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Organic intercalation of structure modified vermiculite

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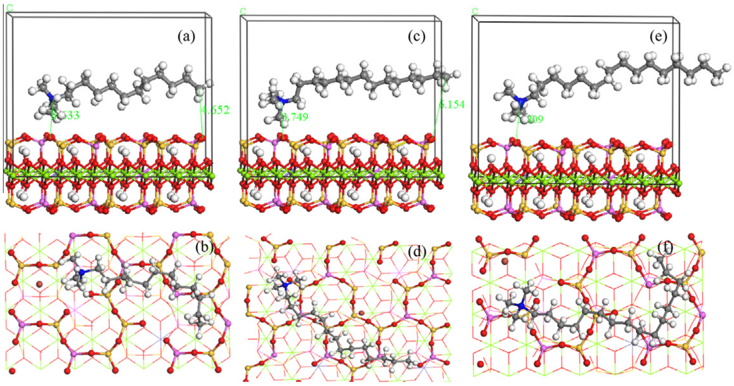
GRAPHICAL ABSTRACT

Interlayer organics align almost parallel to structure sheet of vermiculite, with alkyl chain stretching to the middle of gallery.



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ABSTRACT

The experiment used cationic surfactants of different chain lengths to intercalate structure modified vermiculites. The influences of structure modification, chain length and dosage of surfactants on the intercalation behavior of vermiculites were studied, and intercalation mechanism and features of interlayer chemical reactions were discussed. Results indicate that structure modified vermiculites with different layer charge have different intercalation behavior. The basal spacing of the organic intercalated modified vermiculite is the largest when acid concentration used in structure modification is 0.003 mol/L, and increases with increasing the chain length and dosage of the organics. Molecular dynamics simulation verifies that interlayer organics align almost parallel to structure layer of vermiculite, with alkyl chain stretching to the middle of interlayer space. –N^+ groups of the three surfactants locate above the leached [SiO_4], which has stronger interaction with interlayer organic cations. Electrostatic force is the main interaction force between interlayer organics and structure layer of vermiculite, and then is Van der Waals force, no chemical bond formed.

1. Introduction

Vermiculite is one kind of 2:1 type layered structural aluminum silicate minerals, which has water molecules and exchangeable cations in the interlayer space [1]. The structural unit of vermiculite is composed of two opposing tetrahedral [SiO4] layers and one [MgO6] and/or [FeO6] octahedral layer in between, which is about 1 nm in thickness and stacks periodically in *c* axis to form the vermiculite crystal [2,3]. The interlayer space of vermiculite, characterized by ion exchange, adsorption

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etc., provides a good place for chemical reactions [4–5]. Organic or inorganic species can be introduced into vermiculite interlayer space by physicochemical method, such as ion exchange, adsorption, pillaring and intercalation, resulting in the change of vermiculite properties. Previous study [6] shows that physicochemical properties, like adsorption ability, of vermiculite were improved greatly after the above modifications, which widens the application of vermiculite.

Because of isomorphous replacement in the tetrahedral and octahedral layers, which resulting in a residual negative charge of the structure unit, natural vermiculite has charge balancing inorganic cations, like Na^+, Ca^{2+}, Mg^{2+}, and water molecules in the interlayer space, which can be mutually exchanged or exchanged by organic cations [7–9].This feature of vermiculite makes it possible for organic species to be intercalated into the interlayer space, obtaining organic vermiculite. The electric charge of vermiculite sheet, which affects its interaction with interlayer cations, can be changed by structural modification. In one of our previous studies, we modified the vermiculite structure by leaching in HCl with different concentrations [10]. Results indicate that Si, Al, Mg, Fe, Ca etc. were leached out from the structure and Si in tetrahedral was leached out prior to Al and other ions, which resulted in the increase of the layer charge of vermiculite. The increment of layer charge is proportional to the acid concentration used in the structure modification.

Vermiculites with different layer charge should have different organic intercalation behavior. This study is to investigate the organic intercalation behavior of structure modified vermiculites with different layer charges which were prepared by acid leaching. Three surfactants with different chain lengths, dodecyl trimethyl ammonium bromide (DTAB), tetradecyl trimethyl ammonium bromide (TTAB) and cetyl trimethyl ammonium bromide (CTAB), were used to intercalate the structure modified vermiculites. By XRD and TG-DTA analyses and contact angle measurement, the influences of structure modification, the chain length and dosage of surfactants on organic intercalation of vermiculite are studied. Then, molecular dynamics simulation is carried out to reveal the configuration of surfactants in the interlayer space and the interactions between them and the structure layer of vermiculite, which helps to understand the organic intercalation mechanism of structure modified vermiculite [11].

2. Materials and methods

2.1. Materials

The vermiculite used was purchased from Lingshou, Hebei province, P.R.China. Its main phases are vermiculite, vermiculite-mica mixed layer mineral, and a small amount of mica, hornblende, etc. Purified raw vermiculite, mainly composed of vermiculite and vermiculite-mica mixed layer mineral (which are very difficult to separate) (Fig. 1), was obtained after sedimentary separation, natural drying, machine grinding and 200-mesh sieving. It is a vermiculite with Mg as main interlayer cation and made of SiO_2 37.46%, Al_2O_3 14.19%, MgO 11.42%, K_2O 1.83%, Fe_2O_3 13.07%, CaO 3.47%, FeO 0.8%, TiO_2 1.51% and H_2O 7%.

The purified raw vermiculite was structure modified by leaching in hydrochloric acid of different concentrations (0.003 mol/L, 0.01 mol/L, and 0.1 mol/L). The leaching process includes mixing of 3 g vermiculite in 100 mL HCl of certain concentration, stirring for 1 h at 70 °C, centrifuging, washing with distilled water for 3 times, then natural drying in air for 48 h.

Three alky ammonium ions with the same structure of nitrogen headgroup but varying chain length (DTAB, TTAB, and CTAB) were used as the intercalating agents.

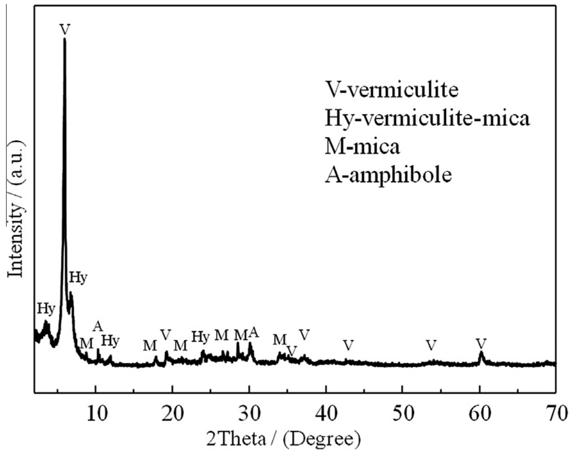

Fig. 1. X-ray diffraction patterns of vermiculite raw material.

These hydrochloric acid (CAS#: 7647-01-0), dodecyl trimethyl ammonium bromide (CAS#: 1119-94-4), tetradecyl trimethyl ammonium bromide (CAS#: 1119-97-7), cetyl trimethyl ammonium bromide (CAS#: 57-09-0) were purchased from Shanghai Hualen Chemical Technology Co. Ltd (purity > 99%).

2.2. Methods

5 g of raw vermiculite or structure modified vermiculite were put into erlenmeyer flasks (about 80 g distilled water inside), then stirred at 60 °C in water bath. A certain amount of intercalating agents (DTAB, TTAB, CTAB) were dissolved in 120 mL distilled water, then moved in twice (once a half)into the flask with vermiculite dispersion. The mixtures were stirred for 2 h, stand for 2 h, then centrifuged and washed until no Br^- ion was detected. The centrifugates were dried at low temperature to get organic intercalated vermiculite samples.

Powder X-ray diffraction (XRD) analyses were performed on a Rigaku D/max-IIIa diffracto meter (Tokyo, Japan) with a Ni-filtered CuK radiation at 30 kV and 20 mA. Orientated samples were scanned from 3° to 20° at 2°/min with a scanning step of 0.01°. Powder samples were packed in horizontally held trays. The changes in the XRD reflection positions reflect the size of the hydrated metal cations and organic cations in the interlayer of vermiculite.

Thermo gravimetric (TG) analyses were carried out on TGA Q-500 (TA Instruments, New Castle, USA) from room temperature to 800 °C, at a heating rate of 10 °C/min under a nitrogen flow of 60 mL/min. TG curves were used to determine the content of mass loss. Differential scanning calorimetry (DSC) was performed using a differential scanning calorimeter (TA Instruments Q100) fitted with a cooling system using liquid nitrogen. It was calibrated with an indium standard. Samples of 6 mg of vermiculite were accurately weighed into aluminum pans, sealed and then heated from 30 to 800 °Cat 10 °C/min under a nitrogen flow of 60 mL/min.

The water contact angle (CA) and sliding angle (SA) were measured at ambient temperature with a SL200B apparatus from ZhongChen Digital Equipment Co. Ltd., Shanghai. The CAs reported here were the mean values measured with a ca. 5 μL water droplets at five different positions on each sample. The samples used were shaped into a circle piece using a tablet machine under 15 MPa at room temperature.

2.3. Computation details

Molecular simulation was performed under the module 'CASTEP' of Materials Studio 6.0 software to investigate the