Thermochimica Acta, 86 (1985) 281–289
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SYNTHESIS OF γ-TITANIUM PHOSPHATE. STUDY OF THE SOLIDS OBTAINED BY USING WATER OR ACETONE AS WASHING AGENTS

R. LLAVONA, J.R. GARCÍA, M. SUÁREZ and J. RODRÍGUEZ

Departamento de Química Inorgánica, Facultad de Química, Universidad de Oviedo, C/Calvò Sotelo s/n, Oviedo (Spain)

(Received 18 October 1984)

ABSTRACT

The preparation of γ-titanium phosphate from mixtures of β and γ phases by treatment with NaCl and subsequent reverse reaction with HCl, is described. The hydration process of β-TiP was studied. Solids with a P_2O_5/TiO_2 ratio greater than one were obtained and their thermal behaviour and hydration capacity were determined. The materials were characterised by chemical analysis, thermal analysis (DTA and TG) and X-ray diffraction.

INTRODUCTION

The interest in inorganic ion-exchangers due to technical problems derived from the instability of organic resins against high temperatures and strong ionizing radiation, has made possible the wide development reached in the study of insoluble acid salts of tetravalent metals.

Several crystalline varieties of these salts have been described and those having an α-structure, such as the α-zirconium bis(monohydrogen orthophosphate)monohydrate, have been widely studied [1,2]. To be specially noted are the titanium phosphates because, in addition to their exchange properties, they are low-priced raw materials.

The behaviour of these compounds as ion-exchangers is a function of their crystallinity and structure and, therefore, their perfect characterisation is of primordial importance.

From the literature, different methods of preparation of inorganic ion-exchangers with layered structure can be seen, the most commonly found being the reflux method. In recent years, various preparations of titanium bis(monohydrogen orthophosphate) with several hydration degrees by means of this method have been described. Among them, titanium bis(monohydrogen orthophosphate) with a γ-structure should be noted owing to its great interlayer distance (11.6 Å) [2,3].

In 1975, Kobayashi [4] prepared a crystalline titanium phosphate with the

0040-6031/85/$03.30

composition $Ti(HPO_4)_2 \cdot \frac{1}{2}H_2O$, by refluxing a titanium phosphate gel in concentrated H_3PO_4 for 24 h and washing the solid obtained with acetone or ethanol. Later, by refluxing a $TiOSO_4$ solution in concentrated H_3PO_4, he obtained a solid which, washed with water, had the chemical composition $Ti(HPO_4)_2 \cdot 0-\frac{1}{2}H_2O$ [5].

Alberti et al. [6], following a similar procedure to the first one described by Kobayashi, but with a greater reflux time (1 week) and by washing with distilled water, obtained a crystalline compound ($Ti(HPO_4)_2 \cdot 2H_2O$) which they called γ-TiP [7] because of its similarity to γ-ZrP. Recently, Kobayashi [8] investigated the characteristics of various types of hydrated titanium bis(monohydrogen orthophosphate), the previously reported $Ti(HPO_4)_2 \cdot 0-\frac{1}{2}H_2O$ [4,5] is called the (β–γ) form which, as a mixture, is a quasi-stable form.

γ-TiP loses its two molecules of hydration water in the temperature range 40–100°C, being transformed into β-$Ti(HPO_4)_2$ which tends to rehydrate in air [9,10].

When amorphous titanium phosphate was refluxed in concentrated H_3PO_4, a product with a different composition was obtained depending on the eluent used in the elimination of the phosphoric acid [4–8]. In this paper, the results obtained by using water or acetone as washing agents, are examined.

EXPERIMENTAL

Reagents

All chemicals used were of reagent grade.

Analytical procedures and experimental techniques

The determination of the concentration of phosphorus and titanium in the solid was carried out gravimetrically [11]. The water content of the γ-$Ti(HPO_4)_2 \cdot 2H_2O$ and β-$Ti(HPO_4)_2$ phases was determined from the weight loss of the solids, in an electric furnace at 1000°C. The H_3PO_4 content in the $Ti(HPO_4)_2 \cdot zH_3PO_4$ solid was obtained by shaking the solid in deionized water for several hours and analysing the H_3PO_4 amount in solution by titration with 0.05 mol l^{-1} NaOH, using phenolphthalein or methyl orange as indicator. The thermogravimetric analyses (TG) were performed in a Setaram MTB10-8. The differential thermal analyses (DTA) were performed in a Setaram MTB-M4. The X-ray diffraction was performed in a Philips PV 1050/23 ($\lambda = 1.5418$ Å).

Reflux experiments

Amorphous titanium phosphate obtained by the method of Alberti et al. [12] was refluxed in 15.5–17.0 mol l^{-1} H_3PO_4 in the ratio 20 cm^3 : 1 g for 7–10 days and, after cooling, the solid was separated by centrifugation. A portion was washed several times with deionized water until pH 3.5 and stored over a saturated solution of $BaCl_2$ at room temperature ($P/P^0 = 0.9$). The remaining solid was washed with acetone several times and stored over P_2O_5.

Preparation of the γ-Ti(HPO₄)₂ · 2H₂O phase

The $Ti(HPO_4)_2 \cdot xH_2O$ solid obtained in the reflux was equilibrated with a 0.5 mol l^{-1} solution of NaCl in the ratio 100 cm^3 : 0.75 g for 3 h. The solid was centrifugally separated and treated with 0.5 mol l^{-1} HCl at the same ratio for 3 h. This process was repeated three times. After centrifugation, the product was washed with deionized water until pH 3.0–3.5 and stored over a saturated solution of $BaCl_2$.

Preparation of the β-Ti(HPO₄)₂ phase

The γ-$Ti(HPO_4)_2 \cdot 2H_2O$ solid was heated at 210°C for 48 h and stored over P_2O_5.

Hydration of the Ti(HPO₄)₂ · zH₃PO₄ and β-Ti(HPO₄)₂ solids

In the presence of water, both solids transformed originating phases with X-ray patterns showing reflections corresponding to the initial solids and characteristics of γ-$Ti(HPO_4)_2 \cdot 2H_2O$. The degree of transformation with time was determined quantitatively from the calibration curves of X-rays obtained from mixtures of the pure solids (γ-$Ti(HPO_4)_2 \cdot 2H_2O$ + $Ti(HPO_4)_2 \cdot zH_3PO_4$ and γ-$Ti(HPO_4)_2 \cdot 2H_2O$ + β-$Ti(HPO_4)_2$) and by calculating the area corresponding to the first reflection of each phase [13].

RESULTS AND DISCUSSION

Water as eluent

The product obtained in the reflux washed with deionized water had the composition $Ti(HPO_4)_2 \cdot xH_2O$ ($x = 0.8$–1.1). The X-ray pattern of this solid (Table 1) showed many reflections, all of them corresponding to the β-TiP and γ-TiP phases. To be specially noted were the values at $d = 9.12$ and 11.56 Å of the interlayer distance of these phases. The TG curve (Fig. 1)

TABLE 1

X-ray diffraction data for γ-TiP, β-TiP and the reflux solids

γ-TiP	β-TiP	γ-TiP [10]	β-TiP [10]	$Ti(HPO_4)_2 \cdot xH_2O$	$Ti(HPO_4)_2 \cdot zH_3PO_4$	$Ti(HPO_4)_2 \cdot 1/2H_2O$ [6]
11.56vs		11.55vs		11.56s		11.47w
	9.12ms		9.20ms	9.12m	9.12ms	9.21m
5.54w		5.56mw		5.56w		
	5.20m		5.21m	5.20w	5.19s	5.21s
	4.47m		4.48vw	4.47w	4.47m	4.48m
4.29mw		4.29mw		4.30w		4.39w
	3.99w			4.01vw	3.99w	
3.87vw	3.90w	3.86w		3.89w	3.90w	3.90w
	3.67vw			3.68vw	3.66vw	3.66w
3.45ms		3.46ms				
	3.42vs		3.42s	3.43vs	3.42vs	3.42s
3.29vw		3.30w				
3.16w	3.16m	3.17w	3.13w	3.16w	3.16m	3.16m
3.04w		3.05w				
	3.00w		2.99vw	3.02w	3.00w	3.00w
2.78w		2.78w		2.79vw		
	2.74vw		2.75vw			
2.58vw	2.57w	2.58vw		2.58w	2.57w	2.57w
2.55w		2.55w				

vs, very strong; s, strong; ms, moderately strong; m, moderate; mw, moderately weak; w, weak; vw, very weak.

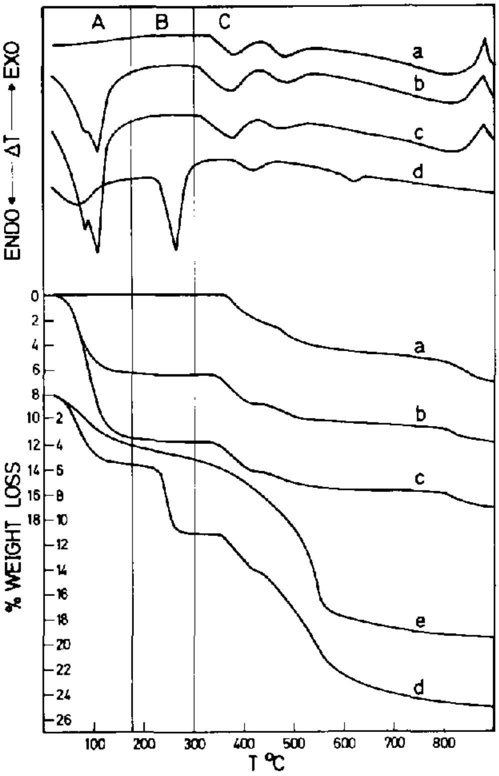

Fig. 1. DTA and TG curves of β-TiP (a), $Ti(HPO_4)_2 \cdot xH_2O$ (b), γ-TiP (c), $Ti(HPO_4)_2 \cdot zH_3PO_4$ (d) and $Ti(HPO_4)_2 \cdot zH_3PO_4$ heated at 210°C for 40 h (e).

showed four endothermic peaks and one exothermic peak, and two well-defined weight losses; the former between room temperature and 160°C and the latter over 330°C.

Zone A in these curves corresponds to the transformation of the γ-phase into the β-phase. The process occurred in two overlapped steps corresponding to each water molecule of γ-TiP. The subsequent endothermic reactions (zone C) were a result of the condensation of the hydrogen phosphate groups of the β-TiP phase, producing α-TiP_2O_7. Two defined processes again appeared; they were explained by La Ginestra and Massucci [9] as being due to the formation of an intermediate pyrophosphate/phosphate phase with an interlayer distance of 8.3 Å which explained the delay in the condensation process. At 880°C, α-TiP_2O_7 was transformed into its high-temperature form.

It has been reported [9,10] that the β-phase tends to produce the γ-phase in air. Nevertheless, when the solid described above was at high relative humidity (in a desiccator with water or a saturated solution of $BaCl_2$) or in contact with water or diluted solutions of H_3PO_4, an evolution towards the γ-phase was observed though the total conversion was never reached. Under the present working conditions, the hydration of the β-form was not an adequate method for obtaining γ-TiP.

Owing to the importance of the attainment of pure materials in the study of ion-exchange properties, it is necessary to find an alternative method for the transformation of β-TiP into γ-TiP. Since γ-ZrP was obtained through an Na phase [14] a similar behaviour might be expected for γ-TiP. When the β and γ mixtures were treated with a diluted solution of NaCl, a product was obtained whose X-ray pattern (Table 2) is similar to that described by Allulli et al. [3] for the $TiNa_{0.5}H_{1.5}(PO_4)_2 \cdot H_2O$ phase. By means of treatment of the Na phase with a diluted solution of HCl the acid exchanger was obtained. Characterisation by chemical analysis, X-ray diffraction (Table 1), DTA and TG (Fig. 1) suggested that the solid was γ-TiP. By heat treatment at 210°C it was transformed into a solid which, characterised in a similar way (Table 1, Fig. 1), turned out to be β-TiP.

The attainment of the pure β and γ phases made possible the quantitative determination of mixtures of these solid phases by X-ray diffraction. The study of the hydration of the β-TiP phase at a relative humidity of 100% initially showed a high hydration rate which subsequently decreased, a conversion of 76% being reached in 17 days. These results explain why Kobayashi and Yamazaki [8] considered the β–γ mixtures as "quasi-stable" phases.

TABLE 2

X-ray diffraction data of the sodium phase of γ-TiP

$TiH_{1.5}Na_{0.5}(PO_4)_2 \cdot H_2O$ [5]	Reflux solid treated with NaCl
11.0vs	11.05s
6.21vw	6.15w
5.88w	6.00w
5.06w	4.96w
4.67vw	4.65w
4.23w	
	3.91vw
3.78m	3.78s
3.73m	3.73s
3.66w	3.55w
3.13w	3.16w
3.11w	3.10m
3.01w	3.01w
2.98w	2.98w
2.86vw	2.89vw
2.77w	2.78w

Acetone as eluent

The reflux product washed with acetone had the composition $Ti(HPO_4)_2 \cdot zH_3PO_4$ ($z = 0.3$–0.5). The *d*-values of the reflections observed in the X-ray patterns are shown in Table 1. A total agreement with the *d*-values of β-TiP can be seen, though the reflections were less strong. Thermal analysis (Fig. 1) showed a different behaviour to that of the β and γ phases. Four endothermic processes were observed corresponding to well-defined weight losses. Zone B, characteristic of this product, should be noted.

$Ti(HPO_4)_2 \cdot zH_3PO_4$ quickly absorbed water from the air giving rise to an X-ray pattern with reflections characteristic of γ-TiP in addition to the initial ones. When the solid was stored over water similar behaviour was observed; the intensity of the reflections characteristic of the γ phase increased with time, and after 50 h a conversion degree of 34% was reached (Fig. 2). Thermal analysis of these partially hydrated samples showed that the initial pattern was maintained with stronger losses in zone A. The two water molecules of γ-TiP should be lost in this zone, as happened in the solid washed with water.

In order to explain the process occurring in zone B of the pattern, a sample of $Ti(HPO_4)_2 \cdot zH_3PO_4$ was heated at 210°C for 1 h. Its pattern showed reflections characteristic of α-TiP_2O_7 which were the only ones remaining when the treatment lasted for 40 h (Table 3). In this case, the TG curve did not show weight losses in zone B. In this temperature range, the condensation of the hydrogenphosphate groups into pyrophosphate took place.

Weight loss at temperatures over 300°C (zone C) was verified in two steps increasing with the H_3PO_4 content in each sample. X-ray patterns corresponded to those of α-TiP_2O_7. The shape of the TG curve can be attributed to the behaviour of the P_2O_5/H_2O system in the liquid phase [15] because in these systems a loss of water initially takes place, H_3PO_4 starting to evaporate from temperatures about 300°C until the azeotrope with 92% in P_2O_5 (boiling point 840°C) is reached.

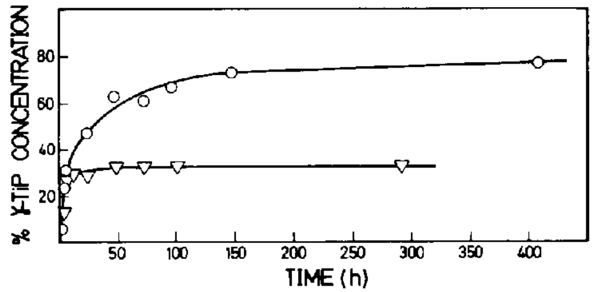

Fig. 2. Conversion–time curves of β-TiP (○) and $Ti(PO_4)_2 \cdot zH_3PO_4$ (▽) at a relative humidity of 100%.

TABLE 3

X-ray diffraction data for the heating products of titanium hydrogen phosphate

$Ti(HPO_4)_2 \cdot zH_3PO_4$ (210, 500, 1000°C)	α-TiP_2O_7 [a]	γ-TiP (800°C) [10]
4.50w	4.51m	4.51m
3.91vs	3.91vs	3.91vs
3.50s	3.50s	3.50s
3.19s	3.19s	3.19s

[a] According to Levi and Peyronel (1935). ASTM X-ray data cards.

Although in similar materials to those studied in this paper the insertion of basic groups used to be easier [16], compounds with interlayer H_3PO_4 have also been detected [16–18]. They are highly unstable in contact with liquid water or water vapour. The presence of interlayer H_3PO_4 should explain the loss of crystallinity of the material and the premature appearance of α-TiP_2O_7 in the heat treatment.

When $Ti(HPO_4)_2 \cdot zH_3PO_4$ was in water for 15 h, all its H_3PO_4 passed into the solution and the X-ray pattern showed reflections corresponding to a mixture of β and γ phases. At the same time, in TG curves the disappearance of weight losses in zone B can be observed, it behaving in the same way as the $Ti(HPO_4)_2 \cdot xH_2O$. The easy extraction of H_3PO_4 by means of water detracts from the results attainable in the study of $Ti(HPO_4)_2 \cdot zH_3PO_4$ as an ion-exchanger in an aqueous medium.

REFERENCES

1 A. Clearfield, G.H. Nancollas and R.H. Blessing, in J.A. Marinsky and Y. Marcus (Eds.), Ion-Exchange and Solvent Extraction, Vol. 5, Marcel Dekker, New York, 1973.
2 A. Clearfield (Ed.), Inorganic Ion Exchange Materials, CRC Press, Boca Raton, FL, 1982.
3 S. Allulli, C. Ferragina, A. La Ginestra, M.A. Massucci and N. Tomassini, J. Inorg. Nucl. Chem., 39 (1977) 1043.
4 E. Kobayashi, Bull. Chem. Soc. Jpn., 48 (1975) 3114.
5 E. Kobayashi, Bull. Chem. Soc. Jpn., 51 (1978) 2306.
6 G. Alberti, M.G. Bernasconi, M. Casciola and U. Costantino, J. Inorg. Nucl. Chem., 42 (1980) 1637.
7 G. Alberti, U. Costantino and M.L. Luciani, J. Inorg. Nucl. Chem., 41 (1979) 643.
8 E. Kobayashi and S. Yamazaki, Bull. Chem. Soc. Jpn., 56 (1983) 1632.
9 A. La Ginestra and M.A. Massucci, Thermochim. Acta, 32 (1979) 241.
10 C. Ferragina, A. La Ginestra and M. Tamanini, J. Calorim. Anal. Therm., 9A, B4 (1978) 27.
11 I.M. Kolthoff, E.B. Sandell, E.J. Meehan, and S. Bruckenstein, Quantitative Chemical Analysis, Nigar, Buenos Aires, 1972.
12 H. Alberti, P. Cardini-Galli, U. Constantino and E. Torracca, J. Inorg. Nucl. Chem., 29 (1967) 571.

13 H.P. Klug and L.E. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley, New York, 1974.

14 A. Clearfield, R.H. Blessing and J.A. Stynes, J. Inorg. Nucl. Chem., 30 (1968) 2249.

15 J.R. van Wazer, Phosphorus and its Compounds I, Interscience, New York, 1958, 748.

16 K. Beneke and G. Lagaly, Inorg. Chem., 22 (1983) 1503.

17 E. Torracca, G. Alberti, R. Platania, P. Scala and P. Galli, Ion Exch. Process Ind., Pap. Conf., 1969, Soc. Chem. Ind., London, 1970, p. 315.

18 N.G. Chernorukov, N.P. Egorov and V.F. Kutsepin, Russ. J. Inorg. Chem., 24 (1979) 987.