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Research paper

Thermal transformation of pyrophyllite and alkali dissolution behavior of silicon

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ABSTRACT

Thermochemical behavior of pyrophyllite was characterized by using XRD, FTIR, TG-DTA and MAS NMR techniques. Pyrophyllite experiences a series of solid-state phase transformations during thermal treatment. Dehydroxylation of pyrophyllite is completed at 880 °C, and the original layered framework is inherited in dehydroxylated pyrophyllite. Up to 1100 °C, the layered framework is collapsed thoroughly, with formation of amorphous SiO_2 and mullite. Above 1200 °C, cristobalite crystallizes from amorphous SiO_2, and mullitization is promoted dramatically. The alkali leaching results show that amorphous SiO_2 in the thermally activated pyrophyllite is soluble in caustic soda liquor, while mullite is not, and the formation of sodium aluminosilicate hydrate of $0.95Na_2O{\cdot}Al_2O_3{\cdot}3.25SiO_2{\cdot}4.79H_2O$ during alkali leaching diminishes the dissolution ratio of silica. The alkali dissolution behavior of silicon demonstrates an innovative process for removing silica from pyrophyllite by using thermochemical activation (TCA) followed by alkali leaching, which can be applied to desilication of bauxite ore and preparation of alumina-base porous material. A desilication of 84% was obtained from the tested ore containing 90% pyrophyllite at the optimal thermochemical activation conditions of temperature 1100–1150 °C and time 90–20 min. The good alkali dissolution characteristic of silica also is a cogent evidence on the formation of amorphous silica during the thermal treatment of pyrophyllite.

1. Introduction

Pyrophyllite possesses a layered dioctahedral 2:1 structure. In the unit cell of pyrophyllite, a sheet of Al–O(OH) octahedra is sandwiched between two linked sheets of SiO_4 tetrahedra, with each octahedral aluminum bonded with the tetrahedral silicon via an apical oxygen and with an adjacent aluminum via two hydroxyl groups. According to the crystal structure of pyrophyllite, its theoretical formula can be expressed as $Al_2[Si_4O_{10}](OH)_2$ and the chemical composition is Al_2O_3 28.35%, SiO_2 66.65%, and H_2O 5.0% (Rayner and Brown, 1966; Wardle and Brindley, 1972).

Pyrophyllite is a relatively rare mineral. It has been widely applied in many industries, particularly in the manufacture of refractories, ceramics, fiber glasses, paints, rubbers, paper, porous materials and insulating materials. And most of these applications are due to its good technological properties following thermal treatment (Robertson, 1973; Virta, 2005).

As to the thermal transformation of pyrophyllite, a few researches have been carried out for its industrial applications (Fitzgerald et al., 1996; Mackenzie et al., 1985; Sánchez-Soto et al., 1993; Wang et al., 2002; Zhang and Wang, 1998).

Mackenzie et al. (1985) studied the thermal reactions of pyrophyllite by high-resolution solid-state ^{27}Al and ^{29}Si NMR Spectroscopy, thermal analysis and XRD analysis. It was observed that dehydroxylated pyrophyllite appears after heating to 783 °C, and survives further heating up to 1100 °C. Mullite gradually grows at the expense of the dehydroxylated pyrophyllite on heating above 1100 °C. At 1150 °C, a small amount of cristobalite appears.

Fitzgerald et al. (1996) reported the thermal transformation of pyrophyllite up to 1350 °C with XRD, ^{27}Al and ^{29}Si NMR and ^{1}H CRAMPS measurements. It was reported that pyrophyllite experiences a series of transformations: (1) Dehydroxylation of pyrophyllite occurs between 150 and 550 °C. (2) The thermally induced transformation of pyrophyllite anhydride results in separation of the silica–alumina layer at 950 °C. (3) A transition-alumina-type phase, containing 4- and 6-coordinate aluminum is formed between 950 and 1050 °C. In addition, a high content of amorphous silica glass and a small amount of a poorly ordered Si/Al-containing mullite phase form. (4) At 1250–1350 °C, the glassy silica is converted to cristobalite, accompanied by conversion of octahedral aluminums to tetrahedral aluminums.

An overall summary on thermal transformation stages of pyrophyllite was also presented by Zhang and Wang (1998): (1) unchanged state of pyrophyllite (room temperature—450 °C); (2) dehydroxylation of pyrophyllite into dehydroxylated pyrophyllite (500–900 °C); (3) decomposition of dehydroxylated pyrophyllite into amorphous SiO_2 and mullite (950–1100 °C); and (4) crystallization of cristobalite from

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amorphous SiO_2 (1150–1200 °C). The results were similar with those obtained by Sánchez-Soto et al. (1993), except that the starting and finishing temperatures of each stage are not accurately identical.

According to the above overview, the previous studies fail to draw a unanimous and consistent conclusion on thermal transformation of pyrophyllite. The phase and constituent of decomposition products of dehydroxylated pyrophyllite remain controversial.

In recent years, some new researches have been carried out to remove silicate gangues from bauxite ores (Li, 2002; Li et al., 2009) and prepare porous material by using pyrophyllite as the precursor (Yang and Du, 2008) via thermochemical activation (TCA) and subsequent leaching. The removal efficiency of gangues and properties of porous material are related with thermal treatment. Therefore, it is necessary and meaningful to make the thermal transformation of pyrophyllite clear.

The aim of the present study is to shed light on the structural changes and phase transformations of pyrophyllite, relying on multiple instrumental techniques. Based on that, the alkali dissolution characteristic of silicon in thermally treated pyrophyllite was characterized and desilication ratio of pyrophyllite ore by TCA process was studied further. The alkali dissolution characteristic of silica verifies the formation of amorphous silica in thermally treated pyrophyllite conversely.

2. Experimental

2.1. Mineral material

Pyrophyllite ore used in this study was obtained from Beijing, China. The pyrophyllite ore sample was firstly purified by hand picking and then crushed to 100 mass% passing 3 mm. The sample for instrumental measurement was further ground to 80–85 mass% passing 76 μm with a laboratorial porcelain mill.

The phase and chemical compositions of the sample are shown in Fig. 1 and Table 1, respectively. The main minerals in the sample are pyrophyllite and diaspore, whose contents are about 90% and 5–6% respectively. The minor minerals are kaolinite, feldspar and quartz.

2.2. Methods

2.2.1. Thermal treatment

The thermal treatment experiments were carried out in an electrically heated furnace. A Pt/Pt–Rh thermocouple was used for measuring temperature. Samples were loosely packed in an alumina vessel or alumina crucible and calcined isothermally at a uniform temperature for a given period. The calcined samples were cooled in the air, and then ground to 100 mass% passing 76 μm.

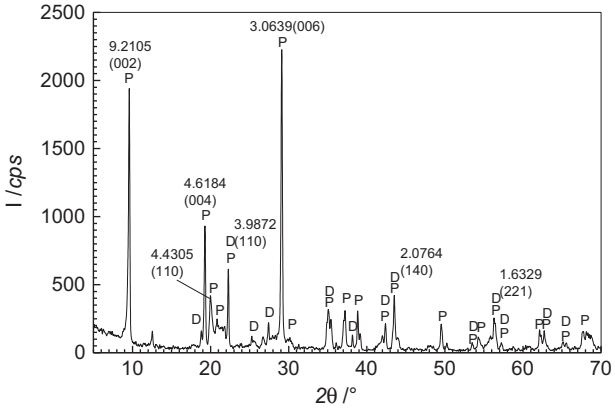

Fig. 1. XRD patterns of raw pyrophyllite ore. P—pyrophyllite and D—diaspore.

Table 1
Chemical composition of raw pyrophyllite ore/%.

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	LOI[a]
30.59	59.83	0.83	1.14	0.50	0.43	0.30	0.11	6.25

[a] LOI—loss on ignition.

2.2.2. Alkali leaching

Alkali leaching tests were conducted in a DY-8 autoclave. The autoclave was equipped with eight 150 mL stainless steel pots that can rotate end to end (the rotating velocity varies from 20 rpm to 120 rpm) in glycerin bath, which was electrically heated and the temperature was controlled by a thermostat.

At the beginning of each trail, caustic soda solution and calcined pyrophyllite at a given mass ratio of liquid to solid were added to the pots. The sealed pots were soaked in the bath and agitated. The temperature of glycerin was maintained at a constant level. Filtration was performed immediately after a period of leaching. The contents of SiO_2 and Al_2O_3 in solution and solid residue were measured respectively.

2.2.3. Instrumental techniques

2.2.3.1. X-ray diffraction (XRD) analysis. Mineralogical analysis was performed by a Japanese Rigaku D/max-rA diffractometer equipped with a graphite monochromator under the conditions of CuKα, 50 kV, 100 mA, and a scanning rate of 4° 2θ/min.

2.2.3.2. Fourier transform infrared spectroscopy (FTIR) analysis. Infrared absorption spectra of samples were obtained from the KBr pellets by a Fourier transform infrared spectrometer (Nicolet-470, USA).

2.2.3.3. Thermogravimetric and differential thermal analysis (TG-DTA). A NETZSCH STA 449C thermal analyzer was used. The pulverized sample was heated from ambient temperature to 1300 °C at a rate of 10 °C/min under a static atmospheric condition. The reference was alumina calcined at 1200 °C in advance.

2.2.3.4. Magic angle spinning nuclear magnetic resonance (MAS NMR) analysis. ^{29}Si MAS NMR spectra of pulverized samples were recorded at 79.49 MHz in an Avance (DSC) 400FT-NMR spectrometer (Bruker, Germany) at 9.4 T. Cross-polarization and proton decoupling were not used. The spinning frequency was 6 kHz. The ^{29}Si spectra were acquired using a 6 μs–π/2 pulse with 15 s recycle delay, and referred to tetramethylsilane (TMS). It should be noted that the ^{27}Al MAS NMR spectra of pyrophyllite cannot be identified due to the strong resonance signal of α-Al_2O_3 which forms during dehydration of diaspore in the raw pyrophyllite ore.

3. Results and discussion

3.1. Thermal transformation of pyrophyllite

Thermal transformation of pyrophyllite was characterized by comparing XRD patterns, FTIR transmission spectra and ^{29}Si MAS NMR spectra of raw pyrophyllite ore and samples calcined at different temperatures for 60 min.

3.1.1. XRD analysis

XRD analysis was carried out to characterize the phase transformation of pyrophyllite during thermal treatment. The XRD patterns of samples calcined at different temperatures are shown in Fig. 2.

The sharp, symmetrical and clear diffractions are still observed in Fig. 2a, which implies that the layered framework of pyrophyllite remains unchanged after being calcined at 500 °C.