



Research paper

Calcination-induced changes in structure, morphology, and porosity of allophane



Peixin Du^{a,b}, Peng Yuan^{a,b,*}, Dong Liu^{a,b}, Shun Wang^{a,b}, Hongzhe Song^{a,b}, Haozhe Guo^{a,b}

^a CAS Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Key Laboratory of Mineral Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehua Street, Guangzhou 510640, China

^b University of Chinese Academy of Sciences, 19 Yuquan Road, Beijing 100049, China

ARTICLE INFO

Keywords:

Allophane
Imogolite
Calcination
Heating
Structure
Porosity
Soil

ABSTRACT

Allophane with an Al/Si molar ratio of 1.6 was hydrothermally synthesized, followed by calcination at defined temperatures up to 1300 °C. The heated products were then characterized using a combination of techniques including X-ray diffraction, Fourier transform infrared spectroscopy, thermal analyses, nuclear magnetic resonance, transmission electron microscopy, and N₂ physisorption. In allophane, the imogolite local structure (ImoLS) had a relatively low thermal stability, and the adsorbed water was removed at a low temperature. Five major steps were outlined for the thermal evolution process of allophane. (i) At 200 °C or lower, the loss of adsorbed water and partial dehydroxylation of Si–OH accompanying with the formation of Si–O–Si resulted in the loss of ImoLS. (ii) As the temperature rose, further dehydroxylation of Si–OH as well as disassociation of Al–OH occurred, leading to decreases in the specific surface area and porosity due to the continued agglomeration of hollow spherules, whereas the spherical morphology of allophane was largely retained. (iii) At approximately 500 to 900 °C, the disconnection of AlO octahedra and SiO tetrahedra caused increased disintegration of the allophane structure and formation of amorphous alumina and silica. (iv) At approximately 1000 °C, nanosized mullite was crystallized by the reaction between the yielded amorphous alumina and silica. (v) Finally, further growth of the already-formed mullite crystals and formation of cristobalite occurred, with the consumption of excess silica.

1. Introduction

Allophane is a short-range ordered clay mineral of ubiquitous occurrence in soils of volcanic origin (Wada, 1989; Rampe et al., 2012). It has a chemical composition of 1–2SiO₂·Al₂O₃·5–6H₂O (Toyota et al., 2017a). This varied Al/Si molar ratio arises from the fact that naturally occurring allophane is a mixture of Al-rich allophane (Al/Si = 2) and Si-rich allophane (Al/Si = 1); it can be a mixture of unit particles or a mixture of structures within the unit particles (Parfitt, 1990). Al-rich allophane is composed of a curved gibbsite-like sheet with isolated orthosilicate groups attached to its inside, as in the case of imogolite (Cradwick et al., 1972; Yuan et al., 2016). For Si-rich allophane, although some orthosilicate groups may still be present, the silicate group is polymerized with some Al³⁺ substituting for Si⁴⁺ in tetrahedral sites (Brigatti et al., 2006). The layered structure of allophane contains vacancies, especially in octahedral sheets. Clusters of such defects in the wall give rise to openings with a diameter of about 0.35 nm (Theng and Yuan, 2008).

Irrespective of chemical composition, the unit particles of allophane

appear as hollow spherules with an external diameter of 3.5–5.5 nm and a wall thickness of 0.7–1.0 nm (Kitagawa, 1971; Wada and Wada, 1977), forming micro-aggregates (clusters) of various sizes and shapes (Brigatti et al., 2006). Due to its special nanosized hollow spherical structure and the large specific surface area and high surface activity it endows, many applications for allophane are envisaged, such as adsorption (Reinert et al., 2011; Huang et al., 2016), catalysis (Garrido-Ramirez et al., 2012; Zhou and Zeng, 2017), drug delivery (Toyota et al., 2017b), and nanocomposites (Nishikiori et al., 2014, 2017). However, due to the hydrophilic nature that originated from surface hydroxyls and the presence of openings in the wall, the hollow lumen of allophane is filled with adsorbed water at ambient conditions, which limits applications of the lumen.

Heating is a frequently used method to remove the adsorbed water. However, as the dehydration of the adsorbed water and the dehydroxylation of the allophane structure may occur continually without any clear boundaries, how to select a suitable temperature at which the physisorbed water is almost removed while dehydroxylation seldom occurs is of vital importance. In addition, heating is one of the most

* Corresponding author at: Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, China.
E-mail address: yuanpeng@gig.ac.cn (P. Yuan).

commonly used methods to tune the structure, porosity, and solid acidity of clay minerals, for both industrial and scientific purposes (Bergaya et al., 2006). The structural changes of allophane under heating have been studied by several research groups to clarify the structure of allophane (Kitagawa, 1974; Henmi, 1980; Henmi et al., 1981; van der Gaast et al., 1985; Wilson et al., 1988; MacKenzie et al., 1991). Because of the difficulties in characterization on its ultrafine size and short-range ordered structure, many issues remain to be investigated regarding the changes in allophane induced by thermal treatment. Particularly, in studies of the heating treatment of allophanes, impurities inevitably hinder interpretation of the spectroscopic results and thus decrease the reliability of the mechanism proposed, as in the case of halloysite (Yuan et al., 2012). However, most of the samples used in studies on the calcination of allophane were separated from soils, which are commonly found in association with other clay minerals such as imogolite and halloysite (Levard and Basile-Doelsch, 2016). As highlighted by Calabi-Floody et al. (2011), the isolation of allophane particles with a high purity grade from the soil is difficult, even after repeated pretreatments. Moreover, the structural changes caused by chemical and/or physical purification methods cannot be avoided. Consequently, there lacks first-hand information regarding the structural and morphological changes of allophane under heating, and this topic quite deserves in-depth investigation.

In this study, a pure allophane sample was obtained via hydrothermal synthesis and used for calcination at various temperatures up to 1300 °C. Changes in the structure, morphology, and porosity of allophane were explored using a combination of characterizations, including X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), thermal analyses, transmission electron microscopy (TEM), and N₂ physisorption.

2. Experimental

2.1. Materials and methods

Orthosilicate sodium (Na₄SiO₄) was purchased from Alfa Aesar, USA. Aluminium chloride hexahydrate (AlCl₃·6H₂O) was provided by Guangzhou Chemical Reagent Factory, China. All chemicals and reagents used in this study were of analytical grade and were used as received. Ultrapure water with a resistivity of 18.25 MΩ·cm was used throughout the experiments.

Allophane used in this study was synthesized following a procedure previously reported (Ohashi et al., 2002). In a typical run, the precursors were prepared by mixing 0.10 M aluminium chloride solution and 0.10 M orthosilicate sodium solution at an initial Al/Si molar ratio of 4/3 with stirring for 1 h. The byproduct NaCl was removed by centrifugation of the obtained dispersion at 4000 rpm for 10 min. The resulting white gel was autoclaved at 100 °C for 48 h, dialyzed in water for 4 days, and freeze-dried. White powder was obtained and labelled as Allo; its Al/Si molar ratio was 1.60, as determined by X-ray fluorescence.

The Allo was heated at defined temperatures (200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200 and 1300 °C) in a muffle furnace (Carbolite, England) for 4 h. The heated products were denoted as Allo_{*n*}, where *n* was the value of the heating temperature in degrees Celsius. For example, Allo₅₀₀ was the product obtained after heating Allo at 500 °C for 4 h.

2.2. Characterizing techniques

The XRD patterns were collected with 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.

The FTIR spectra were recorded on a Bruker Vertex 70 IR

spectrometer. The specimens were prepared by mixing 0.9 mg of sample and 80 mg of KBr, followed by pressing the mixture into pellets. A pure KBr wafer was measured as the background. All spectra were collected over 64 scans in the range of 4000–400 cm⁻¹ at a resolution of 4 cm⁻¹.

Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were performed using a Netzsch STA 409PC instrument (Selb, Germany). Approximately 10 mg of sample was heated in a corundum crucible from 30 to 1000 °C at a rate of 10 °C/min in an N₂ atmosphere (60 cm³/min).

Solid-state ²⁷Al magic-angle-spinning (MAS) NMR spectra were recorded using a Bruker AVANCE III 600 spectrometer in a static magnetic field of 14.1 T at a resonance frequency of 156.4 MHz. ²⁷Al MAS NMR spectra were recorded on a 4 mm probe by 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 ²⁷Al NMR were referenced to 1 mol/L Al(NO₃)₃.

The TEM images, high-resolution TEM (HRTEM) images, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images, and energy-dispersive X-ray (EDX) spectroscopy results were collected on a FEI Talos F200S field-emission transmission electron microscope operating at an accelerating voltage of 200 kV. The samples were ultrasonically dispersed in water (pH 4.0) for 10 min, and the specimens were prepared by dropping two droplets of the as-received dispersion onto a carbon-coated copper grid.

Nitrogen physisorption analysis was performed using a Micromeritics ASAP 2020 instrument (Micromeritics Co. Norcross, USA) at liquid-nitrogen temperature (−196 °C). Before measurements, the samples were outgassed at defined temperatures for 12 h. The specific surface area (S_{BET}) value was calculated using the multiple-point Brunauer-Emmett-Teller (BET) method (Rouquerol et al., 2007), and the total pore volume (V_{total}) was evaluated from the N₂ uptake at a relative pressure of approximately 0.97 (Gregg and Sing, 1982). The t-plot method was used to calculate the microporous specific surface area (S_{micro}) and the micropore volume (V_{micro}). The pore size distributions, ranging from 0.45 to 10 nm, were analyzed by means of the non-local density functional theory (Thommes et al., 2015).

3. Results and discussion

3.1. Structure and phase transformation of allophane under heating

3.1.1. XRD results

The XRD patterns of Allo and its heated products are shown in Fig. 1. As a typical short-range ordered aluminosilicate, the XRD pattern of Allo exhibited a major broad reflection at 27° (2θ, with a *d*-spacing of 3.3 Å) and two weak ones at 40° (2.25 Å) and 66.5° (1.4 Å) (Fig. 1a). The former reflection was ascribed to an interference between neighbouring SiO tetrahedra (Henmi et al., 1981), and this reflection is similar to that of synthetic silica gel, which showed only one broad reflection at 3.7–3.8 Å. The latter two reflections might arise from a structure similar to the imogolite local structure (ImoLS) (Du et al., 2017), which corresponds to the (063) and (006) reflections of the XRD pattern of imogolite, respectively (Cradwick et al., 1972). In addition to the three reflections mentioned above, two maxima at 2.8–3.1° (28.5–31.5 Å) and 6° (14.6 Å) were also observed in the XRD pattern of Allo (Fig. 1a). According to van der Gaast et al. (1985), the former might arise from the interference between the neighbouring allophane particles, whilst the latter arose from some long-range order associated with the structural water in allophane, reflecting its chemical composition and hydration status.

The XRD pattern of Allo₂₀₀ was almost identical to that of Allo (Fig. 1a,b), indicating that few structural changes occurred during calcination at 200 °C. The reflection at 14.6 Å nearly disappeared in the XRD pattern of Allo₃₀₀ (Fig. 1c), which indicated that some kind of dehydroxylation occurred, resulting in irreversible changes in the

Download English Version:

<https://daneshyari.com/en/article/8046021>

Download Persian Version:

<https://daneshyari.com/article/8046021>

[Daneshyari.com](https://daneshyari.com)