

Thermal analysis of dehydroxylation of Algerian kaolinite

F. Sahnoune · N. Saheb · B. Khameh ·
Z. Takkouk

Received: 28 March 2011 / Accepted: 27 April 2011 / Published online: 11 May 2011
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Abstract Thermal analysis techniques remain important tools amongst the large variety of methods used for analysis of the dehydroxylation of kaolinite. In the present study, the kinetics of dehydroxylation of Algerian kaolinite, wet ball milled for 5 h followed by attrition milling for 1 h, was investigated using differential thermal analysis (DTA) and thermogravimetry (TG). Experiments were carried out between room temperature and 1350 °C at heating rates of 5, 10 and 20 °C min⁻¹. The temperature of dehydroxylation was found to be around 509 °C. The activation energy and frequency parameter evaluated through isothermal DTA treatment were 174.69 kJ mol⁻¹ and 2.68 × 10⁹ s⁻¹, respectively. The activation energies evaluated through non-isothermal DTA and TG treatments were 177.32 and 177.75 kJ mol⁻¹, respectively. Growth morphology parameters *n* and *m* were found to be almost equal to 1.5.

Keywords Kaolinite · Dehydroxylation · Thermal analysis · DTA · TG

Introduction

It is well known that kaolinite undergoes a series of reactions and finally forms mullite [1] which is used in the preparation of technical ceramics for functional and structural applications [2]. Thermal analysis techniques [3–10] remain important tools amongst the large variety of methods [11–13] used for analysis of the kinetics of dehydroxylation of kaolinite. Thermogravimetry and infrared emission spectroscopy were used to investigate thermal behavior and decomposition of kaolinite-potassium acetate intercalation complex [3]. Changes observed at 48, 280, 323, and 460 °C were attributed to the loss of adsorbed water; loss of the water coordinated to acetate ion in the layer of kaolinite; loss of potassium acetate in the complex; and water through dehydroxylation. Franco and co-workers [4] studied the influence of particle-size reduction on the dehydroxylation process. They reported that particle-size reduction caused an increase of the mass loss between 140 and 390 °C which was attributed to the loss of the hydroxyl groups exposed on the external surface of kaolinite; a shift to lower temperatures of the endothermic effect related with the mass loss between 390 and 600 °C; and a shift of the end of dehydroxylation to lower temperatures. Thermal characterization of Brazilian kaolinitic clays [5] showed three endothermic transformations identified as water loss within the 60–64, 268–276 and 499–503 °C ranges. The changes were mainly interpreted as the release of free moisture, dehydration of gibbsite and dehydroxylation of kaolinite. Kristóf and co-workers [6] investigated thermal behaviour of mechanochemically treated kaolinite under dynamic and controlled rate thermal analysis (CRTA) conditions. CRTA technology enabled the observation of dehydroxylation of the ground mineral in four overlapping stages at 385, 404, 420 and 433 °C instead of a single mass

F. Sahnoune
Laboratoire de Physique et Chimie des Materiaux, Université de M'sila, 28000 M'sila, Algeria

N. Saheb (✉)
Department of Mechanical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Kingdom of Saudi Arabia
e-mail: nouari@kfupm.edu.sa

B. Khameh · Z. Takkouk
Department of Physics, Ferhat Abbas University, Jijel 18000, Algeria

loss stage between 400 and 600 °C. Ptáček and co-workers [7] investigated the kinetics of the dehydroxylation of kaolinite under isothermal conditions by TG. They evaluated the overall activation energy (E_A) and pre-exponential (frequency) factor (A) from a series of thermogravimetry experiments in the temperature range from 370 to 500 °C. They found that dehydroxylation of kaolinite and metakaolinite formation up to the temperature 410 °C was controlled by the rate of the second-order chemical reaction. The E_A and A values were reported as 257 kJ mol⁻¹ and 1.9×10^{19} s⁻¹. Above 410 °C, the course of thermal decomposition of kaolinite corresponded to a third-order reaction with the E_A and A values of 202 kJ mol⁻¹ and 2.9×10^{15} s⁻¹. In other studies the same authors investigated dehydroxylation of kaolinite under non-isothermal conditions using TG [8] and DTG [9]. The reported values of E_A and A were 227 kJ mol⁻¹ and 9.4×10^9 s⁻¹, respectively, from TG results; and 195 kJ mol⁻¹ and 8.58×10^{14} s⁻¹, respectively, from DTG results. Bich and co-workers [10] tested three kaolins heated between 500 and 850 °C. The reactivity of the samples was evaluated by the determination of the residual quantity of Ca(OH)₂ by DTA performed on hydrated mixtures of 50% metakaolin and 50% Ca(OH)₂. The authors did not find a direct relationship between the pozzolanic activity of metakaolin and the degree of dehydroxylation. They reported a highest activity when the degree of dehydroxylation was more than 95%. Researchers who investigated dehydroxylation of kaolinite concluded that it is hard to reach a single value of overall activation energy and the difference between reported values was attributed to many factors such as kaolinite structure [14], impurities [15], and heating rate [16]. In previous investigations, the authors synthesized mullite from Algerian kaolinite [1] and evaluated the temperature of formation, activation energies and growth morphology parameters [17]. The objective of the present study is to investigate the kinetics of the dehydroxylation of Algerian kaolinite through thermal analysis.

Materials and experimental procedure

Raw kaolinite (DD3, from Guelma, Algeria) was used in this investigation. More information on this kaolinite and its chemical composition were reported elsewhere [1, 17]. The raw kaolinite was wet milled in planetary ball mill with alumina grinding media for 5 h, then attrition milled for 1 h using ZrO₂ balls (diameter of 1.2 μm) at a speed of 1250 rev min⁻¹. The slurry was dried at 150 °C, powdered and sieved through a 163 μm mesh. DTA and TG experiments were performed on samples using a SETARAM Labsys thermal analyser. The samples were heated from room temperature up to 1350 °C at heating rates of 5, 10

and 20 °C min⁻¹. The DTA scans were conducted in flowing air using platinum crucibles.

Results and discussion

Figure 1 shows typical DTA/TG curves of kaolinite powder heated from room temperature to 1350 °C at a heating rate of 10 °C min⁻¹. The DTA curve reveals an endothermic peak at 509.14 °C and an exothermic peak at 997.87 °C. The endothermic peak is due to the dehydroxylation of kaolinite while the exothermic peak corresponds to the formation of primary mullite. On the TG curve, two step mass losses are observed. The first mass loss (about 1.5%) corresponds to the evaporation of adsorbed water. The second mass loss (about 13%) corresponds to the endothermic and exothermic peaks. The mass loss remained unchanged with heating above 800 °C.

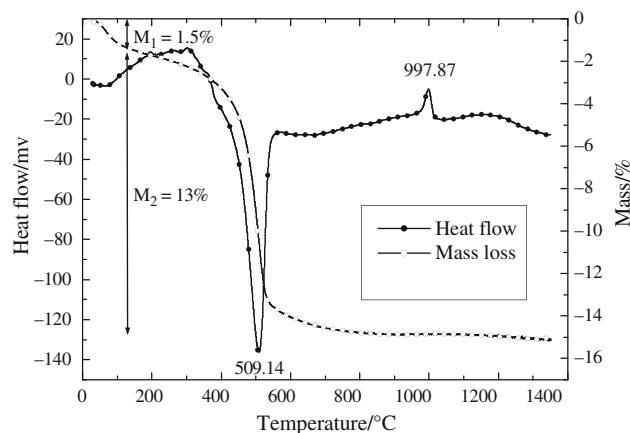


Fig. 1 DTA and TG curves of kaolinite powder heated at 10 °C min⁻¹

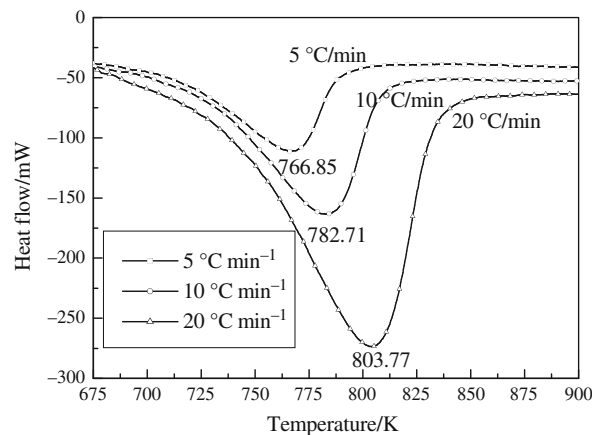


Fig. 2 DTA curves for kaolinite heated at different heating rates

Figure 2 shows DTA curves for kaolinite heated at different heating rates. It can be clearly seen that the increase of heating rate from 5 to 20 °C min⁻¹ shifts the temperature of the maximum of the endothermic peak position, T_p , to higher temperature from 766 to 803 K.

The variation of the crystallised fraction of metakaolin (dehydroxylated kaolinite) with temperature under different heating rates is presented in Fig. 3. The crystallised fraction x can be determined from the DTA results [18] as:

$$x = \frac{A_T}{A_0}$$

where A_T is the area of the endothermic peak in the DTA curve at temperature T and A_0 is the total area under the peak.

The rate of dehydroxylation of kaolinite with time for different heating rates is shown in Fig. 4. The rate of dehydroxylation increases with increasing heating rate.

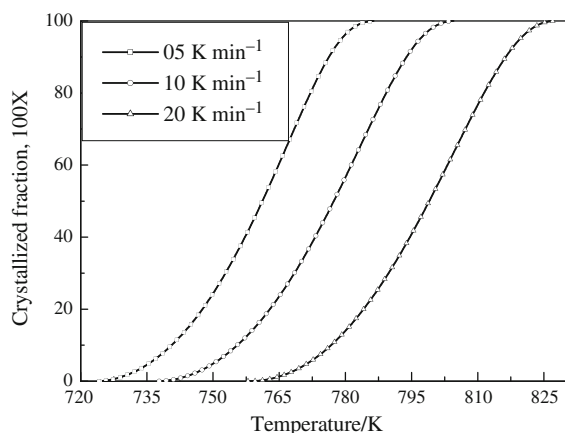


Fig. 3 Variation of crystallised fraction of metakaolin with temperature for kaolin powder under different heating rates

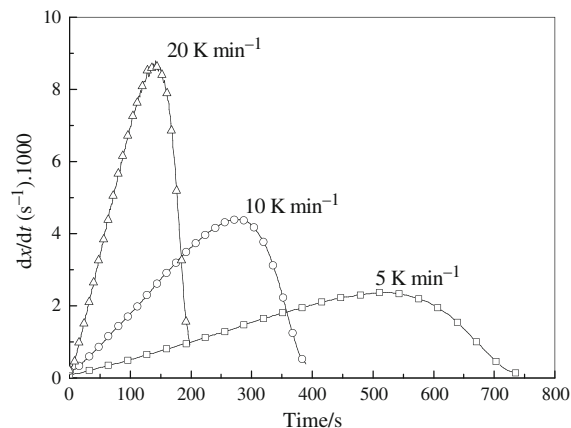


Fig. 4 Rate of dehydroxylation of kaolinite at different heating rates

The Johnson–Mehl–Avrami theory [18, 19] can be used to evaluate the crystallised fraction of dehydroxylation under isothermal condition as follows:

$$x = 1 - \exp[-(kt)^n] \tag{1}$$

where x is the volume fraction crystallised versus time t , n is the Avrami exponent and k is the reaction rate constant, given by the Arrhenian type equation

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where k_0 is the frequency factor, E is the apparent activation energy, R is the ideal gas constant and T is the isothermal temperature in Kelvin.

Rearrangement of Eqs. 1 and 2 leads to [18]:

$$\begin{aligned} \ln\left(\frac{dx}{dt}\right) &= \ln[K_0n] + \frac{n-1}{n} \ln[-\ln(1-x)] + \ln(1-x) - \frac{E}{RT} \\ &= \ln[k_0f(x)] - \frac{E}{RT} \end{aligned} \tag{3}$$

A mathematical method through non-isothermal techniques was proposed by Ligeró and co-workers [20]. If the same value of x in every experiment at different heating rates is selected; and $\ln\left(\frac{dx}{dt}\right)$ is plotted as function of $1/T$, the result will be a linear curve, Fig. 5, with a slope equal to the activation energy, E .

Table 1 presents the activation energy E for different crystallised fraction, which was calculated by the average of the slopes of the lines (Eq. 3). The average activation energy of dehydroxylation is 174.69 kJ mol⁻¹.

Values of $\ln[k_0f(x)]$ for different crystallised fraction for kaolinite powder heated at a heating rate of 20 °C min⁻¹ are listed in Table 2.

The Avrami parameter which indicates the crystallisation mode, n , was determined by the selection of many pairs of x_1

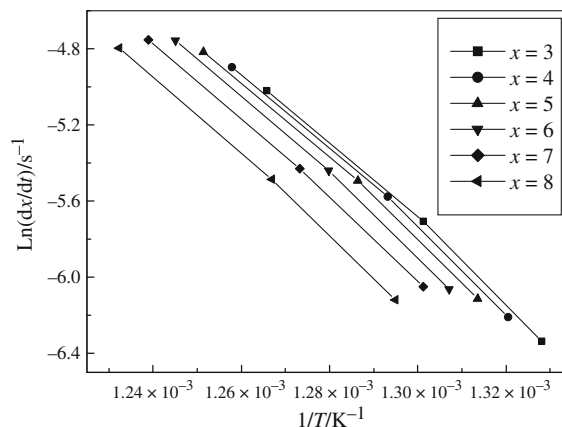


Fig. 5 Plot of $\ln\left(\frac{dx}{dt}\right)$ versus $1/T$ at same value of crystallised fraction x from experiments at different heating rates

Table 1 Values of the activation energy, E , for different crystallised fraction

x	r	$E/\text{kJ mol}^{-1}$
0.1	0.998	176.54
0.2	0.997	175.77
0.3	0.998	175
0.4	0.998	173.76
0.5	0.998	172.66
0.6	0.999	174.04
0.7	0.999	172.65
0.8	0.999	174.90
0.9	1	176.87

Table 2 Values of $\ln[k_0f(x)]$ for different crystallised fraction for kaolin powder heated at heating rate of $20\text{ }^\circ\text{C min}^{-1}$

X	0.1	0.2	0.3	0.4	0.5	0.7	0.8	0.9
$\ln[k_0f(x)]$	21.78	21.76	21.65	21.42	21.19	20.99	21.15	21.08

and x_2 that satisfied the condition $\ln[k_0f(x_1)] = \ln[k_0f(x_2)]$ and using Eq. 3, the following equation is derived [18]

$$n = \frac{\ln[\ln(1-x_2)/\ln(1-x_1)]}{\ln[(1-x_2)\ln(1-x_2)/(1-x_1)\ln(1-x_1)]} \quad (4)$$

The average values of n for each heating rate are listed in Table 3. The average Avrami parameter is 1.6. This value is close to 1.5, which suggests that the process of dehydroxylation is diffusion controlled.

The frequency factor, k_0 , can also be calculated by the following equation [18]

$$\ln[k_0f(x)] = \ln[k_0n] + \frac{n-1}{n}[\ln(-\ln(1-x))] + \ln(1-x) \quad (5)$$

The average of k_0 is equal to $2.68 \times 10^9\text{ s}^{-1}$.

For a non-isothermal DTA experiment, the temperature is changed linearly with time.

$$T = T_0 + \phi \left(\phi = \left(\frac{dT}{dt} \right) \right)$$

According to Kissinger method [13, 21]

$$\ln\left(\frac{\phi}{T_p^2}\right) = -\frac{E}{RT} + C \quad (6)$$

where E , R , T , ϕ and C are the activation energy, gas constant, peak temperature, heating rate and integrating

Table 3 Values of the Avrami parameter n for different heating rates

$\emptyset/\text{ }^\circ\text{C min}^{-1}$	5	10	20
n	1.6	1.59	1.61

constant, respectively. A plot of $\ln\left(\frac{\phi}{T_p^2}\right)$ versus $1/T_p$ should be a linear curve, whose slope yields the activation energy for crystallisation E .

A modified form of the Kissinger equation was proposed by Matusita and coworkers [22–24] as follows:

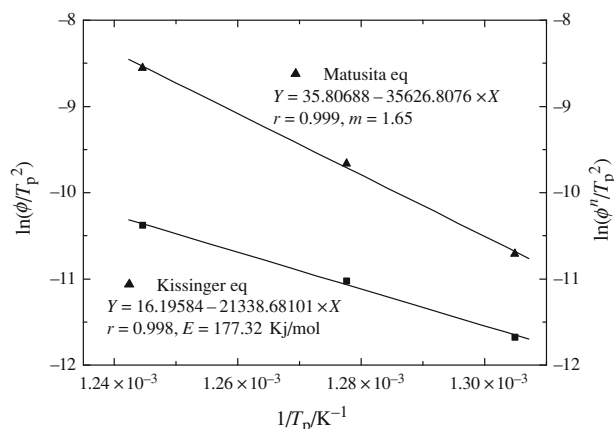
$$\ln\left(\frac{\phi^n}{T_p^2}\right) = -\frac{mE}{RT} + C \quad (7)$$

where n is the Avrami parameter which indicates the crystallisation mode and m is a numerical factor which depends on the dimensionality of crystal growth.

Figure 6 shows plots of $\ln\left(\frac{\phi}{T_p^2}\right)$ and $\ln\left(\frac{\phi^n}{T_p^2}\right)$ versus $1/T_p$ according to Kissinger and Matusita equations respectively [18, 22].

The activation energy calculated from the slope of the Kissinger plot (non-isothermal DTA treatment) is $177.32\text{ kJ mol}^{-1}$; it is in good agreement with that of $174.69\text{ kJ mol}^{-1}$ estimated by the Ligeró method (isothermal DTA treatment). The above values of the activation energy fall in the range $140\text{--}250\text{ kJ mol}^{-1}$ [8, 15, 25–29]. The difference between reported values of activation energy of dehydroxylation of kaolinite was attributed to many factors such as kaolinite structure [14], impurities [15], and heating rate [16]. The parameter m , according to Matusita equation, is found to be equal to 1.65 for dehydroxylation of kaolinite. Both growth morphology parameters n and m are close to 1.5, an indication of a 3D growth of metakaolin crystals.

According to the definition, $\text{DTG} = dm/dt$ is the DTG value at time t . Using a group of DTG curves at different heating rates [30], we can determine the corresponding DTG and T values at certain conversion degrees Y [8, 31].

**Fig. 6** Plots of $\ln\left(\frac{\phi}{T_p^2}\right)$ and $\ln\left(\frac{\phi^n}{T_p^2}\right)$ versus $1/T_p$ according to Kissinger and Matusita equations respectively

$$Y = \frac{m_t - m_0}{m_0 - m_\infty} \quad (8)$$

where m_t , m_0 and m_∞ are mass at instantaneous, initial and final time of system and Y is the conversion degree.

Plots of $\ln(-DTG)$ as function of $1/T$ are linear curves. The activation energy E can be determined from the slope of these lines [30, 31].

$$\ln\left(-\frac{dm}{dt}\right) = -\frac{E}{RT} + C \quad (9)$$

where E , R and T are activation energy, universal gas constant and temperature, respectively.

According to the temperature corresponding to the given conversion degree shown in Fig. 7a, the time required to reach the temperature can be determined, and the corresponding DTG value plotted as presented in Fig. 7b.

Figure 8 shows fitted lines of $\ln(-DTG)$ versus $1/T$ at different conversion degree of 20, 40, 60, and 80%. The slopes of these lines are similar to each other. The activation energy E of the dehydroxylation is calculated as $177.75 \text{ kJ mol}^{-1}$. This value is almost equal to the value of

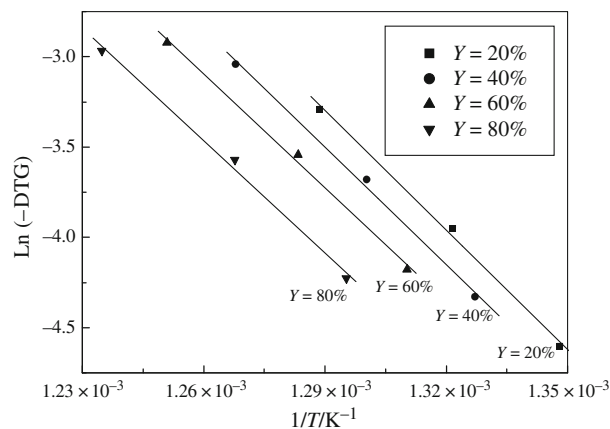


Fig. 8 Fitting lines of $\ln(-DTG)$ vs. $1/T$ at different conversion degree

$177.32 \text{ kJ mol}^{-1}$ calculated from the slope of the Kissinger model (non-isothermal DTA treatment). Also, it is in good agreement with that of $174.69 \text{ kJ mol}^{-1}$ estimated by the Ligeró method (isothermal DTA treatment).

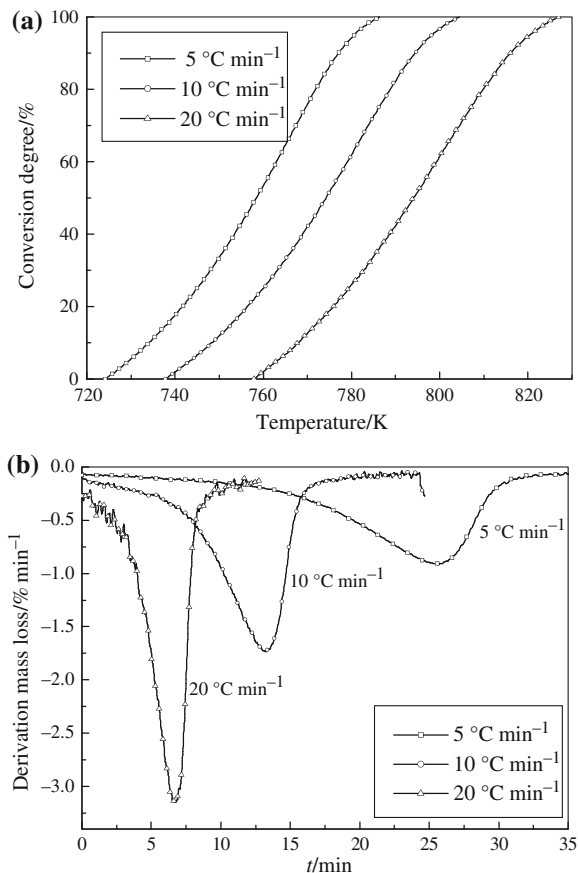


Fig. 7 Conversion degree (a) and DTG (b) curves at different heating rates

Conclusions

The kinetics of dehydroxylation of Algerian kaolinite was investigated using DTA and TG techniques. The temperature of dehydroxylation was found to be around $509 \text{ }^\circ\text{C}$. The activation energy and frequency parameter evaluated through isothermal DTA treatment were $174.69 \text{ kJ mol}^{-1}$ and $2.68 \times 10^9 \text{ s}^{-1}$, respectively. The activation energies evaluated through non-isothermal DTA and TG treatments were 177.32 and $177.75 \text{ kJ mol}^{-1}$, respectively. Growth morphology parameters n and m were found to be almost equal to 1.5.

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