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THERMAL DECOMPOSITION OF BASIC ALUMINIUM POTASSIUM SULPHATE (BAPS) IN HYDROGEN ATMOSPHERE

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ABSTRACT

The dissociation of basic aluminium potassium sulphate (BAPS) in hydrogen atmosphere was studied using thermal analysis, X-ray phase analysis and chemical analysis. It was found that under these conditions the desulphurisation of the basic salt is more complete and occurs at lower temperatures in comparison with this process in air. The solid products of decomposition of the studied compound at 1223 K are α-Al_2O_3 and β''-KAl_5O_8.

The present work was preceded by a thermodynamic analysis of the reactions which could occur during desulphurisation of basic salt in a hydrogen atmosphere; the results of the calculations were compared with the experimental results.

INTRODUCTION

From previous studies on the calcination of BAPS in air, it is known [1] that a mixture of $KAl(SO_4)_2$ and γ-Al_2O_3 is formed after dehydration; however we cannot exclude the possibility of obtaining an aluminium sulphate.

Within the temperature range 870–1200 K, dissociation of aluminium potassium sulphate leads to the formation of a mixture of K_2SO_4 and $Al_2(SO_4)_3$; further decomposition of aluminium sulphate yields γ-Al_2O_3 and sulphur oxides.

From literature data [2] and from our earlier investigations of the decomposition of this salt in the presence of carbon and water vapour [3], we can state that in the presence of a reducing agent, the course of the last stage of the decomposition, i.e. desulphurisation, is different from that taking place in air. Investigations into the thermal dissociation of BAPS in hydrogen were preceded by thermodynamic analyses of the reactions expected to take place in these conditions.

THERMODYNAMIC ANALYSIS OF THE PROCESS

Calculations were made for the reactions occurring in the presence of the solid dehydration products of the basic salt. Thermodynamic potentials were

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TABLE 1

Standard thermodynamic potentials of reactions occurring during desulphurisation of BAPS in hydrogen

No.	Reaction	$\Delta G^{\ominus}$ (kcal mol^{-1})			
		298 K	600 K	800 K	1000 K
1	$KAl(SO_4)_2 \rightarrow 1/2K_2SO_4 + 1/2Al_2O_3 + 3/2SO_2 + 3/4O_2$	80.54	49.64	29.70	9.96
2	$KAl(SO_4)_2 \rightarrow 1/2K_2SO_4 + 1/2Al_2(SO_4)_3$	7.22	6.91	6.60	6.00
3	$KAl(SO_4)_2 + 2H_2 \rightarrow 1/2K_2O + 1/2Al_2O_3 + 2SO_2 + 2H_2O$	54.30	20.05	1.56	−22.34
4	$KAl(SO_4)_2 + 3/2H_2 \rightarrow 1/2K_2SO_4 + 1/2Al_2O_3 + 3/2SO_2 + 3/2H_2O$	−1.43	−27.11	−43.28	−59.11
5	$KAl(SO_4)_2 + 7/2H_2 \rightarrow 1/2K_2S + 1/2Al_2O_3 + 3/2SO_2 + 7/2H_2O$	−2.93	−33.70	−52.84	−70.29
6	$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_2 + 3/2O_2$	146.62	85.45	46.21	7.91
7	$Al_2(SO_4)_3 + 3H_2 \rightarrow Al_2O_3 + 3SO_2 + 3H_2O$	−17.30	−68.03	−99.74	−130.21
8	$Al_2(SO_4)_3 + 12H_2 \rightarrow Al_2S_3 + 12H_2O$	−86.99	−125.30	−147.22	−167.10
9	$Al_2S_3 + 3H_2O \rightarrow Al_2O_3 + 3H_2S$	−66.63	−64.59	−63.07	−61.57
10	$K_2SO_4 + H_2 \rightarrow K_2SO_3 + H_2O$	4.18	1.64	0.17	−1.03
11	$K_2SO_3 + 3H_2 \rightarrow K_2S + 3H_2O$	−7.18	−14.83	−19.30	−21.33
12	$K_2SO_4 + 4H_2 \rightarrow K_2S + 4H_2O$	−3.00	−13.19	−19.13	−22.36
13	$K_2SO_4 + H_2 \rightarrow K_2O + SO_2 + H_2O$	111.46	94.30	83.44	73.54
14	$K_2S + 2H_2O \rightarrow 2KOH + H_2S$	−78.06	−65.70	−59.36	−51.79
15	$K_2S + H_2O \rightarrow K_2O + H_2S$	69.02	66.87	65.72	63.08
16	$K_2S + H_2O + Al_2O_3 \rightarrow K_2O \cdot Al_2O_3 + H_2S$	−2.41	−4.11	−5.17	−6.19
17	$K_2SO_4 + Al_2O_3 + 4H_2 \rightarrow K_2O \cdot Al_2O_3 + H_2S + 3H_2O$	−5.55	−18.92	−26.82	−33.22
18	$SO_3 + H_2 \rightarrow SO_2 + H_2O$	−37.86	−41.22	−43.16	−44.88
19	$SO_3 + 4H_2 \rightarrow H_2S + 3H_2O$	−83.80	−81.84	−80.01	−77.70
20	$SO_3 + 3H_2 \rightarrow 1/2S_2 + 3H_2O$	−75.40	−67.37	−67.88	−67.19
21	$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$	−45.44	−40.62	−36.85	−32.82
22	$SO_2 + 2H_2 \rightarrow 1/2S_2 + 2H_2O$	−37.54	−26.15	−24.72	−22.31

calculated at 298, 600, 800 and 1000 K using ref. 4 or by calculating [5] the standard thermodynamic potentials of the appropriate reagents being formed. The results of the calculations are shown in Table 1.

Calculations show that the desulphurisation of BAPS in the reducing atmosphere of hydrogen should occur at lower temperatures and be more complete compared with the course of dissociation in air. The solid products of the decomposition of the basic salt under these conditions would be expected to include aluminium oxide and potassium aluminate and, in the gaseous phase, a mixture of SO_2, H_2S and elementary sulphur would be found [6].

EXPERIMENTAL AND RESULTS

Basic aluminium potassium sulphate with the following composition was investigated: Al_2O_3, 30.94%; K_2O, 10.55%; SO_3, 41.71%; H_2O, 16.80%.

Thermogravimetric analyses of the decomposition of the basic salt in hydrogen or argon were made using a Mettler thermoanalyser. The measurements were performed on samples of approximately 20 mg with variable rates of temperature increase. Figure 1 shows a typical thermogram of BAPS decomposed in hydrogen atmosphere with a heating rate of 15 °C min^{-1}. Figure 2 is the thermogram of the same compound in argon at a heating rate of 40 °C min^{-1}.

In the next series of measurements, samples of basic salt were heated in a pipe reactor in a stream of hydrogen at the following temperatures and times: 803 K, 1 h; 943 K, 2 h; 1123 K, 2 h; 1223 K, 2 h.

The solid products of partial decomposition of BAPS were analysed by X-ray phase analysis, thermal analysis and chemical analysis.

The X-ray diffraction analyses were performed using a Philips diffractometer PM991/00 (The Netherlands) and a Carl Zeiss Jeno diffractometer HZG-4C (Germany), using Co Kα radiation. The results of these analyses are presented in Table 2.

Thermogravimetric curves of the samples were recorded on a MOM OD102 derivatograph (Hungary). The solid products determined were: K_2O,

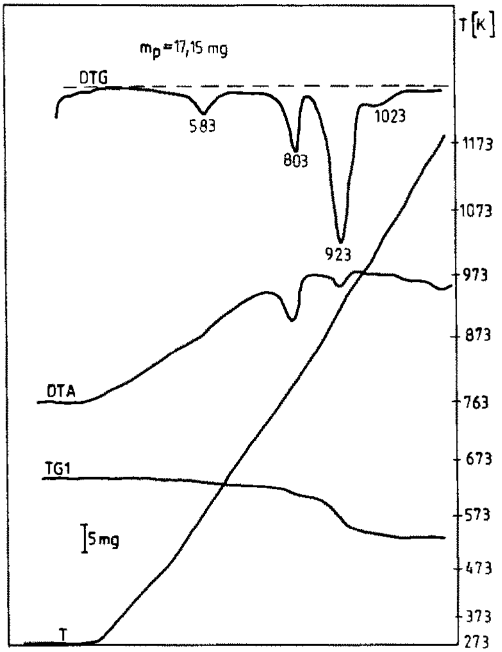

Fig. 1. Thermogravimetric curves of BAPS in hydrogen atmosphere.

TABLE 2

X-ray diffraction analyses of intermediate and final products of the decomposition of BAPS in hydrogen

Sample 803 K 1 h	Mirkin's standard [7] K_2SO_4		Sample 943 K 2 h	Mirkin's standard [7] γ-Al_2O_3		Sample 1123 K 2 h	Sample 1223 K 2 h	Standard ASTM [8] α-Al_2O_3		Standard ASTM [8] β''-KAl_5O_8	
d (Å)	*d*(Å)	*I*	*d* (Å)	*d* (Å)	*I*	*d* (Å)	*d* (Å)	*d* (Å)	*I*	*d* (Å)	*I*
4.185	4.19	24	4.18	2.39	19	2.77	5.62	3.479	75	5.70	70
3.75	3.73	8	3.00	2.275	13	2.72	3.46	2.552	90	2.798	70
3.38	3.38	5	2.88	1.975	72	2.41	2.79	2.379	40	2.511	40
2.97	3.00	80	2.38	1.396	100	1.97	2.55	2.085	100		
2.91	2.88	100	2.09	1.139	13	1.399	2.51	1.740	45		
2.50	2.50	12	1.985				2.41	1.601	80		
2.42	2.41	20	1.399				2.38	1.404	30		
2.37	2.21	24					2.08	1.374	50		
2.23	2.08	40					1.97	1.239	16		
2.08	1.88	10					1.74				
							1.60				
							1.40				
							1.374				
							1.24				

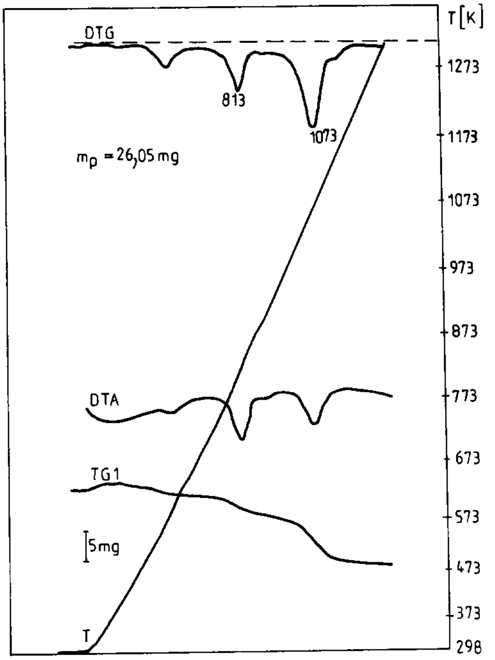

Fig. 2. Thermogravimetric curves of BAPS in argon atmosphere.

by titrating the sample with 0.1 N HCl in the presence of phenolphthalein; SO_4^{2-}, by weighing the precipitate formed with barium sulphate; and S^{2-}, iodometrically and also semi-quantitatively with a sodium nitroprussate.

The results of these analyses facilitated determination of the molar composition of the intermediate dissociation products of BAPS in hydrogen at various temperatures.

Gaseous products released during decomposition of the compound in hydrogen were absorbed in 30% NaOH and determined using Wiele's method [9] for S^{2-} and SO_3^{2-} ions. It was found that during decomposition of the basic salt in hydrogen at 1223 K, the gaseous products released are a mixture of SO_2 and H_2S in a 1 : 1 ratio. It was also observed that elementary sulphur accumulated in cooler parts of the apparatus.

DISCUSSION

Comparing thermograms of the studied compound in hydrogen and argon (Figs. 1 and 2), one can state that dehydration of the salt occurs in the same temperature range, 298–823 K, in both atmospheres and in both cases this is followed by a mass loss of 17.9%. In the dehydration of solid products in hydrogen, the sample being heated at 803 K for 1 h, only K_2SO_4 was detected using X-ray phase analysis (see Table 1). Aluminium compounds in sulphate form have an X-ray-amorphous, finely grained, highly hygroscopic structure. The molar composition of the dehydration products in the form of oxides is $K_2O \cdot 3Al_2O_3 \cdot 4SO_3$ which can be equal to the mixture K_2SO_4, $Al_2(SO_4)_3$ and $2Al_2O_3$. The basic difference in the decomposition of basic aluminium potassium sulphate in hydrogen compared with the decomposition in argon can be observed during the desulphurisation of the compound.

In hydrogen, within the range 823–943 K, one can observe a peak at 923 K in the DTG curve and a slight effect on the DTA curve. As can be seen from the TG curve, the loss in weight at this stage of decomposition is 31.7%, which indicates the release of sulphur combined with aluminium. X-ray diffraction studies of the intermediate product of the decomposition of BAPS obtained as a result of heating at 943 K for 2 h show weaker reflections from K_2SO_4 compared with those on the X-ray diffractogram of the sample obtained at 803 K, and also reflections corresponding to γ-Al_2O_3 (see Table 2).

Chemical analyses of the contents of SO_4^{2-}, K_2O and S^{2-} in the sample, and also the thermogravimetric data, allowed the following molar composition of the solid phase to be deduced: $0.25K_2O$, $0.75K_2SO_4$ and $3Al_2O_3$.

In an argon atmosphere, the sulphur released from a basic salt combines with aluminium in the temperature range 823–1273 K with the peak in the DTG curve at 1073 K (Fig. 2); a 31.7% mass loss takes place in this range (see the TG curve).

Above a temperature of 943 K in the DTG curve of BAPS decomposed in hydrogen (Fig. 1), there is a peak at 1023 K associated with a 7.6% loss in weight. During this stage, the reduction of K_2SO_4 occurs with no clearly observable endothermic effect in the DTA curve. There is no proper dissociation stage for potassium sulphate in the decomposition of the basic salt in argon. The X-ray diffraction data of the sample heated at 1123 K for 2 h (see Table 2) indicate the presence of γ-Al_2O_3. Chemical analysis indicated the presence of a solid phase of K_2O but no sulphates or sulphides were found.

Dissociation of BAPS in hydrogen at 1223 K for 2 h yields α-Al_2O_3, β''-KAl_5O_8 and a small amount of γ-Al_2O_3 as solid products (see X-ray data in Table 2). Chemical analyses do not indicate the presence of SO_4^{2-} or S^{2-} and only a small amount of K_2O (about 0.04 mole) was found. The results of experimental studies are confirmed by the results of thermodynamic calculations. The absence of any sulphides in the solid products, despite the thermodynamic possibility of their occurring in a reducing atmosphere, is explained in another paper [6].

CONCLUSIONS

The results of experimental studies lead us to suggest the following scheme for the desulphurisation of BAPS in hydrogen atmosphere.

The first stage is the desulphurisation of aluminium compounds at 823–943 K

$$2KAl(SO_4)_2 \rightarrow K_2SO_4 + Al_2(SO_4)_3 \qquad (1)$$

$$Al_2(SO_4)_3 + 3H_2 \rightarrow \gamma\text{-}Al_2O_3 + 3SO_2 + 3H_2O \qquad (2)$$

At this stage the decomposition product of BAPS is a mixture of γ-Al_2O_3 and K_2SO_4, from which potassium sulphate can be washed to obtain active Al_2O_3 which can be used as sorbent.

The second stage is the desulphurisation of K_2SO_4 and the simultaneous sublimation of potassium compounds (943–1123 K)

$$K_2SO_4 + Al_2O_3 + 4H_2 \rightarrow K_2O \cdot Al_2O_3 + H_2S + 3H_2O \qquad (3)$$

At temperatures close to 1223 K the following reactions occur

$$\gamma\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3 \qquad (4)$$

$$K_2O \cdot Al_2O_3 + 4Al_2O_3 \rightarrow K_2O \cdot 5Al_2O_3 \qquad (5)$$

The low temperature of the phase transformation of γ-Al_2O_3 to α-Al_2O_3, about 1223 K, is probably caused by the presence of potassium cations in the system; such a phase transformation is rarely observed below 1373 K.

In the gaseous phase, there are three possible reactions in the presence of hydrogen

$$SO_3 + H_2 \rightarrow SO_2 + H_2O \qquad (6)$$

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O \qquad (7)$$

$$SO_2 + 2H_2 \rightarrow 1/2S_2 + 2H_2O \qquad (8)$$

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