



Research paper

The molecular structure of kaolinite–potassium acetate intercalation complexes: A combined experimental and molecular dynamic simulation study



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ABSTRACT

The kaolinite (Kaol) intercalated with potassium acetate (Ac) was prepared and characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and thermogravimetry. Molecular dynamic simulation was performed to investigate the structure of Kaol–Ac intercalation complex and the hydrogen bonds between Kaol and intercalated Ac and water using INTERFACE forcefield. The acetate anions and water arranged in a bilayer structure in the interlayer space of Kaol. The potassium cations distributed in the interlayer space and strongly coordinated with acetate anions as well as water rather than keyed into the ditrigonal holes of tetrahedral surface of Kaol. Strong hydrogen bonds formed between the hydrogen atoms of hydroxyl on the octahedral surface and oxygen atoms of both acetate anions and water. The acetate anions and water also weakly bonded hydrogen to the silica tetrahedral surface through their hydrogen atoms with the oxygen atoms of silica tetrahedral surface.

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1. Introduction

Kaolinite (Kaol) is an important industrial material having wide-spread application e.g. in the manufacturing of paper, inks and paints, as well as in the production of rubber and polymers as an additive (Kristóf et al., 1999; Franco et al., 2004). Kaol is commonly used for the production of clay-based nanocomposites that exhibit unexpected hybrid properties such as enhanced mechanical, thermal, dimensional and barrier performance properties, and flame retardant characteristics. Especially, one of the most commonly studied systems to date is the intercalation of synthetic polymers within layered aluminosilicates. While being intercalated within the inorganic structure, organic polymers naturally reduce their structural mobility and some of them assume a highly organized conformation within the layered structure. In this way, it is possible to produce clay polymer nanocomposites that usually present unique properties if compared to the corresponding properties of the isolated starting materials and/or their mechanical blends (Gardolinski et al., 2000a,b). The composite of Kaol intercalated by organic molecules have gained much attention over the last decades,

essentially making the clay into a single layered mineral (Franco and Ruiz Cruz, 2004; Franco et al., 2004; Gardolinski, 2005; Gardolinski and Lagaly, 2005a,b). The inserting molecule breaks the hydrogen bonds formed between the Kaol hydroxyl groups and the oxygens of the next adjacent siloxane layer, then forms hydrogen bonds with either the hydrophobic surface of the Kaol (the siloxane layer) or the hydrophilic part of the Kaol surface (the hydroxyl surfaces of the gibbsite-like layer). A further possibility exists in that the inserting or adsorbing molecule may interact with the end surfaces of the Kaol (Frost et al., 1999).

Compared to the intercalation by formamide, DMSO, urea, and their derivatives, there are more debates on the mechanism of the intercalation by potassium acetate (Ac). This is especially true regarding the layer structure and arrangement of intercalated Ac in the interlayer space of Kaol. Previous researches on the supposed molecular structure of kaolinite–potassium acetate (Kaol–Ac) intercalation complex were based on the X-ray diffraction (XRD) and Fourier transform infrared spectroscopic analysis (FTIR) analysis together with the geometrical structure of Ac, and no unanimous conclusion was generated. The paper of Wada (1961) was the first investigation to propose the possible structural arrangement of Ac between Kaol layers. The potassium was keyed into the ditrigonal holes of tetrahedral surface of Kaol, and water formed a monolayer between the acetate ions located at the middle position of interlayer space and hydroxyl groups of octahedral surface of Kaol. However, contradicted to Wada's proposal, Kristóf et al. (1993) reported that the potassium was hydrated by intercalated water and distributed

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randomly in the interlayer space of Kaol based on the FTIR study of Kaol intercalated with Ac. The molecular structure of Kaol intercalation complexes is hardly investigated by the commonly used experimental techniques. Molecular dynamic simulation have been proven to be an effective way for probing into the molecular structure at an atomistic scale, and have made a great contribution to the research field of functional material and drug design. In recent years, molecular dynamic simulation has been brought in the investigation of interface between clay minerals and organics, and demonstrated its utility in the microstructural investigation (Teppen et al., 1997, 1998; Heinz et al., 2003; Zeng et al., 2003; Heinz and Suter, 2004b; Zeng et al., 2004; Heinz et al., 2006b). Lots of researches on molecular dynamic simulation of clay minerals were mainly focused on the montmorillonite and its related intercalation compounds with surfactant (Zeng et al., 2004; Skipper et al., 2006; Aggarwal et al., 2007; Cygan et al., 2012; Zhao and Burns, 2012; Zhu et al., 2012). To the best of our knowledge, there is little information about the molecular dynamic simulation of Kaol–Ac intercalation complex.

Due to the extensive use of Kaol in industrial processes and its excellent feature for the preparation of organic/inorganic nanocomposites, the intercalation of Kaol has gained increasing interest both in industrial field and academic field. In the present study, molecular dynamic simulations and experimental measurements (XRD and FTIR analysis) were used to investigate the structural properties of Kaol–Ac intercalation complex.

2. Experimental methods and simulations

2.1. Materials

The Kaol used in the present study was naturally pure Kaol with the size of 45 μm from Zhangjiakou, Hebei Province, China. The chemical composition of the sample in mass % was: SiO_2 , 44.64; Al_2O_3 , 38.05; Fe_2O_3 , 0.22; MgO , 0.06; CaO , 0.11; Na_2O , 0.27; K_2O , 0.08; TiO_2 , 1.13; P_2O_5 , 0.13; MnO , 0.002; and loss on ignition, 15.06. The major mineral constituent was a well-ordered Kaol (95%) with a Hinckley index of approximately 1.31. All reagents were purchased from Xilong Chemical Company, Ltd. (China) in purities of at least 98% and used without further treatment.

2.2. The intercalation complex preparation

The Kaol–Ac intercalation complex was prepared by immersing 10 g of Kaol in 20 mL of Ac solution at a mass percentage concentration of 30%. The samples were shaken for 2 h at room temperature. The complex was allowed to dry at room temperature before the TG–DTG, XRD and FTIR analysis.

2.3. Characterization

The powder X-ray diffraction (XRD) analysis was performed using a Japan Rigaku D/max-rA X-ray diffractometer (40 kV, 100 mA) with Cu ($\lambda = 1.54178 \text{ \AA}$) irradiation at the scanning rate of $4^\circ/\text{min}$ in the 2θ range of $2.6\text{--}50^\circ$.

Fourier transform infrared (FTIR) spectroscopic analysis was undertaken using a NICOLET 750 SX spectrometer. FT-IR spectra between 400 and 4000 cm^{-1} were obtained. The samples were prepared at KBr pellets (ca. 2% by mass in KBr).

The simultaneous TG–DTG measurements were carried out in a Mettler-Toledo TG–DSC I/1600 HT simultaneous thermal analyzer, under the flowing nitrogen atmosphere (100 mL/min). About 30 mg of sample was placed into alumina crucibles and heated from room temperature to 1100°C at a heating rate of $5^\circ\text{C}/\text{min}$.

2.4. Models and simulations

The unite cell of Kaol with the chemical composition of $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ was built as a basic cell for the present simulation work based on the data of Young and Hewat (1988). The unit cell exhibits P1 symmetry with the following lattice parameters: $a = 0.515 \text{ nm}$, $b = 0.893 \text{ nm}$, $c = 0.738 \text{ nm}$, $\alpha = 91.93^\circ$, $\beta = 105.04^\circ$, and $\gamma = 89.79^\circ$. Then the supercell composed of 16 ($4 \times 4 \times 1$) unite cells with a total of 544 atoms was constructed. The corresponding overall sizes of the supercell in a and b dimensions are 2.060 nm and 3.574 nm, respectively. To simulate the Kaol/Ac + water interface, an aqueous box having the same size as that of Kaol supercell in a and b dimensions and containing 12 Ac molecules and 131 water molecules was constructed. Then the Ac and water aqueous box was sandwiched between two Kaol supercells by build layer tool to create the initial Kaol/Ac + water interface. The molar ratio of Ac molecules to water molecules in this study was determined based on the study carried out by Kristóf et al. (2002). Although the mass loss of thermal decomposition of the samples in this study can be obtained readily according to the thermal analysis, no clear break in the slope of TG curves was observed when interlayer Ac and associated water were deintercalated upon heating. Consequently, it is challenging to discriminate the decomposition process of interlayer water from that of Ac, which make the calculation of intercalated Ac and water in mass difficult. A recently developed INTERFACE forcefield (Heinz et al., 2005, 2012), in this simulation case, was adopted, which have already proven itself quite successful in describing many inorganic–organic and inorganic–bimolecular interfaces in quantitative agreement with available experimental data (Heinz and Suter, 2004a,b; Heinz et al., 2006a,b; Fu and Heinz, 2010; Heinz et al., 2012).

The MD simulations were carried out employing the Forcite program (Material Studio) (Zhu et al., 2012). The Kaol/Ac + water complex system were geometrically optimized through energy minimization prior to performing simulations. To calculate the d -value of complex system, MD simulation was performed using an isothermal–isobaric (NPT) ensemble, where the pressure and temperature were controlled by the Nose thermostat (Nosé, 1984) and Berendsen barostat (Berendsen et al., 1984), respectively. In this simulation step, the total simulation time is 300 ps, in which the first 100 ps run was for the system equilibrium, and the last 200 ps production run were used for d spacing calculation. In order to derive the structural and dynamic properties of complex systems, subsequently, a further NVT with a period of 300 ps was performed following the previous 300 ps NPT simulation. The starting frame of the NVT simulation was that obtained from the last frame of the NPT simulation. All simulations in the present study, periodic boundary conditions were applied in three dimensions. The velocity Verlet algorithm with a time step of 1 fs was used to integrate the particle motion. The trajectory frame was recorded every 20 fs. The long-range electronic interactions were calculated by the Ewald summation method, and the van der Waals interactions were calculated using Lennard-Jones potential. During the simulations, all particles of the simulation systems were allowed to move freely in three dimensions.

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns show that the basal $d_{(001)}$ of Kaol expands from 0.71 to 1.42 nm; the increment of 0.71 nm in d -value of Kaol indicates the intercalation of Ac in the interlamellar space (Fig. 1), which is similar to the results published before (Frost et al., 1998b; Deng et al., 2002; Franco and Ruiz Cruz, 2004; Cheng et al., 2010b,d,e). The (020), ($\bar{1}10$), ($\bar{1}\bar{1}1$), ($\bar{2}01$), ($\bar{1}\bar{3}1$) (200), (003), ($\bar{2}02$), and (131) reflection of original Kaol in the middle- 2θ and high- 2θ regions almost disappear, suggesting that the well crystallized Kaol suffered structural degradation after the intercalation action (Frost and Johansson, 1998; Frost

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