

THERMAL BEHAVIOUR OF COBALT(II) DIHYDROGENPHOSPHATE TETRAHYDRATE*Korechko S. A.*, Antraptseva N. M.National University of Life and Environmental Sciences of Ukraine, Kyiv, Ukraine
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Heat treatment of crystal hydrates is one way to obtain anhydrous salts. This process in many respects is defined by extent of hydration of crystalline hydrate. The thermal transformation of cobalt(II) dihydrogenphosphate dihydrate $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ have been determined. Thermal properties of a tetrahydrate – $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ – are studied insufficiently.

The aim of this work was to study thermal behaviour of the $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, to determine the sequence of thermal and structural transformations and how the extent of hydration affects these transformations.

Thermal transformations were studied on a Q-1500D derivatograph.

According to results of the differential and thermal analysis, $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ resistant when heating on air with a rate of 2.5 K/min to 60 °C. Further temperature increase is followed by loss of weight. It on curve TG is registered four accurate steps.

Interpreting the results of the complex characterization of the products of partial and complete dehydration of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$, we found the following: heat treatment of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ in the range of 60–120 °C is followed by removal of two molecules of water on the molecular mechanism and formation of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. At the same time partly the process of disproportionation of anion will be realized with formation of $\text{CoHPO}_4 \cdot 1.5\text{H}_2\text{O}$ and H_3PO_4 .

The second stage of dehydration comes to an end with formation in the range of 120–165 °C mixes of two crystal phases: $\text{Co}(\text{H}_2\text{PO}_4)_2$ and $\text{Co}_5(\text{HPO}_4)_2(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. The quantity of free H_3PO_4 in the thermolysis products of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ increases and at 165 °C makes 2.10 wt % (based on P_2O_5). Process of anion condensation begins on the third stage thermolysis of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$.

At 185 °C losses of weight correspond to removal of 4.57 mol of H_2O . In composition of a salt component are formed condensed phosphate with $n = 2 \div 5$, in composition of acid – polyphosphoric acids of the general formula $\text{H}_{n+2}\text{P}_n\text{O}_{3n+1}$ ($n = 2 \div 4$).

Most difficult is composition of products heating of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ to 280 °C. He is presented mixture condensed phosphates and polyphosphoric acids with $2 \leq n \leq 7$. The condensed phosphates with $n = 3–8$ are X-ray amorphous.

At heating of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ to 310 °C anionic composition of products of thermolysis is simplified. The finish products of dehydration appears. He is identified as cyclotetraphosphate with composition of $\text{Co}_2\text{P}_4\text{O}_{12}$. Crystallization of him closes at 345 °C.

Thus, the sequence of thermal solidphase transformations accompanying thermolysis of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ was established. The composition of products of his partial and full dehydration is identified; the temperature intervals of their formation and thermal stability are concretized.

It is shown, that formation the final product of the thermolysis of the composition $\text{Co}_2\text{P}_4\text{O}_{12}$ (monoclinic system, sp. gr. $C2/c$, $Z = 4$; $a = 1.2080$, $b = 0.8473$, $c = 1.0176$ nm; $\beta = 119.27^\circ$) is realized on two directions. The first direction provides thermal dehydration of the protonated condensed phosphates (up to 65 %). According to the second direction, up to 35 % of $\text{Co}_2\text{P}_4\text{O}_{12}$ is formed as a result solidphase interactions of intermediate products of thermolysis. The general scheme of thermal solidphase transformations of $\text{Co}(\text{H}_2\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ was proposed.