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A STUDY OF THE REACTIONS DURING FORMATION OF $c\text{-}Ni_2P_4O_{12}$

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ABSTRACT

The reaction course of the calcination of $Ni(H_2PO_4)_2 \cdot 2H_2O$ to give nickel cyclotetraphosphate has been studied by thermogravimetry under quasi-isothermal-isobaric conditions. Isothermal calcination was also carried out in an electric furnace at various temperatures for 20 min. The reaction products were analysed by chromatography, IR and NMR spectroscopy and X-ray diffraction. The compositions of the calcinates were determined through extraction with various inorganic and organic solvents. It was found that the water-vapour pressure has a great influence on the course of these condensation reactions, as well as on the temperature and velocity of the reactions, and on their results. Depending on the vapour pressure, there is a partial splitting of the first condensation product, the dihydrogendiphosphate.

INTRODUCTION

In our laboratory, the cyclotetraphosphates of some bivalent metals for use as special thermostable inorganic pigments have been synthesised and tested [1–4]. These compounds are formed by the calcination of dihydrogenphosphates of bivalent metals or by the calcination of a mixture containing the phosphorus and bivalent metal components in the corresponding ratio [5–8]. $c\text{-}Ni_2P_4O_{12}$ is a very important product of such a process [9]. The published literature [5–8,10,11] does not provide sufficiently precise data on the conditions of preparation. Therefore, we have followed the processes taking place during calcination of nickel(II) dihydrogenphosphate by means of thermal analysis (TA) with both dynamic (non-isothermal) and quasi-isothermal, quasi-isobaric (Q-TA) conditions.

EXPERIMENTAL

The measurements were carried out with a derivatograph, type Q-1500 (MOM Budapest, Paulik–Paulik–Erdey system). Platinum crucibles of various types were used, capable of trapping the water vapour released from the

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phosphate sample at various pressures [12]. Then the individual products and intermediates were prepared by calcination of the starting phosphate in an electric oven, and they were analysed by instrumental analytical methods (IAMs): thin layer chromatography [13], infrared spectroscopy [14] and X-ray diffraction analysis [15]. The surface changes were observed using electron microscopy. Extractions of the calcinates with various solvents (acetone, water, 0.3 M HCl) made it possible to determine the temperature ranges in which the individual intermediates exist [16] and the degree of conversion of the calcinates to the $c\text{-Ni}_2P_4O_{12}$ product [17].

RESULTS AND DISCUSSION

Non-isothermal TA

With non-isothermal conditions of TA (temperature increase 5 ° C min^{-1}), see Fig. 1, the release of four water molecules (two of water of crystallization and two of constitutional water) from the initial $Ni(H_2PO_4)_2 \cdot 2H_2O$ can be seen to take place in three steps. These are accompanied by endothermal effects within the temperature intervals 130–230 ° C, 230–350 ° C and 350–450 ° C using a labyrinth crucible in which the water vapour pressure is 100 kPa. Using an open crucible (vapour pressure 5 kPa), the temperatures are 30–60 ° C lower. The TG, DTA and DTG curves apparently indicate that the two molecules of crystal water are released in one process. An interesting difference can be seen in the course of the TG curves after the four water molecules have been lost from the starting phosphate (24.94%): in the labyrinth crucible, the sample mass does not change any more, while in the open crucible, there is a slight, steady mass loss (by about 1% of the original sample mass up to 600 ° C).

Quasi-isothermal, quasi-isobaric TA

The thermogravimetric curves (Q-TG) recorded with quasi-isothermal, quasi-isobaric conditions (decomposition rate 0.3 mg min^{-1}) indicate that both molecules of water of crystallization are lost from $Ni(H_2PO_4)_2 \cdot 2H_2O$ (Fig. 2) in the first step (weight loss 12.5%), within the following temperature intervals for the different crucible types: multi-plate (A), 50–90 ° C; open crucible (B), 70–120 ° C; crucible with lid (C), 85–140 ° C; and labyrinth crucible (D), 110–150 ° C (180 ° C). It is clear from the Q-TG curves that this reaction proceeds practically isothermally. Thus it follows that this reaction leads to equilibrium. The presence of anhydrous $Ni(H_2PO_4)_2$ in the temperature interval from 150 to 180 ° C in the labyrinth crucible was confirmed by IR spectra and by X-ray diffraction analysis, confirming its crystalline character.

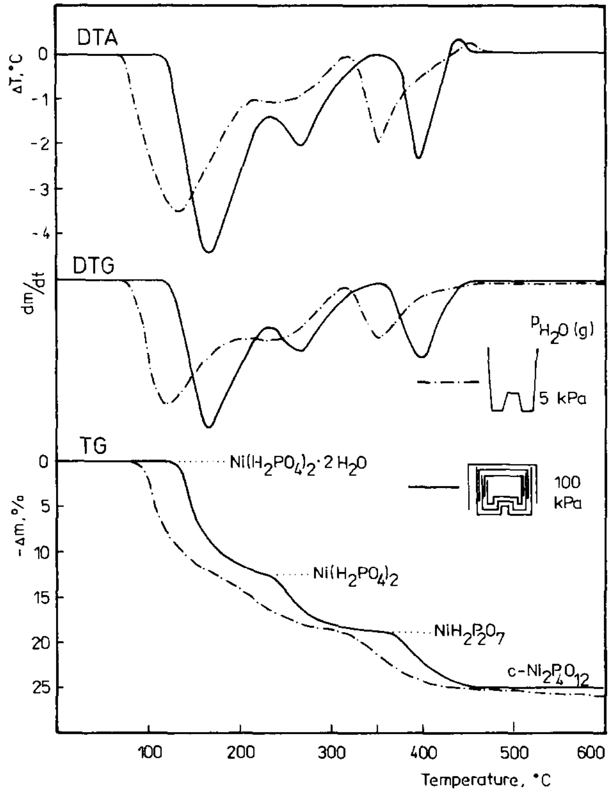

Fig. 1. Simultaneous TG, DTG and DTA curves of $Ni(H_2PO_4)_2 \cdot 2H_2O$ under non-isothermal (dynamic) conditions. Apparatus, Derivatograph Q-1500; heating rate, 5 °C min^{-1}; sample weight, 600 mg; standard, α-Al_2O_3. Sensitivity of the balances: TG, 200 mg; DTA and DTG, 1/3. Atmosphere, air; –·–·–, open crucible, $pH_2O(g) = 5$ kPa; ———, labyrinth crucible, $pH_2O(g) = 100$ kPa.

The formation of the first condensation product, NiH_2P_2O, corresponding to the loss of the first molecule of constitutional water, extends over a broader temperature interval which depends on the crucible type used, i.e. on the water-vapour present: 95–240 °C (A); 120–270 °C (B); 140–310 °C (C); and 180–360 °C (D). Consequently, the Q-TG curves show inflexion points at the mass loss corresponding to $NiH_2P_2O_7$. The existence of $NiH_2P_2O_7$ was confirmed by means of TLC and IR spectroscopy (the presence of absorption bands corresponding to valence vibrations of dihydrogendiphosphate [14]. The amorphous nature of the intermediate $NiH_2P_2O_7$ formed within the given temperature interval was confirmed by X-ray diffraction analysis and electron microscopy, which indicated a certain degree of porosity in this intermediate (this degree probably depends on the water-vapour pressure).

The intermediate (which was also prepared by calcination of the starting sample, temperature increase 2 °C min^{-1}) was subjected to extraction ex-

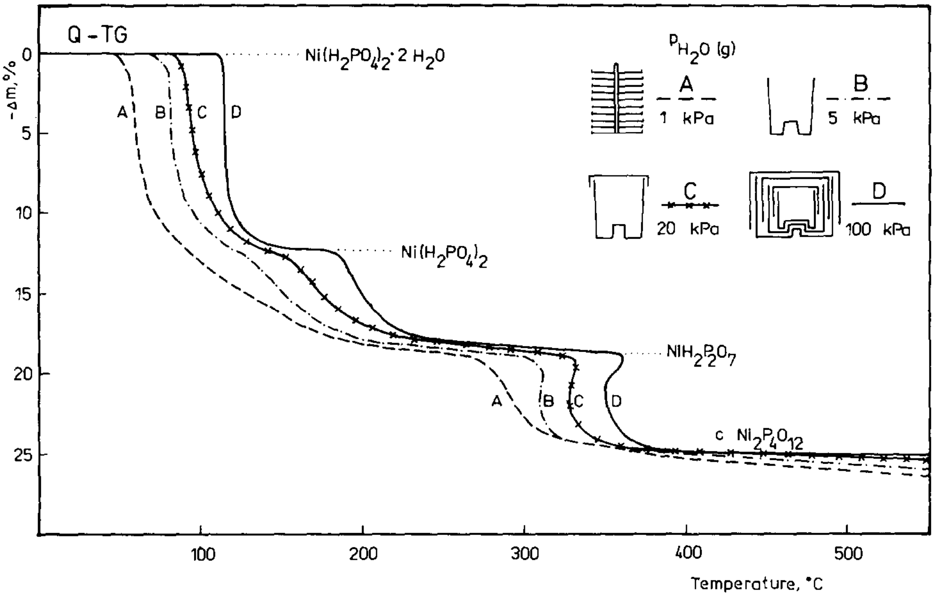

Fig. 2. Thermogravimetric curves of $Ni(H_2PO_4)_2 \cdot 2H_2O$ under quasi-isothermal, quasi-isobaric conditions. Apparatus, Derivatograph Q-1500; decomposition rate, 0.3 mg min^{-1}; sample weight, 300 mg; atmosphere, air. A, Multi-plate crucible, $pH_2O(g) = 1$ kPa; B, open crucible, $pH_2O(g) = 5$ kPa; C, crucible with a lid, $pH_2O(g) = 20$ kPa; D, labyrinth crucible, $pH_2O(g) = 100$ kPa.

periments which indicated, see Fig. 3, that part of the phosphate component is split off, either in the form of phosphoric acid from the intermediate anhydrous dihydrogenphosphate, or in the form of diphosphoric acid from the first condensation product, dihydrogendiphosphate. Figure 3 shows a distinct region of enhanced extractability of P_2O_5 by acetone from calcinates prepared in crucible A at 125–270 °C and in crucible D at 200–380 °C. These regions correspond to the formation and existence of the first condensation product, $NiH_2P_2O_7$. The phosphate component is partially extracted with acetone from this intermediate which, at the same time, is partially transformed into the normal diphosphate, $Ni_2P_2O_7$ (the ratio of NiO/P_2O_5 found approaches 2).

The temperatures at which the last of the water is released from the calcined sample, i.e. the second molecule of constitution water from the initial dihydrogenphosphate, and which correspond to the second condensation reaction, the formation of c-$Ni_2P_4O_7$, again depend on the type of crucible employed, i.e. on the partial pressure of water vapour between the grains of the calcined sample. At the same time, however, it was found that this transformation did not exhibit an isothermal course, occurring within fairly wide temperature intervals: A, 240–360 °C; B, 270–370 °C; C, 310–380 °C; and D, 360–400 °C. These results imply that the decomposition

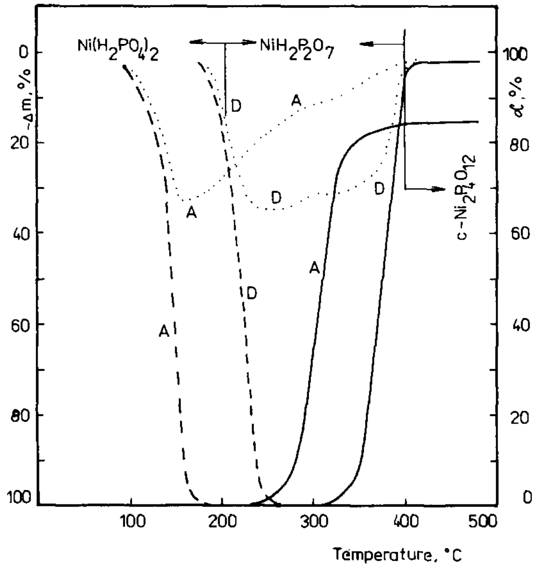

Fig. 3. Extraction experiments of calcinates of $Ni(H_2PO_4)_2 \cdot 2H_2O$. Calcination conditions: 2 °C min^{-1}; $pH_2O(g) = 1$ kPa (A) or 100 kPa (D). Weight changes determined by extraction using acetone (······); water (— — —) or 0.3 M HCl (———) (α, degree of conversion for c-$Ni_2P_4O_{12}$).

reaction leads to equilibrium. This conclusion, however, is not in accordance with the loss of the second molecule of constitutional water. Considering all the circumstances, we can conclude that the reaction probably leads to equilibrium, but that its course is affected by the different degrees of porosity of the crust formed on the grains. With crucible D the total mass loss is 25.0%, and it does not change further with increasing temperature. This agrees well with the theoretical value of 24.94% corresponding to the total release of four water molecules from the starting $Ni(H_2PO_4)_2 \cdot 2H_2O$. The analytically determined c-$Ni_2P_4O_{12}$ content in the labyrinth-type crucible was more than 98%. When using crucibles which produce lower water vapour pressures, a slight mass decrease continued even when the temperature was higher than that of the formation of c-$Ni_2P_4O_{12}$; in the case of the multi-plate crucible it was about 2% of the starting mass up to 550 °C, i.e. to the end of the TA measurement. This is connected with side reactions involving splitting of the phosphate components and the origin of ultraphosphates. This lowers the yield of the main product, c-$Ni_2P_4O_{12}$: when a multi-plate type of crucible was used, the determined content of cyclotetraphosphate was 85%; in the open crucible, the content was 91%; and in the crucible with a lid, 95%.

These conclusions were confirmed by extraction experiments performed on the calcinates prepared under the respective conditions in an electric furnace (0.3 M HCl was used for the extraction, see Fig. 3). At the water-vapour pressure of about 100 kPa, the calcinations of $Ni(H_2PO_4)_2 \cdot 2H_2O$

produce the first yield of final product, $c\text{-}Ni_2P_4O_{12}$ above 330 °C ($pH_2O(g) \approx 1$ kPa above 250 °C); the final steady-state degree of conversion found in the calcinate at $pH_2O(g) \approx 100$ kPa was 98% $c\text{-}Ni_2P_4O_{12}$ (at 425 °C) and at $pH_2O(g) \approx 1$ kPa was about 85% $c\text{-}Ni_2P_4O_{12}$ (at 450 °C).

CONCLUSIONS

The above-described investigation of the effect of the presence of water vapour on the course of condensation reactions during the calcination of $Ni(H_2PO_4)_2 \cdot 2H_2O$ indicates that the individual reactions taking place at the water-vapour partial pressure of 100 kPa can be represented by the following scheme

$$Ni(H_2PO_4)_2 \cdot 2H_2O \xrightarrow[-2H_2O]{100\text{–}150\,^\circ C} Ni(H_2PO_4)_2 \xrightarrow[-H_2O]{180-360\,^\circ C} NiH_2P_2O_7 \qquad (1)$$

$$2NiH_2P_2O_7 \xrightarrow[-2H_2O]{360(350)\text{–}400\,^\circ C} c\text{-}Ni_2P_4O_{12} \qquad (2)$$

At lower vapour pressures, the reaction proceeds at temperatures 20–100 °C lower, the yield of the final $c\text{-}Ni_2P_4O_{12}$ also being lower.

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