



## Research paper

# High morphological stability and structural transition of halloysite (Hunan, China) in heat treatment



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## ABSTRACT

Halloysite is one of the nanoscale tubular minerals in nature. This article reports the mineralogical character, dispersion treatment, structural, and morphological stabilities of a 10 Å-type halloysite mineral from Hunan, China. X-ray diffraction (XRD), transmission electron microscopy (TEM), particle-size distribution and N<sub>2</sub> adsorption-desorption isotherms were adopted to characterize the raw and calcined minerals. Ammonium lauryl sulfate was used as the surfactant to obtain mono-dispersed halloysite nanotubes.

The raw mineral is a kind of tubular nanotube with a hollow interior channel, the specific surface area is 56.7 m<sup>2</sup>/g. Alunitization occurred in the impure mineral. Thermal treatment to the mineral induced shrinkage of the c-axis and yielded a 7 Å-type structure. The tube wall was transformed to an amorphous structure in the dehydration process at 450 °C. Phase segregation occurred to yield amorphous SiO<sub>2</sub> and γ-Al<sub>2</sub>O<sub>3</sub> at around 1000 °C. The tubular morphology can be maintained even after it is calcined at 1100 °C for 6 h, and the specific surface area is enlarged slightly to 65.7 m<sup>2</sup>/g. While after being calcined to 1300 °C, the mineral will generate mullite and silica, accompanied with collapse of the tubular walls. A schematic diagram is proposed to illustrate the structural transformation procedure. The results provide assurance to the use of halloysite in high temperature circumstances, such as three-way catalysts.

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## 1. Introduction

Halloysite (abbreviated as Hal (Bergaya et al., 2006; Yuan et al., 2012b)) is one of the naturally generated tubular minerals, which is widely distributed in many places around the world (Bates and Hildebrand, 1950; Clarke, 2008; Garcia et al., 2009; Joussein et al., 2005; Rawtani and Agrawal, 2012; Singer et al., 2004). It has a kaolinite-like crystal lattice, in which the layered [SiO<sub>4</sub>] and [AlO<sub>6</sub>] polyhedrons are arranged in a 1:1 style manner (Bergaya et al., 2006; Clarke, 2008; Joussein et al., 2005; Rawtani and Agrawal, 2012). The kaolinite layers curve to the [AlO<sub>6</sub>] side to form a closed hollow channel, yielding the tubular morphology in Hal. The lengths of the tubes vary from 0.1 to 1 μm. The interior diameter of the channels is about 20–35 nm, and the wall thickness is about 10–20 nm. So far, the largest reported specific surface area of the Hal mineral is 156 m<sup>2</sup>/g (Joussein et al., 2005).

Hal was often used as raw material to produce fine ceramics in the past. The specific morphology and unique properties of the mineral determine that it should be applied in some high-tech fields, such as its use as a support for catalysts and other functional materials. Many investigations have been carried out to expand the application fields of this unique mineral. For example, some magnetic particles were assembled in hollow tubes to obtain magnets with high coercivity (Zhang and

Yang, 2012b). Pd, Co<sub>3</sub>O<sub>4</sub>, and ZnS nanoparticles were loaded on Hal, and excellent catalytic performances were observed (Zhang and Yang, 2012a, 2013; Zhang et al., 2013b). Furthermore, it was proved that Hal was capable of storing considerable amounts of hydrogen molecules (Jin et al., 2013). Some other applications such as in controlled drug loading and delivering (Lvov et al., 2008; Tan et al., 2014; Yuan et al., 2012a), metal or metal oxides support for catalyst applications (L. Wang et al., 2011; R. Wang et al., 2011; Wang et al., 2013), high-performance, polymer-based composites (Abdullayev et al., 2013; Pan et al., 2011; Zhou et al., 2010), biological antibacterial membranes (Chen et al., 2012; Zhang et al., 2013a) and oil capture were also reported (Cavallaro et al., 2013). Many delicate techniques have been developed in the synthesis of these functional materials: for example, the acid-leaching treatment to prepare silica nanotubes (Zhang et al., 2012); surface modification with organosilane, dopamine, or carboxylic (Chao et al., 2013; Joo et al., 2012; Yah et al., 2011, 2012; Yuan et al., 2008, 2012a); and selective leaching of aluminium to enlarge the tube diameter (Abdullayev et al., 2012). The synthesis and characterization of Hal nanotube-based functional materials is a hot spot both in mineral and in material areas, and the trend will not face a downturn in the near future (Clarke, 2008).

Hal will inevitably be used under some high temperature conditions in industries. To what extent the tubular morphology of Hal can keep its stability will determine the possibility of using this mineral as functional materials, such as catalysts. Some groups have reported the

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morphological stability and structural transformation of Hal under high temperature circumstances (Garcia et al., 2009; Nicolini et al., 2009; Yuan et al., 2012b). The surface activity, electron paramagnetic resonance (EPR) spectroscopy and porosity of Hal from different areas (Linfen, China; Utah, USA and New Zealand) have also been acquired in these literatures. Calcinations of Hal at varied temperatures have been conducted by different researchers. All of these references have showed the dehydration and phase transformation in Hal at high temperatures. Amorphization at around 500 °C followed by mullite formation at around 1250 °C has been detected (Garcia et al., 2009; Yuan et al., 2012b).

The tubular morphology of a Hal mined in Hunan province, China has been reported by our group (Zhang and Yang, 2012b). Based on the unique morphology of this mineral, a possible application is to introduce Hal to three-way catalysts, which is a kind of ceria-based mixed oxides used in the field of automobile exhaust cleaning, and this will allow Hal to encounter hot exhaust gases from a gasoline fuel engine cylinder, where the temperature is often elevated to about 600–800 °C (Collins and Twigg, 2007; Muroi et al., 2010). Therefore, morphological stability is the key to evaluate whether or not the Hal at Hunan can be applied in this field. As a result, a series of experiments were conducted to study the structural, porous and morphological characteristics of the raw and calcined Hal. The results show an incredible morphological stability. The tubular morphology of Hunan Hal can be maintained, even after calcination at 1100 °C for 6 h, which is slightly different with the performance of Linfen Hal reported by Yuan et al. (2012b). The result will provide sufficient evidence and assurance for utilizing Hal from Hunan, China in high temperature circumstances, such as three-way catalysis.

## 2. Experiment

Hal raw mineral was obtained from Chenxi, Hunan, P.R. China. Before the mineral was characterized, impurities were manually eliminated. Dispersion of the raw mineral was conducted before morphology characterizations. According to previous work (Lun et al., 2014), anionic surfactants such as sodium dodecyl sulfonate (SDS) can be an effective dispersant in the pH range 7–10. Another ionic molecule, ammonium lauryl sulfate ( $\text{NH}_4\text{SO}_4\text{C}_{12}\text{H}_{25}$ , abbreviated as ALS), was chosen to facilitate the following treatments, because ALS could be totally decomposed through simple calcining below 400 °C. ALS was industrial grade and was supplied by Lichen Chemical Ltd., Changsha. All of the other chemicals were analytical grade and were used without further purification. In a typical dispersion procedure, 10 g of the manually milled Hal raw mineral was dispersed in 300 mL de-ionized water. About 1.0% of ALS was dissolved into the mixture after the pH was adjusted to 9.0 using diluted ammonia. To avoid the sedimentation of the dispersed Hal, 0.1% PVA and PVP were also added. The mixture was first emulsified by high-speed dispersion at 2000 rpm (higher speed is not recommended as the tubular morphology would be destroyed), and then ultrasonic vibration was applied for 10 min. The mixture was stirred at 300 rpm for 2 h to obtain the final white dispersion. A part of the mineral powder may be deposited from the dispersion in 1 h. The un-deposited powder will remain in the dispersion for more than 7 days. The stable dispersion is suitable for the preparation of many kinds of functional materials. 100 mL of the dispersion was dried at 105 °C to estimate the mass percentage of the Hal; the result was revealed to be 1.14%. The dried product was calcined at different temperatures for a designated time to evaluate the structural, porous and morphological stability of Hal.

The chemical composition of the raw mineral was analyzed by a PANalytical Axios PW4400/40 X-ray fluorescent technique (XRF) and chemical analysis. The results are shown in Table 1. The pure Hal mainly contains  $\text{SiO}_2$  (39.59 wt.%) and  $\text{Al}_2\text{O}_3$  (33.544 wt.%), which is in good agreement with the theoretical ratio of pure and stoichiometric Hal. While the mineral with impurities contains some  $\text{SO}_3$  (4.225 wt.%)

**Table 1**  
Chemical compositions of the blue and brown minerals.

Components/%	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{K}_2\text{O}$	$\text{SO}_3$	NiO	$\text{Cr}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	Ig
Brown sample	34.123	35.46	1.409	4.225	0.4	0.496	0.76	22.87
Blue sample	33.544	39.59	0.02	0.225	0.1	0.02	0.33	26.1

and  $\text{K}_2\text{O}$  (1.409 wt.%), which will be discussed detailedly with the combination with XRD results. TG/DSC curves of the pure Hal powder was measured by a Mettler thermometer in air; the heating rate was set at 10 °C/min. The crystal structure was characterized by a RIGAKU D/max-2550VB<sup>+</sup> 18 kW powder diffractometer with  $\text{CuK}\alpha$ -radiation ( $\lambda_1 = 1.5405983 \text{ \AA}$ ). Data were collected from 5° to 80° of  $2\theta$  with a step width of 0.02°. Morphology of the sample was observed by a JEOL-3010 transmission electron microscopy (TEM) equipped with an Oxford EDAX analyzer; the accelerating voltage was set at 200 kV. Before the samples were subjected to the observation, the sample suspensions were dropped onto an amorphous carbon-coated 300-mesh copper grid and then dried at 80 °C. Nitrogen adsorption–desorption isotherms of the samples were measured by an Nova 2000e system (Quantachrome Co. Ltd.) using liquid nitrogen as the medium at 78.3 K. Data were collected in a relative pressure from 0.0 to 1.0. The Barrett–Joyner–Halenda (BJH) pore size distributions were deduced from adsorption branch of isotherm curves. Brunauer–Emmett–Teller (BET) specific surface area was deduced by nitrogen adsorption at 78.3 K, which was performed after degassing the sample at 423 K for 6 h under vacuum. For the raw Hal, the degassing was conducted at 373 K for 3 h to maintain the natural character of the mineral. The size distribution of particles was tested by an Oumeike LS-POP6 laser particle-size analyzer.

## 3. Results and discussions

Hal mineral deposits in Chenxi, China are located underground at –30 to –10 m; they are found between every two layers of limestones. The height of the Hal mineral layer varies from 0.5 m to 2.0 m; photos of the Hal raw mineral are displayed in Fig. 1. The photos show two kinds of raw minerals, which are the typical sediments in the well. The slight blue mineral is the pure Hal. But they are surrounded by the red kaoline minerals. Therefore, Fig. 1(B) shows the Hal contaminated by red impurities, yielding the brown-and-blue appearance. This article denotes these two kinds of Hal as the blue and brown minerals hereafter. The chemical compositions of the two raw minerals are shown in Table 1. Impurities are clearly observed in the brown sample, while very little of them exist in the blue source.  $\text{K}_2\text{O}$ ,  $\text{SO}_3$ , and  $\text{Fe}_2\text{O}_3$  are revealed to be the major impurities in the brown mineral, which will be discussed further in combination with the XRD results.

To detect the crystal structure and the possible preferred development of the crystal facets in the two kinds of Hal, bulk minerals were cut into  $1 \times 1 \times 1 \text{ cm}^3$  cubes according to the sediment-layer orientations shown in Fig. 1. The XRD patterns of the two kinds of bulk Hal minerals are shown in Fig. 2. The pattern acquired from the blue block and powder showed a pure Hal with 10 Å-type structure (JCPDS No. 29-1489,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ , hexagonal structure (Primitive),  $a = 5.118 \text{ \AA}$ ,  $c = 10.03 \text{ \AA}$ ). The clear and sharp reflections on XRD patterns of blue sample indicate the well-crystallized Hal mineral; the broadened asymmetry peak could have originated from the curved crystal lattice of kaolinite slices, which is the building block of Hal. XRD patterns from each facet of the blue cube are similar. No preferred orientation can be detected according to the XRD patterns of the blue block and powders. The situation is different for the brown block. The XRD patterns of the brown cube show the typical Hal-10 Å structure, too. But an individual diffraction emerged at  $2\theta = 30.95^\circ$ , which should be attributed to the diffractions from certain kinds of silicates containing impurities. The pattern of the powder milled from the brown mineral clearly shows the coexistence of Hal-10 Å and the alunite phase (JCPDS No. 73-1652,

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