ELSEVIER

Journal of Alloys and Compounds 262–263 (1997) 292–295

Journal of
ALLOYS AND COMPOUNDS

Morphological evolution of zinc oxide originating from zinc hydroxide carbonate

F.A. Sigoli*, M.R. Davolos, M. Jafelicci, Jr.

Instituto de Química, Universidade Estadual Paulista-UNESP, PO Box 355, 14801-970 Araraquara, SP, Brazil

Abstract

Zinc oxide can be obtained by thermal decomposition of hydrozincite, a topochemical reaction. This work reports the relation between zinc oxide morphology and the precursor zinc hydroxide carbonate precipitation time. The morphological evolution was monitored by SEM, IR and XRD. Zinc oxide obtained from initially precipitated hydrozincite consists of porous spherical aggregates and shows a single Zn–O IR vibrational band. At longer periods of precipitation time the aggregates were transformed into spherulitic-shaped zinc oxide particles showing the Zn–O split vibrational band. X-ray patterns show that the hexagonal zinc oxide phase is substantially increased as a function of hydrozincite precipitation time. © 1997 Elsevier Science S.A.

Keywords: Zinc oxide; Hydrozincite; Morphology; Zinc hydroxide carbonate

1. Introduction

Zinc oxide is a white powder with exceptional and unique properties. It is produced industrially in great quantities by oxidation of zinc vapors resulting in various morphologies [1]. Morphology, structure, size, composition and crystallinity play an important role in technology of varistors, luminescent devices and pigments [2]. Several methods concerning the preparation of colloidal metal oxides are available in the literature. In recent years a large number of techniques have been developed to yield particles of different but uniform shapes and of narrow size distributions within the micron and sub-micron range [3]. The most convenient method for preparation of such products is based on the control of chemical process taking place in homogeneous solutions.

Zinc oxide can also be obtained by thermal decomposition of zinc hydroxide carbonate topotatic precursor. This precursor is prepared by aging aqueous zinc salt solutions in the presence of urea at elevated temperatures [4]. Recently, spherulitic needle-aggregates were obtained from a chloride medium and large porous spherical aggregates from a sulfate medium using the latter technique [5]. The chemical composition and morphology of the resulting particles depend on a large number of parameters, such as pH, reagent concentrations, temperature, anion species in solution, method mixing rate and precipitation time [6,7], and therefore is one of the problems to be solved when preparing zinc oxide.

The aim of this work is to study the influence of zinc hydroxide carbonate precipitation time on the morphology and crystallinity characteristics of zinc oxide samples obtained as a product of thermal decomposition.

2. Experimental

All chemicals were MERCK products, reagent grade purity. Zinc hydroxide carbonate was precipi-

---

* Corresponding author. Fax: +55 16 222 79 32, e-mail: fsigoli@iq.unesp.br

0925-8388/97/$17.00
PII S0925-8388(97)00404-0

tated at pH = 5 from standard 3.3×10^{-2} mol l^{-1} zinc chloride and 2.4×10^{-2} mol l^{-1} urea solutions aged at 90°C during different precipitation times: 0 (initial turbidity), 75, 180, and 440 min. The products were filtered, washed with deionized water and then thermally decomposed in an alumina crucible at 300°C for 4 h under static air atmosphere to give zinc oxide. Samples were characterized by X-ray powder diffractometry (XRD- DIFFRACTOMETER HGZ 4/B) using iron-filtered CoK_α radiation and by scanning electron microscopy (JEOL JSM T330A). The IR (FT-IR NICOLET IMPAC 400) KBr pellets were recorded in the range 4000– 200 cm^{-1} with resolution of 2 cm^{-1}.

3. Results and discussion

The SEM analysis shows that spherically shaped particles of zinc oxide are obtained within the periods of time from first turbidity until 75 min of precipitation (Figs. 1a,b). Then, at longer periods of precipitation they are transformed into spherulitic and acicular particles (Figs. 1c,d). This evolution is in agreement with the thermodynamic principles and consequently with the natural occurrence of the precursor, as stated by Ghose [8].

Recently IR spectroscopy has successfully been applied for the morphological characterization of several metal oxide powders, such as αFe_2O_3, TiO_2 and ZnO. Calculated IR absorption spectra of ZnO microcrystals have been assigned to their shapes corresponding to slab, where the ratio of the crystallographic axis is $c/a < 1$ to sphere ($c/a = 1$) and to cylinder ($c/a \gg 1$) [9,10]. The IR absorptions presented are characteristic of Zn-O vibrations and their splitting depends on particle morphology. Porous spherical specimens (Figs. 1a–b) show two bands with maxima at 420 and 565 cm^{-1} (Figs. 2a–b). The absorption at 420 cm^{-1} splits progressively as a function of the precursor precipitation time giving rise to three separate absorption bands at 425, 410, 387 cm^{-1} for the final spherulitic and acicular shapes (Figs. 2c–d). Particle shapes, state of aggregation and method of preparation have a strong effect on the experimental IR powder spectra as predicted by the theory of

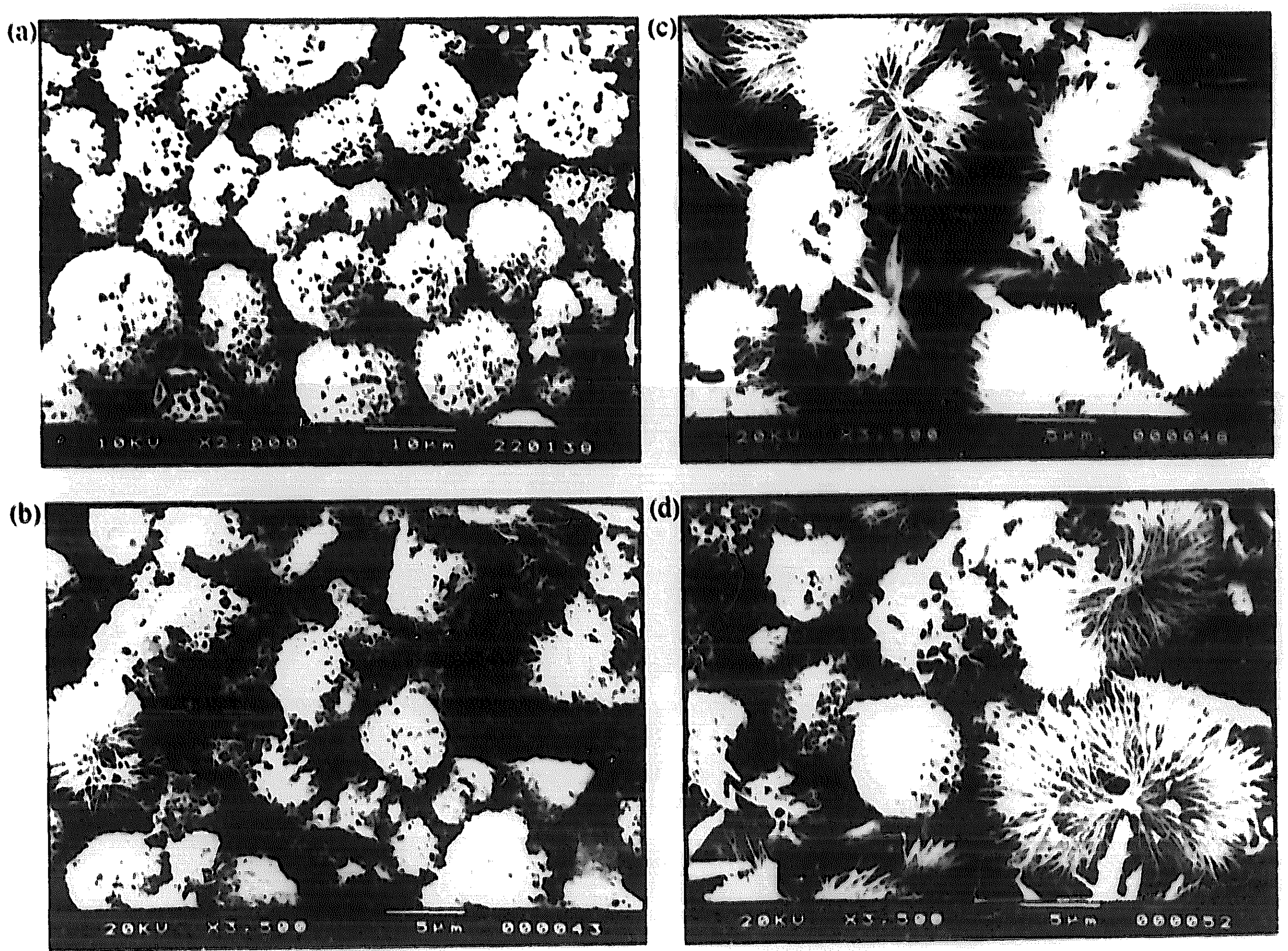

Fig. 1. (a) Zinc oxide obtained from thermal decomposition of 300°C of initiallty precipitated ($t = 0$ min) zinc hydroxide carbonate. (b) Zinc oxide obtained from thermal decomposition at 300°C of zinc hydroxide carbonate precipitated after 75 min. (c) Zinc oxide obtained from thermal decomposition at 300°C of zinc hydroxide carbonate precipitated after 180 min. (d) Zinc oxide obtained from thermal decomposition at 300°C of zinc hydroxide carbonate precipitated after 440 min.

average dielectric constant (TADC) [11]. On the other hand, surface effects related to particle size can result in the appearance of new bands as the surface to volume ratio increases. To better evaluate this result other IR and SEM experiments were performed with uniform porous spherical aggregates and acicular-shaped zinc oxide obtained with different reagent concentrations (Figs. 3a–b). The results showed that a single band at 416 cm^{-1} corresponds to porous spherical aggregates and the splitting bands at 430, 406, and 385 cm^{-1} correspond to the acicular shape.

The morphological evolution can also be evaluated by XRD of different zinc oxide shapes (Fig. 4): (i) all the samples obtained by thermal decomposition are crystalline and their diffractograms are characteristic of zincite; (ii) the intensity of the reflection (002) is substantially increased as a function of the precursor precipitation time. The intensity changes are in agreement with the morphological evolution illustrated by SEM and IR spectra. Porous spherical aggregates have a crystallographic axis ratio $c/a = 1$, however, the reflections (002) and (100) have the same intensities (Fig. 4a). Spherulitic-shaped aggregates are formed from various acicular single particles with crystallographic axis ratio $c/a \gg 1$, resulting in a (002) reflection intensity stronger than (100) one corresponding to a hexagonal zinc oxide phase.

4. Conclusions

This work showed that morphological characterization of non-uniform samples can be evaluated using the theory of average dielectric constant making careful IR spectra analysis. It also showed that it is possible to monitor the particle morphology and crystallinity as a function of precursor precipitation time and to have better reliability of the products.

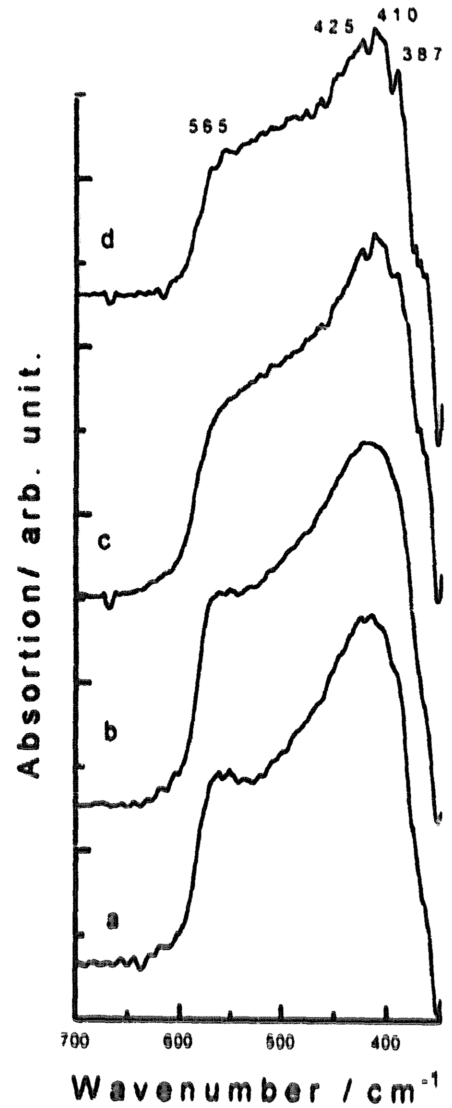

Fig. 2. Infrared absorption spectra from zinc oxide samples corresponding to SEM figures: (a) Zinc oxide from initially precipitated zinc hydroxide carbonate; (b) zinc oxide from precipitated zinc hydroxide carbonate after 75 min; (c) zinc oxide from precipitated zinc hydroxide carbonate after 180 min; (d) zinc oxide from precipitated zinc hydroxide carbonate after 440 min.

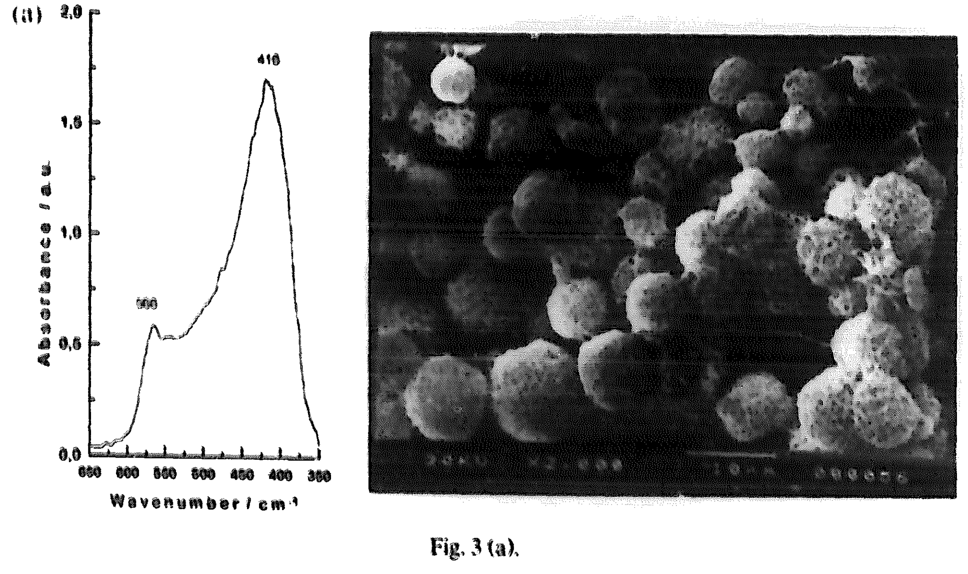

Fig. 3 (a).

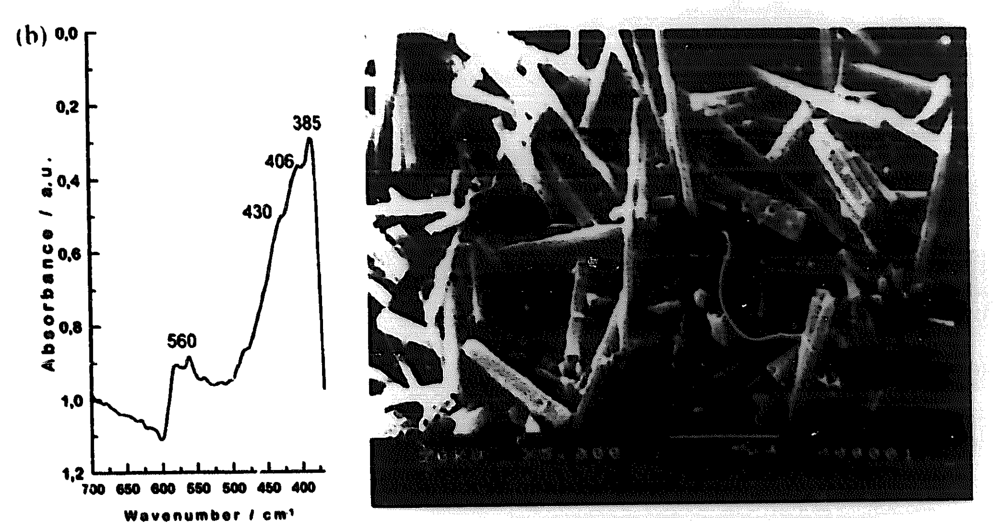

Fig. 3. (a) Infrared absorption spectrum of zinc oxide spherical particles obtained from thermal decomposition at 300°C of zinc hydroxide carbonate precipitated after 180 min: [urea] = 0.40 mol $^{-1}$; [$ZnCl_2$] = 0.055 mol l^{-1}. (b) Infared absorption spectrum of zinc oxide needle-like particles obtained from homogeneous precipitation at 90°C after 180 min: [urea] = 8.0×10^{-3} mol l^{-1}; [$ZnCl_2$] = 1.1×10^{-3} mol l^{-1}; and [HCl] = 5.0×10^{-5} mol l^{-1}.

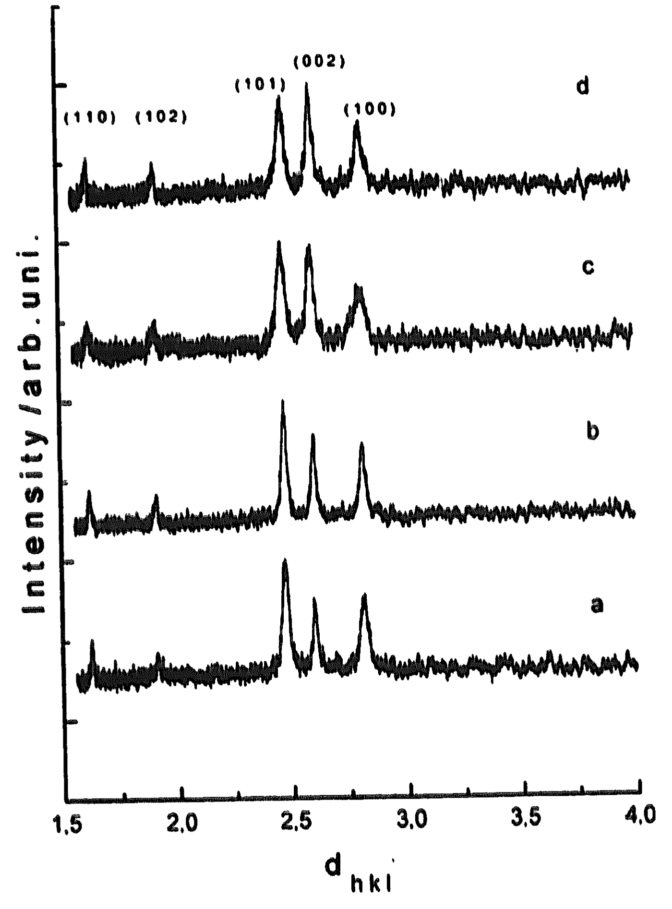

Fig. 4. X-ray diffractogram of zinc oxide samples corresponding to SEM figures: (a) zinc oxide from inicially precipitated zinc hydroxide carbonate; (b) zinc oxide from zinc hydroxide carbonate precipitated after 75 min; (c) zinc oxide from zinc hydroxide carbonate precipitated after 180 min; (d) zinc oxide from zinc hydroxide carbonate precipitated after 440 min.

Acknowledgements

Financial support by CNPq and FAPESP is gratefully acknowledged. F.A.S thanks for CNPq scholarship.

References

[1] A. Hausmann, B. Utsch, Z. Phys. B 21 (1975) 217.
[2] I.R. Collins, E.S. Taylor, J. Mater. Chem. 2 (1992) 1277.
[3] E. Matijevic, Annu. Rev. Mater. Sci. 15 (1985) 483.
[4] M.A. Castellano, E. Matijevic, Chemistry of Materials 1 (1989) 78.
[5] C.G. Zampronio, M.R. Davolos, E.B. Stucchi and M. Jaffelicci Jr., Mater. Res. Soc. 372 (1995).
[6] A. Chittofrati, E. Matijevic, Colloid. Surf. 48 (1990) 65.
[7] F.A. Sigoli, M.R. Davolos, E.B. Stuchi, and M. Jaffelicci Jr. (to be published elsewhere)
[8] S. Ghose, Acta Cryst. 17 (1964) 1051.
[9] J.C. Serna, M. Ocanâ, E.J. Iglesias, J. Mater. Sci. Lett. 7 (1988) 970.
[10] M. A Verges, A. Mifisud, C.J. Serna, J. Chem. Soc. Faraday Trans 86 (1990) 959.
[11] S.I. Hayash, N. Nobuyuki, K. Hitoshi, J. Phys. Society Japan 46 (1979) 177.