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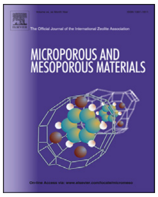

Preparation and characterization of a novel porous silicate material from coal gangue

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A B S T R A C T

A novel porous silicate material (PSM) derived from coal gangue was successfully prepared and characterized by N_2 adsorption–desorption isotherms, thermogravimetric analysis, Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, and X-ray diffraction measurements. The preparation procedure involved two steps: (1) SiO_3^{2-} leaching from coal gangue by both activation and chemical approaches, and (2) preparation of the PSM by reaction of the leachate with $Ca(OH)_2$. It was found that the maximum SiO_3^{2-} leaching yield was achieved at calcination temperature of 1000 °C, reaction temperature of 106 °C for 2 h, NaOH concentration of 25%, and the ratio of coal gangue to alkali of 0.5:1. The PSM was then easily prepared from the SiO_3^{2-} leaching at 98 °C for 2 h with a Ca/Si ratio of 1.2:1 and the pH value of 12.70. The spectroscopic results showed that the PSM was mainly composed C, Ca, O, Si and Na, in the form of Ca^{2+}, Na^+, SiO_3^{2-}, and CO_3^{2-} ions. Some adsorbed water and/or surface water was observed. The adsorption behavior revealed that the CO_2 adsorbed amount on PSM was 36.69 mg g^{-1} at 293.15 k and ambient pressure with a pure CO_2 flow rate of 120 mL min^{-1} during 90 min.

1. Introduction

Coal gangue is the hazardous solid waste of coal produced in excavation and washing processes. Currently, it has been one of the largest industrial residues in terms of land-occupying area, annual emissions, and cumulative burden in China. In statistics [1], the accumulated amount of coal gangue in China has already reached 3.8 billion tons in an increasing rate of 0.2 billion tons per year. Such a large quantity of this solid waste would occupy enormous tracts of farmland, destroy ecological environment, pollute water, soil, and atmosphere, and even cause geological disasters [2–4]. Therefore, the resource recovery of coal gangue has become an important research topic in the world. In China, many studies are carried out to investigate the use of coal gangue; however, the utilization rate of coal gangue is always lower than 15% [5]. Furthermore, although some progresses in the resource recovery of coal gangue have been made, the overall depth is still underdeveloped. So it is of great importance to study efficient approaches for the resource recovery of coal gangue.

At present, there are some reports to discuss how to utilize coal gangue, for example, in China coal gangue is mainly used to generate power and pile on land [6,7]. However, serious environmental impacts, especially the atmospheric and water pollution, could be caused [8,9]. Even so, only a small portion of coal gangue is consumed. The useful ingredients of coal gangue are also not reasonably utilized, for example, most of coal gangue is used for traditional construction materials, including pottery, cement and brick [10–12]. In recent years, the coal gangue with high content of carbon, SiO_2, and Al_2O_3 has been increasingly used to fabricate chemical materials, such as zeolite-activated carbon composite adsorbents [13,14], zeolites [15], and activated carbons [16]. However, nowadays these technologies are still in the process of development. Moreover, the scale and level as a whole are very low because of low value-added products, secondary pollution, and difficult large-scale industrial production. Some reports show another application of coal gangue to prepare ceramic separation membranes, for example, Lu et al. [17] prepared a porous mullite ceramic membrane from coal gangue. These membranes exhibit disadvantages of high production cost and application limitation in traditional industry, such as food and beverage.

In this work, a new and facile route of coal gangue application was provided to prepare the novel porous silicate material (PSM) as

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adsorbents for the high adsorption capability towards CO_2, which had made a sizeable contribution to global warming as one of the primary greenhouse gas. The PSM was characterized by techniques of thermogravimetric analysis (DG-DTG), fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction measurements (XRD), and N_2 adsorption–desorption isotherm. This work was not only to provide a new and facile insight for solving environment problems caused by coal gangue, but also to present a technology for the high adsorption capability towards CO_2. Furthermore, it also might lead to a breakthrough in the field of coal gangue resource recovery that has been used to sluggish process for decades.

2. Experimental section

2.1. Materials

The sample (coal gangue) was mainly composed by SiO_2 and Al_2O_3, as shown in Table S1, which was friendly supplied by Wujialiang coal preparation plant from Inner Mongolia province, China. NaOH, $Ca(OH)_2$, and other chemicals were analytical grade and used without further purification.

2.2. The preparation of SiO_3^{2-} leachate from coal gangue

Coal gangue could be used as a SiO_3^{2-} source [18] to synthesis PSM in this work. Firstly, the raw coal gangue was milled and sieved. The obtained 200-mesh particles were calcined at 600–1100 °C for 2 h to generate thermal activated coal gangue (TAE). Secondly, the TAE was added into a 15–35% NaOH solution with a coal gangue/alkali ratio of 0.2–0.8 at 80–106 °C and stirred for 30–210 min. The suspension liquid was then filtered and washed to obtain leachate.

In this process, based on quantitative analysis of SiO_3^{2-} with silico-fluoride natrium volumetry method, the optimum SiO_3^{2-} leaching condition, including calcination temperature T_1, reaction temperature T_2, reaction time t, concentration of NaOH (mass fraction) w, and coal gangue to alkali mass ratio (C/A) R, was investigated. The method principle was shown in Formula (1)–(4).

$$SiO_3^{2-} + 6F^- + 6H^+ \rightarrow SiF_6^{2-} + 3H_2O \tag{1}$$

$$SiF_6^{2-} + 2Na^+ \rightarrow Na_2SiF_6\downarrow \tag{2}$$

$$Na_2SiF_6 + 3H_2O \rightarrow 2Na^+ + 2F^- + H_2SiO_3 + 4HF \tag{3}$$

$$HF + OH^- \rightarrow F^- + H_2O \tag{4}$$

The SiO_3^{2-} leaching yield was calculated as in Formula (5).

$$y(SiO_3^{2-}) = C(SiO_3^{2-}) \times V \times M/m_1 \tag{5}$$

where $y(SiO_3^{2-})$ is the SiO_3^{2-} leaching yield, wt %; M is molar mass of SiO_2, g/mol; $C(SiO_3^{2-})$ is the molar concentration of SiO_3^{2-} in the leachate, mol/L; V is the volume of leachate, L; and m_1 is the mass of SiO_2 in the raw coal gangue, g.

2.3. The preparation of the PSM

As-prepared SiO_3^{2-} leachate was reacted with $Ca(OH)_2$ suspension liquid in the range of room temperature to 98 °C for 1–5 h under stirring. Then the obtained liquid mixture was transferred into a beaker and then the pH value was adjusted by washing using deionized water. Finally, the liquid mixture was filtrated and dried to get the ultimate PSM. In this process, the influence of the preparation condition, such as $Ca(OH)_2$ to SiO_3^{2-} mole ratio (Ca/Si), pH, the preparation temperature, and time, on the properties of the final products was also systematically studied. The schematic preparation procedure was presented in Fig. 1.

2.4. Characterization

The chemical composition of the coal gangue was determined by X-ray fluorescence (XRF) analyzer spectrometer (Rigaku ZSX Primus II). The phase structure of coal gangue before and after calcination and crystallinity of the sample were checked by XRD analysis (Shimadzu, D/max-2200/PC) with Cu K_α radiation operated at 40 kV and 40 mA. The phase transition characteristics and functional groups of the samples were determined through FTIR technology, using the KBr pellet technique (Nicolet, Nexus 670), in the frequency region of 4000 to 400 cm^{-1}. The microstructure and morphology of sample was analyzed by SEM analysis (HITACHI, S-3400N) with an energy dispersive X-ray spectrometer (EDS). TEM analysis was carried out by using a JEOL JEM-2100F field emission electron microscope with an acceleration voltage of 200 kV. The BET specific surface areas of the samples were calculated by N_2 adsorption isotherms obtained from a Quadrasorb SI-MP analyzer at 77 K. All the samples were degassed under vacuum at 300 °C for 4 h before testing. The pore size distributions in the adsorption branches of the isotherms were obtained by using the Barret-Joyner-Halenda (BJH) method. The pore size and total volume were calculated based on pore size distribution curves. The thermal stability of the sample was determined by thermogravimetry and differential thermogravimetry (TG-DTG) analysis by using an America Thermal Analysis Q50TGA at a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) data were obtained with a KRATOS Axis ultra X-ray photoelectron spectrometer with a monochromatized AlKα X-ray ($h\nu = 100$ MeV) operated at 225 W.

2.5. Adsorption test

The CO_2 adsorption experiment was carried out in a flow system at 293.15 k and ambient pressure, as shown in Fig S1, based on the following procedure. A fixed column loaded with the PSM was placed in a thermostatic water bath to maintain the temperature constant. The pure CO_2 (99.999 vol %) with flow rate of 120 mL min^{-1} was introduced into the sample and adsorbed for 90 min. The adsorbed amounts of CO_2 were calculated by the weight difference of the sample before and after CO_2 adsorption. All measurements of mass were performed on an electronic balance with an accuracy of 0.1 mg (Sartorius BS224S), and the uncertainty of mole fraction was estimated about ±0.0001.

3. Results and discussion

3.1. Effect of thermal activation

3.1.1. XRD analysis

The calcination temperature of samples was set at 600–1100 °C based on the previous report [19], in which the calcination temperature of 600–700 °C was found to significantly improve the cementitious activity of coal gangue. Fig. 2 (a) shows the XRD patterns of original and calcined coal gangue.

As illustrated in Fig. 2 (a), the major mineralogical composition of uncalcined coal gangue is quartz (PDF card NO. 65-0466), kaolinite (PDF card NO. 14-0164), gismondine (PDF card NO. 20-0452), clinochlore (PDF card NO. 29–0701), albite (PDF card NO. 41-1480), and illite (PDF card NO. 43-0685). At the calcination