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Organic modification of synthesized clay-magadiite

Sea-Fue Wang *, Ming-Liang Lin, Yaw-Nan Shieh, Yuh-Ruey Wang, Shea-Jue Wang

Department of Materials and Mineral Resources Engineering, National Taipei University of Technology,
1, Sec. 3, Chung-Hsiao E. Rd., Taipei, Taiwan, ROC

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Abstract

A synthesized magadiite has been organically modified by *n*-hexadecyl trimethyl-ammonium bromide (CTAB), and then grafted by γ-aminopropyltriethoxysilane (APTS). The formation of the CTAB-magadiite was confirmed by XRD, which the basal spacing increases from 1.54 to 2.46 mn. The formation of the organic derivatives of magadiite was confirmed by XRD, FTIR, and ^{29}Si CP-MAS NMR spectra. A silylating reagent of APTS was reacted to the CTAB exchanged magadiite. The copolymerization of the APTS modified magadiite presents a new layered silicate-organic compound. In this compound, a covalently bond formed between the interlayer spaces. It is dissimilar to the conventional clay-polymer systems in which the ionic interactions between silicates and organic modifiers are dominant.

Keywords: Magaditte; Silylation; Intercalation; Organic modification

1. Introduction

The construction of organic–inorganic nanocomposites has attracted considerable attention in materials chemistry. Composite materials are typically formed when at least two distinctly dissimilar materials are mixed to form a monolith. The overall properties of a composite material are determined not only by the properties of the parent components but also by the morphology, volume fractions, and connectivity of the phases as well as the interfacial properties [1,2]. Host-gust composites based on the intercalation of guest molecules into inorganic layered hosts represent a new class of premier functional materials such as catalyst and molecular sieving properties, which possess unique chemical and physical characteristics [3–9]. The intercalation of the inorganic layered hosts can be used to facilitate exfoliation of the inorganic nanolayers into a polymer network, which maximizes the interfacial contact between the organic and inorganic phases. The exfoliated nanocomposites show a better phase homogeneity than the intercalated nanocomposites, and effectively improve the performances of clay composite materials [2,10].

Layered silicate clay of magadiite is a good candidate for the formation of organic–inorganic nanocomposites, in part, because it has chemically stable siloxane surfaces and a high surface area [11,14]. It also possesses a high aspect ratio and a high strength. Magadiite forms a series of sodium polysilicate with the formula of $Na_2O{\cdot}14SiO_2{\cdot}nH_2O$ [8,11,12]. The model structure of magadiite is shown as Fig. 1. It is composed of one or multiple negatively charged sheets of SiO_4 tetrahedra with abundant silanol-terminated surfaces. The negative charges in the layers of magadiite are balanced by either Na^+ or H^+ in the interlayer spaces [13]. Magadiite has a high capacity for ion exchange, whereby the sodium ions can be replaced by protons, other cations or large quaternary ammonium ions [6,11,14–20]. The surfaces of magadiite contain silanol group (χ Si–OH) and siloxide group (χ Si–O). The interface between these layers contains Na^+ and H_2O. Organic groups can be grafted to these groups by reaction with silane to modify the interlayer space. The grafting of organic derivative of inorganic layered materials has the capability of further accommodation of organic molecules because of the organophilicity of the interlayer surfaces. By choosing the bulkiness and the amount of the modifying organic groups, unique properties, such as selective and specific introduction of guest species, have emerged. In this study, *n*-hexadecyl trimethyl-ammonium bromide (CTAB) was applied as intercalation agent to exchange the cation ions and thus to organically modify the

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* Corresponding author. Tel.: +886 2 2771 2171x2735;
fax: +886 2 2731 7185.
E-mail address: sfwang@ntut.edu.tw (S.-F. Wang).

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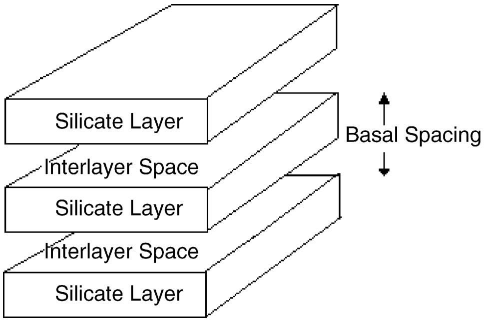

Fig. 1. A schematic diagram of the makatite structure, and, equally, kanemite, octosilicate, magadiite and kenyaite: two-dimensionally infinite silicate layer, separated by interlayer spaces.

magadiite. γ-Aminopropyltriethoxysilane (APTS), a silane coupling agent, was used as silylating reagent to react with CTAB exchanged magadiite. The organically modified magadiite was characterized using X-ray diffraction (XRD), infrared spectroscopy and ^{29}Si CP-MAS Solid-State nuclear magnetic resonance (NMR) spectroscopy.

2. Experimental procedure

2.1. Materials

Commercial hydrothermal synthesized clay (Na-magadiite) with CEC = 100 meq/100 g (Chang-chun Petrochemical Co., Taiwan), solvent of *N*-dimethylacetamide (DMAC, 98%; Tedia Co.), intercalation agent of *n*-hexadecyl trimethyl-ammonium bromide (CTAB, 99%; Acros Co., Japan), and coupling agent of γ-aminopropyltrimethoxysilane (APTS, 99%; Acros Co., Japan) were used in this study throughout.

2.2. Intercalation of layer silica

A proper amount of Na-magadiite was added into DMAC solvent and mixed for several hours. CTAB was poured into a separated beaker with DMAC solvent and mixed for several hours. The above two solutions were then poured into a reactor together and stirring for 36 h at the temperature of 60 °C. Subsequently, the reacted product was separated by centrifugation and washed with the acetone for several times. Finally, the intercalation product was dried in air and grinded.

For comparison, H-magadiite was prepared by mixing an aqueous Na-magadiite suspension with a HCl solution. The former was obtained by stirring 10 g Na-magadiite in 800 ml D.I. water for an hour, and the latter was prepared by stirring 4 g HCl (35%) in 200 ml D.I. water for an hour. The mixture was then stirring for 5 days in room temperature. Finally, the H-magadiite was separated by centrifugation, washed with deionized H_2O until Cl-free, and then dried in air and grinded.

2.3. Silylation of intermediate (CTAB-magadiite)

A certain amount CTAB-magadiite was baked for 2 h at the temperature of 100 °C. The powder sample was then mixed with DMAC solvent under nitrogen atmosphere and stirred for several hours at the room temperature. A grafting agent of APTS was added into the above suspension, mixed for 48 h at the temperature of 60 °C, and then washed with DMAC for several times. After filtrating and drying, the final product was obtained. For comparison, Na-magadiite and H-magadiite were silylated by APTS-DMAC solution using the same process.

2.4. Characterizations

X-ray diffraction analysis on the samples was performed to evaluate the layer spacing of the magadiite, using a Rigakm D/max-B diffractometer with monochromatic Cu Kα radiation (λ = 0.154 nm) and an acceleration voltage of 40 kv. The surface treated magadiite was also characterized using the Fourier transform infrared (FTIR) and ^{29}Si CP-MAS Solid-State NMR spectra. For the FTIR measurement, spectra were recorded using a Perkin-Elmer Model 2000 spectrometer at the resolution of 4 cm^{-1}. Samples were mixed with dry KBr before analysis. The ^{29}Si CP-MAS Solid-State NMR (500 MHz) spectra were performed using a Varian Inova spectrometer.

3. Results and discussion

The XRD patterns of Na-magadiite, H modified magadiite, and CTAB modified magadiite samples are shown in Fig. 2. The basal spacing of Na-magadiite calculated from the XRD result shown in Fig. 2(a) is 1.54 nm, which is consistent with that reported by Brindley [21]. Peaks due to impurity were not detected. In order to be successful in the interlayer silylation with bulky organosilyl group, the H- and CTAB-exchanged silicates were used as intermediates for the silylation. They were prepared by ion exchange reaction between Na-magadiite and an aqueous HCl solution or a CTAB-DMAC solution. XRD pattern for H-magadiite, shown in Fig. 2(b), has a small peak at 2*θ* of 7.83°, which is corresponding to the basal spacing of 1.12 nm. This is similar to that reported in the literature [18,19]. The basal spacing of H-magadiite is smaller than that of Na-magadiite, which is due to the loss of water molecules at the interlayers during the exchange reaction. From the XRD pattern shown in Fig. 2(c), the basal spacing of CTAB-magadiites is 2.46 nm. It is apparent that large quaternary ammonium ions of

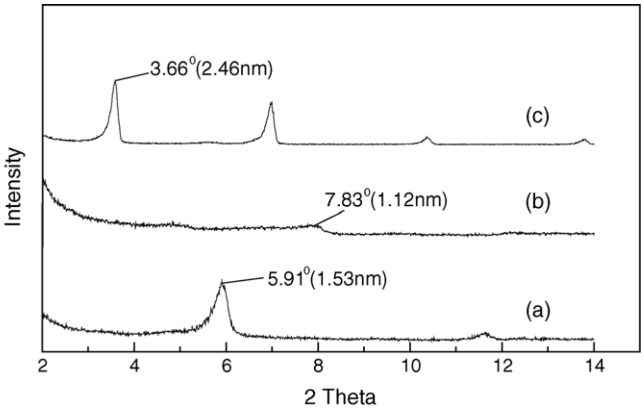

Fig. 2. X-ray diffraction (XRD) patterns of (a) Na-magadiite, (b) H-magadiite, and (c) CTAB-magadiite.

CTAB have replaced the sodium ions and intercalated into the interlayer space, which causes the expansion of basal spacing. The expanded hydrophobic interlayer space made it possible to introduce bulky organic groups. The use of CTAB as an intercalation agent, to expand the interlayer spaces of magagiite, appears to be as effective as that observed at the $C_{12}TMA$ (dodecyltrimethylammonium)-magadiite system reported by Ogawa and coworkers [10,11].

Fig. 3 shows the XRD patterns of the Na-magadiite, H-magadiite, and CTAB modified magadiite after silylation reactions with the APTS. The silylated Na-magadiite has a basal spacing of 1.54 nm, indicated in Fig. 3(a), which is nearly identical to that of the original Na-magadiite. It manifests that the silane coupling agent does not react with Na-magadiite. Fig. 3(b) shows the XRD pattern for the APTS-magadiite prepared from the intermediate of H-magadiite. It exhibits a sharp diffraction peak at 3.60° and a small peak at 5.56°. The large sharp peak is corresponding to the basal spacing of 2.47 nm, due to the incorporation of APTS. The smaller peak is similar to the (0 0 1) reflection of the original Na-magadiite, which indicates that part of magadiite has not been exchanged by the silane of APTS. The long-chain coupling agent is not evenly distributed between the interlayer spaces. Fig. 3(c) shows that, after the silylation of APTS to CTAB-magadiite, the basal spacing of APTS-magadiite increases slightly to 2.50 nm compared to that of CTAB magadiite. The XRD pattern only shows the expanded layers, and the reflections of the original magadiite are absent. Only slightly increases in basal spacing is due to the fact that the chain length of the organosilyl group of APTS is shorter than that of CTAB that consists of 12 carbon atoms per chain. Carefully compare the diffraction peaks at Figs. 2(c) and 3(c), a broadening of XRD peaks was obtained. This observation indicates that the CTAB has been exchanged by the silane of APTS and a greater stacking disorder occurred. The introduction of the APTS in the interlayer space of magadiite was also evidenced by IR and NMR analysis.

Infrared spectra of Na-magadiite, CTAB-magadiite, and APTS-magadiite are shown in Fig. 4(a)–(c), respectively. In Fig. 4(a), the IR spectrum exhibits the bands due to C–H stretching at around 2900 cm^{-1}. A broad band centered at 3460 cm^{-1} corresponds to the strong hydrogen bonding Si–OH stretching. A small sharp peak appearing at 3650 cm^{-1} refers to the weakly hydrogen bonded free Si–OH stretching of isolated silanol groups on the surface of magadiite. This weakly bonded free Si–OH is responsible for reacting with the coupling agents [22]. However, the small peak becomes less significant in Fig. 4(b) and even disappears in the spectra shown in Fig. 4(c), which could be due to the formation of Si–C bonds from organosilyl group as the intercalation and silylation proceed.

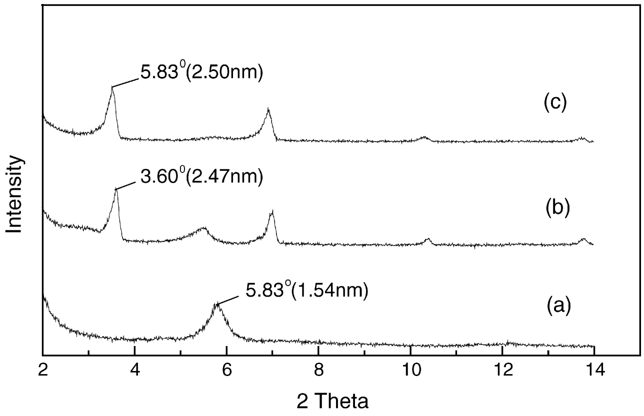

Fig. 3. X-ray diffraction (XRD) patterns of (a) Na-magadiite, (b) H-magadiite, and (c) CTAB-magadiite, after APTS silylation with APTS treatment.

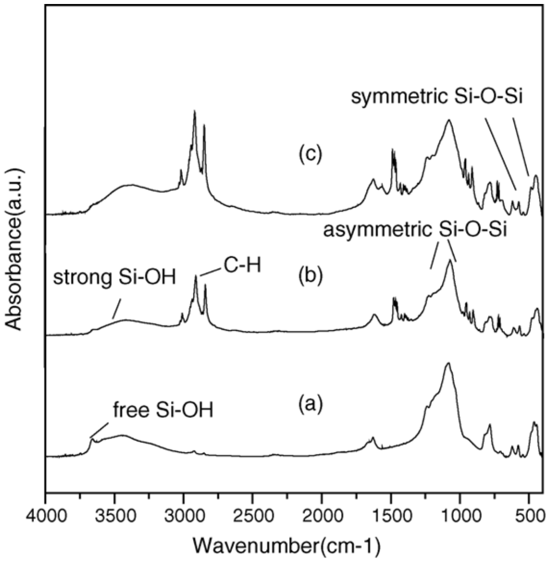

Fig. 4. Infrared (IR) spectra of (a) Na-magadiite, (b) CTAB-magadiite, and (c) APTS-magadiite.

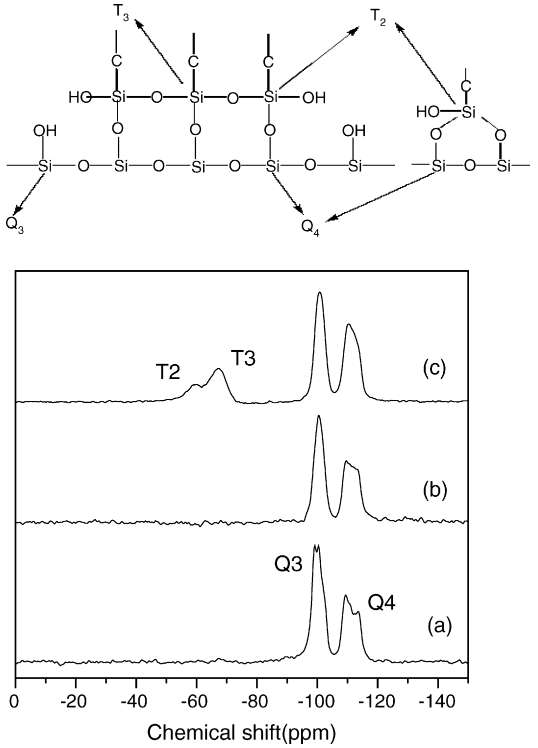

Fig. 5. ^{29}Si solid-state NMR spectra of (a) Na-magadiite, (b) CTAB-magadiite, and (c) APTS- magadiite.

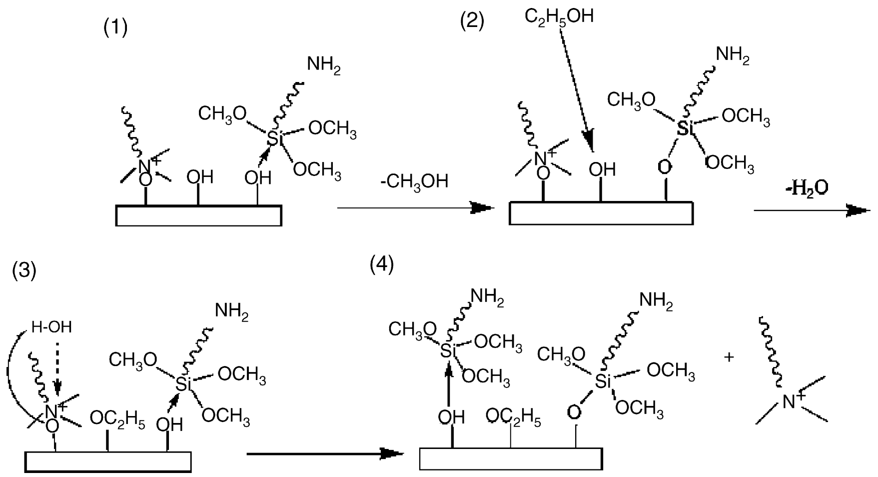

Fig. 6. A model for silylation reaction between the APTS silane and the magadiite surfaces [15].

The successful grafting of the isolated silanol groups in the interlayer space of magadiite was performed with organic chemicals such as quaternary ammonium of CTAB or APTS silane. A few new sharp bands of 2900 cm^{-1} appear at Fig. 4(b) and (c) due to asymmetric CH stretching vibration, indicating that the organic group has intercalated into the interlayer space of magadiite [11]. On the other words, a silane of APTS has grafted to the silanol group at the surface of the magadiite to form a covalent bond.

Fig. 5(a)–(c) show the ^{29}Si Solid-State NMR spectra of Na-magadiite, CTAB-magadiite and APTS-magadiite, respectively. From Fig. 5(a), one can find that Na-magadiite have one Q^3 peak (~100 ppm) and two Q^4 peaks (~110 ppm and ~114 ppm), which are very similar to those reported previously [15,16]. The Q^3 peak represents the presence of $[Si(OSi)_3O–]$ or $[Si(OSi)_3OH]$ and the Q^4 peaks characterizes the $[Si(OSi)_4]$ which is a hydrophilic group on the surface of magadiite [15]. Fig. 5(b) shows that the characteristic peaks of the CTAB-magadiite, which are similar to those of the Na-magadiite. It is evident that the structure of Na-magadiite did not vary after the intercalation and cation-exchange reactions, which indicates the retention of the silicate framework. However, as shown in Fig. 5(c), not only the Q^3 and Q^4 peaks exist but also a T^2 (~61 ppm) and a T^3 (~69 ppm) peaks appear as well. T^2 peak symbolizes the structure of $[Si(OSi)_2(OR')R]$ and T^3 peak corresponds to the $[Si(OSi)_3R]$ [17]. Both are organic functional groups, which have bonded to the surfaces of the layer silicates after silylation process. This observation indicates that silane of APTS has been successfully grafted to the interlayer space of magadiite. In other words, the surface of magadiite has been silylated. The signal of the T^2 increases associated with the ratio of Q^4/Q^3 decreases as the level of the silylation increases. The absorption refers to the isolated silanol group at 3650^{-1} disappears in the IR spectrum of the silyated-magadiite, while Q^3 still remained after silylation. This observation suggests that hydrogen-bonded silanol groups remained even after silylation. A covalent bond has been formed between one end of the APTS chain and the surface of magadiite. It is dissimilar to the conventional clay-polymer system in which the ionic interactions between silicates and organic modifiers are dominant [15]. However, the results indicated in DTA, FTIR, and ^{29}Si Solid-State NMR spectra do not rule out the facts that some of the CTAB may retain in the interlayer spaces after the silylation. Similar to other intercalation agents, particularly for long chain organoammonium ions, reported in the literature, they can significantly enlarge the interlayer spaces of the silicates, but may retain after silylation, [15] which leads to the existence of some ionic bond in the product.

Fig. 6 is a proposed model represents the silylation reaction between the APTS silane and the surface of magadiite, as suggested by Isoda et al. [15] on the study of grafting of γ-methacryloxypropylsilyl (γ-MPS) group on magadiite and copolymerization with methyl methacrylate. One can observe from this model, the hydroxyl group of APTS produced by the hydrolysis process reacts with the free Si-OH group at the surface of magadiite to form the hydrogen bonding. After removing the water as the condensation proceeds, a covalent bond is formed between the APTS and the magadiite finally.

4. Summary

XRD results proved the basal spacing of Na-magadiite can be expanded by intercalating a large quaternary ammonium ion of CTAB. APTS-magadiite was successfully prepared by reacting the CTAB-magadiite with γ-aminopropyltrimethoxysilane (CTAB), as confirmed by the XRD, FTIR and ^{29}Si Solid-State NMR spectra.

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