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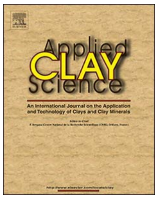

Research paper

Decomposition and phase transformation mechanism of kaolinite calcined with sodium carbonate

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ABSTRACT

Thermal decomposition, phase transformation and microstructure change for the mixture of kaolinite and sodium carbonate (Na_2CO_3) calcined at different temperatures were studied through experimental investigation and theoretical analysis. Thermo-gravimetric and differential scanning calorimetric coupled with mass spectrometer (TG-DSC/MS) were utilized to determine the reaction temperature of kaolinite and Na_2CO_3. The calcinated products at different temperatures were characterized by X-ray diffraction (XRD), magic angle spinning nuclear magnetic resonance (MAS-NMR) and Fourier transform infrared (FT-IR). The results showed that the solid-state reaction between kaolinite and Na_2CO_3 mainly occurred within the temperature of 300–850 °C. During the calcining process, kaolinite was decomposed and transformed into meta-kaolin (MK), low-temperature carnegieite (L-phase), nepheline and zeolite in turn, which can be interpreted in terms of the combination change of different oxygen coordination. With the increase of temperature, the [AlO_6] octahedron in kaolinite gradually transformed into the [AlO_4] tetrahedron in MK by dehydroxylation, and the bridging oxygen between [AlO_4] and [SiO_4] layers together with the bridging oxygen in [AlO_4] layer and [SiO_4] layer were broken with the participation of Na_2CO_3. Subsequently, the obtained individual [AlO_4] and [SiO_4] tetrahedrons alternately recombined and formed an anion frame-like structure by sharing the oxygen atom owing to the limitation of Pauling's electrostatic valence rule. In order to further maintain the charge neutrality and structural stability, Na^+ ions were filled in the anion frame-like structure of L-phase, nepheline and zeolite. This research is of some theoretical significance for the Na_2CO_3-assisted thermal activation of kaolinite and kaolinite-based solid wastes.

1. Introduction

With the increase in alumina demand and the diminishing of bauxite resources, exploring a potential substitute for bauxite in alumina production is of great importance (Ding et al., 2016; Guo et al., 2016; Yao et al., 2014). In recent decades, kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) and kaolinite-based solid wastes such as coal gangue and oil shale have attracted considerable attention for alumina extraction (Guo et al., 2016; Lima et al., 2014; Livingston et al., 1983; Miao et al., 2011; Qiao et al., 2008; Xiao et al., 2015). The extraction process sequentially includes feedstock activation, acid leaching, solid-liquid separation and crystallization or precipitation to produce alumina products (Livingston et al., 1983; Miao et al., 2011). Among these processes, feedstock activation plays a key role due to the high chemical stability of kaolinite (Guo et al., 2014a; Li et al., 2011). Thermal activation is a common method by which kaolinite can be partly activated, but it has been confronted with low extraction of aluminum and difficult utilization of acid slag (Cui et al., 2015; Qiao et al., 2008). Sodium carbonate (Na_2CO_3) is widely considered as a good additive for completely activation of kaolinite and kaolinite-based solid wastes. When the calcinated product was leached in acid, the consequent dissolution percentage of aluminum can even reach > 95%. Meanwhile, the obtained acid slag is mainly consist of amorphous silica with uniform particle sizes, high special surface area and chemical activity (Guo et al., 2014a; Xiao et al., 2015; Zakharov et al., 2012). Therefore, Na_2CO_3-assisted thermal activation has been considered as a promising method for the simultaneous extraction of aluminum and silicon in kaolinite and kaolinite-based solid wastes.

As to the calcination mechanism of kaolinite-based materials and Na_2CO_3, it has been the concern of many researchers and has achieved some results (Guo et al., 2014a; Kosminski et al., 2006; Kubo et al., 1966, 1967, 1968). Kubo et al. investigated the solid-state reaction between kaolinite and Na_2CO_3 within the temperature range of 600–1200 °C. They found that kaolinite decomposed at about 600 °C

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and transformed to low-temperature carnegieite (L-phase), nepheline and high-temperature carnegieite in turn with the increase of temperature (Kubo et al., 1966, 1967, 1968). In our previous work, sodium aluminum silicates such as nepheline and carnegieite were also found to be formed during the calcination of coal gangue and Na_2CO_3 at 850 °C (Guo et al., 2014a,b). In addition, Kubo et al. further investigated the structure inheritance from reactants to products for the reaction of kaolinite and Na_2CO_3. They speculated that the reaction process can be interpreted in terms of the random distribution of Na^+ in kaolinite because both L-phase and nepheline have a similar Si—O framework to that of the kaolinite (Kubo et al., 1968). Meanwhile, Kosminski et al. deemed that the hexagonal crystal structure of kaolinite was preserved during the transformation from kaolinite to nepheline (Kosminski et al., 2006). Cited works showed that the reaction process of kaolinite-based materials and Na_2CO_3 underwent a series of phase transformations. However, the microstructure change and reaction mechanism during this process are still unclear.

In this work, the thermal decomposition, phase transformation and microstructure change for the mixture of kaolinite and Na_2CO_3 calcined at different temperatures were studied through experimental investigation and theoretical analysis. Based on this, the decomposition and phase transformation mechanism of kaolinite calcined with Na_2CO_3 was analyzed in detail. This research is expected to provide a theoretical guide to the Na_2CO_3-assisted thermal activation of kaolinite and kaolinite-based solid wastes.

2. Experimental

2.1. Materials

Kaolinite was purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing. The chemical compositions and loss on ignition (LOI) of raw material were measured. Table 1 lists SiO_2 and Al_2O_3, whose sum accounts for > 82%, as the main chemical compositions of the kaolinite. The ratio of aluminum and silicon (Al/Si) was approximately 0.93, slightly lower than the theoretical value due to the presence of quartz (Fig. 1). Sodium carbonate (A.R.) was purchased from Beichen Chemical Reagent Factory, Tianjin.

2.2. Sample preparation

The as-received kaolinite was dried at 105 °C for 12 h and ground to fine powder (< 75 μm) using a planetary ball mill (Nanjing University Instrument Plant, QM-3SP2). The pulverized kaolinite was homogenized with a certain amount of Na_2CO_3 (molar ratio of 1:1.2) in an agate mortar. The mixed samples were transferred into a platinum crucible and heated in a muffle furnace (Shanghai Hongji Instrument Plant, SX2–12-10) at the desired temperature for 2 h. The calcined samples were cooled to room temperature in a desiccator and then ground into powder again.

2.3. Sample characterizations

Thermo-gravimetric and differential scanning calorimetric (TG-DSC) analyses were performed simultaneously by a thermal analyzer (SETARAM, Setsys Evolution). Approximately 25 mg sample was taken in platinum crucible with a blank platinum crucible as reference. It should be noted that the blank platinum crucible is run with α-Al_2O_3 powder that does not present any transformations from ambient temperature to 1000 °C. (Yang et al., 2016) The measurements were conducted from ambient temperature to 1000 °C with a linear heating rate of 10 °C/min under a nitrogen flow of 100 mL/min. A quadrupole mass spectrometer (MS, OMNISTAR, GSD 320 O3) coupled to the thermal analyzer was used for the evolved gas analysis. The mass signals of 18 (H_2O) and 44 (CO_2) were continuously detected during the analysis (Sonobe and Worasuwannarak, 2008).

The mineral compositions of calcined samples were identified using an X-ray diffraction (XRD) spectrometer (BRUKER, PHASERD 2) equipped with a Cu Kα radiation and an advanced linear detector. The acceleration voltage and electrical current were 30 kV and 10 mA, respectively. The scans were performed between 10° and 60° with a 0.01° step size and a counting time of 0.1 s step^{-1} (Yan et al., 2016).

The ^{27}Al and ^{29}Si coordination structure of calcined samples were measured by a BRUKER AVANCE III 600 MHz wide bore magic angle spinning nuclear magnetic resonance (MAS-NMR) spectrometer (14.2 T). A 4-mm probe was used with a spinning frequency of 13,000 Hz for ^{27}Al, and a 7-mm probe was used with a spinning frequency of 6000 Hz for ^{29}Si. ^{27}Al spectra were recorded with a single pulse excitation (SPE) using a short pulse length (1 μs) and a recycle delay of 1 s. ^{29}Si spectra were recorded using a 90° pulse length of 5.7 μs with a recycle delay of 60 s. ^{27}Al and ^{29}Si chemical shifts were, respectively, referenced using $Al(NO_3)_3$ and $(CH_3)_4Si$ solutions as the external reference (chemical shift at 0 ppm) (Maia et al., 2014; Mantovani et al., 2009).

Fourier transform infrared (FT-IR) spectra were recorded on a Fourier transform infrared spectroscopy (PerkinElmer, Spectrum 2) using a KBr Pellet Method (Guo et al., 2016). The KBr Pellet Method was performed as follows: weighing the dry samples and KBr in a mass ratio of 1:100, grinding in an agate mortar and pressing to form the pellet. The spectrum of each sample was recorded in triplicate by accumulating 64 scans at 4 cm^{-1} resolution between 4000 cm^{-1} and 400 cm^{-1}.

Table 1
Chemical compositions and loss on ignition of kaolinite.

Oxides	SiO_2	Al_2O_3	TiO_2	Na_2O	CaO	MgO	K_2O	Fe_2O_3	LOI
Contents (wt %)	45.71	35.95	0.73	0.60	0.57	0.33	0.29	0.16	15.66

LOI denoted the loss on ignition at 850 °C.

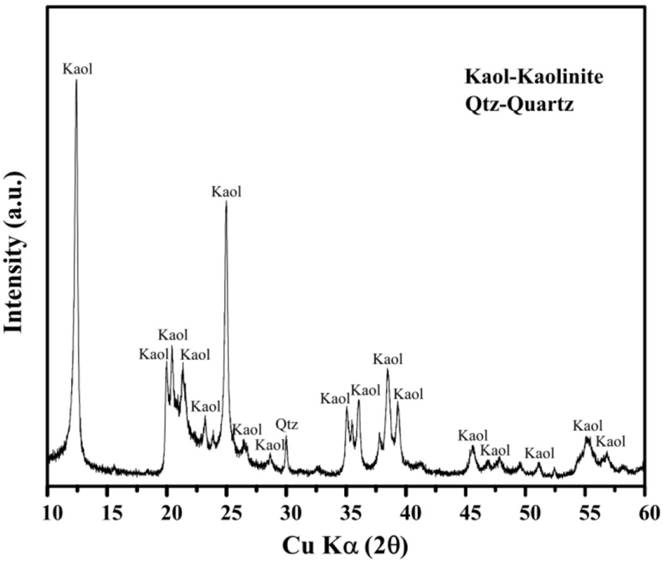

Fig. 1. XRD patterns of as-received kaolinite.

3. Results and discussion

3.1. Thermal decomposition behavior

TG-DSC/MS analyses were used to clarify the thermal decomposition behavior of kaolinite calcined with or without Na_2CO_3. As shown by the TG-DSC/MS curves of kaolinite in Fig. 2(a), a significant weight