The composition of the products of Co (II) -Zn dihyphosphates heat treatment under isothermal conditions

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Polymeric phosphates of bivalent metals are widely used as the basis for creating various inorganic materials. For practical realization of their synthesis by heat treatment of hydrated salts the data on their composition, formation temperature and thermal stability of the products of partial and complete dehydration are needed. Such data on the products of Co(II) –Zn dihydrogen phosphates heat treatment under isothermal conditions are absent in the literature. Their preparation is the aim of this work.

Heat treatment of $Co_{1-x}Zn_x(H_2PO_4)_2 \cdot 2H_2O$ ($0 < x < 1.0$) was performed in the range of 100–350 °C (±5 °C). The sample was held at a predetermined temperature for 0.5, 1.5, 3.0, 5.0 and 7.0 hours. The total phosphorus content and anionic composition were determined with quantifying the percentage of each of the polymeric phosphates in the dehydration products.

According to our data, at the heat treatment of $Co_{0.5}Zn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ at 100 °C for 0.5–7 hours a heterophase mixture of solid and liquid phases containing only monophosphate anion is formed. Condensation of the anion in the solid phase begins upon heating up to 150 °C starting a crystalline hydrate. It treatment at this temperature for 0.5 hours leads to the formation of 12.6 wt. % diphosphate and 1.2 wt. % triphosphate. At the increase in the calcination time to 7 hours the degree of polycondensation of the phosphate anion (*n*) rose to 4. The most complex mixture of polymeric phosphates with linear structure of the anion (the *n* value reaches 9) is formed on calcining $Co_{0.5}Zn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ for7 hours at 225°C.

Phosphate with cyclic anion structure, cyclotetraphosphate (up to 5.8 wt. % in terms of P_2O_5), has been identified in the products of $Co_{0.5}Zn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ heat treatment at 275 °C for 3 hours. An increase in the calcination time at this temperature to 7 hours results in the simplification of the anionic composition of the heat treatment product. It consists of cyclotetraphosphate up to 86 % of the total P_2O_5 content. The solid phase obtained at 350 °C practically completely is formed by the condensed phosphate which is $CoZnP_4O_{12}$anhydrous cyclotetraphosphate.

The total percentage of free phosphoric acids in the heat treatment products of $Co_{0.5}Zn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ is maximal, when it is heated for 0.5 hour at 150°C. It presents 8.8 wt.% of P_2O_5 in the form of monophosphate acid. Anionic condensation processes begin at prolonging the heat treatment to 1.5 hours.

Besides monophosphate acid, diphosphate acid (up to 6 % of the total P_2O_5) is formed. The similar changes in the anionic composition of the acid component occur at heat treatment in the range of 150–185 °C. When the temperature rises to 350 °C the percentage of free phosphoric acids decreases. They are absent in the products of thermal treatment of $Co_{0.5}Zn_{0.5}(H_2PO_4)_2 \cdot 2H_2O$ at 350 °C.

The results obtained make it possible to select the optimum conditions for the synthesis of dihydrophosphates $Co_{1-x}Zn_x(H_2PO_4)_2 \cdot 2H_2O$ with different composition and structure of the anion polymeric products of heat treatment. Changing the value of *x* in the range $0 < x < 1.0$ does not almost affect on their composition. When increasing the percentage of cobalt(II), the temperature ranges of polymeric products formation shifts by 10–15 °C to higher temperatures.