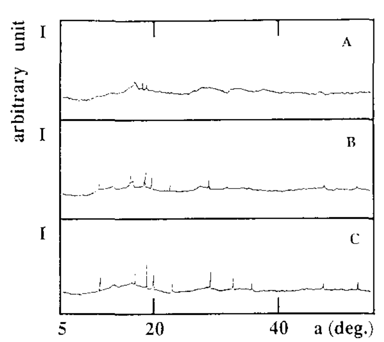


Fig. 13. Grain size distributions of cerium oxides prepared from tetrahydrated cerium(IV) sulphate: A 2 mol kg^{-1} NaOH; B 12.5 mol kg^{-1} NaOH; C 25 mol kg^{-1} NaOH.

Fig. 14. Grain size distributions of cerium oxides prepared from hexahydrated cerium(III) nitrate: A 2 mol kg^{-1} NaOH; B 12.5 mol kg^{-1} NaOH; C 25 mol kg^{-1} NaOH.



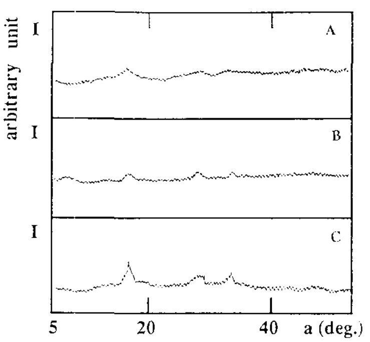


Fig. 15. X-ray spectra of the cerium oxides prepared from tetrahydrated cerium(IV) sulphate: A 2 mol kg^{-1} NaOH; B 12.5 mol kg^{-1} NaOH; C 25 mol kg^{-1} NaOH.

Fig. 16. X-ray spectra of the cerium oxides prepared from hexahydrated cerium(III) nitrate: A 2 mol kg^{-1} NaOH; B 12.5 mol kg^{-1} NaOH; C 25 mol kg^{-1} NaOH.

grains when more concentrated media are used. For example, the products obtained in 25 mol kg^{-1} NaOH, whatever the nature of the precursor, have modes of 9.2 μm (sulphate) and 7.6 μm (nitrate). In comparison, those obtained in 2 mol kg^{-1} NaOH have modes of 29.6 μm and 33.5 μm respectively. In particular, we can notice that the product prepared in 25 mol kg^{-1} NaOH from cerium(IV) sulphate, is bipopulated, the second mode (2.4 μm) corresponding to very small grains. We noticed that some of these grains agglomerate forming lumps of about 40–60 μm. These lumps may represent up to 10%–20% of the sample. These results are compared with the SEM results. In Fig. 8 packs with these dimensions are observed.

4.2.4. X-ray diffraction

Uncalcined products. The X-ray spectra in Figs. 15 and 16 show that the medium viscosity (which increases with the NaOH mole fraction) favours the crystallization of the resulting product by slowing down the diffusion process. When the tetrahydrated cerium(IV) sulphate is used as a precursor, an X-ray amorphous product is formed when the NaOH concentration is 2 mol kg^{-1} (Fig. 15, spectrum A). However, a partially crystallized product is obtained when the preparation medium is 12.5 mol kg^{-1} NaOH (Fig. 15, spectrum B). The crystallization of the product is improved when 25 mol kg^{-1} NaOH (Fig. 15, spectrum C) is used.

Using the hexahydrated cerium(III) nitrate, we can observe something similar (Fig. 16), but without ever obtaining good crystallization of the product, even with 25 mol kg^{-1} NaOH (Fig. 16, spectrum C). The difference observed in the behaviour of the two precursors might be explained by the higher stability of the sulphato complex of the cerium(IV).

Calcined products. Three products, whose formula is $CeO_{1.76} \cdot 0.55H_2O$ (yellow coloured), obtained in 12.5 mol kg^{-1} NaOH with cerium(IV) sulphate precursor, were calcined, the first at 300 °C for 6 h, the second at 600 °C for 6 h and the last at 800 °C for 6 h (samples A, B and C). We can observe in Fig. 17 that the higher the calcination temperature, the better the crystallization. Moreover, we noticed that the final colour and specific surface area of the products depend on the calcination temperature (Table 3). Calcination progressively transforms the non-stoichiometric cerium oxide into cerium dioxide (Fig. 18).

5. Conclusion

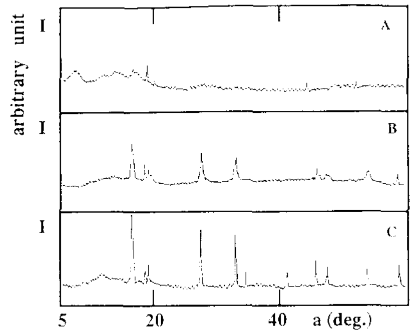
In H_2O–NaOH mixtures, it was possible to prepare cerium oxides at room temperature using cerium(IV) sulphate or cerium(III) nitrate as a precursor. The oxidation states of these oxides ranged from 3.3 to 3.8.

The chemical composition and the morphology of the oxides formed strongly depend on the method of preparation. It appeared that the essential factors were the viscosity of the medium and the nature of the precursor used.

TABLE 3

Calcination temperature dependence of the colour and specific surface area of the cerium oxide $CO_{1.76} \cdot 0.55H_2O$

	Sample		
	A	B	C
Calcination temperature (°C)	300	600	800
Colour	Yellow	White	White
Specific surface area (m^2 g^{-1})	19.0	6.0	1.5



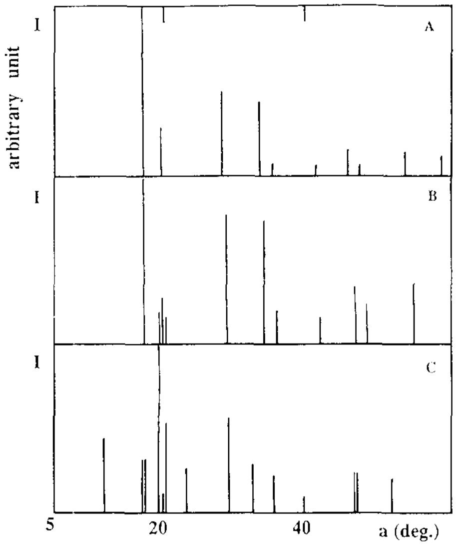


Fig. 17. X-ray spectra of the cerium oxides prepared from tetrahydrated cerium(IV) sulphate in 12.5 mol kg^{-1} NaOH and calcined for 6 h at 300 °C (A), 600 °C (B) and 800 °C (C).

Fig. 18. Comparison between the spectra of stoichiometric CeO_2 (A), cerium oxide prepared from tetrahydrated cerium(IV) sulphate from 12.5 mol kg^{-1} NaOH calcined at 800 °C for 6 h (B), and cerium oxide prepared from tetrahydrated cerium(IV) sulphate from 25 mol kg^{-1} NaOH and not calcined (C).

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