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The kinetic analysis of the thermal decomposition of kaolinite by DTG technique

Petr Ptáček *, František Šoukal, Tomáš Opravil, Jaromír Havlica, Jiří Brandštetr

Centre for Materials Research, Faculty of Chemistry, Brno University of Technology, Purkyňova 464/118, Brno, CZ-621 00, Czech Republic

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ABSTRACT

The thermal decomposition of kaolinite was studied by differential thermogravimetry (DTG) technique under non-isothermal conditions. Samples of industrially treated (washed) kaolin with high content of the medium ordered kaolinite were calcined using a heating rate from 1 to 40 K min^{-1}. The apparent activation energy and frequency factor for the dehydroxylation of kaolinite was evaluated by Kissinger method as 195 ± 2 kJ × mol^{-1} and $(8.58 \pm 0.33) \times 10^{14}$ s^{-1}, respectively. Avrami exponent of the process was estimated using Kissinger empirical kinetic models and Carne equation.

1. Introduction

The human life and the existence of many organisms on this planet are connected with clays. The catalytic surface of clays has an essential importance for origin of life and clay–humus complex of soils. Clay minerals, such as minerals of kaolinite, smectite, vermiculite, mica, chlorite and palygorskite and sepiolite groups, are among the world's important and useful raw minerals. One of the most important clay minerals is kaolinite ($Al_2Si_2O_5(OH)_4$) [1–5].

The raw kaolin contains kaolinite as a main mineral phase, white mica (muscovite and newly formed illite or mixed-layer structures of illite and smectite), quartz and residues of undecomposed silicates, mostly feldspars, biotite and accessory minerals. The accessory minerals can be divided in original (e.g. tourmaline, zircon, garnet, ilmenite and rutile) and newly formed minerals (e.g. siderite, pyrite, marcasite, chlorite, goethite, akaganeite, hematite, anatase and rutile) [1]. The commercial kaolins are treated by grinding, sieving, washing, hydroclassification and magnetic separation [6].

The kaolin is an important raw material for the production of ceramics, refractoriness and many others fields of industry, e.g. as an industrial filling for paper, rubber, plastics, dyes and paints [1,2,5]. Utilization of calcined clays as pozzolanic admixtures for cement has been known since the time of the Romans [7]. Furthermore, kaolin can be utilized for waste management [8,9] and preparation of geopolymers and geopolymer based composites [10–12], zeolites [13,14] and intercalates [15,16].

Thermal behaviour of kaolinite is in most cases described via sequence of following reactions [5,6,17,18]:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \xrightarrow{450-700^\circ C} Al_2O_3 \cdot 2SiO_2 + 2H_2O_{(g)} \tag{1}$$

$$2(Al_2O_3 \cdot 2SiO_2) \xrightarrow{925-1050^\circ C} 2Al_2O_3 \cdot 3SiO_2 + SiO_{2(amorphous)} \tag{2}$$

$$3(2Al_2O_3 \cdot 3SiO_2) \xrightarrow{\geq 1050^\circ C} 2(3Al_2O_3 \cdot 2SiO_2) + 5SiO_2 \tag{3}$$

$$SiO_{2(amorphous)} \xrightarrow{\geq 1200^\circ C} SiO_{2(cristobalite)} \tag{4}$$

On the other hand, the thermal treatment of kaolin shows considerable complexity with regard to nonstoichiometric composition of originating phases, predehydroxylation process [7,19], gradual disappearing of residual hydroxyl groups [19] and mullite formation processes (mullitization) [20]. The process is also influenced by material properties, such as degree of disorder of the kaolinite structure [21], by pressure and partial water vapour pressure [22,23], heating rate [6,23], mechanical treatments and ultrasound processing of sample [24,25].

The thermal decomposition kinetics of kaolinite has been widely studied due to its aforementioned industrial importance. Table 1 provides an overview of the results published in the current literature.

The aim of the present paper is a kinetic analysis of the thermal decomposition of kaolinite. Kinetic parameters, i.e. apparent activation energy and pre-exponential factor, were derived from Kissinger equation using results of differential thermogravimetry. This article reflects the kinetic aspect of DTG data from previous published paper [34].

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* Corresponding author. Fax: +420 541 149 389.
E-mail address: ptacek@fch.vutbr.cz (P. Ptáček).

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Table 1
The kinetics of the thermal decomposition of kaolinite overview.

Experimental method	Experimental technique	Signature	Technique specification	Signature	EA [kJ × mol^{-1}]	Comments	References
Thermal analysis (TA)	Thermogravimetric analysis	TGA	Non-isothermal Thermogravimetric analysis	TGA	~197	450–600 °C; F_1, A_1 and A_3	[26]
					163	F_2	[27]
					227 ± 1	F_3	[34]
			Isothermal Thermogravimetric analysis	ITGA	208	F_2	[27]
					257 ± 8	up to 410 °C, F_2	[28]
					202 ± 3	over 410 °C, F_3	
					140–300		[29]
	Differential thermogravimetry	DTG	–	–	195 ± 2	Kissinger kinetic equation	This article
	Differential thermal analysis	DTA	Non-isothermal assessment	–	178	Kissinger kinetic equation	[30]
	Effluent gas analysis	EGA	Non-isothermal assessment	–	227 ± 1	Kissinger kinetic equation	[31]
			Controlled transformation rate evolved gas analysis	CREGA		D_3	[32]
	Sample controlled thermal analysis	SCTA	Controlled rate thermal analysis	CRTA	233 ± 15	10^{-3} hPa; D_3	[23]
					188 ± 10	5 hPa; F_1	
Molecular spectroscopy	Mass spectroscopy	MS	–	–	145 ± 15	280–600 °C	[33]

F_1 $-\ln(1-y)$ Avrami–Erofeev equation, $n = 1$. Process is controlled via instantaneous random nucleation followed by growth of nuclei.
A_2 $(-\ln(1-y))^{-2}$ Avrami–Erofeev equation, $n = 2$. Process is controlled via instantaneous random nucleation followed by two-dimensional growth of nuclei.
A_3 $(-\ln(1-y))^{-3}$ Avrami–Erofeev equation, $n = 3$. Process is controlled via instantaneous random nucleation followed by three-dimensional growth of nuclei.
F_2 $(1-y)^{-1}$ Second order process is controlled via second-order chemical reaction.
F_3 $(1-y)^{-2}$ Third-order process is controlled via third-order chemical reaction.
D_3 $[1-(1-y)^{1/3}]^2$ Jander equation process is controlled via three-dimensional diffusion through layer of products on the spherical particles.

2. Experimental and methodology

2.1. Sample characterization and measurement

The washed kaolin Sedlec Ia from the region Carlsbad (Czech Republic) produced by the company Sedlecký kaolin a.s. was used for the study of thermal decomposition of kaolinite. This high quality kaolin, originally mined in open-cast mine near village Sedlec, is commercially available since 1892 and it is often allowed to be the world's standard. The content of kaolinite guaranteed by the producer is higher than 90 wt.%. with equivalent grain diameter median in the range 1.2–1.4 μm. The main impurities are mica group minerals and quartz. The colorant oxides content — hematite (α-Fe_2O_3) and tetragonal TiO_2 (rutile), is lower than 0.85 and 0.2wt.%, respectively. The initial state, properties and chemical composition of applied kaolin is described elsewhere [28].

2.2. DTG experiment and data processing

Dehydroxylation of kaolinite was investigated using the TG-DTA analyzer SDT Q600. The 10 mg sample was put into a Pt crucible and heated up to 1200 °C with rate in the range from 1 to 40 °C min^{-1} under flow of argon (100 cm^3 min^{-1}). The number of TGA experiments is six and if needed they were repeated more times to find an average result without outliers. The variation coefficient has to be lower than 5% for all sets of results. The numerical derivation of TG curve provides DTG plot used for determination of temperature at the peak maximum and other important peak parameters (Fig. 1).

The DTG effect was characterized by extrapolated temperature of beginning of peak (T_i), peak temperature (T_p), height of peak (H), width ($W = T_e - T_i$) and half width ($W_{1/2}$) of peak. The shape index (SI) of the peak defined by Eq. (14) can be also determined graphically (see details of Fig. 1). The temperatures of T_i (onset) and T_e (outset) were determined from the intersection of the extrapolated initial baseline and the tangent to the frontal (T_1) and terminal (T_2) inflection points, respectively. Thus the peak's width is equal to the length of the linear interpolated baseline. The peak height is the vertical distance between T_p and interpolated baseline. The peak width at ½H is termed as the peak's half width (semi-breadth of the peak).

2.3. Mathematical background

The Kissinger approach is commonly applied to the kinetic analysis of data from DTA, DTG or DSC experiments. The method can be directly used for the calculation of activation energy from the shift of peak with heating rate ($\Theta = dT/dt$) [35–37]. The shape of the TA curve corresponds to the kinetics of running process, which can be described by substitution of Arrhenius law into the mass action law:

$$\frac{dy}{dt} = kf(y) = A\,exp\left(-\frac{E_A}{RT}\right)f(y). \tag{5}$$

The term dy/dt denotes the reaction rate, k is rate constant, function $f(y)$ represents an applied empirical kinetic model, y is the degree of conversion (fractional conversion), A is the pre-exponential (frequency) factor, E_A is the apparent activation energy, T is the absolute scale temperature and R is the universal gas constant (8.314 J × K^{-1} × mol^{-1}).

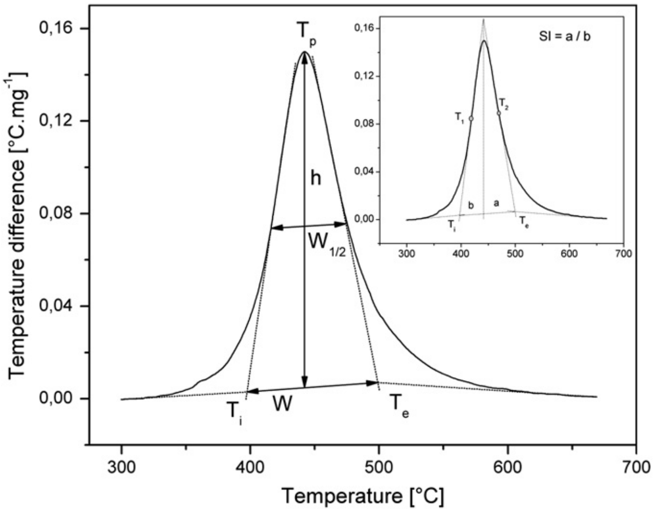

Fig. 1. Monitored peak parameters and method for the determination of the shape index (SI) from DTG curve.