Thermal activation of copper carbonate

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Much interest focuses on the use of nano-scale copper and copper oxide for catalyst use [1]. The copper oxide may be used as a solid solution or as a mixture of mixed oxides [2-6]. The application of these mixed oxides is in environmental applications such as the catalytic oxidation of carbon monoxide and the wet oxidation of organics in aqueous systems [5,6]. These nano-scale chemicals are produced through the thermal decomposition of copper salts such as copper carbonate, copper hydroxy-carbonate either synthetic or natural (malachite) [7-9]. Many studies of the thermal treatment of these copper carbonates have been undertaken [9-16].

The use of thermogravimetry to assess the effect of mechanochemical activation by dry grinding of malachite determined the mass loss of water and carbon dioxide separately and/or together for $Cu_2(OH)_2CO_3$ samples untreated and ground for different times [17,18]. Often the thermal analysis is used to determine the effectiveness of catalyst precursors [19]. Indeed copper carbonates and nitrates can form part of the basic synthesis of superconductors. Thus there is a need to understand the thermal decomposition and surface reactions during thermal decomposition of copper carbonate and copper hydroxy-carbonate.

Thermal decomposition of the copper salts was carried out in a TA high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere (80 cm^3/min) at a pre-set, constant decomposition rate of 0.15 mg/min. (Below this threshold value the samples were heated under dynamic conditions at a uniform rate of 0.5 °C/min). The samples were heated in an open platinum crucible at a rate of 0.5 $°C/min^{-1}$ up to 300°C. With the quasi-isothermal, quasi-isobaric heating program of the instrument the furnace temperature was regulated precisely to provide a uniform rate of decomposition in the main decomposition stage. The TGA instrument was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. Only selected gases were analyzed.

The thermogravimetric (DTG) and differential thermogravimetric analyses (DTGA) of copper carbonate and copper hydroxy-carbonate are displayed in Figure 1a. The DTGA curve of copper oxide contains 5 peaks in the 150 to 300°C region. Hence there are five steps in the thermal decomposition of copper carbonate. These occur at 189, 232, 242, 260, 276 and 328°C with weight losses of 8.1, 10.6, 33.3, 13.8

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and 22.7% respectively. Figure 1b displays the TGA and DTGA patterns for copper carbonate and copper hydroxy-carbonate in the 400 to 900°C region. For copper carbonate four weight losses are observed at 475, 600, 643 and 840°C. The first three weight losses are not observed for copper hydroxy-carbonate. The DTGA pattern for this chemical shows a sharp weight loss at 850°C.

The mass spectrum of H_2O, CO_2, O_2 together with the DTGA pattern for copper carbonate are illustrated in Figure 2. The mass spectra coincides with precision with the DTGA pattern of $CuCO_3$, thus confirming the thermal decomposition of copper carbonate in five steps in the 150 to 350°C region. Figure 2 clearly shows that the there is the simultaneous loss of water, carbon dioxide and some oxygen. The first step (marked 1 in Figure 1a) at 150°C is thus assigned to the loss of water. Similarly the weight loss at 350°C (step 6) is assigned to water loss. Steps 2 to 5 are all associated with the loss of CO_2, H_2O and O_2. The slow heating of the copper carbonate with simultaneous loss of oxygen may have resulted in the formation of some copper carbide. The weight loss steps at 475, 600 and 643°C are not due to the loss of CO_2, H_2O and O_2. It is not known what are these weight loss steps. The weight loss step at 845°C is easily attributed to the loss of oxygen and this step is ascribed to the conversion of copper oxide to metallic copper.

Previous studies of the thermal decomposition of malachite are varied and the results depend upon the way the experiment is undertaken. Wide variation in the interpretation of the results for naturally occurring malachite is reported. Figure 1 shows the thermal decomposition of malachite. Six stages of decomposition are identified for malachite (a) firstly five steps in the 180 to 430°C region and (b) in the ~840°C region. Step 1 is simply attributed to a loss of water observed at 250°C for malachite. The second thermal decomposition stage is observed at 321°C. Stage 3 is observed at 332°C for malachite. A weight loss of 32.5% is observed. For this decomposition stage, the loss of water and carbon dioxide is simultaneous and follows an identical pattern. Stage 4 is readily observed as a separate step for malachite at 345°C. The water and carbon dioxide are lost simultaneously across each of these steps. Figure 1b displays the thermogravimetric and differential thermogravimetric patterns for malachite over the 400 to 1000°C temperature range. What is readily observed is the weight loss step at 855°C. This weight loss is associated with a loss of oxygen and it is proposed that at this temperature copper oxide changes to metallic copper. It should be kept in mind that the furnace in which the thermal analysis is undertaken is neutral. No oxygen is present. Mansour proposed a scheme for the thermal decomposition of azurite in which an initial loss of water occurred with a conversion of the azurite to malachite followed by a simultaneous loss of water and carbon dioxide [11]. Such conclusions are in harmony with the results observed in this work. However five steps are observed for the thermal decomposition as opposed to the two steps at 320 and 430°C reported previously [11]. Mansour reported the continuous loss of water and carbon dioxide up to 700°C. In this work, the loss is complete by 400°C for malachite.

Figure 3 displays the mass spectra of CO_2, H_2O and O_2 for malachite together with the DTGA pattern. There is a simultaneous loss of both H_2O and CO_2 across the first five weight loss steps. The weight loss steps 4 and 5 appear to have a greater weight loss of water than of carbon dioxide. The weight loss step at 850°C is associated with oxygen loss. In this set of data as compared with that for copper carbonate, the evolution of the CO_2 and H_2O appear to follow after the DTGA weight loss step. From 320 to around 450°C, there appears to be a continuous loss of CO_2 and H_2O.

A number of conclusions may be drawn:

(a) The thermal decomposition of copper carbonate and copper hydroxy-carbonate (malachite) are different. The temperatures of decomposition are higher for malachite than for copper carbonate.
(b) The decomposition of copper carbonate is complex with five overlapping thermal decomposition steps identified.
(c) The mass spectrum of carbon dioxide follows the differential thermal analysis pattern with precision
(d) A high temperature weight loss is identified at 850°C for both copper carbonate and copper hydroxy-carbonate with a loss of weight attributed to oxygen loss
(e) For copper hydroxy-carbonate, stages 1 and 2 result from the loss of water.
(f) For copper hydroxy-carbonate, Stages 3 and 4 result from the simultaneous loss of water and carbon dioxide.
(g) The stages identified in the mass spectrometric analyses are in harmony with the steps identified in the differential thermogravimetric patterns.

The thermal activation of copper carbonate takes place at temperatures below 300°C. Increased temperatures result in agglomeration and further heat treatment means that copper metal will be formed.

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