Thermochimica Acta, 75 (1984) 129–137
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL DECOMPOSITION OF ORGANIC BASIC ALUMINIUM SALTS—FORMATE AND ACETATE

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(Received 10 November 1983)

ABSTRACT

The thermal transformation of anhydrous alumina by the decomposition of the formate and acetate of basic aluminium has been examined by thermal analysis (TG and DTA), infrared spectrophotometry and X-ray diffraction studies. It is found that under an atmosphere of air the organic basic aluminium salts decompose to anhydrous amorphous alumina which transforms to α-alumina via γ-, δ- and θ-aluminas

$$\begin{tikzcd}
Al(OH)(HCOO)_2 \arrow[r] & Al_2O(HCOO)_4 \arrow[r] & AlO(HCOO) \arrow[r] & Al_2O_3(\text{amorphous}) \arrow[r] & \gamma \arrow[r] & \delta \arrow[r] & \theta \arrow[r] & \alpha \\
Al(OH)(CH_3COO)_2 \arrow[r] & Al_2O_3 \cdot xCO_2 \cdot yH_2O \arrow[urr] & & & & & &
\end{tikzcd}$$

INTRODUCTION

The transformation of anhydrous alumina prepared by the thermal decomposition of the hydrates of aluminium chloride, nitrate and sulphate, and ammonium alum into α-alumina has been reported in previous papers [1,2]. In connection with these results, the present study extends the work to the thermal transformation of anhydrous alumina by the decomposition of organic basic aluminium salts.

EXPERIMENTAL

Reagents

The basic aluminium salts such as formate and acetate were used as samples. Basic aluminium acetate was of analytical reagent grade (Koso Chemical Co., Ltd.). Basic aluminium formate was prepared by the reaction between amorphous aluminium hydroxide and formic acid: the white precipitate from the formic acid solution containing aluminium ion on the addition of acetone was filtrated and washed with acetone repeatedly. Both

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0040-6031/84/$03.00

basic aluminium salts were insoluble in water. All chemicals were of analytical reagent grade.

Analysis

Organic basic aluminium salts were examined by thermal analysis (TG and DTA), and the salts and their thermally decomposed products were examined by infrared spectrophotometry and X-ray diffraction as follows: X-ray powder diffraction diagrams were obtained using a Geigerflex recording X-ray diffractometer (Rigaku Denki Co., Ltd.) with filtered copper radiation, generator operating at 30 kV and 15 mA, divergence slits $1^\circ \times 1^\circ$, scanning speed 2 and/or $1/4^\circ$ 2θ min^{-1}, chart speed 1 cm min^{-1}, time constant 2 s, scale factor 16, multiplier constant 1.0; infrared spectra were determined by the Nujol or Fluorube mull and potassium pellet methods on the grating infrared spectrophotometers Model IR-Al and Model IR-F (Japan Spectroscopic Co., Ltd.) for measurements at 4000–650 and 700–200 cm^{-1}, respectively, as a capillary film between thallium halide plates or polyethylene films. The decomposition products were prepared by heating each salt at a state temperature for 2 h under atmospheric pressure, after heating to the required temperature at a rate of 5°C min^{-1}. The TG and DTA were carried out on an automatic recording thermobalance and DTA apparatus, made by the Agne Research Centre, using platinum–platinum/rhodium thermocouples, and a Shinku-Riko Co., Ltd. Model TGD-1500RH-P differential thermobalance, equipped with an infrared heater. The sample (100 mg; for formate 20–55 mg were used) was heated at a rate of 5°C min^{-1} under an air or nitrogen stream at a rate of 50 ml min^{-1}. In DTA at a higher temperature, however, 300–450-mg samples were used for the materials derived from the specimens preheated for 2 h at 700°C. For the measurement of differential thermal electromotive force, α-alumina was used as a reference material.

The aluminium concentration was determined by EDTA titration using Xylenol Orange as indicator [3]. The carbonate ion contained in the thermally decomposed products was examined by passing the gas, evolved on reaction with sulphuric acid, through baryta water. The formate ion content was determined by weighing the mercurous chloride produced on the reduction of mercuric chloride by the formate ion.

RESULTS AND DISCUSSION

Thermal decomposition of organic basic aluminium salts

The TG curve of basic aluminium formate (Fig. 1a), having the stoichiometric composition $\text{Al(OH)(HCOO)}_2 \cdot 0.5\ \text{H}_2\text{O}$, reveals the weight-losses of

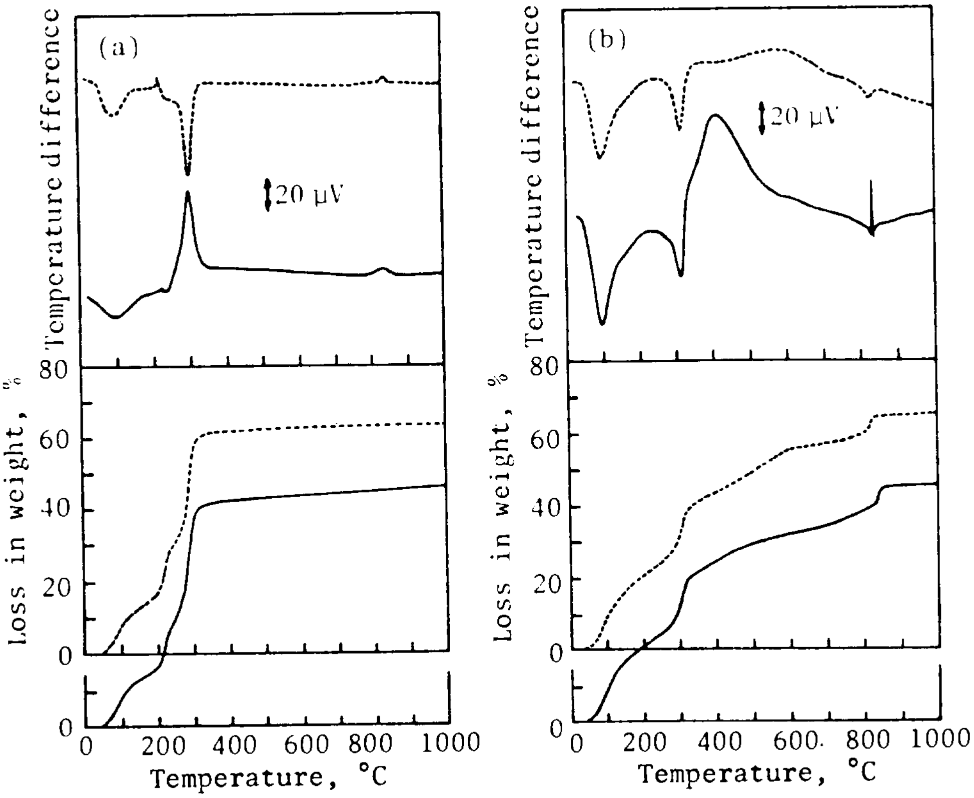

Fig. 1. TG and DTA curves of organic basic aluminium salts (———) air, (- - - - -) nitrogen. (a) Formate, (b) acetate.

about 17, 32 and 62% at 200, 260 and 350°C, respectively, in air. These correspond to the respective calculated losses from $Al(OH)(HCOO)_2$ to $Al_2O(HCOO)_4$, $AlO(HCOO)$ and Al_2O_3 of 12.6, 38.5 and 64.3%. In a nitrogen atmosphere, the TG curve shows that the weight-losses are in good agreement with calculated values. The DTA curve of aluminium formate (Fig. 1a) exhibits a broad endothermic reaction at 50–150°C due to the liberation of a water molecule, the reaction at 300°C arises from its decomposition to alumina and some gaseous products, and the weak exotherm at about 840°C is attributed to the crystallization to alumina. In air, however, the endothermic reaction at 300°C is not observed, but the exothermic one arising from the combustion of the gases appears at the same temperature. Additionally, a weak exotherm is observed at 220°C this is an explosive reaction accompanied by a steep loss in weight. Therefore, when a large amount of sample is used in thermal analysis, the sample powder breaks out of the platinum crucible, suggesting the decomposition of peroxoacid. The infrared spectrum of basic aluminium formate (Fig. 2a) exhibits the broad OH stretching vibration (3600–3000 cm^{-1}), the strong CO stretching bands

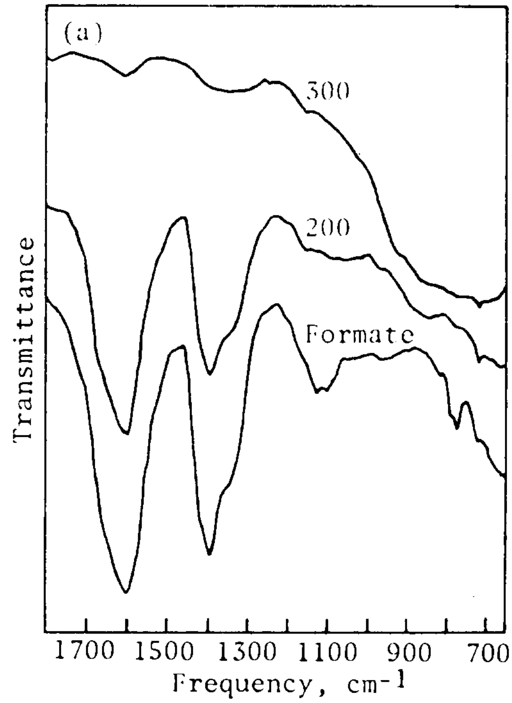

Fig. 2. Infrared spectra of the materials derived from organic basic aluminium salts heated at various temperatures (figures on curves are heating temperatures, °C). (a) Formate.

at 1600 (which superimposes to the OH bending band) and 1390 cm^{-1}, the CH bending frequency (shoulder) at about 1340 cm^{-1}, and the broad OH bending band at 1200–900 cm^{-1}. On heating to 200°C the OH absorptions become weaker, and at 300°C the CO and CH bands almost disappear but the absorption below 1000 cm^{-1} due to the formation of alumina appears.

In an atmosphere of air or nitrogen, the TG curve of basic aluminium acetate (Fig. 1b) shows weight-losses in three steps (at about 40, 20 and 5% at < 320, 320–830 and 840°C, respectively; the final weight-loss is 64.5%, although the calculated value as $\mathrm{Al(OH)(CH_3COO)_2}$ is 68.6%). Thus, the number of the bonded OH moiety of the original basic acetate is expected to be in the region 1.4–1.5. The DTA curve (Fig. 1b) in air gives three endothermic reactions at 100, 310 and 840°C, and two exothermic ones at 420 and 835°C. The endothermic peak at 100°C followed by the weak reaction up to 200°C is due to the release of a part of the OH and the acetate groups, the endothermic reaction at 310°C is attributed to the thermal decomposition of the remaining acetate group, the broad exothermic one centered around 420°C ascribed to the combustion of the decomposed products, and the endothermic one at 840°C due to the dehydroxylation. The exothermic reaction at 835°C, resulting from the crystallization of

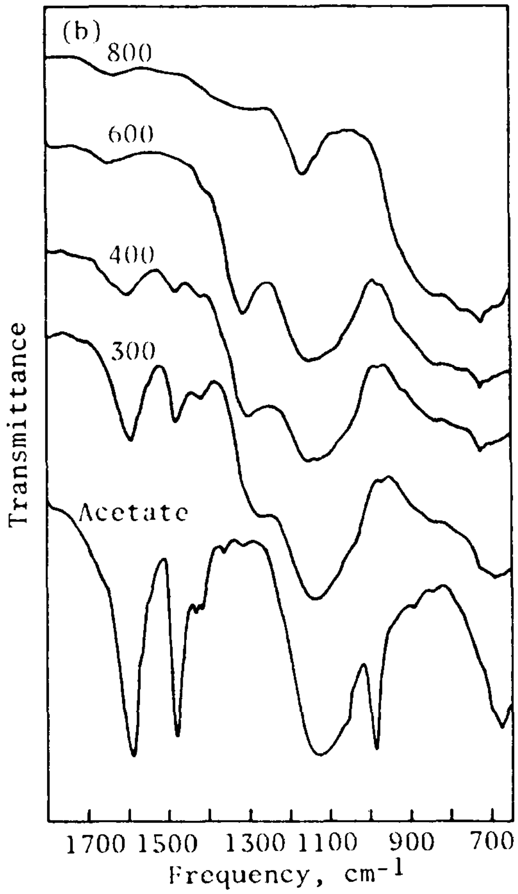

Fig. 2. (b) Acetate.

alumina, is not observed in the DTA curve under nitrogen atmosphere showing the weak endotherm at 350–550°C instead of the exotherm at 420°C in air. The infrared spectrum of basic aluminium acetate (Fig. 2b) reveals the strong CO stretching vibrations at 1590–1480 cm^{-1}, and the CH and OH bending frequencies at 1430 and 1250–950 cm^{-1}, respectively. By heating to 300°C the CO and CH vibrations become weaker because of the thermal decomposition of the acetate group, but the OH bending band still remains. The absorption at 1300 cm^{-1} which appears at 400–600°C indicates the presence of a carbonate group. From the test with baryta water for the products collected by the DTA at 550–650°C in air, it is found that the amount of carbonate group is maximum at about 550°C and decreases with increasing temperature, suggesting the formation of aluminium basic carbonate. In addition, the absorption below 1000 cm^{-1}, due to the formation of alumina, appears on heating at 400°C. But the CO vibration at 1150 cm^{-1} still remains even at 800°C.

Hence, it is concluded that formate and acetate of basic aluminium thermally decompose to anhydrous alumina under an atmosphere of air as follows

$$Al(OH)(HCOO)_2 \rightarrow Al_2O(HCOO)_4 \rightarrow AlO(HCOO) \rightarrow Al_2O_3$$

and

$$Al(OH)(CH_3COO)_2 \rightarrow Al_2O_3 \cdot xCO_2 \cdot yH_2O \rightarrow Al_2O_3$$

in which the transformation of $Al(OH)(CH_3COO)_2$ to $Al_2O_3 \cdot xCO_2 \cdot yH_2O$ proceeds via the dehydroxylation, the decomposition of the skeleton and the combustion of its decomposed products. According to Grigorév et al. [4], however, aluminium triacetate loses acetic anhydride to form basic acetates on composition to $Al_2O(CH_3COO)_4$ or $Al_3O(CH_3COO)_7$ on heating at about 120–140°C; further decomposition to $AlO(CH_3COO)$ occurs at 200°C.

Thermal transformation of anhydrous alumina to α-alumina

X-ray diffraction results for the products derived from organic basic aluminium salts and their respective diagrams are illustrated in Table 1 and Fig. 3, respectively. In comparison with the infrared spectral results (Fig. 2), it is therefore deduced that under an atmosphere of air anhydrous amorphous alumina is formed by the thermal decomposition of the formate and acetate of basic aluminium at 300 and 800°C, respectively, and that the resulting amorphous alumina transforms to α-alumina via γ-, δ- and θ-aluminas. The DTA curves of the formate and acetate of basic aluminium (Fig. 4) exhibit the exothermic reactions due to the crystallization of amorphous alumina to γ-alumina at 820 and 835°C, respectively, and the exothermic ones resulting from the transformation of θ- to α-alumina at 1080 and 1230°C, respectively.

TABLE 1

X-ray diffraction results for the products derived from organic basic aluminium salts heated at various temperatures

Temperature (°C)	Formate	Acetate
700	Am [a]	Am [a]
800	γ	γ
900	γ	γ
950	γ + (δ) [b]	γ
1000	γ + δ + α	γ + δ
1050	α + θ	δ
1100	α	δ + θ + α
1200	α	α

[a] Am = amorphous alumina.

[b] Parentheses indicate a small amount.

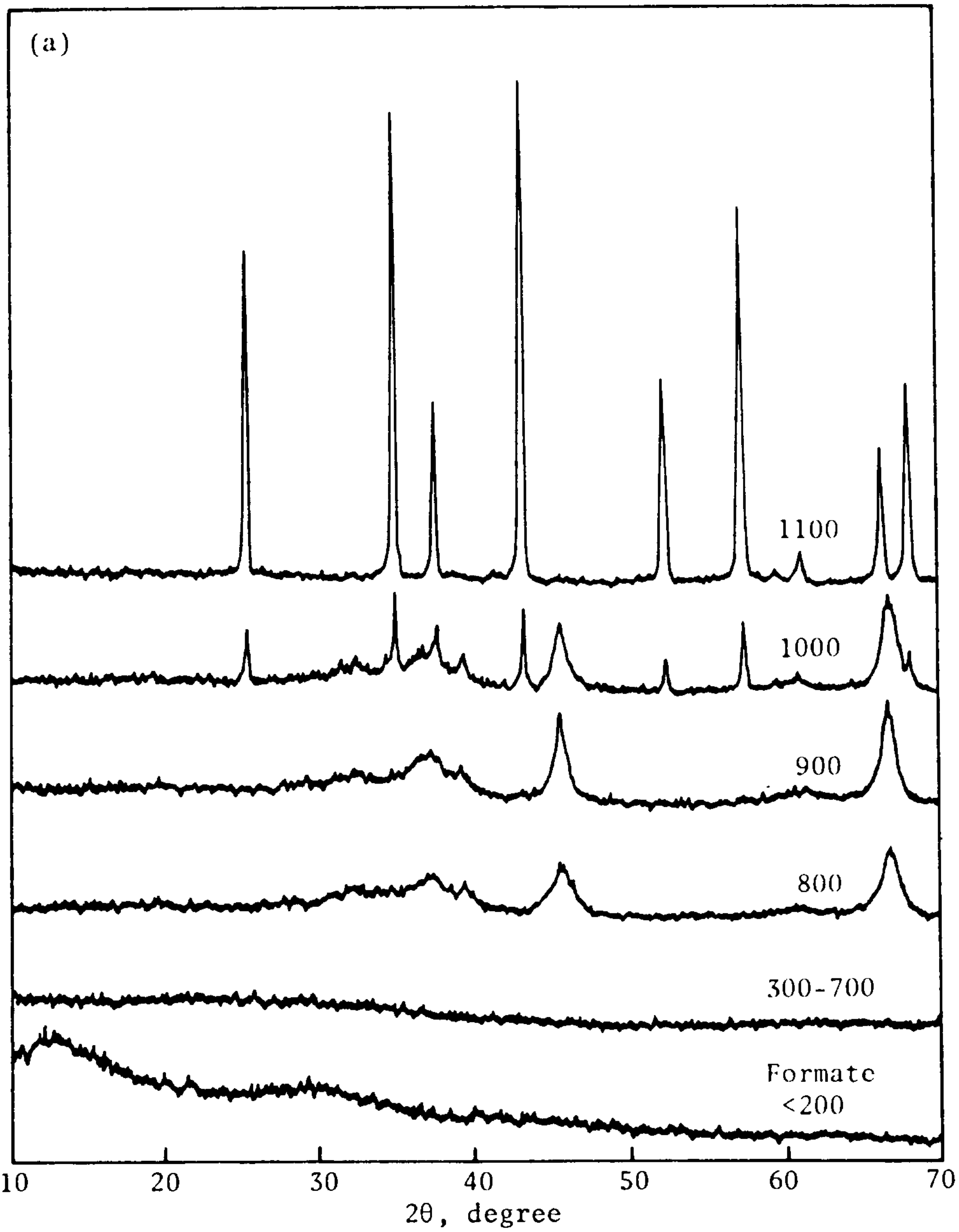

Fig. 3. X-ray diffraction diagrams of the materials derived from organic basic aluminium salts heated at various temperatures (figures on curves are heating temperatures, °C). (a) Formate.

In these processes, it is considered that the reactions ascribed to the transformations from γ- to δ-alumina and from δ- to θ-alumina are masked by those from θ- to α-alumina. According to Dollimore et al. [5], however, the thermal decomposition of aluminium oxalate forms χ-alumina.

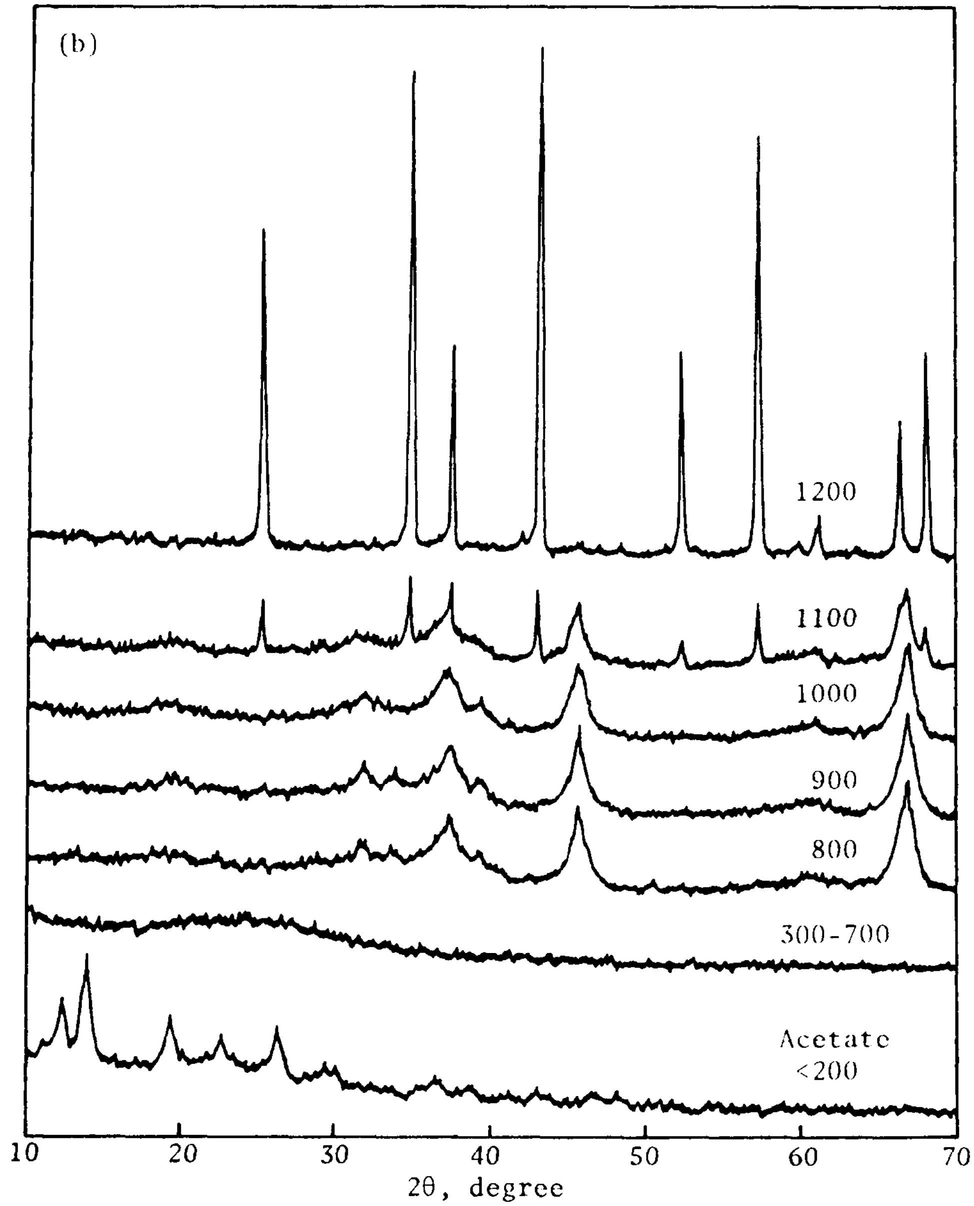

Fig. 3. (b) Acetate.

Consequently it is inferred that the thermal transformation to α-alumina of anhydrous alumina by the thermal decomposition of organic basic aluminium salts proceeds in the sequence $Al(OH)(HCOO)_2$ or $Al(OH)(CH_3COO)_2$ → amorphous alumina → γ-alumina → δ-alumina → θ-alumina → α-alumina. This process consists essentially of the transformation of alumina derived from the hydrates of aluminium chloride, nitrate and sulphate, and alum [1,2].

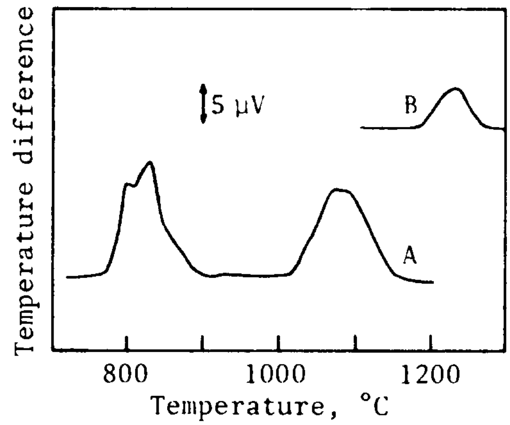

Fig. 4. DTA curves of the materials derived from organic basic aluminium salts preheated at 700°C for 2 h, under an atmosphere of air. (A) Formate, (B) acetate.

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