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KINETIC STUDY OF THERMAL DECOMPOSITION OF CoOOH

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ABSTRACT

The kinetics of the thermal decomposition of CoOOH powder has been studied isothermally in a temperature range of 260–310°C in air. The reaction was found to proceed by the advance of a two-dimensional reaction interface. The kinetics results indicate that there are two phases in the decomposition in this temperature range: up to 280°C with an activation energy $E_1 = 34.75$ kcal mol^{-1} and above 280°C with $E_2 = 18.91$ kcal mol^{-1}. A reaction mechanism is proposed to account for these observations.

INTRODUCTION

In the past 50 years a number of papers have appeared on the Co(III)–hydroxide system[1]. The interest in this compound is not accidental, for it involves a small number of stable simple compounds of trivalent cobalt, which is also its most stable hydroxide[2] occurring in nature in the form of various minerals[3]. Considerable light on the properties and structure of the CoOOH phase has been shed recently by Schrader and Petzold[1,3-5]. However, the process of the thermal decomposition[6]

$$12\text{CoOOH} \rightarrow 4\text{Co}_3\text{O}_4 + 6\text{H}_2\text{O} + \text{O}_2 \qquad (1)$$

and, more in particular, its kinetics and mechanism on which there are no literature data have not yet been properly studied. However, this reaction is important not only as a basic property of CoOOH but also with a view to its product, i.e., as a process of spinel formation leading to the obtainment of Co_3O_4, which is an excellent catalyst of many chemical processes and, moreover, is widely used in modern semiconductor technique.

A study of the kinetics and mechanism of this process seemed therefore appropriate and, this is the purpose of this work.

EXPERIMENTAL

Material

A commercial product (VO/Sojuzchimexport, U.S.S.R., grade č) was used, which was subjected to chemical analysis. The cobalt was determined gravimetrically[7], Co(III) by iodometric titration[8], and H_2O by absorption in P_2O_5 after thermal decomposition. The composition (wt. %): Co, 62.70; Co(III), 61.20; and H_2O, 11.56; which corresponds approximately to the formula $CoOOH \cdot 0.1\ H_2O \cdot 0.025\ Co(OH)_2$ (theor. wt. %: Co, 62.88; Co(III), 61.37; H_2O, 11.71). The presence of a small quantity of Co(II) is inevitable in all CoOOH samples[1,9]. The weight loss (%) on ignition between 250 and 600°C in air was 14.64 (theor. 14.35).

X-Ray analysis

The sample Debyegram (apparatus TUR-M60, Co-K_α-radiation) showed a crystal structure corresponding to the CoOOH phase[9,10]. The solid product was identified as Co_3O_4. Since thermal dissociation is one of the structure-sensitive properties of the solid state, it is of the utmost importance to obtain information on the state of the crystal lattice of the initial CoOOH. Its diffractogram (Fig. 1) suggests a semi-recrystallized CoOOH lattice form[1].

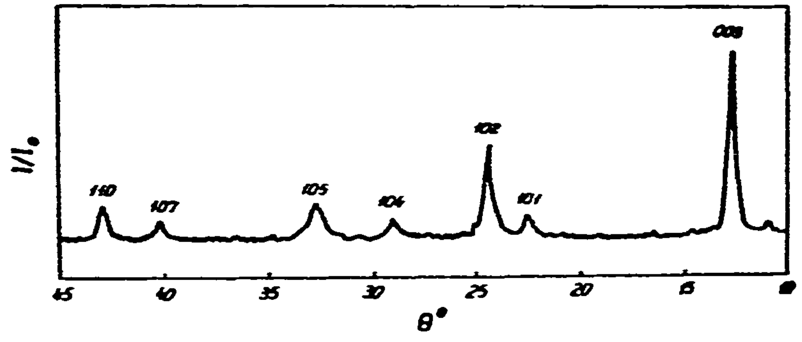

Fig. 1. CoOOH diffractogram (apparatus TUR-M61, Fe-K_α-radiation, rotation rate: 1° min^{-1}) after heating at 210°C for 20 min.

Electron microscopy

The samples, prepared by means of a carbon-platinum technique, were photographed with a D2-Zeiss instrument (× up to 12,000). The CoOOH powder consists chiefly of disc-like particles with an average $\phi \sim 4$–$5\ \mu m$ and an uneven surface.

Thermal decomposition apparatus

The apparatus for isothermal gravimetric study has been described elsewhere[11]. The volumetric investigations of the O_2 formed by reaction (1) were made according to Berg[12] by the absorption of H_2O with P_2O_5.

RESULTS

The kinetic study was made gravimetrically, proceeding from the well-known fact (confirmed by us volumetrically) that H_2O and O_2 separate simultaneously by eqn (1). The presence of even the small quantity ($\sim$0.1 mole) of non-stoichiometric

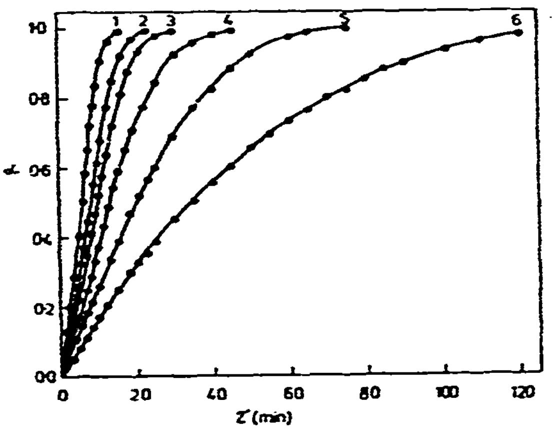

Fig. 2. Thermal decomposition curves for CoOOH. 1 = 310°C; 2 = 300°C; 3 = 290°C; 4 = 280°C; 5 = 270°C; and 6 = 260°C. Sample weight = 1 g.

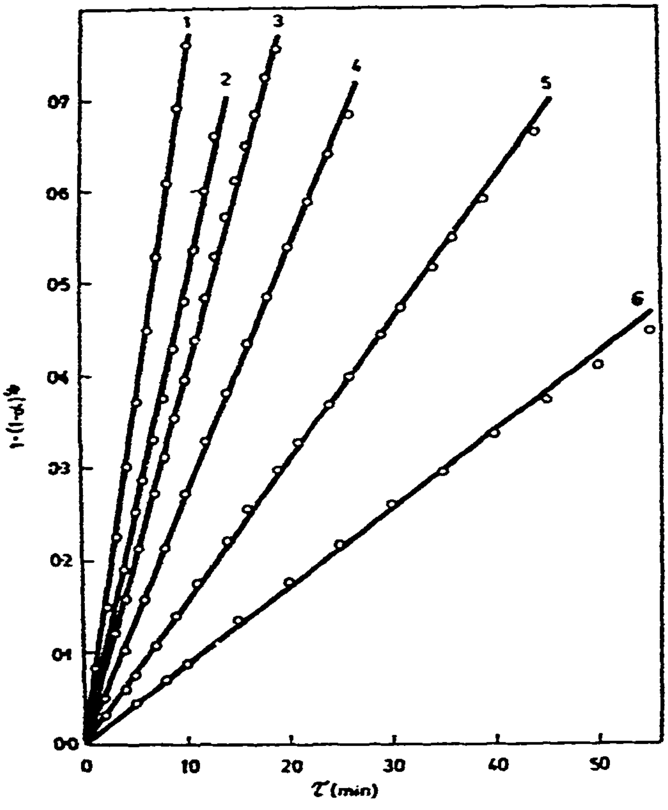

Fig. 3. Plots of eqn (2). 1 = 310°C; 2 = 300°C; 3 = 290°C; 4 = 280°C; 5 = 270°C; and 6 = 260°C.

bound water in the initial CoOOH may affect the initial period of the kinetic curves. In order to avoid this, the samples were heated beforehand up to 210°C for 20 min, during which most of the non-stoichiometrically bound water was removed without the onset of decomposition by eqn (1), as was established volumetrically.

Typical gravimetric decomposition curves for CoOOH are shown in Fig. 2, where the degree of decomposition α is calculated as a ratio of weight loss during time τ to final weight loss. The shape of the curves is not sigmoid and the reaction tends to be deceleratory throughout. A correction was made of the non-isothermal period during the first 1–3 min by extrapolating the straight sector of the curves to their intersection with the abscissa. Several kinetic laws were tested to obtain the best fit to these results. The most satisfactory one is given by a 'contracting-circle' law, which is obeyed for $0.00<\alpha<0.90$ (at 260°C, $0.00<\alpha<0.70$). The kinetics of the decomposition according to this model should follow the equation (Fig. 3)

$$1-(1-\alpha)^{\frac{1}{2}}=K\tau \tag{2}$$

where α is the degree of decomposition; the constant $K=k/a$; k (cm min^{-1}) is the rate constant; a is the initial mean radius of the circled particles; τ is the time.

The activation energy is determined as usual from the Arrhenius plot (Fig. 4). The graph shows a change in the slope at 280°C. Two values for activation energy have correspondingly been calculated: up to 280°C, $E_1=34.75$ kcal mol^{-1} and above 280°C, $E_2=18.91$ kcal mol^{-1}. An analogous character of the Arrhenius plot was found when the ordinates are taken from the initial linear decomposition rate (Fig. 2), as well as when other less suitable kinetic equations are used.

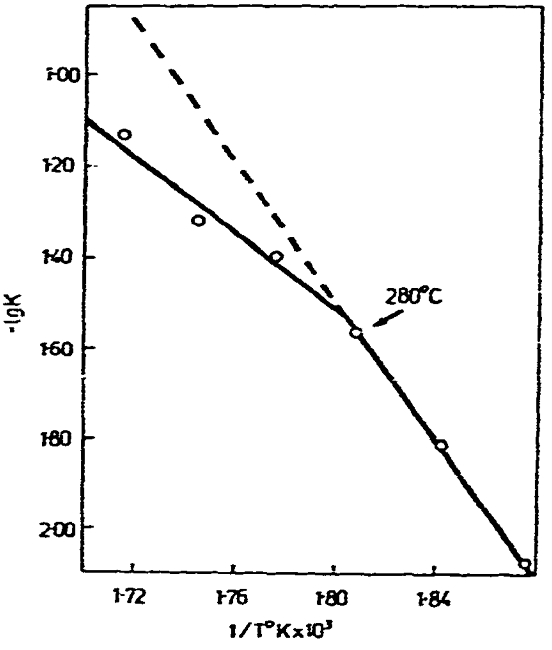

Fig. 4. Arrhenius plot for CoOOH decomposition, using eqn (2).

DISCUSSION

Modern conceptions about the nature of the thermal decomposition of solids are chiefly based on the theory of the nucleation and growth of a new phase. When studying the mechanism of this process, it is important to determine the rate-controlling step in the chain of the numerous stages through which it passes. In our case the absence of an induction period, which was found in all the kinetics experiments (Fig. 2), showed that the nucleation of the new phase proceeds quickly and relatively without hindrance and consequently cannot be the rate-controlling step of the general process. This is also confirmed by crystallographic considerations. Analogous to the decomposition of $Mg(OH)_2$[13], reaction (1) may be supposed to represent one of the simplest examples of a solid decomposition reaction, since both reactant and product possess only one known crystal structure and the conversion of the hexagonal hydroxide lattice to the cubic oxide lattice (Co_3O_4) represents a fairly simple crystallographic transformation. On the other hand, the presence of a semi-recrystallized CoOOH lattice (Fig. 1), which may be considered richer in strains and defects, should promote nucleation.

Thus, our kinetic results of the thermal decomposition of CoOOH are consistent with a reaction mechanism, in which the rate process is controlled by the movement of an interface reaction. Crystals undergoing this type of decomposition have been represented by "contracting circle" and "contracting sphere" models[14]. Our microscopic studies, as well as the fact that CoOOH belongs to the brucite type with a CdJ_2 layer lattice, made the first model more logical[15]. The fit of this model to reaction (1) is not unexpected, as this type of kinetic behaviour is exhibited by a number of other structurally similar hydroxides ($Mg(OH)_2$[13,16], $Al(OH)_3$[16], $Fe(OH)_2$[15], $Co(OH)_2$[15] and $Ni(OH)_2$[15]).

The interface reaction consists of a number of separate physicochemical processes in solids. Besides the proton transfer ($2OH^- \rightarrow H_2O+O^{2-}$) and H_2O escape from the crystal, typical of the decomposition of every hydroxide[17], in this case there is also an electron transfer ($2Co^{3+}+O^{2-} \rightarrow 2Co^{2+}+\frac{1}{2}O_2$) with O_2 removal, as a result of the partial reduction of Co(III) to Co(II), which is specific of CoOOH dehydration. It is quite logical for this typical feature of the process to be reflected in some way on its kinetics, as was also confirmed by our results. The Arrhenius plot (Fig. 4) shows a certain change in the kinetics of the reaction at higher temperatures (above 280 °C) with the accepted kinetic law remaining in force (Fig. 3). It follows that the difference should be referred to the mechanism of the interface reaction. The considerably higher value of the activation energy (34.75 kcal mol^{-1}) for the period up to 280 °C in comparison with that of the above-mentioned hydroxides should be attributed to the presence of an electron transfer in the general course of the interface reaction. At higher temperatures (above 280 °C), however, with an increase of the decomposition rate, the rapid escape of H_2O between the layers of the CoOOH lattice, which has a highly pronounced layer structure[18], is increasingly impeded. Dehydration thereby begins to produce a predominant effect on the kinetics. As a result, the value of the activation energy drops (18.91 kcal mol^{-1}) and approximates that (18.75 kcal $mole^{-1}$) of the thermal dissociation of $Co(OH)_2$[17], which crystallographically is very close to CoOOH[9]. Proceeding from these considerations, it may be concluded that the kinetics of the process at temperatures below 280°C, including also the electron transfer, expresses more fully the thermal decomposition of CoOOH.

The proposed kinetic model, based on some experimentally established facts, offers a probable explanation of the mechanism of the investigated process by associating it kinetically with the group of hydroxides in general, while at the same time expressing its specificity.

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