

Dehydration Kinetics of Tincalconite from Thermogravimetric Data

¹Fatih Sevim, ²Hilal Küçükarslan, ¹Fatih Demir* and ³Hayrettin Eroglu, ⁴Mehmet Aktan

¹Department of Chemical Engineering, Engineering Faculty, Atatürk University, 25240, Erzurum, Turkey.

²TŞFAŞ, Research and Development Dept., Ortaköy Yolu Üzeri, 17. km, Kırşehir, Turkey.

³Department of Biomedical Engineering, Engineering Faculty, Atatürk University, 25240, Erzurum, Turkey.

⁴Department of Industrial Engineering, Engineering Faculty, Atatürk University, 25240, Erzurum, Turkey.
fatihdemir@atauni.edu.tr*

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Summary: Kinetic parameters of tincalconite during thermal decomposition were explored with TGA data. Coats-Redfern and Suzuki methods were implemented for the kinetics analysis. Decomposition kinetics of tincalconite occurred in two steps and both suitably fit a first-order kinetic model. Activation energy and frequency factor were observed as 149.17 kJ.mol⁻¹ and 1.2x10¹⁶ min⁻¹ for region I, and 5.45 kJ.mol⁻¹ and 5.23x10⁸ min⁻¹ for region II, respectively with the Coats-Redfern method. Activation energy and frequency factor were observed as 60.95 kJ.mol⁻¹ and 67.21x10⁵ min⁻¹, respectively for the Suzuki method.

Keywords: Tincalconite; Thermal Decomposition; Suzuki Method and Coats-Redfern Method.

Introduction

To acquire a porous and an active structure and to provide an advantage for economic and management respects by changing some surface characteristics, thermal processes are usually applied with the elimination of some volatile compounds. During thermal analysis, effects of temperature change over physical properties of a substance and its reaction products are investigated. Several methods were developed to support the kinetic analysis of TG and DSC data [1]. Differential thermal analysis and kinetic parameters for carbonate minerals are broadly reported in the literature [1–5]. Demir *et al.* [6] investigated the kinetic parameters of thermal decomposition for magnesite with TG data.

Thermal dehydration of boron minerals and boron products has been investigated by using different methods. Şener *et al.* [7] explored dehydration kinetics of ulexite by TG, DTA and DTG and determined the structural changes in ulexite by means of X-ray diffractometry by scanning electron microscopy and mercury porosimeter. Park *et al.* [8] proposed a kinetic analysis method with a dynamic model that works for the varying thermal decomposition behavior of polymers. They stated that the process fits a first order kinetic model and Coats-Redfern method gives more reliable results than Suzuki method. Okur and Eymir [9] investigated calcination kinetics of ulexite using TGA data. In this study, reaction parameters were determined by using Coats-Redfern and genetic algorithm methods, and the results were compared. Malecka *et al.* [10] examined thermal decomposition of cadmium malonate hydrates. They stated that dehydration of

cadmium malonate hydrate occurs in the range of 80–170 °C, and the amount of hydration water in the initial sample has a strong effect on decomposition reaction.

In this study, thermal decomposition related kinetic parameters for tincalconite were analyzed with TGA data and by means of Coats-Redfern [11] and Suzuki methods [12]. Particle size effect of tincalconite was not investigated since the particle size of tincalconite produced by Eti Bor A.Ş. change in a narrow region. This study is the first investigation of thermal decomposition kinetics of tincalconite.

Results and Discussion

For studying the dehydration kinetics of tincalconite from thermogravimetric data, tincalconite particle sizes between 0.075–1.2 mm and 3 different heating rates were chosen, which were 5, 10 and 12 °C min⁻¹. For a heating rate of 10 °C min⁻¹, the in Fig. 1 was obtained. For other heating rates of 5 and 12 °C min⁻¹, the same process was applied. Peak temperature values in DTA are consistent with the values given in the literature [13–14].

The major peak value around 149 °C is due to the first dehydration of tincalconite and the second peak value around 700 °C is due to the second dehydration and subsequent boiling of the sample. In addition, the endothermic peak values, which were observed above 700 °C, are related with melting and bubbling of the sample. Two DTA regions with

*To whom all correspondence should be addressed.

different nominal mass loss rates and two TG peaks imply two steps for the dehydration process (Fig. 1).

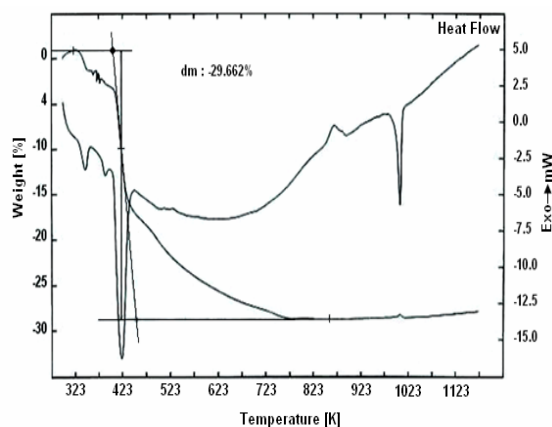
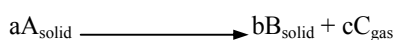


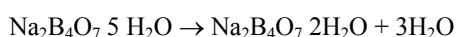
Fig. 1: Differential Thermal and Thermogravimetric Analysis Curves of Tincalconite (0.075-1.2 mm).

In this study, Coats-Redfern method was used for determining the kinetic parameters of a reaction with the following type:



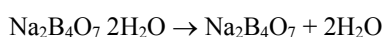
According to the results, the dehydration of tincalconite probably occurs in two steps as given below:

Region I; mass loss: %21, temperature range: 190-215 °C



Partial loss of water from hydrated minerals is represented in this step.

Region II; mass loss: %29, temperature range: 215-503 °C



Complete loss of water is represented in this step. Both steps are attributed to the dehydration of tincalconite.

The reaction order was determined from the plot of $\ln(f(\alpha)/T^2)$ vs. $(1/T)$, which is given in Fig. 2. It would be more suitable to take two dissimilar regions into account in the calculations of kinetic parameters, as can be seen in Fig. 2. Because of that, Coats-Redfern method was used for both regions

separately. After application of the method, the regions were determined as below and the calculations were made accordingly.

For the first and second regions, the results implied that the reaction is a first-order kinetic model. Slopes of straight lines in Eq. (10) were used to find the frequency factor and the activation energy as $1.2 \times 10^{16} \text{ min}^{-1}$ and $149.17 \text{ kJ mol}^{-1}$ for the first region, and $5.23 \times 10^8 \text{ min}^{-1}$ and 5.45 kJ mol^{-1} for the second region, respectively. R-square values for the other orders were calculated with Coats-Redfern method and the results are given in Table 1 and shown in Fig. 2. Table 1 shows activation energies and frequency factors which were calculated with the Coats-Redfern method for several heating rates.

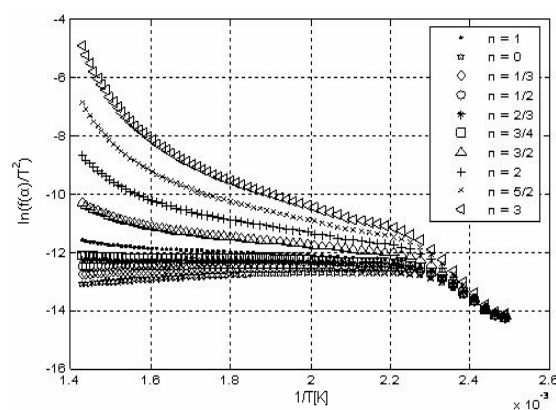


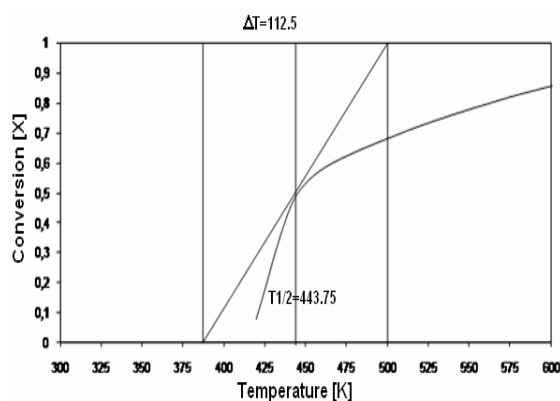
Fig. 2: Coats-Redfern treatment for tincalconite dehydration.

Conversion fraction vs. temperature graphs were plotted as in Fig. 3 for using the Suzuki method [12]. ζ was obtained from the slope in Fig. 3 and ϕ was calculated by using Eq. (11). The graph suggested by Suzuki was used for estimating the z value. Frequency factor was calculated by Eq. (13). Values of ΔT and $T_{1/2}$ obtained from these plots were 71.87 K and 431.25 K, respectively. Frequency factor and activation energy values calculated according to the Suzuki method were found as $67.21 \times 10^5 \text{ min}^{-1}$ and $60.95 \text{ kJ mol}^{-1}$, respectively. Table-2 presents the frequency factor and activation energy values calculated with this method for other heating rates. It is observed that the activation energy increases with increasing heating rate. A linear regression model for the activation energy, E (kJ mol^{-1}) against the heating rate ($^\circ\text{C min}^{-1}$) is constructed with the data given in Table 2 as below:

$$E = -4.250 + 5.461 \times \text{heating rate}$$

Table-1: Frequency factor and activation energy and r-square and order values which are evaluated due to the Coats-Redfern method for both (two) regions.

		Particle Size (mm)					
		0.075		0.075-1.2		1.2	
		1.Region	2. Region	1. Region	2. Region	1. Region	2. Region
5°C	E(kJ/mol)	22.92	3.03	56.61	2.70	77.48	2.89
	k_0 (s ⁻¹)	71.90×10^5	1.96×10^8	7.94×10^5	1.84×10^8	3598.06×10^5	2.02×10^8
	n	1	1	1	1	1	1
	r ²	0.9936	0.9875	0.9998	0.9933	0.9973	0.9856
10°C	E(kJ/mol)	149.17	5.45	133.36	2.97	35.83	4.80
	k_0 (s ⁻¹)	1215.26×10^{13}	5.23×10^8	685.28×10^{13}	3.77×10^8	6.11×10^{13}	4.06×10^8
	n	1	1	1	1	1	1
	r ²	0.9991	0.9956	0.9877	0.9944	0.9890	0.9909
12°C	E(kJ/mol)	80.05	6.09	91.31	7.46	118.65	5.19
	k_0 (s ⁻¹)	16.76×10^8	3.79×10^8	267.63×10^8	3.00×10^8	4.77×10^{13}	4.06×10^8
	n	1	1	1	1	1	1
	r ²	0.9996	0.9869	0.9947	0.9794	0.9976	0.9716

Fig. 3: Conversion-Temperature Curve Obtained by TGA for the Suzuki Method (particle size 0.075-1.2 mm and heating rate 10 °C min⁻¹).Table-2: Frequency factor and activation energy and T_{1/2} (K) and ΔT(K) values which are evaluated due to the Suzuki method.

		Particle Size (mm)		
		0.075	0.075-1.2	1.2
5°C	E(kJ/mol)	24.00	24.39	23.98
	k_0 (s ⁻¹)	47.046	49.95	38
	T _{1/2} (K)	435.5	440.62	443.75
	ΔT(K)	168.75	156.25	175
10°C	E(kJ/mol)	60.95	54.17	33.20
	k_0 (s ⁻¹)	67.21×10^5	8.04×10^5	1440.54
	T _{1/2} (K)	431.25	434.37	443.75
	ΔT(K)	271.87	81.25	112.5
12°C	E(kJ/mol)	63.65	134.53	63.60
	k_0 (s ⁻¹)	12.74×10^6	266×10^{13}	7.72×10^6
	T _{1/2} (K)	437.5	449.5	450
	ΔT(K)	75	38.88	75

The regression model has an R^2 value of 0.79, and the p -value of the heating rate is 0.018, which implies that the heating rate has a statistically significant effect on the activation energy at significance level of $\alpha=0.05$. This result is expectable because the dehydration of tinalconite is an endothermic reaction.

The r-square values obtained from DTA-TGA curves fit a first order kinetic model. As can be seen from TG curve, mass loss increases with temperature. For a given temperature, conversion fraction was found by dividing the mass loss by the total mass loss at the end of the process. In order to determine the kinetic parameters, Coats-Redfern and Suzuki methods were applied, and the results were compared. It was determined that Coats-Redfern method gives more reliable results than Suzuki method since it can be applied to both regions successfully.

Tables 1 and 2 show that kinetic parameters reported in the literature is close to the results obtained from this work. Results of this work are reasonably compatible with those given by Ersahan *et al.* [15] and Sevim *et al.* [16].

Experimental

Tinalconite was obtained from Bandırma Boron and Acid Plants Works of Eti Bor A.Ş. Table 3 shows the chemical decomposition of tinalconite. The X-ray diffraction analysis is given in Fig.4, in which the primary peaks of the concentrate correspond to those of tinalconite. Hence, the concentrate was mainly formed from tinalconite crystals. Na₂B₄O₇·5H₂O (Tinalconite) analysis were made by the volumetric method. Impurities were determined by atomic absorption spectrometer (Varian SpectrAA-300). TG experiments were carried out using a SETARAM Labsys 3.0 simultaneous DTA-TG System. Fig. 1 presents DTA and TGA graphs of tinalconite. The results are presented for a heating rate of 10°C min⁻¹. An endothermic peak is seen for DTA at 740 °C. A sample size of 20 mg and a temperature range of 50–850 °C was applied in the thermal experiments. After the sample is inserted in a platinum crucible,

its mass loss was measured at heating rates of 5, 10 and 12 °C min⁻¹ using flowing nitrogen atmosphere with a purge time of 20 min and a flow rate of 25 ml min⁻¹. The thermo balance was measured with a mass of 0.001mg, and with an accuracy of ±1%.

Table-3: Chemical analysis of tincalconite.

Component	Value (wt %)
B ₂ O ₃	48.37 %
Na ₂ O	21.05 %
Ca	148 ppm
Cr	1.33 ppm
Fe	5.11 ppm
Al	10.29 ppm
Sr	10.50 ppm
Li	35 ppm
Mg	29 ppm
K	107 ppm
Ti	0.16 ppm
Zn	13 ppm
Ni	4.25 ppm
Moisture	30.22 %

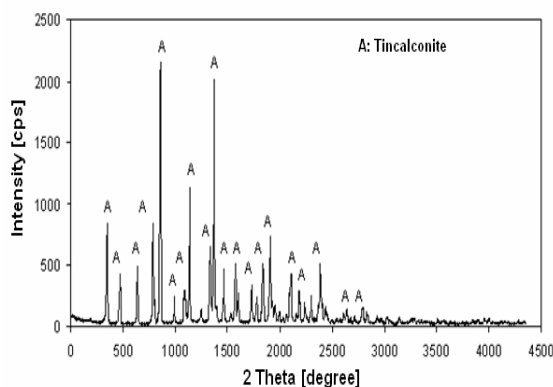


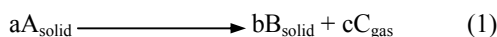
Fig. 4: RD Spectrum of Tincalconite.

Mathematical Models

There are several approaches for studying the kinetic analysis of thermal decomposition two of them were used in this study based on TG. These approaches are briefly explained below:

Coats-Redfern Method

In this method, decomposition reaction of a solid can be defined as a thermal decomposition of the solid and the reaction type can be expressed as below:



where, A_{solid} is the decomposition rate of the solid material. It can be defined as

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (2)$$

where, t is time, α is the conversion fraction, n is the reaction order and k is the rate constant. If s (heating

rate) is defined as $q = dT/dt$, and k is expressed as $k = k_o \exp(-E/RT)$, Eq.(2) can be defined as

$$\frac{d\alpha}{dT} = \frac{k_o}{q} (1-\alpha)^n \exp\left(\frac{-E}{RT}\right) \quad (3)$$

where, T is the absolute temperature, k_o is the frequency factor, R is the universal gas constant and E is the activation energy. Eq. (4) can be obtained by integrating Eq. (3) with the boundary conditions $T \rightarrow T_0$ for temperature, and $\alpha \rightarrow 0$ for the conversion fraction.

$$\frac{1-(1-\alpha)^{1-n}}{(1-n)} = \frac{k_o R}{q} \int \exp\left(\frac{-E}{RT}\right) dT \quad (4)$$

Since the right hand-side of this equation does not have an exact integral, the following equation can be obtained if the right-hand side is expanded into an asymptotic series and high-order terms are ignored

$$\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \frac{k_o R}{qE} \left(1 - \frac{2RT}{E}\right) \exp\left(\frac{-E}{RT}\right) (n \neq 1) \quad (5)$$

With an assumption of $2RT/E \ll 1$, Eq. (5) becomes

$$\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} = \frac{k_o R}{qE} \exp\left(\frac{-E}{RT}\right) (n \neq 1) \quad (6)$$

Eq. (7) can be obtained from Eq. (3) for $n=1$:

$$\frac{-\ln(1-\alpha)}{T^2} = \frac{k_o R}{qE} \exp\left(\frac{-E}{RT}\right) (n=1) \quad (7)$$

If the following functions are defined,

$$f(\alpha) = \frac{1-(1-\alpha)^{1-n}}{(1-n)} (n \neq 1) \quad (8)$$

$$f(\alpha) = -\ln(1-\alpha) (n=1) \quad (9)$$

Eq. (10) can be written:

$$\ln \frac{f(\alpha)}{T^2} = \ln \left(\frac{k_o R}{qE} \right) - \left(\frac{E}{RT} \right) \quad (10)$$

The plot of $\ln(f(\alpha)/T^2)$ vs. $1/T$ forms a line with a slope of $-E/R$. The intercept of this straight line is frequency factor [11].

Suzuki Method

In order to obtain the kinetic parameters, a conversion vs. temperature plot of TGA data is used. $T_{1/2}$, which is the temperature for 50% conversion, and ΔT , which is the slope at 50% conversion, can be determined from the plot. Eq. (11) is then defined as:

$$\xi = \frac{\Delta T}{T_{1/2}} = \frac{2}{\ln 2} \varphi \left(\frac{E}{RT_{1/2}} \right) \quad (11)$$

where

$$\varphi \left(\frac{E}{RT_{1/2}} \right) = 1 - \left[z e^{-z} E_1(z) \right] \quad (12a)$$

$$E_1(z) = \int_0^{\infty} \left[\frac{\exp(-z)}{z} \right] dz \quad (12b)$$

$z = E/RT_{1/2}$. For determining the activation energy of the process, ξ can be obtained from the conversion vs. temperature plot, and φ can be calculated by Eq. (11). The graph of Suzuki *et al.* [12] is used to estimate the value of z . Eq.(13) can be used to find the frequency factor:

$$k_0 = \frac{2q}{\Delta T} \exp \left(\frac{E}{RT_{1/2}} \right) \quad (13)$$

Conclusions

Kinetic parameters of tinalconite during thermal decomposition were explored with TGA data. More reliable results were obtained by the Coats-Redfern method compared to the Suzuki method, since the Coats-Redfern method can successfully be applied on both regions. It was observed that the decomposition kinetics of tinalconite occurred in two steps and both regions suitably fit a first-order kinetic model. Coats-Redfern method calculated the activation energy and frequency factor values as 149.17 kJ mol⁻¹ and 1.2x10¹⁶ min⁻¹ for region I, and 5.45 kJ mol⁻¹ and 5.23x10⁸ min⁻¹ for region II, respectively. Suzuki method found the activation energy and frequency factor values as 60.95 kJ mol⁻¹ and 67.21x10⁵ min⁻¹, respectively. In order to determine whether our system is external-diffusion limited or reaction-rate limited, extra experimental studies should be carried out [17]. The effect of parameters such as particle size and flow rate of inert gas is to investigate detail as a future work.

In addition, the following findings are within the scope of work done:

- 1- Unprocessed raw material compounds of boron and other foreign substances eliminate the extra weight and reduce the amount of water,
- 2- Reduce the production cost of energy and transportation of anhydrous borates,
- 3- Disintegration of calcined samples was carried out more quickly due to the dehydration process.

Nomenclature

- E - Activation Energy, kJ mol⁻¹
 K -Rate Constant, s⁻¹
 k_0 - Frequency Factor, s⁻¹
 n - Reaction Order
 Q - Heating Rate, K s⁻¹
 R - Universal Gas Constant, 8.314 J.mol⁻¹K⁻¹
 T - Absolute Temperature, K
 α - Fraction Reacted

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