

# Stable Silanetriols That Contain *tert*-Alkoxy Groups: Versatile Precursors of Siloxane-Based Nanomaterials

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**Abstract:** Novel *tert*-alkoxysilanetriols (ROSi(OH)<sub>3</sub>, R = adamantyl and 3-ethyl-3-pentyl) have been prepared from the corresponding *tert*-alkoxytrichlorosilanes and successfully used as molecular building blocks to produce ordered siloxane-based nanomaterials. Controlled hydrolysis of the alkoxytrichlorosilanes led to the formation of crystalline powders of alkoxy-silanetriols that were stable under ambient conditions. Solid-state polycondensation of the alkoxy-silanetriols occurred

upon heating, which led to the formation of ordered silica-organic nanocomposites with laminated morphologies. On the other hand, silylation of the *tert*-alkoxysilanetriols with chlorotrimethoxysilane enabled us to synthesize well-defined oligomeric alkoxy-

lanes (ROSi[OSi(OMe)<sub>3</sub>]<sub>3</sub>). Hydrolysis and polycondensation of these oligomers followed by acid treatment gave microporous silica with narrow pore size distributions. Thus, *tert*-alkoxy groups serve not only as protecting groups of siloxane species to regulate hydrolysis and polycondensation, but also as templates to generate micropores thereby providing unique synthetic pathways for the design of ordered silica-based materials.

**Keywords:** building block approach • microporous materials • nanostructures • silanes • sol-gel processes

## Introduction

Molecular routes to inorganic solids with designed structures have received increasing attention in modern materials chemistry. The polymerization of silicic acids or silicates by

condensation of SiOH groups is probably the most studied process that allows the production of siloxane-based materials under mild conditions.<sup>[1,2]</sup> Tetrafunctional silanes, such as Si(OR)<sub>4</sub> and SiCl<sub>4</sub>, are widely used as precursors. However, concurrent hydrolysis and polycondensation generally lead to the formation of amorphous silica with randomly cross-linked networks. Control of the reaction kinetics is therefore crucial to tailor the structures of the final products. Although the use of organic structure-directing agents or templates has made it possible to control silica structures on various length scales,<sup>[3–5]</sup> the molecular design of the alkoxy- or chlorosilanes that serve as single precursors of ordered silica-based materials is still a great challenge.

It is known that several kinds of silanetriols can be obtained by controlled hydrolysis of the corresponding trichloro- or trialkoxysilanes in which organic groups are bonded to silicon atoms through Si–C, Si–N, or Si–O bonds.<sup>[6–12]</sup> Polycondensation is retarded by the steric effects of the organic groups and also by hydrogen-bonding between silanol groups. Such molecules have been used as molecular building blocks in the construction of well-defined oligomeric siloxane and cage-like metallosiloxane species.<sup>[7,8]</sup> Furthermore, solid-state polycondensation of crystalline silanetriols offers an interesting approach to ordered siloxane-based materials.<sup>[11,12]</sup> We have previously reported the for-

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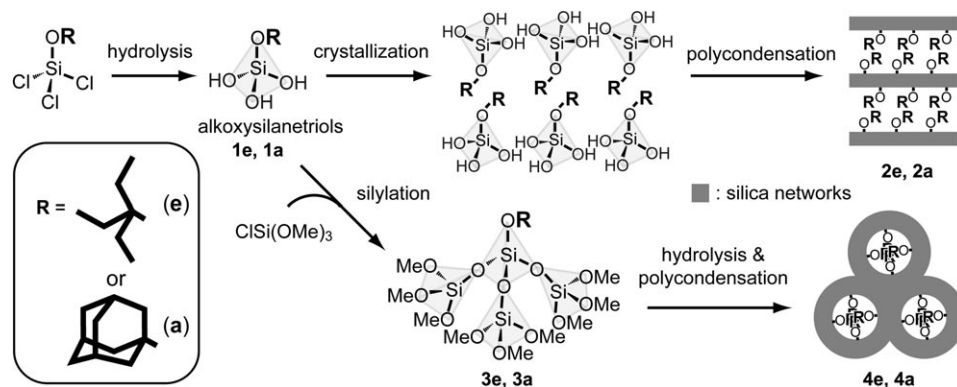
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mation of layered silica–organic hybrids by solid-state polycondensation of lamellar assemblies of alkylsilanetriols derived from long-chain alkyltriethoxysilanes.<sup>[10]</sup> More recently we synthesized long-chain *n*-alkoxysilanetriols that underwent spontaneous polycondensation and cleavage of Si–O–C linkages to form layered silica–alcohol nanocomposites.<sup>[13]</sup>

Alkoxysilanetriols are particularly important as molecular building blocks because alkoxy groups and silanols can be used in chemical reactions. One of the aims of research in this field is to produce porous solids with well-defined pore sizes by using alkoxy groups as templates that can be hydrolyzed under mild conditions. To produce spherical or cylindrical assemblies with three-dimensional silica frameworks, additional siloxane units should be attached to the Si–OH groups of alkoxysilanetriols to enlarge the size of the head group. Recently we demonstrated that oligomeric alkoxysilanes in which three trialkoxysilyl groups are attached to an alkylsilane unit formed cylindrical assemblies.<sup>[14]</sup> The design of similar oligomeric species with alkoxy groups instead of alkyl groups will open a new route to porous silica. However, the chemical modification of long-chain alkoxysilanetriols is difficult because of the instability of alkoxysilanetriols under ambient conditions.

Herein, we report the synthesis of stable *tert*-alkoxysilanetriols as effective molecular building blocks for producing silica-based nanomaterials with well-regulated structures, morphologies, and porosities. We chose highly bulky alkoxy groups, 3-ethyl-3-pentoxy and 1-adamantoxy groups (Scheme 1), as protecting groups of siloxane species to pro-



Scheme 1. Design of various silica nanomaterials by using *tert*-alkoxysilanetriols as building blocks.

duce alkoxysilanetriols (**1e** and **1a**, respectively). Solid-state polycondensation of the molecular crystals of these alkoxysilanetriols, induced by heating, led to ordered alkoxylated silica materials (**2e** and **2a**). Furthermore, the high stability of the alkoxysilanetriols enabled us to design novel oligomeric alkoxysilanes (**3e** and **3a**) by silylation. These molecules formed xerogels with ordered structures (**4e** and **4a**); removal of the alkoxy groups of **4e** and **4a** gave microporous silica with controlled pore sizes.

## Results and Discussion

**Formation of alkoxysilanetriols **1e** and **1a** from alkoxytrichlorosilanes:** The solutions obtained after hydrolysis of *tert*-alkoxytrichlorosilanes were analyzed by liquid-state NMR spectroscopy. The <sup>29</sup>Si NMR spectra of the hydrolyzed solutions of 3-ethyl-3-pentoxy- and 1-adamantoxytrichlorosilanes (Figure 1) exhibit single signals at  $\delta = -77.8$  and

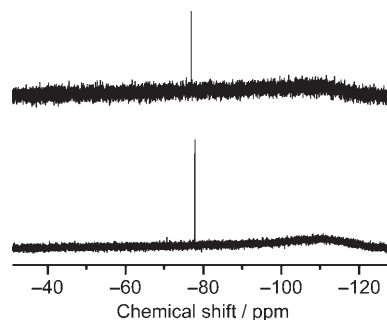


Figure 1. Liquid-state <sup>29</sup>Si NMR spectra of hydrolyzed solutions of 3-ethyl-3-pentoxytrichlorosilane (bottom) and 1-adamantoxytrichlorosilane (top).

–76.9 ppm, respectively, which are very different from those of the *tert*-alkoxytrichlorosilanes ( $\delta = -52.0$  and  $-49.3$  ppm). These signals can be tentatively assigned to  $\text{ROSi}(\text{OH})_3$  based on the fact that the signal of the silicic acid monomer ( $\text{Si}(\text{OH})_4$ ) appears at around  $\delta = -72$  ppm and is shifted upfield when one hydroxy group is substituted by an alkoxy group.<sup>[11]</sup> The differences in the chemical shifts of the *tert*-alkoxysilanetriols compared with those of *n*-alkoxysilanetriols (for example,  $\delta = -73.4$  ppm)<sup>[13]</sup> can be attributed to a higher electron-donating ability of the *tert*-alkoxy groups. The broad signal centered at  $\delta = -110$  ppm is due to the glass tube used for the measurement.

The retention of the *tert*-alkoxy groups was clearly confirmed by <sup>13</sup>C NMR spectroscopy (Figure 2). The spectra exhibit signals arising from the alkoxy groups along with strong signals from the solvent (THF). For the hydrolyzed solutions of 3-ethyl-3-pentoxy- and 1-adamantoxytrichlorosilanes, the chemical shifts of the  $\alpha$ -carbon atoms ( $\delta = 76.7$  and  $70.7$  ppm, respectively) are different to those of either the *tert*-alkoxytrichlorosilanes ( $\delta = 90.0$  and  $80.8$  ppm) or the *tert*-alkyl alcohols ( $\delta = 74.7$  and  $68.2$  ppm). Taking into account the fact that the  $\alpha$ -carbon signals of *n*-alkoxy groups appear 1.0–1.5 ppm downfield of those for the corresponding alcohols,<sup>[13,15,16]</sup> it is reasonable to assign these signals to

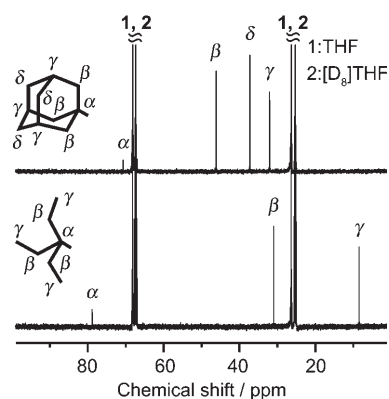


Figure 2. Liquid-state  $^{13}\text{C}$  NMR spectra of hydrolyzed solutions of 3-ethyl-3-pentoxytrichlorosilane (bottom) and 1-adamantoxytrichlorosilane (top).

the  $\alpha$ -carbon atoms of *tert*-alkoxy groups. From these NMR data we conclude that *tert*-alkoxysilanetriols **1e** and **1a** were selectively formed by partial hydrolysis of the corresponding alkoxytrichlorosilanes.

Importantly, alkoxytranetriols **1e** and **1a** were isolated as crystalline precipitates by adding hexane to concentrated solutions of these triols. The solid-state  $^{29}\text{Si}$  MAS NMR spectra of **1e** and **1a** show sharp  $Q^0$  signals with no signals being observed in the  $Q^2$ ,  $Q^3$ , and  $Q^4$  regions (Figure 3a).

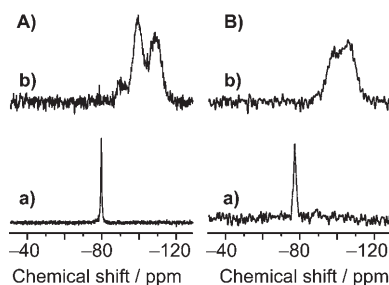


Figure 3. Solid-state  $^{29}\text{Si}$  MAS NMR spectra of A) 3-ethyl-3-pentoxysilanetriol (**1e**) and B) 1-adamantoxysilanetriol (**1a**) for the compounds as synthesized (a) and after thermal treatment (b).

These precipitates were soluble in THF and the liquid-state  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR spectra showed signals assigned to 3-ethyl-3-pentoxy- and 1-adamantoxysilanetriols (see the Supporting Information). These results provide evidence that the polycondensation of **1e** and **1a** is strictly retarded both in the solid-state and in THF. To the best of our knowledge, these are the first stable alkoxytranetriols to be synthesized even though several stable organosilanetriols with organic groups linked to the silicon atom through stable Si–C bonds have been previously reported.<sup>[6–11]</sup>

**Factors stabilizing alkoxytranetriols:** We have previously reported the formation of *n*-alkoxytranetriols with long alkyl chains ( $\text{C}_{12}$ – $\text{C}_{20}$ ).<sup>[13]</sup> Hydrophobic interactions between alkyl groups appeared to play a crucial role. However, crystalline precipitates of *n*-alkoxytranetriols were only obtained at a

low temperature ( $-20^\circ\text{C}$ ) and both polycondensation of the silanol groups and cleavage of Si–O–C bonds rapidly occurred at room temperature. In contrast, **1e** and **1a** were readily crystallized at room temperature by adding a poor solvent (hexane) and were stable for a long period of time (at least for 1 month). This suggests that hydrophobic interactions between the alkoxy groups are not the main factor stabilizing alkoxytranetriols. Furthermore, our preliminary experiments revealed that *tert*-butoxy- or 2-methyl-2-heptoxytrichlorosilanes do not afford stable silanetriols. It is therefore concluded that bulky alkoxy groups with more than two carbon atoms in each of the side-chains are essential for the formation of stable alkoxytranetriols. The rigidity of the alkoxy groups appears to have little effect because both 3-ethyl-3-pentoxy- and adamantoxysilanetriols were obtained under similar conditions.

These results clearly show that the stability of alkoxytranetriols is dominated by the steric effects of the alkoxy groups. Similar behavior has also been reported for organosilanetriols with stable Si–C bonds. It is known that molecular crystals of organosilanetriols are stabilized by steric repulsion between bulky organic groups and also by hydrogen-bonding between adjacent silanol groups.<sup>[6]</sup> For example, *tert*-butyl- and cyclohexylsilanetriols are stable in the solid state, whereas *n*-alkylsilanetriols undergo polycondensation.<sup>[10]</sup> It is plausible that the bulky organic groups attached to the silicon atoms hinder the attack of neighboring silanol groups to form Si–O–Si bonds. In addition, the presence of bulky alkoxy groups leads to an increase in the lateral distances between silanetriol molecules, which should be unfavorable for condensation.

#### Thermal polycondensation of alkoxytranetriols **1e** and **1a**:

Although alkoxytranetriols **1e** and **1a** are stable at room temperature, they underwent solid-state polycondensation at higher temperatures. Thermal treatment of **1e** and **1a** was performed at 100 and  $200^\circ\text{C}$ , respectively. These temperatures are still lower than the decomposition temperatures of the *tert*-alkoxy groups ( $\approx 250$  and  $\approx 380^\circ\text{C}$ , respectively). The samples became insoluble in THF after thermal treatment for one day (designated as **2e** and **2a**), which suggests that polycondensation of the silanol groups had occurred. In the  $^{29}\text{Si}$  MAS NMR spectra of **2e** and **2a** (Figure 3b), three new signals appeared at around  $\delta = -90$ ,  $-100$ , and  $-110$  ppm, and the  $Q^0$  signal disappeared. These signals generally correspond to the  $Q^2$ ,  $Q^3$ , and  $Q^4$  sites ( $Q^x = (\text{Si}(\text{OSi})_x(\text{OH})_{4-x})$ ) of silica-based materials.<sup>[1]</sup> However, the  $Q^1$ ,  $Q^2$ , and  $Q^3$  sites with *tert*-alkoxy groups may overlap them because *tert*-alkoxy groups induce upfield shifts of the  $^{29}\text{Si}$  signals. The formation of siloxane networks was also confirmed by IR spectroscopy (data not shown). The bands due to Si–OH ( $925\text{ cm}^{-1}$ ) and OH ( $3230\text{ cm}^{-1}$ ) almost disappeared, and bands due to Si–O–Si networks ( $1060$ – $1220\text{ cm}^{-1}$  and  $\approx 460\text{ cm}^{-1}$ ) appeared.

Further information was obtained from the solid-state  $^{13}\text{C}$  cross-polarization (CP)/MAS NMR spectra of *tert*-alkoxytranetriols **1e** and **1a**, and of **2e** and **2a**, as shown in

Figure 4. All of the signals have been assigned to the 3-ethyl-3-pentyl and 1-adamantyl groups with the signals becoming broader upon thermal treatment. It appears that the

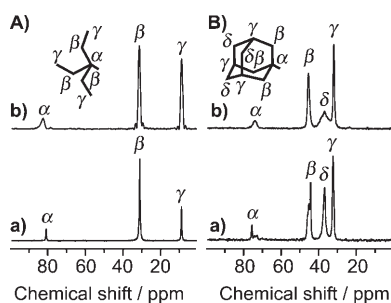


Figure 4. Solid-state  $^{13}\text{C}$  CP/MAS NMR spectra of A) 3-ethyl-3-pentoxysilanetriol (**1e**) and B) 1-adamantoxysilanetriol (**1a**) for the compounds as-synthesized (a) and after thermal treatment (b).

alkoxy groups remain intact in the products owing to the lack of  $\alpha$ -carbon signals in the NMR spectra that arise from the corresponding alcohols. However, a combination of thermogravimetric (TG) and CHN analyses revealed that the molar ratios of alkoxy groups per  $\text{SiO}_2$  decreased to around 0.40 and 0.34 for **2e** and **2a**, respectively. This suggests that some Si–O–C linkages were cleaved and the resulting alcohols eliminated from the samples at high temperatures. The alkoxy groups can be cleaved either by the condensation of Si–OR and Si–OH groups (i.e., alcohol-producing condensation) or by hydrolysis with water formed by the condensation of Si–OH groups.<sup>[13]</sup>

**Structural considerations:** Figure 5 shows the powder XRD patterns of **1e** and **1a** and those obtained after thermal treatment (**2e** and **2a**). The powder XRD patterns of alkoxy-silanetriols **1e** and **1a** exhibit several sharp diffraction peaks that are indicative of their crystalline nature. The XRD pattern of **1e** shows the strongest peak with a  $d$  spacing of 1.29 nm accompanying higher order reflections. On the other hand, compound **1a** exhibits a rather complicated pattern consisting of three peaks close together with  $d$  spacing values of 1.68, 1.53, and 1.41 nm and many other peaks in the higher  $2\theta$  regions. After thermal treatment, broad peaks with  $d$  spacing values of 1.56 and 1.65 nm were observed for **2e** and **2a**, respectively, which implies that the crystalline order of alkoxy-silanetriols was partly retained even after polycondensation.

The crystal structures of several organosilanetriols have previously been elucidated by X-ray analyses, and those with *tert*-butyl and cyclohexyl groups were found to adopt a double-sheet structure in which the organic groups point towards each other.<sup>[6,7]</sup> Although the detailed crystal structures of **1e** and **1a** have not yet been clarified, the layered structure of these samples was suggested by the slight increase in  $d$  spacing when treated with decyl alcohol and also by the collapse of their structures after calcination (at 500 °C for 8 h). The  $d$  spacings of the XRD peaks in the lowest  $2\theta$  re-

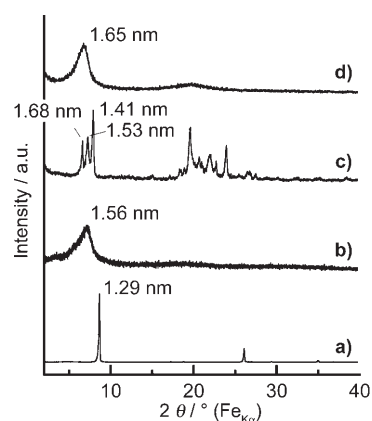


Figure 5. Powder XRD patterns of alkoxy-silanetriols a) **1e** and c) **1a**, and those obtained after thermal treatment b) **2e** and d) **2a**.

gions roughly correspond to twice the extended lengths of *tert*-alkoxy-silanetriol molecules which suggests that they have bilayer structures.

The layered structures of the alkoxy-silanetriols were also suggested by their specific particle morphologies. The SEM image of **1e** shows irregular, angular particles with laminated surfaces, whereas **1a** is shown to be composed of randomly shaped flakelike particles several micrometers in size (Figure 6a and c). No major change in the morphologies of

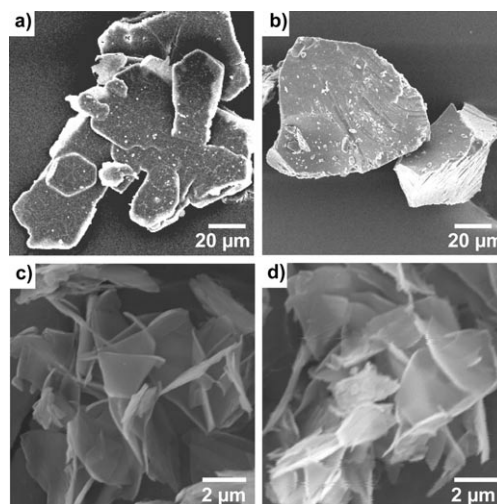


Figure 6. FE-SEM images of alkoxy-silanetriols a) **1e** and c) **1a**, and those obtained after thermal treatment b) **2e** and d) **2a**.

**1e** and **1a** was observed even after thermal treatment (Figure 6b and d). Layered hybrids with similar flakelike morphologies have been prepared by the self-assembly of several organoalkoxy-silanes that have stable Si–C bonds,<sup>[10,17,18]</sup> but **2e** and **2a** are unique because the organic groups are attached through hydrolyzable Si–O–C bonds.

The slight increases in the  $d$  spacings upon thermal polycondensation are presumably as a result of increases in the thickness of the siloxane layers, as expected from the forma-



tion of the Q<sup>2</sup>, Q<sup>3</sup>, and Q<sup>4</sup> units (Figure 3b). Because of the large volume of bulky alkoxy groups relative to the Si–O–Si moiety, partial cleavage and removal of alkoxy groups upon thermal treatment should play an important role in satisfying the spatial restriction demanded for the formation of cross-linked siloxane networks.

**Molecular design of 3e and 3a:** A significant feature of *tert*-alkoxysilane triols is that they can be used as building blocks for further modification. Figure 7 shows the liquid-state

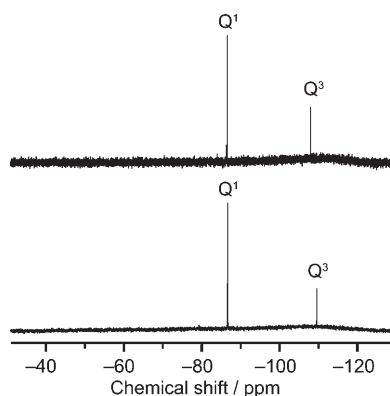


Figure 7. Liquid-state <sup>29</sup>Si NMR spectra (in CDCl<sub>3</sub>) of **3e** (bottom) and **3a** (top) prepared by trimethoxysilylation of **1e** and **1a**, respectively.

<sup>29</sup>Si NMR spectra of **3e** and **3a** prepared by trimethoxysilylation of **1e** and **1a**, respectively. Both spectra show Q<sup>1</sup> and Q<sup>3</sup> signals with intensity ratios of 3:1 which suggests that three trimethoxysilyl groups are bonded to *tert*-alkoxysilyl cores. The appearance of the Q<sup>3</sup> signals (at  $\delta = -109.6$  and  $-108.1$  ppm for **3e** and **3a**) upfield from that generally observed at around  $\delta = -100$  ppm has been attributed to the presence of *tert*-alkoxy groups bonded to silicon atoms. The <sup>13</sup>C NMR spectra of **3e** and **3a** exhibit signals arising from the  $\alpha$ -carbon atoms of *tert*-alkoxy groups ( $\delta = 81.0$  and  $72.9$  ppm, respectively) in addition to the methoxy signal at  $\delta = 51$  ppm (see the Supporting Information). These data demonstrate the successful synthesis of novel oligomeric alkoxy silanes with well-defined structures and two kinds of alkoxy groups.

**Hydrolysis and polycondensation of 3e and 3a:** After hydrolysis and polycondensation of **3e** and **3a** in THF under acidic conditions, several signals appeared in the Q<sup>1</sup>, Q<sup>2</sup>, and Q<sup>3</sup> regions of the <sup>29</sup>Si NMR spectra (see the Supporting Information). These signals may be assigned to cyclic species formed by hydrolysis of the methoxy groups and subsequent intramolecular polycondensation of the silanol groups, as we recently reported for similar oligomeric alkoxy silanes with *n*-alkyl groups bonded to the silicon atom through stable Si–C bonds.<sup>[14b]</sup> In fact, complete hydrolysis of the methoxy groups was confirmed by the <sup>13</sup>C NMR spectra (data not shown) in which the signals of the methoxy groups ( $\delta = 51.1$  ppm) had almost disappeared and a strong signal aris-

ing from methanol ( $\delta = 49.8$  ppm) had appeared. It was also shown that the *tert*-alkoxy groups were partially hydrolyzed to 3-ethyl-3-pentanol and 1-adamantanol. However, the hydrolysis rate appeared to be much lower and therefore most of the alkoxy groups (at least 70%, as estimated from the signal intensity ratio) were preserved. This may be owing to steric hindrance of the bulky alkoxy groups, which prevents nucleophilic attack of water molecules on silicon atoms.

Figure 8 shows the <sup>29</sup>Si MAS NMR spectra of **4e** and **4a** prepared by casting and drying hydrolyzed solutions of **3e** and **3a**, respectively. Both spectra exhibit three signals at

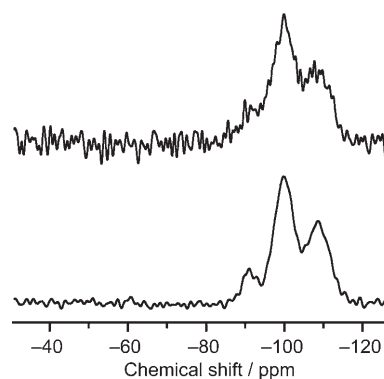


Figure 8. Solid-state <sup>29</sup>Si MAS NMR spectra of **4e** (bottom) and **4a** (top) prepared by casting and drying of hydrolyzed solutions of **3e** and **3a**, respectively.

$\delta = -91.1$ ,  $-99.8$ , and  $-108.6$  ppm with intensity ratios of 1:5:4 and 1:5:3, respectively. As mentioned above, the silicon atoms bonded to *tert*-alkoxy groups appear upfield from those bonded to *n*-alkoxy or hydroxy groups. However, considering that 75% of the silicon units arise from the branched –Si(OMe)<sub>3</sub> groups of **3e** and **3a**, it is reasonable to assign these signals to the Q<sup>2</sup>, Q<sup>3</sup>, and Q<sup>4</sup> units rather than to the Q<sup>1</sup>, Q<sup>2</sup>, and Q<sup>3</sup> units that have *tert*-alkoxy groups.

Partial cleavage of the alkoxy groups was suggested by the <sup>13</sup>C CP/MAS NMR spectra (see the Supporting Information). The  $\alpha$ -carbon atoms of the 3-ethyl-3-pentoxy and 1-adamantoxy groups appear at  $\delta = 82.5$  and  $74.4$  ppm in the spectra of **4e** and **4a**, respectively. Other signals observed at  $\delta = 77.3$  and  $69.0$  ppm might be due to 3-ethyl-3-pentanol and 1-adamantanol, respectively, formed by cleavage of Si–O–C linkages. The organic content of **4e** and **4a** was evaluated by elemental analysis in combination with TG analysis. The number of residual alkoxy groups (and/or alcohol molecules) per 4 SiO<sub>2</sub> was 0.62 and 0.89 for **4e** and **4a**, respectively, which confirms that alkoxy groups were partly lost during synthesis, possibly through condensation in the drying process.

**Removal of alkoxy groups from 4e and 4a:** The large siloxane units of **3e** and **3a** resulted in the formation of ordered three-dimensional siloxane networks that are preserved even after the removal of alkoxy groups. It is of particular

importance that alkoxy groups can be removed by hydrolysis at room temperature as well as by calcination. Acid-catalyzed hydrolysis appears to be suitable for the removal of organic groups without the rearrangement of siloxane networks. The removal of organic groups from silica–organic hybrids that contain C–C triple bonds adjacent to silicon atoms has previously been achieved by chemical treatment in the presence of fluoride ions, however, the rearrangement of siloxane networks also occurred.<sup>[19,20]</sup>

Figure 9 shows the XRD patterns of **4e** and **4a** and those recorded after acid treatment or calcination. The as-synthesized XRD patterns of **4e** and **4a** exhibit broad peaks that

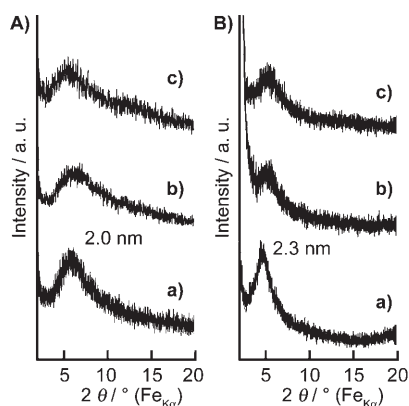


Figure 9. Powder XRD patterns of A) **4e** and B) **4a** for the compounds as-synthesized (a), after acid treatment (b), and after calcination (c).

correspond to *d* spacings of 2.0 and 2.3 nm, respectively, which suggests the products have an ordered structure. These peaks are still observed after acid treatment or calcination. The slight decreases in the *d* spacings are as a result of shrinkage of the siloxane networks by further polycondensation of the silanol groups. The complete removal of the organic groups was confirmed by IR spectroscopy (see the Supporting Information); the absorption bands arising from the *tert*-alkoxy groups (typically a C–H stretching vibration at 2890–2980 cm<sup>-1</sup>) had almost disappeared. The bands due to Si–OH stretching ( $\approx 925$  cm<sup>-1</sup>) are more prominent after acid treatment than after calcination owing to the formation of new Si–OH groups as a result of hydrolysis of alkoxy groups.

The generation of micropores upon removal of alkoxy groups was confirmed by nitrogen adsorption measurements. Figure 10 shows the adsorption–desorption isotherms for **4e** and **4a** after acid treatment. Although as-synthesized **4e** and **4a** are almost nonporous, after acid treatment they show type I isotherms that are characteristic of microporous silica. The Brunauer–Emmet–Teller (BET) surface areas increased to 350 and 670 m<sup>2</sup>g<sup>-1</sup> for **4e** and **4a**, respectively. The pore sizes estimated by the Saito–Foley (SF) method were around 0.6 nm in both cases. This value corresponds well to the molecular size of the alkoxy groups, which implies that the alkoxy groups acted as molecular templates to

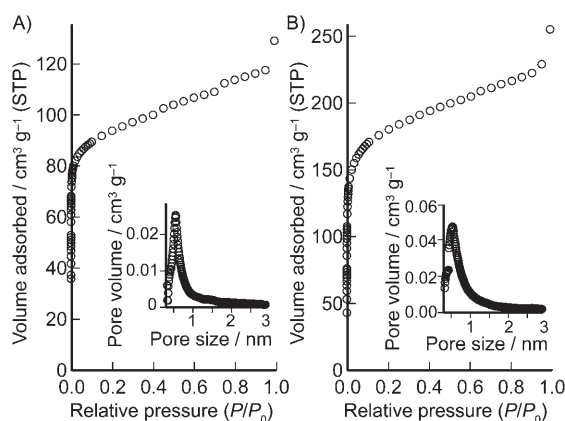


Figure 10. Nitrogen adsorption isotherms for A) **4e** and B) **4a** after acid treatment. The insets show pore size distribution curves obtained by the SF method.

create well-regulated pores. As expected from the broad XRD peaks, a disordered, wormhole-like pore architecture was observed by TEM (Figure 11).

On the other hand, when alkoxy groups were removed by calcination, **4e** gave a solid with a very small surface area (10 m<sup>2</sup>g<sup>-1</sup>). Thermal shrinkage of siloxane networks might leave no pores and/or only closed pores. In contrast, microporous silica was obtained from **4a**. This result is probably owing to the higher thermal stability of adamantyl groups. The networks could be retained while shrinkage of the networks occurred, thus leaving voids even after calcination. However, the BET surface area was smaller (370 m<sup>2</sup>g<sup>-1</sup>) than that of the material produced after acid treatment. These results proved that the removal of alkoxy groups as a molecular template under mild conditions is a promising way to produce microporous silica materials.

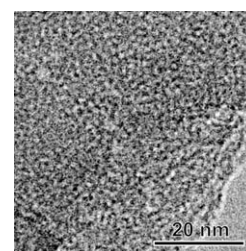


Figure 11. TEM image of **4e** after acid treatment.

## Conclusion

We have demonstrated the first successful synthesis of stable alkoxy-silane-triols that contain *tert*-alkoxy groups and their use as novel molecular building blocks in the construction of ordered silica-based materials. Solid-state polycondensation of crystalline alkoxy-silane-triols led to the formation of alkoxy-silane-triols with ordered nanostructures that could be utilized as a new class of nanofillers for composite materials. Well-defined oligomeric alkoxy-silane-triols were also obtained by trimethoxysilylation of alkoxy-silane-triols. Hydrolysis and polycondensation of these oligomers led to the formation of nanostructured networks that gave microporous solids by hydrolysis of the *tert*-alkoxy groups under acidic conditions. This is a sort of molecular imprinting technique that allows

the design of microporous silica with well-regulated pores. The simple sol–gel processing of the oligomeric precursors is suitable for morphological control, which is very important for various applications. The molecular design of further alkoxytri-chlorosilanes with bulky alkoxy groups is underway, the aim of which is to create a diverse class of materials with ordered structures at the molecular level.

## Experimental Section

**Materials:** Tetrachlorosilane ( $\text{SiCl}_4$ , Tokyo Kasei Co. Ltd., 98%), 3-ethyl-3-pentanol ( $\text{C}_2\text{H}_5$ )<sub>3</sub>COH, Tokyo Kasei, 99%), and 1-adamantanol ( $\text{C}_{10}\text{H}_{15}\text{OH}$ , Aldrich, 99%) were used for the synthesis of the alkoxytri-chlorosilanes. Other chemicals, which included aniline, pyridine, dehydrated tetrahydrofuran (THF), and *n*-hexane (all from Kanto Chemical Co.), were used as received.

**Synthesis of *tert*-alkoxytrichlorosilanes ( $\text{ROSiCl}_3$ ):** The *tert*-alkoxytrichlorosilanes were synthesized by the reaction of  $\text{SiCl}_4$  and *tert*-alkyl alcohols (3-ethyl-3-pentanol and 1-adamantanol). Typically, a solution of one of the alcohols in THF was added slowly to a solution of  $\text{SiCl}_4$  in hexane and the mixture was stirred at room temperature for 1.5 h. The gaseous HCl generated by the reaction was allowed to leave the vessel. An excess of  $\text{SiCl}_4$  ( $\text{SiCl}_4$ /*tert*-alkyl alcohol, 5:1) was used to suppress the generation of  $\text{Cl}_2\text{Si}(\text{OR})_2$ .  $^{29}\text{Si}$  NMR spectroscopic analyses of the mixtures revealed the formation of *tert*-alkoxytrichlorosilanes as the predominant species. After removal of hexane and unreacted  $\text{SiCl}_4$  under reduced pressure, the residue was distilled under vacuum to yield alkoxytrichlorosilanes as clear and colorless liquids.

**3-Ethyl-3-pentoxytrichlorosilane:**  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.06 ( $\gamma$ ), 30.37 ( $\beta$ ), 90.10 ppm ( $\alpha$ );  $^{29}\text{Si}$  NMR (99.3 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –52.78 ppm.

**1-Adamantoxytrichlorosilane:**  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 31.28 ( $\gamma$ ), 35.84 ( $\delta$ ), 44.91 ( $\beta$ ), 80.86 ppm ( $\alpha$ );  $^{29}\text{Si}$  NMR (99.3 MHz,  $\text{CDCl}_3$ ):  $\delta$  = –49.41 ppm.

**Synthesis of *tert*-alkoxysilanetriols (**1e** and **1a**):** *tert*-Alkoxytrichlorosilane ( $\text{ROSiCl}_3$ , 1 g) in THF (10 mL) was added dropwise to a mixture of THF (40 mL), aniline, and water (molar ratio of  $\text{ROSiCl}_3$ /aniline/ $\text{H}_2\text{O}$  = 1:3.3:3.3) in an ice bath. Aniline acts as an acceptor of the HCl generated by hydrolysis of the Si–Cl groups, and therefore, maintains the solution at neutral pH. After stirring for 1.5 h, precipitates of aniline hydrochloride were removed by filtration. The resulting clear solution was concentrated to about 10 vol% under reduced pressure. The addition of hexane (50 mL) to this solution led to the formation of precipitates that were separated by filtration, washed with hexane, and dried under vacuum to give **1e** and **1a** as white powders.

**Synthesis of trimethoxysilylated derivatives (**3e** and **3a**) of the *tert*-alkoxysilanetriols:** The silylating agent (chlorotrimethoxysilane ( $\text{ClSi}(\text{OMe})_3$ )) was synthesized by adding methanol (40 mL) to  $\text{SiCl}_4$  (38 mL) under a flow of nitrogen (3:1 molar ratio of  $\text{MeOH}/\text{SiCl}_4$ ) and the mixture was stirred for 20 min.  $^{29}\text{Si}$  NMR spectroscopy confirmed that the resulting liquid was a mixture of chlorotrimethoxysilane ( $\text{ClSi}(\text{OMe})_3$ ) and tetramethoxysilane in an approximate molar ratio of 7:3. This mixture was directly used for silylation because tetramethoxysilane is relatively inert towards silylation to cause little or no side reactions. Trimethoxysilylation of the alkoxytri-chlorosilanes was performed by adding a solution of **1e** (or **1a**) in THF to a mixture of the silylating agent, pyridine, and hexane, which was then stirred at room temperature for 1 h. The molar ratio of silanetriols/pyridine/chlorotrimethoxysilane was 1:18:12. After removal of the resulting pyridine hydrochloride by filtration and evaporation of the solvent under vacuum, a slightly viscous liquid was obtained. Finally, **3e** and **3a** were isolated by GPC with dried THF as the eluent.

**Hydrolysis and polycondensation of **3e** and **3a**:** Hydrolysis and polycondensation reactions were performed with a molar ratio of **3e** (or **3a**)/THF/ $\text{H}_2\text{O}/\text{HCl}$  = 1:50:18:0.002 whilst stirring at room temperature for

3 h. The solutions were then cast onto glass substrates and air-dried to give **4e** and **4a** as thick films. They were pulverized for characterization. Removal of the alkoxy groups was carried out either by acid treatment or by calcination at 500 °C for 8 h in air. For the acid treatment, **4e** (or **4a**) (0.1 g) was dispersed in a mixture of THF (10 mL) and an aqueous solution of 0.1 N HCl (0.1 mL). After stirring the dispersion at room temperature for 1 d, precipitates were recovered by centrifugation and dried for 1 d under vacuum.

**Characterization:** Liquid-state  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR spectra were obtained by using a JEOL Lambda-500 spectrometer with resonance frequencies of 99.25 and 125.65 MHz, respectively. The sample solutions were put into 5 mm glass tubes and tetramethylsilane (TMS) was added as an internal reference;  $\text{CDCl}_3$  or  $[\text{D}_8]\text{THF}$  was used to obtain lock signals. A small amount of  $[\text{Cr}(\text{acac})_3]$  was also added as a relaxation agent for  $^{29}\text{Si}$  nuclei. Solid-state  $^{29}\text{Si}$  magic-angle spinning (MAS) NMR spectroscopy was performed by using 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  $^{13}\text{C}$  CP/MAS NMR spectra were obtained by using 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. The chemical shifts in both the  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR spectra were referenced to tetramethylsilane at 0 ppm. Powder X-ray diffraction (XRD) patterns were recorded by using a Mac Science M03XHF22 diffractometer with Mn-filtered  $\text{FeK}\alpha$  radiation. Field-emission scanning electron microscopy (FE-SEM) was performed on samples coated with Pt/Pd by using a Hitachi S-4500S microscope at an accelerating voltage of 15 kV. FTIR spectra of the products in KBr pellets were obtained by using a Perkin–Elmer Spectrum One spectrometer with a nominal resolution of 0.5  $\text{cm}^{-1}$ . TG analysis was carried out with a RIGAKU TG8120 instrument under a flow of dry air at a heating rate of 10  $\text{K min}^{-1}$ . The  $\text{SiO}_2$  content in the products was determined by the residual weight after heating to 900 °C and the amounts of organic constituents were determined by CHN analysis (Perkin–Elmer PE-2400). Nitrogen adsorption measurements were performed by using an Autosorb-1 instrument (Quantachrome Instruments, Inc) at 77 K. Samples were preheated at 120 °C for 3 h under a pressure of  $1 \times 10^{-2}$  Torr.

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