

Investigations of thermal decomposition of aluminium sulphate by the emf method

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Abstract

An investigation of the thermal decomposition of aluminium sulphate in an atmosphere of argon containing 1 vol% of hydrogen was carried out by the emf method. The results indicate that the decomposition is a multistep process in which $\text{Al}_2\text{O}(\text{SO}_4)_2$ is formed as an intermediate product. The IR spectra of the decomposition products confirm the findings.

INTRODUCTION

In previous work [1,2] it has been found that aluminium oxysulphate is an intermediate product of the thermal decomposition of hydrated aluminium sulphate in different gaseous environments. Pysiak et al. showed that the thermal decomposition of basic aluminium sulphates proceeds in several stages; moreover, $\text{Al}_2\text{O}(\text{SO}_3)_2$ and $\text{Al}_2\text{O}(\text{SO}_4)_2$ were formed as intermediate products [3,4].

The purpose of this work was to investigate the thermal decomposition mechanism of aluminium sulphate by the emf method in a reducing atmosphere.

EXPERIMENTAL

The investigations were carried out using the laboratory device shown in Fig. 1. This apparatus contains two electric furnaces. One of them is used to heat the samples at given temperatures, and the second to determine the partial pressure of oxygen in the gaseous phase from the first furnace. Measurements were performed by the emf method using zirconia solid electrolyte stabilized by CaO and Y_2O_3 . The furnace with the solid elec-

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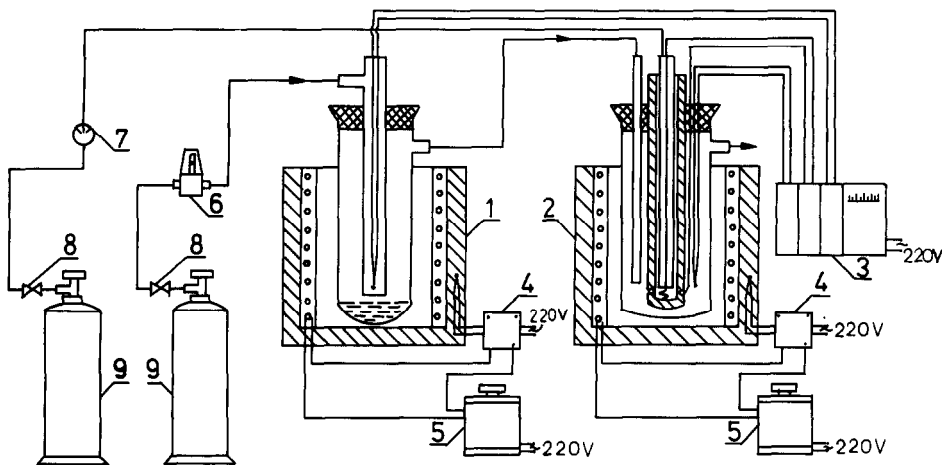


Fig. 1. Scheme of apparatus: 1, furnace reactor; 2, furnace with solid electrolyte; 3, recorder; 4, thermoregulator; 5, adjustable resistor; 6, rotameter; 7, manometer; 8, valve; 9, gas cylinders.

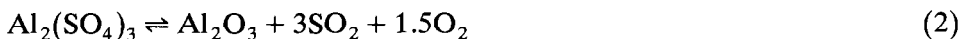
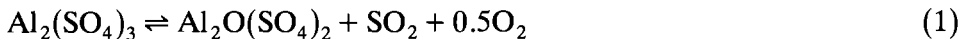
trolyte operated at 1123 K, and the reference electrode was placed in a pure oxygen atmosphere. The weight of the investigated samples amounted to 500 mg. Gas having the composition: H_2 1 vol%, Ar 99 vol% was passed into the furnace at a rate of 20 l h^{-1} . The gas mixture had a low partial pressure of oxygen ($p_{\text{O}_2} = 3.16 \times 10^{-18} \text{ Pa}$) in the reactor space.

The subject of the experiments was $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ c.p. of 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 0.001, and others.

The starting material was dried at 573 K for 2 h to obtain anhydrous aluminium sulphate. The experiments were carried out in the range 873–1213 K. The solid products were analysed by infrared spectroscopy.

RESULTS AND DISCUSSION

Joint interpretation of the thermogravimetric results of the thermal decomposition of $\text{Al}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ [1] and the physicochemical investigation data of the intermediate and final products makes it possible to propose the following mechanism of the process



Thus the formation of aluminium oxysulphate in the range 950–1045 K (reaction (1)) is related to changes in the aluminium sulphate structure and

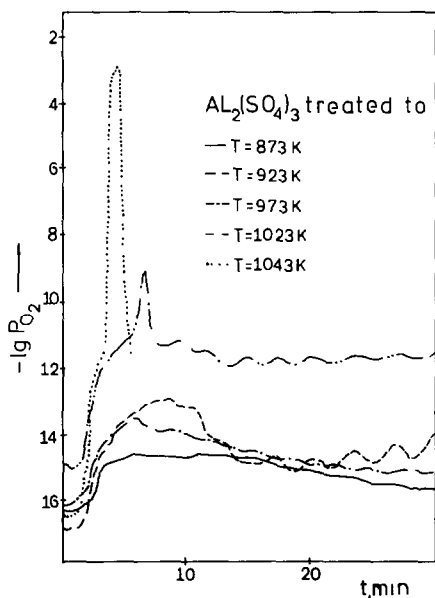


Fig. 2. The relationship between $\lg p_{\text{O}_2}$ and time, obtained during thermal decomposition of $\text{Al}_2(\text{SO}_4)_3$ at different temperatures in a mixture of hydrogen (1 vol%) and argon (99 vol%).

the formation of SO_2 and O_2 in the gas phase. The evolution of oxygen may be confirmed by the p_{O_2} measurement using the emf method.

Figure 2 represents the relationship between $\lg p_{\text{O}_2}$ and time in the temperature range 873–1043 K. It can be seen that the change in p_{O_2} is negligible at 873 K. At 923 and 973 K in the first 13 min in the p_{O_2} in the gas phase is represented by a broad, tailing peak and $\lg p_{\text{O}_2}$ changes from (–16.1 to –16.8) to (–13.5 to –13). The greatest changes in p_{O_2} are registered at 1023 and 1043 K, where within only a few minutes the $\lg p_{\text{O}_2}$ increased to –9.0 at 1023 K and to –2.9 at 1043 K. The results obtained prove that the process proceeds with the evolution of oxygen. At the same time it is evident that the temperature is the rate determining factor in the release of oxygen.

At higher temperatures such as 1073 and 1123 K the character of the $\lg p_{\text{O}_2}$ –time curves changes, which indicates the progress of desulphurization reactions such as (2) and (3). At the highest investigated temperatures, 1173–1213 K, this process is complete within 15–22 min.

The IR spectra are shown in Fig. 3, and they provide further confirmation of the process mechanism. The IR spectrum of the starting material shows absorption bands at 1620 and 3450 cm^{-1} , corresponding to the stretching and bending vibrations of OH groups in the aluminium sulphate structure. The absorption band at 1170 cm^{-1} , which is characteristic of the bending vibrations of SO_4^{2-} , indicates the presence of sulphate in the compound.

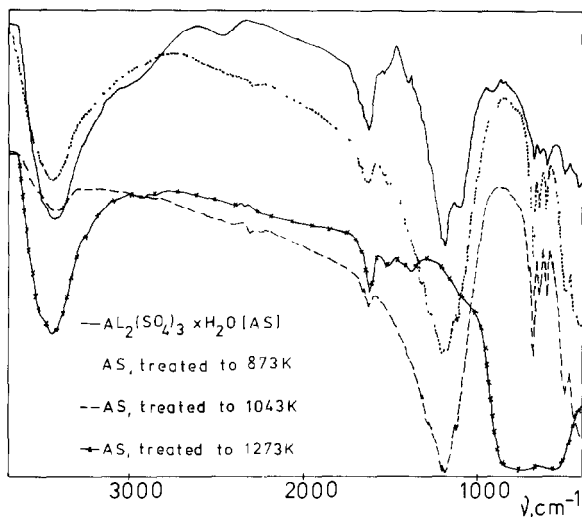


Fig. 3. The infrared spectra of the products of thermal decomposition of $\text{Al}_2(\text{SO}_4)_3$ at different temperatures in a mixture of hydrogen (1 vol%) and argon (99 vol%).

The absorption bands in the range $600\text{--}700\text{ cm}^{-1}$ (characteristic triplet for Al–O–Al group [1,4]) indicate the presence of $\text{Al}_2\text{O}(\text{SO}_4)_2$ in the sample. The content of moisture in the samples is due to their method of preparation. Analyses of the IR spectra and the relationship between $\lg p_{\text{O}_2}$ and time prove that the change of $\lg p_{\text{O}_2}$ at 923 K (Fig. 2) corresponds to the evolution of hygroscopic water from the samples. At temperatures of 923 and 973 K the first sign of the partial decomposition of $\text{Al}_2(\text{SO}_4)_3$ to $\text{Al}_2\text{O}(\text{SO}_4)_2$ (reaction (1)) can also be observed. It is evident that 1043 K is close to the optimum temperature for reaction (1) to proceed.

Probably at this temperature decomposition of the investigated compound to aluminium oxide is possible, but the reactions (2) and (3) proceed very slowly. In view of this, one can state that under the above conditions only reaction (1) takes place. The relationships presented in Fig. 4 confirm our assumptions. The temperature of 1073 K is sufficiently high for reaction (1) as well as for reactions (2) and (3) to start. The simultaneous course of all three reactions causes the fundamental increase of the partial pressure of oxygen in the gaseous atmosphere (Fig. 4). On the other hand, a temperature of 1073 K is not sufficiently high for the complete desulphurization of the salt.

The experiments performed by the emf method provide the final information to explain the mechanism of the thermal decomposition of aluminium sulphate. The derivatograms provide data to confirm the existence of $\text{Al}_2\text{O}(\text{SO}_4)_2$ as the intermediate product. The IR results show that aluminium oxysulphate develops at a temperature as low as 873 K, but the continuous registration of $\lg p_{\text{O}_2}$ changes in the gaseous phase leads to the

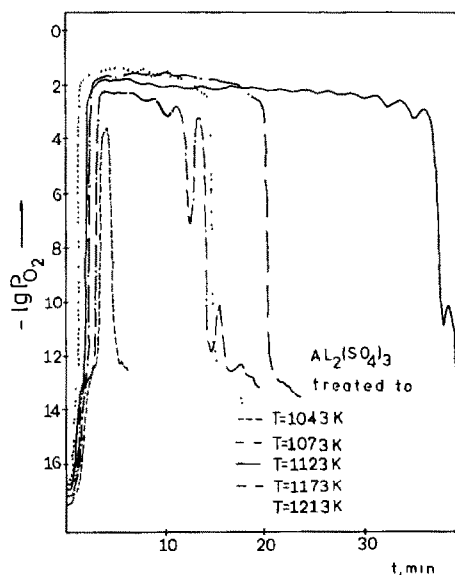


Fig. 4. The relationship between $\lg p_{\text{O}_2}$ and time, obtained during thermal decomposition of $\text{Al}_2(\text{SO}_4)_3$ at different temperatures in a mixture of hydrogen (1 vol%) and argon (99 vol%).

conclusion that the range of temperature 1023–1043 K affords optimum conditions for the course of reaction (1). Above 1043 K decomposition of $\text{Al}_2(\text{SO}_4)_3$ and $\text{Al}_2\text{O}(\text{SO}_4)_2$ to Al_2O_3 begins.

The optimum temperature range for the decomposition of aluminium sulphate to Al_2O_3 is 1173–1213 K.

CONCLUSIONS

Results of measurements performed by the emf method are consistent with the thermal decomposition of aluminium sulphate by a multistep process in which aluminium oxysulphate is formed as an intermediate product.

The optimum range of temperature to obtain $\text{Al}_2\text{O}(\text{SO}_4)_2$ is 1023–1043 K and that for the formation of Al_2O_3 is 1173–1213 K. The addition of a reducing agent to the gaseous phase causes lowering of the desulphurization temperature range and accelerates the process, but does not change its mechanism.

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