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REACTION OF FORMATION OF c-$Co_2P_4O_{12}$, A STUDY USING THERMAL ANALYSIS METHODS

M.TROJAN, D.BRANDOVÁ and Z.ŠOLC
Institute of Chemical Technology Pardubice, 532 10 Czechoslovakia

ABSTRACT

The thermal behaviour of $Co(H_2PO_4)_2.2H_2O$ and reaction of formation of c-$Co_2P_4O_{12}$ is described in this paper. Increasing temperature evolves the hydrate water at first, then follows the constitute water and the condensation reactions of the phosphate anions. It was found that this water vapour pressure has a great influence on the course of these condensation reactions, on the temperature and velocity of the reactions and their result too. According to the vapour pressure there occurs a partial splitting of the first condensation product - dihydrogendiphosphate.

INTRODUCTION

Dicobalt cyclo-tetraphosphate is formed on calcination of cobalt (II) dihydrogen phosphate or calcination of a mixture containing the phosphorus and the cobalt components in the corresp. ratio (ref. 1,2). Available papers do not give sufficiently precise data on conditions of the preparation. Therefore, we have followed the processes taking place during calcination of dihydrogenphosphate by means of thermal analysis (TA) at both dynamic-non-isothermal and quasi-isothermal-isobaric (Q-TA) conditions.

METHODS

The measurements were carried out with a Q-Derivatograph type Q-1500 (MOM Budapest, system F.Paulik, J.Paulik, L.Erdey). Platinum crucibles of various types (Fig. 2, ref. 3) were used which enabled trapping of the water vapour released from the phosphate sample at various tensions . The TG curves from dynamical TA were evaluated mathematically. Then the individual products and intermediates were prepared by calcination of the starting phosphate in an electric oven, and they were analyzed by instrumental methods (IMA) - thin layer chromatography, infrared spectroscopy and X-ray diffraction analysis. The surface changes were observed using electron microscopy. Extractions of the calcinates with various solvents enabled a determination of temperature regions of

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the existence of the individual intermediates.

RESULTS AND CONCLUSIONS

As shown by Q-TA (Fig.2) the crystal water is released from the starting phosphate in two steps - at 105-150°C and 150-155°C- if the labyrinth arrangement is used. Formation of the first condensation product $CoH_2P_2O_7$ is extended over a broader temperature interval 130-250°C (depending on the crucible type used, i.e. on tension of water vapour). The extraction experiments with the calcinates prepared in electric oven established the temperature region of the existence of $CoH_2P_2O_7$ within 180 and 240°C with the maximum in the range 200-230°C. The IMA methods confirmed its composition, molecular structure, and amorphous character. Different values of water vapour tension in the calcinated sample caused different surface porosity of this intermediate. The extraction experiments showed that the microcrystalline cyclo-tetraphosphate begins to be formed from the temperature of 240°C already. This temperature corresponds to Q-TA in the crucible type A. The open crucible (B) and that with a lid (C), however, exhibited higher corresponding temperature (270°C), whereas with the labyrinth arrangement the range was 280-295°C. The crucibles with low water vapour tension (A,B) showed, however, a subsequent decrease of the sample temperature. Hence, the nucleation which initiates the condensation reaction takes place at a higher temperature than that corresponding to the proper reaction, i.e. at higher energy content in the compound. If a sufficient amount of the nuclei are formed, the equilibrium is re-established, and the reaction proceeds at the speed chosen (0.4 mg/min) and at the temperature corresponding to the actual water vapour pressure. At the same time, however, the intermediate $CoH_2P_2O_7$ is partially split. A part of the phosphorus component is released in the form of phosphoric or diphosphoric acid which undergoes independent condensation reaction. At the beginning, these reactions also proceed at temporarily decreased temperature; with the temperature further increasing, higher polyphosphoric acid condensates are formed. An enhanced portion of the cobalt component in the calcinate is compensated by partial formation of $Co_2P_2O_7$. Thus the yield of the main reaction product (cyclo-tetraphosphate) is decreased. Up to the temperature of the Q-TA measurement (380°C), the calcinate only contained 80% c-$Co_2P_4O_{12}$, the total weight decrease being lower than that corresponding to libera-

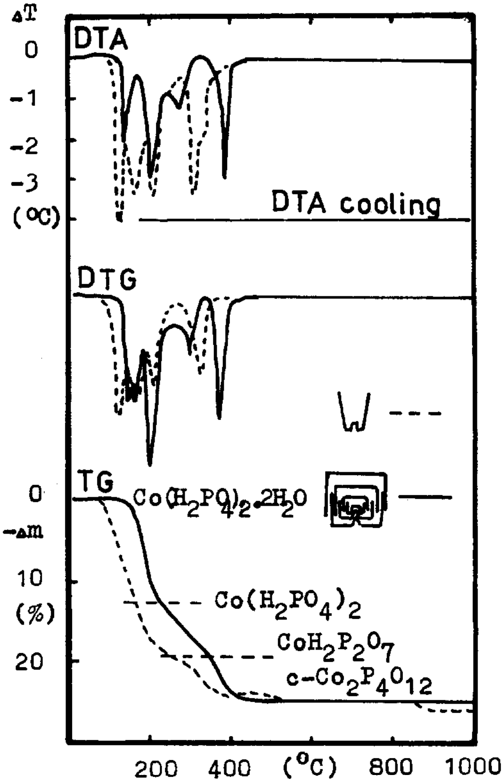
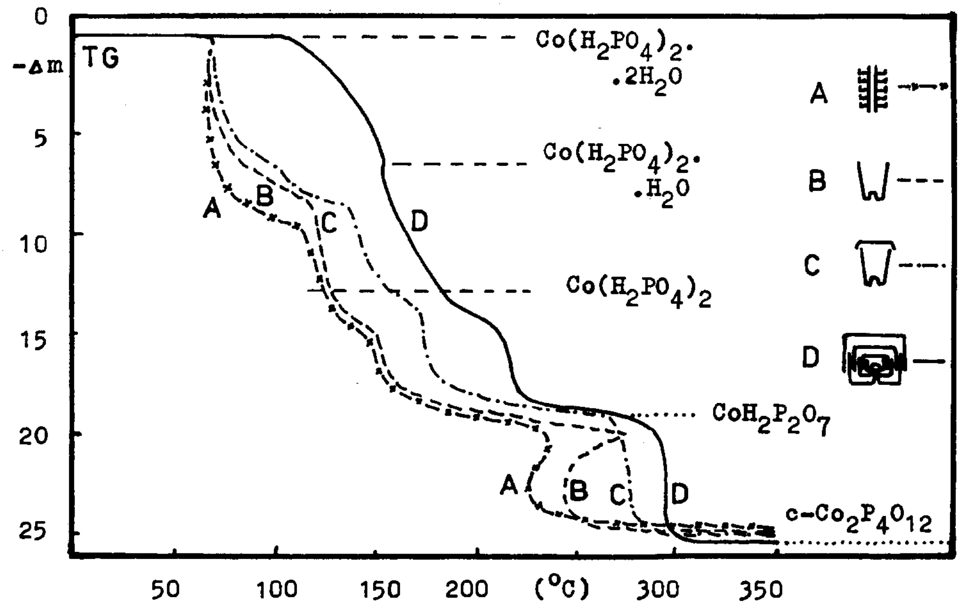


Fig. 1. DTA, DTG, TG curves $Co(H_2PO_4)_2.2H20$ recorded at dynamic conditions

Sample weight: 800 mg
Atmosphere: air
Sensitivity of the balance:
TG 200 mg; DTA, DTG 1/3
Temperature increase:
$2,5^oC.min^{-1}$

Fig. 2. TG curves $Co(H_2PO4)_2.$ $.2H_2O$ recorded at quasi-isothermal-quasi-isobaric coditions
Sample weight: 800 mg
Decomposition rate: $0,4mg.min^{-1}$



tion of four water molecules. This is due to the fact that both the independent condensation of the phosphorus component and formation of $Co_2P_2O_7$ are shifted to higher temperatures (ref.4) than that of formation of cyclo-tetraphosphate. The same fact explains the unexpected weight decrease of the sample in the open crucible above 840°C which was recorded by the dynamic TA (Fig.1). At this temperature the highly condensed phosphoric acid is decomposed, and the liberated phosphorus pentoxide is evaporated (ref.4). During the Q-TA in the labyrinth crucible (D), the formation of cyclo-tetraphosphate proceeds almost isothermally (280-295°C) and leads to an equilibrium. Above 300°C the degree of conversion into $c\text{-}C_2P_4O_{12}$ was higher than 95%, and the total sample weight decrease corresponded precisely to four water molecules. Hence, the processes taking place during calcination of $Co(H_2PO_4)_2.2H_2O$ at the water vapour tension corresponding to atmospheric pressure (100 kPa) can be described by the following scheme:

$$Co(H_2PO_4)_2.2H_2O \xrightarrow[-H_2O]{105\text{-}150^\circ C} Co(H_2PO_4)_2.H_2O \xrightarrow[-H_2O]{155\text{-}180^\circ C}$$

$$\rightarrow Co(H_2PO_4)_2 \xrightarrow[-H_2O]{180\text{-}240^\circ C} CoH_2P_2O_7 \xrightarrow[-H_2O]{280\text{-}295^\circ C} \frac{1}{2}\ c\text{-}Co_2P_4O_{12}$$

Mathematical treatment of the TG curves from dynamical TA revealed diffusion to be the controlling process of the condensation reaction. This is best expressed by the anti-Jander equation $[((1+\alpha)^{1/3} - 1)^2 = kt]$ for the so-called countercurrent diffusion (ref.5). This result agrees with the consideration of the porosity of the sample surface and its effect on the condensation reaction course.

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