



## Research paper

## A new data in the kinetic and thermodynamic analysis of non-isothermal decomposition of super-fine kaolin powder

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## ABSTRACT

Kinetic and thermodynamic analysis of non-isothermal decomposition of super-fine kaolin powder was examined. It was established that the decomposition process proceeds through liberation of adsorbed water, the loss of the water of hydration and dehydroxylation process, which produces highly disordered metakaolin. By applying the distributed reactivity approaches, it was found that dehydroxylation can be described with simultaneous two-parallel reactions model. By applying the Exner-Linert statistical method on estimated Eyring plots, the true isokinetic temperature was confirmed. The appearance of entropy – enthalpy compensation (EEC) showed the direct cause-and-effect relationship between these thermodynamic observables resulting by physically real factors such as the steric factors. It was shown that the phenomenon of true compensation effect arises from conformational (geometrical) changes, which occur during metakaolin formation.

## 1. Introduction

The industrial mineral kaolin has many uses. It has favorable properties such as natural whiteness, fine particle size, non-abrasiveness, and the chemical stability. The kaolinite is a clay mineral, part of the group of industrial minerals, with the chemical composition  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ . It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedra (Deer et al., 1992; Talabi et al., 2012). Kaolin contains 20–26% by weight of alumina. Consequently, it can be suitable material for production of  $\gamma$ -alumina because of its abundance and having considerable content of alumina in kaolin structure.

For industrial application, kaolin is an important member of the kaolinite group of clay minerals. This clay mineral is also the principal constituent in China clay. The main constituent in kaolin is kaolinite. The primary industrial application of kaolin is in the paper making as coating and paper filler. As filler, the kaolin is mixed with cellulose fibers in wood pulp and as a coating, the kaolin is mixed with water, adhesives, and various additives and coated onto the surface of the paper (Murray, 2007). Kaolin is also widely used as filler in plastics industry because of its inert chemical nature and its unique size, shape and structure. Due to the very white color, the fine particle size and layer-like structure, kaolin is suitable as pigment for paint, ceramic raw

material, functional filler, extender, cosmetic, food additive, adhesives, sealant, etc.

Kaolin powder has direct application in the fields of paper-making, ceramics, plastics, coating, etc. (Gamelasa et al., 2014; Bai, 2010; He and Jia, 2013). In industrial applications, the different grades of kaolin powder were classified based on fineness and whiteness. The ultra-fine kaolin is used in the new materials of refractory castable, 4A zeolite, carbon-white, etc. (Shaoxia and Qinhu, 2010). After all, for obtaining the ultra-fine ( $d_{50} < 5 \mu\text{m}$ ) or super-fine ( $d_{97} = 3\text{--}10 \mu\text{m}$ ) kaolin powders, the different mechanical methods and centrifugal sedimentation techniques were used (Dellisanti and Valde, 2012; Sivamohan and Vachot, 1990; Debras et al., 2016).

It should be noted that the kaolin can be used in a variety of useful purposes after transformation, via calcination, into its dehydroxylated phase,  $\text{Al}_2\text{Si}_2\text{O}_7$ , which is much more reactive. This is the first reaction step which occurs through the heating of kaoline usually in the temperature range  $\Delta T = 400\text{--}700 \text{ }^\circ\text{C}$ , and after the water desorption sub-step at the temperatures up to  $100 \text{ }^\circ\text{C}$  (Ptáček et al., 2013). However, above  $700 \text{ }^\circ\text{C}$ , there are another two reaction steps leading to formation of thermodynamically stable phases (mullite and cristobalite) from the kaolin sample (Ptáček et al., 2012).

In this article, the decomposition of the kaolin in the programmed heating modes of the test sample in a temperature range from room

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temperature up to 800 °C has been under monitoring. Therefore, attention has been focused on dehydroxylation process.

Thermal treatment of kaolin exhibits the complexity in respect to nonstoichiometric composition of originating phases, pre-dehydroxylation reaction (Balek and Murat, 1996), the gradual disappearance of the residual hydroxyl groups (Lee et al., 1999), and mullite formation processes (mullitization) (Chakraborty, 2003). The entire process is also influenced by a several material parameters such as: the degree of disorder of structure (DeLuca and Slaughter, 1985), by the pressure and partial water vapor pressure (Smykatz-Kloss and Warne, 1991), the heating rate (Castelein et al., 2001) and mechanical treatments (Vizcayno et al., 2005) of the sample.

The kinetics of thermal decomposition process of kaolin were widely investigated. The kinetics behavior was studied in both, isothermal (static) (Gasparini et al., 2013) and non-isothermal (dynamic) (Ptáček et al., 2010, 2011; Cheng et al., 2010) experimental conditions, in a wide range of fineness of the used kaolin powder, as well as the applied temperature range and flow rate of carrier gas. The kinetics of dehydroxylation of kaolin has been extensively studied preferably by applying thermo-analytical (TA) techniques (such as thermogravimetric analysis (TGA) which is suitable for evaluating the kinetic parameters (the pre-exponential factor ( $A$ ) and the apparent activation energy ( $E_a$ )) involving corresponding mass losses) (Dion et al., 1998; Redfern, 1987).

However, it can be observed through a review of the literature that there is a wide dispersion in the values of the kinetic parameters, as well as the proposals of the reaction mechanism through which the process of interest occurs. It has been found that, depending on the experimental conditions used during TA measurements, then kinetic methods used (which may differ from each other according to their reliability and introduced errors), the particle size of the powder, the sintering process, etc., the mechanism of dehydroxylation may varies from  $n$ -th order reaction mechanisms (with different values of reaction orders ( $n$ )) via nucleation and growth models up to diffusion models (Ptáček et al., 2010). Specifically, such discrepancies are due to the fact that many parameters affects the kinetics of dehydroxylation, which range from the structure defectivity to the shape and particle sizes and size homogeneity, to heating rate used and heating conditions and also the presence of impurities.

The aim of this study is the kinetic and thermodynamic analysis of non-isothermal decomposition process of super-fine kaolin powder in an argon atmosphere. In this study, the main attention was focused on the kinetic and thermodynamic behaviors of dehydroxylation reaction step.

The kinetic parameters and reaction mechanism were determined using distributed reactivity model (DRM) based on parsing of complex mechanistic scheme on the set of reactions that belong to multi-reaction scheme. The DRM was implemented through prediction of conversion rate curves and numerically derived kinetic parameters. Thermodynamic analysis was based on the mutual correlation between thermodynamic quantities with implementation of the procedure for checking the existence of entropy - enthalpy ( $S$ - $H$ ) compensation.

## 2. Experimental

### 2.1. Material

The raw material used for actual study was imported from Czech Republic as industrial kaolin, and which was provided by the Company Sedlecký kaolin a. s., Czech Republic (CZ).

### 2.2. Characterization of materials

The chemical composition of supplied kaolin was determined by X-ray fluorescence (XRF) analyzer (Lab-X3500, Oxford Instruments, Abingdon, United Kingdom, UK) and the results are as follows: SiO<sub>2</sub>

66.00%, Al<sub>2</sub>O<sub>3</sub> 30.98%, Fe<sub>2</sub>O<sub>3</sub> 0.80%, TiO<sub>2</sub> 0.57%, Na<sub>2</sub>O + K<sub>2</sub>O 0.50% and CaO + MgO 0.50%, LOI 0.65%. The particle size analysis was performed on YX-3000A (Xiamen Yuxiang Magnetic Materials Ind. Co., Ltd. Xiamen, China) disc particle size analyzer (PSA) which adopts high-speed disc centrifugal sedimentation. Medium value of analyzed particle sizes of kaolin powder was ~10 μm. Corresponding particle size distribution of kaolin powder is shown in Fig. S1 (Supplementary material).

### 2.3. Thermo-analytical (TA) measurements under dynamic heating modes

Thermo-analytical (TA) measurements were carried out using a simultaneous non-isothermal thermogravimetric analysis (TG) and differential thermal analysis (DTA) on the SETARAM SETSYS Evolution 1750 (SETARAM Instrumentation 7, rue de l'Oratoire 69,300 Caluire, France) instrument. The high purity argon (Ar) gas (99.999%) was used as carrier gas at a flow rate of  $\varphi = 20 \text{ mL min}^{-1}$ . A Pt crucible was filled with about 10 mg of powder sample and heated at different heating rates:  $\beta = 10, 15, 30$  and  $40 \text{ °C min}^{-1}$ . The tested sample at a given heating rates was heated from the room temperature up to 800 °C. Differential thermal analysis (DTA) was carried out simultaneously with thermogravimetry (TG) under same conditions as described above, with a 1750 °C DTA cell, and noise RMS and resolution of 20 μW and 0.4 μW, respectively. For each recording, duplicate non-isothermal runs for the selected heating rate were performed under the same conditions, and it was found that the data overlaps with each other indicating the satisfactory reproducibility.

### 2.4. The FTIR spectroscopy

The procedure used for FTIR spectroscopy analysis was conducted in accordance with the FTIR procedure proposed for clay minerals (Ojima, 2003). The Fourier transform infrared (FTIR) spectrum was acquired using a Thermo Nicolet 380 FT-IR (Thermo Fisher Scientific Ltd., Waltham, MA, USA) instrument equipped with a Smart Orbit™ ATR attachment, which contains a single-reflection diamond crystal. The FTIR spectrum was taken in the attenuated total reflectance (ATR) mode where typically 64 scans are performed for each spectrum at a resolution of  $4 \text{ cm}^{-1}$ , in the wavenumber range of 400–4000  $\text{cm}^{-1}$ . About the 1 mg of the sample (the dried sample, which was previously dried for 2 h at the temperature of 105 °C) accompanied with 100 mg KBr (the dried powdered sample was homogenized in spectrophotometric grade KBr in an agate mortar and pressed at 3 mm pellets with a instrument distributed hand press) was done. The FTIR peaks were reported based on the % transmittance to a given wavenumbers ( $\text{cm}^{-1}$ ).

## 3. Theoretical background

### 3.1. Kinetic analysis

In general, for the process as  $aA_{[\text{solid}]} \rightarrow bB_{[\text{solid}]} + cC_{[\text{gas}]}$ , the disappearance of component A can be described by the formal kinetic expression in a form:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot f(\alpha) \quad (1)$$

while  $k(T) = A \cdot \exp(-E_a/RT)$  represents the temperature-dependent rate constant expressed by the Arrhenius equation;  $d\alpha/dt$  is the rate of the process,  $t$  is the time,  $\alpha$  is the conversion fraction,  $A$  is the pre-exponential factor,  $E_a$  is the apparent (effective) activation energy,  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature (K), and  $f(\alpha)$  is the kinetic (conversion) function, which takes different forms depending on the particular reaction rate equation. In non-isothermal kinetics, the time dependence on the left-hand side of the Eq. (1) is eliminated using constant heating rate  $\beta = dT/dt$ , so that

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