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Stability of the compounds obtained by intercalating potassium acetate molecules into kaolinite from coal measures

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ABSTRACT

The intercalation compounds of kaolinite/potassium acetate were prepared by grinding and aging mixtures of potassium acetate and kaolinite from coal measures. The techniques of XRD, ICP-AES, IR, DSC, SEM and particle-size distribution analysis were used to characterize the microstructure and stability of the as-obtained intercalation compounds. The basal spacing increased from 0.72 nm for the raw kaolinite to 1.42 nm for the intercalation compound. The intercalation compounds were very stable in the anhydrous ethanol at room temperature, whereas deintercalation occurred when the as-obtained intercalation compounds were treated with water or heated at 296 °C.

1. Introduction

Kaolinite is a layered aluminosilicate with a 1:1 structure built from one tetrahedral silica sheet and one octahedral aluminium hydroxide sheet. The tetrahedral silica sheet and the octahedral aluminium hydroxide sheet are linked by oxygen atoms. Kaolinite has been widely used as hosts to prepare kaolinite/organic intercalation compounds since the 1960s [1]. Kaolinite/organic intercalation compounds have been extensively investigated due to their wide applications in scientific and industrial aspects such as in the delamination of kaolinite [2] and in the preparation of composites [3–6].

Potassium acetate [1,7–10], dimethylsulfoxide (DMSO) [10,11], urea [2,12,13], formamide [10] and hydrazine [10,14,15] are the commonly used intercalation reagents. Being low-molecular-mass polar compounds, they can be intercalated into the interlayer spaces of kaolinite directly. However, most organic compounds cannot be intercalated into kaolinite directly because they do not have suitable polarity and chemical properties. Based on this fact, the displacement technique has been developed to enable intercalation of alternative compounds into kaolinite. Intercalation is therefore obtained after the interlamellar structure of kaolinite is expanded through preintercalation of potassium acetate, DMSO, etc. The displacement can be carried out in water, ethanol and other solvents, or under a melting condition. Therefore, it is necessary to investigate the stability of kaolinite/organic intercalation compounds.

Many kinds of kaolinite all over the world have been utilized to prepare kaolinite/organic intercalation compounds. It is found that a lot of factors, including the type, the crystal structure and the particle-size of the kaolinite, can affect the intercalation reactions and the characteristics of the resultant intercalation compounds.

In China, kaolinite-rich rocks are widespread in the Permo-Carboniferous, late Triassic, Jurassic, early Cretaceous and Tertiary coal measures strata, especially in the Permo-Carboniferous. The deposits of the kaolinite-rich rocks from the coal measures are sedimentary in origin, and have some features that are uncommon in deposits elsewhere in the world. Most of them are grey hard rocks made of organic matter, and the content of the kaolinite mineral is up to ~90–95% in many good quality deposits in coal measures [16]. However, they are usually piled up on the ground as refuse derived from the mining or processing of coal, which pollutes the environment seriously. It is important to utilize the kaolinite-rich rocks from the coal measures from the point of view of the resources and environment protection.

Herein, intercalation compounds of kaolinite/potassium acetate are prepared using kaolinite-rich rocks (kaolin rocks) from the coal measures in China as the host material. The structures and the stability of the as-prepared intercalation compounds are investigated.

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2. Experimental procedure

Kaolin rock from coal measures of Datong coal district, Shanxi province, China, was used as the host material. It was a hard rock with grey color due to some included organic matter. After milling at Raymond mill, the kaolin powders had a particle-size distribution of less than 43 μm (325 mesh). Potassium acetate (analytically pure, ≥92%, the Regent Chemical Co., Ltd., Tianjin, China) was used as the guest reagent. Anhydrous ethanol (analytically pure, ≥99.7%) was obtained from Yantai Shuangshuang Chemical Co., Ltd., China. Distilled water was used in the experiment.

The intercalation process was carried out under ambient environmental conditions. Kaolin powder and potassium acetate, with a mass ratio of 1:1, were well ground and aged alternately in air and in mortar for 24 h. Then, a mushy mixture was obtained, due to the moisture absorption of potassium acetate. The mushy mixture was washed with anhydrous ethanol under magnetic stirring for 5 min. Then, solid particles were separated from the solution by centrifugation at 2500 rpm for 20 min using a TDZ5-WS benchtop low speed self balancing centrifuge (Changsha Xiangyi Centrifuge Instrument Co., Ltd., China). The resulting sample was dried at 60 °C for 8 h in the presence of air to remove the residual anhydrous ethanol. Finally, the kaolinte/potassium acetate intercalation compound (sample K–K) was obtained.

In order to investigate its stability, sample K–K was washed with water (sample K–KW) and with anhydrous ethanol (sample K–KA1) under magnetic stirring for 10 min, respectively. K–KA1 was washed with anhydrous ethanol for another 10 min (sample K–KA2), and then K–KA2 was washed with anhydrous ethanol for 30 min (sample K–KA3). Each sample was centrifuged and dried via the process mentioned above.

XRD analysis was carried out on a Panalytical Xpert-Pro diffractometer using CuKα radiation. The intercalation ratio (I.R.) was determined from the X-ray diffractograms using the following formula: $I.R.=(I_{(0\,0\,1)\text{compound}}/(I_{(0\,0\,1)\text{compound}}+I_{(0\,0\,1)\text{kaolinite}}))\times 100\%$ [17], where I was the integrate intensity of 001 peak of the intercalated compound and the origin kaolinite. IRIS-Intrepid ICP-AES (Thermo Fisher Scientific, USA) was used to analyze the potassium (K) content of all the samples. Infrared spectra of the powdered samples were recorded using a Nicolet 460 Fourier-transform infrared spectrometer (Nicolet, USA) with the scanning range between 4000 and 400 cm^{-1}. A STA 449C DSC/TG (Netzsch, Germany) was used to study desorption, melt, decomposition and combustion processes. DSC/TG curves of all samples were recorded under an air atmosphere from ambient temperature to 800 °C with a heating rate of 10 °C/min. The morphology of kaolinite particles was observed using a Quanta-200 scanning electron microscope (FEI, Holland). Samples were coated with a layer of gold film and the SEM images were obtained using a secondary electron detector. Using the laser method of particle-size analysis (Zetasizer 3000HS, Malvern), particle-size distribution of powder samples was measured for suspended particles in water for the water washed samples or in anhydrous ethanol for the anhydrous ethanol washed samples.

3. Results and discussion

Fig. 1 shows the XRD patterns of the raw kaolin and the intercalation compounds. The raw kaolin is mainly composed of kaolinite (JCPDF card no. 80-0886) with the Hinckley index of 1.18 [18], and no other minerals are identified in the pattern (Fig. 1(a)). The kaolinite/potassium acetate intercalation compound is prepared successfully, as the basal spacing increases from 0.72 nm for the raw kaolinite to 1.42 nm for the intercalated compounds (Fig. 1(b)). However, the weak 001 diffraction peak

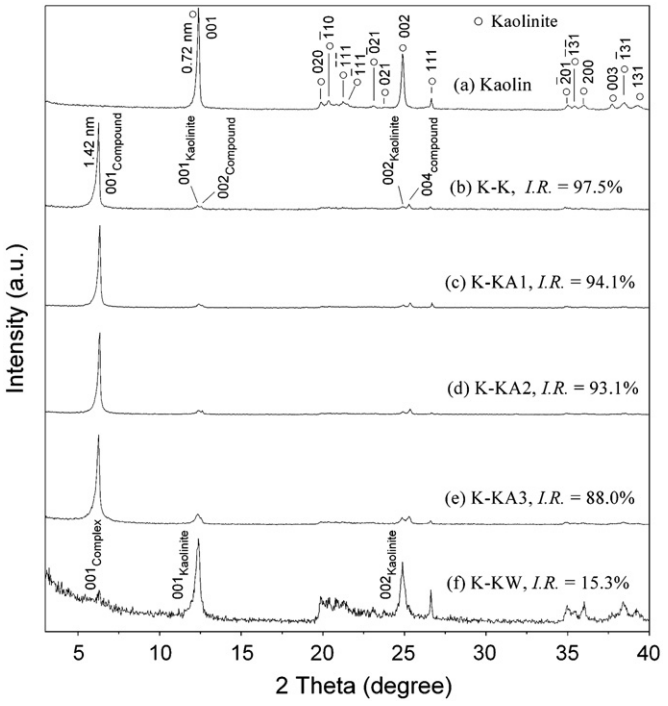

Fig. 1. XRD patterns of (a) the raw kaolin and (b)–(f) the intercalation compounds.

Table 1
Potassium contents of the raw kaolin and its intercalated compounds.

Sample	Raw kaolin	K–K	K–KW	K–KA1	K–KA2	K–KA3
K content (wt%)	0.19	9.18	2.83	6.75	5.50	5.03

of kaolinite appearing in the patterns indicates that a few kaolinite crystals were not intercalated. When washed with anhydrous ethanol for 5 min, the calculated *I.R.* of the K–K compound is 97.5%. After washing with anhydrous ethanol for 15, 25 and 55 min, the *I.R.* of the compounds is 94.1% (Fig. 1(c)), 93.1% (Fig. 1(d)) and 88.0% (Fig. 1(e)), respectively.

On the contrary, the *I.R.* value of the compound decreases rapidly from 97.5to 15.3%, when the samples are washed with anhydrous ethanol for 5 min and then with water for 10 min. The decrease in *I.R.* indicates the deintercalation of potassium acetate molecules from the interlayer spaces of kaolinite (Fig. 1(f)).

Table 1 gives the ICP-AES analysis results for the potassium contents of all the samples. The potassium content of the raw kaolin is 0.19 wt%. It increases to 9.18 wt% for sample K–K, confirming the intercalation of potassium acetate molecules into the interlayer spaces of kaolinite. The potassium content of the intercalated compounds decrease rapidly from 9.18 (K–K) to 2.83 wt% (K–KW) when K–K is washed with water for 10 min. The decreases in potassium content suggests the deintercalation of a large amount of potassium acetate molecules from the compound after washing with water. However, when sample K–K is washed with anhydrous ethanol for 10, 20 and 50 min, the potassium contents of K–KA1, K–KA2 and K–KA3 are 6.75%, 5.5% and 5.03%, respectively. This result indicates that the kaolinite/potassium acetate intercalation compound is more stable in anhydrous ethanol than in water, which is in accordance with the XRD results.

Figs. 2 and 3 present the Fourier-transform infrared (IR) spectra of the raw kaolin and the intercalated compounds. The raw kaolin exhibits all the four characteristic hydroxyl stretching vibration bands of kaolinite at 3694, 3670, 3651 and 3620 cm^{-1} (Fig. 2(a)). The three high frequency vibrations can be assigned to the