Formation of Layered Silica−Alcohol Nanostructured Materials from Alkoxytrichlorosilanes

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Novel layered silica−organic nanostructured materials were prepared by hydrolysis and condensation of alkoxytrichlorosilanes (n-$C_nH_{2n+1}OSiCl_3$, $n = 12$, 14, 16, 18, and 20) as single precursors. The formation relies on the self-assembly of alkoxysilanetriols (n-$C_nH_{2n+1}OSi(OH)_3$) generated by the preferential hydrolysis of Si−Cl groups in the precursors. The products exhibited the XRD patterns indicative of layered structures whose *d* spacings varied in the range of 3.95 to 6.13 nm depending on the alkyl chain lengths. The SEM images of the products showed well-defined platelike morphologies on micrometer length scales, reflecting the layered structures of the products. Further structural characterization by solid-state ^{29}Si and ^{13}C NMR and FTIR revealed that the layered structures consisted of bimolecular layers of long-chain alcohols and thin silica layers. Condensation of alkoxysilanetriols proceeded in the solid state to form silica networks, being accompanied by the cleavage of the alkoxy groups. The present results provide a new approach for the construction of silica-based nanostructured materials with well-regulated organic arrays and silica networks.

Introduction

The preparation of ordered inorganic−organic nanostructured materials has been attracting significant interest from both scientific and technological viewpoints.[1,2] Recently, self-organization of amphiphilic molecules has developed as an efficient and versatile way to create highly ordered nanomaterials with wide varieties of compositions, structures, and morphologies. It is well-established that silica−surfactant mesostructured (lamellar, hexagonal, or cubic) materials can be prepared by using surfactants as structural directors for the condensation of silicate species.[3,4] However, their formation process is very complicated due to the random polymerization of silicate species during the self-assembly, and also to the weak interactions between surfactants and silicate species.

The use of specific precursors where organic molecules are covalently attached to inorganic species opens up a possibility for the preparation of unique inorganic−organic nanostructured materials.[5−10] Self-organization of organosilane molecules during hydrolysis and condensation has been studied intensively.[6−10] We have reported the formation of multilayered hybrids via the hydrolysis and condensation of alkyltriethoxysilanes ($C_nH_{2n+1}Si(OEt)_3$, $n = 12{-}18$).[9] This process involves the self-assembly of hydrolyzed monomers having both hydrophobic alkyl chains and hydrophilic silanol groups. Such methods based on the use of the single precursors allow facile control of the reaction. Moreover, better control of the nanostructure is expected because the siloxane formation should be regulated to some extent by the steric restriction in the self-assembled structures.

Our recent interest is focused on the incorporation of organic groups by Si−O−C bonds instead of Si−C bonds to control the nature of the inorganic−organic interface. This is quite important to tailor the structure and properties of the resulting silica-based nanomaterials.[1,2] One of the most promising precursors is alkoxysilanetriols ($ROSi(OH)_3$) with long *n*-alkyl chains, which are expected to have self-assembling ability. In contrast to the stable Si−C bonds in organosilanetriols, alkoxy groups (Si−O−C) can be cleaved easily to form alcohol molecules, implying the potential of such precursors to afford novel ordered silica−alcohol nanocomposites. The

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resulting nanostructured silica materials are of interest for their potential applications, such as adsorbents and nanofillers in polymer matrixes.

Although alkoxysilanetriols are commonly present in partially hydrolyzed solutions of tetraalkoxysilanes,[11] and also in alkali solutions of silicate and short chain alcohols,[12] their isolation is generally very difficult. Our preliminary study on the use of alkoxytrimethoxysilanes ($C_nH_{2n+1}OSi(OMe)_3$, $n = 12$ and 18) resulted in the formation of amorphous silica and alcohols even when the reaction was carefully performed with a controlled amount of water.[13] On the other hand, several kinds of silanetriols are known to be obtained by the controlled hydrolysis of the corresponding trichlorosilanes where organic groups are attached to Si atom via Si−C, Si−N, and Si−O bonds.[14−16] However, there has been no report on the selective formation of alkoxysilanetriols, and their use as self-assembling precursors for silica-based nanostructured materials has not been explored.

In this paper, we report the formation of layered silica−alcohol nanostructured materials from alkoxytrichlorosilanes with various alkyl chain lengths. We employed a new class of precursor molecules and reaction processes, and succeeded in the formation of amphiphilic alkoxysilanetriols. The structures of the resulting nanostructured materials were characterized in detail, and their formation processes, including the self-assembly of alkoxysilanetriols and the subsequent condensation step, are described here.

Experimental Section

Materials. Tetrachlorosilane (Tokyo Kasei Co., >98%) and alkyl alcohols ($C_nH_{2n+1}OH$, abbreviated as C*n*OH, $n = 8$ (Tokyo Kasei Co., >98%), $n = 10$ (Kanto Chemical Co., 95%), $n = 12$ (Tokyo Kasei Co., 99%), $n = 14$ (Tokyo Kasei Co., 98%), $n = 16$ (Wako Pure Chemical Co., 95%), $n = 18$ (Wako Pure Chemical Co., 98%), and $n = 20$ (Tokyo Kasei Co., 96%)) were used as received for the preparation of the precursors (see below). Other chemicals, including aniline, diethyl ether, *n*-hexane, and tetrahydrofuran (THF), were purchased from Kanto Chemical Co., and used as received.

Synthesis of the Precursors. *n*-Alkoxytrichlorosilanes ($C_nH_{2n+1}OSiCl_3$, abbreviated as C*n*OTCS, $n = 8$, 10, 12, 14, 16, 18, and 20) were synthesized by the reactions of $SiCl_4$ and the corresponding C*n*OH with the molar ratio of $SiCl_4$/C*n*OH = 1:1. In a typical procedure, C*n*OH dissolved in *n*-hexane was added dropwise to a hexane solution of $SiCl_4$ under a nitrogen flow, and the mixture was stirred at room temperature for 1.5 h. The resulting solution contains $(CnO)_mSiCl_{4-m}$ ($m = 0-3$), which was confirmed by ^{29}Si NMR (see below). Removal of hexane and residual $SiCl_4$ followed by vacuum distillation yielded C*n*OTCS as a clear liquid.

The ^{29}Si NMR spectrum of the reaction mixture of $SiCl_4$ and C16OH, for example, exhibits four signals at −18.7, −38.6, −55.8, and −70.1 ppm, which can be assigned to unreacted $SiCl_4$, (C16O)*Si*Cl_3, $(C16O)_2$*Si*Cl_2, and $(C16O)_3$*Si*Cl, respectively.[17] The isolation of C16OTCS was confirmed by the appearance of a single signal at −38.6 ppm (see Figure S1 in Supporting Information). The ^{13}C NMR spectrum of C16OTCS showed the signals assigned to the alkoxy groups (Figure S2), where the signal assigned to the carbon atom adjacent to oxygen atom (α carbon) appears at 66.6 ppm, being shifted from that of C16OH (62.5 ppm). The spectroscopic data for C*n*OTCS ($n = 8-20$) are contained in the Supporting Information.

Hydrolysis and Condensation of C*n*OTCS. C*n*OTCS (ca. 1.0 g) dissolved in diethyl ether (10 mL) was added dropwise to the mixture of diethyl ether (20 mL), THF (20 mL), aniline, and H_2O under vigorous stirring in an ice bath. The molar ratio of C*n*OTCS/H_2O/aniline was 1.0:3.3:3.3. Aniline was used as an acceptor of HCl generated by the hydrolysis of Si−Cl groups in the precursors. After stirring for 1.5 h, the precipitate of aniline hydrochloride was removed by filtration to give a clear solution. In the cases of $n = 16$, 18, and 20, white precipitates were readily formed on cooling the solutions below −20 °C, whereas precipitation did not occur in the cases of $n = 8$, 10, 12, and 14. Precipitates were obtained for $n = 12$ and 14 by adding hexane (50 and 30 mL, respectively) in the solutions, followed by cooling the solutions in a similar manner. However, we could not obtain any solid products from C8OTCS and C10OTCS. The resulting precipitates were filtered, washed with hexane, and air-dried for 1 day to afford powdered samples.

Characterization. Liquid-state ^{29}Si and ^{13}C NMR spectra were obtained on a JEOL Lambda-500 spectrometer with resonance frequencies of 99.25 and 125.65 MHz, respectively. The sample solutions were put in 5-mm glass tubes, and tetramethylsilane (TMS) was added as an internal reference, and $CDCl_3$ or THF-d_8 was used to obtain lock signals. A small amount of $Cr(acac)_3$ was also added as a relaxation agent for ^{29}Si nuclei. Powder X-ray diffraction (XRD) patterns were recorded on a Mac Science M03XHF[22] diffractometer with Mn-filtered Fe Kα radiation. Field-emission scanning electron microscopic (FE-SEM) observations were performed for the samples coated with Pt−Pd using a Hitachi S-4500S field-emission microscope at an accelerating voltage of 15 kV. Solid-state ^{29}Si magic-angle spinning (MAS) NMR measurements were performed on a JEOL JNM-CMX-400 spectrometer at a resonance frequency of 79.42 MHz, with a pulse width of 45°, and a recycle delay of 100 s. Solid-state ^{13}C cross-polarization (CP)/MAS NMR spectra were obtained on the same spectrometer at a resonance frequency of 100.54 MHz, with a contact time of 1.5 ms, and a recycle delay of 5 s. Chemical shifts for both ^{29}Si and ^{13}C NMR were referenced to TMS at 0 ppm. FTIR spectra of the products in KBr pellets were obtained using a Perkin-Elmer Spectrum One spectrometer with a nominal resolution of 0.5 cm^{-1}. Thermogravimetry (TG) was carried out with a RIGAKU TG8120 instrument under a dry air flow at a heating rate of 10 °C/min, and the amounts of SiO_2 fractions in the products were determined by the residual weight after heating to 900 °C. The amounts of organic constituents were determined by CHN analysis (Perkin-Elmer PE-2400).

Results and Discussion

Formation of Alkoxysilanetriols by Controlled Hydrolysis of C*n*OTCS. We initially analyzed the solutions obtained by the hydrolysis of C*n*OTCS to confirm the formation of alkoxysilanetriols. The liquid-state ^{29}Si and ^{13}C NMR spectra of the solution obtained by the hydrolysis of C16OTCS are representatively shown in Figure 1. The ^{29}Si NMR spectrum (Figure 1a) shows a single signal at −73.4 ppm, being different from that of the precursor (−38.6 ppm). The signal can be assigned to C16O*Si*$(OH)_3$, based on the general findings that the signal due to silicic acid monomer (*Si*$(OH)_4$) appears at around −72 ppm, and shifts to lower

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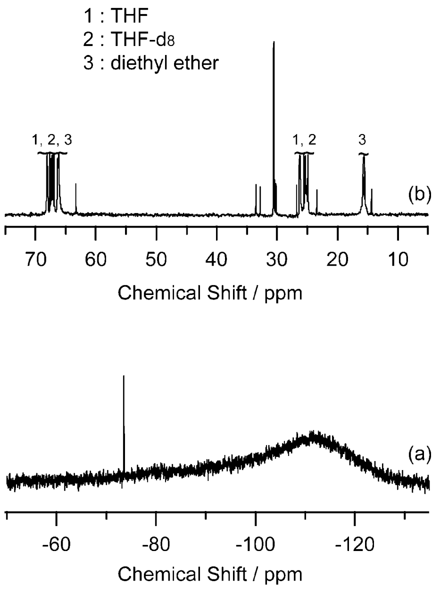
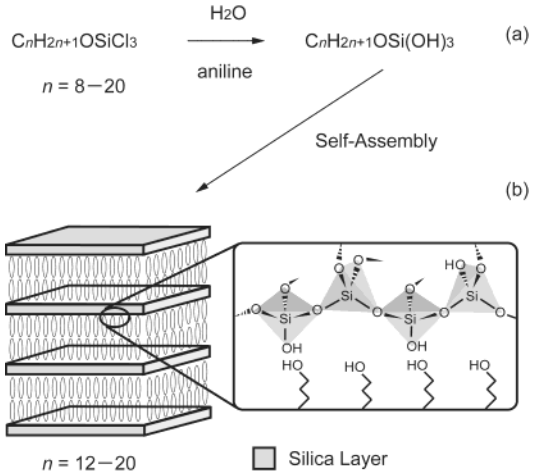


Figure 1. Liquid-state (a) ^{29}Si NMR and (b) ^{13}C NMR spectra of the solution obtained by the controlled hydrolysis of C16OTCS.

Scheme 1. (a) Formation of Alkoxysilanetriols from C*n*OTCS, and (b) Proposed Structural Model of the Resulting Layered Nanocomposites



frequency (~2 ppm) when one hydroxy group is replaced by an alkoxy group.[11,18−20] The low signal/noise ratio of the spectrum is attributed to the low concentration of C16OTCS in the initial reaction mixture, and the broad signal centered at −110 ppm arises from the glass tube used for the measurement. Furthermore, the ^{13}C NMR spectrum (Figure 1b) shows the signals due to C16 chains along with the strong signals due to the solvents (THF and diethyl ether). It is important that the signal assigned to the α carbon is observed at 63.3 ppm, and the value is different from that of either starting C16OTCS (66.6 ppm) or C16OH (62.5 ppm).[21] This result suggests that C16OTCS was fully reacted without the hydrolysis of alkoxy groups, being consistent with the ^{29}Si NMR data.

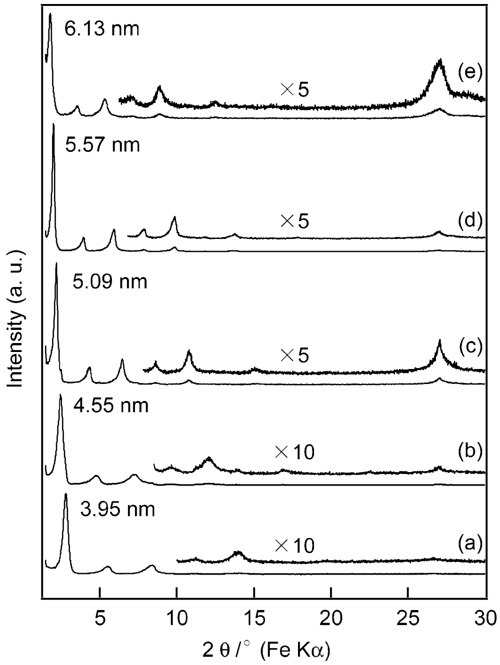


Figure 2. Powder XRD patterns of the products obtained by hydrolysis and condensation of C*n*OTCS with (a) $n = 12$, (b) $n = 14$, (c) $n = 16$, (d) $n = 18$, and (e) $n = 20$.

Similar ^{29}Si and ^{13}C NMR results were also obtained for $n = 8$, 10, 12, 14, 18, and 20, confirming the formation of alkoxysilanetriols ($C_nH_{2n+1}OSi(OH)_3$) (Scheme 1 (a)). The formation relies on the addition of a controlled amount of water ($H_2O/Si = 3.3$) for the reaction, in addition to the much higher reactivity of Si−Cl groups than that of Si−OR groups, which resulted in the preferential hydrolysis of Si−Cl groups in C*n*OTCS. The addition of aniline is also necessary to avoid rapid condensation of hydrolyzed species in the presence of hydrochloric acid. Although the similar synthetic procedure has been applied for preparing various organosilanetriols,[14,15] this is the first report on the selective formation of alkoxysilanetriols with *n*-alkyl chains.

Structures of Hydrolyzed and Condensed Products derived from C*n*OTCS. The powder XRD patterns of the products obtained by hydrolysis and condensation of C*n*OTCS ($n = 12−20$) are shown in Figure 2. The products exhibit low-angle diffraction peaks at the *d* spacings of 3.95, 4.55, 5.09, 5.57, and 6.13 nm for $n = 12$, 14, 16, 18, and 20, respectively. The patterns also show higher order diffraction peaks up to seventh order, suggesting the well-ordered layered structures of the products. It is noted that the *d* values of the products are apparently larger than those of the solid alcohols with the corresponding chain lengths. For example, hexadecanol crystal is reported to exhibit three different polymorphic structures with the basal spacings of 3.71, 4.49, and 4.43 nm.[22,23] No diffraction peaks due to alcohol crystals are observed in Figure 2. At higher 2θ

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[20] Actually, we monitored the initial hydrolysis processes of tetraalkoxysilanes ($Si(OC_nH_{2n+1})_4$, $n = 2$ and 4) in $THF−H_2O−HCl$ mixtures by ^{29}Si NMR, and confirmed that the signals due to $Si(OC_nH_{2n+1})(OH)_3$ appeared at −73.8 and −73.7 ppm for $n = 2$ and 4, respectively. It appears that the number of carbon atoms in the alkoxy groups has little effect on the chemical shifts when $n \geq 2$.

[21] When C16OH was added to the hydrolyzed solution of C16OTCS, the ^{13}C NMR spectrum exhibited several new signals in addition to those originated from C16OTCS derived species. In the spectrum, the signal due to the α carbon in C16OH was observed at 62.5 ppm.

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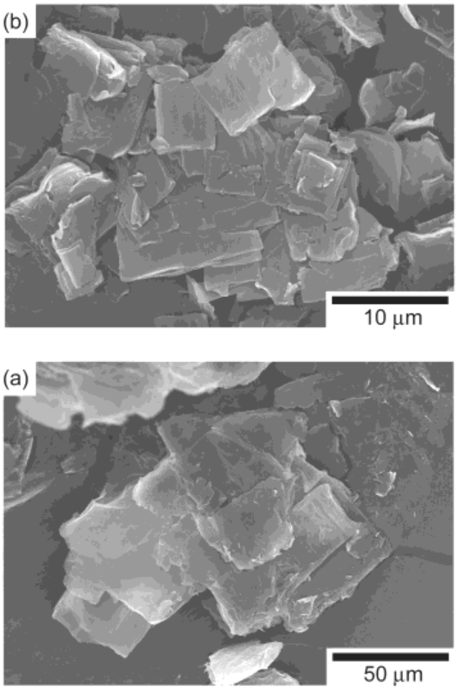

Figure 3. Typical FE-SEM images of the products derived from (a) C14OTCS and (b) C16OTCS.

angles, broad peaks at around $2\theta = 27°$ ($d = \sim 0.42$ nm) are observed, and the peaks are attributable to the packing of alkyl chains.[9]

Figure 3 shows the typical FE-SEM images of the C14OTCS- and C16OTCS-derived products. Both products show, for the most part, the square-shaped particles with well-defined platelike morphologies, reflecting the layered structures of the products. Similar morphologies were also observed for other systems with different alkyl chain lengths, although the particle sizes varied in the range of several micrometers to several tens of micrometers.

The ^{29}Si MAS NMR spectra of the products are shown in Figure 4. All of the products display similar profiles with the signals corresponding to the Q^2, Q^3, and Q^4 units (Q^m; $\mathit{Si}(OX)_{4-m}(OSi)_m$, X = H or alkyl). The relative intensity ratios of the signals are listed in Table S1 in the Supporting Information. The products have essentially the same extent of reaction ($^1/_2(Q^2) + {}^3/_4(Q^3) + (Q^4) = \sim 79\%$). The presence of the Q^4 units indicates that Si−OR groups as well as Si−OH groups in alkoxysilanetriols were condensed to form Si−O−Si bonds, which is described in detail below. The formation of siloxane networks was also confirmed by the FTIR spectra of the products (see Supporting Information Figure S3), which show the bands assigned to the Si−O−Si stretching vibration (1060−1230 cm^{-1}) and the Si−O−Si bending vibration (~460 cm^{-1}). It is interesting to note that the profile of the ν_{as}(Si−O−Si) bands, which is split into two well-defined bands, is quite different from that of the sol−gel-derived silica xerogels which typically show very broad peaks at this region.[11] This result implies the structural feature of the products, although the details are not yet well-understood.

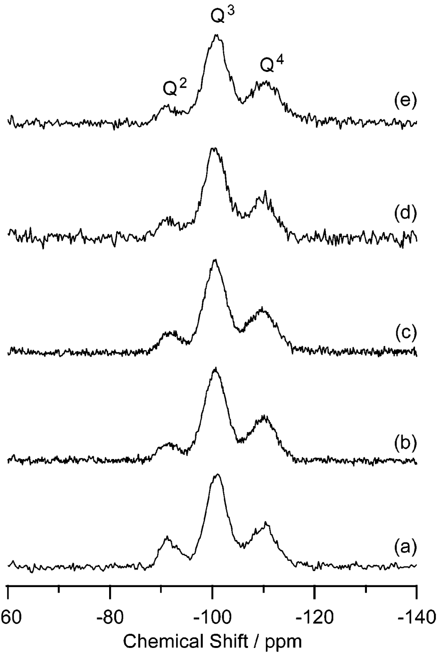

Figure 4. Solid-state ^{29}Si MAS NMR spectra of the products derived from C*n*OTCS with (a) $n = 12$, (b) $n = 14$, (c) $n = 16$, (d) $n = 18$, and (e) $n = 20$.

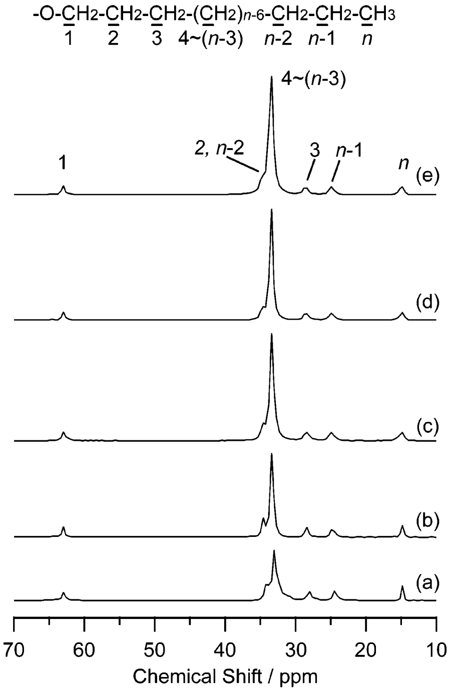

Figure 5. Solid-state ^{13}C CP/MAS NMR spectra of the products derived from C*n*OTCS with (a) $n = 12$, (b) $n = 14$, (c) $n = 16$, (d) $n = 18$, and (e) $n = 20$.

The organic moieties derived from the alkoxy groups in C*n*OTCS were investigated by IR and ^{13}C CP/MAS NMR. The IR spectra of all of the products show the typical absorption bands due to alkyl chains (e.g., the methylene stretching modes and the methylene scissoring mode) in addition to the bands due to the siloxane networks (Figure S3). More detailed information was obtained by the ^{13}C CP/MAS NMR spectra of the products. As shown in Figure 5, the spectra exhibit the signals corresponding to the carbon atoms in the alkyl chains. It has been reported that the signals due to the α carbon in alkoxysilyl groups ($SiO\mathit{C}H_2C$) appear at higher frequencies (ca. 1.0−1.5 ppm) than those of alcohol molecules ($HO\mathit{C}H_2C$).[24,25] We confirmed that the signals ascribed to the α carbon (labeled as 1) appear

Table 1. Amounts of Alkyl Chain Per SiO_2 in the Products

n	mass % C	mass % H	mass % N	% SiO_2[a]	amt of alkyl chains (C_nH_{2n+1})/SiO_2
12	56.4	10.6	0.0	32.6	0.72
14	60.0	11.4	0.0	19.1	1.1
16	61.9	11.1	0.0	18.1	1.1
18	64.6	12.2	0.0	19.0	0.95
20	65.8	12.2	0.0	18.2	0.91

[a] Evaluated by TG.

at the same position as those found for the corresponding solid alcohols. This result suggests that the organic layers consist of alcohol molecules (C*n*OH) rather than alkoxy groups (C*n*OSi), which is consistent with the ^{29}Si MAS NMR data showing the presence of Q^4 units. Further support was obtained by the fact that the organic moiety in the products was considerably reduced (e.g., ~84%, in the case of $n = 16$) by simply dispersing the products in hexane followed by stirring for 1 day.

We also examined the conformation of the interlayer alkyl chains in the layered nanocomposites. It is generally reported for ^{13}C CP/MAS NMR spectra of long alkyl chains that signals due to internal methylene carbons appear at 33 ppm for all-trans conformation and at 30 ppm for trans-gauche conformation.[26] As shown in Figure 5, the signals due to the internal methylene carbons appear at 33.3 ppm, suggesting the all-trans conformation of the interlayer alkyl chains. However, in the case of $n = 12$, a small signal was also observed at 30 ppm indicative of the presence of disordered chains. The all-trans conformations of the alkyl chains with $n = 14-20$ were also evidenced by the IR spectra of the products (Figure S2). The absorption bands due to methylene stretching vibrations (ν_s CH_2 and ν_{as} CH_2) are observed at 2849 and 2918 cm^{-1}, respectively, which is characteristic of the long alkyl chains in a closely packed all-trans state.[27,28]

The chemical compositions of the layered nanocomposites were evaluated by TG and CHN analyses (Table 1). The absence of nitrogen in all of the products ensures the complete removal of aniline hydrochloride formed as a byproduct in the hydrolysis step. In the cases of $n = 14-20$, the amounts of alkyl chains (C_nH_{2n+1}) per SiO_2 are estimated to be 0.9−1.1, which strongly suggests that the products were formed by the assembly of C*n*OSi$(OH)_3$. The lower amount of organic fractions in the case of $n = 12$ (0.72 per SiO_2) can be explained by the loss of interlayer alcohol molecules during the drying process due to the relatively low molecular weight and the low melting point (23.4 °C) of C12OH.

Figure 6 displays the relationship between the number of carbon atoms in the alkoxy groups in C*n*OTCS and the *d* values of the resulting layered nanocomposites. The relation is linear and the average increment of the *d* value per one CH_2 group is calculated to be 0.26 nm/CH_2. The calculation was performed in the range of $n = 14-20$ because C12OTCS-derived product contains conformationally disordered chains as described above. The average increment roughly corresponds to twice the average C−C distance in the long axis of all-trans alkyl chains (0.127 nm/CH_2), suggesting that the interlayer chains are adopting a bimolecular arrangement and are oriented normal to the silica layers. Furthermore, by subtracting the theoretical thickness of alcohol bilayers (i.e., twice the extended lengths of C*n*OH molecules) from the *d* values of the products, the average thickness of the silica layers of ca. 0.7 nm is obtained. The value is extremely small, and is comparable to the thickness of layered silicic acids consisting of single or double layers of SiO_4 tetrahedra (e.g., ~0.60 nm for $H_2Si_2O_5$−III and ~0.74 nm for H-octosilicate).[29,30] This represents the potential of the present method for the control of the silica structures on a molecular scale.

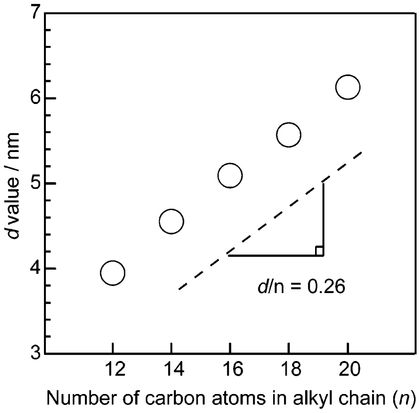

Figure 6. Relationship between the number of carbon atoms in the alkoxy groups in C*n*OTCS and the *d* values of the resulting layered nanocomposites.

Structural Model. The proposed structural model of the layered nanocomposites, based on the above results, is illustrated in Scheme 1(b). The products have layered structures consisting of thin silica layers and bimolecular layers of alcohol molecules with almost all-trans alkyl chains. The nanostructure is similar to those of layered hybrids obtained by hydrolysis and condensation of alkyltrichlorosilanes[10] or alkyltriethoxysilanes,[9] whereas the nature of the inorganic−organic interface is quite different. In comparison with the alkylsilane-derived layered hybrids with the interface linked by Si−C bonds, the present nanocomposites exhibit slightly larger *d* spacings (ca. 0.3 nm), which can be explained by the presence of terminal hydroxy groups and noncovalent bonding between siloxane layers and alkyl chains.

Various layered silica−organic nanocomposites have previously been synthesized by the hydrolysis and condensation of alkoxysilanes in the presence of organic assemblies such as double-chain or single-chain ammonium cations,[31−33] alkylamines,[34] nonionic alkyl poly-

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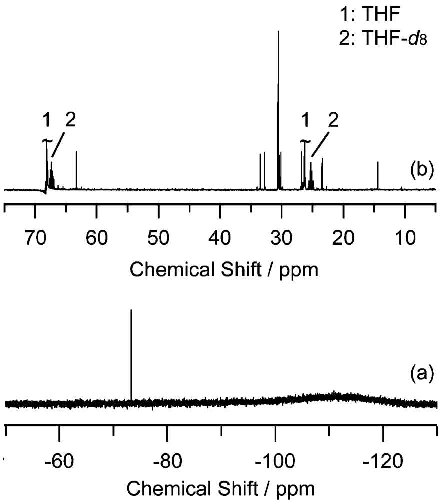

Figure 7. Liquid-state (a) ^{29}Si and (b) ^{13}C NMR spectra of the THF solution of as-formed precipitate ($n = 16$).

(oxyethylene) surfactants,[35] and amphiphilic block copolymers.[35,36] However, there has been no report on the use of alkyl alcohols as structure directing agents, possibly due to their low self-assembling ability and relatively weak (hydrogen bonding) interaction with silicate species. An alternative approach for preparing layered silica−organic nanocomposites is the intercalation of organic guest molecules into crystalline layered silicates. However, there have been few reports on the intercalation of alcohol molecules. We have reported the esterification of interlayer silanol groups in a layered silicate magadiite with various alcohols, but the amounts of the introduced alcohol molecules were limited (0.2−0.96/$Si_{14}O_{30}$).[25] Thus, the present methodology based on the self-assembly of alkoxylated silicic acid has realized the single precursor synthesis of novel layered nanocomposites that are difficult to be accessed by conventional methods.

Formation Processes. In the present system, the layered nanocomposites were formed by the precipitation in the solutions of alkoxysilanetriols on cooling and by a subsequent drying process at room temperature. We found that the precipitates immediately after filtration (as-formed products) were soluble in THF, and became insoluble during the drying process. The ^{29}Si and ^{13}C NMR spectra of the THF solution of the as-formed product in the case of $n = 16$ are shown in Figure 7. Interestingly, both spectra show the signals identical to those observed for the partially hydrolyzed solution of C16OTCS (see Figure 1), indicating that the as-formed product is the aggregate of alkoxysilanetriol. In addition, the as-formed product showed the XRD pattern indicative of the layered structure. It is therefore concluded that the self-assembly of alkoxysilanetriols into lamellar structures is the driving force for the formation of the layered nanocomposites. Although the precipitation of alkoxysilanetriols can also be explained in terms of crystallization, it seems to be strongly related to the self-assembly of amphiphilic molecules into lamellar phases, because the as-formed precipitates have a lower structural ordering if compared with that of crystalline solids such as alcohol crystals.

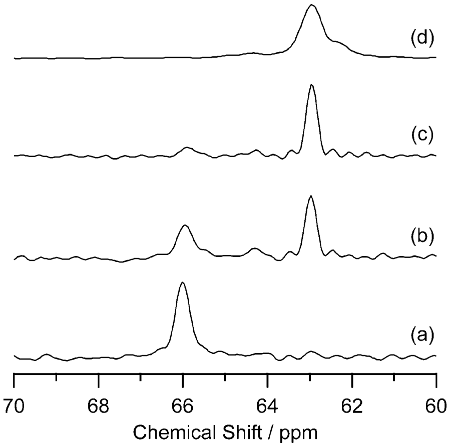

Figure 8. Solid-state ^{13}C CP/MAS NMR spectra of (a) as-formed product derived from C16OTCS; the products after drying at 20 °C for (b) 15 min and (c) 30 min; and (d) final product (after drying for 1 day).

The self-assembly induced by lowering of the solution temperature can be attributed to the decrease of the solubility of alkoxysilanetriols. Such a behavior is generally observed for long-chain amphiphiles, and is actually observed for hydrolyzed alkyltriethoxysilanes to form layered hybrids.[9] In the cases of $n = 12$ and 14, precipitation of alkoxysilanetriols occurred only when appropriate amounts of hexane were added as a cosolvent, followed by cooling of the solutions. It should be noted here that hexane is typically used for the crystallization of organosilanetriols due to their low solubility in nonpolar solvents. However, solid products have never been obtained from the alkoxysilanetriols with shorter alkyl chains ($n = 8$ and 10) even when large amounts of hexane were added. These results show that strong hydrophobic interaction of long alkyl chains is essential for the self-assembly of alkoxysilanetriols.

It is clear that the formation of the siloxane networks proceeded in the solid state during the drying process. Previously, solid-state condensation of silane monomers was also found in the systems using alkylsilanetriols[9] and organically bridged bistrichloro- or bistrimethoxysilanes[37,38] to form ordered hybrids. Because the aggregates of alkoxysilanetriols became insoluble in THF within 2 h of the drying process, condensation appeared to proceed at the early stage of the drying process. However, the condensation was mostly inhibited at lower temperature of ca. −20 °C, which should play a crucial role in the present system to afford aggregates of alkoxysilanetriols without condensation.

It is of particular interest that the alkoxysilanetriols undergo condensation with the cleavage of Si−O−C bonds to form layered silica−alcohol nanocomposites. The cleavage of Si−O−C bonds during the drying process of as-formed product ($n = 16$, hexadecoxysilanetriol) was monitored by ^{13}C CP/MAS NMR. Figure 8 shows the ^{13}C CP/MAS NMR spectra of the as-formed product (measured at −20 °C to avoid condensation),

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the products after drying at 20 °C for 15 and 30 min, and the final product (after drying for 1 day). The as-formed product shows a signal at 66 ppm (Figure 8a) which can be assigned to the α carbon of the solid-state alkoxysilanetriol. At higher temperature of 20 °C, the signal at 66 ppm immediately decreases and a new signal appears at 63 ppm (Figure 8b and c). This signal is also observed in the spectrum of the final product (Figure 8d), and can be assigned to C16OH.[24] The cleavage of alkoxy groups can proceed by the condensation between Si−OR groups and neighboring Si−OH groups (eq 1), and/or by the hydrolysis of Si−OR groups (eq 3) with water formed by the condensation of Si−OH groups (eq 2).

$$\equiv\mathrm{Si{-}OR} + \equiv\mathrm{Si{-}OH} \rightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{ROH} \qquad (1)$$

$$\equiv\mathrm{Si{-}OH} + \equiv\mathrm{Si{-}OH} \rightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O} \qquad (2)$$

$$\equiv\mathrm{Si{-}OR} + \mathrm{H_2O} \rightarrow \equiv\mathrm{Si{-}OH} + \mathrm{ROH} \qquad (3)$$

Previous reports demonstrated that the siloxane formation is sterically restricted in the closely packed two-dimensional array of long-chain alkylsilanes.[9,10,39] In the case of the lamellar hybrids derived from alkyltrialkoxysilanes, the siloxane layers are mainly composed of the T^2 units along with relatively small portions of the T^1 and T^3 units (T^m; $\mathrm{C}Si(\mathrm{OH})_{3-m}(\mathrm{OSi})_m$). On the basis of this fact, the condensation of alkoxysilanetriols should result in the formation of the Q^2 units for the most part, if the alkoxy groups remain intact during the reaction. However, the products in this system exhibited an unexpectedly high degree of condensation, as shown by the appearance of the Q^2, Q^3, and even Q^4 signals (∼25%) in the ^{29}Si MAS NMR spectra. The cleavage of Si−O−C bonds may permit the partial rearrangement of the $\mathrm{SiO_4}$ tetrahedra and further condensation reaction to form well-condensed silica networks. The resulting silica layers are therefore expected to have specific characters such as rigidity and higher thermal stability if compared with those derived from trifunctional organosilanes.

Conclusions

Novel multilayered inorganic−organic nanostructured materials, consisting of alternating thin silica layers and bimolecular layers of alcohol molecules, were prepared by using alkoxytrichlorosilanes as single precursors. The formation depends on preferential hydrolysis of alkoxytrichlorosilanes, the self-assembly of formed alkoxysilanetriols, and subsequent condensation in the solid state. This is quite different from the conventional sol−gel processing of alkoxysilanes, where hydrolysis and condensation occur concurrently. The present results extend the self-assembly process of organotrialkoxysilanes to the use of tetrafunctional silanes for the first time, providing a new approach for control of the polymerization of silicate monomers in the confined two-dimensional arrays. The design of various types of precursors where alcohol molecules are covalently bonded to Si or other metal atoms will lead to the creation of novel nanomaterials with unique structures, morphologies, and compositions.

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Supporting Information Available: Spectroscopic data for the precursors, ^{29}Si NMR spectra of C16OTCS together with the reaction mixture of $\mathrm{SiCl_4}$ and C16OH, FTIR spectra of the products, and signal intensity ratios for the ^{29}Si MAS NMR spectra in Figure 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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