Research paper

Thermal decomposition behavior and de-intercalation mechanism of acetamide intercalated into kaolinite by thermoanalytical techniques

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ABSTRACT

De-intercalation is the inverse of the intercalation process, which can be easily and rapidly determined by thermal analysis. Research on the de-intercalation process is beneficial to exploring the intercalation mechanism that is still unclear in the case of kaolinite intercalation. The objectives of this study were (a) to investigate the thermal decomposition behavior of the intercalation compound of kaolinite and (b) to determine the kinetics of de-intercalation process by thermal analysis to study the mechanism of de-intercalation reaction in kaolinite. Here, the kaolinite–acetamide intercalation compound that was prepared by the direct intercalation method was investigated. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy results showed that acetamide molecules were inserted into the interlayer space of kaolinite and apparently formed new hydrogen bonds with the inner surface hydroxyl groups of kaolinite. The basal spacing of kaolinite increased from 0.721 to 1.102 nm upon intercalation with acetamide. The thermogravimetric (TG) and differential scanning calorimetry (DSC) curves indicated that the decomposition process of the intercalation compound could be divided into two steps. The first step was attributed to the de-intercalation of the intercalated molecules at a temperature of about 181 °C, and the second step corresponded to the dehydroxylation of kaolinite at a temperature of about 502 °C. The completed kinetic triplet of the de-intercalation reaction was obtained through thermal analysis kinetics methods. The apparent activation energy E_a of the de-intercalation process was calculated to be about 73.6 kJ mol^{-1} by an iterative procedure. The pre-exponential factor A was estimated to be in the range of 1.06×10^{10} s^{-1} to 7.92×10^{10} s^{-1} by the Dollimore method. The optimized mechanism function of the de-intercalation process of acetamide was determined to be an nth-order chemical reaction through the Malek method. The mechanism function is $G(\alpha) = [1 - (1 - \alpha)^{1-n}]/(1-n)$, $f(\alpha) = (1 - \alpha)^n$ and experiments showed that the value of n increased with increased heating rate.

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1. Introduction

Recently, there has been a growing interest in preparing organic–inorganic nanocomposites by intercalation (Solin, 1997; Mittal, 2009). Traditional materials, such as naturally occurring clay minerals, have been widely used in intercalation research, due to their special layer structure. Kaolinite is a member of the 1:1 type layered silicates consisting of one silica tetrahedral [SiO$_4$] sheet combined with an alumina octahedral [AlO$_6$] sheet. The 1:1 layers are stacked together with little or no interlayer space between the layers, but can accommodate some molecules to form organic–inorganic intercalation compounds that may greatly improve the performance and value of kaolinite. Such compounds have a wide variety of applications as novel functional materials because of its asymmetric layer structure and nonlinear optical characteristics (Takenawa et al., 2001; Wang et al., 2005). In addition,

they can serve as promising precursors for preparing clay–polymer nanocomposites by replacing the intercalated molecules with polymers (Gardolinski et al., 2000a; Pomogailo, 2000). Until now, various organic species such as formamide (Frost et al., 2000), dimethylsulfoxide (Olejnik et al., 1968), methanol (Komori and Sugahara, 1998), N-methylformamide (Olejnik et al., 1971a), etc. have been reported to be intercalated into the interlayer space of kaolinite. However, most of the intercalation processes take a very long time, at least above 24 h, to reach equilibrium. Also, most of the molecules are difficult to insert into the interlayer space because of the strong hydrogen bonds with no space or exchangeable cations in the kaolinite structure (Brindley and Brown, 1980). Therefore, it is necessary to investigate and understand the intercalation mechanism of kaolinite in order to synthesize many new inorganic–organic nanocomposites for potential applications. However, the complexity of the nano-scale process of kaolinite intercalation makes it very difficult to monitor and explore the mechanism of intercalation by existing techniques. The reverse process of intercalation however, i.e., de-intercalation can throw new light on the intercalation mechanism.

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On one hand, de-intercalation is the inverse process of the intercalation that is rapid and can be easily investigated by thermal analysis (Kristof et al., 2002; Qin et al., 2007). Some researchers previously investigated the intercalation compounds using thermal analysis methods (Horte et al., 1988; Kristof et al., 1999; Lapides and Yariv, 2009; Cheng et al., 2014) but most of these studies are focused on the thermal stability of the compounds with few or none studying the mechanism. Using thermal analysis techniques and determining the kinetics of the de-intercalation reaction will open up new avenues for studying the mechanism of the intercalation process. On the other hand, to achieve intercalation of polymer, the precursor clay–organic nanocomposite and the polymer require a match with respect to their thermal properties (Pomogailo, 2000). During the de-intercalation reaction a large amount of intercalated guest molecules may be set free from the precursor before the polymer could melt and intercalate in the interlayers. Rapid release of interlayer organic molecules can lead to little or no intercalation of polymer. Therefore, reaction control, i.e. a careful temperature control during the de-intercalation reaction, is essential for the production of high-quality polymer composites. Understanding the de-intercalation kinetics will result in a control of the reaction rates and provide a theoretical basis for the preparation of kaolinite–polymer composites.

In this work, the structure of the kaolinite–acetamide intercalation compound, its thermal decomposition behavior and de-intercalation reaction were investigated by XRD, FTIR, DSC and TG techniques and kinetics. The objectives of this research were (1) to study the thermal decomposition behavior of the kaolinite–acetamide intercalation compound; (2) to investigate the mechanism of the de-intercalation reaction of acetamide from kaolinite and (3) to develop thermokinetic methods for the de-intercalation process.

2. Materials and methods

2.1. Materials

The sample used in this experiment was a pure kaolinite from Commerce Company of China University of Geosciences. Laser particle size analyzer showed its average diameter was 2.56 μm. Methanol and acetamide (Ac) were purchased from Shanghai Sinopharm Company, China with purity of A.R. grade. All chemicals were used directly without further purification. Deionized water was obtained from a Milli-Q system, which was stored at <5 °C and used within a month of preparation.

2.2. Preparation of intercalation compounds

Firstly, 4.0 g of kaolinite was mixed with 20.0 g Ac by grinding carefully. The mixture was heated up to 85 °C in oil bath and was then stirred at this temperature for 48 h. After cooling down to room temperature in air, the resulting mixture was washed by methanol. The final product was allowed to dry at 60 °C for 12 h.

2.3. Characterization

Powder X-ray diffraction patterns of different materials were obtained with a diffractometer (Rigaku D/max-β B) using Cu Kα radiation ($\lambda = 0.15432$ nm) at the scanning rate of 8° min^{-1} in the two theta range of 3° to 45° with a step size of 0.02° and a counting time of 1 s. The FTIR spectra were recorded using a spectrometer (Bruker Tensor 27), in the range of 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. Samples (ca. 5 mg) were mixed with 100 mg dehydrated KBr and ground together. One hundred scans were collected using KBr pellets at room temperature. Simultaneous TG-DSC measurements were carried out on a thermal analyzer (Netzsch STA 409 PC) under a flowing nitrogen atmosphere (30 mL/min). Approximately 20 mg of the samples was placed in alumina crucibles and heated from room temperature to 1000 °C at heating rates of 1, 3, 5, 7, 10, 15, 20 or 30 °C/min.

3. Results and discussion

3.1. Crystal structures of the prepared intercalation compound

The two-dimensional layer structure of kaolinite crystals can accommodate organic molecules to form intercalation compounds. When the kaolinite was inserted with Ac, the distance between the layers will increase, which can be determined by XRD through the d_{001}-value directly. The XRD patterns of the kaolinite and its Ac intercalation compound (Kaol-Ac) are shown in Fig. 1. The typical pattern of the kaolinite exhibits a characteristic reflection with a d_{001}-value of 0.721 nm. When the kaolinite was inserted with Ac molecules, its d_{001}-value increased to 1.102 nm, which is consistent with the literature data (Frost et al., 1999, 2002). Noticeably, there was no evidence for crystalline acetamide in the X-ray diffractogram of Kaol-Ac, indicating that the only crystalline materials found within the matrix were kaolinite and Kaol-Ac. The intercalation rate of the compound was calculated to be 61.2% according to the formula, $IR = I_{(001)(c)} / [I_{(001)(c)} + I_{(001)(k)}]$ (Gardolinski et al., 2000b), where $I_{(001)(c)}$ is the intensity of the 001 reflection of the intercalate compound, and $I_{(001)(k)}$ is the intensity of the 001 reflection of kaolinite.

3.2. FTIR spectroscopy

FTIR spectra of the untreated and Ac intercalated kaolinites together with the spectrum of Ac in full spectral regions and several characteristic vibration regions are presented in Fig. 2. There was no residual un-intercalated acetamide in the final compound as indicated by the absence of characteristic infrared vibrations of pure acetamide in FTIR spectrum. These results are in agreement with the XRD results given above.

The presence of interlayer Ac was detected on the FTIR spectrum (Fig. 2A) by the C=O stretching at 1674 cm^{-1} and by the modification of the inner surface OH stretching mode (Farmer, 1974) at 3697, 3670 and 3651 cm^{-1} (Fig. 2B) due to interactions of the C=O groups in acetamide with the surface Al–OH group of the clay. The blue shift to 3701 cm^{-1} and decrease of the intensity of the band at 3697 cm^{-1} are related to the interaction of the inner surface hydroxyl with the C=O group in the acetamide molecule (Brindley and Brown, 1980). Clearly two new bands were observed in the FTIR spectra of the intercalated kaolinites at 3481 cm^{-1} and 3373 cm^{-1} (Fig. 2C). These bands are
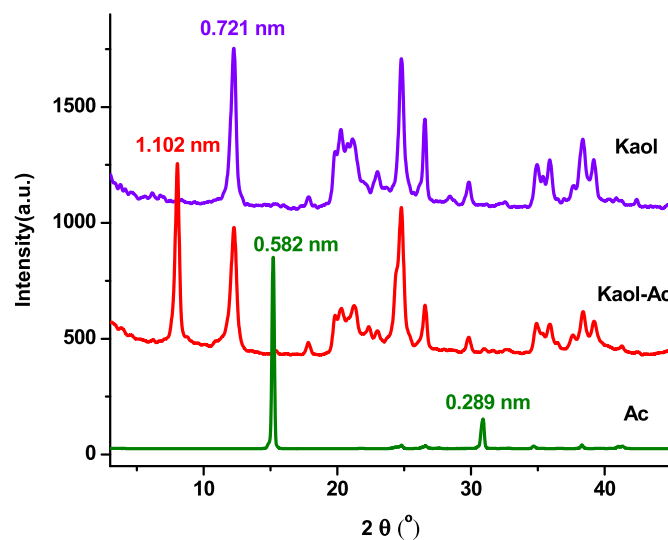

Fig. 1. XRD patterns of kaolinite (Kaol), acetamide (Ac) and kaolinite–acetamide (Kaol-Ac) intercalation compound.