Thermal analysis and infrared emission spectroscopic study of halloysite–potassium acetate intercalation compound

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ABSTRACT

The thermal decomposition of halloysite–potassium acetate intercalation compound was investigated by thermogravimetric analysis and infrared emission spectroscopy. The X-ray diffraction patterns indicated that intercalation of potassium acetate into halloysite caused an increase of the basal spacing from 1.00 to 1.41 nm. The thermogravimetry results show that the mass losses of intercalation the compound occur in main three main steps, which correspond to (a) the loss of adsorbed water, (b) the loss of coordination water and (c) the loss of potassium acetate and dehydroxylation. The temperature of dehydroxylation and dehydration of halloysite is decreased about 100 °C. The infrared emission spectra clearly show the decomposition and dehydroxylation of the halloysite intercalation compound when the temperature is raised. The dehydration of the intercalation compound is followed by the loss of intensity of the stretching vibration bands at region 3600–3200 cm^{-1}. Dehydroxylation is followed by the decrease in intensity in the bands between 3695 and 3620 cm^{-1}. Dehydration was completed by 300 °C and partial dehydroxylation by 350 °C. The inner hydroxyl group remained until around 500 °C.

1. Introduction

Halloysite is a polytype of kaolinite ($Al_4[Si_4O_{10}](OH)_8$) and differs mainly in the morphology of the crystals, which are curved or rolled [1]. The structure and chemical composition of halloysite are similar to those of kaolinite. However, halloysite can be intercalates with a monolayer of water molecules, resulting a basal spacing near 10 Å [2]. Halloysite occurs mainly in two different polymorphs, the hydrated form (basal distance around 10 Å) with the minimal formula of $Al_2Si_2O_5(OH)_4\cdot2H_2O$, and the dehydrated form (basal distance around 7 Å) with the minimal formula of $Al_2Si_2O_5(OH)_4$ which is identical to that of kaolinite. The hydrated form converts irreversibly into the dehydrated form when dried at temperatures below 100 °C [3,4]. This halloysite ($d = 10$ Å) easily dehydrates in atmospheric pressures at temperatures around 60 °C or in vacuum at room temperature. This anhydrous form with a basal spacing near 7.2 Å and is metastable, and can recover its interlayer water when placed in moist air. Because the 1:1 layers in hydrated halloysite are separated from each other by a water layer and occur in a scroll-like morphology, halloysite has a larger cations exchange capacity and surface area than kaolinite [3,5,6].

Various inorganic and organic species can be used in the intercalation of halloysite into its interlayer spaces, such as formamide [2,7], dimethylsulfoxide [8], urea [3], potassium acetate [1], aniline [9] and hydrazine [10]. Studies have already been know for decades and have recently began to gain increasing importance, mainly due to the possibility of using this class of compounds for potential industrial application [3]. These studies have been carried out either for differentiating halloysite from kaolinite or gaining the insight into the reactivity of halloysite to organic compounds [11].

Although the extensive use of halloysite in industrial processes and its excellent characteristics for the preparation of organic/inorganic intercalation compounds, there is little information about the thermal stability of intercalation compounds. However, heating treatment of intercalated halloysite is necessary for its further application, especially in the rubber industry. Infrared emission spectroscopy allows the possibility of studying the decomposition, dehydration and dehydroxylation of halloysite intercalation compound at elevated temperatures. This measurement of discrete vibrational frequencies emitted by thermally excited molecules, known as Fourier transform infrared emission spectroscopy (FT-IES) has not been widely used for study of thermal stability of clay intercalation compound [12–15]. Thermal decomposition analysis using thermogravimetric analysis and infrared emission spectroscopy techniques enables the thermal transformation of halloysite intercalation compound, the modification of the structure and the mechanism in response to heat

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treatment to be determined [14,16–19]. It has proven extremely useful for determining the stability of minerals [13,20]. To the best of the authors knowledge no thermal decomposition analysis of halloysite–potassium acetate intercalation compound have been undertaken; although differential thermal decomposition analysis of some related minerals intercalation complex have been published [21–25]. This paper reports the thermal decomposition analysis of halloysite intercalation compound using XRD, thermogravimetric analysis and infrared emission spectroscopy.

2. Experimental methods

2.1. Materials

The sample used in this study was the natural halloysite from Xianrenwan, Hunan province of China. Its chemical composition in wt% is SiO_2 35.47, Al_2O_3 34.51, Fe_2O_3 1.36, MgO 0.81, CaO 0.47, Na_2O 0.01, K_2O 0.32, TiO_2 0.065, P_2O_5 0.03, MnO 0.22, loss on ignition 26.69. These data are consistent with the theoretical one. It illustrated that this halloysite was almost clear from impurities. The potassium acetate (A.R.) was purchased from Beijing Chemical Reagents Company, China.

2.2. The intercalation compound preparation

The potassium acetate (KAc) intercalate was prepared by immersing 10 g of halloysite in 20 ml of KAc solution at a concentration of 30%. The sample was stirred for 10 min at room temperature. The compound after aging for 24 h was allowed to dry at room temperature before the XRD, thermogravimetric analysis and infrared emission spectroscopy analysis.

2.3. X-ray diffraction

X-ray diffraction patterns were collected using a PANalytical X'Pert PRO X-ray diffractometer (radius: 240.0 mm). Incident X-ray radiation was produced from a line focused PW3373/10 Cu X-ray tube, operating at 40 kV and 40 mA, with Cu Kα radiation of 1.540596 Å. The incident beam passed through a 0.04 rad soller slit, a 1/2° divergence slit, a 15 mm fixed mask, and a 1° fixed antiscatter slit.

2.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of the sample was carried out in a TA® Instruments incorporated high-resolution thermo gravimetric analyser (series Q500) in a flowing nitrogen atmosphere (60 cm^3 min^{-1}). Approximately 50 mg of each sample underwent thermal analysis, with a heating rate of 5 °C/min, with resolution of 6, from room temperature to 1000 °C.

2.5. Infrared emission spectroscopy

FTIR emission spectroscopy was carried out on a Nicolet Nexus 870 FTIR spectrometer, which was modified by replacing the IR source with an emission cell. A description of the cell and principles of the emission experiment have been published elsewhere [12–15,26]. Approximately 0.2 mg of halloysite–KAc intercalation compound was spread as a thin layer on a 6 mm diameter platinum surface and held in an inert atmosphere within a nitrogen-purged cell during heating. The infrared emission cell consists of a modified atomic absorption graphite rod furnace, which is driven by a thyristor-controlled AC power supply capable of delivering up to 150 A at 12 V. A platinum disk acts as a hot plate to heat the intercalation compound sample and is placed on the graphite rod. An insulated 125-μm type R thermocouple was embedded inside the
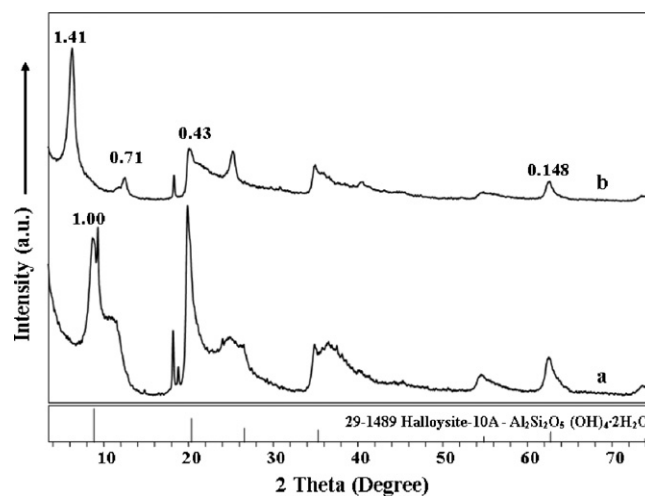

Fig. 1. the XRD patterns for (a) halloysite, (b) halloysite–KAc intercalation compound.

platinum plate in such a way that the thermocouple junction was less than 0.2 mm below the surface of the platinum. Temperature control of ±2 °C at the operating temperature of the sample was achieved using a Eurotherm Model 808 proportional temperature controller, coupled to the thermocouple.

In the normal course of events, three sets of spectra are obtained over the temperature range selected and at the same temperatures; those of the black body radiation, the platinum plate radiation, and the platinum plate covered with the sample. Normally only one set of black body and platinum radiation is required. The emission spectrum at a particular temperature was calculated by subtraction of the single beam spectrum of the platinum backplate from that of the platinum covered with the sample, and the result ratioed to the single beam spectrum of an approximate black body (graphite). This spectral manipulation is carried out after all the spectral data has been collected.

The emission spectra were collected at intervals of 50 °C over the range 100–1000 °C. The time between scans (while the temperature was raised to the next hold point) was approximately 100 s. It was considered that this was sufficient time for the heating block and the powdered sample to reach temperature equilibrium. The spectra were acquired by co-addition of 128 scans for the whole temperature range, with an approximate scanning time of 1 min, and a nominal resolution of 4 cm^{-1}. Good quality spectra can be obtained providing the sample thickness is not too large. If too large a sample is used then the spectra become difficult to interpret due to the presence of combination and overtone bands. Spectral manipulation such as baseline adjustment, smoothing and normalization was performed using the Spectra calc software package (Galactic Industries Corporation, NH, USA).

3. Results and discussion

3.1. X-ray diffraction (XRD)

X-ray diffraction was the preliminary technique to verify whether the layered structure was altered or not [27], the halloysite after the intercalation treatment with KAc solution, and to detect the possible change of the basal spacing after the intercalation reactions. The XRD patterns of the halloysite and halloysite intercalation compound samples are shown in Fig. 1. Halloysite shows an identical XRD pattern to the standard. The halloysite shows a characteristic first basal peak at 10 Å, which tends to disappear when intercalated by KAc. It was observed that after the halloysite crystal
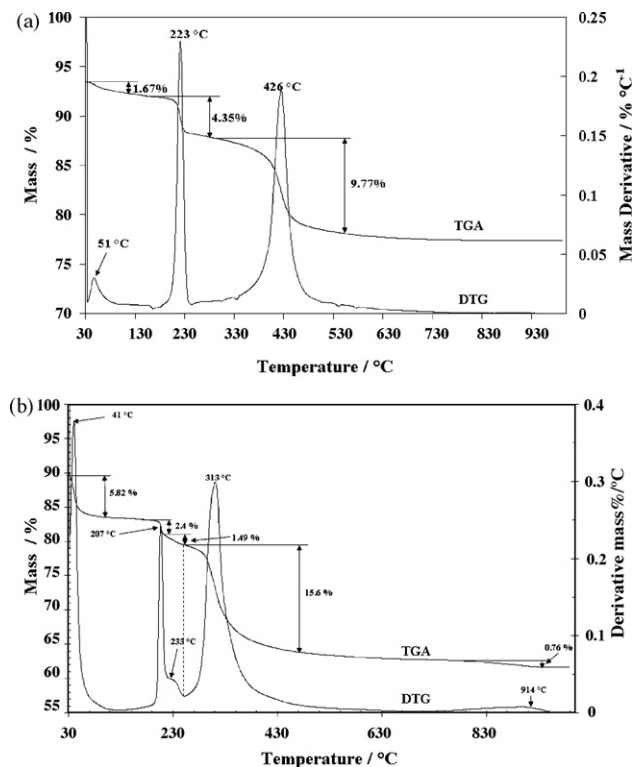
Fig. 2. Thermal analysis curves (TGA–DTG) of (a) halloysite and (b) halloysite–KAc intercalation compound.

was intercalated with KAc, increasing the basal distance from 10 to 14.2 Å, which is consistent with the results published before [1].

3.2. Thermal analysis

To evaluate the thermal stability of halloysite–KAc intercalation compound, the thermogravimetry and differential thermogravimetric (TGA–DTG) analyses of the halloysite and halloysite–KAc intercalation compound are presented in Fig. 2a and b, which show the TGA and DTG curves for these two samples. Thermal decomposition properties of the halloysite and halloysite–KAc intercalation compound are discussed in details as followed.

Fig. 2a shows the thermal decomposition of the halloysite. There are three main mass losses in TGA curve of halloysite. The first small mass loss is observed at 51 °C and mass loss is 1.67%. This is attributed to the elimination of adsorbed water molecules on the external surfaces of the halloysite particles. A second mass loss is observed at 223 °C with a mass loss of 4.35%, which is assigned to the thermal dehydration of halloysite in the structural layer. The last mass loss is observed at 426 °C with a mass loss of 9.77%, which is attributed to dehydroxylation of halloysite. It is calculated according the formula that the theoretical mass loss value is 13.95%, which is similar to the detected mass loss in these two steps. However, four distinct mass losses are observed in the TGA–DTG curves of halloysite–KAc intercalation compound in Fig. 2b. The TGA–DTG curve of the intercalation compound presented a peak at 41 °C associated with dehydration of the intercalation compound with a 5.82% mass loss of physically absorbed water. The second peak appeared at 207 °C, accompanied by a mass loss of 2.4% caused by thermal dehydration of halloysite in the structural layer. Another small band is observed at 233 °C with a mass loss of 1.49%, which is assigned to the decomposition of the intercalation compound. This step can be interpreted as being due to the loss of adsorbed water which is coordinated to KAc in the interlayer of halloysite. The last mass loss of 15.6% at 313 °C is observed, which is attributed to the loss of
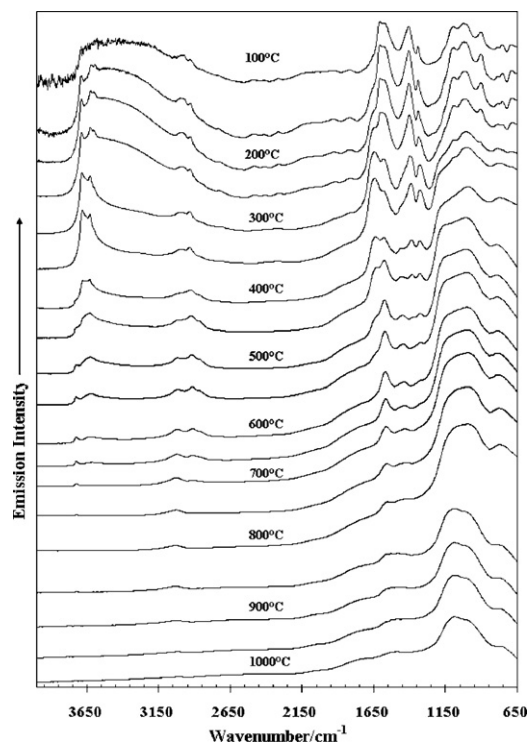

Fig. 3. Infrared emission spectra of halloysite–KAc intercalation compound over the 100–1000 °C temperature range.

KAc in the layer of intercalation compound and dehydroxylation of halloysite.

It is proposed that the halloysite–KAc intercalation compound is stable below 200 °C. It is generally considered that there are steps for the dehydration, loss of KAc and dehydroxylation of the intercalation compound at the elevated temperature. According to the structural model, KAc coordinated to water molecules serves as molecular props between the halloysite layers, resulting in the observed 1.428 nm spacing. Partial loss of water drives the remaining KAc molecules into the ditrigonal holes of the oxygen-atom surface of the 1:1 layer [25]. Two notable observations can be made: firstly, a new mass loss peak is observed at 233 °C, which is assigned to the loss of water coordinated to KAc. Secondly, the temperature of dehydroxylation and dehydration of halloysite is decreased about 100 °C. Thus this is beneficial to the calcinations in the industrial process.

3.3. Infrared emission spectroscopy

In order to confirm the results obtained from TGA and understand the thermal decomposition of intercalation compound better, infrared emission spectroscopy was undertaken. TGA curves clearly show at which temperature the mass loss. However, infrared emission spectroscopy will give the evidence on the changes of structure. These make all explanation have the sufficient evidence. Typical infrared emission spectra of halloysite–KAc intercalation compound are shown in Fig. 3. The spectra clearly show the temperatures at which the OH group is lost and at which the compound decomposed. In the 200–400 °C temperature range obvious structure changes are observed. In order to follow these thermal decompositions three spectra at 200, 300 and 400 °C were selected for further analysis. The infrared emission spectra at these temperatures for intercalation compound in the 2850–3750 cm^{-1} range are shown in Fig. 4. For the 200 °C infrared emission spectrum bands are observed at 3693, 3675, 3653, 3625, 3604, 3573, 3453,3280, 3089, 2985 and 2930 cm^{-1}. The bands at 3693, 3675 and 3653 cm^{-1}
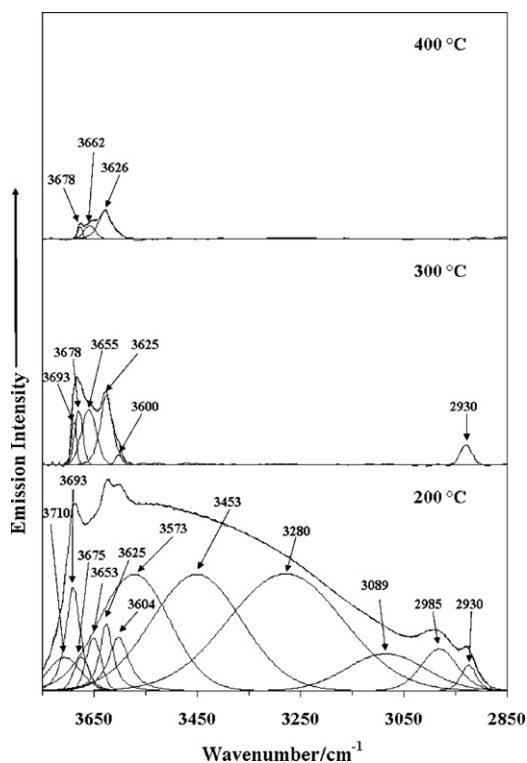
Fig. 4. Infrared emission spectra of halloysite–KAc intercalation compound in the 2850–3750 cm^{-1} region at 200, 300 and 400 °C.

Fig. 5. Infrared emission spectra of halloysite–KAc intercalation compound in the 1250–1750 cm^{-1} region at 200, 300 and 400 °C.

are attributed to the vibrations of inner surface hydroxyls and this region is specifically assigned to stretching vibrations of hydroxyl groups [11]. The band at 3625 cm^{-1} is due to the inner hydroxyl stretching vibration [1]. The four bands positioned at 3573, 3453, 3280 and 3089 cm^{-1} are attributed to the hydroxyl stretching frequencies of water in various states (interlayer water and water coordinated to KAc) [13]. These bands are very broad, suggesting that more than one type of water molecule is present. This broad spectral profile is assigned to water–hydroxyl stretching frequencies. It also known that water is intercalated together with KAc and the water molecules serve to hydrate the cation and fill the interlayer spaces [11]. They are more intense and broader in halloysite in comparison with kaolinite [11,28]. The other bands at 2985 and 2930 cm^{-1} may be attributed to some impurities in the intercalation compound. These bands diminish in intensity on heating and no intensity remains in the spectrum at 400 °C. Only six bands are observed for halloysite–KAc intercalation compound at 300 °C at 3693, 3678, 3655, 3625, 3600 and 2930 cm^{-1}. It is important to note that the vibration of adsorbed and interlayer water almost disappeared. The intensity of inner surface hydroxyl vibration at 3693 cm^{-1} decreased alone with the increase of temperature, and until at 400 °C, no peak intensity remains. This corresponds to the results of thermal analysis (Fig. 2b). In the 400 °C spectrum, only three bands are found at 3678, 3662 and 3626 cm^{-1}, which are due to the stretching vibrations of inner surface hydroxyl and inner hydroxyl.

When halloysite is intercalated with KAc significant changes occurred in the region 1250–1750 cm^{-1} of vibration spectra. The intercalation reaction destroys the inherent hydrogen bond of halloysite and presents some new bonds [11]. The infrared emission spectra of halloysite–KAc intercalation compound in the 1250–1750 cm^{-1} region at 200, 300 and 400 °C are shown in Fig. 5. In the 200 °C spectrum bands are observed at 1666, 1610, 1579, 1463, 1403, 1355 and 1345 cm^{-1}. The strong band is observed at 1666 cm^{-1} which is attribute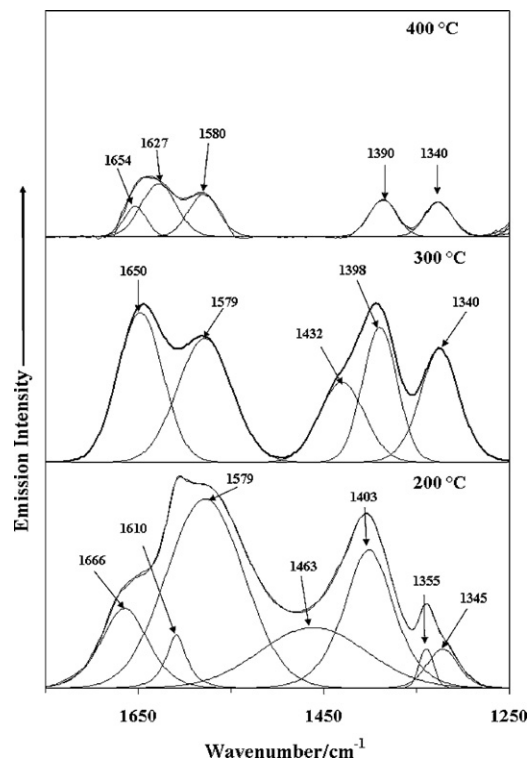d to bending vibrations of absorbed water. The bands are observed at 200 °C at 1610 and 1580 cm^{-1}, which are due to the antisymmetric and symmetric ν(COO) stretching vibrations [23]. The band at 1463 cm^{-1} may be assigned to the C–H bending vibration. The symmetric stretching band of the O–C–O unit at 1420 cm^{-1} in KAc shifted to 1403 cm^{-1} as a result of hydrogen-bonding with inner surface OH groups in the compound. At the same time, the symmetric deformation band of the CH$_3$ group was reduced in intensity at 1345 cm^{-1}. It is proposed that the CH$_3$ group of the acetate is interacting with the silica sheet [23]. The 300 °C spectrum shows a small shift in these bands, which are now observed at 1650, 1579, 1432, 1398 and 1340 cm^{-1}. In the 400 °C spectrum, five bands are found at 1654, 1627, 1580, 1390 and 1340 cm^{-1}. The bands at 1650, 1579, 1398 and 1340 cm^{-1} show a decrease in relative intensity as temperature is increased.

The infrared emission spectra at 200, 300 and 400 °C for halloysite–KAc intercalation compound in the 650–1250 cm^{-1} range are shown in Fig. 6. At 200 °C, the spectrum in this region presents the band at 694 cm^{-1} which is assigned to the Al–OH vibrations. Two bands are observed at 755 and 792 cm^{-1}, which are typical of the OH translational vibrations. The bands at 912 cm^{-1} are attributed to the OH bending vibrations. The strong band at 1033 cm^{-1} is assigned to the Si–O–Si in-plane vibrations. The band occurring at 1115 cm^{-1} is the Si–O stretching mode. A band is observed at 1157 cm^{-1}. The probable assignment of this band is to the C=O symmetric stretching mode from the acetate ion. The 300 °C spectrum shows small shift in these bands, which are now observed at 688, 755, 792, 904, 1005, 1033, 1115 and 1180 cm^{-1}. Two bands at 694 and 1033 cm^{-1} disappeared and a new band is observed at 1005 cm^{-1}. These shift and disappearance are attributed to that the water coordinated to KAc is lost when the temperature is raised. These also illustrate that when KAc is actually intercalated into the layer of halloysite and attached with the inner surface hydroxyl of halloysite it will result in the shift of Al–O. These bands are observed at 735, 781, 1005, 1115, 1168 and 1207 cm^{-1} in the 400 °C spectrum.
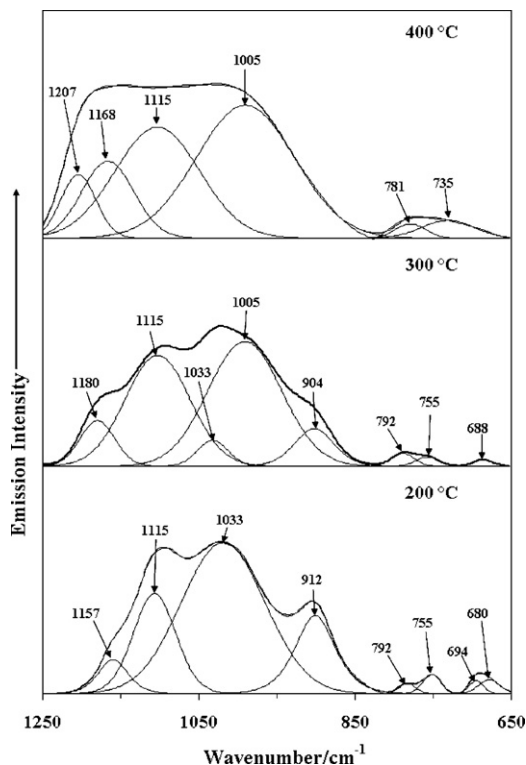
Fig. 6. Infrared emission spectra of halloysite–KAc intercalation compound in the 650–1250 cm^{-1} region at 200, 300 and 400 °C.

The results of the thermal analysis are in harmony with the infrared emission spectroscopic results. Both techniques show the thermal decomposition occurs between 200 and 400 °C.

4. Conclusions

The thermal decomposition of halloysite–KAc intercalation compound has been studied using XRD, TGA–DTG and infrared emission spectroscopy. The XRD results show that the KAc have been successfully intercalated into halloysite with an obvious basal distance increase of the first basal peak. The TGA–DTG results show that the halloysite–KAc intercalation compound is stable below 200 °C. A comparison of TGA–DTG curves of halloysite and halloysite–KAc intercalation compound gives new discovery that not only a new mass loss peak is observed at 233 °C, but also the temperature of dehydroxylation and dehydration of halloysite is decreased about 100 °C.

The technique of infrared emission spectroscopy allows the possibility of studying a compound of minerals such as halloysite intercalation compound and kaolinite group minerals intercalation and to study the thermal degradation and decomposition of these compounds in situ at the elevated temperature. The technique also makes the results of TGA clearly about the chemical process. Minerals intercalation compounds such as halloysite–KAc intercalation and kaolinite–KAc intercalation have application as filler in rubber and infrared emission spectroscopy enables the study of these compounds for potential use as filler in more fields.

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