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New Layered Calcium Organosilicate Hybrids with Covalently Linked Organic Functionalities

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A series of layered calcium organosilicate hybrids containing covalently linked organic functionalities was synthesized by a sol−gel process from the reaction of calcium salt and organotrialkoxysilane with alkyl (from methyl to octadecyl) and phenyl functionalities in an aqueous/ethanolic basic solution at room temperature. These hybrid organic−inorganic materials were characterized by XRD, TEM, FTIR, and solid state ^{29}Si, ^{1}H, and ^{13}C NMR spectroscopy. The comparison of the basal distance measured by XRD and the length of the alkyl groups is consistent with a bilayer arrangement of the organic group inside the interlayer. The degree of basal ordering does not depend on the alkyl group length. Broad in-plane diffraction peaks are best explained by a smectite-like layer than by the parent inorganic calcium silicate hydrate (C−S−H) structure. This suggests the existence of edge-sharing $Ca(O,OH)_6$ layers separated by well-organized organosilicates. FTIR, ^{13}C, and ^{29}Si NMR spectra exhibit the typical features of Si−C bonds, showing that the organic groups have not been cleaved. Moreover, the ^{29}Si NMR spectrum shows that silanes are fully hydrolyzed but weakly condensated. To our knowledge, this is the first report of the synthesis and characterization of layered calcium silicate with organic functionalities directly bonded to the inorganic framework via Si−C bonds.

Introduction

Many ordered inorganic materials can be prepared under nonhydrothermal conditions by biomimetic template synthesis using self-organized assemblies of organic molecules.[1,2] Since the discovery of M41S in 1992,[3] synthesis routes of organized inorganic materials using surfactant micelles and liquid crystals have attracted considerable attention. A number of layered materials such as silicates, transition-metal oxides, and metallic phosphates have been obtained using ionic and nonionic surfactants.[4−14] The ordering is thought to proceed by the coassembly of the inorganic monomers or oligomers and surfactant headgroups through electrostatic or H-bonding interactions. Another strategy consists of using a surfactant with a polar head, which becomes an integral part of the inorganic framework during condensation leading to a layered covalent linked organic−inorganic hybrid. For example, Huo et al.[15,16] prepared lamellar phases using soluble precursors of Mg, Al, Mn, Fe, Co, Ni, and Zn oxides with surfactants containing sulfate ($C_nH_{2n+1}OSO_3Na$) or phosphate ($C_nH_{2n+1}OPO_3H_2$) polar heads. In these layered hybrids, the surfactant heads were presumably forming a part of the inorganic framework. A similar approach has been employed to produce multilayered organic−inorganic films with covalently attached organic functionalities between silica layers by hydrolysis and condensation of alkyldimethylmethoxysilanes or alkylmethyldimethoxysilanes in the presence of tetramethoxysi-

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(1) Mann, S.; Ozin, G. A. *Nature* **1996**, *382*, 313.
(2) Stupp, S. I.; Bruan, P. V. *Science* **1997**, *277*, 1242−1248.
(3) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834−10843.
(4) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147−1160.
(5) Oliver, S.; Kuperman, A.; Coombs, N.; Lough, A.; Ozin, G. A. *Nature* **1995**, *378*, 47−50.
(6) Sayari, A.; Karra, V. R.; Reddy, J. S.; Moudrakovski, I. L. *Chem. Commun.* **1996**, 411−412.
(7) Ogawa, M. *J. Am. Chem. Soc.* **1994**, *116*, 7941−7942.
(8) Dubois, M.; Gulik-Kryzywicki, T.; Cabane, B. *Langmuir* **1993**, *9*, 673−680.
(9) Tanev, P. T.; Liang, Y.; Pinnavaia, J. *J. Am. Chem. Soc.* **1997**, *119*, 8616−8624.
(10) Xu, A.-W. *Chem. Mater.* **2002**, *14*, 3625−3627.
(11) Clearfield, A. *Chem. Rev.* **1988**, *88*, 125−148.
(12) Clearfield, A. *Chem. Mater.* **1998**, *10*, 2801−2810.
(13) Khan, A. I.; O'Hare, D. *J. Mater. Chem.* **2002**, *12*, 3191−3198.
(14) Bujoli, B.; Pena, O.; Palvadeau, P.; Lebideau, J.; Payen, C.; Rouxel, J. *Chem. Mater.* **1993**, *5*, 583−587.
(15) Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176−1191.
(16) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317−321.

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lane.[17,18] Syntheses of layered organoclay materials with organic functionalities occupying the interlayer and covalently bonded to silicon have been recently reported.[19−28] A series of layered magnesium, nickel, and aluminum phyllo(organo) silicate hybrids have been prepared by a one-step direct association of Mg (Ni, Al) chloride and organotrialkoxysilane in alkaline conditions at room temperature. For Mg and Ni, these hybrid organic−inorganic materials have a lamellar structure analogous to 2:1 trioctahedral phyllosilicates (end member, talc $Si_8Mg_6O_{20}(OH)_4$) and, for Al-organoclay, a structure similar to dioctahedral phyllosilicate. Hydrothermal methods have been used as an alternative method to prepare crystallized organo-modified clays. Organo-grafted magnesium silicate based on hectorite has been obtained by refluxing aqueous slurries of magnesium hydroxide, LiF, and phenyltriethoxysilane.[29] However, these experimental conditions lead to partial breaking of the Si−C bonds and, consequently, to a limited loading of phenyl group. Well-crystallized organo-layered nickel phyllosilicate has been synthesized under hydrothermal conditions from nickel acetate, (aminopropyl)triethoxysilane, and ammonium fluoride as the mineralizing agent at neutral pH.[30] The low content of Si in the hybrid (Si/Ni = 1/3), as compared to the 4Si/3Ni of the initial ratio, suggests the formation of siloxane oligomers that remain soluble in the filtrate. Recently, Fujii et al. succeeded in synthesizing alkylammonium/magnesium phyllosilicate hybrids by hydrothermal reaction from $Mg(OH)_2$, silica sol, and octadecyldimethyl(3-trimethoxysilylpropyl)ammonium chloride.[31]

In most of the Mg-organoclays, comparisons between the $d_{(001)}$ spacing and the length of the organic functionalities are consistent with an alternating or interdigitated arrangement of the organic groups between the inorganic sheets. However, Ukrainczyk et al.[28] observed a bilayer arrangement of the organic groups in the case of Al-organoclays and an increase of ordering with a longer (alkyl) organic group. The authors concluded that the ordering in Al-organoclays is mainly due to hydrophobic surfactant chain interactions and the formation of liquid crystals, rather than the grafting of silanes to the preformed gibbsite-like sheet. On the contrary, the authors suggest that the organization of Mg-organoclays is likely to be driven by the formation of brucite-like sheets. This may lead to a decrease of surfactant interactions and an interpenetration of the organic group in the interlayer.

In this study, we report for the first time the synthesis and the characterization of a series of new covalently linked inorganic−organic hybrids with lamellar structure obtained by condensation of organotrialkoxysilane in the presence of calcium ions. Unlike magnesium, the inorganic 2:1 phyllosilicate structure is incompatible with calcium. On the other hand, calcium silicate hydrate (C−S−H), which is the major product of Portland cement hydration, is thought to form a layer structure related to tobermorite or jennite.[32] The present work demonstrates that organic hybridization of calcium silicate layers can be successfully achieved with a high level of crystallinity. The inorganic component of these layered hybrids is much closer to those of phyllosilicate than that of C−S−H derived materials. In this work, the structure and comparison of Mg and Ca layered organosilicate hybrids are discussed.

Experimental Section

Materials. All of the chemicals used were reagent grade and were used as received without further purification. The silanes used were methyltriethoxysilane (MTES), ethyltriethoxysilane (ETES) *n*-butyltrimethoxysilane (BTMS), *n*-hexyltriethoxysilane (HTES), *n*-octyltriethoxysilane (OTES), *n*-dodecyltriethoxysilane (DDTES), *n*-octadecyltrimethoxysilane (ODTMS), phenyltriethoxysilane (PTES), and tetraethoxysilane (TES). Alkyltrialkoxysilanes and PTES were purchased from Gelest. The other reagents were obtained from Aldrich. The desired organosilane (5×10^{-3} mol) was hydrolyzed for 1 h in a solution containing 0.46 g of $CaCl_2$ dissolved in 0.1 M HCl (1.35 cm^3) and ethanol (6.9 cm^3). In this mixture, the Si/Ca/H_2O/ethanol molar ratio was 1/0.83/15/30. The Ca/Si molar ratio of 0.83 is the typical molar ratio found in well-crystallized calcium silicate hydrates C−S−H.[32] All of these mixtures are homogeneous except for DDTES and ODTMS as starting silanes which are not soluble in the solution. In the case of ODTMS, a precipitate is observed in less than 10 min. To all of these mixtures was rapidly added 1 cm^3 of aqueous sodium hydroxide solution (14 mol dm^{-3}) under stirring. The base addition to the Ca−silane solution resulted in a rapid precipitation. The precipitate was aged for 12 h at room temperature and then washed twice by centrifugation with deionized water. The white solid was dried at room temperature at an atmosphere of 11% RH for 2 weeks (equilibrium with saturated aqueous $LiCl\cdot H_2O$). Mg−DDTES and Mg−ODTMS hybrids were obtained following the same procedure by substituting $CaCl_2$ for $MgCl_2\cdot 6H_2O$. Ca and Mg hybrids were also synthesized following the same procedure but without the acidic hydrolysis stage. Finally, inorganic calcium silicate hydrate (C−S−H) was obtained with TES as the starting silane.

Characterization. Elemental analysis was performed using ICP atomic absorption for calcium and silicon after heat treatment of the samples at 1200 °C to remove organic groups. X-ray diffraction patterns were performed on an INEL CPS120 curved-detector powder diffraction set up in transmission mode (Debye−Scherrer geometry) with Cu Kα_1 radiation (30 mA × 30 kV).[33] 0.5 mm Lindemann capillaries were used as sample

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(17) Shimojima, A.; Sugahara, Y.; Kuroda, K. *J. Am. Chem. Soc.* **1998**, *120*, 4528−4529.

(18) Shimojima, A.; Umeda, N.; Kuroda, K. *Chem. Mater.* **2001**, *13*, 3610−3616.

(19) Fukushima, Y.; Tani, M. *J. Chem. Soc., Chem. Commun.* **1995**, 241−242.

(20) Burkett, S. L.; Press, A.; Mann, S. *Chem. Mater.* **1997**, *9*, 1071−1073.

(21) Mann, S.; Burkett, S. L.; Davis, S. A.; Fowler, C. E.; Mendelson, N. H.; Sims, S. D.; Walsh, D.; Whilton, N. T. *Chem. Mater.* **1997**, *9*, 2300−2310.

(22) Whilton, N. T.; Burkett, S. L.; Mann, S. *J. Mater. Chem.* **1998**, *8*, 1927−1932.

(23) Muthusamy, E.; Walsh, D.; Mann, S. *Adv. Mater.* **2002**, *14*, 969−972.

(24) Fonseca, M. G. d.; Airoldi, C. *J. Chem. Soc., Dalton Trans.* **1999**, 3687−3692.

(25) Fonseca, M. G. d.; Silva, C. R.; Airoldi, C. *Langmuir* **1999**, *15*, 5048−5055.

(26) Fonseca, M. G.; Silva, C. R.; Barone, J. S.; Airoldi, C. *J. Mater. Chem.* **2000**, *10*, 789−795.

(27) Fonseca, M. G.; Airoldi, C. *J. Mater. Chem.* **2000**, *10*, 1457−1463.

(28) Ukraincky, L.; Bellman, R. A.; Anderson, A. B. *J. Phys. Chem. B* **1997**, *101*, 531−539.

(29) Carrado, K. A.; Xu, L.; Csencsits, R.; Muntean, J. V. *Chem. Mater.* **2001**, *13*, 3766−3773.

(30) Richard-Plouet, M.; Vilminot, S.; Guillot, M.; Kurmoo, M. *Chem. Mater.* **2002**, *14*, 3829−3836.

(31) Fujii, K.; Hayashi, S.; Kodama, H. *Chem. Mater.* **2003**, *15*, 1189−1197.

(32) Taylor, H. F. W. *Cement Chemistry*, 2nd ed; Thomas Telford: London, 1997.

(33) Evain, M.; Deniard, P.; Jouanneaux, A.; Brec, R. *J. Appl. Crystallogr.* **1993**, *26*, 563−569.

Table 1. Elemental Composition of Ca−Organosilicate Hybrids

materials	Ca/Si molar ratio
Ca−TES	1.10
Ca−MTES	0.93
Ca−ETES	0.74
Ca−BTMS	0.74
Ca−HTES	0.92
Ca−OTES	0.84
Ca−DDTES	1.02
Ca−ODTMS	0.86
Ca−PTES	1.18

holders. $Na_2Ca_3Al_2F_{14}$ (cubic, $a = 10.257(1)$ Å)[34] and silver behenate ($d(001) = 58.380(3)$ Å)[35] were chosen as standards for linearization at high and low angles, respectively (step size = 0.06°). Patterns were collected with an exposure time of about 5 h. Infrared spectra were carried out in transmission mode from powder diluted in a dried KBr pellet on a Perkin-Elmer model 1600 FTIR spectrophotometer. Solid-state NMR experiments were carried out on a Bruker ASX 500 spectrometer. For the ^{29}Si nuclei, cross-polarization magic angle spinning (CP-MAS) was employed with the following: contact time, 2 ms; recycling time, 5 s; spinning rate, 5 kHz; and TMS as standard reference. ^{13}C CP-MAS NMR spectra were acquired with a recycling time of 8 s at a spinning rate of 7 kHz and with glycine as standard reference. ^1H simple pulse experiments were carried at high spinning rate (12 kHz) with adamantane as the standard reference. Transmission electron microscopy (TEM) was performed on samples dispersed on a carbon membrane using a Philips CM-30 microscope operating at 300 keV.

Results

Elemental Analysis. The elemental analysis of the calcium organosilicates is listed in Table 1. The Ca/Si molar ratios of the products are close to those of the starting reaction mixture (Ca/Si = 0.83). The weight loss of the samples after heat treatment at 1200 °C increases as the content of carbon in the organic group linked to Si increases, suggesting that the Si−C bond remained intact during synthesis. This assertion will be confirmed by NMR measurements (see NMR section).

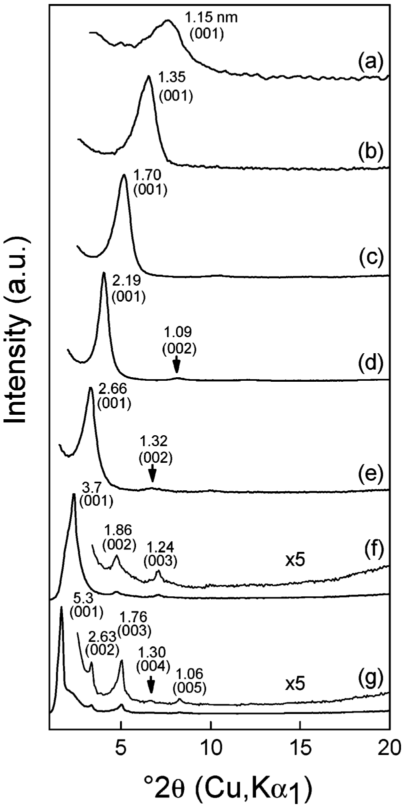

Figure 1. XRD patterns of Ca−organosilicates made with hydrolyzed alkyltrialkoxysilanes. (a) Ca−MTES, (b) Ca−ETES, (c) Ca−BTMS, (d) Ca−HTES, (e) Ca−OTES, (f) Ca−DDTES, (g) Ca−ODTMS. Interlayer spacing (d_{00l}) is given in nanometers.

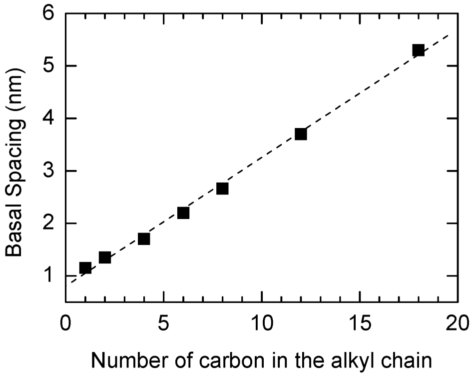

Figure 2. Basal distance of Ca−organosilicates versus the number N of carbon atoms in alkyl functionalities. Dotted line: linear fit, $0.85 + 0.25N$ (nm).

X-ray Diffraction and TEM. The powder diffraction patterns of the synthesized Ca−organosilicates are consistent with a lamellar structure model (Figure 1). In each case, the basal d_{001} reflection increases with the organic functionality size, suggesting the presence of organic moieties in the interlayer space as in Mg-organoclays.[20] Ca−organosilicates with a long alkyl chain exhibit n-order reflections of the basal distance. Figure 2 shows that the variation of d_{001} with the number N of carbon from 1 to 18 in the n-alkyl functionalities may be fitted by a straight line equal to $0.85 + 0.25N$ (nanometers). The value of 0.25 nm is approximately equal to twice the carbon−carbon distance (0.127 nm) projected on the axis along an extended paraffinic chain.[36] This suggests a bilayer arrangement of the alkyl functionalities between inorganic sheets. The tactoid sizes calculated from the fwhm of the d_{001} peak with the Scherrer equation (no correction for instrument broadening and Lorentz polarization factor) are comprised between 4 and 6 scattering layers ($1/d_{001}$) in the alkyl series from $N = 1- 12$, and 12 for Ca−ODTMS.

The TEM image of Ca−HTES (Figure 3) clearly reveals the ordered lamellar morphology of the hybrids, indicating that the particles are well crystallized.

Several broad higher angle (in-plane) reflections may be observed in XRD patterns (Figure 4). XRD patterns of samples with small organic moieties show in-plane peaks at $2\theta = 29.6°$ ($d = 0.30$ nm) and $2\theta = 51.3°$ ($d = 0.178$ nm). To compare in-plane reflections of Ca−organosilicates and parent inorganic calcium silicate hydrates (C−S−H), the XRD pattern of Ca−TES is shown in Figure 4. The calcium silicate hydrate prepared with TES and calcium chloride presents an XRD

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[34] Courbion, G.; Ferey, G. *J. Solid State Chem.* **1988**, *76*, 426−431.

[35] Huang, T. C.; Toraya, H.; Blanton, T. N.; Wu, Y. *J. Appl. Crystallogr.* **1993**, *26*, 180−184.

[36] Kitaigorodskii, A. I. *Organic Chemical Crystallography*; Consultant Bureau: New York, 1961.

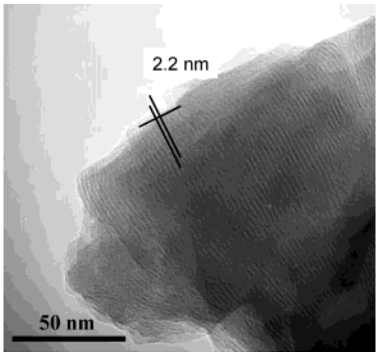

Figure 3. TEM micrograph of Ca−HTES showing layered morphology.

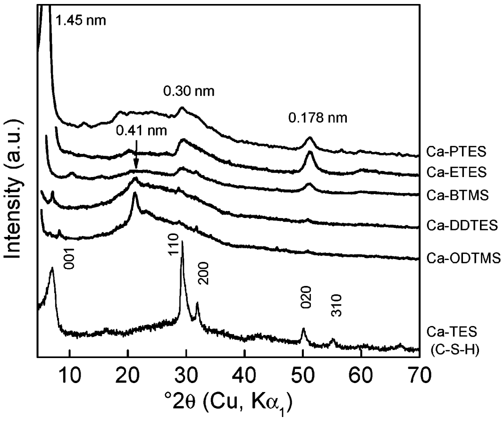

Figure 4. XRD patterns at high angle of layered calcium organosilicate hybrids and C−S−H (Ca−TES).

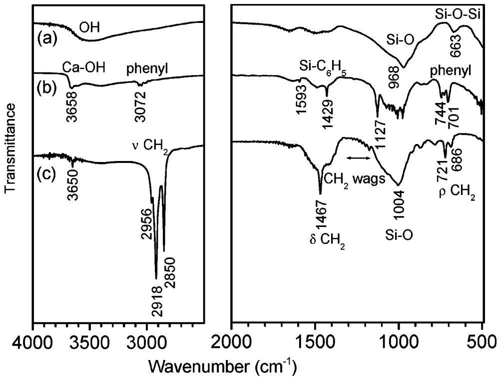

Figure 5. Infrared spectra of (a) Ca−TES, (b) Ca−PTES, and (c) Ca−ODTMS.

pattern typical of a relatively highly crystalline specimen of C−S−H.[32] The structure of C−S−H has not been fully determined, but may be inferred from 1.1 nm-tobermorite ($Ca_5Si_6O_{15}(OH)_3{\cdot}2H_2O$).[32] Tobermorite has a layer structure with a layer thickness from 1.1 to 1.4 nm depending on the water content. In tobermorite, silicate chains with a period of three tetrahedra are condensed onto each side of a distorted calcium octahedra bilayer.[37] In each level of the calcium bilayer, polyhedra share edges, whereas polyhedra from one level to the other are linked via vertices. In C−S−H, some tetrahedra are missing, depending on the Ca/Si ratio, but the Ca−O bilayer does not seem to be modified by the breaking of silicate chains.[38] The broad in-plane (*hk*0) peaks of C−S−H may be indexed in an orthorhombic cell with $a = 0.560$ nm and $b = 0.364$ nm. Many differences exist between the in-plane reflections of Ca−organosilicates and the parent calcium silicate. In particular, the reflection at $2\theta = 51.3°$ in the hybrids does not exist in C−S−H, suggesting a modification of the Ca/Si inorganic framework as compared to C−S−H. Assignment of in-plane reflections of Ca−alkylsilicates may be suggested on the basis of the 2:1 trioctahedral phyllosilicate structure. In 2:1 Mg−phyllosilicate, such as smectite, the *hk*0 reflections are indexed in rectangular base with $a \approx 0.53$ nm and $b \approx 0.93$ nm, where $a = \sqrt{3}d_{\mathrm{Mg-Mg}}$ and $b = 3d_{\mathrm{Mg-Mg}}$, and $d_{\mathrm{Mg-Mg}} \approx 0.31$ nm is the distance between magnesium atoms in the brucite-like sheet. In smectite, the most intense in-plane reflections are (110, 020), (130, 200), and (060, 330). Assuming that the 29.6° and 51.3° reflections of Ca−organosilicates are assigned to (130, 200) and (060, 330), respectively, we obtain a Ca−Ca distance of 0.351 ± 0.005 nm. This distance is close to the Ca−Ca distance ($d_{\mathrm{Ca-Ca}} = 0.359$ nm) found in portlandite ($Ca(OH)_2$), which crystallizes into the brucite-like structure.

As the length of the organic group increases, the *hk*0 peaks disappear, but a new reflection at $2\theta = 22°$ ($d = 0.41$ nm) can be observed. Due to the high ordering of long-chain samples, it may be suggested that the peak at 0.41 nm corresponds to the regular spacing between alkyl chains as it is observed in langmuir monolayers of *n*-alkyltrialkoxysilanes ($d = 0.47$ nm),[39] lamellar silicate mesophases obtained by the hydrolysis of *n*-octadecyltrichlorosilane ($d = 0.41$ nm),[40] TES in the presence of alkylammonium surfactant ($d = 0.41$ nm),[4] and the alkylammonium/magnesium phyllosilicate hybrid ($d = 0.41$ nm).[31]

The XRD diagram of Ca−PTES (Figure 4) is similar to the diagrams of short alkyl calcium silicate hydrates with $d_{001} = 1.45$ nm, which is a higher value than the one reported for Mg−PTES ($d_{001} = 1.18$ nm).[20,28] The lamellar distance seems too small to accommodate a bilayer arrangement, suggesting that phenyl molecules are partially interdigitated or arranged in an inclined disposition. Intralayer reflection, (130, 200) and (060, 330), characteristics of 2:1 trioctahedral phyllosilicate are also observed with phenyl moieties.

Infrared Spectroscopy. Figure 5 and Table 2 show IR data for the parent inorganic structure (Ca−TES), calcium phenyl-silicate (Ca−PTES), and calcium octadecyl-silicate (Ca−ODTMS). Comparisons between spectra of Ca−PTES and reported spectra of Mg−PTES[20,29] reveal that hybrid materials are similar. The same absorption bands assigned to the phenyl moiety are observed in Ca and Mg structures at 3072, 1429, 744, and 701 cm^{-1}, assigned to aromatic CH stretching, Si−C_6H_5 aromatic stretching, aromatic CH wagging, and aromatic ring bending, respectively. In Ca−PTES, the peak at 3658 cm^{-1} can be assigned to CaO−H. The spectrum of Ca−ODTMS given in Figure 5 shows the presence of three distinct peaks in the high-frequency region at 2956, 2918, and 2850 cm^{-1} assigned to CH_3

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(37) Hamid, S. A. *Z. Kristallogr.* **1981**, *154*, 189−198.

(38) Lequeux, N.; Morau, A.; Philippot, S.; Boch, P. *J. Am. Ceram. Soc.* **1999**, *82*, 1299−1306.

(39) Fontaine, P.; Goldmann, M.; Rondelez, F. *Langmuir* **1999**, *15*, 1348−1352.

(40) Parikh, A. N.; Schivley, M. A.; Koo, E.; Seshadri, K.; Aurentz, D.; Mueller, K.; Allara, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 3135−3143.

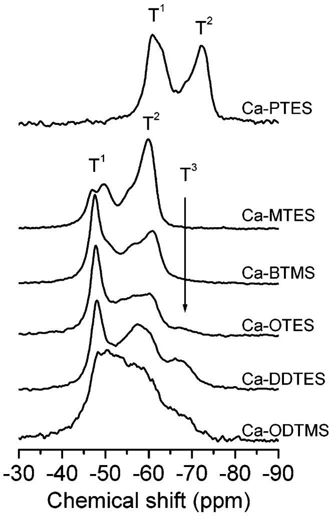
Table 2. Assignments of IR Bands for Calcium Organosilicate Hybrids (Ca−PTES and Ca−ODTMS)

materials	assignments	frequency (cm^{-1})
Ca−TES (C−S−H)	interlayer water molecules, H-bending, O−H str	∼3600
	Si−O str	968
	Si−O−Si bend	663
Ca−PTES	Ca−OH	3658
	aromatic C−H str	3072
	aromatic C═C ring str	1593
	Si− aromatic str	1429
	R−SiO	1127
	Si−O str	∼1000
	aromatic C−H wagging	744
	aromatic C−H str	701
Ca−ODTMS	Ca−OH	3650
	CH_3 (r$^-$)	2956
	CH_2 (d$^-$, d$^+$)	2918, 2850
	CH_2 (δ)	1467
	CH_2 wagging	1175−1275
	Si−O str	∼1000
	CH_2 (ρ)	721, 686

asymmetric stretching (r$^-$), CH_2 antisymmetric (d$^-$), and CH_2 symmetric (d$^+$), respectively.[41] The position and the fwhm values of the CH_2 mode peaks, 20 and 15 cm^{-1}, estimated for the d$^-$ and d$^+$ are consistent with highly ordered, *all-trans* chains.[42] In addition, the sharp peak at 1467 cm^{-1} (fwhm ≈ 13 cm^{-1}) assigned to the CH_2 scissoring deformation mode (δ) and the series of band between 1175 and 1275 cm^{-1} attributed to CH_2 wag modes are indicative of the presence of conformationally ordered alkyl chains in agreement with XRD results.[40,43] As in Ca−PTES, a band at 3650 cm^{-1} assigned to Ca−OH is observed in Ca−alkylsilicates. Whereas this band position is similar to that observed in Portlandite, Ca(OH)$_2$, this mineral phase is not detected by XRD, suggesting that Ca−OH bonds are integrated within the inorganic part of the hybrids.[44] This result agrees with the assumption of a phyllosilicate-like inorganic layer rather than a parent C−S−H structure, because C−S−H with a low calcium-to-silicon ratio does not contain Ca−OH groups[45] (see Figure 5).

The low frequency of the Si−O−Si stretching band centered at ∼1000 cm^{-1} in Ca−ODTMS as compared to about 1100 cm^{-1} in *n*-octadecylsiloxane[40] and in Mg−octadecylsilicate[28] is characteristic of a low degree of silicate polymerization. This observation is consistent with previous studies which showed a shift of this band toward lower frequency with the decrease of the silicate polymerization.[45,46]

NMR. ^{29}Si CP-MAS NMR spectra of Ca−organosilicates (Ca−MTES, Ca−BTMS, Ca−OTES, Ca−ODTES, Ca−DDTES) and Ca−PTES are shown in Figure 6. All of the spectra have peaks in the chemical shift range of trifunctional silicon ($T^n = RSi(OR')_{3-n}(OSi)_n$), confirming the chemical stability of the Si−C bond. The chemical shifts of T^n silicon with phenyl groups are shifted upfield by approximately 12 ppm with respect to alkyl groups, in agreement with results observed in Mg−organosilicates[20] and various organosiloxanes.[47,48] In all of the samples, T^1 and T^2 species are observed in addition with T^3 species for the long-chain alkyl groups. In contrast to Mg−organosilicates which contain in general a large proportion of fully condensed T^3 silicon,[20,28] the proportion of T^3 in Ca−organosilicates quantified by MAS NMR (not reported here) does not exceed 30%. The low degree of condensation in Ca−organosilicates suggests that in these hybrids Ca−O−Si bonds are promoted with respect to Si−O−Si bonds, assuming that silanol groups Si−OH are in low content due to the high pH condition of synthesis and that alkoxy groups Si−OR do not remain in the solid because composites are extensively washed with deionized water (see ^{13}C NMR results). As the length of the alky chains increases, peak broadening is observed, indicating a disorder increase of the T^n silicon species.



	Chemical Shift (ppm)		
	T^1	T^2	T^3
Ca-PTES	-61	-72	
Ca-alkylsilanes	-47 to -50	-56 to -61	~ -67

Figure 6. ^{29}Si CP-MAS NMR spectra of Ca−organosilicates. $T^n = RSi(OSi)_n$.

The ^{13}C CP-MAS NMR and ^{1}H NMR spectra of Ca−PTES are shown in Figure 7. The sample was dried under vacuum at 100 °C during 1 day prior to measurements to remove residual ethanol and water molecules. The ^{13}C NMR spectrum shows one peak at 135 ppm related to the phenyl group and a very small peak at 58 ppm related to residual alkoxy groups bonded to silicon.[49] The broad resonance of the phenyl group and the presence of sidebands indicate that the organic groups are in a rigid solidlike environment. The ^{1}H NMR spectrum of Ca−PTES shows two resolved peaks at 7.1 and −0.5 ppm. The peak at 7.1 ppm may be assigned to protons in phenyl groups. The contribution

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(41) Snyder, R. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145−5150.

(42) MacPhail, R. A.; Strauss, H. L.; Snyder, R. G.; Elliger, C. A. *J. Phys. Chem.* **1984**, *88*, 334−341.

(43) Snyder, R. G. *J. Chem. Phys.* **1967**, *47*, 1316−1358.

(44) Ryskin, Y. I. In *The Infrared Spectra of Minerals*; C., F. V., Ed.; Mineralogy Society: London, U. K., 1974; pp 137−181.

(45) Yu, P.; Kirkpatrick, R. J.; Poe, B.; McMillan, P. F.; Cong, X. *J. Am. Ceram. Soc.* **1999**, *82*, 742−748.

(46) McMillan, P. F.; Wolf, G. H. In *Structure, Dynamics and Properties of Silicate Melts*; Stebbins, J. F., McMillan, P. F., Dingwell, D. B., Eds.; Mineralogy Society of America: Washington, 1994; Vol. 32, pp 247−215.

(47) Engelhardt, G.; Jancke, H.; Magi, M.; Pehk, T.; Lippmaa, E. *J. Organomet. Chem.* **1971**, *28*, 293.

(48) Engelhardt, G.; Magi, M.; Lippmaa, E. *J. Organomet. Chem.* **1973**, *54*, 115−122.

(49) Loy, D. A.; Baugher, B. M.; Baugher, C. R.; Schneider, D. A.; Rahimian, K. *Chem. Mater.* **2000**, *12*, 3624−3632.

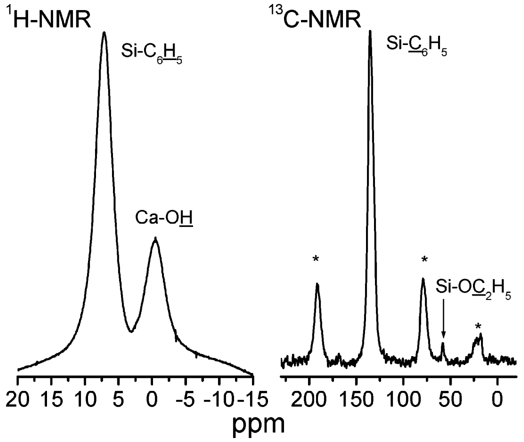

Figure 7. ^{1}H MAS NMR and ^{13}C CP-MAS NMR spectra of Ca−PTES. (* denotes spinning sidebands.)

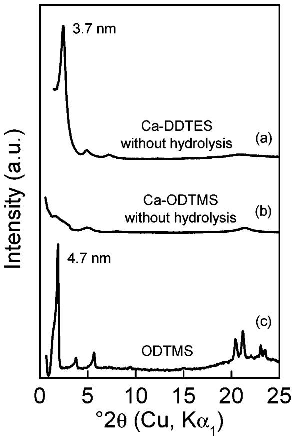

Figure 8. Powder XRD diagrams of (a) Ca−DDTES and (b) Ca−ODTMS synthesized without the acidic hydrolysis stage of the organotrialkoxysilanes prior to precipitation, and (c) *n*-octadecyltrimethoxysaline (ODTMS) after acidic hydrolysis in water/ethanol solution.

of protons of Si−OH groups, which are generally observed between +16 and +5 ppm in calcium silicates hydrates,[50] cannot be ruled out. The chemical shift of the peak at −0.5 ppm is clearly in the chemical shift range of the protons of Ca−OH (+4 to −1 ppm).[50] This result is consistent with FTIR data which showed the presence of CaOH groups in the hybrids.

Acidic Hydrolysis Effect. A series of Ca−organosilicates was synthesized without the acidic hydrolysis stage of the organotrialkoxysilane. No difference between the XRD and ^{29}Si NMR spectrum of hydrolyzed and nonhydrolyzed samples is found except for Ca−ODTMS which does not present a lamellar order when the silane is not hydrolyzed before the addition of sodium hydroxide solution, as seen in Figure 8. The behavior of *n*-octadecyltrimethoxysilane in alcohol/water solution differs significantly from the behavior of the other alkylsilanes. In the case of ODTMS without acidic hydrolysis, a nonmiscible oily phase is observed which is stable for more than 1 h. Lowering the pH by addition of HCl results in a rapid formation of a white gelatinous precipitate. XRD diffraction of the precipitate after 1 h of hydrolysis is consistent with the formation of a layered organosilane crystal with a basal distance of 4.7 nm (Figure 8c). Parikh et al. have shown that simple hydrolysis of *n*-octadecyltrichlorosilane in water leads to the formation of layered crystals constituted from stacks of head-to-head bilayers in which each layer is comprised of conformationally ordered alkyl chains.[40] They observed a basal distance of 5.3 nm higher than the theoretical value predicted for a bilayer arrangement and then concluded to the presence of a single molecule layer of intercalated water in the $RSiO_x-O_x$-SiR interface layer. In the present case of *n*-octadecyltrimethoxysilane, the basal distance lower value of the crystalline organosilane may be due to the crystalline difference assemblies of the alkyl chains. This may be attributed to the difference of reactivity of the silanes used in both experiments and the difference of the synthesis conditions. Moreover, in the case of *n*-ODTMS precursor, many details of the lateral ordering of the hydrocarbon chains can be seen by XRD between 20° and 25° (2θ), whereas only one broad peak centered at 21.45° (chain−chain distance) is reported with *n*-octadecyltrichlorosilane. Complementary experiments show that the basal distance of *n*-ODTMS layered crystals precipitated in acidic media is not modified if calcium chloride is absent from the starting solution. This result indicates that calcium ions are not incorporated in the *n*-ODTMS crystals after the acidic hydrolysis stage. When the pH is raised by addition of sodium hydroxide solution, the basal distance of the layered organosilicate increases from 4.7 to 5.3 nm, suggesting that it is only at this stage that calcium ions are incorporated into the layered hybrids by formation of Si−O−Ca bonds.

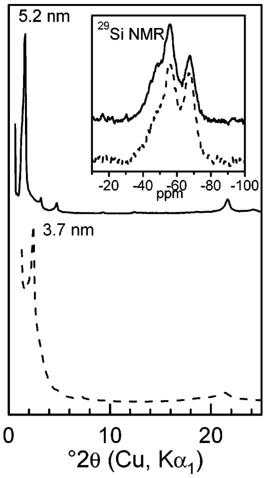

Figure 9. XRD patterns and ^{29}Si CP-MAS NMR spectra (inset) of Mg−ODTMS (line) and Mg−DDTES (dots).

Magnesium−Calcium Substitution. Mg−DDTES and Mg−ODTMS have been synthesized following the same procedure as for Ca−organosilicates and have been characterized by XRD and ^{29}Si CP-MAS NMR (Figure 9) spectroscopy. The substitution of Ca by Mg does not significantly modify the basal distance of the layered nanocomposites. As for Ca−alkylsilicates, the XRD results of Mg−alkylsilicates are consistent with a bilayered stack of *trans*-conformational alkyl chains in the interlayer. Several features are observed when comparing ^{29}Si NMR spectra of Mg−DDTES and Mg−ODTMS to those corresponding to Ca−alkylsilicates. It can be seen for Mg−DDTES and Mg−ODTMS that the

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(50) Heidemann, D. In *Application of NMR Spectroscopy to Cement Science*; Colombet, P., Grimmer, A. R., Eds.; Gordon, Breach: London, 1994; pp 77−102.

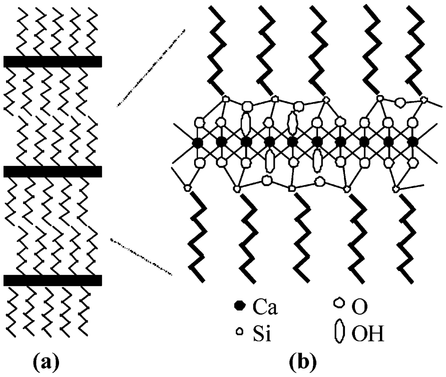

Figure 10. (a) Schematic representation of the layered calcium alkyl-silicate. (b) Tetrahedral silicate layers partially condensed to the central calcium octahedral layer. Alkyl chains are organized into lamellar bilayers.

T^1 peak (−49 ppm) is less intense and the T^3 peak (−67 ppm) is more intense as compared to those observed in Ca−DDTES and Ca−ODTMS, indicating a higher degree of condensation in nanocomposites made with Mg. The ^{29}Si NMR spectrum of Mg−DDTES is very similar to that obtained by Ukainczyk et al., whereas the layer spacing in the present case is much higher (3.7 vs 2.4 nm).[28]

Finally, without the prehydrolysis stage, Mg−DDTES is well crystallized and Mg−ODTMS is amorphous (XRD not presented here).The effect of acidic prehydrolysis of the silane on the hybrid structure appears to be similar whatever the nature of the ion used (Ca or Mg).

Discussion

The characterization data presented in the earlier sections led to a conclusion that the layered calcium organosilicate hybrids consist of an inorganic part with a structure analogous to that of smectites, and an organic part of alkyl chains grafted to the Ca phyllosilicate part through an Si−C bond and organized in an *all-trans* conformation (Figure 10). However, as compared to an ideal 2:1 trioctahedral phyllosilicate structure, the condensation of the silanes onto the calcium octahedral sheet is mainly modified due to the presence of organic groups pointing in the interlayer. Assuming an ideal Ca/Si ratio of 4/5, the calcium organosilane hybrids can be expressed as $(RSi)_5Ca_4O_{11.5-z/2}(OH)_z$.

Despite the previous works in the area of phyllosilicate hybrids, the mechanism of their assembly process is far from being well understood. The formation of these layered hybrids could be dominated by the self-organization of partially condensed organosilane molecules that form a template for condensation of aqueous metals species, leading to the formation of a claylike inorganic framework. This mechanism was proposed to describe the precipitation of Al−alkylsilicate at pH $\approx$ 5 by the observation that the degree of ordering of lamellar hybrids increases with the length of the alkyl chain, suggesting that the hydrophobic surfactant interactions of precursor silane molecules play an important role in the assembly process. However, in the case of Mg−alkylsilicates synthesized at pH $\approx$ 11.5, Ukrainczyk et al. obtained poorly ordered layers structure with interpenetrating long-chain alkyl groups in the interlayer.[28] It was postulated that the formation of Si−O−Si and Si−O−Mg promoted at high pH, related to the silane hydrolysis, spaces out the silane organic groups and decreases the surfactant interaction. So, in the case of magnesium, an alternative mechanism was proposed consisting of the grafting of silanol groups to the preexisting cationic octahedral sheets. In the present study, this last assumption may be ruled out because highly ordered Ca-organoclays and Mg-organoclays have been obtained at high pH. Moreover, the acidic prehydrolysis of the alkyltrialkoxysilane, which favors the formation of silanol groups and promotes the liquid crystal formation, does not seem to have an effect on the crystallinity (number of coherently scattering layers) of the lamellar hybrids, except for *n*-ODTMS. The high degree of organization of the organoclays obtained in the present work with alkylsilanes from methyl to octadecyl alkyl groups could be due to the much higher pH conditions (pH > 13.5) as compared to the reported synthesis. In extreme high pH conditions, the alkoxysilane hydrolysis rate becomes faster than the condensation rate because siloxane bonds are unstable, and it is likely that Si−O−Ca (or Si−O−Mg) and Ca−O−Ca (or Mg−O−Mg) bonds are promoted as compared to Si−O−Si bonds.[51] However, the degree of ordering in Ca−organosilicates does not seem to depend on the size of the alkyl chain (for $N < 18$), suggesting that ordering is not totally due to hydrophobic surfactant interaction. All of these results suggest that the precipitation of layered hybrids involves the cooperative assembly of inorganic and organic components similar to that described for silica-surfactant mesophases.[52,53] The formation of layered calcium organosilicate hybrids may be favored by the electrostatic matching between highly charged anionic organosilicate and calcium ions. Once the Si−O−Ca condensation is triggered, these precursors can condensate into a lamellar structure via hydrophobic interaction of the organic chains of the silane and via the formation of Ca−O−Ca bonds.

The mechanism of the precipitation of Ca−ODTMS and Mg−ODTMS seems to be slightly different because the crystallization of the *n*-octadecyltrimethoxysilane into the lamellar structure, promoted by acidic hydrolysis, plays a key role in the formation of lamellar Ca or Mg organoclays. It is apparent that for this long alkyltrialkoxysilane, the final lamellar structure of the calcium (or magnesium) organosilicate hybrid is strongly directed by the self-organization of the silane in solution due to strong hydrophobic interaction. Moreover, the interactions between the long alkyl chains seem able to disorder the organization of the inorganic part of the hybrid because the in-plane reflection disappears and the ^{29}Si NMR peaks are broadened.

The main differences between Ca and Mg organoclays are observed by ^{29}Si NMR. Silicon is more condensed in hybrids made with magnesium than those made with calcium. Because both (calcium and magnesium) organosilicate hybrids present about the same degree of

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(51) Brinker, C. J.; Scherer, G. W. In *Sol−Gel Science*; Academic Press, Ed.; Harcourt, Brace, Jovanovich: Boston, 1990.

(52) Beck, J. S.; Vartuli, J. C. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 76.

(53) Soler-Illia, G.; Sanchez, C.; Lebeau, B.; Patarin, J. *Chem. Rev.* **2002**, *102*, 4093−4138.

ordering, the condensation difference is likely to be due to the difference between the cation size in the brucite-like layer rather than a difference in assembly process. This difference can influence the mismatch that can be tolerated at the interface between the octahedral and organosilicate layers. It is interesting to note that in layered calcium silicate minerals, due to the large size of the calcium ion, the calcium octahedral sheet can accommodate only unbranched silicate chains.[54] This structure of chains seems to persist in the calcium organosilicates.

Conclusions

Novel layered calcium organosilicates with covalently linked organic functionalities can be synthesized via a simple low-temperature route. The functionalized calcium silicates obtained by hydrolysis and polycondensation in water/ethanolic solution of trialkoxysilanes and calcium ions at high pH show long-range order. In the case of *n*-alkyltrialkoxysilanes as starting precursors, XRD data are consistent with a bilayer chain arrangement in the interlayer. The structure of the inorganic part of the nanocomposite does not look like the parent calcium silicate hydrate (C−S−H) structure but is similar to a 2:1 trioctahedral phyllosilicate-like structure. Except for the longer alkylsilane used in this study (*n*-octadecyltrimethoxysisilane), the degree of ordering does not increase with the length of the alkyl groups from methyl to dodecyl and does not depend on a (acidic) prehydrolysis stage of the silanes before the precipitation of the hybrids. These results suggest a cooperative assembly process of the inorganic and organic components during precipitation of the nanocomposites.

Magnesium alkylsilicate layered hybrids have been also synthesized in this study. The substitution of Ca by Mg does not affect the organization of the hybrid. A very high pH condition of syntheses seems to be the key of successful well-crystallized calcium or magnesium organosilicate hybrids.

All of the results suggest a new methodology for the linking of organic moieties to inorganic silicates, and, in the case of the calcium silicate system, this simple approach may offer a very powerful tool to design new cement-based materials.

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(54) Liebau, F. *Structural Chemistry of Silicates*; Springer-Verlag: Berlin, 1985.