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Study of the mechanism of the thermochemical decomposition of ferrous sulphate monohydrate

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Abstract

A derivatograph study has been carried out for the thermal decomposition of ferrous sulphate monohydrate in an oxidizing gaseous atmosphere. Based on the results from the derivatographic, thermogravimetric, and X-ray phase analyses, and from Mössbauer spectroscopy, a two-stage process for oxidizing Fe^{2+} to Fe^{3+} is suggested with formation of intermediate products, such as $FeOHSO_4$ and $Fe_2O(SO_4)_2$. A new mechanism is suggested for the thermal decomposition of $FeSO_4{\cdot}H_2O$ in an oxidizing gaseous atmosphere, that takes into account the effect of the partial pressure of the gaseous components on the rate of certain parallel reactions.

Keywords: Decomposition; Derivatographic analysis; Mössbauer; TGA; XRD

1. Introduction

The mechanism of the thermochemical decomposition of ferrous sulphate monohydrate in an oxidizing atmosphere has been studied by a number of authors [1–11]. Some results of the investigations confirm the formation of two intermediate phases, $FeOHSO_4$ and/or $Fe_2O(SO_4)_2$. Radionov et al. [1], Pannetier et al. [2] and Bristoti et al. [3] assume a single-stage oxidation of Fe^{2+} to Fe^{3+} following the formation of $FeOHSO_4$, which is then decomposed to $Fe_2O(SO_4)_2$. Lorant [4] also confirmed the single-stage course of the oxidation, but with direct formation of $Fe_2O(SO_4)_2$. Gallagher et al. [5], Saphiulin et al. [6] and Skeff Neto and Garg [7] consider that the oxidation is a two-stage process and that it is accompanied by the parallel dehydration of $FeSO_4{\cdot}H_2O$ and decomposition of $FeOHSO_4$ to $Fe_2O(SO_4)_2$.

The aim of the present work is to study the mechanism of the thermochemical decomposition of ferrous sulphate monohydrate in an oxidizing atmosphere and to understand these discrepancies.

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2. Experimental

The investigations were carried out using a MOM-derivatograph (type Q-1500D) under dynamic heating conditions at a heating rate of 5 K min^{-1} in the temperature range 293–1273 K. The sample weight was 1000 mg, with air flowing over the sample at a rate of 25 l h^{-1}. Zirconium crucibles with an internal diameter of 8 mm, a height of 20 mm and a low thermal capacity were used. The initial $FeSO_4 \cdot H_2O$ was produced by a preliminary drying of $FeSO_4 \cdot 7H_2O$ at 353 K in a vacuum of 0.6×10^{-5} Pa. The dried product contained 55.93% SO_4^{2-}, 34.57 Fe^{2+} and 9.5% crystallization water.

The intermediate and end products obtained from the thermochemical decomposition of $FeSO_4 \cdot H_2O$ were analysed by X-ray phase analysis (Phillip's X-ray diffractometer, Germany) and Mössbauer spectroscopy.

The Mössbauer analyses were performed using a standard Mössbauer spectrometer, operating at a constant acceleration of the radioactive source ^{57}Co in Pd. The labelling of the rate scale is given in relation to α-Fe.

3. Results and discussion

Fig. 1 presents the derivatogram of the thermal decomposition of $FeSO_4 \cdot H_2O$ in an oxidizing atmosphere. From an analysis of the TG, DTG and DTA dependences, it is possible to assume a three-stage pattern for the process. The weight loss of 1.9% found up to $T = 545$ K can be explained as the evolution of the moisture absorbed during the treatment of the specimen. A mass loss of 6.6% found in the 545–645 K temperature range of the TG dependences can be assigned to the dehydration of the last water molecule from the monohydrate structure. In the high temperature range (823–1073 K), a desulphurization of the specimen takes place (mass loss, 46.3%).

Along with these clear results, the derivatograph dependences suggest that some other parallel reactions are also taking place, thus making the process rather complicated. Firstly, there are the mass losses, lower than those that are theoretically possible, for the dehydration interval 545–645 K. Secondly, there are the changes observed in the DTA dependence in the temperature range of 680–823 K. All these changes are related to the effect of overlapping of two reactions: the endothermal over the exothermal.

It might be assumed that, in the low temperature range, the oxidation of Fe^{2+} by oxygen from the air, and also the formation of various unstable basic ferrous sulphates, $FeOHSO_4$ and/or $Fe_2O(SO_4)_2$, are possible.

The thermodynamic analysis of the Fe–S–O system and the phase diagram constructed from the results (see Fig. 2) also suggest the formation of $FeOHSO_4$ and/or $Fe_2O(SO_4)_2$ in relation to the values of P_{SO_3}, P_{H_2O} and P_{O_2}. The thermodynamic balance between $FeOHSO_4$ and $Fe_2O(SO_4)_2$ is determined by the reaction:

$$2FeOHSO_4 = Fe_2O(SO_4)_2 + H_2O \tag{1}$$

With balanced values of the partial pressure of the water vapour at $T = 500$ K, both compounds in the system can be produced simultaneously. At $P_{H_2O} > P_{H_2O(balanced)}$, $FeOHSO_4$ is the thermally stable product; at $P_{H_2O} < P_{H_2O(balanced)}$, it is $Fe_2O(SO_4)_2$.

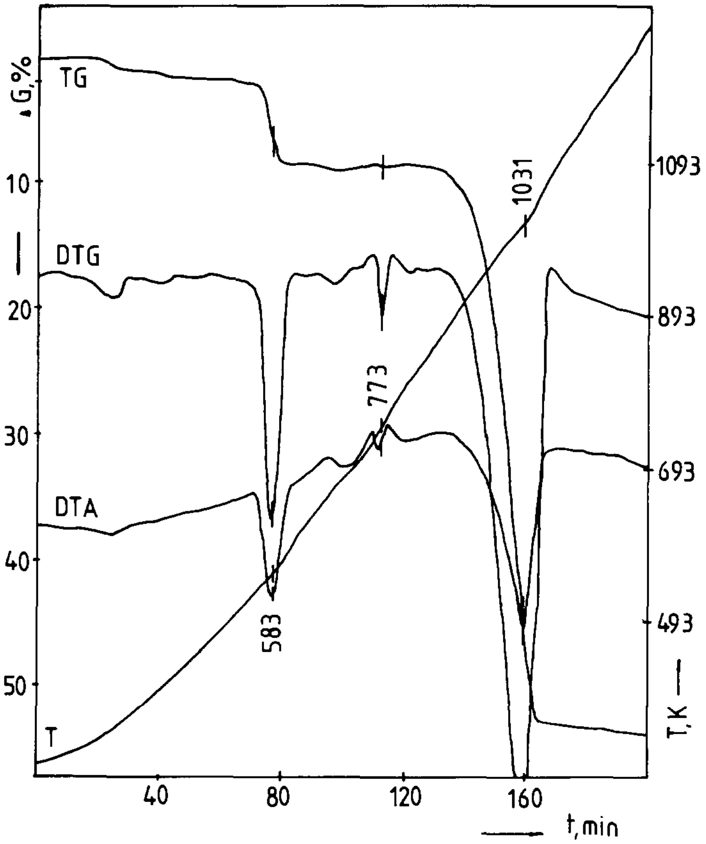

Fig. 1. Derivatogram of the thermal decomposition of $FeSO_4{\cdot}H_2O$ in an oxidizing medium at a heating rate of 5 K min^{-1}.

The changes in the TG, DTA and DTG dependences, as well as the results of the thermodynamic analysis, are a reasonable basis for a study of the intermediate products resulting from the decomposition of $FeSO_4{\cdot}H_2O$ up to $T = 605$ K and $T = 793$ K, analysed by Mössbauer and X-ray spectroscopy (Figs. 3–5 and Table 1).

The results from the X-ray phase analysis prove the existence of a mixture consisting of $FeSO_4{\cdot}H_2O$, $FeSO_4$, $FeOHSO_4$ and $Fe_2O(SO_4)_2$ in the solid decomposition products, which are closely related to the temperature of the process. The oxysulphate was identified with reference to the data from the X-ray analysis reported by Swamy and Prasad [10]. The values for d, Å:3.19; 2.39; 2.28; 1.84, are in full agreement with the reported results [10], but they differ from those published by Saphiulin et al. [6–8].

The Mössbauer spectrum of the solid product, taken from the decomposition process at $T = 605$ K (Fig. 3, curve b and Table 1) presents mainly a combination of two doublets. The first one, with parameters $\delta_{is} = 1.27$ mm s^{-1} and $\Delta E_Q = 2.67$ mm s^{-1}, proves the existence of $FeSO_4$ in the tested sample; the second one, with parameters

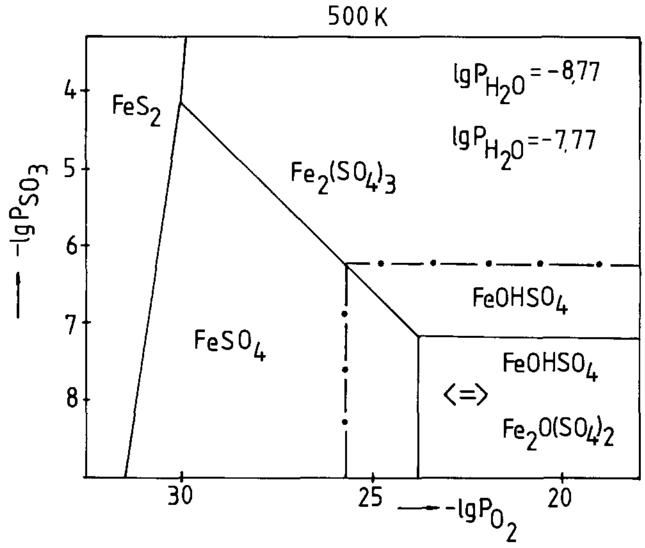

Fig. 2. Phase diagram of the system Fe–S–O at $T = 500$ K.

$\delta_{is} = 0.42$ mm s^{-1} and $\Delta E_Q = 1.43$ mm s^{-1} proves the existence of $FeOHSO_4$, according to the results reported by Bristoti et al. [3], Gallagher et al. [5] and Skeff Neto and Garg [9]. The relative Fe^{3+} percentage from the hydro-oxysulphate, evaluated from its spectrum area, is 63%, which proves that it is the predominant semi-product from the decomposition of $FeSO_4 \cdot H_2O$ in an oxidizing gaseous atmosphere and $T = 605$ K. In addition to these well-defined doublets, on the same spectrum one can also just observe a single line with an isometric displacement close to the zero point. Its intensity in relation to the remaining phases is about 5%. Most probably, with reference to the data available in the literature [3,5,9], this spectrum can be assigned to $Fe_2O(SO_4)_2$.

The distribution of Fe in the solid product as a result of the decomposition at $T = 793$ K is quite different to that at $T = 605$ K (Fig. 3, curve c). The spectrum looks like a slightly broadened single line with isometric displacement $\delta_{is} = 0.41$ mm s^{-1} and width $\Gamma = 0.50$ mm s^{-1} and proves that 87% of the Fe is present as $Fe_2O(SO_4)_2$. The second most intense phase is that of α-Fe_2O_3, about 10% of the Fe; and the third, 3%, is for $FeSO_4$.

The oxysulphate, as well as the remaining forms of the ferrous sulphate, are sensitive to atmospheric moisture, and they hydrate on exposure to air. The Mössbauer spectrum of the same hydrated specimen now presents a doublet (Fig. 3, curve d, Table 1). Probably, the absorbed moisture is bound in the structure of the $Fe_2O(SO_4)_2$ as crystallization water and, as a result of this, there is a split in its spectrum. This is also confirmed by the studies of Bristoti et al. [3]. Our tests do not show, however, the presence of a magnetically split spectrum, which was assigned to $Fe_2O_2SO_4$ by Gallagher et al. [5]. The Mössbauer spectra characterize the intermediate products $FeOHSO_4$ and $Fe_2O(SO_4)_2$ as paramagnetic at ambient temperature.

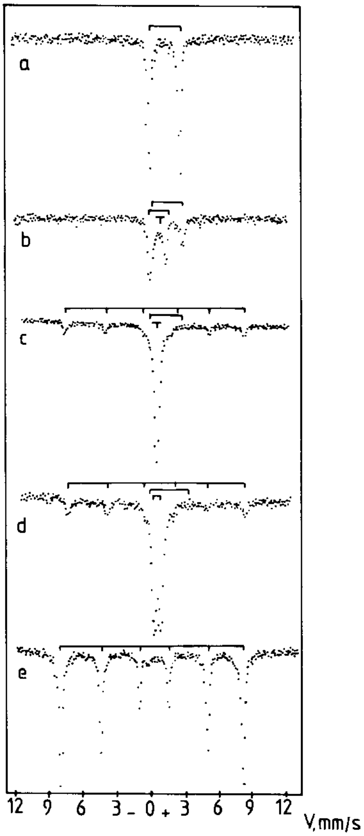

Fig. 3. Mössbauer spectra of the solid products of the decomposition of $FeSO_4{\cdot}H_2O$ at: curve a, initial product; curve b, T = 605 K; curve c, $T = 793$ K; curve d, $T = 793$ K after dehydration and secondary drying; curve e, $T = 1273$ K.

The experimental data confirm the different theories that have been published in the literature for the mechanism of the thermal decomposition of $FeSO_4{\cdot}H_2O$ in oxidizing gaseous atmosphere, with the formation of intermediate compounds (such as $FeOHSO_4$ and $Fe_2O(SO_4)_2$). However, the results provide the basis for determining the process mechanism with evaluation of the gaseous components of the system.

The results from the analysis show that, along with the process of dehydration of $FeSO_4{\cdot}H_2O$ to $FeSO_4$ in the temperature range 545–645 K, another oxidation process of Fe^{2+} to Fe^{3+} is also taking place. It is related to the simultaneous production of $FeOHSO_4$ and $Fe_2O(SO_4)_2$. The amount of the latter is lower and this is explained by the fact that during dehydration of $FeSO_4{\cdot}H_2O$ the value of P_{H_2O} is expected to be higher than the balance value for those temperatures, so that $FeOHSO_4$ is normally produced. With a temperature rise to 763–823 K, $FeOHSO_4$ becomes thermally unstable and is decomposed to $Fe_2O(SO_4)_2$ which is an endothermal reaction. At the

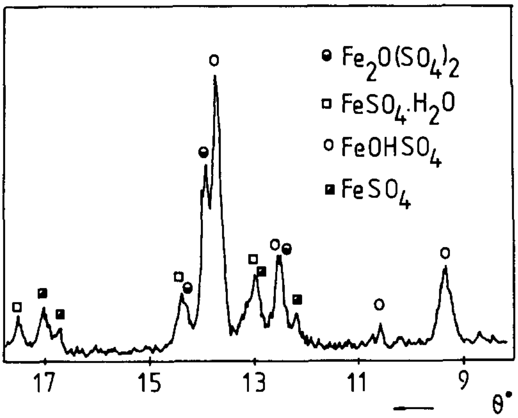

Fig. 4. X-ray pattern of the solid product from decomposition of $FeSO_4 \cdot H_2O$ at $T = 605$ K and a heating rate of 5 K min^{-1}.

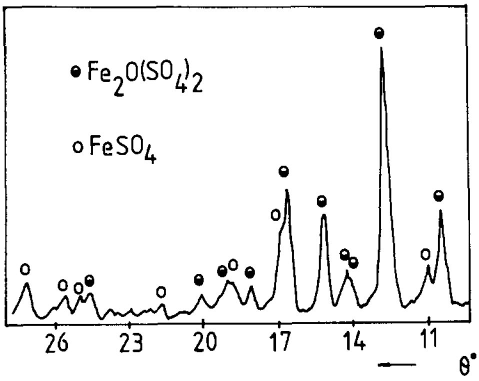

Fig. 5. X-ray pattern of the solid product from decomposition of $FeSO_4 \cdot H_2O$ at $T = 793$ K and a heating rate of 5 K min^{-1}.

same time, a second stage is taking place, that of oxidation of Fe^{2+} to Fe^{3+}, i.e. the direct transformation of $FeSO_4$ in $Fe_2O(SO_4)_2$, an exothermal reaction. The simultaneous progress of both reactions leads to an overlapping of their effects in the DTA dependences and also to compensation and insignificant integral change of the weight losses. Thus, in the system with $T = 823$ K, Fe is mainly in the form of $Fe_2O(SO_4)_2$. This is probably more unstable than the ferrous sulphate and the initial destruction of its structure explains the presence of some quantities of α-Fe_2O_3, even at $T = 793$ K (Fig. 3, curve c).

The latter results definitely show that the quantity and thermal stability of $FeOHSO_4$ and $Fe_2O(SO_4)_2$ are defined not only by the temperature, but also by the ratio between the partial pressures of the gaseous components, the water vapour and

Table 1
Results for the intermediate products from the thermal decomposition of $FeSO_4{\cdot}H_2O$, analysed by Mössbauer spectroscopy and X-ray analysis

No	T/K	Parameters			Fe^{n+}	Quantity of Fe^{n+}/%	Identified phases from	
		δ_{is} mm s^{-1}	ΔE_Q/ mm s^{-1}	H_{eff}/ kOe			Mössbauer spectroscopy	X-ray diffraction
1	298	1.18	2.67	–	Fe^{2+}	100	$FeSO_4{\cdot}H_2O$	$FeSO_4$ $FeSO_4{\cdot}H_2O$
2	605	1.27	2.75	–	Fe^{2+}	32	$FeSO_4$	$FeSO_4{\cdot}H_2O$,
		0.42	1.43	–	Fe^{3+}	63	$FeOHSO_4$	$FeOHSO_4$,
		0.40	–	–	Fe^{3+}	5	$Fe_2O(SO_4)_2$	$Fe_2O(SO_2$, $FeSO_4$
3	793	0.44	–	–	Fe^{3+}	87	$Fe_2O(SO_4)_2$,	$Fe_2O(SO_4)_2$,
		0.40	0.42	516	Fe^{3+}	10	α-Fe_2O_3	$FeSO_4$
		1.12	2.67	–	Fe^{2+}	~3	$FeSO_4$	
4	793	0.33	0.61	–	Fe^{3+}	87	$Fe_2O(SO_4)_2{\cdot}xH_2O$	–
		0.40	0.42	516	Fe^{3+}	10	α-Fe_2O_3	
		1.35	3.27	–	Fe^{2+}	~3	$FeSO_4{\cdot}xH_2O$, $\alpha = 4–7$	
5	1273	0.40	0.42	516	Fe^{3+}	100	α-Fe_2O_3	α-Fe_2O_3

oxygen, in the reaction tract. The variations in the values of P_{O_2}/P_{H_2O} are the result of dissimilarities in the equipment used; however, they are also related to the ongoing dehydration of $FeSO_4{\cdot}H_2O$. All this explains the changes in the content of the basic ferrous sulphates in the solid phase. From this point of view, the different and quite diverse conclusions of various authors [2,3,5,6,11] can be easily explained. The production of only $FeOHSO_4$, or $Fe_2O(SO_4)_2$ obviously requires the maintenance of strictly defined test conditions for temperature, and P_{O_2} and P_{H_2O}, and their transport in and out of the system.

On the basis of the quantitative results obtained from the thermogravimetric and spectroscopic investigations, the following mechanism can be proposed for the thermal decomposition of ferrous sulphate monohydrate in an oxidizing medium:

I. Dehydration with partial oxidation, 563–605K

$$3FeSO_4{\cdot}H_2O = 3FeSO_4 + 3H_2O - Q \tag{2}$$

$$2FeSO_4{\cdot}H_2O + 0.5O_2 = 2FeOHSO_4 + H_2O - Q \tag{3}$$

$$FeSO_4{\cdot}H_2O + 0.25O_2 = 0.5Fe_2O(SO_4)_2 + H_2O - Q \tag{4}$$

II. Intermediate partial oxidation of Fe^{2+} to Fe^{3+}, 683–800K

$$2FeSO_4 + 0.5O_2 = Fe_2O(SO_4)_2 + Q \tag{5}$$

$$2FeOHSO_4 = Fe_2O(SO_4)_2 + H_2O - Q \tag{1}$$

III. Desulphurization, 823–1073K

$$2.5Fe_2O(SO_4)_2 = 2.5Fe_2O_3 + 5SO_2 + 2.5O_2 - Q \quad (6)$$

$$FeSO_4 = 0.5Fe_2O_3 + SO_2 + 0.25O_2 - Q \quad (7)$$

4. Conclusions

From the obtained test data, a new mechanism is proposed for the thermal decomposition of $FeSO_4 \cdot H_2O$ in an oxidizing gaseous medium. It is a complex three-stage process of dehydration, intermediate oxidation and desulphurization. The mechanism of this process is described by a complex of seven possible reactions. A process of oxidation of Fe^{2+} to Fe^{3+} in two stages was confirmed. The ratio of the speeds of the reactions running in parallel is mainly determined by the temperature and the ratio between the partial pressures of water vapour and of oxygen. Depending on their values, it is possible to obtain intermediate products with different phase ratios.

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