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Mechanism and kinetics of thermal decomposition of ammoniacal complex of copper oxalate

R. Prasad

Department of Chemical Engineering, Institute of Technology, Banaras Hindu University, Varanasi 221005, India

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Abstract

A complex precursor has been synthesized by dissolving copper oxalate in liquor ammonia followed by drying. The thermal decomposition of the precursor has been studied in different atmospheres, air/nitrogen. The mechanism of decomposition of the precursor in air is not as simple one as in nitrogen. In nitrogen, it involves endothermic deammoniation followed by decomposition to finely divided elemental particles of copper. Whereas in air, decomposition and simultaneous oxidation of the residual products (oxidative decomposition), make the process complex and relatively bigger particle of cupric oxide are obtained as final product. The products of decomposition in different atmospheres have been characterized by X-ray diffraction and particle size analysis. The stoichiometric formula, $Cu(NH_3)_2C_2O_4$ of the precursor is established from elemental analysis and TG measurements, and it is designated as copper amino oxalate (CAO).

In nitrogen atmosphere, the deammoniation and decomposition have been found to be zero and first order, respectively. The values of activation energy have been found to be 102.52 and 95.38 kJ/mol for deammoniation and decomposition, respectively.

Keywords: Thermal decomposition; Ammoniacal complex; Copper oxalate; Novel catalysts

1. Introduction

Ammoniacal complex of copper oxalate has been shown to be a good precursor [1,2] for the preparation of highly active and novel catalysts. The novelty of the catalysts is that the ‘reduction step’ is eliminated which is an essential and very sensitive step of activation of the conventional catalysts. In addition the novel catalysts are proved to be superior to the traditional ones, exhibiting better activity, selectivity and stability in dehydrogenation of alcohol. Calcination of the precursor in an inert atmosphere directly produces copper in active state without reduction. Thus, the decomposition of the complex precursor is an important step in the preparation of catalytically active copper. It is desirable to understand the process as well as the factors influencing the morphology of the decomposition products.

The influence of atmospheres (air/nitrogen) on the mechanism of thermal decomposition of copper oxalate is well known [3]. Dollimore et al. in a recent review [4] pointed out that in the early publications the interaction of the oxalate upon decomposition with the atmosphere had been neglected whilst as a generalization it might be said that many recent publications did not pay enough attention to the morphological form of the material. Impregnation of copper on supports through an ammoniacal solution of copper oxalate is advantageous because it results in uniform dispersion [5]. As the thermal decomposition of the

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E-mail address: prasad_r@satyam.net.in (R. Prasad).

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complex precursor obtained by drying of ammoniacal solution of copper oxalate has not been thoroughly studied before, the aim of the present work is to determine the stoichiometric formula of the precursor and to investigate the influence of the experimental conditions on the mechanism and kinetics of the decomposition process and also on the morphology of the decomposition products. The results of this work can be useful in the design and development of copper catalysts.

2. Experimental

2.1. Sample preparation

The complex precursor was synthesized by dissolving pure precipitated copper oxalate in aqueous ammonia (12 wt.% NH_3) at ambient conditions followed by evaporation over a steam bath and drying at 378 K for 5 h in an oven. All analytical grade chemicals were used in the synthesis of the sample. The prepared sample was stored in a decicator over anhydrous calcium chloride.

2.2. Elemental analysis

A Perkin-Elmer 2400 CHN elemental analyzer and a Perkin-Elmer 373 atomic absorption spectrophotometer were used to determine the composition of the complex precursor.

2.3. Thermal analysis

The thermograms were recorded on a Stanton Redcroft STA-781, simultaneous thermal analysis system in still air and nitrogen flow of 40 cm^3/min at a heating rate of 10 K/min. Platinum sample pan and αAl_2O_3 as reference were used. Sample of particle size 200–300 mesh and weight of 12–15 mg were taken. The sample was thoroughly dried before analysis.

2.4. Phase and morphological analyses

X-ray powder diffraction spectra of the samples were obtained in a Seifert, Model ID 3000 diffractometer (Germany) using Cu Kα radiation (40 kV/30 mA) to identify the phases present. The scanning speed was maintained at 2°/min. Morphological studies include particle size analysis and BET surface area determination from low temperature N_2 adsorption. The particle size analysis was carried out with the help of a Micron Photosizer, SKC-2000, Seishin (Japan), using toluene as a dispersant media.

3. Results and discussion

3.1. Elemental analysis of the precursor

The composition of carbon, hydrogen, nitrogen and copper, determined by the CHN analyzer and atomic absorption spectrophotometer are given in Table 1. Composition of oxygen was determined by the difference and it was found to be equivalent to the carbon content in the sample as C_2O_4. The ratio of nitrogen and hydrogen (experimental value) shows that they are only present as NH_3. The results of the weight losses by elemental analysis (Table 1) and also by thermogravimetry in nitrogen atmosphere (Table 2) are consistent with the rational formula of the complex precursor to be $Cu(NH_3)_2C_2O_4$. The precursor is designated as copper amino oxalate (CAO).

The results are reproducible for five samples prepared under identical conditions and also for a sample washed with water and dried at 378 K for 5 h. The complex is stable under ambient conditions.

Table 1
Elemental analysis of copper amino oxalate

Element	Composition (%)	
	Experimental	Theoretical
Carbon	13.01	12.93
Hydrogen	3.17	3.23
Nitrogen	14.90	15.09
Copper	34.23	34.26
Oxygen (by difference)	34.69	34.49
N/H ratio		
Experimental = 4.70		
Theoretical in NH_3 = 4.67		
Decomposition loss		
By elemental analysis (C + H + N + O) = 65.777%		
By thermal analysis = 65.71%		
By theoretical calculation = 65.74%		

Table 2
Thermogravimetric analysis of copper amino oxalate in nitrogen and in air

Step	DTA peak temperature (K)	Weight loss (%)	
		Theoretical	Experimental
In air			
Deammoniation	489 (endothermic)	18.32	–
Decomposition to Cu and CO_2	531 endothermic)	65.74	–
Oxidation of Cu to Cu_2O	574 (exothermic)	61.43	59.11
Oxidation of Cu_2O to CuO	Hump (exothermic)	57.12	57.25
In nitrogen			
Deammoniation	484 (endothermic)	18.32	–
Decomposition to Cu and CO_2	531 (endothermic)	65.74	65.71

3.2. Mechanism of thermal decomposition of copper amino oxalate

The thermograms for the decomposition of the precursor indicate that the overall process in air (Fig. 1a) occurs in four steps whereas in nitrogen it completes in just two steps. The decomposition steps along with the weight losses and the temperatures corresponding to the peaks on DTA curves for each step are given in Table 2.

The TG curve in nitrogen shows a continuous loss in weight of the sample to a final value of 65.71%. In air continuous loss in weight occurs up to 59.11% followed by an increase in the weight in the last step decreasing the percentage loss to 57.25%. Since the increase in weight is observed in the presence of oxygen, this would be ascribable to the oxidation of the resulting solid product. These results suggest that decomposition in the inert atmosphere produces elemental copper and cupric oxide is the product of decomposition in the air. These conclusions are in accordance with X-ray diffraction (Fig. 2) studies. Table 2 shows that the experimental results are in perfect agreement with the stoichiometric calculations for the final steps of transformations in air as well as in nitrogen. Although the intermediate steps are distinct but there exact positions are difficult to locate on TG curve. This is due to overlapping reactions, as evident by the overlapping DTG and DTA peaks, respectively.

According to the DTA curve in nitrogen (Fig. 1b) the thermal transformation of CAO is wholly endothermic process consisting of a peak and a plateau

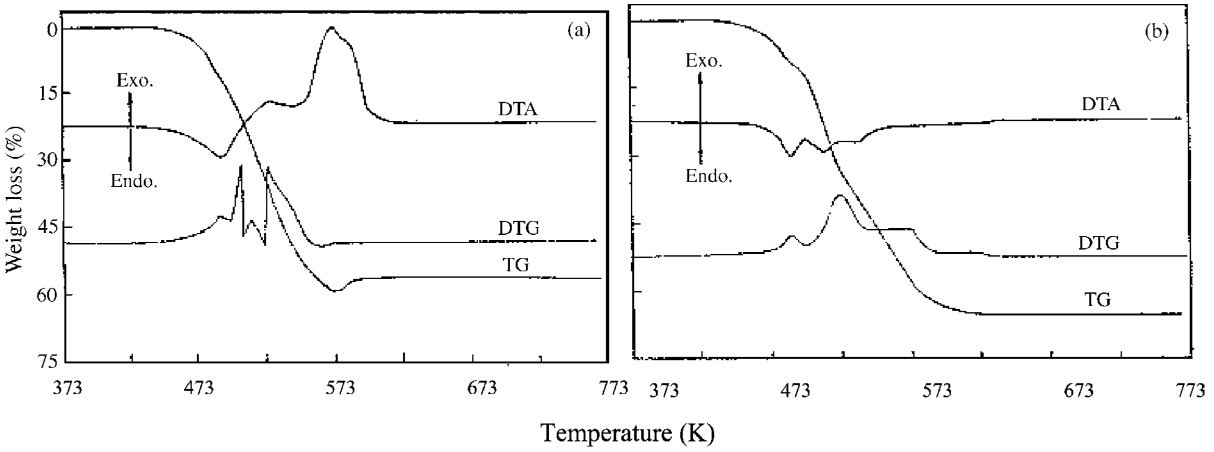


Fig. 1. Thermograms of copper amino oxalate: (a) heating rate 10 K/min in static air and (b) N_2 flow.

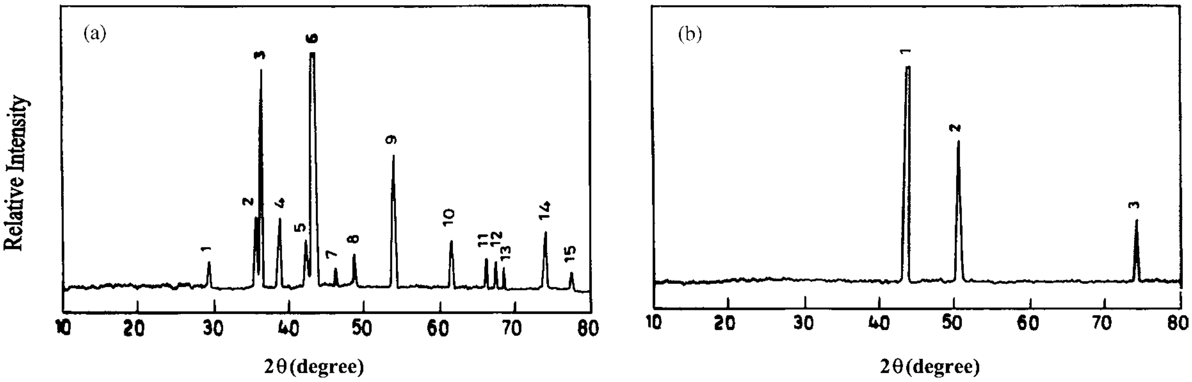


Fig. 2. XRD spectra of decomposed mass of CAO: (a) in air and (b) N_2 atmosphere.

corresponding to the deammoniation and decomposition to Cu and CO_2 steps, respectively. While, the net effect of overall transformation is highly exothermic in air (Fig. 1a). Except the first step of endothermic deammoniation all other steps seem to be exothermic and overlapping. Probably the released ammonia is catalytically oxidized by resulting solid product showing exothermic character to the DTA peak. Further, simultaneous decomposition to copper and oxidation of the resulting solid products occur in the next steps.

Data of the third step (Table 2) suggest that the oxidation of the resulting copper to Cu_2O is completed in itself along with the decomposition of the oxalate as well as its partial oxidation to CuO. Fourth step is exclusively oxidation of remaining Cu_2O to CuO. Corresponding to the fourth step an exothermic hump following the DTA peak of the third step can be seen. The intensities of the exotherms are several times more than the endothermic steps, which can lead to substantial heating of the residue in air. The violent exothermic oxidations, especially at the temperature of decomposition, completely overwhelm the endothermic decomposition of oxalate. The pyrophoric nature of the copper is mainly due to its finely divided state.

Fig. 2 shows the XRD spectra of the products of decomposition of CAO in air and in nitrogen atmosphere. The three peeks of the spectrum of the product resulting in nitrogen atmosphere (Fig. 2b) correspond to copper metal. There are 15 peaks in the diffractogram of the product obtained in air (Fig. 2a), most of the peaks are of CuO with few peaks of copper and cuprous oxide.

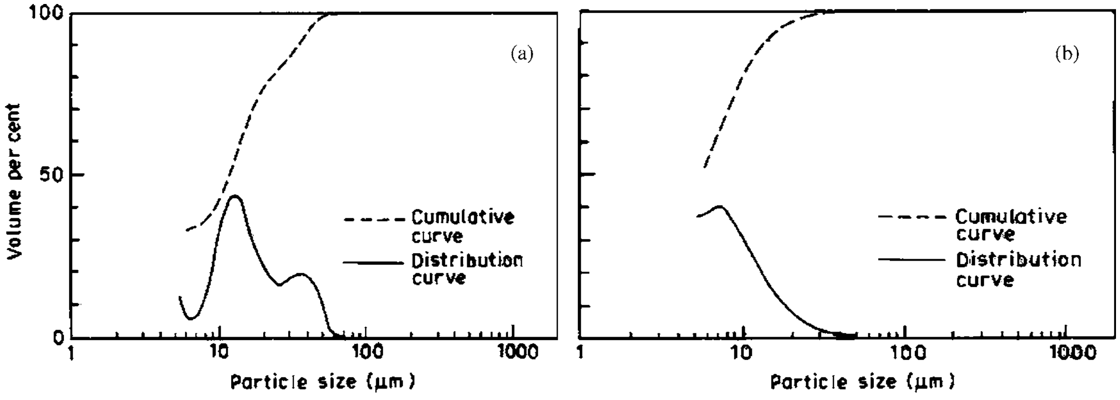


Fig. 3. Particle size distribution of the products of CAO decomposition: (a) in air and (b) in N_2.

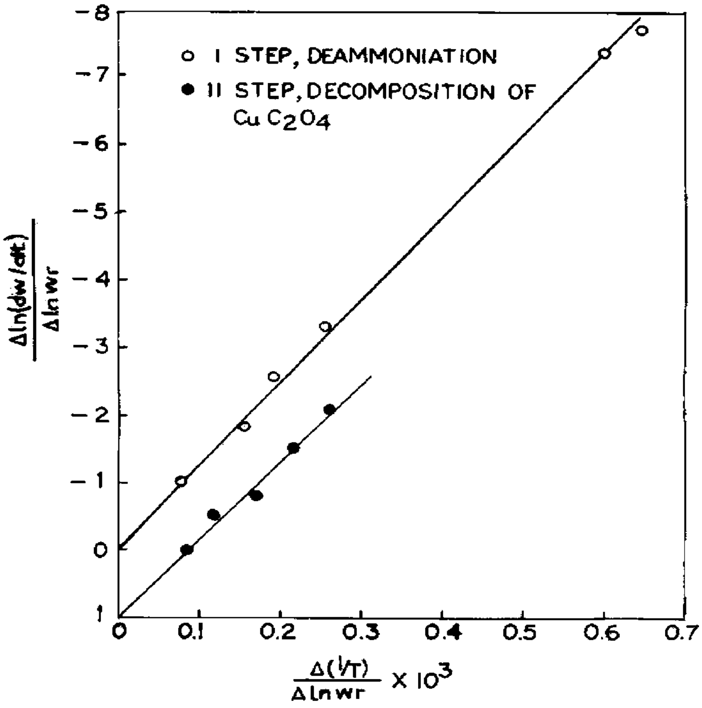


Fig. 4. Kinetics of non-isothermal decomposition of CAO in N_2, heating rate 10 K/min.

It can be concluded from these results that the thermal decomposition of CAO follows the following routes:

In nitrogen

$$Cu(NH_3)_2C_2O_4 \xrightarrow{-2NH_3} CuC_2O_4 \xrightarrow{-2CO_2} Cu \quad (1)$$

In air

$$2Cu(NH_3)_2C_2O_4 \xrightarrow{-4NH_3} 2CuC_2O_4 \xrightarrow{-4CO_2} 2Cu \xrightarrow{1/2O_2} Cu_2O \xrightarrow{1/2O_2} 2CuO \quad (2)$$

3.3. Morphological characterization of the samples

It is apparent from the particle size distribution curves that the particles resulted by thermal decomposition of CAO in air (Fig. 3a) are bi-dispersed with most probable sizes of 12 and 35 μm, and are larger than mono-dispersed particles with most probable size of 7 μm obtained in nitrogen atmosphere (Fig. 3b). Also, the BET surface area (40.73 m^2/gm) of the particles resulting in nitrogen is higher than that of air (28.35 m^2/gm). These differences in morphology of the particles produced under different conditions may be interpreted in terms of decomposition mechanism of CAO. It is to be noted that the elemental copper is the product of endothermic decomposition of CAO in nitrogen atmosphere, while CuO is the result of violent exothermic processes in air.

$$Cu + \tfrac{1}{2}O_2 \rightarrow CuO \quad \Delta H = -161.70\,\mathrm{kJ/mol} \quad (3)$$

The exothermic processes simultaneously causes sintering of the particles due to local over heating which resulted in bigger particle size and lower surface area of CuO than that of finely divided elemental copper.

3.4. Kinetics of the thermal decomposition of CAO

The most important thermal decomposition steps of CAO, from the point of view of its catalytic activity, are the deammoniation and decomposition in nitrogen atmosphere. The catalyst with the highest activity and selectivity for dehydrogenation of alcohol was obtained when CAO was decomposed in nitrogen below 573 K.

Kinetics of decomposition of CAO has been studied non-isothermally under conditions of sample temperature increasing at the rate of 10 K/min in a flowing atmosphere of nitrogen. The following equation derived by Freeman and Carroll [6] is used to determine the activation energies and orders of deammoniation and decomposition steps.

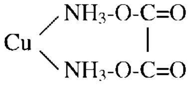
$$\frac{\Delta \ln(\mathrm{d}W/\mathrm{d}t)}{\Delta \ln W_\mathrm{r}} = n - \frac{(E/R)\Delta(1/T)}{\Delta \ln W_\mathrm{r}} \qquad (4)$$

where, $W_\mathrm{r} = W_\mathrm{c} - W$, W_c are the weight loss at completion of reaction, W the total weight loss upto time, t, E the energy of activation, R the universal gas constant, T the absolute temperature, and n the order of reaction with respect to reactant.

Fig. 4 is a plot of $\Delta\ln(\mathrm{d}W/\mathrm{d}t)/\Delta\ln W_\mathrm{r}$ versus $\Delta(1/T)/\Delta\ln W_\mathrm{r}$ for deammoniation and decomposition steps of CAO. Values of $\mathrm{d}W/\mathrm{d}t$ and W_r are determined from the thermograms. The intercepts and slopes of the respective lines yield the values of the orders and energies of activation for the two decomposition reactions. The deammoniation and decomposition are found to be zero order and first order, respectively. The energies of activation are found to be 102.52 and 95.38 kJ/mol for deammoniation and decomposition steps, respectively.

4. Conclusions

The rational formula of the complex precursor, CAO has been derived,



The mechanism and kinetics of the thermal decomposition of CAO in nitrogen have been established. Finely divided, mono-dispersed elemental particles of copper are obtained through endothermic decomposition of the precursor in nitrogen. Exothermic decomposition of CAO results in bi-dispersed, relatively lower BET surface area and bigger particles of cupric oxide due to sintering. It is important to consider the formation of different decomposition products during the thermal treatment of CAO in air for the correct assessment of the kinetics of decomposition. Thus, using CAO as a source of active component in the preparation of supported copper catalysts and calcining it in an inert atmosphere, particles of most favorable morphology can be derived for catalyzing chemical reactions of industrial importance.

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