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# Synthesis of $Ga_2O_3$-pillared fluorine micas

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Synthesis of gallium oxide pillared fluorine micas has been undertaken by using hydroxogallium solutions having different OH/Ga ratios and aging conditions as pillaring agents. The gallium oxide pillared fluorine micas obtained from aged hydroxogallium solutions have larger basal spacings and higher specific surface areas than those obtained from freshly prepared hydroxogallium solutions. Thermal durability of the pillared structure depends on the aging conditions of the hydroxogallium solutions; thermal durability of the pillared micas was enhanced by using the solutions aged under the optimized conditions. The pillared micas obtained from the hydroxogallium solution (OH/Ga = 2.0) aged at room temperature for 24 hours retained larger basal spacings and specific surface areas even after heated up to 750 °C. © *2000 Kluwer Academic Publishers*

## 1. Introduction

The intercalation of bulky inorganic polycations between the layers of swellable clays followed by calcination leads to the formation of pillared clays. In these pillared clays, the intercalated oxides prop the layers apart as pillars, providing microporous characters. These pillared clays exhibit interesting properties for catalysis, adsorption and separation.

The present authors have focused their attention on swellable synthetic fluorine micas [1, 2] as host crystals for preparing pillared clays. These synthetic fluorine micas are featured by large cation exchange capacity and high crystallinity. The variability of layer charge in the synthetic mica groups also leads to the controlled pillar density and microporous properties for alumina [3, 4], chromia [5, 6] and titania [7, 8] pillared fluorine micas.

The thermal durability related with the properties of both pillars and host crystals is important for applications of the pillared clays, such as selective gas adsorptions, catalyses, etc. For the potential for thermal stability and different types of catalytic activity, new pillaring agents of hydroxogallium solutions [9–11] were used for preparing gallium oxide pillared clays [12–14]. However, the knowledge of the chemical species in hydroxogallium solutions prepared under various conditions has not been fully obtained although some detailed studies have been reported [12–14]. Therefore, further investigations are needed on the preparations and properties of $Ga_2O_3$-pillared clays.

In this study, Li-taeniolite series expandable fluorine mica, $Li_{0.5}Mg_{2.5}Li_{0.5}Si_4O_{10}F_2$, which was prepared from $Na_{0.5}Mg_{2.5}Li_{0.5}Si_4O_{10}F_2$ by cation exchange [3–8] was used as host crystals for preparing $Ga_2O_3$-pillared fluorine micas. The aims of this paper are 1) to clarify the effects of an OH/Ga ratio and aging conditions of the hydroxogallium solutions on formation and thermal durability of $Ga_2O_3$-pillared fluorine micas and 2) to obtain the $Ga_2O_3$-pillared micas with high thermal durability. The microporous characteristics of the pillared micas were also examined.

## 2. Experimental

The starting Na-taeniolite having a layer charge of 0.5, $Na_{0.5}Mg_{2.5}Li_{0.5}Si_4O_{10}F_2$, was synthesized by the same procedure as described previously [2], and ground into powder of $<75$ $\mu$m by an agate mortar. It was then exchanged three times with a 2 mol/dm$^3$ solution of LiCl for 1 hour at room temperature to transform into the homoionic $Li^+$-exchanged form [3–8].

The hydroxogallium ion (hereafter abbreviated to Hyd-Ga) solutions were prepared using $GaCl_3$ (Wako Pure Chemical Industries, Ltd., 99.9%) solution. The solutions of 0.2 mol/dm$^3$ $GaCl_3$ were hydrolyzed to form the hydroxogallium ions by the dropwise addition of NaOH solution, until Ga concentration of 0.06 mol/dm$^3$ and the OH/Ga ratios of 1.8, 2.0 and 2.25 were reached. These solutions were then aged at room temperature for 12–36 hours or at 40 °C for 2–24 hours.

Separate samples of $Li^+$-exchanged micas dispersed in distilled water were allowed to react with the Hyd-Ga solutions at room temperature for 2 hours. The amounts of intercalated Ga were measured by the wet chemical analysis from the differences in Ga concentrations of the Hyd-Ga solutions between before and after the intercalation reactions. The reaction products were centrifuged, washed with distilled water several times to remove the excess ions and dried in air at room temperature. A portion of the dried reaction products was heated at the temperatures in the range of 350–800 °C for 1 hour. The samples were then characterized by

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X-ray diffraction (XRD) using Cu $K_\alpha$, scanning electron microscopy (SEM) and $N_2$ adsorption-desorption measurements.

## 3. Results and discussion

### 3.1. Effects of the OH/Ga ratio of solutions on pillared mica formation

Fig. 1 shows XRD patterns around the (001) profile of the reaction products ($Ga_2O_3$-pillared fluorine micas) heated at different temperatures. The $Ga_2O_3$-pillared fluorine micas were obtained from freshly hydrolyzed Hyd-Ga solutions with the different OH/Ga ratios of 1.8, 2.0 and 2.25. For all the air-dried samples, XRD patterns exhibited a (001) reflection having a long basal spacing (1.92 nm) with a sub-phase of 1.52 nm, indicating a segregation of interstratified structures. The (001) profiles were broadened and shifted gradually to larger diffraction angles with increasing heating temperatures for the samples obtained from the solutions of OH/Ga = 1.8 and 2.25. On the other hand, the (001) profile of the long spacing is partly retained at higher temperatures for the complexes prepared from the solution of OH/Ga = 2.0. The appearance of a strong peak around 5.0° (Cu $K_\alpha$) at 600 °C was remarkable. These results suggest that the formation and thermal durability of $Ga_2O_3$-pillared micas having larger basal spacings are affected by the OH/Ga ratio of the solutions and that the appropriate OH/Ga ratio is probably 2.0.

Kloprogge *et al*. reported that the basal spacing of $Ga_2O_3$-pillared montmorillonite prepared from fleshly hydrolyzed Hyd-Ga solution with a OH/Ga ratio of 2.25 decreased from 1.77 nm to 1.23 nm after calcination at 150 °C, collapsing to 0.95 nm at 350 °C [14]. These results indicate that $Ga_2O_3$-pillared micas with high thermal durability can't be synthesized from freshly hydrolyzed Hyd-Ga solutions.

Fig. 2 shows the relation between intercalated Ga content and the OH/Ga ratio of the Hyd-Ga solutions used for the intercalation. The as-prepared solutions were used. The intercalated Ga content increases with increasing the OH/Ga ratio of the solutions. This indicates that the degree of hydrolysis of hydroxogallium species increases with increasing the OH/Ga ratio of

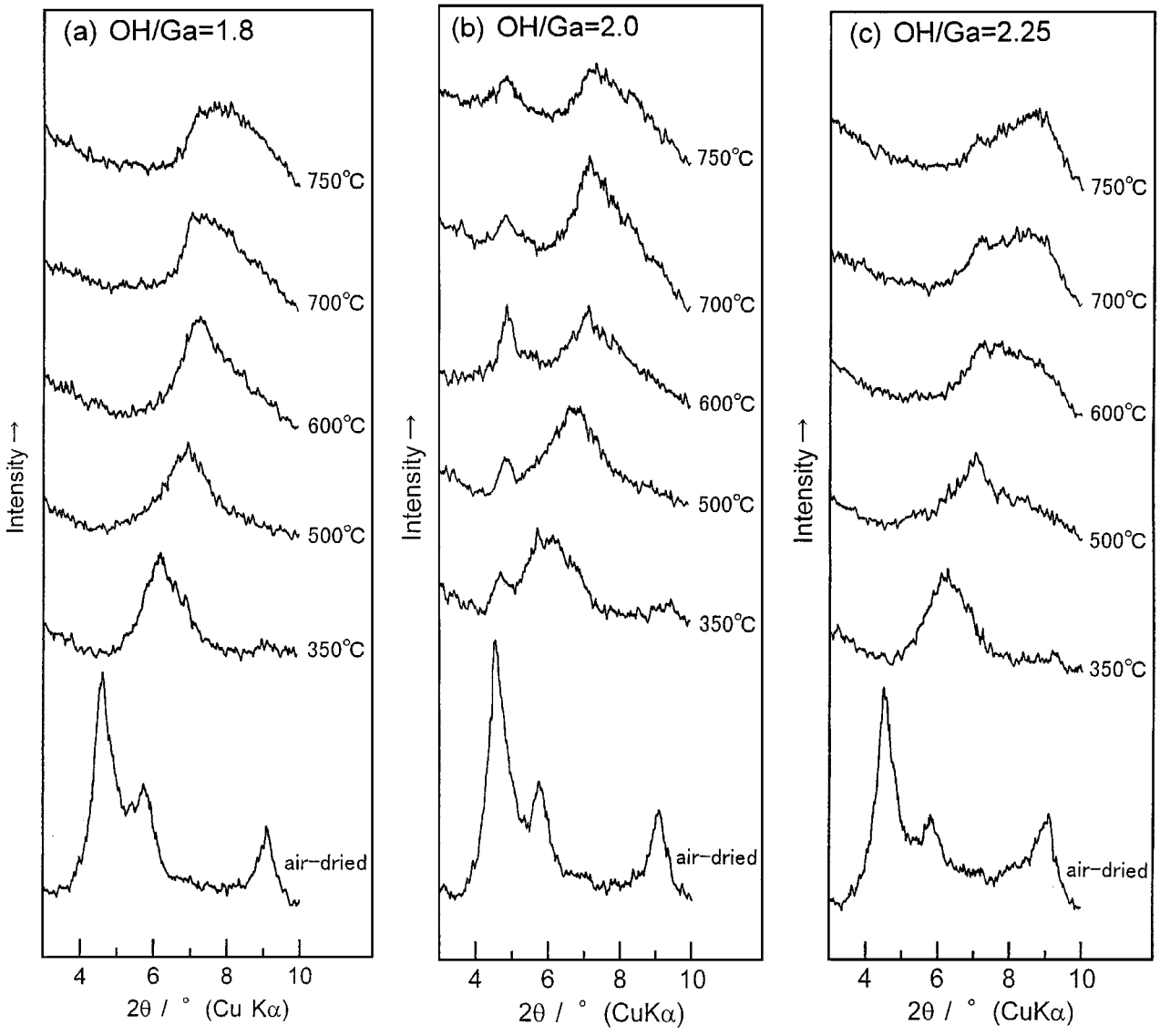


*Figure 1* XRD patterns of $Ga_2O_3$-pillared fluorine micas obtained from the Hyd-Ga solutions (without aging) having the OH/Ga ratios of (a) 1.8, (b) 2.0 and (c) 2.25, when heated at different temperatures.

the solutions. If the intercalated Ga cations were not hydrolyzed, or monomeric $Ga^{3+}$ cations were intercalated, the Ga content of the complex should be 0.5/3 mol $(Si_4O_{10})^{-1}$ at its maximum since the layer charge of the host crystals is 0.5 e $(Si_4O_{10})^{-1}$. Therefore, the $Ga_2O_3$-pillared fluorine micas have the Ga content 3.5–4.9 times as large as the theoretical value of the monomeric Ga ions. It is astonishing that the thermal durability of the pillared micas thus obtained is very low despite of the high contents of the intercalated $Ga_2O_3$. The reason is discussed later.

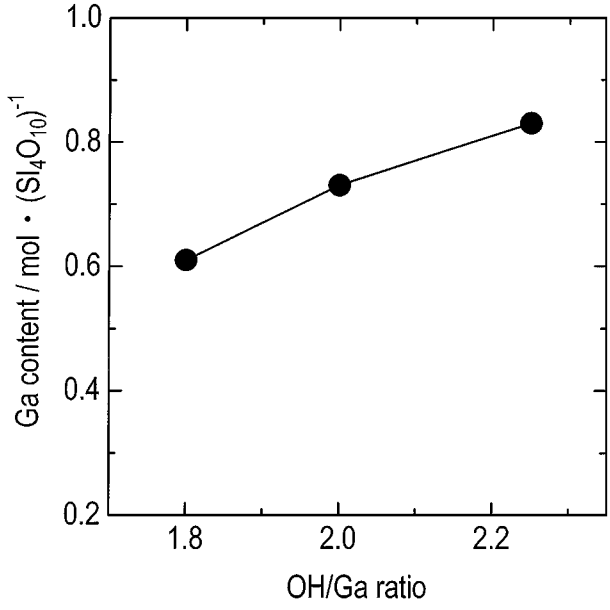


*Figure 2* Intercalated Ga content of $Ga_2O_3$-pillared fluorine micas as a function of the OH/Ga ratio of the Hyd-Ga solutions (without aging).

### 3.2. Effects of the aging of solutions on pillared mica formation

Fig. 3 shows XRD patterns around the (001) profile of the reaction products obtained from the aged Hyd-Ga solutions (OH/Ga = 2.0) having the different aging times at room temperature, when calcined at different temperatures. The samples dried at room temperature exhibited a strong peak at 4.6° (Cu $K_\alpha$) along with a weak peak at 5.7° (Cu $K_\alpha$). The stacking sequences of the pillared micas are again somewhat irregular with segregation of the minor secondary phase having a smaller basal spacing. However, the latter peak, which is ascribable to the (001) profile of a segregated phase, was smaller for the sample obtained from the solution aged for 24 hour than for those obtained from the solutions aged for 12 and 36 hours. When the samples were heated, the sharp (001) diffraction peaks around 5° (Cu $K_\alpha$) were dominant at higher temperatures and

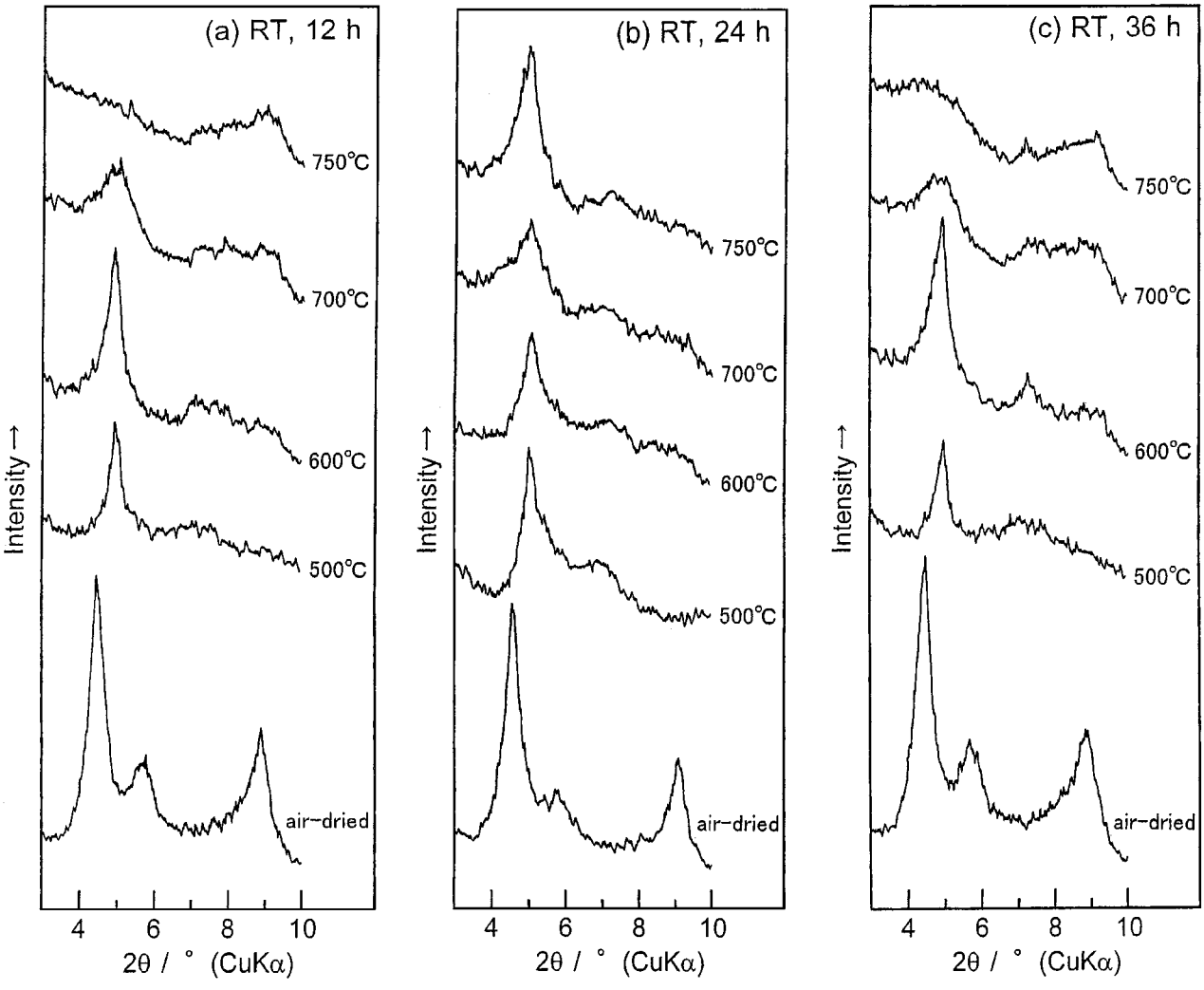


*Figure 3* XRD patterns of $Ga_2O_3$-pillared fluorine micas obtained from the Hyd-Ga solutions aged at room temperature for (a) 12 h, (b) 24 h and (c) 36 h.

did not shift any more at least up to 600 °C, being in contrast to Fig. 1. Moreover, the sample obtained from the solution aged for 24 hours retained the (001) reflection of 5° (Cu $K_\alpha$) even when heated up to 750 °C. Therefore, the formation of pillared mica having nearly regular stacking sequences is a good first approximation. These results indicate that $Ga_2O_3$-pillared fluorine micas having larger basal spacings and higher thermal durability can be synthesized by using the aged Hyd-Ga solutions, especially by using the solution aged for 24 hours. When heating temperature was above 800 °C, the pillared structures collapsed even for the sample obtained from the solution aged for 24 hours.

Using the solutions aged at higher temperatures for prolonged times never led to the formation of the regular-interstratified pillared micas having large basal spacings with high thermal stability. This is probably due to the formation of larger polymers of hydroxogallium ions which are difficult to intercalate into the interlayer regions of mica crystals.

Fig. 4 shows the relation between intercalated Ga content and the aging time of the Hyd-Ga solution (OH/Ga = 2.0) used for the intercalation. The intercalated Ga content tends to increase gradually with increasing the aging time of the solution. The intercalated Ga content of the $Ga_2O_3$-pillared micas obtained from the solution aged for 24 hours was 0.78 mol $(Si_4O_{10})^{-1}$. There was not so significant difference in Ga contents among the samples having the different aging times of more than 12 hours. Therefore, the direct correlation was not found between thermal durability and the Ga content of the pillared micas. This probably indicates that the selectivity and configuration of different hydroxogallium cations in the interlayer regions are predominant factors for determining the thermal durability of $Ga_2O_3$-pillared micas because variable hydrolyzed species of hydroxogallium ions are formed, depending on the OH/Ga ratio, aging conditions and concentration of solutions.

### 3.3. Properties of gallium oxide pillared fluorine micas

Fig. 5 shows the change of the basal spacing with increasing heating temperature for the $Ga_2O_3$-pillared fluorine mica prepared from the solution aged for 24 hours. The sample dried at room temperature gives a basal spacing of 1.92 nm. Thus, the average dimension of intercalated hydroxogallium cations perpendicular to the silicate layer is estimated to be about 0.98 nm, which is calculated by subtracting the thickness of the silicate layer (0.94 nm) from the basal spacing at room temperature. The basal spacing decreases to 1.84 nm at 350 °C, and further decreases to reach the constant value of 1.77 nm at heating temperatures above 500 °C. The decrease is due to the dehydration and dehydroxylation of hydroxogallium cations to form gallium oxides in the interlayer regions of host crystals. The basal spacing reached 0.98 nm when heated at 800 °C, indicating the collapse of the pillared structure.

In our previous study of alumina pillared fluorine micas using the same host micas [3, 4], the basal spacing gradually decrease above 600 °C. The $Ga_2O_3$-pillared micas in the present study, however, retain the constant value of the larger basal spacing between 500–750 °C. This probably indicates that the thermal stability of gallia pillars in the $Ga_2O_3$-pillared micas, if synthesized successfully, is superior to that of alumina pillars in the alumina-pillared micas. On the other hand, the basal spacing of the $Ga_2O_3$-pillared montmorillonite [13] was reported to decrease gradually with increasing heating temperatures up to 600 °C and to fall below 1.6 nm at 700 °C. This difference in the thermal durability is ascribable to the difference of host crystals; i. e. host fluorine micas are thermally more stable and better in crystallinity than natural smectites.

It is reported that there are highly polymerized species of Keggin $Al_{13}$ cations in concentrated hydroxoaluminum solutions [3, 4]. High performance

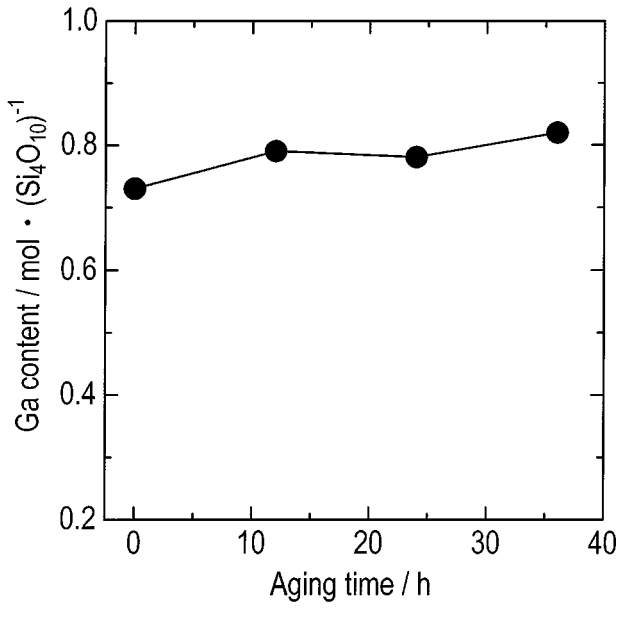


*Figure 4* Intercalated Ga content of $Ga_2O_3$-pillared fluorine micas as a function of the aging time of the Hyd-Ga solution.

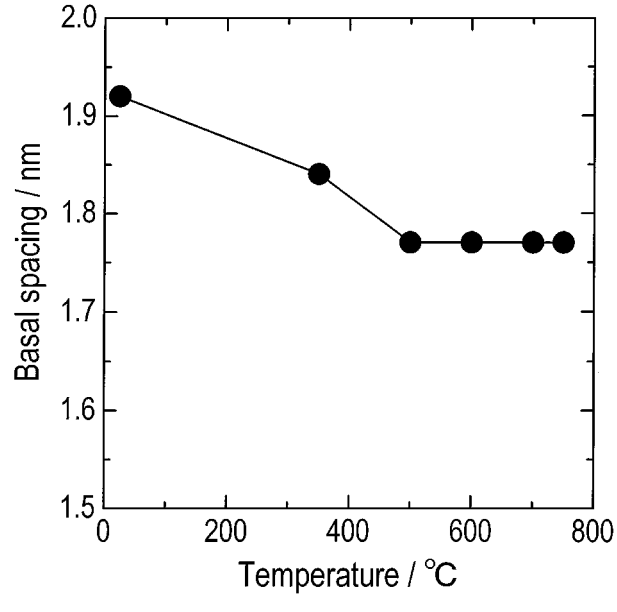


*Figure 5* Basal spacing of the $Ga_2O_3$-pillared fluorine mica plotted against heating temperature. The Hyd-Ga solution used: OH/Ga = 2.0, aged at room temperature for 24 h.

liquid chromatography (HPLC) is a powerful tool for estimating the chemical species in hydroxoaluminum and hydroxochromium solutions, showing variable species having different degrees of hydrolysis and polymerization [3–6]. It is also reported that the $Ga_{13}$ species ($GaO_4Ga_{12}(OH)_{24}(H_2O)_{12}^{7+}$) is much less stable in solution than the analogous $Al_{13}$ species ($AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$) [11, 13]. The hydrolyzed species and their amounts in the Hyd-Ga solutions should vary with the OH/Ga ratio, aging conditions and Ga concentration although a little information was obtainable from HPLC analysis of Hyd-Ga solutions up to now. Selectivity of the species for intercalation is also determined by solution loadings per gram of host crystals [12] and the nature of host crystals, such as layer charge and the site of substitution. All these factors explain the reason why there are optimum conditions for the intercalation of hydroxogallium cations with fluorine micas.

Fig. 6 shows the relationship between the specific surface area (Langmuir) and heating temperature for the $Ga_2O_3$ pillared fluorine micas obtained from the solution aged at room temperature for 24 hours and the as-prepared solution. The pillared micas obtained from the aged solution have larger specific surface areas than those obtained from the as-prepared solution. The specific surface areas of the pillared micas obtained from the aged solution were above 100 $m^2\,g^{-1}$ in the heating temperature range between 600 and 750 °C while those obtained from the as- prepared solution were ca. 30 $m^2\,g^{-1}$ in the same temperature range. The unusual decrease in the specific surface areas was recognized at 500 °C in each sample. The maximum surface area, 120 $m^2\,g^{-1}$, was obtained at 700 °C for the pillared micas obtained from the aged solution. On the other hand, the specific surface areas of the $Ga_2O_3$-pillared micas obtained from the solutions which were aged for 12 and 36 hours were 21.3 and 34.4 $m^2\,g^{-1}$, respectively, when heated at 700 °C. Fig. 7 shows the micropore area of the products plotted against heating temperature. The samples are the same as in Fig. 6. The micropore area was obtained from the *t*-analysis [15]. The pillared micas obtained from the aged solution have larger micropore areas than those obtained from the as-prepared solution. This agrees well with the results of Fig. 6.

The relatively small specific surface areas of $Ga_2O_3$-pillared micas, compared with those of pillared clays obtained from natural clays, are due to the stuffed interlayer oxide pillars resulted from the higher layer charge of host crystals as well as larger host crystals with the maximum dimension of 75 $\mu$m.

Fig. 8 shows the pore size distribution curve of the $Ga_2O_3$-pillared fluorine mica obtained from the aged solution of 24 hours, when heated at 600 °C. The sample gave a sharp peak corresponding to a pore diameter of 4.0 nm. The pore of 4.0 nm is ascribable to the so-called slit pores which originate from the regularly interstratified structure of pillared micas. These sorts of

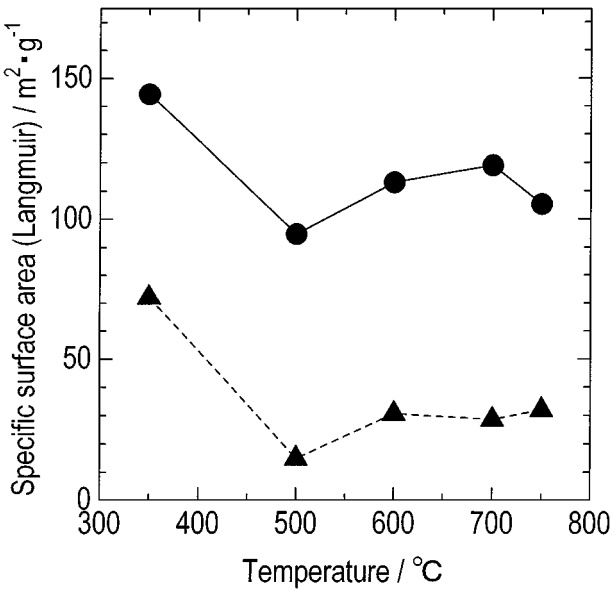


*Figure 6* The relationship between specific surface area and heating temperature for $Ga_2O_3$ pillared fluorine micas prepared from the Hyd-Ga solution having the OH/Ga ratio of 2.0. ●: obtained from the solution aged at room temperature for 24 h, ▲: obtained from the freshly hydrolyzed solution.

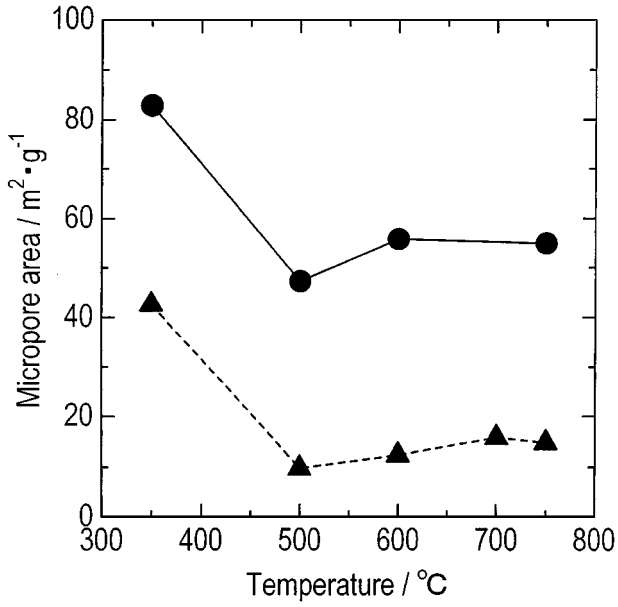


*Figure 7* The relationship between micropore area and heating temperature for $Ga_2O_3$ pillared fluorine micas prepared from the Hyd-Ga solution having the OH/Ga ratio of 2.0. ●: obtained from the solution aged at room temperature for 24 h, ▲: obtained from the freshly hydrolyzed solution.

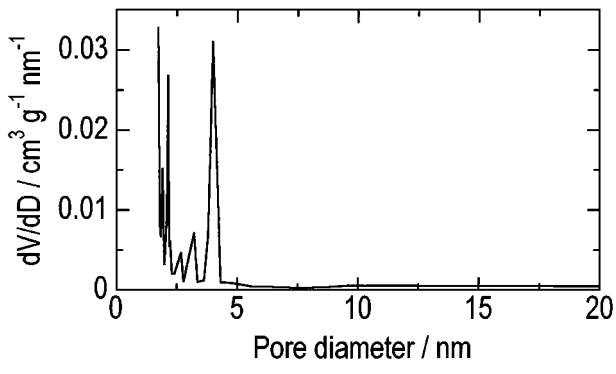


*Figure 8* Pore size distribution curve of the $Ga_2O_3$ pillared fluorine mica heated at 600 °C. The Hyd-Ga solution used: OH/Ga = 2.0, aged at room temperature for 24 h.

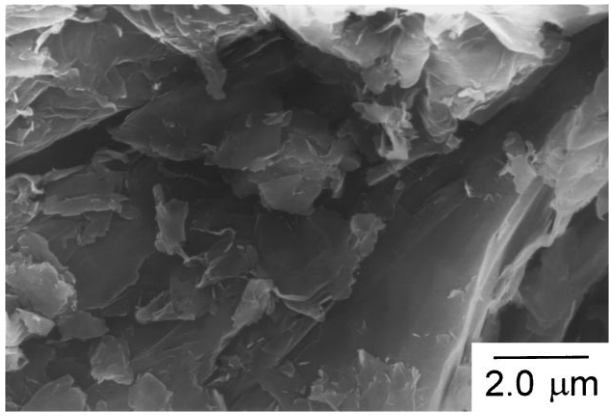


*Figure 9* SEM photograph of the $Ga_2O_3$ pillared fluorine mica heated at 600 °C. The Hyd-Ga solution used: OH/Ga = 2.0, aged at room temperature for 24 h.

pores have also been found in alumina- [4], chromia- [5, 6] and titania-pillared fluorine micas [7, 8]. A shoulder which appears at the smaller diameter sides below 2 nm is observed, illustrating the existence of micropores. This corresponds to the results of Fig. 7.

Fig. 9 shows a SEM photograph of the $Ga_2O_3$-pillared fluorine mica obtained from the aged solution, when heated at 600 °C. The $Ga_2O_3$-pillarerd fluorine micas are featured by their larger flakes with high crystallinity, however, the surface of which are sometimes covered with smaller delaminated platelets.

## 4. Conclusion

Synthesis of gallium oxide pillared fluorine micas has been undertaken by using hydroxogallium solutions having different OH/Ga ratios and aging conditions as pillaring agents in order to clarify the effects of an OH/Ga ratio and aging conditions of the hydroxogallium solutions on formation and thermal durability of $Ga_2O_3$-pillared fluorine micas and to obtain the $Ga_2O_3$-pillared micas with high thermal durability. The results are summarized as follows.

1. Thermal durability and microporous characteristics of gallium oxide-pillared fluorine micas depend on the OH/Ga ratio and the aging conditions of hydroxogallium solutions used for complex formation.

2. The gallium oxide pillared fluorine micas obtained from aged hydroxogallium solutions have larger basal spacings and higher specific surface areas than those obtained from freshly prepared hydroxogallium solutions.

3. Although there was not so significant difference in Ga contents among the pillared micas obtained from the solutions having different aging times, the most appropriate solution for pillaring had the OH/Ga ratio of 2.0 and the aging time of 24 hours at room temperature.

4. The gallium oxide-pillared fluorine mica thus obtained retained the large basal spacing of 1.77 nm in the temperature range between 500 and 750 °C, showing the highest thermal durability.

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