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Thermal Dehydroxylation Kinetics of Algerian Halloysite by Differential Thermal Analysis

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In this study, the dehydroxylation of Algerian halloysite (DD1) was studied using differential thermal analysis. Measurements of samples were performed between room temperature and 1400 °C, at different heating rates of 10, 20, 30, 40 and 50 °Cmin^{-1}. The activation energy calculated from isothermal (using Johnson-Mehl-Avrami and Ligero methods) and non-isothermal treatments (using Kissinger-Akahira-Sunose) were 135 kJ/mol and 153 kJ/mol, respectively. The Avrami parameter obtained by method of Ligero and the m parameter (a numerical factor) obtained by Matusita method were 1.55 and 1.59, respectively. The results show that bulk nucleation was dominant in halloysite transformation, followed by three-dimensional growth of meta-halloysite. This growth is controlled by diffusion from a constant number of nuclei. The frequency factor calculated by the isothermal treatment is equal to 4.16×10^6 s^{-1}.

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PACS/topics: differential thermal analysis (DTA)

1. Introduction

Halloysite is a clay mineral belonging to the group of kaolinite. Chemical formula of halloysite is $Al_2Si_2O_5(OH)_4{\cdot}2H_2O$ [1]. Halloysite, as well as kaolinite, is exploited commercially and used in ceramic and porcelain industry [2]. Furthermore it is also used now for the filling and coating of paper, rubber and plastics, as an addition to pesticides, lubricants and sealing materials [1].

Many researchers have studied thermal decomposition of halloysite by differential thermal analysis (DTA). It is the most common technique [3] for the study of the kinetics of phase transformations and chemical reactions. It has been used to determine type of crystal nucleation and to obtain the activation energy [3].

In the present study the dehydroxylation of halloysite mineral was investigated by DTA in order to estimate the activation energy, based on isothermal and non-isothermal methods, the growth methods, the growth morphology parameters and the frequency factor. The studied materials originate from the deposits from the Djebel Debbagh area in northeastern Algeria.

2. Materials and equipment

Algerian raw halloysite (DD1, from Djabal Debagh) was used in this investigation. The ball milling technique was used to prepare a homogeneous mixture of halloysite. The mixture of the raw powders was charged into zirconia vials (250 ml in volume) together with 15 zirconia balls (10 mm in diameter). The milled mixture was dried at 150 °C for 24 hours. Differential thermal and thermogravimetric analyses (TGA) were performed on the samples using a SETARAM Labsys thermal analyzer. The samples were heated from room temperature up to 1400 °C at heating rates of 10, 20, 30, 40 and 50 °C/min.

3. Results and discussion

Figure 1 shows the typical DTA/TG curves of halloysite powder during heating from room temperature to 1400 °C, at a heating rate of 50 °C/min. These experiments show that the decomposition process of the halloysite takes place in three major steps.

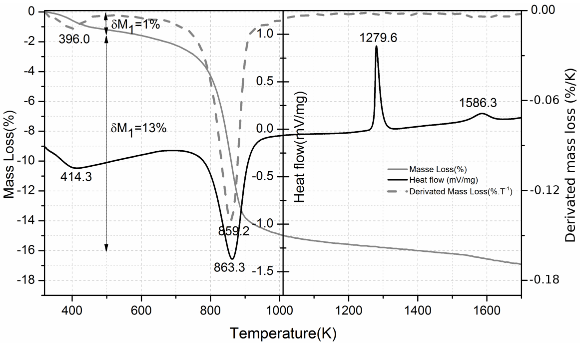

Fig. 1. DTA and TG/D(TG) curves of halloysite powder heated at 50 °C/min.

The first endothermic peak in the range of 360–450 K corresponds to the liberation of water adsorbed on the surface of the particles (dehydration) [4]. The second step of structural decomposition of halloysite occurs in the endothermic peak between 700 and 950 K. The peak centered at about 863.3 K is assigned to the dehydroxylation of halloysite and the formation meta-halloysite.

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An exothermic peak between 1200–1400 K, centered at about 1279.6 K (transformation from the amorphous metahalloysite into crystalline phases), could be explained by the formation of Si-Al spinel [4]. An exothermic peak between 1500–1650 K, centered at about 1586.3 K, corresponds to the formation of primary mullite and transformation of amorphous SiO_2 into a crystalline phase called cristobalite.

In the thermogravimetric curve, the first weight loss (of about 1 wt.%) is due to the evaporation of adsorbed water. The second weight loss (of about 13 wt.%) in the temperature range of 600–900 K is due to the dehydration of the hallosyite and the formation of metahalloysite. It is correlating with the second endothermic peak at 859.2 K.

Figure 2 shows the crystallized fraction and rate of crystallized fraction of meta-halloysite formation under different heating rates (10, 20, 30, 40 and 50 °C/min) measured using DTA analyses.

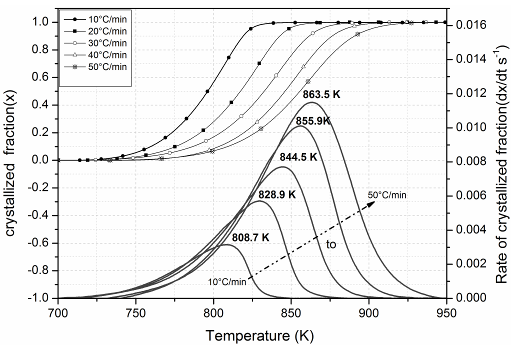

Fig. 2. Rate of crystallized fraction and crystallized fraction of metahalloysite formation under different heating rates, measured using DTA analysis.

It can be seen that temperature of the position of maximum of the peak, T_p, shifts to higher temperatures from 808.7 to 868.6 K, as the heating rate increases from 10 to 50 °C.

A mathematical method of calculation of activation energy through non-isothermal technique was suggested by Ligero, et al. [5]. Activation energy E can be calculated from the slope of the function $\ln(\mathrm{d}x/\mathrm{d}t) = f(1/T)$ [6] for the same value of the crystallized fraction x, measured at different heating rates. The resulting linear curve is shown in Fig. 3.

The values of E which were calculated by the slopes of the lines $\ln(\mathrm{d}x/\mathrm{d}t) = f(1/T)$ for different values of crystallized fraction are listed in Table I. The correlation coefficient was $R^2 \geq 0.99$ for different values of $x = 0.1$–0.5. The median activation energy of the transformation of halloysite to meta-hlooysite is 135.7 kJmol^{-1}.

The Avrami parameter n estimated by non-isothermal DTA treatment was determined by the selection of many pairs of x_1 and x_2 that satisfied the condition $\ln[kf(x_1)] = \ln[kf(x_2)]$ [5] and using Eq. (1).

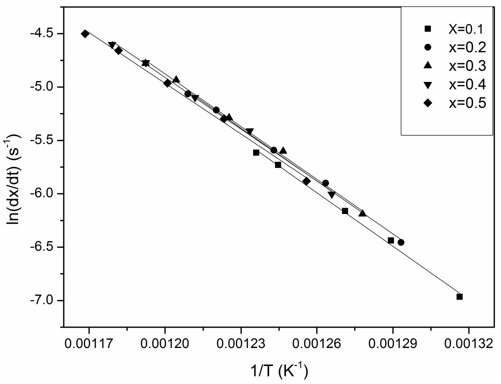

Fig. 3. Plot of $\ln(\mathrm{d}x/\mathrm{d}t)$ vs. $1/T$ for the same value of crystallized fraction x, from experiments at different heating rates.

TABLE I

Values of the activation energy, E, for different crystallised fraction.

X	R^2	E [kJmol^{-1}]
0.1	0.995	138.7
0.2	0.996	137.1
0.3	0.996	136.7
0.4	0.996	134.5
0.5	0.995	131.6

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

The median values of Avrami parameter n for each heating rate are listed in Table II. The average Avrami parameter is $n = 1.55$, which indicates that the crystallization process of meta-halloysite has to be controlled by a diffusion growth [7].

The value of the frequency factor K for the different heating rates (10, 20, 30, 40 and 50 °C/min) can be calculated using Eq. (2). The average value of K calculated using values from Table II is equal to 4.16×10^6 s^{-1}.

$$\ln\left(K_0 f\left(x\right)\right) = \ln\left(K_0\right) + \ln\left(n\right)$$
$$+\frac{n-1}{n} \times \left[\ln\left(-\ln\left(1-x\right)\right)\right] + \ln\left(1-x\right). \quad (2)$$

TABLE II

Values of the Avrami parameter and the frequency factor for different heating rates.

Heating rate [°C/min]	n	K
10	1.66	4.59×10^6
20	1.59	4.11×10^6
30	1.54	3.91×10^6
40	1.51	3.67×10^6
50	1.47	4.51×10^6

Figure 4 shows the plots of Y versus $1/T_\mathrm{p}$ at different heating rates according to the methods of Ozawa, Boswell and Kissinger. The values of the activation energies of dehydroxylated halloysite, calculated from the slope of the function $Y_i = f(1/T_\mathrm{p})$ are listed in Table III. The average activation energy for isothermal DTA treatment is 157 kJ mol^{-1}.

Table IV presents the values of the Avrami parameter n which shows the crystallization mode. The average of n for different heating rates is equal to 1.65 using Eq (3).

$$n = -\frac{2.5T_\mathrm{p}^2 R}{\Delta T_\mathrm{p} E_\mathrm{A}}. \tag{3}$$

Figure 5 shows the plots of $\ln(\varphi^n/T^2)$ versus $1/T_\mathrm{p}$ according to Matusita (see Eq. (4)). The dimensionality of crystal growth m was found to be equal to 1.70.

$$\ln\left[\frac{\varphi^n}{T_\mathrm{p}^2}\right] = C - \frac{mE_\mathrm{A}}{RT_\mathrm{p}}, \tag{4}$$

where c is a constant, φ is the heating rate, E_A is the activation energy, T_p is the absolute peak temperature in DTA curves and R ($R = 8.314$ JK^{-1}mol^{-1}) is the ideal gas constant.

Both, the the Avrami parameter ($n = 1.65$) of the growth morphology and the dimensionality of crystal growth ($m = 1.70$) are close to 1.5. This indicates that the bulk nucleation is the dominant mechanism in crystallization of metahalloysite, and that the crystal growth is controlled by diffusion from a constant number of nuclei [8].

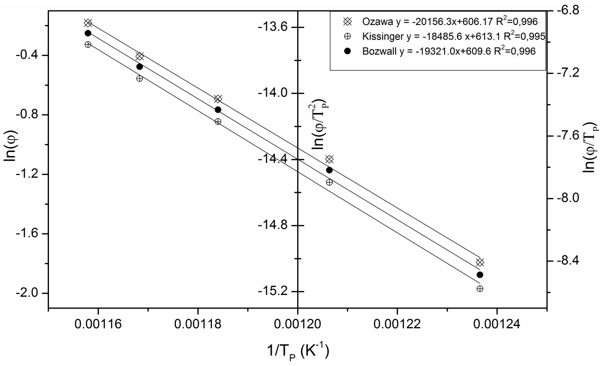

Fig. 4. Plots of Y versus $1/T_\mathrm{p}$ of dehydroxylation of halloysite at different heating rates, obtained using DTA analysis.

TABLE III

Values of E_A and R^2 of dehydroxylated kaolinite calculated using Ozawa, Boswell and Kissinger methods from DTA experiment.

Method	Ozawa	Boswell	Kissinger
E_A [kJ/mol]	159	160	153
R^2	0.996	0.996	0.995

4. Conclusions

In conclusion, the kinetics of dehydroxylation of the halloysite (DD1, from Djabal Debagh, Algeria) was investigated using DTA techniques. Experimental results show that the activation energy of dehydroxylation, calculated by the Ligero method and the non-isothermal Kissinger method is 135 and 153 kJ mol^{-1}, respectively. The Avrami parameter n of growth morphology and the numerical factor m, which depends on the dimensionality of the crystal growth, calculated using non-isothermal and isothermal treatments, are found to be 1.5. The bulk nucleation was dominant in halloysite transformation, followed by three-dimensional growth of metahlloysite. The value of the frequency factor calculated via the isothermal treatment is equal to 4.16×10^6 s^{-1}.

TABLE IV

Values of the Avrami parameter n for different heating rates, obtained from DTA experiments.

Heating rate [°C/min]	10	20	30	40	50
ΔT	50.19	53.16	58.35	62.47	66.2
T_p peak	808.7	828.9	844.5	855.9	863.5
Avrami par.	1.76	1.75	1.65	1.59	1.52

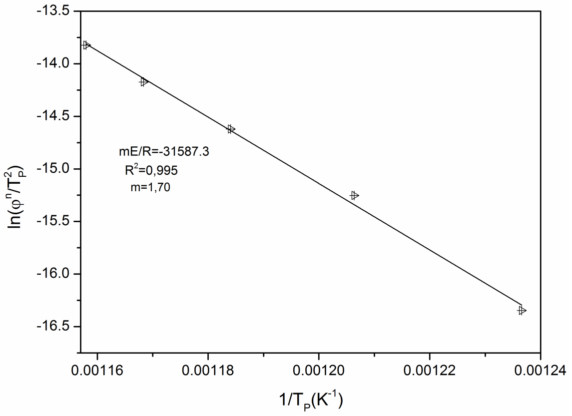

Fig. 5. Plot of $\ln\left[\varphi^n/T_\mathrm{p}^2\right]$ versus $1/T_\mathrm{p}$ according to Matusita equation.

References

[1] E. Joussein, S. Petit, J. Churchman, B. Theng, D. Righi, B. Delvaux, *Clay Minerals* **40**, 383 (2005).

[2] I.R. Wilson, *Clay Minerals* **39**, 1 (2004).

[3] M.C. Weinberg, *J. Am. Ceram. Soc.* **74**, 1905 (1991).

[4] K. Samir, L. Salima, M.K. Kheira, S. Jacques, G.B. Isabelle, K. Amine, *Micropor. Mesopor. Mater.* **158**, 47 (2012).

[5] R.A. Ligero, J. Vazques, M. Casas-Ruiz, R. Jimenez-Garay, *J. Mater. Sci.* **26**, 211 (1991).

[6] M. Romero, J. Martin-Marquez, J.M. Rincon, *J. Eur. Ceram. Soc.* **26**, 1647 (2006).

[7] P. Ptáček, F. Šoukal, T. Opravil, M. Nosková, J. Havlica, J. Brandštetr, *J. Powder. Technol.* **203**, 272 (2010).

[8] K. Matusita, K. Miura, T. Komatsu, *Thermochim. Acta* **88**, 283 (1985).