Synthesis of Gallium-sodalite from a Layered Silicate with a Half Cup-type Sodalite Cage Structure

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Gallium-sodalite (Ga-SOD) was synthesized from a half cup-type sodalite cage layered silicate (named; HLS: $[(CH_3)_4N]_2Na_2$ $[Si_{10}O_{20}(OH)_4]$ $5.6H_2O$) by solid-state transformation. HLS was easily converted to the Ga-SOD by mixing it with $Ga(OH)_3$ and heating at 150 °C for 3 h after adding a small amount of H_2O as the solvent. Ga was inserted into the T-site of the SOD cage obtained.

The crystallization of zeolite and its related materials generally involves the mixing of an aluminate source with a silicate source in a basic medium to form an amorphous aluminosilicate gel. This is followed by hydrothermal treatment at some predetermined elevated temperature. The mechanisms of crystallization have been investigated,[1,2] however, these investigations were conducted primarily by using large amounts of solutions with an intricate nucleation step followed by crystal growth. Another preparation method of zeolites, the vapor-phase transport (VPT) method, was reported by Xu et al.[3] who synthesized MFI from dry aluminosilicate gels under mixed vapors of ethylenediamine, triethylamine and H_2O. Thus far, the framework substitution of sodalite (SOD) has been attempted only by in situ hydrothermal synthesis.[4] A quantitative limit exists for framework substitution by the hydrothermal synthesis, because the chemical composition of the starting material will inevitably change.

Recently, we synthesized a novel half cup-type sodalite cage layered silicate (HLS) by using the system of SiO_2–1,4-dioxane–tetramethylammonium hydroxide (TMAOH)–NaOH–H_2O.[5,6] According to ab initio structure analysis based on X-ray powder diffraction data[7] and ^{29}Si MAS NMR analysis, HLS has a cup-shaped cage topology with four- and six-membered rings that are composed of Q^3–Q^4–Q^3 silicon networks. Such a unique network is expected to be constituents of zeolite frameworks, or nano-sized building blocks. From this viewpoint, we investigated the synthesis of zeolite from the HLS by solid-state transformation.

The HLS was prepared by employing the method reported previously.[5] The molar composition of the starting gel was SiO_2:3.05R:0.133TMAOH:0.1NaOH:10.2H_2O; (R: 1,4-dioxane).

A typical synthesis was carried out in the following manner. First, 10 g of Cab-O-Sil (M5) was mixed with 61.8 g of distilled H_2O, and then 13.2 g of TMAOH (Tokyo Kasei: 25 wt % in water), 60.0 g of 1M NaOH aq. (Wako Pure Chemical Ltd.) and 50.0 g of 1,4-dioxane (Wako Pure Chemical Ltd.) were successively added to the solution. After vigorous stirring for 1 h, the gel mixture was poured into a Teflon-lined autoclave with a volume of 300 mL, the autoclave was then heated at 150 °C for 5 days. The resulting powder was filtered and washed with 200 mL of acetone, and dried at 70 °C for a few hours. The yield of the powder was 9.72 g. The powder was identified to be HLS by the X-ray diffraction (XRD) pattern. $Ga(OH)_3$ ($=Ga_2O_3 \cdot nH_2O$, Kishida Chemical Co., Ltd., Japan) was used as an intercalation modifier. The starting powder for the solid-state transformation was prepared by the mechanical mixing of the HLS and $Ga(OH)_3$ under dry condition. The mixed powder was then heated in an autoclave (Parr, No. 4749, 23 mL volume) at 150 °C for 3–24 h. H_2O was added separately in the autoclave, when required.

The X-ray diffraction (XRD) patterns were recorded on a MAC Science MXP instrument using Cu Kα radiation with a graphite monochromator. Thermogravimetry and differential thermal analyses (TG-DTA) were carried out on a MAC Science TG-DTA 2000 instrument in dried air. Scanning electron microscope (SEM) observations were performed with a Hitachi S-800 equipped with a Kevex EDX system.

Typical conditions for the solid-state transformation of the HLS-$Ga(OH)_3$ powder are summarized in Table 1. Pure sodalite (SOD) with high crystallinity was obtained in the presence of $Ga(OH)_3$. The HLS was not converted to SOD in the absence of $Ga(OH)_3$. This result indicates that $Ga(OH)_3$ plays an important role in the transformation of HLS into SOD. SOD was obtained even in the absence of extra H_2O (Table 1, run No. 2). A small amount of H_2O (0.1 g) promoted the transformation into SOD. On the other hand, in the presence of a large amount of H_2O (18 g) in the autoclave, only the amorphous phase was obtained (Table 1, run No. 10), because the precursor HLS terminal Si–OH groups were dissolved in H_2O and the layer structure was damaged or shattered. The dehydration condensation of the HLS terminal Si–OH groups and elimination of H_2O were promoted by adding of $Ga(OH)_3$. In other words, it was shown that the adjacent HLS interlayer could be combined (Figure 1). Therefore,

Table 1. Crystallization conditions of HLS-$Ga(OH)_3$ powder (in weight ratio/g)

Run	$Ga(OH)_3$	H_2O	Time/h	Product
1	0	0	24	HLS
2	0.1	0	24	SOD
3	0.1	0.1	3	SOD
4	0.1	0.1	5	SOD
5	0.1	0.1	10	SOD
6	0.1	0.1	24	SOD
7	0.3	0.1	10	SOD
8	0.5	0.1	10	SOD
9	1.0	0.1	10	SOD
10	0.5	0.5	10	SOD
11	0.5	18	10	Amorphous

HLS: 1.0 g, 150 °C in autoclave. H_2O was added separately in the autoclave.

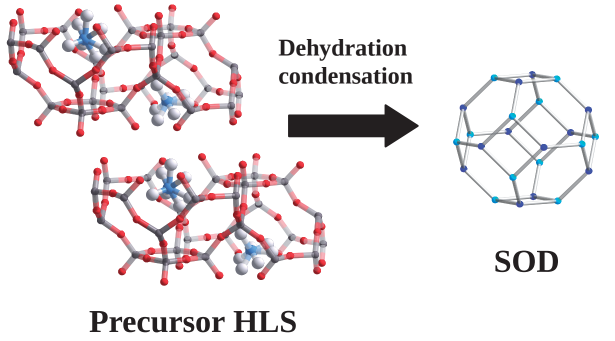

Figure 1. Plausible mechanism for synthesis of SOD from HLS.

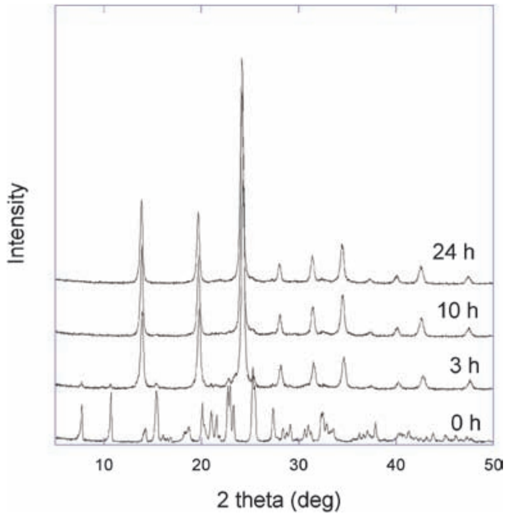

Figure 2. Time course of the XRD pattern in the transformation of HLS to Ga-SOD. (before the transformation and run Nos. 1, 3, 5, and 6).

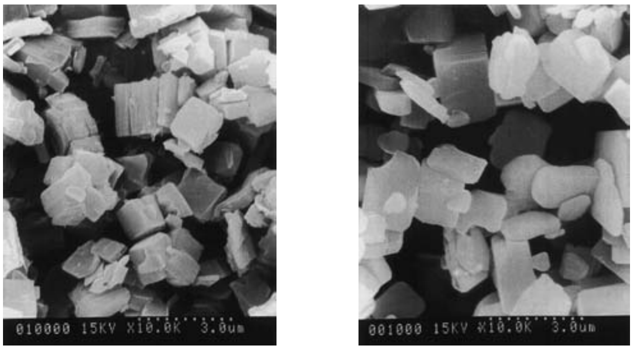

Figure 3. SEM images of HLS (Left) and Ga-SOD (Right).

Ga-SOD could be obtained directly from the HLS and Ga(OH)$_3$.

Figure 2 represents the time course of the XRD pattern in the transformation of the HLS to Ga-SOD (before the transformation and run Nos. 3, 5, and 6 in Table 1). It was found that the pattern suddenly changed to that of SOD after heating at 150 °C for 3 h. The HLS directly changed to the SOD phase without converting into the amorphous phase. Moreover, the XRD pattern did not change further after the appearance of SOD although the heating was continued for at least 24 h.

The EDX measurement revealed the existence of Ga in the obtained SOD. The amount of Ga in the Ga-SOD was proportional to that of Ga(OH)$_3$ added during the reaction. It was possible to control the Si/Ga ratio from ca. 300 to 1 by changing the adding amount of Ga(OH)$_3$. It grew more than the Al-SOD (space group: *P*43*n*) because of the high accuracy of lattice spacing determined by powder X-ray analysis. It is considered that the Ga exists in the T site of SOD.

The content of TMA$^+$ in the Ga-SOD was 13.70 wt % and it was consistent with the value of the starting HLS. The TG-DTA curves of the HLS indicated weight loss with an exothermic peak at 365 °C that corresponds to the release of TMA$^+$ between the sheets. However, Ga-SOD showed an exothermic weight loss of 8.7 wt % due to TMA at 716 °C. This difference in the TMA release temperature between the HLS and Ga-SOD suggested that most TMA$^+$ ions in Ga-SOD were occluded within the SOD cages. Moreover, Ga-SOD was observed to be dark blue in color after the XRD measurement. This suggested that Ga-SOD easily generated a color center with X-ray irradiation. It was known that the Na$_4{}^{3+}$ cluster in SOD could function as a color center by electron capture.[8,9] Thus, TMA$^+$ and Na$^+$, which were located between the HLS layers, were occluded into the SOD-cages during the transformation to SOD. It is noteworthy that SOD was formed with the inclusion of the molecules located in the interlayer. The morphology of the obtained Ga-SOD crystals was cubic (1–2 µm in size) with a layer habit. A comparison between the precursor HLS and Ga-SOD, revealed that the morphology and crystal size were almost the same. In other words, no crystal dissolution and crystal growth occurred during the transformation to Ga-SOD from the HLS precursor. This result suggested that the solid-state transformation was topotactic (Figure 3).

In summary, pure Ga-SOD was successfully synthesized from a half cup-type sodalite cage layered silicate. The mechanism of the transformation into Ga-SOD was directly related with the interlayer dehydration condensation of the HLS terminal Si–OH groups and Ga–OH groups.

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