



## EFFECT OF CRYSTALLIZATION TIME ON HYDROTHERMAL SYNTHESIS AND PHYSICO-CHEMICAL CHARACTERIZATION OF CUO/ZNO/AL<sub>2</sub>O<sub>3</sub> NANOPOWDER

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### ABSTRACT

Hydrothermally synthesis of CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> nanopowder successfully carried out. The effect of crystallization time on product properties was observed and 6 h reaction time, based on powder XRD analysis and FESEM imaging, was selected as the best crystallization duration in range of 3-12 h. Nanopowders were characterized using XRD, FESEM, EDX mapping, FTIR, TG and BET techniques. The XRD patterns confirmed crystalline metal oxide formation. Good crystallinity of samples was observed with FESEM image which confirmed XRD analysis results. Scherrer equation calculations showed average crystallite size of 20 nm for products and FESEM images showed nano scale particles. The BES surface area measurement showed acceptable values for synthesized CZA samples. FTIR spectroscopy confirmed metal oxides formation during hydrothermal and calcination process. TGA results illustrated high thermal stability of the synthesized nanopowders.

### INTRODUCTION

Hydrothermal synthesis of nano scale material is a single step and easy route which produces crystalline powders. The term hydrothermal has a geological origin and now days implies to a chemical process in which reactions occur under high temperature in a closed system. Temperature increment leads to pressure rise in closed system and generates an intense condition which intensifies reactions [1-3]. Numerous effective parameters such as reaction temperature, precursor's concentration and type, reaction or crystallization duration and etc. affects products quality and features. Among these effective factors reaction duration or crystallization time has

the most important effect on hydrothermal process output [1]. Products crystallinity and particles size distribution considerably change with crystallization time. Crystalline metal oxides like CuO or ZnO has wide technological application. These semiconductor materials play very important rule as catalyst material in petrochemical industries. Nanostructured CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> (CZA) powder has been used as methanol synthesis catalyst from synthetic gas. Its admixed with an acid catalyst is also used for direct dimethylether (DME) synthesis [4-6]. CZA powder has been widely synthesized and studied using conventional methods like precipitation or impregnation [4-6].

In our recent work [7] the properties of hydrothermally synthesized CZA was studied. Perfect crystallinity and narrow size distribution of produced particles were observed. In this work we investigated crystallization time effect on hydrothermally synthesized CZA. Four CZA samples with atomic ratio of 6:3:1 were synthesized hydrothermally in 3 h reaction duration up to 12 h with 3 h incremental steps. The synthesized samples crystallinity was studied with powder XRD method. The morphology of particles was investigated using FESEM imaging. Surface area of nano-powder measured using nitrogen adsorption at 77 K and BET method; and physicochemical properties of products were studied with FT-IR technique. The thermo-gravimetric behavior of samples was investigated using TGA-DT analysis.

### MATERIALS AND METHODS

**Materials:** Copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Merck, extra pure), zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Merck, extra pure),

and aluminium nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Merck, extra pure) were used as CZA precursor; while sodium hydroxide ( $\text{NaOH}$ , Merck, pellet pure) was employed as alkaline precipitant. All of the reagents were used without further purification.

**Preparation and Procedures:** The CZA nano powder synthesized as explained in our recent work [7]. Figure 1 shows schematic diagram of CZA preparation steps. The precursor concentrations were adjusted to produce 6:3:1 atomic ratio of components. The metal salts were dissolved in deionized water to produce CZA nanocomposite with vigorous mixing. Sodium hydroxide was dissolved in deionized water under drastic stirring; then alkaline solution was added into transparent dark blue metal salt solution (solution color is due to high concentration of copper) and mixed for 20 minutes. Mixture becomes opaque immediately after alkaline addition. Opaque blue mixture was transferred into poly tetra fluoro ethylene (PTFE) lined stainless steel vessel and heated at  $180^\circ\text{C}$  for 3, 6, 9 and 12 h. Then vessel was cooled down naturally to room temperature. Dark brown product deposited in bottom of vessel was collected and washed with deionized water until pH reached to 7. Then cake dried at  $110^\circ\text{C}$  for 16 hrs and calcined in air at  $350^\circ\text{C}$  for 5 hours.

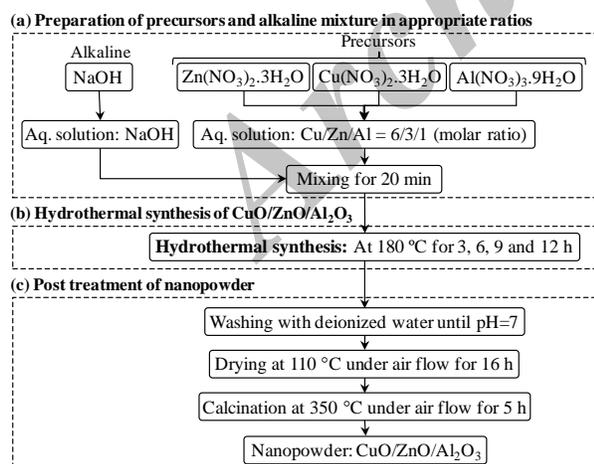


Figure 1

Schematic flow chart for the preparation steps of CZA nanopowder via hydrothermal method.

**Characterization Techniques:** Nanocomposite X-ray diffraction was carried out by *D5000 Siemens X-*

ray diffractometer (Cu K $\alpha$  radiation, 0.154056 nm) with a X-ray tube operated at 30 kV and 40 mA; average crystallite size was estimated using Scherrer algorithm and obtained XRD patterns. The relative crystallinity of samples was calculated with patterns integration. The morphology of sample was investigated using HITACHI 4160-s field emission scanning electron microscope. The physicochemical properties of samples were determined at room temperature using FTIR spectra, collected by a Unicam 4000 FTIR spectrometer using KBr plate. All the spectra were recorded over the 400-4000  $\text{cm}^{-1}$ . The BET surface areas of samples were determined by nitrogen adsorption at 77K and desorption at room temperature using a Quanta Chrome Chem-Bet 3000 analyzer which samples was degassed at  $200^\circ\text{C}$  for 30 min. Thermogravimetric properties (TGA-DTG) of samples was investigated using PerkinElmer Pyris Diamond apparatus. The sample temperature was linearly raised from room temperature to  $500^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$  under air flow.

## RESULTS AND DISCUSSIONS

**XRD Analysis:** Figure 2 shows obtained XRD patterns of as synthesized samples. Hydrothermally synthesized CZA nanopowders exhibited monoclinic crystallite system for copper oxide (JCPDS 01-080-1268) and hexagonal system for zinc oxide (JCPDS 01-076-0704), while as expected  $\text{Al}_2\text{O}_3$  was undetectable due to low loading and its high dispersion. As shown in figure, crystallization duration increment leads to higher peaks in patterns. The peaks sharpness implies to perfect crystallinity of samples; therefore crystallization time increment improves products crystallinity. Table 1 illustrates detail calculations of XRD data for CZA nanopowders. As can be seen in all samples, the CZA crystals are approximately in same range of size. The average crystallite size calculated for both CuO and ZnO is about 20 nm. So reaction duration has not considerable effect on crystallite size and only facilitates lattice planes extension and particle growth.

**FESEM Analysis:** The FESEM images of samples are shown in figure 3. From figure 3, it is obvious that increase in crystallization time leads to larger particles. The images in agree with XRD patterns depicts that higher reaction duration significantly increases particle size and to achieve perfect particle size distribution the crystallization time must be

optimized. As shown in second column of the Figure 3, particles synthesized in 6 h crystallization time have good uniformity and fairly size distribution. Also from XRD patterns, these particles have proper crystallinity.

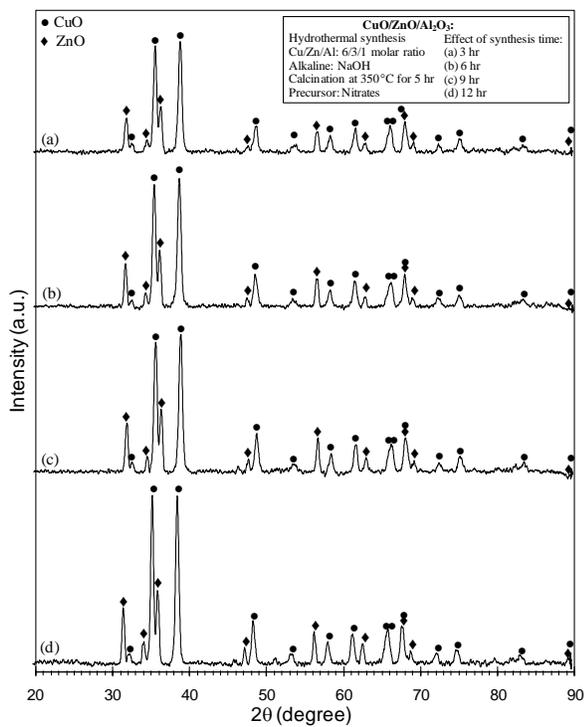


Figure 2

XRD patterns of synthesized CZA nanopowders at various crystallization times: (a) 3, (b) 6, (c) 9 and (d) 12 hr.

Table 1. Structural properties of synthesized CZA nanopowder via hydrothermal method.

Synthesis time	S <sub>BET</sub> (m <sup>2</sup> /g)	Crystallite size <sup>b</sup> (nm)		
		CuO <sup>c</sup>	ZnO <sup>d</sup>	Al <sub>2</sub> O <sub>3</sub> <sup>e</sup>
3	9	19.43	19.63	-
6	10	20.57	20.97	-
9	10	19.23	21.03	-
12	9	19.23	19.80	-

- a. Relative crystallinity: XRD pattern peak area.
- b. Crystallite size estimated by Scherre's equation.
- c. Crystallite phase: monoclinic (JCPDS: 01-080-1268)
- d. Crystallite phase: hexagonal (JCPDS: 01-076-0704)
- e. Crystallite phase: cubic (JCPDS: 00-004-0880)

**BET Analysis:** BET specific surface area analysis for CZA nanopowder results are illustrated in table 1. Approximately specific surface area of all is same. Generally, copper oxide and other composites with high copper content have low specific surface area because of favorability for bulk crystal formation. CZA

composite synthesized using other methods, such as co-precipitation, impregnation and sol-gel, may have specific surface area in the range of 30-60m<sup>2</sup>/gr [8]. This considerable increasing of surface area emanates from amorphous structure of powder. Since hydrothermally synthesized CZA nanopowder has completely crystalline and compact structure, a low surface area was anticipated, but its nano-scale structure leads to enhance the surface area. From data given in Table 1, it can be concluded that for hydrothermally synthesis of high copper content materials reaction time increment has not significant effect on product surface area.

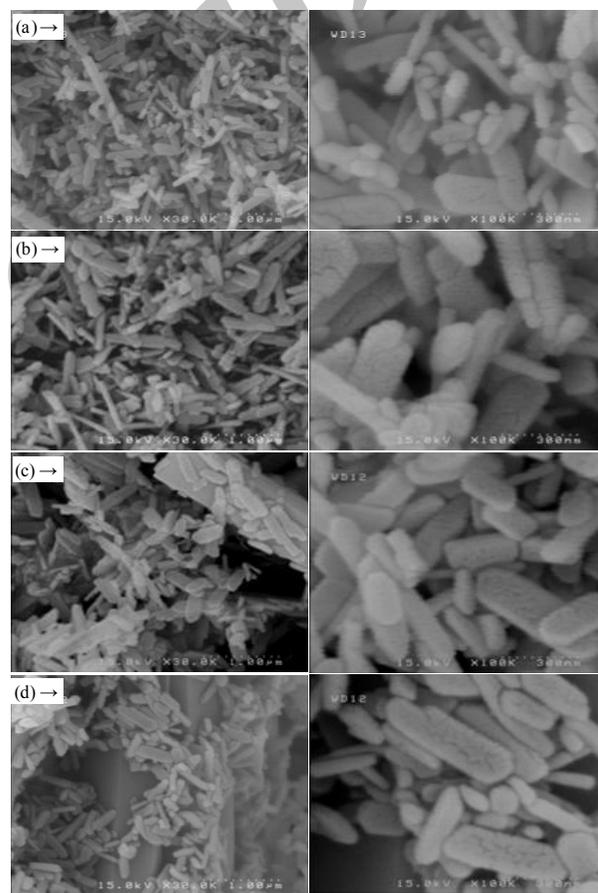


Figure 3

FESEM images of synthesized CZA nanopowders at various crystallization times: (a) 3, (b) 6, (c) 9 and (d) 12 hr.

**FTIR Analysis:** FTIR spectra of CZA nanopowder with crystallization time of 3, 6, 9 and 12 h are shown in Figure 4. Generally metal oxide (CZA) peaks can be classified as bellow:

peaks around  $512\text{ cm}^{-1}$  is the signature of ZnO existence [9, 10]; O-Cu-O bonding cause bending close to  $500$  and  $1384\text{ cm}^{-1}$  [11] and bending near  $582\text{ cm}^{-1}$  is identified to be the characteristic of  $\text{Al}_2\text{O}_3$  [12]. As shown in the Figure, the FTIR spectrums of samples contain main band for metal oxide, in the range of  $450\text{--}550\text{ cm}^{-1}$ , and this proves metal oxides production in hydrothermal process. Bending around  $1225\text{ cm}^{-1}$  and  $1740\text{ cm}^{-1}$  which seem only on sample b spectra corresponds to  $\text{CO}_2$  adsorption [13]; it may during FT-IR test sample was exposed to  $\text{CO}_2$  source.

The Figure 5 shows FTIR spectrum of the sample with 6 h crystallization time before (a) and after (b) calcination. The broad bands in the ranges of  $3300\text{--}3500$  and  $1200\text{--}1700\text{ cm}^{-1}$  correspond to O-H stretching and banding [[9, 14]; this proves metal hydroxide existence in sample ( $\text{Cu}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$ ) and calcination necessity to complete metal oxide production process (Figure 5-b). It must be noticed that strong bending corresponds to O-H bonding eliminates CuO peak near  $1400\text{ cm}^{-1}$  in non-calcined sample that appears clearly in FTIR spectra of calcined sample. Two peaks in the range of  $1200\text{--}1700\text{ cm}^{-1}$  deal with physically adsorbed  $\text{H}_2\text{O}$ .

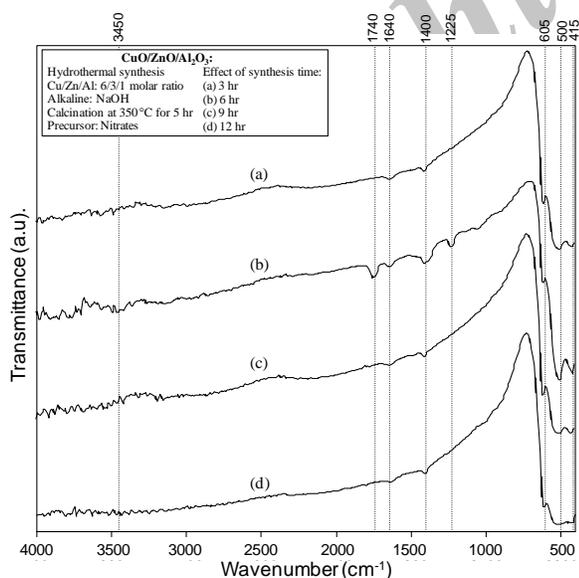


Figure 4

FTIR spectrum of synthesized CZA nanopowders at various crystallization times: (a) 3, (b) 6, (c) 9 and (d) 12 hr.

**TG-DTG Analysis:** TG-DTG results of the sample with 6 hr crystallization time before (a) and after (b) calcination are shown in Figure 6. The obtained TG curves can be divided into 3 zones. At the first zone (room temperature to  $150^\circ\text{C}$ ), the physically adsorbed water is desorbed. The smooth decreasing trend in calcined sample (b), and some intense trend in non-calcined sample (a), corresponds to water desorption. At the second thermal zone ( $150\text{--}400^\circ\text{C}$ ), a considerable weight loss can be seen in non-calcined sample around  $220^\circ\text{C}$ . This weight loss is clearly denoted by the derivate curve maxima which can be deduced conversion of metal hydroxide to metal oxide which take place at this zone. At the last zone ( $400\text{--}500^\circ\text{C}$ ), sample weight become stable and metal oxide formation reaction is terminated. The negligible weight loss of calcined sample (less than 0.5%) is due to desorption of physically adsorbed components.

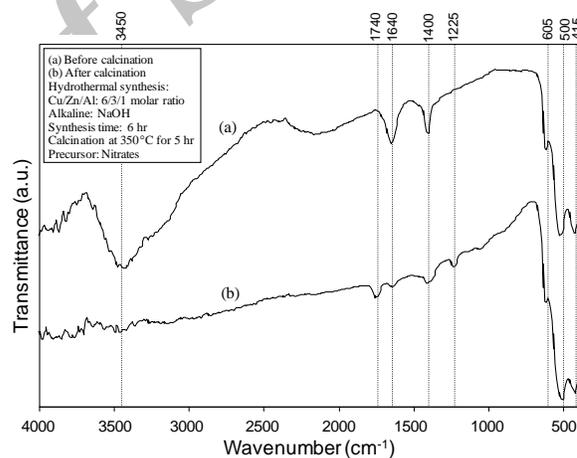


Figure 5

Effect of calcination temperature on FTIR spectrum of synthesized CZA nanopowder at crystallization time of 6 hr.

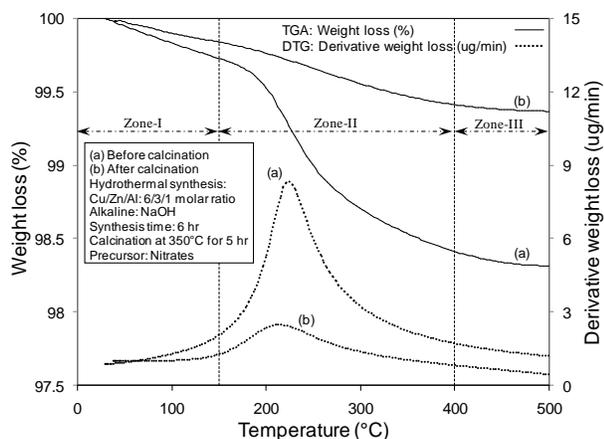


Figure 6

TG-DTG spectrum of synthesized CZA nanopowders at various crystallization times: (a) 3, (b) 6, (c) 9 and (d) 12 hr.

## CONCLUSIONS

The effect of crystallization time on physiochemical properties of  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  nanopowder was studied. The XRD patterns showed perfect crystallinity and nano scale particles for CZA samples synthesized hydrothermally. FESEM images confirmed the results of XRD patterns and also showed a fair particle size distribution for samples. The BET surface area measurements revealed that CZA nanopowder have an acceptable specific surface area in contrast with their compact and crystalline structure. FTIR spectroscopy confirmed desired metal oxides formation in product. TGA-DGT analysis showed good thermal stability of product. 6 h was selected as the optimum crystallization duration for hydrothermally synthesis of CZA nanopowder.

## ACKNOWLEDGMENTS

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