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Synthesis, Characterization, and Reactivity of Layered Inorganic−Organic Nanocomposites Based on 2:1 Trioctahedral Phyllosilicates

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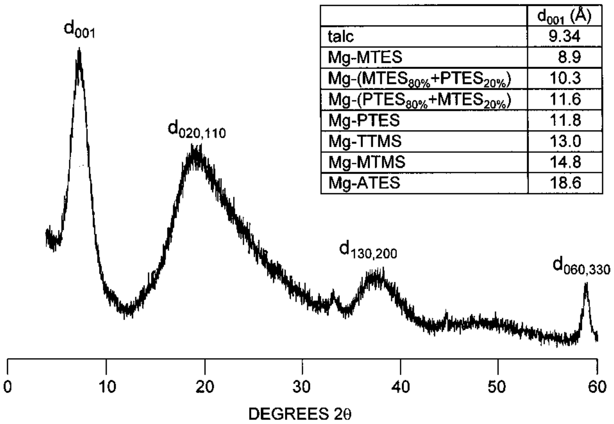
Layered inorganic−organic composite materials such as zirconium organophosphates and organophosphonates are of interest because they provide an ordered array of organic moieties within a stable inorganic matrix.[1] Tailoring of the organic components allows for a variety of applications in ion exchange, catalysis, and the construction of nanoscale assemblies. In the present work, a series of analogous materials, based on layered magnesium silicate materials that contain covalently linked organic functionalities, have been prepared by a one-step, direct-synthesis procedure involving mild reaction conditions. These hybrid materials are members of a family of 2:1 trioctahedral phyllo(organo)-silicates with approximate compositions of $Si_8R_8Mg_6O_{16}(OH)_4$, based on the composition of the parent structure, talc,[2] $Si_8Mg_6O_{20}(OH)_4$. To date, only one layered magnesium organosilicate (the (3-(methacryloxy)propyl)-siloxane derivative) has been briefly reported.[3] Because the direct synthesis of covalently linked organoclays should have wide applicability, we have investigated the potential of this approach by extending the synthesis protocol to a range of organic functionalities. In each case, the layered magnesium organosilicates have been characterized by a range of physical methods. In addition, the in situ reactivity of the organic moieties (e.g., phenyl, thiol) within the layered inorganic−organic nanocomposites and the potential use of the thiol-containing materials as host matrixes for the organized deposition of gold nanoparticles are described.

Layered magnesium organosilicates were synthesized using several different organosiloxanes, including methyltriethoxysilane (MTES; R = CH_3), phenyltriethoxysilane (PTES; R = C_6H_5), (3-mercaptopropyl)trimethoxysilane (TTMS; R = $(CH_2)_3SH$), (3-aminopropyl)-triethoxysilane (ATES; R = $(CH_2)_3NH_2$), (3-(methacryloxy)propyl)trimethoxysilane (MTMS; R = $(CH_2)_3OC(O)CH(CH_3)CH_2$) and mixtures of MTES and PTES.[4] In each case, the layered structure of the magnesium organosilicate materials was confirmed by X-ray powder diffraction (XRD, Figure 1). The observed reflections were broader than those from the parent inorganic structure (talc[5]), suggesting significant intralayer disorder due to the presence of the organic moieties. In particular, the (020) reflection was more intense and modified in shape in the organoclay materials. The intralayer reflection ($d_{060,330}$ = 1.56−1.57 Å) was characteristic of the 2:1 trioctahedral phyllosilicate structure[6,7] and remained unchanged among the various magnesium organosilicate materials synthesized. This indicates that the layered inorganic framework can accommodate a range of pendent organic functionalities without the loss of long-range periodicity. Furthermore, the interlayer d_{001} spacing increased with the steric size of the organosiloxane (Figure 1), suggesting that the organic fragments were directed into the interlayer space of the inorganic−organic hybrid material. The absolute values of the interlayer spacings are too small to be consistent with a bilayer motif, and suggest that the organic moieties are interdigitated between adjacent magnesium organosilicate sheets.



	d_{001} (Å)
talc	9.34
Mg-MTES	8.9
Mg-($MTES_{80\%}$+$PTES_{20\%}$)	10.3
Mg-($PTES_{80\%}$+$MTES_{20\%}$)	11.6
Mg-PTES	11.8
Mg-TTMS	13.0
Mg-MTMS	14.8
Mg-ATES	18.6

Figure 1. XRD pattern of Mg−PTES. Assignments are based on the 2:1 trioctahedral phyllosilicate structure of talc.[3] Note that the interlayer spacing indicated for talc is d_{002}, with two 2:1 trioctahedral phyllosilicate sheets per unit cell.[5]

Solid-state ^{29}Si NMR spectroscopy performed with $^1H-^{29}Si$ cross polarization (CP) and magic angle spinning (MAS) indicated that the silicon species were not fully condensed, possibly due to geometric constraints as they pack or to slow condensation kinetics, or both. Silanol-containing T^1 and T^2 species were observed in addition to the fully condensed T^3 (T^n = $RSi(OMg)(OSi)_{n-1}(OH)_{3-n}$) (Figure 2). However, quantitative evaluation of the silanol content of these materials to determine the exact composition ($Si_8R_8Mg_6O_{16-x/2}(OH)_{4+x}$, where x indicates the number of silanol groups) was not possible due to the CP technique used to accommodate the long ^{29}Si relaxation times. Interestingly, no T^3 species were present in the amino derivative, Mg−ATES, perhaps due to the disfavored condensation chemistry of hydrolyzed ATES.[8] Solid-state ^{13}C CP MAS NMR spectroscopy also indicated that the organic moieties were intact within the magnesium silicate-based materials.[9]

Characteristic framework vibrational modes observed in the infrared spectra of all samples were consistent

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(1) Cao, G.; Hong, H.-G.; Mallouk, T. E. *Acc. Chem. Res* **1992**, *25*, 532.

(2) Aranda, P.; Ruiz-Hitzky, E. *Chem. Mater.* **1992**, *4*, 1395.

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(4) In a typical preparation, 16.5 mmol (3.40 g) of magnesium chloride hexahydrate was dissolved in 100 mL of methanol and 22.0 mmol of the organosiloxane species (Aldrich, Mg/Si molar ratio = 0.75) was added. The cloudy suspension, which was obtained upon addition of 400 mL of 0.05 M aqueous sodium hydroxide, was stirred overnight at room temperature, and the resulting finely divided white precipitates collected by vacuum filtration or centrifugation and repeatedly washed with water.

(5) JCPDS card 13-0558.

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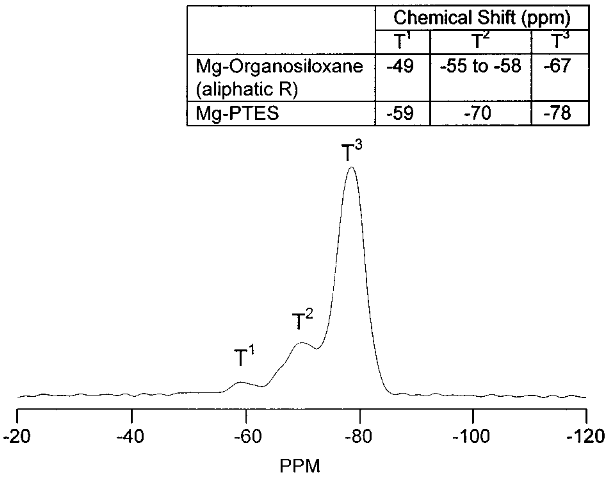
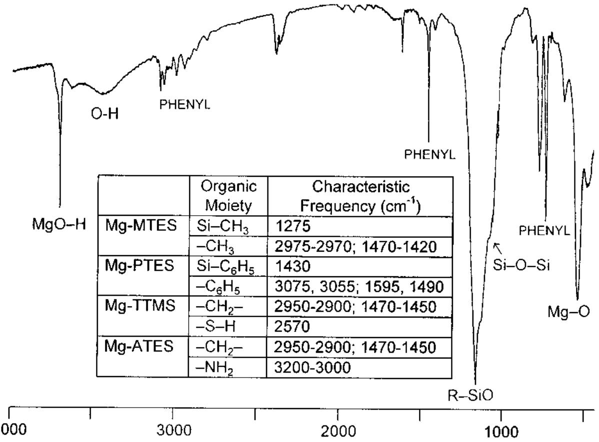


	Chemical Shift (ppm)		
	T^1	T^2	T^3
Mg-Organosiloxane (aliphatic R)	-49	-55 to -58	-67
Mg-PTES	-59	-70	-78

Figure 2. ^{29}Si CP MAS NMR of Mg−PTES. Chemical shifts are given relative to tetramethylsilane at 0 ppm. T^n = $RSi(OMg)(OSi)_{n-1}(OH)_{3-n}$.



	Organic Moiety	Characteristic Frequency (cm^{-1})
Mg-MTES	$Si–CH_3$	1275
	$–CH_3$	2975-2970; 1470-1420
Mg-PTES	$Si–C_6H_5$	1430
	$–C_6H_5$	3075, 3055; 1595, 1490
Mg-TTMS	$–CH_2–$	2950-2900; 1470-1450
	$–S–H$	2570
Mg-ATES	$–CH_2–$	2950-2900; 1470-1450
	$–NH_2$	3200-3000

Figure 3. IR spectrum of Mg−PTES.

with the proposed talc-like structure (Figure 3). These included the Mg−O stretch (500−550 cm^{-1}, which is not present in any of the starting materials), Si−O−Si within a 2:1 phyllosilicate (1015−1040 cm^{-1}),[10] Si−C (1120−1150 cm^{-1}), O−H (adsorbed water; silanol groups; 3400−3450 cm^{-1}), and MgO−H (3700 cm^{-1}).[10] In addition, resonances indicative of the specific organic moieties were observed by IR spectroscopy (Figure 3), thus confirming that the organosiloxanes were incorporated into the layered solids. The amine groups in the Mg−ATES clay appeared to be protonated (weak IR band at 1900−2100 cm^{-1}), suggesting the presence of salt formation with an intercalated chloride counterion. This is consistent with the observation of a larger interlayer spacing for Mg−ATES relative to that for the corresponding (mercaptopropyl)siloxane in Mg−TTMS (Figure 1).

The results indicate that a range of layered magnesium organosilicates containing covalently linked organic functionalities can be synthesized at room temperature. These inorganic−organic hybrid nanocomposites are constructed from individual layers of octahedrally coordinated magnesium oxide/hydroxide chains (brucite sheet) overlaid with a layer of tetrahedral organosilicate units on both sides of the brucite sheet. It has been proposed that in the formation of hectorite (a 2:1 trioctahedral phyllosilicate), brucite sheets form initially in solution, followed by condensation of the tetrahedral silicate layers.[11] That is, the preferred octahedral coordination of magnesium is the primary structural determinant in the formation of 2:1 trioctahedral phyllosilicate lamellae; this is analogous to the self-assembly of zirconium organophosphates and organophosphonates in that structure formation is controlled by the coordination chemistry of the inorganic components.[1] The limited coordination of the organosiloxane units, the hydrophobicity of the organic moieties, and the resulting microphase segregation possibly facilitate formation of lamellar structures. For example, we have observed that layered magnesium silicate structures do not form at room temperature in the absence of hydrophobic organosiloxanes, such as when triethoxysilane (HTES; R = H) or tetraethoxysilane (TEOS; R = OCH_2CH_3) is used in lieu of the organosiloxane component in the synthesis. The layered magnesium organosilicate materials appear to be hydrophobic powders, as suggested by their aggregation behavior and inability to be suspended in aqueous solution, both of which are dependent on the nature of the organic groups covalently linked into the structure.

The reactivity of organic functionalities within assembled Mg organosilicates was also investigated. Oxidation of the Mg−TTMS thiols to disulfides via treatment with aqueous hydrogen peroxide was suggested by the disappearance of the SH band (2570 cm^{-1}) and of bands characteristic of a thiol-containing methylene group (2930, 1450, 1260 cm^{-1}) from the IR spectrum. Similarly, reaction of the phenyl groups of Mg−PTES with $Mo(CH_3CN)_3(CO)_3$ to form molybdenum arene carbonyl complexes was apparent by IR spectroscopy.[12] The mercaptopropyl functionality was used to synthesize nanosized gold particles within the layers of the Mg−TTMS material via in situ reduction of tetrachloroauric(III) acid.[13] The light brown-colored samples were characterized by XRD, which revealed two new, sharp peaks assigned to Au(0) (d = 2.35, 2.04 Å) in addition to the original, broad, clay-based reflections. However, the d_{001} reflection of the clay was no longer observed upon deposition of the gold nanoparticles, perhaps because of exfoliation or expansion of the interlayer spacing beyond the working range ($d \leq 22$ Å) of the X-ray diffractometer in use. The presence of gold was also confirmed by EDX analysis (data not shown). Uniform gold particles (diameter ≈ 2 nm), the

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[9] ^{13}C NMR chemical shift values (ppm); Mg−PTES, 127.8, 130.5, 134.1; Mg−TTMS, 13.0, ~25 (sh), 28.5; Mg−ATES, 13.7, 23.5, 43.4. No resonance corresponding to the Si−C carbon of Mg−PTES (expected at approximately 131 ppm) was observed; this may be due to inefficient CP and a long relaxation time for this carbon, or broad neighboring peaks obscuring this resonance.

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[12] Sims, S. D.; Burkett, S. L.; Mann, S., manuscript in preparation.

[13] A suspension of 0.05 g of the Mg−TTMS clay ([SH] ≈ 6 mmol g^{-1}) in 10 mL of water was stirred overnight with 1.5 mL of the appropriate solution of tetrachloroauric(III) acid (Aldrich) in methanol (approximate Au/SH molar ratios = 0.02, 0.2, 2). Reduction of $[AuCl_4]^-$ to Au(0) was apparent from the change of color of the solution from yellow to colorless and the change of color of the suspended solid from white to light brown. The products were filtered, washed with methanol and water, and dried in air. Although the observations suggest that Au(III) reduction occurs in the vicinity of the mercaptopropyl functionalities, reaction with poly(mercaptoorgano)siloxane byproducts cannot be ruled out.

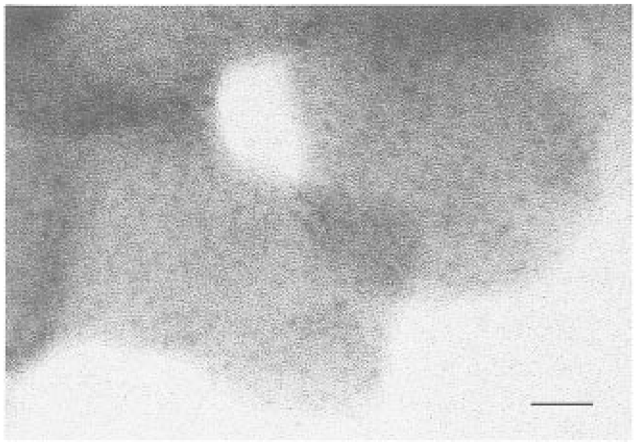

Figure 4. TEM micrograph of gold nanoparticles synthesized in situ within Mg−TTMS. Scale bar = 10 nm.

size of which appeared to be independent of the starting Au/SH ratio, were observed by TEM to be located in the interlayer space of the Mg−TTMS clays (Figure 4). Microtomed, resin-embedded samples revealed that for low starting Au/SH ratios, the gold particles did not penetrate to the center of the clay particle. However, the uniformity of the gold colloid suggested that the particles were formed within the interlamellar space in Mg−TTMS. Initial attempts to synthesize isolated nanoscale particles of cadmium sulfide in Mg−TTMS yielded only bulk precipitates.

In summary, a range of layered magnesium organosilicates with covalently linked organic functionalities can be synthesized via a simple low-temperature route. The general applicability of this method suggests that it should be possible to prepare appropriate lamellar hybrid materials for the intra- and interlayer construction of molecular and superlattice arrays of inorganic and organometallic guest species. To test the feasibility of this approach, we have demonstrated that the in situ reactivity of covalently linked thiol moieties can be used to prepare Au nanoparticles within the interlayer spacings of Mg−TTMS. There are many other possibilities which remain unexplored.

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