



# Thermal decomposition and transformation mechanism of mullite with the action of sodium carbonate



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## ABSTRACT

Mullite as one of the major aluminum-containing minerals in pulverized coal fly ash (PCFA) has a stable crystal structure, resulting in the difficulty in aluminum extraction from PCFA.  $\text{Na}_2\text{CO}_3$ -assisted thermal activation of PCFA is an efficient approach to activate the reactivity of mullite in PCFA. A clear understanding of the decomposition and transformation mechanism of mullite calcined with  $\text{Na}_2\text{CO}_3$  is of great significance to clarify the activation mechanism of PCFA and the further process optimization. In this work, the thermal decomposition behavior, the phase transformation and the microstructure change were investigated in detail using thermo-gravimetric and differential scanning calorimetric (TG-DSC), X-ray diffraction (XRD) and magic angle spinning nuclear magnetic resonance (MAS-NMR). The results showed that the phase transformation process was mullite firstly converting into sodium aluminum silicate (SAS,  $\text{Na}_{1+x}\text{Al}_{1+x}\text{Si}_{1-x}\text{O}_4$ ,  $0 < x < 1$ ) at  $< 800^\circ\text{C}$  and then to other minerals with higher structure stability, such as sodium aluminate and sodium silicate, with the increasing of  $\text{Na}_2\text{CO}_3$  amount at  $> 800^\circ\text{C}$ . The reaction mechanism could be interpreted in terms of the combination change of different oxygen coordination. During the calcination, the  $\text{Na}_2\text{O}$  decomposed from  $\text{Na}_2\text{CO}_3$  would enter in mullite through filling oxygen vacancies and then react with the oxygen atoms around the  $\text{Al}^{\text{VI}}$ , resulting in the formation of the  $\text{AlO}_4$  in SAS. Further increase in the calcination temperature and the  $\text{Na}_2\text{CO}_3$  amount, the transforming from mullite to SAS would be obviously enhanced. When the temperature was  $> 800^\circ\text{C}$ , the residual  $\text{AlO}_6$  originated from mullite was further transformed into  $\text{AlO}_4$  with the larger amount of  $\text{Na}_2\text{CO}_3$ . Meanwhile, the bridging oxygen bonds between  $\text{AlO}_4$  and  $\text{SiO}_4$  in SAS were broken by the attacking of  $\text{Na}_2\text{O}$ . Subsequently, all the obtained  $\text{AlO}_4$  and  $\text{SiO}_4$  as well as  $\text{Na}^+$  ion could be further recombined in a specific manner to transform into sodium aluminates ( $\text{AlO}_4\text{-AlO}_4$ ), sodium silicates ( $\text{SiO}_4\text{-SiO}_4$ ) and sodium aluminosilicates ( $\text{AlO}_4\text{-SiO}_4$ ).

## 1. Introduction

Alumina extraction from coal fly ash as an effective waste disposal and high-value resource utilization way has attracted extensive attentions recently [1–4]. Pulverized coal fly ash (PCFA) produced from coal combustion above  $1200^\circ\text{C}$  mainly consists of mullite, quartz and amorphous phases [5,6]. Mullite as one of the major aluminum-containing minerals in PCFA has a stable crystal structure, resulting in the difficulty in aluminum extraction from PCFA [7–9]. The activation of PCFA by adding a certain amounts of additives during the thermal treatment could destroy the structure of mullite and improve the dissolution of aluminum in the leaching agents effectively [8,10–16]. Many literatures have shown that PCFA activated with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) at  $800\text{--}900^\circ\text{C}$  exhibited a high aluminum dissolution of  $> 90\%$  in acid, and the silicon in PCFA was transformed

into a highly active anhydrous silicon during the leaching process, which is beneficial to the synchronous utilization of aluminum and silicon in PCFA [8,17]. A clear understanding of the thermal decomposition and transformation mechanism of mullite with the action of  $\text{Na}_2\text{CO}_3$  is of great significance to clarify the activation mechanism of PCFA and the further process optimization.

To date, the investigations on the reactions between mullite and  $\text{Na}_2\text{CO}_3$  are more concentrated on the phase identification of calcined products and the speculation of reaction process [8,18–20]. Guo et al. investigated the role of  $\text{Na}_2\text{CO}_3$  in improved thermal activation of PCFA for alumina extraction. The results indicated that mullite, quartz and amorphous phases in PCFA transformed into nepheline, sodium silicate and some other sodium aluminum silicates with the addition of  $\text{Na}_2\text{CO}_3$  at  $> 850^\circ\text{C}$ , and the dissolution percentage of aluminum from PCFA could reach more than 90% accordingly [8]. Stjernberg et al.

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studied the degradation of mullite/corundum refractories by calcination with  $\text{Na}_2\text{CO}_3$ , and found that  $\text{Na}_2\text{CO}_3$  could react with mullite at 700–1350 °C to form a series of sodium aluminum silicates, such as feldspar and nepheline, which accelerated the degradation of mullite/corundum refractories [18]. Wang et al. found that mullite would completely transform into nepheline when the mass ratio of  $\text{Na}_2\text{CO}_3$  and PCFA was more than 1.2:1. Although all these cited works intended to reveal the transformation process of mullite with the action of  $\text{Na}_2\text{CO}_3$ , the understanding is still limited [19]. Li et al. tried to speculate the transformation process between mullite and  $\text{Na}_2\text{CO}_3$  based on the ab initio quantum chemical modeling and density functional theory. The results showed that mullite was easier to combine with  $\text{Na}^+$ , an electron acceptor, which can enter into the crystal lattice of mullite and then rupture the Al–O bonds in  $\text{AlO}_6$ , resulting in the transformation from mullite to the other phases with a lower binding energy such as nepheline, feldspar and corundum [20]. The study provides valuable information for further understanding about this reaction process, however, it have not been verified by any effective experimental results.

In this work, the thermal decomposition and transformation of mullite calcined with  $\text{Na}_2\text{CO}_3$  were analyzed in detail using thermal gravimetric and differential scanning calorimetric (TG-DSC) and X-ray diffraction (XRD). Meanwhile, the microstructure change during the transformation process was characterized by magic angle spinning nuclear magnetic resonance (MAS-NMR). On the basis of these results, the solid-state reaction mechanism of mullite with the action of  $\text{Na}_2\text{CO}_3$  was proposed combining the experimental data and the computational chemistry reports from literatures.

## 2. Experimental

### 2.1. Materials

Mullite sample was purchased from Dongyuan Coal Aluminum Technology Co., Ltd., China. Chemical compositions of the as-received sample were determined using X-ray fluorescence analyzer spectrometer (Rigaku Simultix 12 XRF spectrometer). Table 1 lists alumina and silica, whose sum accounts for more than 95 wt%, as the main chemical compositions of mullite sample. Besides, the as-received sample also contains trace amounts of  $\text{TiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , etc. Crystal components of the as-received sample were also measured using X-ray diffraction spectrometer (Bruker Advance D2 XRD spectrometer). XRD pattern in Fig. 1 shows that mullite in this sample is well-crystallized. In addition, sodium carbonate sample used in this study is an analytical-grade reagent purchased from Sinopharm Chemical Reagent Co., Ltd., China.

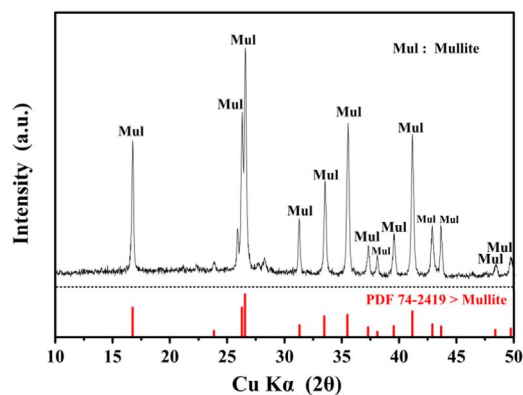
### 2.2. Sample preparation

The as-received sample was dried in an oven at 105 °C for 12 h and ground in an agate mill to pass through a 200-mesh sieve (< 75  $\mu\text{m}$ ). The pulverized sample was homogenized in an agate mortar with different amount  $\text{Na}_2\text{CO}_3$  (molar ratio of 1:1.5, 1:3.0, 1:4.5 and 1:6.0, respectively). The mixtures were immediately transferred into a platinum crucible and heated in a muffle furnace at the desired temperature for 120 min; then subsequently cooled to room temperature in a desiccator. The calcined samples were ground into fine powder again and labeled according to its calcination temperatures.

**Table 1**

Chemical compositions of the as-received mullite sample.

Components	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{TiO}_2$	$\text{CaO}$	$\text{Fe}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	Others
Contents (wt%)	67.50	27.70	1.43	1.20	0.77	0.43	0.11	0.86



**Fig. 1.** XRD pattern of the as-received mullite sample.

### 2.3. Sample characterizations

Thermo-gravimetric and differential scanning calorimetric (TG-DSC) analysis was measured in a simultaneous thermal analyzer (NETZSCH, STA409PC). About 12 mg of the mixed sample was exposed to a nitrogen atmosphere with gas flow rate of 100 mL/min. The programmed temperature was conducted from room temperature to 1100 °C with a linear heating rate of 10 °C/min.

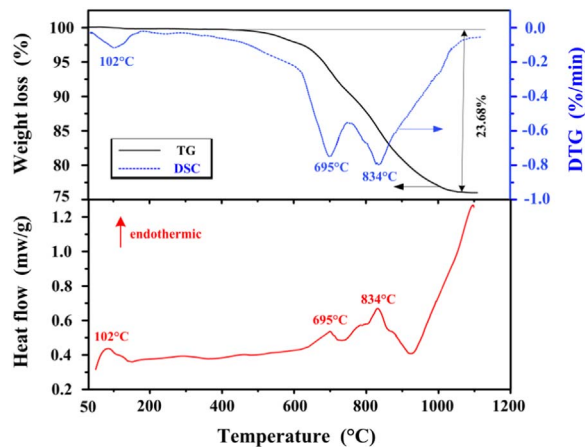
Phase compositions of the calcined products were identified using an X-ray diffraction spectrometer (XRD, BRUKER, PHASERD 2) equipped with a Cu K $\alpha$  radiation and an advanced linear detector. The acceleration voltage and electrical current were 30 kV and 10 mA, respectively. The scans were performed between 10° and 50° with a 0.01° step size and a counting time of 0.1 s step<sup>-1</sup>.

Magic angle spinning nuclear magnetic resonance (MAS-NMR) analysis of <sup>27</sup>Al and <sup>29</sup>Si were performed on a 600 MHz wide bore spectrometer (BRUKER, AVANCE III 14.2 T). The 4 mm probe with a spinning frequency of 13000 Hz and the 7 mm probe with a spinning frequency of 6000 Hz were used for <sup>27</sup>Al and <sup>29</sup>Si, respectively. The detailed operation procedures were described elsewhere [21]. Note that the standard chemical shift of <sup>27</sup>Al and <sup>29</sup>Si (chemical shift at 0 ppm) in this work were referenced using  $\text{Al}(\text{NO}_3)_3$  and  $(\text{CH}_3)_4\text{Si}$  solution, respectively.

## 3. Results

### 3.1. Thermal decomposition behavior

TG/DTG-DSC analysis was used to investigate the thermal decomposition behavior of the mixture of mullite and  $\text{Na}_2\text{CO}_3$ . As shown in



**Fig. 2.** TG/DTG-DSC curves of the mixture of mullite and  $\text{Na}_2\text{CO}_3$ . (Molar ratio = 1:6.0).

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