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Influence of interlayer cations on organic intercalation of montmorillonite

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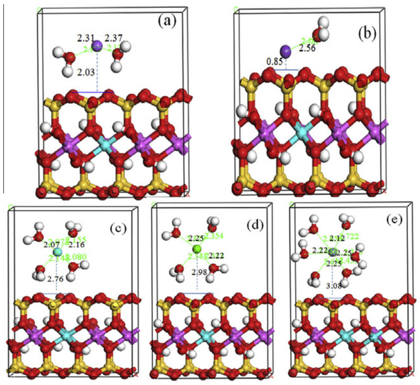
GRAPHICAL ABSTRACT



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ABSTRACT

The influence of the types of interlayer cations on organic intercalation of montmorillonite (Mt) was studied in this paper. The distribution of Na^+, K^+, Mg^{2+}, Ca^{2+} and Fe^{3+} in montmorillonite interlayer, their interaction with structure layers and the effect of interlayer cations on the basal spacing of Mt, the amount of binding water for different interlayer cations and the binding force between them were investigated systematically. 1-Hexadecy1-3-methylimidazolium chloride monohydrate (C_{16}mimCl) was intercalated into montmorillonites with different interlayer cations. The influence of interlayer cations on organic intercalation was investigated. Molecular dynamics (MD) modeling was used to speculate the interlayer microstructures of the organically intercalated Mt with different interlayer cations. These simulations help to predict the microstructure of organo-Mt and guide their relevant engineering applications.

1. Introduction

Montmorillonites (Mts) are clay minerals with regular layer structure composed of octahedral sheet between two tetrahedral sheets. Intercalating organic and inorganic species into layered host materials has drawn researchers' increasing interests. It is an effective way to construct ordered inorganic–organic and inorganic–inorganic assemblies with unique microstructures and properties [1,2]. The Mts have attractive features, such as large surface area, swelling behavior, adsorption and ion exchange properties [3,4]. The Mts have been extensively used as the host materials

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and the other possible applications such as catalysis, separation, delivery and storage [5–11] because of their attractive properties and ability to accommodate various kinds of organic and inorganic guest species [12]. The intercalated nano-sized Mt particles (dimension of a single layer is 0.6–1 nm) are ideal dispersing additives for the synthesis of organic–inorganic hybrid nano-composites to enhance mechanical, thermal and chemical stabilities. The composites have been applied into the fields of plastic, paint, petroleum engineering, etc. [12–19]. Most of these Mt-based materials take advantages of their specific laminar structures in which a variety of ions, molecules and polymers can be adsorbed [20–24]. These properties can be affected directly by the types of cations in the interlayer of Mt.

Interlayer hydrated cations are mainly stabilized by electrostatic interaction, and they could be exchanged by other cations in solution. The species of interlayer hydrated cations would affect interlayer spacing, surface area, adsorption, swelling, dispersion, and crystal stability and other properties of Mt. The common cations in the interlayer of Mt are Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, etc. Certain difference in properties can be expected in Mt with different interlayer cations. Recently, utilization of computer simulation on study of clay material like Mt has attracted more and more interest due to its possibility in providing micro-view on structure and properties and layed ground for experimental work. Cations in the interlayer of Mt, such as Li^+, Na^+ and K^+, are hydrated, so the spacing of Mt is actually a function of water content. With different types of interlayer cations, their distribution, hydration and diffusion properties in the interlayer of Mt are different [25–27]. For example, swelling property of Mt depends on the size and charge of the interlayer cations. The behaviors of Li^+, Na^+ and K^+ in the interlayer of Mt are significantly different, especially for their interaction with the sheet. Li^+ and Na^+ hydrate more easily than K^+, so they can be separated from the silicon oxygen tetrahedral surface of Mt. On the other hand, K^+ is close to Mt's layer sheet and bound to the surface of silicon oxygen tetrahedra. So far, most of the studies on Mt have been focused on the hydration of interlayer cations, interlayer structure and swelling property, etc. Few have been done to reveal the relationship between organic intercalation and the type of interlayer cations.

Molecular modeling recently has been recognized as an efficient method for understanding the interlayer microstructure of clay minerals [28–33]. In molecular dynamic simulation, energy of the system is an important parameter to represent the stability of montmorillonite with different interlayer cations and their difficulty in ion exchange. A higher total energy of interaction means a better distribution in the interlayer space and more combining water. However, lower electrostatic energy will leading to weaker interaction with structure sheet, more easily exchanged by other cations. In montmorillonite, the energy involved is mainly non-bonded energy, including mostly Van der Waals energy and some other energie like coulomb's force, angle torsion interaction and bond stretching. During the molecular dynamic simulation, except for slightly increase in energy caused by structure distortion, all the other bonding energy and non-bonding energy decreased in varying degrees, especially for bonding energy and Van der Waals energy.

In the present paper, we investigated in details the nature of the exchangeable interlayer cations (Na^+, K^+, Mg^{2+}, Ca^{2+} and Fe^{3+}) in montmorillonite and its influence on organic intercalation. Properties of montmorillonite with different interlayer cations were studied systematically. The content of binding water molecules for interlayer cations and the force between them, the distribution of cations in the interlayer and the interaction between interlayer cations and structure layers were investigated from a microcosmic view.

2. Materials and methods

2.1. Materials

The montmorillonite(Mt) used was obtained from the Clay Mineral Repositories in Purdue University (West Lafayette, IN) without further purification. It has a chemical formula of $(Ca_{0.12}\ Na_{0.32}\ K_{0.05})[Al_{3.01}\ Fe(III)_{0.41}\ Mg_{0.54}][Si_{7.98}\ Al_{0.02}]O_{20}(OH)_4$, a Cation exchange capacity (CEC) of 85 ± 3 $mmol_c$/100 g [34], a layer charge of 0.32 eq/mol per $(Si,Al)_4O_{10}$ [35], an external surface area (ESA) of 23 m^2/g [36], and a mean particle size of 3.2 μm with a d_{25} to d_{75} in the range of 3–10 μm.

2.2. Methods

The homoionic Mt samples were generated from exchanging the interlayer cations of the Mt with Na^+, K^+, Ca^{2+}, Mg^{2+}, and Fe^{3+} to produce, Na-Mt, K-Mt, Mg-Mt, Ca-Mt, and Fe-Mt. Weigh a certain amount of Mt, mix them with water to from slurries. Weigh NaCl, KCl, $CaCl_2$, $MgCl_2$, and $FeCl_3{\cdot}H_2O$ at 3 times of Mt CEC and dissolve them in water. Mix the slurry and the solution separately, and then stir the mixture at 60 °C, hooding for 30 min. The supernatant was rejected and the clay mineral was washed repeatedly until the chloride level was not measurable.

The initial 1-Hexadecy1–3-methylimidazolium chloride monohydrate (C_{16}mimCl) concentrations varied from 10 to 5000 mg/L for the adsorption isotherm study. The mass of Mt used was 0.2 g while the volume of solution used was 25 mL for all studies except the kinetic study. The solid and solution were combined in each 50 ml centrifuge tube and shaken for 2 h at 150 rpm and room temperature for all studies except the kinetic study. After the mixtures were centrifuged at 10,000 rpm for 20 min, the supernatants were filtered through 0.22 μm syringe filters before being analyzed for equilibrium C_{16}mimCl concentrations.

The equilibrium C_{16}mimCl concentrations were analyzed by a UV–Vis spectrophotometer (Model T6 New Century 1650, made by General Instrument, Inc. LLT, Beijing China) at the wavelength of 210 nm, corresponding to its maximal absorbance. Calibrations were made using standards of 10, 20, 30, 40, 50, and 60 mg/L with a regression coefficient of 0.9998. The amount of adsorbed C_{16}mimCl was calculated from the difference between the initial and final concentrations.

The exchangeable cations desorbed were determined by atomic absorption on a Perkin Elmer AAnalyst-100 Atomic Absorption Spectrometer (Waltha, MA, USA). In the ammonium acetate method, Na^+, K^+, Ca^{2+}, Mg^{2+} and Fe^{3+} ions were exchanged by small ammonium cations (NH_4^+) which is more intimate to the Mt. It used a solution of ammonium acetate in excess to assure that all cations were exchanged. The dispersion of the Mt in 1 M ammonium acetate solution was shaken overnight. It was filtered in a Buchner funnel. If the filtrate was not clear, it was passed again through the filter. After that, the Mt was washed four times with 25 mL ammonium acetate. Then, the Mt was washed with eight separate aliquots of ethanol to remove the excess cations. The calibration was made using seven standard solutions with concentrations from 0.2 to 3.0 mg/L for K^+, Na^+, and Mg^{2+}, 1.0 –25.0 mg/L for Ca^{2+}, and 0.5–20.0 mg/L for Fe^{3+}. The detection wavelengths were 766.5, 589.0, 285.2, 422.7, 248.3 nm with a detection limit of 0.01, 0.006, 0.06, 0.04, and 0.06 mg/L for K^+, Na^+, Mg^{2+}, Ca^{2+}, and Fe^{3+}, respectively. The relative standard deviation is 0.2%.

Powder XRD analyses were performed on a Rigaku D/max-IIIa diffractometer (Tokyo, Japan) with a Ni-filtered Cu Kα radiation at 30 kV and 20 mA. Orientated samples were scanned from 1° to 10° at 2°/min with a scanning step of 0.01°. Powder samples were packed in horizontally held trays. The changes in the XRD peak