*Thermochimica Acta*, 53 (1982) 281–288
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

# THERMAL DECOMPOSITION OF GALLIUM HYDROXIDES

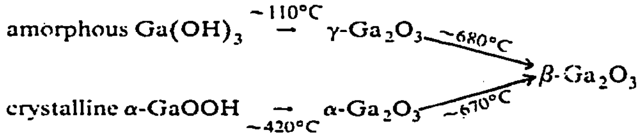
TAICHI SATO and TAKATO NAKAMURA

*Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu (Japan)*

(Received 10 August 1981)

## ABSTRACT

The thermal decomposition of gallium hydroxides [amorphous $Ga(OH)_3$ and crystalline $\alpha$-GaOOH] prepared from aqueous gallium chloride solution by addition of alkali at various values of pH, has been studied by thermal analyses (thermogravimetry and differential thermal analysis), X-ray diffraction and IR spectrophotometry. From the results obtained, it is concluded that gallium hydroxides decompose thermally according to



$$\begin{tikzcd}
\text{amorphous Ga(OH)}_3 \arrow[r, "\sim 110^\circ C"] & \gamma\text{-Ga}_2\text{O}_3 \arrow[dr, "\sim 680^\circ C"] & \\
& & \beta\text{-Ga}_2\text{O}_3 \\
\text{crystalline } \alpha\text{-GaOOH} \arrow[r, "\sim 420^\circ C"'] & \alpha\text{-Ga}_2\text{O}_3 \arrow[ur, "\sim 670^\circ C"'] &
\end{tikzcd}$$

## INTRODUCTION

A crystalline hydroxide, $\alpha$-gallium oxyhydroxide with a diaspore structure, and some oxides are known for gallium which, like aluminium, are amphoteric [1,2]. However, since there have been few investigations on the thermal decomposition of gallium hydroxide by means of thermal analysis, the present study considers the thermal transformation of amorphous and crystalline gallium hydroxides.

## EXPERIMENTAL

Aqueous gallium chloride solution was prepared by dissolving gallium metal (99.9999%, Swiss Aluminium Ltd., Switzerland) in concentrated hydrochloric acid and dilution with deionized water to a selected concentration. Other chemicals were of analytical reagent grade.

Precipitates were obtained from an 0.5 M aqueous solution of gallium chloride in 0.9 M hydrochloric acid at various values of pH by the addition of 3 N sodium hydroxide solution at a rate of 5 ml min$^{-1}$ at 20°C and were aged in the mother liquors for a given period of time. Examination of the precipitates showed that gallium hydroxide exists in two amorphous forms, $Ga(OH)_3$ and a crystalline form, α-GaOOH, as illustrated in Table 1. On the basis of this result, when the precipitates were prepared at pH 8 by the addition of 3 N sodium hydroxide at 20, 50 and 80°C, it was found that their crystallization was enhanced by raising the temperature and the TG and DTA curves of the crystalline precipitate prepared at the higher temperature indicated the decrease in combined water. Consequently, the following gallium hydroxides were used as samples: the amorphous precipitate, separated immediately from the mother liquor after preparation at pH 8 by the addition of 3 N sodium hydroxide at 30°C, and the crystalline precipitate, prepared at pH 8 by the addition of 3 N sodium hydroxide and aged for 6 h at 80°C. They were centrifuged, washed with distilled water until as free as possible from alkali and anion, and then dried with acetone. The gallium concentration in the aqueous solution was determined by EDTA titration using Xylenol Orange [3]. The thermally decomposed products were prepared by maintaining the samples at the stated temperatures for 2 h after heating to this temperature at a rate of 5°C min$^{-1}$.

The materials so obtained were examined by thermogravimetry (TG) and differential thermal analysis (DTA), X-ray diffraction and IR spectrophotometry according to the procedures described previously [4–6]. TG and DTA were carried out on an automatic recording thermobalance and DTA apparatus (made by the Agne Research Center) using 100 mg of specimen at a heating rate of 5°C min$^{-1}$ [4–6]. X-Ray powder diffraction diagrams were obtained on a Rigaku Denki diffractometer [4]. Infrared spectra at 4000–650 cm$^{-1}$ and 700–200 cm$^{-1}$ were determined as a KBr disk and/or a capillary film between thallium halide plates or polyethylene on Japan Spectroscopic Co. Ltd. Model IRA-1 and IR-F double beam grating spectrophotometers, respectively.

## RESULTS AND DISCUSSION

The TG and DTA curves for amorphous and crystalline specimens are shown in Fig. 1. The molar ratio $[H_2O]/[Ga_2O_3]$ determined by the loss in weight for the TG curve is given in Table 2. Figures 2–4 and Table 3 give the IR and X-ray results for the gallium hydroxide specimens and their thermally decomposed products, but only

TABLE 1

Crystallographic composition of the precipitates prepared at various values of pH and by ageing in mother liquors for a period of time

| Ageing time (days) | Crystallographic composition [a] | | | | |
|---|---|---|---|---|---|
| | pH 6 | pH 7 | pH 8 | pH 9 | pH 10 |
| 0 | A | A | A | A | A |
| 1 | A, α | A, α | A, (α) | A, (α) | A, (α) |
| 3 | A, α | α, A | α | α | α, A |
| 7 | A, α | α, (A) | α | α | α, A |

[a] A and α represent amorphous gallium hydroxide and α-gallium oxyhydroxide, respectively.

the representative X-ray diffraction diagrams and IR spectra for the materials derived from the specimens heated at various temperatures are shown.

The results of the thermal analyses (Fig. 1 and Table 2) suggest that the thermal decomposition behaviour of gallium hydroxide precipitates occurs in two ways: the DTA curve of amorphous gallium hydroxide, $Ga(OH)_3$, exhibits a broad endothermic reaction at ~ 110°C and an exothermic reaction at ~ 680°C, and that of the crystalline gallium hydroxide, $\alpha$-GaOOH, exhibits a weak broad endotherm at 200–300°C, an endothermic peak at ~ 420°C and an exothermic reaction at

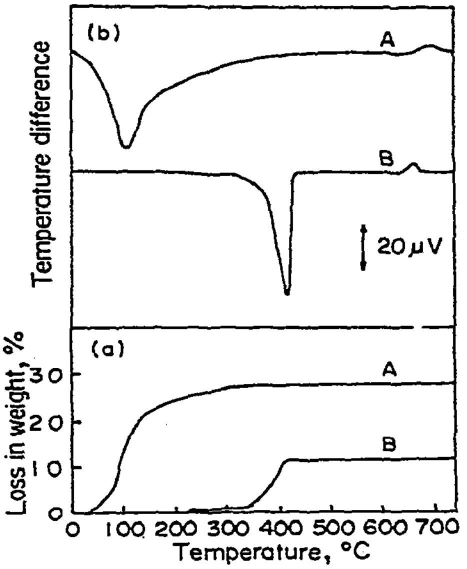


Fig. 1. (a) TG and (b) DTA curves of gallium hydroxides. A and B represent amorphous $Ga(OH)_3$ and $\alpha$-GaOOH, respectively.

TABLE 2

Molar ratio $[H_2O]/[Ga_2O_3]$ of gallium hydroxides heated at various temperatures

| Temp. (°C) | Molar ratio $[H_2O]/[Ga_2O_3]$ | |
|---|---|---|
| | A [a] | $\alpha$ [a] |
| Room temp. | 4.07 | 1.29 |
| 100 | 2.16 | 1.29 |
| 200 | 0.57 | 1.29 |
| 300 | 0.30 | 1.19 |
| 400 | 0.09 | 1.11 |
| 420 | 0.08 | 0.05 |
| 500 | 0.06 | 0.02 |
| 600 | 0.04 | 0.01 |
| 700 | 0.02 | 0 |

[a] A and $\alpha$ represent amorphous gallium hydroxide and $\alpha$-gallium oxyhydroxide, respectively.

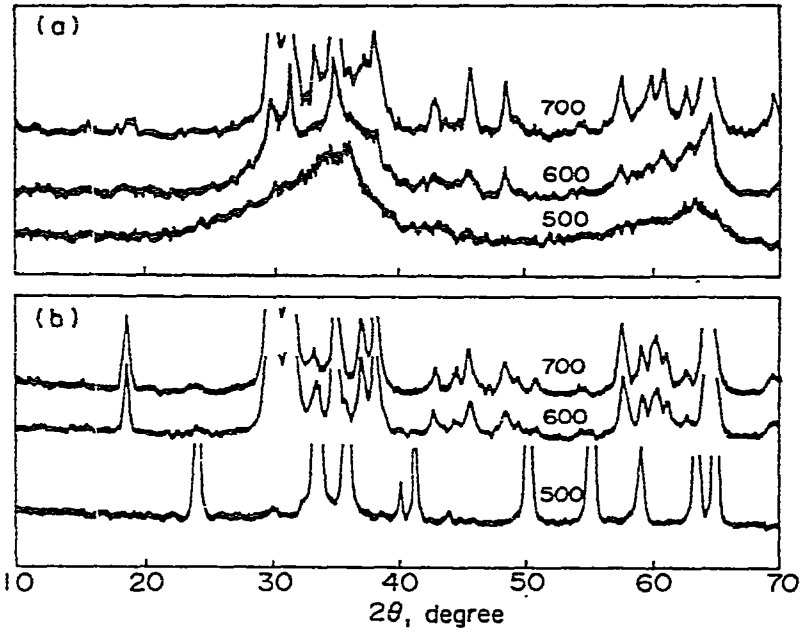


Fig. 2. X-Ray diffraction diagrams for the materials derived from gallium hydroxides heated at various temperatures. The numerals on the curves represent the heating temperatures (°C) of (a) amorphous $Ga(OH)_3$ and (b) α-GaOOH.

~670°C. In both the hydroxides, the respective endothermic reactions show the corresponding weight loss in the TG curve, while the exothermic reactions are not accompanied by the loss in weight. Accordingly, it is presumed that the endotherms arise from dehydroxylation during the thermal decomposition of gallium hydroxides

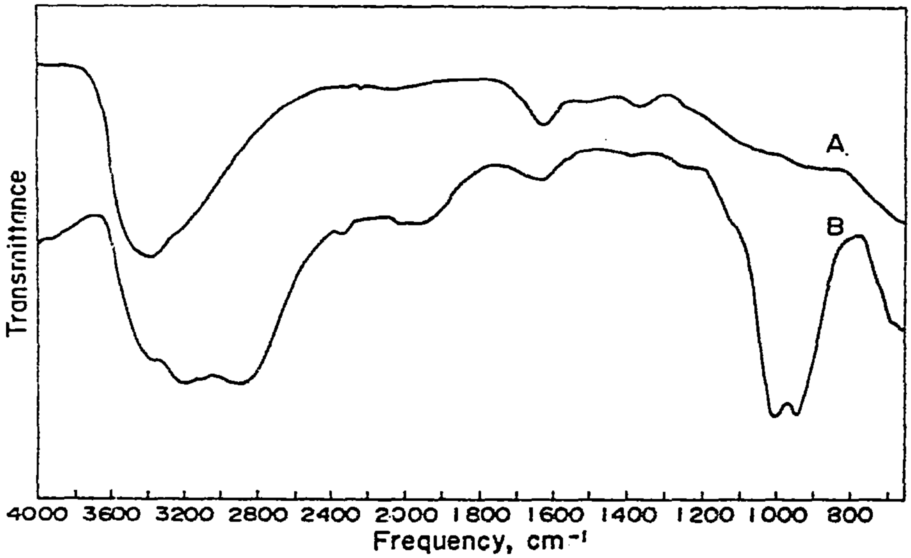


Fig. 3. IR spectra for gallium hydroxides. A and B represent amorphous $Ga(OH)_3$ and α-GaOOH, respectively.

to anhydrous gallium oxide and the exotherms are attributed to thermal transformation of the oxide at higher temperatures.

In the X-ray diffraction results (Table 3 and Fig. 2), the material derived from the

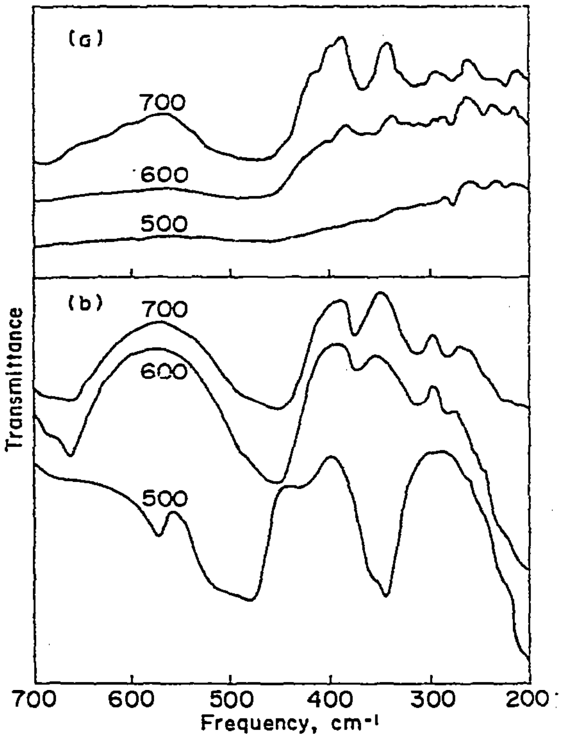


Fig. 4. IR spectra in the lower frequency region for the materials derived from gallium hydroxides heated at various temperatures. The numerals on the curves represent the heating temperatures (°C) of (a) amorphous Ga(OH)$_3$ and (b) α-GaOOH.

TABLE 3

X-Ray diffraction results for the products derived from gallium hydroxides heated at various temperatures

| Temperature (°C) | Phase detected [a] | |
|---|---|---|
| | Ga(OH)$_3$ | α-GaOOH |
| 100 | γ | α-GaOOH |
| 200 | γ | α-GaOOH |
| 300 | γ | α-GaOOH |
| 400 | γ | α |
| 500 | γ | α |
| 600 | γ+β | β+α |
| 700 | β | β |
| 800 | β | β |

[a] α, β and γ indicate α-, β- and γ-Ga$_2$C$_3$, respectively: γ+β and β+α denote a mixture of the respective Ga$_2$O$_3$.

amorphous specimen by heating at 100°C gives the characteristic pattern of γ-gallium oxide. The material obtained from α-gallium oxyhydroxide by heating at 450°C gave the α-gallium oxide pattern, and by heating at 700°C, their products revealed the same β-gallium oxide pattern. It is seen that the amorphous specimen is thermally transformed to stable β-gallium oxide via γ-gallium oxide, but the crystalline precipitate forms via the α-form. These facts correspond to the IR spectral results, i.e. a distinct difference is observed between the spectra of the materials heated at 500 and 600°C, athough each band is not always easily assigned because of the contained lattice vibration (Fig. 4). According to Roy et al. [2], amorphous gels decompose to the α-form by heating at 500°C for 12 h. However, X-ray diffraction patterns for the materials heated at 400, 500 and 550°C for 24 h show the γ-form and never the α-form. In addition, it is observed that the product prepared hydrothermally from the amorphous precipitate and γ-gallium oxide at 280°C for 2 h is α-gallium oxyhydroxide. It is thus considered that the amorphous hydroxide has a structure similar to γ-gallium oxide and the lattice structure is maintained during dehydration. When the crystalline specimen is heated at below 300°C, the diffraction lines arising from α-gallium oxyhydroxide shift to a higher angle with increasing temperature, as given in Table 4. This tendency perhaps implies that the crystal lattice in the precipitate is swollen by non-stoichiometric water, as shown in Table 2.

The IR spectrum of α-gallium oxyhydroxide (Fig. 3), however, shows the absorption bands at 3380 and 1620 $cm^{-1}$ due to the OH stretching and bending modes of $H_2O$, respectively, the OH stretching bands at 3200 and 2850 $cm^{-1}$, the Ga–OH bending bands at 1010 and 950 $cm^{-1}$ and their overtones at 2040 and 1940 $cm^{-1}$ [7,8]. On heating below 300°C, the IR spectra reveal the following changes with increasing temperature: the intensities of the OH stretching band at 3380 $cm^{-1}$ and the OH bending band at 1620 $cm^{-1}$ decrease; the OH stretching band at 2850 $cm^{-1}$ is split into two bands at 2900 and 2810 $cm^{-1}$; the Ga–OH bending band at 1010 $cm^{-1}$ shifts to the higher frequency of 1020 $cm^{-1}$. In addition, all the bands in the range 4000–700 $cm^{-1}$ disappear above 400°C. These changes indicate that the OH stretching band at 3380 $cm^{-1}$ is due to free water and that the OH stretching bands at 2900 and 2810 $cm^{-1}$ arise from Ga–OH vibration. In contrast, the IR spectrum of amorphous gallium hydroxide (Fig. 3) exhibits the OH stretching band at 3400 $cm^{-1}$ and the OH bending band at 1610 $cm^{-1}$. These absorption bands decrease in intensity with increasing temperature. Therefore the following interpretation may be given for the endotherms of the DTA curves: for the amorphous precipitate, the endothermic reaction is due to the transformation of γ-gallium oxide accompanied by the release of combined water; for the crystalline precipitate, the first endotherm is due to the release of water fixed in the α-gallium oxyhydroxide lattice and the second one is due to the dehydration of α-gallium oxyhydroxide to α-gallium oxide. In addition, the exotherm of the DTA curve for the amorphous precipitate may be explained as the rearrangement of the crystal lattice due to the transformation from the γ-form to the β-form and for the crystalline specimen, to the transformation

TABLE 4

X-Ray diffraction data for α-gallium oxyhydroxide and its products heated at various temperatures

| α-GaOOH | | 100 [a] | | 200 [a] | | 300 [a] | | I [b] | | II [c] | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $d$ (A) | $I/I_0$ | $d$ (A) | $I/I_0$ | $d$ (A) | $I/I_0$ | $d$ (A) | $I/I_0$ | $d$(A) | $I/I_0$ | $d$ (A) | $I/I_0$ |
| 4.929 | 6 | 4.929 | 7 | 4.929 | 8 | 4.902 | 8 | 4.906 | 5 | 4.891 | w |
| 4.611 | 1 | 4.611 | 1 | 4.576 | 2 | 4.576 | 2 | 4.580 | 2 | | |
| 4.172 | 100 | 4.172 | 100 | 4.153 | 100 | 4.134 | 100 | 4.134 | 100 | 4.094 | vs |
| 3.351 | 9 | 3.351 | 9 | 3.351 | 10 | 3.327 | 15 | 3.34 | 10 | 3.316 | m |
| | | | | | | | | | | 2.966 | vw |
| 2.667 | 31 | 2.667 | 30 | 2.660 | 34 | 2.652 | 42 | 2.659 | 35 | 2.639 | vs |
| 2.550 | 12 | 2.550 | 14 | 2.550 | 15 | 2.546 | 15 | 2.543 | 12 | 2.536 | s |
| 2.502 | 3 | 2.502 | 3 | 2.495 | 4 | 2.488 | 5 | 2.49 | 1 | 2.479 | m |
| 2.449 | 13 | 2.449 | 14 | 2.455 | 16 | 2.449 | 18 | 2.45 | 3 | 2.444 | m |
| 2.417 | 40 | 2.417 | 43 | 2.417 | 40 | 2.417 | 47 | 2.414 | 40 | 2.404 | vs |
| 2.287 | 3 | 2.281 | 3 | 2.271 | 3 | 2.260 | 6 | 2.286 | 4 | 2.255 | w |
| 2.217 | 7 | 2.217 | 6 | 2.214 | 5 | 2.207 | 5 | 2.214 | 8 | 2.210 | w |
| | | | | | | | | | | 2.193 | w |
| 2.166 | 10 | 2.166 | 10 | 2.161 | 11 | 2.156 | 11 | 2.161 | 11 | 2.149 | m |
| | | | | 2.058 | 1 | 2.049 | 1 | | | | |
| 1.989 | 4 | 1.989 | 3 | 1.981 | 3 | 1.981 | 3 | 1.981 | 4 | 1.973 | w |
| 1.896 | 2 | 1.896 | 3 | 1.896 | 3 | 1.892 | 3 | 1.894 | 2 | 1.886 | w |
| 1.783 | 6 | 1.783 | 6 | 1.778 | 6 | 1.774 | 7 | 1.781 | 8 | 1.767 | m |
| 1.753 | 2 | 1.753 | 2 | 1.749 | 2 | 1.746 | 2 | | | 1.743 | m |
| 1.701 | 19 | 1.701 | 20 | 1.692 | 20 | 1.687 | 24 | 1.697 | 29 | 1.686 | s |
| 1.678 | 6 | 1.678 | 6 | 1.663 | 6 | 1.663 | 9 | 1.671 | 9 | 1.657 | m |
| 1.640 | 1 | 1.640 | 1 | 1.634 | 2 | 1.634 | 2 | 1.640 | vw | 1.629 | w |
| 1.585 | 3 | 1.585 | 3 | 1.578 | 5 | 1.575 | 6 | 1.583 | 4 | 1.573 | m |
| 1.544 | 12 | 1.544 | 12 | 1.542 | 13 | 1.540 | 13 | 1.541 | 12 | 1.536 | s |
| | | | | | | | | | | 1.521 | m |
| | | | | | | | | | | 1.490 | m |
| 1.488 | 6 | 1.488 | 6 | 1.480 | 5 | 1.488 | 6 | 1.486 | 8 | 1.485 | m |
| | | | | | | 1.482 | 5 | | | 1.477 | m |
| 1.457 | 3 | 1.455 | 3 | 1.445 | 3 | 1.439 | 7 | 1.453 | 5 | 1.436 | w |
| 1.435 | 6 | 1.435 | 5 | 1.432 | 5 | 1.433 | 6 | 1.432 | 4 | 1.429 | m |
| 1.401 | 2 | 1.432 | 2 | 1.402 | 2 | 1.401 | 3 | 1.40 | 2 | | |
| 1.381 | 2 | 1.381 | 2 | 1.361 | 2 | 1.370 | 3 | 1.38 | 4 | | |
| 1.358 | 2 | 1.354 | 2 | | | | | | | | |

[a] The products heated at 100, 200 and 300°C, respectively.
[b] ASTM data.
[c] Ref. 9.

from the α-form to the β-form. Hence it is concluded that the thermal decomposition of gallium hydroxide proceeds according to

$$\begin{tikzcd}
\text{amorphous Ga(OH)}_3 \arrow[r, "\sim 110^\circ\text{C}"] & \gamma\text{-Ga}_2\text{O}_3 \arrow[dr, "\sim 680^\circ\text{C}"] & \\
 & & \beta\text{-Ga}_2\text{O}_3 \\
\text{crystalline } \alpha\text{-GaOOH} \arrow[r, "\sim 420^\circ\text{C}"'] & \alpha\text{-Ga}_2\text{O}_3 \arrow[ur, "\sim 670^\circ\text{C}"'] &
\end{tikzcd}$$

## ACKNOWLEDGEMENT

We wish to thank the Research and Development Department, Swiss Aluminium Ltd., Neuhausen a. Rhf., Switzerland, for a gift of gallium metal.

## REFERENCES

1 H.B. Weiser and W.O. Milligan, J. Phys. Chem., 44 (1940) 1081.
2 R. Roy, V.G. Hill and E.F. Osborn, J. Am. Chem., Soc., 74 (1952) 719.
3 J. Kinnunen and B. Wennerstrand, Chemist-Analyst, 46 (1957) 92.
4 T. Sato, T. Yamashita and F. Ozawa, Z. Anorg. Allg. Chem., 370 (1969) 202.
5 T. Sato, F. Ozawa and S. Ikoma, J. Appl. Chem. Biotechnol., 28 (1978) 811.
6 T. Sato, F. Ozawa, T. Nakamura, H. Watanabe and S. Ikoma, Thermochim. Acta, 34 (1979) 211.
7 V.A. Kolesova and Ya.I. Ryskin, Zh. Strukt. Khim., 3 (1962) 680.
8 T. Dupuis, Mikrochim. Acta, (1964) 228.
9 A.N. Christensen, Mater. Res. Bull., 6 (1971) 691.