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DERIVATOGRAPHIC STUDY OF CoOOH DECOMPOSITION

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ABSTRACT

The thermal decomposition of $CoOOH(H_2O)_{0.1} \cdot 0.025\ Co(OH)_2$ material was investigated derivatographically up to 500 °C in air and in N_2. The reaction proceeds in three stages: separation of the non-stoichiometrically bonded water (20–220 °C), decomposition of $Co(OH)_2$ (220–252 °C) and CoOOH decomposition (244–312 °C). The effect of impurities on the last stage is discussed.

INTRODUCTION

In refs. 1 and 2 we investigated the kinetics and the mechanism of CoOOH decomposition. The experiments were facilitated by a detailed derivatographic analysis of the initial material in order to elucidate the thermal behaviour of the phase CoOOH which it contained. It was considered more expedient to make a separate report on the data obtained in this analysis.

The following considerations justify such a decision. The thermoanalytical curves of CoOOH decomposition have been insufficiently studied. They are either only partially dealt with[3,4] or do not constitute the main object of the relevant studies[5,6]. As will be shown here, only the simultaneous representation of the four thermoanalytical curves (TG, DTG, DTA, T) and their comparison can lead to a deeper insight in the general evolution of the process. Furthermore, CoOOH is usually not the only phase in the initial material but is accompanied by small but detectable amounts of $Co(OH)_2$ and by non-stoichiometrically bonded water. This makes it necessary to elucidate the relationship between these three compounds during the general decomposition and their effect on the basic process of CoOOH decomposition which can be studied by appropriate derivatography.

EXPERIMENTAL

Materials and methods

The characteristics of the material with an approximate composition $CoOOH(H_2O)_{0.1} \cdot 0.025\ Co(OH)_2$ have been described[1]. The derivatographic unit has been given elsewhere[7]. Heating rates employed were 3 and 6 °C min^{-1}; DTG, DTA and TG sensitivities, 1/5, 1/5 and 200 mg, respectively. The experiments

were carried out in static air atmosphere and in dry nitrogen (99.99%) with a flow-rate of 30 ml min^{-1}.

RESULTS AND DISCUSSION

The character of a given decomposition can be properly understood by studying the effect of several factors on it during its derivatographic investigation. In the present case two such factors were selected: heating rate and atmosphere. The effect of the latter on the evolution of a reaction, which can be most generally described as $A_s \rightarrow B_s + C_g$, may acquire great importance, particularly in the case of transition metal compounds[8-11].

Larger samples (about 800 mg) were used in order to elucidate the effect of the impurity phases on the basic process of CoOOH decomposition. The thermal behaviour of $Co(OH)_2$ and of the non-stoichiometrically bonded water was recorded on the derivatograms of these samples.

The derivatograms shown in Fig. 1 and particularly in Fig. 2 clearly delineate the existence of three stages in the decomposition of the initial material in the temperature range 20–500 °C.

The portion AB from 20 to 220 °C on the TG curve shows a slight and gradual decrease in weight for a rather long period of time. It was established analytically that this is due to the release of water only[1]. The absence of a pronounced peak on the differential curves in this region indicates the absence of

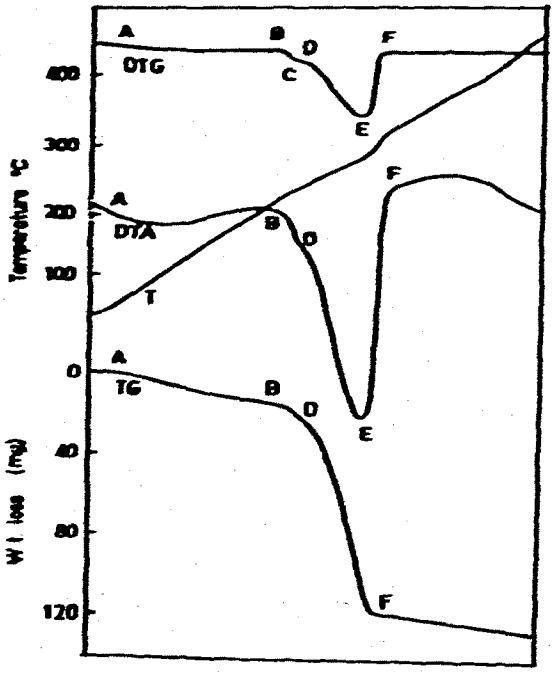

Fig. 1. Derivatogram for $CoOOH(H_2O)_{0.1} \cdot 0.025\ Co(OH)_2$ in air. Heating rate 3 °C min^{-1}.

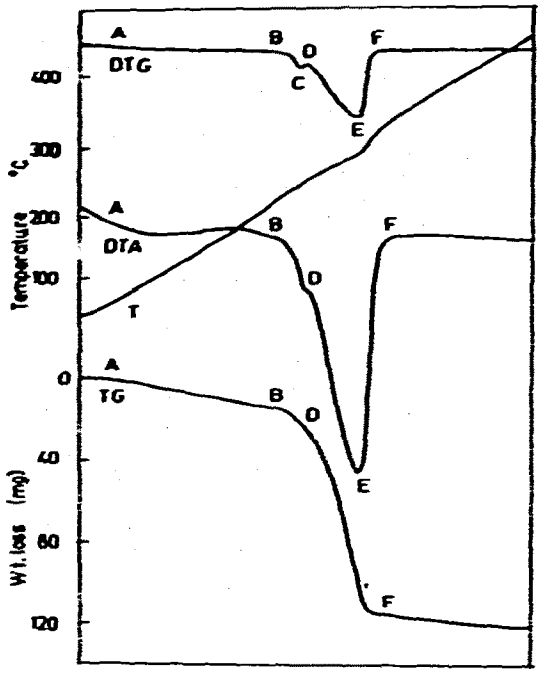

Fig. 2. Derivatogram for $CoOOH(H_2O)_{0.1} \cdot 0.025\ Co(OH)_2$ in N_2. Heating rate 3 °C min^{-1}.

an abrupt qualitative change at a strictly determined temperature and shows that his water is physically bonded (adsorption and capillary).

A small but well-defined peak appears on the DTG curve in N_2 in the region BCD from 220 to 252 °C (Fig. 2). Its small size as well as the insignificant change in this region on the TG curve testify to a minor process at a well determined temperature, which leads to a chemical transformation. This process is considerably weaker on the DTG curve recorded in air (Fig. 1), thus revealing its dependence on the oxidizing atmosphere. The same stage can be identified on the DTA curves of the two figures by the presence of an inflexion in the same region (point D) which is more pronounced in N_2. This goes to show that the thermal effect of this process, just as the weight loss, is less in an oxidizing atmosphere.

These facts can be easily explained by taking into account the chemical composition of the initial material, in particular the presence of a certain amount of $Co(OH)_2$ which decomposes in approximately the same temperature range[12,13], according to the equations

in air

$$6\,Co(OH)_2 + O_2 \rightarrow 2\,Co_3O_4 + 6\,H_2O \qquad (1)$$
$$(\text{theor. } \Delta m = 13.66\,\%)$$

in N_2

$$Co(OH)_2 \rightarrow CoO + H_2O \qquad (\text{theor. } \Delta m = 19.36\,\%) \qquad (2)$$

At that, the thermal effect of the first reaction is smaller, as in this case it constitutes the algebraic sum of the endothermic effect of dehydration and of the exothermic effect of partial oxidation of Co(II) to Co(III) accompanying the formation of Co_3O_4.

Upon further heating in the temperature range 244–312 °C, a sharp peak appears on all three curves (Figs. 1 and 2). The main CoOOH decomposition proceeds according to the equation

$$12\,CoOOH \rightarrow 4\,Co_3O_4 + 6\,H_2O + O_2 \qquad (3)$$

The gaseous products of this reaction were identified chemically on runs made under the same temperature conditions and the solid ones by X-ray diffraction.

As regards its mechanism, this reaction is the result of two major physicochemically different solid-state processes: a proton transfer

$$OH^- + OH^- \rightarrow H_2O + O^{2-} \qquad (3')$$

an electron transfer

$$2\,Co^{3+} + O^{2-} \rightarrow 2\,Co^{2+} + O \qquad (3'')$$

due to the partial reduction of Co(III) to Co(II) in the formation of Co_3O_4.

The two derivatograms and particularly the differential curves suggest that these two processes take place in one stage, i.e., simultaneously on a macroscopic scale. Derivatographic investigations confirm unambiguously the simultaneous release of H_2O and O_2 according to reaction (3). This finding, verified volumetrically[1], was made use of in refs. 1 and 2. On the other hand, the pronounced endothermic effect of the reaction, which constitutes the sum of the endothermic effects of the above two major processes, is reflected by the strong endothermic peak on the DTA curves. A comparison of the two derivatograms shows that reaction (3) is not affected by the presence of an oxidizing atmosphere (air). The slight decrease after the main stage on the TG curves, which is not reflected on

TABLE 1

DERIVATOGRAPHIC RESULTS OF $CoOOH(H_2O)_{0.1} \cdot 0.025\ Co(OH)_2$ IN N_2

Decomposition transition	*Range of temp. (°C)*	*DTG peak temp. (°C)*	*DTA peak or inflection temp (°C)*	*Weight loss %*	
				Exp.	*Theor.*
$CoOOH(H_2O)_{0.1} \cdot 0.025\ Co(OH)_2 \rightarrow$ $\rightarrow CoOOH \cdot 0.025\ Co(OH)_2 + 0.1\,H_2O$	20–220	—	—	1.85	1.87
$CoOOH \cdot 0.025\ Co(OH)_2 \rightarrow$ $\rightarrow CoOOH + 0.025\ CoO + 0.025\ H_2O$	220–252	246	250	1.00	0.48
$12\ CoOOH \rightarrow 4\ Co_3O_4 + 6\ H_2 + O_2$	244–312	290	290	11.68	12.43

the differential curves, is attributed to the slow release of the last portions of gas from the solid reaction product.

The results of the derivatographic analysis are summarized in Table 1 for the case in N_2.

The calculated weight losses during the different stages support the suggested course of the process. The partial slight overlapping of the second and the third stage explains the small differences between the experimental and the calculated values of the weight losses.

The derivatograms recorded at a heating rate of 6 °C min^{-1} have the same shape. On derivatograms of 160 mg samples the second stage remains unnoticeable[2], as it proceeds to a minor degree.

CONCLUSION

The results of the derivatographic analysis of $CoOOH(H_2O)_{0.1} \cdot 0.025\ Co(OH)_2$ permit a deeper insight into the relationship between the three phases of this material during its thermal decomposition. The presence of non-structurally bonded water, which is apparent when comparing the thermoanalytical curves of the first stage, is quite well reflected by the formula proposed by Schrader and Petzold[5], $CoOOH(H_2O)_{>0\text{ to }1}$, which takes into account the difference between the non-structural and the constitutional water in the compound. We succeeded in eliminating the major portion of the former by heating the initial material at 210 °C for 20 min. This did not affect the course of reaction (3)[1].

All CoOOH synthetic samples obtained so far[3-6,14] contain a certain amount of Co(II) identifiable by ordinary analytical techniques. The stoichiometric ratio Co:O (oxidation number of Co) is used as a measure of this content. Theoretically, in the absence of Co(II), this ratio should be 1:1.5. In our material its value was 1:1.488. Schrader and Petzold[6] merely admitted the possibility that in some cases the decomposition of the impurity $Co(OH)_2$ might appear on the differential thermoanalytical curves of the CoOOH decomposition. Our investigations in air and in N_2 may be said to prove derivatographically the presence of a $Co(OH)_2$ impurity in CoOOH and its independent decomposition according to eqns (1) and (2), depending on the operating conditions. The thermal decomposition of $Co(OH)_2$ proceeds, therefore, in this case at a much higher rate than its oxidation to CoOOH according to the equation

$$4\,Co(OH)_2 + O_2 \rightarrow 4\,CoOOH + 2\,H_2O \qquad (4)$$

which takes place under different conditions[15].

The important problem of the nature of this impurity remains, however, still unsolved. Indeed, it is not known whether $Co(OH)_2$ is a heterophase in the CoOOH crystals or whether Co^{2+} partly replaced Co^{3+} in the CoOOH lattice, thus forming a substitutional solid solution[5]. The elucidation of this problem is of considerable importance[16] for understanding the effect of the $Co(OH)_2$ impurity on

the kinetics and the mechanism of CoOOH decomposition. In the former case this phase may be expected not to affect essentially the CoOOH decomposition, because of its small amount. In the presence of a solid solution, however, the Co^{2+} ions, even in a very small amount, will tend to deform considerably the CoOOH lattice and may, therefore, strongly affect its decomposition. Although this problem cannot be unambiguously solved within the framework of this study, some facts suggest a probable conclusion. The existence of an independent region of decomposition of $Co(OH)_2$ on our derivatograms and the very small amount of sample (0.025 mol) make its existence as a discrete phase more logical than as a solid solution. This opinion is supported by thermoanalytical investigations of some solid carbonate[17] and hydroxide[18] solid solutions which, judging by their corresponding thermoanalytical curves, behave as a single phase. This stresses an additional advantage of derivatography, i.e., its possible use as a direct visual criterion of the formation of solid solutions. Until now this could be done only by X-ray diffraction experiments.

The problem of the effect of the Co(II) impurity on CoOOH decomposition calls for additional studies, in particular on CoOOH that does not contain this impurity, provided that such samples can be obtained. In this context it is interesting to note that natural CoOOH known as the mineral stainiérite (86.8% CoOOH) does not contain Co(II)[6].

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