An experimental study on thermal decomposition of microwave synthesized Cu$_2$(OH)$_3$Cl to copper oxide nanoparticles

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Abstract
This work presents the thermal decomposition of dicopper chloride trihydroxide [Cu$_2$(OH)$_3$Cl] into a stable phase of copper oxide under nitrogen atmosphere. A dedicated single-mode sealed-vessel microwave reactor is used to synthesize the precursor, Cu$_2$(OH)$_3$Cl. Based on the thermogravimetric (TG) curve, Cu$_2$(OH)$_3$Cl is subjected to pyrolysis at different temperatures in the range of 250°C to 900°C in a tubular furnace, mimicking the TGA operating conditions. The resulting sequential products are investigated using powder x-ray diffraction technique to understand the fundamental chemical and the structural changes of the precursor during the thermal decomposition process. Further, transmission electron microscopy studies of the precursor, as well as pyrolyzed samples, their stability under e-beam, and associated phase transitions of copper oxide, are also presented.

Introduction
The current research in the synthesis of inorganic nanomaterials is driven by the fact that the physical and chemical properties of these materials can be tailored to meet the requirements of the intended application by varying the particle size and shape [1, 2]. However, the subtle control of particle size and shape of the final nanomaterials is a challenging task and depends upon many parameters including synthesis route [3]. In this regard, the liquid-phase synthesis techniques are believed to be more flexible than gas-phase processes. These techniques include co-precipitation, hydrolytic as well as non-hydrolytic sol-gel processes, hydrothermal or solvothermal methods, template synthesis and biomimetic approaches [4–7]. In recent times, microwave-assisted liquid phase routes to synthesize inorganic nanomaterials have received much attention due to several advantages compared to conventional heating, including energy efficiency, higher yield, fewer byproducts, short reaction times, improved reproducibility, and remarkable control of reaction parameters [8, 9]. It is theoretically possible to combine microwave irradiation with any of liquid-phase synthesis techniques. Consequently, this idea provides exciting opportunities as well as unique challenges for the synthesis of inorganic nanomaterials.

Nano-sized copper oxide is one of the most attractive inorganic nanomaterials. Copper oxide nanomaterials find numerous applications in various fields including catalysis, medicine, energy generation and storage, electronics, environmental remediation, food technology, chemical sensors and heat transfer [10–17]. Thousands of publications related to synthesis, characterization, and applications of copper oxide nanostructures and nanoparticles can be found in the literature. However, much of the publications deal with liquid-phase synthesis techniques. Many other publications related to microwave synthesis have employed a domestic microwave oven as a heating source. Domestic microwave ovens are considered inferior to dedicated microwave equipment in terms of safety and parameter control. The physical and chemical properties of copper oxide nanomaterials are mainly dependant on the synthesis route [18]. In particular, the nature of the precursor and conditions of pyrolysis or calcination are the main governing factors [19].

In light of these aspects, the present work employed a dedicated single-mode sealed-vessel microwave reactor to obtain the precursor. The precursor, dicopper chloride trihydroxide [Cu$_2$(OH)$_3$Cl], was then
characterized by electron microscopy and powder x-ray diffraction techniques. The precursor transforms into copper oxide nanoparticles upon pyrolysis. In order to optimize the pyrolysis temperature, the following protocol was used. A known quantity of precursor was subjected to simultaneous thermogravimetry and differential thermal analysis (TG-DTA). Based on thermal decomposition profile thus obtained, the fresh precursor sample was then subjected to pyrolysis under inert N₂ atmosphere for 2 h using a tubular furnace at series of temperatures separately (250 °C, 350 °C, 400 °C, 500 °C, 700 °C and 900 °C). The resulting products were then analyzed using powder x-ray diffraction technique.

Materials and methods

Analytical grade chemicals and the ultrapure water of type 1 obtained from Milli-Q have been used throughout the experiment. Copper chloride dihydrate (CuCl₂ 2H₂O) was procured from Merck (India) and urea, ethylene glycol was procured from Fischer Scientific International, Inc.

Synthesis of copper oxide nanoparticles

The synthesis of copper oxide nanoparticles involves two main steps. In the first step, Cu₂(OH)₃Cl was synthesized from 0.1 M CuCl₂ 2H₂O stock solution through homogeneous precipitation reaction using a dedicated microwave reactor (Anton Paar, Monowave 200). The reactor is equipped with an infra-red (IR) sensor for temperature measurement and is capable of controlling the pressure inside the sealed vessel by regulating MW power output. Appropriate quantities of CuCl₂ 2H₂O and urea (1:5 molar ratio) were dissolved in a mixture of ethylene glycol and water (3:1 volume ratio) to obtain the 0.1 M CuCl₂ 2H₂O stock solution. The sealed glass vial (G30) containing a known volume of stock solution (~20 cm³) and a magnetic stir bar was kept inside the reactor chamber. The reaction was programmed to 150 °C using heat in time option for 15 min. After 15 min, the compressed air was passed into the chamber to cool the vial. During the reaction, the dark green solution turned into dark blue with a greenish precipitate. The precipitate was subjected to centrifugation (at 7000 rpm)—washing cycle for several times. It was then dried at laboratory temperature (~30 °C) to obtain the precursor.

In the second step, the precursor obtained in the first step was pyrolyzed at different temperatures as explained in section 1.

Characterization techniques

The powder x-ray diffraction (PXRD) patterns were recorded on a Bruker D8 ADVANCE ECO x-ray diffractometer equipped with a Cu Kα radiation source (0.154 nm). Simultaneous measurements of thermogravimetry and differential thermal analysis (TG-DTA) were performed using Shimadzu thermal instrument (DTG-60). A known quantity of precursor was heated at a rate of 10 °C min⁻¹ under inert atmosphere (N₂ at a flow rate of 50 cm³ min⁻¹) from 30 °C to 900 °C. The surface morphology of samples was studied using scanning electron microscope (SEM) images, which were obtained from Carl Zeiss, Neon 40 FESEM instrument coupled with an energy dispersive x-ray (EDX) spectroscopy (INCA, Oxford). The sample was dispersed in ultrapure water. Few drops of dispersion were allowed to dry on a clean Si substrate and this was used as an SEM specimen. Transmission electron microscopy (TEM) studies were carried out in a 200 keV JEOL 2010 machine. The specimen was prepared by placing a drop of dispersion on a 300-mesh carbon-coated copper grid and allowed to dry. Fourier transform infrared ray (FTIR) analysis (Perkin Elmer FTIR spectrum 2) was carried out by recording the spectrum in the range of 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹.

Results and discussion

Figure 1(a) shows the scanning electron micrograph of the precursor. The precursor appears to be an aggregate of loosely bound micron-sized faceted particulates. It seems to be unstable under the electron beam as the image shows poor contrast and streaks. This feature is more evident in the TEM image as a higher energy beam impinges on the surface of particulates (figure 1(c)). The EDS spectrum (figure 1(b)) confirmed the presence of copper, oxygen, and chlorine with an additional Si signal from the substrate used for dispersion.

The PXRD pattern of the precursor is shown in figure 2. The pattern corresponds to paratracamite, Cu₂(OH)₃Cl (PDF Number 01–087–0679). The peaks at 17.6° and 32.4° indicate that the material also contains atacamite polymorph in little quantity (PDF Number 00–025–0269). Further analysis using Diffraction Eva, XRD software, showed about 68% crystallinity. The average size of crystallites, calculated using Scherrer formula, was found to be around 39 nm. However, SEM analysis revealed the presence of clusters having an
average size in the micrometer range (figure 1(a)). Hence, it can be suggested that the material essentially consists of clusters of tiny nanocrystallites being embedded in the amorphous matrix. As already mentioned, these larger micron-sized clusters are unstable and susceptible to structural as well as phase transitions in the presence of an electron beam, an external source of energy. This is confirmed by TEM analysis, which uses higher energy beam compared to SEM technique. The SAED pattern in figure 2 shows several peaks. Major reflections designated as ‘A’ correspond to paratacamite phase. Other reflections designated as ‘B’, ‘C’ and ‘D’ correspond to Cu$_4$O$_3$, CuO, and Cu$_2$O phases of copper oxide. This suggests that the precursor material transforms into different phases of copper oxide under the electron beam.

The above observation can be justified as follows. It is well known that a high energy electron beam generates a considerable amount of localized heat at the level of nanoscale. The rise in temperature could be in the range of 100 s of degrees Celsius. In other words, for a thermally unstable material, the electron beam might act as a miniaturized heating source similar to those used for pyrolysis in chemical synthesis. In the present case, paratacamite has a rhombohedral structure involving loosely bound chlorine atoms and interconnecting hydrogen bonds [7]. Consequently, it exhibits low melting point (250 °C). Hence, it transformed into copper oxide types upon exposure to electron beam, even for a few seconds.

These results and discussions signify the conditions of pyrolysis conditions to obtain copper oxide nanoparticles. Hence, the precursor was investigated by thermogravimetric analysis. Figure 3 shows the TGA-DTA curves of Cu$_2$(OH)$_3$Cl. The TGA curve shows a multi-step decomposition. The first step, corresponding to a 13% weight loss, was observed in the temperature range of 280 °C to 305 °C. In the second step, about 6% weight loss was observed in the temperature range of 450 °C to 466 °C. The DTA curve exhibited two sharp endothermic peaks corresponding to these two steps of decomposition. Further, the TGA curve showed a relatively broader step in the temperature range of 580 °C to 643 °C, corresponding to 23% weight loss. The absence of corresponding peak in the DTA curve might be because of no thermal effect being associated with this step process or the DTA instrument might not have been sensitive enough to detect the large gradual decomposition process.
In order to gain insight into the influence of pyrolysis conditions on nature of final product, the fresh precursor sample was subjected to pyrolysis at different temperatures, namely 250 °C, 350 °C, 400 °C, 500 °C, 700 °C and 900 °C using a tubular furnace under inert N₂ atmosphere. The resulting products were analyzed using the PXRD technique and the PXRD patterns are shown in figure 4. The precursor exhibited both paracetamite and atrachite polymorphs with 68% crystallinity as already discussed. Pyrolysis at 250 °C has not produced any significant changes in the PXRD pattern of resulting material compared with that of the precursor. When the precursor sample was pyrolyzed at 350 °C, a drastic change in the PXRD pattern of resulting material was observed. Major peaks corresponding to Cu₂(OH)₃Cl are either completely disappeared or exhibited a sharp decline in intensity (d). Additionally, a couple of new peaks appeared in the 2-theta range of 30° and 40°. The peak at 35.6° corresponds to both Cu₄O₃ (■) and CuO (□). The Cu₄O₃ is commonly known as paramecaonite and has a tetragonal structure (PCPDF: 00–033–0480). The tenorite, CuO, has a monoclinic structure (PCPDF: 01–073–6023). Further, crystallinity reduced to 42%. It can be deduced that the decomposition of precursor has already commenced at 350 °C. This is further confirmed from TGA curve, which showed 13% weight loss in the temperature range of 280 °C to 305 °C. Stoichiometric calculation of 13% weight loss approximately corresponds to a loss of 1.5 moles of water from Cu₂(OH)₃Cl. The exact mechanism of decomposition with relevant equations could not be proposed at this stage due to inadequacy of experimental evidence. However, considering the reduction in crystallinity of resulting material and insights obtained from electron microscopy analysis of precursor, it is speculated that the precursor must have decomposed into several products including Cu₄O₃, CuO, CuOCl, and CuOCl₂. Some of these intermediates should have been amorphous and unstable in nature and hence their presence is not reflected in PXRD pattern. This becomes clear with the analysis of PXRD.
patterns of precursor pyrolyzed at 400 °C as well as at 500 °C. The intensity of peaks corresponding to precursor (○) reduced further in the PXRD pattern of precursor pyrolyzed at 400 °C. Meanwhile, intensity of peaks corresponding to Cu₄O₃ (■) and CuO (□) increased slightly, indicating an enhanced crystallinity (about 47%). The peaks corresponding to precursor (○) have disappeared completely in the PXRD pattern of precursor pyrolyzed at 500 °C. The TGA curve also shows 6.5% weight loss in this temperature range, which might be attributed to further loss of 0.75 moles of water. Meanwhile, two major new peaks appeared at 28.1° and 47.5°. These peaks correspond to Cu₄O₃ (■) exclusively. Several more peaks appear at higher angles corresponding to CuO (□). The peak at 35.6°, common to both Cu₄O₃ and CuO, becomes sharper as it loses contribution from Cu₄O₃. The percentage of crystallinity also increased to 58%. Thus, the resulting product is essentially a mixture of Cu₄O₃ and CuO to a larger extent.

In the PXRD pattern of precursor pyrolyzed at 700 °C, all the peaks correspond to CuO (□) exclusively, indicating that the resulting material is essentially CuO. The crystallinity is further increased to 71%. Interestingly, the TGA curve shows a maximum weight loss of 22.5%. There is no corresponding signal in the DTA curve. It is, therefore, speculated that Cu₄O₃ must have reacted with other amorphous intermediates in the temperature range of 500 °C to 700 °C in various ways. These several reactions might have been both exothermic and endothermic, leading to no net thermal effect. The observed weight loss could be attributed to the removal of chlorine atoms and some oxygen atoms in the form of volatile gaseous products.

The PXRD pattern of precursor pyrolyzed at 900 °C shows a definite crystalline phase transition. Evidently, the resulting product is a mixture of tenorite, CuO (□) and cubic cuprite, Cu₂O (●). Hence, it was concluded that the precursor, Cu₂(OH)₃Cl, undergoes complete transformation into copper oxide nanoparticles in the temperature range of 700 °C to 900 °C. Subsequently, the remaining precursor obtained from microwave synthesis was subjected to pyrolysis at 900 °C under the inert N₂ atmosphere for 2 h using a tubular furnace and the resulting product was taken up for further study.

Figure 5 shows the FTIR spectrum of copper oxide nanoparticles. In general, metal oxides show absorption bands in the fingerprint region due to inter-atomic vibrations. Here, the spectrum shows a single prominent sharp band around 430 cm⁻¹, which can be attributed to Cu–O stretching vibration [20–22]. The remaining spectrum was relatively smooth and thus confirms the formation of highly pure copper oxide nanoparticles.

Figure 6 (a) shows the surface morphology of copper oxide nanoparticles. At first glance, it appears to be aggregates of tiny particles. A closer look at individual particles reveals that each individual particle consists of numerous loosely bound grains (figure 6(b)). The EDS spectrum shows the presence of copper and oxygen only, confirming the purity of copper oxide nanoparticles.

Transmission electron microscopy analysis shows that the material contains well-dispersed nanoparticles with an average size of 30 nm (figure 7(a)). The specimen is more stable under the electron beam compared to the precursor. However, the analysis of the SAED pattern revealed unanticipated interesting facts (figure 7(b)). The pattern shows a predominant polycrystalline ring corresponding to Cu₄O₃ (designated as ‘A’). Other reflections that are either close or having overlapping 2θ values correspond to multiple copper oxides such as CuO, Cu₂O, and Cu₄O₃ (designated as ‘B’). As already demonstrated in previous paragraphs, the resulting product from the pyrolysis of the precursor at 900 °C is predominantly CuO with traces Cu₂O only. Hence, it
can be deduced that high energy electron beam again causes phase transformations in CuO/Cu₂O, resulting Cu₃O₄. In figure 7(a), the arrow marks were indicted to show darker regions inside many particles. This can be a result of the combination of mass contrast (Z) and diffraction contrast. As it is evident from SAD that the specimen is a mixture of 3 phases of copper oxides by now, the darker and lighter regions could be seen as a result of mixture these phases of varying mass densities.

The electron beam induced reduction of CuO to Cu was reported in literature very long back by NJ Long and AKP Long [23]. The authors investigated the phase transformation of CuO nanoparticles into metallic copper by comparing electron energy loss spectra (EELS) spectra for CuO and Cu metal in the region of the L₂ and L₃ edges. They concluded that the reduction of CuO to Cu proceeds via two intermediate phases, namely Cu₄O₃ and Cu₂O, under prolonged exposure (a few minutes) to focused e- beam. Apparently, the transformation from CuO to Cu₄O₃ was very rapid, while further transformation to Cu₂O and Cu was relatively slow. A similar phenomenon must have happened in the present case also under the influence of e-beam during the acquisition of images. While describing the structure of paramelaconite, Cu₄O₃, another study revealed that Cu₄O₃ could be obtained by sequential removal of oxygen atoms from CuO, while further removal of oxygen atoms results in the formation of Cu₂O [24]. Based on these observations, it can be said that even in the present case, the electron beam induces the reduction of CuO through successive stages. Hence, the SAED pattern shows a major polycrystalline ring corresponding to Cu₄O₃ and a few other weaker reflections, which could be attributed to different stages of the reduction process.

Conclusion

Dicopper chloride trihydroxide, [Cu₂(OH)₃Cl] was synthesized under controlled pressure and temperature in a dedicated microwave reactor. Later, this precursor material was subjected to thermal decomposition. Following conclusions were drawn regarding the stability, chemical and structural changes, and the associated phase transformations on the basis of PXRD and electron microscopy results:
(i) The precursor material is highly unstable under the electron beams of SEM and TEM.

(ii) Significant loss of weight is observed at three specific temperatures ranges, namely 280 °C–305 °C, 450 °C–466 °C, and 580 °C to 643 °C, which corresponds to a net weight loss of 42%.

(iii) PXRD spectra taken around these temperatures suggest that the precursor loses weight mainly due to loss of chlorine, hydrogen and also oxygen to some extent. Exact molecular forms of the lost elements could not be ascertained as the PXRD does not account for any intermediate amorphous materials. Stoichiometric calculations suggest that precursor loses weight in the form of water and some volatile gases containing chlorine.

(iv) Even after the weight stabilization, we observe a partial phase transformation of CuO to Cu$_2$O. These phase transformations among different polymorphs of copper oxide seem to be reversible as suggested by the TEM study of the pyrolyzed specimen. Under the high energy electron beam, electron diffraction pattern shows signatures of CuO, Cu$_2$O, and Cu$_4$O$_3$ which were seen at different temperatures in the sequential PXRD studies.

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