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MECHANISM OF THE DEHYDRATION OF $CoHPO_4 \cdot 1.5H_2O$

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The dehydration of $CoHPO_4 \cdot 1.5H_2O$ has been followed by means of thermal analyses at quasi isothermal–isobaric conditions. The intermediates and products prepared in the course of the TA and by calcination of the starting hydrogen phosphate in electric ovens at various temperatures have been analyzed and identified by means of thin-layer chromatography, IR spectroscopy, X-ray diffraction analysis and electron microscopy.

Condensed phosphates of divalent metals are thermally and chemically stable compounds [1, 2] whose properties allow their applications in two areas: as long-acting microelement fertilizers and as special inorganic pigments. The cobalt-containing products possess distinct colour hues [3, 4] as well as certain anticorrosion effects.

The condensed phosphates can be prepared by calcination of hydrogen or dihydrogen phosphates of the respective metals or from mixtures containing the corresponding amounts of the phosphoric and the divalent components [1]. The formation of dicobalt diphosphate ($Co_2P_2O_7$) by calcination of cobalt hydrogen phosphate ($CoHPO_4 \cdot 1.5H_2O$) was given considerable attention by some authors [5–8]. The papers, however, are not quite concordant with respect to the formation of the condensation intermediates [5, 6, 8] and to mutual interconversions of the two diphosphate modifications [7, 8, 17]. Structure [9], magnetic properties [10] and application of dicobalt phosphate in the above-mentioned areas [8] were also studied.

On the basis of the results [11] of thermal decompositions of Ca^{2+} and Mg^{2+} hydrogen phosphates carried out by means of the thermogravimetric method at quasi isothermal–isobaric conditions [12, 13] it was presumed that also in the case of

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$CoHPO_4 \cdot 1.5H_2O$ it would be possible to apply the same method to complete the picture of the course of the respective condensation reactions. The present paper gives an account of the experiments carried out in this respect.

Experimental

Pure cobalt(II) hydrogen phosphate in the form of pink-violet fine crystals was prepared [11] by the reaction of cobalt(II) hydroxyde-carbonate with trihydrogen-phosphoric acid. Its X-ray diffraction analysis confirmed a layer structure of the crystalline substance whose typical, most intensive line lies at $d = 7.5 \cdot 10^{-10}$ m. It contained the cobalt(II) and phosphoric components in the molar ratio $CoO/P_2O_5 = 1.997$, and the water content found by calculation was 14.9% which corresponded to 1.5 molecule of crystal water. The thermal analyses carried out at quasi isothermal–isobaric conditions were performed by means of Derivatograph Q–1500 D apparatus (Hungarian Optical Works MOM Budapest). The decomposition rate was 0.5 mg min^{-1} (calculated for 100 mg total weight change). The sample weight was 350 mg, and the examination was carried out in the presence of air.

Various types of platinum crucibles [12, 13] (Fig. 1) were used to the measurements: A) multiplate sample holder, B) open crucible, C) crucible with a lid and D) a labyrinth crucible. The last arrangement (D) holds back the water vapour released by calcination up to the point where its partial pressure in the inside of the crucible reaches 100 kPa (quasi isobaric conditions) [12, 13]. In the case of the

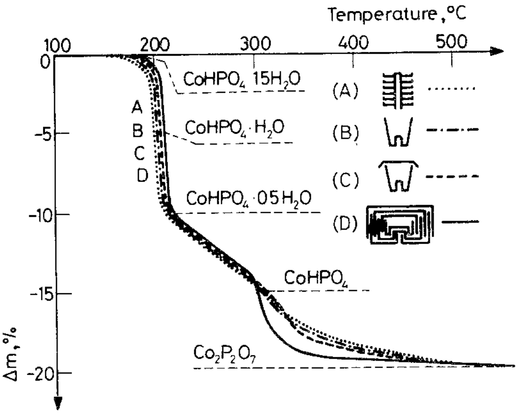

Fig. 1 Thermogravimetric curves traced under quasi isothermal and quasi isobaric conditions by using different kinds of sample holder

multiplate sample holder (A) the water vapour pressure in the course of the calcination can be neglected since it is about 1 kPa. The water vapour pressure in the open (B) and covered (C) crucible is cca 5 and 20 kPa, respectively [12, 13]. The calcinates of the hydrogen phosphate were prepared on the multiplate sample holder (A) and in the labyrinth crucible (D). They were analyzed by means of thin-layer chromatography [14] (the TLC II set), IR spectroscopy [15] (Perkin–Elmer 684 Infrared Spectrophotometer), and X-ray diffraction analysis [9] with an HZG–4 apparatus (GDR).

Results and discussion

From the thermogravimetric (Q–TG) curves recorded under quasi-isothermal, quasi-isobaric conditions (Fig. 1) it is obvious that, at first, one molecule water of crystallization is released from $CoHPO_4 \cdot 1.5H_2O$. This is a single-step process (the weight loss: 9.8%) taking place at different temperatures in the individual sample holders: 208° (A), 212° (B), 216° (C), 220° (D) resp. Accordingly, the decomposition temperatures hardly changed with the decreasing partial pressure of water vapour. From the Q–TG curves it can be seen that the reaction proceeds practically isothermally. From this follows that the reaction leads to an equilibrium. The X-ray diffraction analysis and electron microscopy revealed non-crystalline character of the intermediates corresponding to the molecular formulas $CoHPO_4 \cdot 0.5H_2O$ and $CoHPO_4$ independently whether they were obtained on the multiplate sample holder or in the labyrinth crucible.

The course of the release of the remaining crystal water (4.9% theor) was independent of the type of the sample holder applied i.e. of the partial pressure of water vapour within the sample. At the same time, however, it was also shown that the release of this one half of crystal water molecule does not proceed isothermally but proceeds within a temperature interval of 210–310°. From the facts given it is obvious that the release of this part of crystal water does not lead to any equilibrium. It can be presumed that this remainder of crystal water is bound in another way than the first departing one molecule water of crystallization. The release of the last part of water connected with the condensation reaction investigated (i.e. formation of $Co_2P_2O_7$) began at 300° and finished at about 500°. It also can be stated that this process depends on the type of the crucible used i.e. on the water vapour pressure within the sample, but just in the reverse way as it could be expected. Viz. at about 300° the sequence of the curves turns just the reverse. As the Q–TG curves show in the labyrinth crucible (D) the constitutional water departed at the lowest while on the multiplate sample holder at the highest temperature. This phenomenon can be explained as follows: a higher water vapour pressure in the area of the thermoanalyzed sample promotes the porosity of the $CoHPO_4$ intermediate and hence, facilitates the release of the water molecules. On the other hand, in the case of the multiplate sample holder, in which the water vapour pressure is negligible, and the crust of the formed $CoHPO_4$ intermediate is more compact, the escape of water molecules proceeds slowly.

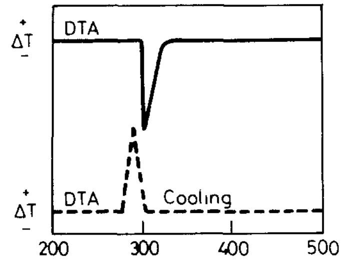

Fig. 2 DTA curves of $Co_2P_2O_7$

With application of DTA [8] a mild exothermic effect was observed at 480° which was ascribed to crystallization of $Co_2P_2O_7$ in accordance with the authors [7, 15]. The said substance is formed in an amorphous form at first, and then it is transformed directly into the high-temperature β-modification, which was confirmed by the X-ray diffraction analysis. This conclusion agrees with that of Ref. [15], which also states a transformation of the amorphous diphosphate into the high-temperature β-modification. On the other hand, the authors [7] present another mechanism: at first the amorphous product is transformed into the α-modification (up to 300°) which is allegedly transformed into the β-modification at temperatures as high as about 500°, the latter transition being connected with the above-mentioned mild exothermic effect in this region. But the energy characteristic of the reversible modification transformation $\alpha \rightarrow \beta$ of $Co_2P_2O_7$, which was observed at 295–300° with pure $Co_2P_2O_7$ (Fig. 2), is endothermic, which supports our conclusions.

Conclusion

The reactions taking place during thermal preparation of dicobalt(II) diphosphate from cobalt(II) hydrogen phosphate and the physical process taking place during further heating or cooling of diphosphate at 100 kPa water vapour pressure can be described as follows:

$$2CoHPO_4\cdot 1.5H_2O \xrightarrow[-2H_2O]{190\text{–}200^\circ} 2CoHPO_4\cdot 0.5H_2O \xrightarrow[-H_2O]{220\text{–}300^\circ} 2CoHPO_4 \rightarrow$$

$$\xrightarrow[-H_2O]{300\text{–}480^\circ} Co_2P_2O_7 \text{ amorph.} \xrightarrow[\text{crystallization}]{500^\circ} \beta\text{-}Co_2P_2O_7 \xrightarrow[\substack{\text{reversible}\\ \text{modification}\\ \text{transformation}}]{300\text{–}295^\circ}$$

$$\rightarrow \alpha\text{-}-Co_2P_2O_7$$

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Zusammenfassung — Mittels thermischer Untersuchungen unter quasiisothermen und quasiisobaren Bedingungen wurde die Dehydratierung von $CoHPO_4\cdot 1.5H_2O$ analysiert. Die im Ergebnis der Thermoanalyse und der Kalzinierens des Hydrogenphosphatausgangsmaterials in einem elektrischen

Ofen bei verschiedenen Temperaturen entstandenen Zwischenprodukte und Produkte wurden mittels Dünnschichtchromatographie, IR-Spektroskopie, Röntgendiffraktion und Elektronenmikroskopie untersucht und identifiziert.

Резюме — С помощью термического анализа в квази-изотермических и квази-изобарных условиях изучена дегидратация $CoHPO_4 \cdot 1.5H_2O$. Методом тонкослойной хроматографии, ИК спектроскопии, рентгенофазового анализа и электронной микроскопии проведен анализ и идентификация промежуточных продуктов дегидратации и продуктов, получаемых в процессе ТА и при обжиге исходного гидрофосфата в электрических печах при различных температурах.