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Kinetics of thermal decomposition of howlite mineral at different heating rates

Gamze ARSLAN SEN[1], Muge SARI YILMAZ [1*], Emek MOROYDOR DERUN[1]

ABSTRACT

In this work, the thermal decomposition kinetics of howlite were investigated at different heating rates by using Coats–Redfern, Ozawa, and Kissinger–Akahira–Sunose kinetic models under non-isothermal conditions. The thermal decomposition of howlite occurred in two dehydroxylation stages. Results indicated that it decomposes in the first dehydroxylation stage at a very slow rate due to the higher thermal stability of the mineral. Kinetic parameters were determined using the above-mentioned models for all decomposition stages. The activation energies calculated from the Ozawa and Kissinger–Akahira–Sunose isoconversional methods fit well with each other, while the activation energies calculated with the Coats–Redfern method were different. It was also seen that the activation energy of the decomposition reaction changed with the degree of conversion, suggesting that the reaction mechanism is not single-step.

Keywords: *Howlite, Kinetics, Thermal Decomposition, Dehydroxylation, Isoconversional.*

INTRODUCTION

Turkey has approximately 73% of the world's known boron reserves [1, 2]. These reserves have many different kinds of boron minerals such as tincal, colemanite, kernite, ulexite, pandermite, boracite, howlite, and hydroboracite. Among them, howlite is a calcium borosilicate hydroxide mineral and it has a monoclinic structure (space group P21/c) with a = 12.82 Å, b = 9.35 Å, c = 8.61 Å, β = 104.84° [3]. Finney et al. found the correct structural formula for howlite as Ca2[B3O4(OH)2.OSiB2O4(OH)3] [4]. The thermal behavior of howlite was investigated by high-temperature X-ray diffraction and differential thermal analysis in a previous study. It was found that the thermal expansion of howlite was strongly anisotropic, which is probably due to the hinge mechanism of the colemanite chains in the structure [5]. The only study on dehydration kinetics of howlite was investigated by Erdogan et al. in the literature. The activation energy and pre-exponential factor for dehydration reaction of howlite were found as 65 kJ.mol−1 and 50.8×105, respectively [6]. In this study, the thermal decomposition kinetics of howlite were discussed in detail differ from the literature.

Boron minerals and products are widely used in different industries including glass, detergents, ceramics, fertilizers, fuels, nuclear energy, military vehicles, electronics, and communications [7, 8]. Knowledge about the thermal behavior of boron minerals and products has great importance for being able to use them in industry. Therefore, thermal behavior and decomposition kinetics of boron minerals and products have been investigated for many years. Recently, some studies concerning the thermal decomposition kinetics of boron minerals obtained by thermal analysis methods have been reported in the literature. Ekmekyapar et al. examined the dehydration kinetics of tincal and borax. They calculated the activation energies, frequency factor, and order of reaction for both minerals by using various kinetic methods [9]. Tunc et al. determined the kinetic parameters of the thermal decomposition of ulexite by using thermal gravimetric analysis. The Suzuki and Coats–Redfern methods were used, and it was revealed that the process was first-order and the activation energy and frequency factor decreased with decreasing particle size [10]. The dehydration kinetics of inderite mineral was examined by different non-isothermal kinetic methods. The activation energy of the dehydration reaction in the different models varied from 76 to 107 kJ/mol [11]. The thermal behavior and dehydration kinetics of tunellite were investigated at different heating rates. It was found that the activation energies obtained by the isoconversional Ozawa method were more reliable for all dehydration stages [12]. Furthermore, the dehydroxylation kinetics of tunellite were studied by thermogravimetric technique. The

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[1] *Department of Chemical Engineering, Yıldız Technical University, Istanbul, Turkey*
**E-mail address: mugesari@yildiz.edu.tr*
Orcid id: https://orcid.org/0000-003-4908-4594; 0000-0003-0441-7586; 0000-0002-8587-2013
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average activation energy for tunellite was computed as 144.38 kJ/mol in non-isothermal dehydroxylation studies [13]. Thermal kinetics and thermodynamics of the dehydration reaction of inyoite mineral were also studied. Reaction orders of dehydration and dehydroxylation stages were found as 1.7 and 1.3, respectively. In addition, it was seen that the decomposition process of inyoite was an endothermic, non-spontaneous, and slow reaction [14]. Kipcak et al. synthesized zinc borates and they investigate of dehydration kinetics the boron product by using the Coats–Redfern and Horowitz–Metzger kinetic methods. The activation energies were found in the ranges 225.40–254.33 and 570.63–518.22 kJ/mol by using the Coats–Redfern and Horowitz–Metzger methods, respectively [15]. Asensio et al. investigated thermal dehydration kinetics of the synthesized potassium borate. Coats–Redfern and Doyle non-isothermal kinetic methods were used for the determination of activation energies and found to be 110.12-202.43 kJ/mol and 107.77-304.18 kJ/mol, respectively [16]. Thermal dehydration kinetics of synthesized admontite mineral was examined by using various methods. The results of kinetic analysis show that activation energies values were in good agreement with each other [17].

The objective of this study is to investigate and compare different kinetic methods including the Coats–Redfern, Ozawa, and Kissinger–Akahira–Sunose models for the thermal decomposition kinetics of howlite. In addition, the effect of the heating rate on the kinetic parameters is determined using the Coats–Redfern model.

EXPERIMENTAL

Materials and Characterization

Howlite mineral was obtained from the region of Sultancayiri, Balikesir, in Turkey. Before the analyses, the mineral was milled and sieved through 250 mesh, and then stored in a desiccator. Powder X-ray diffraction (XRD) analysis was conducted for the phase identification analysis of the mineral on PANalytical X'Pert Pro XRD equipment with CuKα radiation at operating parameters of 40 mA and 45 kV. The chemical composition of the mineral was determined by using a PerkinElmer Optima 2100 DV inductively coupled plasma-optical emission spectrometer (ICP-OES). The mineral was analyzed three times and mean values were used as one observation. The IR spectra of the mineral was obtained using a Fourier transform infrared (FT-IR) spectrometer (PerkinElmer Spectrum One). The sample was powdered and mixed with potassium bromide (KBr) and determined in the wavenumber range of 4000–400 cm−1.

The thermogravimetry (TG)/derivative thermogravimetry (DTG)-differential thermal analysis (DTA) curves were obtained on a PerkinElmer Diamond thermogravimetric analyzer with a non-isothermal temperature program. 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 as the sample. Approximately 10 mg of sample was used for each experiment. The sample was heated from ambient temperature to 900 °C at different heating rates of 2, 5, 10, 15, and 20 °C/min under nitrogen atmosphere at a flow rate of 150 mL/min. The mass loss of the sample and the temperature were recorded during the experiment for kinetic analysis.

Kinetic Methods

Thermal analysis techniques are commonly used to investigate the mechanism of solid-state decomposition reactions. In order to calculate the kinetic parameters, many non-isothermal kinetic models have been suggested. In the present study, the Coats–Redfern, Ozawa, and Kissinger–Akahira–Sunose kinetic models were used to determine the activation energy of howlite decomposition. Also, the reaction order and the effect of the heating rate on the kinetic parameters were determined using the Coats–Redfern model.

Coats-Redfern: The non-isothermal solid decomposition rate is mathematically expressed as:

$$\frac{d\alpha}{dt} = \beta . \frac{d\alpha}{dT} = k(T) . f(\alpha) \tag{1}$$

where β is the heating rate (°C/min) and f(α) and k(T) are functions of conversion and temperature, respectively. α is the conversion rate of the reaction; that is:

$$\alpha = \frac{w_o - w_t}{w_o - w_\infty} \tag{2}$$

where w_o, w_t, and w_∞ are the initial weight of the sample (mg), the sample weight at any temperature T, and the final sample weight (mg), respectively.

The temperature dependence of the rate constant, k(T), is described by the Arrhenius equation:

$$k(T) = A.e^{\left(-\frac{E}{RT}\right)} \tag{3}$$

where E is the activation energy (kJ/mol), A is the pre-exponential factor (min^{-1}), and R is the gas constant (8.314 J/K.mol).

The function f(α) can be written as:

$$f(\alpha) = (1-\alpha)^n \tag{4}$$

If all terms are substituted in Eq. 1, the following equation is obtained:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(-\frac{E}{RT}\right)} (1-\alpha)^n \tag{5}$$

From the solution of Eq. 5, the Coats–Redfern method is obtained. This equation is as follows:

$$In\left[\frac{-In\,(1-\alpha)}{T^2}\right] = In\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad n = 1 \tag{6}$$

$$In\left[\frac{1-\,(1-\alpha)^{1-n}}{(1-n)T^2}\right] = In\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad n \neq 1 \tag{7}$$

The Coats–Redfern method can be applied to TG/DTG data, assuming the reaction order (n). The correct n is presumed to lead to the best linear plot with the highest correlation coefficient value (R^2), from which the activation energy is determined [18]. The Arrhenius parameters (E and A) can be computed from the slope and intercept of the linear plot.

Ozawa: The Ozawa method is an isoconversional method in which the activation energy is predicted without knowledge of the reaction mechanism. In this method, temperatures were determined for each α value that occurred at different heating rates to find the kinetic parameters of the decomposition reactions of howlite. The acquired α values were detected at intervals of 0.1 in the range of 0.1–0.9 and temperatures at different heating rates were recorded on a graph [19]. The expression in logarithmic form is as follows:

$$\log\beta = \log\left(\frac{AE}{R}\right) - 2.315 - 0.4567\left(\frac{E}{RT}\right) - \log g(\alpha) \tag{8}$$

The E value can be calculated using the slope of the straight line of log β versus 1/T, which is equal to 0.4567(E/R) based on the established conversion rate.

Kissinger-Akahira-Sunose: The Kissinger–Akahira–Sunose method is an evaluation of the Arrhenius equation using the differential method. This model can be defined as in the following equation:

$$\text{In}\left(\frac{\beta}{T^2}\right) = \text{In}\left(\frac{\text{AR}}{Eg(\alpha)}\right) - \left(\frac{E}{RT}\right) \tag{9}$$

The slope of the plot of the left side of Eq. (9) versus 1/T at constant conversion rate for the tested heating rates allowed the calculation of the E value [20, 21].

RESULTS AND DISCUSSION

The powder XRD pattern of the mineral is given in Figure 1. All detected peaks are indexed and XRD analysis of the mineral indicated that it was defined as howlite with the chemical formula of Ca2B5SiO9(OH)5. The crystal system, the space group, and the lattice parameters of howlite were monoclinic, P21/c, and a = 12.81, b = 9.35, and c = 8.61 Å, respectively. (PDF no: 00-035-0630).

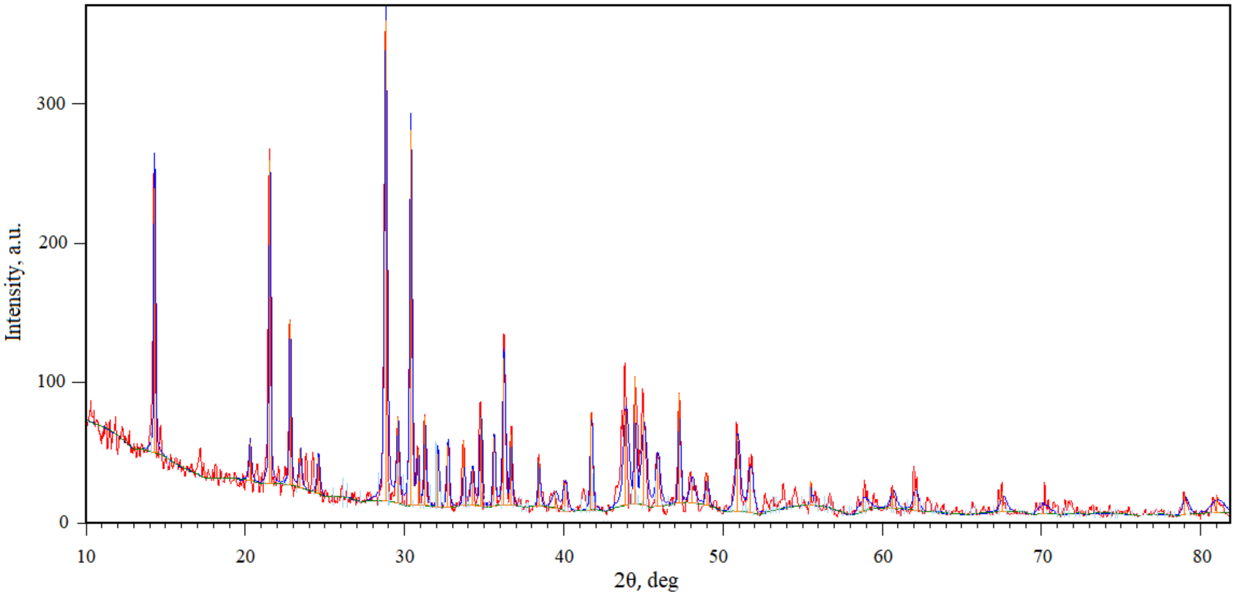


Figure 1. XRD pattern of mineral

The chemical composition of the howlite mineral was found as 43.47% B2O3, 28.61% CaO, and 16.13% SiO2 according to ICP-OES analysis results. The remaining amount of 11.79% is water content in the mineral. This result was convenient with the TG analysis result.

The FT-IR spectrum of the howlite mineral is presented in Figure 2. The bands at 3562.18 and 3217.07 cm^{-1} formed due to the presence of O-H stretching vibrations. Two bands at 1455.86 and 1325.34 cm^{-1} confirmed the presence of the asymmetric stretching mode of B(3)-O. Two bands at 1227.82 and 1012.23 cm^{-1} corresponded to O-H deformation and bending vibration. Bands between 959.11 and 859.89 cm^{-1} were attributed to the asymmetric stretching modes of B(4)-O. Bands at 829.60 and 749.36 cm^{-1} formed due to the presence of out-of-plane bending of B(3)-O. Bands between 706.78 and 467.84 cm^{-1} were assigned to the symmetric stretching modes of B(4)-O [22].

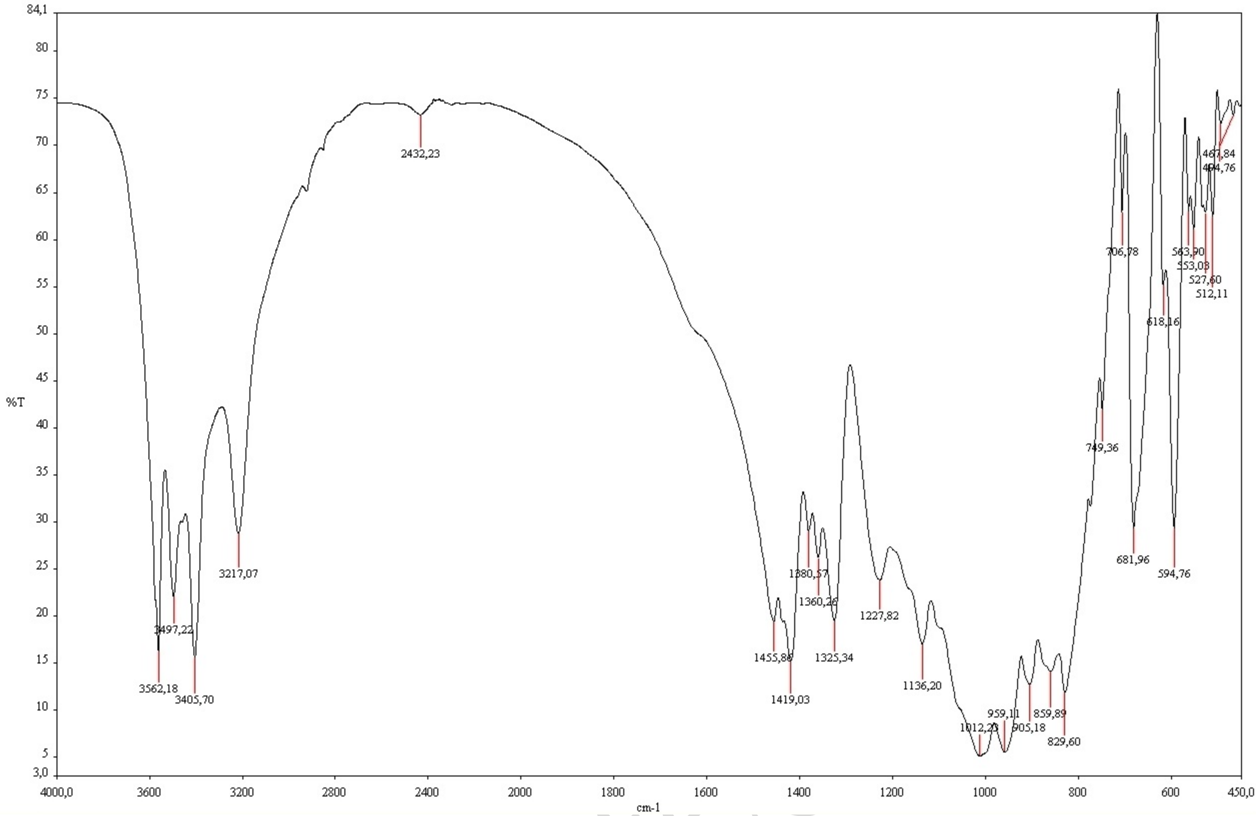


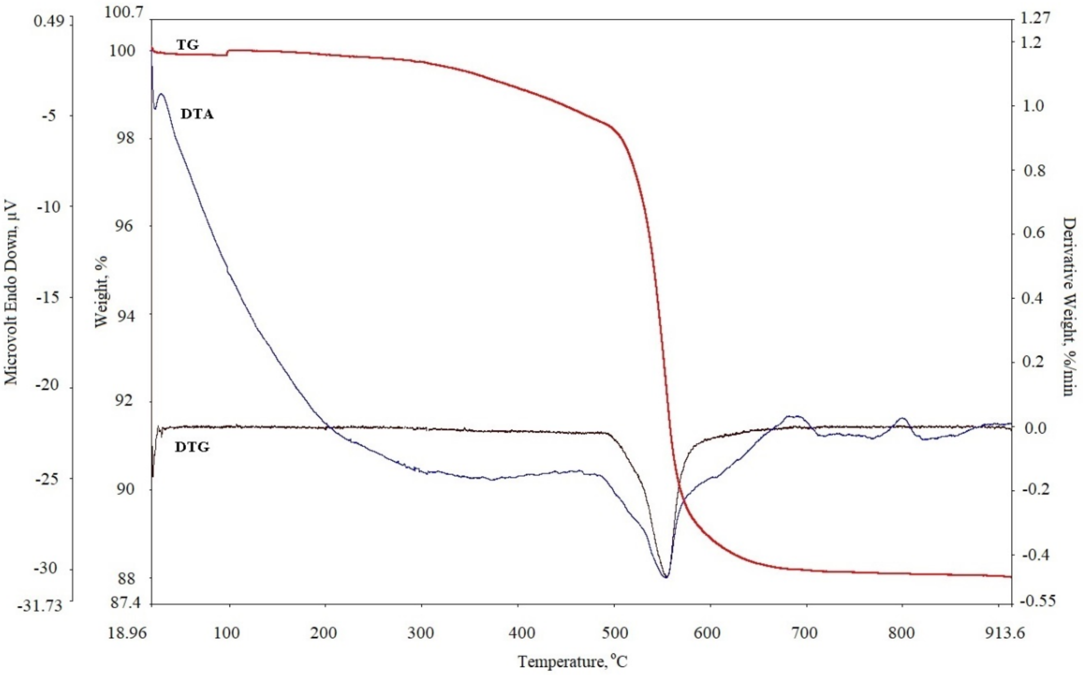
Figure 2. FT-IR spectra of howlite

The thermal behavior of howlite was investigated at different heating rates of 2, 5, 10, 15, and 20 °C/min between 30 and 900 °C under nitrogen atmosphere. Figure 3 shows thermal analysis curves of howlite at different heating rates. From the TG curve, it was observed that weight losses of howlite occurred in two stages. The first dehydroxylation stage of howlite began at about 100 °C and continued up to 512.17 °C. No sharp peak was observed in this region; therefore, it can be concluded that the howlite decomposes at a very slow rate over a wide temperature range due to the higher thermal stability of the mineral. The second dehydroxylation reaction, which corresponds to the releasing of hydroxyl groups (OH-) from the polyanion structure, proceeded up to 716 °C. The total weight losses were calculated as 11.79% for the heating rate of 10 °C/min (Table 1).

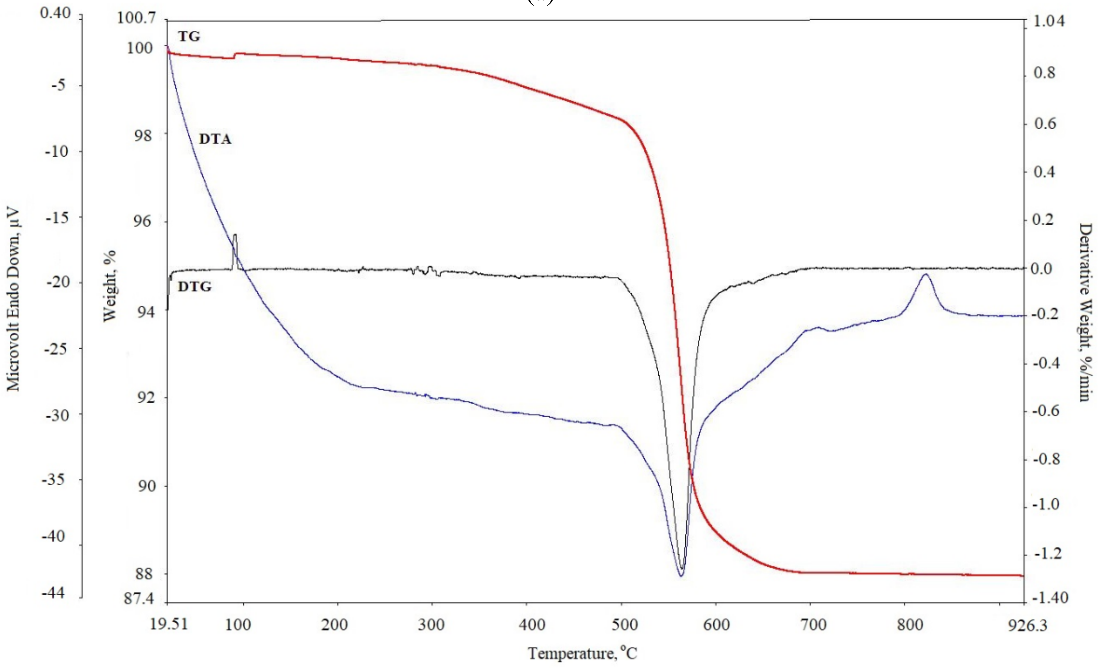
Table 1 Weight losses of all reaction stages at different heating rates

Heating Rate (°C/min)	Reaction Stage	Temperature Range (°C)	Weight Loss (%)
2	First	84.02-493.24	1.60
	Second	493.24-706.38	10.14
5	First	93.54-507.25	1.60
	Second	507.25-713.38	9.99
10	First	100.37-512.04	1.16
	Second	512.04-716.34	10.63
15	First	115.01 -513.49	1.38
	Second	513.49-717.30	10.72
20	First	119.42 -515.17	1.19
	Second	515.17-723.82	10.52

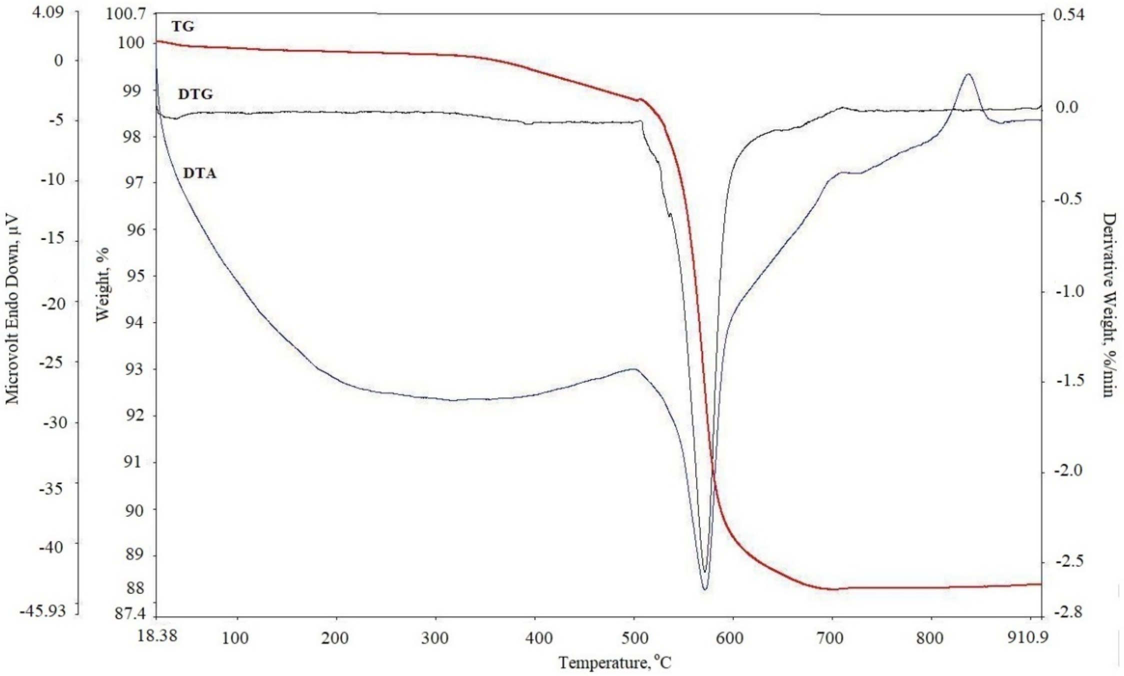
The results of DTA demonstrated that there were two endothermic peaks related to the dehydroxylation and one exothermic peak related to the crystallization (Figure 3). A sharp peak formation was not observed in the first endothermic peak of the DTA curves due to its very slow reaction rate. In addition, the effect of heating rate was also investigated and the results are summarized in Table 1. The position of the peak for the first and second stages shifted to higher temperatures when the heating rate was increased. This may have occurred due to the presence of increased thermal lag between the furnace temperature and sample temperature.



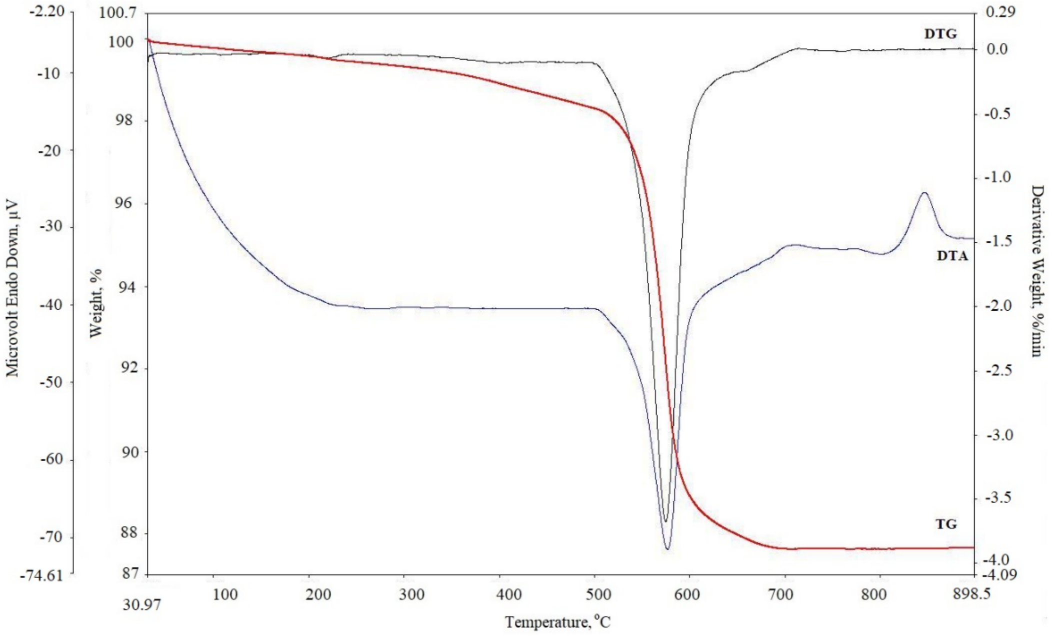
(a)



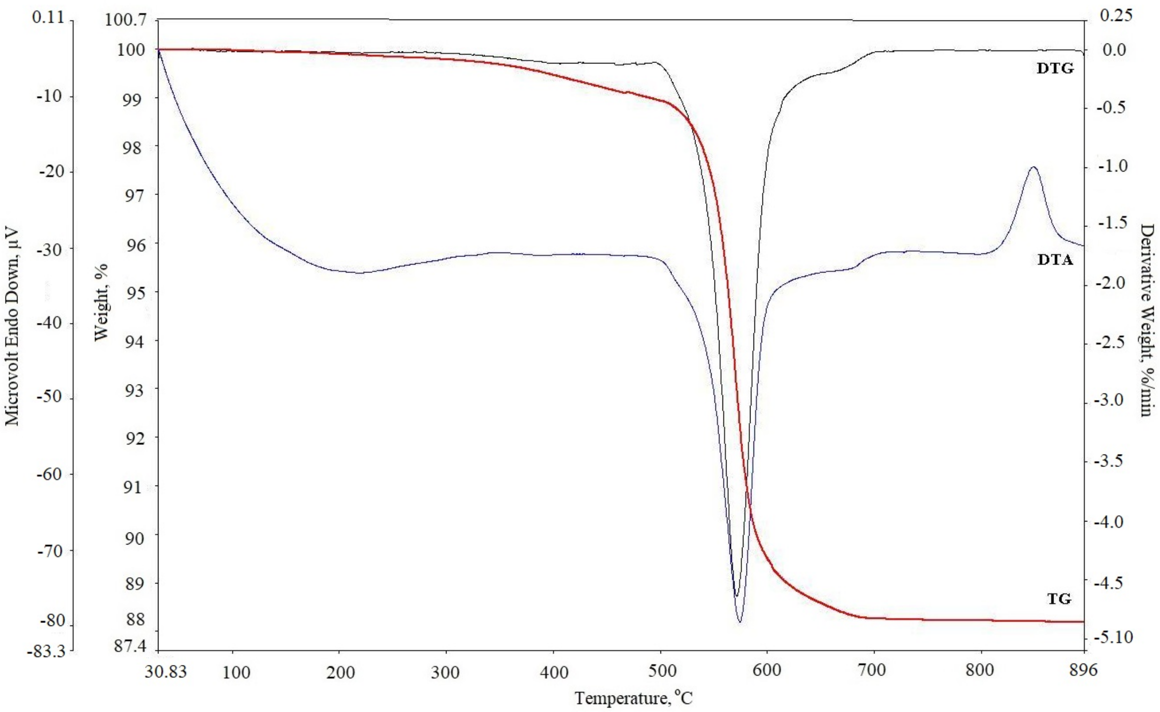
(b)


TG
DTG
DTA
4.09
0
-5
-10
-15
-20
-25
-30
-35
-40
-45.93
Microvolt Endo Down, µV
100.7
100
99
98
97
96
95
94
93
92
91
90
89
88
87.4
Weight, %
0.54
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-2.8
Derivative Weight, %/min
18.38
100
200
300
400
500
600
700
800
910.9
Temperature, °C

(c)


DTG
DTA
TG
-2.20
-10
-20
-30
-40
-50
-60
-70
-74.61
Microvolt Endo Down, µV
100.7
100
98
96
94
92
90
88
87
Weight, %
0.29
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.09
Derivative Weight, %/min
30.97
100
200
300
400
500
600
700
800
898.5
Temperature, °C

(d)



(e)

Figure 3. TG/DTG/DTA curves of howlite at different heating rates, °C/min a) 2, b) 5, c) 10, d) 15, and e) 20

Kinetic Analysis

In order to determine the activation energy of howlite, different non-isothermal methods such as Coats–Redfern, Ozawa, and Kissinger–Akahira–Sunose are used in this study. In the Coats–Redfern method, n values are estimated until the best straight line is obtained for all stages. The correct n value thus estimated leads to straight plots with maximum square correlation coefficients (R^2), from which E is determined. Thus, reaction orders of several values in the range of 0–3 were considered, the related R^2 values were calculated, and the kinetic parameters calculated using the Coats–Redfern method for the thermal decomposition of the howlite are listed in Table 2. It can be seen that in the first dehydroxylation stage the E and A values varied between 10.48 and 49.74 kJ/mol and between 0.16 and 4.83×102 min–1, while these values were 428.91–574.35 kJ/mol and 2.40×1026–9.57×1035 min–1 for the second dehydroxylation stage, respectively. Also, it is seen from the table when the reaction order increased, the calculated activation energy also increased. The value of n was found to be less than 1 for the first stage and greater than 1.5 for the second stage. This result is different from the kinetic model of the dehydration reaction of howlite (First order (n=1) thermal decomposition model) reported in previous study [6].

Table 2. Kinetic parameters calculated from Coats-Redfern method for decomposition reactions of howlite

Heating Rate (°C/min)		First Stage				Second Stage			
2	n	0	0.5	0.76	1	0	1	1.5	1.92
	R^2	0.9859	0.9970	0.9983	0.9973	0.9571	0.9888	0.9951	0.9965
	E (kJ/mol)	30.41	37.56	41.74	45.88	209.33	307.37	369.75	428.91
	A (min^{-1})	1.67	8.75	22.60	57.08	6.22×10^{11}	2.12×10^{18}	3.00×10^{22}	2.40×10^{26}
5	n	0	0.18	0.5	1	0	1	1.5	1.98
	R^2	0.9941	0.9949	0.9928	0.9831	0.9556	0.9878	0.9945	0.9962
	E (kJ/mol)	21.00	22.78	26.19	29.88	228.26	334.50	402.12	475.93
	A (min^{-1})	0.55	0.87	2.08	5.35	1.75×10^{13}	1.71×10^{20}	4.41×10^{24}	2.80×10^{29}
10	n	0	0.5	0.89	1	0	1	1.5	1.80
	R^2	0.9838	0.9961	0.9987	0.9985	0.9619	0.9909	0.9961	0.9969
	E (kJ/mol)	34.71	42.64	49.74	51.89	239.92	348.69	417.63	463.59
	A (min^{-1})	17.50	102.57	482.64	766.33	1.44×10^{14}	1.74×10^{21}	4.97×10^{25}	4.55×10^{28}
15	n	0	0.01	0.5	1	0	1	1.5	1.93
	R^2	0.9680	0.9682	0.9463	0.9213	0.9568	0.9886	0.9951	0.9966
	E (kJ/mol)	10.42	10.48	13.81	17.73	241.36	351.04	420.60	488.13
	A (min^{-1})	0.14	0.16	0.42	1.34	2.25×10^{14}	2.87×10^{21}	8.56×10^{25}	1.82×10^{30}
20	n	0	0.42	0.5	1	0	1	1.5	2.43
	R^2	0.9899	0.9935	0.9934	0.9882	0.9385	0.9795	0.9899	0.9959
	E (kJ/mol)	24.38	29.27	30.28	37.13	237.68	348.54	419.18	574.35
	A (min^{-1})	3.97	13.45	17.05	84.76	1.90×10^{14}	2.99×10^{21}	1.07×10^{26}	9.57×10^{35}

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[1] Department of Chemical Engineering, Yıldız Technical University, Istanbul, Turkey
**E-mail address: mugesari@yildiz.edu.tr*
Orcid id: https://orcid.org/0000-003-4908-4594; 0000-0003-0441-7586; 0000-0002-8587-2013
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In the Ozawa and Kissinger–Akahira–Sunose isoconversional methods, the E values were calculated according to the degree of conversion (α). E values were calculated in the α range of 0.1–0.9 with an increment of 0.1 for all stages. E and R^2 for each α value at different stages are listed in Table 3 for all decomposition stages. The average E values using the Ozawa and Kissinger–Akahira–Sunose methods were found as 457.64 kJ/mol and 382.47 kJ/mol for the first dehydroxylation stage and 539.60 kJ/mol and 590.12 kJ/mol for the second dehydroxylation stage, respectively. It was seen that the E values varied substantially with α. This significant variation of E with temperature suggests that the decomposition of howlite took place by complex reactions. A comparison of the E values obtained with the Coats–Redfern, Ozawa, and Kissinger–Akahira–Sunose methods showed similar trends for all methods. In all of the cases, the E values for the second dehydroxylation stage were higher than those for the first dehydroxylation stage. This is consistent with the decomposition of howlite in this region.

Table 3. Kinetic parameters obtained from isoconversional methods for the decomposition reactions of howlite

α	Ozawa				Kissinger-Akahira-Sunose			
	E_1 (kJ/mol)	R^2	E_2 (kJ/mol)	R^2	E_1 (kJ/mol)	R^2	E_2 (kJ/mol)	R^2
0.1	231.27	0.9858	470.40	0.9946	435.51	0.9785	505.09	0.9697
0.2	407.94	0.9895	484.19	0.9944	345.48	0.967	521.95	0.9542
0.3	282.83	0.9431	496.58	0.9974	393.05	0.9659	548.10	0.9477
0.4	435.40	0.9708	518.61	0.9933	346.81	0.9638	565.16	0.9440
0.5	596.22	0.9514	538.56	0.9927	329.58	0.9628	582.21	0.9399
0.6	524.33	0.9144	556.20	0.9928	416.09	0.9507	600.62	0.9337
0.7	683.03	0.9790	572.95	0.9863	425.20	0.9541	609.35	0.9381
0.8	422.64	0.9516	552.85	0.9997	368.03	0.9459	636.37	0.9539
0.9	535.09	0.9187	666.08	0.9979	490.15	0.9224	742.20	0.9604
Average E	457.64	-	539.60	-	382.47	-	590.12	-

Activation energy is defined as the minimum energy requirement that must be overcome before molecules can get close enough to react and form products [23]. The E values obtained from the Ozawa and Kissinger–Akahira–Sunose isoconversional models were similar for all decomposition stages, while the calculated E values obtained from the Coats–Redfern model for all decomposition stages differed from the other methods' results due to the different conceptions of the kinetic models. The Coats–Redfern method involves a systematic error since it is based on a single heating rate method. On the other hand, the isoconversional Ozawa and Kissinger–Akahira–Sunose methods are based on multiple heating rate methods. The isoconversional method provides the dependency of kinetic parameters using the conversion information obtained from TG and DTG curves, determined by measurements at different heating rates, without any assumptions about the reaction function and the order of the reaction [12]. Isoconversional methods are the most reliable techniques for describing the kinetic analysis of thermal data, as noted in the ICTAC Kinetic Project [24, 25]. Therefore, activation energies calculated by the Ozawa and Kissinger–Akahira–Sunose methods are more reliable than those obtained from the Coats–Redfern method.

CONCLUSION

In this study, the decomposition kinetics of howlite mineral were investigated by using the Coats–Redfern, Ozawa, and Kissinger–Akahira–Sunose non-isothermal kinetic models. Thermal decomposition of the mineral occurred in the temperature range of 84–724 °C with two dehydroxylation stages. The E values calculated by the Ozawa and Kissinger–Akahira–Sunose methods fit well with each other. Since the Coats–Redfern method has

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[1] Department of Chemical Engineering, Yıldız Technical University, Istanbul, Turkey
**E-mail address: mugesari@yildiz.edu.tr*
Orcid id: https://orcid.org/0000-003-4908-4594; 0000-0003-0441-7586; 0000-0002-8587-2013

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different assumptions, the calculated E value from this method was different. Therefore, the consistency of the results from the Ozawa and Kissinger–Akahira–Sunose models shows the accuracy and reliability of the calculated E values. Moreover, the investigation by isoconversional methods of E, corresponding to the dehydroxylation stages, revealed the presence of complex reactions since it varied significantly with the conversion.

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