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STUDY OF THERMAL DECOMPOSITION OF $FeC_2O_4.2H_2O$

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SUMMARY

Thermal decomposition of $FeC_2O_4.2H_2O$ was investigated in air, oxygen and inert atmosphere, using DTA, TGA, Mössbauer spectroscopy and X-ray phase analyses. The temperatures of dehydration and decomposition, the types of the end products and the conditions of α-Fe_2O_3 production by oxalate decomposition were determined.

INTRODUCTION

Thermal decomposition of $FeC_2O_4.2H_2O$ has been the subject of a number of investigations /1-5/. Although the obtained and generalized results are rather contradictory /6/, the conclusion may be drawn, that the thermal effects and types of the end products are substantially influenced by the atmosphere, the rate of heating, the quantity of the sample and the final temperature of heating. It is the aim of the present study of $FeC_2O_4.2H_2O$ decomposition to clarify the effect of those factors and to establish the conditions of producing α-Fe_2O_3 by oxalate decomposition.

MEASURING METHODS

DTA and TGA were carried out by the help of "Derivatograph Q" (Hungary). Samples of 0,25, 0,50 and 0,75 g were used in air, oxygen and nitrogen atmosphere at 5^o/min., 10^o/min and 20^o/min. rate of heating. The X-ray phase investigations were carried out on X-ray difractometer TUR M62 (GDR). Mössbauer spectra were taken on a standard Mössbauer spectrometer, operating in a regime of constant acceleration and were computed. The isomeric shift (IS) was determined with respect to metal Fe. Magnetic measurements were carried out by the help of a magnetic balance.

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RESULTS AND DISCUSSION

The derivatograms, obtained for $FeC_2O_4.2H_2O$ decomposition in air and oxygen atmosphere, are of one and the same type, but in oxygen atmosphere the mentioned effects have 5-25° lower values. A part of the obtained results are presented in Table 1.

Table 1

Differential and thermal analysis of $FeC_2O_4.2H_2O$

No	Atmosphere	Peaks, °C			Products of decompos.	References
		I	II	III		
1	air	~200(-)	~230(+)		Fe_2O_3	1
2	air		~220(+)		70% FeO+ +Fe_2O_3	2
3	air	225(-)	365(+)	485(+)	α-Fe_2O_3	our data
4	oxygen	~200(-)	~230(+)		Fe_2O_3	1
5	oxygen	220(-)	360(+)	460(+)	α-Fe_2O_3	our data
6	nitrogen	250(-)	450(-)		Fe_3O_4+Fe	1
7	argon		384(-)		>93% FeO	2
8	nitrogen	225(-)	425(-)		Fe,Fe_3O_4,Fe	our data

In contrast to references/6/ the carried out investigations show the existence of two distinct exoeffects. The first exoeffect is related to weight loss and the second to an increase, which shows that a more pronounced sequence of the completion of the thermal processes is observed. The endoeffect at 225°C is due to $FeC_2O_4.2H_2O$ dehydration. In quasi isobaroisothermal conditions the determined temperature of dehydration of the studied $FeC_2O_4.2H_2O$ is 187°C. Up to 350°C decomposition of the obtained FeC_2O_4 takes place though to a lower degree. FeC_2O_4 and some Fe_3O_4 are obtained when heating the initial $FeC_2O_4.2H_2O$ up to 350°C, which is proved by X-ray phase analysis. The process of decomposition proceeds up to ~460°C, and in isobaroisothermal conditions - at 378°C.

The probable mechanism of $FeC_2O_4.2H_2O$ thermal decomposition may be described by the following equations on the grounds of the results from DTA, TGA and X-ray phase analysis:

$FeC_2O_4 \cdot 2H_2O \longrightarrow FeC_2O_4 + 2H_2O$ (1)

$FeC_2O_4 \longrightarrow FeO + CO_2 + CO$ (2)

$4FeO \longrightarrow Fe_3O_4 + Fe$ (3)

$2Fe_3O_4 + 0{,}5O_2 \longrightarrow 3Fe_2O_3$ (4)

$2Fe + 1{,}5O_2 \longrightarrow Fe_2O_3$ (5)

CO oxidation, according to eq.(2) and Fe_3O_4 and Fe oxidation according to eq.(4) and eq.(5), leads to the appearance of the two exoeffects of the derivatograms.

The descrepancy between the obtained results and the previously published ones is, according to us, due to the different rate of heating and the different quantities of the samples. When the rate of heating (5°/min.) and the weight of the sample (0,25 g) are decreased, an exoeffect is observed at 300–400°C.

It was established by the help of X-ray analysis and Mösbauer spectroscopy, that the pure phase α-Fe_2O_3 is obtained at temperatures above 600°C. At temperatures below 500°C mainly the phases Fe_3O_4 and γ-Fe_2O_3 are observed, their ratio depending mainly on the temperature and oxygen content of the atmosphere.

In nitrogen atmosphere the taken derivatograms show the presence of two distinctly pronounced endoeffects, related to dehydration and decomposition of $FeC_2O_4 \cdot 2H_2O$. The X-ray analysis shows the presence mainly of FeO and less Fe_3O_4 and Fe. FeO disproportionates to Fe_3O_4 and Fe, which are the end products of $FeC_2O_4 \cdot 2H_2O$ decomposition in inert atmosphere and vacuum. The FeO phase /2,4/ is observed in certain conditions.

The results of Mössbauer spectroscopy of the initial oxalate and the decomposition products are presented in Table 2.

Table 2

Results of Mössbauer measurements of the samples

No	Compound	Isomeric shift, mm/s	Quadrupole splitting, mm/s	Intrinsic magnetic field, kOe
1	$FeC_2O_4 \cdot 2H_2O$	1,180±0,005	1,724±0,005	0
2	γ-Fe_2O_3	0,388±0,005	0,164±0,005	499,2±0,5
3	α-Fe_2O_3	0,437±0,005	-0,269±0,005	515,3±0,5

Phases Fe_3O_4, γ-Fe_2O_3 and an unidentified compound are observed in the obtained Mösbauer spectrum when $FeC_2O_4.2H_2O$ is heated at limited air access, which is, most probably, a non-stechiometric FeO.

CONCLUSIONS

The processes of dehydration and decomposition of $FeC_2O_4.2H_2O$ are carried out consecutively at the temperatures of 187°C and 378°C. α-Fe_2O_3 is produced in an oxidizing atmosphere. In an inert atmosphere the end products are FeO, Fe and Fe_3O_4. Mössbauer investigations show, that at limited air access mainly Fe_3O_4 and some γ-Fe_2O_3, as well as an unidentified third phase of small quantity are produced in the decomposition of $FeC_2O_4.2H_2O$.

The transition γ-Fe_2O_3 —— α-Fe_2O_3 is investigated by the help of differential and thermal analyses and magnetic measurements. The temperatures of transition for the two methods are 510°C and 520°C, respectively.

Pure γ-Fe_2O_3 could be obtained by $FeC_2O_4.2H_2O$ decomposition controlling the oxygen content of the atmosphere and temperature lower than 500°C. The process could be carried out in two stages, too: production of Fe_3O_4 and its oxidation to γ-Fe_2O_3.

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