



Interlamellar silylation of magadiite by octyl triethoxysilane in the presence of dodecylamine

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ABSTRACT

Magadiite was modified by interlamellar silylation with octyl triethoxysilane (OTES) in the presence of dodecylamine (DDA) in ethanol without a pre-swelling step. Dodecylamine expanded the interlayer space and acted as silylation catalyst. The well ordered silylated magadiite had basal spacings between 1.18 and 1.38 nm. Solid-state ²⁹Si MAS NMR showed Q³ and Q⁴ signals as well as T² and T³ signals. The increase in the relative intensity of Q⁴ for Q³ and the appearance of T² and T³ signals were attributed to the grafting of OTES to the interlayer surface silanol groups. The described method provides a promising route for the preparation of functional nanomaterials.

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1. Introduction

Layered materials have been often used to design and construct organic–inorganic nanomaterials because of the ease and variety of modification (Landis et al., 1991; Daily and Pinnavaia, 1992; Ogawa and Kuroda, 1997; Jeong et al., 1995; Kwon et al., 1996; Kwon and Choi, 1999; Kwon and Shin, 2000; Kwon and Park, 2001; Galarneau et al., 1995). Chemical modification into the interlayer surface of layered materials became the focus of increased research. Interlamellar silylation of magadiite by grafting reactions was described by Ruiz-Hitzky and Rojo (1980), Ruiz-Hitzky et al. (1985), Beneke and Lagaly (1983) and Kwon et al. (1996). Shimojima et al. (2001), Okutomo et al. (1999), Ogawa et al. (1998) and Yanagisawa et al. (1988) reported trimethylsilylation, diphenylmethylsilylation and octyldimethylsilylation of magadiite, kenyaite and kanemite using the quaternary ammonium-exchanged form of the silicates as intermediates. Thiesen et al. (2002) described the silylation of H⁺-kenyaite using alkylamines together with a silylating agent.

We now report the introduction of functional groups in the interlayer space of magadiite by grafting reactions. Such materials can offer new opportunities for designing nanocomposite with desired functions because of the accessibility of the interlayer spaces by various compounds. In combination with polymers, functional groups attached on the internal and external surfaces can interact with active groups in the polymer matrix. In particular, attached amine groups

can react with functional groups of epoxy, nylon, and urethane polymers. The expanded interlayer space can store drugs or enzymes (Corma et al., 2002). These materials can also be used as fillers in gas permeation membranes (Choi et al., 2008). Layered materials with attached amine groups may adsorb heavy metal ions for photosensitive species. In spite of the wide range of applications for the modification of organic functional groups in the interlayer surface of layered materials these studies have not yet been conducted.

Here, we report the silylation of acid-activated magadiite (H⁺-magadiite) by octyl triethoxysilane (OTES) in the presence of dodecylamine. Magadiite is an Al-free layered silicate and can be synthesized under hydrothermal conditions (Beneke and Lagaly, 1983). Octyl triethoxysilane has been extensively used for chemical modification of silica and alumina particles (Caravajal et al., 1988; Kelly and Leyden, 1991; Impens et al., 1999). As the interlayer surfaces of H⁺-magadiite contain reactive Si-OH groups, OTES can be intercalated and react with the Si-OH groups.

Dodecylamine (DDA) expands the interlayer space and acts as silylation catalyst so that the reaction proceeds without a pre-swelling step.

2. Materials and methods

2.1. Synthesis of Na⁺-magadiite and H⁺-magadiite

Synthetic Na⁺-magadiite was hydrothermally synthesized (Kwon et al., 1995) from silica gel (Wakogel, Q-63), sodium hydroxide, sodium

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carbonate and water in molar ratios $\text{SiO}_2/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 5$ and $\text{H}_2\text{O}/(\text{NaOH} + \text{Na}_2\text{CO}_3) = 100$. The synthesis was carried out in a stainless steel autoclave (72 h, 150 °C, autogenous pressure) without stirring. The product was filtered and washed with deionized water to remove the excess of NaOH, Na_2CO_3 and dried at 70 °C.

H^+ -magadiite was obtained by ion exchange of Na^+ -magadiite with a 0.1 N HCl solutions (Beneke and Lagaly, 1983). A suspension of 10 g Na^+ -magadiite in 200 ml deionized water was titrated slowly with a 0.1 N HCl solution to a final pH of 2.0 and then allowed to stand for 24 h. H^+ -magadiite was recovered by filtering, washed with deionized water (until Cl^- free), and air dried at 40 °C. Octyl triethoxysilane (OTES) and dodecylamine (DDA) were purchased from Aldrich.

2.2. Silylation

DDA-OTES mixed solutions were prepared by dissolving OTES and DDA in ethanol (95%). The concentration of OTES in solution was varied between 0.01 and 0.1 M, and the DDA concentration was held constant at 0.1 M. H^+ -magadiite (0.44 g, about 0.5 mmol) was then dispersed in 6 ml of these solutions (ultrasound, 20 min, at room temperature). Ethanol was evaporated and the silylated magadiite was dried for 24 h at 50 °C (DDA-OTES-MA). Some amounts of DDA-OTES-MA were washed with ethanol to remove dodecylamine and dried in air at 70 °C (OTES-MA). As a part of the dodecylamine molecules may have been protonated by the proton transfer from silanol groups, only a part of dodecylammonium ions were removed by washing with ethanol.

2.3. Characterization

The scanning electron micrographs (SEM) were obtained from a JEOL JSM-840A scanning electron microscope. X-ray diffraction (XRD) patterns were obtained with a Bruker AXS D8 DISCOVER diffractometer with $\text{Cu K}\alpha$ radiation. Transmission electron micrographs (TEM) were obtained with a JEOL JEM-200 CX transmission electron microscope operating at 200 kV. Powdered samples were embedded in Epoxy resin. Microtome sectioned samples were examined. Solid-state ^{29}Si MAS NMR experiments were performed on a Bruker DSX-400 spectrometer (KBSI Daegu center, Korea) operating at 79.5 MHz. ^{29}Si MAS NMR spectra were obtained using 30–40° pulse width at a spinning rate of 6 kHz. Cross-polarization experiments were carried out with delay times of 3 s, 90° pulse of 5 s, and contact times of 2000 μs . The chemical composition of Na^+ -magadiite and H^+ -magadiite was determined by EDX (AS1000-85S) and thermogravimetric analysis (TGA, 10 °C/min to 900 °C, 100 cm^3/min N_2 purge). The carbon content was determined by CHN analysis (CHNS-932(Leco)).

3. Results and discussion and summary

Well-crystallized Na^+ -magadiite were obtained by the hydrothermal reaction of silica gel for 72 h at 150 °C. The X-ray powder diffraction pattern of air-dried Na^+ -magadiite exhibited several (001) reflections, indicating a basal spacing of 1.54 nm (Fig. 1). Air-dried H^+ -magadiite also reveals several (001) reflections corresponding to a basal spacing of 1.18 nm. The decrease in basal spacing indicates the loss of interlayer H_2O after the ion exchange. Na^+ -magadiite particles were composed of platy particles. H^+ -magadiite and OTES-MA showed a similar morphology (Fig. 2). The chemical compositions of Na^+ -magadiite and H^+ -magadiite were obtained by combining the results of TGA and EDS analysis (the content of silica and sodium) as $\text{Na}_2\text{Si}_{14}\text{O}_{29} \cdot 9\text{H}_2\text{O}$ and $\text{H}_2\text{Si}_{14}\text{O}_{29} \cdot \text{H}_2\text{O}$ respectively. All these observations are consistent with previous results (Beneke and Lagaly, 1983; Kwon et al., 1995). The XRD patterns of OTES-MA are shown in Fig. 3. OTES-MA consists of H^+ -magadiite with intercalated OTES dodecylamine, and also dodecylammonium ions (by proton transfer from silanol groups) and condensation between adjacent layers cannot occur

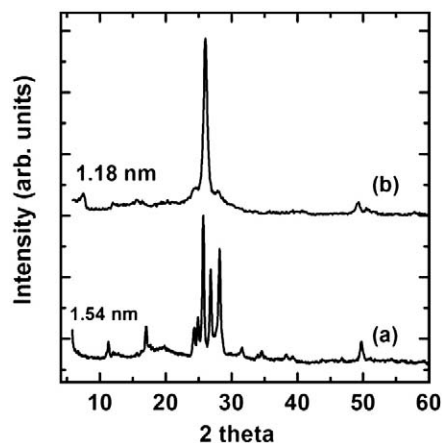


Fig. 1. XRD patterns of (a) Na^+ -magadiite and (b) H^+ -magadiite.

because of the expansion of the interlayer space, with basal spacings between ~1.38 (Fig. 3b, c, d) by DDA. However, increasing concentrations of OTES broaden the reflections and decrease the basal spacing because of the high degree of grafting that reduces the amount of intercalated DDA. The XRD patterns of OTES-MA (after washing DDA-OTES-MA) with ethanol showed the same behavior (Fig. 3e, f, g). The basal spacing was ~1.28 nm (Fig. 3e, f, g). This basal spacing indicated

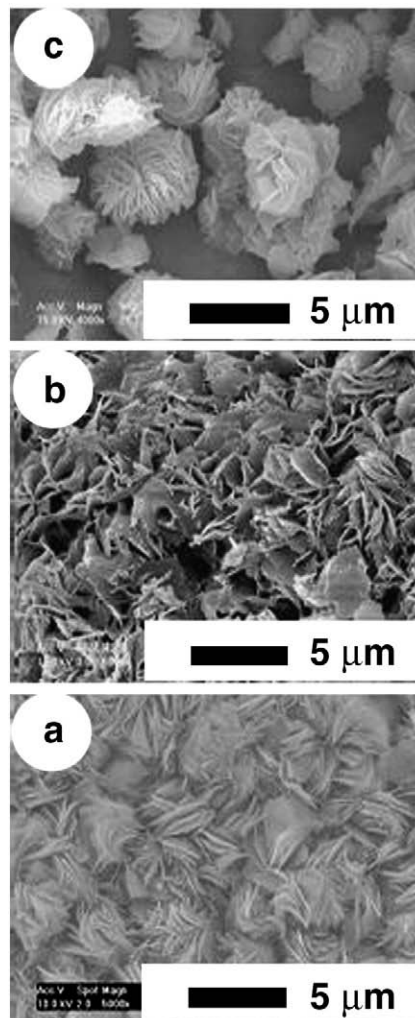


Fig. 2. SEM of (a) Na^+ -magadiite, (b) H^+ -magadiite and (c) OTES-magadiite.

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