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THERMAL DECOMPOSITION OF SODIUM ALUMINIUM SULPHATE CRYSTALLOHYDRATE

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Abstract

Dynamic TG investigations were carried out to elucidate the mechanism of thermal decomposition of aluminium sodium sulphate crystallohydrate.

Shimadzu 31H and MOM Derivatograph X-ray diffraction and other techniques were used to determine data on the decomposition, activation energy, structure and phases in the solid products. Isothermal study in the temperature ranges 883–958 K and 983–1113 K in air or a reducing gas atmosphere revealed different reaction mechanisms. Depending on the experimental conditions, mainly Al_2O_3 can be obtained.

Keywords: aluminium sodium sulphate crystallohydrate

Introduction

Sodium aluminium sulphate crystallohydrate (SASCH) is one of the semiproducts of the process of aluminium oxide production from some aluminium-containing raw materials [1]. Their thermal decomposition determines to a great extent the efficiency of the whole technology. Research work has been reported on the thermal decompositions of aluminium sulphate and sodium and potassium alums in various atmospheres [2, 3]. These studies were carried out in connection with the establishment of alternative methods of aluminium oxide production from nephelines and alunites [4, 5] and they refer mainly to the thermal decompositions of aluminium sulphate, potassium aluminium sulphate and mixed potassium sodium aluminium sulphate.

The object of the present studies to establish the mechanism of the thermal decomposition of SASCH and to characterize the end-products.

Experimental

Tests were carried out on a Q-1500 D derivatograph, (MOM, Budapest) under the following conditions: sample mass 100 mg, heating rate 10 $\text{deg}\cdot\text{min}^{-1}$, atmosphere air or a mixture of 5% H_2 and 95% Ar with a flow rate of 30 $l\cdot h^{-1}$.

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The subject of the studies was SASCH produced from solution after acid decomposition under optimal conditions of enriched bulgarite [6]. The chemical composition of the alum used was as follows, %: Al_2O_3 9.39; Na_2O 7.15; Fe_2O_3 0.47; moisture 1.35. The kinetics of the process was examined with a Shimadzu 31H thermoanalyzer under isothermal heating. The product obtained after SASCH dehydration at 673 K was used for the studies. The tests were carried out with a gas mixture containing 2% H_2 and 98% Ar, at a flow rate of 25 l·h^{-1}, on a sample of 10 mg, within the temperature range 883–1113 K.

Results and discussion

The thermal curves of SASCH decomposition in air and in the reducing atmosphere are shown in Figs 1a, b. The TG curve in Fig. 1a has a clearly expressed two-stage character, the first stage, within the temperature range 293–633 K, characterizing the process of dehydration. Four stages of water loss are recorded at a low heating rate: within the range 293–363 K, about 20% of the water is lost, which corresponds to 4 moles of water of crystallization; from 363 K to 395 K, the loss increases up to 29.5%, when a further 2 moles of water are released; within the range 395–471 K, a further 3 moles of crystallization water are evolved; and within the temperature range 471–631 K, a further 2 moles of water, about 11 moles of water per mole of sulphate. The process of desulphurization starts above 873 K, the highest rate occurring at

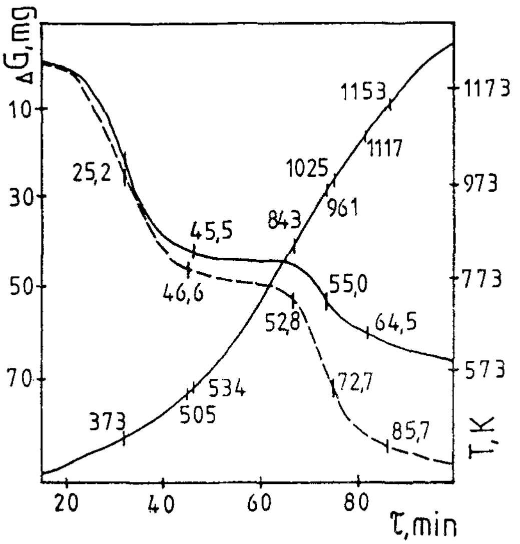

Fig. 1 Thermal curves of SASCH at gas flow rates 25 l·h^{-1} and heating rate 10 deg·min^{-1}; a) — air ; b) - - - reducing gas

1025 K. The overall mass loss is 64.5%, which corresponds to a desulphurization degree of 97.6%. The following decomposition is indicated:

$$2NaAl(SO_4)_2 = Na_2SO_4 + Al_2O_3 + 3SO_3 \quad (1)$$

In a reducing medium (Fig. 1b), the TG dependence exhibits three stages, the first being dehydration, within the temperature range 293–603 K, characterized by a mass loss of 50.1%, which corresponds to almost complete dehydration. Two stages are observed in the temperature range 773–1243 K. The first is in the range 863–941 K, with maximum rate at 911 K and a mass loss of 64.6%. The process of thermal decomposition within this range is assumed to follow the equation:

$$2NaAl(SO_4)_2 + 3H_2 = Na_2SO_4 + Al_2O_3 + 3SO_2 + 3H_2O \quad (2)$$

the degree of desulphurization then being 91.0%. The second stage is within the temperature range 961–1157 K, with maximum rate of decomposition at 1010 K. The rate of decomposition decreases above 1073 K. The total mass loss in this stage suggests the following scheme of thermal decomposition:

$$Na_2SO_4 + H_2 = Na_2SO_3 + H_2O \quad (3)$$

$$Na_2SO_3 + Al_2O_3 = 2NaAlO_2 + SO_2 \quad (4)$$

$$Na_2SO_4 + 4\ H_2 = Na_2S + 4\ H_2O \quad (5)$$

$$Na_2S + Al_2O_3 = 2NaAlO_2 + H_2S \quad (6)$$

To shed light on the mechanism proposed for the process of thermal decomposition, X-ray phase analysis of the products of thermal decomposition in air (Fig. 2) and in a reducing atmosphere (Fig. 3) was carried out. The X-ray phase analysis results confirmed the scheme proposed for the thermal decomposition. The results in the reducing medium clearly showed the presence of phases of Na_2SO_4 and $NaAlO_2$, while in air only Al_2O_3 and Na_2SO_4 were indicated.

The data from the derivatographic analysis were treated by a computer program with an algorithm based on the following equation:

$$\log(K_T B) = \log A + \frac{E}{R}\left[\left(\frac{W_{max}}{R_{T_{max}} \cdot T^2_{max}}\right)\log W - \frac{1}{2.3\ T}\right]$$

where $B = dT/d\tau$, the linear heating rate; R = gas constant; W = mass loss; E = apparent activation energy.

The apparent activation energies calculated for the process of SASCH decomposition were as follows:

in air: $E_a = 116.5\ \mathrm{kJ{\cdot}mol^{-1}}$
in a reducing medium: stage I $E_a = 105.7\ \mathrm{kJ{\cdot}mol^{-1}}$
stage II : $E_a = 122.3\ \mathrm{kJ{\cdot}mol^{-1}}$

High precision was attained, the correlation index ranging from 0.9946 to 0.9969.

TG curves showing the change in sample mass as a function of time are depicted in Figs 4, 5 and 6. Figure 4 presents results on the isothermal decomposition of SASCH dehydrated at 673 K in air medium. On elevation of the temperature, the process rate increases considerably. At 923 K, the time needed for a high degree of decomposition to be achieved is 36–40 min, while at 998 K a

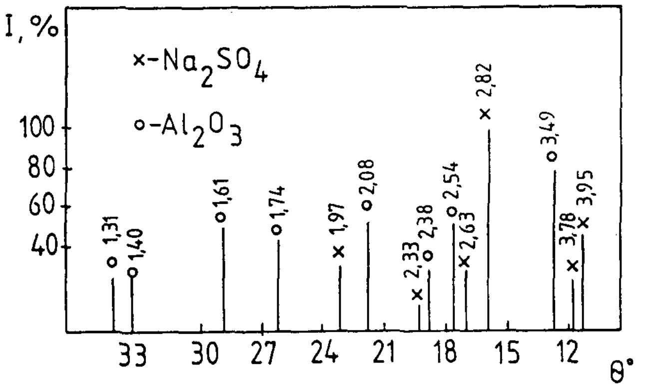

Fig. 2 X-ray diffractogram of a product from thermal decomposition of SASCH in air

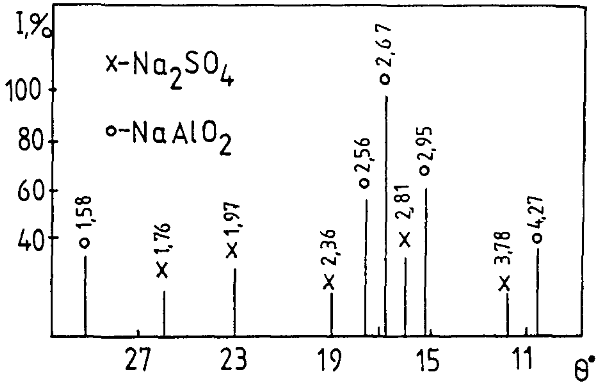

Fig. 3 X-ray diffractogram of a product from thermal decomposition of SASCH in a reducing atmosphere

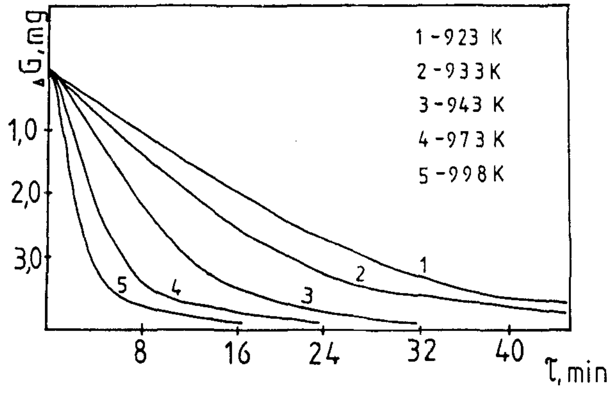

Fig. 4 TG-relationships of SASCH decomposition in air

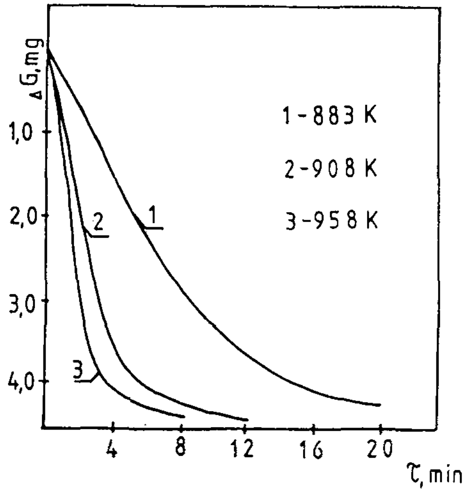

Fig. 5 TG-relationships of SASCH decomposition in a reducing atmosphere

high degree of desulphurization is achieved in 8–12 min. The rate constant of the process changes from 0.0244 min^{-1} at 923 K to 0.1159 min^{-1} at 998 K. The apparent activation energy for this temperature is 162.3 $\text{kJ}\cdot\text{mol}^{-1}$. The final mass loss corresponds only to the decomposition of the aluminium sulphate contained in the starting SASCH. The results of the isothermal studies in a reducing medium are shown in Figs 5 and 6. Figure 5 demonstrates the results on the first stage of decomposition, within the range 883–958 K, and Fig. 6 those on the second stage, within the range 983–1113 K. The apparent activation energy of the first stage of thermochemical decomposition, where $Al_2(SO_4)_3$ desulphurization in the range 883–958 K, is 99.9 $\text{kJ}\cdot\text{mol}^{-1}$, and that of the second

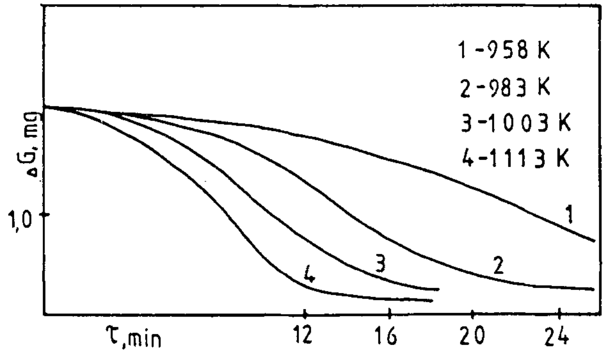

Fig. 6 TG-relationships of SASCH decomposition in a reducing atmosphere at T =958–1113 K

stage, where Na_2SO_4 decomposes in the range 983–1113 K, is 127.7 $kJ \cdot mol^{-1}$. The rate constant of the process in the first stage changes from 0.0363 min^{-1} at 883 K to 0.1018 min^{-1} at 958 K, while in the second stage it changes from 0.1077 at 983 K to 0.5273 min^{-1} at 1113 K.

Conclusions

Sodium aluminium sulphate crystallohydrate is dehydrated within the temperature range up to 633 K in air medium and up to 603 K in a reducing atmosphere. A process of desulphurization of the anhydrous product then begins. Na_2SO_4 and Al_2O_3 are the products of decomposition in air medium, while Na_2SO_4 and $NaAlO_2$ are formed in a reducing atmosphere.

The apparent activation energy of the process in air is 162.3 kJ/mol for the temperature range 923–998 K. The process is a two-stage one in the reducing medium, the apparent activation energy being 99.9 kJ/mol within the temperature range 883–958 K and 127.7 kJ/mol within the range 983–1113 K.

The mechanism of thermal decomposition in air is described by reaction 1 and in the reducing medium by reactions 2–6.

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Zusammenfassung — Es wurden DTG Untersuchungen zur Aufklärung des Mechanismus der thermischen Zersetzung von Aluminiumnatriumsulphat-Kristallohydrat durchgeführt.
Ein Shimadzu 31H und MOM Derivatograph, Röntgendiffraktion und andere Techniken wurden zur Bestimmung von Daten über die Zersetzung, Aktivierungsenergie, Struktur und Phasen in den Feststoffprodukten zu ermitteln. Eine isotherme Untersuchung im Temperaturintervall von 883 bis 958 K und von 983 bis 1113 K in Luft oder reduzierender Atmosphäre legte verschiedene Reaktionsmechanismen offen. In Abhängigkeit von den Versuchsbedingungen konnte hauptsächlich Al_2O_3 beobachtet werden.