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Improved extraction of alumina from coal gangue by surface mechanically grinding modification

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ABSTRACT

Coal gangue, a type of kaolinite clay in coal measures, is one of the largest categories of solid industrial wastes in China. Alumina extraction from coal gangue could offer an alternative to bauxite as a source of alumina. Mechanically modification by grinding is an effective activation method to improve alumina recovery from coal gangue. The effect of grinding on coal gangue, however, had not been investigated systematically. Present understanding regarding the effects of grinding on coal gangue is still restricted to that on kaolinite. Furthermore, the differences in the inherent mechanisms between grinding and thermal activation on coal gangue have not been investigated so far. This study aimed to clarify the differences among them. Changes in particle size, surface area, and morphology were followed by means of laser particle size analysis, nitrogen adsorption/desorption isotherms, and scanning electron microscopy (SEM). Possible modifications of the chemical structure, mineral phase and thermal behavior were monitored using X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Infrared analysis (IR), and Thermogravimetry (TG). The results showed that the alumina dissolution from coal gangue increased with longer grinding time. Grinding followed by calcination further improved the alumina extraction. After the calcined coal gangue was ground for 20 h, the alumina extraction reached ~95%. The results of XRD, XPS, and IR analysis implied that grinding produced defects in the coal gangue kaolinite; however the main kaolinite layer structure (Si—O—Al^{VI}) were unaffected in the absence of calcination. In this case, the improved activity might be due to reduced particle size, increased surface area, and aluminum enrichment at the surface. The primary structure of kaolinite in coal gangue was destroyed by calcination after grinding, and kaolinite was altered to amorphous metakaolinite with Si—O—Al^{IV} structure, which facilitated alumina extraction.

1. Introduction

With the increased global depletion of bauxite reserves and the concurrent growth in the demand for alumina resources, it is important to search for the alternatives to bauxite [1–3]. Coal gangue produced from coal mining and coal processing is one of the largest amounts of industrial solid wastes in China [4,5]. The current simple disposal method and the low utilization can cause severe environmental issues and constitute a significant waste of finite resources [6]. Coal gangue as a type of kaolinite-rich material contains 15–40% Al_2O_3 by weight; the extraction of alumina from such materials has, therefore, attracted considerable academic interest [7–9]. The common alumina extraction method is acid leaching by which alumina, aluminum chloride, and poly-aluminum chloride could be produced [7–9]. Activation of coal gangue is necessary as kaolinite, the major aluminum-containing component, is chemically inert. Thermal activation is a common method by which coal gangue has been activated that is simple to implement but relatively inefficient. The percentage recovery of alumina after thermal activation typically fails to reach 70% [8]. A method that achieves higher efficiency to activate coal gangue will be essential to the industrial application for the extraction of alumina from coal gangue.

Mechanical activation by grinding is an important physical activation method commonly used on the activation of the minerals with poor reactivity. Prior research has consistently shown that grinding enhanced the reactivity of solid particles [10–12]. Aglietti et al. [13] demonstrated that grinding not only dehydrated clays, but could also change their structure. Other researches have shown that grinding increased the specific surface area [14], decreased the mean particle size [15], changed the crystal structure [16], and increased the reactivity [17,18].

Kaolinite has been widely used in the production of paper, ceramic, polymer, and cement, as well as in the application of alumina extraction [19–21]. Previous studies have shown that mechanical activation by grinding of kaolinite decreased the particle size [22–25], increased surface area [13,26–28], and changed the pore size distribution [29]. Other studies reported that grinding resulted in kaolinite amorphization [23, 30] and changes in its physical and chemical properties such as cation

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exchange capacity [31], base exchange capacity [22,32], water-adsorption capability [33] and acid solubility [31].

Recent studies also discussed the effects of grinding on kaolinite. Consensus exists that improved reactivity of kaolinite upon grinding is caused by removal of hydroxyls [13,30,34–36]. Improved alumina extraction from kaolinite after grinding has been demonstrated [19,21]. Such works focused on more interest in the performance of alumina extraction. The understanding is still restricted to the dehydroxylation and amorphization of kaolinite.

Coal gangue is a type of kaolinitic clay in coal measures. In addition to kaolinite, it contains carbonaceous organic matter and minerals such as quartz, illite, pyrite, and calcite [37]. Improved alumina extraction from coal gangue by grinding has been reported. Wang et al. [38] reported that alumina extraction increased from 7% to 88% after 10 h ball milling. Liu et al. [39] achieved a 98% alumina extraction after 400 °C calcination and 30 min grinding. Their primary results indicated that the improved alumina extraction was due to the removal of hydroxyl groups from kaolinite by grinding [21,38,39], which is consistent with the results for kaolinite [19,21]. Few previous studies have systematically addressed the effects of grinding on coal gangue. The responses of kaolinite and coal gangue to grinding, however, may be not the same due to the differences in their chemical compositions. In addition, the results from grinding are similar to those from thermal activation, which showed that improved alumina extraction after thermal activation was due to the removal of hydroxyl from kaolinite in coal gangue [40,41]. The differences in activation mechanisms between thermal and mechanical processes for coal gangue remain unclear.

This study investigates on the influence of mechanical activation by grinding on the variations of the physical properties and chemical structure of coal gangue, such as the particle size, bulk density, specific surface area, and Al—O or Si—O chemical bonding.

2. Experimental

2.1. Materials

The sample of coal gangue used in this study was obtained from Changcun Coal Mine, Lu'an Coal Mining Industry, Shanxi, PR China. The chemical composition of raw material and LOI (Loss on ignition) (Table 1) are 41.1% SiO_2, 22.9% Al_2O_3, 2.4% Fe_2O_3, 2.0% K_2O, and 33.2% LOI respectively. The content of Carbon is 17.9% according to ultimate analysis. The mineral compositions analyzed by X-ray diffraction spectrometer (XRD) showed that the raw material contains quartz, kaolinite, illite, calcite, etc. (Fig. 1). The crystallinity index (HI) for kaolinite calculated by the Hinckley (1963) method is 0.19 (Fig. 2) [42]. Samples were labelled based on the treatment conditions. The "As-received" sample was obtained by crushing the raw material using jaw crusher, ground using a planetary mill, and sieved to 60–100 mesh (0.25–0.15 mm). The activated samples were obtained by calcination and/or grinding of the as-received coal gangue; "(n)h-Uncal" denoted coal gangue ground for "n" hours, and "(n)h-Cal" were coal gangue ground for "n" hours and then calcined at determined temperature.

2.2. Methods and processes

2.2.1. Mechanical and thermal activation

Coal gangue samples were initially crushed using Jaw crusher (PE60X100), then ground using a planetary mill (QM-3SP2) and sieved to 60–100 mesh (0.25–0.15 mm) to obtain As-received samples. As-received samples then ground using a planetary mill (QM-3SP2) continually for 2 to 20 h at a 35 Hz rotational speed to obtain mechanical activation samples. Each milling was carried out with a 200 g air-dried sample in a sealed 600 cm^3 capacity stainless steel pot using 469 g (ball gradation was 65:288 and weight were 3.45 g and 0.85 g respectively) stainless steel balls. The applied rotation speed was 220 rpm. Thermal activation (after grinding, and only when annotated) was performed in a muffle furnace (SX2-12-10, Ningbo Hinotek Technology Co. Ltd., Zhejiang, PR China) at 750 °C for 2 h.

Table 1
Chemical composition and loss on ignition of coal gangue.

Chemical composition (wt%)							
SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	TiO_2	MgO	Loss on ignition (wt%)
41.1	22.9	2.4	2.0	0.73	0.86	0.34	33.2

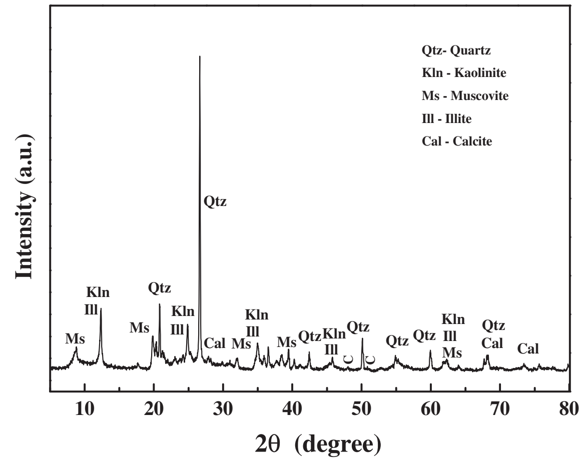

Fig. 1. XRD analysis of coal gangue raw material.

2.2.2. Leaching alumina from coal gangue

Alumina dissolution was used to evaluate the activation efficiency of coal gangue samples. It was performed by mixing As-received or activated coal gangue samples by thermal or grinding activation in a 4-neck flask with 20% by weight (6.02 mol/L) hydrochloric acid solution at a solid to liquid mass ratio of 1:3, heating the resulting mixture to boiling point with a reflux for 2 h. Afterwards, the mixture was cooled to room temperature and was separated into the solution and the solid residues by filtration. The major components in the solution are $AlCl_3$ and $FeCl_3$. Furthermore, it contains some small amount of other soluble salts such as $CaCl_2$, $MgCl_2$, and KCl. The matters, for example SiO_2, TiO_2 etc., being insoluble are remained in the solid residues. The

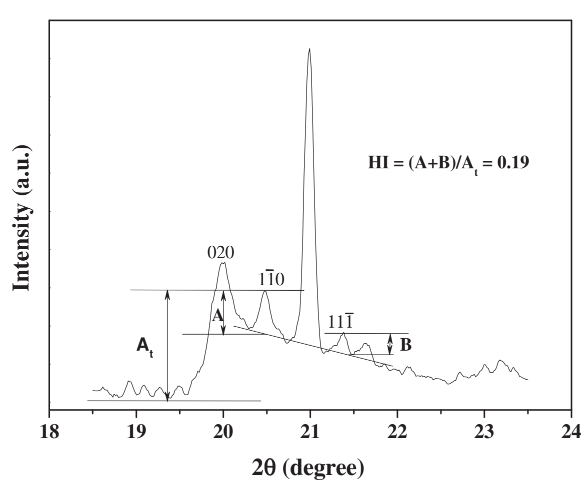

Fig. 2. Diagram of the crystallinity index (HI) for kaolinite calculation.