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Variation of interlayer binding energy of muscovite in its swelling

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ABSTRACT

The interlayer binding energy of natural muscovite after thermal and ionic exchange treatments has been investigated using X-ray diffraction, molecular dynamics simulation and one-dimensional Patterson function. The results showed that the interlayer binding energy was reduced to less than 1/30th of its strength subsequent to thermal and ionic exchange treatments. The decrease of the binding strength after thermal treatment might be due to the modification of atomic positions within the layer and a slight increase of interlayer spacing. A dramatic decrease of the binding strength from 110.05 kJ/mol to 19.09 kJ/mol was observed after the $LiNO_3$ treatment. The mechanism might be explained by a combination of an increase of interlayer spacing and Li^+ immersion into the layers. In addition, interlayer spacing was increased to 3 nm when octadecyl trimethyl ammonium ion (OTA^+) intercalation was used, resulting in the interlayer binding energy approaching 0 kJ/mol.

1. Introduction

Muscovite is a 2:1 layered silicate. Several layers together form a particle. The layers are built of an octahedral sheet, sandwiched between two Si-O sheets [1]. The Si-O tetrahedral sheet is connected at the vertices with the oxygen atoms to form a coplanar hexagonal lattice. A hydroxyl group at the center of each hexagon gives rise to a triangular lattice providing the bottom face of the $AlO_4(OH)_2$ octahedron. An inverted Si-O tetrahedral sheet is then attached to the top face of these octahedrons to complete the muscovite layer [2]. The binding between the muscovite layers has electrostatic and van der Waals interactions [3]. The origin of the ionic binding is from the substitution of Si^{4+} and Al^{3+} in the layers by low-charge cations that gives the silicate layers a negative charge and attracts K^+ in the interlayers to balance the negative charge [4]. It has been reported that the binding energy between the adjacent layers of 6.02×10^{23} muscovite molecules is 134 kJ [5], which tightens the interlayer strongly. Therefore, cleaving natural muscovite into individual layers is difficult.

The exfoliation of muscovite could be realized through applying strong external forces or modifying the interlayer structure. Mechanical forces, for example grinding [6], are important external forces. Ultrasonic treatment has been used to separate adjacent layers. Caseri et al. indicated that the specific surface area of muscovite determined by methylene blue (MB) adsorption was increased from 3.4 m^2/g to more than 100 m^2/g after ultrasound cleavage of muscovite in a $LiNO_3$ solution [7]. Another method is to heat muscovite up to 800 °C, followed by adding it immediately to a saturated Na_2CO_3 or $NaHCO_3$ solution and neutralizing the mixture by HCl [8]. It is believed that in the presence of acid, CO_3^{2-} or HCO_3^- penetrates into the interlayers. The muscovite layers are then separated by the pressure of the evolved CO_2. Commercially, this method can produce muscovite particles with a thickness of about 130 nm, corresponding to approximate 130 silicate layers. However, the methods fail in producing nanoscale particles because the binding strength is intimately related to the ability of muscovite exfoliation and the quality of resulting particles.

In our previous paper, we presented a novel method for the exfoliation of natural muscovite into monolayers. It consists of swelling the interlayers through thermal treatment followed by ionic exchange to reduce the interlayer binding strength, and then exfoliation with ultrasound [9,10]. The key to achieve the exfoliation is to modify the bonds in the interlayer structure. Therefore, it is of great significance to understand the variations of interlayer binding energy when the natural muscovite is swollen, in order to optimize the thermal and ionic exchange treatments.

In this study, we attempted to investigate the variations of interlayer binding energy in muscovite using the molecular dynamics (MD) simulation, X-ray diffraction (XRD) and the one-dimensional (1D) Patterson function. The MD simulation was used to obtain muscovite structure after each treatment, while XRD was

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used to determine the basal spacing of muscovite. The peaks in the 1D Patterson function represent the interatomic distance vectors, which provide a good description of the distance between atom planes. The interlayer spacing and atomic positions after the thermal and ionic exchange treatments were then calculated and the binding energy was obtained. The objective was to obtain a better understanding of the exfoliation mechanisms of natural muscovite.

2. Methods

2.1. Determination of interlayer binding energy

The interlayer binding energy (IBE) is defined as the energy difference between a single crystal and one which has been cleaved, exposing two open surfaces [5,11], as shown in Eq. (1):

$$IBE = E_{layer1} + E_{layer2} - E_{total} \quad (1)$$

where E_{layer1} and E_{layer2} are energies of two layers, while E_{total} is the energy of the crystal before being separated. The lattice energy E consists of the attraction terms caused by the Coulomb and van der Waals interactions and nonelectrostatic repulsion term. The value of the Coulomb energy can be readily calculated from Eq. (2) [12]

$$U = -\frac{e^2}{2}\sum_{j=1}^{N}\sum_{i=1}^{\infty}\frac{k \cdot z_i z_j}{r_{ij}} \times 10^7 \quad (2)$$

where U is the Coulomb energy, kJ; k is the factor to convert the unit of U, 9.0×10^9 N•m^2/C^2; N is the number of atoms in the unit cell; Z is the valence of the ion; r is the interionic distance, Å; and e is electrical charge, 1.6×10^{-19} C; 10^7 is 10^{-3} divided by 10^{-10} because the unit of U and r is in kJ and Å, respectively. The Lennard-Jones expression is most commonly used to approximate the van der Waals interactions and nonelectrostatic repulsion, as shown in Eq. (3) [13]

$$V_{LJ} = \varepsilon\left[\left(\frac{r_m}{r}\right)^{12} - 2\left(\frac{r_m}{r}\right)^{6}\right] \quad (3)$$

where ε is the depth of the potential well, kJ/mol; r is the distance between the atoms, Å; and r_m is the distance at which the potential reaches its minimum, Å. The atomic positional parameters are the prerequisites in calculating the IBE according to Eqs. (1)–(3). Accordingly, in this work, these parameters can be obtained through a combination of molecular dynamics (MD) simulation, XRD and 1D Patterson function, followed by computing IBE with the above equations using the software of *Materials Studio* (MD) *6.0*.

2.2. Muscovite swelling

The natural muscovite sample (termed M) used in this work for swelling tests was collected from Liaoning Science Co., Ltd, China. The XRD pattern shown in Fig. 1 indicated that the main composition of the sample was monoclinic muscovite 2M1, without any other impurities being determined. The inductively coupled plasma atomic emission spectroscopic and thermogravimetric analysis showed that the chemical formula of one muscovite molecule in the natural sample was $(K_{0.81}Na_{0.09})(Mg_{0.05}Fe_{0.17})(Si_{3.04}Al_{2.65}Rb_{0.01}Ti_{0.01})O_{10}(OH)_{1.5}$. Therefore, one mole natural muscovite has 6.02×10^{23} of the above muscovite molecules.

The muscovite swelling tests were carried out in three steps: (1) the muscovite powder (M) was roasted at 750 °C to obtain the calcinated product (M750); (2) the M750 was further treated in molten lithium nitrate ($LiNO_3$) at 300 °C to exchange all K^+, yielding a product of Li-M750; (3) the Li-M750 was finally treated in the saturated octadecyl trimethyl ammonium chloride (OTAC) solution to insert large molecules into the interlayers to obtain the product OTA-M750. The details of the experimental method were described in our previous publication [10].

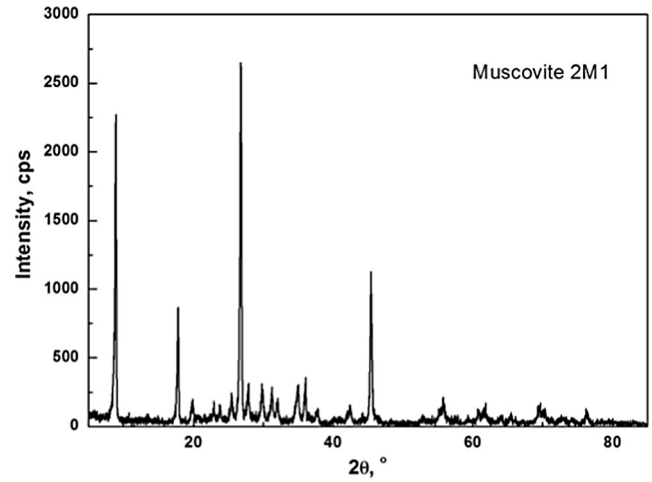

Fig. 1. The XRD pattern of the natural muscovite sample.

The chemical reagents used in this work were all of analytical grade, purchased from Sinopharm Chemical Reagent Co., Ltd, China. Ultrapure Milli-Q water was used throughout.

2.3. Measurements

The elemental analysis of muscovite was performed using the PerkinElmer Optima4300DV ICP.

Mineral phase and structure changes before and after treatments were determined using a Bruker D8 Advance X-ray diffractometer with Cu K_α radiation. The diffraction patterns, ranging from 5° to 80° (2θ), were collected with a step-scanning speed of 10°/min, while small-angle diffraction patterns from 1° to 10° (2θ) were collected with a step-scanning speed of 1°/min.

FT-IR measurements were conducted using a Thermo Scientific Nicolet 6700 FT-IR spectrometer, with the pellets being prepared by pressing a mixture of 1–2 mg of the sample and 200–300 mg of dried KBr.

2.4. Molecular dynamics simulation

Muscovite has a monoclinic space group *C2/c* [14]. The original muscovite model was based on the structure defined in Guggenheim's work [15]. The lattice parameters were $a = 0.52$ nm, $b = 0.9021$ nm, $c = 2.007$ nm, and $\beta = 95.71°$ and the atom positional coordinates are shown in Table 1, where no atom substitution is listed. The perfect structure model of muscovite was built with software *Materials Studio 6.0* by importing the space group, lattice parameters and atom positional coordinates. It is common that substitution occurs in the natural sample; therefore, based on the chemical formula obtained in this study, two tetravalent Si atoms and one trivalent Al atom were substituted by two Al atoms and one divalent Fe atom, respectively. After that, the energy of the structure was minimized by the Discover Module using the *Materials Studio 6.0* software. The lattice parameters ($a = 0.5217$ nm, $b = 0.9185$ nm, $c = 2.022$ nm, $\beta = 95.75°$) and atom positions of dehydroxylated muscovite (Li-M750) were given by Gridi-Bennadji et al. [16] (shown in Table 1), according to which the structure of dehydroxylated muscovite was built with *Materials Studio 6.0*. The same Al/Si and Fe/Al substitutions took place in the dehydroxylated muscovite as in the original. In the interaction simulation of $LiNO_3$ into dehydroxylated muscovite, a dehydroxylated muscovite model was cut parallel to the (*010*) direction to