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SYNTHESIS OF SILVER (II) OXIDE BY OXIDATION OF SILVER OR SILVER OXIDE BY MEANS OF OZONE

R. DALLENBACH[†], J. PAINOT[‡] and P. TISSOT[*]
Département de Chimie Minérale, Analytique et Appliquée, Sciences II, 30, quai E. Ansermet, CH-1211 Genève, Switzerland

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Abstract—The oxidation by ozone of a suspension of silver or silver oxide in an aqueous solution of sodium hydroxide is described. It has been shown that the oxidation proceeds in two steps:

$$Ag \xrightarrow{O_3} Ag_2O \xrightarrow{O_3} AgO.$$

The experimental results are in good agreement with a mechanism of dissolution and precipitation. The silver (II) oxide obtained has remarkable properties of stability in alkaline solution and of reducibility to metallic silver. These special properties are probably due to the large size of the particles.

INTRODUCTION

Since the work of Marignac,[1] who was the first to observe the formation of AgO by reaction of O_3 on silver, some authors have studied this solid–gas reaction both on silver and on silver oxide.[2–5] The oxidation by ozone of the ion Ag^+ in solution has formed the subject of a greater number of studies with several silver salts in acid, neutral or alkaline solutions.[5–7] As far as we know, there has been no work on the oxidation by O_3 of an aqueous suspension of silver or silver oxide; this possibility to obtain the silver peroxide has been mentioned in the review published by McMillan[8] and in a patent application.[9] We describe in this paper a detailed study of the synthesis of AgO by oxidation of a suspension of silver or silver oxide in an aqueous solution of sodium hydroxide, and we compare the properties of the product obtained (named OSK) with those of a commercial silver (II) oxide (Merck suprapur, named Msp) obtained by oxidation of Ag^+ by persulphate.

EXPERIMENTAL

Equipment

All the runs were done in a 10 l. reactor, fitted with a double mantle, a stirrer, an input and an output for the gaseous mixture O_2–O_3. The ozone was produced by a brush-discharge device providing a maximum flow of $2.6\,gh^{-1}O_3$ with a total flow ($O_2 + O_3$) of $150\,lh^{-1}$. The 2N sodium hydroxide solution contained either 100 g of silver powder (mean dia. 20 μm) or 100 g of silver oxide (mean dia. 2 μm).

Analytical methods

During the course of the synthesis, we took samples and analysed the mixture Ag–Ag_2O–AgO. The titration of this mixture is complicated by the dismutation reaction (1)

$$Ag^{+2} + Ag^0 = 2\,Ag^{+1} \qquad (1)$$

which proceeds in solution and prevents the use of a chemical titration of the oxidizer power of AgO in the presence of metallic silver.[10] We used this method only for the samples taken at the end of the synthesis. In the other cases we used thermogravimetry; this method is well known[11–13] and is based on the loss of weight associated with the reactions (2) and (3):

$$2\,AgO \xrightarrow{\sim 120^\circ C} Ag_2O + 1/2\,O_2 \qquad (2)$$

$$Ag_2O \xrightarrow{\sim 400^\circ C} 2\,Ag + 1/2\,O_2. \qquad (3)$$

Unfortunately between the two steps, there is a continuous small weight loss, so that the accuracy of the method is not better than ±2% for AgO alone. In the presence of metallic silver, the solid–solid reaction (1′)

$$AgO + Ag = Ag_2O \qquad (1')$$

proceeds at the same time as the reaction (2). However the reaction (1′) is slow, and we have made a correction curve taking into account this phenomenon for several AgO–Ag ratios. The accuracy of the thermogravimetric method is ±5% in the case of the mixtures.

In addition each sample was checked by X-ray diffraction and with the scanning electron microscope.

STUDY OF THE SYNTHESIS

The stirring of the suspension and the flow of ozone are the main factors which influence the yield, calculated as the ratio of the silver oxidized ($Ag_2O + AgO$) over the total amount of ozone introduced. Figure 1 shows the results obtained for the maximum flow of ozone; with our experimental equipment, the optimum rotation speed of the stirrer is 480 rpm, which we used in all runs.

Figure 2 represents the change of the concentration during the course of a synthesis. All the runs show the same aspect, which is characteristic of two successive reactions; the oxidation proceeds then in two steps, $Ag^0 \rightarrow Ag^+ \rightarrow Ag^{+2}$.

The complete oxidation (to 96 ± 2% AgO) of 100 g of silver takes about 20 hr. A prolongation of the ozone

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[*] Author to whom correspondence should be addressed.

[†] Present address: Union Carbide, 43, rue J. L. Chevrolet -CH-2301 La Chaux-de-Fond, France.

[‡] Present address: Thermocompact SA, 10 rue Richemont, CH-1202 Geneve, Switzerland.

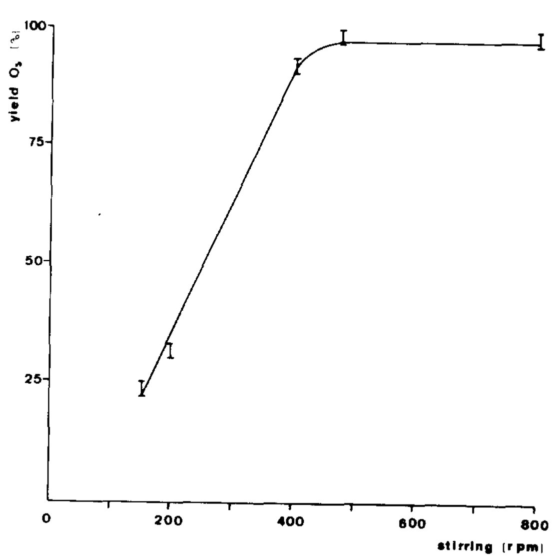

Fig. 1. Consumption of ozone as a function of stirring. Total flow (O_2+O_3), 150 l H^{-1}; flow of O_3, 2.6 gh^{-1}; temperature, 25°C; reaction mixture, 100 g of Ag in 10 l NaOH 2N.

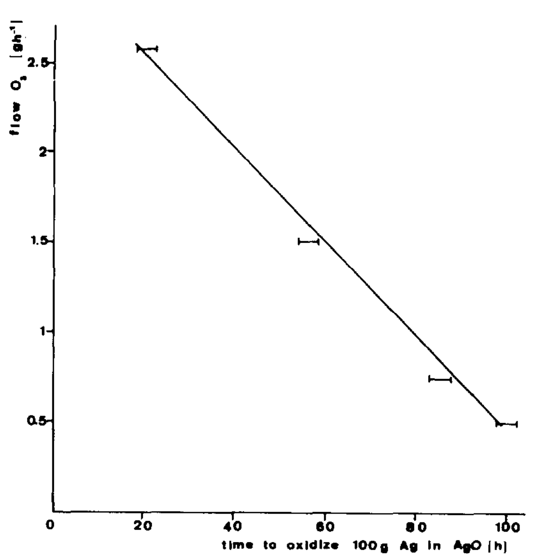

Fig. 3. Rate of oxidation as a function of ozone flow-rate. Temperature, 25°C.

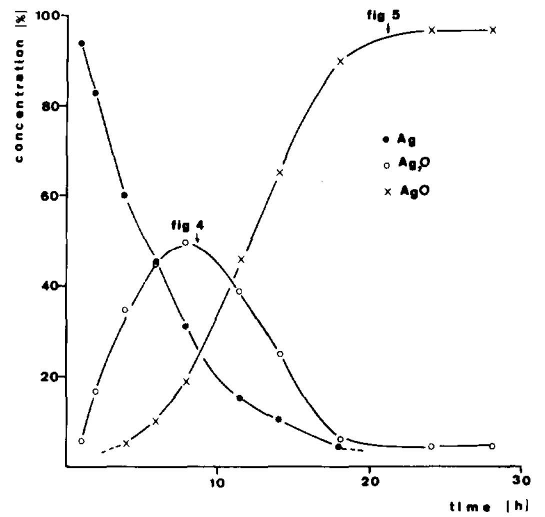

Fig. 2. Change of the concentration during the synthesis. Total flow (O_2+O_3), 150 lh^{-1}; flow of O_3, 2.6 gh^{-1}; temperature, 25°C; reaction mixture, 100 g of Ag in 10 l NaOH 2N.

bubbling does not change the percentage of AgO. With the same experimental conditions, we have observed the same rate of oxidation (100 g in 20 hr) with batches of 50–400 g of silver. The influence of the flow of ozone is shown in the Fig. 3, which represents the linear relation between the flow rate of ozone and the time required to oxidize 100 g of silver. It was not possible to test higher flow rates of ozone than 2.6 gh^{-1}, but it is likely that a linear relation exists for larger rates of flow.

All tests were made at 25°C; at O and 50°C we observed a slower rate of oxidation.

By starting with Ag_2O instead of Ag, we obtained the same product; in this case, the rate of oxidation is about two times greater. This is in good agreement with the hypothesis that the oxidation of silver proceeds in two steps. The examination with the SEM of the samples taken during the synthesis also confirms this hypothesis; as a matter of fact, one initially observes the formation of small protuberances of Ag_2O on the surface of the silver grains, whose sizes diminishes. We never observed the formation of a film over the surface of silver, and so we think that the Ag_2O is formed by a mechanism of dissolution and precipitation. After some hours AgO appears in the shape of flakes (Fig. 4); at the end of the oxidation, the AgO flakes enlarge and theAg_2O disappears (Fig. 5). The size of the particles obtained is exceptionally big, as compared with the usual AgO (Fig. 6). However, the two products shown in Fig. 5 and 6 have the same X-ray pattern, corresponding to the usual monoclinic form of AgO.

PROPERTIES OF THE SILVER (II) OXIDE

The main difference observed between AgO obtained by oxidation of silver by ozone and AgO obtained by oxidation of silver ions is the shape and the size of the particles. With the procedure described in this paper, we obtained large flakes of 10–30 μm of length and 0.1–1 μm of thickness. The specific area of this product is less than 0.1 m^2g^{-1}, when the specific area of Msp is 0.8 m^2g^{-1} as measured by the BET method. The thermal stability of the two kinds of silver oxide has been tested by thermograviemetry and differential thermal analysis. The starting temperature of decomposition according to the reaction (2) is about 10°C lower for the Msp sample.

We have also compared the stability of the two types of oxide in 7N KOH solution at 60°C, by measuring the volume of oxygen evolved. Figure 7 shows the remarkable stability of OSK; we have tested more than 15 types of AgO of different origins, and never obtained the same stability.

Another outstanding property of the OSK type AgO is the possibility to reduce it (by hydrogen or hydrazine for example) to metallic silver, well before the complete

Fig. 4. Scanning electron microscope photography of reaction-mixture after 8 hr (see Fig. 2) (1000×) Ag: 30%; Ag_2O: 50%; AgO: 20%.

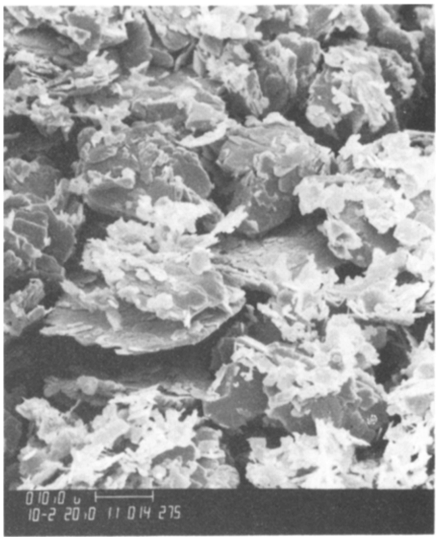

Fig. 5. SEM photography of AgO (types OSK) (1000×).

reduction of AgO to Ag_2O. This reduction proceeds in two steps:

$$2\,AgO + H_2 = Ag_2O + H_2O \quad (4)$$

$$Ag_2O + H_2 = 2\,Ag + H_2O. \quad (5)$$

With all samples tested except OSK, we did not detect silver by X-ray analysis until 90% of AgO had been transformed into Ag_2O; with OSK, on the other hand, we have detected metallic silver when only 30% of AgO had been reduced to Ag_2O. This property could be very useful in the preparation of the cathodic mass of electrical cells.

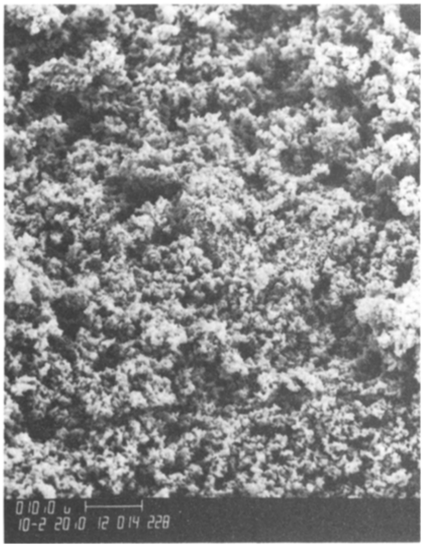

Fig. 6. SEM photography of AgO (type Msp) (1000×).

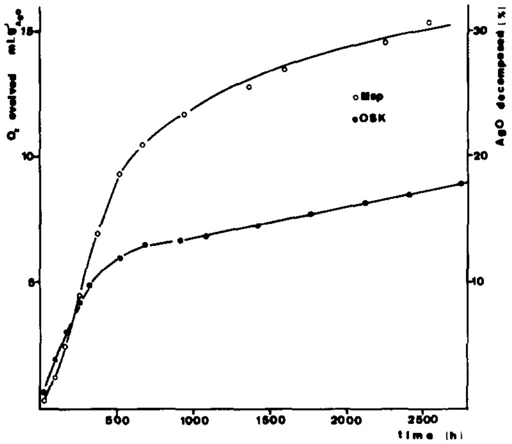

Fig. 7. Decomposition of AgO in 7N KOH at 60°C.

CONCLUSIONS

The overall reaction of formation of silver (II) oxide by oxidation of silver by ozone can be written as follow:

$$Ag + O_3 = AgO + O_2. \quad (6)$$

We have clearly demonstrated that this reaction takes place in two steps, with the intermediary formation of Ag_2O. Moreover, it seems that solid silver is not oxidized directly by gaseous ozone, but rather that we have a reaction between soluble species. The silver is not soluble in alkaline solution, and the first step must be the oxidation of silver. Silver oxides present some solubility, and several authors[5,11,14] have proposed $Ag(OH)_2^-$, AgO^-, $Ag(OH)_3^-$ and $Ag(OH)_4^-$ as the soluble species.

The solubility of ozone in alkaline solution has also been studied by several authors;[15,20] most of them have mentioned that the decomposition of O_3 goes through the ozonide ion and that the concentration of OH radicals is high.

All our experimental results are in good agreement with a mechanism involving successive steps of dissolution-oxidation-precipitation. The slow rate of oxidation observed could be partly explained by one or the other of the two folowing reactions:

$$2\,Ag(OH)_3^- = 2\,Ag(OH)_2^- + H_2O + 1/2\,O_2 \quad (7)$$

or

$$Ag(OH)_3^- + Ag = Ag_2O + OH^- + H_2O. \quad (8)$$

Finally, the outstanding properties of the OSK type AgO is probably due to the size of the particles obtained by this synthesis.

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