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PREPARATION OF CADMIUM ORTHOPLUMBATE AT NORMAL PRESSURE BY DECOMPOSITION OF THE RESPECTIVE COPRECIPITATED CARBONATES

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ABSTRACT

The thermal decomposition of lead and cadmium coprecipitated carbonates was found to be a good method for the preparation of cadmium orthoplumbate.

By heating carbonates coprecipitated in the molar ratio Pb/Cd = 1/2, at 500–525°C, in an oxygen stream at normal pressure, it is possible to prepare an almost pure cadmium orthoplumbate.

The X-ray diffractogram of the orthoplumbate prepared in this way coincides almost exactly with that diffractogram given in the literature, both with regard to the interplanar spacing (d) and the relative intensities, I/I_1. However, the line 1.971 Å ($I/I_1 = 33$) does not appear in the diagram given in the literature, whereas this line is repeated in all the samples studied by us.

INTRODUCTION

Only a few papers on mixed oxides of lead and cadmium have been published. Up to now, only the following compounds have been identified: Cd_2PbO_4, $CdPb_2O_5$, $CdPbO_3$ (I) and $CdPbO_3$ (II). The first and second compounds were obtained by Keester and White [1] in the CdO–PbO system studied in the temperature range 200–750°C and at an oxygen pressure of 100–1500 bar.

The compounds $CdPbO_3$ (I) and $CdPbO_3$ (II) were obtained by dehydration of $CdPb(OH)_6$ prepared in aqueous solution by "controlled precipitation from the homogeneous phase" [2,3].

Cadmium compounds possess a number of photoconductor properties [4] and, therefore, preparing further compounds or obtaining those already prepared by other methods would seem to be of interest.

Our experience with the coprecipitation of carbonates [5–11], and in the study of the compounds obtained during thermal decomposition, induced us to study the coprecipitation of Pb^{2+}/Cd^{2+} solutions with an ammonium

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carbonate solution in three different Pb^{2+}/Cd^{2+} molar ratios: 2/1, 1/1 and 1/2. We consider that a mixed oxide could be obtained during the thermal decomposition of the double carbonates.

The study of the precipitates by X-ray powder diffraction has allowed us to establish that, in every case, the precipitate is a mixture of $PbCO_3$ and $CdCO_3$ and, on decomposition, Cd_2PbO_4 is formed as an intermediate compound.

With the experimental conditions used, it was possible to obtain Cd_2PbO_4 without employing high oxygen pressures.

EXPERIMENTAL

Products

$Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2CO_3$ were from Merck (AR quality).

Preparation of the samples

Twenty-seven samples were prepared by precipitation from aqueous solutions of mixtures of $Pb(NO_3)_2$ and $Cd(NO_3)_2 \cdot 4H_2O$ with an $(NH_4)_2CO_3$ aqueous solution. The amount of carbonate employed was seven times larger than the theoretical value.

The Pb/Cd molar ratios in aqueous solutions of nitrates were: 2/1, 1/1 and 1/2.

The precipitates were obtained by adding the $(NH_4)_2CO_3$ aqueous solution, at boiling point, to the aqueous solution of nitrates, also at boiling point, and vice versa. The digesting times of the precipitates in the mother liquors were: 0, 0.5, 1 and 3.5 h. The precipitates obtained were filtered by means of an N.4 coarse filter, washed with cold distilled water, and dried at room temperature.

The composition of the different precipitates was determined by quantitative chemical analysis. CO_3^{2-}: elemental microanalysis of C, Perkin-Elmer 240 analyser; Pb^{2+}: complexometric titration.

Mechanical mixtures of $PbCO_3/CdCO_3$ were prepared in the same molar ratios as the coprecipitated samples, using the isolated carbonate precipitates obtained by us in the same way as the double carbonates.

Apparatus

TG

A Chevenard thermobalance (model 93) from Adamel was used with photographic recording. Heating rate, 300°C h^{-1}.

DTA

This was constructed in the laboratory using a vertical furnace and a temperature regulation system, both from Adamel. A differential chromel/alumel thermopar was used. Heating rate, 300°C h^{-1}.

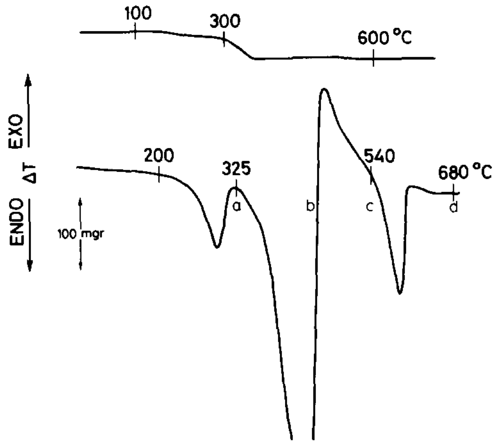
X-ray powder diffraction

A Siemens D-500 diffractometer was used with a graphite monochromater, K 805 generator and Cu $K\alpha_1$ radiation.

RESULTS AND DISCUSSION

A study of the precipitates by X-ray powder diffraction showed that mixtures of $PbCO_3$ and $CdCO_3$ were obtained with all precipitation conditions. The chemical analysis showed that the precipitation of all the Pb^{2+} and Cd^{2+} present in the solution is quantitative; therefore, the lead/cadmium molar ratio in the precipitates is the same as in the respective nitrate solutions. We have also proved that maintaining the precipitates at boiling point for a prolonged period does not change the composition nor the crystalline structure of the same.

The thermal study of the precipitates was carried out in an open atmosphere and with an oxygen stream. All the samples showed the same thermal behaviour: the successive decomposition of $PbCO_3$ and $CdCO_3$ led to the formation of their respective oxides with the intermediate formation of lead



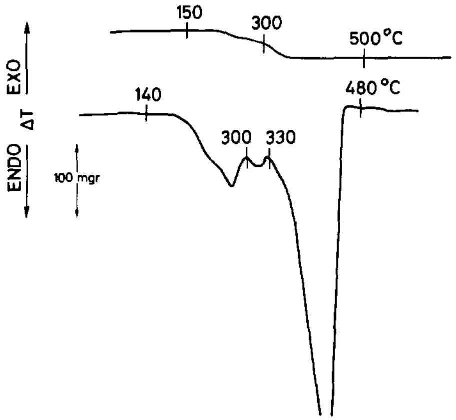


Fig. 1. TG and DTA curves of a coprecipitated sample of molar ratio Pb/Cd = 1/2. Sample weight, 206.4 mg.

Fig. 2. TG and DTA curves of a mechanical mixture of molar ratio Pb/Cd = 1/2. Sample weight, 198.7 mg.

dioxycarbonate, minium and cadmium orthoplumbate. This being so, in Fig. 1 only the TG and DTA curves of a coprecipitated sample of molar ratio Pb/Cd = 1/2 are shown.

The TG curve shows three weight losses and one increase in weight, which correspond to the three endothermic peaks and the one exothermic peak of the DTA curve, respectively.

The analysis by X-ray powder diffraction of samples taken at predetermined points of the DTA curve (a, b, c, d) and the thermogravimetric data allow us to establish the reactions that take place in the coprecipitated samples during heating.

$$\text{(a) } PbCO_3 + CdCO_3 \xrightarrow{200-325^\circ C} PbCO_3 \cdot 2PbO + CdCO_3$$

$$\text{(b) } PbCO_3 \cdot 2PbO + CdCO_3 \xrightarrow{325-540^\circ C} Pb_3O_4 + Cd_2PbO_4 + CdO + PbO$$

$$\text{(c) } Pb_3O_4 + Cd_2PbO_4 \xrightarrow{540-680^\circ C} PbO + CdO$$

In Fig. 2 we give the TG and DTA curves corresponding to a mechanical mixture of molar ratio Pb/Cd = 1/2, in which it is shown that the thermal behaviour is different to that of the coprecipitated samples; in these curves there are no oxidation phenomena.

On making the thermal study of this mixture and examining samples taken at predetermined points of the DTA curve by X-ray powder diffraction, we established the reactions which take place in the mechanical mixtures during heating.

$$\text{(a) } PbCO_3 + CdCO_3 \xrightarrow{200-300^\circ C} PbCO_3 \cdot 2PbO + PbCO_3 \cdot PbO + CdCO_3$$

$$\text{(b) } PbCO_3 \cdot 2PbO + PbCO_3 \cdot PbO + CdCO_3 \xrightarrow{300-330^\circ C} PbCO_3 \cdot 2PbO + PbO + CdCO_3$$

$$\text{(c) } PbCO_3 \cdot 2PbO + CdCO_3 \xrightarrow{330-480^\circ C} PbO + CdO$$

The results obtained throughout our experiments show that during the heating of the coprecipitated samples, minium and cadmium orthoplumbate were obtained, due to the reaction of lead oxide issuing from cerussite decomposition with air oxygen and with CdO from the otavite decomposition, which occurred at the same time as $PbCO_3 \cdot 2PbO$ decomposition.

Therefore, we are able to establish that it is possible to obtain cadmium orthoplumbate from coprecipitated carbonates at normal pressure, whether or not the Pb/Cd molar ratio is stoichiometric.

We carried out two isothermal series, employing a temperature increase of 25°C, between the temperatures of 450 and 550°C at normal pressure, one in an open atmosphere and the other in an oxygen stream, in order: (1) to

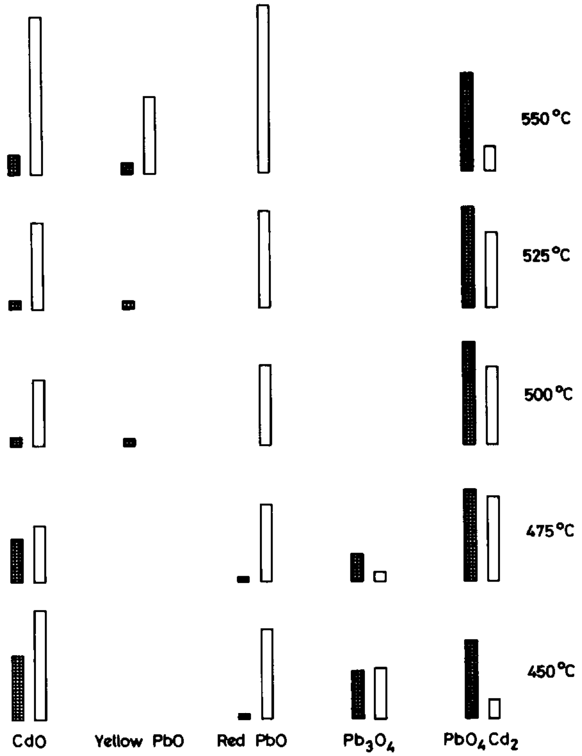


Fig. 3. Bar chart constructed of the height of determined lines of the X-ray diagrams at different temperatures. Shaded bars, oxygen stream; open bars, open atmosphere.

establish the optimum temperature for the formation of cadmium orthoplumbate; (2) to obtain a practically pure compound; and (3) to determine the maximum temperature of stability. The isothermal series were left for 2 h. Samples of molar ratio Pb/Cd 1/2 were used for this isothermal study.

The ten residues of isothermal calcination were studied by X-ray powder diffraction. In order to compare the height of the lines given by different compounds, we employed the same weight of residue in all cases. This way it was possible to observe the evolution of the components at each temperature.

In Fig. 3 we give a bar chart showing the values obtained from the heights of the determined lines of the X-ray diagrams: spacing $(d) = 4.918$ Å for Cd_2PbO_4; 3.3807 Å for Pb_3O_4; 3.1121 Å for red PbO; 2.9463 Å for yellow PbO and 2.3492 Å for CdO. The value given for the line at 3.1121 Å was obtained by deducting the value of the height of the Pb_3O_4 line, overlapped with it.

It is clear from Fig. 3 that, as was foreseen, the oxidation of Pb^{2+} to Pb^{4+} in an oxygen stream is improved and, therefore, the formation of orthoplumbate increased. At all temperatures the amount of orthoplumbate obtained was greater than in an open atmosphere. Using an oxygen stream, the stability interval of Cd_2PbO_4 was between 475 and 550°C, which was slightly superior to that observed in an open atmosphere.

On the other hand, practically pure Cd_2PbO_4 was obtained when an oxygen stream was employed at temperatures of 500 or 525°C, the CdO and PbO impurities being minimal.

It was also observed that red PbO, which shows no reaction at 475°C, is transformed into yellow PbO at 500°C.

Finally, we would mention that the X-ray diffractogram of Cd_2PbO_4 obtained here, coincided in every case with that obtained by Keester and White [1], but it also presented the spacing 1.971 Å with $I/I_1 = 33$, which does not appear in the X-ray diffractogram given by the above-mentioned authors.

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