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The influence of structure order on the kinetics of dehydroxylation of kaolinite

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Abstract

The structural order of kaolinite is an important factor that shows a substantial effect on the processes which take place during the thermal treatment of kaolin. The influence of structural order on the dehydroxylation process was investigated by simultaneous thermogravimetry and differential thermal analysis (TG-DTA). The thermal analysis was performed on the samples with gradually decreasing structural order prepared by milling procedure. The apparent activation energy of dehydroxylation process decreases with decreasing structural order according to the exponential function. The extrapolation of experimental data leads to the estimation of apparent activation energy of 76.6 kJ mol^{-1} and of frequency factor of 0.12×10^4 s^{-1} related to completely disordered form of kaolinite, while the ordered form shows the apparent activation energy of 216.17 kJ mol^{-1} and the frequency factor of 9.26×10^4 s^{-1}. The relationships between features such as the infrared pattern of treated material, the degree of structural order and the apparent activation energy were established.
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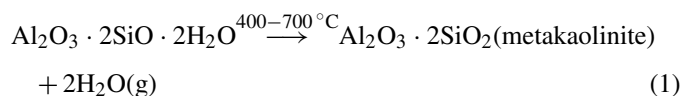*Keywords:* Kaolinite; Structural order; Dehydroxylation; Activation energy; Kinetics

1. Introduction

Clays are important and useful raw minerals in ceramics, chemical, cosmetics and food industry. The industrial meaning and the utilization of clay minerals, such as kaolinite, smectites, and palygorskite and sepiolite, are itemized in works.[1,2] The knowledge on the processes taking place during the thermal treatment of clay minerals is necessary for understanding the sintering behavior of ceramic materials and the influence of additives on the process.[3] Clay minerals fixed in natural raw materials are exposed to the thermal and physical treatment during manufacturing.

Grinding and milling of clay minerals is applied in industrial processes to obtain materials of homogeneous fine particles. While the reduction of materials to a powder of fine or very fine particle size takes place during grinding, the milling procedure is accompanied by structural and chemical changes resulting from friction forces induced in vibratory, oscillating and planetary mills. Short grinding time reduces the kaolinite particles size and increases the surface area.[4] But milling[5,6] and ultrasound treatment[7–11] of well-ordered kaolinite lead to the reduction of particle-size, delamination, increased structure disorder and subsequent amorphization of the material, which affects physical and thermal properties.

Different structural orders of clay minerals obtained by different milling times influence the dehydroxylation process and the formation of cubic spinel phase, mullite and cristobalite during the thermal treatment of kaolin. The processes which take place during the thermal treatment of kaolinite were studied by a number of authors by means of large variety of methods.[2–15] The following reaction was often applied to describe the process of dehydroxylation:

$$Al_2O_3 \cdot 2SiO \cdot 2H_2O \overset{400-700\,^\circ C}{\longrightarrow} Al_2O_3 \cdot 2SiO_2 (\text{metakaolinite})$$
$$+ 2H_2O(g) \tag{1}$$

Besides applied conditions which include heating rate, relative water vapor pressure, particle size distribution, accessory minerals and impurities, and sample pre-treatment, the course of

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dehydroxylation is strongly affected by the degree of crystallization and the order of kaolinite structure.[16–19] It was found that ordered kaolinite structure is transformed into metakaolinite.[20]

The paper deals with the investigations of the kinetics of kaolinite dehydroxylation using the samples with gradually decreasing structural order which were prepared by milling process. The kinetics triplet, that consisted in the identification of most probable mechanism, apparent activation energy and frequency factor, was investigated by non-isothermal thermogravimetric analysis.

2. Experimental

2.1. Kaolin and sample treatment

Washed kaolin Sedlec Ia from the Carlsbad region (Czech Republic) produced by the Sedlecký kaolin company was used for the study of thermal decomposition of kaolinite. This high quality kaolin, originally mined in open-cast mine near Sedlec village, is commercially available since 1892 and is often accepted to be the world's standard. The content of kaolinite guaranteed by producer is higher than 90 wt.% with equivalent grain diameter median in the range of 1.2–1.4 µm. The main impurities are mica group minerals and quartz. The contents of colorant oxides – hematite (α-Fe_2O_3) and tetragonal TiO_2 (rutile) are lower than 0.85 and 0.2 wt.%, respectively. The initial state, properties and chemical composition of applied kaolin are described elsewhere.[21]

The structural defects which lead to the decrease of structural order of kaolinite were reached by milling kaolin in vibratory mill for the time of 0, 10, 30, 60, 120 and 180 min. The samples treated for time longer than 30 min were milled upon 30 min intervals to prevent them from heating to the temperatures higher than 60 °C.

2.2. Assessment of the structural order

The structure of milled samples was characterized by X-ray diffraction analysis (XRD) using X-ray diffractometer (X'pert Empyrean, PANanalytical) with Cu$K\alpha$ radiation at 40 kV and 40 mA. The XRD patterns were used for the assessment of structural order via calculation of Hinckley (HI), Aparicio-Galán-Ferrell (AGFI) and weighted intensity ratio index (WIRI) from weighted intensity of (0 2 1 1) diffractions.

The Hinckley index (HI) can be expressed as follows[22]:

$$HI = \frac{A + B}{I_A} \qquad (2)$$

where values representing individual parameters can be assessed from XRD pattern according to Fig. 1.

The Hinckley index is an empirical method for measuring relative levels of defects in kaolinite powder and it is related to the physical properties of kaolin, namely the particle size. High-defect kaolinite presents broad X-ray peaks, while low-defect one has sharp diffraction peak. Higher value of index indicates lower density of defects. However, the method is applicable only
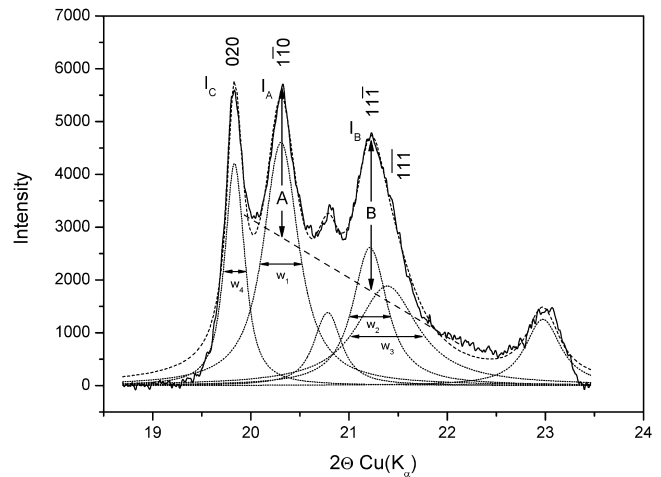

Fig. 1. An example illustrating the determination of values for the calculation of HI, AGFI and WIRI indexes from XRD data for investigated sample of kaolin.

in case that the content of kaolinite in kaolinitic material is more than 20 wt.%.

The empirical methods defined as Aparicio-Galán-Ferrell (AGFI) and weighted intensity ratio (WIRI) indexes can be applied to estimate the structural order of kaolinite as well. The AGFI index is defined by following relation[23]:

$$AGFI = \frac{I_A + I_B}{2I_C} \qquad (3)$$

and the law for weighted intensity ratio index (WIRI) can be expressed as[24]:

$$WIRI = 1 - \exp\left[\frac{-w_1^{-1}I(1\,\bar{1}\,0) + w_2^{-1}I(1\,1\,\bar{1}) + w_3^{-1}I(1\,\bar{1}\,\bar{1})}{w_4^{-1}I(0\,2\,0)}\right] \qquad (4)$$

where w is half-width of diffraction according to Fig. 1. The value of WIRI index ranges from 0 to 1, while maximum values of other indexes (HI and AGFI) are higher than one.

The relation between WIRI and HI indexes can be described by the following linear law[24]:

$$HI = 0.1 + 1.44\,WIRI \qquad (5)$$

2.3. Kinetics of dehydroxylation

The determination of apparent activation energy, pre-exponential (frequency) factor and the most probable mechanism, i.e. the kinetic triplet of dehydroxylation is based on the model fitting method that was described in detail in previous work.[25] The thermal analyses were performed using TG-DTA analyzer SDT Q600 (TA Instruments). 10 mg of sample were introduced into Pt cup and heated under the heating rate of 10 °C min^{-1} and the flow of argon (100 cm^3 min^{-1}) to the temperature of 1000 °C.