

Structure Determination of H-LDS: An Acidified Form of the Layered Silicate K-LDS

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The crystal structure of H-LDS ($\text{Si}_8\text{O}_{20}\text{H}_8$)—an acidified form of the layered silicate K-LDS—was determined. Structure analysis from X-ray powder diffraction data shows that its layer structure comprises a six-membered Si atom ring network. ¹H MAS NMR spectroscopy indicates strong intra- and inter-layer hydrogen bonding between neighboring terminal oxygen atoms. Electron density distributions attributed to hydrogen bonding are obtained by the maximum entropy method. The structure of H-LDS is stabilized by the hydrogen bonds without an alkali metal cation.

Layered silicates are one of the most functional materials for various industrial applications such as adsorbents, catalysts, ion exchangers, separators, and hybrid porous organic–inorganic materials like pillared clays. In the past decade, novel layered silicates such as RUB-39, PLS-1, and Nu-6(1) have been synthesized. By thermal treatment, these silicates form new zeolites, namely, RUB-41, CDS-1, and Nu-6(2), respectively, which have topotactic framework structures with two-dimensional micropores.^{1–3}

Kanemite is a well-known hydrous layered silicate composed of a six-membered Si atom ring network (6-MR), and it is used as a nanosized building block for inorganic compounds.⁴ For example, porous materials such as zeolites and mesoporous silicas have been synthesized using kanemite; FSM-16⁵ and KSW-2⁶ are kanemite-derived mesoporous silicas that are obtained via the organic–inorganic interaction between the self-assembled surfactant and the siliceous framework. More recently, new layered silicates PLS-3 and PLS-4, which are topotactic precursors of FER- and CDO zeolites, respectively, were synthesized using a protonated form of kanemite (H-kanemite) as a silica source.⁷ However, the detailed crystal structure of H-kanemite has not yet been reported.

Recently, Komura et al. discovered a new anhydrous layered silicate K-LDS (potassium low-dimensional silicate).⁸ The crystal structure of K-LDS, which is an isostructural compound of $\text{Cs}(\text{Si}_3\text{O}_6(\text{OH}))$ and $\text{Rb}(\text{Si}_2\text{O}_4(\text{OH}))$, consists of a 6-MR layered framework and potassium ions in the interlayer.⁹ A simple layered silicate H-LDS was prepared by acid treatment of K-LDS. The crystal morphology of H-LDS obtained by scanning electron microscopy (SEM) shows an attractive large cleavage parallel to the layer plane. This suggests that delamination of the layered structure took place. Therefore, we anticipate that a silica nanosheet can be prepared if each layer of H-LDS is completely exfoliated by acid treatment. In this study, we determine the crystal structure of H-LDS by ab initio analysis using powder X-ray diffraction (PXRD) and solid-state nuclear magnetic resonance (NMR) spectroscopy to understand the structural stability of H-LDS. Additionally, we investigate the structural similarities between H-kanemite and H-LDS.

K-LDS was obtained from a steam-assisted solid-state reaction according to a previous report.⁸ Subsequently, a solution of 0.5 M aqueous HCl (7.5 mL) was added to K-LDS (0.5 g) at room temperature. The resulting mixture was stirred for 30 min. H-LDS was separated by filtration, thoroughly washed with distilled water, and dried at 60 °C overnight. Na-kanemite was prepared as follows: 1.0 g of $\delta\text{-Na}_2\text{O}\cdot 2\text{SiO}_2$ powder (Tokuyama Siltech Co., Ltd.) was stirred in distilled water (100 mL) for 3 h at room temperature. Na-kanemite powder was separated by filtration, washed with deionized water, and air-dried overnight. An acidified form of Na-kanemite (denoted as H-kanemite) was prepared via a procedure similar to the one described for H-LDS, using 1N aqueous HCl solution for 2 h at ambient temperature.

It is well known that clays typically swell in water, enhancing the effective ion-exchange ability between intercalated cations and/or siliceous frameworks. However, the fact that K-LDS does not swell in water suggests that there is a strong interaction between its layers. However, we found that a protonated H-LDS having unknown structure is easily produced by treating K-LDS with an aqueous HCl solution. The XRD pattern of K-LDS drastically changed after 1 min of acid treatment; however, the complete formation of H-LDS was observed after 30 min. The diffraction peaks attributed to H-LDS were not significantly changed to amorphous or impurity phases even after 48 h. Additionally, H-LDS was also obtained by acid treatment using a 0.5 M aqueous acetic acid solution (This synthesis is not discussed here).

Figure 1 shows the XRD patterns of (a) K-LDS and (b) H-LDS. Broad peak patterns of H-LDS are obtained by the acid treatment of K-LDS, which are due to structural disorder and/or small domain size resulting from local delamination. We

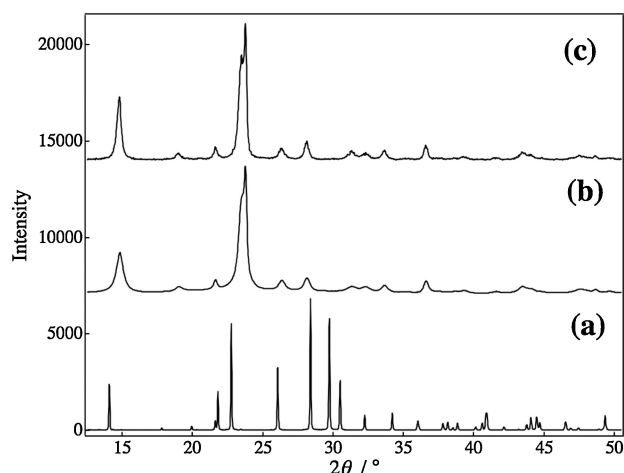


Figure 1. PXRD patterns of (a) K-LDS, (b) H-LDS, and (c) H-kanemite.

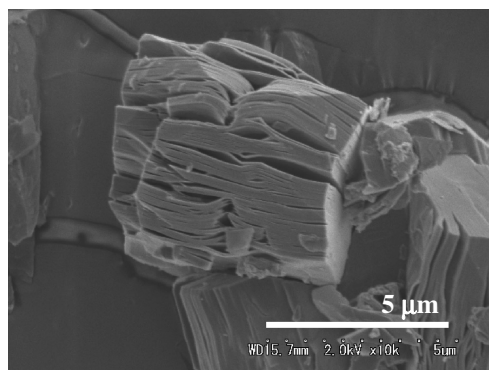


Figure 2. Crystal morphologies of H-LDS by the FE-SEM observation.

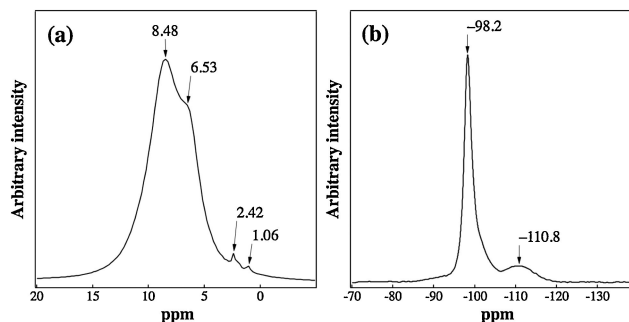


Figure 3. (a) ^1H MAS NMR and (b) ^{29}Si MAS spectra of H-LDS.

accidentally found that H-kanemite had a crystal structure similar to that of H-LDS; their XRD patterns were similar, as depicted in Figure 1c. However, the well-defined crystal structure of H-kanemite has not yet been clarified.

SEM images of the sample are shown in Figure 2. Interestingly, H-LDS has a rather unique morphology that shows a cleavage of blocks with a specific direction. This may indicate that the exfoliation of K-LDS can be performed effectively by acid treatment. Potassium ions were scarcely observed by the EDX analysis, indicating that a complete proton exchange took place. Although no micropore was observed by the Ar gas adsorption measurement, the presence of a macropore was estimated by the abrupt increase in the adsorption volume at a relative pressure of $P/P_0 \approx 1$ (Figure S1).¹⁰ The macropore is probably attributed to the large cleavages observed in H-LDS.

We measured the ^{29}Si MAS and ^1H MAS NMR spectra of the samples to clarify the retention of the siliceous framework of K-LDS (Figure 3). In the ^1H MAS NMR spectra (Figure 3a), a broad peak at 8.48 ppm with a shoulder peak at 6.53 ppm was observed. The O–O distances with hydrogen bonding were estimated as 2.77 and 2.84 Å for the resonances at 8.48 and 6.53 ppm, respectively, according to the equation $\delta = 79.05 - 0.255 \times d(\text{O}-\text{H}\cdots\text{O})/\text{pm}$ (picometer).¹¹ From these findings, it is reasonable to infer that two types of hydrogen bonding exist between terminal silanols; one type of hydrogen bonding is within a layer, and the other is between adjacent layers. Additionally, two small resonance peaks at 2.42 and 1.06 ppm, which are attributed to isolated silanols, were observed, indicating the presence of a Si atom defect in the framework.

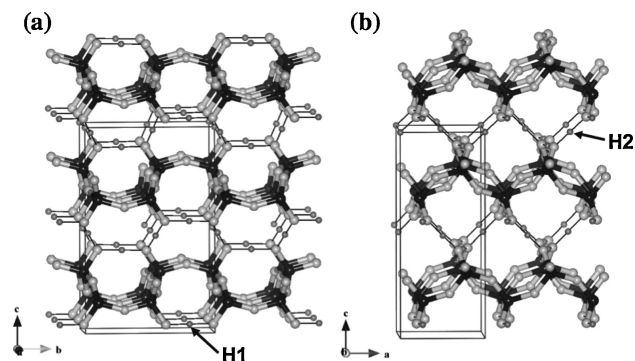


Figure 4. Crystal structure model of H-LDS along (a) [100] and (b) [010] direction. H1 and H2 show proton positions contributing to hydrogen bonds estimated by MEM analysis.

A sharp peak at -98 ppm in the ^{29}Si MAS NMR spectra (Figure 3b) revealed that the layered framework was almost completely retained after the acid treatment of K-LDS. However, partial dehydration condensation of the silicate layers occurred during the acid treatment; this was indicated by the Q^3 or Q^4 shoulder peak that corresponds to an amorphous siliceous framework. This implies that H-LDS is preferably obtained by an HCl solution with a small amorphous phase.

The TG-DTA curve of K-LDS shows an endothermic weight loss of ca. 5% at 450°C , whereas that of H-LDS shows a weight loss of ca. 7% at a lower temperature of 180°C . High-temperature PXRD shows that H-LDS is easily dehydrated and condensed between adjacent layers because of the absence of a K^+ cation at 180°C (Figures S2 and S3).

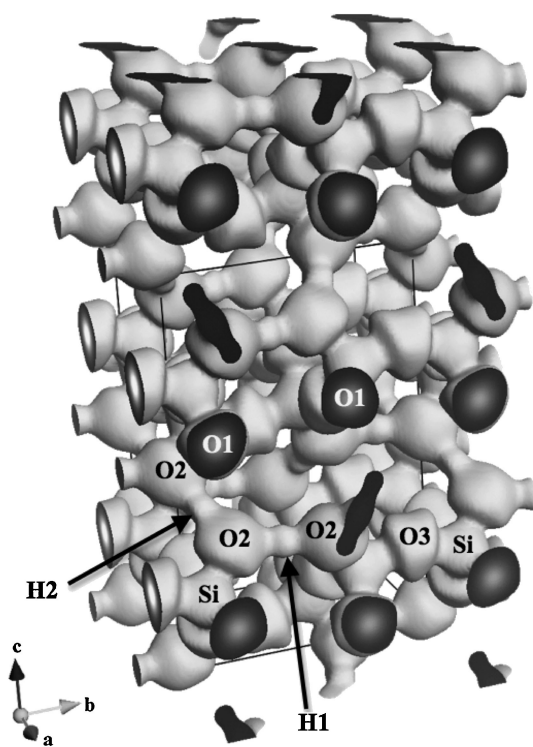
Lattice constants with an orthorhombic cell were determined as $a = 11.90$ Å, $b = 7.47$ Å, and $c = 4.90$ Å, using the indexing program N-treor built into the integrated package EXPO2004.¹² The most suitable space group for H-LDS was estimated to be $Pnaa$. Preliminary observed integral intensities were extracted using the Le Bail method.¹³ As a result, the direct method analysis (EXPO2004) easily provided the framework structure as an initial model. The structure of this model was verified to be composed of one Si site and three O sites; site O1 possessed a terminal silanol oxygen atom. No K^+ ion site was found in the interlayer.

The initial structural model was then refined by Rietveld analysis using the program RIETAN-FP.¹⁴ The space group, whose ab plane is parallel to the layer plane, was converted to $Pccn$ by transforming the axis from (a, b, c) to (c, b, a) . Anisotropic line broadening was clearly observed in several reflections at $2\theta < 38^\circ$. Then, a partial profile relaxation with a modified split pseudo-Voigt function was applied to these reflections, resulting in a significant improvement in the fit between their observed and calculated intensities (Figure S4). Furthermore, electron density distributions of H-LDS were analyzed by a MEM-based pattern fitting (MPF) using RIETAN-FP and the MEM analysis program PRIMA.¹⁵ Structure models and electron density images were visualized by using the program VESTA.¹⁶

Figure 4 shows a model of the refined crystal structure of H-LDS. This framework topology is similar to that of K-LDS or kanemite in that it also has a six-membered Si atom ring network. The stacking ordering of the adjacent layer framework

Table 1. The crystallographic data and *R* factors for H-LDS

Compound name	H-LDS
Chemical formula	Si ₈ O ₂₀ H ₈
Space group	<i>Pccn</i> (No. 56)
<i>a</i> /Å	4.9058(2)
<i>b</i> /Å	7.4815(3)
<i>c</i> /Å	11.9014(7)
Unit-cell volume/Å ³	436.81(3)
<i>R_F</i> (Rietveld)	0.0040
<i>R_{Bragg}</i> (Rietveld)	0.0039
<i>R_{wp}</i> (Rietveld)	0.0319
<i>R_c</i> (Rietveld)	0.0128

**Figure 5.** Electron density distribution image of H-LDS obtained by the MPF analysis. Equi-density level is 0.5 e/Å.

is identical without in-plane layer displacement. At this stage, the proton site was not taken into account in the structural model; nevertheless, the presence of hydrogen bonding between terminal oxygen atoms was estimated by a preliminary MEM analysis. On the basis of the obtained ¹H MAS NMR spectra, two proton sites were added in the structural model to compensate for the charge. The fractional coordinates of the two proton sites were fixed as (1/4, 3/4, *z*(O₂)) for site H1 and (0, 0, 0) for site H2; however, these protons would be distributed disorderly between neighboring O₂ sites. The chemical formula of H-LDS was determined to be H₂Si₂O₅. Detailed crystallographic information is summarized in Table 1 and in Supporting Information.¹⁰

Figure 5 shows the final electron density distribution according to the MPF analysis, which revealed the existence of hydrogen bonding between neighboring O₂ sites in the intra- and interlayer. This fact strongly suggests that the layered

framework of H-LDS might be stabilized by the hydrogen bonds. Electron densities of the O₂ site are isotropic, whereas those of the O₁ and O₃ sites are anisotropic due to tight covalent bonding.

The *R* factors obtained from the Rietveld analyses were also sufficiently low (Table 1). The *l*(Si–O) and *φ*(O–Si–O) values range from 1.55 to 1.63 Å and from 106.3 to 111.4°, respectively. The average *l*(Si–O) value of ca. 1.58 Å seems to be unusually short compared to the ideal value of 1.60 Å. The reason for this has not yet been clarified. However, it is probable that the covalent bonding of Si–O might be affected by the strong hydrogen bonding. The atomic distances, *l*(O₂–O₂), between neighboring layers was 2.74 Å, whereas the *l*(O₂–O₂) between adjacent silanols in the silicate layer was 2.86 Å. These distances are in good agreement with those values estimated from the ¹H MAS NMR spectra. Furthermore, it is shown that this defined crystal structure of H-LDS is also acceptable for the acidified H-kanemite framework structure. In conclusion, H-LDS has a metastable structure that is immobilized because of strong hydrogen bonding.

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