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HYDROTHERMAL SYNTHESIS AND REACTIVITY OF RHODIUM DIOXIDE AND OXYHYDROXIDE

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ABSTRACT

The hydrothermal synthesis, interrelations and thermal decomposition of RhOOH and RhO_2 in different atmospheres are studied. Although the final product of the decomposition is always rhodium metal, there is a marked influence of the atmosphere on the intermediate products. The reactions that have been observed include the disproportionation of RhOOH in vacuum and the hydrothermal reduction of the dioxide to the oxyhydroxide.

INTRODUCTION

The majority of the trivalent oxyhydroxides adopting the InOOH-type structure are high pressure phases [1]. This structure can be considered as an orthorhombic deformation of the rutile-type structure. Such a deformation appears to be due to the presence of hydrogen bonds in the trivalent compound [2]. Given such a structural analogy, interesting chemical interrelations are expected when the same metal is known to form compounds of both these two types, as is the case of rhodium.

Following our early work [3] on the interconversion between orthorhombic CrOOH and rutile-like CrO_2, we present in this paper a study of the thermal decomposition and interconversion between orthorhombic RhOOH and tetragonal RhO_2 whose preparation has, for the first time, been achieved hydrothermally at pressures of the order of 1500 bar.

EXPERIMENTAL

Polycrystalline samples of RhOOH and RhO_2 were obtained by hydrothermal synthesis in gold tubes, sealed at both ends, and treated within a steel autoclave heated externally in an experimental set up fully described elsewhere [4]. The pressures, of the order of 1–2 kbar, were measured during

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the experiments by means of an Ashcroft manometer, the temperature being controlled by a Cr–CrAl thermocouple located outside the autoclave. Previously, an approximate calibration of the gradient between the internal and external temperatures was performed with the autoclave filled with alumina.

DTA experiments were performed on a Mettler T1 thermoanalyzer, while TG experiments were made on a thermogravimetric apparatus based on a Cahn balance. X-Ray diffraction analysis was carried out on a Phillips 1310 unit using CuK_α radiation and high purity silicon as internal standard.

We found that the best conditions to obtain RhOOH are a suspension of Rh_2O_3 in a 0.1 M solution of hydrochloric or nitric acid at 2000 bar and 600°C for 48 h; lower pressure or shorter time results in a less well-crystallized product; below 1000 bar, neither the oxyhydroxide nor the dioxide are obtained. With regards to RhO_2, the best procedure appears to be a suspension of Rh_2O_3 in 7 M HNO_3 or 2.7 M $HClO_3$ at about the same pressure, temperature and heating time as in the case of the oxyhydroxide. For lower concentrations of oxidizing acid, a mixture of both RhO_2 and RhOOH was obtained. The only previously reported synthesis of these materials required much higher pressure: 3000 bar of oxygen pressure for RhO_2 [5,6] or 80 kbar and a NaOH suspension in the case of RhOOH [1]. Our attempts to prepare RhO_2 at atmospheric pressure by the thermal decomposition in air of rhodium oxide gels, as suggested by Bayer and Wiedemann [7], failed. The only product observed under these circumstances was α-Rh_2O_3, crystallized on heating $Rh_2O_3 \cdot 5\,H_2O$ at 550°C after 115 h.

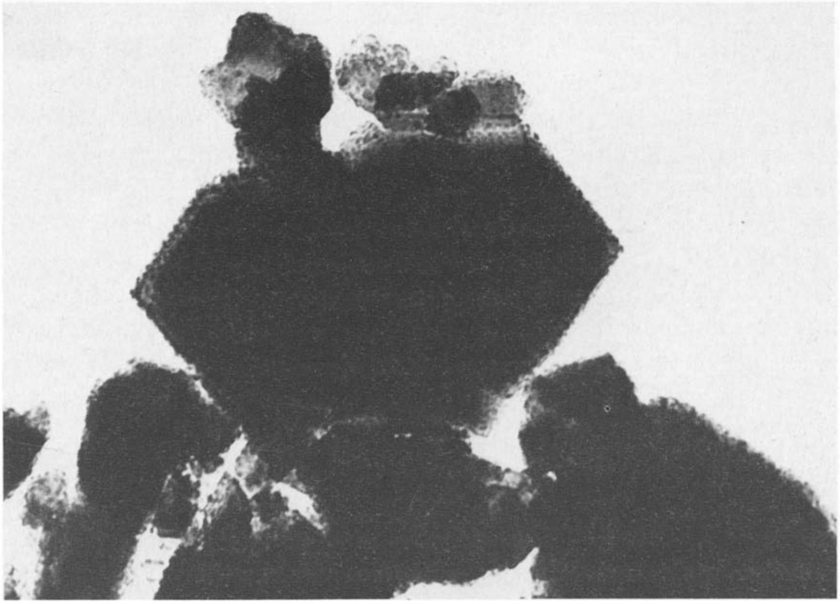

Fig. 1. Electron micrograph of hydrothermally synthetized RhOOH. Magnification, × 125,000.

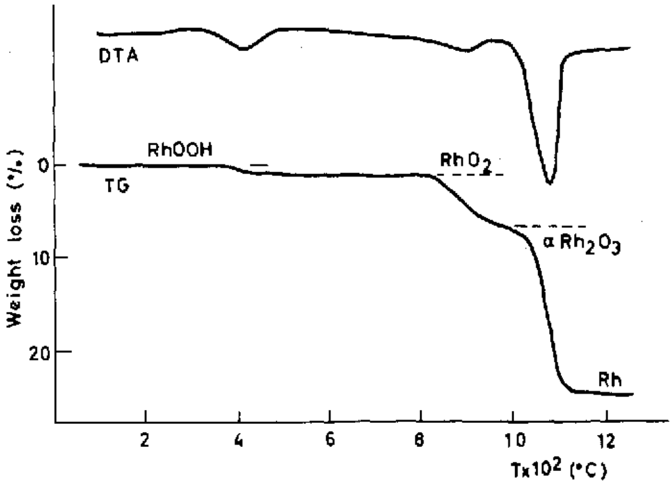

Fig. 2. Thermal decomposition of RhOOH in air. Heating rate 10°C min^{-1}.

However, RhO_2 can be obtained in a well-crystallized form from this gel by hydrothermal synthesis under the conditions indicated above.

Both materials were obtained as polycrystalline powders and electron microscopy revealed an almost hexagonal crystal shape, the crystal size being of the order of 0.5 μm (Fig. 1).

RESULTS AND DISCUSSION

In still air, a DTA experiment performed at 10°C min^{-1} (Fig. 2), shows the presence of three endothermic peaks at the 470, 900 and 1080°C, respectively. The corresponding weight losses, 0.64, 6.10 and 18.52%, appear to conform to the decomposition reactions

$$2\ RhOOH + \tfrac{1}{2}\ O_2 \xrightarrow{400\text{–}500^\circ C} 2\ RhO_2 + H_2O \qquad (1)$$

$$2\ RhO_2 \xrightarrow{800\text{–}900^\circ C} \alpha\text{-}Rh_2O_3 + \tfrac{1}{2}\ O_2 \qquad (2)$$

$$\alpha\text{-}Rh_2O_3 \xrightarrow{1000\text{–}1100^\circ C} 2\ Rh + \tfrac{3}{2}\ O_2 \qquad (3)$$

for which the calculated values are 0.73, 5.93 and 18.90%, respectively.

It is interesting to note that reaction (1) is endothermic, something rather unusual for an oxidation process, e.g. CrOOH oxidizes exothermically to CrO_2 [3]. This seems to reflect a higher stability of RhOOH with respect to RhO_2 than that of orthorhombic CrOOH with regards to CrO_2. This fact could be due to a higher hydrogen bonding energy of the former.

Of the three well-established forms of Rh_2O_3, the one obtained in the above processes is the corundum-like α-form. This is somewhat surprising since, according to Wold et al. [8], this should transform to the so called high temperature, or β-form at temperatures of the order of 750°C. Nevertheless, it should be recalled that these authors indicated that the low to high temperature form transition was sluggish. On the other hand, and according to Shannon, there is a three-dimensional relationship between the rutile-type structure of CrO_2 and the corundum-type structure of Cr_2O_3 whose transformation can be considered as topotactic [9]. In this way, it would appear that the transformation of RhO_2 to Rh_2O_3 will be kinetically easier.

In vacuum ($P < 10^{-4}$ torr), the thermal treatment of RhOOH at 400°C produces rhodium metal and the dioxide according to

$$4\ RhOOH \rightarrow 3\ RhO_2 + Rh + 2\ H_2O \tag{4}$$

as determined by X-ray diffraction. It is interesting to mention that the RhO_2 so produced decomposes according to

$$RhO_2 \rightarrow Rh + O_2 \tag{5}$$

at temperatures of the order of 500°C in vacuum while hydrothermally synthesized RhO_2 can be heated to 680°C under the same conditions without decomposition. This result was somewhat unexpected since, according to Muller and Roy [6], RhO_2 decomposes in air at 680°C, and an oxygen pressure of 10 atm. increased the decomposition temperature to over 850°C. This effect is likely to be due to a particle size effect. It is perhaps worth recalling in this connection the good crystallinity of our RhO_2 hydrothermally obtained samples, as seen by electron diffraction [4].

In air, RhO_2 is stable up to 800°C, suggesting that the rutile-type structure is somewhat stabilized in an oxidizing atmosphere (cf. CrO_2 [3]). At higher temperatures in air, it decomposes according to eqns. (2) and (3).

By analogy with the system CrO_2–CrOOH [3,10], it could be expected that the hydrogen reduction of RhO_2 would be an interesting procedure for the preparation of RhOOH. However, in the presence of hydrogen, RhO_2 is very unstable, giving the metal at a temperature as low as 50°C after a week ($P_{H_2} = 50$ torr) and no intermediate products are formed. In a DTA experiment, it was observed that this process is exothermic and peaked at 170°C at a heating rate of 2°C min^{-1}.

$$RhO_2 + 2\ H_2 \rightarrow Rh + 2\ H_2O \tag{6}$$

The experimental weight loss (23.90%) is in good agreement with the calculated value (23.70%). The kinetics of this reduction process appear to follow an Avrami-type equation: $[-\ln(1-\alpha)]^{1/2} = kt$. The ease of the reduction of RhO_2 could explain the disproportionation of RhOOH in vacuum. That is, if under these circumstances RhOOH liberates hydrogen on heating, the hydrogen so produced will reduce the corresponding stoichiometric amount of RhO_2 formed; the balance of the total reaction will be that indicated in eqn. (4).

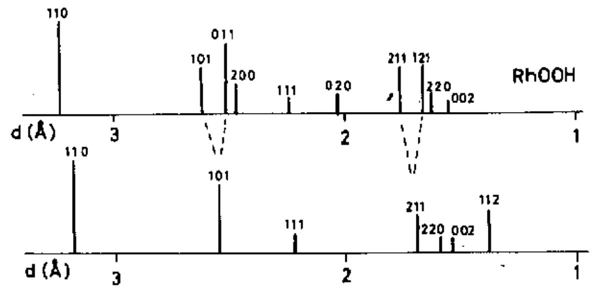

Fig. 3. X-Ray diffraction patterns of RhOOH (top) and RhO_2 (bottom). CuK_α radiation.

Nevertheless, it is still possible to obtain RhOOH from RhO_2 by hydrothermal synthesis in pure water at 600°C and 1500 bar.

$$4\ RhO_2 + 2\ H_2O \rightarrow 4\ RhOOH + O_2 \tag{7}$$

In this way, RhO_2 and CrO_2 closely resemble each other [3,11]; the facility of this interconversion between RhO_2 and RhOOH can be explained, as in the case of CrO_2–CrOOH, by the close analogy between both crystal structures. Figure 3 shows the X-ray diffraction data for both compounds where the splitting of the lines with $h \neq k$, reflecting the change in symmetry from tetragonal to orthorhombic, is clearly seen.

We have also observed that any of the three known polymorphs of rhodium sesquioxide is easily reduced by hydrogen and this happens at temperatures as low as 150°C. These processes, which appear to be quite endothermic, contrast with the much more strongly reducing conditions needed to obtain chromium from chromia (1500°C, H_2) [12] and is another reflection of the "nobility" of rhodium.

A final point worth mentioning is that, in the course of our work, we have observed that rhodium oxyhydroxide can be slightly non-stoichiometric. The amount of variation in composition appears to be related to the synthesis conditions. A detailed report of these aspects of our work will be published elsewhere.

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