THERMOANALYTICAL INVESTIGATION OF LAYERED TITANIUM SALTS

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Abstract

The investigated materials have similar routes of thermal decomposition; i.e. they lose their crystal water first, then at a higher temperature their structural one. At least the result TiP_2O_7 goes through a phase change at about 1000 K. The amorphous titanium phosphate lost its crystal and structural water at higher temperature than those of crystalline forms. Both α- and γ-titanium phosphates and also their transition metal containing forms have layered structure. In case of α- and γ-forms after the loss of crystal water a phase change occurs which is followed by the decomposition of the molecule.

Various transition metals containing γ-titanium phosphates lose their crystal water at the same temperature, with the exception of Ni containing ones. The process is finished in this case at temperature 90 K higher than that of the others.

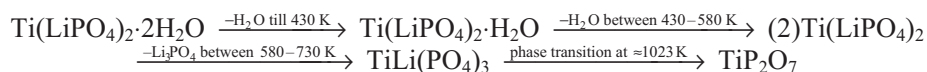**Keywords:** phosphate, thermal analysis, titanium, transition metals

Introduction

Among the acidic salts of tetravalent metals, after the corresponded zirconium compounds, titanium phosphate and related materials have been widely investigated. Crystalline titanium phosphate (TiP) has been obtained independently in various laboratories by refluxing the amorphous gel in phosphoric acid with different concentration [1–3] for a few days or by direct precipitation via fluoro-complex [4–5]. Titanium phosphate and other related salts have their own interest as catalysts in some dehydrogenation reactions, especially, in nuclear chemistry practice as ion exchangers for the separation of the products of various nuclear reactions and as a target material for the production of $^{m}Tc^{99}$ isotope, which is widely used in medicine [6, 7].

The γ-crystalline form was later synthesized by Alberti *et al*. [8]. They used a so-called direct precipitation method which goes through the fluoro complex of titanium. This method resulted in a layered monoclinic crystalline form with higher density of fixed charges than there are in α-zirconium phosphate. Later the structure of γ-titanium phosphate was investigated in detail by Christensen *et al*. [9]. They determined the cell

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parameters, the binding distance between the ions and gave a possible arrangement of them in the molecule. In addition to the structure and ion exchange behaviour it is very important to know the thermal behaviour of such materials. Only few works were done on this topic. From them, data of thermal decomposition of zirconium and titanium phosphates, given by La Ginestra *et al*. [10] could be mentioned. Chernorukov *et al*. [11] during the titration of α-TiP with Li ions investigated the thermal behaviour of the resulted material by DTA. They found that the dehydration process is

$$Ti(LiPO_4)_2 \cdot 2H_2O \xrightarrow{-H_2O \text{ till } 430 \text{ K}} Ti(LiPO_4)_2 \cdot H_2O \xrightarrow{-H_2O \text{ between } 430-580 \text{ K}} (2)Ti(LiPO_4)_2$$
$$\xrightarrow{-Li_3PO_4 \text{ between } 580-730 \text{ K}} TiLi(PO_4)_3 \xrightarrow{\text{phase transition at } \approx 1023 \text{ K}} TiP_2O_7$$

The titanium salts especially the transition metal containing forms can act as semi-conductors. Investigating this behaviour of the mentioned materials we must learn more information on them. For this reason the thermal decomposition of various crystalline forms of titanium phosphate and their derivatives containing various first-row divalent transition metals (Co(II), Ni(II), Mn(II), Cu(II) and Zn(II), respectively) was investigated. The results are collected in this paper.

Experimental

All used chemicals were of MERCK analytical grade.

Sample preparation

The amorphous titanium phosphate (TiPa) was prepared by mixing the stoichiometric quantity of $TiCl_4$ in 1 M solution of HCl and 4 M H_3PO_4 at 80°C. The precipitate was filtered, washed till pH=4 and dried in exsiccator above P_2O_5. α- and γ-titanium phosphates (α-TiP, γ-TiP) were prepared by the methods proposed first by Alberti *et al*. [4, 8], respectively.

Preparation of ion exchange forms

γ-TiP was equilibrated with solutions containing various first-row divalent transition metal ions under the following conditions:

100 cm^3 of 0.1 M *M*(II)-acetate solution was added to 3 g of γ-TiP. The mixture was stirred and heated to 353 K and held at this temperature – with constant stirring and solution level – for 200 h, respectively. After the equilibration was complete the precipitate filtered and air dried. The quantity of added solution was calculated taking into consideration the exchange capacity (≈30% of total capacity). The supernatant liquid was stored for analytical determination.

Methods

The metal(II) content both of the original and the residual solutions was checked, by spectrophotometry [12], using a Spectromom 195D photometer. The quantity of exchanged ions was calculated from the difference between the *M*(II) contents of the

initial and the residual acetate solutions. The concentration values obtained are given in Table 1. The samples were subsequently checked by elemental (carbon) analysis to ascertain whether any acetate remained. The titanium and phosphate were determined using methods described by Sandell [12].

Table 1 Analytical data

Solution	Concentration of M(II)/mM mL^{-1}				
	Co(II)	Ni(II)	Mn(II)	Cu(II)	Zn(II)
Initial	0.08	0.10	0.10	0.10	0.10
*	0.008	0.01	0.01	0.01	0.01
Residual	0.017	0.025	0.016	0.015	0.016
Ion uptake	0.063	0.075	0.084	0.085	0.084
%	78.75	75.0	84.0	85.2	84.0

* – dilution ×10 for standard

Identification

Identification of the samples were carried out using XRD method at the conditions described earlier [13].
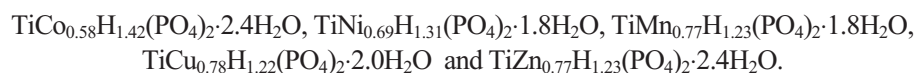
Thermal analysis

The measurements were carried out with a Mettler TA-1-HT computer controlled thermobalance that simultaneously provided DTA and TG data. The heating rate was chosen 5°C min^{-1}. The temperature range was 273–1100 K, the reference material was Al$_2$O$_3$, ambience: air, the experiments were carried out in a Pt crucible. The data were evaluated by means of a computer program.

Result and discussion

The measured values of titanium and phosphate give a ratio of 1:2. The elemental (carbon) analysis showed no acetate in the investigated samples. Evaluating the analytical data (Table 1) we found that during 200 h equilibration 78.75, 75.0, 84.0, 85.2, and 84.0% of Co(II), Ni(II), Mn(II), Cu(II) and Zn(II) were taken up, respectively. During the shorter contacting time these quantities are drastically decreased independently whether α- or γ-crystalline form titanium phosphate was used. At the end of the process the ion uptake became slower and slower and the total (100%) change of hydrogen to transition metal ions could not be achieved under the given experimental conditions. Taking these data into consideration the following Ti/M(II) ratios could be calculated: 1/0.58, 1/0.69, 1/0.77, 1/0.78 and 1/0.77 for Co(II), Ni(II), Mn(II), Cu(II), and Zn(II) containing samples, respectively.

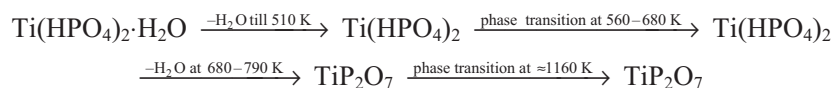Consequently the following compositions are suggested for the samples:

$$TiCo_{0.58}H_{1.42}(PO_4)_2 \cdot 2.4H_2O, \ TiNi_{0.69}H_{1.31}(PO_4)_2 \cdot 1.8H_2O, \ TiMn_{0.77}H_{1.23}(PO_4)_2 \cdot 1.8H_2O,$$
$$TiCu_{0.78}H_{1.22}(PO_4)_2 \cdot 2.0H_2O \ \text{and} \ TiZn_{0.77}H_{1.23}(PO_4)_2 \cdot 2.4H_2O.$$

α-TiP have similar structure to that of α-zirconium phosphate but since the length of the Ti–O bond is shorter than that of the Zr–O one, consequently other dimensions were found for the unit cell. Namely: it has layered monoclinic structure with interlayer distance of $d_{002}=0.750\pm0.0001$ nm and elementar cell parameters of $a=0.864\pm0.0001$ nm, $b=0.501\pm0.0001$ nm, $c=1.617\pm0.0001$ nm and $\beta=110°$. For γ-TiP the following parameters were found: interlayer distance $d_{002}=1.16\pm0.0001$ nm and the elementar cell has dimensions of $a=0.521\pm0.0001$ nm, $b=0.644\pm0.0001$ nm, $c=2.316\pm0.0001$ nm and $\beta=110°$. The XRD diffractogram of the first-row transition metal containing γ-TiP samples showed a new peak around $2\Theta=10°$ region. Detailed analysis of the reflections shows that these materials also have monoclinic structure and they are inhomogeneous from the crystallographic point of view. They consist of reflections (with decreased intensity) characteristic of γ-TiP. The cell parameters of transition metal containing titanium phosphate samples are collected in Table 2.

Table 2 Unit cell parameters and interlayer spacing of various transition metal containing (γ-titanium phosphate materials

	a/nm	b/nm	c/nm	β/°	d_{002}/nm
Co(II)	1.0722	0.5407	2.4611	106.8	1.1409
Ni(II)	0.9944	0.5556	1.9778	105.3	0.9603
Mn(II)	0.9296	0.5519	2.1556	104.6	1.0220
Cu(II)	0.9333	0.5557	2.5500	103.3	1.2596
Zn(II)	0.9994	0.5370	1.9334	107.8	0.9255

Data concerning the thermal behaviour discussed as follows: For the amorphous titanium phosphate two endothermic processes with mass loss were found (Fig. 1a). The first covers the crystal water loss while the second is related with the structural water loss. In case of α-TiP three endothermic processes (the first and third with mass loss) were found. In addition, an exothermic process without mass loss (with a peak at 1160 K) was observed (Fig. 1b). The total mass loss was found of 24.3%, which divided the endothermic processes practically into two equal parts. Taking into consideration the initial molecule composition 1–1 mole H_2O per molecule unit is lost during the discussed processes. In agreement with these data the decomposition of α-TiP can be described as follows:

$$Ti(HPO_4)_2 \cdot H_2O \xrightarrow{\ -H_2O \ till \ 510 \ K\ } Ti(HPO_4)_2 \xrightarrow{\ phase \ transition \ at \ 560-680 \ K\ } Ti(HPO_4)_2$$

$$\xrightarrow{\ -H_2O \ at \ 680-790 \ K\ } TiP_2O_7 \xrightarrow{\ phase \ transition \ at \ \approx1160 \ K\ } TiP_2O_7$$
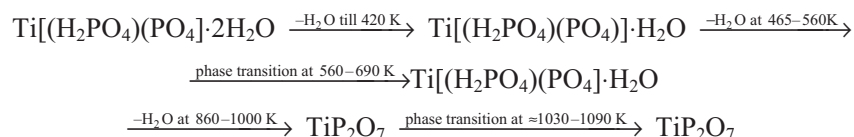
The second endothermic process (without mass loss) is related with the reversible solid phase transition. It takes place in the temperature range of 560–680 K. This process
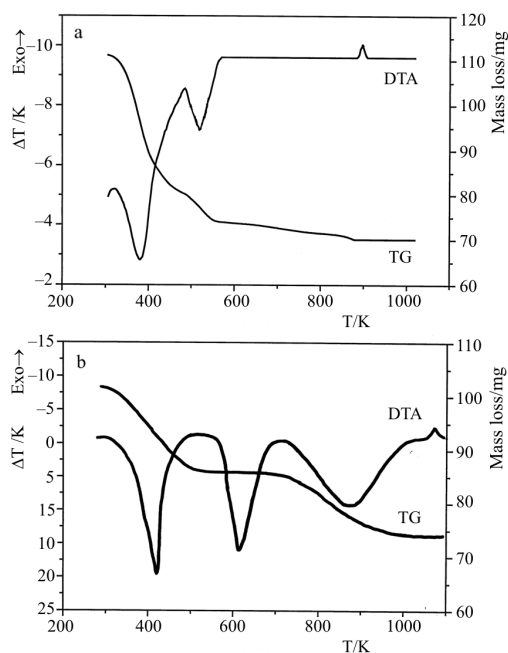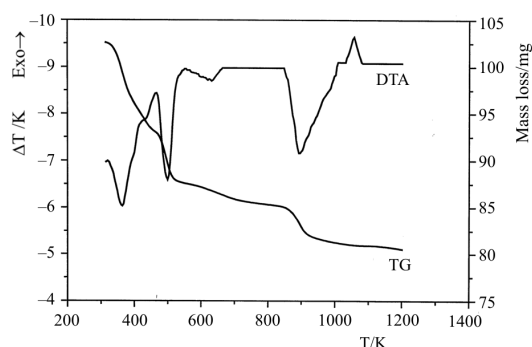
Fig. 1 DTA and TG curves of α-titanium phosphate; a – amorphous, b – α-form

requires less heat as it is neccessary for the loss of the first mole of water, as it was declared by Moraglio *et al.* [14]. The layered structure is prescribed till 1123 K, while at this temperature a rearrangement to cubic, three dimensional structure was observed.

γ-titanium phosphate (γ-TiP) showed characteristic similarities with γ-zirconium phosphate not only in its structure but in its thermal behaviour, too (Fig. 2). Namely, taking into consideration the analytical data 2 mole per molecule unit of crystal water were found, which were bound in different strength as suggested by XRD data. The second mole of crystal water is lost at a relatively high temperature which made us suppose that it must have been some bonding role between the layers. Immediately after that a reversible solid phase change takes place. The fourth endothermic process with mass loss can be ordered to the loss of structural water originating from the decomposition of hydrogen phosphate groups and at least the exothermic process characterises the rearrangement of titanium pyrophosphate to a cubic three-dimensional structure. Combining the analytical and thermal analytical data the initial material could be described by the formula of $Ti[(H_2PO_4)(PO_4)]\cdot 2H_2O$ and its thermal decomposition is characterized as follows:

$$Ti[(H_2PO_4)(PO_4)]\cdot 2H_2O \xrightarrow{-H_2O\ \text{till}\ 420\ K} Ti[(H_2PO_4)(PO_4)]\cdot H_2O \xrightarrow{-H_2O\ \text{at}\ 465-560K}$$

$$\xrightarrow{\text{phase transition at}\ 560-690\ K} Ti[(H_2PO_4)(PO_4]\cdot H_2O$$

$$\xrightarrow{-H_2O\ \text{at}\ 860-1000\ K} TiP_2O_7 \xrightarrow{\text{phase transition at}\ \approx 1030-1090\ K} TiP_2O_7$$

Fig. 2 DTA and TG curves of γ-titanium phosphate

Data concerning the transition metal containing TiP samples are collected in Table 3 and are shown on Figs 3–7.

Practically, the thermal decomposition of these materials takes place in the same way; i.e. the crystal water is lost in two steps which is followed by the structural water loss and the crystalline phase change (about 1000 K). The two-step-character of crystal water loss is involved that it is bound so strongly in γ-TiP that it retained its original place in the structure during the whole ion exchange process, and after.

Table 3 Data of thermal decomposition of transition metal containing γ-titanium phosphate

Ion exchange form	Temperature range/K	Mass loss/ %	DTG$_{max}$/K endo	exo	DTA$_{max}$/K
Co(II)	370–405 405–610 610–660 980–1010	17.6	18/660	–	–0.35/465
Ni(II)	450–495 495–620 620–840 995–1120	19.1	19.5/840	–	–1.25/495
Mn(II)	320–415 495–620 620–725 905–960	15.7	15.6/725	–	–8.85/425
Cu(II)	340–405 405–495 590–780 945–990	15.8	15.0/780	–	–10.6/440
Zn(II)	325–380 380–410 515–590 950–990	15.5	15.8/590	–	–9.75/360

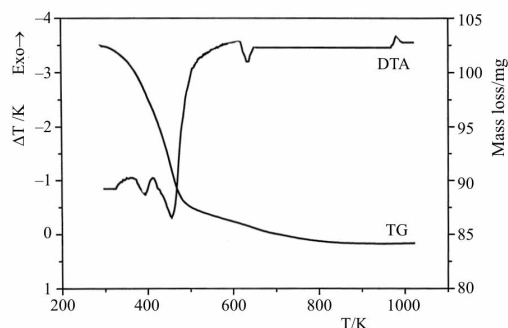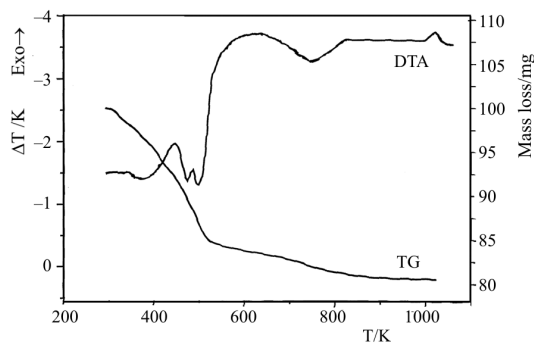**Fig. 3** DTA and TG curves of Co(II) containing γ-titanium phosphate

Fig. 4 DTA and TG curves of Ni(II) containing γ-titanium phosphate

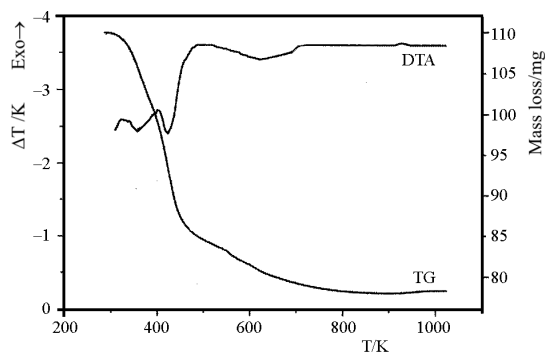**Fig. 5** DTA and TG curves of Mn(II) containing γ-titanium phosphate

Comparing these samples which each other some differences can be observed, namely: in case of sample with Ni(II) ions the crystal water loss is finished at temperature higher (~100 K) than with the sample containing Zn(II) ions. The samples with Mn(II) or Co(II) ions showed similar conditions to the latter one, while the sample containing Cu(II) ions seems to take place between these two kinds of mentioned materials. We found that these two steps followed each other fast (with the exception of Mn containing
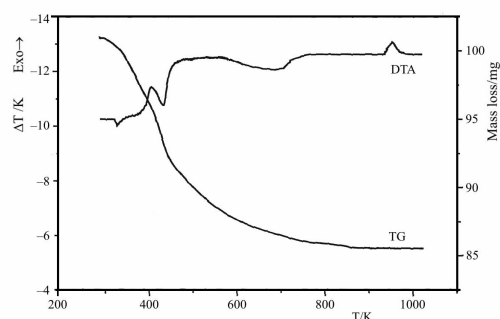
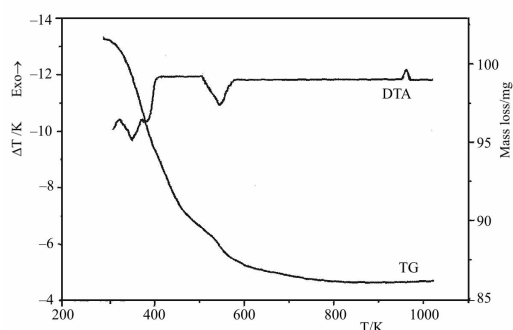**Fig. 6** DTA and TG curves of Cu(II) containing γ-titanium phosphate

Fig. 7 DTA and TG curves of Zn(II) containing γ-titanium phosphate

sample). It seems that the samples containing transition metal ions after losing the first mole of crystal water have some structural rearrangement which results in the quick loss of the second mole of crystal water.

As can be seen from Figs 3–7 the structural water loss is different in samples containing different transition metal ions. In case of sample containing Zn(II) ions the endotherm process is quick and takes place at higher temperature compared to the samples with Mn(II) or Cu(II) ions. In the latter cases the endotherm process is much slower. The sample containing Ni(II) ions showed some extremity, in this case the endotherm process is very slow and finishes at temperature higher (~100 K) than that is for Co(II) containing sample.

In our opinion the different behaviour of these samples is in connection with the different hydration state of used first-row transition metal ions. Based on knowing the ion exchange process we postulated that these ions must initially be exchanged in unhydrated or partially hydrated state which is necessary on a steric basis to permit the ions to diffuse into the layers of titanium phosphate. This process must entail an expenditure of energy which is continuously compensated by the rehydration of the ions and the strong electrostatic interaction between the transition metal cations and fixed anionic sites of γ-TiP. Ni(II) has the largest hydration energy [15] among the used cations. This energy difference may be sufficient to account for reduced uptake of Ni ions and, on the other hand,

for the extremity of the sample containing this ion and, in general, for different behaviour of the others during the thermal decomposition process.

Conclusions

Generally, all investigated materials have a similar route of thermal decomposition. One endotherm process occurs at low temperature, another one at high temperature, both with mass loss, and at last at about 1000 K an exotherm process was found to be existed without mass loss.

In case of α-and γ-crystalline forms an additional endotherm process without mass loss takes place.

According to the above mentioned we propose a way of thermal decomposition: the investigated materials first lose their crystal water which is followed by a crystal phase change (in case of -α- and γ-crystalline forms) after which at a higher temperature the phosphate groups (the loss of structural water is taken place) decompose and at last the result titanium pyrophosphate goes through a phase change (turn to cubic from monoclinic).

The thermal decomposition of transition metal containing γ-titanium phosphates showed big similarities to those of original γ-titanium phosphate.

Considerable differences were not found among the samples containing various transition metal ions, with the exception of Ni(II) containing one. The extremities found in this case are connected with the high hydration energy (higher among the other used cations) of Ni(II) ion. As a result the position of Ni(II) ions in the molecule differ from the other investigated one.

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