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MECHANISM OF DEHYDRATION OF $ZnHPO_4 \cdot H_2O$

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Thermal analyses under quasi-isothermal-isobaric conditions were used to follow the condensation reactions proceeding during the calcination of zinc hydrogenphosphate. Its calcination in an electric oven under isothermal conditions was adopted for preparation of the intermediates and the main product, which were analysed by chromatography, IR spectroscopy, NMR spectroscopy, X-ray analysis and electron microscopy.

The condensed phosphates of divalent metals are relatively stable compounds both thermally and chemically [1, 2]. They exhibit some properties (colour) [3], anticorrosion ability [4, 5] and luminescence [6] which allow their application as special inorganic pigments [7]. On the other hand, they dissolve very slowly, which predetermines their application as slowly-acting micro-element fertilizers [8]. Diphosphates are formed by calcination of the hydrogenphosphates of the respective metals, or of mixtures of phosphoric acid with the oxide, hydroxide or carbonate with the $M^{II}O/P_2O_5$ molar ratio equal to two [1, 9]. Dizinc diphosphate can be prepared by the calcination of zinc hydrogenphosphate monohydrate ($ZnHPO_4 \cdot H_2O$). The available papers [10, 17] dealing with the problem of the formation of dizinc disphosphate do not give consistent data on the temperatures of release of the crystal water and the subsequent condensation reaction. Our earlier research showed that the temperatures of these processes and their course are markedly affected by the calcination or thermal analysis conditions. Besides the rate of temperature increase, the water vapour pressure in the calcination area also has a distinct effect. As these factors are technologically important, the aim of the present work was to follow the above-mentioned dehydration and condensation reactions under conditions approaching isothermal-isobaric ones.

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Experimental

Pure $ZnHPO_4 \cdot H_2O$ in the form of colourless crystals was prepared by the reaction of an aqueous suspension of zinc hydroxide-carbonate with phosphoric acid at 80° for 5 h [18]. The quality of the starting product was confirmed by X-ray diffraction analysis, and its morphology by electron microscopy.

For separation of the individual processes taking place during the calcination, and for investigation of the effect of water vapour pressure on the course of these processes, the starting hydrogenphosphate monohydrate was submitted to simultaneous TG, DTG and DTA examinations under quasi-isothermal-isobaric conditions [19, 21] by means of the latest type derivatograph fitted with a microcomputer [22] (Derivatograph–C produced by the Hungarian Optical Works (MOM), Budapest). The selected decomposition rate was 0.2 mg min^{-1}. The sample weight was 200 mg; the examination was carried out in the presence of air. Figure 1 is an original chart.

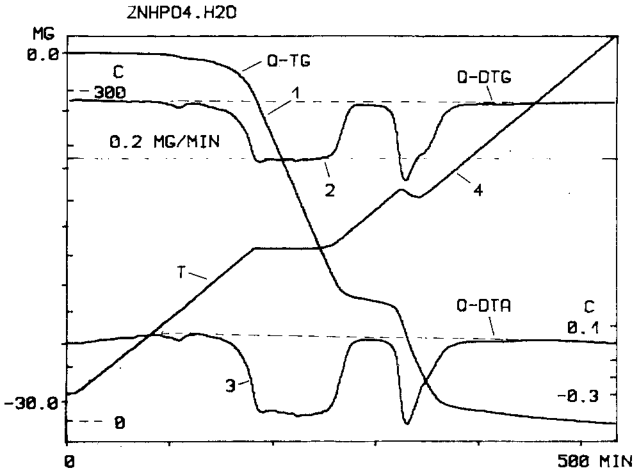

Fig. 1 Simultaneous TG, DTG and DTA curves of $ZnHPO_4 \cdot H_2O$, traced under quasi-isothermal—quasi-isobaric conditions

Various types of platinum crucible (Fig. 2) were used for the measurements [19, 21]: a multiplate sample holder (curve A), an open crucible (curve B), a crucible with a lid (curve C) and a labyrinth crucible (curves 1, 2 and 3 in Fig. 1 and curve D in Fig. 2). The last arrangement holds back the water vapour released by calcination of the starting hydrogenphosphate monohydrate; its partial pressure in the inside of the crucible is about 100 kPa and constant (quasi-isobaric conditions) [19–21]. On the other hand, in the case of the multiplate sample holder (A), the partial

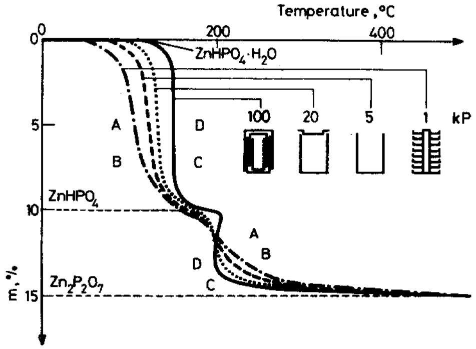

Fig. 2 Q–TG curves traced by using a multiplate sample holder (A), an open (B), a covered (C) and a labyrinth crucible (D)

pressure of the water vapour is so low that it can be neglected in the course of the calcination (it is about 1 kPa). The water vapour pressures given [19–21] for the arrangements (B) and (C) are about 5 and 20 kPa, respectively.

The conditions determined from the thermal analysis results were then adopted for preparation of the main condensation product and intermediates by means of the above mentioned derivatograph–C by quenching. The calcined samples for analyses were also prepared in electric resistance furnaces. The analyses of the individual samples prepared and the identification of the products obtained from the thermal analysis were carried out by means of thin-layer chromatography [23], IR spectroscopy [11, 23] (Perkin–Elmer 684 infrared spectrophotometer), X-ray diffraction analysis [12] (HZG–4, GDR), NMR spectroscopy (JEOL JNM–FX 100) and electron microscopy [24, 25].

Results and discussion

According to the Q–TG curves traced by using the labyrinth sample holder (curve 1 in Fig. 1 and curve A in Fig. 2), the zinc hydrogenphosphate monohydrate first lost the water of crystallization at 155° upon heating. The material lost its constitutional water at 200–210°.

Comparison of the courses of the Q–TG curves in Fig. 2 permits the conclusion that the loss of the water of crystallization is a process leading to equilibrium. Experience indicates [19–21] that if the curves follow one another with a lesser or greater temperature difference in a sequence corresponding to the partial pressure of the gaseous decomposition products, and the process takes place isothermally as occurred in the present case, then it can be stated with high probability that the reaction is a process leading to equilibrium. In contrast, if the curves are either congruent or not congruent, but the sequence does not show regularity, or shows the reverse sequence to that expected from the partial pressure of water vapour prevailing in the sample holders, and if the course of the curves is nonisothermal, then in all probability the reaction does not lead to equilibrium.

A special phenomenon can be observed at about 200° in the course of the Q–TG curves in Fig. 2. In the vicinity of this temperature the sequence of the curves (A, B, C, D) is reserved (D, C, B, A).

The explanation of this phenomenon is as follows.

In accordance with earlier papers [3, 10, 11, 16], it could be stated that amorphous $Zn_2P_2O_7$ was first formed, which was then transformed into crystalline form. The crystallization process took place gradually. Examination of the sample surface by electron microscopy showed that in the multiplate sample holder the original morphology of the starting phosphate particles was maintained to a major extent, while in the sample prepared in the labyrinth crucible a phase composed of new, needle-shaped crystals of the $ZnHPO_4$ intermediate was observed.

Thus, it seems that the pure water vapour atmosphere formed in the labyrinth crucible was favourable for the higher mobility of the lattice elements of zinc pyrophosphate, which promoted the recrystallization and hastened the end of the decomposition process. In fact, such an effect of water vapour is not unknown in thermal analysis [20].

The Q–TG curve in Fig. 1 reveals that the process of loss of constitutional water started with some delay, which caused the overheating of the sample by about 7 degrees. After the hindering factors were eliminated, the sample cooled down spontaneously to 202° again. Thereafter, the temperature of the sample began to increase with growing rapidity up to 250°, where the process practically ended. Accordingly, the course of this section of the curve was not isothermal, i.e. the reaction did not lead to equilibrium. The last traces of water departed from the sample at 500°. This temperature is lower than that given by Duval [14], but higher than those given by other authors [13, 14, 16] or those found in dynamic thermal analysis investigations. Above 550°, the mass of the total sample no longer changed, and the total mass decrease amounted to 15.1%, which corresponds to a release of 1.5 molecule of water (theoretical value: 15.05%).

When $ZnHPO_4 \cdot H_2O$ was calcined in an electric oven, i.e. under isothermal conditions, a mass decrease of 15.1% was attained at 500° (at this temperature, the TLC analysis also revealed the last remnants of simple phosphate anions: less than 3%. Above 500° only $Zn_2P_2O_7$ exists, as confirmed by X-ray diffraction analysis [11, 12] and IR spectroscopy [11, 23]. From the results of thermal and chromatographic analyses, it is obvious that shift in the release of the last portions of constitutional water to relatively high temperatures is connected with the course of the condensation reaction of diphosphate formation and not with the hydration properties of $Zn_2P_2O_7$, as some authors have stated [16]. The X-ray analysis of samples calcined in an oven at temperatures from 220° to 250° already showed the diffraction lines of crystalline $Zn_2P_2O_7$.

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Zusammenfassung — Es wurde eine thermische Analyse unter quasi-isothermen-isobaren Bedingungen zur Untersuchung der während des Kalzinierens von Zinkhydrogenphosphat ablaufenden Kondensationsreaktion durchgeführt. Das Kalzinieren in einem elektrischen Ofen wurde zur Darstellung der Zwischenprodukte und des Hauptproduktes benutzt, welche mittels Chromatographie, Infrarot- und NMR-Spektroskopie sowie Röntgenstrukturanalyse und Elektronenmikroskopie untersucht wurden.

Резюме — Квази-изотермический-изобарный термический анализ был использован для исследования реакций конденсации, протекающих при кальцинировании кислого фосфата цинка. Обжиг, проведенный в электропечи в изотермических условиях, был использован для получения промежуточных продуктов и основного продукта реакции, анализ которых проводился с помощью хроматографии, ИК спектроскопии и спектроскопии ЯМР, рентгеноструктурного анализа и электронной микроскопии.