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Formation of a New Crystalline Silicate Structure by Grafting Dialkoxysilyl Groups on Layered Octosilicate

Dai Mochizuki,[†] Atsushi Shimojima,[†] and Kazuyuki Kuroda*[,†,‡]

Department of Applied Chemistry, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan, and Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Shinjuku-ku, Tokyo 169-0051, Japan

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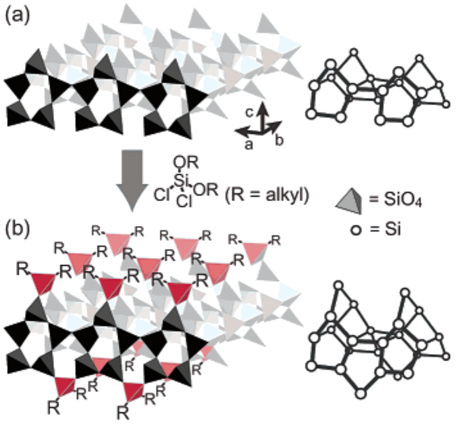
Nanoarchitecture of ordered silicate frameworks is important from the viewpoints of both basic chemistry and applications. Various layered polysilicates and zeolites are basically prepared hydrothermally.[1] However, precise control of silicate frameworks by hydrothermal synthesis is limited, and we have not yet established a soft chemical methodology for the design of silicate structures. Mesostructured silicas are synthesized by various interactions between supramolecular assemblies and silicate species.[2] However, such methods do not afford an approach for nanoarchitecture at a molecular level. Here we report the formation of novel crystalline layered silicate as a novel approach by the reaction of octosilicate with dialkoxydichlorosilanes.

Layered polysilicates are ideal as a substrate for this reaction because of the ability of the two-dimensional silicate frameworks to be modified variously.[3] The most suitable silicate is layered octosilicate ($Na_8[Si_{32}O_{64}(OH)_8{\cdot}32H_2O]$, Na-Oct).[4] The layered structure is composed of five-membered rings as the structural unit,[5] as shown in Scheme 1a. The layer thickness is thicker than that of a single layered polysilicate kanemite, resulting in the rigidity. The distances among Si−OH and/or $Si{-}O^-$ sites arranged along one axis are different from those along the other. Consequently, the bonding direction on the interlamellar surfaces should be arranged regularly when appropriate silylating reagents are grafted onto the surfaces. We have recently reported the reaction of kanemite with various alkylchlorosilanes, resulting in the formation of novel silica-organic nanostructures with newly formed ring structures.[6] However, because of both the flexibility of the single-layered structure and the high silanol density, it is difficult to create a novel crystalline silicate framework.

As the silylating reagent, we used dialkoxydichlorosilane ($(RO)_2SiCl_2$, R = alkyl).[8a] Although both Si−OR and Si−Cl groups are reactive, the reaction rate of Si−Cl groups is much higher than that of Si−OR groups. By utilizing the difference, dialkoxysilyl groups can be grafted onto octosilicate, as schematically shown in Scheme 1. Up to now, there have been no reports on the design of the framework by such a soft process. Also, the silylated products can be regarded as a planar polymer of silicon alkoxide. Ordered alkoxyl groups can be hydrolyzed, and the formed silanol groups can condense to form novel silica-based materials.

It is difficult to directly graft the interlayer surface of Na-Oct with dialkoxysilyl groups. Dodecyltrimethylammonium-exchanged octosilicate (DTMA-Oct)[7] was used as an intermediate. Dialkoxysilylated derivatives of octosilicate ($(C\textit{n}O)_2$Si-Oct, n = 4, 6, 8, 10, and 12) were prepared by the reaction of DTMA-Oct with the corresponding dialkoxydichlorosilanes.[8b]

Scheme 1. Grafting of Dialkoxysilyl Groups onto Octosilicate



The powder XRD patterns of $(C\textit{n}O)_2$Si-Oct exhibit different profiles from those of Na-Oct and DTMA-Oct. The basal spacing of DTMA-Oct (d = 2.37 nm) changed to d = 1.66 nm (n = 4), 2.07 nm (n = 6), 2.49 nm (n = 8), 2.87 nm (n = 10), and 3.20 nm (n = 12) after the reaction (Figure 1 and Supporting Information Figure S1). The amounts of nitrogen in all of the silylated products became zero, whereas that of DTMA-Oct was 2.4%, indicating complete removal of DTMA ions. The basal spacing increased with the increase in the carbon number (n) of alkoxyl groups. The relation is linear, and $\Delta d/CH_2$ was 0.19 nm, being larger than that of a monolayer (0.13 nm/CH_2), suggesting a bilayer arrangement of the organic groups. The interlayer alkoxyl groups (n = 8−12) take gauche−trans conformations, as proved by the chemical shift (δ = 31 ppm) of the interior methylene chains in the ^{13}C CP/MAS NMR spectra of the products (Supporting Information Figure S2).[10] The scanning electron microscopic (SEM) images of the silylated products (Supporting Information Figure S3) showed the retention of the particle size and morphology of starting Na-Oct.

The ^{29}Si MAS NMR spectra of the products (Figure 2) show quite different profiles from those of DTMA-Oct. The signals due to dialkoxysilyl ($(RO)_2\textit{Si}(OSi)_2$, R = alkyl) groups are observed at −96 ppm, characteristic of dialkoxylated Q^2 units.[11] The Q^2 signal at −93 ppm is ascribable to ($(RO)(HO)\textit{Si}(OSi)_2$).[11] The small broad signals at around −104 ppm can be assigned to unsilylated Q^3 units, and the shift from −100 to −104 ppm is probably caused by the distortion of neighboring silylated sites, being in agreement with the small lattice expansion based on the powder XRD data. The distortion also affects the profiles in the Q^4 region, and the peaks were split into several signals, −111, −113, and −114 ppm for $(C4O)_2$Si-Oct and −108, −110, −112, −114, and −115 ppm for $(C\textit{n}O)_2$Si-Oct (n = 8−12). The intensity of the Q^3 signal of DTMA-Oct (the ratio of the intensities due to Q^3 (−100 ppm) and Q^4 (−111 ppm) is 1:1) decreased substantially after silylation, and the degree

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[*] To whom correspondence should be addressed. E-mail: kuroda@waseda.jp.
[†] Department of Applied Chemistry.
[‡] Kagami Memorial Laboratory for Materials Science and Technology.

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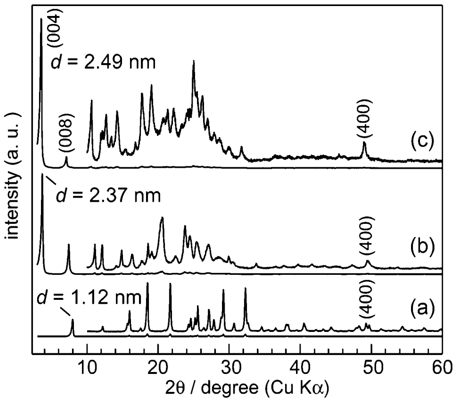

Figure 1. Powder XRD patterns of (a) Na-Oct, (b) DTMA-Oct, and (c) $(C8O)_2$Si-Oct. (Rigaku RINT-2500X diffractometer with graphite monochromated Cu Kα radiation.)

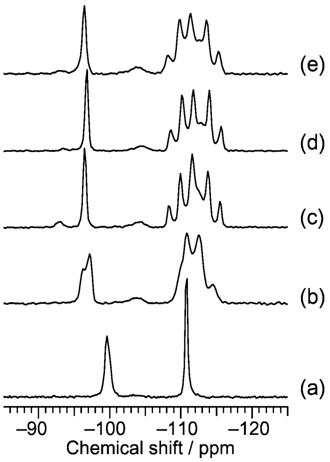

Figure 2. ^{29}Si MAS NMR spectra of (a) DTMA-Oct, (b) $(C4O)_2$Si-Oct, (c) $(C8O)_2$Si-Oct, (d) $(C10O)_2$Si-Oct, and (e) $(C12O)_2$Si-Oct. The spectra were recorded on a JEOL JNM-CMX-400 spectrometer at a resonance frequency of 79.42 MHz with a 45° pulse and a recycle delay of 200 s.

of the decrease (Supporting Information Table S1) clearly indicates that about 90% of the interlayer surface reactive sites are silylated. The amounts of the introduced alkoxyl groups, based on the ^{29}Si MAS NMR data, were 0.8−1.1 per Si−OH, which are larger than those reported for esterified layered silicates[12] and silicas.[13]

The XRD patterns of the products exhibited many peaks at higher angles ($2\theta = 10-60°$). The peaks are due to the ordering of the framework, which has not been observed for all other silylated derivatives of layered polysilicic acids.[3,6] All of the diffraction peaks in the pattern of $(C8O)_2$Si-Oct, for example, are easily assigned to a tetragonal cell (space group $I4_1/amd$), the same group as that of Na-Oct. The same structure is retained because the reactive sites are specifically arranged on each side of the silicate layers. The lattice constants of the a-axis for all of the products are $a = 0.743$ nm, and the value is slightly larger than that of Na-Oct ($a = 0.733$ nm).[5] This slight difference is ascribable to the distortion in the silicate framework by forming new ring structures.

The bonding state of the silyl groups can take two types (Supporting Information Chart S1). One silylating reagent reacts with two confronting silanol groups on the surface to form a cyclic siloxane ring (model A). The other type is the formation of siloxane bonds between adjacent Si−Cl groups of silylating reagents in which one group reacts with the surface of octosilicate (model B). The signal intensity ratios of Q^4 and Q^2 ($(Q^4 - 1)/Q^2$) should be 2 and 1 for models A and B, respectively. The value for $(C4O)_2$-Oct is 1.6 (Table S1), suggesting the combination of both models. On the other hand, the values for $(C8O)_2$Si-Oct and $(C12O)_2$Si-Oct become 2.0, which strongly suggests the bonding shown by model A. The difference with the carbon number is similar to that found for the alkylsilylation of kanemite[6] and is explained by the different degree of silylation due to the steric hindrance of alkoxyl groups.

All of the results prove the formation of alkoxysilylated layered polysilicates with a novel crystalline silicate framework. The dialkoxysilyl groups are grafted in a controlled manner to form new five-membered rings regularly on both sides of the silicate layers (Scheme 1b). The products are a new type of layered silicates with thicker layers where only Q^4 and Q^2 units are present, being in clear contrast to all known layered silicate structures composed of Q^3 and Q^4 units. This material is structurally unique and potentially applicable as precursors for silicate-based materials by hydrolysis and condensation. The interlayer alkoxysilyl groups can act as functional groups and provide *geminal* silanol groups by hydrolysis which could be utilized as a bridging part to form a three-dimensional framework. Further silylation will also afford a well-designed silicate framework, which means the viability of the method for the design of silicate framework at a molecular level.

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Supporting Information Available: XRD patterns of $(CnO)_2$-Oct ($n = 4$, 6, 10, and 12), SEM images of Na-Oct and $(C8O)_2$-Oct, ^{13}C CP/MAS NMR spectra of $(CnO)_2$-Oct ($n = 8$, 10, and 12), ^{29}Si MAS NMR data, and possible models for the bonding state of silyl groups (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) (a) $SiCl_4$ was dissolved in hexane, and *n*-alcohol (C*n*OH, $n = 4$, 6, 8, 10, or 12) was added dropwise ($SiCl_4$/C*n*OH = 1:2) under N_2 flow. The mixture was allowed to react at room temperature for 1 h. The products were the mixtures of $(CnO)_mSiCl_{4-m}$ ($m = 0-4$), and the dialkoxydichlorosilanes were purified by distillation (0.1 Torr, bp; 340 K ($n = 4$), 360 K ($n = 6$), 380 K ($n = 8$), 400 K ($n = 10$), and 420 K ($n = 12$)). Each ^{29}Si NMR spectrum of the products showed a signal at −55.8 ppm for $(CnO)_2SiCl_2$. Each ^{13}C NMR spectrum showed a signal due to $SiOCH_2$ at 65.4 ppm.[9] (b) DTMA-Oct (1.5 g) dispersed in dehydrated toluene (30 mL) containing dehydrated pyridine (15 mL) was mixed with an excess amount (32 mmol) of dialkoxydichlorosilane and stirred at room temperature for 2 d. The products were centrifuged and washed with toluene to remove unreacted silylating reagents, followed by washing with dichloromethane to remove pyridine hydrochloride and deintercalated DTMACl. The resulting products were dried in vacuo to yield $(CnO)_2$Si-Oct.
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