A Green Approach to Fabricate CuO Nanoparticles from Low Cost Raw Materials

H. Abdizadeh¹, H. R. Baharvandi², M.A. Tadjrishi³, H. Nami⁴ and M.A. Baghchesara⁵*

Abstract—Nanostructured CuO powders have been synthesized using chemical methods. Ammonium oxalate and copper nitrate were used as the precursor materials. The weight ratios of the raw materials (ammonium oxalate/copper nitrate) were 1.1, 1.2, 1.3, and 1.4. As a result of chemical reaction (between them), copper oxalate was synthesized. Produced samples were analyzed by XRD and SEM. The results show that the best ratio (for ammonium oxalate/copper nitrate) is 1.2. Produced copper oxalate powder was heated at 600, 700 and 800°C. The final product was CuO nanopowder. XRD studies indicate that the highest ratio of Cu₂O to CuO was observed in the specimen heated at 700°C.

Keywords—CuO, nano, synthesis, oxalate.

I. INTRODUCTION

Recently, nanostructures of ceramics have been attracted considerably due to the unique physical properties for the applications, which are quite different from those of bulk phases [1]. The synthesis of inorganic materials of high quality, specific size and morphology is a key aspect in the development of new materials in fields such as catalysis, medicine, electronics, ceramics, pigments and cosmetics [2–5]. The synthesis step is decisive for particle properties such as the primary particle size, morphology, crystallinity and purity. These in turn determine the product properties and the quality of the end product [6].

Copper oxide nanopowder is a black and incombustible material which is insoluble in water, but soluble in acids. This material has been used in various applications such as microelectronic, microcircuits, nanowires, microbacteria and nanofluids. Copper oxides, especially, which are p-type semiconductor have been widely used as heterogeneous catalysts in oxidizing processes of organic synthesis [7,8]. It is also used in polymers to increase their electrical conductivity, as well as in car industries to reduce pollution, and so on. One of the most important applications of this powder is replacement of expensive catalysts such as platinum and palladium. In the present work, CuO nanopowder was synthesized using cheap organic raw materials [9–18].

In this work we have tried to produce the precious nano size copper oxide powder from ammonium oxalate and copper nitrate, the low cost industrial materials by chemical synthesis and pyrolysis.

II. EXPERIMENTAL PROCEDURE

The starting material was ammonium oxalate with the purity of 99% and copper nitrate with the purity of 99%. These materials were mixed according to the weight ratios of (NH₄)₂C₂O₄/Cu(NO₃)₂ equal to 1.1, 1.2, 1.3, and 1.4, then they were reacted together at ambient temperature and under atmospheric pressure. As a result of chemical reaction, blue sediment consisting of copper oxalate was formed. Chemical reaction between ammonium oxalate and copper nitrate is performed according to the following equation:

\[
(\text{NH}_4)_2\text{C}_2\text{O}_4 + \text{Cu(NO}_3)_2 \rightarrow \text{CuC}_2\text{O}_4 + 2\text{NH}_4\text{NO}_3
\]

Ammonium nitrate (2NH₄NO₃) is soluble in water. Therefore, the sediment was washed several times with distilled water; then it was dehydrated with centrifuge and dried at 150°C, subsequently.

The phases which have been formed during chemical treatment were measured by a powder X-ray diffractometer (XRD) (Philips Xpert pro). The specimen with highest copper oxalate yield was identified as the optimum sample. This sample was studied with DTA and TGA up to 850°C to determine its phase transition behavior. The optimum sample was heated at 600, 700, and 800°C for 1 hr. The size and microstructure of the particles were identified by a Scanning Electron Microscope (SEM) (Cam Scan MV 2300).

III. RESULTS AND DISCUSSION

X-ray diffraction patterns of the produced samples with different weight ratios are shown in figure (1). As it can be seen in the patterns, the reaction products are identical in all of the trials. However, their amounts are different. The (NH₄)₂C₂O₄ (ammonium oxalate) has not been detected in any of the samples indicating that ammonium oxalate was consumed completely in all ratios. The patterns also show that

1,3,4,5 Hossein Abdizadeh, Mohammad Ali Tadjrishi and Haled Nami, School of Metallurgy and Materials Engineering, University of Tehran, Tehran-Iran (e-mail: abdizade@ut.ac.ir).
2 Hamid Reza Baharvandi, Malek Ashtar University of Technology, Tehran-Iran (e-mail: baharvandee@yahoo.com).
5 Mohammad Amin Baghchesara, Department of Metallurgy and Materials Engineering Masjed Soleyman Branch, Islamic Azad University, Masjed Soleyman, Iran. (corresponding author to provide phone: (+98) 919-4798823; fax: (+98)21-88006076; e-mail: amsara2000@Gmail.com).
existed in the products, due to the presence of water in the reaction environment. Comparison between pattern (1-b), (produced sample with weight ratio of 1.2 for \((\text{NH}_3)_2\text{C}_2\text{O}_4\) to \(\text{Cu} (\text{NO}_3)_2\)) with patterns (1-a), (1-c) and (1-d) (produced samples with weight ratios of 1.1, 1.3 and 1.4) shows that maximum amount of copper oxalate \((\text{CuC}_2\text{O}_4)\) and minimum amount of copper nitrate \((\text{Cu(NO}_3)_2)\) (the optimum condition) were resulted at weight ratio of 1.2.

Figure 2-a shows the micrograph of oxalate particles with ratio \((\text{NH}_4)_2\text{C}_2\text{O}_4/\text{Cu(NO}_3)_2\)=1.3. The size of oxalate particles is less than 100 nm but they are in agglomerate shape. The micrograph of the same particles treated at 800°C is shown in figure 2-b. It can be seen that the particle size is about 80-140 nm.

Figure (3) presents the XRD patterns of the produced sample with weight ratio of 1.2, which were heated at 600, 700 and 800°C. The patterns indicate that synthesized powder consists of \(\text{CuO}\) and \(\text{Cu}_2\text{O}\). As the patterns show, the specimen heated at 700°C has the highest ratio of \(\text{Cu}_2\text{O}\) to \(\text{CuO}\). The amount of \(\text{CuO}\) is increased with temperature decreasing to 600°C, while the amount of \(\text{Cu}_2\text{O}\) is decreased with temperature decreasing. It can be expected that the \(\text{CuO}\) amount increases with further temperature decreasing. The amount of \(\text{Cu}_2\text{O}\) and therefore the ratio of \((\text{Cu}_2\text{O}\) to \(\text{CuO})\) are decreased with temperature increasing up to 800°C. It seems that the main reason for this behavior is reduction of \(\text{Cu}^{2+}\) to \(\text{Cu}^{+}\) by existing carbon. Equations 2-4 show the possible chemical reactions which may occur in this process.

$$
\begin{align*}
4\text{CuO} + \text{C} & \rightarrow 2\text{Cu}_2\text{O} + \text{CO}_2 : \Delta G^{298}_\text{rxn} = -158.8732\text{KJ/mol} & (2) \\
2\text{CuO} + \text{C} & \rightarrow \text{Cu}_2\text{O} + \text{CO} : \Delta G^{298}_\text{rxn} = -19.351\text{KJ/mol} & (3) \\
2\text{CuO} + \text{CO} & \rightarrow \text{Cu}_2\text{O} + \text{CO}_2 : \Delta G^{298}_\text{rxn} = -139.5222\text{KJ/mol} & (4) \\
\text{C} + \text{CO} & \rightarrow 2\text{CO} : \Delta G^{298}_\text{rxn} = 120.0818\text{KJ/mol} & (5)
\end{align*}
$$

Reactions 2 - 4 are thermodynamically possible. However, reaction 5 (named as Bodward reaction) is not thermodynamically possible at temperatures lower than 900°C [19].

DTA/TG patterns are shown in figure (4). The patterns indicate that the process contains some reactions at 280°C to 380°C. The abovementioned reactions are completed at 800°C. Therefore, reactions 2 to 4 perform during the process and \(\text{Cu}^{2+}\) changes to \(\text{Cu}^{+}\) throughout pyrolysis.
The microstructures of the CuO powders (different weight ratio of starting materials), synthesized at 800°C, are shown in figure 2-b illustrating the particle size of the products in range of 80 – 140 nm. Due to high surface area of powder and therefore their high electrostatic energy, they are agglomerated.

**IV. CONCLUSION**

1) The best result was obtained with weight ratio of 1.2. In this condition, the amount of copper oxalate (CuC₂O₄) was maximum, while the amount of copper nitrate (Cu(NO₃)₂) was minimum.

2) The synthesized powder consists of CuO and Cu₂O. The highest ratio of Cu₂O to CuO was observed in the specimen heated at 700°C.

3) The effect of weight ratio of (NH₄)₂C₂O₄/Cu(NO₃)₂, on the relative amount of Cu₂O to CuO is insignificant.

4) The particle size of synthesized powder is in the range of 80 – 140 nm.

**REFERENCES**