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Thermoelectrical and thermal analyses of copper(II) acetate monohydrate ZnO–matrix composite powder obtained by freeze-drying

Jusmar Valentin Bellini [a,*], Edgardo Alfonso Gomez Pineda [b], Raquel de Almeida Rocha [a], Andre Luis de Lima Ponzoni [a], Andrea Paesano Jr. [a]

[a] *Department of Physics, State University of Maringá, CEP 87020-900 Maringá, PR, Brazil*
[b] *Department of Chemistry, State University of Maringá, CEP 87020-900 Maringá, PR, Brazil*

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Abstract

The thermal history of freeze-dried mixtures of composite powders containing ZnO–matrix and $(CH_3COO)_2Cu\cdot H_2O$ (copper(II) acetate monohydrate) was undertaken by thermal analysis (TA) coupled to thermoelectrical analysis (TEA). Experiments were carried out on compacted samples, under non-isothermal conditions, in air, up to 350 °C, by measuring the electrical resistance during heating, called thermoelectrical resistometry (TER), and by differential scanning calorimetry (DSC). Activation energy (E_a) for exothermal events related to the decomposition of $(CH_3COO)_2Cu$ (copper(II) acetate, $CuAc_2$), observed within the range 225–325 °C, was estimated according to ASTM E 698 method. Values of E_a equal to 154 and 155 kJ/mol were obtained by TER and DSC, respectively. TER showed that the thermal decomposition of $CuAc_2$ involves the liberation of electrons. Results also indicated that TER may be used as an alternative or complementary method for the study of the thermal decomposition mechanisms of transition metal(II) acetates.

Keywords: Copper(II) acetate monohydrate; Freeze-drying; Zinc oxide; Thermoelectrical analysis; DSC

1. Introduction

Transition metal(II) acetates, commercially available in the form of powders, are very useful reagents mainly used in industrial processes. Their hydrated general form is $(CH_3COO)_2M\cdot xH_2O$, where M is a transition metal cation with valence 2+, e.g., Mn, Cd, Hg, Pb, Mg, Ca, Ba, Co, Ni, Cu or Zn; CH_3COO is an acetate group and x is the number of crystallisation water molecules. Similar to nitrates, oxalates, sulphates, etc., the metal acetates are soluble in water. Despite the technological importance of these materials, systematic data on their solubility in water have only recently been published [1,2].

Since metal acetates are water-soluble salts, they may be freeze-dried individually or in multi-components. In the conventional powder processing by freeze-drying, or cryochemical process [3], the initial aqueous mixture containing high purity salts is rapidly frozen to avoid precipitation or segregation of the components, followed by ice sublimation under vacuum. Resulting powders obtained by freeze-drying are expected to be chemically more homogeneous, free from contamination by impurities and highly reactive. After thermal decomposition and solid-state reactions at high temperatures, the precursors give rise to more uniform mixtures on the atomic scale. Freeze-drying of acetates have been used to improve powder synthesis of a great variety of materials, including carbon nanotubes [4], La–Sr-manganates [5], Co-perovskites [6], Ca-phosphates [7], catalysts [8], proton conductors [9], superconductors [10–13] and ferrites [14,15]. Recently, Bellini et al. [16–18] showed that freeze-drying may also be used to synthesise mixtures of powders containing ZnO and $(CH_3COO)_2Cu\cdot H_2O$ (copper(II) acetate monohydrate, henceforth termed $CuAc_2\cdot H_2O$) which were employed for the fabrication of Cu-doped ZnO-based ceramics.

Thermoanalytical studies on the thermal decomposition course of transition metal acetates, carried out under various conditions, will contribute towards the understanding of related thermal events and the identification of either the gaseous/volatile

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[*] Corresponding author. Tel.: +55 44 32614330; fax: +55 44 32634623.
E-mail addresses: jvbellini@dfi.uem.br, jvbellini@irapida.com.br (J.V. Bellini).

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or the solid intermediate products or the final solid ones. Temperature range, in which thermal events occur, and the products depend on the kind of atmosphere, heating rate and powder morphology. Ehrensberger et al. [19] reported that, at the temperature range 300–400 °C, the main solid products encountered during the decomposition of transition metal(II) acetates, such as Mn, Fe, Co, Ni and Cu, in air, were Mn_2O_3, γ-Fe_2O_3, Co_3O_4, NiO, and CuO, respectively. However, in N_2 atmosphere, the solid products were MnO, Fe_3O_4, CoO, Ni^0 and Cu^0 (i.e., metallic Ni and Cu), respectively.

During the last decades, several researches have been published on $CuAc_2 \cdot H_2O$ [10,19–37]. This material has been investigated by differential thermal analysis (DTA) [10,22,24,29,30,33,35], thermogravimetry (TG) [20–22,24,26, 27,29,30,33,34], differential scanning calorimetry (DSC) [20,21,27], X-ray diffractometry (XRD) [10,20,21,24,25,31, 35–37], scanning electron microscopy (SEM) [10,20,22,24], infrared (IR) [10,21,23,24,33,34] and Raman spectroscopy [23], mass spectrometry [28,32,35]. According to thermal analyses data in the above-mentioned works, it may be briefly pointed out that this material decomposes via two well defined processes of mass loss (thermal events I and II) over the temperature range 25–350 °C. Event I (25–175 °C) corresponds to dehydration, with a single (sometimes double) endothermic peak, either in air or in N_2, or in Ar, forming anhydrous salt $(CH_3COO)_2Cu$ (denoted by $CuAc_2$). Event II (175–350 °C) corresponds to the decomposition of $CuAc_2$ which is greatly affected by ambient atmosphere. As a rule, the decomposition solid products in air may contain Cu^0, CuO, Cu_2O or Cu_4O_3. The occurrence of only CuO depends on the temperature of the thermal treatment, normally above 500 °C. Under vacuum, H_2, N_2 or Ar, the solid product is usually Cu^0. With regard to the decomposition of $CuAc_2$ in air, within this range, the presence of two exothermic peaks, followed sometimes by a third one, may at least be observed. However, in N_2, the presence of two endothermic peaks is also reported. The gaseous or volatile products have been mainly composed by acetone (CH_3CH_3CO), acetic acid (CH_3COOH), acetaldehyde (CH_3CHO), methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), and hydrogen (H_2). Amount of gaseous products formed during thermal decomposition depends on the atmosphere and on the types of metal(II) acetates [19].

Changes in physical quantities (variables of state) of a sample as a function of temperature such as heat and mass are generally measured by thermal analysis (TA) and calorimetry methods. Actually DSC and TG are very useful to determine the processes in certain thermal events, although these methods frequently involve substantial instrumentation and are limited to small samples. Alternatively, a secondary classification criterion of methods of thermal analysis considers thermoelectrical analysis (TEA) as a generic term which may be applied to the study of the electrical properties with or without any kind of applied electric field. Thus, TEA may be performed by measuring electrical resistance [38–40], since the specimen may be a sufficient conductor. For this purpose, a freeze-dried mixture has been used with a specific composition of a composite powder containing ZnO (semiconductor) and $CuAc_2 \cdot H_2O$ so that the changes in the electrical resistance caused by the thermal decomposition of $CuAc_2 \cdot H_2O$ could be observed (as-called thermoelectrical resistometry, TER). Just for comparison, it may be stated that samples in the form of compacted pellets were characterised by DSC and TER in air up to 350 °C.

In current research the exothermal events, registered in DSC curves, within the range 175–350 °C, mainly related to the thermal decomposition of $CuAc_2$, may be associated to changes (decrease of several orders of magnitude) in the electrical resistance of the sample that occur in that same range of temperatures. Further, the authors applied the concepts related to TA and TEA, from DSC and TER data, and presented, comparatively, a calculated kinetic parameter, the activation energy (E_a) for exothermal reactions, according to the ASTM (American Society for Testing and Materials) standard, ASTM E 698.

2. Experimental

2.1. Freeze-drying

Initially a specific composition of powders containing ZnO (99.9%, Uniroyal, with a mean particle diameter $D_{50} \approx 0.5\ \mu m$) and $CuAc_2 \cdot H_2O$ (98.7%, Mallinckrodt) was homogeneously diluted in 150 ml of distilled-deionised water, at room temperature. In current experiment the mass of $CuAc_2 \cdot H_2O$ was below its solubility limit in water (0.38 mol/kg), at 25 °C [1]. Next, the aqueous mixture containing ZnO + 7.2 wt.% $CuAc_2 \cdot H_2O$, equivalent to ZnO + 3 mol% Cu^{2+}, was transferred to an appropriate glass flask and freeze-dried. The freeze-drying process consists of two stages: (i) freezing: the aqueous mixture is slowly frozen inside the flask which rotates in contact to a refrigerant fluid (semi-dipped) in a continuous system (Edwards, Shell Freezer) at −50 °C, at atmospheric pressure, for 45 min; (ii) drying: the flask is connected to the freeze-drier which consists of a vacuum pump (Edwards, E2M2) and a water trap (Edwards, Micromodulyo). During the drying stage, the frozen water sublimates under low pressure at 3.2 Pa (2.4×10^{-2} Torr) and is captured in the trap maintained at −45 °C. After about 18 h the powder is completely dried.

2.2. Thermoelectrical and thermal analyses

A scheme of the homemade system used for measuring thermoelectrical resistance on ceramic pellets is shown in Fig. 1. The system is composed of a heating element connected to a temperature controller (Novus) for time-dependence programming of the sample's temperature (i.e. heating rate). The data of electrical resistance as a function of temperature are collected by a GPIB interface computer, from a digital multimeter (Tectronix, DM5520). The heat flux coming from the side in contact with the heat source enters the sample. Electrical connections, made of very thin wires of gold with small silver-painted electrical contacts, lie in the diagonal extremities of the opposite surface. The sample is electrically insulated from the heat source by a thin mica layer, whereas the system is flexible enough to permit the analysis of sample either in vacuum, dynamic or static gas atmospheres, or in air at atmospheric pressure.

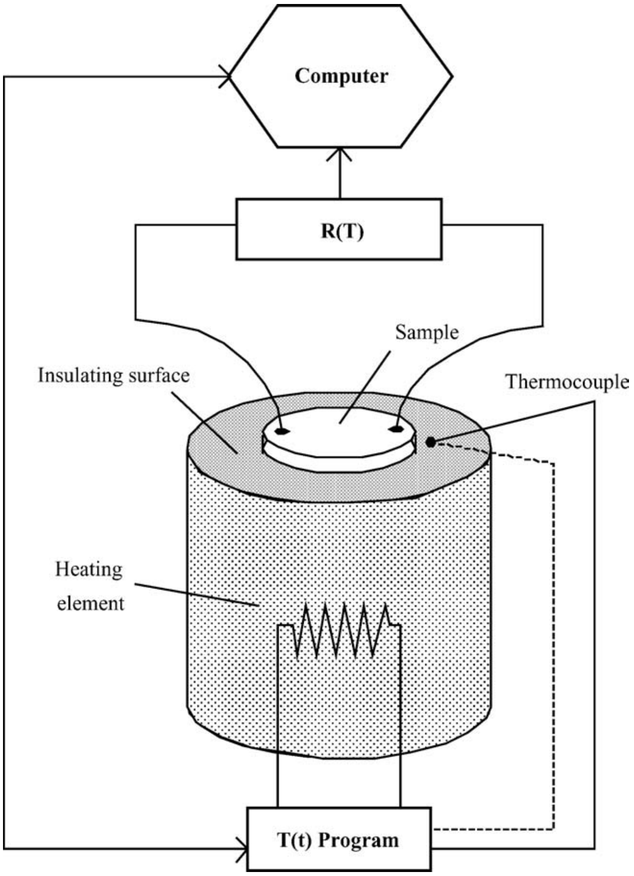

Fig. 1. Device scheme for measurements of the pellet's electrical resistance during heating.

In the case of DSC and TER measurements, the freeze-dried powders were previously uniaxially compacted into the shape of a disk (2 mm in thickness, 8 mm in diameter), with a pressure of 76 MPa, using a steel die without any pressing additives. The thermal decomposition course of the pellets was examined by DSC (Shimadzu, DSC-50) on heating up to 350 °C in aluminium crucibles. DSC and TER were carried out in static air with heating rates $\beta = (2.5, 5, 10 \text{ and } 20\,^\circ\text{C/min})$ and $\beta = (1, 5, 10, 15 \text{ and } 20\,^\circ\text{C/min})$, respectively.

3. Results and discussion

Fig. 2 shows the results of DSC performed in static air, with $\beta = (2.5, 5, 10 \text{ and } 20\,^\circ\text{C/min})$, for ZnO + 3 mol% Cu^{2+} samples consisting of small pieces (about 6 mg) carefully cut out from a compacted pellet. Two important thermal events, shifted to the right as heating rate is increased, have been observed in the temperature range 25–350 °C. Event I corresponds to the dehydration process and shows the presence of endothermic peaks with maximum values occurring at 149, 151, 158 and 163 °C. Event II is related to the thermal decomposition of $CuAc_2$ and corresponds to the maximum exothermic events occurring at 260, 268, 280 and 291 °C. It is worthwhile reporting that event II may contain two very close peaks, as may be seen in the DSC curves. The existence of at least two exothermic peaks and sometimes a third one has been documented in the literature [10,20,22,24,35,41].

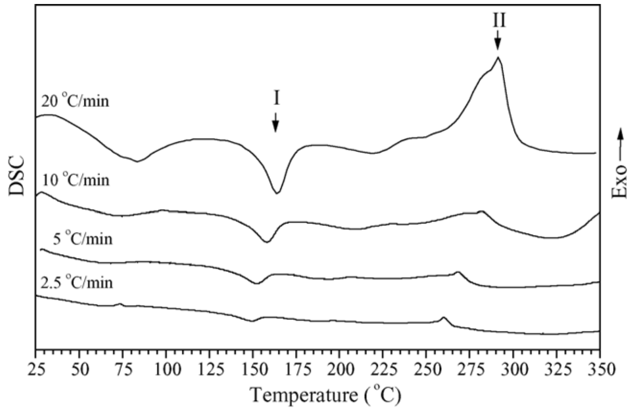

Fig. 2. DSC in static air, with heating rates $\beta = (2.5, 5, 10 \text{ and } 20\,^\circ\text{C/min})$, for ZnO + 3 mol% Cu^{2+} freeze-dried samples.

Fig. 3 shows the results of TER (logarithmic scale) performed in air, with heating rates $\beta = (1, 5, 10, 15 \text{ and } 20\,^\circ\text{C/min})$, for ZnO + 3 mol% Cu^{2+} pellets (about 0.4 g). Two important thermal events that, similar to DSC, shift to the right and increase in intensity as the heating rate increases, have been registered in the range 25–350 °C. Comparatively, event I (25–175 °C), which corresponds to the dehydration process (from DSC), appears as a decreasing peak in the electrical resistance whose minimum values occur at 80, 103, 115 and 135 °C as β increases from 5 to 20 °C/min, respectively. Moreover, this peak becomes more pronounced as β increases. Event II (175–350 °C) presents two successive decreasing peaks in electrical resistance, whose temperature differences increase as heating rate increases. Temperatures related to the first minimum peak occurred at 255, 276, 288, 296 and 300 °C as β increased from 1 to 20 °C/min, respectively. Event II is believed to be related to the thermal decomposition of $CuAc_2$.

Fig. 4 shows the results of a linear fit of $-\ln(\beta/T^2)$ as a function of $1/T$, deducted from DSC and TER results, where β is

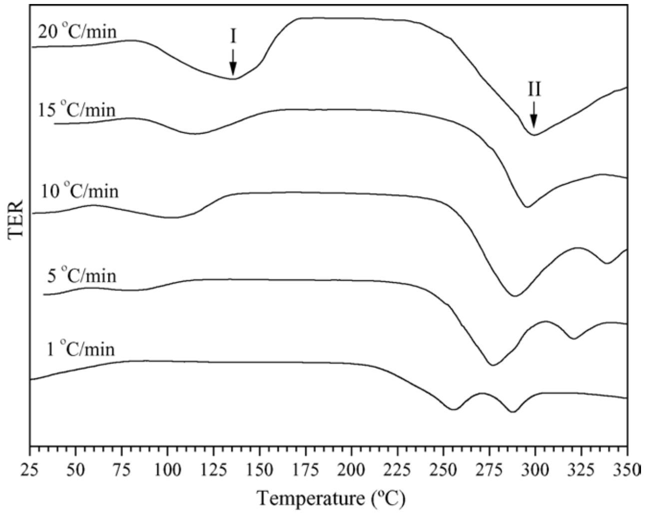

Fig. 3. TER in static air, with heating rates $\beta = (1, 5, 10, 15 \text{ and } 20\,^\circ\text{C/min})$, for ZnO + 3 mol% Cu^{2+} freeze-dried samples.

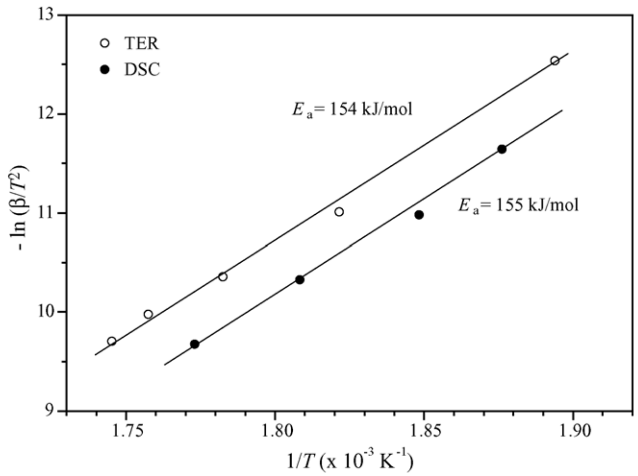

Fig. 4. Plot of $-\ln(\beta/T^2)$ vs. $1/T$ where β is the heating rate (in K/min) and T is the thermodynamic temperature (in K) of the corrected maximum peak (from DSC, Fig. 2) and minimum in electrical resistance (from TER, Fig. 3), related to the exothermic event II, respectively.

the heating rate (in K/min) and T is the thermodynamic temperature (in K) identified by an arrow, related to event II: the exothermic event in Fig. 2 and the first minimum in electrical resistance in Fig. 3, respectively. For comparison, the activation energy (E_a) for the corresponding thermal processes was estimated by using the values of the angular coefficients, calculated according to the ASTM E 698 standard. Values of E_a obtained from DSC ($E_a = 155$ kJ/mol) and from TER ($E_a = 154$ kJ/mol) are very close, which indicates that TER can be used for the calculation of E_a of a previously known exothermic event.

Kinetic parameters for the dehydration and decomposition of $CuAc_2 \cdot H_2O$ in air has been calculated by isothermal or non-isothermal methods [22,24,26,27,29,41]. Related to the decomposition step, Obaid et al. [22] tested various methods of analysis and obtained $E_a = 71.2$ kJ/mol for isothermal and values between 100 and 117.1 kJ/mol for non-isothermal ones, respectively. Based on TG and DTA results, Mansour [24] obtained $E_a = 227$ kJ/mol as non-isothermal kinetic parameter for the decomposition of $CuAc_2$. Using thermogravimetric analysis, Maslowska and Baranowska [29] obtained $E_a = 191.5$ kJ/mol for the thermal decomposition reaction of $CuAc_2$ to produce Cu^0 + gaseous products. When the results previously presented are compared, in current research the obtained value of E_a, around 154 kJ/mol, lies within similar value range.

Studies published in the literature by Bellini et al. [20] on the thermal decomposition of $CuAc_2 \cdot H_2O$ freeze-dried powders showed that, after thermal treatment at 125 or 225 °C, in air, this material dehydrates to $CuAc_2$. After thermal treatment at 325 °C, $CuAc_2$ decomposes to a mixture of phases containing Cu^0, Cu_2O and CuO. These phases have also been found by Zhang et al. [41] as solid residue after thermal decomposition in air at 310 °C. Since the single CuO phase was encountered after thermal treatment above 500 °C [20,24,33–35], complex oxidation processes from Cu^0 to CuO were shown. Therefore, in the temperature range 250–300 °C, the exothermic transition observed in DSC, coupled to a decrease in several orders of magnitude within the electrical resistance observed in TER, is related to the decomposition of $CuAc_2$ initially involving the formation of Cu^0.

Different mechanisms were proposed for acetate decomposition [19,41,42] so that the generation of different volatile products and the partial reduction of the transition metals even in inert atmospheres could be explained. Interestingly, two schemes of a catalysed acetate conversion mechanism describing the formation of intermediate acetic anhydride and liberation of electrons, which in turn may reduce the metal ions, have been proposed by Bowker and Madix [42] and Madix et al. [43]. Current results agree with these models because a strong decrease in the electrical resistance (liberation of electrons) during the thermal decomposition of $CuAc_2$ has been reported. Besides, the formation of Cu^0 as solid product (which could contribute to the decrease in the electrical resistance) indicates that possibly catalytic reactions may reduce Cu^{2+} ions to Cu^+ and Cu^0, in overlapped consecutive processes [22].

It may be stated that, in the context of the decomposition process of $CuAc_2$ in compacted samples from ZnO + $CuAc_2 \cdot H_2O$ freeze-dried composite powders, E_a is approximately 154 kJ/mol. Moreover, TER in association with DSC, or other methods of thermal analysis, may be very useful for the understanding of exothermic events that occur in metal acetates and for the testing of decomposition mechanism models.

4. Conclusions

Freeze-drying is a useful processing technique to produce highly homogeneous mixtures of composite powders containing ZnO + 7.2 wt.% $CuAc_2 \cdot H_2O$, equivalent to ZnO + 3 mol% Cu^{2+}. Due to the polymeric characteristic of $CuAc_2 \cdot H_2O$, pellets of that mixture were compacted without any pressing additives. Compacted samples were characterised by TER and DSC, in static air, with heating rates at 1–20 °C/min. Since DSC results showed the presence of exothermic events within the range 250–350 °C and since, in the same range of temperatures, TER results revealed a decrease in electrical resistance, such events were associated to the thermal decomposition of $CuAc_2$. The activation energy, E_a, for exothermic reactions, was estimated according to ASTM E 698 standard. Values of E_a equal to 154 and 155 kJ/mol were obtained by TER and DSC, respectively. Results indicate the possibility of using TER as an alternative or complementary method for the study of the thermal decomposition course of transition metal(II) acetates.

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