



Research paper

The pyrolysis kinetics of the conversion of Malaysian kaolin to metakaolin



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ABSTRACT

The aim of this work was to study the pyrolysis kinetics of the thermal transformation of kaolin to metakaolin with the aid of models and model free isoconversional methods. Thermal treatment in the range of 600–850 °C is used to convert kaolin into an amorphous and highly reactive metakaolin (MK). In this study, the thermal transformation of kaolin to metakaolin was investigated using thermokinetics and instrumental analysis. Kaolin was subjected to thermogravimetric analysis (TGA) at heating rates of 10, 20 and 40 °C/min, in the temperature range of 50–800 °C. Approximately, 14.2% of mass loss was recorded during the TG analysis. 95% of the degree of dehydroxylation was attained at 635 °C, representing the minimum temperature for this process. The TGA and its related data were analyzed using model free (based on DTG, DTA and TG) and model based kinetics methods. Both DTG and DTA peak temperatures were employed for the thermokinetics of kaolin using Ozawa, Kissinger and Starink methods; giving an E_a in the range of 246.6–252.5 kJ·mol⁻¹. A slight higher average E_a (266–267 kJ·mol⁻¹ vs 246.6–252.5 kJ·mol⁻¹) was observed when TGA based integral methods (KAS, FWO and Starink) were used. The mechanism of the thermokinetics was investigated using the Redfern model and the best fitting was given by 3rd order chemical reaction (F_3) function. Both model-free and model based thermokinetics methods could be used to validate the thermal transformation of kaolinite to metakaolinite.

1. Introduction

The existence of life on this planet is closely associated with the clay minerals owing to their vital role in different forms. Various types of the most important clay minerals include sepiolite, smectite, palygorskite and kaolinite etc. Both in raw and pure forms, these clays have been used in different reactions and applications (Bergaya and Lagaly, 2006; Ptáček et al., 2014). Kaolinite (Al₂Si₂O₅(OH)₄) is the major phase present in kaolin, a phyllosilicate that is comprised of alternating sheets of SiO₄ tetrahedra and Al octahedra of O and OH, respectively, having a theoretical composition of 46.54% SiO₂, 39.5% Al₂O₃ and 13.96% water. Along with kaolinite, traced amounts of other phases e.g. illite, muscovite, smectite and quartz etc. can exist in kaolin (Bergaya and Lagaly, 2006; Rashad, 2013b).

Currently, the total global production of kaolin is more than 25 million tons/year (Nkoumbou et al., 2009). Kaolin has been used as a raw precursor for the synthesis of ceramics, nano aluminum oxide, nano SiO₂, along with its use in the paper, coating, fireproofing, pharmaceuticals and petrochemical industries (Bukhari et al., 2015; Yang et al., 2010). Moreover, kaolin has been frequently utilized in cement

industry, and in the alternative green cementing materials called geopolymers (Provis and Bernal, 2014; Rashad, 2013a; Souri et al., 2015; Temuujin, 2011). With the emergence of geopolymer technology in the last decade, kaolin and metakaolin have received the attention of the geopolymer scientists around the globe. Geopolymers are the three dimensional aluminosilicates, which are most frequently used as low-CO₂ cementing/binder material (Davidovits, 1982, 2008; Khan et al., 2015). Necessary to mention, the alkali activation of kaolin has been hindered by the presence of the well-ordered layered structure of kaolinite (Provis and Bernal, 2014). Thermal treatment or calcination at 600 °C–850 °C is used to convert kaolin to an amorphous and highly reactive material, metakaolin (Ambroise et al., 1985; Meinhold et al., 1992; Ptacek et al., 2010, Ptacek et al., 2011a, 2011b, 2014). In this process, it is considered that the Al octahedra of O and OH are probably transformed to a reactive tetrahedral geometry (Provis and Bernal, 2014). Fundamentally, metakaolin (MK) has been used for the synthesis of geopolymers and alkali activated materials since 1968; the time the first geopolymer was reported by Davidovits (1982, 2008). Besides the use of metakaolin in geopolymers, it has also got many applications in the cement and concrete industry (Dunster et al., 1993; Sabir et al.,

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2001). Different procedures have been used for the transformation of kaolin to MK including mechanical activation and thermal treatment (Mitrović and Zdujić, 2014; Fitos et al., 2015; Ilić et al., 2016). Rashad (2013b) reviewed the thermal treatment conditions used by various researchers and concluded that two hour treatment at 800 °C was sufficient for the preparation of MK. Davidovits (1991) calcined kaolinite at 500, 650, 700 and 750 °C, whereas Palomo et al. (2014) recommended the temperatures in the range of 600–700 °C for metakaolination process. Dehydroxylation of kaolin is dependent on many factors, including mineralogy, particle size, and crystallinity of the raw materials. Moreover, it is also influenced by the water vapour pressure formed. The reaction is complicated by intricate diffusion problems associated with diffusion of water vapour molecules in the powder mass and diffusion occurring in the crystal itself (Bulens and Delmon, 1977; Gastuche et al., 1963; Kakali et al., 2001; Temuujin et al., 1999). Thermal analysis, X-ray diffraction (XRD) and infra-red (IR) spectroscopy are used to confirm the formation of MK from kaolin (Ptacek et al., 2011a, 2011b; Bich et al., 2009). Using thermal analysis, the kinetics of dehydroxylation of kaolin to MK has been investigated to find the activation energy (E_a) and pre-exponential factor (lnA) of that process (Brindley and Nakahira, 1957; Ptacek et al., 2010; Wang et al., 2011; Zemenová et al., 2014). The process of dehydroxylation of kaolin is influenced by the method used, nature of the clay, the experimental design and water vapour pressure, among others (Kakali et al., 2001; Temuujin et al., 1999). Thermal dehydroxylation of kaolin produced E_a in the range of 145–265 kJ mol⁻¹, in different studies (Brindley and Nakahira, 1957; Ptacek et al., 2011a; Wang et al., 2011).

Model-free and model based methods using Kissinger, Ozawa, Flynn-Wall-Ozawa (FWO), Kissinger Akahira and Sunrose (KAS) and Redfern equations have frequently been used for the investigation of thermokinetics parameters of different materials (Vyazovkin et al., 2011, 2014). Recently, Ptacek et al. (2010, 2011a, 2014) studied the thermokinetics of MK formation using isothermal TGA and differential thermograms (DTG) techniques and the mechanism of metakaolination was function of heating rate and temperature. Recently, S. Vyazovkin et al. (2011) concluded that more reliable and accurate results were produced with the aid of Starink method (Starink, 2003; Vyazovkin et al., 2011). Previously, the Starink method has been used by employing thermogravimetric analysis (TGA) data at varying heating rates. Starink (2003) suggested that the equation can be applied to the derivative curves, i.e. DTG and differential thermal analysis (DTA), in a fashion similar to Kissinger equation.

In the previous studies, the thermokinetics of the dehydroxylation of kaolinite was not investigated using the Starink method. Moreover, it was necessary to support model-free methods with the Redfern model based methods to confirm the mechanism of that process. This study is the first detailed kinetics study of the metakaolination process using TGA employing both model free and model based methods. In this work, Ozawa, Kissinger and Starink methods were applied to both DTG and DTA data to calculate the activation energy and pre exponential factor (min⁻¹). Moreover, KAS, FWO and Starink methods were applied to the TG data and lastly the mechanism of the thermal transformation was retrieved using Redfern model.

2. Material and methods

2.1. Materials

Kaolin was purchased from R & M Chemicals Sdn. Bhd. Malaysia, and was used without further treatment. The chemical composition of the kaolin determined using X-rays fluorescence spectroscopy (XRF) was SiO₂ (55.9%), Al₂O₃ (37.7%), TiO₂ (1.76%), Fe₂O₃ (1.74%), P₂O₅ (1.70%), CaO (0.46%), K₂O (0.37%), along with traced components (0.37%). The moisture content of the sample was 0.4% as determined by the mass loss procedure.

2.2. Methods

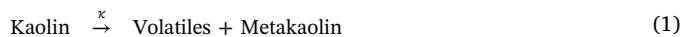
Raw kaolin was dried in an oven at 110 °C in the air for three hours, and was transformed into metakaolin by sintering in a muffle furnace at 700 °C for 4 h (Lima et al., 2014). Kaolin and the fabricated metakaolin were characterized using different analytical techniques to compare the changes taking place during the metakaolination process. X-rays diffraction analysis was run on an X-ray diffractometer (D8 advance, Bruker, Germany) equipped with a copper tube operating at 40 KV and 200 MA, producing CuK_α radiation having a wavelength of 1.5406 Å. The samples were scanned from 2° – 80° (2θ) at a rate of 2°/s, a step size of 0.02, a receiving slit width (RS) of 0.02 mm. The XRD analysis was used for the qualitative and quantitative analysis (Rietveld analysis) of the phases present in kaolin and metakaolin. Rietveld analysis was carried on using freeware, Material Analysis Using Diffraction (MAUD), with the input phases of kaolinite, illite and quartz. Fourier Transformed Infra-Red (FTIR) analysis of both samples was recorded using an IR spectrophotometer (Spectrum One, Perkin Elmer, US), using KBr pellet technique. Approximately, 5 mg of the sample was mixed with 200 mg of KBr, pressed to pellet at a pressure of 9 MPa and was analyzed in the FTIR instrument at a scanning rate of 24 scans per sample at a resolution of 1 cm⁻¹, in the wavenumbers range of 4000–400 cm⁻¹. Both FTIR and XRD analysis were used to determine the transformation of kaolinite to metakaolinite. To investigate the microstructural changes happened during metakaolination, field emission scanning electron microscopic (FESEM) micrographs of the powdered samples were recorded using FESEM (VP55, Zeiss supra, Germany) at an acceleration voltage of 20–30 keV and magnification of 20,000 ×, using the secondary electron technique.

Thermogravimetric analysis (TGA) of kaolin was carried out with a simultaneous thermal analyzer (STA-6000, Perkin Elmer, US), under nitrogen atmosphere, with a flow rate of 20 ml min⁻¹ at three different heating rates of 10, 20 and 40 °C min⁻¹. The sample (~10 μg) was placed in an alumina crucible and was dried from laboratory temperature to 105 °C and then was analyzed in STA-6000 from 50 to 800 °C and the results were recorded in the form of mass loss (%) vs. temperature. Derivatives of the TGs (DTGs) were calculated using in-built software “Pyris” and were smoothed, whenever necessary.

Kinetics study of the dehydroxylation of kaolinite in kaolin was obtained using TGA, DTG and DTA techniques, employing model-free and model based kinetics methods. The theory of the kinetics using thermogravimetric data is discussed in next section.

2.3. Kinetic theory

The thermal dehydroxylation of kaolin can be represented using Eq. (1) as a one-step universal model by assuming that degradation reaction occurs in a single step;



volatiles and k represent the water of dehydroxylation and the rate constant of reaction, respectively. The Arrhenius equation expresses the temperature dependence of k in Eq. (2).

$$k = Ae^{-\left(\frac{E_a}{RT}\right)} \quad (2)$$

where A , E_a , R and T indicate the pre exponential factor (min⁻¹), activation energy (KJ·mol⁻¹), gas constant (8.314 J·K⁻¹·mol⁻¹) and the absolute temperature (K), respectively. The rate of transformation of a material from solid state to volatile product is described by Eq. (3)

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

where α , t , $k(T)$, $f(\alpha)$ represent the degree of conversion of the reactants to products, time taken, rate constant and the reaction model, respectively. The normalized form of mass loss of the sample is termed as conversion (α) and is represented by Eq. (4).

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