

A Novel Layered Silicate Having the Intercalated Potassium Cation: Synthesis, Characterizations, and Modification by Acid Treatment

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Synthesis and structure determination of the potassium cation intercalated crystalline materials having the lower dimensional siliceous frameworks and the modification by the acid treatment were successfully investigated. The materials were characterized by using a powder XRD, TG-DTA, solid ²⁹Si MAS NMR, and FE-SEM.

The clays in nature such as kanemite and smectite, having a layered siliceous framework and intercalated alkaline metal cations, have been widely used in industry and focused on the functional and valuable inorganic materials.¹ The use of clays has been also investigated as an additive for the composite materials and the organic–inorganic hybrid materials, so far. As one of the recent potential applications, clays have been utilized as a nanosized building-block toward the sophisticated formations of the inorganic matrix architects. For example, mesoporous silica FMS-16² and KSW-2³ can be prepared from layered silicate Na–kanemite as a starting nanosized building-block via interaction of silicate frameworks and assembled organic surfactants.

On the other hand, the solid-state transformations of kanemite into microporous materials, in particular zeolites (BEA,⁴ ZSM-5,⁵ and Silicalite-1⁶), have been also reported, in which kanemite was used as an important raw silicate crystal. Instead of Na–kanemite, the novel microporous materials synthesis has also investigated by using the artificial novel layered silicates.^{7,8} Very recently, it is reported that the Ga–SOD can be successfully prepared from the mixture of the layered silicate β -HLS⁹ and Ga(OH)₃.¹⁰ These potential applications for the synthesis of microporous materials let us realize utilization as a nanosized building block of the layered silicate and the importance of the exploration of the new layered silicate.

Here, we report the synthesis and characterizations of potassium cation-intercalated layered silicate and provide its structure determined by ab initio analysis using high-resolution powder XRD data. The modification of the obtained layered silicate by acid was also discussed.

We named and abbreviated the obtained crystal discussed here as K-LDS (Potassium-type Lower Dimensional Silicate), and this can be obtained from a dry-gel powder by a steam-assisted conversion (SAC)¹¹ method, of which dry-gel powder was prepared from the mixture of silica-sol and aqueous K₂CO₃ solution.¹²

Figure 1A shows the XRD patterns of K-LDS. No steam treatment gave an only amorphous phase; however, the crystal of K-LDS can be successfully obtained by SAC. After screening of synthetic temperature and time, it revealed that the pure crystal of K-LDS can be formed after 5 h and above 100 °C and also found that the concentration of SiO₂ in the prepared silica-sol

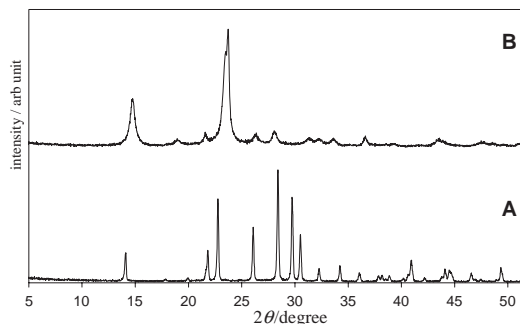


Figure 1. XRD patterns of K-LDS (A) and H-LDS (B).

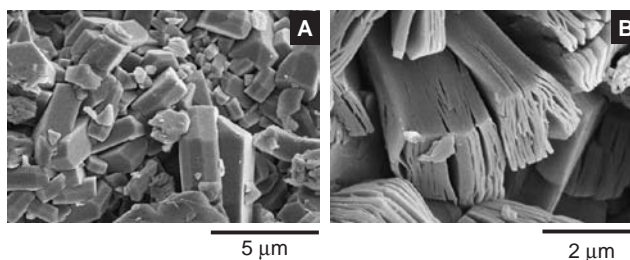


Figure 2. FE-SEM images of K-LDS (A) and H-LDS (B).

did not affect the crystal formation of K-LDS. Further, it is noted that K-LDS is not swelled even in the presence of water. This is a quite unique property compared with conventional clays. TG-DTA analysis indicates that a slightly weight decrease (ca. 1%) was observed at 200–420 °C, and the drastic weight loss (ca. 5%) was detected at 420–550 °C with an endothermic change. This endothermic reaction is ascribed to the release of water by the dehydrate-condensation of K-LDS (see Figure S1 in Supporting Information).¹³

As one of the extensive application, we examined the modification of K-LDS by the acid treatment in order to synthesize the proton-type LDS. The treatment of K-LDS using 0.5 M aqueous HCl solution at room temperature for 24 h yielded the H-formed LDS (H-LDS) as a white powder. Figure 1B shows XRD pattern of H-LDS; the pattern was drastically changed, and broadening profile due to the degraded crystallinity by stacking faults and/or delamination of siliceous layers was observed.

FE-SEM images of K-LDS and H-LDS are shown in Figure 2. The morphology of K-LDS is not characteristic, and the shape are not uniform (Figure 2A). However, the interesting morphology was observed in H-LDS (Figure 2B), which shows the cleavage of block along with specific direction. This may indicate that the effective exfoliation of K-LDS can be performed by the acid treatment. This is a quite unique property

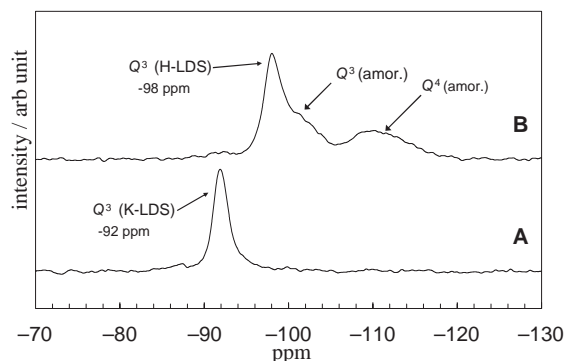


Figure 3. Solid ^{29}Si MAS NMR of K-LDS (A) and delaminated H-LDS (B).

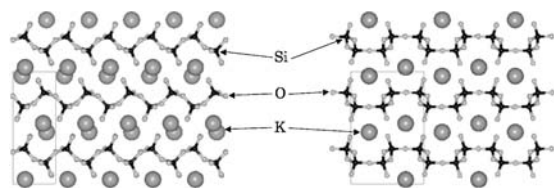


Figure 4. Structural drawing of K-LDS along [001] (left) and [010] (right) directions.

of K-LDS because the same treatment of Na-kanemite gave only amorphous phase.

Solid ^{29}Si MAS NMR showed that the only sharp Q^3 (HO-SiO_3) peak of K-LDS can be detected at -92 ppm (Figure 3A). This clearly indicates that the framework of the K-LDS is constructed by only Q^3 silicate unit. This unique single peak is also found in Na-kanemite: its ^{29}Si NMR of appears in -97 ppm.¹⁴ On the other hand, the Q^3 peak of K-LDS was shifted to -98 ppm by the acid treatment owing to the different environment of the exposing Q^3 silanols (Figure 3B). It is obvious that the siliceous layered framework can be almost retained after acid treatment of K-LDS. However, the dehydration-condensation of silicate layers partially occurred during the acid treatment; the Q^3 silanols of K-LDS changed to the broad Q^3 and Q^4 peaks corresponding to the amorphous framework. In order to avoid the dehydration-condensation, the use of a weak acid such as acetic acid was attempted; however, no improvement of the amorphous broad peaks in H-LDS was observed.

Crystal data and structure determination of K-LDS are as follows (see S2 in Supporting Information);¹³ the lattice parameters and space group were $a = 12.5472(2)$, $b = 4.75163(6)$, $c = 8.13813(10)$ Å and $P2_12_12_1$, respectively, from the indexing analysis. Fractional coordinates of all Si, O, and K atoms for K-LDS were uniquely determined by a direct method and refined by the Rietveld method from the XRD data as shown in Figure 1. It is found that the silicate framework of K-LDS is similar to that of Na-kanemite (Figure 4), which bearing Q^3 silicate sheets exposing alternative terminal silanols, and, instead of Na^+ , the potassium cations are robustly sandwiched between their silicate layers. Cs^+ or Rb^+ -containing layered silicates with kanemite-like siliceous framework (Cs - or Rb -kanemite) are known;¹⁵ however, K-LDS is a novel crystalline form of K-type kanemite.

In conclusion, K-LDS having potassium cations between silicate layers can be successfully synthesized by the steam-

assisted conversion method of dry-gel powder and characterized by XRD, TG-DTA, FE-SEM, and solid NMR analyses. Ab initio structure analysis using powder XRD data elucidated that the K-LDS has similar framework geometry to that of kanemite. The treatment of K-LDS with an acid yielded the corresponding proton-type silicate H-LDS with a partially amorphous framework. Further investigations of K-LDS to use a nanosized building block will be our task and will be reported elsewhere in a near future. Crystal structure analysis for H-LDS is now in progress.

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- The procedure of K-LDS is as follows; the concentrated HNO_3 (2.1 g) was added dropwise to the mixture of TEOS (17.4 g), EtOH (147 mL), and distilled water (3.2 g) with stirring at room temperature. After stirring for 2 h at ambient temperature, the resulting solution was stored at refrigerator for 3 days. This solution was used as a silica-sol for the preparation of K-LDS. The K_2CO_3 (3.55 g) was resolved into 3.8 mL of aqueous NaOH solution (ca. pH 11.5). Then, this solution was added slowly into the 41 mL of prepared silica-sol at room temperature. Very soon, a white precipitate appeared, and the resulting heterogeneous solution was evaporated at 80°C with stirring to obtain dry powder. Obtained dry powder (5.25 g) was transferred into a Teflon autoclave and added distilled water (1.0 mL). After standing at 140°C for 24 h, an autoclave was cooled down to room temperature, then the white solid was washed with distilled water. Obtained white solid was dried at 90°C for overnight to give the K-LDS.
- Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/>.
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