# THERMAL DECOMPOSITION OF BASIC ALUMINIUM - AMMONIUM SULFATE (BAAS) IN HYDROGEN ATMOSPHERE

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The stages of thermal decomposition of basic aluminium-ammonium sulfate (BAAS) in hydrogen atmosphere were studied with use of differential thermal analysis (DTA), thermogravimetric (TG), X-ray diffraction phase analysis (XRD), and chemical analyses. It has been found that hydrogen greatly influences the process of the desulfurization of the investigated compound: this process occurs at lower temperatures as compared to the desulfurization process in air. The final decomposition product of the basic salt at 1223 K is $\gamma$-$Al_2O_3$. The experimental part is preceded by the thermodynamic analysis of the desulfurization process of BAAS in hydrogen atmosphere, and its results have been correlated with experimental tests.

## Introduction

In a previous paper [1] the authors presented results of the study of decomposition of BAAS in air. The product of a partial dehydration of the basic salt is $3Al_2O_3 \cdot 4SO_3 \cdot (0-2)H_2O$, which next dissociates towards $\gamma$-$Al_2O_3$ and sulfur oxides. Investigations of decompositions of BAAS in the presence of carbon [2] shows that reducing environment influences significantly the course of alunite desulfurization.

The present work is devoted to the study of the stages of the degradation of BAAS in hydrogen atmosphere.

## Thermodynamic analysis of the process

Thermodynamic calculations for the reactions, which can constitute the decomposition process of a basic salt, were conducted with an assumption that can be expected decisive influence of reducing atmosphere of hydrogen

in the third stage of the compound dissociation, i. e. during its desulfurization. These thermodynamic calculations were limited to reactions occuring during decomposition of $Al_2(SO_4)_3$ and secondary reactions which could happen in the gaseous phase. For the presented reactions there have been calculated standard thermodynamic potentials at temperatures 298, 600, 800 and 1000 K while using standard thermodynamic potentials typical for forming reagents, $\Delta G_f^0$.

Standard thermodynamic potentials typical for forming gaseous reagents were taken from the Tables [3], and for solid reagents they were calculated on the basis of values of function [4]:

$$H_{f298}^0, S_{298}^0, S_T^0 - S_{298}^0, H_T^0 - H_{298}^0$$

Results of calculations are given in Table 1.

Table 1 Standard thermodynamic potentials of reactions occurring during desulfurization process of BAAS in hydrogen atmosphere

| $N^o$ | Reactions | $\Delta G^o$, kcal/mole | | | |
|---|---|---|---|---|---|
| | | 298 K | 600 K | 800 K | 1000 K |
| 1 | $Al_2(SO_4)_3 = Al_2O_3 + 3SO_2 + 3/2O_2$ | 146.62 | 85.45 | 46.21 | 7.91 |
| 2 | $Al_2(SO_4)_3 = Al_2S_3 + 6O_2$ | 568.69 | 488.62 | 436.58 | 385.38 |
| 3 | $Al_2(SO_4)_3 + 3H_2 = Al_2O_3 + 3SO_2 + 3H_2O$ | −17.30 | −68.03 | −99.74 | −130.21 |
| 4 | $Al_2(SO_4)_3 + 12H_2 = Al_2S_3 + 12H_2O$ | −86.99 | −125.30 | −147.22 | 167.10 |
| 5 | $Al_2S_3 + 3H_2O = Al_2O_3 + 3H_2S$ | −66.63 | −64.59 | −63.07 | −61.57 |
| 6 | $SO_3 + H_2 = SO_2 + H_2O$ | −37.86 | −41.22 | −43.16 | −44.88 |
| 7 | $SO_3 + 4H_2 = H_2S + 3H_2O$ | −83.30 | −81.84 | −80.01 | −77.70 |
| 8 | $SO_3 + 3H_2 = 1/2S_2 + 3H_2O$ | −75.40 | −67.37 | −67.88 | −67.19 |
| 9 | $SO_2 + 3H_2 = H_2S + 2H_2O$ | −45.44 | −40.62 | −36.85 | −32.82 |
| 10 | $SO_2 + 2H_2 = 1/2S_2 + 2H_2O$ | −37.54 | −26.15 | −24.72 | −22.31 |

Comparing values $\Delta G^o$ for reactions 2 and 3 (cf. data in Table 1), allows to include that it is more probable that the course of the reaction 2 leads to obtaining aluminium sulphide as the final dissociation product.

If, however, it is taken into consideration the idea of cation acidity understood as an ability of the cation to bind negative ligands [5] quantitatively expressed with an "electronegative force" with a formula:

$$E_f = -E_j / r$$

where: $E_f$ – an electronegative force

$E_j$ – the last ionization energy leading to the cation in the given oxidation state
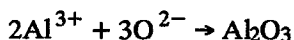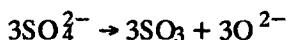
$r$ – the standard cation radius for the coordination number 6

These values for $Al^{3+}$ are as follows:

$$E_j = 28.44 \text{ eV} \quad r = 0.53 \text{ Å} \quad E_f = 85.96 \text{ nN}$$

So one can find that $Al^{3+}$ belongs to cations with high acidity and capabilities for combining to oxide anions.

Thus the reaction course of releasing sulfur trioxide can occur as follows:

$$3SO_4^{2-} \rightarrow 3SO_3 + 3O^{2-}$$

$$2Al^{3+} + 3O^{2-} \rightarrow Al_2O_3$$

In the gaseous phase probably occur the following secondary reactions:

$$SO_3 + H_2 \rightarrow SO_2 + H_2O$$

$$SO_3 + 4H_2 \rightarrow H_2S + 3H_2O$$

$$SO_3 + 3H_2 \rightarrow 1/2S_2 + 3H_2O$$
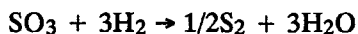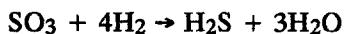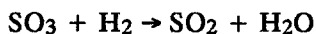
Reduction of $SO_3$ with hydrogen causes releasing of primary product from gaseous phase during these reactions.

It is especially significant for the course of desulfurization of the basic salt, because at the temperature range 778–973 K while releasing sulfur oxides from the BAAS the equilibrium of the reaction:

$$SO_3 \leftarrow \rightarrow SO_2 + 1/2O_2$$

is shifted towards $SO_3$ [1].

In solid products of decomposition of BAAS in hydrogen atmosphere one should expect the presence of aluminium oxide, and in the gaseous phase a mixture of $SO_2$, $H_2S$, and elementary sulfur.

## Experimental and results

The subject of the studies was the basic aluminium-ammonium sulfate of the following composition:

$$Al_2O_3 \ 35.2\% \quad NH_3 \ 3.5\% \quad SO_3 \ 42.0\% \quad H_2O \ 19.3\%$$
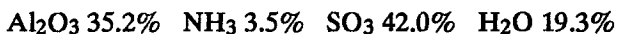
An approximate formula is $(NH_4)_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot (6-8)H_2O$. The thermogravimetric studies were performed in an atmosphere of argon or hydrogen with a Mettler thermoanalyser TA 2 and TA 4000. Examples for results of the thermogravimetric studies are presented in Fig. 1 and Fig. 2. Figure 1 shows a thermogram made for 18 mg samples with heating rate 15 deg/min in streaming hydrogen. Figure 2 shows thermogravimetric curves of the same compound decomposed in the inert argon atmosphere registered under the same conditions as above.
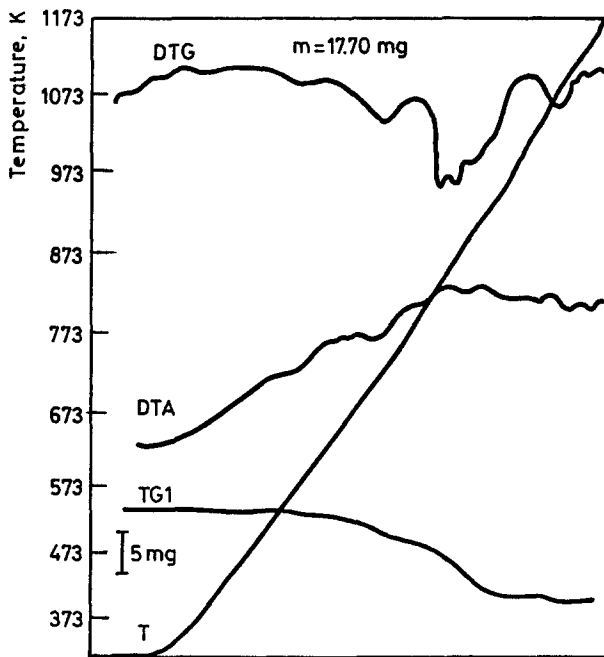


Fig. 1 Thermoanalytical curves of BAAS in hydrogen atmosphere

The samples of basic salt were heated isothermally in a pipe-reactor where the stream of hydrogen was flowing at the following temperatures and time: 773 K, 2 h; 973 K, 1 h; 1123 K 2 h; 1223 K, 2 h. X-ray phase analysis of solid products of decomposition was carried out in the Philips diffractometer PM 9901/00 using $CoK_\alpha$ radiation. Results are shown in Table 2 and Fig. 3.

Intermediate solid products of dissociation of basic salt were also analysed thermogravimetrically with a MOM derivatograph type OD-102.
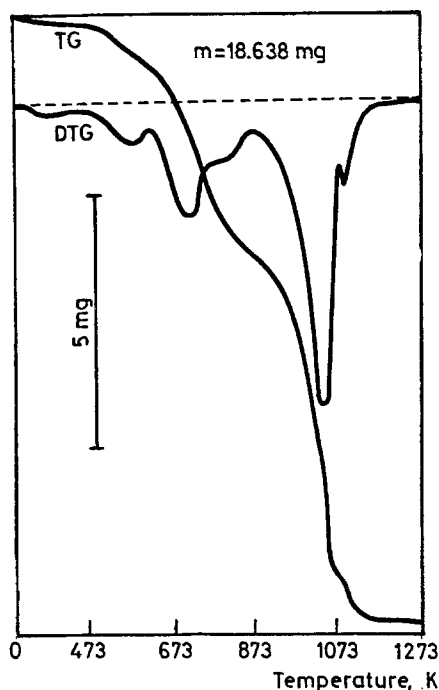
Fig. 2 Thermoanalytical curves of BAAS in argon atmosphere

The thermogram for the sample decomposed at 973 K during 1 h is shown in Fig. 4 as an example.

There were also conducted semiqualitative tests for the contents of $S^{2-}$ with sodium nitroprussiate. No sulfides were found in the intermediate and final products.

Table 2 X-ray diffraction analyses of intermediate and final products of decomposition of BAAS in hydrogen atmosphere

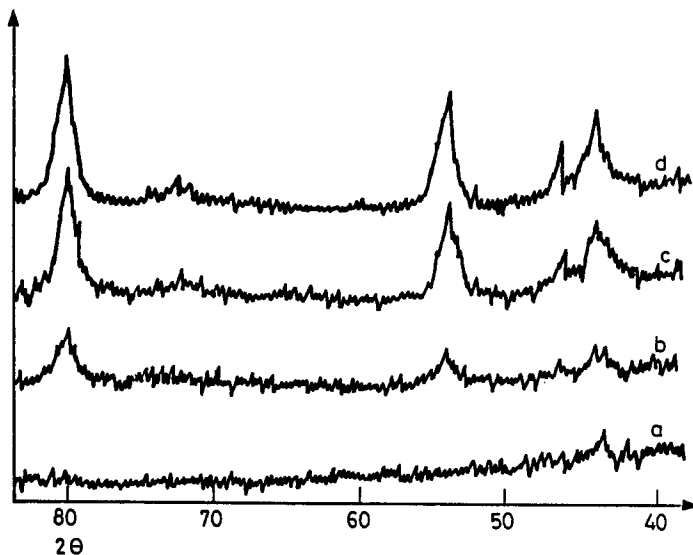| Standard [7] $\gamma-Al_2O_3$ Mirkin's | | Sample 773 K 2 h | Sample 973 K 1 h | Sample 1123 k 2 h | Sample 1223 K 2 h |
|---|---|---|---|---|---|
| $d$, Å | $I$ | $d$, Å | $d$, Å | $d$, Å | $d$, Å |
| 2.390 | 19 | amorphous | 2.390 | 2.390 | 2.390 |
| 1.975 | 72 | substance | 1.980 | 1.980 | 1.975 |
| 1.396 | 100 | | 1.398 | 1.398 | 1.398 |

Fig. 3 X-ray diffraction analysis of BAAS heated in variable conditions of temperature and
time; a: 773 K, 2 h, b: 973 K, 1 h, c: 1123 K, 2 h, d: 1223 K, 2 h

In order to achieve the semiquantitative analysis of the composition of
gaseous products of the compound dissociation, they were absorbed in 30%
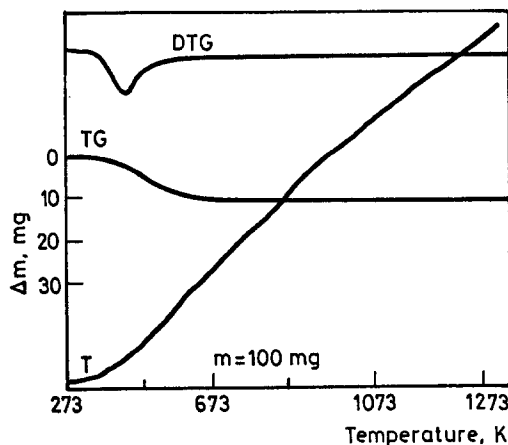NaOH and contents of ions $S^{2-}$ and $SO_3^{2-}$ were determined with Wiele



Fig. 4 Thermoanalytical curves of intermediate dissociation product of BAAS in hydrogen
atmosphere (973 K, 1 h)

method [6]. While heating the BAAS at 1223 K for 2 h, there were found $H_2S$ and $SO_2$ occurring in gaseous products in the mole ratio 3:2.

Elementary sulfur was observed in the form of the yellow bloom accumulating at the cooler parts of the apparatus.

**Discussion**

Thermogravimetric analyses of the studied compound conducted in atmosphere of $H_2$ or Ar (Fig. 1 and Fig. 2), allow to declare that in the temperature range 298–773 K the loss in weight is about 20% and it is connected with release of water (except 1 mole) and ammonia from the BAAS. Results of thermogravimetric analysis do not signify any influence of reducing hydrogen atmosphere on the course of alunite dehydration.

The X-ray diffraction analysis of basic salt roasted at 773 K for 2 h does not show any presence of products with alunite structure in the sample. Its structure is radiographically amorphous (Fig. 3 and Table 2). One can only assume that the product of a partial dehydration of BAAS is $AlH(SO_4)_2$, which next decomposes into $Al_2(SO_4)_3$, $Al_2O(SO_4)_2$ and $\gamma$-$Al_2O_3$.

The crystallographic structure of the sample heating at 773 K for 2h is not sufficiently developed and its X-ray diffractogram does not show presence of any reflections. Above 773 K on the DTG curve one can observe the wide peak within the temperature range 773–973 K, which is connected with 39% loss of sample mass (3.5 moles of $SO_3$ and remained water), and a small peak on the DTG curve at 1073 K, which accompanied by about 4% loss of sample weight (TG curve) corresponds to the evolution of 0.5 molecule of $SO_3$ (Fig. 1).

The same stage in argon atmosphere occurs at the temperature range 773–1273 K, with the maximum rate of releasing sulfur oxides at 1053 K (DTG curve in Fig. 2).

Thermal decomposition of BAAS in hydrogen atmosphere occurs differently in dynamic and isothermal conditions, when at temperature 973 K within 1h takes place a complete release of sulfur oxides from a basic salt. This can be confirmed by both X-ray diffraction studies of this sample, where one states only presence of $\gamma$-$Al_2O_3$ (Fig. 3 and Table 2), and results of the thermogravimetric analysis in which there is no peak responsible for decomposition of sulfates (Fig. 4).

Further heating of the sample at temperatures 1123 K and 1223 K for 2h causes only a better arranged of $\gamma$-$Al_2O_3$ structure observed as more clear

reflections on X-ray diffraction spectrum (Fig. 3). In the solid products of degradation sulfide anions are not found at all.


## Conclusions

1. The product of dehydration of BAAS in hydrogen atmosphere is a radiographically amorphous, fine-crystalline and hygroscopic phase of sulfate compounds of aluminium.

2. In hydrogen atmosphere the last stage of decomposition of basic salt, i.e. the desulfurization of BAAS occurs in lower temperatures as compared with dissociation in air.

3. Gaseous products of desulfurization of BAAS are $H_2S$, $SO_2$, and elementary sulfur.

4. At 973 K in hydrogen atmosphere in 1h one can obtain $\gamma$-$Al_2O_3$, at higher temperatures the structure of $\gamma$-$Al_2O_3$ is only better arranged.


## References

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**Zusammenfassung** — Die Stufen der thermischen Zersetzung von basischem Aluminium Ammonium Sulfat (BAAS) in Wasserstoffatmosphäre wurden unter Verwendung von Differenzthermoanalyse (DTA), Thermogravimetrie (TG), röntgenographischer Phasenanalytik (XRD) und chemischer Analytik untersucht. Es wurde festgestellt, dass Wasserstoff den Desulfurierungsprozess der untersuchten Verbindung stark beeinflusst, indem dieser bei tieferer Temperatur abläuft als die Desulfurierung in Luft. Das Endprodukt der Zersetzung des basischen Salzes bei 1223 K ist $\gamma$-$Al_2O_3$. Die experimentellen Resultate wurden mit den Ergebnissen einer vorgängig durchgeführten thermodynamischen Betrachtung der Desulfurierung von BAAS in Wasserstoffatmosphäre korreliert.