Journal of Thermal Analysis, Vol. 48 (1997) 403-411

DEHYDRATION KINETICS OF ULEXITE FROM THERMOGRAVIMETRIC DATA

M. Tunç[*], *H. Erşahan, S. Yapici and S. Çolak*

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

(Received November 29, 1995; in revised form March 28, 1996)

Abstract

In the present study, the kinetic parameters of the thermal decomposition of ulexite were investigated by using TGA data. For the kinetic analysis, the Suzuki and Coats-Redfern methods were applied. It was determined that the process fits a first-order kinetic model, and the value of the activation energies and frequency factors decreased with decreasing particle size, which can be attributed to the increasing particle internal resistance to the escape of water as the grain size increases. The activation energy values were found to be 47.34–60.01 kJ mol^{-1} for region I and 0.225–1.796 kJ mol^{-1} for region II for the range of particle size fraction used. The frequency factors were calculated to be 9821.8–524.9 s^{-1} for region I and 3.05×10^{-4}–2.807×10^{-5} for region II for the same conditions.

Keywords: dehydration, dehydration kinetics, thermal decomposition, thermogravimetry, ulexite

Introduction

Most of the world's commercially recoverable boron reserves are in the form hydrated borate minerals, such as ulexite, pandermite, tincal and colemanite. An important extent of the world's ulexite reserves, together with colemanite and other boron minerals, was discovered in the Bigadiç region in Turkey. It is estimated that about 54% of the world's known boron reserves are in Turkey which has a substantial boron extraction industry [1–4]. Ulexite, a hydrated calcium-sodium borate with the chemical formula $Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$, is a commercially important boron mineral. At present, it is commonly used in the production of fire-resistant chemical substances, insulators and fiberglass [3]. When substances containing hydrate water are heated to a certain temperature, they lose mass by giving off H_2O, a process called dehydration. Dehydration processes can be used for different tech-

---

[*] Present address: Van Yüzüncü Yil University, Faculty of Science, Department of Chemistry, Van, Turkey.

0368–4466/97/ $ 5.00

John Wiley & Sons, Limited
Chichester

nological and economical purposes; to decrease the mass of a material in order to reduce transportation costs if it includes hydrated water in large amounts, or it can be a necessary stage of a chemical process. The purpose of applying thermal dehydration to ulexite is to obtain a high rate of extraction of boric acid with acidic solutions from the dehydrated mineral.

To predict and understand an industrially important dehydration process, its kinetic must be known. In recent years, procedures have been introduced into almost all fields of material sciences for the determination of kinetic parameters, utilizing non-isothermal TG data. These methods have been applied to obtain experimental thermogravimetric data on materials and kinetic parameters of reactions. The mass change of a material heated at a constant heating rate is recorded continuously, and these thermogravimetric data are then interpreted with the use of different approaches, such as the Suzuki method [5], the Coats-Redfern method [6], Doyle's approximation and McCarty's approximation [7].

The thermal dehydration of ulexite has been studied by various investigators [8–12], but studies on the dehydration kinetics from the thermogravimetric data are scarce. Therefore, the aim of this work was to investigate the dehydration kinetics of ulexite by using TG data. For this purpose, DTA and TG curves of an ulexite mineral were obtained for five samples with different particle sizes, and the dependence of the kinetic parameters on the particle size was investigated by employing two different kinetic models on the basis of the TG curves.

Theoretical backround

For a kinetic analysis employing thermal decomposition data, various approaches have been developed. Two of them, based on TG, explained briefly below, were used in the present study.

Coats-Redfern method [6]

For a decomposition reaction of a solid material

$$aA_s \rightarrow bB_s + cC_g \tag{1}$$

the decomposition rate of the solid material, A_s, can be expressed as

$$\frac{dx}{dt} = k(1-x)^n \tag{2}$$

where x is the conversion fraction, t is time, k is the rate constant and n is the reaction order. If the heating rate is expressed as $q=dT/dt$, and the rate constant $k=k_0\exp(-E/RT)$, Eq. (2) can be expressed as

$$\frac{dx}{dT} = \frac{k_0}{q}(1-x)^n \exp\left(\frac{-E}{RT}\right) \tag{3}$$

where k_0 is the frequency factor, T is the absolute temperature, E is the activation energy and R is the universal gas constant. Integration of Eq. (3) with the boundary conditions $0 \rightarrow x$ for the conversion fraction and $T_0 \rightarrow T$ for the temperature gives the following expression:

$$\frac{1-(1-x)^{1-n}}{(1-n)} = \frac{k_0}{q}\int_{T_0}^{T} \exp\left(\frac{-E}{RT}\right)\mathrm{d}T \qquad (4)$$

The right-hand side of this equation has no exact integral, but the following equation can be obtained when the right-hand side of the equation is expanded into an asymptotic series and the higher-order terms are ignored:

$$\frac{1-(1-x)^{1-n}}{T^2(1-n)} = \frac{k_0R}{qE}\left(1-\frac{2RT}{E}\right)\exp\left(\frac{-E}{RT}\right) \qquad (\text{for } n \neq 1) \qquad (5)$$

where k_0R/qE is constant for any definite value of n and of heating rate. Assuming that $2RT/E \ll 1$, Eq. (5) reduces to

$$\frac{1-(1-x)^{1-n}}{T^2(1-n)} = \frac{k_0R}{qE}\exp\left(\frac{-E}{RT}\right) \qquad (\text{for } n \neq 1) \qquad (6)$$

For $n=1$, the following equation can be obtained from Eq. (3) with the same assumptions:

$$\frac{-\ln(1-x)}{T^2} = \frac{k_0R}{qE}\exp\left(\frac{-E}{RT}\right) \qquad (\text{for } n = 1) \qquad (7)$$

If the following functions are defined:

$$f(x) = \frac{1-(1-x)^{n}}{T^2} \qquad (n \neq 1) \qquad (8)$$

$$f(x) = \frac{-\ln(1-x)}{T^2} \qquad (n = 1) \qquad (9)$$

the following general equation can be written:

$$\ln\frac{f(x)}{T^2} = \ln\left(\frac{k_0R}{qE}\right) - \left(\frac{E}{RT}\right) \qquad (10)$$

A plot of $\ln(f(x)/T^2)$ *vs.* $1/T$ gives a straight line of slope $-E/R$. The frequency factor can be calculated from the intercept of this straight line.

Suzuki method [5]

In this method, a conversion *vs.* temperature plot obtained from TG data is used to obtain kinetic parameters. The temperature corresponding to 50% conversion,

$T_{1/2}$, and ΔT, which is the slope of the plot at the point of 50% conversion, are determined by using this plot. The following function is then defined:

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

where

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

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

where $z = E/RT_{1/2}$. To calculate the activation energy of the process, ξ is obtained from the conversion *vs.* temperature plot, and the term φ is then calculated from Eq. (11). For estimation of the value of z, the graph prepared by Suzuki [5] is used. The frequency factor is obtained from the following equation:

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

Experimental

The ulexite used in the present work was obtained from the deposits around Eskisehir-Kirka in Turkey. The composition of the sample was determined by X-ray diffraction and analytical analysis (Table 1). Five different particle sizes of the mineral were used in the thermogravimetric experiments. A Shimadzu Model 50 DTA-TG system was employed for the DTA and TG measurements. For TG, a given amount of the sample was put into a platinum crucible, and its mass loss due to dehydration was recorded at a constant heating rate of 10°C min^{-1} at a N_2 gas flow rate of 0.83 mLs^{-1}.

Results and discussion

DTA and TG curves of the mineral are given in Figs 1a and 1b, respectively, for the particle size fraction of $-2000+1000$ μm. For all particle size fractions, two basic endothermic peaks were observed; one of them at 155–165°C, and the other, larger than the first one, at 185–190°C. The size of the peaks decreased as the temperature was raised. The TG curves showed that the mass loss started in the temperature range 62–71°C for all particle size fractions. In the DTA experiments, the rate the dehydration process was very high in the interval 90–230°C; after 230°C, the process continued at a very low rate up to 530°C, at which almost no mass loss was observed. Two TG peaks and two DTA regions with different nominal mass

Table 1 Chemical composition of ulexite

Component	Wt%
CaO	13.67
B_2O_3	42.44
Na_2O	7.24
H_2O	35.42
Impurity	1.23

loss rates revealed that the dehydration process takes place in two steps. Stoch and Waclawska [12] studied the mechanism of thermal decomposition of ulexite and observed a three-step dehydration process. The difference in step number between their work and the present study may result from the difference in heating rates; they used heating rates of 10 and 2.5°C min^{-1}, but without mentioning at which heating rate they observed three steps. It could have been 2.5°C min^{-1}, which is much lower than that used in this study. They recorded the three peaks at temperatures of 118, 152 and 181°C, while in our work the two peaks were observed at 158 and 189°C, i.e. in good agreement with the last two temperatures obtained by Stoch and Waclawska. This difference in peak number can be explained by the faster heating in our investigation. From the TG experiments, it was observed that the second step of the process started at a conversion fraction of approximately 0.74 for all particle size fractions used in the investigation, but that the beginning temperature of the second step decreased with decreasing particle size, from 240 to 210°C.

The dehydration reaction taking place in the process is given as

$$Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O \rightarrow$$
$$Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}nH_2O+(16-n)H_2O \qquad (14)$$

where n is the number of moles of water remaining after dehydration. The conversion fractions were calculated as the ratio of the mass loss at a given temperature to the total mass loss at the end of the process.

The reaction order of the process must first be determined in order to calculate the kinetic parameters by the Coats-Redfern method. The reaction order was determined as the value giving the best fit to the plot of $\ln(f(x)/T^2)$ *vs.* $(1/T)$ by iteration. This was done by increasing the value of the reaction order by a certain interval and then testing the fit of the $\ln(f(x)/T^2)$ *vs.* $(1/T)$ plot. For the first region, the results for all particle sizes showed that the reaction fitted a first-order kinetic model with regression coefficients between 0.9929 and 0.9984. Since the Coats-Redfern method is applicable for conversion values from 0.05 to 0.8, and the second step of the reaction covers the range from approximately 0.74 to 0.97, i.e. partly out of the range of application of this method, taking the reaction in the second stage as of first order can be considered an approximation. However, application of the Coats-Redfern method confirmed the DTA and TG results, i.e. the process occurred in

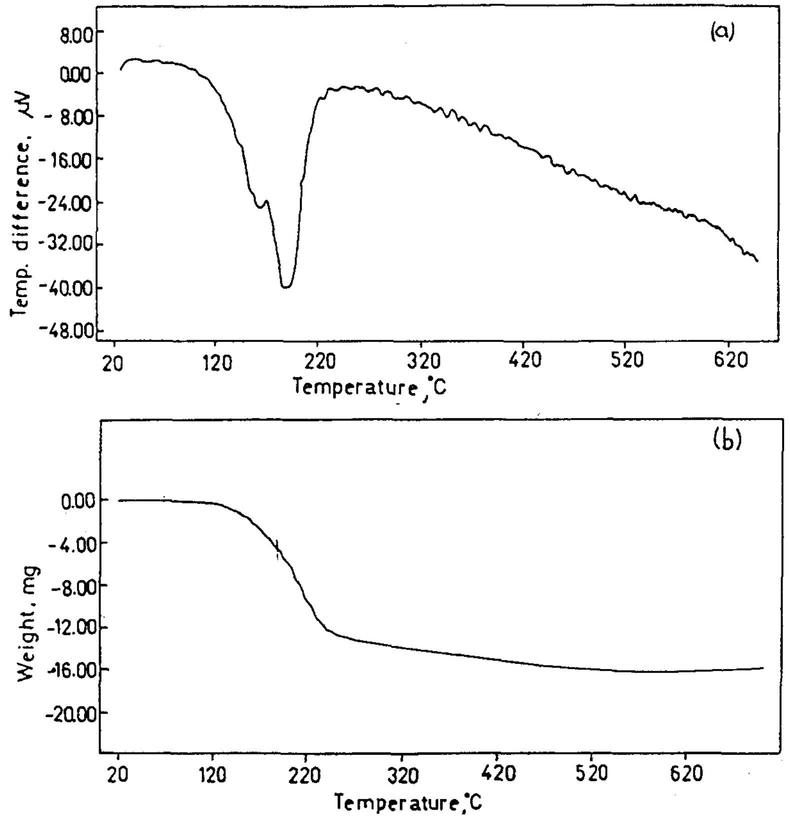

Fig. 1 (a) DTA, (b) TG curves of ulexite

two steps. The plot of $\ln(f(x)/T^2)$ *vs.* $(1/T)$ includes two regions, due to two different types of dehydration behaviour, as seen in the TG curve in Fig. 1b, now shown in Fig. 3 for the particle size fraction –2000+1000 μm. Therefore, the Coats-Redfern method was applied to both regions separately. From the slopes of the straight lines and Eq. (10), the activation energies and frequency factors for both regions were calculated, and are given in Table 2.

Table 2 Activation energies and frequency factors from Coats-Redfern method

	Region I		Region II	
Particle size μm	E/kJ mol^{-1}	k_0/s^{-1}	E/kJ mol^{-1}	k_0/s^{-1}
–2000+1000	60.01	9821.8	1.796	3.05×10^{-4}
–1000+710	54.50	4105.8	0.709	8.910×10^{-5}
–710+600	53.20	3635.8	0.510	6.900×10^{-5}
–425+300	47.90	818.8	0.333	4.310×10^{-5}
–300+250	47.34	524.9	0.225	2.807×10^{-5}

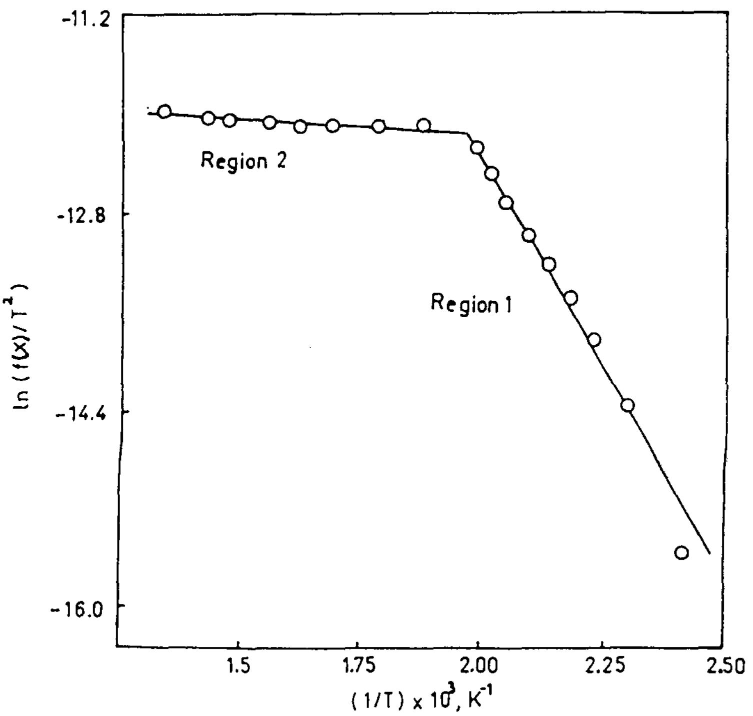

Fig. 2 Coats-Redfern treatment for ulexite dehydration

To apply the Suzuki method, the plots of conversion fraction *vs.* temperature were constructed, as shown in Fig. 2 for the particle size fraction –2000+1000 μm. The values of ΔT and $T_{1/2}$ obtained from these plots, and the calculated values of the activation energies and frequency factors of the process are given in Table 3. As seen in Tables 2 and 3, the values of activation energies and frequency factors show a general tendency to decrease with decreasing particle size fraction. The effect of particle size on the activation energy can be explained by the increasing diffusional resistance to the escape of water from the particle interior as the particle size increases.

Table 3 Activation energies and frequency factors from Suzuki method

Particle size	$T_{1/2}$/K	ΔT/K	E/kJ mol^{-1}	k_0/s^{-1}
–2000+1000	488	69.7	66.7	69338
–1000+710	468	87.5	53.0	3150
–710+600	465	82.0	53.1	3879
–425+300	464	85.0	50.0	1725
–300+250	475	97.5	48.2	707

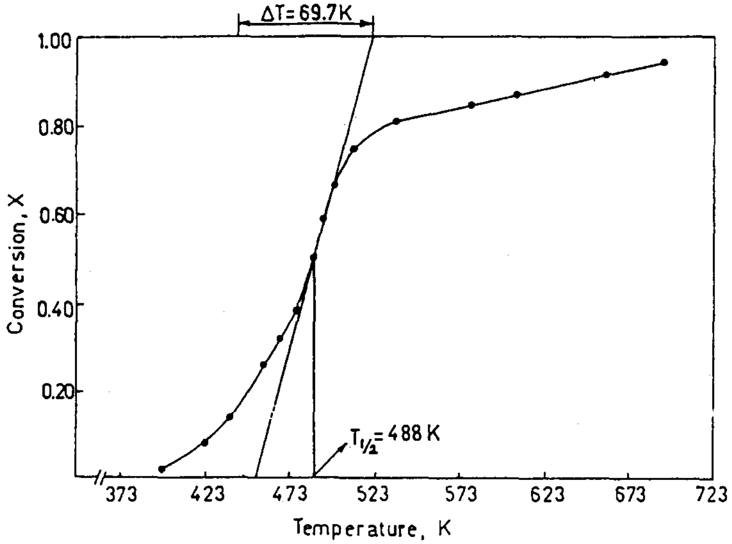

Fig. 3 Suzuki treatment for ulexite dehydration

If a comparison is made between the two methods used in the kinetic analysis, it can be seen that there is good agreement between the activation energy values obtained by the Coats-Redfern method for region I and the Suzuki method. It can be said that the values obtained by the Suzuki method represent only region I, where the main part of the conversion takes place. It is clear that the Coats-Redfern method is more suitable for the processes with more than one region. The Suzuki method can be applied to a process with one region, but is not suitable for processes with multi-regions. It can also be said that the Suzuki method leads to an overall approach, while the Coats-Redfern method gives the facility of a more detailed investigation, and therefore the Coats-Redfern results can be said to be more reliable. A similar study was performed by Khadikar *et al.* [13], in which the thermal decomposition of thallium(III) citrate was investigated. They observed a three-region decomposition process and applied the Coats-Redfern method for estimation of the kinetic parameters.

Conclusions

In the present study, the kinetic parameters of the thermal decomposition of ulexite were investigated by using TG data. It was established that the process fits a first-order kinetic model, and the values of the activation energies and frequency factors decreased with decreasing particle size, which can be attributed to the increasing intraparticle resistance to the escape of water. The results of the Coats-Redfern method can be said to be more reliable, since the Suzuki method includes more hand-fitting procedure. Application of the Coats-Redfern method also confirmed the DTA and TG results that the process consisted of two regions. The activation energy values were found to be 47.34–60.01 kJ mol^{-1} for region I and 0.225–1.796 kJ mol^{-1} for region II for the range of particle size fraction used. The frequency factors were calculated as 9821.8–524.9 s^{-1} for region I and 3.05×10^{-4}–2.807×10^{-5} for region II for the experimental conditions of the system.

Explanation of symbols

Symbol	Meaning	Unit
E	activation energy	kJ mol^{-1}
k	rate constant	s^{-1}
k_0	frequency factor	s^{-1}
n	reaction order	
q	heating rate	Ks^{-1}
R	universal gas constant	8314 kJ mol^{-1}K^{-1}
T	temperature	K
x	conversion fraction	

References

1 P. H. Kemp, The Chemistry of Borates, Part I. Borax, Consolidated Ltd., S. W. I., 1956, p. 1.
2 Bull. Mine. Res. Explor. Inst. of Turkey, Report, 187 (1982).
3 F. I. Karayazici, N. Nal and F. Celayir, Türkiye Sinai Kalkinma Bankasi, Yayin, 19 (1980) 72.
4 T. W. Davies, S. Çolak, S. R. M. Hooper, Proc. Chemeca'90, 1990, 1164–1171.
5 M. Suzuki, M. D. Misic, O. Koyama and K. Kawazoe, Chem. Eng. Science, 33 (1978) 271.
6 A. Ersoy-Mericboyu, S. Küçüdbayrak and B. Dürüs, J. Thermal Anal., 39 (1993) 707.
7 A. A. Duswalt, Thermochim. Acta, 8 (1974) 57.
8 H. Gülensoy, Türkiyedeki bor mineralleri ile bunlarm dehidrolanmalari, çözünürlükleri ve kati cisim reaksiyonlari hakkinda, Şirketi Mürettibiye Basimevi, Istanbul, 1961, pp. 1–45.
9 H. Gülensoy and J. Savci, Bull. Miner. Res. Explor. Ionst. of Turkey, 86 (1976) 75.
10 H. Gülensoy and M. M. Kocakerim, Bull. Miner. Res. Explor. Inst. of Turkey, 89 (1977) 36.
11 M. Tugtepe and Ü. Sanigök, Chimia Industrielle, Serie C, 27 (1962) 98.
12 L. Stoch and J. Waclawska, J. Thermal Anal., 36 (1990) 2045.
13 P. Khadikar, A. Joshi, S. Parnerkar, S. Karmarkar and S. Karmarkar, Chimica Acta Turcica, 21 (1993) 117.