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Insight into morphology and structure of different particle sized kaolinites with same origin

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ABSTRACT

The particle size, morphology, crystallinity order and structural defects of four kaolinite samples are characterized by the techniques including particle size analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) and magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR). The particle size of four kaolinite samples gradually increases. Four samples all belong to the ordered kaolinite and show a decrease in structural order with the increase of kaolinite particle size. The changes of structural defect are proved by the increase of the band splitting in Raman spectroscopy, the decrease of the intensity of absorption bands in infrared spectroscopy, and the decrease of equivalent silicon atom and the increase of non-equivalent aluminum atom in MAS NMR spectroscopy. The differences in morphology and structural defect are attributed to the broken bonds of Al–O–Si, Al–O–Al and Si–O–Si and the Al substitution for Si in tetrahedral sheets.

1. Introduction

Kaolinite is a 1:1 type layer structure mineral with the basic unit consisting of a tetrahedral sheet of SiO_4 units and an octahedral sheet of AlO_2 $(OH)_4$ [1,2]. The ideal chemical composition of kaolinite is Al_2O_3 39.53%, SiO_2 46.51% and H_2O 13.96%. The octahedral sheets have hydroxyl groups, whereas the tetrahedral sheets have oxide surfaces, providing an asymmetric environment. The layers are less tightly linked together through hydrogen-bonding between hydroxyl sites in the gibbsite basal plane and the oxygen of the silicon tetrahedral sheet in the '*c*-axis' direction and hence can be separated easily [3].

Kaolinite has a wide variety of applications in industry, and can be used as a major component of ceramics, paper filler, coating pigment, an extender in water-based paints and ink, and rubber filler [4,5] and other polymeric materials [6,7]. It is also commonly used as a component of catalysts for the catalytic cracking process of oil, adsorbent for water purification treatments, and a support for drug adsorption and controlled release [8,9]. The use of kaolinite/silica particles as reinforcing materials for styrene butadiene rubber (SBR) has been studied [10,11]. In addition, kaolinite may be used as a matrix for photocatalyst and can enhance a material's photocatalytic activity [12,13]. The relationship between the crystallinity, thermal stability and surface properties of four soft kaolinites from China have been studied [14]. However, little attention has been paid to the physicochemical characteristics of the same source kaolinites with different aspect ratios and the role of the variation in these characteristics of the mineral is rarely discussed in the preparation of materials. Some characteristics of kaolinite, including the morphology, crystal order, structural defect and surface properties directly determine the kaolinite technical applications. Therefore, a detailed study on the mineralogical characteristics of kaolinite should be required, and would be most useful in the field of mineral-based functional composites [15,16].

In this work, the focus is the analysis of the relationship between the kaolinite particle size, morphology, crystallinity degree and structural defect of four classification kaolinites from the same source.

2. Materials and methods

Raw kaolinite samples, with hydrothermal alteration origin, originate from Zhangjiakou in China. Four kaolinite samples are obtained by free settling method. The raw kaolinite was blended

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with water at a weight ratio of 1:4, and added 0.5% sodium hexametaphosphate as dispersant. The pH of suspension was adjusted to 10.0 using a suitable sodium hydroxide solution. The suspension was stirred for 2 h. Then the upper suspension was extracted to another container with siphon method after settling for 10 min. The sand and mud at the bottom were separated from the kaolinite suspension. The new suspension was resettled according to a specified time. After settling for 480 min, the 2 cm height suspension extracted in the upper was labeled as FS-1. The rest of the suspension was stirred 1 h again and resettled 184 min. The 1 cm height part of the stable suspension in the upper was obtained through siphoning, and labeled as FS-2. According to the same processing method of FS-2, FS-3 was also obtained after resettled 114 min. The residual suspension was labeled as FS-4.

The particle size distribution of the four kaolinite samples was measured by using a Mastersizer 2000 laser particle size analyzer of Malvern company (wet, cycle injection mode, and test time: 1–2 min). For electron microscope examination, the kaolinite powders were adhered to Cu stubs using conductive adhesive, and scanning electron microscopy (SEM) micrographs were obtained with a S4800 LV electron microscope under 5.0 kV. Variation in kaolinite crystallinity was assessed by the powder X-ray diffractometer traces of unoriented powders, acquired with a RigaKu D/max-2000 18 kW X-ray diffractometer with Cu Kα radiation, 40 kV, 150 mA, and a scanning rate of 2°/min over the range 2.5–75° (2θ). The Raman spectra were recorded at a resolution of 4 cm^{-1} using an inVia Laser confocal Raman spectroscopy system, at the conditions of 514.5 nm laser wavelength, 65 μm slit-width, 10 s time constant and 3 scanning times. The FTIR spectra of the kaolinite samples were recorded on a Bruker Tensor27-spectrometer in the region 4000–400 cm^{-1} using potassium bromide/kaolinite pellet technique at the ratio of 200–1. ^{29}Si and ^{27}Al MAS NMR spectra of four kaolinite samples were measured with a Bruker AVANCE III 400 NMR spectrometer 79.3 and 104.0 kHz, respectively, using TMS as external reference with a 2 μs pulse width and a 30 s recycle delay and using solution of $AlCl_3$ as external standard reference with a 0.6 μs pulse width and a 0.2 s recycle delay, respectively. Rotors were spun in air at 5–12 kHz. The decompositions of ^{27}Al and ^{29}Si MAS NMR spectra were performed by PeakfitV4.0 simulation program using the Gaussian/Lorentzian functions. The parameters were fitted to the original data using the standard error ($SE < 10^{-2}$) and the correlation coefficient ($R^2 > 0.999$) as metrics for goodness of fit. The influence of the baseline was reduced by performing baseline correction before curve fitting. ^{29}Si MAS NMR spectra were fitted using three fixed peaks at −93.6 ppm, −90.6 ppm and −87.9 ppm. ^{27}Al MAS NMR spectra were fitted using two peaks at around1.0 ppm and 7.0 ppm.

3. Results and discussion

3.1. Particle size of kaolinite

The particle size distributions of the classification kaolinite samples measured by laser analyzer are shown in Fig. 1. The particle size indices of kaolinite, including the average particle size (D_{50}) and particle size cumulative volume frequency (D_{10}, D_{90}), are reported in Table 1. In Fig. 1 three peaks of the particles size distribution can be observed in the curves of FS-1, FS-3 and FS-4, whereas only two peaks is found in that of FS-2. Meanwhile, most particles are in the range of 0.5–4.0 μm for four kaolinite samples. Fig. 1 indicates that FS-3 and FS-4 contain more particles beyond 4 μm than FS-1 and FS-2. In the samples of FS-1 and FS-2, the particles larger than 5 μm are close to zero. Therefore, D_{50} and D_{90} of FS-1 and FS-2 are smaller than that of FS-3 and FS-4 (Table 1). The

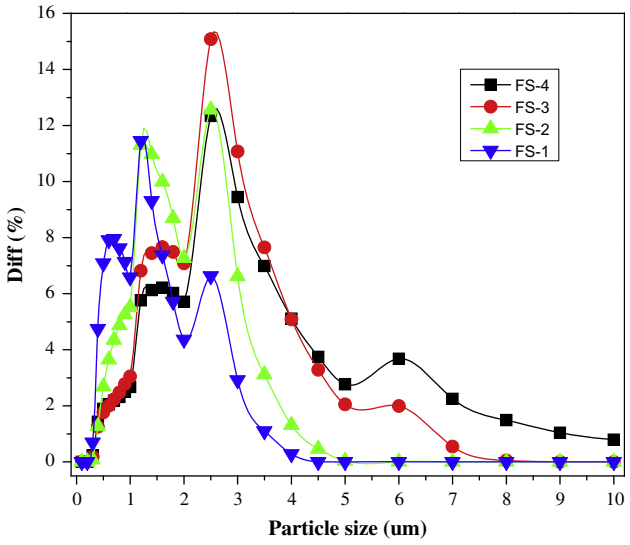

Fig. 1. Particle size distributions for four kaolinite samples.

Table 1
Particle size characteristic (D_{10}, D_{50}, D_{90}) and specific surface area (S_{BET}).

Samples	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	S_{BET} (m^2/g)
FS-1	0.466	1.004	2.115	7.01
FS-2	0.655	1.401	2.590	5.13
FS-3	0.804	1.935	3.871	3.99
FS-4	0.796	2.184	6.305	3.69

most particles of FS-1 are distributed in the range of 0.5–2 μm, and that of FS-2 are in the range of 1.5–3 μm; the particle size of FS-3 and FS-4 focus in the range of 2–4 μm; in addition, FS-4 has much more particles large than 5 μm than FS-3. The particle size gradually increases from FS-1 to FS-4.

3.2. Morphology and specific surface area

Kaolinite is a layered clay mineral in which each layer in the structure consists of two sub-layers, as shown in Fig. 2. The AlO_6 sub-layer consists of octahedrally coordinated Al and structural water in the form of hydroxyl groups. The other sub-layer consists of SiO_4 tetrahedrally coordinated Si. Two sub-layers are held together by Al–O–Si bonds formed in sharing the oxygen atom surface. The atoms, such as Al and Al, Al and Si, Si and Si, are linked by the way of sharing the O atoms and form the structures of

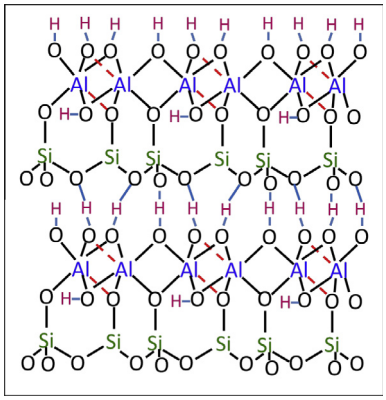

Fig. 2. Kaolinite structure diagram.