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Electrosynthesis and thermal characterization of basic copper carbonate nanoparticles

Research Article

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Abstract: The present study concerns the electrochemical synthesis of basic copper carbonate nanoparticles by oxidation of metallic copper on the anode in an aqueous bicarbonate solution. This simple and one-step preparation can be considered as green synthesis. The scanning electron microscopy (SEM) analysis indicates that average particle size of the product is in the range of about 70 nm. On the other hand, basic copper carbonate micro-powder has been prepared, by mixing solutions of copper(II) sulphate and sodium bicarbonate. The SEM analysis showed that the size of particles prepared in the same way is in the range of about 1 μm. In another part of this study, the thermal decomposition of micro and nanoparticles of copper carbonate produced by various methods was studied in air using TG-DTA techniques. The results of thermal study show that the decomposition of both samples occurs in single step. Also, the TG-DTA analysis of the nanoparticles indicates that the main thermal degradation occurs in the temperature range of 245 - 315ºC. However, microparticles of $Cu(OH)_2 \cdot CuCO_3$ decomposed endothermally in the temperature range of 230 - 330ºC.

Keywords: *Nanoparticle • Electrosynthesis • Basic copper carbonate • Thermal decomposition • TG-DTA*

1. Introduction

Copper carbonate, $Cu(OH)_2 \cdot CuCO_3$, as a basic salt, is used widely in pyrotechnics (such as deflagration catalyst in gas-generators, flare composition) [1-3], pigments (and it is still in use for artist's colours), insecticides, fungicide for seed treatment, feed additive (in small amounts), coloring brass black, astringent in pomade preparation, antidote for phosphorus poisoning, inorganic industry, organic synthesis catalyst in organic industry, antidote for phosphorous toxin, desulfurizer of raw oil, wood preservative. Copper carbonate is bulkier than the oxide form, thus it tends to disperse better to give more even results. It is also more reactive chemically than the oxide form and thus melts better. As such, it is ideal for use in brush work where minimal speck is required. However it produces gases as it decomposes and these can cause pinholes or blisters in glazes. Also the carbonate form contains less copper per gram; therefore colors are less intense than the oxide form. The hydroxyl component is an important aid in dispersing the powder throughout the glaze slurry and thus avoids specks in the fired glaze [4-9].

Many product properties that are of relevance in industrial use can be adjusted by changing the particle size and particle size distribution of the powder. This statement is valid in several fields, ranging from polymers to pharmaceutical and inorganic powders [10,11]. On the other hand, from pioneering efforts in the late 1980·s the electrodeposition of nanostructures has advanced rapidly to commercial application as a result of (1) an established industrial infrastructure (*i.e.,* electroplating and electroforming industries), (2) a relatively low cost of application whereby nanomaterials can be produced by simple modification of bath chemistries and electrical parameters used in current plating and electroforming operations, (3) the capability in a single-step to produce metals, alloys, and metal-matrix composites in various forms, and most importantly (4) the ability to produce fully dense nanostructures free of extraneous porosity [13-18].

The combined use of different thermoanalytical methods allows the extensive characterization of inorganic salts and their fundamental properties. In addition, these methods can be used for the determination of physical characteristics such as melting, sublimation, evaporation behaviour or decomposition temperature [19].

The main purpose of the present work is to investigate the electrochemical synthesis of nanostructured basic copper carbonate powder by anodic oxidation of copper in the alkali sodium bicarbonate solution, evaluating its thermal properties and comparison with conventional

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prepared microparticle copper carbonate powder. To the best of our knowledge, the synthesis of microparticles of copper carbonate by reacting copper salts with alkali carbonate in aqueous solution at elevated temperatures, stirring, and subsequently isolating the copper carbonate have been reported [5,20], previously. Also, some reports could be found on its thermal characterization [21-22]. But there is no report on the synthesis and thermal behaviour of nano-powder of basic copper carbonate.

2. Experimental Procedures

2.1 Electrosynthesis of nanoparticles

All reagents were purchased from Merck (Tehran, Iran). For bulk synthesis, the electrolyte solution was prepared by dissolving sodium bicarbonate with 0.033 mol dm^{-3} concentration in deionized water. Electrochemical experiments were carried out in an undivided conventional two electrode Pyrex cell (V = 400 cm^3) at room temperature (22 ± 1 ºC). The working electrode consisted of a plate of copper with a geometric surface area (3 cm^2) and the cathode was a stainless steel (AISI 316) electrode with 10 cm^2 surface area. Prior to electrodeposition, the stainless steel and copper electrode were cleaned with detergent and electrochemically polished as described elsewhere [23]. The synthesis was carried out at constant cell voltage for 60 minutes. To collect the product, the solution was centrifuged and the precipitate washed with dionized water three times, and dried at 40 - 50ºC.

2.2 Preparation of microparticles

The microparticles of basic copper carbonate were prepared, as described in [5], by mixing 200 mL solution of copper(II) sulphate 0.05 M with 200 mL sodium bicarbonate 0.05 M alkalified with KOH at room temperature (22 ± 1ºC), filtering, washing and drying the precipitate, at 40 - 50ºC, which was green in color.

2.3 Characterization of the samples

All samples were characterized by induced coupled plasma (ICP), carbon, hydrogen, nitrogen elemental analysis (CHN), scanning electron microscopy (SEM) and thermogravimetry/ differential thermal analysis (TG-DTA). Scanning electron micrographs were recorded using a Philips XL30 series instrument using a gold film

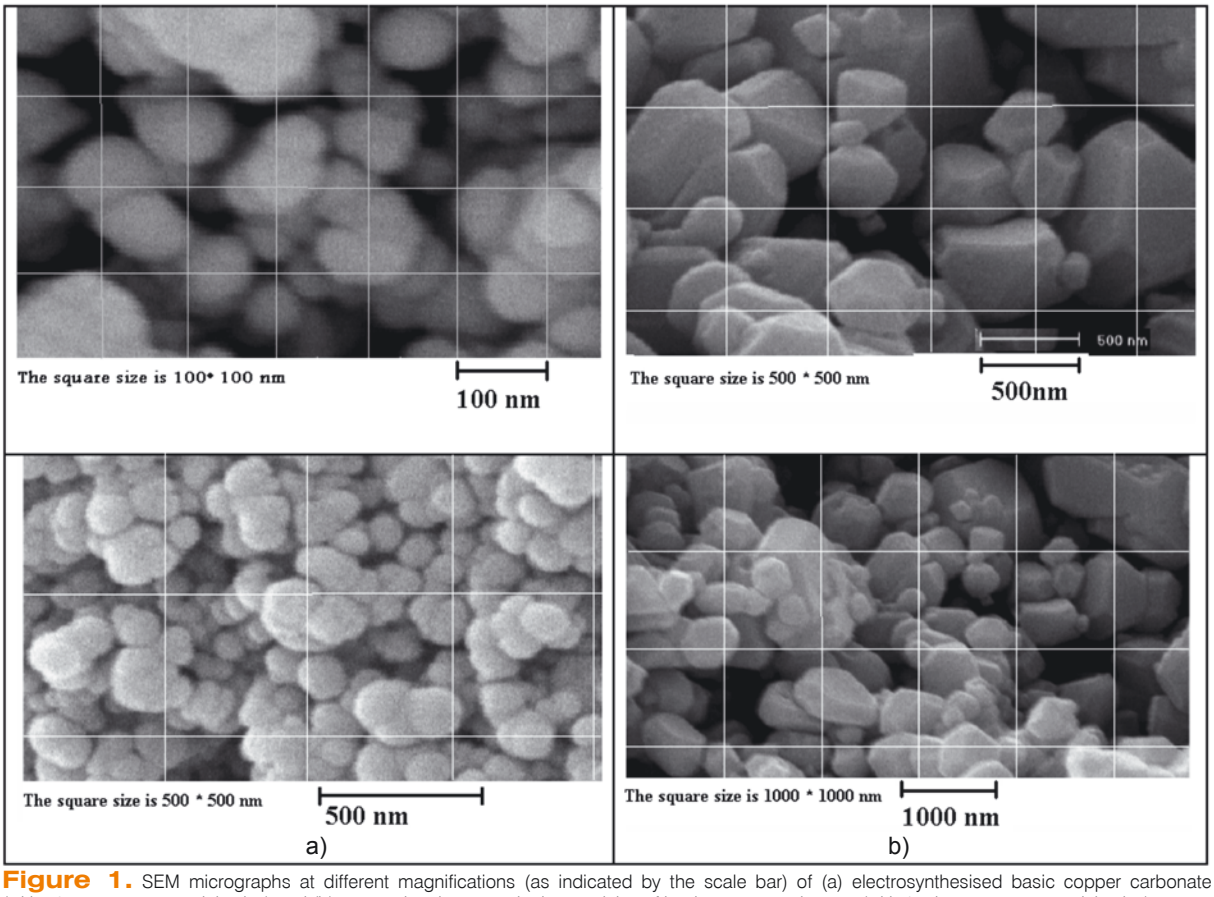

Figure 1. SEM micrographs at different magnifications (as indicated by the scale bar) of (a) electrosynthesised basic copper carbonate (with 70 nm average particle size) and (b) conventional prepared microparticles of basic copper carbonate (with 1 micron average particle size).

for loading the dried particles on the instrument. Gold films were prepared by a Sputter Coater model SCD005 made by BAL-TEC (Switzerland).

A thermobalance (Stanton, model TR-01, sensitivity 0.1 mg) with a differential thermal analysis attachment (STA 1500) was used for TG-DTA studies of samples. Approximately, 2.0 mg of sample and reference (Pt foil) were placed in alumina pans and heated 10ºC min^{-1} from 30 to 800ºC. In this study, the flow rate of purge gas (air) was 10ºC min^{-1} at 1 bar. TG mass, DTA baseline and temperature calibrations were performed prior to the experiments [24].

3. Results and discussion

On electrolysis of an aqueous sodium bicarbonate solution, both bicarbonate reduction and hydrogen evolution reactions take place at the cathode leading to the generation of hydroxyl ions. The resulting increase in pH of the solution causes the shift of bicarbonate and carbonate to the generation of a greater amount of carbonate. On the other hand, copper oxidation takes place at the anode. The resulting Cu^{+2} ions cause the formation and hence the precipitation of basic copper carbonate.

The elemental analysis was performed by ICP and CHN. The analysis confirmed the presence of corresponding elements in stochiometric percentage. The effect of electrolysis voltage on the particle size of product was investigated. The copper carbonate nanoparticles were prepared by electrolysis of copper electrode in bicarbonate solution at three different voltages (3, 7 and 12 V). It was found that the particle size of the product decreased as the electrolysis voltage was enhanced.

On the other hand, SEM images of electrosynthesized copper carbonate particles were obtained using a gold film for loading the derived particles on the instrument. The SEM pictures for the copper carbonate obtained at optimum electrolysis voltage (12 V) showed nano-sized particles with majority in the range of about 70 nm (Fig. 1a).

In contrast, basic copper carbonate was prepared by mixing the copper(II) sulphate, at room temperature, with basic sodium bicarbonate solution. A green precipitate was formed. The precipitate was filtered, washed several times with water and dried at 40 - 50ºC for 4 hours. In the present case, the powder has much bigger particles as seen by SEM pictures. It is seen from the picture (Fig. 1b) that the particle size of the sample is about 1µm. Also, the elemental analysis was performed by ICP and CHN and their results showed the formation of the product.

3.1 Thermal characterization of the samples

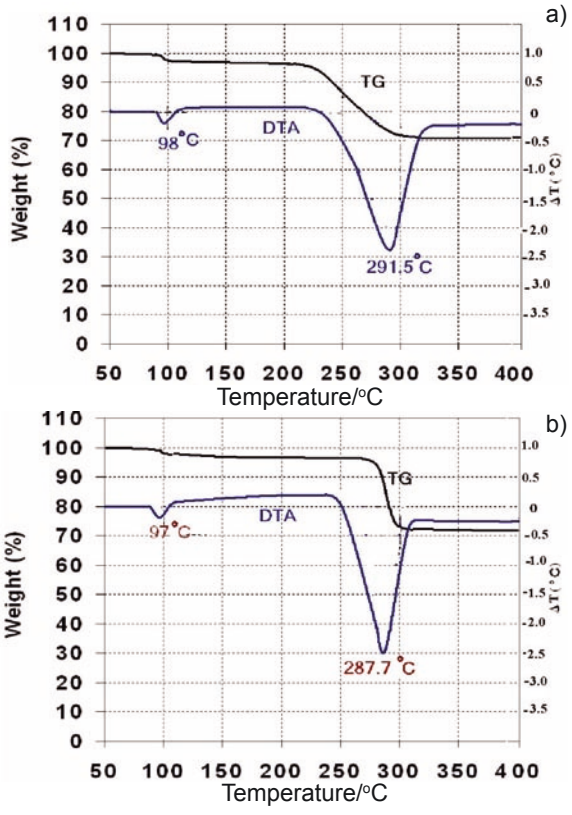

Figure 2. TG and DTA Curves for Basic Copper Carbonate (a) Microparticles (with 1 micron average particle size) (b) Nanoparticles (with 70 nm average particle size); (Sample Weight 2.0 mg; Heating Rate 10˚C min^{-1}; Air Atmosphere).

Fig. 2a represents the TG-DTA curves of $Cu(OH)_2 \cdot CuCO_3$ microparticles. There is a small, broad DTA endotherm below 100ºC, which corresponds to a mass loss of about 2.5% (moisture loss). The results of TG-DTA for microparticles sample showed that the major endothermic decomposition occurred around 291.5ºC. On the other hand, the TG thermogram of this sample showed that the decomposition of the compound started at about 230ºC and the final stages of the decomposition were not complete until about 330ºC. The TG curve indicates only one step (with 27% mass loss) for the process of thermal decomposition [21,25,26].

$$\tfrac{1}{2}\, CuCO_3 \cdot Cu(OH)_2 \xrightarrow{230\text{-}330^{\circ}C} CuO + \tfrac{1}{2}\, CO_2 + \tfrac{1}{2}\, H_2O$$

The single peak for DTA and for the complementary TG run, suggests that the loss of CO_2 and H_2O occurs at the same time which agrees with findings of Henmi *et al.* [27,28].

Fig. 2b represents the TG-DTA thermogram of nanoparticles. In this sample, there is a small, DTA endotherm about 100ºC, with mass loss of 1.5%, which corresponds to retained moisture. After this, the nano-sample rapidly decomposes endothermally at 287.7ºC. This result agrees with the TG curve (about 27% mass losses) for this sample.

3.2 Comparison of thermal behaviour of two samples

Thermal behaviour of micro and nanoparticles of basic copper carbonate was studied under identical condition. Fig. 2 and Table 1 give the thermal properties of the samples. For microparticles of basic copper carbonate, DTA endothermic decomposition occurs at 291.5ºC, and the TG mass loss range is 230 - 330ºC. However, nano-sample decomposed endothermally at 287.7ºC and its mass loss range is about 245 - 315ºC. Such behaviour may indicate that the decomposition temperature range for nanoparticles is narrower than the microparticles. Also, the results showed that the decomposition temperature for the nano-sample (287.7ºC) is lower than the micro-sample (291.5ºC).

Table 1. Summary of DTA-TG Results.

Factor	Micro-particles	Nano-particles
Average particle size	1 μm	70 nm
First T* (ºC)	90 - 100	90 - 100
First mass loss (%)	2.5	1.5
Second T* (ºC)	230 - 330	245 - 315
$^{\#}T_p$ (endothermally) (ºC)	291.5	287.7
Second mass loss (%)	27	27

T is the Temperature Range when There is Fall in a Sample's Mass*
$^{\#}T_p$: temperature at minimum peak

4. Conclusions

In this paper, we reported a novel method to obtain basic copper carbonate nanostructures by single-step oxidation of metallic copper on the anode, in the bicarbonate electrolyte, which is clean, mild and controllable. On the other hand, the conventional method is used for production of copper carbonate micro-particles. The results of TG-DTA showed that, the thermal decomposition of basic copper carbonate (micro and nano-particle) samples occur in air in a single step. However, copper carbonate nano-particles have a different decomposition temperature than the micro-particles, but both of them have similar mass loss. Finally, from a viewpoint of practical application this present study describes a process which can be easily scaled up for production of nano-sized basic copper carbonate powder.

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