Effect of Heat Treatment on Structure, Morphology and Surface Properties of Halloysite

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Abstract. Halloysite was one of the nanoscale tubular minerals in nature. The objective of the present study was to investigate the effect of heat treatment on structure, morphology and surface properties of tubular halloysite, which were significant in the applications of halloysite as functional materials but had received scant attention in comparison with kaolinite. X-ray diffraction (XRD), thermo gravimetric analysis (TG-DSC), field scanning electron microscope (FSEM), transmission electron microscope (TEM) and surface area measurement (BET) were adopted to characterize raw and heated minerals. The interior diameter of halloysite tube was about 50 nm, and the length of tube was in the range of 0.5-1.0 μm. A series of substantial changes in crystalline structure and phase state occurred in halloysite after heated treatment. The FSEM and TEM images of halloysite showed that the unheated halloysite particles possessed typical cylindrical shapes and contained transparent central areas that run longitudinally along the cylinder, indicating that the cylinders were hollow and open ended. The morphology of the halloysite had no obvious change before and after heat treatment. Specific surface areas (SBET) of the raw and heated mineral below 800 °C were similar (in the range of 35-36 m²/g), suggesting that it still maintained tubular structure.

1. Introduction

Halloysite is an aluminosilicate mineral of the kaolin group with the dominant form of nanotubular structure[1-5]. It has a kaolinite-like crystal lattice, in which the layered [SiO₄] and [AlO₆] polyhedrons are arranged in a 1:1 style manner[2, 6, 7]. The main difference between halloysite and other clay minerals is its unique nanotubular structure. In general, halloysite nanotubes vary in length from the submicron scale to several microns, sometimes even >30 μm [8], in external diameter from approximately 30 to 190 nm, and in internal diameter from approximately 10 to 100 nm[9, 10].

In recent years, researchers focus on many studies and applications of halloysite due to its nanotubular structure, high surface area and unique surface properties. Halloysite was often used to produce fine ceramics and as additive fillers in polymers, plastics, and other similar composites[3, 11]. The tubular form of halloysite had attracted most interest for new technology application, such as,
nanoscale reactor, catalyst carrier and adsorbent[9, 12-16]. In order to improve properties of halloysite, the functionalization by various methods had been studied[17, 18]. For example, halloysite could load by some magnetic particles and other nanoparticles to obtain magnets and catalysts[19-22]. And more applications such as in controlled drug loading and delivering, biological antibacterial membranes, oil capture and metal or metal oxides support for catalyst applications were also reported[23-27]. Therefore, halloysite is always a hotspot for future research as a functional material. Actually, in some applications, preparation of halloysite functional material was done via calcination process. Some advanced applications, such as catalyst support, required more excellent thermal stability. Numerous studies on the calcination of kaolinite have been conducted, but much less attention of halloysite has been paid to the thermal transformation. The reaction mechanism of halloysite with heat treatment had been postulated to be analogous to that of Kaolinite because halloysite was structurally and chemically similar to kaolinite. This assumption was supported by Smith[28]. In Smith’s work, structure changes on thermal decomposition of halloysite with progressive heating up to 1400 °C had been studied, and showed that thermal transformations closely followed those pervious outline for the related mineral kaolinite. But the halloysite used in this work contained considerable impurities of quartz and cristobalite, which inevitable affected the reliability of the results obtained. The morphological and textual characteristics of halloysite could cause some differences from kaolinite under heating. If stereotype tubular morphology of the mineral is taken into account, the structural and morphological stability of halloysite with heat treatment should be carefully studied. Consequently, further understanding of the mineralogical characteristics, such as the laws for the structure and morphology development under different heat treatment temperature, would be the important foundation of expanding the new application fields for halloysite.

Differential testing methods had been used in the phases and microstructure of halloysite[29]. In the previous studies, the reaction conditions were maintained fixedly generally and phases were observed with heating in differential thermal apparatus[30, 31]. Peng yuan et.al investigated changes in the structural, textual, and surface properties of tubular halloysite under heating[1]. However, it could not determine the exact temperature of phase transition with heating. The present study was undertaken in an effort to resolve these uncertainties.

Herein, a very pure tubular halloysite sample was used in the present work. A series of experiments were conducted to study the structural, porous and morphological characteristics of the raw and heated halloysite, which were investigated by XRD, HT-XRD, TG-DSC, FTIR, FSEM, TEM and BET. The results could provide sufficient evidence and assurance for applications in high temperature circumstances.

2. Experimental

2.1. Material and methods
Halloysite raw mineral was obtained from Shiyan, Hubei, P.R. China. Before the mineral was characterized, impurities were manually eliminated by scrubbing, grinding, settling and separation. And then purified halloysite was heated in a programmed, temperature-controlled muffle furnace at scheduled temperature for 1h.

2.2. Characterization techniques
The chemical composition of purified halloysite was analyzed by chemical analysis. X-ray powder diffraction was recorded on a Philips X’Pert PRO diffraction using Cu Kα radiation (40 kV, 40 mA) with a scanning rate of 2°/min from 5° to 70° (2θ). For in situ high-temperature phase change studies, the XRD patterns of samples were recorded from 2θ = 5-70°, in the temperature range 20-1200 °C on a Philips X’Pert PRO unit equipped with Anton Paar HTK attachment with Pt sample holder at the vacuum(6.3 Pa). The temperature was controlled by a PID-type temperature controller unit to within ±1°C during the XRD measurement. The samples were heated with the rate of 10 °C /min and held for 5 minutes at each temperature before XRD measurement. The thermal behaviors of halloysite were
studied by TG-DSC analysis, in air atmosphere at heating rates of 10 °C/min within a temperature range of 20-1200 °C with a Netsch STA 449 C simultaneous thermal analyzer. The secondary electron images of samples calcined at different temperature were obtained by FSEM (SU8010, Hitachi, Japan). The bright field images were observed by high-resolution transmission electron microscope (JEOL JEM-2100, Tokyo, Japan). N₂ adsorption-desorption isotherms were determined with a Micromeritics ASAP2020 system (Norcross, Georgia, USA) at boiling nitrogen temperature. The specific surface area of the powder, S BET, was calculated by the multiple-point Brunauer-Emmett-Teller method.

3. Results and discussion

3.1. Structure and phase transformations of halloysite under heating

The chemical composition of purified halloysite as determined from chemical analysis was, in percent by mass of the respective oxide forms: SiO₂ 44.68, Al₂O₃ 38.16, TFe₂O₃ 0.11, CaO 0.3, MgO 0.07, K₂O 0.03, Na₂O 0.21, TiO₂ 0.01, MnO 0.01, P₂O₅ 0.17, S 0.015, and loss on ignition 16.55. The pure halloysite mainly contained SiO₂ (44.68 wt.%) and Al₂O₃ (38.16 wt.%), which was in good agreement with theoretical ratio of pure and stoichiometric halloysite based on calculation.

Purified halloysite showed a (001) reflection at ~12.05° 2θ (Figure 1), which corresponded to a basal spacing of 7.3405 Å and identified it as 7 Å halloysite. This basal reflection of halloysite was

Figure 1. XRD patterns of purified halloysite.

Figure 2. In situ XRD patterns of halloysite heated from room temperature to 400 °C.
due to its tubular structure, higher order degree and smaller crystal size. In addition, a diagnostic
feature of the X-ray pattern of halloysite with common tubular morphology was the very intense
reflection at 4.4356 Å.

For in situ high-temperature phase change studies, the diffraction patterns of heated samples were
compared.

The position of diffraction peaks did not change obviously when halloysite heated from room
temperature to 400 °C (Figure 2). The peak intensity increased with increasing temperature, and the
full width at half maximum (FWHM) decreased (Figure 3). Actually, FWHM reflected the order
degree of the sample. However, in halloysite adsorbed water led to increasing of the interlayer spacing,
mainly embodied in \( d_{001} \), resulting a shift to higher angle in diffraction peak. Because of the difference
in adsorbed water in the interlayer, it would cause inconsistency on spacing of layers, which
manifested as a relatively wide peak and low degree in XRD pattern. The decrease of interlayer
distance caused by dehydration of absorbed water under heat treatment, and then they were consistent
with each other. Thus, order degree increased. This meant that FWHM was decreasing with increasing
of intensity.

![Figure 3. FWHM of (001) diffraction peak at different
temperature.](image)

Octahedra layer in halloysite collapsed and diffraction intensity decreased rapidly with increasing
temperature which was attributed to the evolution of structural water (Figure 4). The structural water
lost largely at 500 °C. Pseudomorphic aggregate in tetrahedral sheet could keep stable in a certain
temperature extent because of tubular structure in halloysite, therefore, some peaks could still be
observed.

\[
\text{Al}_4\text{Si}_4\text{O}_{10}\text{[OH]}_8 \xrightarrow{\Delta} 2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 4\text{H}_2\text{O} \\
\text{Halloysite} \quad \text{Meta} - \text{halloysite}
\]

(1)

\[
\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \xrightarrow{\Delta} \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \\
\text{Meta} - \text{halloysite} \quad \text{Amorphous}
\]

(2)

As temperature increased, tetrahedral sheet would also collapsed. The diffraction peak disappeared
and the crystalline transformed into the amorphous. Finally, mullite and cristobalite appeared (Figure
5).
\[ 3(\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) \xrightarrow{\Delta} 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 4\text{SiO}_2 \]  
Amorphous \hspace{1cm} \text{Mullite} \hspace{1cm} \text{Cristobalite} 

(3)

Figure 4. In situ XRD patterns of halloysite heated from 400°C to 800 °C.

Figure 5. In situ XRD patterns of halloysite heated from 800°C to 1200 °C.

TG/DSC curves of the halloysite (Figure 6) presented an endothermic peak at 70 °C associated with dehydration of the material with a 1.5% mass loss of physic adsorbed water. An endothermic peak appeared at 500°C caused by losing of hydroxyl water. Andothermic peak appeared at 640 °C reflected structure adjustment in halloysite after evolution of the structural water. No loss in mass could be observed in the range of 800-1200 °C, with an exothermic peak at 1002°C. This exothermic process was an evidence of the mullite and cristobalite phase segregation in the mineral, while the results were in accordance with the in situ XRD.
3.2. Changes in morphology and micro-structure of halloysite under heating

The FSEM (Figure 7a) images of halloysite showed it had a regular tubular morphology, with smooth surface and orderly fracture. The length of the halloysite nanotube was 0.5-1.0 μm. Halloysite could preserve its tubular structure at 400 °C, thereby partial halloysite with lower order degree formed microcrack on the tube surface due to dehydration (Figure 7b). Obvious distortion occurred so the tubes were scarred and ruptured at 600 °C (Figure 7c). With temperature increasing, the tubes broke up and fractured (Figure 7d and 7e). Reaction sintering and distortion of tube were obviously in the system at 1200 °C (Figure 7f). Although tubular morphology still existed, mullite and cristobalite were generated. The morphology of the halloysite did not change considerably after heat treatment. This suggested that the regular morphology of the halloysite was stable, which could act as a positive template role.

The TEM image of halloysite showed that the unheated halloysite particles possessed typical cylindrical shapes and contained transparent central areas that run longitudinally along the cylinder (Figure 8a). Cross-sectional TEM images showed that the lumen (inner cavity of the nanotube) diameter of the halloysite particles was 20 nm. No evident morphological changes of halloysite particles at 400°C observed. And the most tubular morphology intactly remained at 600°C, 800°C and...
1000°C. However, surface mottling and distorted tubular outlines were observed, reflecting a high degree of structural disordering. In view of the thermal analysis and XRD results, all these were probably caused by the structural disordered associated with dehydroxylation and the phase transition.

![Figure 8. TEM images of halloysite: (a) original kaolinite; (b) 400 °C; (c) 600 °C; (d) 800 °C; (e) 1000 °C.](image)

![Figure 9. BET surface areas of heated halloysite.](image)

### 3.3. Changes in specific surface area of halloysite under heating

BET surface areas of heated halloysite were shown in Figure 9. Specific surface areas ($S_{BET}$) of the raw and heated mineral below 800 °C were similar (in the range of 35-36 m$^2$/g), suggesting that it still maintained tubular structure. After being treated at 1000 °C, $S_{BET}$ value began to decrease because partial tubular was destroyed. And at 1200 °C, tubular was mostly destroyed, $S_{BET}$ value was lower
(8.12 m²/g). This was in good agreement with the FSEM and TEM observation that the tubular morphology of halloysite intactly remained when the heating temperature did not exceed 1000 °C. It proved that halloysite could be adapted to different application because of its excellent thermal stability, such catalyst support, fillers and adsorbent.

4. Conclusions

The pure halloysite with a hollow nanotube morphology mainly contained SiO₂ (44.68 wt.%) and Al₂O₃ (38.16 wt.%) , which was in good agreement with theoretical ratio of pure and stoichiometric halloysite based on calculation. The interior diameter of the tube was about 50 nm, and the length of the tube was in the range of 0.5-1.0 μm.

Nanotubular halloysite heated at temperatures up to 1400 °C resulted in a series of substantial changes in crystalline structure and phase state. Dehydroxylation of halloysite occurred at 500 °C, leading to a collapsing of octahedra layer, which was attributed to the evolution of structural water. As temperature increased to 1200 °C, tetrahedral sheet would also collapse. The FSEM and TEM images of halloysite showed that the unheated halloysite particles possessed typical cylindrical shapes and contained transparent central areas that run long-itudinally along the cylinder. The morphology of the halloysite did not change considerably after heat treatment. Specific surface areas (S BET) of the raw and heated mineral below 800 °C were similar (in the range of 35-36 m²/g), suggesting that it still maintained tubular structure.

The present study revealed that heating caused changes in structure, morphology and surface reactivity of nanotubular halloysite, offering potential uses for catalyst support, fillers and adsorbent.

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