

Nanosized Cr₂O₃ hydrate spherical particles prepared by the urea method

M. Ocaña *

Instituto de Ciencia de Materiales de Sevilla (CSIC-UNSE), Americo Vespucio s/n, Isla de La Cartuja, 41092 Seville, Spain

Received 22 July 2000; received in revised form 26 September 2000; accepted 11 October 2000

Abstract

A procedure for the preparation of non-agglomerated spherical particles of narrow size distribution in the nanometer range, based on the aging at 100°C of aqueous solutions of Cr(III) nitrate in the presence of sodium sulfate, urea and polyvinyl pyrrolidone is reported. The mean particle diameter could be controlled by altering the Cr(III) concentration in the starting solutions. The so produced particles consisted of an amorphous Cr₂O₃ hydrate containing a certain amount of carbonate and sulfate anions. The carbonate anions decomposed when these particles were heated at 325°C which also resulted in the crystallization of α-Cr₂O₃. The decomposition of the sulfate groups requires a further annealing at 500°C. The surface area of the particles increased considerably as increasing heating temperature up to 325°C. However, an important decrease of this magnitude was detected after calcination at 500°C as a consequence of particle sintering. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Calcination; Cr₂O₃; Powders-chemical preparation

1. Introduction

Chromic oxide (Cr₂O₃) is an important refractory material due to its high melting temperature (about 2300°C) and oxidation resistance, although its sinterability is very poor and requires special sintering condition to achieve high density.¹ For such an application, the availability of nanosized powders would be desirable since they usually present high surface areas and may favor the sintering process.^{2,3} In addition, this kind of powders is essential for preparing nanocrystalline ceramics, which may present improved properties (hardness, stiffness, etc.) over the conventional ones.⁴

It is well known that the use of spherical and non-agglomerated particles as starting powders in ceramic processing results in materials of improved mechanical properties since this kind of particles can be better compacted and sintered.² These particles are also very useful as models for fundamental studies since many

properties of the dispersed matter are affected by particle size and shape.⁵

Nanosized Cr₂O₃ particles have been prepared by several methods including the sol-gel process,¹ gas-condensation,³ thermal decomposition of Cr(III) nitrate solutions,⁶ microwave plasma⁷ and by sonochemical reactions.⁸ However, except in the case of the plasma method,⁷ ill defined and irregular morphologies and particle aggregation were obtained. It has also been reported the preparation of spherical particles of narrow size distribution of amorphous Cr₂O₃ hydrate by forced hydrolysis of very diluted solutions (2×10^{-4} – 1×10^{-3} mol dm⁻³) of chrome alum [CrK(SO₄)₂] at moderated temperatures (60–90°C) for long periods of time (18 h to several days).^{9,10} This procedure yielded particle sizes in the micrometer range (>0.3 μm).

In this paper, a method for the preparation of non-agglomerated spherical particles of narrow size distribution in the nanometer range, consisting of an amorphous Cr₂O₃ hydrate based on the aging at moderated temperature (100°C) of aqueous solutions of Cr(III) nitrate in the presence of sodium sulfate, urea and polyvinyl pyrrolidone is described. The effects of the reagent concentrations on the size and shape of the

* Tel.: +34-954-48-9533; fax: +34-954-46-0665.

precipitated particles are reported. The so obtained powders were analyzed in terms of chemical composition, crystallinity, electrokinetic behavior (isoelectric point) and specific surface area. The evolution of the powders characteristics on heating up to α -Cr₂O₃ crystallization was also evaluated.

2. Experimental

The powders were prepared by aging at 100°C for 24 h aqueous solutions of Cr(III) nitrate (Aldrich, 99%), sodium sulfate (Aldrich, 99%), urea (Merk, > 99%) and polyvinyl pyrrolidone K-30 (PVP, Fluka, purum). For such a purpose, Pyrex test tubes (10 cm³) containing freshly prepared solutions were tightly closed with Teflon caps and placed in an oven preheated at 100°C. After aging, the dispersions were cooled in a water bath and centrifuged at 18 000 rpm. The obtained precipitates were washed several times with doubly distilled water, filtered and dried at room temperature before analyses. The concentration of 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.

For calcination, the samples were heated for 1 h in a furnace preheated at the desired temperature, after which they were slowly cooled to room temperature.

The Cr(III) content in the supernatant solutions was measured (ICP, Perkin-Elmer 5500) in order to gain information on the yield of the precipitation reaction. The qualitative composition of the precipitated particles was assessed by energy dispersive X-ray analysis (EDX, Philips DX4).

The particle shape was examined by transmission electron microscopy (TEM) (Philips 200CM). For this, the samples were dispersed in water after which, a droplet of the suspension was deposited on a copper grid coated with a transparent polymer and dried. The particle size distribution was obtained from the micrographs by counting several hundreds of particles.

X-ray diffraction (Siemens D501) was used to identify the crystal structure of the samples. The infrared spectra of the powders diluted in KBr were recorded in a Nicolet 510 FT-IR spectrometer.

Differential thermal (DTA) and (TGA) analyses (Setaram 92-16.18) were performed in air atmosphere at a heating rate of 10°C min⁻¹.

The isoelectric point (iep) of the solids was determined by measuring (Malvern Zetamaster) electrophoretic mobilities of aqueous dispersions as a function of pH, at constant ionic strength (10⁻² mol dm⁻³ NaCl). The pH was varied by adding HCl or NaOH, as needed.

The surface areas were evaluated in a Micromeritics ASAP 2010 apparatus using the BET nitrogen gas adsorption method. Before analyses, the samples were heated at 150°C for several hours under vacuum.

3. Results and discussion

Table 1 summarizes the effects of the reagents concentrations on the morphological characteristics (size and shape) of the particles precipitated after aging at 100°C for 24 h, Cr(NO₃)₃ solutions in the presence of urea, Na₂SO₄ and PVP. As observed, the aging of solutions with Cr(NO₃)₃ concentrations ranging from 0.003

Table 1

Effects of the reagents concentrations on the size and shape of the particles precipitated by aging solutions of Cr(III) nitrate at 100°C for 24 h in the presence of urea, sodium sulfate and PVP^a

Cr(NO ₃) ₃ (mol dm ⁻¹)	Sulfate/Cr(III) (mol ratio)	Urea (mol dm ⁻¹)	PVP (g dm ⁻¹)	Particle shape	Mean particle diameter (S.D.) (nm)
0.001	0.6	0.02	20	Ill defined	
0.003	0.6	0.02	20	Spherical	62 (17)
0.005	0.6	0.02	20	Spherical	81 (20)
0.007	0.6	0.02	20	Spherical	138 (16)
0.009	0.6	0.02	20	Spherical	150 (18)
0.012	0.6	0.02	20	Agglomerates	
0.015	0.6	0.02	20	Agglomerates	
0.007	0.6	0.02	—	Agglomerates	
0.007	0.6	—	20	No precipitation	
0.007	0.2	0.02	20	Gel-like	
0.007	0.4	0.02	20	Ill defined	
0.007	0.8	0.02	20	Spherical	Polydispersed (~60–500 nm)
0.007	1.0	0.02	20	Spherical	Polydispersed (~60–800 nm)
0.007	1.2	0.02	20	Spherical	Polydispersed (~60–800 nm)
0.007	2.0	0.02	20	Spherical	Polydispersed (~60–800 nm)
0.007	2.6	0.02	20	Spherical	Polydispersed (~60–800 nm)

^a The minimum and maximum particle diameter in the polydispersed systems are included in parenthesis.

to 0.009 mol dm⁻³, keeping constant the urea concentration (0.02 mol dm⁻³), the PVP content (20 g dm⁻³) and the sulfate/Cr(III) mol ratio (0.6), produced non-agglomerated particles of spherical shape and narrow size distribution, the mean diameter of which increased

(from 62 to 150 nm) as increasing the Cr(III) concentration (from 0.003 to 0.009 mol dm⁻³). An example of such uniform particles prepared under the conditions described in the legend is shown in Fig. 1. It should be noted that more diluted Cr(III) solutions (0.001 mol

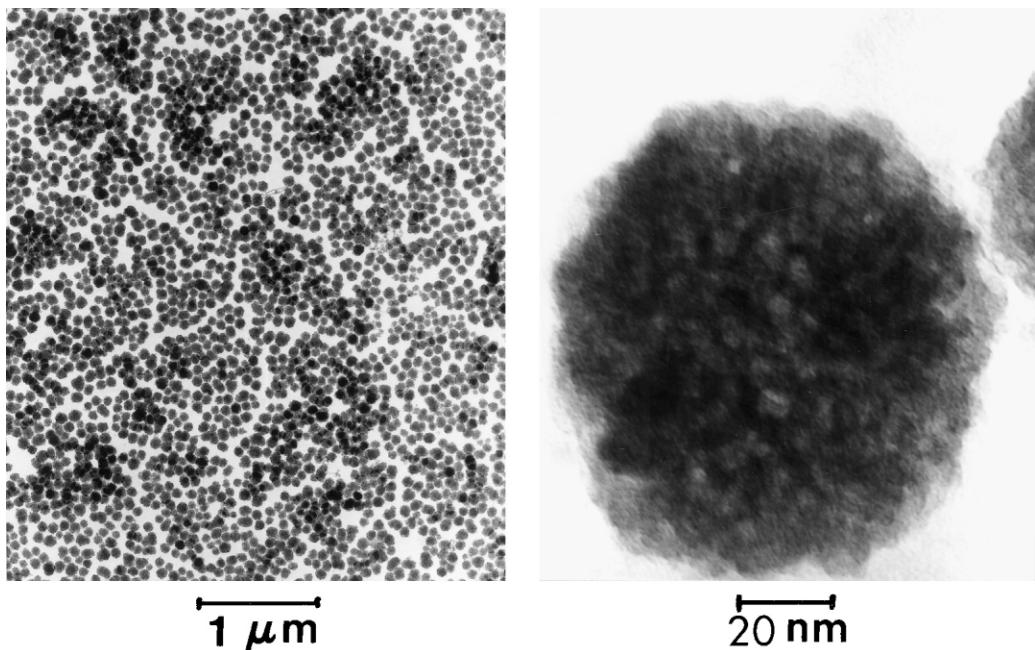


Fig. 1. TEM micrographs at different magnifications of the sample obtained by aging at 100°C for 24 h solutions containing 0.005 mol dm⁻³ of Cr(NO₃)₃, 0.003 mol dm⁻³ of sodium sulfate [sulfate/Cr(III) mol ratio = 0.6], 0.02 mol dm⁻³ of urea and 20 g dm⁻³ of PVP.

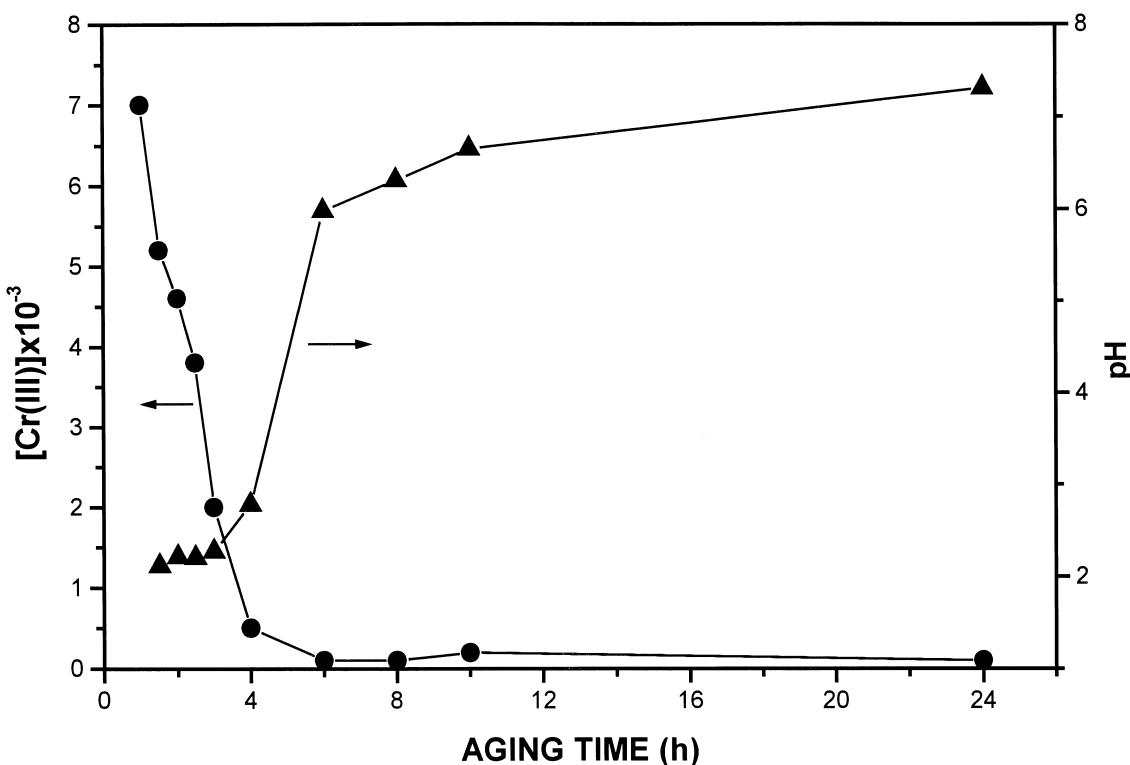


Fig. 2. Cr(III) concentration and pH measured after aging at 100°C for 24 h solutions containing 0.007 mol dm⁻³ of Cr(NO₃)₃, 0.0042 mol dm⁻³ of sodium sulfate [sulfate/Cr(III) mol ratio = 0.6], 0.02 mol dm⁻³ of urea and 20 g dm⁻³ of PVP.

dm^{-3}) yielded ill-defined and strongly aggregated particles whereas for Cr(III) concentrations $> 0.009 \text{ mol dm}^{-3}$ ($0.012\text{--}0.015 \text{ mol dm}^{-3}$) only hard agglomerates were obtained. The sulfate/Cr(III) mole ratio range required for the formation of such uniform dispersions is even more restrictive, since for values lower than 0.6 either gel-like precipitates [sulfate/Cr(III) ratio = 0.2] or ill-defined systems [sulfate/Cr(III) ratio = 0.4] were observed while for higher values [sulfate/Cr(III) ratio = 0.8–2.6] polydispersed spheres with sizes ranging from 60 to 500 nm resulted.

The addition of urea to the starting solutions was found to be essential in order to produce precipitation in the here described systems. Thus, in the absence of

this compound no precipitation was detected after 24 h of aging at 100°C in solutions containing $0.007 \text{ mol dm}^{-3}$ of Cr(III), $0.0042 \text{ mol dm}^{-3}$ of sodium sulfate (sulfate/Cr(III) ratio = 0.6) and 20 g dm^{-3} of PVP. This behavior is explained by the increase of pH generated by the decomposition of urea on heating, which has been amply used for the homogenous precipitation of several metal oxides from aqueous solutions of the corresponding metal salts. Finally, when the above solution was aged in the presence of 0.02 mol dm^{-3} of urea but in the absence of PVP, strongly agglomerated particles were formed, which indicated that the addition of a certain amount (20 g dm^{-3}) of this surfactant was also needed to prevent particle aggregation.

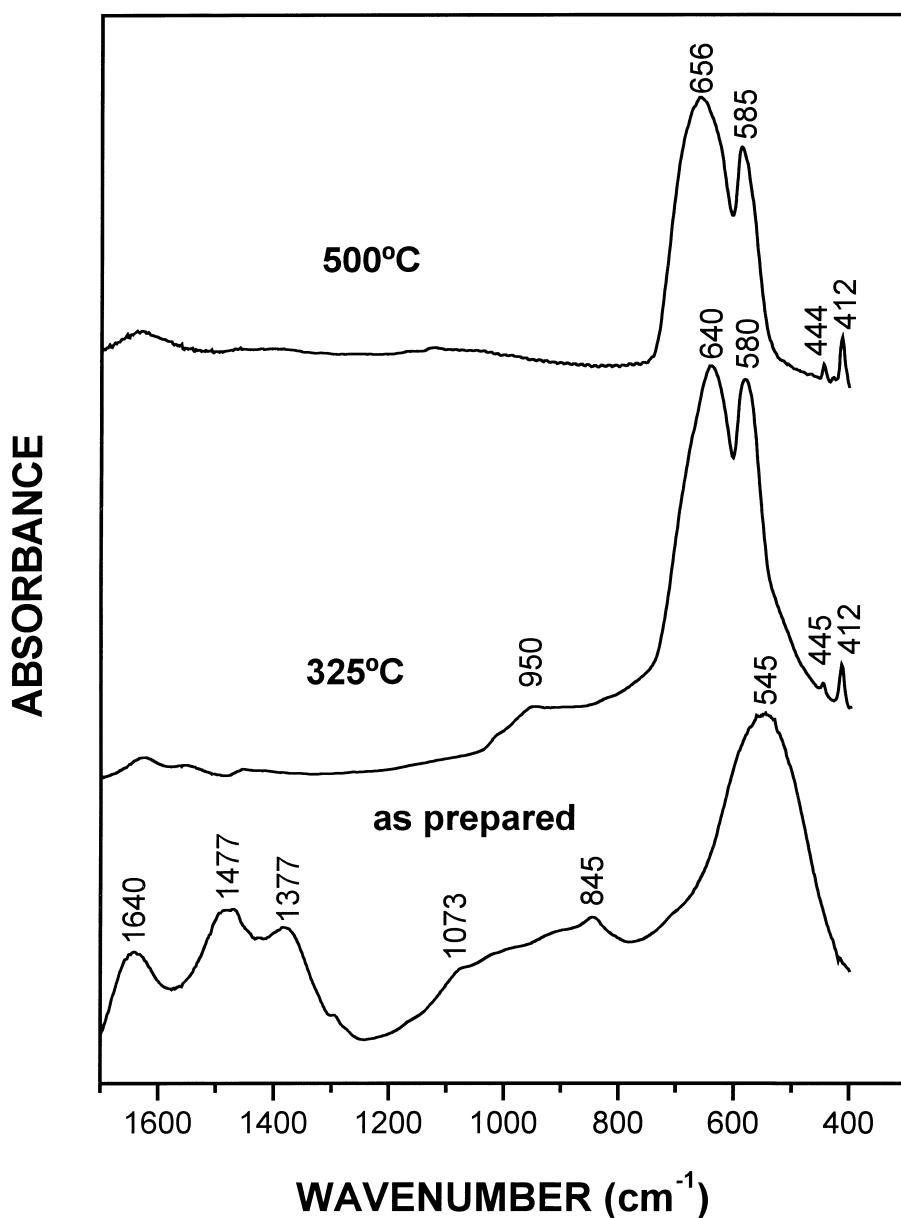


Fig. 3. Infra-red spectra of sample shown in Fig. 1, as prepared and after heating at different temperatures.

The effects of aging time on the precipitation yield were also analyzed. For such a purpose, solutions containing $0.007 \text{ mol dm}^{-3}$ of $\text{Cr}(\text{NO}_3)_3$, $0.0042 \text{ mol dm}^{-3}$ of sodium sulfate [sulfate/Cr(III) mol ratio = 0.6], 0.02 mol dm^{-3} of urea and 20 g dm^{-3} of PVP were aged at 100°C for different periods of time. As observed in Fig. 2, after an induction period of 75 min, the Cr(III) amount in solution continuously decreased during the first 6 h of aging, whereas no significant variations in this magnitude were detected for longer aging times. This behavior clearly indicates that the precipitation reaction was almost accomplished after 6 h of aging. It is outstanding that under these conditions, the corresponding yield was very high ($\sim 98\%$) for which, this procedure produces a much higher amount of uniform particles of Cr(III) oxide ($\sim 500 \text{ mg dm}^{-3}$) than that based on the forced hydrolysis of chrome alum solutions ($\leq 0.001 \text{ mol dm}^{-3}$) in the absence of urea ($\sim 10 \text{ mg dm}^{-3}$).¹⁰

Most of the characterization efforts were conducted on the sample having a mean particle size of 81 nm

(Table 1), which was chosen as a representative example. X-ray diffraction revealed that this sample was amorphous. Its infra-red spectrum in the $1700\text{--}400 \text{ cm}^{-1}$ region displayed bands at 545 , 845 , 1377 , 1477 and 1640 cm^{-1} as well as several broad absorptions between 900 and 1100 cm^{-1} (Fig. 3). The first absorption maximum (545 cm^{-1}) must be ascribed to the Cr-O vibrations, whereas that at 1640 cm^{-1} is due to adsorbed water. The broad bands at $900\text{--}1100 \text{ cm}^{-1}$ indicate the presence of a small amount of sulfate anions in the particles,¹¹ which was confirmed by EDX analyses (Fig. 4). Finally, the absorptions at 845 , 1377 and 1477 cm^{-1} can be attributed to carbonate anions.¹¹ It should be noted that both, sulfate and carbonate bands, persisted with unaltered intensity in the spectrum of the sample after a further extensive washing with doubly distilled water, suggesting that both anions are not simply adsorbed onto the particles surface. The carbonate anions are originated during the decomposition of urea, which, as it has been amply reported, liberate such

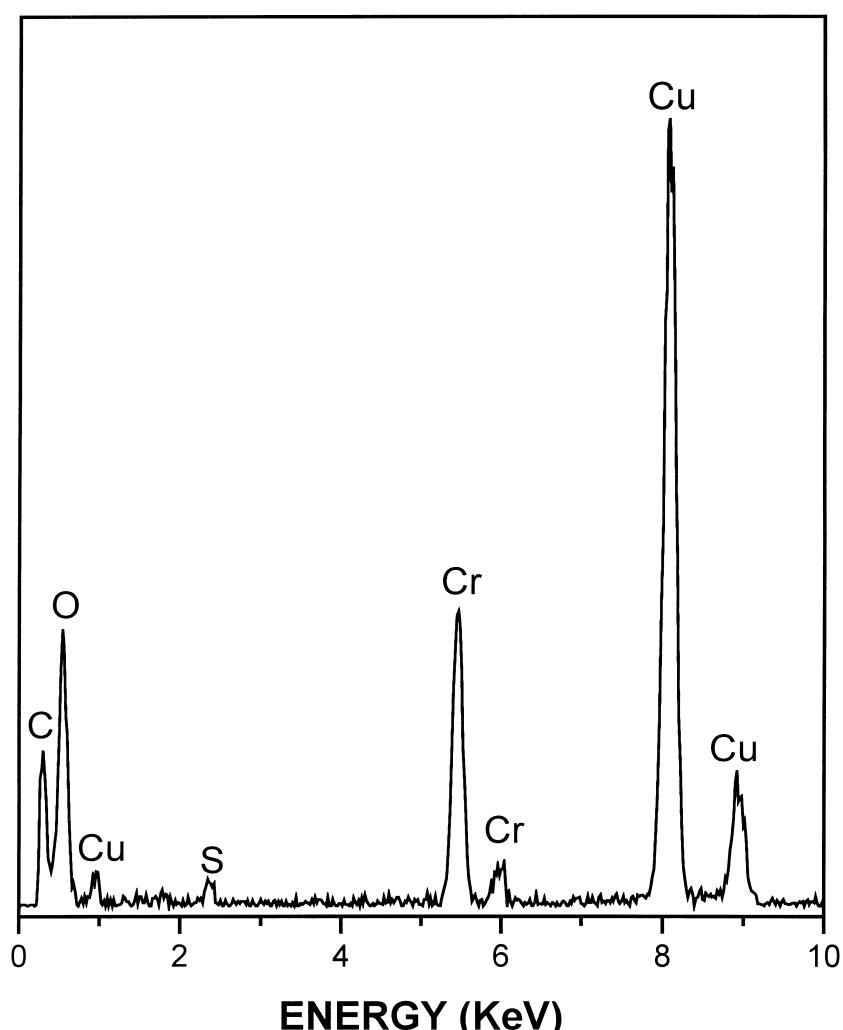


Fig. 4. EDX spectrum of the sample shown in Fig. 1. The carbon and copper peaks are due to the TEM grid.

anions when heated in neutral or alkaline media causing the precipitation of basic carbonates. In this case, a basic pH value was only reached at the last steps of aging (Fig. 2), for which the amount of carbonate anions incorporated to the particles must be rather small.

The presence of sulfate and carbonate anions in the amorphous nanoparticles also affected their iep, which was lower (7.2 ± 0.1) (Fig. 5) than that previously reported for chromium (III) oxide (8.4).¹²

The BET surface area of the selected sample was higher ($42 \text{ m}^2 \text{ g}^{-1}$) than that calculated assuming only geometrical considerations ($\sim 14 \text{ m}^2 \text{ g}^{-1}$), which may be due to both, the surface roughness of the particles and the presence of a certain internal porosity (Fig. 1). It should be noted that the measured surface area was also higher than that previously reported for the spherical particles of the same composition prepared in the absence of urea ($\leq 20 \text{ m}^2 \text{ g}^{-1}$), which presented a higher mean diameter ($\sim 0.4 \mu\text{m}$) and smoother surface.¹⁰

The differential thermal and thermogravimetric curves obtained for the amorphous chromium (III) oxide nanoparticles are shown in Fig. 6. As observed, the main features of the DTA curve are an endothermic peak centered at 155°C followed by two exothermic ones at 240 and 390°C , respectively. The endothermic effect, which is accompanied by a weight loss of 27%,

measured between 25 and 230°C , is ascribed to the release of adsorbed water. The first exothermic peak (240°C) and its associated weight loss detected between 230 and 350°C ($\sim 12\%$) can be attributed to the decomposition of the carbonate anions as substantiated by the infrared spectrum of the sample heated at 325°C , in which the carbonate bands disappeared (Fig. 3). This spectrum also shows additional variations when compared with that of the original sample. Thus, the absorption corresponding to the sulfate anions (900 – 1100 cm^{-1}) changes in intensity and position indicating changes in the sulfate coordination and probably a certain decrease in the sulfate content. In addition, some bands at 412 , 445 , 580 and 640 cm^{-1} were developed which can be attributed to crystalline $\alpha\text{-Cr}_2\text{O}_3$ (eskolaite)¹³ manifesting the crystallization of the initially amorphous particles, which still retained the spherical shape (Fig. 7A). The X-ray diffraction of the heated sample (Fig. 8) was consistent with $\alpha\text{-Cr}_2\text{O}_3$ ¹⁴ confirming such a crystallization process. It should be noted that after this heat treatment, the surface area of the sample increased up to $95 \text{ m}^2 \text{ g}^{-1}$ suggesting an increase in the internal porosity of the particles as a consequence of the release of water¹⁰ and carbonates.

Finally, the exothermic effect at 390°C and its corresponding weight loss (5.5%) may be attributed to the decomposition of sulfate groups as confirmed by the

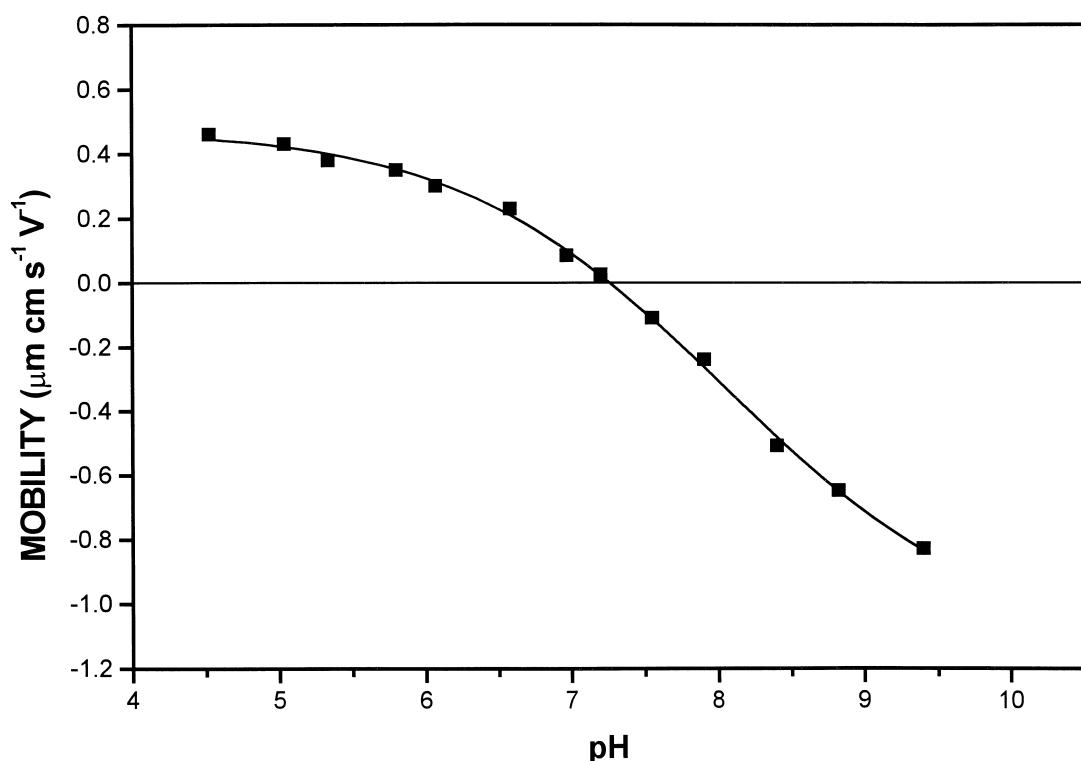


Fig. 5. Electrophoretic mobilities measured as a function of pH for the sample shown in Fig. 1.

infrared spectrum of the sample annealed at this temperature which only showed the bands corresponding to eskolaite (Fig. 3). This treatment also resulted in an

important decrease of the surface area of the sample ($12 \text{ m}^2 \text{ g}^{-1}$) mainly due to the sintering process observed by TEM (Fig. 7B).

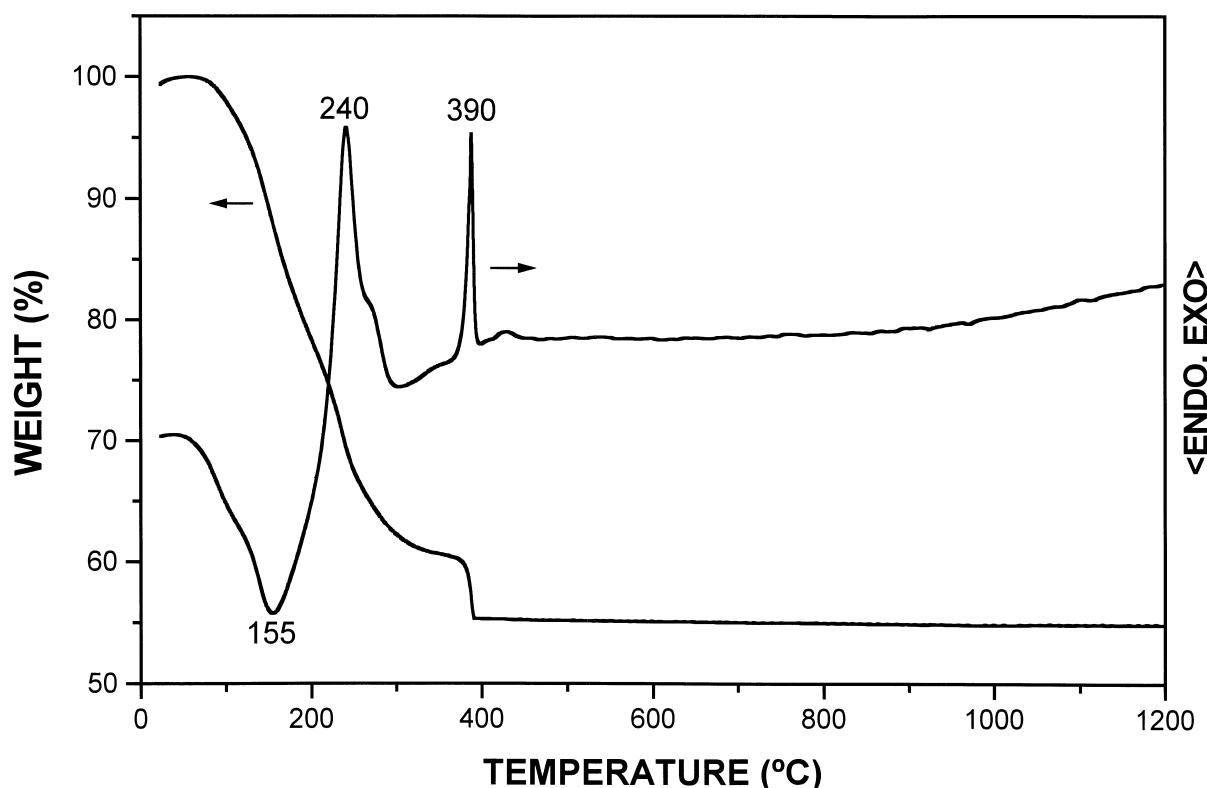


Fig. 6. Differential thermal and thermogravimetric analyses obtained for the sample shown in Fig. 1.

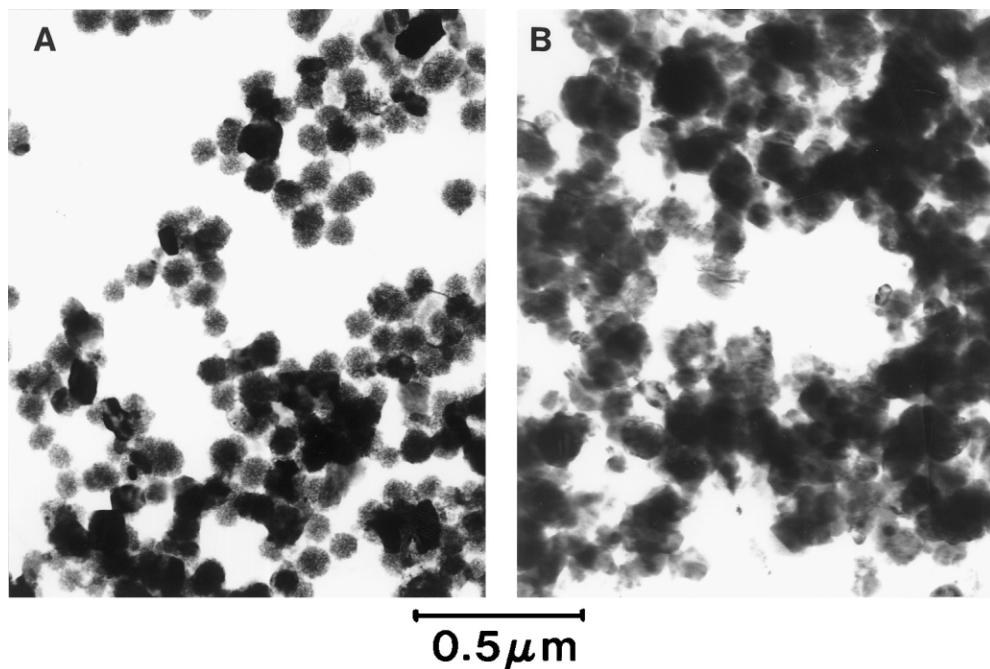


Fig. 7. TEM micrographs of the sample shown in Fig. 1A after heating at (A) 325°C and (B) 500°C.

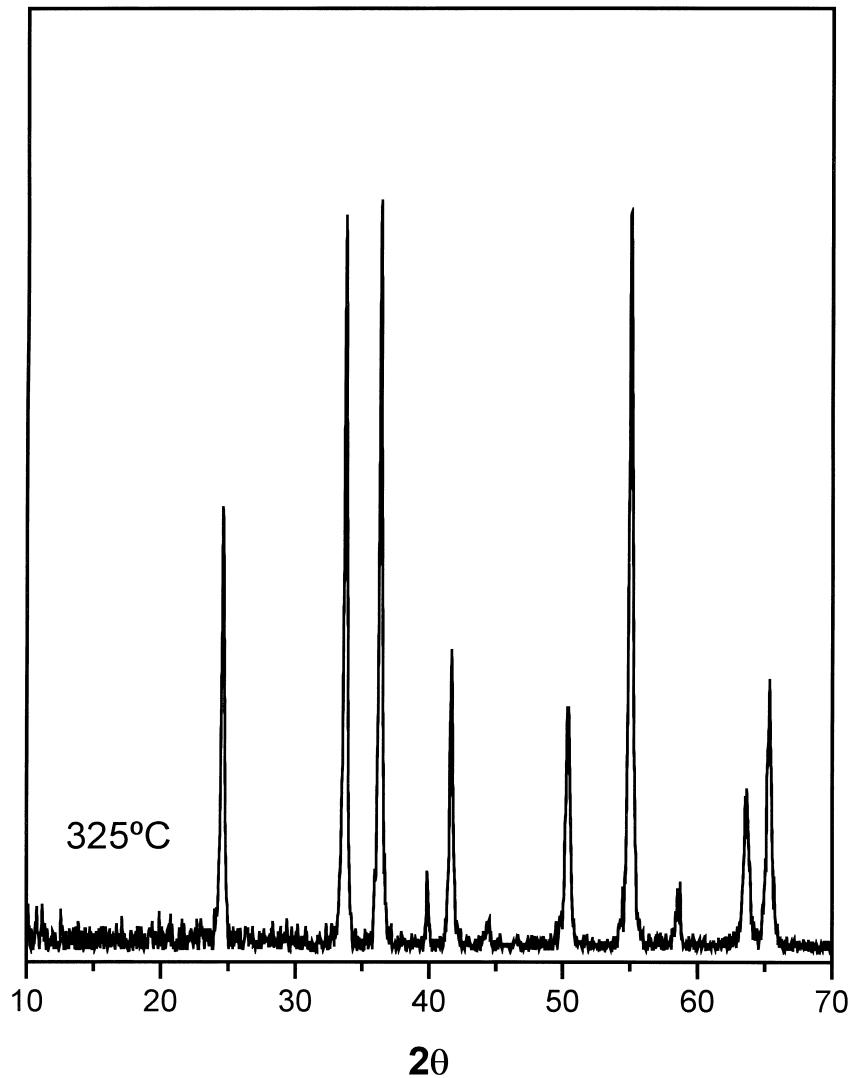


Fig. 8. X-ray diffraction pattern of the sample shown in Fig. 1 after heating at 325°C.

4. Conclusions

Non-agglomerated spherical particles of narrow size distribution in the nanometer range have been prepared by aging at 100°C aqueous solutions of Cr(III) nitrate (0.003–0.009 mol dm⁻³) in the presence of sodium sulfate [sulfate/Cr(III) mol ratio=0.6], urea (0.2 mol dm⁻³) and polyvinyl pyrrolidone (20 g dm⁻³). It was found that the mean particle diameter increased (from 62 to 150 nm) as increasing the Cr(III) concentration (from 0.003 to 0.009 mol dm⁻³). A sample composed by particles having a mean diameter of 81 nm was characterized in detail as a representative example. This sample consisted of an amorphous Cr₂O₃ hydrate containing a certain amount of carbonate and sulfate anions and presented a surface area of 42 m² g⁻¹. The carbonate anions decomposed when the particles were heated at 325°C. This process was accompanied by the crystallization of α -Cr₂O₃ and by a considerable

increase of the surface area up to 95 m² g⁻¹. A further annealing at 500°C gave rise to the decomposition of the sulfate groups and to an important decrease of the surface area (12 m² g⁻¹) as a consequence of particle sintering.

Acknowledgements

This work was supported by the Spanish CICYT and the European Union under project No. 1FD97-0697. The technical assistance of Mrs. Immaculada Rosa Cejudo is acknowledged.

References

- Kawabata, A., Yoshinaka, M., Hirota, K. and Yamaguchi, O., Hot isostatic pressing and characterization of sol-gel derived chromium(III) oxide. *J. Am. Ceram. Soc.*, 1995, **78**, 2271–2273.

2. Ring, T. A., Processing of fine ceramics. *MRS Bull.*, 1990, **15**, 34–40.
3. Balachandran, U., Siegel, R. W., Liao, Y. X. and Askew, T. R., Synthesis, sintering and magnetic properties of nanophase Cr₂O₃. *Nanostruct. Mater.*, 1995, **5**, 505–512.
4. Verweij, H., Nanocrystalline and nanoporous ceramics. *Adv. Mater.*, 1998, **10**, 1483–1486.
5. Haruta, M. and Delmon, B., Preparation of homodisperse solids. *J. Chim. Phys.*, 1986, **83**, 859–868.
6. Hou, B., Ji, X., Xie, Y., Li, J., Shen, B. and Qian, Y., ESR study of nanocrystalline and amorphous Cr₂O₃. *Nanostruct. Mater.*, 1995, **5**, 599–605.
7. Vollath, D., Szabó, D. V. and Willis, J. O., Magnetic properties of nanocrystalline Cr₂O₃ synthesized in a microwave plasma. *Mater. Letter*, 1996, **29**, 271–279.
8. Arul Dash, N., Koltypin, Y. and Gedanken, A., Sonochemical preparation and characterization of ultrafine chromium oxide and manganese oxide powders. *Chem. Mater.*, 1997, **9**, 3159–3163.
9. Demchak, R. and Matijević, E., Preparation and particle size analysis of chromium hydroxide hydrosols of narrow size distribution. *J. Colloid Interface Sci.*, 1969, **31**, 257–262.
10. Zettlemoyer, A. C., Siddiq, M. and Micale, F. J., Surface properties of heat-treated chromia of narrow particle size distribution. *J. Colloid Interface Sci.*, 1978, **66**, 173–182.
11. Colthup, N. B., Daly, L. H. and Wiberley, S. E., *Introduction to Infrared and Raman Spectroscopy*. Academic Press, San Diego, 1990.
12. Hunter, R. J., *Zeta Potential in Colloid Science*. Academic Press, New York, 1981.
13. McDevitt, N. T. and Baun, W. L., Infrared absorption study of metal oxides in the low frequency region (700–240 cm⁻¹). *Spectrochim. Acta*, 1964, **20**, 799–808.
14. JCPDS file No. 6-504.