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OBTAINING OF CHROMIUM(III) PHOSPHATES(V) IN THE SOLID-STATE AND THEIR THERMAL STABILITY

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As a result of solid-state reactions four chromium(III) phosphates(V) have been obtained, i.e. $Cr(PO_3)_3$, $Cr_4(P_2O_7)_3$, $Cr_2P_4O_{13}$ and $CrPO_4$. $Cr_2P_4O_{13}$ has been obtained as a result of a solid-state reaction between Cr_2O_3 and $(NH_4)_2HPO_4$ as well as between $CrPO_4$ and $Cr(PO_3)_3$ mixed at a molar ratio of 1:1 or between $Cr_4(P_2O_7)_3$ and $Cr(PO_3)_3$ mixed at a molar ratio of 1:2. Melting temperatures and the products of thermal decomposition have been determined for the obtained chromium(III) phosphates(V).

Keywords: *chromium(III) phosphate(V), DTA, XRD*

Introduction

Phosphates(V) of transition metals, owing to their interesting properties, can find many practical applications, e.g. as catalysts, anticorrosive pigments, sensors or materials used in the production of lasers [1–3].

The following compounds are known in the binary system Cr_2O_3–P_2O_5: orthophosphate $CrPO_4$ [4–6], pyrophosphate $Cr_4(P_2O_7)_3$ [7, 8], metaphosphate $Cr(PO_3)_3$ [8, 9], metatetraphosphate $Cr_4(P_4O_{12})_3$ [9], orthotriphosphate $Cr_5(P_3O_{10})_3$ [7], metahexaphosphate $Cr_2P_6O_{18}$ [10]. All the listed above chromium(III) phosphates(V) have been obtained by mixing in appropriate proportions a solution of ammonium phosphate(V) with a solution of chromium(III) nitrate(V), evaporating them to dryness and next heating the residue at selected temperatures [4–10].

Some of the three latter phosphates correspond to the same molar ratio Cr:P as one of the first three phosphates – namely: $Cr_2P_6O_{18}$ and $Cr_4(P_4O_{12})_3$ exhibit a ratio of Cr:P=1:3 just like the metaphosphate. The formation of different compounds at the same composition of the reacting mixture is explained by some authors as due to variational conditions of heating the solid residue after the evaporation of the reacting mixture [7, 10].

The recently obtained orthotetraphosphate $Cr_2P_4O_{13}$ has been reported to be a co-product found in a non-stoichiometric mixture when a chromium analogue of $Mo_3P_5SiO_{19}$ was tired to be prepared [11]. $Cr_2P_4O_{13}$ has not been obtained in a pure state, but it contained small amounts of Cr_2O_3 and P_2O_5 as impurities [11]. For the purpose of indexing and structure solution one single crystal of $Cr_2P_4O_{13}$ was mechanically selected. The results showed a monoclinic cell, space group $P2_1/c$, the unit cell parameters: a=0.8097(2) nm, b=0.8787(3) nm, c=1.3098(4) nm, β=105.54(2)°, Z=4 [11].

The aim of this work was investigating which chromium(III) phosphates(V) can be obtained as a result of solid-state reactions between Cr_2O_3 and $(NH_4)_2HPO_4$ under normal pressure and performing a synthesis of $Cr_4P_2O_{13}$ that would allow a pure product to be obtained. Because of inconsistent literature information about thermal properties of chromium(III) phosphates(V), it seemed interesting to conduct a research aimed at establishing precisely the ranges of thermal stability of individual chromium(III) phosphates(V) and determining the kind of their decomposition products.

Experimental

Preparation of samples

All samples were prepared from Cr_2O_3, p.a. (Aldrich, Germany) and $(NH_4)_2HPO_4$, pure (POCh, Poland) by the conventional calcination method [12, 13]. Appropriate portions of the reactants were homogenized by grinding, pressed into pellets and heated in the atmosphere of air in several stages, until an equilibrium state had been attained. The heating conditions of individual samples differed, depending on their composition, both as to the heating temperature and the heating time period at given temperature.

After the final heating stage all samples were cooled very gradually (together with the furnace) to ambient temperature and next the pellets were ground and subjected to DTA and XRD investigations. Such procedure was realized in order to obtain monophase samples. The individual phosphates(V) were obtained in the following cycles:

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$Cr(PO_3)_3$: 450°C (24 h)+650°C (3·24 h)+
700°C (3·24 h)+800°C (24 h)

$Cr_4(P_2O_7)_3$: 450°C (24 h)+700°C (3·24 h)+
800°C (24 h)+850°C (2·24 h)

$CrPO_4$: 450°C (24 h)+700°C (3·24 h)+
800°C (24 h)+850°C (2·24 h)

Methods

Thermal analysis

The DTA investigations were carried out by means of the apparatus SDT 2960 (TA Instruments). All measurements were conducted in the atmosphere of helium. The samples subjected to the measurements weighed as little as ca. 6 mg and were placed in quartz crucibles. The heating rate amounted to $10°C\ min^{-1}$.

XRD investigations

Phases occurring in the samples were identified on the base of the XRD investigations results (diffractometer DRON-3, Bourevestnic, Sankt Petersburg, Russia, radiation CoK_α filter Fe). The identification of individual phases was performed by using the XRD characteristics contained in the PDF files [14] and the data reported in the work [11].

Results and discussion

Products of the solid state reaction

The work was begun with an attempt to obtain pure $Cr_2P_4O_{13}$ by a solid-state reaction. For this purpose a mixture comprising 20 mol% Cr_2O_3 and 80 mol% $(NH_4)_2HPO_4$ was prepared. This mixture was heated at 400°C for 24 h in order to remove NH_3 and H_2O, next the sintering cycles were the following: 850°C (3·24 h), 900°C (3·24 h), 915°C (24 h), 1000°C (3·24 h). The $Cr_2P_4O_{13}$ phase was identified on the base of XRD patterns by comparison with a pattern of $Cr_2P_4O_{13}$ generated from the data of Lii *et al.* [11]. The obtained results prove that the solid-state reaction between Cr_2O_3 and $(NH_4)_2HPO_4$ leads to a formation of pure $Cr_2P_4O_{13}$ according to the equation:

$$Cr_2O_{3(s)}+4(NH_4)_2HPO_{4(s)}= Cr_2P_4O_{13(s)}+8NH_3\uparrow+6H_2O\uparrow \quad (1)$$

The diffraction lines set characteristic for $Cr_2P_4O_{13}$ was recorded also in the case of the product of solid-state reactions between $CrPO_4$ and $Cr(PO_3)_3$ mixed at a molar ratio of 1:1 as well as between $Cr_4(P_2O_7)_3$ and $Cr(PO_3)_3$ mixed at a molar ratio of 1:2. The corresponding samples were heated in the following stages: 650°C (2·24 h), 900°C (2·24 h), 950°C (2·24 h), 1000°C (2·24 h). The equations of the occurring reactions can be written as follows:

$$CrPO_{4(s)}+Cr(PO_3)_{3(s)}=Cr_2P_4O_{13(s)} \quad (2)$$

$$Cr_4(P_2O_7)_{3(s)}+2Cr(PO_3)_{3(s)}=3Cr_2P_4O_{13(s)} \quad (3)$$

Further investigations were aimed at establishing which chromium(III) phosphates(V) can be obtained as a result of solid-state reactions under normal pressure. Table 1 presents the composition of samples prepared for the research, their preparation conditions and the kind of phases detected in individual samples after the final heating stage. The DTA method can provide the information about the temperature region of the formation about samples. The heating was interrupted if the results were identical after last two successive stages of heating. The data compiled in Table 1 prove that as a result of solid-state reactions four chromium(III) phosphates(V) can be obtained under normal conditions, namely $Cr(PO_3)_3$, $Cr_2P_4O_{13}$, $Cr_4(P_2O_7)_3$ and $CrPO_4$.

Diffraction patterns of samples comprising in their initial mixtures 17.50, 22.50 or 25.00 mol% Cr_2O_3 (mixed with $(NH_4)_2HPO_4$), taken after the last heating cycle, revealed only the presence of diffraction lines characteristic for $Cr(PO_3)_3$. Thus it can be assumed that a formation of $Cr(PO_3)_3$ occurred in them according to the equation:

$$Cr_2O_{3(s)}+6(NH_4)_2HPO_{4(s)}= 2Cr(PO_3)_{3(s)}+12NH_{3(g)}\uparrow+9H_2O_{(g)} \quad (4)$$

while the excess of P_2O_5 in the samples 1 and 2 underwent a sublimation in the conditions of this synthesis.

Diffractograms of samples that had comprised 26.50, 29.50 or 31.00 mol% Cr_2O_3 in their initial mixtures, taken after heating at 930°C, contained two sets of diffraction lines, characteristic for $Cr(PO_3)_3$ and $Cr_2P_4O_{13}$, whereas in the case of a sample comprising 33.33 mol% Cr_2O_3 in its initial mixture only one set of diffraction lines was recorded, characteristic for $Cr_2P_4O_{13}$. This corroborates a conclusion that the formation of this compound can occur according to Eq. (1).

Diffraction patterns of subsequent samples comprising in their initial mixtures 34.50, 37.00 or 39.00 mol% Cr_2O_3, recorded after the final heating stage, contained two sets of diffraction lines, characteristic for $Cr_2P_4O_{13}$ and $Cr_4(P_2O_4)_3$, and it was only in the case of a sample comprising 40.00 mol% Cr_2O_3 in its initial mixture that one alone set of lines was registered, characteristic for $Cr_4(P_2O_7)_3$. This allows a conclusion that this compound can be formed in the solid state according to the equation:

$$2Cr_2O_{3(s)}+6(NH_4)_2HPO_{4(s)}= Cr_4(P_2O_7)_{3(s)}+12NH_{3(g)}\uparrow+9H_2O_{(g)} \quad (5)$$

Table 1 Composition of initial mixtures in terms of system components, conditions of synthesis and kind of phases detected in equilibrium samples

No.	Composition of samples in terms of system components/mol%		Conditions of synthesis	Phases detected after final heating stage
	Cr_2O_3	P_2O_5		
1	17.5	82.5	450°C (24 h)+600°C (3·24 h)+ 600°C (2·24 h)	$Cr(PO_3)_3$
2	22.5	77.5		
3	25	75	450°C (24 h)+650°C (3·24 h)+ 700°C (3·24 h)+800°C (2·24 h)	$Cr(PO_3)_3$
4	26.5	73.5	450°C (24 h)+650°C (3·24 h)+ 800°C (3·24 h)+900°C (24 h)+930°C (2·24 h)	$Cr(PO_3)_3$, $Cr_2P_4O_{13}$
5	29.5	70.5		
6	32	68		
7	33.33	66.67	450°C (24 h)+850°C (3·24 h)+ 900°C (3·24 h)+915°C (24 h)+1000°C (3·24 h)	$Cr_2P_4O_{13}$
8	34.5	65.6	450°C (24 h)+850°C (3·24 h)+ 900°C (3·24 h)+930°C (2·24 h)	$Cr_2P_4O_{13}$, $Cr_4(P_2O_7)_3$
9	37	63		
10	39	61		
11	40	60	450°C (24 h)+750°C (3·24 h)+ 800°C (24 h)+850°C (2·24 h)	$Cr_4(P_2O_7)_3$
12	41.5	58.5		$Cr_4(P_2O_7)_3$, $CrPO_4$
13	44.5	55.5		
14	48	52		
15	50	50		$CrPO_4$
16	55	45	450°C (24 h)+850°C (3·24 h)+ 900°C (3·24 h)+930°C (2·24 h)	$CrPO_4$, Cr_2O_3
17	65	35		
18	75	25		
19	85	15		
20	95	5		

Diffractograms of samples that had comprised in their initial mixtures 41.50, 44.50 or 48.00 mol% Cr_2O_3, taken after the last heating cycle, revealed beside a set of diffraction lines characteristic for $Cr_4(P_2O_7)_3$ also the presence of a line set characteristic for $CrPO_4$. This set as the only one was recorded in the case of a sample comprising 50.00 mol% Cr_2O_3 in its initial mixture, which indicates that the formation of $CrPO_4$ occurred according to the equation:

$$Cr_2O_{3(s)}+6(NH_4)_2HPO_{4(s)}= \\ 2Cr(PO_3)_{3(s)}+12NH_{3(g)}\uparrow+9H_2O_{(g)} \qquad (6)$$

Diffraction patterns of all samples comprising in their initial mixtures more than 50.00 mol% Cr_2O_3 contained two sets of diffraction lines, characteristic for $CrPO_4$ and Cr_2O_3.

The presented research results prove that it is possible to obtain, as a result of solid-state reactions under normal pressure, four from among chromium(III) phosphates(V), namely $Cr(PO_3)_3$, $Cr_4(P_2O_7)_3$, $Cr_2P_4O_{13}$ and $CrPO_4$, while three other phosphates(V) described in literature, i.e. $Cr_4(P_4O_{12})_3$, $Cr_5(P_3O_{10})_3$ and $Cr_2P_6O_{18}$, failed to be obtained in this way.

The thermal behaviour of the phosphate compounds

The present work comprises moreover some investigations of the thermal stability of the obtained chromium(III) phosphates(V).

Figure 1 presents DTA curves of four obtained chromium(III) phosphates(V). In the DTA curve of $Cr(PO_3)_3$ (Fig. 1a) four endothermic effects were recorded with their onset temperatures amounting respectively to: 1325, 1360, 1425 and 1450°C, accompanied by varying mass losses. The first from among these effects was assumed to be due to the decomposition of chromium(III) metaphosphate(V). The mass loss associated with the first endothermic effect was equal to 25 mass%, which allows a conclusion that the first stage of decomposition occurs probably according to the equation:

$$2Cr(PO_3)_3=Cr_2P_4O_{13}+P_2O_5 \qquad (7)$$

The calculated mass loss corresponding to this reaction amounts to 24 mass%.

The second endothermic effect with its onset at 1360°C, recorded also in the DTA curve of $Cr_2P_4O_{13}$ (Fig. 1b) and not recorded in the DTA curves of $Cr_4(P_2O_7)_3$ and $CrPO_4$ (Figs 1c and d), can

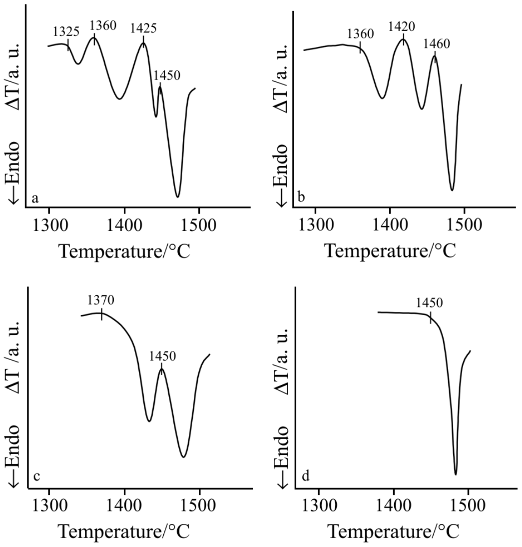

Fig. 1 DTA curves of: a – $Cr(PO_3)_3$, b – $Cr_2P_4O_{13}$, c – $Cr_4(P_2O_7)_3$, d – $CrPO_4$

be ascribed to the decomposition of chromium(III) orthotetraphosphate(V) that occurs probably according to the equation:

$$2Cr_2P_4O_{13}=Cr_4(P_2O_7)_3+P_2O_5\uparrow \qquad (8)$$

The calculated mass loss during the decomposition of $Cr_2P_4O_{13}$ is equal to 16 mass%, whereas the mass loss read from the TG curves amounted to 17 mass%.

The third endothermic effect that was also registered in the DTA curves of chromium(III) orthotetraphosphate(V) (Fig. 1b) and chromium(III) diphosphate(V) (Fig. 1c), but was not registered in the case of chromium(III) orthophosphate(V) (Fig. 1d), can be attributed to the thermal decomposition of $Cr_4(P_2O_7)_3$ occurring as follows:

$$Cr_4(P_2O_7)_3=4CrPO_4+P_2O_5\uparrow \qquad (9)$$

The corresponding mass decrease read from the TG curve that amounted to 21 mass% is consistent with the calculated mass decrease equal to 19 mass%.

The last from among the endothermic effects, beginning at the onset temperature of 1450°C, occurs also in the DTA curves of chromium(III) orthotetraphosphate(V) (Fig. 1b), diphosphate(V) (Fig. 1c) and orthophosphate(V) (Fig. 1d), and is associated with the decomposition of $CrPO_4$ that takes place probably according to the equation:

$$2CrPO_4=Cr_2O_3+P_2O_5\uparrow \qquad (10)$$

This reaction is accompanied by a mass loss that was read from the TG curve and amounted to 50 mass%, whereas the calculated mass loss is equal to 48 mass%.

The thermal decomposition of the compound $Cr_2P_4O_{13}$ is a three-stage reaction and begins at 1360°C (Fig. 1b). The mass decrease read from the TG curve and equal to ca. 16 mass% indicates that the first stage of decomposition occurs according to Eq. (8). The second endothermic effect that begins at 1420°C is due to the decomposition of $Cr_4(P_2O_7)_3$ in accordance with the Eq. (9), whereas the third stage takes place according to the Eq. (10). The total mass loss read after the last decomposition stage amounts to 67 mass%, while the theoretical mass loss consistent with the proposed equations is equal to 65 mass%.

In the DTA curve of $Cr_4(P_2O_7)_3$ two endothermic effects were recorded, which proves a two-stage course of the thermal decomposition of chromium(III) diphosphate(V) (Fig. 1c). The first stage occurs according to Eq. (9) and the corresponding mass decrease read from the TG curve, equal to 18 mass%, remains in good agreement with the calculated value amounting to 19 mass%. The other stage with its onset at 1450°C is associated with the decomposition of $CrPO_4$ that takes place according to Eq. (10).

The thermal decomposition of $CrPO_4$ starts at 1450°C (Fig. 1d). The mass loss read from the TG curve amounts to 51 mass%, which corresponds exactly to the value calculated for the reaction (10) and equal to 48 mass%.

Conclusions

The results of the conducted research allow the following statements:

- The solid-state reaction between Cr_2O_3 and $(NH_4)_2HPO_4$ leads to a formation of pure $Cr_2P_4O_{13}$ according to Eq. (1). This compound in a pure state can also be obtained as a result of solid-state reactions between $CrPO_4$ and $Cr(PO_3)_3$ mixed at a molar ratio of 1:1 as well as between $Cr_4(P_2O_7)_3$ and $Cr(PO_3)_3$ mixed at a molar ratio of 1:2, in accordance with the Eqs (2) and (3).
- $Cr_2P_4O_{13}$ decomposes thermally in three stages. The decomposition starts at 1360°C. The product of the first stage of decomposition is $Cr_4(P_2O_7)_3$, second – $CrPO_4$ and third – Cr_2O_3.
- As a result of the solid-state reaction between Cr_2O_3 and $(NH_4)_2HPO_4$ four stable chromium(III) phosphates(V) can be obtained, namely $Cr(PO_3)_3$, $Cr_2P_4O_{13}$, $Cr_4(P_2O_7)_3$, $CrPO_4$. The remaining three phosphates reported in literature either correspond to the same molar ratio Cr:P as one of the above-mentioned phosphates – namely $Cr_2P_6O_{18}$ and $Cr_4(P_4O_{12})_3$ exhibit a ratio of Cr:P=1:3 just like the metaphosphate – or cannot be found in samples after a sufficiently long-time and high-temperature sintering – as it is in the case of the $Cr_5(P_3O_{10})_3$ phase. Thus, these three phosphates cannot be stable under the normal conditions, unlike the meta-, orthotetra-, pyro- or orthophosphate.

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