

Surface Modification of Montmorillonites by Chlorosilanes

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Montmorillonite was modified by chlorosilane derivatives (trimethylchlorosilane and *tert*-butyldimethylchlorosilane) based on the reaction between OH group and chlorosilane. Fourier-transformed infrared spectra (FTIR) confirmed that chlorosilanes did react with the OH groups of montmorillonite. The effect of reaction time and dispersing agents on the intercalation was studied by wide angle X-ray diffraction (WAXD) method. Further experiments proved that there is no reactive OH group on the surface of layers in the interlayer galleries of montmorillonite. The cation exchange capacity (CEC) of montmorillonites was measured, showing that after modification by chlorosilane derivatives, CEC values drastically decreased. The dispersibility measurements of montmorillonites were conducted, which showed that the dispersibility of modified montmorillonites both in H₂O and toluene were improved due to the decrease of attractions of particles and layers.

Keywords montmorillonite, chlorosilane, modification, dispersibility

Introduction

Clays play important roles in the fields of petrochemical engineering, materials, pharmacy, coatings, cosmetics, environmental protection, *etc.* There are different ways to modify clays, such as, molecular adsorption,¹ polymer encapsulation,² ion exchange with organic ammonium cations³ or organic phosphonium cations,⁴ modification by organic polyions,⁵ acidification,⁶ chemical grafting with silane coupling agents⁷⁻¹⁰ or chlorosilanes.^{11,12} After modification, clays exhibit special properties, including the decreased attraction of particles¹ and the increased degree of hydrophobization.⁷ Owaga *et al.*^{11,12} have studied the modification of magadiite (Na₂Si₁₄O₂₉ · nH₂O). Magadiite was ion-exchanged with quaternary ammonium salt firstly, and then reacted with chlorosilanes. Solid-state ²⁹Si nuclear magnetic resonance and Fourier-transformed infrared spectra indicated that the chlorosilanes were grafted on the surface of magadiite. Elemental analysis and X-ray diffraction showed the deintercalation of quaternary ammonium salt during the process of silylation.

Montmorillonite is known for its high cation exchange

capacity (CEC), good swellability and high specific surface area. It is a layered silicate, the crystal structure consists of a 2:1 layer formed by one Al—O octahedral sheet sandwiched within two Si—O tetrahedral sheets, and the layer thickness is approximately 1 nm. Stacking of these layers leads to vander Waals' gaps or galleries. The galleries (also referred to as interlayers) are occupied by exchangeable cations, typically Na⁺ and/or Ca²⁺, which balance the charge deficiency due to the isomorphous substitution of partial Si⁴⁺ and Al³⁺ by lower-valent metal ions. Because of the existence of ionic bonds and ability to form hydrogen bond with H₂O, montmorillonite exhibits high hydrophilicity. However, it was demonstrated by the Toyota group¹³ that via ion exchange with alkylammonium surfactants, the surface of montmorillonite changed from a hydrophilic to a hydrophobic one, and could be compatible with the hydrophobic polymer matrix to fabricate polymer-layered silicate nanocomposites. These nanocomposites afford the superior properties as compared to those of conventional polymer-inorganic composites.¹⁴⁻¹⁷

Although the coordinated OH groups of Al—O octahedral sheet wrapped by Si—O tetrahedral sheets are non-reactive, there are a few OH groups at the edges of layers that can act as anchoring groups to modify montmorillonite. In an earlier study, covalently bonded organic moieties were formed in the interlayer regions by treating protonated montmorillonite with triethoxysilane derivatives,¹⁸ but whether or not there are reactive OH groups on the surface of layers in the interlayer galleries of montmorillonite is under dispute.¹⁹ In this paper, montmorillonite was modified by chlorosilane derivatives. Special experimentation was designed for investigating if there are OH groups on the surface of layers in the interlayer galleries of montmorillonite. Modified montmorillonites were characterized by wide angle X-ray diffraction (WAXD) and Fourier-transformed infrared spectra (FTIR). The cation exchange capacity (CEC) values of the montmorillonites were measured, and their results of dispersibility in H₂O and toluene were compared and discussed.

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Experimental

Materials

Na-montmorillonite (MMT, Zhangjiakou Qinghe Chemical Factory, China) was dried for 8 h at 100 °C in vacuum before used. Chlorosilane derivatives, trimethylchlorosilane ((CH₃)₃SiCl; industrial-grade; abbreviated as TMSCl), *tert*-butyldimethylchlorosilane ((CH₃)₃CSi-(CH₃)₂Cl; industrial-grade; abbreviated as TBDMSCl) and intercalating agents, sodium chloride (A. R.), and ammonium chloride (A. R.) were purchased from Beijing Chemical Reagent Corporation and used as received. Dispersing agents, 1,4-dioxane (A. R.), toluene (A. R.) and ethanol (A. R.) were used without further purification; acetone (A. R.) was dried by anhydrous MgSO₄, and then distilled before use.

Preparation

MMT (10 g) and chlorosilane derivative (12 g) were mixed and refluxed in the dispersing agent (100 mL) under agitation. Except for the samples used for investigating the effect of reaction time on the intercalation, the fixed reaction time was 36 h. The products were filtered and washed with acetone for two times, then washed with 95% ethanol until no Cl⁻ was detected by AgNO₃ (0.1 mol/L) solution. The products were dried for 8 h at 100 °C *in vacuo*, and then ground into powder (diameter about 40–70 μm) to get silylated montmorillonites (samples of MMT modified by TMSCl in acetone and toluene, by TBDMSCl in dioxane and toluene for 36 h were marked as TMA, TMT, TBDO and TBT, respectively).

TMA (3 g) was treated with 60 mL NaCl (2.0 g/L) ethanol solution at 75 °C for 3 h under agitation, and then filtered. Such treatment was repeated for 6 times in total. The final product was washed with 95% ethanol until no Cl⁻ was detected by AgNO₃ (0.1 mol/L) solution, dried for 8 h at 100 °C in vacuum, then ground into powder (diameter about 40–70 μm) to get TMA-Na.

Measurements

Wide angle X-ray powder diffraction (WAXD) pattern was obtained using a Rigaku D/max 2400 diffractometer and Cu Kα radiation (λ = 0.154 nm, 40 kV, 120 mA) at room temperature. The diffractograms were scanned from 3° to 30° in the 2θ range in 0.02° steps, scanning rate was 8 (°)/min. Infrared spectra of KBr disks were recorded on a Perkin-Elmer System 2000 Fourier-transform infrared spectrometer.

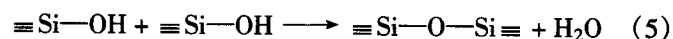
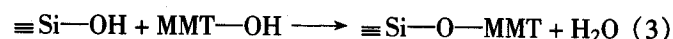
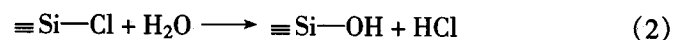
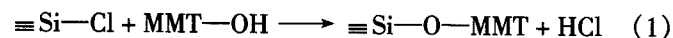
Cation exchange capacity (CEC) values of montmorillonites were measured using NH₄Cl as intercalating agent by the method described by Peech.²⁰

Dispersibility experiments were performed by putting 0.100 g sample and 10 mL dispersing agent (de-ionized water or toluene) into the tube with a 10 mL scale accu-

rately, then ultrasonic dispersing for 4 h. After being laid aside for 48 h, the dispersibility results were observed and recorded.

Results and discussion

There were reactive OH groups at the edges of montmorillonite layers, and dried montmorillonite also contained a small amount of water, which could react with chlorosilanes as follows:



Chlorosilane derivatives were grafted on the montmorillonite via the reactions (1) and (3).

During the process of reaction, there had HCl detected by pH indicator paper at the outlet of condenser tube. Fig. 1 showed the WAXD patterns of MMT modified by TMSCl in acetone for different reaction time. With the reaction time increasing, the (001) plane diffraction peak shifted to lower angle. There was a tendency towards larger interlayer spacing. At the initial stage of the reaction, diffraction peak became wider and wider with the reaction time prolonged, but after 24 h, the diffraction peak became narrower. This can be explained by that at the initial stage of reaction, some interlayers of montmorillonite had been intercalated, but others had not, so the interlayer spacings were non-uniform, the diffraction peak became wider; after a given reaction time (24 h), the majority of the interlayers had been intercalated, the interlayer spacings became uniform, corresponding diffraction peak became narrower.

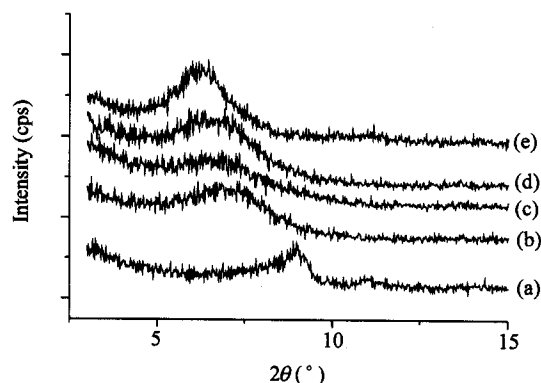


Fig. 1 WAXD of the MMT modified by TMSCl in acetone for (a) 0 h, (b) 6 h, (c) 12 h, (d) 24 h and (e) 36 h.

Fourier-transformed infrared spectra for silylated and unmodified montmorillonites were compared, and the results are shown in Fig. 2. The sharp band at 3620 cm^{-1} was the stretching vibration of isolated OH group (not forming hydrogen bond), and the band at 3440 cm^{-1} was the stretching vibration of OH group formed hydrogen bond.²¹ After silylation, the adsorptions at 3620 and 3440 cm^{-1} weakened, and the new bands at 2925 and 2855 cm^{-1} appeared that belong to the characteristic adsorptions of methyl group. The results indicated that the chlorosilane derivatives reacted with the OH groups of montmorillonite successfully.

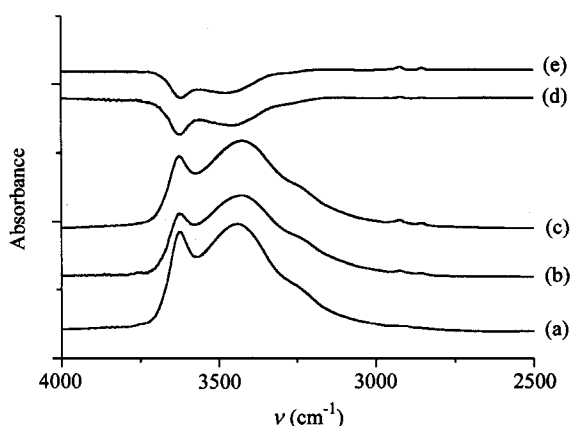


Fig. 2 FTIR and differential spectra of montmorillonites. (a) MMT, (b) TMA, (c) TBDO, (d) TMA-MMT and (e) TBDO-MMT.

The above results indicated that chlorosilanes reacted with OH groups of montmorillonite and something had been intercalated into the interlayer galleries, but what was the intercalated component remained unclear. In order to investigate this subject, TMA was treated with NaCl ethanol solution. Fig. 3 shows the WAXD difference between TMA before and after treated with NaCl ethanol solution. After treated with NaCl, the (001) plane diffraction peak of TMA came back to the position almost identical to that of MMT. This indicated that the intercalated component almost completely deintercalated from the interlayers during the process of NaCl treatment. The intercalated component and the montmorillonite layers were not combined by a covalent interaction but by a physical one. It showed that there is no reactive OH group on the surface of layers in the interlayer galleries of montmorillonite. The final intercalated component could not be chlorosilanes or silanols, but should be dimmer of them (siloxane) because chlorosilanes and silanols are very reactive, just as reactions (4) and (5).

The interlayer spacings of montmorillonites are given in Table 1. After silylated in polar dispersing agents (acetone, dioxane), the interlayer spacing was increased to 1.41 (TMA) and 1.40 nm (TBDO) from 0.99 nm (MMT), increased 0.42 and 0.41 nm respectively. This just corresponded to the thickness of dimer of TMSCl and TBDMSCl lay flatly into the interlayers, indicating that

dimer of chlorosilane derivatives had successfully intercalated into the interlayers of montmorillonite and arranged in a single layer. But in apolar dispersing agent (toluene), the interlayer spacing increased to 1.33 (TMT) and 1.27 nm (TBT), increased 0.34 and 0.28 nm respectively, less than the thickness of dimer of TMSCl and TBDMSCl, demonstrated that dimer of chlorosilane derivatives intercalated only into a part of interlayers of montmorillonite. The polarity of dispersing agents was in favor of the intercalation of montmorillonite.

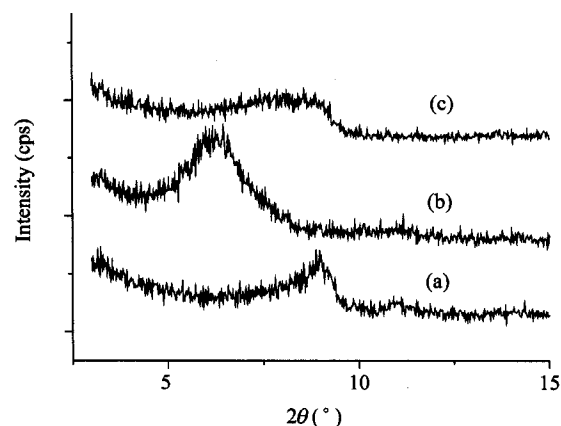


Fig. 3 WAXD patterns of (a) MMT, (b) TMA and (c) TMA-Na.

Table 1 Interlayer spacings and CEC values of montmorillonites

Sample	MMT	TMA	TBDO	TMT	TBT	TMA-Na
d001 (nm)	0.99	1.41	1.40	1.33	1.27	1.03
CEC (mmol/100 g)	89	42	46	60	56	58

Table 1 also gave the CEC values of MMT and modified montmorillonites. Compared with MMT, the CEC values of silylated montmorillonites had drastically decreased. Protonation or loss of hydroxyl groups decreases the anionic charge of smectites.²² After modification by chlorosilane derivatives, partial OH groups had lost, CEC values decreased. The CEC value of TMA was less than the value of TMA-Na, it is probably because the intercalated component of TMA overlapped the partial Na^+ and affected the ion exchange with NH_4^+ . In polar dispersing agent, the degree of both OH groups be reacted and the intercalation were higher, corresponding CEC values were less.

The dispersibility and swellability are two important properties of montmorillonite in dispersing agents. Table 2 shows the dispersibility measurements of MMT and silylated montmorillonites in H_2O and toluene. In H_2O , because of the intrinsic hydrophilic property and the effect of charge repulsion, MMT exhibited good dispersibility. But it was interesting that the dispersibility of silylated montmorillonites in H_2O became better. After modification by chlorosilane derivatives, the loss of hydroxyl groups at the edges of montmorillonite layers decreased the attraction be-

tween the montmorillonite particles, and attraction between layers was also decreased due to the reduce of the anionic charge and increase of the interlayer spacing. However, the hydrophilicity of silylated montmorillonites were not changed greatly because the amount of grafted alkyl chains was little. Their dispersibility in H₂O became better. The cloudy supernatants observed in the experiment were colloid solutions, and Tyndall phenomena were clearly observed. This showed that the particles of silylated montmorillonites were dispersed exiguously. In toluene, MMT exhibited worse dispersibility, and the volume was no swelling. After modification by chlorosilane derivatives, the particles' and layers' attraction were decreased, but their hydrophilicity was not changed distinctly, their dispersibility in toluene was also bad, merely the volumes were swelling. Whether the silylating reagents (TMSCl or TBDMSCl) or the dispersing agents (polar or apolar) was used in the modification reaction, the dispersibility result of silylated montmorillonite had no apparent difference. This indicated that under the experimental conditions in this paper, the key factors affecting the dispersibility are the particles' and layers' attraction and the characterization of hydrophilicity or hydrophobicity of corresponding montmorillonite. It was probably because although the degree of OH groups being reacted and the intercalation were different, particles' and layers' attraction of silylated montmorillonites and their hydrophilicity changed insignificantly. Corresponding investigations still need to be further studied.

Table 2 Dispersibility of montmorillonites in H₂O and toluene^a

Sample	MMT	TMA	TBDO	TMT	TBT
Agent					
H ₂ O	+	++	++	++	++
Toluene	-	+-	+-	+-	+-

^a - : Worse dispersibility, supernatant is clear, lower sample is no swelling. +- : Bad dispersibility, supernatant is clear, lower sample is swelling. + : Good dispersibility, supernatant is cloudy and non-uniform, lower sample is swelling. ++ : Better dispersibility, supernatant is cloudy, but uniform, lower sample is swelling.

Conclusion

Montmorillonite was modified by chlorosilane derivatives. After silylation, chlorosilane derivatives reacted with OH groups at the edge of Montmorillonite layers, dimer of them intercalated into the interlayer galleries. There is no

reactive OH group on the surface of layers in the interlayer galleries of montmorillonite. The CEC values of silylated montmorillonites were drastically decreased, and their dispersibility in H₂O and toluene was improved.

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