

Thermal activation of copper nitrate

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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 activation of copper salts such as copper carbonate, copper hydroxy-carbonate, either synthetic or natural (malachite), and other copper salts, for example copper nitrate [7-9]. Many studies of the thermal treatment of these copper carbonates to produce nanoscale copper oxide or metallic copper have been undertaken [9-16].

Many patents exist for the use of copper nitrate in the preparation of superconductors and catalysts [17-23]. Copper ammoniated nitrates have also been used to produce copper oxides or copper metal on a nano-particle scale [24]. The

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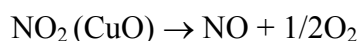
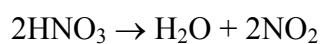
results of simultaneous DTA-TG-DTG and DSC studies on the thermal decomposition of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in air have been reported. The mechanism and enthalpies of the investigated processes were determined as well as the kinetic parameters of the processes run under non-isothermal conditions [17]. In order to make copper oxide on the nanometer scale, montmorillonitic clays have been dispersed into copper nitrate solutions [25,26]. The copper oxide generated through the thermal treatment of the copper nitrate adsorbed onto the montmorillonitic clays enables an efficient catalyst to be produced. Our interest lies with the behaviour of copper oxide and copper nano-particles supported on kaolinitic and montmorillonitic clays for the wet oxidation of organics. Hence it is important requirement to understand the thermal activation of copper nitrate.

Thermal decomposition of the copper nitrate was carried out in a TA high-resolution thermogravimetric analyzer (series Q500) in a flowing nitrogen atmosphere ($80 \text{ cm}^3/\text{min}$) at a pre-set, constant decomposition rate of $0.15 \text{ mg}/\text{min}$. (Below this threshold value the samples were heated under dynamic conditions at a uniform rate of $2.0 \text{ }^\circ\text{C}/\text{min}$). The samples were heated in an open platinum crucible at a rate of $2.0 \text{ }^\circ\text{C}/\text{min}^{-1}$ 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. Differential scanning Calorimetry was undertaken using a TA Q100 instrument.

The thermogravimetric (TGA) and differential thermogravimetric (DTGA) curves for copper nitrate over the ambient to 300°C temperature range are shown in Figure 1. Two distinct weight loss regions are observed. These are centred on 125, and 200°C. Four steps in the DTGA pattern are observed. Figure 2 displays the peak component analysis of this region and shows the temperature at which the weight losses are occurring. A relative weight loss of 48.0% is observed at ~81°C attributed to the loss of adsorbed water. At 109°C a large weight loss of 10.5% is observed. This value is much lower than the theoretical value of 22.4% calculated from the formula for copper nitrate trihydrate. A third weight loss is observed at 132°C of 15.8%. A final weight loss of 25.7% is observed at 194°C. This large weight loss is observed in the mass spectrum of water (Figure 3).

The weight loss steps 2 and 3 are also associated with a loss of water. However nitric oxide is also released from the sample. The ratio of the weight loss of nitric oxide to nitrogen dioxide should be in the ratio of 100 to 30. If the ratio is higher as is the case here, then the nitric oxide is being produced as a result of a chemical reaction and not as the daughter mass from the decomposition of nitrogen dioxide. It is proposed that during the thermal decomposition of copper nitrate a high surface energy material is produced which causes the reduction of nitrogen dioxide to nitric oxide. Further it is suggested that the copper nitrate dissolves in its own water of crystallisation, the copper nitrate then hydrolyses to copper oxy-nitrate and nitric acid. This nitric acid then decomposes on the copper oxide surface to nitric oxide and nitrogen dioxide. The following reactions are postulated:





Differential scanning calorimetry of copper nitrate displays four distinct exothermic reactions at 107, 126, 225 and 305°C. These values are in agreement with the values noted in the DTGA patterns at 105, 123 and 132, 211 and 347°C. The exotherms as determined by DSC occur at the same temperatures at which the principal weight losses are occurring (Figure 4).

Infrared emission spectroscopy of copper nitrate in the OH stretching region shows that the water is lost slightly above 200°C. This value is in agreement with both the DTGA and DSC results. The infrared emission spectra of the low wavenumber region shows that the nitrate bands are retained up to 300°C. A comparison of the infrared emission and DTGA results is not strictly valid as the IES is a dynamic continuously heating experiment, whereas the TGA experiment is a controlled heating rate experiment in which the weight changes occur isothermally.

A number of conclusions may be drawn:

- (a) The thermal decomposition occurs in stages
- (b) Two high temperature stages are identified at 350 (and 850°C)
- (c) Water and nitric oxide are lost simultaneously and over all the decomposition stages

- (d) The amount of oxide produced is higher than anticipated and it is suggested that the copper oxide surface produced during the decomposition of copper nitrate reduces the NO₂ to NO.
- (e) The DSC exothermic stages correspond with the differential weight changes.

It is apparent that the thermal decomposition of copper nitrate results in a high surface area material, which may act as a surface for the oxidation of organics. Such an activated copper oxide surface has applications in the wet oxidation of organics in water systems and for water purification.

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Figure 1 Thermogravimetric and differential thermogravimetric analysis of copper nitrate.trihydrate over the 50 to 1000°C range

Figure 2 Peak Analysis of the differential weight loss in the 50 to 400°C region of hydrated copper nitrate.

Figure 3 Mass spectrum of water vapour evolved during the thermal treatment of copper nitrate.

Figure 4 Differential scanning calorimetry of copper nitrate.