Research Paper

Changes in the structure and porosity of hollow spherical allophane under alkaline conditions

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ABSTRACT

This work investigated changes in the chemical composition, structure and porosity of hollow spherical allophane under alkaline conditions, which are significant not only for understanding its fate in natural environment but also for its functional applications. Hollow spherical allophane with a silicon/aluminium (Si/Al) molar ratio of 0.77 was hydrothermally synthesised followed by treatment with dilute sodium hydroxide (NaOH) solutions with different concentrations (indicated by pH values). The allophane and its alkali-treated products were then characterized using a combination of techniques, such as Fourier-transform infrared spectroscopy, nuclear magnetic resonance and nitrogen physisorption analysis. Allophane showed a weak structural stability in alkaline conditions. At pH ≤ 11.0, the framework of allophane particles was almost intact; its polymerised silicates showed only slight dissolution. At a higher pH (> 11.0), desilication and dealumination enhanced, resulting in the destruction of the imogolite local structure (ImoLS) along the edges of defect pores and the formation of amorphous materials. Most of the defect pores increased in size, becoming accessible to nitrogen and the textural parameters of the micropores reached their maximum values at a pH of 12.5. However, the damage to some secondary pores and the collapse of some hollow spherules reduced total pore volume (V_{total}). At a pH of 13.0, most of the hollow spherules were observed to have collapsed, resulting in remarkable decrease in the textural parameters. However, some unbroken and/or mildly broken allophane particles might remain, deduced from the relatively high BET specific surface area (SSA) and V_{total} and the considerable proportion of micropores for $Allo_{13.0}$. These results reveal the dissolution behaviour of allophane in alkaline conditions and the mechanism underlying this behaviour, providing essential insights into the mineral's potential applications.

1. Introduction

Allophane is a short-range ordered hydrous aluminosilicate mineral commonly found in weathering environments associated with volcanic activities (Wada, 1989; Rampe et al., 2012). Its typical parent materials are volcanic ash, pumice and pyroclastic materials of different compositions (Harsh et al., 2002). Its chemical composition, $1-2SiO_2 \cdot Al_2O_3 \cdot 5-6H_2O$, is variable, which suggests two typical end-members with Si/Al molar ratios of 0.5 and 1, corresponding to Al-rich and Si-rich allophane, respectively (Parfitt, 1990; Levard et al., 2012; Huang et al., 2016). The structure of allophane is complicated because of its variable Si/Al molar ratios. The most common type is Al-rich allophane, which is comprised of an outer curved gibbsite-like sheet with isolated orthosilicate groups linked to the inside (Brigatti et al.,

2006; Thill et al., 2017). Allophane with a higher Si/Al molar ratio exhibits a similar framework with Al-rich allophane, and the extra Si attaches to the isolated SiO tetrahedra forming the polymerised silicates (MacKenzie et al., 1991; Abidin et al., 2005). The amount of polymerised silicates increased with the Si/Al ratio, and Al^{3+} often substitutes Si^{4+} in polymerised silicates (Levard et al., 2012). An individual particle of allophane is usually described as a hollow spherule with an external diameter of 3.5–5 nm, a wall thickness of 0.7–1.0 nm and several defect pores (perforations) of approximately 0.3 nm in diameter on the surface (Abidin et al., 2004; Iyoda et al., 2012). Commonly, allophane appears as nano- or micro-aggregates (clusters) differing in size and shape. These unique characteristics endow allophane with abundant porosity and high specific surface area (Brigatti et al., 2006). Therefore, numerous applications have been envisaged for

allophane in fields such as composite materials (Nishikiori et al., 2012), catalysis (Zhou and Zeng, 2017), adsorption (Kaufhold et al., 2010; Huang et al., 2016) and biological medicine (Toyota et al., 2017).

Pretreatment of allophane, for example, by acid or thermal activation, have been investigated to modify the structure and properties of allophane (Jong, 1989; Ono and Katsumata, 2014; Du et al., 2018). In addition, alkali treatment is another method that is commonly used to modify clay minerals. In the last few decades, alkali treatment has been used to remove reactive silica-alumina gels from natural soils to obtain pure allophane (Farmer et al., 1977; Hiradate, 2005). Recently, researchers focused on the theoretical reaction pathways and the kinetics of allophane dissolution in dilute NaOH solutions, and proposed a dissolution mechanism with the aid of the molecular orbital calculation (Abidin et al., 2004, 2005). Later, they pointed out that defect pores on the allophane wall were enlarged from 0.35 nm to 0.45 nm by treatment with 10 mmol/L NaOH solution, which was determined using the cation exchange method (Abidin et al., 2007). Despite of these advances, however, changes in the hollow spherical structure and the porosity of allophane in alkaline conditions have received little attention, and the characteristics of allophane products during alkali treatment at different pHs – the key to understanding the dissolution of allophane in alkaline conditions, have also been neglected. In addition, the lack of research data regarding the structural stability of allophane might have frustrated the studies on its functional modification as well as its potential applications. In fact, studies on the modifications and applications of allophane are far fewer than that of other clay minerals, such as halloysite (Yuan et al., 2016) and montmorillonite (Bergaya and Lagaly, 2013). Therefore, more research attentions should be paid on the chemical and structural stability of allophane under alkaline conditions, which is significant not only for acquiring a good knowledge of how the structure of allophane changes with environments, but also for the development of functional materials based on allophane.

In this work, the effects of alkali treatment on the structure and porosity of hollow spherical allophane were systematically investigated. To monitor changes in the chemical composition, nanostructure and porosity of allophane, a combination of characterisation techniques was used, including wavelength dispersive X-ray fluorescence spectrometry (XRF), inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectroscopy, solid-state nuclear magnetic resonance (NMR) and nitrogen (N_2) physisorption analysis.

2. Experimental section

2.1. Chemicals and materials

Sodium orthosilicate (Na_4SiO_4) and aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$) were purchased from Alfa Aesar and Sigma-Aldrich, respectively. Sodium hydroxide (NaOH) and sodium chloride (NaCl) were provided by Guangzhou Chemical Reagent Factory, China. All of reagents were of analytical grade and were used as received, without further treatment. Ultra-pure water (18.25 MΩ·cm) was used in all of the experiments.

The high-purity allophane used in this study was synthesised following the procedures reported by Ohashi et al. (2002). In a typical run, 0.1 mol/L of Na_4SiO_4 solution and $AlCl_3 \cdot 6H_2O$ solution were mixed rapidly at an initial Si/Al molar ratio of 0.75 under continuous stirring. One hour later, the as-received dispersion was centrifuged at 4000 r/min for 10 min, and the resulting white precursors were heated to and maintained at 100°C for 48 h. Next, the products were dialysed with ultra-pure water to achieve a near-neutral pH, and then freeze-dried. The final products were ground in a mortar and denoted 'Allo'.

2.2. Alkali treatment

Pretests showed that alkali treatment at pH < 10.0 did not result in detectable changes in the Allo. Therefore, pHs higher than 10.0 (pH = 10.0, 11.0, 12.0, 12.5 and 13.0, respectively) were adopted in this work. With a solid/liquid ratio of 0.5 g/200 mL, the dispersion was shaken at a constant rate of 200 spm (shaking per minute) for 24 h. Subsequently, 20 mL of saturated sodium chloride solution were added to the dispersion, which was then centrifuged at 11,000 g for 30 min. The supernatants were used to determine the concentrations of dissolved Si and dissolved Al, and the sediments were dialysed against ultra-pure water for one week and then freeze-dried. The residual solids were labelled 'Allo$_n$', where n represented the initial pH value of the NaOH solution used to treat the Allo.

2.3. Characterisation methods

The transmission electron microscopy (TEM) images were collected on a FEI Talos F200S field-emission transmission electron microscope operating at an accelerating voltage of 200 kV. Two droplets of ultrasonically dispersed Allo dispersion were dropped on a carbon-coated copper grid followed by drying it at the ambient condition.

Atomic force microscopy (AFM) characterisation was performed on a Bruker Multimode 8 scanning probe microscope with a silicon tip on a nitride lever. A newly cleaved mica sheet was dipped into a dispersion of Allo for 30s followed by cleaning steps in water to eliminate excess material. And then, the specimens were dried in air for one week. ScanAsyst-air mode was used for scanning Allo.

XRD patterns were obtained using a Bruker D8 Advance diffractometer (Manheim, Germany) with an Ni filter and Cu Kα radiation (λ = 0.154 nm) generated at 40 kV and 40 mA. The specimens were investigated from 2° to 70° (2θ) with a step size of 0.02° and a measuring time of 0.4 s per step.

Chemical composition of samples was analyzed by XRF on Rigaku RIX2000 (Rigaku, Japan). To determine loss on ignition (LOI), 1000 mg of sample powder was heated to and maintained at 1000°C for 10 min. The concentrations of dissolved Si and dissolved Al were determined using ICP-AES (Optima 2000DV PerkinElmer, USA).

FT-IR absorbance spectra were obtained on a Bruker Vertex 70 FT-IR spectrometer (Manheim, Germany). Pure spectroscopic-grade KBr (Aladdin, China) was measured and used as a reference. Each specimen used for FT-IR measurement was prepared by blending and grinding 0.9 mg of sample powder with 80 mg of KBr followed by pressing the mixture into wafer. The spectra were collected over 64 scans in the range of $4000–400\ cm^{-1}$ with a resolution of $4\ cm^{-1}$. Diffuse reflectance infrared Fourier-transform (DRIFT) technique is able to provide a rapid method for analyzing samples without any interference from the sample preparation, and the technique is particularly suitable for studying the hydroxyl stretching vibration of power samples (Frost and Johansson, 1998). DRIFT spectra in the hydroxyl region were collected (64 scans at $4\ cm^{-1}$ resolution) on the diffuse reflectance attachment. To avoid the interference of adsorbed water, pretreatment of degassing in vacuum (at 200°C for 8 h) was employed, and then a portion of the powder was packed immediately into a 4 mm inner-diameter micro-sample cup for DRIFT spectra collection. The spectra were normalized against a KBr reference.

The solid-state ^{29}Si cross-polarization magic-angle-spinning (CP/MAS) NMR spectra and ^{27}Al MAS NMR spectra were recorded using a BRUKER AVANCE III 600 spectrometer (magnetic field strength of 14.1 T) equipped with a 4 mm triple resonance probe operating at resonance frequencies of 119.2 MHz and 156.4 MHz, respectively. ^{29}Si CP/MAS NMR spectra were recorded using a contact time of 6 ms, a π/2 pulse length of 2.3 μs, a recycle delay of 2 s and a spinning rate of 8 KHz. ^{27}Al MAS NMR spectra were acquired using a small-flip angle technique with a pulse length of 0.5 μs (< π/12), a recycle delay of 1 s and a spinning rate of 14 kHz. The chemical shifts of ^{27}Al and ^{29}Si were referenced to 1 mol/L $Al(NO_3)_3$ and tetramethylsilane (TMS), respectively.

N_2 adsorption-desorption isotherms were measured on a