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Thermal, Structural and Morphological Characterisation of Freeze-dried Copper(II) Acetate Monohydrate and its Solid Decomposition Products

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In the present study the thermal decomposition of a freeze-dried copper(II) acetate monohydrate powder, $(CH_3COO)_2Cu{\cdot}H_2O$, ($FDCuAcH_2O$), was analysed by a combination of high-temperature X-ray diffractometry; differential scanning calorimetry and thermogravimetry, up to 700 °C. The structure and morphology of the calcined freeze-dried powders were analysed by scanning electron microscopy and X-ray diffractometry. The results showed that $FDAcCuH_2O$ decomposes during heating in two stages: I) (25-225 °C) $FDCuAcH_2O$ dehydrates giving rise to copper(II) acetate, $(CH_3COO)_2Cu$, (AcCu), and II) (225-525 °C) AcCu decomposes to CuO through complex oxidation reactions of Cu and Cu_2O, simultaneously. SEM showed that $FDCuAcH_2O$ powder has a scale-like morphology, which is created in the freezing stage and retained after freeze-drying. After calcination at 125 and 225 °C, clusters of elongated tubes (or filaments) compose the resulting powder (AcCu). Subsequent calcination at temperatures above 325 °C resulted in hard clusters of spheroid-like CuO particles.

Keywords: *freeze-drying, copper(II) acetate monohydrate, thermal decomposition, Cu oxides, high-temperature X-ray diffractometry*

1. Introduction

In general, powders of hydrate metal acetates have the form $(CH_3COO)_2M{\cdot}xH_2O$, where M is a metal cation, CH_3COO is an acetate group and x is the number of water molecules. These materials are useful reagents commercially available and are used mainly in industrial processes. Although metal acetates are technologically important materials only recently systematic data about their solubilities in water as a function of temperature have been published[1].

The fact that metal acetates (including nitrates, oxalates, sulphates, etc.) are water-soluble salts indicates that they can be freeze-dried individually or in multi-components. In the conventional freeze-drying[2] (or cryochemical) process, the starting salts of high purity are initially dissolved in an adequate solvent, rapidly frozen to avoid precipitation or segregation of the components, followed by solvent sublimation under vacuum. The resulting powders obtained in this way are expected to be chemically more homogeneous, free of contamination by impurities and highly reactive. After thermal decomposition and solid state reactions in high temperature the precursors give rise to a more uniform mixture of metal oxides in atomic scale. Freeze-drying have been used to make improvements in the powder synthesis of catalysts[3], PLZT[4,5], ferrites[6] and superconductors[6-9]. Recently, scientific and technological efforts have been carried out through the utilisation of the freeze-drying technique to produce homogenous mixtures of powders such as oxides with copper(II) acetate monohydrate $(CH_3COO)_2Cu{\cdot}H_2O$ (denoted $CuAcH_2O$ in the text for simplification) which have been used as precursors to preparation of ZnO-based varistors[10,11].

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In the last decades much work has been published in the literature[9,10,12-18] on thermal decomposition of $CuAcH_2O$, under various conditions, to understand the thermal events involved in the solid-gas-solid reactions and the products of such reactions. This material has been investigated by differential thermal analysis (DTA)[9,12,14,15,18], thermogravimetry (TG)[13-16,18], differential scanning calorimetry (DSC)[18], X-ray diffractrometry (XRD)[9,12,16,18,19-21], scanning electron microscopy (SEM)[9,17,18], both infrared (IR) and Raman spectroscopy[9,13,14,18,22]. These previously mentioned works pointed out that thermal decomposition course of $CuAcH_2O$ occurs in two stages: I) dehydration of $CuAcH_2O$ producing copper(II) acetate ($(CH_3COO)_2Cu$) (denoted by CuAc) and II) decomposition of CuAc producing solid products such as Cu, Cu_2O, CuO or more rarely to Cu_4O_3, and gaseous or volatile products such as acetic acid, acetone, acetaldehyde, methane, carbon dioxide, and hydrogen. The range of temperatures of such thermal events and the resulting solid products may depend on the atmosphere, heating rate and origin of the powder.

In this work, the thermal decomposition course of a freeze-dried $(CH_3COO)_2Cu{\cdot}H_2O$ powder (denoted $FDCuAcH_2O$) have been studied by DSC and TG, in static air, up to 700 °C. The structural and morphological changes have been characterised by RXD and SEM, at ambient temperature, after calcination in air, in various temperatures up to 625 °C. For the first time on literature the results of *in situ* characterisation by high-temperature X-ray diffractometry (HTXRD) up to 600 °C of a $FDCuAcH_2O$ powder are showed. The main aim of this study was to obtain more information about thermally-induced structural modifications to decide for a better condition of thermal treatment to get a desired phase.

2. Experimental

From literature[1], a solubility limit value of 0.38 $mol.kg^{-1}$, for $AcCuH_2O$, in water, at 25 °C, corresponds to about 19 g of $AcCuH_2O$ for 250 ml of water. Thus, a certain mass of $AcCuH_2O$ was chosen in this wok to be below of its solubility limit. Initially, 15 g of copper(II) acetate monohydrate $(CH_3COO)_2Cu{\cdot}H_2O$ powder (Mallinckrodt, 98.7%) was homogeneously diluted in 250 ml of distilled-deionized water, at ambient temperature. The pH value of the resulting aqueous mixture was around 6.7 indicating that there was no excess of acid products formed. In this work, the freeze-drying process consisted of two stages: *i*) *freezing*: the aqueous mixture was transferred to an appropriate glass flask and connected to a continuous freezing system (Edwards Shell Freezer). In this system, the flask (semi-dipped) rotated slowly and continuously (~45 min) in contact to a refrigerant fluid (-50 °C), at atmospheric pressure, until the aqueous mixture was completely frozen. After this step, overlapped thin frozen layers were created inside the flask; *ii*) *drying*: the flask was transferred and connected into the freeze-drier. A vacuum pump (Edwards E2M2) and a water trap (Edwards Micromodulyo) compose this equipment. During this stage the water sublimates and it was captured in the trap (-45 °C). After about 16 hours the powder was completely dry. During freeze-drying, the pressure inside the vacuum system (trap) was maintained at 2.4×10^{-2} torr. The pH of the trapped water, at ambient temperature, after freeze-drying was around 6.2.

The thermal decomposition course of the resulting $FDCuAcH_2O$ powder was examined on heating up to 600 °C, at heating rate of 5 °C/min, in static air, by DSC and TG (Netzsch). The solid products from the thermal decomposition of $FDCuAcH_2O$ were identified *in-situ* using HTXRD (Siemens D5000). The powder was Joule-heated inside a Pt-crucible, at heating rate of 5 °C/min. The X-ray diffraction measurements were performed in a fixed range $34 < 2\theta < 40°$, at ambient temperature, and in intervals of 100 °C during heating up to 600 °C; at 300 °C and at ambient temperature, during cooling.

The $FDCuAcH_2O$ powders were calcined at various temperatures up to 625 °C, in intervals of 125 °C. The powders were calcined during 1h; in static air atmosphere, using a Al_2O_3-crucibles, in a electric furnace (EDG3000). During the calcinations, a constant heating and cooling rate of 5 °C/min was used. XRD measurements (Siemens D5000) were performed, at ambient temperature, for the $FDCuAcH_2O$ and calcined powders, in the range $5 < 2\theta < 80°$. The morphological aspects of the powders were analysed by SEM (Leica StereoScan 440) using secondary electrons, after Au-recovering.

3. Results and Discussion

The curves of thermal analysis of the $FDCuAcH_2O$ powder by DSC and TG are presented in the Fig. 1. DSC and TG measurements indicate that $FDAcCuH_2O$ decomposes via two processes of weight loss (thermal events I and II) over the temperature range 100-325 °C:

Event I: (100-190 °C) corresponds to dehydration, with an endothermic maximum peak at 145 °C, corresponding to a weight loss about 11.9% at 190 °C. Normally, in both DTA and DSC, the obtained maximum or minimum temperature values are dependent on heating rate, shifting to right as heating rate is increasing[18]. Evidences from literature[9,12,14-16,18] show that the first stage is mainly related to dehydration of $(CH_3COO)_2Cu{\cdot}H_2O$ ($CuAcH_2O$) leading to formation of copper(II) acetate $(CH_3COO)_2Cu$ (CuAc). The theoretical mass loss of water molecules of $CuAcH_2O$ corresponds to 9.0%. In this study, the greater weight loss than that expected for the formation of CuAc could be also attributed to the volatilisation of CuAc or water excess, in the

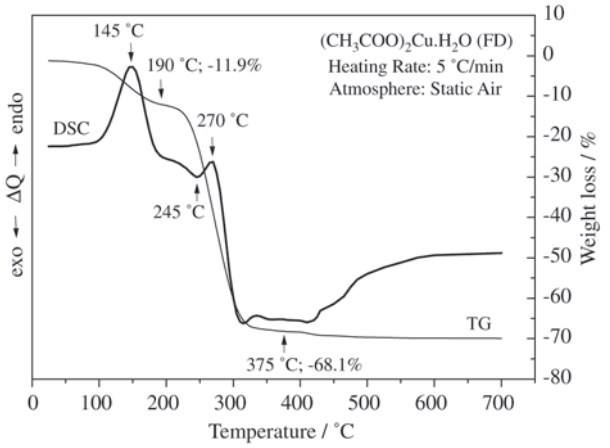

Figure 1. Curves of DSC and TG for a freeze-dried copper(II) acetate monohydrate powder.

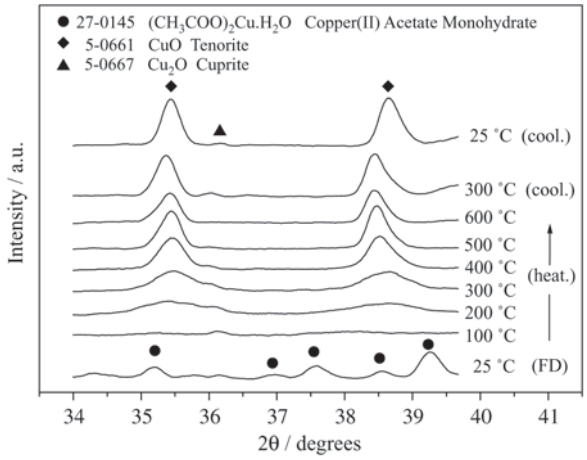

Figure 2. HTXRD spectra for a freeze-dried copper(II) acetate monohydrate.

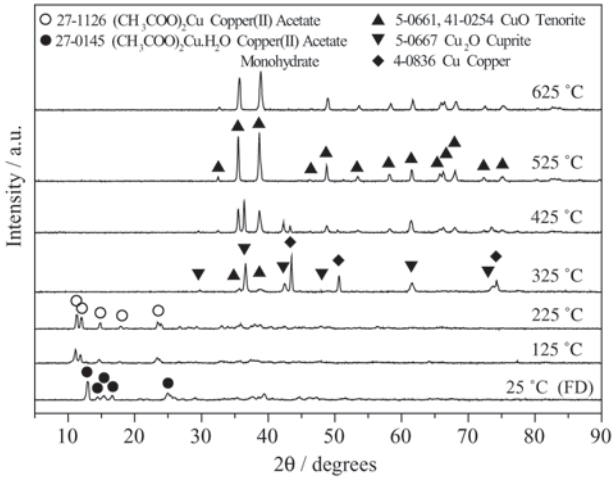

Figure 3. XRD spectra for the copper(II) acetate monohydrate powder: freeze-dried; and calcined at 125 to 625 °C, in air for 1h.

$FDCuAcH_2O$ powder. The gas atmosphere significantly affects the mechanism of dehydration of $CuAcH_2O$. Under vacuum, dynamic Ar or N_2, CuAc sublimates and copper is lost[9,13,15,18].

Event II: (220-325 °C) corresponds to decomposition of CuAc. In this range, DSC showed two double peaks: an exothermic at 245 °C, followed by an endothermic at 270 °C. These peaks are related to complex solid-gas-solid reactions involving probably the production of solid metallic copper (Cu^0) and volatile or gaseous products. TG showed that the mass loss at 375 °C was about 68.1%, which is equivalent to the theoretical mass loss to formation of Cu^0 (68.17%). The decomposition of $CuAcH_2O$ is greatly affected by the ambient atmosphere. In general, researchers[9-18] have been relating that in vacuum, N_2 or Ar, and in air, the main solid products have been Cu^0 and Cu_2O, CuO or Cu_4O_3, respectively. 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), and hydrogen gas (H_2).

The results of HTXRD for the range $34° < 2\theta < 40°$ performed in air, at atmospheric pressure, are showed in Fig. 2. This range of study was especially chosen because it includes the diffraction planes of relative maximum intensity for the crystalline phases CuO and Cu_2O, *i.e.*, (-111) at $2\theta = 35{,}55°$ and (111) at $2\theta = 36{,}41°$, respectively. Three phases were monitored and identified by card number from *powder diffraction files* (PDF) of *the joint committee on powder diffraction standards* (JCPDS): CuO (*tenorite*) or *copper(II) oxide* (PDF 5-0661); Cu_2O (*cuprite*) or *copper(I) oxide* (PDF 5-0667); $(CH_3COO)_2Cu.H_2O$ (*copper(II) acetate monohydrate*) or *copper acetate hydrate* (PDF 27-0145). At ambient temperature (25 °C), XRD showed that the $FDCuAcH_2O$ powder is $CuAcH_2O$. Comparing the XRD data for $FDCuAcH_2O$ powder with previous XRD data for the commercial material powder (not presented here) did not indicate any secondary phase. At 100 °C occurs the dehydration of $FDCuAcH_2O$ leading to formation of CuAc. At 200 °C is the beginning of the thermal decomposition process of CuAc leading probably to formation of Cu_2O and CuO phases, simultaneously. In the range 200-400 °C, these amorphous phases crystallise to CuO in an oxidation process. At 500 and 600 °C, on heating and on cooling from 600 °C to ambient temperature the present phase is CuO.

The XRD spectra for the $FDCuAcH_2O$ calcined powders are presented in Fig. 3. At ambient temperature the

$FDCuAcH_2O$ is identified as $CuAcH_2O$. After calcination at 125 °C and 225 °C, $FDCuAcH_2O$ dehydrates leading to formation of AcCu. Calcination at 325 °C gives rise to formation of various coexisting phases that were identified as Cu^0, Cu_2O and CuO. This indicates that from solid decomposition products of CuAc in air, Cu^0, Cu_2O and CuO can be formed simultaneously, between 225 and 325 °C. XRD analyses of the calcined powders at 325, 425 and 525 °C, indicate that CuO is formed through oxidation reactions of Cu^o and Cu_2O. Above 525 °C the final product is CuO.

In function of the previously obtained results by DSC-TG, HTXRD, and XRD, the probably reactions giving rise to the solid products of the thermal decomposition of the $FDCuAcH_2O$ are:

Stage I (25-225 °C):

$$(CH_3COO)_4Cu_2{\cdot}2H_2O \rightarrow 2(CH_3COO)_2Cu + 2H_2O$$

Stage II (225-525 °C):

$$6n(CH_3COO)_2Cu + \tfrac{1}{2}O_2 \rightarrow Cu + Cu_2O + 3n\text{Product}_{(\text{gas, volatile})}$$

$$Cu + \tfrac{1}{2}O_2 \rightarrow CuO$$

$$2Cu + \tfrac{1}{2}O_2 \rightarrow Cu_2O$$

$$Cu_2O + \tfrac{1}{2}O_2 \rightarrow 2CuO$$

The morphological evolution of the $FDCuAcH_2O$ powder after calcination was examined by SEM. Figure 4a, 4b and 4c) shows the morphological aspects of the $FDCuAcH_2O$ powders at ambient temperature (25 °C), and calcined from 125 to 225 °C/1h, respectively. The $FDCuAcH_2O$ powder, showed in Fig. 4a, has a clear scale-like aspect. The origin of this morphology is probably due to the freeze-drying processing technique used in this work. When the mixture is frozen overlapped solid thin layers are created inside the glass flask. During water sublimation that solid layers are retained giving rise to this interesting and unusual morphology. In a recent work, the characterisation by SEM of a freeze-dried $CuAcH_2O$ powder, obtained by spray-freeze-drying, showed morphology composed by very thin filaments or chained agglomerates[9]. Studies about the crystalline structure of $CuAcH_2O$ show that this material tends to form dimmers, $(CH_3COO)_4Cu_2$, bonded by water molecules, which package in the monoclinic system[19-22]. The

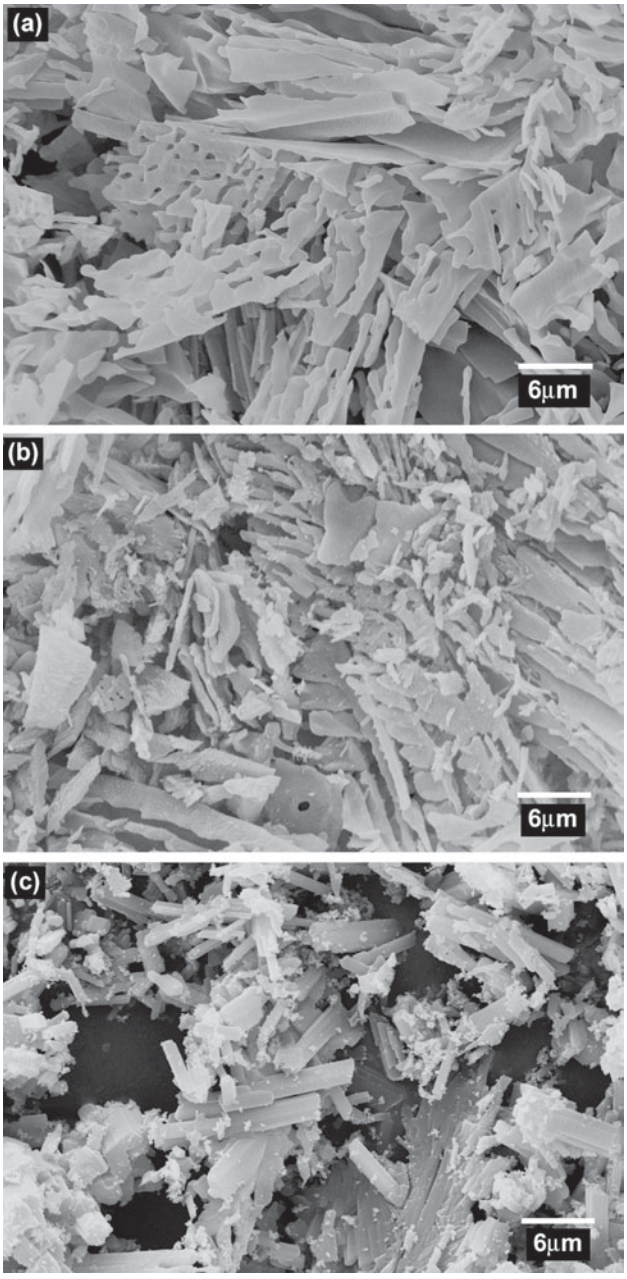

Figure 4. SEM morphological aspects for the copper(II) acetate monohydrate powder: (a) freeze-dried; and calcined at (b) 125 °C; and (c) 225 °C, in air for 1 h.

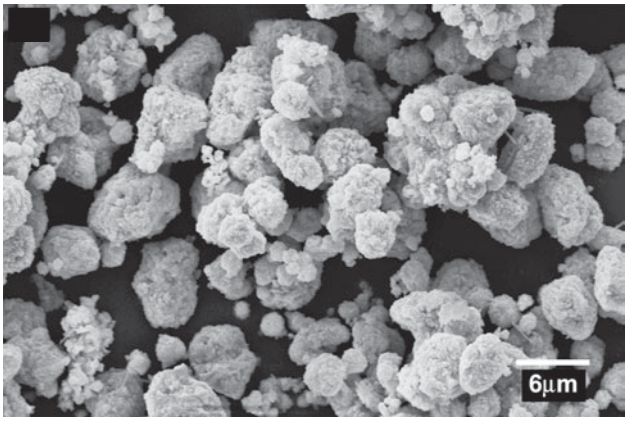

Figure 5. SEM morphological aspects for the copper(II) acetate monohydrate powders, calcined at 425 °C in air for 1 h.

morphology of giant $CuAcH_2O$ single crystals have been reported as been composed by flat faces[17,18]. Analysis of both powder morphology, the $FDCuAcH_2O$ calcined at 125 and 225 °C, shows that after dehydration the powders form elongated solid tubes, which is characteristic of the open tetragonal structure of CuAc. After calcination at 325, 425 and 525 °C, CuAc decomposes to Cu^0, Cu_2O and CuO, in an oxidation reaction, resulting in hard clusters of spheroid-like CuO particles (Fig. 5).

4. Conclusions

Results obtained in this study show that the freeze-drying synthesis process is reliable for producing copper(II) acetate monohydrate powder ($FDAcCuH_2O$), with an unusual scale-like morphology created in the freezing stage and retained after freeze-drying. Results of the solid decomposition products show that the copper(II) acetate monohydrate powder ($FDAcCuH_2O$) decomposed during heating in two stages: I) (25-225 °C) $FDCuAcH_2O$ dehydrates giving rise to copper(II) acetate, (AcCu), and II) (225-525 °C) AcCu decomposes to CuO through complex oxidation reactions of Cu and Cu_2O, simultaneously.

The morphological aspect of the products from decomposition of copper(II) acetate monohydrate powder ($FDAcCuH_2O$), between 125 and 225 °C, are elongated solid tubes or filaments of AcCu and after subsequent calcination above 325 °C the morphological aspect resulted in hard clusters of spheroid-like CuO particles.

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