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Methylene-Functionalize Saponite: A New Type of Organoclay with CH₂ Groups Substituting for Bridging Oxygen Centers in the Tetrahedral Sheet

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Abstract

The synthesis of saponite in the presence of bis(triethoxysilyl)methane (BTESM) as an organosilicon reagent results in the replacement of up to 33.3 % of the oxygen atoms in the tetrahedral sheet by bridging methylene groups. The methylene-functionalized saponites represent a new form of covalently-bonded organoclay that truly is isomorphic with purely inorganic saponite made under equivalent reaction conditions from sodium silicate as the silicon source. The isoelectronic and isolobal relationship between methylene and bridging oxygen centers is essential for methylene saponite formation. Bridging ethylene groups are not incorporated into the Kagome net of the basal surfaces due to a mismatch in bridging group size. The textural properties of the methylene saponites are similar to those for purely inorganic magnesium saponite made under equivalent synthetic conditions in the absence of BTESM. Layer stacking disorders afford large surface areas (~550 to 650 m²/g), making the methylene saponites attractive candidates for use as adsorbents and functional fillers for polymer composites.

Keywords

saponite; synthesis; methylene saponite; bissiloxane; organoclay

1. Introduction

Saponite clay is among the more easily synthesized smectite clay minerals (Vogels et al., 1995; Klopogge et al., 1993). Owing to their submicron size (Brindley and Brown, 1980) smectite clays serve as important industrial materials, and find applications in process industries, agriculture, environmental remediation, construction, pigments, coatings, ceramics, catalysts and polymer materials (Murray, 1999). Similar applications are envisioned for synthetic saponites. The major structural building blocks of 2:1 clay minerals are tetrahedral SiO₄ units and octahedral MO₆ units, where M = Al, Mg, Fe, Zn and the like. In the case of saponite the 2:1 layers are made of tetrahedral silica sheets and octahedral brucite-like sheets, with aluminum substitution for silicon occurring primarily in the tetrahedral sheet. The general unit cell formula for saponite may be written as (M⁺_{x-y}nH₂O)[Mg_{6-y}Al_y](Si_{8-x}Al_x)O₂₀(OH)₄, where M⁺ is the exchangeable gallery cations.

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Smectite clays can be synthesized through sol-gel methods under conditions varying from mild room-temperature conditions (Vogels et al., 1995; Klopogge et al., 1993; Carrado, 2000) to extreme hydrothermal conditions (Klopogge, et al., 1999; Reinholdt, et al., 2001; Prihod'ko, et al., 2002). The low temperature methods at ambient pressures are especially attractive for the cost-effective preparation of this clay for materials applications. In the present work we make use of previously reported low temperature (≤ 100 °C) pathway for the preparation of saponite (Vogels et al., 1995; Klopogge et al., 1993). We then use the analogous pathway to prepare organic – inorganic hybrid derivatives in which the bridging oxygen atoms in the tetrahedral sheet are replaced in part by bridging CH₂ groups.

Normally, organic modification of smectite clay is achieved through organocation exchange. In the present work, organic modification is achieved through the isostructural integration of covalently bonded Si-CH₂-Si linkages in place of Si-O-Si units in the tetrahedral sheet of the 2:1 layer lattice structure. The replacement of bridging oxygen atoms by bridging methylene groups is schematically illustrated in Figure 1. To our knowledge, this is the first example of a smectite organoclay in which the organic moiety is covalently linked to the tetrahedral sheets with retention of the 2:1 layer lattice structure.

Previous approaches to the synthesis of covalently linked organoclay derivatives have used monosiloxanes of the type RSi(OR')₃ as the organosilicon reagent (Chastek, et al., 2005a, 2005b; Whilton, et al., 1998; Burkett et al., 1993). The resulting products indeed are layered, but they cannot be isostructural with a 2:1 layered silicate structure type for the following reasons. If the three oxygen atoms of the RSiO₃ moiety occupy three oxygen positions on the Kagome net of oxygen atoms on the gallery surfaces, then the silicon center must lie above the basal plane in order to spatially accommodate the R group. That is, the silicon center must “invert” its tetrahedral position in the 2:1 layered lattice. Under this scenario, neither the silicon atom nor the R group of the Si-R moiety occupy positions equivalent to those characteristic of the 2:1 layer lattice structure. On the other hand, if only one or two oxygen atoms of the RSiO₃ moiety occupy positions in the Kagome net, then the symmetry of the Kagome net is interrupted and the product is no longer isostructural with smectite clay.

In the approach reported here bis(triethoxysilyl)methane (BTESM), serves as an organosilicon reagent that allows the methylene group to substitute for the bridging oxygen atoms that define the Kagome net of smectite clay. This reagent been used previously for the synthesis of hybrid organozeolites (Yamamoto, et al., 2003) and periodic mesoporous organosilicates (PMOs) (Hatton, et al., 2005), but it has not been shown to be effective in forming methylene-functionalize layered silicate structures. The results of the present work demonstrate that BTESM indeed is effective in providing methylene functionalized saponites and that the compositions represent a new type of organoclay that truly is isostructural with the purely inorganic form of the clay.

2. Experimental Section

2.1. Materials

BTESM was purchased from Gelest and used without purification. All other chemicals were purchased as reagent grade chemicals from Aldrich and used without purification.

2.2. Inorganic saponite synthesis

A synthetic magnesium saponite, denoted Mg-SAP, was prepared at 90 °C by modification of previously described methods (Vogels et al., 1995) using water glass (27 wt% silica, 14 wt% NaOH), Al(NO₃)₃·9H₂O, Mg(NO₃)₂·6H₂O, NaOH and urea as reagents. In a typical synthesis, 38.5 g of the sodium silicate solution (contained 0.173 mol silica) and 7.22 g (0.019 mol) Al(NO₃)₃·9H₂O were mixed in 346 g deionized water at room temperature for 1.5 h under stirring

in a round bottom flask fitted with a reflux condenser. Then 28.8 g (0.480 mol) of urea was introduced to the white suspension, followed by another 1.5 h of stirring at room temperature. The mixture was then brought to 90 °C and stirred for 30 min, followed by the addition of 37.0 g (0.144 mol) of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. After a digestion period of 24 h at 90 °C, the pH was increased to a value of 11.0 through the addition aqueous NaOH and the mixture was heated for another 15 h. The resulting product was centrifuged, washed, and dried at 50 °C under N_2 flow.

An analogous procedure and set of reaction conditions were used to prepare a zinc analog of Mg-SAP, wherein zinc replaces magnesium in the 2:1 layer lattice. This latter sample was denoted Zn-SAP.

A second, well-crystallized magnesium saponite, denoted was obtained under hydrothermal reaction conditions in a sealed autoclave at 200 °C (Kloprogge et al., 1993). In a typical synthesis, 0.35 g of 28 wt% NH_4OH solution (2.8 mmol NH_4OH), 0.61 g (3.0 mmol) $\text{Al}(\text{OC}_3\text{H}_7)_3$, 1.6 g (27 mmol) fumed silica, and 4.77 g $\text{Mg}(\text{CH}_3\text{CO}_2)_2$ (22 mmol) were introduced to 40 g deionized water one by one. During the addition of the chemicals, the mixture was stirred for 10 minutes after the addition of each reagent to allow sufficient mixing. The entire mixture was then stirred at room temperature for 24 h before being added to an autoclave. The reaction was carried out at 200 °C for 6 days, and then the autoclave was cooled to room temperature. The resulting SAP-200 product was centrifuged, washed with water, and dried at 50 °C under N_2 flow.

2.3 Methylene saponite synthesis

Saponites with methylene groups substituting for bridging oxygen atoms in Kagome network of the gallery surfaces of saponite were made by following the same methodology described for the synthesis of inorganic Mg-SAP except that bis(triethoxysilyl)methane (BTESM) was mixed with water glass solution (27 wt% silica, 14 wt% NaOH), or used exclusively, as the Si source for the synthesis. When a mixture of BTESM and Na_2SiO_3 is used as the silica source, the molar ratio of BTESM and Na_2SiO_3 is varied from 1/10 to 1/2 to afford an organic / inorganic silicon ratio of 1/5 or 1/1, respectively, and the mixture is equilibrated at room temperature overnight to complete the hydrolysis of the BETSM component. The resulting products were denoted $\text{CH}_2\text{-SAP-1}$ and $\text{CH}_2\text{-SAP-2}$, respectively. When BTESM was used exclusively as the Si source, the product was denoted $\text{CH}_2\text{-SAP-3}$. In this latter case, 2.0 moles of NaOH per mole of BTESM was added to the aqueous BTESM solution and then the mixture was stirred at room temperature overnight to complete the hydrolysis. After the hydrolysis of BTESM, the synthesis of the hybrid saponites was carried out using the same method used for Mg-SAP synthesis. The molar ratio of total Si (BTESM plus Na_2SiO_3), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was 3.6 : 0.40 : 3.0, consistent with the Mg-SAP synthesis.

2.5. Product Characterization

X-ray diffraction (XRD) patterns were obtained on a Rigaku rotaxflex 200B diffractometer equipped with Cu $\text{K}\alpha$ X-rays and a curved crystal graphite monochromator, operating at 45 kV and 100 mA. Powder samples were pressed onto a glass X-ray sample holder.

N_2 adsorption-desorption isotherms were recorded at -196 °C on a Micrometrics ASAP 2010 sorptometer. Prior to analysis samples were outgassed at 150 °C and 10^{-6} Torr for a minimum of 12 h. BET surface areas were calculated from the linear part of the BET plot and BJH pore sizes were obtained from adsorption isotherms.

Transmission electron microscopy (TEM) images were obtained on a JEOL 2200FS field emission microscope with a ZrO/W Schottky electron gun and an accelerating voltage of 200

kV. The powdered samples were sonified in ethanol, and the resulting suspension was dripped onto 300 mesh copper grids.

Scanning electron microscope energy dispersive X-ray microanalysis (SEM EDS) was performed on a JEOL 6400V microscope with LaB₆ emitter, and the EDS detector was an INCA x-sight. The powder samples were mounted on aluminum stubs and coated with carbon before analysis. Quantitative analysis was performed using an INCA suite version 4.07 (Oxford Instruments) analysis program.

²⁹Si MAS NMR spectra were obtained at 79 MHz on a Varian VXR-400S solid-state NMR spectrometer equipped with a magic angle-spinning probe. The samples were spun at 4 kHz for each measurement. The pulse delay for was 400 s. Talc was used as a chemical shift reference (-98.1 ppm).

FTIR spectra of samples dispersed in KBr disks were recorded at ambient temperature on a Mattson Galaxy 3000 FTIR spectrometer over the range 400 to 4000 cm⁻¹.

3. Results

3.1. Inorganic saponite derivatives

In order to better understand the relationship between the textural properties of methylene-functionalized saponites and those of purely inorganic saponites, we first examine the properties of purely inorganic saponites made under conditions equivalent to those used for the preparation of methylene saponites, but in the absence of BTESM as a silicon reagent.

Figure 2 provides the XRD patterns of synthetic saponite clays made at 90 °C with Mg cations and Zn cations in the octahedral positions of the brucite sheet (denoted Mg-SAP and Zn-SAP, respectively). Included for comparison is a well crystallized magnesium saponite made under hydrothermal conditions at 200 °C. In-plane diffraction peaks characteristic of smectite clay are observed in all three cases. Mg-SAP does not possess a well-stacked nanolayer morphology, as indicated by the absence of a 001 peak in the XRD pattern (Figure 2b). However, once the powder is compacted in a hydraulic press at 10,000 psi for 1 min to form a pellet, a 001 peak is observed (Figure 2a), indicating that the as-made Mg-SAP has an irregularly stacked platelet morphology. In contrast, Zn-SAP and SAP-200 exhibited a sharp 001 peak, indicating a well-stacked morphology. Zn-SAP and SAP-200 have better crystallinity compared with Mg-SAP, as indicated by their narrower line widths of the clay in-plane diffraction peaks. The difference in the diffraction feature of Zn-SAP and MG-SAP indicates that the nature of the divalent cation in the octahedral sheet is important in determining the aspect ratio and layer stacking order of the nanolayers.

The platy morphologies of the synthetic saponites are shown clearly in TEM images (Figure 3). The dark thin lines in the images represent clay platelets with edge-on orientations to the electron beam. The length of such edges increases dramatically in the order of Mg-SAP < Zn-SAP < SAP-200, indicating an increase in lateral dimension. Additionally, the number of the edges appearing in the TEM images decreases in the reverse order, indicating a higher order of layer stacking. The in-plane dimensions of the Mg-SAP platelets are on the order of 50 nm, whereas Zn-SAP has in-plane platelet dimensions of several hundred nanometers, and SAP-200 had an even larger lateral dimensions. Layer stacking was evident for both Zn-SAP and SAP-200. Although the layer stacking is highly disordered in Mg-SAP, the clay platelets are aggregated into bundles.

Table 1 provides the textural properties of Mg-SAP, Zn-SAP and SAP-200, as determined from nitrogen adsorption-desorption isotherms shown in Figure 4a. Mg-SAP exhibits a large

BET surface area ($920 \text{ m}^2/\text{g}$) and a large pore volume ($1.98 \text{ cm}^3/\text{g}$). The well-stacked Zn-SAP and SAP-200 derivatives exhibit substantially lower surface areas and pore volumes. The sodium exchange form of naturally occurring sodium montmorillonite usually exhibits a surface area $< 50 \text{ m}^2/\text{g}$ and virtually no pore volume. Clearly, the exceptionally high surface area and porosity of Mg-SAP are the result of the relatively small platelet size and the aggregation of the platelets in poorly stacked form. The small layer aspect ratio and imperfect stacking of the layers also accounts for the presence of micropores that are manifested in the abrupt nitrogen uptake at low pressure indicates the presence of micropores (c.f., Figure 4a). The lack of well-ordered stacking in the case of Mg-SAP also accounts for the mesopore distributions shown in Figure 4b for this clay and its potassium, cesium and calcium exchanged forms. A synthetic Mg-SAP used previously as a reinforcing agent for epoxy polymers (Xue and Pinnavaia, 2007) exhibits similar textural properties.

Vibration modes typical of a 2:1 layered silicate structure are observed in the FTIR spectrum of Mg-SAP (Figure 5). The broad adsorption band $3000\text{--}3600 \text{ cm}^{-1}$ is the stretching vibrations of -OH from structural hydroxyl groups, the symmetric and asymmetric -OH stretching frequencies of surface water molecules, and gallery NH_4^+ ions. The adsorption bands at 1646 and 1385 cm^{-1} are assigned to the bending vibrations of -OH from surface water and gallery NH_4^+ ions, respectively. The strong adsorption band at 1050 cm^{-1} is assigned to Si-O stretching. The band at 476 cm^{-1} is assigned to Si-O-Si bending (Madejova and Komadel, 2001).

A Si : Mg : Al atomic ratio of 17 : 13 : 2 for is obtained for Mg-SAP by SEM-EDS methods. The corresponding to a unit cell formula is $(\text{Na}^+, \text{NH}_4^+)_{0.5}(\text{Si}_{7.3}\text{Al}_{0.7})[\text{Mg}_{5.8}\text{Al}_{0.2}]\text{O}_{20}(\text{OH})_4$. A 19 : 15 : 2 ratio is obtained for Zn-SAP, which is consistent with a unit cell formula $(\text{Na}^+, \text{NH}_4^+)_{0.4}(\text{Si}_{7.4}\text{Al}_{0.6})[\text{Zn}_{5.8}\text{Al}_{0.2}]\text{O}_{20}(\text{OH})_4$. The ratio 18 : 14 : 3 obtained for SAP-200, corresponds to the unit cell composition $(\text{NH}_4^+)_{0.4}(\text{Si}_{7.2}\text{Si}_{0.8})[\text{Mg}_{5.6}\text{Al}_{0.4}]\text{O}_{20}(\text{OH})_4$.

The Na^+ and NH_4^+ gallery exchange cations of as-made Mg-SAP are replaced by K^+ , Cs^+ , and Ca^{2+} without a substantial change in lamellar nanoparticle morphology, as indicated by the textural properties in Table 1 and the pore size distributions in Figure 4b. However, the nature of the exchange cation can affect the degree of nanolayer aggregation, as indicated by the decreases in surface area upon K^+ , Cs^+ , and Ca^{2+} exchange. The disordered aggregation of nanolayers for the exchanged forms of Mg-SAP is further verified by the XRD patterns equivalent to Mg-SAP (Figure 6). The reduction in the relative intensity of the 110 diffraction peak for Cs-[Mg-SAP] may arise from differences in the degree of hydration in comparison to the K^+ and Ca^{2+} forms of the clay.

The presence of Ca^{2+} , Cs^+ , and K^+ in the exchanged forms of Mg-SAP saponite is verified through SEM-EDS analysis. As shown by the results in Table 2, the Si : Mg : Al atomic ratios for the exchanged saponites are consistent within experimental error with the as-made Mg-SAP and with the replacement of the gallery Na^+ cations by Ca^{2+} , Cs^+ , and K^+ . It is noteworthy that NH_4^+ is not detected by EDS, but the presence of this ion is necessary in order to achieve electrical neutrality. For an analogous reason, the calcium cation in Ca-[Mg-SAP] is written in hydrolyzed $\text{Ca}(\text{OH})^+$ form.

3.2. Methylene saponite derivatives

When bis(triethoxysilyl)methane (BTESM) is used for the synthesis of a 2:1 smectite clay, the bridging methylene group may substitute for bridging oxygen atoms in the basal plane of the saponite clay structure (c.f., Figure 1). The resulting methylene-functionalized clay, denoted CH_2 -SAP differs fundamentally from organoclays synthesized from monosiloxanes of the type

RSi(OR')₃. [9-12]. Unlike the bridging methylene group in BTESM, the terminal R group of the latter moiety cannot bridge two silicon centers in the tetrahedral sheet.

The method used for Mg-SAP synthesis also is effective for the preparation of methylene-functionalized except that BTESM is used in part or in total as the silicon source. CH₂-SAP in which 16.7%, 50% and 100% of the silicon centers in the tetrahedral sheet are in the form CH₂SiO₃ groups are denoted CH₂-SAP-1, -2 and -3, respectively. The XRD patterns of the CH₂-SAP derivatives (Figure 7) exhibit the characteristic 060 clay diffraction peak for smectite clay. The diffraction pattern of CH₂-SAP-1 is equivalent to that of Mg-SAP. But as the amount of organosilicon is increased in samples CH₂-SAP-2 and CH₂-SAP-3, the relative intensities of the reflections change and a small carbonate impurity phase appears in the pattern of CH₂-SAP-3 due to reaction with CO₂ formed in the hydrolysis of urea. The intensity changes and broadening of the diffraction peaks most likely reflect in-plane disorder and a reduction in the scattering domain size at higher levels of CH₂ group incorporation.

The incorporation of methylene groups in the tetrahedral sheets is verified using ²⁹Si MAS NMR. As shown in Figure 8 the spectrum for CH₂-SAP-1 shows two Q³ bands (-93.5, -87.0 ppm) corresponding to silicon centers of the type Si(OSi)₃ and Si(OAl)(OSi)₂ (Xue and Pinnavaia, 2007; Lipsicas, et al. 1984). Also, a T² band is observed at -55.1 ppm verifying the presence of a O₃Si-CH₂-SiO₃ centers in the structure. Deconvolution of the Q and T bands reveals an inorganic / organic Si species ratio of 4.2, close to the expected value of 5 from the ratio of BTESM / Na₂SiO₃ in the synthesis. Similarly, both Q and T bands are observed in the spectrum of CH₂-SAP-2, and the ratio of organic / inorganic Si species is 1, consistent with the expected value. Also, as expected, when BTESM is used exclusively as the Si source for the preparation of CH₂-SAP-3, only a T² band (-57.1 ppm) is observed in the spectrum. The increased broadness of the T² resonances with increasing incorporation of BTESM suggests the increasing presence of multiple oxygen and methylene near-neighbor environments for the methylene groups on the Kagome net.

The presence of methylene groups in the CH₂-SAP derivatives also is verified using FTIR. As shown in Figure 9 all of the CH₂-SAP derivatives exhibit the lattice vibrations characteristic smectite (e.g., compare with the spectrum of Mg-SAP in Figure 5). In addition, the C-H stretching bands at 2937 and 2866 cm⁻¹ reveal the presence of the methylene groups. The weak band at 1280 cm⁻¹ in CH₂-SAP-2 and -3 are assigned to Si-C stretching, but the same band is too weak to be observed in CH₂-SAP-1 due to the comparatively low organic silicon content. CH₂-SAP-3 shows a sharp structural hydroxyl stretching band at 3705 cm⁻¹, while the same band is buried in the hydroxyl stretching of the surface water molecules of the more hydrophilic derivatives CH₂-SAP-1, CH₂-SAP-2 and Mg-SAP. CH₂-SAP-3 shows additional C-O stretching bands at 1497 and 1427 cm⁻¹ which are assigned to carbonate byproducts formed by reaction with CO₂ generated in the hydrolysis of urea (Frost and Klopogge, 1999; Botha and Strydom, 2001, 2003).

As summarized in Table 3, the BET surface areas of the CH₂-SAP derivatives are in the range of 550 - 650 m²/g, as expected for aggregates of poorly stacked nanolayers. The lack of regular layer stacking is verified by the absence of a 001 reflection in the XRD powder patterns (c.f., Figure 7). Figure 10 provides TEM images of the CH₂-SAP derivatives. The dimensions of the CH₂-SAP-1 particles are in the range of 20~80 nm, while CH₂-SAP-2 and -3 have larger dimension of 100~200 nm. Unlike the corresponding inorganic Mg-SAP saponite, the CH₂-SAP derivatives exhibit little edge-face platelet interactions. Nevertheless, the layer stacking order is not regular, as evidenced by the absence of a 001 XRD reflection.

4. Discussion

4.1. Inorganic saponite derivatives

The textural properties of the synthetic inorganic saponite products are determined by the synthesis temperature and the composition of the octahedral sheet. Comparing Mg-SAP made at 90 °C and SAP-200 made at 200 °C, we see that the higher synthesis temperature results in larger in-plane platelet dimensions and ordered layer stacking. Consequently, SAP-200 exhibits a well stacked layered morphology, while the stacking is not regular for Mg-SAP. The nature of the cation in the octahedral positions of the 2:1 layer also plays an important role in determining the clay particle morphology. With Zn as the octahedral cation, the in-plane growth of the nanolayers is accelerated in comparison to Mg-SAP. Thus, Zn-SAP exhibits larger in-plane particle dimensions and better layer stacking order, in agreement with earlier observations (Vogels et al., 1995).

The layer stacking order of Mg-SAP is not substantially affected by ion-exchange of Na^+ and NH_4^+ cations on the basal surfaces of the as-made mineral. Although K^+ , Cs^+ , Ca^{2+} , Na^+ and NH_4^+ have different atomic diameters that could result in different gallery spacings, the stacking of nanolayers of Mg-SAP is not improved by ion exchange, as judged by X-ray diffraction. However, the nature of the exchange cation does affect to some extent the aggregation of the 2:1 sheets, because the surface areas and pore volumes of the exchanged derivatives generally decrease in comparison to the parent Mg-SAP. Thus, the replacement of Na^+ and NH_4^+ cations in as-made Mg-SAP by less hydrophilic K^+ , Cs^+ , and Ca^{2+} tends to reduce the exposure of the basal planes through improved layer stacking, but the order of the stacking is not sufficient to observe a 001 reflection for the exchanged derivatives.

4.2. Methylene saponite derivatives

The results of the current work demonstrate that methylene groups are effectively incorporated into the gallery surfaces of synthetic saponite through the use of bis(triethoxysilyl)methane (BTESM) as an organosilicon reagent. On the basis of evidence provided by XRD, FTIR, ^{29}Si NMR, TEM and nitrogen adsorption measurements we show that the methylene-substituted form of saponite (denoted $\text{CH}_2\text{-SAP}$) is structurally analogous to inorganic saponite with magnesium ions occupying octahedral interstices (denoted Mg-SAP). The isoelectronic and isolobal relationship between the methylene group and a bridging oxygen atom is essential for the successful incorporation of the organic moiety into positions defined by the Kagome net of the gallery surfaces. Replacing the methylene group by a larger ethylene group, however, does not result in the formation of a saponite structure as judged by powder XRD. Ethylene is too large to serve as an isomorphic replacement of bridging oxygen in the Kagome net.

Lamellar 2:1 $\text{CH}_2\text{-SAP}$ structures are formed from reaction mixtures in which 16.7, 50.0, and 100 % of the silicon centers originate from BTESM as the organosilicon reagent. The product made from BTESM as the sole silicon source allows for the replacement of 33.3 % of the bridging oxygen positions in the Kagome net. Reducing the level of organosilicon centers to 16.7 and 50.0 mole % allows for the replacement of 6.7 % and 16.5% of the oxygen atoms, respectively. Thus, the methylene groups at 6.7% replacement are largely site-isolated. But at 16.5 and 33.3% replacement, multiple sites become possible and this substitution disorder leads to broadening of NMR resonance lines and shifts in the intensities and positions of in-plane XRD reflections (c.f., Figures 7 and 8). With increasing amounts of BTESM used in the hybrid saponite synthesis, there also is the possibility of one of the siloxane centers of BTESM being in the clay basal plane while the other is inverted and oriented out of the basal plane. This also will contribute to in-plane disorder.

Although the basic 2:1 layer lattice structure is retained in methylene saponite, the aspect ratio of the layers and the morphology of the aggregates differ from those of inorganic Mg-SAP. Methylene substitution results in a reduction of the lateral dimensions of the nanolayers and a more compact agglomeration of the nanolayers (c.f., Figures 3 and 10). For both materials, however, the layer stacking is disordered and neither material exhibits a 001 X-ray reflection. The stacking disorder and small aspect ratio of the nanolayers imparts large surfaces in the range 550 to 650 m²/g (c.f., Table 3). The large surface area and anticipated hydrophobic nature of the nanolayers may make methylene saponite well suited for the removal of organic pollutants from water. This new form of organoclay may also exhibit interesting properties as a functional additive in engineering polymers and provide barrier and reinforcement benefits similar to those known for conventional alkyl ammonium ion exchange forms of smectite clays. Studies along these lines are in progress.

Another opportunity for future studies is the incorporation of methylene groups in other layered silicates systems. Although methylene groups are known to replace bridging oxygen atoms in zeolites (Yamamoto, 2003), the present work to our knowledge is the first example of the incorporation of methylene bridges in a layered silicate. There are many layered silicates other than smectites that contain Q³ centers, such as magadiite and kanemite, among others. These layered structure also should be good candidates for the preparation of methylene-functionalized derivatives.

5. Conclusions

Bis(triethoxysilyl)methane (BTESM) is an effective reagent for replacing up to 33.3 % of the bridging oxygen atoms in the basal surfaces of saponite by bridging methylene groups. The methylene -functionalized saponites represent a new type of organoclay that may be useful for the adsorption of organic pollutants from water or as functional additives for engineering polymers, among other materials applications. BTESM also should be an effective reagent for the preparation of complementary methylene-functionalized layered silicate structures such as magadiite, kanemite, and the like.

Acknowledgments

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Figure 1. Schemes illustrating the tetrahedral sheet structure for (a) an inorganic clay and (b) an organo hybrid clay made from BTESM.

Figure 2. Wide angle hkl X-ray diffractions of (a) pressed Mg-SAP, (b) as-made Mg-SAP, (c) Zn-SAP and (d) SAP-200.

Figure 3.
TEM images of (a) Mg-SAP; (b) Zn-SAP and (c) SAP-200.

Figure 4.

(a) Nitrogen adsorption-desorption curves and (b) BJH adsorption pore size distributions (offset by 0.1 for clarification) of as-made Mg-SAP and its Ca^{2+} -, Cs^+ -, and K^+ -exchanged derivatives.

Figure 5.
The FTIR spectrum of Mg-SAP.

Figure 6. Wide angle hkl X-ray diffractions of the Ca(OH)^+ -, Cs^+ -, and K^+ -exchanged Mg-SAPs, compared with that of as-made Mg-SAP.

Figure 7. XRD patterns of the CH₂-SAP derivatives. The *hkl* values are labeled in the diffraction pattern for CH₂-SAP-1. The peaks marked by an asterisk are assigned to the presence of carbonate byproducts. In samples CH₂-SAP-1, -2, and -3, 16.7%, 50%, and 100 % of the silicon is in the form of CH₂SiO₃ organosilicon.

Figure 8.
 ^{29}Si MAS NMR spectra of $\text{CH}_2\text{-SAP}$ derivatives.

Figure 9.
FTIR spectra of CH₂-SAP derivatives

Figure 10. TEM images of (a) CH₂-SAP-1, (b) CH₂-SAP-2, and (c) CH₂-SAP-3.

Table 1

The BET surface areas and pore volumes of Mg-SAP, Zn-SAP, and SAP-200 and the K⁺-, Cs⁺-, and Ca (OH)⁺-, exchanged forms of Mg-SAP.

	BET surface area (m ² /g) *	Total pore volume (cm ³ /g)	BJH adsorption pore size (nm)
Mg-SAP	920	1.98	3
Zn-SAP	310	0.70	-
SAP-200	270	0.10	-
K-[Mg-SAP]	820	1.16	-
Cs-[Mg-SAP]	700	0.98	-
Ca-[Mg-SAP]	690	1.02	2

* The relative standard deviations of the BET surface areas are less than 0.5%.

Table 2

Elemental atomic ratios for Mg-SAP and its exchanged derivatives obtained from quantitative SEM-EDS analyses.^a

	Si	Mg	Al	Exchange Cation
Mg-SAP	19.0	14.7	2.0	0.5 Na ⁺ , 0.5[NH ₄ ⁺] ^b
Ca-[Mg-SAP]	19.6	14.6	2.0	1.1 Ca[(OH)] ⁺
Cs-[Mg-SAP]	18.1	15.0	2.0	1.0 Cs ⁺
K-[Mg-SAP]	19.0	15.5	2.0	1.1 K ⁺

^aMeasurements were performed on three different regions of each sample.

^bNH₄⁺ is not detected by EDS, but the presence of this ion is necessary in order to achieve electrical neutrality.

Table 3BET surface areas and pore volumes of the CH₂-SAP derivatives.

	BET surface area (m ² /g) *	Total pore volume (cm ³ /g)
CH ₂ -SAP -1	606	0.43
CH ₂ -SAP -2	558	0.31
CH ₂ -SAP -3	654	0.46

* The relative standard deviations of the BET surface areas are less than 0.5%.