



Thermal decomposition kinetics of Algerian Tamazarte kaolinite by thermogravimetric analysis



D. REDAOUI¹, F. SAHNOUNE^{2,3}, M. HERAIZ¹, H. BELHOUCHE¹, M. FATMI³

1. Physics and Chemistry of Materials Laboratory, Department of Physics, University of M'sila, M'sila 28000, Algeria;

2. Department of Physics, University of M'sila, M'sila 28000, Algeria;

3. Research Unit on Emerging Materials (RUEM), University Ferhat Abbas of Setif 1, Setif 19000, Algeria

Received 30 June 2016; accepted 4 October 2016

Abstract: The decomposition kinetics of Algerian Tamazarte kaolinite (TK) was investigated using thermogravimetric analysis (TG). Differential thermal analysis (DTA) and TG experiments were carried out between room temperature and 1400 °C, at different heating rates from 10 to 40 °C/min. The activation energies, measured by DTG from isothermal treatments using Johnson–Mehl–Avrami (JMA) and Ligeró methods and by non-isothermal treatments using Ozawa, Boswell and Kissinger methods, were around 151 and 144 kJ/mol, respectively. The Avrami parameter of growth morphology (indicating the crystallization mode) was found to be around 1.57 using non-isothermal treatments; however, when using isothermal treatments it is found to be equal to 1.35. The numerical factor, which depends on the dimensionality of crystal growth, is found to be 1.53 using Matusita equation. The frequency factor calculated by the isothermal treatment is equal to $1.55 \times 10^7 \text{ s}^{-1}$. The results show that the bulk nucleation is followed by three-dimensional growth of metakaolinite with polyhedron-like morphology controlled by diffusion from a constant number of nuclei.

Key words: kaolinite; decomposition kinetics; Avrami parameter; activation energy; growth morphology

1 Introduction

Kaolin is widely used in a diverse applications in the industry of ceramics: conventional, structural and refractory ceramics, dielectrics and infrared transmitting materials [1,2]. Further than ceramics applications, kaolin also is utilized as an industrial filler agent for paper, rubber, plastics, cosmetics and paints [1,2]. Also, kaolin can be utilized for management of waste and preparation of geopolymers, geopolymer based composites and zeolites [1,3]. All these applications contain the thermal transformation of kaolinite and main mineral phase of kaolin. So, the course of metakaolinite development from kaolinite has been proved by some techniques and methods such as thermogravimetric analysis (TG), differential thermal analysis (DTA), differential scanning calorimetry (DSC) and dilatometry [2,3,4,5,6–14].

By using different factors such as the degree of structural ordering, adsorbed and substituted ions, shape and particle size, the thermal decomposition of kaolinite

were determined. Also, the influence of instrumental conditions on the rate of decomposition is discussed in many works. In the range of temperature between 450 and 700 °C, the water release of kaolinite and the formation of the metakaolinite $\text{Al}_2\text{Si}_2\text{O}_7$ are well known. During the thermogravimetric investigation, the difference between the thermogravimetric mass loss (between 11.2% and 14.5% [4,5]) and the theoretical value of 13.95% is commonly reported.

In published works [6–16] the kinetics and mechanism of thermal decomposition of kaolinite and general clay mineral give large interesting. A full spectrum of methods, including molecular spectroscopy [6,7], electron microscopy [9] and thermal analysis techniques [8,10–12] were investigated in a massive process.

The aim of the present work is to study two corresponding processes during thermal decomposition of kaolin, such as dehydroxylation of kaolinite and the mechanism of dehydroxylation. The important kinetic parameters (overall activation energy and frequency factor) will be determined on the basis of TG experiments.

2 Experimental

Raw kaolin of Tamazarte (from Jijel, Algeria) was used in this investigation. Its chemical composition was determined by X-ray fluorescence (XRF) as shown in Table 1. The raw kaolin was milled by planetary ball with alumina grinding media for 4 h, after that it was milled by attrition for 2 h using ZrO₂ balls (diameter of 1.25 mm) at a speed of 700 rev/min. The slurry was dried at 150 °C, crushed manually then sieved through a 63 μm mesh.

Table 1 Chemical composition of raw kaolin (mass fraction, %)

| Al ₂ O ₃ | SiO ₂ | Na ₂ O | P ₂ O ₅ | SO ₃ |
|--------------------------------|------------------|-------------------|--------------------------------|-----------------|
| 33.00 | 61.73 | 0.14 | 0.03 | 0.03 |
| K ₂ O | MgO | CaO | Fe ₂ O ₃ | |
| 2.96 | 0.44 | 0.44 | 0.80 | |

Thermal analysis (DTA/TG) at the same time was carried out on a Setaram LABSYS Evo TG–DSC 1600 °C equipment, operated under Argon atmosphere. The samples were heated from room temperature up to 1400 °C at heating rates of 10 to 40 °C/min. The phases and their transformations were characterized by diffractometer system (XPERT-Pro) with a scan step of 0.0167° (Cu K_α radiation and a Ni filter) operated at 40 kV and 40 mA. The morphology of powders was characterized by a JEOL scanning electron microscope (SEM) model JMS 5600. The mechanism and kinetics of kaolinite transformation have been investigated by two different isothermal and non-isothermal methods. According to the information obtained about the thermal activities of kaolin, each technique gave excellent results.

Many methods have been introduced to calculate the activation energy (E_A) in the case of the non-isothermal method. In this study, just three of methods Ozawa [15,16], Boswell [17] and Kissinger were used [18–20]. The principle basics were listed by three formulas below:

$$\ln v = -1.0518 \frac{E_A}{RT_p} + C_1 \quad (1)$$

$$\ln \frac{v}{T_p} = -\frac{E_A}{RT_p} + C_2 \quad (2)$$

$$\ln \frac{v}{T_p^2} = -\frac{E_A}{RT_p} + C_3 \quad (3)$$

where C_i ($i=1, 2$ and 3) is a constant, v is the heating rate in the DTG analysis, E_A is the activation energy, T_p is the absolute peak temperature in DTG curves, and R is the gas mole constant. The activation energy can be calculated by the slope obtained. The value of Avrami

exponent, n , was determined from the shape of DTG curves at any heating rates as [21,22]

$$n = \frac{2.5T_p^2 R}{\Delta T_p E_A} \quad (4)$$

where ΔT_p is the width of crystallization peak at half maximum.

MATUSITA and SAKKA [23] have proposed a method to change Kissinger method as follows:

$$\ln \frac{v^n}{T_p^2} = C_3 - \frac{mE_A}{RT_p} \quad (5)$$

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

Now in the second method (isothermal treatment of the TG/DTG obtained curves) the theoretical basis for interpreting TG results is determined by the Johnson–Mehl–Avrami (JMA) theory. Under an isothermal condition, the evolution of the crystallization fraction with the time (t) during a phase transformation can be described as

$$x = 1 - \exp[(-kt)^n] \quad (6)$$

where x is the volume fraction crystallized versus time (t), it was determined from the DTG results presented in the formula below:

$$x = \frac{A_T}{A_0} \quad (7)$$

where A_0 is the total area of the peak in the DTG curve between the temperature T_i (the initial of crystallization) and T_f (the completion of crystallization); A_T is the area under the peak between T_i and T ; k is the reaction rate constant. Its temperature dependence is expressed by the Arrhenius type equation:

$$k = k_0 \exp\left(-\frac{E_A}{RT}\right) \quad (8)$$

where k_0 is the frequency factor. Equations (6) and (8) lead to

$$\begin{aligned} \ln\left(\frac{dx}{dt}\right) &= \ln(K_0 n) + \frac{n-1}{n} \ln[-\ln(1-x)] + \ln(1-x) - \frac{E_A}{RT} \\ &= \ln[k_0 f(x)] - \frac{E_A}{RT} \end{aligned} \quad (9)$$

LIGERO et al [24] suggested a mathematical method through non-isothermal techniques. The activation energy can be deduced from the slope of Eq. (9) if the authors select the same value of x in every experiment at different heating rates and plot for a given x . The function $\ln(dx/dt)$ versus $1/T$ shows that the plot of $\ln(dx/dt)$ versus $1/T$ at the same value of crystallized

Download English Version:

<https://daneshyari.com/en/article/8011849>

Download Persian Version:

<https://daneshyari.com/article/8011849>

[Daneshyari.com](https://daneshyari.com)