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SYNTHESIS AND CHARACTERIZATION OF COPPER HYDROXYNITRATE AND COPPER OXIDE BY HYDROTHERMAL METHOD

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Abstract: In this study, copper hydroxynitrate ($Cu_2(OH)_3NO_3$) and copper oxide (CuO) were synthesized by using the reactants $Cu(NO_3)_2.3H_2O$ and $Na_2B_4O_7.10H_2O$ with the addition of SB12 surfactant by hydrothermal method. The prepared samples were characterized by X-ray diffraction (XRD), Thermal gravimetric analysis (TGA), Fourier Transform Infrared (FTIR) spectra, and scanning electron microscopy (SEM) techniques. According to X-ray diffraction results, copper hydroxynitrate was obtained by borax hydrolysis. Then, the monoclinic phase of copper oxide by calcination of $Cu_2(OH)_3NO_3$ at 400 °C was obtained. TG-DTA analysis showed single stage weight loss. The weight loss of 33.27% at 350°C represents a simultaneous dissociation of HNO_3 and H_2O. The FTIR analysis indicates the samples have O-H, O-NO_2, N-O and Cu-OH group bands. The SEM results reveal that the copper hydroxynitrate have micrometer-size elongated hexagonal plates.

Keywords: Hydrothermal Method, borax, copper nitrate, copper hydroxynitrate, copper oxide.

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INTRODUCTION

Basic copper salts have become suitable precursor applicants for synthesis of unusual CuO nanostructures because of their unique and well-known layered structures. For example, $Cu_2(OH)_3NO_3$, $Cu_2Cl(OH)_3$, $Cu_2(OH)_2CO_3$, $Cu_4SO_4(OH)_6$, and $Cu_7Cl_4(OH)_{10}{\cdot}H_2O$ have been broadly used to prepare $Cu(OH)_2$ and CuO nanostructures with new morphologies (1). Copper-based hydroxynitrate (CuHN) with composition $Cu_2(OH)_3NO_3$ crystallizes in orthorhombic and monoclinic crystal systems (2). The crystal structure of monoclinic copper hydroxynitrate [$Cu_2(OH)_3NO_3$ or $Cu(OH)_{1.5}(NO_3)_{0.5}$] is comprised of copper hydroxide layers in which some of the hydroxyl ions (x = 0.5) are replaced by the nitrate ions and are directly coordinated to the sheets. Copper occupies two different distorted octahedral sites within the layer and the structure of copper hydroxynitrate ($Cu_2(OH)_3NO_3$) is shown in Figure 1.

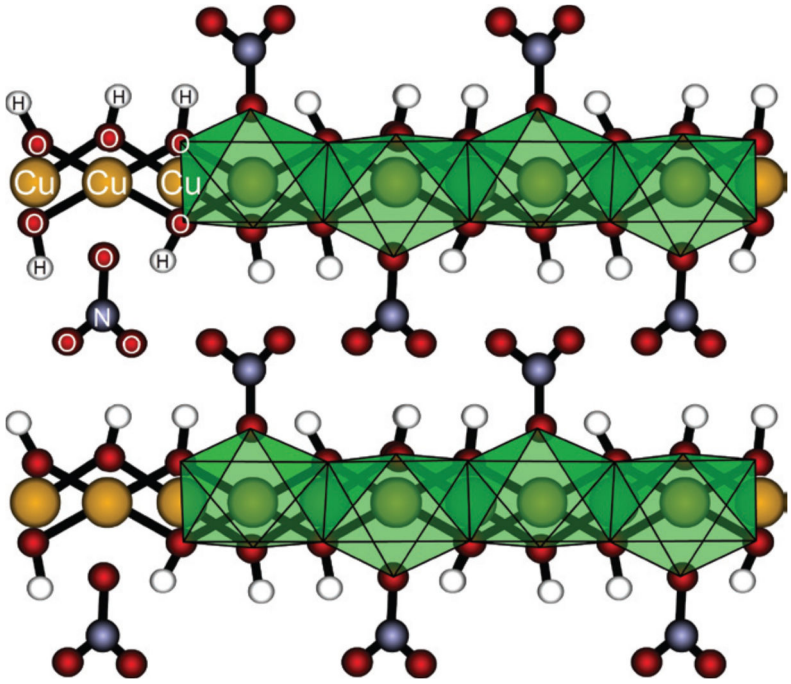

Figure 1. Schematic representation of the structure of copper hydroxynitrate, ($Cu_2(OH)_3NO_3$)(3).

Owing to such an extraordinary structure, copper hydroxyl nitrate has different applications, particularly for the swelling of vehicle airbags, low-ash solid propellants, ion exchangers and ignition compositions (4).

A diversity of inorganic and organic substances such as carbon materials, pure and doped metal oxides/hydroxides, and polymers have been successfully plated onto various substrates for particular aims (5). Metal oxide nanoparticles are crucial in inorganic material investigation owing to their numerous applications in catalysis, energy technology,

data storage and coating fields. One of them, namely copper oxide (CuO), gained increasing attention for its eventual practices in many areas (6). Copper oxide (CuO) is one of potential p-type semiconductors and gains considerable attention due to its excellent physical, electrical, optical and magnetic properties (7). CuO is widely used in gas sensors, photovoltaic cells, electrochemical cells, magnetic storage media, light emitters, thermoelectric materials, heat transfer nanofluids, and for catalysis (8).

There are several methods used to synthesize $Cu_2(OH)_3NO_3$ and copper oxide (CuO) such as chemical precipitation, ultrasound assisted synthesis, polyol mediated synthesis, thermal decomposition and hydrothermal synthesis methods, and so on (1, 3, 6, 9, 10). In the literature, (3) have prepared mixed metal hydroxynitrate such as $Cu_2(OH)_3$ (NO_3 using $Cu(NO_3)_2{\cdot}6H_2O$, and urea as starting material, (9) studied ($Cu(NO_3)_2.2.5H_2O$) and ($Na_2B_4O_7.10H_2O$) as reactants and Span 60 as surfactant by precipitation method, (10) prepared uniform $Cu_2(NO_3)(OH)_3$ nanoparticles using $Cu(NO_3)_2.2H_2O$ and $NaHCO_3$ by polyol-mediated method,

In this study, copper hydroxynitrate ($Cu_2(OH)_3NO_3$) and copper oxide (CuO) were prepared from $Cu(NO_3)_2.3H_2O$ and $Na_2B_4O_7.10H_2O$ as reactants with the addition of SB12 as the surfactant by hydrothermal method. The obtained particles were characterized by XRD, TGA, FTIR, and SEM techniques.

MATERIAL AND METHOD

Materials

Commercially available $Na_2B_4O_7{\cdot}10H_2O$ (borax, Merck, 99%) and copper(II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$; Merck, 99.5%), 3-(N,N-dimethyldodecylammonio) propanesulfonate (SB12;Fluka, 97%) deionized water and absolute alcohol were used in the experiments. All of the chemicals were of analytical grade.

Synthesis

The experimental procedure was as follows: 50 mL 0.1 M borax, 40 mL 0.5 M $Cu(NO_3)_2$ solution and required amount of surfactant zwitterionic SB12 in between its critical micellar concentration (CMC) range were mixed completely for 10 minutes at 60 °C. The critical micellar concentration of the surfactant (SB12) was $1.2x10^{-3}$ M (11). The solution was transferred to a 100 mL Teflon-lined stainless steel autoclave, stamped, and kept at 180 °C for 24 h without stirring and then was allowed inherently to cool to room temperature. The obtained sample was filtered, washed with deionized water and absolute alcohol, then dried at 80 °C for 8h. The sample was calcined at 400 °C for 2h.

Characterization

The morphology and structure of the synthesized products were studied by X-ray diffraction (XRD), Fourier transform infrared (FTIR), thermal gravimetric analysis (TGA/DTA) and scanning electron microscopy (SEM) techniques. Phase compositions of powder samples before and after calcination were characterized by X-ray diffraction (XRD, Rigaku advance powder X-ray diffractometer, λ=1.54 A°).Thermal gravimetric analysis and differential thermal analyses (TGA–DTA) curves were simultaneously obtained on a NETZSCH STA 409 PC Luxx at a heating rate of 10 °C min^{-1} under nitrogen atmosphere in the temperature range from 30 to 1000 °C using Al_2O_3 as the standard material. Fourier transform infrared (FTIR) spectra were recorded in the 500–4000 cm^{-1} range, using Perkin–Elmer Spectrum One FTIR spectrometer. The structure and morphology of the samples were observed by a scanning electron microscope (SEM, Zeiss Ls-10).

RESULTS AND DISCUSSION

Using $Cu(NO_3)_2.3H_2O$ and $Na_2B_4O_7.10H_2O$ as reactants with the addition of SB12 as the surfactant at 180ºC by hydrothermal method was synthesized copper hydroxynitrate ($Cu_2(OH)_3NO_3$). Powder XRD was very important in the identification of the phase formation. Powder X-ray diffraction patterns of both copper hydroxide nitrate and sample obtained by its calcination at 400 °C are shown in Figure 1, section (a) of which shows the powder X-ray diffraction patterns of copper hydroxynitrate obtained by borax hydrolysis. In the XRD patterns of ($Cu_2(OH)_3NO_3$), successive reflections, up to at least the third order, indicate the lamellar structure and could be indexed to monoclinic crystal system space using the JCPDS No. 75-1779 file.

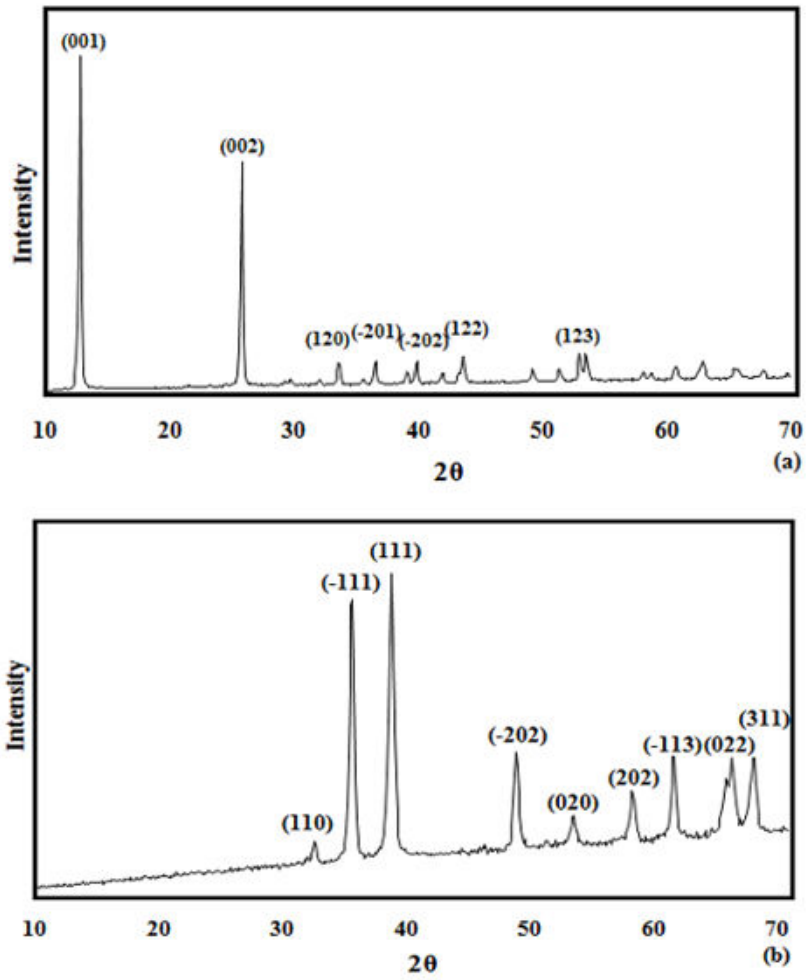

Figure 1. X-Ray diffraction of copper hydroxynitrate (a) raw and (b) calcined sample.

Fig. 1(b) shows the powder X-ray diffraction patterns of sample obtained by calcination at 400 °C of $Cu_2(OH)_3NO_3$. As can be seen from Figure 1(b), the decomposed product could be indexed to monoclinic phase of copper oxide (JCPDS No. 44-0706).

Thermal decomposition of layered hydroxynitrate follows dehydration, denitration, and disruption of layered framework under atmospheric conditions. The elimination of hydroxyl and nitrate groups from the precursors has great influence on the crystallinity of metal oxides, and new intermediate phase might also form during the disruption of the original structure.

TGA/DTA curves of $Cu_2(OH)_3NO_3$ shown in Figure 2. The total weight loss in the whole temperature range of 30–1000 °C is 33.26%, which is in good agreement with the theoretical value of $Cu_2(OH)_3NO_3$(33.6%). Meanwhile, most of the weight loss occurs within a narrow temperature range of 230–280 °C.

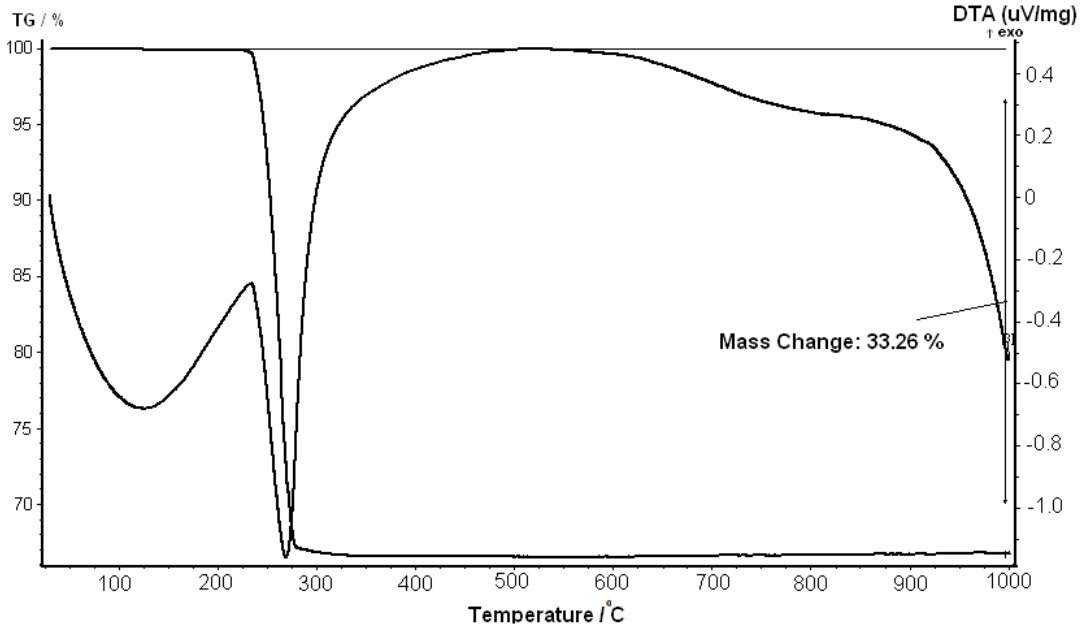

Figure 2. TGA/DTA curves of copper hydroxynitrate.

Thermal decomposition of copper hydroxynitrate occurs at single step in which dehydroxylation and decomposition of the nitrate in the interlayer space take place simultaneously leading to the destruction of the layered structure (Figure 2).

The copper hydroxynitrate undergoes decomposition in a single step producing CuO according to the equation:

$$Cu_2(OH)_3NO_3 \rightarrow 2CuO + HNO_3 + H_2O \qquad \text{(Eq. 1)}$$

It was shown that the results of TG/DTA curves was in agreement with the results obtained from the XRD analysis.

Fourier transform infrared (FTIR) spectroscopy analysis was carried out to identify the functional groups. FTIR results are given in Fig. 3.The peaks at 3539 and 3412 cm^{-1} belong to isolated and hydrogen bonded OH stretching peaks. The peaks at 1420 and 1347 cm^{-1} are asymmetric and symmetric stretching peaks of O-NO_2 respectively. The peak at 1046 cm^{-1} is connected to N-O stretching pulsation of monodentate O-NO groups. The peaks at 874, 771 and 665 $cm^{-1}$are due to bending vibrations of Cu-OH groups with different hydrogen bonds.

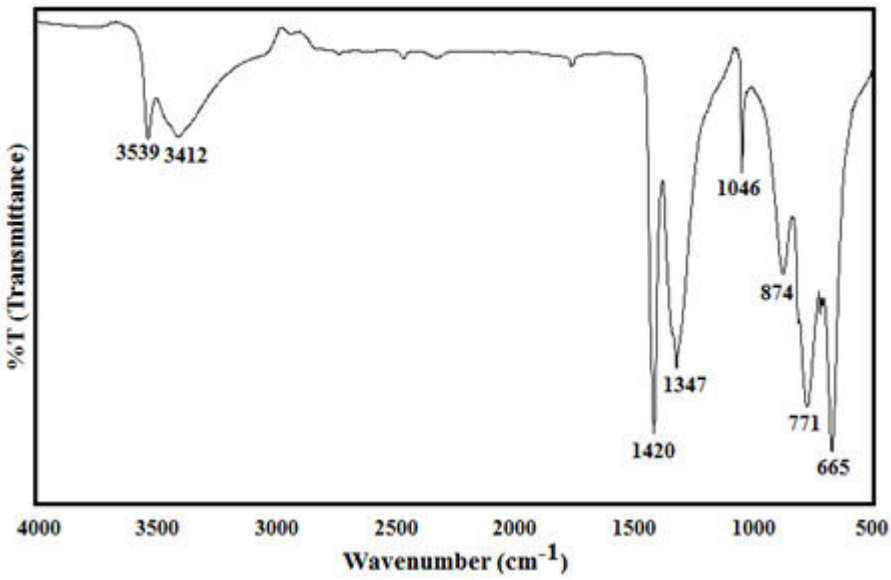

Figure 3. FTIR spectrum of copper hydroxynitrate.

Fig. 4 and 5 shows the scanning electron micrographs before and after calcination of obtained samples. It can be seen from Figure 4, copper hydroxyhydrate ($Cu_2(OH)_3NO_3$) exhibits well-defined and separated tabular particles with the micrometer-size elongated hexagonal plates. Their size was not accurately determined butSEM micrographs show that a 10 mm size is easily attained. The particles CuO obtained by calcination at 400 °C of $Cu_2(OH)_3NO_3$ are characterized by relatively different morphologies formed by disruption of hexagonal structure, which are displayed in the SEM micrographs in Fig. 5.

CONCLUSIONS

From the results that have been described above, some guidelines can be proposed concerning the production of copper hydroxynitrate ($Cu_2(OH)_3NO_3$) by a hydrothermal method starting from $Cu(NO_3)_2.3H_2O$ and $Na_2B_4O_7.10H_2O$ solutions.According to TG-DTA analysis, the synthesized products are seen that only a single sharp decomposition step, which is in accordance with a simultaneous dissociation of HNO_3 and H_2O. The FTIR analysis shows the samples have O-H, O-NO_2, N-O and Cu-OH group bands. In hydrothermal method at 180 °C synthesized the monoclinic copper hydroxynitrate ($Cu_2(OH)_3NO_3$)(gerhardite) hexagonal plate structure. On the other hand, working with the borax as a source of hydroxyl ions allows a slow and better controlled formation of the precipitate.

Figure 4. SEM image of copper hydroxynitrate.

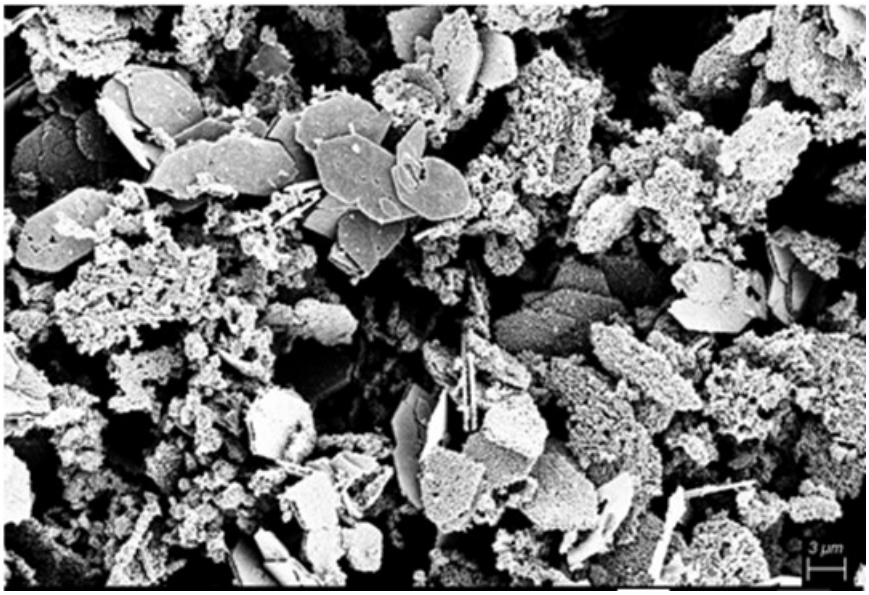

Figure 5. SEM image of copper oxide.

The present work has supplied an elementary and fast method to the micrometer-size well-defined elongated hexagonal plates of copper hydroxynitrate, which can be further processed to CuO structures. Particularly, the conversion of copper hydroxynitrate into CuO, which possess much more applications in vast technological fields, has also been demonstrated.

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Türkçe Öz ve Anahtar Kelimeler

HİDROTERMAL YÖNTEM İLE BAKIR HİDROKSİ NİTRATIN SENTEZ VE KARAKTERİZASYONU

Eda Keleş Güner[1] ve Abdulkadir Özer[2]

Öz: Yapılan çalışmada, hidrotermal yöntemle bakır nitrat $Cu(NO_3)_2.3H_2O$ ve boraks ($Na_2B_4O_7.10H_2O$) başlangıç maddeleri ile SB12 surfaktanı kullanılarak bakır hidroksi nitrat ($Cu_2(OH)_3NO_3$) ve bakır oksit (CuO) sentezlenmiş ve elde edilen ürünler XRD, FTIR, TG ve SEM teknikleri ile karakterize edilmiştir. XRD sonuçlarına göre, 180 ºC'de hidrotermal yöntemle elde edilen örneklerin monoklinik bakır hidroksi nitrat ($Cu_2(OH)_3NO_3$) oluştuğu ve 400ºC'de kalsinasyonu sonucunda tamamen bakır oksit (CuO)'e dönüştüğü görülmektedir. Elde edilen bakır hidroksi nitratların TG analiz sonuçlarına bakıldığında sentezlenen ürünün HNO_3 ve H_2O'un eş zamanlı ayrışmasından meydana geldiği görülmektedir. Sentezlenen ürünün FTIR analizlerinde O-H, $O-NO_2$, N-O ve Cu-OH gruplarının bantları tespit edilmiştir. SEM analizi sonuçlarından, SB12 surfaktan ortamında altıgen plaka şeklinde nano/mikro yapıda partiküllerden oluştuğu görülmektedir.

Anahtar kelimeler: Hidrotermal yöntem; boraks; bakır nitrat; bakır hidroksi nitrat; bakır oksit.

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