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DTA STUDY OF RuO_2 FORMATION FROM THE THERMAL DECOMPOSITION OF RUTHENIUM(III) HYDRATE

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ABSTRACT

Ruthenium(III) hydrate has been precipitated in aqueous solution from the soluble hydrated $RuCl_3$. The thermal behavior of ruthenium(III) hydrate has been investigated by DTA and TG in air and in nitrogen. The compound undergoes a disproportionation reaction between 100 and 150°C yielding Ru(metal)$+RuO_2 \cdot xH_2O$. In nitrogen, the metal crystallizes beyond 450°C whereas it is fully oxidized in air in the temperature range 150–300°C. RuO_2 crystallizes on a sharp exothermic peak, the temperature of which depends on the residual water content. An estimate of the enthalpy of crystallization is given, and the oxidation mechanism is discussed.

INTRODUCTION

RuO_2 coatings (electrodes or catalysts) are usually prepared by decomposing $RuCl_3$ on heated substrates. On the other hand, hydrated $RuCl_3$ is water soluble so that ruthenium hydrates can be (co)-precipitated from aqueous solutions. This is a convenient way to prepare conductive ruthenates phases or solid solutions with other rutile-type oxides, i.e. SnO_2 or TiO_2. However, the stability and thermal behavior of the ruthenium hydrates is not very well known. For many years, some German authors have investigated the nature of the hydroxides and oxides only by chemical methods [1–4]. The lack of thermal data led us to an extended investigation of the oxidation and dehydration of Ru(III) hydrate based upon differential thermal analysis, thermogravimetric analysis, X-ray diffraction and IR spectroscopy.

PREVIOUS WORK

The important oxidation states in acid solution are Ru(III) and Ru(IV). According to Latimer [5], in chloride solution these states are in the form of $RuCl_5^{2-}$ and $RuCl_5OH^{2-}$ complexes. The $RuCl_5^{2-}/RuCl_5OH^{2-}$ potential is about -1.2 V so that the Ru(III) state is more stable. On the other hand, the only stable solid phases are Ru, $Ru(OH)_3$ and $Ru(OH)_4$. The potential–pH equilibrium diagram [6] shows that $Ru(OH)_2$ is only stable in aqueous solutions free from oxidizing agents and can be easily oxidized to $Ru(OH)_4$ or reduced to elementary ruthenium.

In a previous paper [7] we have shown that 3 mequiv. NH_4OH are needed to precipitate 1 mequiv. $RuCl_3$ in aerated water. This result confirms the stability of Ru(III) in chloride solution. However, the brownish-black precipitate dried at 60°C in air was rather a mixture of Ru(IV) and Ru(III) hydrates. According to Hanke [8], $Ru(OH)_3$ can be obtained as a yellow-green precipitate in the absence of oxygen. The IR spectrum of this compound shows an –OH band at 3560 cm^{-1} whereas the hydrated dioxide ($RuO_2 \cdot 2\,H_2O$) does not. Both hydrates are amorphous and cannot be differentiated by X-ray diffraction. The question of whether $Ru(OH)_3$ can give rise to a Ru(III) oxide (Ru_2O_3) prior to oxidation remains. The existence of Ru_2O_3 is doubtful. Earlier, Wöhler [2] assumed that Ru_2O_3 undergoes the disproportionation

$$2\,Ru_2O_3 \rightarrow 3\,RuO_2 + Ru$$

as soon as it is formed in a flow of carbon dioxide.

Wöhler [2] could not properly isolate a pure metal fraction from the oxide since the oxygen content of the former was about 17%. Nevertheless, such a mechanism, in a more complex form, is thought to occur since crystalline Ru was observed at 500°C by us and by Hanke [8]. According to Chatterij and West [9], at this temperature the pressure of dissociation of RuO_2 should be about 10^{-11} atm, so that in any available inert gas the metal formation results from the reduction of the Ru(III) oxide or hydroxide rather than from the Ru(IV) oxide. In addition, TG measurements [10,11] show that Ru-black is completely oxidized to RuO_2 at 500°C under $pO_2 = 100$ Torr.

EXPERIMENTAL

Two batches of $RuCl_3 \cdot 3\,H_2O$, one from Alpha-Ventron (36.5 wt.% Ru), and the other from Johnson, Matthey and Pauwels (39 wt.% Ru), were used. Both were dissolved in distilled water and hydrates were precipitated with 1 *N* ammonia up to pH 8.5. In a previous procedure [7], referred to here as procedure A, the water was not deaerated and the precipitate was dried at 60°C in air. The present procedure (procedure B) consists of working in water deaerated by nitrogen (< 5 ppm O_2) and drying under vacuum at ambient temperature. This latter procedure does not change to a significant extent the weight of dry precipitate recovered; e.g. 0.920 g of precipitate was recovered from 1.523 g of starting material.

Taking into account the losses during filtration, the precipitate composition was assumed to be close to $Ru(OH)_3 \cdot H_2O$. The amount of chlorine was less that 1%. In addition, the color of the precipitate was never yellow but brownish-black, as in procedure A. No specific –OH band was detected by IR spectroscopy. The surface area measured by a BET method was 70 $m^2\,g^{-1}$.

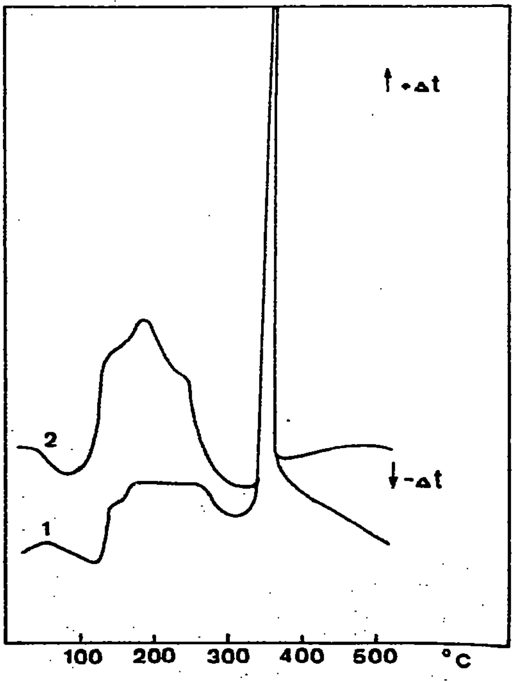
The DTA and TG measurements were determined in air and in nitrogen flow at a heating rate of 8°C min^{-1}. The DTA detector was a Mettler ME-93629 system with an alumina crucible holder. The TG apparatus was an MTB 10-8 Setaram microbalance. X-Ray powder diagrams were recorded with a σ 2080 CGR diffractometer using Cu$K_{\alpha 1}$ radiation.

RESULTS AND DISCUSSION

Figure 1 compares the DTA curves in a flow of air samples (Alpha-Ventron) prepared by procedures A and B. A first endothermic effect is observed in both cases at 90–100°C. This is followed by an exothermic effect up to 300°C which is much stronger in sample B than in sample A. In addition, a shoulder is quite visible in sample B left of the maximum, i.e. at 150°C. Beyond 300°C a sharp exothermic effect is observed in any case. Samples removed from the DTA furnace at 370°C, i.e. at peak top, become crystalline and exhibit the X-ray powder pattern of rutile-type RuO_2. The surface area is kept nearly constant during the overall process and reaches 79.4 m^2 g^{-1} at 400°C.

From this comparison it is assumed that:

(i) the first exothermic peak corresponds to an oxidation mechanism. In fact, the samples prepared by procedure A may have been substantially oxidized during the



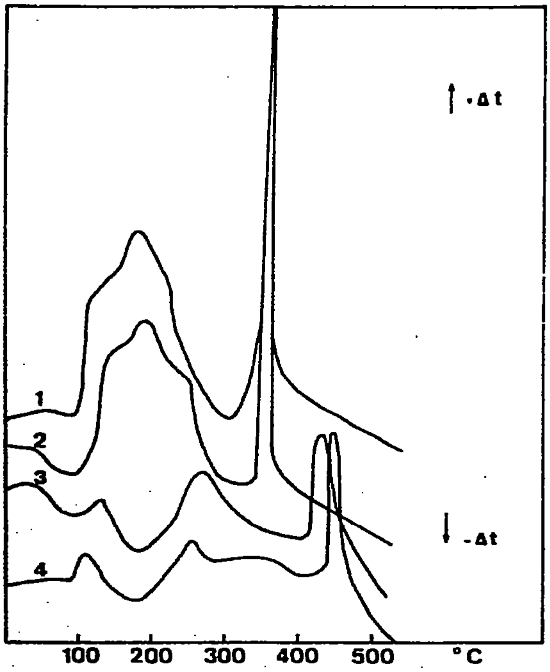


Fig. 1. DTA curves of Ru(III) hydrate prepared by 1, procedure A; and 2, procedure B.

Fig. 2. DTA curves of Ru(III) hydrates: 1, from JMP in air; 2, from alpha in air; (3) from alpha in nitrogen; 4, from JMP in nitrogen.

precipitation and the drying in air whereas samples B have been kept at least in the bulk in the form of a Ru(III) hydrate;

(ii) the second exothermic peak is ascribed to the cristallization of RuO_2 from the Ru(IV) hydrated oxide formed in either case at lower temperature.

Evidence for these hypotheses will be supported by DTA and TG experiments carried out on samples B.

The DTA curves of samples B heated in air and in nitrogen are shown in Fig. 2. First, JMP and Alpha compounds give very similar results so that only one behavior will be assumed in what follows. Fig. 2 also shows large differences for the same batch heated in nitrogen and in air. In nitrogen the first exothermic effect in the temperature range 90–350°C is reduced to rather weak peaks separated by a consistent endothermal one. The first exothermic peak occurs at the same temperature as that of the left shoulder of the strong exothermic peak in air. Finally, the last exothermic effect is shifted to 450°C in nitrogen. X-Ray diffraction shows that beyond this temperature RuO_2 and Ru(metal) crystallize (Fig. 3). The peak areas correspond to a Ru/RuO_2 ratio $= 0.3 \pm 0.05$. In this oxygen pressure range ($pO_2 \approx 10^{-5}$ atm) Ru(metal) is not in equilibrium, as mentioned above, so that Ru(metal) cannot issue from a Ru(IV) hydrate or oxide but from the disproportionation of Ru(III) hydrate.

The TG and DTA curves in air and in nitrogen are plotted in Fig. 4. The different behavior in air and in nitrogen is confirmed:

(i) the weight loss is greater in air than in nitrogen at any temperature. The total weight loss taken at 900°C is 25.8% in air and 24.2% in nitrogen;

(ii) in air the differential curves (Fig. 4) show three separated phenomena, the maxima of which are 175, 300 and 370°C. In nitrogen, the separation of the two first maxima, at 175 and 280°C, is less obvious. The third maximum occurs at 420°C.

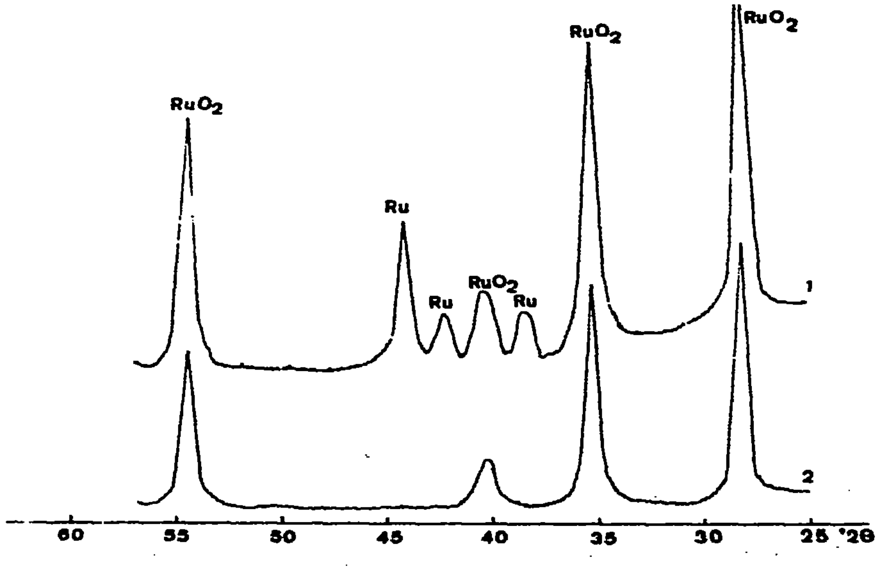


Fig. 3. X-Ray diffraction of Ru(III) hydrate heated at 500°C in 1, nitrogen; and 2, air.

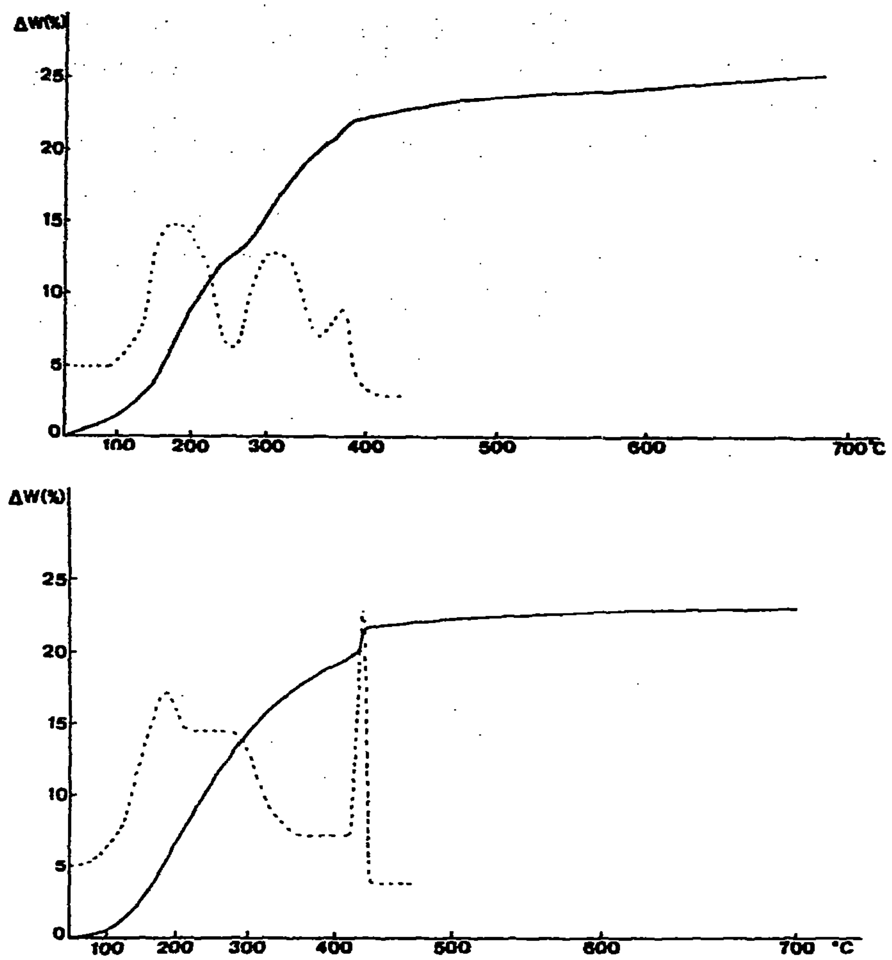


Fig. 4. (a) ————, TG curve of Ru(III) hydrate; - - - - - -, differential curve. In air. (b) ————, TG curve of Ru(III) hydrate; - - - - - -, differential curve. In nitrogen.

Point (i) will be discussed first: let us assume, according to the X-ray analysis for the overall reactions

(1) in air

$$4[Ru(OH)_3 \cdot H_2O] + O_2 \rightarrow 4\,RuO_2 + 10\,H_2O$$

the calculated weight loss is 21.75%, and

(2) in nitrogen

$$4[Ru(OH)_3 \cdot H_2O] \rightarrow 3\,RuO_2 + Ru + 10\,H_2O$$

the calculated weight loss is 26.45%.

In nitrogen, the experimental weight loss is less than that calculated (2.25%). This difference can be accounted for by the surface oxidation of the metal particles resulting from the disproportionation. In fact, it is known [10,11] that the metal can be protected from further oxidation by a thin oxide film. This interpretation is consistent with the two exothermic peaks in the temperature range 90–300°C. The first, which corresponds to the shoulder at about 140°C of the strong exothermic phenomenon in air, is ascribed to the disproportionation reaction. The second, which is seen at 250°C when the endothermic dehydration is slowing down (Fig. 2), is ascribed to surface oxidation of Ru(metal).

In air, the experimental weight loss is somewhat greater than that calculated (+4.05%). As discussed below, the strong exothermic effect in the temperature range 80–300°C includes (i) the disproportionation reaction giving a Ru(IV) oxide hydrate + Ru(metal); and (ii) the oxidation of Ru(metal) into Ru(IV) oxide or hydrate. It is believed that a fraction of Ru(metal) (no more than 20%) may also be oxidized into volatile RuO_4

$$Ru + 2\,O_2 \rightarrow RuO_{4(g)} \quad \Delta G_{(500K)} = -79.8 \text{ kcal}$$

In fact, the beginning temperature of the strong exothermic effect (150°C) corresponds to that of a "sparking" effect observed when the Ru(III) hydrate powder is quickly introduced into a furnace. The sparks are related to the discrete oxidation of Ru particles resulting from the disproportionation. Owing to the important local temperature increase, volatile oxides RuO_3 and RuO_4 may be evolved. These oxides become stable with respect to RuO_2 towards 1000°C [12].

The partial weight losses will now be discussed in relation to the DTA curves.

(1) In air the first important weight loss (Fig. 4a) is achieved at about 250°C and reaches 12.6%. This loss includes: (i) the disproportionation; (ii) the nearly complete oxidation into Ru(IV); and (iii) the partial dehydration. If the following sequence is assumed

$$4[Ru(OH)_3 \cdot H_2O] \rightarrow 3(RuO_2 \cdot 2\,H_2O) + Ru + 4\,H_2O \qquad (1)$$

$$3(RuO_2 \cdot 2\,H_2O) \rightarrow 3(RuO_2 \cdot H_2O) + 3\,H_2O \qquad (2)$$

$$Ru + O_2 + H_2O \rightarrow RuO_2 \cdot H_2O \qquad (3)$$

the net reaction

$$4(Ru(OH)_3 \cdot H_2O) + O_2 \rightarrow 4(RuO_2 \cdot H_2O) + 6\,H_2O$$

gives a weight loss of 11.17%.

An alternate path for (3) would be

$$Ru + O_2 \rightarrow RuO_2$$

with the net reaction

$$4[Ru(OH)_3 \cdot H_2O] + O_2 \rightarrow 3\,RuO_2 \cdot H_2O + RuO_2 + 7\,H_2O$$

and a weight loss of 13.8%.

The experimental results (weight loss of 12.6%; RuO_2 not detected by X-ray at this temperature) are rather consistent with the first net reaction. The difference may be explained by a ruthenium loss as RuO_4.

The second weight loss, giving 19.9% at 360°C, corresponds to a partial dehydration of the Ru(IV) monohydrate ($RuO_2 \cdot H_2O$). It is probable that at this stage a critical water content is reached on the solid surface below which RuO_2 is able to crystallize. This transformation (sharp DTA peak at 360°C in Fig. 2) accelerates the water escape as shown by the third loss at 360°C (Fig. 4a).

(2) In nitrogen (Fig. 4b) the maximum rate of weight loss occurs at about 175°C and corresponds to the endothermic peak which follows the exothermic peak of the disproportionation. Beyond this temperature, the weight is decreasing at nearly constant rate except towards 270°C when the surface of the metal particles should be oxidized as shown by the second exothermic peak. At 350°C, when the rate is slowing down, the weight loss reaches 17%.

The formation of the Ru(IV) monohydrate + Ru(metal) according to

$$4[\mathrm{Ru(OH)_3 \cdot H_2O}] \rightarrow 3(\mathrm{RuO_2 \cdot H_2O}) + \mathrm{Ru} + 7\,\mathrm{H_2O}$$

yields a weight loss of 18.5%, which is in agreement with the experimental one, keeping in mind that Ru may be slightly oxidized.

As in air, the last exothermic peak corresponds to a sharp decrease in weight. The crystallization of RuO_2 (and Ru) begins when a critical water content has been reached. The water loss (19%) is similar to that observed in air but is obtained at a higher temperature (450°C) instead of 360°C in air. This comparison suggests that the temperature of the RuO_2 crystallization is controlled by the water content of the solid surface.

Finally, additional evidence for Ru oxidation on the strong exothermic peak at 175°C and crystallization of RuO_2 on the sharp exothermic peak at 360°C in air is supported by an estimate of enthalpy of both phenomena. A sample containing 10% $KClO_4$ in Al_2O_3, and another containing 10% $Ru(OH)_3 \cdot H_2O$ in Al_2O_3 have been subjected to DTA in air (Fig. 5). From the ΔH value of the endothermic peak of $KClO_4$ at 299°C (24 cal g^{-1}) [13], a ΔH value of -8.5 kcal $mole^{-1}$ RuO_2 has been found for the exothermic peak assigned to the RuO_2 crystallization. This value is consistent with the order of magnitude of a crystallization from an amorphous phase.

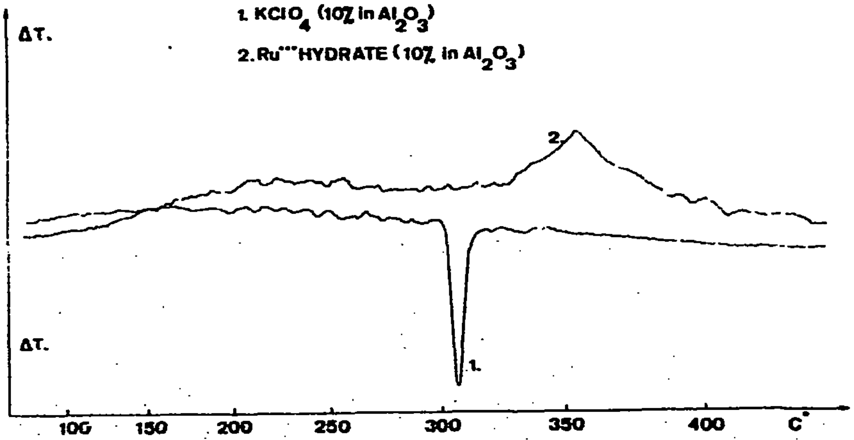


Fig. 5. Comparison of DTA of 1 $KClO_4$ (10% in alumina); and 2, Ru(III) hydrate preheated at 250°C (10% in alumina).

On the other hand, an estimate of 59 kcal mole^{-1} RuO_2 is found for the net exothermic peak in the range 80–300°C, if one assumes that 0.25 mole Ru is formed from 1 mole $Ru(OH)_3 \cdot H_2O$ by the disproportionation reaction. Owing to the opposite effect of the endothermic dehydration, the order of magnitude is consistent with the enthalpy of RuO_2 formation which is -68 kcal mole^{-1} at 600 K.

CONCLUSIONS

Ru(III) hydrate $[Ru(OH)_3 \cdot H_2O]$ can be obtained from $RuCl_3$ if the precipitation and the filtration are carried out in a deaerated medium. The black-brownish color of the precipitate is likely to be related to a surface oxidation to Ru(IV) hydrate.

Beyond 100°C, the Ru(III) hydrate undergoes a disproportionation reaction during dehydration which leads to Ru(metal) + Ru(IV) hydrate. Amorphous or crystalline Ru_2O_3 has not been detected.

The amorphous metal is protected by a thin oxide film in nitrogen. Beyond 450°C it crystallizes at the same time as RuO_2. In air, the metal is oxidized in the temperature range 150–300°C to an amorphous Ru(IV) oxide hydrate.

The monohydrate $RuO_2 \cdot H_2O$ resulting from the disproportionation crystallizes into RuO_2 before complete dehydration. The temperature of the RuO_2 crystallization is likely to be controlled by the water content of the solid surface. The enthalpy of crystallization is estimated as 8.5 kcal mole^{-1} RuO_2.

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