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A MODERN VIEW ON THE THERMOLISIS OF HYDRATE ZINC-MANGANESE(II) PHOSPHATES

Antraptseva N.M.
d.c.s., prof.
ORCID: 0000-0002-5661-6133
Voloshchuk S.V.
student
National University of Life and Environmental Sciences of Ukraine,
Kyiv, Geroev Oboronu, 15
Zhitnetskyi I.V.
c.t.s., as.prof.
ORCID: 0009-0006-3029-7281
Bila G.N.
c.c.s., as.prof.
National University of Food Technologies,
Kyiv, Volodymyrska str., 68, 01601

Abstract. *The work was carried out in order to study the modern view on the thermolysis of zinc-manganese(II) phosphate tetrahydrates of the general formula* $Zn_{3-x}Mn_x(PO_4)_2{\cdot}4H_2O$ $(0<x\leq 1.00)$*. Using the example of phosphate with the composition* $Zn_2Mn(PO_4)_2{\cdot}4H_2O$*, it was established that it is thermally stable when heated to 100-105°C. A further increase in temperature is accompanied by the pairwise removal of four molecules of crystal hydrate water in two stages. The products of partial and complete dehydration were identified as a dihydrate of the composition* $Zn_2Mn(PO_4)_2{\cdot}2H_2O$ *and anhydrous* γ- $Zn_2Mn(PO_4)_2$*. The temperature intervals of their formation and thermal stability are determined. The influence of the heating rate and the nature of the cation on them is shown. Taking into account modern information on thermal transformations of hydrated phosphates of divalent metals, a general scheme for the thermolysis of hydrated zinc-manganese(II) phosphates is proposed. The given for* $Zn_2Mn(PO_4)_2{\cdot}4H_2O$ *dehydration scheme is correct for zinc-manganese(II) phosphates of the general formula* $Zn_{3-x}Mn_x(PO_4)_2{\cdot}4H_2O$ $(0<x\leq 1.00)$ *of various compositions. The influence of the nature of the cation is manifested in the temperature ranges of stability of both the initial crystal hydrates and their dehydration products. They were found to be maximal for phosphates with a higher manganese(II) content, which is due to the energy state of water molecules in their crystal structures.*

Key words: *thermolysis, hydrated phosphates, solid solution, stability, temperature ranges.*

Introduction.

Solid solutions of phosphates of divalent metals, in particular zinc and manganese(II), are used as various construction materials with technically valuable properties that can be purposefully changed by varying the composition of the solid solution and its operating conditions [1,2].

Since most technological processes take place at elevated temperatures, in order to choose the optimal mode of operation of a solid solution, knowledge of its behavior during heating, composition, temperature intervals of formation and thermal stability of products of partial and complete dehydration is necessary.

There is no information on systematic studies of the thermal properties of a solid solution of zinc and manganese(II) hydrated phosphates in the literature.

The purpose of this work is to study the thermolysis of a solid solution of hydrated zinc and manganese(II) phosphates, to determine the composition, temperature intervals of formation and thermal stability of the products of its partial and complete dehydration.

Experimental

A solid solution of the general formula $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$ ($0<x\leq1.00$) ($0<x\leq1.00$) was obtained by the interaction of a mechanical mixture of zinc (77.23 wt.% ZnO) and manganese (53.87 wt.% MnO) hydroxocarbonates with a solution of phosphoric acid (64.13 wt.% P_2O_5) similar to that described in [2]. A saturated solid solution – $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ and phosphates of different cation composition within the homogeneity of the solid solution were used as the main object of the study.

The behavior of phosphates during heating was studied in the temperature range of 25-900°C under dynamic conditions (derivatograph Q-1500D, platinum crucibles with a lid, standard – freshly calcined Al_2O_3, sample weight – 300 mg, heating rate 0.6, 2.5, 5.0 and 10.0 degrees/ min.) and quasi-isothermal (labyrinth crucible, speed 3.0 degrees/min) heating modes. Heat treatment products obtained at temperatures corresponding to thermal effects on the DTA curve were identified similarly [3], using a complex of analysis methods: chemical, X-ray phase analysis, IR spectroscopy.

IR spectra were recorded at 20°C and –190°C in the range of 400-4000 cm-1 on a Nexus-470 spectrometer with Fourier transform and Omnic software. The samples were prepared by pressing a fixed amount (0.05 wt.%) into a KBr matrix.

Results and discussion

According to the results of a thermoanalytical experiment, zinc-manganese(II) phosphate of the composition $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ when heated at a rate of 2.5 degrees/min. thermally stable up to 100-105°C (Table). Its thermal stability can be significantly increased by using a quasi-isothermal mode for heat treatment, in which the partial pressure of water vapor above the sample is close to the thermodynamically balanced one. Under these conditions, mass loss in $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ tetrahydrate begins when heated to 135-145°C, in $Zn_{2.5}Mn_{0.5}(PO_4)_2 \cdot 4H_2O$ – to 130-135°C.

Table – Dependence of formation conditions and thermal stability of thermolysis products $Zn_{3-x}Mn_x(PO_4)_2 \cdot 4H_2O$ ($0<x\leq1.00$) (heating rate 2.5 degrees/min)

Phosphate composition	Thermal stability	First stage of dehydration, °C			Second stage of dehydration, °C		
		Start	End	Maximum speed	Start	End	Maximum speed
$Zn_2Mn(PO_4)_2 \cdot 4H_2O$	100	105	190	160	230	325	305
$Zn_{2,4}Mn_{0,6}(PO_4)_2 \cdot 4H_2O$	95	98	183	155	225	315	295
$Zn_{2,6}Mn_{0,4}(PO_4)_2 \cdot 4H_2O$	90	92	180	152	222	310	285
$Zn_{2,8}Mn_{0,2}(PO_4)_2 \cdot 4H_2O$	85	87	175	150	215	300	280

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An increase in the heat treatment temperature of $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ above 100°C is accompanied by a loss of mass of the sample, which occurs in two stages, each of which corresponds to the removal of two water molecules.

The first stage of dehydration occurs in the range of 105-190°C. The product formed at 190°C is identified as a dihydrate of the composition $Zn_2Mn(PO_4)_2 \cdot 2H_2O$. Its X-ray and IR spectroscopic characteristics (Figure) correspond to those known for isostructural $Zn_3(PO_4)_2 \cdot 2H_2O$ [4,5].

Dihydrate – $Zn_2Mn(PO_4)_2 \cdot 2H_2O$ – is stable during heat treatment in the range of 190-225°C (Table). The X-ray patterns of the samples obtained at 190°C and 225°C show a complete coincidence of the diffraction maxima. Their somewhat higher intensity in $Zn_2Mn(PO_4)_2 \cdot 2H_2O$, obtained at 225°C, indicates its more perfect structure.

The spectrum of the sample obtained under the conditions of heating $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ to 225°C is also completely similar to the previous one (Figure). The two absorption maxima recorded at 20°C in the ν(OH) region are not separated at

-190°C. This indicates that in the interval 190-225°C, the removal of the two least tightly bound water molecules takes place, which is accompanied by the rearrangement of the system of H-bonds in the structure of crystal hydrate.

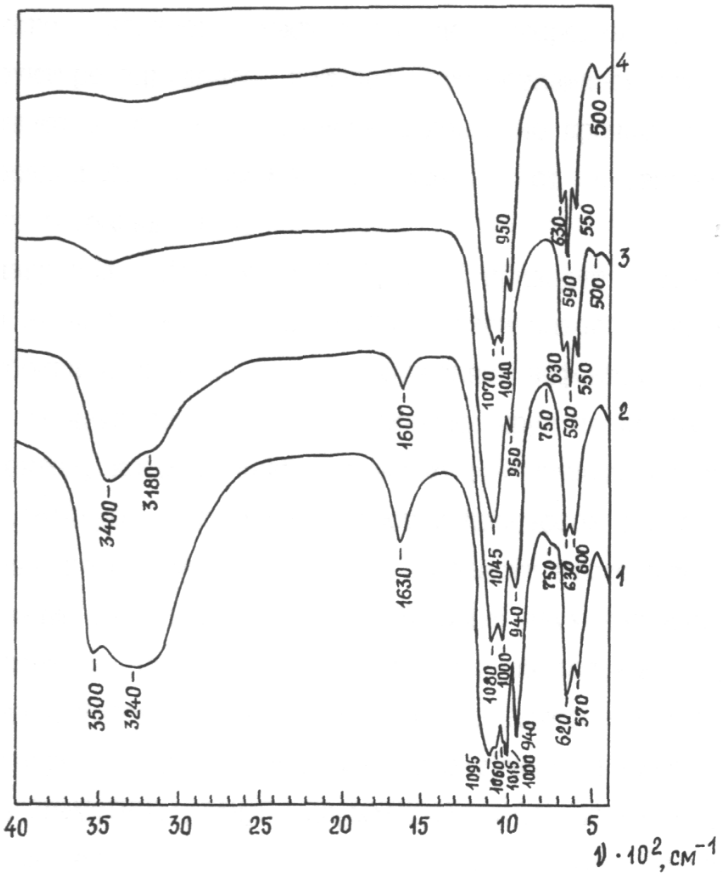

Figure – IR spectra of $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ (1) and its heat treatment products obtained at 190-225°C (2), 325°C (3) and 900°C (4)

When $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ is heated to 230°C, the second stage of dehydration begins. It occurs in the range of 230-325°C and is characterized by the removal of the next two water molecules. At temperatures higher than 325°C, the mass loss of the sample practically stops. Minor changes associated with the removal of the last amounts of water are observed upon heating to 400-450°C.

In the IR spectra, thermal transformations occurring at the second stage of dehydration of $Zn_2Mn(PO_4)_2 \cdot 4H_2O$ are registered as significant changes in the entire spectral range (Figure). Bands of absorption characterizing the oscillations of water molecules are practically absent. The configuration of the absorption bands in the region of the anion's vibrations changes markedly. The spectral range of the main absorption bands narrows even more, and the appearance of a new intense band related to antisymmetric deformation triply degenerate vibrations indicates a significant deformation of phosphate tetrahedra, the interaction of which is weakened by the absence of hydrogen bonds.

The IR spectrum of dehydrated at 900°C $Zn_2Mn(PO_4)_2{\cdot}4H_2O$ is similar to the spectrum of the sample obtained by heating it to 325°C. A clear splitting of absorption bands and an increase in their intensity are evidence of a more perfect structure of dehydrated phosphate. The obtained data complement the results of the X-ray analysis of the dehydration products of $Zn_2Mn(PO_4)_2{\cdot}4H_2O$, according to which the completely dehydrated phosphate is identified as γ-$Zn_2Mn(PO_4)_2$.. It is stable when heated in the range of 325-900°C.

Thus, thermolysis of zinc-manganese(II) phosphate of the composition $Zn_2Mn(PO_4)_2{\cdot}4H_2O$ is accompanied by thermal solid-phase transformations, the sequence of which can be represented by a general scheme:

$$Zn_2Mn(PO_4)_2{\cdot}4H_2O \xrightarrow[-\ 2H_2O]{105\text{-}190^0C} Zn_2Mn(PO_4)_2{\cdot}2H_2O \xrightarrow[-\ 2H_2O]{230\text{-}325^0C} \gamma\text{-}Zn_2Mn(PO_4)_2$$

The specified temperature intervals correspond to heat treatment of $Zn_2Mn(PO_4)_2{\cdot}4H_2O$ with a heating rate of 2.5 degrees/min. A change in speed leads to a shift in the temperature intervals of formation and thermal stability of both the original phosphate and the products of its partial and complete dehydration. So, at a heating rate of 0.6 degrees/min. $Zn_2Mn(PO_4)_2{\cdot}4H_2O$ is stable up to 90°C. In the range of 95-170°C (the first stage of water removal), a phosphate of lower hydration is formed – $Zn_2Mn(PO_4)_2{\cdot}2H_2O$. The dihydrate is stable in the range of 190-215°C and loses 2 molecules of water with the formation of completely dehydrated γ-$Zn_2Mn(PO_4)_2$when heated to 295°C. Under conditions of a heating rate of 10.0 degrees/min. formation of $Zn_2Mn(PO_4)_2{\cdot}2H_2O$ and γ-$Zn_2Mn(PO_4)_2$ is recorded at 115-235°C and 270-345°C, respectively. At the same time, the general regularities of the process are preserved.

The given for $Zn_2Mn(PO_4)_2{\cdot}4H_2O$ dehydration scheme is correct for zinc-manganese(II) phosphates of the general formula $Zn_{3-x}Mn_x(PO_4)_2{\cdot}4H_2O$ ($0<x\leq1.00$) of various compositions. The influence of the nature of the cation is manifested in the temperature ranges of stability of both the initial crystal hydrates and their dehydration products. They were found to be maximal for phosphates with a higher manganese(II) content, which is due to the energy state of water molecules in their crystal structures.

Summary and conclusions

The thermolysis of zinc-manganese(II) phosphate tetrahydrates of the general formula $Zn_{3-x}Mn_x(PO_4)_2{\cdot}4H_2O$ ($0<x\leq1.00$) was investigated. Using the example of phosphate with the composition $Zn_2Mn(PO_4)_2{\cdot}4H_2O$, it was established that it is thermally stable when heated to 100-105°C. A further increase in temperature is accompanied by the pairwise removal of four molecules of crystal hydrate water in two stages.

The products of partial and complete dehydration were identified as a dihydrate of the composition $Zn_2Mn(PO_4)_2{\cdot}2H_2O$ and anhydrous γ-$Zn_2Mn(PO_4)_2$. The temperature intervals of their formation and thermal stability are determined. The influence of the heating rate and the nature of the cation on them is shown.

Taking into account modern information on thermal transformations of hydrated phosphates of divalent metals, a general scheme for the thermolysis of hydrated zinc-manganese(II) phosphates is proposed.

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