PAPER

Novel crystalline organic–inorganic hybrid silicate material composed of the alternate stacking of semi-layered zeolite and microporous organic layers†

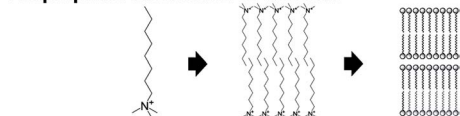Katsutoshi Yamamoto, [iD] *[a] Takuji Ikeda, [iD] *[b] Yusuke Tsukamoto[a] and Takuma Nakaoka[a]

A novel type of crystalline organic–inorganic hybrid microporous silicate material, KCS-5, was synthesized supposedly from a lamellar precursor composed of amphiphilic organosilicic acids. This well-ordered material has a crystalline structure, is thermally stable up to 500 °C and has lipophilic 1-dimensional micropores.

Organic–inorganic hybridization of silicate materials has been diligently studied because it can control surface properties to improve their adsorption capacities and catalytic activities. In these studies, bridged organosilanes, where an organic group connects two trialkoxysilyl species, are frequently employed as a silicon source. For example, Shea *et al.* prepared microporous amorphous materials named bridged polysilsesquioxanes[1] by sol–gel synthesis from various organosilanes with bulky bridging organic groups, such as bis(triethoxysilyl)benzene (BTEB), and Inagaki *et al.* obtained surfactant-templated hexagonally-ordered mesoporous silicates from organosilanes bridged with aliphatic or aromatic organic groups.[2] Tatsumi *et al.* discovered an improvement in catalytic activities and surface hydrophobicity through the syntheses of a mesoporous titanosilicate[3] and zeolites[4] from bridged organosilanes. In particular, Bellussi *et al.* crystallized microporous aluminosilicates called ECS,[5] composed of layered aluminosilicate and bridging organic groups. Such bridged organosilanes were used as a single silicon source, presumably because they can theoretically build a three-dimensional silicate framework without introducing structural defects.
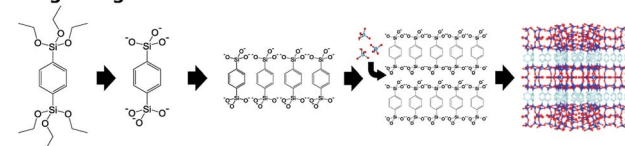
In contrast to bridged organosilanes, terminal organosilanes, where a terminal organic group like a methyl or phenyl group functionalizes trialkoxysilyl species, were not employed as a single silicon source but were subsidiarily added as part of a silicon source because terminal organic groups inevitably cause structural defects which cause a deterioration in the 3-dimensional structure of tectosilicates. However, we conceived an idea to obtain well-ordered materials only from terminal organosilanes inspired by our material KCS-2.[6] KCS-2, also synthesized using a bridged organosilane BTEB, is a crystalline organic–inorganic hybrid material with a large 12-ring micropore and unique amphiphilic inner surface properties. Considering that the finely-designed layered structure of KCS-2 is similar to that of a Langmuir–Blodgett membrane, it is deduced that KCS-2 is crystallized *via* a well-ordered lamellar precursor composed of hydrolysed bridged organosilane (Fig. 1 middle). Because a lamellar structure is formed from amphiphilic surfactant molecules (Fig. 1 top), a well-ordered lamellar precursor should also be formed from amphiphilic organosilicic acid molecules made from terminal organosilanes (Fig. 1 bottom). For example, phenyltriethoxysilane (PTES) was

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† Electronic supplementary information (ESI) available: Materials and methods, X-ray crystallographic data in CIF format, and solid-state MAS NMR spectra. See DOI: 10.1039/c8ra09908a
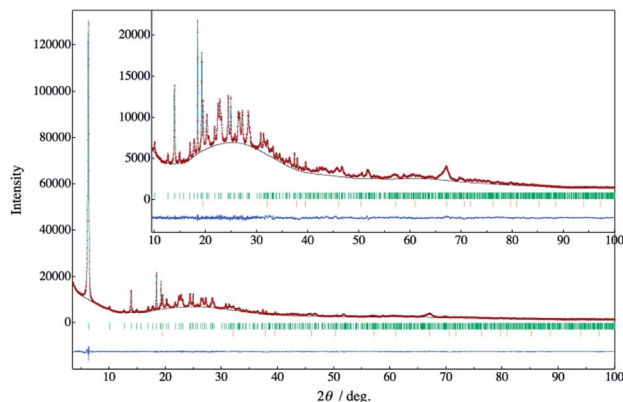

Fig. 1 The induced formation scheme of lamellar precursors from bridged and terminal organosilanes.

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Fig. 2 Observed (red) and calculated (light blue), background (black), and difference (blue) intensity curves of KCS-5 obtained by Rietveld refinement. The green tick marks denote the peak positions of possible Bragg reflections.

Table 1 Conditions for the PXRD experiments and crystallographic information obtained therein for KCS-5

Compound name	KCS-5
Estimated chemical formula	$\|Na_4 \cdot (C_2H_5OH)_{0.28}\| \cdot$ $[Si_8Al_4O_{20}(C_6H_5)_8]$
Space group	$Pca2_1$
a/nm	1.12617(2)
b/nm	1.39679(2)
c/nm	0.92161(5)
Unit-cell volume/nm^3	1.44971(4)
Z	4
2θ Range/°	3.5–100.1
Step size (2θ)/°	0.016346
Profile range in FWHM	12
Number of observations	5933
Number of contributing reflections	843
Number of refined structural parameters	104
Number of constraints	96
R-factors obtained by Rietveld analysis	
R_{wp}	0.019
R_F	0.011
R_{Bragg}	0.017
R_{exp}	0.015
χ^2	1.62

hydrolysed into an amphiphilic molecule with a hydrophilic trihydroxysilyl head group and a hydrophobic phenyl group, which would be self-organized into a lamellar phase. Therefore, through the condensation of silicic acid (with aluminum, if necessary), it would be possible to synthesize a crystalline layered (alumino)silicate.

Actually, we have succeeded in synthesizing a novel crystalline silicate material, KCS-5, from PTES as a single silicon source. In a typical synthesis (please refer to ESI†), a mixture with the molar composition of 1.0 PTES : 1.0 NaOH : 5.0H$_2$O was stirred at r.t. for 2–4 days to promote the hydrolysis of PTES to amphiphilic organosilicic acid, which could be arranged into a lamellar-structured precursor. After the addition of fumed alumina powder (Al$_2$O$_3$/Si = 0.2), this mixture was

hydrothermally treated at 100 °C for 7 days under static conditions. Generally, KCS-5 was obtained preferentially from mixtures with low H$_2$O/PTES ratios, where the concentration of amphiphilic organosilicic acid was high. In addition, no crystalline products were obtained from this organosilane without the addition of an aluminum source.

Fig. 2 exhibits the powder X-ray diffraction (PXRD) pattern of KCS-5. A low and wide background ranging from 15° to 40° would be derived from a concomitant amorphous by-product and a borosilicate glass capillary tube. By an indexing analysis, the lattice constant belonging to an orthorhombic system was uniquely found. A crystal structure model of KCS-5 was tentatively built from local structural units, such as SiO$_4$, AlO$_4$ and C$_6$H$_5$–SiO$_3$, elucidated from the solid-state NMR. (The ^{29}Si, ^{27}Al, and ^{13}C solid-state MAS NMR spectra are shown in ESI.†) The packing structure of these units was solved by the direct-space method with the parallel tempering algorithm using the program FOX.[7] Table 1 lists the crystallographic information obtained by Rietveld analysis[8] using the program RIETAN-FP.[9] Reliability factors obtained in this analysis were small enough. The calculated and difference plots obtained by the Rietveld analyses are also exhibited in Fig. 2.

Fig. 3 shows the crystal structures of KCS-5 viewed along the [100] and [001] directions. As can be easily observed, inorganic aluminosilicate layers and organic layers are stacked alternately, tentatively demonstrating the induced formation scheme illustrated in Fig. 1. The structure of the aluminosilicate layer was identical to that of RUB-15 [10] and HUS-1,[11] which is isomorphic with the (110) slice part of SOD-type zeolite topology (Fig. 4). Between the aluminosilicate layers two kinds of phenyl groups are observed. The conformation of phenyl groups is of course restricted by the bond angle of the silicon atoms in an aluminosilicate framework and the crystal structure of the aluminosilicate layer; one phenyl group stands almost perpendicularly from the aluminosilicate layer (a–c plane), and the other is inclined at approximately 45° from the a–c plane. Due to these different arrangements of phenyl groups, the organic layer located between the aluminosilicate layers has one-dimensional elliptical pseudo-micropores (Fig. 3 inset). The effective diameter of this micropore is calculated at 6.2 Å × 2.9 Å. The 1D pore shape is strictly zigzag viewed along the b-axis.

Fig. 5(a) and (b) show the thermogravimetric curve and the PXRD patterns of heat-treated KCS-5, respectively. It can clearly be observed that the crystal structure of KCS-5 is intact under atmospheric conditions until ca. 540 °C when the terminal phenyl groups are burned out. In addition, the stacking structure of KCS-5 was not spoiled by treatment with several solvents such as water, ethanol, toluene or n-hexane (not shown), also demonstrating the high structural stability of KCS-5.

The nitrogen adsorption isotherm of KCS-5 (Fig. 5(c)) shows a small adsorption step around $P/P_0 = 0$ to support the presence of the above-mentioned micropores. On the other hand, in the benzene adsorption isotherm (Fig. 5 (d)), a type II isotherm was observed, which indicates good affinity against adsorptive molecules. Although the crystal structural model shows that the micropore opening is large enough to adsorb benzene molecules inside, an obvious adsorption step was not observed near $P/P_0 =$
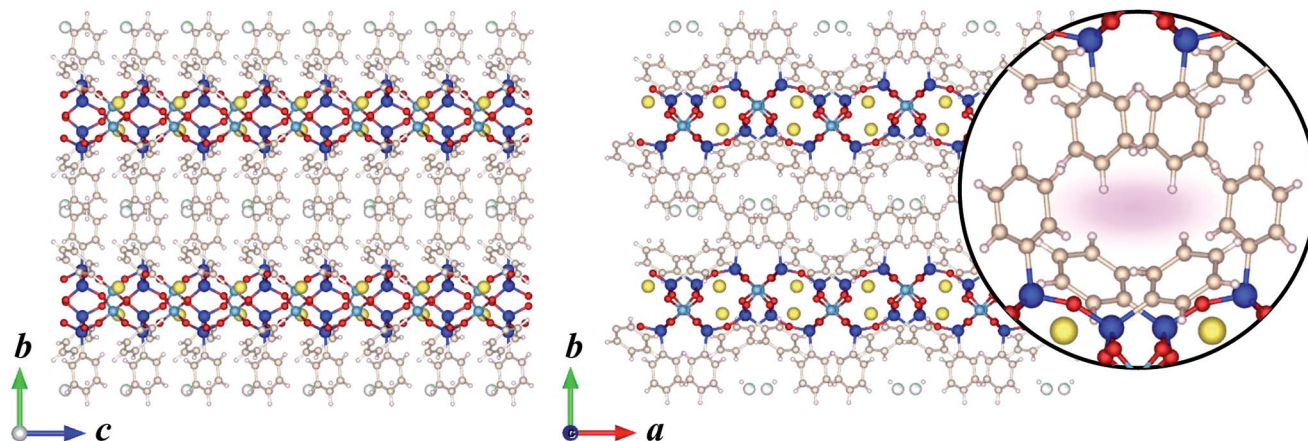
Fig. 3 Crystal structure models of KCS-5 viewed along the [100] (left) and [001] (right) directions. Inset: the magnified drawing clearly shows an elliptical 1-dimensional micropore.
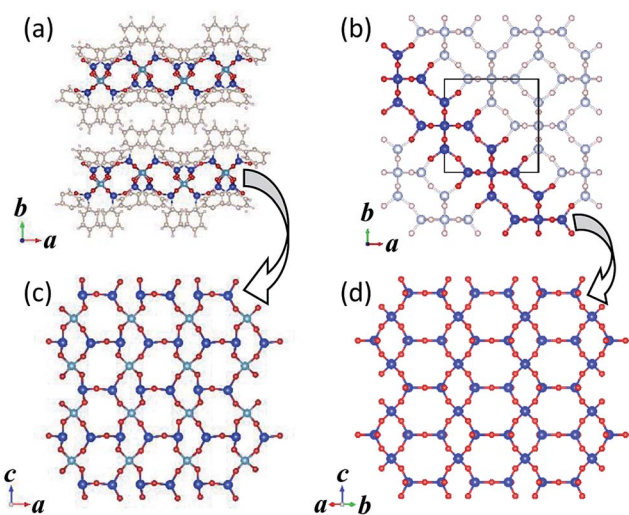

Fig. 4 Crystal structures of (a) KCS-5 and (b) SOD-type zeolites and their component silicate layers (c) and (d), respectively.

Fig. 5 (a) Thermogravimetric curves of KCS-5, (b) PXRD patterns of heat-treated KCS-5 and adsorption isotherms of KCS-5 for (c) nitrogen and (d) benzene.

0. This would be caused by the fact that the size of a benzene molecule and the micropore opening of KCS-5 are very close to each other. In addition, the saturated adsorption volume of benzene is similar to the micropore volume of KCS-5 calculated on the basis of nitrogen adsorption, so the benzene adsorption can be regarded as adsorption inside the micropores. From the experimental results above, KCS-5 with its stable structure and lipophilic inner surface properties would be promising for application to size-selective lipophilic adsorbents.

The synthetic scheme in this study can be applied to other organosilanes with various terminal organic groups, and several crystalline materials have been successfully obtained. These materials are expected to have layered structures providing a lipophilic interlayer space. Therefore, they would stably adsorb or intercalate organic molecules between the silicate layers and might be applicable to host materials having good affinities for organic matter. The structural and physicochemical analyses for these materials are now ongoing, and the results will be reported soon elsewhere.
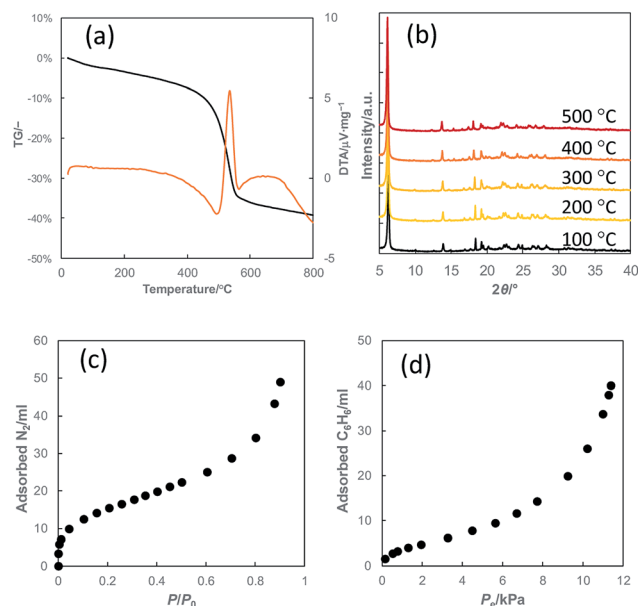
Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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