

Fine spherical particles of narrow size distribution in the $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ system

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The preparation of spherical particles of composite alumina-chromia nature and amorphous character by a procedure of homogeneous precipitation at 100°C for 1 h, from aqueous Al(III) and Cr(III) nitrate solutions containing sodium sulphate, urea and polyvinylpyrrolidone, is described. This method allows controlling the Cr/Al ratio and the mean size of the particles (in the nanometer and the micrometer range) by adjusting the reagents concentrations. The structural and compositional changes originated in the particles on calcination were evaluated. It was found that for alumina-rich compositions (Cr/Al mole ratio ≤ 0.13), the particles transformed into fully developed corundum solid solutions at much lower temperature (1000°C) than those needed for samples prepared by previously reported procedures ($\geq 1300^\circ\text{C}$), which was attributed to the high degree of chemical homogeneity at the atomic level attained in our case. It was also observed that an increase in the Cr/Al mole ratio of the composite systems resulted in an increase of the heating temperature required for the full development of the corundum solid solution.

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1. Introduction

Cr-doped alumina powders, either in amorphous or crystalline forms, have been used for long time as catalysts [1, 2]. Because of their optical properties, $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ solid solutions with corundum structure (ruby) also find important technological applications in solid state lasers [3] and fiber optics [4] and as high temperature pigments [5]. The doping of alumina ceramics with chromia has been found to increase the microhardness and wear resistance of this material for which, its use for ceramic cutting tools in the machining of alloy steel has been proposed [6]. For many of these applications, it would be desirable the availability of powders consisting of uniform particles in order to ensure the reproducibility of their properties [7] and improve their processing [8].

Mixing powders of individual components and subsequent calcination at high temperature is the most usual method of preparation for chromia/alumina powders. This procedure requires high temperatures ($>1300^\circ\text{C}$) [4, 5, 9] to favor the diffusion process required for the formation of solid solutions. Several others procedures including the sol-gel process [2], precipitation from alkoxides [3], coprecipitation from aqueous salts solutions in the presence of hydrazine [9] and the so-called cryosol method [4] have been essayed to achieve a high degree of Al-Cr mixing in the precursors and consequently, to decrease such temperatures.

However, most of these procedures yielded irregular particles in size and shape.

It has been shown that uniform spheres of aluminum [10] and chromium [11] oxides can be prepared by hydrolysis of metal salts solutions in the presence of urea and a certain amount of sulphate anions. In this work, we have modified these methods to produce mixed $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ powders consisting of amorphous spherical particles of narrow size distribution and different modal sizes in the micrometer and nanometer size range. The procedure is based on a co-precipitation process from homogeneous aqueous solutions of Al (III) and Cr (III) nitrates, which were aged at 100°C for 1 h in the presence of urea, sulphate anions and a dispersing agent (polyvinylpyrrolidone). The effects of the reagents concentrations on the composition and morphological characteristics of the precipitated particles are reported. The powders have been heat treated up to full development of the corundum solid solutions. The compositional and structural changes originated in the powders as a consequence of this treatment have been also studied.

2. Experimental

2.1. Powders preparation

Powders of alumina/chromia mixed compositions were prepared by using a procedure similar to those

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previously reported for the preparation of spherical particles of amorphous alumina [10] and chromia [11] introducing some modifications. Essentially, it consisted of the aging at 100°C for 1 h of aqueous solutions containing Al(III) nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Fluka, >99%), Cr (III) nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aldrich, 99%), sodium sulfate (Na_2SO_4 , Aldrich, 99%), urea (Merk, >99%) and polyvinylpyrrolidone K-30 (PVP, Fluka, purum). For such a purpose, Pyrex test tubes (10 cm³) containing freshly prepared solutions were tightly closed with Teflon caps, placed in an oven pre-heated at 100°C and aged for the desired time. After aging, the dispersions were cooled in a water bath and centrifuged at 18000 r.p.m. The obtained precipitates were washed several times with doubly distilled water, filtered and dried at room temperature before analyses. The concentration of the reagents in the starting solutions was systematically varied in order to analyze their effects on the morphological characteristics (particle size and shape) of the powders.

Two dispersions consisting of spherical particles of undoped aluminum and chromium hydrous oxides were also prepared to be used as blanks in the characterization experiments. The first one was obtained by aging at 100°C for 1 h a solution containing $\text{Al}(\text{NO}_3)_3$ (0.0075 mol dm⁻³), Na_2SO_4 (0.0046 mol dm⁻³), urea (0.1 mol dm⁻³) and PVP (20 g dm⁻³). The chromia blank was prepared by aging at 100°C for 24 h a 0.005 mol dm⁻³ $\text{Cr}(\text{NO}_3)_3$ solution in the presence of 0.003 mol dm⁻³ Na_2SO_4 , 0.02 mol dm⁻³ urea and 20 g dm⁻³ PVP [11].

2.2. Characterization

Transmission Electron Microscopy (TEM, Philips 200 CM) was used to examine the morphology of the particles. The particle size distribution was evaluated from the electron micrographs by counting several hundreds of particles.

The qualitative composition of the precipitated particles was assessed in the TEM microscope by energy

dispersive X-ray analysis (EDX, Philips DX4), whereas the quantitative composition of the powders in terms of the Cr and Al contents was determined from the analysis of the supernatants solutions by plasma emission (ICP, Perkin Elmer, Model 5500).

The infrared spectra of the powders diluted in KBr were recorded in a Nicolet 510 FT-IR spectrometer. The different crystalline phases present in the solids were identified by X-ray diffraction (Siemens D501) using $\text{Cu K}\alpha$ radiation.

Unit cell parameters were determined from the X-ray diffraction data collected at intervals of 0.04° (2 θ) and accumulation time for interval of 20 s. The powdered samples were mechanically mixed with a silicon standard (20% by weight). The crystallographic data for α -alumina and silicon were taken from references [12] and [13], respectively.

The isoelectric point (i.e.p.) of the samples was determined (Malvern Zetamaster) by measuring electrophoretic mobilities of aqueous dispersions as a function of pH. For this, 5 mg of sample were dispersed in 100 cm³ of a 0.01 mol dm⁻³ NaCl solution to keep the ionic strength constant, while the pH was varied by adding HCl or NaOH.

Thermogravimetric analyses (Setaram 92-16.18) were carried out in air at a heating rate of 10°C min⁻¹. For isothermal treatments, the solids were heated in a furnace at 10°C min⁻¹ up to the desired temperature at which they were held for 2 h.

3. Results and discussion

Table I summarizes the effects of reagents concentrations on the morphological characteristics (size and shape) of the particles precipitated by aging at 100°C for 1 h, aqueous solutions containing Al(III) nitrate, Cr(III) nitrate, sodium sulfate, urea and polyvinylpyrrolidone (PVP). As observed, the addition of 0.1 mol dm⁻³ of urea to the starting solutions is essential in order to induce precipitation under these conditions, in agreement with previous observations reported for the single

TABLE I Shape, mean diameter (standard deviation) and nominal [(Cr/Al)_{nom}] and experimental [(Cr/Al)_{exp}] Cr/Al mole ratios of the particles precipitated by aging at 100°C for 1 h, solutions containing variable amounts of $\text{Al}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$, Na_2SO_4 , urea and PVP

Sample	$\text{Al}(\text{NO}_3)_3$ mole dm ⁻³	$\text{Cr}(\text{NO}_3)_3$ mole dm ⁻³	$\text{Na}_2\text{SO}_4/\text{Al} + \text{Cr}$ mole ratio	Urea mole dm ⁻³	PVP g dm ⁻³	Particle shape	Mean diameter/nm (standard deviation)	(Cr/Al) _{nom} mole ratio	(Cr/Al) _{exp} mole ratio
A	0.0075	0.0010	0.62		20	No precipitation			
	0.0075	0.0010	0.62	0.1		Agglomerates			
	0.0075	0.0010	0.35	0.1	20	Agglomerates			
	0.0075	0.0010	0.47	0.1	20	Spheres			
	0.0075	0.0010	0.59	0.1	20	Spheres			
	0.0075	0.0010	0.62	0.1	20	Spheres	320 (33)	0.133	0.13
	0.0075	0.0010	0.70	0.1	20	Agglomerates			
	0.0075	0.0010	0.82	0.1	20	Agglomerates			
	0.0075	0.0005	0.62	0.1	20	Spheres	418 (68)	0.066	0.078
	0.0075	0.0015	0.62	0.1	20	Agglomerates			
	0.0075	0.0025	0.62	0.1	20	Agglomerates			
	0.0125	0.0010	0.62	0.1	20	Agglomerates			
B	0.0100	0.0010	0.62	0.1	20	Agglomerates			
	0.0050	0.0010	0.62	0.1	20	Spheres	320 (34)	0.20	0.20
	0.0020	0.0010	0.62	0.1	20	Spheres	125 (13)	0.50	0.49
	0.0010	0.0010	0.62	0.1	20	Spheres	81 (14)	1.00	1.01

alumina [10] and chromia systems [11]. This increase in the precipitation rate in the presence of urea is due to the well-known decomposition of this chemical on heating, which liberates OH anions promoting the precipitation of metal oxides or basic salts. The addition of a certain amount (20 g dm^{-3}) of a dispersing agent (PVP) was also needed to avoid particle agglomeration. This study also revealed that even in these conditions, the formation of unagglomerated spheres requires a very restrictive range of sulphate/M(III) ($M = \text{Al} + \text{Cr}$) mole ratios. Thus, for solutions $0.0075 \text{ mol dm}^{-3}$ $\text{Al}(\text{NO}_3)_3$ and $0.001 \text{ mol dm}^{-3}$ $\text{Cr}(\text{NO}_3)_3$ and the mentioned concentrations of PVP and urea, such a kind of particles was only obtained for sulphate/M(III) ($M = \text{Al} + \text{Cr}$) mole ratios ranging from 0.47 to 0.62. For higher or lower values of this magnitude, hard agglomerates were detected. The influence of the anions on the morphology of the particles formed by homogeneous precipitation from metal salts solutions has been amply recognized and attributed to the ability of such anions to form soluble metal complexes, which act as precursors to the solid phase formation, and/or to affect the zeta potential of the growing particles, which would influence their agglomeration behavior [14].

An increasing number of agglomerates also resulted if under the above conditions and keeping the sulphate/M(III) mole ratio = 0.62, the $\text{Cr}(\text{NO}_3)_3$ concentration was increased over $0.001 \text{ mol dm}^{-3}$ or the $\text{Al}(\text{NO}_3)_3$ concentration over $0.0075 \text{ mol dm}^{-3}$, manifesting that particle morphology is very sensitive to these magnitudes.

It was also found (Table I) that the mean diameter of the spheres increased as decreasing the Cr/Al mole ratio in the starting solutions with values ranging from 81 nm, for solutions $0.001 \text{ mol dm}^{-3}$ $\text{Al}(\text{NO}_3)_3$ and $0.001 \text{ mol dm}^{-3}$ $\text{Cr}(\text{NO}_3)_3$ (Cr/Al mole ratio = 1) to 418 nm, for solutions $0.0075 \text{ mol dm}^{-3}$ $\text{Al}(\text{NO}_3)_3$ and $0.005 \text{ mol dm}^{-3}$ $\text{Cr}(\text{NO}_3)_3$ (Cr/Al mole ratio = 0.066).

Table I also includes the composition of the systems consisting of unagglomerated particles in terms of the Cr and Al contents. As observed, the here reported procedure yields a large variety of Cr/Al mole ratios, ranging from formulations poor in Cr (Cr/Al = 0.068) to equimolecular systems (Cr/Al = 1.01). It should be noted that in all cases, the Cr/Al mole ratio in the powders was very similar to that of the starting solutions, which suggests that most cations precipitated during aging, as it will be later confirmed.

Two samples denoted as A and B (Table I), which presented different mean particle size (320 and 125 nm, respectively) and composition (Cr/Al mole ratio = 0.123 and 0.49, respectively) were chosen for characterization to study the effects of such parameters on the structural characteristics of the particles and their thermal evolution.

Fig. 1A and B illustrate the spherical shape and the size of the particles composing the selected samples, which according to X-ray diffraction were amorphous. The EDX spectra of both samples (Fig. 2) revealed their composite nature (Al/Cr mixed oxides) and the incorporation of a certain amount sulphate anions to the particles during the precipitation process, which could not

be removed by further washing with distilled water suggesting that such anions are not simply adsorbed on the particles surfaces. A similar behavior was observed for the single alumina [10] and chromia [11] systems. The infrared spectrum of sample A (Fig. 3) confirms the presence of sulphate anions in the particles by displaying bands at 1120, 980 and 610 cm^{-1} [15]. The latter was overlapped with a broad absorption, which together with the shoulder at 760 cm^{-1} must be attributed to the M-O ($M = \text{Al}$ or Cr) vibrations. The spectrum of sample B (Fig. 4) was similar to that of sample A, except that the former showed additional weak absorptions at 1485 and 1420 cm^{-1} , due to carbonate anions [15], which were also found in the previously reported chromia particles prepared by similar procedure [11]. As in the latter case, these anions are originated as a consequence of the decomposition of urea at the slightly basic pH (7.24) generated at the end of aging. This explanation is in agreement with the absence of these anions in sample A, since the pH was kept at the acidic values (≤ 3.2) during the entire aging period.

The relative intensity of the Cr and Al peaks in the EDX spectra of the samples (Fig. 2) indicates that the Cr/Al ratio in sample A was lower than that in sample B, in agreement with chemical analyses (Table I). Finally, in both cases, the EDX spectra obtained for several single particles were similar to those shown in Fig. 2, manifesting that the composition of the particles in these samples was very homogeneous.

Several other experiments were conducted in order to gain information on the degree of chemical homogeneity at the atomic level (Al/Cr mixing) inside the precipitated particles. Thus, the Al and Cr precipitation yields were measured as a function of aging time. As observed in Fig. 5, for sample B the values of both magnitudes were very similar during the whole aging period indicating that the precipitation of both cations, Al^{3+} and Cr^{3+} , took place almost simultaneously, which consequently must produce a high degree of Al/Cr mixing in the obtained particles. This figure also revealed that the Cr and Al precipitation yields sharply increased during the first 35 min of aging after which, they reached their maximum values that corresponded to the almost complete precipitation ($\sim 100\%$ yield). A similar behavior to the above one was observed for sample A except that the final yields were slightly lower (Al yield = 89%, Cr yield = 82%).

Fig. 6 shows the values of the electrophoretic mobilities measured as a function of pH for samples A and B. The curves obtained for the undoped alumina and chromia blanks are also included for comparison. As observed, the i.e.p. obtained for sample B (8.5) is between those of the alumina (9.8) and chromia (7.2) blanks, which is in agreement with the composite nature and high degree of Al/Cr mixing present in this sample. However, the i.e.p. of sample A is similar (9.8) to that of the alumina blank suggesting that the presence of a small amount of Cr^{3+} (Cr/Al mole ratio = 0.13) does not have important effects on the surface characteristics of the so obtained alumina particles.

The DTA and TGA curves obtained for samples A and B are shown in Fig. 7. As observed, for sample A,

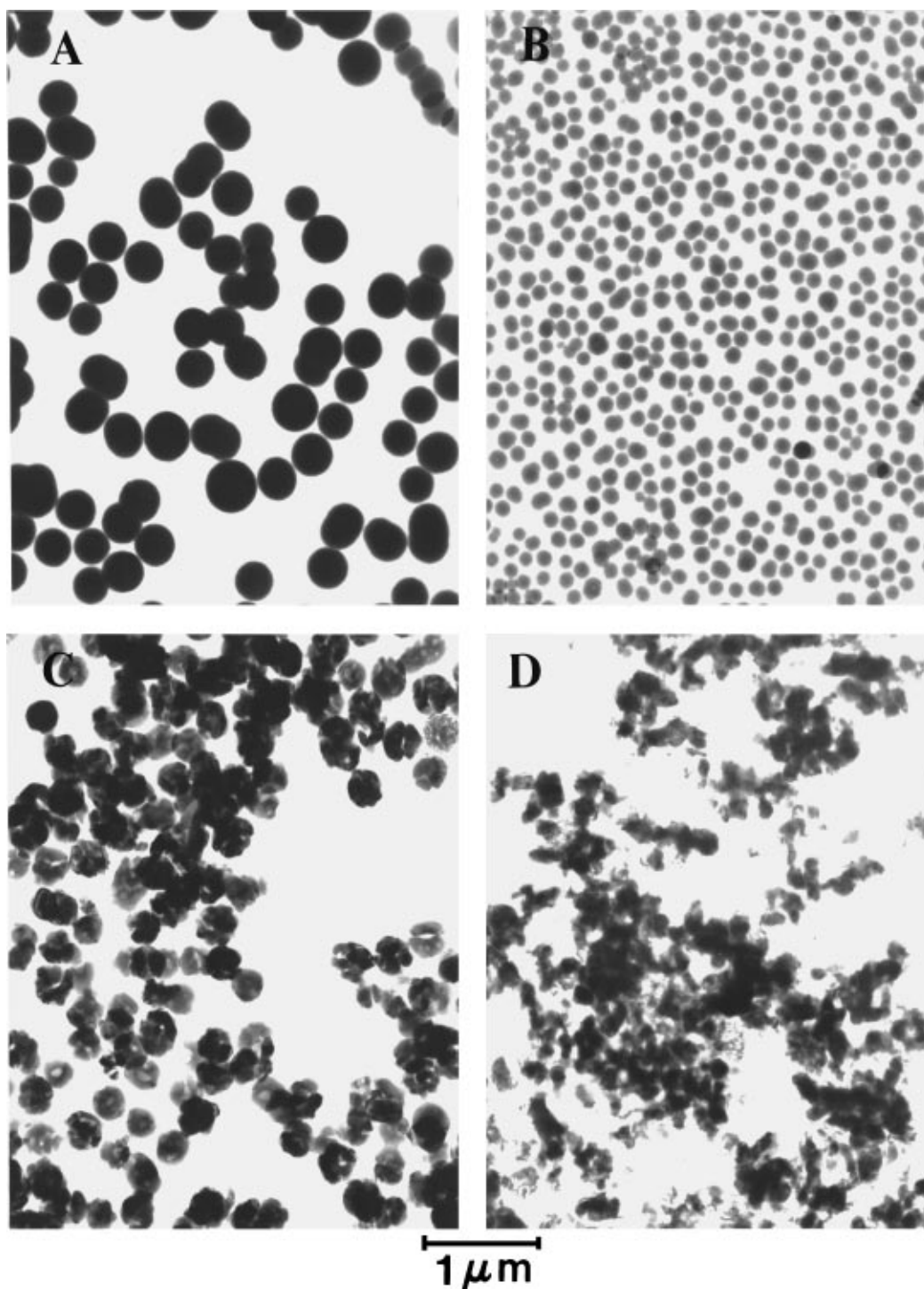


Figure 1 TEM micrographs the samples obtained by: A) aging at 100°C for 1 h solutions containing 0.0075 mol dm⁻³ Al(NO₃)₃, 0.001 mol dm⁻³ Cr(NO₃)₃, 0.00527 mol dm⁻³ sodium sulfate (sulfate/Cr(III) mol ratio = 0.62), 0.1 mol dm⁻³ urea and 20 g dm⁻³ PVP (sample A), B) aging at 100°C for 1 h solutions containing 0.002 mol dm⁻³ Al(NO₃)₃, 0.001 mol dm⁻³ Cr(NO₃)₃, 0.00186 mol dm⁻³ sodium sulfate (sulfate/ Cr(III) mol ratio = 0.62), 0.1 mol dm⁻³ urea and 20 g dm⁻³ PVP (sample B), C) heating sample A at 1000°C for 2 h and D) heating sample B at 1300°C for 2 h.

a broad endothermic effect between 25 and 400°C followed by a sharper one at 875°C and an exothermic peak at 1060°C were detected. The former was due to the release of a high amount of adsorbed water (~40%), whereas the one at 875°C, which is associated with a weight loss of 11.5%, can be ascribed to the decomposition of the sulphate anions as substantiated by the disappearance of the infrared bands at 1120 and 980 cm⁻¹ in the spectrum of the sample heated at 900°C (Fig. 3). The exothermic effect (1060°C) could be attributed to the crystallization of the corundum phase. This pro-

cess was already detected after isothermal treatment at 900°C for 2 h, accompanied by the formation of a certain amount of γ -Al₂O₃ (Fig. 8). It should be noted that the Cr/Al mole ratio obtained from the unit cell *a* parameter of the corundum phase by using the Vegard's law was higher (0.317) (Table II) than that measured by chemical analysis (0.13) in agreement with the presence of the γ -Al₂O₃ phase.

The X-ray diffraction pattern obtained after heating sample A at 1000°C revealed that the spinel phase disappeared during this treatment (Fig. 8) suggesting the

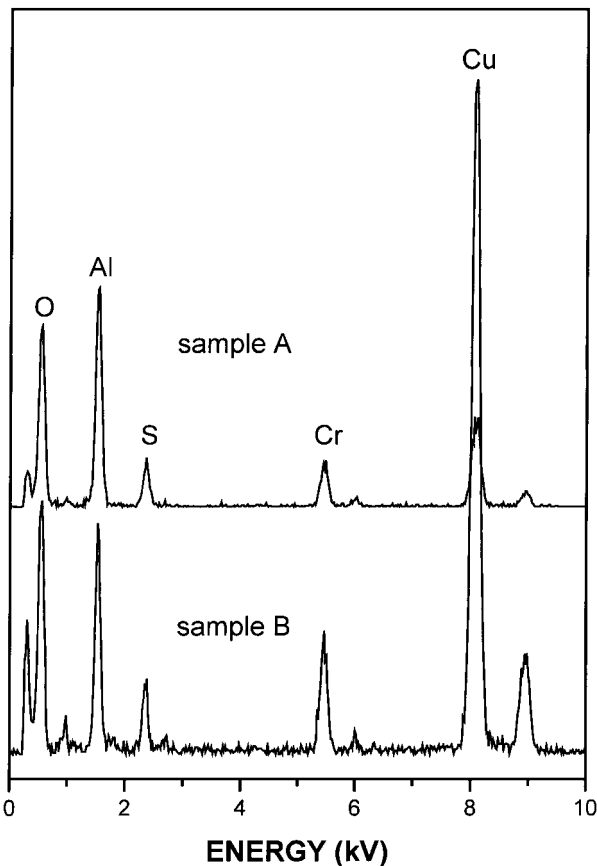


Figure 2 EDX spectra obtained for samples A and B. The copper peak is due to the TEM grid.

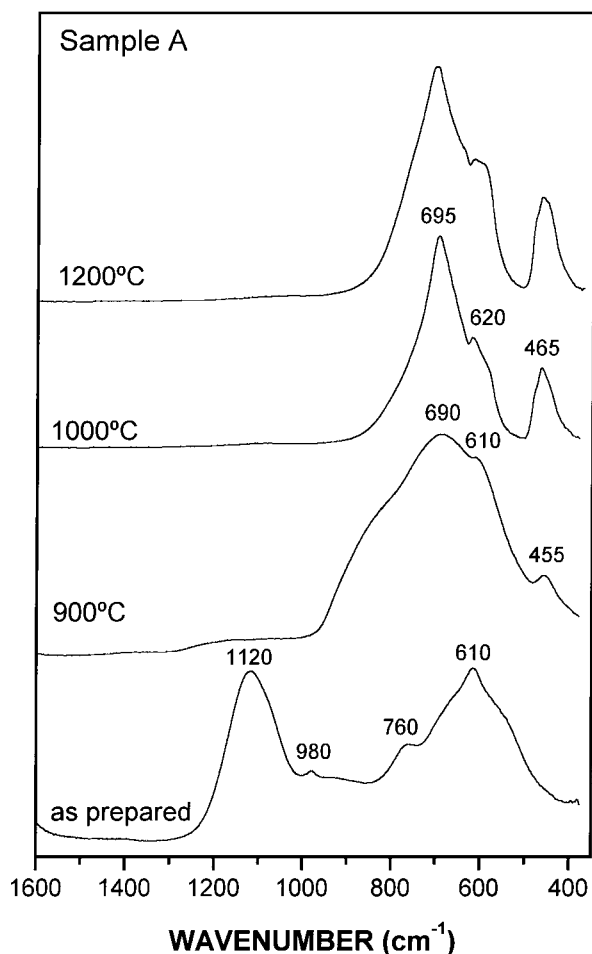


Figure 3 Infrared spectra of sample A, as prepared and after heating at different temperatures.

TABLE II Unit cell a parameter and Cr/Al mole ratio obtained by using the Vegards' law for the corundum solid solutions developed after heating samples A and B at different temperatures

	Temperature (°C)	a (Å)	Cr/Al mole ratio
Sample A	900	4.806 ± 0.006	0.317 ± 0.062
	1000	4.783 ± 0.001	0.143 ± 0.006
	1200	4.783 ± 0.001	0.143 ± 0.006
Sample B	900	4.814 ± 0.004	0.388 ± 0.040
	1000	4.814 ± 0.002	0.388 ± 0.020
	1100	4.816 ± 0.003	0.409 ± 0.030
	1300	4.821 ± 0.002	0.465 ± 0.020

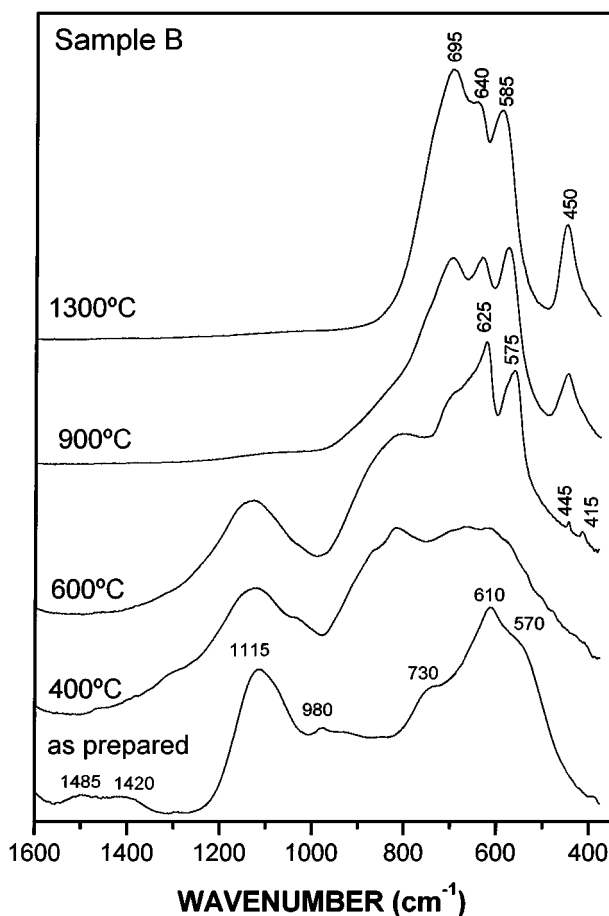


Figure 4 Infrared spectra of sample B, as prepared and after heating at different temperatures.

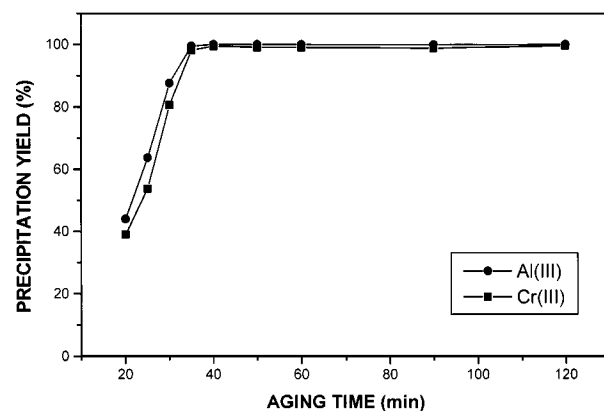


Figure 5 Al(III) and Cr(III) precipitation yields measured after aging at 100°C for different periods of time, solutions containing $0.002 \text{ mol dm}^{-3}$ $\text{Al}(\text{NO}_3)_3$, $0.001 \text{ mol dm}^{-3}$ $\text{Cr}(\text{NO}_3)_3$, $0.00186 \text{ mol dm}^{-3}$ sodium sulfate (sulfate/Cr(III) mol ratio = 0.62), 0.1 mol dm^{-3} urea and 20 g dm^{-3} PVP.

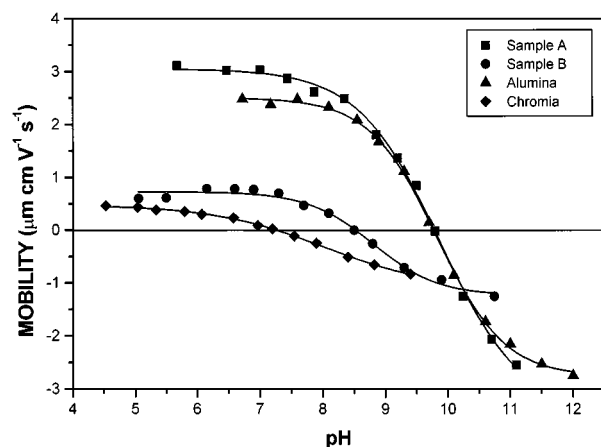


Figure 6 Electrophoretic mobilities measured as a function of pH for samples A and B and for the alumina and chromia blanks.

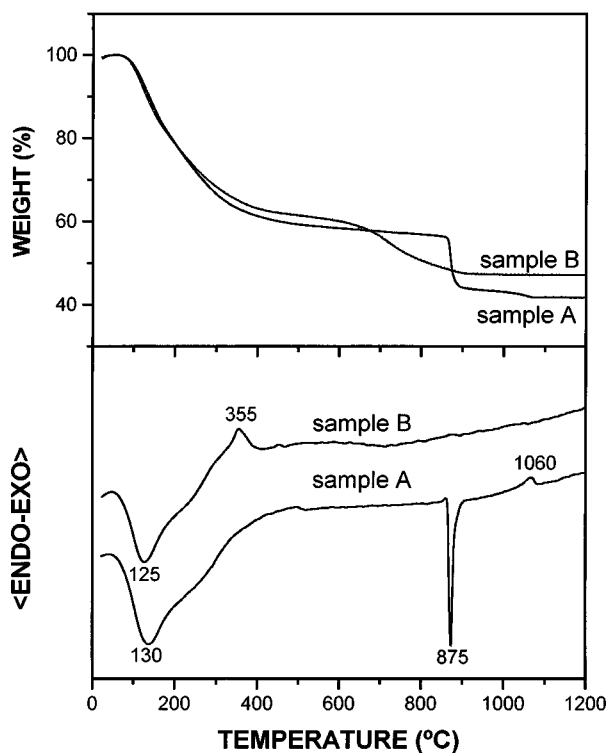


Figure 7 Differential thermal (bottom) and thermogravimetric (top) analyses obtained for samples A and B.

full development of the corundum solid solution. This finding was confirmed by the Cr/Al mole ratio obtained for the solid solution under these conditions which was very close (0.143 ± 0.006) to that measured by chemical analysis (0.13). The infrared spectrum of the sample heated at 1000°C (Fig. 3) was also in agreement with this behavior since it displayed similar features to those previously reported for an alumina/chromia solid solution with similar composition to that of sample A [16]. It must also be mentioned that the particles retained the spherical shape after this heat treatment (Fig. 1C). Finally, a further heating of the sample at higher temperatures (1200°C) did not result in any noticeable change either in its infrared spectrum (Fig. 3) or its X-ray diffraction pattern (Fig. 8, Table II). Therefore, we can conclude that for alumina-rich compositions (Cr/Al < 0.13), the full development of the corundum

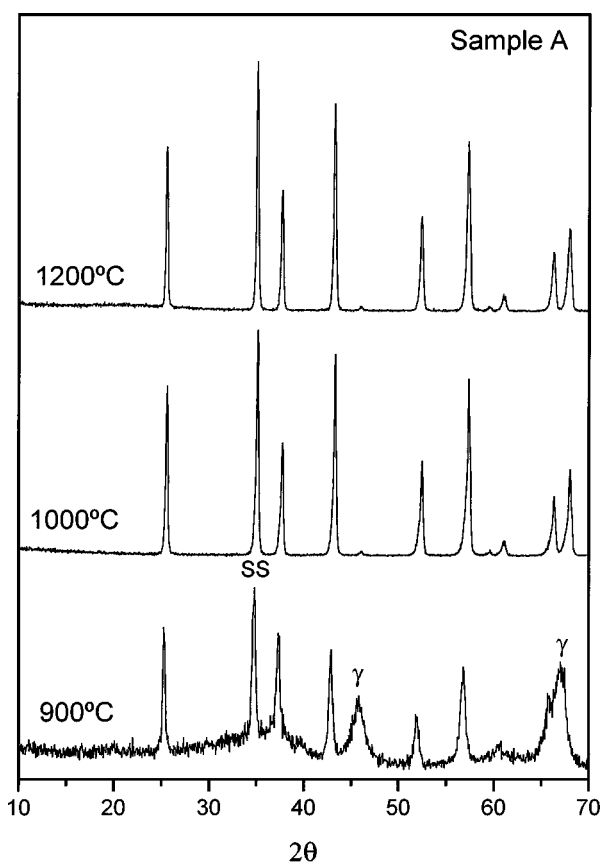


Figure 8 X-ray diffraction patterns of sample A heated at for 2 h at different temperatures. Symbols designating the most intense peaks of the different phases: SS = corundum solid solution, γ = $\gamma\text{-Al}_2\text{O}_3$.

solid solution in the Cr-doped alumina particles prepared by the here reported procedure takes place at lower temperatures than those required in the case of other reported preparation methods ($> 1300^\circ\text{C}$) [3, 9], which may be attributed to the high degree of chemical homogeneity at the atomic level attained in our case.

The DTA curve of sample B (Fig. 7) only showed the broad endothermic peak centered at 125°C due to the release of water and a weak exothermic effect at 355°C , which can be attributed to the decomposition of the carbonate anions, as indicated by the disappearance of their infrared bands in the spectrum of the sample heated at 400°C (Fig. 5). The weight loss associated to both processes was $\sim 40\%$ (Fig. 7). However, some other compositional and structural changes were detected by X-ray diffraction and infrared spectroscopy after heating the sample at higher temperatures. Thus, it was found that chromia segregated at 600°C from the alumina matrix resulting in the crystallization of $\alpha\text{-Cr}_2\text{O}_3$ (Fig. 9). At this temperature the alumina phase remained amorphous and still contained sulphate anions as indicated by the infrared spectrum of the sample (Fig. 4), which also shows the $\alpha\text{-Cr}_2\text{O}_3$ bands ($625, 575, 445$ and 415 cm^{-1}) [11]. From 600 to 900°C , a progressive weight loss (12.5%) took place (Fig. 7) that, according to infrared spectroscopy (Fig. 4), must be ascribed to the decomposition of the sulphate groups. This process was accompanied by the development of an alumina-rich (Cr/Al mole ratio = 0.388, Table II) solid solution, thus decreasing the intensity

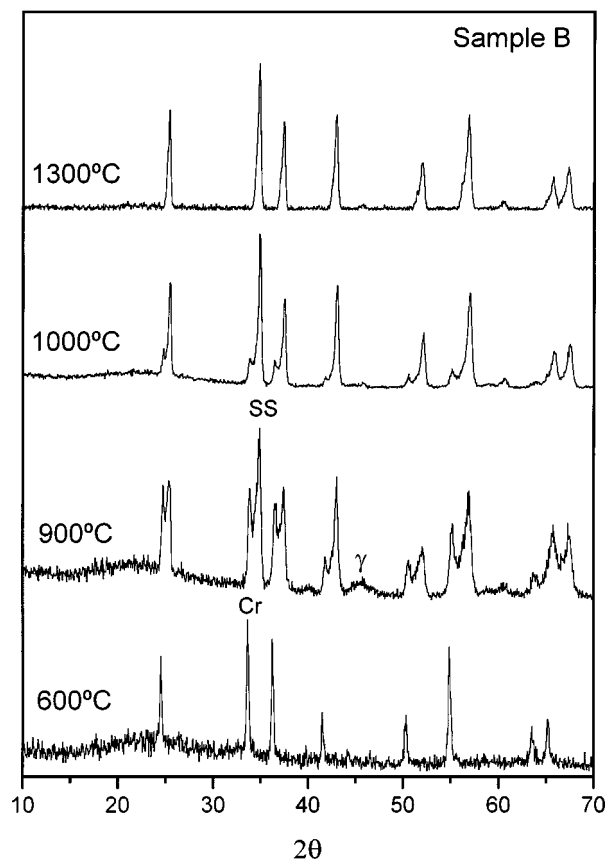


Figure 9 X-ray diffraction patterns of sample B heated at for 2 h at different temperatures. Symbols designating the most intense peaks of the different phases: Cr = α -Cr₂O₃, SS = corundum solid solution, γ = γ -Al₂O₃.

of the α -Cr₂O₃ peaks (Fig. 9). A small amount of γ -Al₂O₃ was also detected after this treatment, which disappeared at 1000°C (Fig. 9). The heating at increasing temperatures (>1000°C) gave rise to a progressive incorporation of Cr³⁺ to the alumina-rich solid solution (Table II). At 1300°C, the Cr content of the latter was very close (Cr/Al mole ratio = 0.465 ± 0.02) to that measured by chemical analysis (Cr/Al mole ratio = 0.49) suggesting the full dissolution of Cr in the alumina lattice, which agrees with the only presence of the peaks corresponding to the corundum phase in the X-ray diffraction pattern of the sample (Fig. 9). It should be mentioned that the infrared spectrum of this solid solution (Fig. 4) showed some variations in bands position respect to that previously reported for a sample with similar composition [16], probably due to differences in particle shape [17, 18], which in our case changed on heating from spheres to irregular morphologies as a consequence of a sintering process (Fig. 1D).

The above results indicate that an increase in the raw Cr content of the composite system prepared by the here described procedure result in an increase in the temperature of calcination required for the full development of the corundum solid solutions.

4. Conclusions

We have shown that unagglomerated spherical particles of composite alumina-chromia nature can be obtained

by homogeneous precipitation at 100°C for 1 h, from aqueous Al(III) and Cr(III) nitrate solutions containing sodium sulphate, urea and polyvinylpyrrolidone, under a very restrictive set of experimental conditions. The Cr/Al ratio and the mean size of the particles could be varied by altering the reagents concentrations. In all cases, the obtained powders were amorphous and contained a certain amount of sulphate anions. The study of the thermal evolution of some selected systems revealed that for alumina-rich compositions (Cr/Al mole ratio ≤ 0.13), the particles transformed into fully developed corundum solid solutions, keeping their spherical shape, at much lower temperature (1000°C) than those needed for samples prepared by previously reported procedures ($\geq 1300^\circ\text{C}$). This behavior was attributed to the high degree of chemical homogeneity at the atomic level attained in our case. It was also found that an increase in the Cr/Al mole ratio of the composite systems resulted in an increase of the calcination temperature required for the full development of the corundum solid solution, which favored particle sintering.

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