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Dehydroxylation Reaction Kinetic Mechanism of İnderite Mineral

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Abstract. Dehydroxylation kinetic of Kirka inderite mineral is investigated based on thermogravimetry analysis (TGA) and fourteen different solid-state mechanisms are applied to determine of dehydroxylation kinetic mechanism. Dehydroxylation experiments were carried out at five different heating rates of 2, 5, 10, 15 and 20°C/min in pure nitrogen atmosphere to obtain the thermal curves under non-isothermal conditions. It is found that random nucleation is the most probable mechanism of dehydroxylation of inderite mineral.

Keywords: Dehydroxylation, inderite mineral, kinetic mechanism, thermogravimetry

1. Introduction

The magnesium borates ($xMgO.yB_2O_3.zH_2O$) are important boron minerals for various application areas because of magnesium and boron contents. In general, they are used as catalyst for the conversion of hydrocarbons, as the luminescent materials for use in fluorescent discharge lamps, as the cathode ray tube screens and X-ray screens, as the electro conductive treating agent and as a reinforcing material for plastics. Especially, they have greater importance in superconductor magnesium diboride (MgB_2) production [1]. Not only inderite and also kurnakovite and inderborite have been first time found in Turkey at Kırka deposits. Turkey has 73% of world's boron mineral reserves based on 851 million tons of B_2O_3 content in the western part. Inderite is found in Kırka borate deposits in Eskisehir providence with borax, ulexite, colemanite, tunellite, meyerhofferite, inyonite, kurnakovite, and inderborite minerals [2]. It is necessary to determine the kinetic mechanism of dehydroxylation in order to predict its stability and transformation. These properties will affect inderite usability in different applications.

There is not available apparent published research concerning the kinetic mechanism of inderite dehydroxylation. There are some published works concerning only dehydration kinetics. ΔH and E_a parameters of some Mg-containing borates as macallisterite ($MgO.3B_2O_3.7.5H_2O$), inderite ($2MgO.3B_2O_3.15H_2O$) and kurnakovite ($2MgO.3B_2O_3.15H_2O$) had been determined by using a DSC thermal analyzer. Kinetic parameters for dehydration reaction are calculated by Kissinger and the simple Ozawa method [3, 4]. According to the non-isothermal kinetic theory, thermal decomposition of a solid can be express by the following function. Also, Coats-Redfern, Arrhenius, Ozawa, Kissinger, and Doyle non-isothermal kinetic models were used to calculate the dynamic kinetic parameters for dehydration reaction of Mg-borate mineral, inderite (Kırka/Turkey) based on thermogravimetric analysis, derivative thermogravimetric analysis and differential thermal analysis [5].

Thermal analysis techniques are used in the evaluation of kinetic parameters of solid-state reactions in the dehydroxylation process.

$$aA_{solid} \rightarrow bB_{solid} + cC_{gas} \quad (1)$$

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$$g(\alpha) = k.t \quad (2) \qquad \alpha = \frac{(W_0 - W_t)}{(W_0 - W_\alpha)} \quad (3) \qquad \ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{k_0}{\beta E_a}\right] - \frac{E_a}{RT} \quad (4)$$

$\ln\left[g(\alpha(\alpha)^2\right]$ function for each mechanism are calculated and plotted against to the 1/T. It is evaluated to determine the linearity of the function and the equitation giving the best fitting of results indicates the most probable mechanism of the reaction. Ea and k_0 can be calculated from the intercept and slope of straight line, respectively [6].

The Ea and k_0 is related with $g(\alpha)$ mechanism function which is listed in Table 1. Urbanovici was suggested a new general equation (5) in order to describe kinetics of solid state reaction and particularly the kinetics of heterogeneous decompositions [7]. This differential equation can be expressed as;

$$\frac{d\alpha}{dt} = k \,.\, \left((1-\alpha)^{\,q} \right)^{x} .\, \left[\left(1-(1-\alpha)^{\,1-q}\right) / \; (1-q)^{\,y} \right] \quad (5)$$

Table 1: Various reaction mechanism of solid thermal decomposition

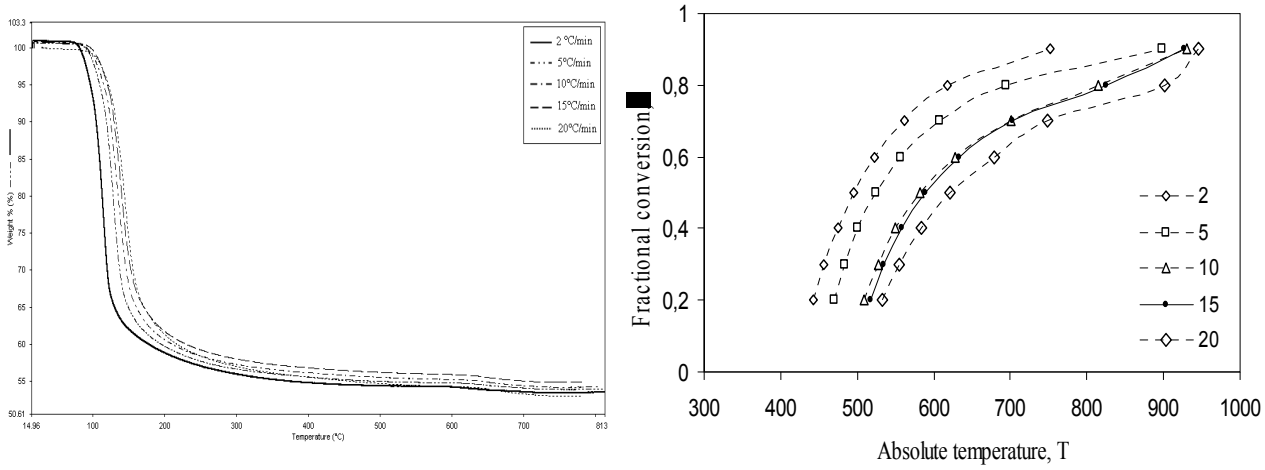
Kinetic mechanism	g(α)	Observation
Power law (P_m)	$\alpha^{1/m}$	m = 1 ,2, 3, 4
Avrami-Erofeev (A_n)	$[-\ln(1-\alpha)]^{1/n}$	n =3/2, 2, 3, 4
nth - Order Reaction (F_n)	$\left[1-(1-\alpha)^{1-n}\right]/(1-n)$	$g(\alpha) = -\ln(1-\alpha)$ (n =1)
One-dimentional diffusion (D_1)	α^2	-
Two-dimentional diffusion (D_2)	$\alpha + (1-\alpha)\ln(1-\alpha)$	-
Three-dimentional diffusion (D_3)	$\left[1-(1-\alpha)^{1/3}\right]^2$	-
Ginstling-Brounshtein (D_4)	$(1-2\alpha/3)-(1-\alpha)^{2/3}$	-

In the present study, the dehydroxylation kinetic mechanism was analyzed according to the Coats-Redfern method using fourteen of solid-state kinetic equitation. TGA were performed at 2, 5, 10, 15 and 20°C/min heating rate under non-isothermal conditions. It was found that the nucleation mechanism ($F_{3/2}$, A_2, A_3, A_4) were the best of fourteen mechanism which describe the experimental data. In the present study, the dehydroxylation kinetic mechanism was analyzed according to the Coats-Redfern method using fourteen of solid-state kinetic equitation. TGA were performed at 2, 5, 10, 15 and 20°C/min heating rate under non-isothermal conditions. It was found that the nucleation mechanism ($F_{3/2}$, A_2, A_3, A_4) were the best of fourteen mechanism which describe the experimental data.

2. Experimental

The inderite mineral used in the study was provided from the region of Kırka, Eskisehir in Turkey. After cleaning the mineral manually from visible impurities, it was ground and sieved with ASTM standard sieves to achieved uniformed size.

TGA were performed at 2, 5, 10, 15 and 20°C/min heating rate at pure N_2 flow rate of 200 ml/min in the temperature range of 30-800°C with a sample size of ~10 mg by Perkin Elmer Diamond TG\DTA. The instrument was calibrated by means of the melting points of indium (156.6 °C) and tin (231.9 °C) as the standard substances under the same conditions with the sample. Obtained TG curves at different heating rates are given in Fig.1a. The thermal curves of the dehydroxylation regions were converted into kinetic curves by plotting the fractional conversion (α) against to the absolute temperature (T) as shown in Fig.1b. The dehydroxylation kinetic mechanism was analyzed according to the Coats - Redfern method (eq. 4) using fourteen of solid-state kinetic equitation which are listed in Table 1.



(a) (b)

Fig. 1: Thermal analysis results (a) TG curves; (b) Kinetic curves of dehydroxylation reaction

3. Results and Discussions

3.1. Thermal Properties

The series of TG curves of inderite at different heating rates are given in Fig.1a. Analysis of these curves estimate the mass loss can be associated with the dehydroxylation reactions are given in below with temperature range. It is observed that all off the characteristic temperature values on the TG curves are increased while increasing heating rate from 2 to 20 °C/min (Table 2).

Table 2: Mass loss of dehydroxylation steps at different heating rates

β (°C/min)	2	5	10	15	20
T_i (°C)	122.01	140.52	150.36	157.36	160.15
(T_f) (°C)	700.15	734.83	759.51	760.84	766.87
m (%)	15.04	13.94	13.74	13.23	15.05
Average	T_i: 146±19		T_f: 744 ±34		m%=14±0.1

3.2. Dehydroxylation Kinetic Mechanism

Fig.2a shows the correlation coefficients (R^2) values of Power-Law kinetic model of inderite mineral. Kinetic mechanism for n=1 was investigated and the R^2 values for this kinetic mechanism were determined as 0.1144, 0.0428, 0.00001, 0.0032, 0.0439 for 2, 5, 10, 15 and 20 °C/min heating rates, respectively.

Fig. Fig.2b shows the R^2 values of n^{th}-order reaction kinetic mechanism of inderite mineral. In the n^{th}-order reaction kinetic mechanism, reaction rate was determined based on random nucleation, one nucleus on each molecule. The results indicated that maximum linearity of the function was obtained for n=3/2 at all the heating rates. The R^2 values for this kinetic mechanism were determined as 0.8693, 0.7158, 0.8234, 0.7574, 0.8234 for 2, 5, 10 15 and 20 °C/min heating rates, respectively.

Fig.2c shows the R^2 values of diffusion kinetic mechanism of inderite mineral. In D_1 mechanism, reaction rate is determined based on one-dimensional diffusion, in D_2 reaction rate is determined based on two-dimensional diffusion and cylindrical symmetry, in D_3 reaction rate is determined based on three-dimensional diffusion, spherical symmetry, Jander's equation. In D_4 reaction rate is determined based on three-dimensional diffusion, spherical symmetry, Ginstling and Brounstein's equations. The results indicated that maximum linearity of the function was obtained at D_3 mechanism for each heating rates. The correlation coefficients for this kinetic mechanism were determined as 0.7882, 0.6532, 0.7313, 0.7268 and 0.7942 for 2, 5, 10, 15 and 20°C/min heating rates, respectively.

Fig.2d shows the R^2 values of Avrami-Erofeev kinetic model of inderite mineral. Kinetic mechanism for n=3/2, 2, 3 and 4 is investigated and maximum linearity of the function was obtained for n=4 at all the

heating rates. The correlation coefficients for this kinetic mechanism were determined as 0.8962, 0.8432, 0.8751, 0.8682 and 0.9031 for 2, 5, 10, 15 and 20 °C/min heating rates, respectively. Results indicated that the dehydroxylation of inderite mineral follows the solid phase mechanism $F_{3/2}$, A_2, A_3, A_4. The values of kinetic parameters of dehydroxylation for the possible solid phase mechanism are listed in Table 3.

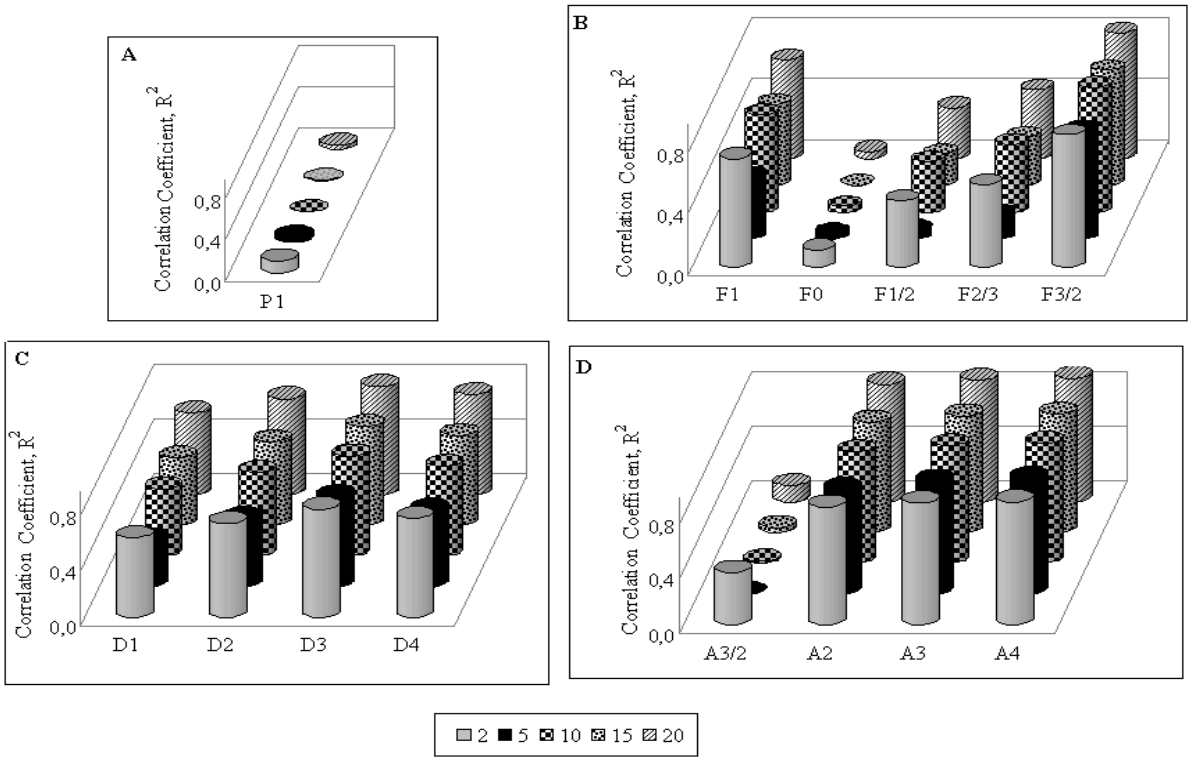


Fig. 2: Kinetic Mechanism - R^2 value, (A) power-law, (B) n^{th}-order reaction, (C) diffusion, (D) Avrami-Erofeev

Table 3: Kinetic parameters of the dehydroxylation reaction of inderite mineral

Mechanism	$F_{3/2}$		A_2	
Heating rate (°C/min)	Ea ($kJmol^{-1}$)	k_o (min^{-1})	Ea ($kJmol^{-1}$)	k_o (min^{-1})
2	15.13	0.41	29.14	11.68
5	9.98	0.16	21.33	2.30
10	12.77	0.33	24.38	4.52
15	11.62	0.45	25.60	8.42
20	12.77	0.65	28.09	13.60
Mechanism	A_3		A_4	
Heating rate (°C/min)	Ea ($kJmol^{-1}$)	k_o (min^{-1})	Ea ($kJmol^{-1}$)	k_o (min^{-1})
2	48.44	$12.39*10^2$	67.73	$11.06*10^4$
5	37.32	95.83	53.31	$32.53*10^2$
10	42.20	$18.17*10^1$	60.02	$60.02*10^2$
15	44.08	$36.86*10^1$	62.55	$13.31*10^3$
20	47.94	$63.42*10^1$	67.78	$24.51*10^3$

4. Conclusions

The results obtained from investigations on dehydroxylation kinetic mechanism from a set of experimental data at different heating rates lead to following conclusion:

1) The dehydroxylation of inderite mineral continued at a very low rate in a wide temperature range up to 767 °C after dehydration step. Release of hydroxyl group (OH^-) from polyanion structure is occurred at dehydroxylation stage.
2) Investigating the different fourteen kinetic mechanisms, it is found that dehydroxylation kinetic mechanism obeyed random nucleation mechanism ($F_{3/2}$, A_2, A_3, A_4) for each heating rate.
3) It is found that random nucleation is the most probable mechanism of dehydroxylation of inderite mineral.

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