

Inverse Co-precipitation Synthesis of Copper Chromite Nanoparticles

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ABSTRACT: In this study, copper chromite (CuCr_2O_4) nanoparticles was prepared by inverse co-precipitation method. In this method, cupric nitrate trihydrate, ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and chromium nitrate nonahydrate, ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) with a mole ratio of 1:2 were used. Characterization of CuCr_2O_4 nanoparticles was performed by Fourier Transform Infrared Spectroscopy (FT-IR), Raman Spectroscopy, X-ray Diffraction Spectroscopy (XRD), Thermo-Gravimetric/Differential Scanning Calorimetry (TG-DSC), and Field Emission Scanning Electron Microscopy (FE-SEM). The results show that CuCr_2O_4 crystal can be obtained at temperature 520°C . Also, phase structure of the CuCr_2O_4 depends on both Cu:Cr molar ratio and temperature in the starting reactants. Based on this method and under optimum conditions, the temperature for calcination (520°C), the crystallite size of nanoparticles (18 nm), the spherical structure particles (30 to 70 nm) were obtained.

KEY WORDS: Copper chromite; Nano particle; Inverse co-precipitation.

INTRODUCTION

Spinels of $\text{M}^{2+}\text{M}^{3+}_2\text{O}_4$ type (for example CuCr_2O_4) attract the research interest due to their unique properties and multiple applications in various fields [1].

The copper chromite (CuCr_2O_4) has wide commercial application such as oxidation [2], hydrogenolysis [3], alkylation [4], clean energy carrier [5], synthesizing methanol [6], sensors [7], semiconductors [8], catalyst, pigment, and drug [9].

Different methods were reported for the synthesis of chromite spinels including wet chemical, micro emulsion, and sol-gel processes [10]. Kawamoto *et al.* [11] have prepared copper chromite via both ceramic and

co-precipitation methods. Patil *et al.* [12] have prepared copper chromite powder via electrochemical method. Prasad *et al.* [9] have discussed various applications and preparation methods of copper chromite catalysts. Xiao *et al.* [13] have controlled preparation and characterization of CuCr_2O_4 catalysts for hydrogenolysis of concentrated glycerol. However, there is no report for preparation of copper chromite via Inverse Co-Precipitation method. Therefore, in this study, CuCr_2O_4 nanocatalyst was synthesized by inverse co-precipitation method and characterized by spectroscopic and microscopic techniques.

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EXPERIMENTAL SECTION

The used reagents and analytical instruments include cupric nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), chromium nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, India Co LOBA Chemie), FT-IR (Perkinelmer, USA), FE-SEM (Hitachi S416002, Holland), XRD (Model: Xpert-MPD, Co: Philips, Holland, λ : 1.74056), and TG-DSC (Metler Toledo, Switzerland). All of the used chemicals in the experiments were of analytical purity. The CuCr_2O_4 catalysts were synthesized by inverse co-precipitation route.

In a typical synthesis procedure, 0.005 mole $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.01 mole $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 100 mL deionized water to obtain a mixed metal nitrate solution. Appropriate amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in stoichiometric ratio of Cu: Cr = 1: 2 were dissolved in deionized water. After stirring for 60 min, the metal nitrate solution was added to the ammonia solution. The pH of the solution was adjusted to 9.0 by slowly dropping metal nitrate solution to the ammonia solution. The fine precipitates of copper chromate were filtered, washed with distilled water, and dried at 110 °C. Then, the powder was calcined at 400, 520, and 800 °C in the air for 2 h at a heating rate of 20°C/min to obtain the final black CuCr_2O_4 nanoparticles).

RESULTS AND DISCUSSION

CuCr_2O_4 Spinel formation mechanism

The probable chemical reactions in the reaction medium are as follows [14]:

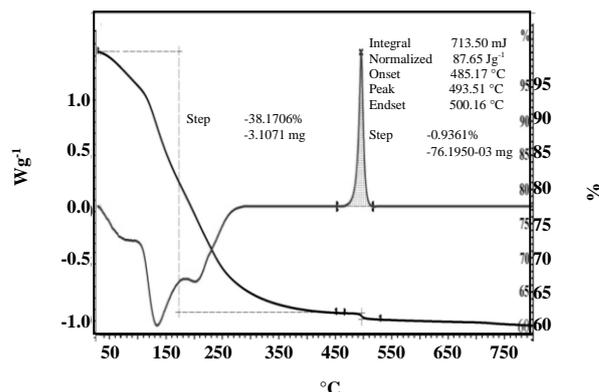
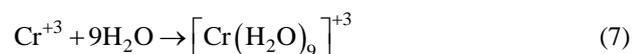
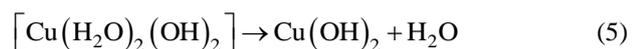
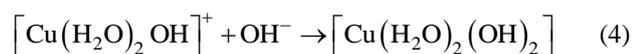
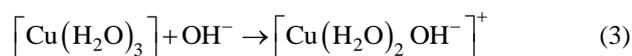
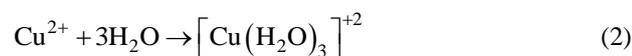
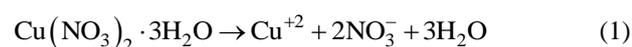
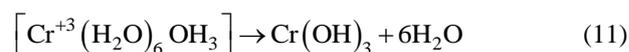
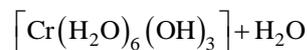
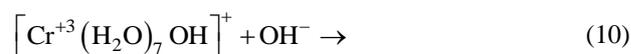
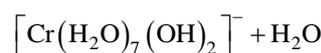
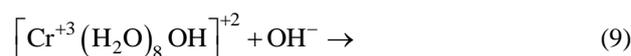
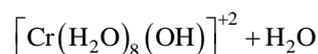
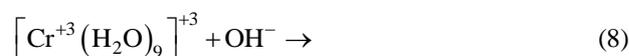
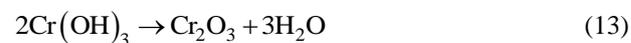


Fig. 1: TG-DSC curves of the synthesized Cu-Cr precursors via inverse co-precipitation method.



Then, in calcination step, water will be exited from hydroxides by two Reactions of (5) and (11) and the product will be CuO and Cr_2O_3 based on the following reactions:



Finally, during calcination and diffusion process the overall reaction will be:



Thermal analysis

Fig. 1 shows the thermal decomposition procedure of the as-obtained Cu-Cr precursors by TG-DSC. Over the temperature range from ambient to 400 °C, there is a continuous weight loss (about 39%) in the TG curve.

The change of weight-loss becomes tiny when the temperature is further increased from 400 to 800 °C. Three discrete regions of thermal decomposition can be observed in the DSC curve at 100-150, 200-300, and 400-500 °C, respectively. The first weight-loss corresponds to the elimination of water. The second weight-loss region can be related to the pyrolysis of NO_3^- to give an amorphous inorganic phase. Subsequently, elimination of the remaining materials occurs in the temperature range from 400 to 500 °C and crystallized CuCr_2O_4 inorganic phase is simultaneously formed.

Crystal structure analysis

Fig. 2 presents the variation of XRD patterns of CuCr_2O_4 sample, prepared via inverse co-precipitation reaction method calcined at 400 °C. It can be observed that the materials calcined at 400 °C are amorphous, while the main planes of (211) and (202) referring to the spinel CuCr_2O_4 . For the sample calcined at 520 °C for 2 h (Fig. 3), all the diffraction peaks can be readily indexed to pure spinel CuCr_2O_4 phase. The wide and weak diffraction peaks are indicative of a very fine particle size of the as-synthesized sample at 520 °C. When the calcination temperature was 800 °C (Fig. 4), intensities of all the diffraction peaks gradually increase and the peak width gradually becomes narrower. No secondary phase diffractions are found in the XRD patterns, which reveals that the particle size increases and the crystallinity improves with temperature while remaining single phase of spinel CuCr_2O_4 . As the results show, the samples calcined at 520 °C are more favorable due to the XRD patterns (Fig 3).

As shown in Fig. 3, the patterns can be readily referred to copper chromite (JCPDS no. 005-0657). In the pattern assigned to copper chromite, diffraction peaks at around 21.64 °, 34.41°, 36.23°, 41.06°, 44.06°, 49.56°, 54.72°, 57.15°, 62.93°, 66.23°, 68.48°, 72.74°, 76.95°, 78.97°, and 83.06° correspond to the (101), (002), (112), (211), (202), (220), (301), (312), (321), (303), (400), (411), (402), and (420) reflections, respectively. The large peak widths are ascribed to the formation of nanosized particles of CuCr_2O_4 . No impurity phases were detected in the XRD patterns. After performing the XRD experiments, the mean crystallite sizes (D) of nanopowders were calculated by Scherrer Formula [15-18] as follows:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (15)$$

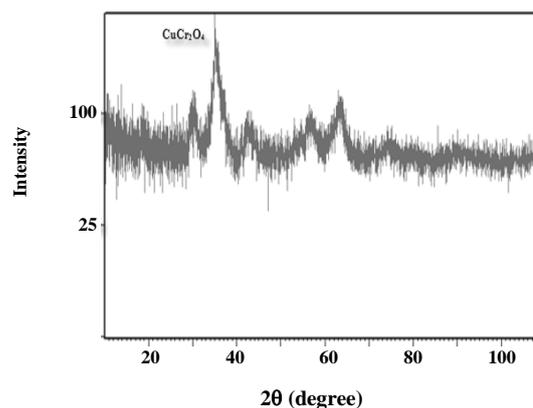


Fig. 2: XRD patterns of the CuCr_2O_4 sample, prepared via inverse co-precipitation reaction method calcined at 400 °C.

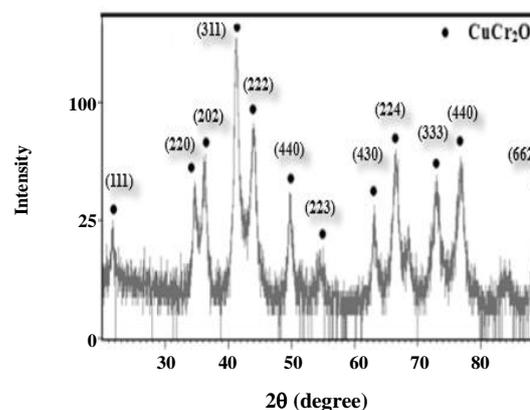


Fig. 3: XRD patterns of the CuCr_2O_4 samples via inverse co-precipitation reaction method calcined at 520 °C.

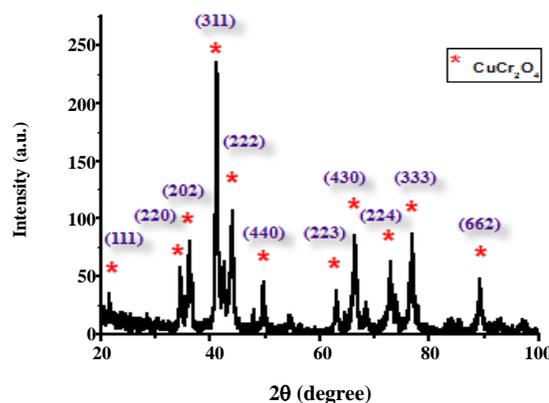


Fig. 4: XRD patterns of the CuCr_2O_4 nanocatalyst calcined at different temperatures for 2 h. (a) 800 °C.

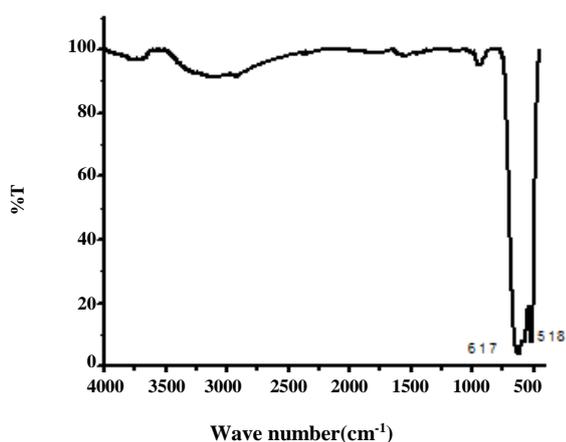


Fig. 5: FT-IR of the copper chromite nanocatalyst synthesized by inverse co-precipitation method calcined at 520 °C.

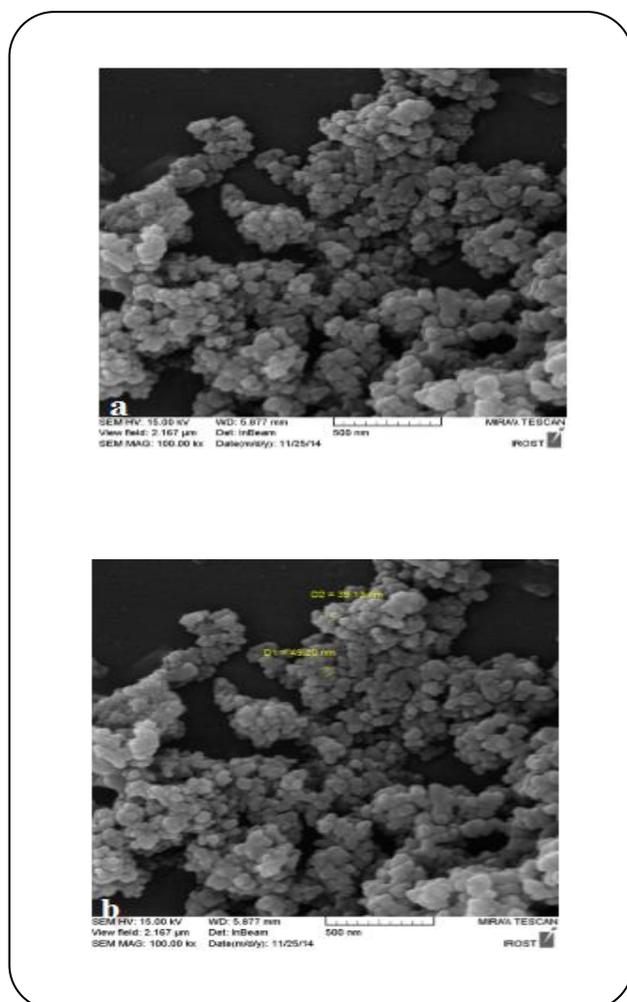


Fig. 6: FE-SEM image of CuCr_2O_4 nanocatalyst prepared by precursor mole ratio of 1:2 and calcination at 520 °C.

Where; β is the width of the highest observed diffraction line at its half-intensity (in radians), λ is the X-ray wavelength of the radiation, and θ is the Bragg diffraction angle. The mean crystallite size, was calculated by Scherrer equation using the (211) peak ($2\theta = 41.06$), is 18 nm.

FT-IR analysis

The Fourier transform infrared (FT-IR) of CuCr_2O_4 is shown in Fig. 5. Transition metal chromite spinel is expected to exhibit the characteristic absorption bands in the short wave region around 617-518 cm^{-1} due to M-O and Cr-O stretching frequencies, respectively. The IR band for chromite sample could be attributed to the stretching vibration of the Cr-O bands of chromium atoms in the tetragonal environment of the O atom. It can be seen that all the samples showed characteristic CuCr_2O_4 absorption bands at 617 and 518 cm^{-1} which refer to the $\text{Cr}_2\text{O}_4^{-2}$ group [19].

Morphologies

Fig. 6 depicts the FE-SEM micrographs of the powders calcined at 520 °C. The micrograph in Fig. 6 shows the formation of powder consisting of spherical structure particles with an average particle size of 72 nm.

CONCLUSIONS

The following results were obtained.

- 1- The inverse co-precipitation method is successful for nanocrystalline copper chromite preparation.
- 2- The optimum temperature for calcination was 520 °C.
- 3- The crystallite size of nanoparticles was determined to be 18 nm.
- 4- FT-IR showed a $\text{Cr}_2\text{O}_4^{-2}$ group formation in the final product.
- 5- FE-SEM micrographs show the spherical structure particles with an average particle size of 30 to 70 nm.

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