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The thermal decomposition of aluminum sulfate in different gas phase environments

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Abstract

The thermal decomposition of hydrated aluminum sulfate has been investigated in air and under reducing conditions. The decomposition proceeds, via an intermediate, at a greater rate under reducing conditions than in air.

INTRODUCTION

Thermal decomposition of aluminum sulfate hydrates is one possible way of obtaining high-purity, fine-grained aluminum oxide.

Several authors have reported that aluminum sulfate decomposes to aluminum oxide via intermediate stages [1–3], not directly. Lorant [4] has found that the alumoxane cation (Al_2O^{4+}) in alumoxane sulfate and sulfite is present in the intermediates formed during the thermal decomposition of $Al_2(SO_4)_3 \cdot 18H_2O$. His hypothesis was confirmed by the results of the investigations of Pysiak and Pacewska [5,6].

The aim of the present work is to establish the mechanism of the thermal decomposition of aluminum sulfate in air and in hydrogen atmosphere.

EXPERIMENTAL

The studies were carried out on a MOM derivatograph model Q-1500D using zirconium sample holders (internal diameter 8 mm, height 20 mm). Sample weights were 500 mg. Measurements were made in the range 298–1273 K at two heating rates, 5 and 10 K min^{-1}. The gas flow was 25 l

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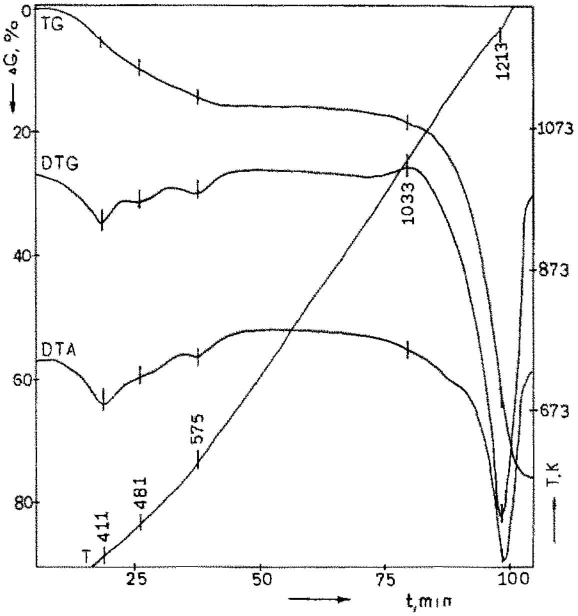

Fig. 1. TG, DTG and DTA curves of $Al_2(SO_4)_3 \cdot xH_2O$: heating rate, 10 K min^{-1}; atmosphere, air; weight of sample, 500 mg.

h^{-1} in air and 20 l h^{-1} in reducing conditions: a mixture of hydrogen (5 vol.%) and argon (95 vol.%) was used as the reducing atmosphere.

The hydrated aluminum sulfate investigated, $Al_2(SO_4)_3 \cdot xH_2O$ c.p. had the following composition (wt.%): main component, 97.106; chlorides, 0.002; ammonium salts, 0.005; heavy metals, 0.001; Fe, 0.003; Ca, 0.007; Na, 0.1; As, 0.0001; and others.

The intermediate and final products of the thermal decomposition of hydrated aluminum sulfate were analyzed by X-ray phase analysis and infrared absorption.

RESULTS

The TG, DTG and DTA curves of the thermal decomposition of $Al_2(SO_4)_3 \cdot xH_2O$ in air at heating rates of 10 and 5 K min^{-1} are presented in Figs. 1 and 2 respectively, and in the reducing environment of the hydrogen (5 vol.%) and argon (95 vol.%) in Fig. 3.

The analysis of the TG, DTG and DTA curves shows that the dissociation of aluminum sulfate proceeds in two stages. The first stage, ending in the region of 603–657 K (Fig. 1), is associated with the dehydration process and the evolution of water of crystallization from the molecule of aluminum sulfate. Comparing the experimental loss in weight (15.6–17.4

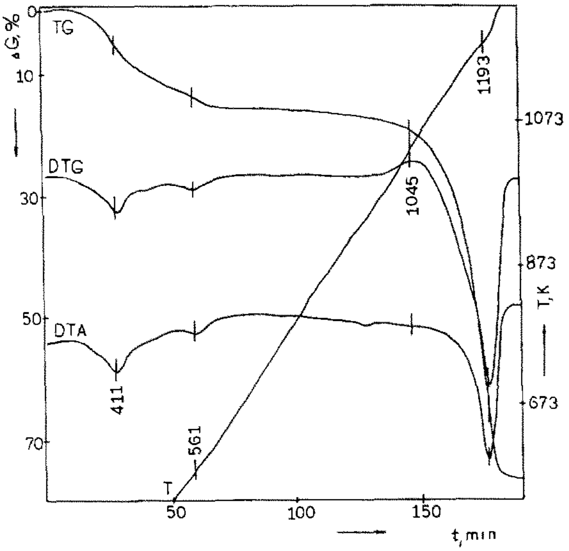

Fig. 2. TG, DTG and DTA curves of $Al_2(SO_4)_3 \cdot xH_2O$: heating rate, 5 K min^{-1}; atmosphere, air; weight of sample, 500 mg.

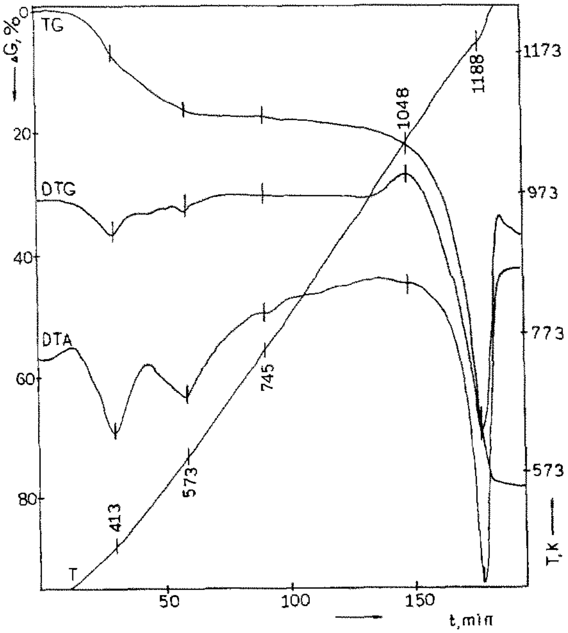

Fig. 3. TG, DTG and DTA curves of $Al_2(SO_4)_3 \cdot xH_2O$: heating rate, 5 K min^{-1}; atmosphere, hydrogen (5 vol.%) and argon (95 vol.%); weight of sample, 500 mg.

wt.%) and the theoretical possibilities, demonstrates that the starting material contains three molecules of water of crystallization. The dehydration of hydrated aluminum sulfate in air at the heating rate 10 K $\min^{-1}$ (Fig. 1) ends at a higher temperature (by about 50 K) than with the heating rate of 5 K $\min^{-1}$ in air (Fig. 2) and in hydrogen atmosphere (Fig. 3).

In the temperature range 603–883 K, one can observe small changes in sample mass. This can be explained by the further slow evolution of crystalline water from the sulfate structure.

In the second stage, at temperatures from 883 to 1263 K, desulfuration of the aluminum sulfate takes place, connected with the intensive endothermic effects on the DTA curves at 1213 K (Fig. 1), 1193 K (Fig. 2) and 1188 K (Fig. 3). During desulfuration in the temperature range 968–1233 K in hydrogen atmosphere at the heating rate of 5 K $\min^{-1}$, the sample loses about 70.2 wt.% of its weight, which indicates complete decomposition of the aluminum sulfate to aluminum oxide.

When performing the experiments in air (Fig. 1) at a heating rate of 10 K $\min^{-1}$, one can observe a weight loss of about 68 wt.%, whereas at 5 K $\min^{-1}$ the weight loss is 68.17 wt.%. This suggests that at the highest heating rate and in the presence of air, the process does not stop at the final experimental temperature of 1273 K. The complete thermal decomposition of aluminum sulfate to 1273 K takes place only in a reducing atmosphere.

The X-ray diffraction data indicate that the final solid product of aluminum sulfate decomposition is a mixture of γ-and ν-Al_2O_3. The low intensity of the XRD peaks shows that much of the material is still amorphous (Fig. 4).

A characteristic property observed for all three thermograms is the presence of maxima on the DTG curves at the following temperatures: 1033 K (Fig. 1), 1045 K (Fig. 2), 1048 K (Fig. 3) and the cut-offs on the TG curves.

From the literature [4–6], it is known that in the same temperature range in air, one can observe the presence of intermediate compounds, such as alumoxane sulfate and sulfite.

To explain these hypotheses, the intermediate solid products of aluminum sulfate decomposition were analyzed by X-ray diffraction analysis and infrared absorption. The results are shown in Figs. 4 and 5.

The infrared spectra of the intermediate products exhibit the bands at 3450 and 1620 cm^{-1} characteristic of the stretching and bending vibrations, respectively, of water. An absorption band at 1170 cm^{-1} indicates a sulfate content in the compound.

The greatest changes in the IR spectrum are observed in the band range 600–700 cm^{-1}. The IR spectrum of aluminum sulfate heated to 1025 K at the heating rate of 2.5 K $\min^{-1}$, compared to the IR spectrum of the starting material, indicates the additional presence of the characteristic

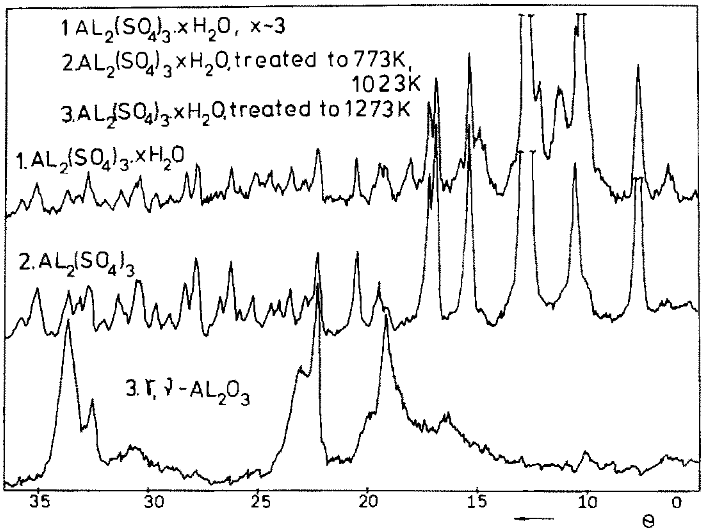

Fig. 4. X-ray diffraction analyses of products of the thermal decompositon of $Al_2(SO_4)_3 \cdot xH_2O$ in air atmosphere.

triplet of absorption bands at 600–700 cm^{-1} (Fig. 5). This may be assigned to the vibrations of the $(Al{-}O{-}Al)^{4+}$ group [5].

Similar IR spectra were obtained for the products of $Al_2(SO_4)_3 \cdot xH_2O$ decomposition in hydrogen atmosphere. When considering the IR results, we can state that $Al_2O(SO_4)_2$ is an intermediate product of the aluminum

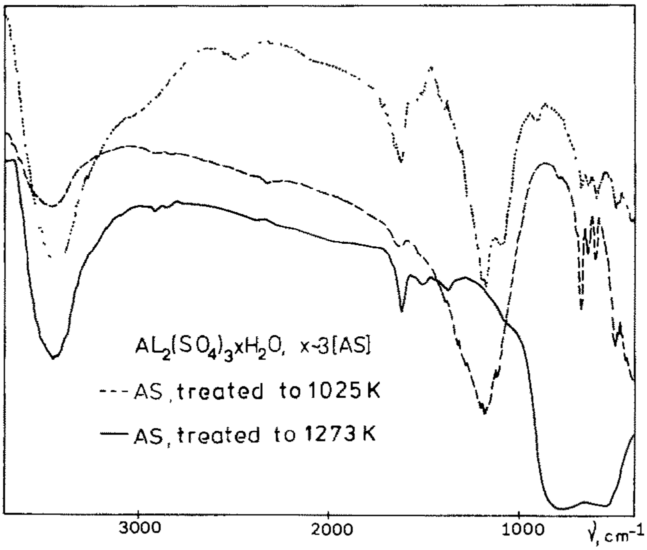

Fig. 5. Infrared spectra of $Al_2(SO_4)_3 \cdot xH_2O$ in air atmosphere.

sulfate decomposition. Therefore, the following mechanism can be proposed:

$$Al_2(SO_4)_3 \rightleftharpoons Al_2O(SO_4)_2 + SO_2 + 0.5O_2 \quad (1)$$

$$Al_2(SO_4)_3 \rightleftharpoons Al_2O_3 + 3SO_2 + 1.5O_2 \quad (2)$$

$$Al_2O(SO_4)_2 \rightleftharpoons Al_2O_3 + 2SO_2 + O_2 \quad (3)$$

The above reactions, which are very dependent on temperature, proceed in parallel.

The formation in the solid phase of $Al_2O(SO_4)_2$, according to reaction (1), and also of SO_2 and O_2 in the gaseous phase, interrupts the course of the main reaction, eqn. (2). Furthermore, this explains the existence of the maximum on the DTG curves (Figs. 1-3).

Contrary to the results obtained by infrared spectroscopy, the X-ray diffraction data do not permit identification of $Al_2O(SO_4)_2$ or other unknown phases in the samples (Fig. 4). One can conclude that the alumoxane sulfate obtained is microcrystalline or amorphous. These results concur with previous observations [5,6]. Pysiak and Pacewska did not identify the intermediate products of the decomposition of basic aluminum sulfate by X-ray diffraction analysis, probably because of insufficiently developed crystalline structures.

CONCLUSIONS

In conclusion, we can state that the thermal decompositon of hydrated aluminum sulfate proceeds at a greater rate in reducing conditions than in air. The contents of reducer in the gaseous phase determine the kinetics, but this is not the result of a change in reaction mechanism. In both air and hydrogen atmosphere, the intermediate product of hydrated aluminum sulfate decomposition is $Al_2O(SO_4)_2$.

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