

Thermal properties of Halloysite nanotubes (HNTs) intercalation complexes-A review

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Abstract: The organic/inorganic intercalated complexes have attracted more interests in past. This paper reviewed the layered structure of halloysite nanotubes (HNTs) intercalated by dimethyl sulfoxide (DMSO), potassium acetate (KAc), N-methylformamide (NMF), urea and acrylamide (AM). The microstructure and model of halloysite intercalated complexes were investigated. The research difficulties and application fields of halloysite intercalated complexes were proposed.

1 Introduction

Halloysite (Hal), with the chemical formula $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, was first described by Berthier as a dioctahedral 1:1 clay mineral of the kaolin group to honour its discoverer, Omalius d'Halloy, who studied a tubular mineral identified in a sample from Liège, Belgium [1, 2]. Halloysite is a multilayer tubular structure mineral composed of siloxane tetrahedral layer and gibbsite-like layers. The siloxane layer is made of SiO_4 tetrahedra linked in a hexagonal array. The bases of the tetrahedral are almost coplanar and the apical oxygen atoms are linked to a second layer containing aluminium ions and OH groups (Fig. 1) [3, 4]. The multilayer tubular structure of halloysite was attributed to the size differences and mismatch between the oxygen-sharing tetrahedral and octahedral sheets in the 1:1 layer [5], and the microstructure and morphology of halloysite was presented in Figure. 1. As a polytype of kaolinite, the structure and chemical composition of Halloysite are similar to those of kaolinite, dickite and nacrite, but the unit layers in halloysite are separated by a monolayer of water molecules [5]; accordingly, halloysite occurs mainly in two different polymorphs, the hydrated form (basal distance around 10 Å) with the minimal formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ and the dehydrated form (basal distance around 7 Å) with the minimal formula of $\text{Al}_2\text{Si}_2(\text{OH})_4$ [4, 6].

The raw halloysite usually mined from natural deposits, which occurs widely in soils of wet tropical and subtropical regions and weathered rocks, being formed by weathering of many types of igneous and non-igneous rocks [7-9]. Worldwide, large Hal deposits have been found in Australia, the United States, China, New Zealand, Mexico, France, Spain, Brazil and others [10, 11]. The stone-like raw halloysite is easily ground into

powder, and its color is usually white but is also sometimes slight red [12]. In general, halloysite has various applications as ceramic raw materials, catalysts, adsorbents, and polymer fillers. Recently, again halloysite nanotubes (HNTs) became a focus of many studies and patents in nanoscience and nanotechnology due to its unique combination of tubular nanostructure, large aspect ratio, good biocompatibility, and high mechanical strength [12].

Various inorganic and organic species can be used in the intercalation of halloysite nanotubes (HNTs) into its interlayer spaces, which is relative easily than do kaolinites [13]. The halloysite intercalation complexes have been carried out either for differentiating halloysite from kaolinite or gaining the insight into the reactivity of halloysite to organic complexes [14, 15]. The purpose of many earlier literatures was to distinguish the halloysite from clay fraction mixtures in soil through intercalation. The complexes of halloysite nanotubes (HNTs) intercalated by organic molecules have recently began to gain much attention, mainly due to the possibility of using this class of complexes to obtain wide choices adsorbent and nanocomposites usually presented unique properties with the isolate starting materials. In this article, the authors have reviewed the layered structure of halloysite nanotubes (HNTs) intercalated by dimethylsulfoxide (DMSO), potassium acetate (KAc), N-methylformamide (NMF), urea and acrylamide (AM). The structure of the organics-intercalated HNTs composites was determined by a series of characterizations such as X-ray diffraction (XRD), Fourier transform infrared (FTIR), Thermogravimetry-Derivative thermogravimetry (TG-DTG), Transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The intercalation mechanism was discussed.

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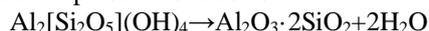
2 Thermal behavior of Halloysite

The thermal stability of halloysite intercalation complexes is very important for their application, because most complexes presented deintercalation phenomenon below 200~300 °C. Thus, the thermal behavior of halloysite should be comprehended firstly to better investigate the halloysite intercalation complexes. There is less research on the thermal behavior and transformation of halloysite, because which is postulated to be generally analogous to those of kaolinite[16]. However, there are some differences in thermal behavior between halloysite and kaolinite, and which are systematically discussed by Peng Yuan, et al[17]. The halloysite (10 Å) undergoes dehydration upon heating attributed to the presence of interlayer water, whereas kaolinite does not. According to the thermal behavior of kaolinite, the thermal reaction of halloysite can be divided into mainly three steps as follows:

1. Dehydration below 400 °C (low-temperature reaction);
2. Dehydroxylation between 450 and 700 °C (Intermediate-temperature reaction);
3. High temperature reactions above 700 °C

It is reported that the dehydration of halloysite (10 Å) normally occur at temperatures ranging from 50 °C to 150 °C, and an obvious endothermic peak correspond to the loss of the physically adsorbed water and the interlayer water [5]. Brindly and Goodyear also observed that heating to 400 °C was required for the complete removal of interlayer water from Indiana halloysite[18].

Dehydration finishes and dehydroxylation begins in the intermediate-temperature region (450~700°C), as confirmed by the results of various studies [5]. In this region, the OH groups release from the octahedral coordinated Al³⁺ ion and the formation of the “metahalloysite” have been reported, and the reaction can be expressed as follows:



The dehydroxylation of halloysite is endothermic, and an intense endothermic peak with the mass loss of 11% ~14% can be observed in the differential thermal analysis (DTA) or differential scanning calorimetry (DSC) curves. Meanwhile, the infrared spectra also could show the dehydroxylation transition process.

The thermal behavior of halloysite in the high temperature region is observed around 900~1000 °C, which is a significant exothermic event. This exothermic peak is believed to be due to the formation of a distinct alumina-rich phase and amorphous SiO₂.

3 The Halloysite intercalation complex

3.1 Dimethylsulfoxide intercalation into halloysite

The dimethylsulfoxide (DMSO) intercalation into kaolinite has been used to distinguish the kaolinite minerals and as the intermediate for the incorporation of other alkali and alkaline metal salts into the kaolinite by replacement of the DMSO. However, there is little

research on the DMSO intercalation in to halloysite[14, 19]. DMSO seems to interact much more strongly with the clay than do other organic molecules due to its strong polar, and the halloysite intercalated by DMSO expand to 1.10~1.12 nm. Costanzo et, al investigated an ordered halloysite intercalation complex treated by DMSO vapor at different time using XRD, and IR spectra. It was reported that a very intense and narrow reflection with the distance of 1.10 nm presented approximately at $2\theta=6\sim 10^\circ$, increasing 0.38 nm relative to that of the raw halloysite. The spectrum of halloysite treated by DMSO vapor at 60 °C is similar to that of the well-ordered kaolinite, and the characteristic bands of $-\text{CH}_3$ and $-\text{CH}_2-$ at 3020 and 2935 cm^{-1} was observed. Their experimental results revealed that halloysite is very sensitive to the temperature of DMSO intercalation. Modest heating for a relatively short time (~ 1hr) is enough to induce a considerable degree of order. The thermal behavior and deintercalation of DMSO intercalated halloysite selected from China was investigated using a combination of thermal analysis techniques, XRD and IR spectroscopy by Li and Zhang et, al[14]. The prepared halloysite DMSO intercalation complex is stable below 150 °C. The XRD data indicated that the relative intensity of the peak with value of 1.12 nm due to the intercalation of DMSO decreased as increasing the temperature and disappeared at 200 °C. In the FT-IR spectra, the appearance of methyl bands at 3022 and 2934 cm^{-1} indicated that the presence of intercalated dimethylsulfoxide, the intensities of which decreased with increasing the temperature and remained until around 150 °C. Xi et, al prepared the stearic acid/halloysite intercalated phase change compound using the halloysite DMSO intercalation complex as intermediates. The DMSO molecules intercalated into halloysite, which resulted in a new reflection appeared at $2\theta=7.95^\circ$ with the value of 1.12 nm. The basal spacing of halloysite-DMSO intercalation complex increased from 1.12 nm to 3.92 nm attributed to the replace of DMSO by stearic acid. The phase change temperature and phase change latent heat of prepared compound is 50.3 °C and 103.9 J/g, respectively. Recently, DMSO is usually used as precursor for the intercalation of non-reactive organic molecules via the displacement of intercalated molecules and addition to the formation of new organoclay nanohybrid materials.

3.2 Potassium acetate intercalation into halloysite

It was reported that the halloysite-potassium acetate (KAc) intercalation complex was formed with the increase of the initial $d_{(001)}$ spacing due to the expansion of potassium acetate molecules, which possessing both proton-donor and proton-acceptor group. The paper of Frost et, al [20] systematically investigated the rehydration of a KAc intercalated halloysite using a combination of XRD and Raman spectroscopy. Compared with the rehydration of potassium acetate-intercalated kaolinite where rehydration takes 20 min, the rehydration of the halloysite intercalation

complex takes 4 h. It is reported that the halloysite with an initial $d_{(001)}$ spacing of 0.713 nm expanded to 1.397 nm with the intercalation of the potassium acetate in the XRD patterns, and which showed the intercalated halloysite to be almost completely expanded. Two expanded phases with $d_{(001)}$ spacing of 1.184 and 0.980 nm were observed upon heating to 250 °C under an atmosphere of nitrogen, which were attributed to two different orientations of the acetate within the halloysite layers. However, Raman spectroscopy showed the halloysite to be incompletely intercalated as evidenced by the intensity of the inner surface hydroxyl band at 3695 cm^{-1} . The interaction between the acetate and the inner surface hydroxyls is observed by the hydroxyl stretching frequency of 3605 cm^{-1} . There are very significant changes in the Raman spectra of the inserting molecule, which suggests that two different molecular structures of the acetate present in the intercalation complex and acetate intercalates into the halloysite structure with two different molecular orientations. After later, a systematic study on the potassium acetate intercalation into halloysite selected from China using XRD, Mid-infrared (MIR) and near-infrared (NIR) spectroscopy was reported by Cheng and Liu [15, 21]. The intercalation of potassium acetate into halloysite caused an increase of the basal spacing from 1.00 to 1.41 nm. The TG-DTG results showed that the prepared intercalation compound is stable below 200 °C. Meanwhile, the dehydroxylation temperature of intercalated halloysite decreased about 100 °C due to the decrease of crystalline degree. The infrared emission spectra showed significant changes occurred in the region 1250–1750 cm^{-1} of vibration spectra when KAc intercalated into halloysite. The bands observed at 1610 and 1580 cm^{-1} are attributed to the anti-symmetric and symmetric (COO) stretching vibrations, and the symmetric stretching band of the O–C–O unit at 1420 cm^{-1} in KAc shifted to 1403 cm^{-1} as a result of hydrogen bonding with inner surface OH groups [22]. These characteristic bands show a decrease in relative intensity as temperature is increased. Based on analysis of the features and assignment for bands of MIR spectra, the NIR spectra provide the significant differences and the obvious structural change between halloysite and halloysite-KAc intercalation complex. The results indicated that the thermal decomposition of halloysite-KAc intercalation complex occurs between 200 and 400 °C. The halloysite–KAc intercalation compound can be used as intermediates for other halloysite intercalations and have application as filler in rubber and other polymer composites. Meanwhile, the combination of different techniques (including XRD, TG-DTG, infrared immersion spectroscopy and Raman spectroscopy) enables better investigated structure change of halloysite and interaction between intercalator molecules and halloysite.

3.3 N-methylformamide (NMF) and Formamide intercalation into halloysite

There are very little research specifically focused on the

N-methylformamide (NMF) halloysite intercalation complex, and only few studies reported the NMF/halloysite and formamide/halloysite intercalation to distinguish the halloysite from kaolinite in mineral mixtures and as intermediates to obtain other halloysite intercalation complex. Churchman et al [23] reported the differences in the rate and extent of formamide intercalation to distinguish the halloysite from kaolinite in mineral mixtures. The intercalation of formamide into untreated halloysite was both rapid and complete, whereas the intercalation occurred with kaolinite was not complete until at least 4 h. The presence of water in the intercalation system (up to 10 % v/v of formamide) could markedly accelerated the formation of interlayer complex for kaolinite and halloysite. Meanwhile, the intercalation of N-methylformamide and formamide are influenced by particle crystallinity and size of clay mineral. Compared that of formamide, the intercalation of N-methylformamide into kaolinite occurred obviously with the basal spacing of 1.09 nm after 4 h reaction. Thus, the N-methylformamide may be used as an alternative to formamide by limiting the time of 1 h or less and an useful intercalating agent for detecting small concentrations of halloysite in the matrix of kaolinite. The behavior of halloysite clay taken from an Udalf B horizon under formamide treatment was systemically studied by Joussein [7]. This study found that the formamide intercalation test greatly underestimates the halloysite content of the clay fractions separated from the stored soil even after repeated treatments with formamide. After immediate formamide treatment, 30% of the re-extracted fine clay ($< 0.1 \mu\text{m}$) fraction intercalates formamide as compared with 79% for the corresponding fraction from the fresh sample, which indicated differences in reactivity between the fresh and re-extracted halloysite. Only 50% of the halloysite is expanded whereas almost all the kaolinite is intercalated after progressive formamide treatment, which consistent with the finding by Churchman et al. Meanwhile, the formamide test clearly indicated that dehydration can modify the behavior and reactivity of K-selective halloysite toward organic compounds. Hofman et al[24] reported that the meta-halloysite treated at 110 °C was intercalated by N-methylformamide, formamide and other organic matter. The interlayer distance of halloysite intercalated with N-methylformamide varied from 1.06-1.12 nm. A patent focused on the preparation of graphene by curling layered halloysite nanotube was reported by Cheng et al[25]. The halloysite was pretreated by N-methylformamide, and then mixed with polymer monomers to substitute the N-methylformamide molecules in the halloysite. Zarei et al [26] reported that dehydrated halloysite was expanded to 1.08 nm through N-methylformamide saturation, which can distinguish the micas and halloysite in the Podzols of the Southern Black Forest.

3.4 Acrylamide (AM) intercalation into halloysite

Acrylamide ($\text{C}_3\text{H}_5\text{NO}$) presented high chemical reactivity with layer structure, and which can occur

hydrolysis, dehydrate, and alcoholysis et. al. Currently, there are less research on the Acrylamide (AM) intercalation into halloysite, and many research focused on the poly-acrylamide and poly(sodium acrylate-acrylamide), which have potential application in paper filler and adsorption water material[5]. The AM molecules were successfully loaded into the lumen of halloysite using vacuum negative pressure method by Zheng [27]. The effect and concentration of AM on the halloysite was evaluated and calculated based on TGA data. It was concluded that the maximum value of loaded AM was the following conditions: reaction time of 5 h, AM concentration of 2%, the ratio of AM and halloysite of 10%, and the ratio of water and ethanol of 10. Based on the above work, the poly-acrylamide (PAM)-halloysite composite was prepared in redox system under N_2 atmosphere, and which was characterized by XRD, TG-DTG and FT-IR. The optimum prepared condition was obtained as follows: reaction time of 3 h, reaction temperature of 50 °C, and the initiator ($(NH_4)_2S_2O_8$ - $NaHSO_3$) content of 10 wt.%. The XRD and FT-IR results showed that the PAM molecule chains presented in the halloysite through the hydrogen bond between hydroxylation and acylamino, and the microstructure of halloysite was stability and completely. Liu et al reported that a (sodium acrylate-acrylamide) superabsorbent nanocomposite incorporating graphene oxide and halloysite nanotubes (PAA-AAm-HNT-GO) was synthesized via the inverse suspension polymerization method. The FT-IR spectra indicated that the stretching vibrations at 3697 cm^{-1} and 3625 cm^{-1} of Al-OH disappeared due to the reaction of H^+ from AA with Al-OH, which also confirmed that during the polymerization process the modified HNTs reacted with or were incorporated into the PAA-AAm copolymer. The average sizes of the PAA-AAm particles decreased from 3-15 μm to 0.3-1 μm attributed to the introduction of HNTs. Thus, The water absorption and retention of prepared PAA-AAm-HNTs nanocomposite was $402.4\text{ g}\cdot\text{g}^{-1}$ and 73.54%, and increased by $124.28\text{ g}\cdot\text{g}^{-1}$ and 3.03 %, respectively. The results revealed that the PAA-

AAm-HNT exhibited a significant improvement in water absorption and water retention ability due to the introduction of HNTs. The paper of Cheng [28] reported that the intercalation of acrylamide into HNTs was successfully achieved through instead KAc by AM in the curling layered nanostructure of HNTs. The XRD data showed that the basal spacing of AM decreased from 1.42 nm of HNTs-KAc to 1.11 nm. The FT-IR further confirmed that the AM molecular has successfully substituted KAc in the HNTs due to the disappearance of characteristic bands the antisymmetric and symmetric stretching vibration of CH_3COO^- . The HNTs-AM intercalation complex can form HNTs-PAM through treating at 300 °C for conducting in-situ polymerization, and which can be used as template to synthesis graphene nanosheets through calcining, acidifying, filtering and drying under appropriate conditions.

3.5 Intercalation of urea and into halloysite

The urea intercalated into kaolinite group (kaolinite, halloysite) was earliest made by Ledoux and White[29]. They reported the intercalation of urea into kaolinite though by washing a hydrazine-kaolinite suspension with saturated urea solution. Subsequently, some researchers prepared and obtained the kaolinite-urea intercalation complex via directly grinding kaolinite and urea procedures[30-32]. A detailed study on the thermal behavior and structural aspects of halloysite-urea intercalation was made by Nicolini et al.[33]. It was reported that the intercalation reaction was carried out mechanochemically by grinding the dehydrated halloysite with urea percentages of 20% in relation to halloysite for 420 min. The XRD patterns showed that basal distance of halloysite expanded from 0.74 nm to 1.07 nm, and the interaction of urea to adjacent layers of halloysite through hydrogen bonds increased the structural order of the matrix. The TG-DTA results indicated that the urea was partially removed and partially decomposed between the layers after heating the sample to 200 °C, which was more stable in halloysite compared that of in kaolinite. Meanwhile, the basal distance collapsed to the original value and the crystals structural disorder was reestablished as the temperature increasing, but part of the structural Fe^{3+} was reduced to Fe^{2+} through an atmosphere of decomposed urea. E. Horváth et al. [34] investigated the urea intercalation into halloysite from Biela Hora (Slovakia) by simultaneous TG-DTA, XRD, FTIR (DRIFT), and Raman spectroscopy. A new diffraction peak appeared at 1.08 nm due to the intercalation of urea, and a significant reduction of the urea band can be seen when the intercalation was treated with isopropanol. The thermal behavior of this complex presented two main stages. The first stage (characteristic endothermic peak at 95 °C, 206 °C and 276 °C) was due to the removal of adsorbed and coordinated water and the decomposition of urea, whereas in the second stage (endothermic peak at 535 °C) was attributed to the thermal dehydroxylation of the halloysite. The DRIFT spectrum presented that the shift of the amide I band (at 1628 cm^{-1} in pure urea) to 1615 cm^{-1} is an indication that the $-NH_2$ groups form hydrogen bonds with the inner surface OH groups, which is in harmony with the model proposed for kaolinite-urea complexes [34]. It is worth mentioning that a structural model of prepared intercalation complex based upon the TO layer model and molecular mechanical calculations was proposed. This model is in harmony with the supposition that the conjugation of the amide groups ceases and both $-NH_2$ groups are connected to the layers and indicated that the carbonyl group likely has an orientation/polarization effect on the inner OH group. During the research of urea intercalation into halloysite, urea can help to break the crystals/layers apart into nanoparticulate mixtures of aluminum and silicon oxides, and the subsequently intercalation complex can potentially be used as a slow release fertilizer, in the white ceramic industry, or after rapid calcination.

4 Conclusions

The studies and patents on halloysite intercalation have began to gain increasing importance mainly due to the increasing interest on naturally occurring nanometric structures of halloysite and the possibility of using this class of compounds as precursor for potential application including catalyst and polymer composites. However, there is still diminutive and inconsistent information on the presence existence form of organic molecules in halloysite interlayer and the thermal decomposition processes of intercalation complexes. Based on above work, there is necessary for a great deal of work and more detailed systematic study on surface chemistry and microstructural or phase transformation for halloysite intercalation complexes. The specific aspects including: (i) the mineral and thermal behavior analysis of raw halloysite selected from different regions, (ii) understand the reactive behavior of halloysite with different organic reagents, (iii) studied the effect of halloysite chemical element composition on intercalation behavior and the phase transition of the intercalation complexes when the temperature of the system is raised, (iv) investigated the intercalation reactions process and decomposition behavior more clear through an effective technique, and (v) proposed the microstructural model and interaction mechanism of halloysite intercalation complexes through combination molecular simulation dynamics and experimental data.

Acknowledgement

The authors gratefully acknowledge the financial support of the School Foundation of Inner Mongolia University of Technology (2016046) and the National Natural Science Foundation of China (51604158).

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