Phase transformation and non-isothermal kinetics studies on thermal decomposition of alunite

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ABSTRACT

Alunite was considered as a potential alternative resource for potassium and alumina production. The disintegration of alunite was a principal step to extract valuable components and therefore was highly relevant to great and efficient utilization. In this research, the phase transformation and kinetics of alunite during thermal decomposition were examined. The results showed that increasing the calcination temperature was beneficial to the decomposition of alunite. The soluble potassium salt K_2SO_4 was recovered by water leaching after calcination. The recovery ratio of K reached 83.9% after calcined at 900 °C for 2 h, and the purity of K_2SO_4 was 83.77%. A crystal structure disintegration mechanism of $KAl_3(SO_4)_2(OH)_6$ was proposed on the basis of the phase transformation sequences characterized by XRD and FTIR. Dehydroxylation was attributed to the breakage of the Al−OH and (Al)O−H bonds. [AlO4] tetrahedrons in alunite were transformed into [AlO6] octahedrons. The S-O linkages between [SO4] tetrahedron and [AlO6] octahedron were broken during desulphation. Then the staged kinetics of alunite decomposition was studied by thermo-gravimetric analysis using the Kissinger-Akahira-Sunose method. The apparent activation energies of dehydroxylation and desulphation were determined.

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1. Introduction

The potash fertilizer was essential and largely consumed for agricultural use [1,2]. At present, the soluble K salt ores were still the dominant raw materials to produce potash fertilizer [3]. Unfortunately, the shortage of potash fertilizer endangered the food production in the countries where the soluble K salt resource was scarce. Thus, other K-bearing minerals received considerable attention as an alternative to produce potash fertilizer [4]. Alunite [$KAl_3(SO_4)_2(OH)_6$] was an important form of insoluble potash ore, where the average content of potassium was >7% [5]. Because the reserve of alunite ore was considerable, it would provide a wider resource of potash fertilizer for agricultural use if this K-bearing mineral could be efficiently utilized.

Natural potassium alunite mainly consisted of K, Al, and S, which can be recovered in the form of K_2SO_4, Al_2O_3, $Al_2(SO_4)_3$ and $KAl(SO_4)_2$. Unfortunately, alunite was insoluble in water and acids unless it was calcined. The main methods to recover valuable compounds from alunite were thermal decomposition [6–11] and

hydrometallurgy leaching [12–15]. For thermal decomposition, dehydration, dehydroxylation, and desulfurization were the three steps in the calcination process of alunite, which occurred at 50–240 °C, 450–550 °C, and 600–830 °C, respectively [7–9]. Kücük [6,7] studied the dehydration/dehydroxylation of alunite and the corresponding kinetics by an isothermal method using thermo-gravimetric analysis. The dehydroxylation conversion of alunite was over 99%. The dehydroxylation of alunite was a first-order homogeneous reaction controlled by chemical reaction. Non-isothermal methods [8] were also used to obtain the activation energy in relation to the degree of conversion. The activation energy of dehydroxylation and desulfurization was 173–303 and 220–318 kJ/mol, respectively. In order to promote the decomposition of alunite, the calcination temperature was usually higher than 700 °C. Thus, the energy consumption was huge.

For hydrometallurgy methods, alunite was calcined and transformed into the soluble potassium and aluminum salts, which were subsequently separated and recovered by leaching and filtration [12–15]. Mohammadi [12] studied direct leaching of natural alunite by KOH solution and its kinetics. Both the leaching fractions of Al and K were >80% at >80 °C. The leaching reaction was controlled by surface chemical reaction with the activation energy of 94.18 kJ/mol. Ozacar [13,14] proposed an optimum process to recover K_2O

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and Al_2O_3 from aluntie. The aluntie ore was calcined at 700 °C for 2 h and then dissolved in NaOH solution at 110 °C for 1 h. Over 90% of Al_2O_3 was leached out by NaOH. In addition, H_2SO_4 and HCl acid were also used to dissolve and leach alunite [14,15]. Zhao [15] developed a H_2SO_4 acid calcination-water leaching method to simultaneously extract Al and K salts. The leaching efficiencies of Al and K were 87.2% and 85.3%, respectively. The products of K_2SO_4 and $Al_2(SO_4)_3$ were extracted and effectively separated by multi-step crystallization [15]. However, large amounts of alkali and acid in leaching alunite were consumed for the dissolution of sulfur (SO_4^{2-}), if dehydroxylation or desulfurization was incomplete.

Therefore, dehydroxylation and desulfurization by calcination are usually the principal steps for the beneficiation of alunite. The key problem of alunite decomposition is to promote the disintegration of the S-O-Al framework structure in $KAl_3(SO_4)_2(OH)_6$, which is highly relevant to the recovery efficiency and energy consumption. The kinetics of dehydroxylation and desulfurization is quite important to identify the factors affecting unit operation design and process control. Therefore, it is necessary to investigate the decomposition mechanisms of alunite and the kinetics characteristic.

The aim of this study was to investigate the thermal behavior of alunite. The disintegration mechanisms of alunite were clarified by characterization of the phase and structure transformation of sulphoaluminate. Then the staged reaction kinetics of alunite decomposition was studied using a non-isothermal method, and the activation energy was determined as a function of the conversion degree.

2. Experimental section

2.1. Materials

Natual alunite ore used in the experiments was provided by Zijin Mining Group in the Fujian province of China. The alunite samples were crushed and milled in a rod mill. Ore powders with an average particle size <74 μm were prepared by sieving. The mineral phase and composition of alunite are listed in Fig. 1 and Table 1, respectively. The impurities were mainly quartz (SiO_2) and dickite ($Al_2Si_2O_5(OH)_4$). The mass fraction of element K was 7.49 wt%. All samples were dried at 110 °C for 24 h.
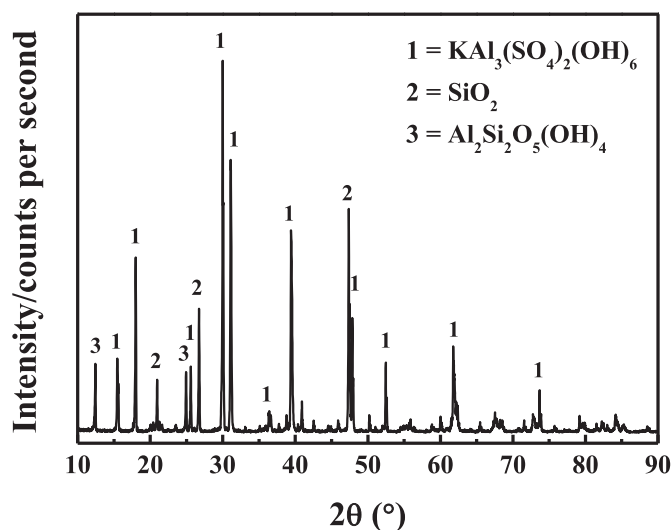

Fig. 1. The mineral phase analysis of the alunite ore used in this study.

2.2. Methods

(1) Thermal decomposition experiment

The thermal decomposition experiment was conducted in a tube furnace at temperatures ranging from 400 to 1000 °C in N_2 atmosphere (>99.9%). Once the temperature reached the desired value, the alunite samples were placed in the furnace. After calcined for 2 h, the samples were taken out to quench at room temperature. Then X-ray diffraction (XRD, X'Pert PRO MPD, The Netherlands) was used to identify the phase composition and lattice structure. Fourier transform infrared spectrometer (FTIR, NICOIET-470, USA) was employed to analyze the phase structure and chemical bonding of sulphoaluminate in the reaction products during the thermal decomposition process. Similar analytical procedures were previously reported [16–29].

(2) Water leaching and crystallization

In order to evaluate the contents of the soluble K, the calcined samples were leached by deionized water at 30 °C for 1 h in a Jacketed PMMA reactor. The solid-liquid ratio and the stirring speed were 1:10 (g/ml) and 300 rpm, respectively. Then the leaching solution containing the soluble K salt was separated by filtration. The concentration of K in the filtrate was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Perkine-Elmer OPTIMA 3000, USA). Finally, the recovery ratio of K (η) was calculated using the equation as followed:

$$\eta = \frac{C_K V_F}{m_a \omega} \times 100\%$$

where C_K is the concentration of K in the filtrate (g/L), V_F is the volume of the filtrate (L), m_a is the mass of alunite (g), ω is the mass fraction of K in alunite (wt%).

After filtration, the leaching residual was separated and dried at 110 °C for 24 h. The filtrate was concentrated and crystallized by evaporation at 80 °C, and the crystallized product was collected. The chemical and phase compositions of the crystallized product and the leaching residual were analyzed by ICP-AES, XRD and X-ray fluorescence (XRF, AXIOS-MAX, The Netherlands).

(3) Thermal decomposition kinetics

The thermal decomposition kinetics of alunite was investigated by thermo-gravimetric analysis based on a non-isothermal method. Simultaneous thermo-gravimetric (TG) and differential thermal analysis (DTA) were performed using a thermo-gravimetric analyzer (STA-409C NETZSCH, Germany), where the mass loss of the sample was measured. For a typical test, about 20 mg of the alunite sample (<74 μm) was heated in a corundum crucible from ambient temperature to 1000 °C at the heating rates of 5, 10, 15, and 20 °C/min under N_2 (>99.99%) gas at a flow rate of 100 ml/min. Standard α-Al_2O_3 was used as the reference material. Typical experimental data of TG and DTA during the thermal decomposition of alunite are illustrated in Fig. 2.

3. Results and discussion

3.1. Recovery of the soluble potassium from alunite

3.1.1. Effect of the calcination temperature on the recovery ratio

The effect of the calcination temperature on the recovery ratio of K was investigated at temperatures ranging from 400 to 1000 °C. All samples were calcined for 2 h. When the temperature was <500 °C,