



Time-resolved powder neutron diffraction study of the phase transformation sequence of kaolinite to mullite

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Abstract

Mullite formation from kaolinite was studied by means of high-temperature *in situ* powder neutron diffraction by heating from room temperature up to 1370 °C. Neutron diffractometry under this non-isothermal conditions is suitable for studying high-temperature reaction kinetics and to identify short-lived species which otherwise might escape detection. Data collected from dynamic techniques (neutron diffraction, DTA, TGA and constant-heating rate sintering) were consistent with data gathered in static mode (conventional X-ray diffraction and TEM). The full process occurs in successive stages: (a) kaolinite dehydroxylation yielding metakaolinite in the ~400–650 °C temperature range, (b) nucleation of mullite in the temperature range ~980–992 to ~1121 °C (primary mullite) side by side with a crystalline cubic phase (Si–Al spinel) detected in the ~983–1030 °C temperature interval; (c) growth of mullite crystals from ~1136 °C, (d) high (or β) cristobalite crystallization at $T > \sim 1200$ °C and (e) secondary mullite crystallization at $T > \sim 1300$ °C. The calculated activation energy for the kaolinite dehydration was 115 kJ/mol; for the mullite nucleation was 278 kJ/mol and for the growth of mullite process was 87 kJ/mol; finally for cristobalite nucleation the calculated apparent activation energy was 481 kJ/mol.

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1. Introduction

Kaolin is extensively used in a diverse number of applications in the ceramic industry: conventional ceramics, structural and refractory ceramics, high-temperature protective coatings, microelectronic packaging, microwave dielectrics, and infrared-transmitting materials. Beyond the ceramics, kaolin is utilized as an industrial filler agent for paper, plastics, rubber, cosmetics, paints, etc.¹ Furthermore, kaolin can be utilized for waste management and preparation of geopolymers and geopolymer based composites, zeolites and intercalates.^{2–4} Metakaolin, produced by calcination of kaolin rock, has found utilizations in food processing industry, oil shale processing and ceramics.^{1–4}

All these applications involve the thermal transformation of kaolinite, main mineral phase of kaolin rock, hence

the need and interest to revisit the conversion of kaolinite ($\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$) to the thermodynamically stable phases, i.e. mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and α -cristobalite (cubic cristobalite, SiO_2) and related subjects, such as its stability as a function of temperature and kinetics of the reactions that allow a better understanding of the development of technical ceramics.⁴ The studies developed to understand this traditional raw material could serve as framework for the study of advanced ceramics.

The processes occurring upon firing kaolinite clay mineral has been the subject of thorough investigation since the early work of Le Chatelier in 1887.⁵ The study of this reaction sequence continues to draw interest from the materials research community due to on-going controversies related to the composition and structure of the intermediate phases.^{6,7} The course of mullite formation from kaolin has been investigated by a number of methods and techniques such as thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC)^{1–4,8} and dilatometry. Unfortunately, although those investigations based on thermal methods provide

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very valuable thermodynamic knowledge, they do not allow a direct *in situ* identification of the phases formed. On the other hand, conventional methods of analysis (powder X-ray diffraction (XRD), ^{27}Al and ^{29}Si Magic-Angle Spinning Nuclear Magnetic Resonance (MAS-NMR)^{9–11} and Transmission Electron Microscopy (TEM))^{12,13} require the reaction process to be abruptly interrupted, hence introducing an external interference. This procedure makes this approach less reliable. Two papers by Belloto et al.^{14,15} report experiments carried out *in situ* using synchrotron radiation diffraction analysis on kaolin specimens. More specifically they study the kinetics of mullite formation in the 1300–1400 °C temperature range and the kinetics of dehydroxylation of two kaolin specimens in the 500–700 °C temperature range.

The use of powder neutron diffractometry (PND), allows the collection of data at a speed appropriate to achieve a resolution acceptable time. The advantage of this technique is that *in situ* recording of diffraction patterns permits the detection of short-lived phases, which otherwise cannot be detected by quenching and more conventional diffraction or microscopic methods.^{16,17} That is why diffraction methods, such as PND, have been used also to identify phases formed and disappeared as the temperature raises. The phase transformation sequence of kaolinite and halloysite to mullite has been examined *in situ*, during heating up to 1500 °C (at room temperature, 600, 900, 1100, 1200, 1400, and 1500 °C on heating), using neutron diffraction methods by Nobuo Tezuka et al.¹⁸ Because of their experimental method these authors cannot detect the possible formation of transitory phases. The high temperature reactions of a natural kaolin were studied using time-resolved powder neutron diffraction by Collins et al.¹⁹ These authors observed the dehydroxylation process in the 440–600 °C range and the initial stages of mullite formation at 950–1000 °C.

The aim of the present paper is to study the thermal transformation of kaolinite at temperatures up to 1370 °C using primarily high-temperature *in situ* powder neutron diffraction methods. Neutron diffractometry under this non-isothermal conditions is suitable for studying high-temperature reaction kinetics and to identify short-lived species which otherwise might escape detection. This technique is also a powerful experimental tool to monitor dehydroxylation process by direct measurement of the background. These data have been complemented and correlated with further thermal and dilatometric analysis. Also specimens of kaolin treated at some prefixed temperatures were analyzed by conventional X-ray diffraction (XRD) and Transmission Electron Microscopy techniques (TEM).

2. Experimental procedure

2.1. Characterization of the sample

The washed kaolin from Poveda de la Sierra,²⁰ Guadalajara, Spain used in this investigation was supplied by Caobar S.A. and their chemical and mineralogical analysis is shown in Table 1. The chemical analysis of kaolin was carried out by ICP-plasma (Iris Duo, Thermo Jarrell Ash Corporation, USA) and flame

Table 1

Chemical analysis and physical properties of the kaolin specimen. Sample dried at 110 °C.

	Kaolin	Kaolin calcined	Theoretical composition
Chemical analysis (wt %)			
Ignition loss	13.0	–	13.95
SiO ₂	48.4	55.9	46.55
Al ₂ O ₃	37.0	42.7	39.50
TiO ₂	<0.005	<0.05	–
Fe ₂ O ₃	0.25	0.29	–
MgO	0.05	0.06	–
CaO	0.31	0.35	–
Na ₂ O	0.13	0.15	–
K ₂ O	0.46	0.53	–
Mineralogical analysis			
Kaolinite	>90		100
Quartz	~5		–
Muscovite (mica)	~5		–
Particle size analysis (d ₅₀ (μm))			
	5.6		
Specific surface area (m ² /g)			
	8.5		

emission spectroscopy (FES 2100, Perkin–Elmer, USA, atomic absorption spectrometer used in the flame emission mode).

This mineral has an average particle size of 5.6 μm (by laser diffraction, Mastersizer S, Malvern, UK) and a specific surface area (S_{BET}) of 8.5 m²/g (by the dynamic method; Monosorb Surface Area Analyzer MS-13, Quantachrome Corporation, USA), using the Brunauer–Emmett–Teller (BET) model.

2.2. Thermal behaviour

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (STA 409, Netzsch, Germany) studies were conducted, in air, using Pt crucibles and α-Al₂O₃ as reference. Samples were heated up to 1400 °C (maximum temperature) at constant heating rates of 2, 5 and 10 °C/min.

The kaolin powders were compacted to form bars of about 5 mm diameter by cold isostatic press under 100 MPa. Samples were heated up in air to 1400 °C (maximum temperature) at constant heating rate of 10 °C/min over periods of time from 2 to 72 h and then program cooled.

2.3. X-ray analysis

The X-ray diffraction (XRD) patterns were acquired using a Siemens D5000 automated diffractometer (Karlruhe, Germany) (Bragg–Brentano geometry) using Cu Kα_{1,2} radiation (λ = 0.1542 nm) and a secondary curved graphite monochromator. To generate X-rays a tube with a Cu anticathode working at 40 kV and 30 mA was used. Data were collected in the Bragg–Brentano (θ/2θ) vertical geometry (flat reflection mode) between 2 and 70° (2θ) in 0.05° steps, counting for 5 s per step. The EVA-version 6.0 Diffrac plus software (Bruker AXS GmbH, Karlsruhe, Germany) was used to evaluate the obtained patterns.

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