STUDIA UBB CHEMIA, LVII, 4, 2012 (p. 167-173)
(RECOMMENDED CITATION)

THERMAL DECOMPOSITION AND KINETICS OF THE PRECURSORS FOR OBTAINING ZnO AND TEAH MODIFIED ZnO NANOPOWDERS

MIHAELA POPA[a,*], AMALIA MESAROS[a], RALUCA A. MEREU[a], IOANA PERHAITA[b], LELIA CIONTEA[a], TRAIAN PETRISOR[a]

ABSTRACT. The thermal decomposition of zinc oxalate, obtained from the precipitation of zinc acetate with oxalic acid, with and without tetraethylammonium hydroxide (TEAH) addition, was investigated. The thermogravimetric analysis (TG) indicated a total mass loss of about 57% in two decomposition steps. FTIR-TG-DTA and MS-TG-DTA indicated mainly CO_2 elimination. The activation energies (E_a) were estimated by Kissinger equation, considering heating rates of 5, 10, 15, 20°C/min. The determined energies were: E_{a1} = 69 kJ/mol, for the dehydration process and of about E_{a2} = 106 kJ/mol, for organic compounds loss.

Keywords: *ZnO, nanopowders, thermal decomposition*

INTRODUCTION

Zinc oxide, ZnO, has attracted much interest because of its possible application in distinct technological fields such as magnetic semiconductors, spintronics, catalysts, sensors, field emission devices, solar cells, etc. [1-5]. The preparation conditions of ZnO nanopowders are important since the purity, the particles size and the presence of organic species on the surface of the particles are strongly influenced by this. The precipitation technique provides a facile way for low cost and large-scale production of ZnO in different sizes and shapes, in a reproducible way [6-11]. The thermal process is important for the reason that physical and chemical properties of a material varies as function of temperature [12-14]. The conventional thermal analysis technique provides information limited to physical properties and indirect information about the identity of the composition and evolved phases [15]. The thermo - FTIR technique provides much more clear information about

[a] *Technical University of Cluj-Napoca, C4S, 28 Memorandumului Street, 400114, Cluj-Napoca, Romania, Phone +40-264-401475. * mip3pim@yahoo.com*
[b] *"Raluca Ripan" Institute for Research in Chemistry, Babes-Bolyai University of Cluj-Napoca, 30 Fantanele Street, Tel:+40-264-580165 Fax: +40-264-420441*

the decomposition pathway, due to the detection of the resulted gases. Such a combination is always an advantage when substances are identified by methods involving a certain loss of mass [16].

In this paper, the thermal decomposition of ZO precursors obtained by precipitation method was performed in order to have an in depth understanding and control of the synthesis process. Furthermore, a small amount of tetraethylammonium hydroxide (TEAH) was added during the precipitation process in order to control the particles shape. Thus, the thermal decomposition in N_2 and static air atmosphere and a kinetic study of TEAH modified ZnO precursor were performed in order to have information about its behavior during the thermal process.

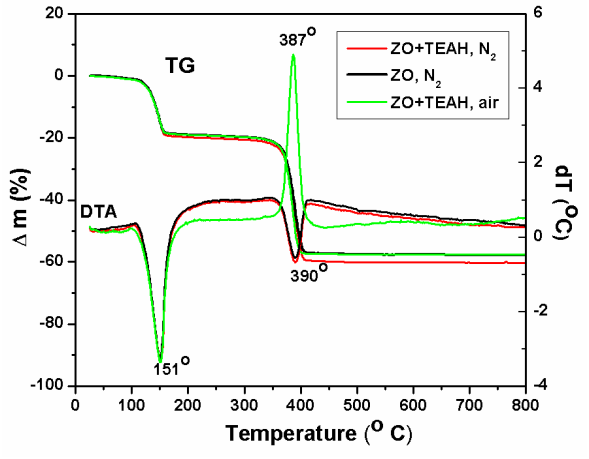
RESULTS AND DISCUSSION

The TG analysis of ZO and ZO+TEAH precursors, performed at a heating rate of 10°C/min, in N_2 and static air atmosphere, indicates a total mass loss of about 57 %, with a ~19 % loss in the first step and ~ 38% in the second step (Fig. 1 a). An insignificantly higher mass loss (57+2.9%) was observed in the case of the ZO+TEAH precursor. The molar masses of ZnO precursors, estimated from the TG curves, were ~ 191 g/mol for the ZO precursor and ~ 204 g/mol for ZO+TEAH precursor. Both values are close to the molar mass of the zinc oxalate hydrated with two molecules of water (189.4 g/mol). This fact suggests that TEAH is present in a very small amount, dispersed in the whole mass of the precursor and that during the synthesis process, zinc acetate has reacted with oxalic acid and deionised water, leading to zinc oxalate and acetic acid elimination, according to the chemical equation:

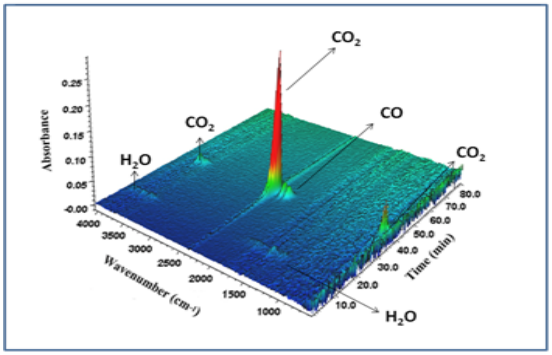
$$Zn(CH_3COO)_{2\,aq} + HOOC\text{-}COOH_{\,aq} + 2\,H_2O \rightarrow Zn(OOC\text{-}COO)\cdot 2H_2O + 2CH_3COOH$$

Comparing the DTA curves in N_2 atmosphere of ZO and ZO+TEAH (Fig. 1 a), unnoticeable difference between the two curves can be remarked. Two endothermic peaks (one at 151°C and one at 387°C) are present. When static air was used, an endothermic peak at 151°C and an exothermic peak at 387°C can be observed. The exothermic behavior is related with the oxygen presence from the air. The FTIR coupled TG-DTA experiment, performed on the ZO+TEAH precursor in N_2 atmosphere, indicates that the 151°C DTA peak corresponds to the water loss (its presence is confirmed in the gas loss 3D FTIR spectra (fig.1 b) at ~ 1600 cm^{-1} and ~ 3600 cm^{-1} (12.7 min). The DTA peak identified at 390°C corresponds to CO_2 (~2400 cm^{-1}) and to CO (~2100-2200 cm^{-1}) simultaneously loss, according to the 3D FTIR spectra (36.5 min). The chemical equation of the gas loss, in inert atmosphere, can be written as follows:

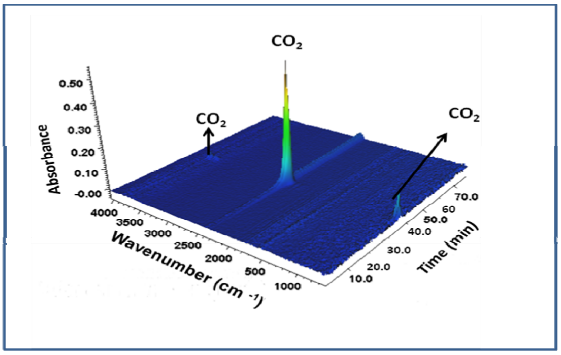
$$Zn(OOC\text{-}COO)\,2H_2O \rightarrow ZnO + CO_2\uparrow + CO\uparrow + 2H_2O$$



a)



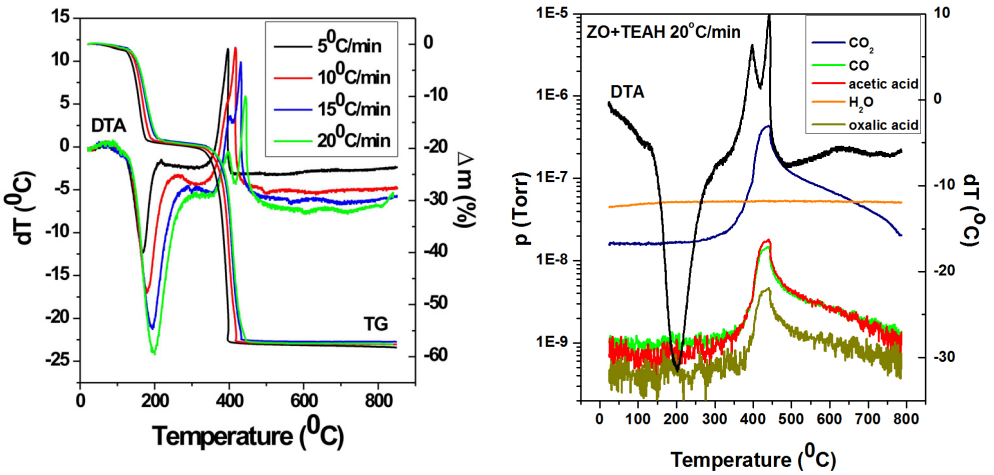
b)



c)

Figure 1. TG-DTA curves in N_2 and static air (a) and FTIR coupled TG - DTA curves of the ZO+TEAH precursor, using a heating rate of 10°C/min, in N_2 atmosphere (b) and static air (c)

The TG-DTA curves of the ZO+TEAH precursor, using different heating rates (5, 10, 15, 20°C/min) - performed in static air, show similar thermograms, with two well defined decomposition steps. A total mass loss in two steps of about 57% was also observed. As can be seen in the DTA curves (Fig.2 a), the mass loss of the ZO+TEAH precursor strongly depends on the heating rate. Using a low heating rate (5°C/min), two peaks can be observed: one endothermic peak at 165°C, corresponding to water elimination and one exothermic peak at 397°C. In disaccord with DTA analysis, the FTIR coupled TG-DTA performed on ZO+TEAH precursor in static air atmosphere and using a heating rate of 10°C/min, indicates only CO_2 (~ 2400 cm^{-1} at 40 min.) and no water elimination (Fig.1 c). As remarked in previous papers [17], by increasing the heating rate, the DTA curves corresponding to water elimination as well as the organic compounds elimination are shifted towards higher temperatures. Using higher heating rates (10 - 15°C/min) a shoulder at about 392°C was observed. Furthermore, a splitting of this peak in two peaks (one at 396°C and one at 445°C) can be noticed by increasing the heating rate at 20°C/min. MS-TG-DTA analysis was performed for clarifying the gases elimination using a heating rate of 20°C/min (Fig. 2 b). As can be seen, the CO_2 elimination in high proportion is accompanied by some CO and acetic acid gases elimination. Furthermore, some traces of oxalic acid were also identified. No water elimination was observed, sustaining FTIR-TG observation (Fig. 1 c) and no N_xO_y gases elimination was identified, probably due to the small amount of TEAH.



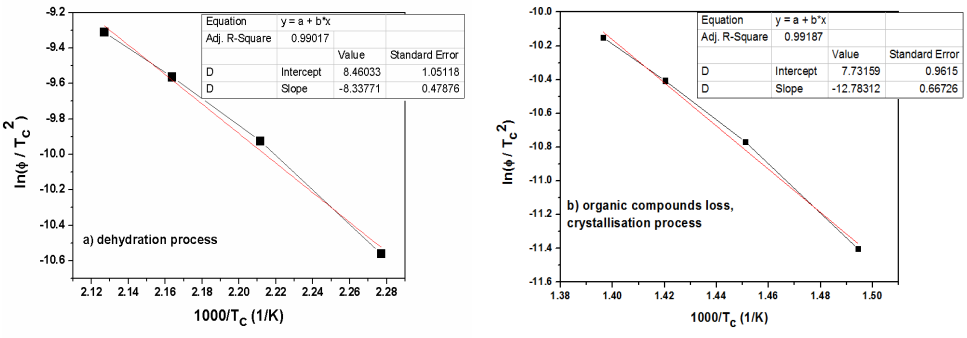
a) b)

Figure 2. TG-DTA curves, performed in static air, heated using different heating rates (5, 10, 15 and 20°C/min) (a) and TG-DTA-MS curves at 20°C/min (b) of the ZO+TEAH precursor

We have approximated the activation energy, using Kissinger equation:

$$(\ln (\phi / T_c^2) = (- E_a / RT_C) + \text{const.},$$

ϕ – heating rate (5, 10, 15, 20 °C/min), T_c – peak temperature, R – gas constant). The activation energy for the dehydration process was E_{a1} = 69 kJ/mol (Fig.3 a) and for the organic compounds loss (determined from the main DTA peaks - 397°C to 442°C) followed by crystallization process (Fig.3 b) was E_{a2} = 106 kJ/mol. The organic compound loss energy value is smaller than the reported value for the zinc oxalate decomposition in helium atmosphere, calculated using Avrami–Erofeev equation[8]. The authors reported an E_a = 181.4–186.5 kJ/mol, using heating rates of 2, 4, 7 and 10 K/min.



a) b)

Fig. 3. The activation energy (E_a) determined according to Kissinger equation a) for the dehydration process, b) for organic compound loss

CONCLUSIONS

The thermal decomposition of zinc oxalate, obtained from the precipitation of zinc acetate with oxalic acid, with and without TEAH addition was investigated. TG-DTA, FTIR-TG-DTA and MS-TG-DTA analyses were used in order to determine the thermal behavior of the samples. The thermal decomposition occurred in two steps, having a total mass loss of about 57%. Two peaks at 151°C and at 387°C were detected in the DTA curves, both in the N_2 and static air atmosphere. The peak at 151°C was assigned to water elimination while the peak at 387°C was assigned to the organic compounds loss followed by a crystallization process. However, FTIR-TG-DTA and MS-TG-DTA indicate only a small amount of water elimination, by using N_2 atmosphere and no water elimination, when static air atmosphere was used. Moreover, no N_xO_y gas elimination was remarked for the TEAH modified precursor. The

influences of different heating rates on the decomposition process and kinetics calculations, using Kissinger equation, were also performed. The activation energy was estimated at about E_{a1} = 69 kJ/mol, for the dehydration process and E_{a2} = 106 kJ/mol, for the organic compounds loss followed by crystallization process.

EXPERIMENTAL SECTION

Sample preparation

High purity chemicals were used in precipitation process. Zinc acetate dihydrate (ZnAc) $Zn(CH_3COO)_2 \cdot 2H_2O$ (Merck, 99,5%), oxalic acid $C_2H_2O_4 \cdot 2H_2O$ (Lach:ner) and deionized water were used. 0.58 M of zinc acetate dihydrate solution and 1.15 M oxalic acid solution were prepared. The two solutions were mixed in stoichiometric ratio, resulting a white precipitate maintained under stirring for 24 h (sample notation – ZO). The mixture pH was 2.8. For one sample, tetraethylammonium hydroxide (Merck, 20% aqueous solution) in 0.0026 volume ratio (TEAH/ZnAc) was added (sample notation ZO+TEAH). The mixture pH increased to 3. The obtained white precipitates were filtered, washed with acetone and then dried at 100°C for 5 h.

Sample characterization

Fourier transform infrared spectroscopy (FTIR) coupled with a thermogravimetric analyser (TG-DTA) (Nicolet 6700 (FTIR) - 851e, 1600°C Mettler-Toledo (TG-DTA)) and thermal analysis coupled with a quadrupole mass spectrometer QMS 200 atmospheric sampling system (Residual Gas Analyzer RGA-Stanford Research System) were used to record the thermal decomposition and the gases loss in the temperature range from 25 to 800°C. The sample mass of about 14 mg was placed in a platinum crucible. Thermal analysis experiments were performed in N_2 and air flow and static state air, using heating rates of 5, 10, 15 and 20 °C/min.

ACKNOWLEDGMENTS

This work was supported by 4D-POSTDOC, contract no. POSDRU/ 89/1.5/S/52603, project co-funded by the European Social Fund through Sectoral Operational Programme Human Resources Development 2007-2013 (M. Popa) and by CNCSIS-UEFISCU project, n° PN II idei code 106/ 2010 (T. Petrisor)

REFERENCES

1 S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, *Progress in Materials Science,* **2005**, *50*, 293.

2 M. Popa, R.A. Mereu, M. Filip, M. Gabor, T. Petrisor Jr., L.Ciontea, T. Petrisor, *Materials Letters,* **2013**, *92*, 267.

3 L. Li, T. Zhai, Y. Bando, D. Golberg, *Nano Energy,* **2013**, *1*, 91.

4 A.B. Djurisic, A.M.C. Ng, X.Y. Chen, *Progress in Quantum Electronics,* **2010**, *34*, 191.

5 Y.Q. Fu, J.K. Luo, X.Y. Du, A.J. Flewitt, Y. Li, G.H. Markx, A.J. Walton, W.I. Milne, *Sensors and Actuators B: Chemical,* **2010**,*143*, 606.

6 K.G. Kanade, B.B. Kale, R.C. Aiyer, B.K. Das, *Materials Research Bulletin,* **2006**, *41*, 590.

7 A. Šaric, S. Music, M. Ivanda, *Journal of Molecular Structures,* **2011**, *993*, 219.

8 B. Małecka, E. Drozdz-Ciesla, A. Malecki, *Thermochimica Acta*, **2004**, *423*, 13.

9 S. Sepulveda-Guzmana, E. de la Rosa, A. Torres-Castroa, V. Gonzalez-Gonzaleza, M. Jose-Yacamane, *Materials Chemistry and Physics,* **2009**, *115*, 172.

10 R.Y. Hong, J.H. Li, L.L. Chen, D.Q. Liu, H.Z. Li, Y. Zheng, J. Ding, *Powder Technology,* **2009**, *189*, 426.

11 J. Zhou, Y. Wang, Y. Zhang, L. Yang, *Journal of Luminescence,* **2007**, *122*, 195.

12 C. C. Lin, Y.-Y. Li, *Materials Chemistry and Physics,* **2009**, *113*, 334.

13 J. Chen, W. Lei, J.L. Song, X.W. Sun, X.B. Zhang, W.Q. Deng, *Physica E,* **2009**, *41*, 822.

14 E. Darezereshki, M. Alizadeh, F. Bakhtiari, M. Schaffie, M. Ranjbar, *Applied Clay Science*, **2011**, *54*, 107.

15 A.V. Ghule, B. Lo, S.-H. Tzing, K. Ghule, H. Chang, Y.C. Ling. *Chemical Physics Letters,* **2003**, *381*, 262.

16 G.W. Ehrenstein, G.R., P. Trawiel, "Thermal Analysis", Hanser Publisher, Munich, **2004**.

17 T. Arii, A. Kishi, *Thermochimica Acta*, **2003**, *400*, 175.