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ORIGINAL CONTRIBUTION

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Preparation and properties of uniform praseodymium-doped ceria colloidal particles

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Abstract A procedure to prepare submicrometre spherical particles of Pr(III), Ce(III) or Pr(III)-doped C(III) hydroxycarbonates with narrow size distribution is reported. The particles were obtained by aging aqueous solutions of Pr(III) chloride and/or Ce(III) nitrate in the presence of urea at 100 °C for 2 h. The effect of Pr and/or Ce salt concentrations in the starting solutions on the size, shape and composition of the precipitated particles is reported. The thermal behaviour of the basic carbonates up to decomposition into the metal oxides was followed by differential thermal and thermogravimetric analyses, X-ray diffraction, IR spectroscopy and transmission electron microscopy. All the systems were also characterized by their electrokinetic behaviour (determination of isoelectric point) and specific surface areas. The colour of the powders was also evaluated as a function of the Pr content and temperature and was compared with previous results on red pigments of similar composition.

Keywords Cerium oxide · Praseodymium oxide · Spheres · Pigments · Catalysts

Introduction

Praseodymium-doped cerium oxide (Pr-CeO_2), as well as its individual components, cerium oxide (CeO_2) and praseodymium oxides (Pr_2O_3 and Pr_2O_3–PrO_2 intermediate phases) are extensively used as catalysts in different processes [1–4]. In particular, Pr-doped ceria was included as a component in three-way automotive catalysts for removing the toxic gases produced in the automobile exhaust [3]. Pr-doped ceria was also suggested as a good candidate for replacing the toxic red ceramic pigments usually employed in the ceramic industry [5, 6]. The convenience of using powders with well-defined characteristics (particle size and shape, specific surface area, etc.) in numerous fields of science and technology is well known [7]. For example, the optical properties of ceramic pigments are strongly dependent on the particle size and shape [8]. The catalytic properties are also influenced by the method of preparation [2]. Therefore, the availability of uniform powders is highly desirable to ensure the reproducibility of their physical and chemical properties.

The most commonly used methods for the preparation of Pr-doped ceria powders are the decomposition of coprecipitated Ce and Pr carbonates and oxalates [1, 5] and the traditional ceramic procedure involving solid-state reactions [6]. In most cases, these methods yield ill-defined powders consisting of particles with heterogeneous size and shape. Uniform spherical colloidal particles of different rare-earth basic carbonates (Gd, Eu, Sm, Tb) were obtained by precipitation from homogenous aqueous solutions of metal salts in the presence of urea [9]. More recently, this method was also successfully applied for the case of Ce(III) hydroxycarbonate [10].

The aim of this work was to prepare spherical particles of Pr-doped CeO_2 with a narrow size distribution using a modified urea method [10]. It is well known that the adequate experimental conditions for the precipitation of uniform particles by this method can only be established after a systematic study of the effects of reagent concentration on the morphological features of the precipitates. To facilitate this procedure for the mixed system, we have previously studied such effects in the case of the single systems. Since the procedure reported here produces basic carbonates, the thermal evolution of the as-prepared powders was investigated up to the formation of the corresponding oxide phases.

Experimental

Powder preparation

Dispersions consisting of uniform spherical particles with narrow size distribution were prepared by precipitation in aqueous solutions containing cerium nitrate [$Ce(NO_3)\cdot 3H_2O$, Fluka, > 99%] and/or praseodymium chloride ($PrCl_3\cdot H_2O$, Strem Chemicals, 99.9%) in the presence of urea (Merck, 99%). The solutions with appropriate reagent concentrations were aged at 100 °C for 2 h in tightly capped Pyrex test tubes. The precipitates obtained were centrifuged and washed with twice distilled water. This purification procedure was repeated several times to eliminate the excess of salts. The purified powders were collected by filtration and dried at 50 °C. The Ce(III) and/or Pr(III) salt concentrations in the starting solutions were systematically varied to investigate their influence on the morphology and composition (Pr/Ce molar ratio) of the precipitated particles.

The samples were calcined in platinum crucibles at 10 $°C min^{-1}$ up to the desired temperature, at which they were held for 1 min, if not otherwise stated.

Powder characterization

The morphology of the particles was studied by transmission electron microscopy (TEM) (Philips 200 CM). The particle size distribution of the powders was evaluated from the electron micrographs by counting several hundred particles.

The Ce and Pr contents were determined by X-ray fluorescence (Siemens, SRS3000). An energy-dispersive X-ray (EDX) analyser, Philips DX4), installed in the TEM microscope, was also used to gain information on the composition of the particles. The analysis of the supernatant solutions was carried out by plasma emission (inductively coupled plasma, PerkinElmer, model 5500).

The IR spectra of the powders in KBr pellets were recorded using a Nicolet 510 FT-IR spectrometer. The crystalline phases present in the solids were identified by X-ray diffraction (Siemens D501, Cu Kα radiation).

The isoelectric point (IEP) was determined (Malvern Zetamaster) by measuring the electrophoretic mobility of aqueous dispersions of the samples (3–5 mg dispersed in 100 cm^3 0.01 $moldm^{-3}$ NaCl solution) as a function of pH.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (Seiko, EXSTAR 6000) were carried out in air at a heating rate of 10 $°C min^{-1}$.

The Brunauer–Emmett–Teller (BET) specific surface area was measured using a Micromeritics ASAP 2010 apparatus with nitrogen at 77 K. Before analysis, the samples were heated at 150 °C for several hours under vacuum.

The colour of the pigments was evaluated according to the Commission Internationale de l'Eclairage through $L^*a^*b^*$ parameters [11]. These parameters were measured for an illuminant D 65, using a Dr. Lange LUCI 100 colourimeter and a white tile ceramic (chromaticity coordinates: $x = 0.315$, $y = 0.335$) as a standard reference. Before the measurements, the samples were gently ground in an agate mortar.

Results and discussion

Praseodymium hydroxycarbonate particles

The effect of the $PrCl_3$ concentration on the morphology and the size of the particles precipitated after aging at 100 °C for 2 h in aqueous solutions of this salt in the presence of 0.5 $moldm^{-3}$ urea is summarized in Table 1. Spheres were only obtained for Pr(III) concentrations between 0.009 and 0.001 $moldm^{-3}$. At concentrations higher than 0.009 $moldm^{-3}$, either big (larger than 5 μm) elongated particles (0.013 $moldm^{-3}$) or mixtures of the

Table 1 Particle shape, mean particle diameter (d_m), relative standard deviation (*SD*) and Pr/Ce molar ratio of samples prepared by aging 0.5 $moldm^{-3}$ urea solutions containing different concentrations of $PrCl_3$ and/or $Ce(NO_3)_3$ at 100 °C for 2 h

	$Ce(NO_3)_3$ ($moldm^{-3}$)	$PrCl_3$ ($moldm^{-3}$)	Particle shape	d_m (nm)	SD (%)	Pr/Ce molar ratio
Sample P		0.0130	Elongated			
		0.0110	Elongated and spherical			
		0.0090	Spherical	865	12	
		0.0070	Spherical	762	17	
		0.0050	Spherical	532	9	
		0.0030	Spherical	399	10	
		0.0010	Spherical	68	19	
		0.0005	Spherical and irregular			
Sample C	0.0130		Elongated and spherical			
	0.0100		0.12	375	12	
	0.0070		0.17	245	17	
	0.0050		0.14	215	14	
	0.0010		0.07	115	7	
	0.0005		Spherical and irregular			
Sample PC1	0.0100	0.0005	Spherical	330	20	0.058
Sample PC2	0.0100	0.0030	Spherical	300	9	0.310
	0.0100	0.0050	Elongated			

latter and spheres (0.011 moldm^{-3}) precipitated, whereas for 0.0005 moldm^{-3} solutions, a mixture of spheres and irregular particles was detected. The mean particle diameter of the spheres decreased from 865 to 68 nm when the Pr(III) concentration decreased from 0.009 to 0.001 moldm^{-3}. In all cases, the spherical particles showed a narrow size distribution with a relative standard deviation of less than 20%. A TEM micrograph of such uniform particles (sample P) is shown in Fig. 1a.

Sample P was identified by X-ray diffraction (Fig. 2) as a basic Pr(III) carbonate with the composition $Pr(OH)CO_3$ [12]. The IR spectrum of this solid (Fig. 3) displayed bands at 1,495, 1,425, 1,075, 840, 725 and 695 cm^{-1} due to carbonate vibrations [13]. In the DTA and TGA diagrams for sample P (Fig. 4), five endothermic effects were detected, at 160, 470, 535, 585 and 990 °C. The one at 160 °C, which was accompanied by a weight loss of ~ 7% (25–300 °C), is due to the release of absorbed water. The peaks at 470, 535 and 585 °C can be attributed to the decomposition of the basic carbonate to form Pr_6O_{11}, which took place in at least two consecutive steps, in agreement with previously reported observations [14]. As indicated by X-ray diffraction (Fig. 2), the first step (300–550 °C) involved the transformation from $Pr(OH)CO_3$ to $Pr_2O_2CO_3$ [15], whereas the second one (550–800 °C) consisted of the decompo-

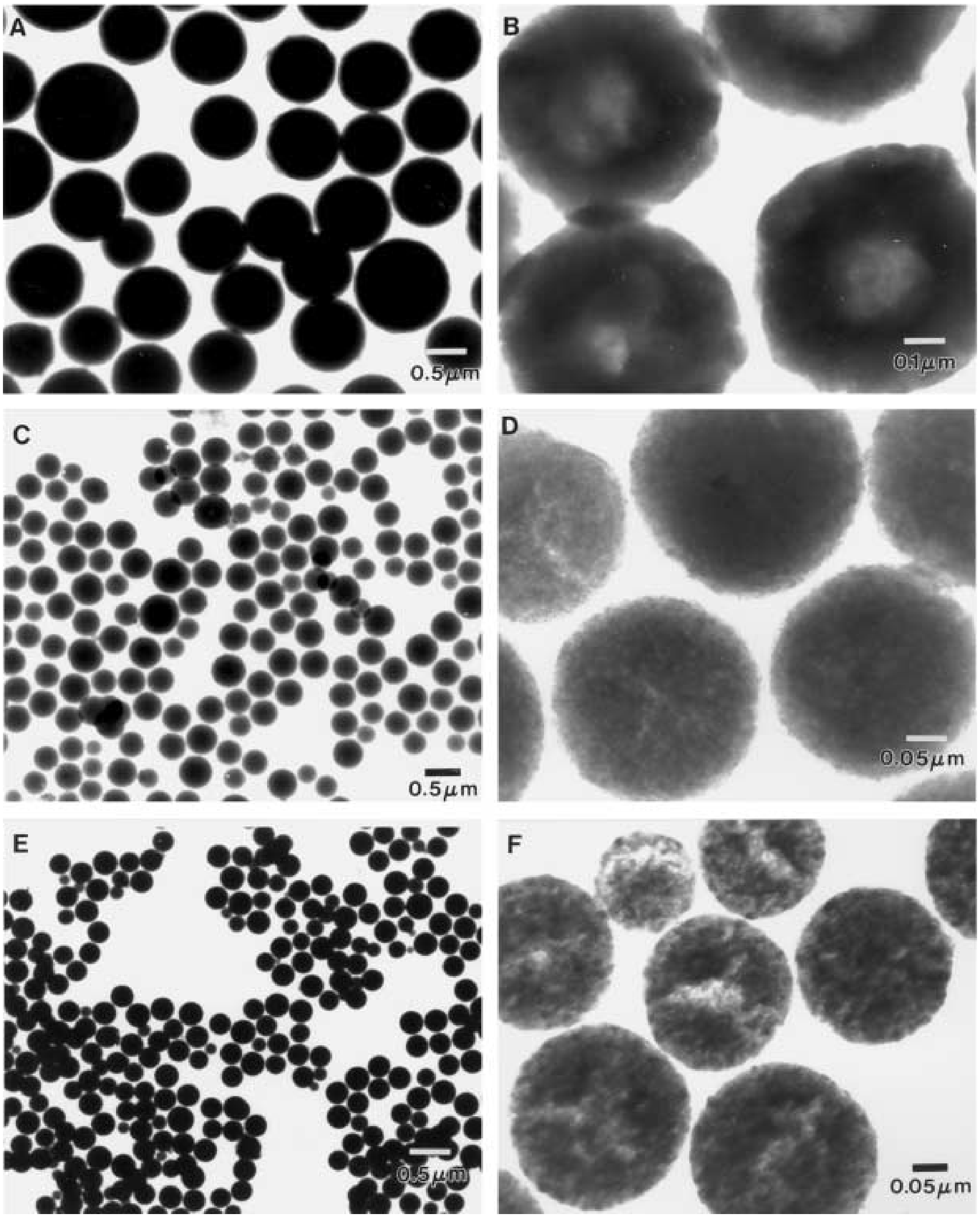

Fig. 1 Transmission electron microscopy (*TEM*) micrographs of **a** sample P as prepared, **b** sample P heated at 800 °C for 1 min, **c** sample C as prepared, **d** sample C heated at 450 °C for 1 min, **e** sample PC2 as prepared and **f** sample PC2 heated at 600 °C for 1 min

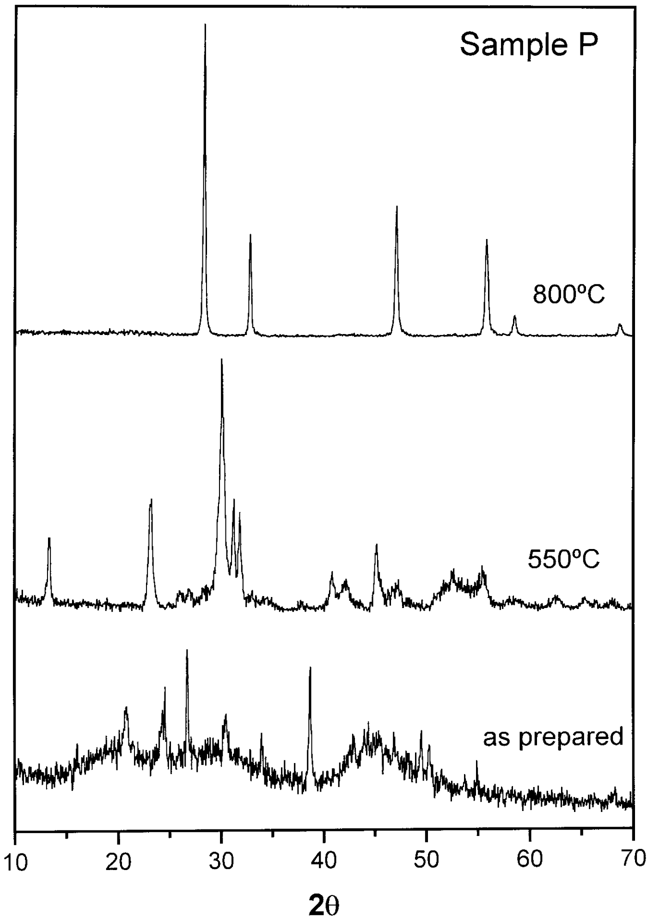

Fig. 2 X-ray diffraction patterns of sample P, as prepared, and after heating for 1 min at different temperatures

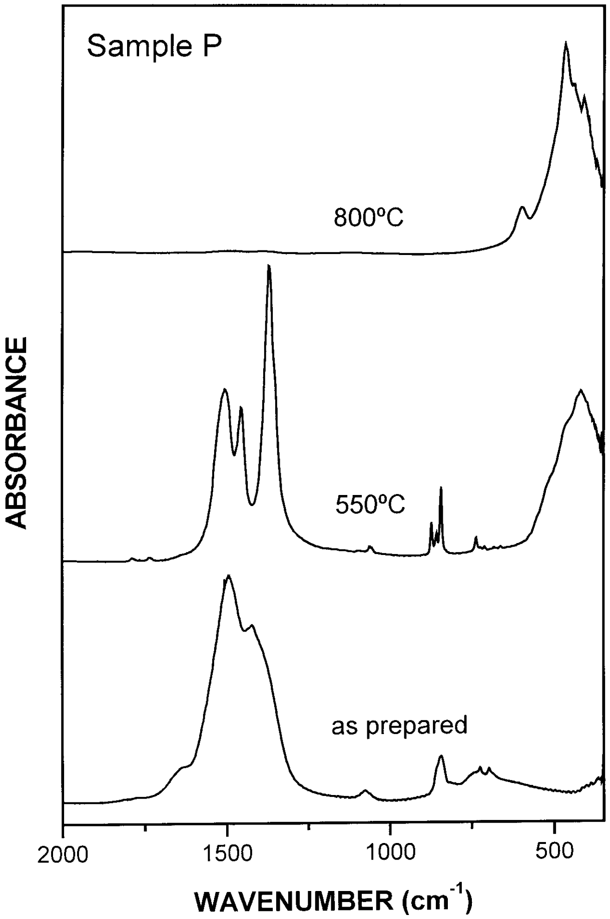

Fig. 3 IR spectra of sample P, as prepared, and after heating for 1 min at different temperatures

sition of the carbonate anions, finally giving Pr_6O_{11} [16]. In agreement with this assignment is the total weight loss of ~ 23% measured between 300 and 800 °C. The number and the position of the carbonate bands (from 1500 to 600 cm^{-1}) in the IR spectrum of the sample changed after heating at 550 °C (Fig. 3), indicating changes in the symmetry of these anions as a consequence of the phase transition. In this spectrum a broad band at 415 cm^{-1} was also observed, which must be ascribed to Pr–O vibrations. The spectrum of the sample heated at 800 °C only displayed the bands due to Pr_6O_{11} [17], confirming the decomposition of the carbonate phase. Finally, the last endothermic effect detected by DTA at 990 °C and its small (0.3%) associated weight loss may be due to the decomposition of a small number of residual carbonate anions.

It should be noted that after heating sample P at 800 °C, the particles still retained a spherical shape (Fig. 1b), although a certain shrinkage, d_m, from 865 (Table 1) to 595 nm (Table 2), was observed as a consequence of the decomposition of the carbonate groups.

The IEP for the calcined sample (Pr_6O_{11}) was slightly lower (8.3) than that corresponding to the original one [$Pr(OH)CO_3$] (8.8) (Fig. 5), in agreement with their different composition.

The BET surface area of sample P ($PrOHCO_3$) was higher (7.2 m^2g^{-1}) (Table 3) than that calculated (1.5 m^2g^{-1}) assuming smooth spheres with a mean diameter of 865 nm (Table 1) and a density of 4.69 gcm^{-3} [12]. This indicates the presence of a certain internal porosity. After calcination at 800 °C, the surface area of the resulting Pr_6O_{11} phase decreased to 3 m^2g^{-1}, which is closer to the theoretical value (1.4 m^2g^{-1}) calculated for a density of 7.32 gcm^{-3} [16] and a mean diameter of 545 nm (Table 2). This decrease in the porosity of the particles is probably due to an internal sintering.

Cerium hydroxycarbonate particles

The aging of cerium nitrate solutions in the presence of 0.5 $moldm^{-3}$ urea at 100 °C for 2 h yielded spherical

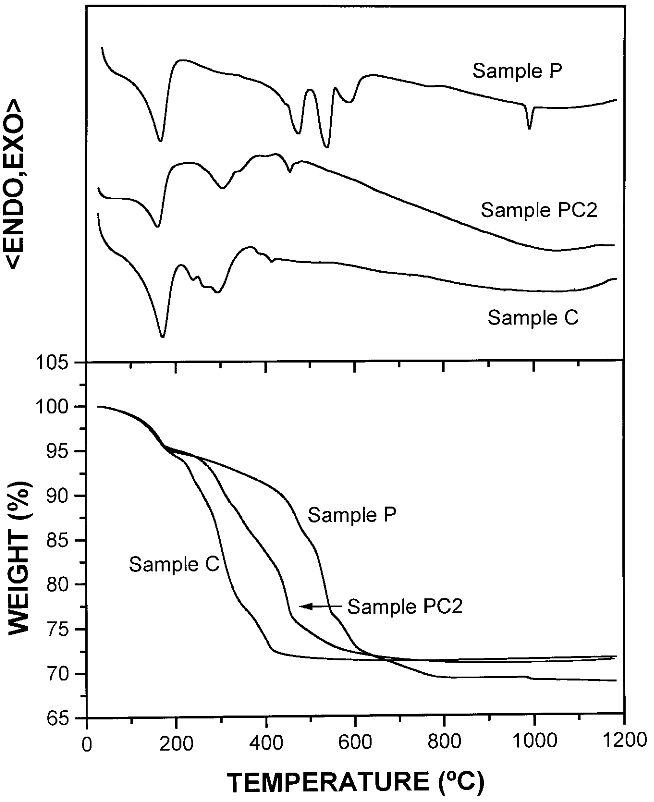

Fig. 4 Differential thermal (*top*) and thermogravimetric (*bottom*) analyses for samples P, C and PC2

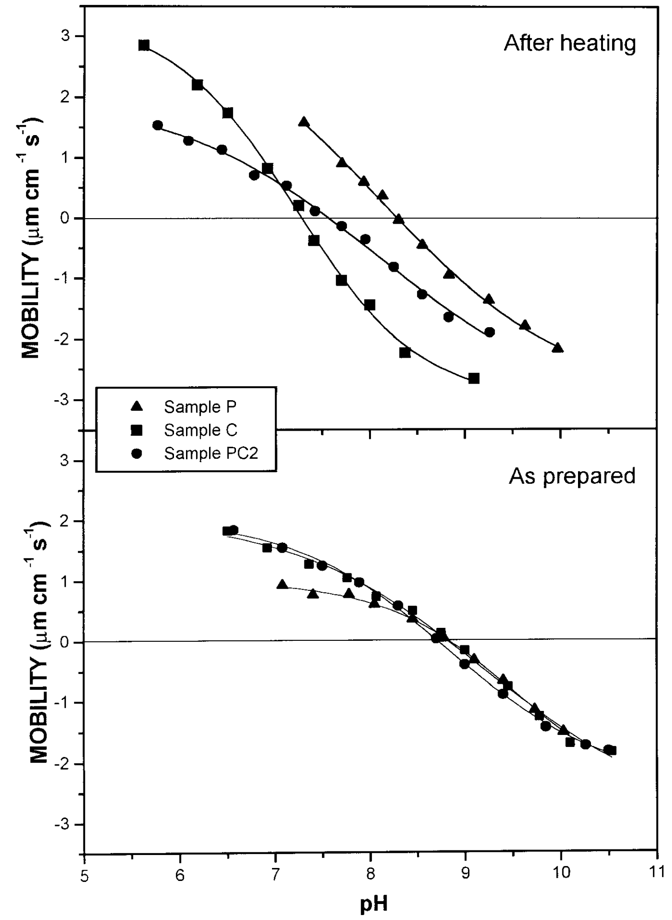

Fig. 5 Electrophoretic mobility measured as a function of pH for samples P, C and PC2, as prepared and after heating for 1 min at 800, 450 and 600 °C, respectively

Table 2 d_m and SD after heating for 1 min at different temperatures. The samples were prepared as described in Table 1

	Temperature (°C)	d_m (nm)	SD (%)
Sample P	800	595	12
Sample C	450	245	16
Sample PC1	600	270	16
Sample PC2	600	200	12

Table 3 Calculated (S_c) and Brunauer–Emmett–Teller (*BET*) (S_{BET}) specific surface area for samples P, C and PC2, as prepared, and after heating at different temperatures

	Temperature (°C)	S_{BET} (m^{2}g^{-1})	S_c (m^{2}g^{-1})
Sample P	As prepared	7.2	1.5
	800	3.0	1.4
Sample C	As prepared	16.8	3.4
	450	33.4	3.4
Sample PC	As prepared	6.7	4.2
	600	10.7	4.1

particles only under a rather restrictive range of Ce(III) concentrations (from 0.01 to 0.001 moldm^{-3}, Table 1). At other concentrations, a mixture of spheres and elongated [0.013 moldm^{-3} Ce(NO$_3$)$_3$] or irregular [0.0005 moldm^{-3} Ce(NO$_3$)$_3$] particles was detected (Table 1). The mean particle diameter (d_m) increased with the Ce(III) concentration; thus, the biggest particles ($d_m = 375$ nm) were obtained for 0.01 moldm^{-3} Ce(NO$_3$)$_3$ solutions and the smallest ones ($d_m = 115$ nm) for 0.001 moldm^{-3}. The relative standard deviation (less than 20%) indicated a narrow size distribution in all the systems (Table 1).

The X-ray diffraction pattern (Fig. 6) of sample C (Fig. 1c) was not consistent with any of the published JCPDF files for Ce compounds; however, it was very similar to that of sample P (Fig. 2), showing a small shift of the peaks towards higher 2θ values. It may be concluded that both samples (P and C) are isostructural and, therefore, sample C consists of Ce(OH)CO$_3$. In agreement, its IR spectrum (Fig. 7) was identical to that of sample P (Fig. 3).

The DTA analysis of sample C showed several endothermic effects at 170, 235, 265, 290, 385 and 410 °C (Fig. 4). The first one and its associated weight loss (5% from 25 to 200 °C) (Fig. 4) were similar to

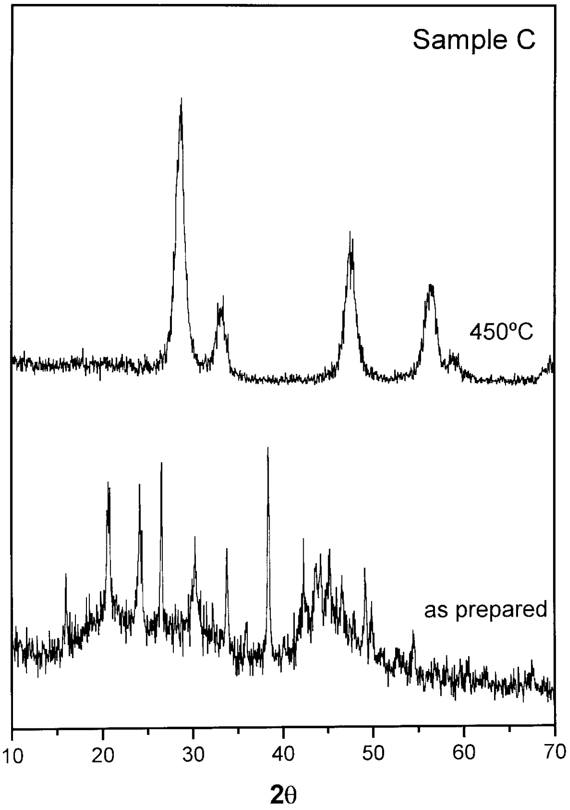

Fig. 6 X-ray diffraction patterns of sample C, as prepared, and after heating for 1 min at 450 °C

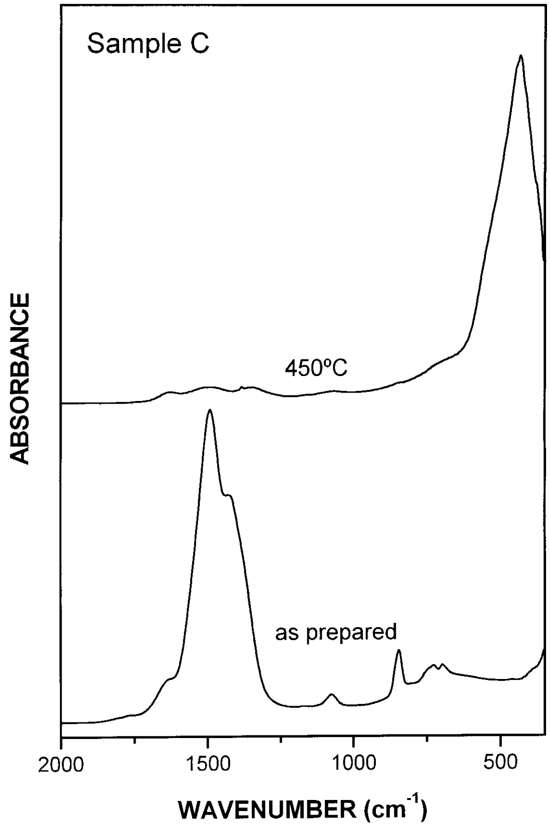

Fig. 7 IR spectra of sample C, as prepared, and after heating for 1 min at 450 °C

those obtained for sample P and were attributed to the release of adsorbed water. The peaks and the 24% weight loss between 200 and 450 °C were related to the decomposition of the Ce(III) hydroxycarbonate [18]. The resulting product showed the X-ray diffraction pattern (Fig. 6) characteristic of CeO_2 with a fluorite structure [19]. The IR spectrum of the sample heated at 450 °C (Fig. 7) corresponded to that reported for this phase [20]. The CeO_2 particles obtained after calcination were still spherical (Fig. 1d), although their mean size was smaller (245 nm) (Table 2) than that of the precursor carbonate (375 nm) (Table 1).

The IEP of samples C and P were identical (8.8) (Fig. 5), indicating that the nature of the metal cation has little influence on the surface charge of these basic carbonates. However, after heating sample C at 450 °C (CeO_2), the IEP was lower (7.3) than that of sample P heated at 800 °C (Pr_6O_{11}) (8.3). The IEP of CeO_2 measured here was in the range of previously reported values (6.1–7.6) [21, 22].

The BET surface area measured for sample C [$Ce(OH)CO_3$] was much higher (16.8 m^2g^{-1}) than the theoretical value (3.4 m^2g^{-1}) (Table 3), indicating that the internal microporosity was more important than for the praseodymium hydroxycarbonate particles (sample P). For the calculation, we used the diameter shown in Table 1 and assumed a density similar to that of $Pr(OH)CO_3$ (4.69 gcm^{-3}). In contrast to sample P, the surface area increased considerably after heating at 450 °C (33.4 m^2g^{-1}), indicating an increase in the internal porosity, which is clearly observed by TEM (Fig. 1d).

Mixed praseodymium–cerium hydroxycarbonate particles

To prepare mixed Pr–Ce systems by aging aqueous Ce(III) and Pr(III) solutions in the presence of 0.5 $moldm^{-3}$ urea at 100 °C for 2 h, we kept the $Ce(NO_3)_3$ concentration constant and varied that of $PrCl_3$. Precipitation of spherical particles of narrow size distribution (relative standard deviation 20% or less) required a Pr(III) concentration of 0.003 $moldm^{-3}$ or lower, since at higher concentrations, elongated particles were formed (Table 1). The mean diameter of these spheres was not strongly influenced by the solution composition. In fact, only a small increase (from 300 to 330 nm) was detected when the Pr/Ce ratio was decreased from 0.3 to 0.05 (Table 1). The Pr/Ce molar ratio of the precipitated particles (Table 1) was similar to that in the starting solutions, which seems to indicate that most Ce(III) and Pr(III) cations precipitated during aging, as confirmed by the absence of an appreciable number of these cations in the supernatants.

Sample PC2 (Fig. 1w) presented the highest Pr/Ce ratio (0.31) that could be obtained by the procedure reported (Table 1). The EDX spectra of several single particles of this sample were identical, showing Ce and Pr peaks (Fig. 8), which shows their mixed composition and suggests a high degree of chemical homogeneity. The X-ray diffraction pattern of sample PC2 was similar to those of the single Pr (Fig. 2) and Ce (Fig. 7) systems. Accordingly, the composite particles consist of a $Pr_{0.237}Ce_{0.763}(OH)CO_3$ solid solution. As expected, the IR spectrum of this sample was also similar to those of the single systems (Figs. 3, 7).

The DTA and TGA curves of sample PC2 were almost similar to those of sample C, with the endothermic peaks and weight losses shifted slightly to higher temperatures (Fig. 4); therefore, the assignment of the effects is identical. The X-ray diffraction pattern and the IR spectrum of the decomposition product (at 600 °C) were similar to those of the Ce(III) single system (Figs. 6, 7) indicating a fluorite structure for the composite system. It should be noted that this calcination temperature is much lower than required for the formation of solid solutions by the conventional ceramic procedure (1,300 °C) [6]. The reason may be the high chemical homogeneity of the precipitated particles. The spherical shape of the particles was retained after calcination at 600 °C (Fig. 1f), although the mean diameter, as for the single systems, was smaller (200 nm) (Table 2) than that of the precursor carbonate (300 nm) (Table 1).

As expected from the data for samples P and C, the IEP of sample PC2 was also at pH 8.8 (Fig. 5); however, after heating sample PC2 at 600 °C the IEP (7.6) was between that of CeO_2 (7.3) and Pr_6O_{11} (8.3) (Fig. 5).

The BET surface area of sample PC2 (6.7 m^2g^{-1}) was much lower than that of the Ce single system (16.8 m^2g^{-1}) (Table 3), indicating a much lower internal porosity because both samples have similar size (Table 1) and density. After the hydroxycarbonate decomposition (heating at 600 °C) the surface area increased to 10.7 m^2g^{-1}. The theoretical surface area (assuming a density similar to that of CeO_2, i.e. 7.22 gcm^{-3} [19] and the diameter shown in Table 2) was lower (4.1 m^2g^{-1}) than the measured value. In fact, the porous structure and the surface roughness was observed by TEM (Fig. 1f). The increase in specific surface area on calcination was less important for the doped system than for sample C, probably owing to the higher temperature (600 °C) required for the total decomposition of carbonates when Pr was present.

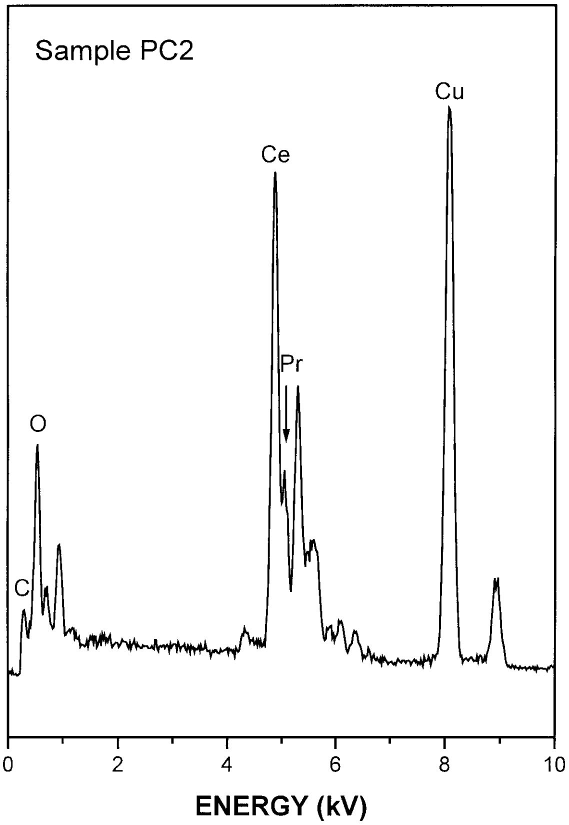

Fig. 8 Energy-dispersive X-ray spectrum obtained for sample PC2 as prepared. The copper peak is due to the TEM grid

Because of the great interest in Pr-doped CeO_2 powders as high-temperature pigments [5, 6], the colour properties of the samples were also measured by the $L^*a^*b^*$ parameters (Table 4). L^* is the colour lightness ($L^* = 0$ for black and $L^* = 100$ for white), a^* is the green (−)/red (+) axis and b* is the blue (−)/yellow (+) axis [11]. After heating sample PC1 (Pr/Ce molar ratio of 0.058, Table 1) at 600 °C for 2 h, a red colour developed, which was characterized by $L^* = 56.3$, $a^* = 17.1$ and $b^* = 15.5$ (Table 4). These parameters are similar to those reported for samples with similar composition (Pr/Ce = 5%) prepared at 600–800 °C using fluxes to decrease the calcination temperature [6], which is not desirable from the environmental point of view [23]. This finding indicates an additional advantage

Table 4 $L^*a^*b^*$ parameters of samples CP1 and CP2 heated at different temperatures

	Temperature (°C)	L^*	a^*	b^*
Sample CP1	600	56.3	17.1	15.5
	800	49.3	18.5	13.0
	1,000	49.3	18.5	13.6
Sample CP2	600	44.3	12.2	8.7
	800	41.0	2.0	−1.5

of the method reported here over previously reported procedures [5, 6]. Heating to 1,000 °C, only caused a slight increase in the colour intensity (L^* decreased from 56.3 to 49.3), whereas a^* and b^* remained almost constant. As previously reported [6], the increase in the Pr content of the pigments (from 0.058 for sample CP1 to 0.31 for sample CP2) did not improve the colour. Thus, decreases in a^* and b^* were detected at 600 °C and were more significant at 800 °C ($a^* = 2.0$, $b^* = -1.5$), being accompanied by a decrease in L^*, indicating a progressive blackening of the pigment.

Summary

We developed a procedure for the preparation of submicrometre spherical particles of Pr(III), Ce(III) or Pr(III)-doped C(III) hydroxycarbonates with a narrow size distribution. The particles were prepared by aging aqueous solutions of Pr(III) chloride and/or Ce(III) nitrate in the presence of urea at 100 °C for 2 h. The mean particle diameter was varied by changing the Pr(III) and/or the Ce(III) concentrations. Calcination at 800 °C of the Pr(III) single system gave Pr_6O_{11}, whereas heating the Ce(III) single system at 450 °C yielded CeO_2 with a fluorite structure. The mixed Pr(III)–Ce(III) systems transformed into Pr-doped CeO_2 after heating at 600 °C. In all cases, the spherical particle shape was retained after the heat treatments, although a certain shrinkage was detected owing to carbonate decomposition. Calcination at 600 °C of a sample with a Pr/Ce molar ratio of 0.058 yielded red pigments of similar colour and a Pr content as reported for samples prepared by the ceramic procedure in the presence of fluxes, which is not desirable from the environmental point of view.

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