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Mechanism of dehydroxylation temperature decrease and high temperature phase transition of coal-bearing strata kaolinite intercalated by potassium acetate

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ABSTRACT

The thermal decomposition and dehydroxylation process of coal-bearing strata kaolinite–potassium acetate intercalation complex (CSKK) has been studied using X-ray diffraction (XRD), infrared spectroscopy (IR), thermal analysis, mass spectrometric analysis and infrared emission spectroscopy. The XRD results showed that the potassium acetate (KAc) have been successfully intercalated into coal-bearing strata kaolinite with an obvious basal distance increase of the first basal peak, and the positive correlation was found between the concentration of intercalation regent KAc and the degree of intercalation. As the temperature of the system is raised, the formation of $KHCO_3$, KCO_3 and $KAlSiO_4$, which is derived from the thermal decomposition or phase transition of CSKK, is observed in sequence. The IR results showed that new bands appeared, the position and intensities shift can also be found when the concentration of intercalation agent is raised. The thermal analysis and mass spectrometric analysis results revealed that CSKK is stable below 300 °C, and the thermal decomposition products (H_2O and CO_2) were further proved by the mass spectrometric analysis. A comparison of thermal analysis results of original coal-bearing strata kaolinite and its intercalation complex gives new discovery that not only a new mass loss peak is observed at 285 °C, but also the temperature of dehydroxylation and dehydration of coal bearing strata kaolinite is decreased about 100 °C. This is explained on the basis of the interlayer space of the kaolinite increased obviously after being intercalated by KAc, which led to the interlayer hydrogen bonds weakened, enables the dehydroxylation from kaolinite surface more easily. Furthermore, the possible structural model for CSKK has been proposed, with further analysis required in order to prove the most possible structures.

1. Introduction

Kaolinite-rich mineral deposits are very abundant in the Permo-Carboniferous coal-bearing strata of North China and are widely used [1–3]. It was found that kaolinite usually existed in the upper part of sedimentary cycle, deposited vertically, which was formed in the hydrodynamic environment from strong to weak [4]. Some deposits have high carbon content and form hard minerals. The majority of coal measures in Northern China contain the industrial kaolinite rocks. Therefore, this kind of kaolinite is called as coal-bearing strata kaolinite (CSK), and the main mineral compound is kaolinite. The color of CSK is rather dark, varying from light gray to gray black to almost completely black [1,5].

The kaolinite intercalation and its application in polymer-based functional composites have attracted great interest, both in industry and in academia fields, since they frequently exhibit remarkable improvements in materials properties compared with the virgin polymer or conventional micro- and macro-composites [6–8]. The intercalation can increase the usability of kaolinite reserves especially CSK. This is due to intercalation can improve the particle size and whiteness or brightness of kaolinite. Therefore, its intercalation complexes are widely used in the fabrication of paper, paints and inks, rubber and plastic, fiberglass, cracking catalysts, cosmetics, medicines, etc. [9–11]. It is useful because of their high specific surface area, chemical and physical stability, and surface structural properties [12]. Various inorganic and organic species can be used in the intercalation of kaolinite into its interlayer spaces, such as formamide [13], dimethylsulfoxide [14], urea [15], potassium acetate [16], aniline [17] and hydrazine [18]. Potassium acetate (KAc) has been shown to readily intercalate within the kaolinite structure [19,20]. Also of significant interest regarding the kaolinite–potassium acetate complex is its thermal behavior and decomposition [19]. This is because heating treatment of intercalated kaolinite is necessary for its further application, especially in the field of plastic

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Table 1
The minerals composition of CSK used in this experiment.

Sample	Content of minerals (%)		
	Kaolinite	Quartz	Illite
Coal bearing strata kaolinite	95	3	2

and rubber industry. Our recent findings showed that the onset of dehydroxylation occurs at a lower temperature than that for nonintercalated kaolinite [21–23]. Meanwhile, the more recent literature [19] also indicated that the kaolinite intercalated by KAc lead to dehydroxylation at somewhat lower temperatures than for the original kaolinite. However, to date there have been few reports regarding the temperature decrease and process interpretations of dehydroxylation for kaolinite intercalation complex.

More recently, there has been increased research on molecular simulation studies on the intercalation of simple molecules in kaolinite [19,24,25]. This is because molecular simulations allow a more detailed interpretation of the experiments and might provide findings that can hardly be derived from experimental data. Although the exact structure of the kaolinite–KAc intercalation complex remains largely unknown, detailed and accurate thermal analysis can be used to furnish evidence or information on the structure of kaolinite–KAc intercalation complex. Therefore, it is very urgent and necessary for the researchers to study on the mechanism of dehydroxylation and thermal decomposition process for kaolinite intercalated by KAc.

This paper, based on authors' previous work [22,23], reports the thermal decomposition process and dehydroxylation mechanism of coal-bearing strata kaolinite–KAc intercalation complex (CSKK) using X-ray diffraction (XRD), infrared transmission and emission spectroscopy and thermal analysis-mass spectrometric analysis. The purpose of the present study is to make clear the dehydroxylation mechanism and high temperature phase transition for CSKK or kaolinite–KAc intercalation complex and provide novel structural insight regarding the structural model of the intercalation complex.

2. Experimental

2.1. Materials

The raw materials used in this work are tonstein, which are kaolinite claystone of volcanic origin found as partings in coal seams of Permo-Carboniferous strata in Datong coal mines from Shanxi province in North China, with size of 45 μm. The beds of tonstein are ~0.5 m thick and are widespread in the coal-bearing strata of the Datong coalfield. The kaolinite content in the rocks is up to 95% with a Hinckley index of 1.10 and the quality is very good for industrial use (Table 1). Its chemical composition in wt% is SiO_2 48.69, Al_2O_3 34.34, Fe_2O_3 0.35, MgO 0.09, CaO 0.11, Na_2O 0.02, K_2O 0.38, TiO_2 0.74, P_2O_5 0.15, MnO 0.059, loss on ignition 15.07. The potassium acetate (A.R) was purchased from Beijing Chemical Reagents Company, China.

2.2. Intercalation reaction

CSKK-5, CSKK-15, CSKK-30 and CSKK-50 were prepared by immersing 10 g of CSK in 20 ml of KAc solution at concentrations of 5%, 15%, 30% and 50%, respectively. The samples were shaken for 2 h at room temperature. The intercalation complexes after aging for 24 h were allowed to dry at room temperature before the XRD, infrared transmission and emission spectroscopy and thermal analysis-mass spectrometric analysis. Only the samples (CSK and CSKK-30) were heated in oven at 500, 600, 700, 800, 900, 1000 and 1100 °C for 4 h before the XRD analysis.

2.3. Characterization

2.3.1. X-ray diffraction (XRD)

The XRD patterns of the prepared samples were performed using a Rigaku D/max 2500PC X-ray diffractometer with Cu (λ = 1.54178 Å) irradiation at the scanning rate of 2°/min in the 2θ range of 2.6–70°, operating at 40 kV and 150 mA.

2.3.2. Thermal analysis-mass spectrometric analysis

The simultaneous thermogravimetry and differential scanning calorimetry (TG-DSC) measurements were carried out by a Mettler-Toledo TG-DSC I/1600 HT simultaneous thermal analyzer in a flowing nitrogen atmosphere (100 ml/min), about 30 mg of samples underwent thermal analysis with a heating rate of 5 °C/min from room temperature to 1200 °C.

The thermal analysis instrument was coupled to a Balzers (Pfeiffer) mass spectrometer (MS) for gas analysis. Only water vapor, carbon dioxide, carbon and oxygen were analyzed. In the MS figures, e.g. Fig. 6, a background of broad peaks may be observed. This background occurs for all the ion current curves. The background becomes more prominent as the scale expansion is increased. It is considered that this background may be due to the loss of chemicals which have deposited in the capillary which connects the thermal analysis instrument to the MS.

2.3.3. Infrared spectroscopy (IR)

Fourier-transform infrared spectroscopy was undertaken by a Thermofisher Nicolet 6700 spectrometer. The samples were prepared at potassium bromide (KBr) pellets (ca. 2% by mass in KBr). The infrared spectra of prepared samples between 400 and 4000 cm^{-1} were recorded.

2.3.4. Infrared emission spectroscopy

Infrared emission spectroscopy was carried out on a Nicolet Nexus 870 Fourier-transform infrared 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 [26,27]. Approximately 0.2 mg of CSKK 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 CSKK sample and is placed on the graphite rod. An insulated 125-μm type R thermocouple was embedded inside the 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 by 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.