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Intercalation of dodecylamine into kaolinite and its layering structure investigated by molecular dynamics simulation

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ABSTRACT

Dodecylamine was successfully intercalated into the layer space of kaolinite by utilizing the methanol treated kaolinite–dimethyl sulfoxide (DMSO) intercalation complex as an intermediate. The basal spacing of kaolinite, measured by X-ray diffraction (XRD), increased from 0.72 nm to 4.29 nm after the intercalation of dodecylamine. Also, the significant variation observed in the Fourier Transform Infrared Spectroscopy (FTIR) spectra of kaolinite when intercalated with dodecylamine verified the feasibility of intercalation of dodecylamine into kaolinite. Isothermal-isobaric (NPT) molecular dynamics simulation with the use of Dreiding force field was performed to probe into the layering behavior and structure of nanoconfined dodecylamine in the kaolinite gallery. The concentration profiles of the nitrogen atom, methyl group and methylene group of intercalated dodecylamine molecules in the direction perpendicular to the kaolinite basal surface indicated that the alkyl chains within the interlayer space of kaolinite exhibited an obvious layering structure. However, the unified bilayer, pseudo-trilayer, or paraffin-type arrangements of alkyl chains deduced based on their chain length combined with the measured basal spacing of organoclays were not found in this study. The alkyl chains aggregated to a mixture of ordered paraffin-type-like structure and disordered gauche conformation in the middle interlayer space of kaolinite, and some alkyl chains arranged in two bilayer structures, in which one was close to the silica tetrahedron surface, and the other was close to the alumina octahedron surface with their alkyl chains parallel to the kaolinite basal surface.

1. Introduction

Orgnoclays, generally defined as organic modified clays, are widely applied in various industries due to their special modified surface characters, including the rheological controlling of paints and greases, selective absorption for toxic pollutants, preparation of polymer nanocomposites, etc. [1,2]. Orgnoclays are usually synthesized through intercalation of clays with organic surfactants, which results in the transition of clay surface from hydrophilic to organophilic. Thus, the modified clays are able to disperse into the polymer matrix to generate novel polymer/clay nanocomposites, which exhibit significantly improved properties on tensile strength, thermostability, barrier performance, and flame retardance compared to those pristine polymers. Layered solids such as clay minerals have been proven to be an ideal host material for the synthesis of orgnoclays by intercalating with organic surfactants in the form of liquids, melts, or concentrated solutions. In previous studies, smectite groups of clay minerals have been investigated extensively as hosts because of their attractive features on swelling behavior, large surface area, and cationic exchangeability [3–10]. Kaolinite, a layer silicate mineral, consists of nanometer thick layers formed by stacking an aluminum octahedron sheet and a silicon tetrahedron sheet along the direction perpendicular to its (001) crystal plane. Unlike montmorillonite, the crystalline network of kaolinite is practically devoid of isomorphic substitutions, so it does not require charge compensation of hydrated interlayer cations, thus, it lacks the expansion behavior and the exchangeable cations in its interlayer pace. In addition, the layers in kaolinite are held together by hydrogen bonds, dipole–dipole interactions, and van der waals forces. These characteristics cause the intercalation of kaolinite with guest molecules to be difficult. However, a limited number of high polar organic species such as urea [11,12], dimethyl sulfoxide [13], formamide [14], hydrazine [15], and potassium acetate [16–19] have been

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validated that they can be successfully intercalated into the kaolinite gallery. Those intercalated derivatives can serve as a precursor for preparing kaolinite-surfactant organoclays, but which are hard to prepare through displacing the preintercalated small molecules with organic surfactants in a direct replacing intercalation method, while a process usually called indirection method has been applied for preparations of several kinds of kaolinite-based organoclays [20–25]. Compared with montmorillonite, Kaolinite presents excellent performance when used as nanofiller in the fabrication of polymer/clay nanocomposites due to its perfect layer structure, less impurity, and substantial deposits in China. Understanding the structure of organoclays and the interaction between kaolinite and surfactants is of significance in design and characterization of polymer/clay nanocomposites. So far, XRD is the most common used technique to determine the layered structure and orientation of intercalated species, which has been applied by Kuroda et al. [24] and Gardolinski et al. [23] to study the structure of kaolinite–alkylamines intercalation compounds. Based on the relation between their basal spacings and the length of alkyl chains, they inferred that the alkyl chains were fully stretched (all-trans conformation) and perpendicular to the basal plane surface, and arranged in a bilayer between the kaolinite layers. Although various structural models have been proposed for the intercalated surfactant, significant structural characteristics of the surfactants, i.e. trans and gauche conformations have not been directly revealed. Molecular dynamics simulation has proven to be an effective technique for a further insight into the structural characteristics in the nano-confined environment. To date, only a few MD simulation studies about the intercalation of kaolinite with some small molecules have been reported [26–28]. As far as we know, almost no investigations on modeling macromolecular surfactants intercalated into the kaolinite gallery have been reported.

In this study, the intercalation of kaolinite with dodecylamine was investigated by using the X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). In addition, molecular dynamics simulation was employed to probe the layer behavior and interlayer structure of dodecylamine confined between the layers of kaolinite at a molecular level. The atomic density profiles and configuration of alkyl chains were produced and discussed.

2. Experimental

2.1. Materials

The kaolinite used in the present study was natural pure kaolinite with the size of 45 μm from Zhangjiakou, Hebei Province, China. The chemical composition of the sample in mass% was as follows: 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 kaolinite (95 mass%) 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. Preparation of kaolinite intercalation complex

The kaolinite intercalation complex with dodecylamine was prepared by the indirect intercalation reaction mentioned above. Firstly, intercalation complex with dimethylsulfoxide (DMSO) as the first intermediate was prepared by adding 50 g kaolinite into a closed container that contained 90 ml DMSO and 10 ml deionized water. The mixture was stirred with the magnetic stirrer at 60 °C for 12 h, and then the suspension was separated by centrifugation with ethyl alcohol. Secondly, after drying the prepared DMSO intercalated samples for 24 h at 60 °C, then dispersing 5 g dried DMSO intercalated samples in 120 ml methanol for preparing the methanol-treated kaolinite. The reaction mixture was stirred with the magnetic stirrer for ten days at room temperature, and the methanol was refreshed every day. Lastly, the dodecylamine intercalation complex was prepared by stirring the mixture of dodecylamine, methanol, and wet methanol-treated kaolinite at 40 °C for 24 h. After centrifugation, the products were dried at room temperature and analyzed by XRD and FTIR.

2.3. Characterization

The XRD analyses of the prepared samples were carried out on a Rigaku D/max 2500PC X-ray diffractometer (Japan) with Cu (λ = 1.54178 Å) irradiation at the scanning rate of 2 °/min operating at 40 kV and 150 mA. The original kaolinite, kaolinite–DMSO intercalation complex, kaolinite–methanol intercalation complex, and crystalline dodecylamine were scanned in the 2θ range of 2–45°, and the kaolinite–dodecylamine intercalation complex was scanned in the 2θ range of 1–45°.

FTIR was performed on a Thermofisher Nicolet 6700 spectrometer (USA). The FTIR spectra of the prepared samples were obtained within the range of 400–4000 cm^{-1} in KBr pellet form (2 mg sample in 300 mg KBr).

2.4. Models and simulation details

Based on the data of Young and Hewat [29], the unite cell of kaolinite with the chemical composition of $A1_4Si_4O_{10}(OH)_8$ was built as a basic cell for the simulation. The unit cell exhibited P1 symmetry with the following lattice parameters: a = 0.515 nm, b = 0.893 nm, c = 0.738 nm, α = 91.93°, β = 105.04°, and γ = 89.79°. The periodic MD simulation supercell consisted of 16 ($4 \times 4 \times 1$) unite cells with a total of 544 atoms was created. The supercell has an overall size of a = 2.060 nm, b = 3.574 nm. All dodecylamine molecules were packed in a cubic box with the lengths a and b matching pretty well with the constructed supercell of kaolinite. Thus they could be stacked upon each other to form a kaolinite–dodecylamine complex system for the following simulations. The Dreiding force field was adopted for these simulations, which was successfully used in the simulations of mineral–organic interfaces by previous studies [2,30]. The partial charges of atoms in kaolinite framework were adopted directly from the studies by Fang et al. [26]. The atomic charges of dodecylamine were assigned by a charge equilibration method [31].

The MD simulations were carried out employing Forcite program (Material Studio 4.1; Accelrys, San Diego, CA, USA) [32] on the supercomputer. All simulations were performed in the NPT ensemble for 500 ps with the pressure fixed at 0.1 Mpa and the temperature fixed at 298 K. The first 200 ps run were chosen to ensure that the system reached equilibrium, and the last 300 ps run were used to collect data for later analyses. 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. Temperature and pressure were maintained by using the Nose thermostat and Berendsen barostat, respectively. During the simulations the Cartesian position of atoms of kaolinite was constrained in the x and y direction, but all atoms of dodecylamine molecules were allowed to freely move.

3. Results and discussion

3.1. XRD analysis

Fig. 1a represents the typical XRD pattern of raw kaolinite with a (001) reflection peak of 0.72 nm at low 2θ side, and a (002)