

The kinetics of thermal dehydration of copper(II) acetate monohydrate in air

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Received 25 February 2005; received in revised form 28 May 2005; accepted 27 June 2005

Available online 1 August 2005

Abstract

The thermal decomposition of copper(II) acetate monohydrate was studied in air using TG-DTG/DTA, DSC, XRD techniques. TG-DTA curves show that the decomposition occurs in four steps. TG and XRD data indicate the reduction of Cu(II) during the decomposition of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$. DTG and DSC data imply at least two steps contained in dehydration reaction, which is verified by the activation energy values estimated with Friedman and Flynn–Wall–Ozawa (FWO) methods. The dependence of activation energy on conversions indicates the dehydration reaction contains an additional initial reversible step. The most-probable kinetic model has been estimated with multivariate non-linear regression method assuming a two-step consecutive reaction. Bna (expanded Prout–Tompkins equation) \rightarrow Cn (n order autocatalytic reaction) model fits the original data best with a high correlation coefficient of 0.9998, and the calculated apparent activation energies of the fitted models are consistent with those calculated by isoconversional methods using original data. The corresponding function $f(\alpha)$, activation energy E and preexponential factor A of Bna, are $(1 - \alpha)^{0.7593} \alpha^{0.2867}$, 128.5 kJ/mol and 1.6×10^{15} , respectively. Those of Cn, are $(1 - \alpha)^{1.0534} (1 + 2.712\alpha)$, 80.5 kJ/mol and 6.9×10^7 , respectively. The combination of model free isoconversional methods and multivariate non-linear regression can give more reasonable and applicable models than commonly used model fitting methods.

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Keywords: Copper acetate monohydrate; Thermal decomposition; Dehydration kinetics; Multiple-step reaction; Multivariate non-linear regression

1. Introduction

Several studies have been performed on the thermal decomposition behavior of metal acetates [1–6], some of which focus on the kinetics of the reactions of copper(II) acetate monohydrate ($\text{CuAc}_2 \cdot \text{H}_2\text{O}$) with different methods [4–6], and contracting-geometry kinetics were observed. The thermal dehydration kinetics of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ in nitrogen have been studied with isothermal mass-loss curves between 353 and 406 K [4], and nucleation-and-growth kinetics (A2) with an activation energy of 154 kJ/mol is obtained at low temperature, which changes to contracting-disc kinetics (R2) at higher temperature with a lower activation energy of

76 kJ/mol. Kinetic analysis of TG curves obtained for the thermal dehydration of single crystalline $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ [5] revealed that the isothermal dehydration is regulated, as a whole, by a phase-boundary controlled reaction law, $R_n = kt$, with $2 < n < 3$. Obaid et al. [6] studied the kinetics of non-isothermal dehydration of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ in air with integral methods including the Ozawa method, but obtained activation parameters, which varied greatly with the extent of conversion. Integral methods such as that of Ozawa, however, introduce some systematic errors in estimating the activation energy, if the latter varies with the extent of conversion [7].

Non-isothermal methods are becoming more widely used because they are more convenient than the classical isothermal methods. Solid-state reactions tend to occur in multiple steps that have different rates. However, the kinetics of thermal transformations are usually described by

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a single-step reaction [8]. Most of the methods of kinetic processing employ data obtained under one heating rate only, which does not allow for a possible change in the rate-limiting step. This limits the application of the kinetic model obtained in solving applied kinetic problems. However, for non-isothermal kinetic analysis, multivariate non-linear regression is a totally different approach [9]. This method, based on multiple heating rates, makes the assumption that the parameters of the model are identical for measurements at all heating rates. It allows a direct fit of the model to the experimental data without a transformation, which would distort the error and consequently the result. An additional advantage lies in the fact that there are no limitations with respect to the complexity of the model, and consequently it is reliable in solving applied kinetic problems.

We have studied the mechanism [10,11] and kinetics [12] of thermal decomposition with non-isothermal analysis techniques. In this work, the dehydration of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ in air was re-examined and a two-step process was observed. The kinetics was studied with a multivariate non-linear regression method.

2. Experimental

$\text{CuAc}_2 \cdot \text{H}_2\text{O}$ crystalline powder (analytical grade) was obtained from Beijing Reagent Factory.

Simultaneous TG-DTA measurements were carried out on a Netzsch STA 449C thermal analyzer. The experiments were performed in static air, at heating rates of 5, 10, 15 and 20 °C/min. The sample mass was kept at 4.50 ± 0.15 mg. The differential scanning calorimetry (DSC) measurement was carried out on a Netzsch DSC 200 analyzer at a heating rate of 10 °C/min. The sample mass was 6.10 mg. The decomposition product was collected at the temperature that was shown on the TG-DTA curves.

For kinetics analysis, Thermokinetics software (Netzsch) was used.

X-ray powder diffraction patterns of the decomposition product were obtained with a Bruker D8-Advance model X-ray diffractometer with a Ni-filter and graphite monochromator, and Cu $K\alpha 1$ radiation ($\lambda = 1.54056$ Å, 40 kV, 50 mA, 4°/min).

3. Results and discussion

3.1. Thermal decomposition

TG curves of the thermal decomposition of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ at four heating rates are shown in Fig. 1. It is observed that the mass loss is independent of the heating rate. TG-DTA curves of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ at a heating rate of 10 °C/min in air are shown in Fig. 2. The DTA peaks closely correspond to the mass changes observed from the TG curve. The curves show that the thermal decomposition of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ in air

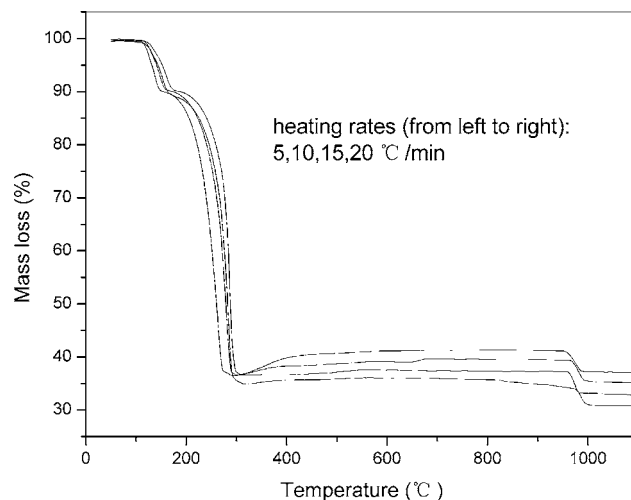


Fig. 1. TG curves of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ at different heating rates in air.

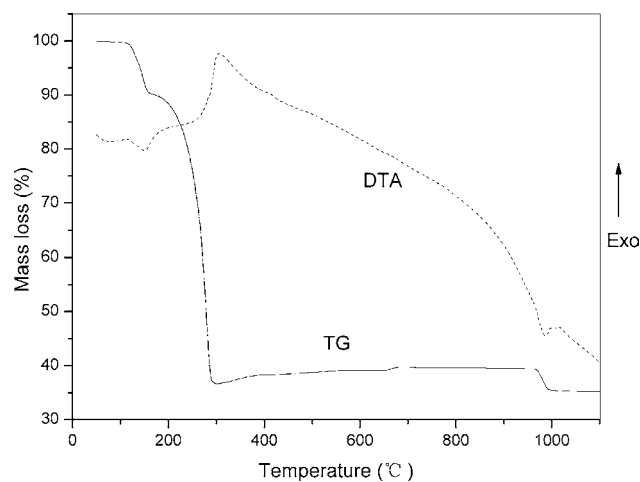


Fig. 2. TG-DTA curves of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ at a heating rate of 10 °C/min in air.

below 1100 °C occurs in four steps. The first step is from 117 to 170 °C, with a mass loss of 8.95% and an endotherm which is attributed to the dehydration of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ and formation of the anhydrous acetate. The second step (at about 170–309 °C) has a mass loss of 54.17% due to the decomposition of anhydrous acetate and the formation of Cu_2O . The mass increase (at about 309–479 °C) results from the oxidation of Cu_2O . The last mass loss step is due to the decomposition of CuO to Cu_2O . All data are listed in Table 1, where the

Table 1
Mass changes of the decomposition of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ at a heating rate of 10 °C/min in air

Steps number	Temperature range (°C)	Mass change (%)		Solid Product
		Experiment	Calculated	
1	117–170	–8.95	–9.02	CuAc_2
2	170–309	–54.17	–55.10	Cu_2O
3	309–479	4.04	4.0	CuO
4	946–1016	–3.96	–4.0	Cu_2O

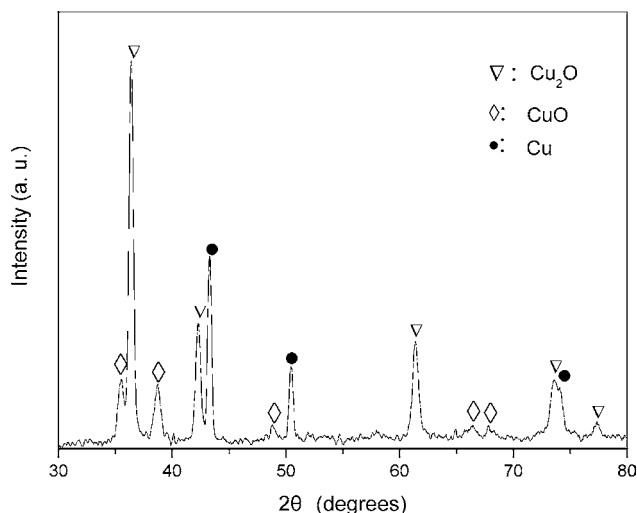


Fig. 3. XRD profile of the residue of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ after decomposition at 310°C in air.

experimental values are consistent with the theory values for all steps. The DTA peak of the second step overlaps with that of the third step. Both exotherms are due to the oxidation of organic residues and Cu_2O , which can be seen more clearly in the DSC curve.

Fig. 3 presents the XRD profile of the residue after decomposition in air at 310°C . It is mainly Cu_2O , while the presence of CuO and even Cu is also observed. The result indicates that the decomposition of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ involves a reduction of Cu(II) , which is consistent with the results obtained before [6].

The DSC curve (Fig. 4) shows that the dehydration step (about $117\text{--}170^\circ\text{C}$) of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ has two endothermic peaks at 130 and 146°C . This implies that the dehydration occurs in at least two steps, which is verified by the DTG curves at different heating rates presented in Fig. 5.

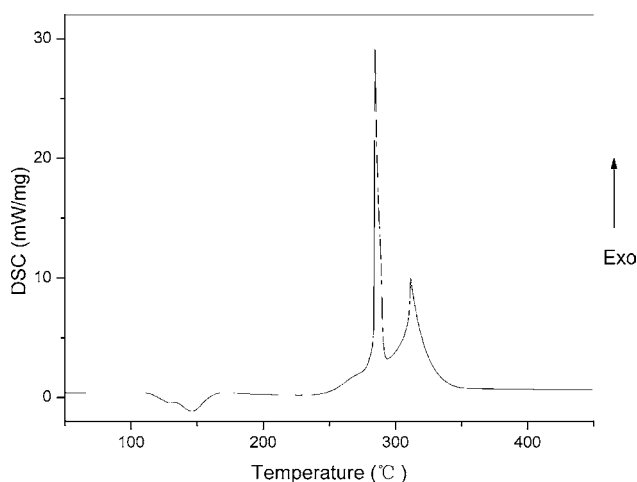


Fig. 4. DSC curve of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ at a heating rate of $10^\circ\text{C}/\text{min}$ in air.

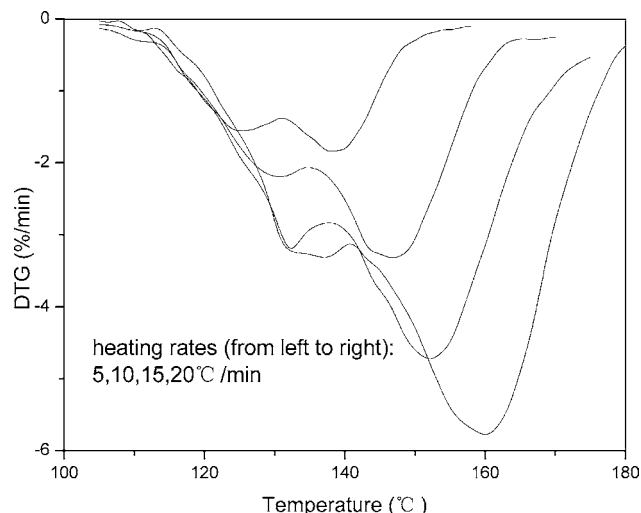


Fig. 5. DTG curves of the dehydration of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ at different heating rates in air.

3.2. Kinetic analysis of dehydration

3.2.1. Estimation of the activation energy E of dehydration

For kinetic analysis, model-free isoconversional methods play an important role. These methods are based on the isoconversional principle that states that the reaction rate at a constant extent of conversion is only a function of the temperature [7].

$$\frac{d \ln \left(\frac{d\alpha}{dt} \right)_\alpha}{dT^{-1}} = -\frac{E_\alpha}{R} \quad (1)$$

Henceforth, the subscript α indicates the values related to a given extent of conversion.

By rearranging Eq. (1), one can easily arrive at Eq. (2)

$$\ln \left(\frac{d\alpha}{dt} \right)_\alpha = \text{constant} - \frac{E_\alpha}{RT} \quad (2)$$

which is the basis of the differential isoconversional method of Friedman [13].

Using Eq. (1) in its integral form and the Doyle's approximation allows one to arrive at Eq. (3)

$$\ln(\beta) = \text{constant} - \frac{E_\alpha}{RT_\alpha} \quad (3)$$

which is the basis of the integral isoconversional methods of Flynn and Wall [14] and Ozawa [15].

The Friedman method and the FWO method are both based on multiple heating rate experiments, where no kinetic model is needed before the activation energy is calculated. The estimated values of the apparent activation energy of dehydration with both methods are presented in Fig. 6. The dependence of E on the extent of conversion (fractional mass loss of dehydration) indicates at least two steps exist

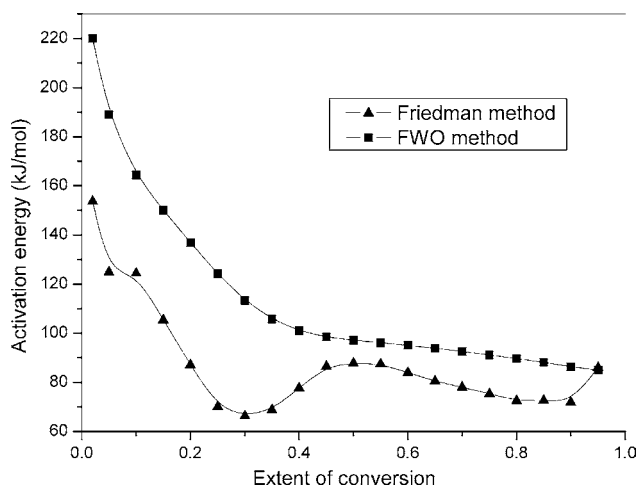


Fig. 6. Calculated apparent activation energies of dehydration using the Friedman method and the FWO method plotted against the extent of conversion.

in the dehydration reaction of the title compound. In addition, at the beginning of the dehydration reaction, the apparent activation energy decreased from a large initial value down to more normal values. This is typical of reaction involving an initial reversible step, which exists in many solid-state decomposition reactions [8,16]. The decreasing dependence of E on α corresponds to the kinetic scheme of an endothermic reversible reaction followed by an irreversible one [17]. E is limited by the sum of the activation energy of the irreversible reaction and the enthalpy of the reversible reaction at low conversions, and only by the activation energy of the irreversible reaction at high conversions.

3.2.2. Determination of the kinetic model of dehydration

Multivariate non-linear regression (Netzsch Thermokinetics) was applied to determine the most-probable kinetic model. Netzsch Thermokinetics is a software module for the evaluation of thermokinetic experiments. The relevant differential equations are numerically solved and the parameters of the differential equations are iteratively optimized. With multivariate non-linear regression as the method of analysis, several dynamic measurements run at different heating rates are brought together during the analysis. Compared to the single curve analysis, the quality of fit diminishes considerably for the non-applicable reaction types [9]. So the distinguish ability between the individual reaction types improves drastically, and the 'correct' reaction type is significantly recognized and the kinetic parameters apply.

As seen from DTG curves and the dependence of E on α , at least two steps exist in the dehydration reaction of the title compound. A possible reversible step exists at the beginning of the decomposition. Because is formed only a small part of the total mass loss, the initial reversible step was omitted.

Table 2

Fitted kinetic parameters of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ resulting from multivariate non-linear regression (heating rate 5, 10, 15 and 20 °C/min) with reaction model of $\text{Bna} \rightarrow \text{Cn}$

Reaction step	E (kJ/mol)	$\log A$	n	a or K_{cat}	Correlation coefficient
Bna	128.5	15.19	0.7593	0.2867	0.9998
Cn	80.5	7.84	1.0534	2.712	

According to Fig. 1, mass loss is independent of the heating rate. So a two-step consecutive reaction $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ was selected. Sixteen commonly used models [9] were tested, and models with a high correlation coefficient and similar E values were the most-probable models. In this work, $\text{Bna} \rightarrow \text{Cn}$ models were determined as the most-probable models. The corresponding function $f(\alpha)$ of Bna, expanded Prout–Tompkins equation, is $(1 - \alpha)^n \alpha^a$; $f(\alpha)$ of Cn, n order autocatalytic reaction, is $(1 - \alpha)^n (1 + K_{\text{cat}}\alpha)$. The fitted kinetic parameters are listed in Table 2. The apparent activation energies of fitted models and those of original measurements, calculated using the Friedman and the FWO methods, are shown in Fig. 7.

It is shown in Fig. 7 that the calculated apparent activation energies of fitted models at different conversions were consistent with those calculated by isoconversional methods. The fact that E values from the FWO method have better consistency is attributed to the sensitivity of the Friedman method to experimental noise [7]. The deviation of E at the beginning of the reaction resulted from an initial reversible step, which was omitted in this fitting process. The larger activation energy of the first step of dehydration may be due to the additional destroy of crystal structure. So the combination of model-free, isoconversional methods and multivariate non-linear regression can give more reasonable and applicable models than commonly used model-fitting methods.

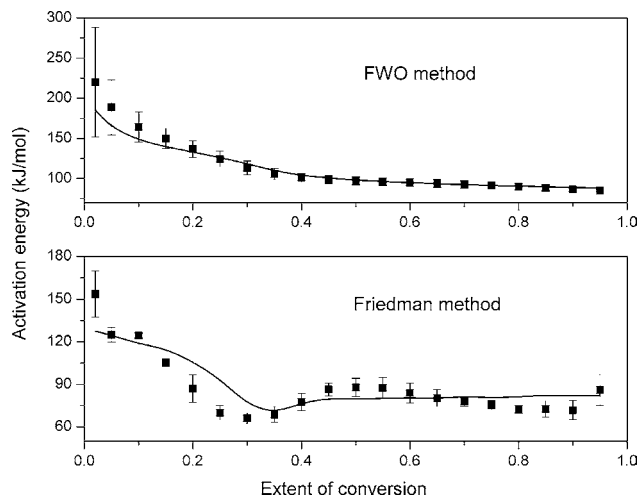


Fig. 7. Calculated apparent activation energies of dehydration using the Friedman and the FWO methods plotted against the extent of conversion. Square: E of measured data; line: E of the $\text{Bna} \rightarrow \text{Cn}$ model fitted data.

4. Conclusions

The thermal decomposition of copper(II) acetate monohydrate in air occurs in four steps, and the reduction of Cu(II) during the decomposition of $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ occurs. The dehydration reaction contains an initial reversible step and two other irreversible steps. The kinetic model has been estimated with multivariate non-linear regression method assuming a two-step consecutive reaction process. Bna \rightarrow Cn model fits the original data best with a high correlation coefficient of 0.9998, and the calculated apparent activation energies of the fitted models are consistent with those calculated by iso-conversional methods using original data. The corresponding function $f(\alpha)$, activation energy E and preexponential factor A of Bna, are $(1 - \alpha)^{0.7593} \alpha^{0.2867}$, 128.5 kJ/mol and 1.6×10^{15} , respectively. Those of Cn, are $(1 - \alpha)^{1.0534} (1 + 2.712\alpha)$, 80.5 kJ/mol and 6.9×10^7 , respectively.

Acknowledgement

We gratefully acknowledge that this work was supported by National Natural Science Foundation of China (20071026).

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