Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Thermochimica Acta 410 (2004) 93–100
thermochimica acta
www.elsevier.com/locate/tca

Thermal decomposition of zinc carbonate hydroxide

N. Kanari[a,*], D. Mishra[b], I. Gaballah[c], B. Dupré[d,e],
Mineral Processing and Environmental Engineering Team

[a] Laboratoire Environnement et Minéralurgie, Institut National Polytechnique de Lorraine, rue du Doyen M. Roubault,
BP 40, 54501 Vandœuvre Cedex, France
[b] Centre National de la Recherche Scientifique, 3 rue Michel-Ange, 75794 Paris Cedex, France
[c] École Nationale Supérieure de Géologie, rue du Doyen M. Roubault, BP 40, 54501 Vandœuvre Cedex, France
[d] Institut National Polytechnique de Lorraine, 2 rue de la Forêt de Haye, 54501 Vandœuvre Cedex, France
[e] Laboratoire de Chimie du Solide Minérale, Associated to CNRS UMR 7555, Université Henri Poincaré, Bvd des Aiguillettes,
BP 239, 54506 Vandœuvre, France

Received 4 April 2003; received in revised form 14 July 2003; accepted 15 July 2003

Abstract

This study is devoted to the thermal decomposition of two zinc carbonate hydroxide samples up to 400 °C. Thermogravimetric analysis (TGA), boat experiments and differential scanning calorimetry (DSC) measurements were used to follow the decomposition reactions. The initial samples and the solid decomposition products were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and laser particle size analyzer. Results showed that zinc carbonate hydroxide decomposition started at about 150 °C and the rate of decomposition became significant at temperatures higher than 200 °C. The apparent activation energies (E_a) in the temperature range 150–240 °C for these two samples were 132 and 153 kJ/mol. The XRD analyses of the intermediately decomposed samples and the DSC results up to 400 °C suggested a single-step decomposition of zinc carbonate hydroxide to zinc oxide with not much change in their overall morphologies.

Keywords: Zinc carbonate hydroxide; Thermal decomposition; Zinc oxide

1. Introduction

Preparation of different grades of zinc oxide has been the subject of many recent researches [1–3]. This is due to the diversified applications of ZnO which include manufacture of varistors, used as protection elements in electric and electronic appliances, as a polymer dispersant and heat absorbent in tyre industry, in cosmetics as UV light absorber and in paints and pigment industry as a color hue [4–6]. This compound is commercially produced by zinc vaporization and its subsequent oxidation (French and American processes), but majority of lab scale R&D activities are focused on precursor calcination methods. Zinc oxides from the decomposition of hydroxy-carbonates are energetically favorable due to their lower decomposition temperature in comparison to other zinc oxide precursors (such as hydroxides, carbonates, acetates, oxalates, etc.). Further, it is well known that the composition and the properties of zinc carbonate hydroxides are largely dependent on the precipitation conditions, variation of which led to different grades of ZnO [7,8].

Thermal decomposition is an essential step for preparation of ZnO from the precipitated precursors. The mechanism and kinetics of thermal decomposition of zinc carbonates (anhydrous, hydrated and hydroxy or basic carbonates) were reported by several authors [9–14]. Recently, thermal decomposition kinetics of anhydrous $ZnCO_3$ was studied by Gotor et al. [9], in the temperature range of 330–452 °C. They suggested two different ‘nucleation and growth’ mechanisms at different temperature ranges by comparing the results of isothermal thermogravimetric analysis (TGA) and constant rate thermal analysis (CRTA). The estimated apparent activation energy (E_a) was found to be 224 and 140 kJ/mol in the temperature ranges of

---

* Corresponding author. Tel.: +33-383-596-343;
fax: +33-383-569-585.
E-mail address: ndue.kanari@ensg.inpl-nancy-fr (N. Kanari).

doi:10.1016/S0040-6031(03)00396-4

347–402 °C and 402–452 °C, respectively. Heide and Knorr [10] reported a value of E_a equal to 113 kJ/mol for the decomposition of smithsonite ($ZnCO_3$) in the temperature range of 269–434 °C. Galvez and Arana [11] had studied the kinetics of non-isothermal decomposition of $ZnCO_3$ by constant heating rate TGA. They reported a value of $E_a =$ 88.6 kJ/mol within the temperature range of 175–462 °C. Similarly, one of the earlier studies on the thermal decomposition of hydrated zinc carbonate ($ZnCO_3 \cdot 2ZnO \cdot 2H_2O$) was performed by Dollimore et al. [12]. They suggested that the decomposition proceeds through two thermally overlapping stages with a constant reaction interface area. On the basis of isothermal TG between 200 and 260 °C, they reported an activation energy 94 ± 9 kJ/mol. The non-isothermal decomposition of a PROLABO zinc carbonate sample was reported by Gadalla [13] by using TGA and DTA under different heating rates. He obtained an average activation energy of 97 kJ/mol. Recently, only one report by Chen et al. [14] on the decomposition kinetics of precipitated $Zn_4CO_3(OH)_6 \cdot H_2O$ is available. Based on the DTA results under different heating rates (4–20 °C/min), they suggested a single-step decomposition process with an activation energy of 113 kJ/mol. The large discrepancy in the value of the activation energies reported by the above authors could be attributed to different sample origins, methods employed for kinetic studies and the poor characterization of the studied samples in most of the cases.

This paper is focused on the thermal decomposition behavior of two well-characterized zinc carbonate hydroxide samples. This work was carried out in the frame of an integrated research program for clean and cost-effective treatment of electric arc furnace dust (EAFD). The objective of this research is to produce commercial grade ZnO from EAFD. Zinc carbonate hydroxide was precipitated by Na_2CO_3 under ambient conditions from the purified dust leach liquor and subsequently thermally treated. The thermal decomposition behavior of this zinc carbonate hydroxide sample was compared with a chemically pure reference PROLABO sample.

2. Materials and experimental procedure

Two zinc carbonate hydroxide samples were used in this study. One chemical grade supplied by PROLABO and designated as reference sample (RFS). The other one was obtained by purification/precipitation of $ZnCl_2$ solution from leaching of electric arc furnace dust. This sample is designated as the industrial sample (INS). The characterization of these samples were done by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray unit (EDS), X-ray diffraction (XRD), Fourier transform infrared (FTIR) in the range of 700–4000 cm^{-1} and chemical analyses.

Thermogravimetric decomposition tests were performed using 60 mg of sample and a SETARAM microbalance having a sensitivity of 10 μg. All the experiments were carried out with constant flow of inert gases (N_2, Ar, dried by P_2O_5 columns) inside the reactor. Experimental tests were carried out under non-isothermal and isothermal conditions. The maximum temperature of the isothermal treatment was chosen so that the weight loss during non-isothermal period did not exceed 7% that is about 28% of the decomposition reaction.

Boat experiments in isothermal conditions were performed using about 2 g of samples. The final decomposed products obtained at several temperatures were subjected to SEM and XRD analyses as well as particle size measurements.

3. Results and discussion

3.1. Characterizations of zinc carbonate hydroxides

The XRD patterns of the two zinc carbonate hydroxide samples are shown in Fig. 1. In both the samples, all the major peak positions correspond to either $Zn_5(CO_3)_2(OH)_6$ (hydrozincite) or $Zn_4(CO_3)(OH)_6 \cdot H_2O$ phase [15]. From this figure, it seems that the sample obtained from EAFD (INS) is less crystalline than the PROLABO (RFS) sample. Laser particle size analysis suggest two size distributions for PROLABO sample with a d_{50} of 12.7 μm, while the industrial sample have a uniform size distribution with a d_{50} of 25.5 μm. Chemical and SEM-EDS (Fig. 2) analysis of INS showed the presence of Na, Ca and Cl as the major impurities. The total impurity percentage of INS is less than 5% with Cl as the major one (2%). Chemical analysis of this sample showed a Zn content of about 50% in contrast to 59% in hydrozincite. The hydrozincite phase was further confirmed from the FTIR spectra (Fig. 3) of the PROLABO sample. The strong and broad band centered at about 3317 cm^{-1} is the characteristic –OH stretching vibrations in hydrozincite [16]. These type of bands correspond to –OH groups co-ordinated to the metal ions indicating the absence of free/loosely bound water molecules. The other peaks in this spectrum can be assigned as: at 1517 and 1390 cm^{-1} (ν_3 mode of carbonate), at 1047, 954 and 890 (sh) cm^{-1} (–OH liberation modes), at 835 cm^{-1} (ν_2 mode of carbonate), at 737 (sh) and 710 cm^{-1} (ν_4 mode of carbonate) and the satellite peaks between 1750 and 2950 cm^{-1} region are due to various combination modes in hydrozincite [16].

3.2. Non-isothermal TG treatment

A series of non-isothermal tests of the reference sample and the sample obtained from EAFD processing (INS), was carried out from room temperature up to 400 °C with an heating rate of 5 °C/min and steady flow of argon as carrier gas. Results are shown in Fig. 4 as evolution of percentage weight loss (% WL) versus temperature. This figure

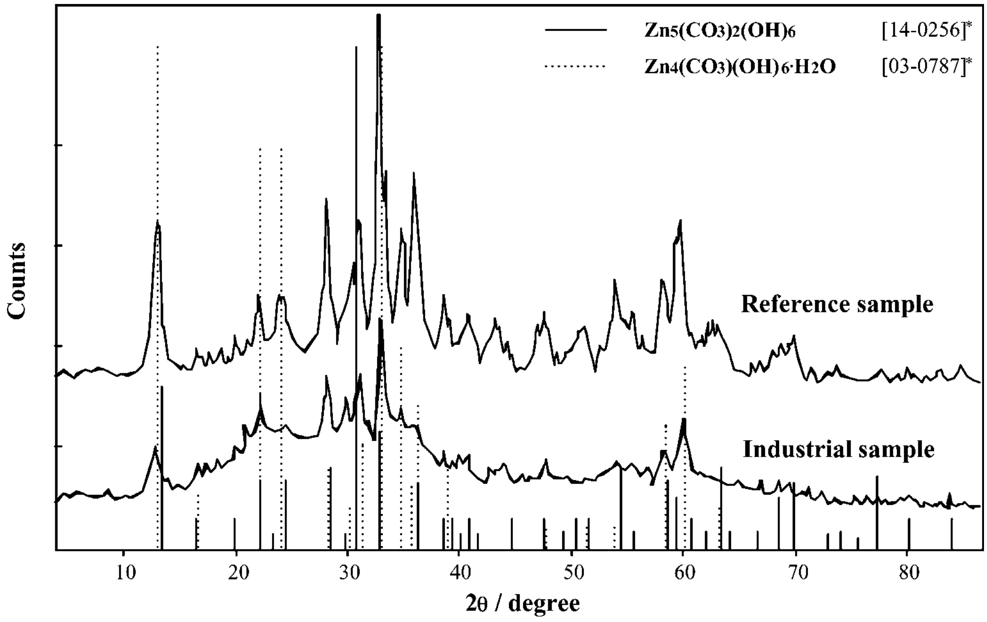

Fig. 1. XRD results of zinc carbonate hydroxide samples.

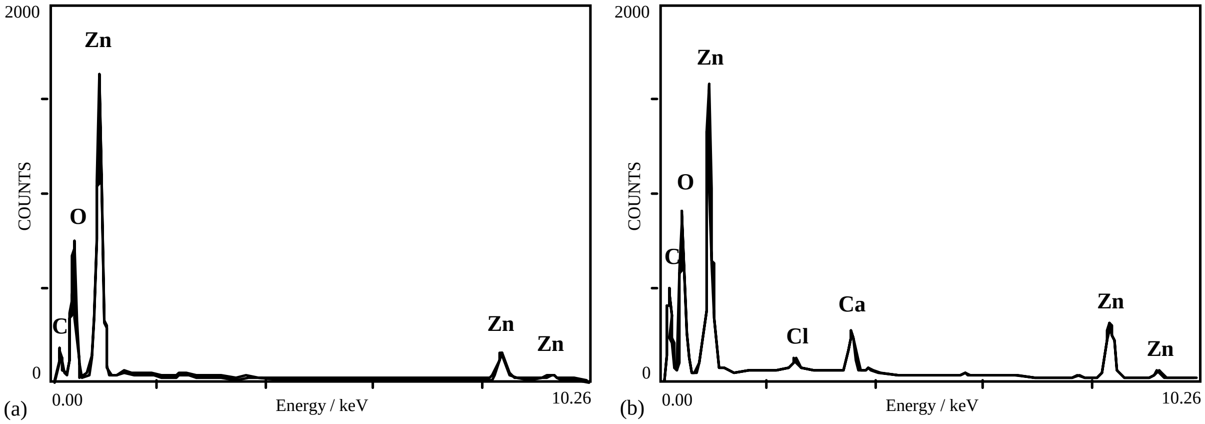

Fig. 2. SEM-EDS spectra of the zinc carbonate hydroxide samples: (a) reference sample; (b) industrial sample.

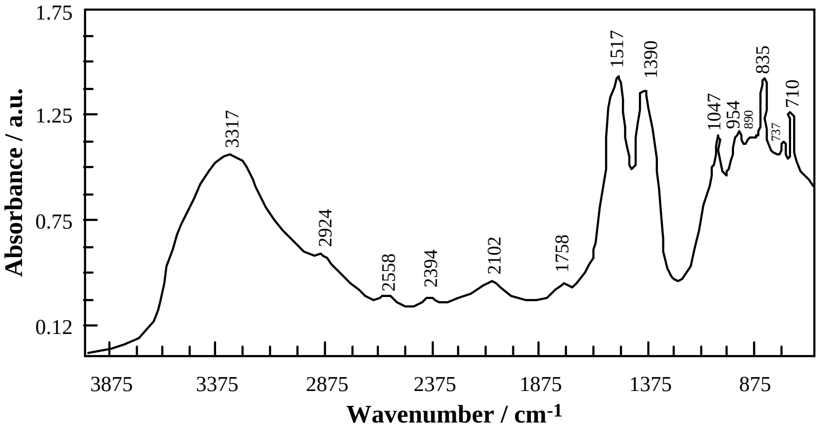

Fig. 3. FTIR of the reference sample.

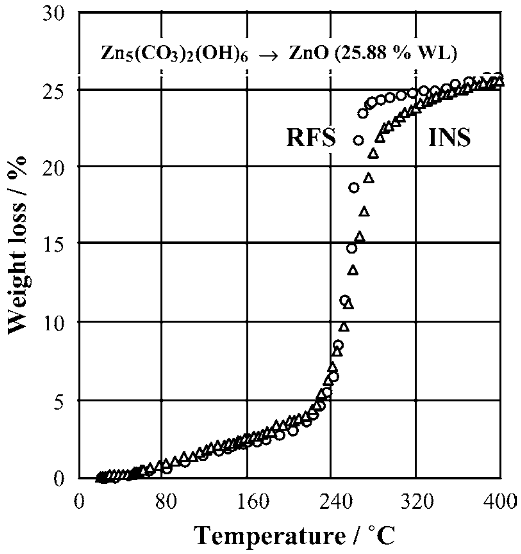

Fig. 4. TG non-isothermal treatment of samples.

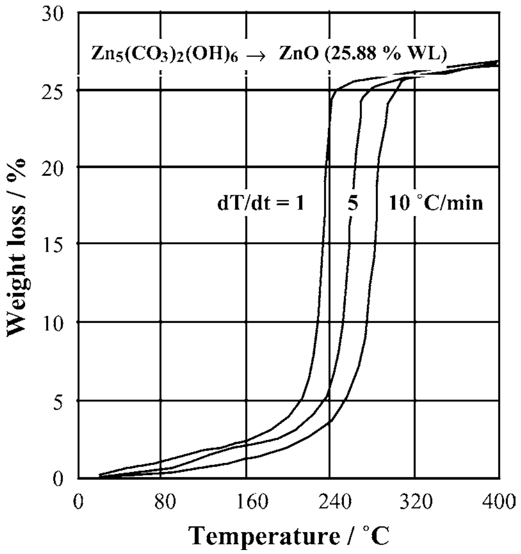

Fig. 5. Treatment of RFS at different heating rates.

also contains the calculated % WL (25.88%) for the decomposition of $Zn_5(CO_3)_2(OH)_6$ to ZnO. The shape of these curves for both samples is similar. However, the INS seems to be more affected by temperature than RFS. As shown by Fig. 4, the weight loss increase slightly with temperature up to 200 °C, since then, the decomposition rate becomes fast and almost full decomposition is reached at about 350 °C.

The decomposition of the reference sample in nitrogen was studied using different heating rates from 1 to 10 °C/min and the results obtained are shown in Fig. 5. With increasing heating rate, the decomposition temperature increased appreciably. This indicates the slow kinetics nature of the thermal decomposition reaction of zinc hydroxy-carbonate into zinc oxide.

3.3. Isothermal TGA

Isothermal decomposition studies on both the samples were performed in the temperature range 150–240 °C under flow of nitrogen. Fig. 6a and b shows the data obtained during the treatment of RFS in the above-mentioned conditions. They represent the evolution of % WL versus time. The weight loss observed at time “zero” correspond to the decomposition of sample from room temperature (20 °C) up to the fixed temperature of the isothermal treatment. As shown by Fig. 6a, more than 160 h are required to achieve 17% WL of the sample at 150 °C. While, about 1 h is sufficient for the full decomposition at 240 °C (Fig. 6b). The sigmoid shape of the obtained curves indicate a most probable nucleation and growth processes. However, suggestion of a mechanism

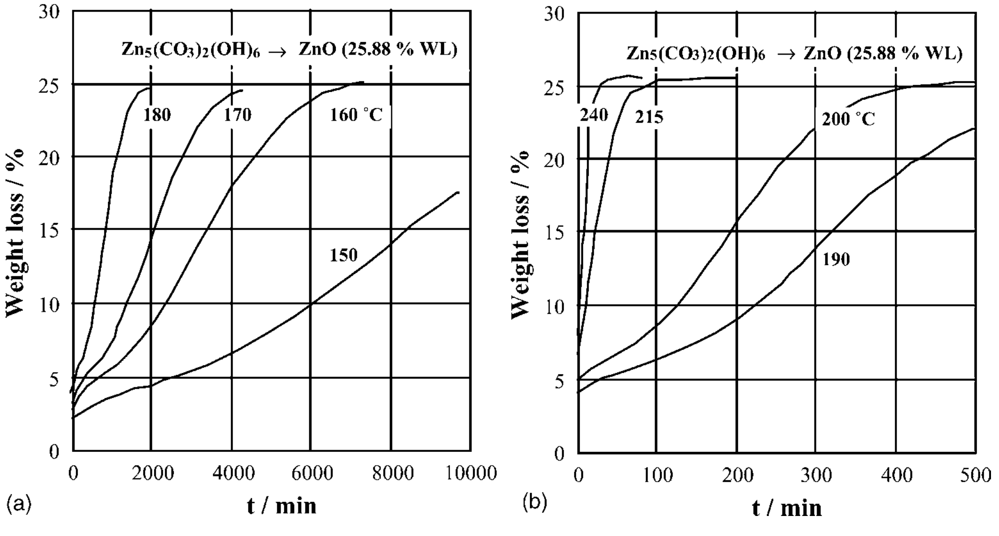

Fig. 6. Isothermal treatment of RFS between 150 and 240 °C.

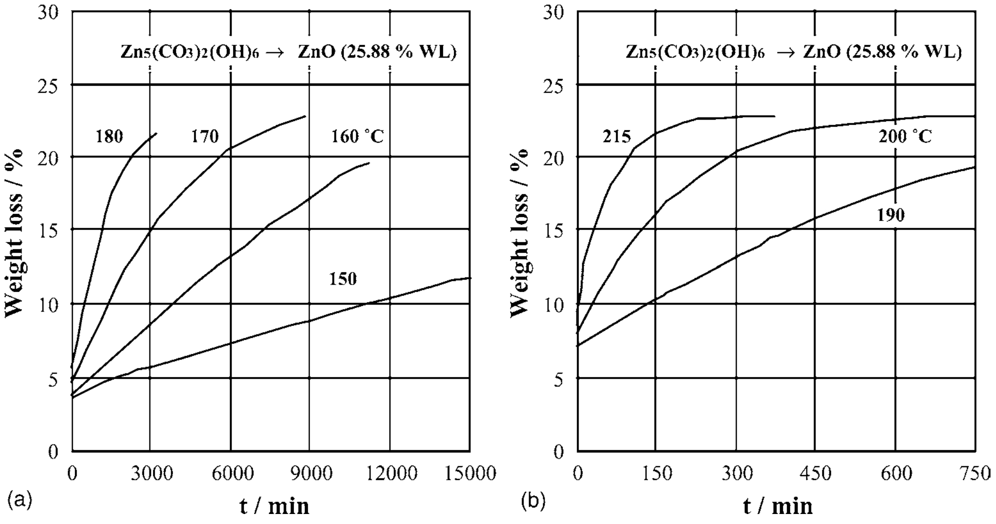

Fig. 7. Isothermal treatment of INS between 150 and 215 °C.

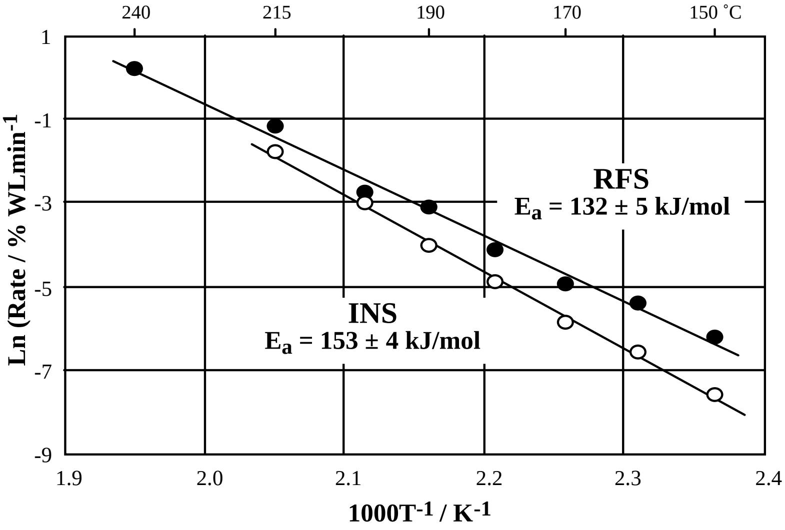

Fig. 8. Arrhenius diagrams of decomposition of both samples.

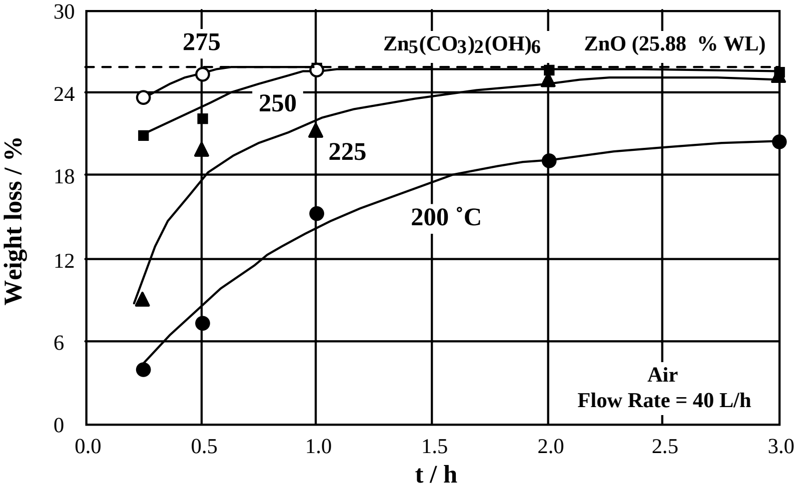

Fig. 9. Treatment of RFS between 200 and 275 °C at different times.

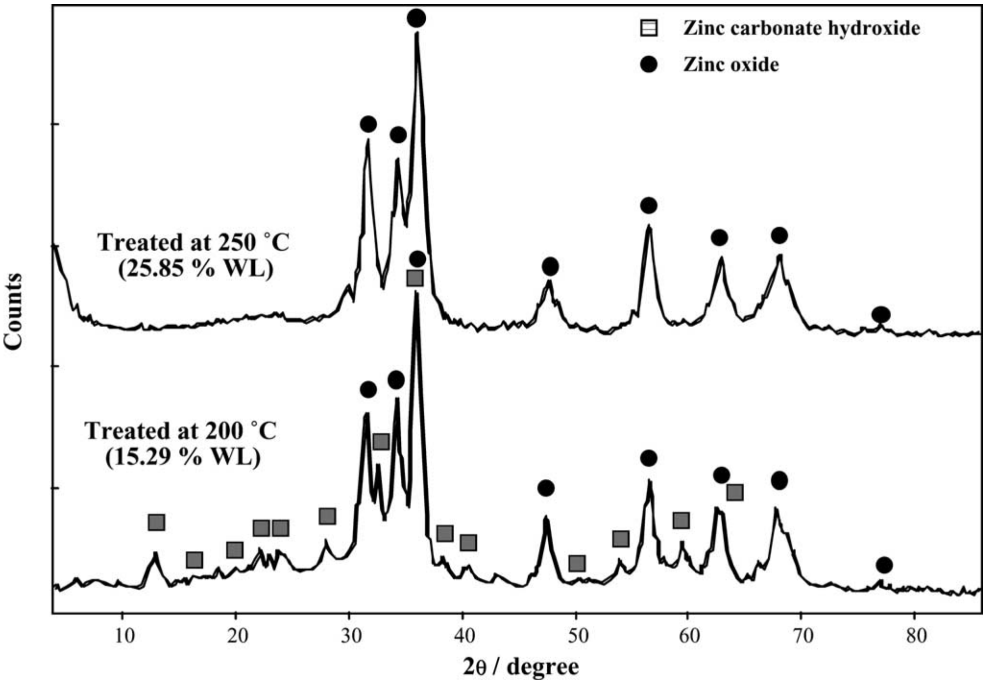

Fig. 10. XRD result of RFS treated at 200 and 250 °C.

will be of over simplification with present experimental data. Similar curves were also obtained in case of the industrial sample (Fig. 7a and b). By comparing Figs. 6 and 7, it is observed that INS takes longer time in comparison to RFS to achieve same weight loss at same temperature, indicating a slower kinetics of decomposition of the former. The slower decomposition rate of INS may be either due to their larger particle size or due to the presence of impurities notably Cl. The Arrhenius diagram obtained with the data of Figs. 6 and 7 are presented in Fig. 8. The apparent activation energy calculated from the slopes of these straight lines are 132 ± 5 and 153 ± 4 kJ/mol for RFS and INS, respectively.

3.4. Isothermal boat experiments and characterization of decomposed products

Isothermal boat experiments (with about 2 g of samples) under air flow were carried on RFS from 200 to 275 °C. The decomposed products obtained at several temperatures were subjected for XRD, SEM, differential scanning calorimetry (DSC), and particle size analyses. The evolution of % WL with time at four different temperatures is presented in Fig. 9. The shape of the curves is almost similar to that obtained in case of vertical TGA. It is observed that full decomposition is achieved within 30 min at 275 °C, whereas about 70% decomposition is achieved at 200 °C for 3 h. This suggests the highly dependence of this decomposition reaction on temperature.

The X-ray diffraction patterns of two typical samples, one fully decomposed obtained at 250 °C (WL = 25.85%), and another intermediately decomposed sample obtained at 200 °C (WL = 15.29%) is shown in Fig. 10. The XRD pattern of the fully decomposed sample shows the peaks for only ZnO while for the sample obtained at 200 °C shows the presence of both ZnO and hydrozincite phases [15]. The presence of anhydrous $ZnCO_3$ was not detected in the latter sample. The DSC plot of RFS (Fig. 11) up to 400 °C

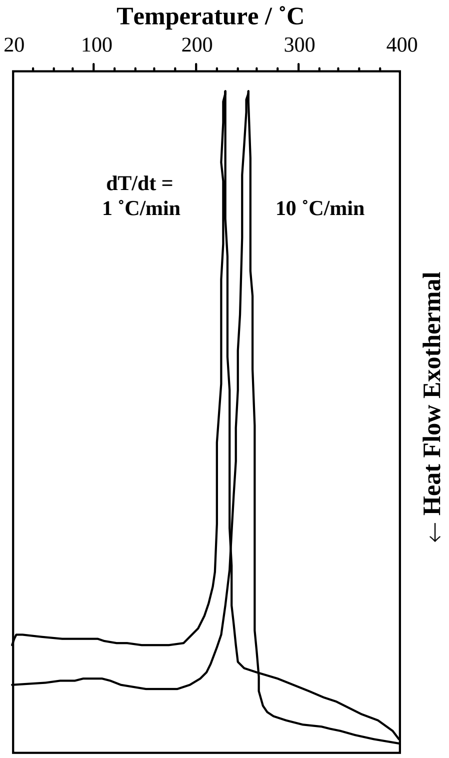

Fig. 11. DSC results of the reference sample.

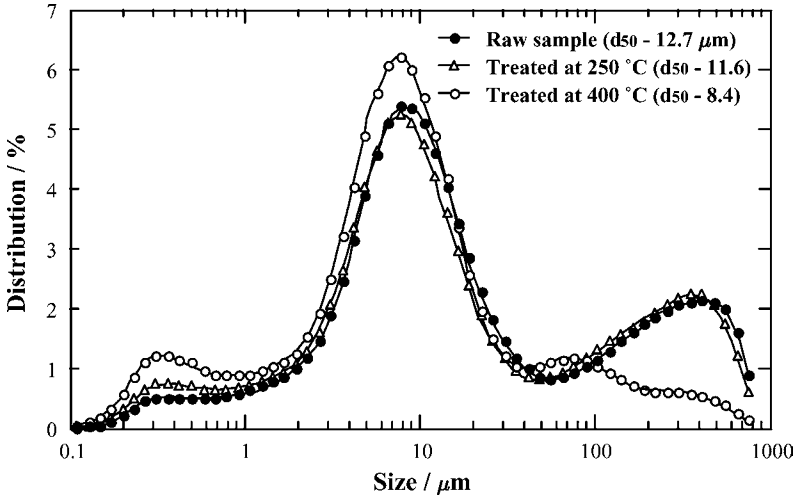

Fig. 12. Evolution of the particle sizes during the treatment of RFS at 250 and 400 °C.

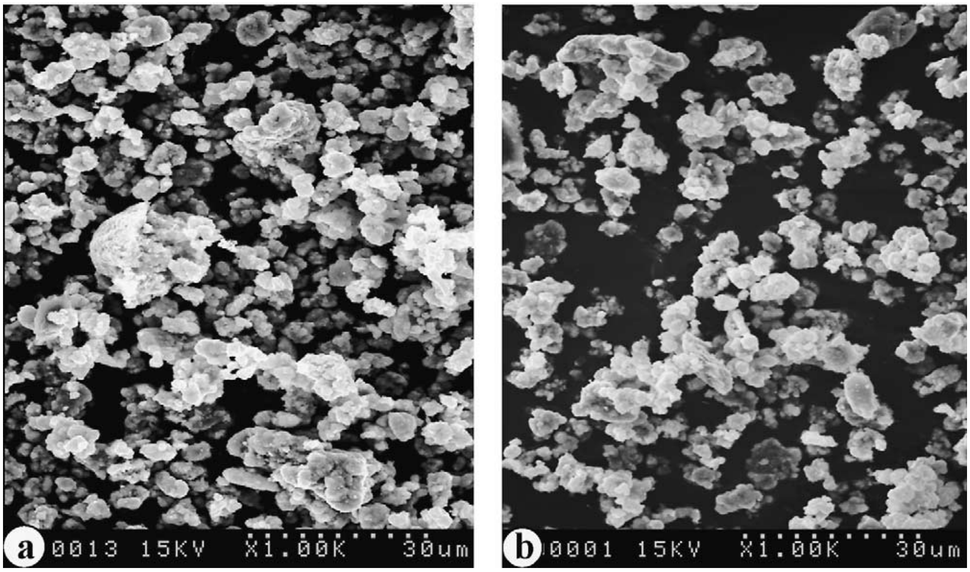

Fig. 13. SEM micrograph of the reference sample: (a) non-treated; (b) decomposed at 250 °C.

with a heating rate of 1 and 10 °C/min show only one sharp endothermic peak at about 230 and 248 °C, respectively. Combining both the XRD and DSC observations, it can be concluded that the decomposition most probably occurs in a single-step with simultaneous de-hydroxylation and de-carboxylation.

Laser particle size measurements were done on RFS and two samples obtained after decomposition of RFS at 250 and 400 °C. These samples were dispersed ultrasonically in ethanol medium prior to their size measurements. The curves are shown in Fig. 12. The size distribution of the initial and the 250 °C treated samples are almost same, having two distinct distributions whereas, the 400 °C treated sample shows more uniform distribution. The d_{50} of this sample is also decreased a little in comparison to the initial and 250 °C treated sample.

SEM micrographs of the reference sample and the sample obtained after its decomposition at 250 °C are compared in Fig. 13. No noticeable change in their morphology is observed. In both the cases, the particles are in a highly agglomerated state making it difficult to measure their sizes. These results are in agreement with that of Castellano and Matijevic [17] on calcination of hydrozincite to zinc oxide. This result further confirmed the iso-morphological thermal transformation of zinc carbonate hydroxides to zinc oxides.

4. Conclusions

From the above study, the following conclusions can be drawn on the thermal decomposition behavior of zinc carbonate hydroxide (hydrozincite):

1. Although the thermal decomposition was started at lower temperature (150 °C) but the reaction rate was appreciable only above 200 °C.
2. Presence of minor amounts of impurities in the sample ‘INS’ resulted a slower decomposition rate in comparison to the chemically pure ‘RFS’ sample.
3. The apparent activation energies obtained from the isothermal TG tests within the temperature range of 150–240 °C are 132 ± 5 kJ/mol for the reference sample and 153 ± 4 kJ/mol for the industrial sample.
4. XRD results of samples obtained in boat experiments at different extent of decomposition as well as the DSC analysis of RFS sample up to 400 °C suggested a most probable single-step transformation of zinc carbonate hydroxides to ZnO.
5. The morphological aspects during the decomposition was more or less unchanged. A minor decrease in the particle size was observed at relatively higher decomposition temperature (400 °C).

Acknowledgements

This work was performed in the frame of EU contract no. G1RD-CT99-00166 thanks to the financial support of the European Union (DG-XII).

References

[1] S.-Y. Chu, T.-M. Yan, S.-L. Chen, J. Mater. Sci. Lett. 19 (2000) 349–352.
[2] J.E. Rodriguez, A.C. Caballero, M. Ocana, P. Duran, J.F. Fernandez, Ceram. Process. Sci. 83 (1999) 19.
[3] P. Sulcova, M. Trojan, J. Therm. Anal. Cal. 60 (2000) 209.
[4] H. Rensmo, K. Keis, H. Lindstrom, S. Sodergren, A. Solbrand, A. Hagfeldt, S.E. Lindquist, L.N. Wang, M. Muhammed, J. Phys. Chem. B 101 (1997) 2598.
[5] W. Preis, E. Konigsberger, H. Gamsjager, J. Sol. Chem. 29 (2000) 605.
[6] Z. Ruirong, C. Jianxun, J. Hanying, J. Cent. S. Univ. Technol. (China) 4 (1997) 13.
[7] L. Wang, M. Muhammed, J. Mater. Chem. 9 (1999) 2871.
[8] S. Music, D. Dragcevic, M. Maljkovic, S. Popovic, J. Mater. Chem. Phys. 77 (2003) 521.
[9] F.J. Gotor, M. Macias, A. Ortega, J.M. Criado, Int. J. Chem. Kinet. 30 (1998) 647.
[10] K. Heide, J.G. Knorr, Chem. Erde Bd 35 (1976) 256.
[11] J. Galvez, R. Arana, Univ. Murcia. Cienc. 38 (1979) 153.
[12] D. Dollimore, J.A. France, B.W. Krupay, R. Witehead, Thermochim. Acta 36 (1980) 343.
[13] A.M. Gadalla, Int. J. Chem. Kinet. 16 (1984) 1471.
[14] J. Chen, R. Zhao, H. Jiang, Y. Li, G. Bao, Trans. Nonferrous Met. Soc. (China) 8 (1998) 149.
[15] Joint Committee on Powder Diffraction Standards (JCPDS), International Center for Diffraction Data (Files 14-0256 and 03-0787), Swathmore, PA.
[16] D. Stoilova, V. Koleva, V. Vassileva, Spectrochim. Acta Part A 58 (2002) 2051.
[17] M. Castellano, E. Matijevic, Chem. Mater. 1 (1989) 78.