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THE ION-EXCHANGE CAPACITY OF Ti AND Zr LAMELLAR HYDROGENPHOSPHATES

TG measurements

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Abstract

Thermogravimetric data were used to calculate the number of acidic Brönsted sites in lamellar α-titanium (α-TiP), γ-titanium (γ-TiP), α-zirconium (α-ZrP) and γ-zirconium (γ-ZrP) hydrogenphosphates. The numbers of acidic sites calculated for these lamellar compounds were 7.81, 5.67, 6.33 and 5.56 for α-TiP, γ-TiP, α-ZrP and γ-ZrP, respectively. These values are in good agreement with those found through potentiometric titration. The data obtained prove that thermogravimetric measurements can be used as a reliable analytical tool to follow the ion-exchange capacity of this kind of crystalline lamellar compounds.

Keywords: ion exchange, lamellar compounds, thermogravimetry, titanium phosphate, zirconium phosphate

Introduction

Hydrogenphosphates of tetravalent metals are normally synthesized as acidic salts in alpha or gamma crystalline forms, giving materials of general formula $\alpha\text{-M(HPO}_4)_2\cdot n\text{H}_2\text{O}$ or $\gamma\text{-M(PO}_4)(\text{H}_2\text{PO}_4)\cdot n\text{H}_2\text{O}$. Such salts have similar lamellar structures, where the inorganic sheets containing cations and phosphate groups are disposed in a regular arrangement, the lamellae being maintained by dispersion forces. The free interlamellar cavities can easily accommodate polar organic molecules in a typical intercalation reaction [1, 2].

These inorganic matrices can also serve as exchangers, with a distinct ion-exchange capacity, by using the free P–OH groups distributed on the lamellae to exchange the proton for other mono-, bi- or trivalent ions, and they also allow chemical interaction with intercalated polar organic species [3, 4]. The number of acidic Brönsted sites is usually determined by potentiometric titration with sodium cation [5].

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In a previous publication, it was shown that thermogravimetry can be successfully used as a reliable tool to calculate the number of silanol groups in silica-gel samples [6], providing a precise description of the superficial composition of that kind of inorganic polymer.

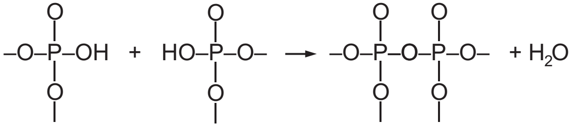
The aim of the present publication is to show that thermogravimetry can be used as a precise analytical tool to perform determinations from direct measurements with a single non-isothermal curve. The number of acidic Brönsted sites in lamellar phosphate materials can be calculated from the total amount of water released by the samples. To achieve this purpose, samples of lamellar α-$M(HPO_4)_2 \cdot H_2O$ (M=Ti and Zr) and γ-$M(PO_4)(H_2PO_4) \cdot 2H_2O$ (M=Ti and Zr) were used as probe compounds.

Experimental

Samples of crystalline lamellar gamma-titanium hydrogenphosphate and alpha and gamma-zirconium hydrogenphosphate were synthesized and characterized as described in detail elsewhere [7–10]. Crystalline lamellar alpha-titanium hydrogenphosphate was prepared by using the previous experimental procedure, with some modifications. Briefly, 0.126 moles of 15% titanium trichloride solution was reacted with 0.50 moles of 85% phosphoric acid during 4 days in a polyethylene beaker at 60°C with periodical stirring [4, 11]. The resulting solid was separated by centrifugation, and washed extensively with bidistilled water until the washings reached the pH range 3.5 to 4.0. The final product was then dried at 40°C. X-ray diffraction patterns were used to follow the crystallinity of each lamellar compound. Thermogravimetric curves for the four samples were obtained on a DuPont model 1090B apparatus under an argon atmosphere at a heating rate of $0.17°C\ s^{-1}$.

Results and discussion

The thermal dehydration of the layered phosphates of general formulae α-$M(HPO_4)_2 \cdot H_2O$ (M=Ti and Zr) and γ-$M(PO_4)(H_2PO_4) \cdot 2H_2O$ (M=Ti and Zr) resulted in the first mass loss step in the thermogravimetric curve, due to the release of water of hydration [5]. The value of this must be neglected in the calculation of the ionexchange capacity. After this stage, the hydrogenphosphate of the inorganic sheets condensed to form the corresponding pyrophosphate [5, 12, 13]. Thus, the mass loss in this stage, which corresponded to the condensation of two hydrogenphosphate groups, must be considered in the calculation of the ion-exchange capacity. The condensation process can be represented schematically as below. This representation shows that, for each water molecule formed, the presence of two –OH groups can be inferred on the hydrogenphosphate moiety:



$$-O-\underset{\underset{|}{O}}{\overset{\overset{|}{O}}{P}}-OH + HO-\underset{\underset{|}{O}}{\overset{\overset{|}{O}}{P}}-O- \longrightarrow -O-\underset{\underset{|}{O}}{\overset{\overset{|}{O}}{P}}-O-\underset{\underset{|}{O}}{\overset{\overset{|}{O}}{P}}-O- + H_2O$$

The number of acidic Brönsted sites calculated by means of thermogravimetry and that obtained through potentiometric titration with Na^+, reported in the literature [5], are listed in Table 1. Thermogravimetric curves and their respective derivatives curves were obtained for γ-$Ti(PO_4)(H_2PO_4)\cdot 2H_2O$ and α-$Zr(HPO_4)_2\cdot H_2O$, as illustrated in Figs 1 and 2. A simple calculation procedure was used as an example for γ-$Ti(PO_4)(H_2PO_4)\cdot 2H_2O$. Thus, the initial mass of 5.76 mg of sample gave a mass loss due to –OH condensation of 5.10%, which was calculated to form $2.94\cdot 10^{-4}$ g or $1.63\cdot 10^{-5}$ moles of water. Each water molecule formed is derived from two –OH groups on the hydrogenphosphate structure of the lamellae. Thus, there are $3.26\cdot 10^{-5}$ moles of –OH in 5.76 mg of the studied compound, γ-$Ti(PO_4)(H_2PO_4)\cdot 2H_2O$. The amount of $3.26\cdot 10^{-5}$ moles of OH, distributed over a sample mass of 5.76 mg, corresponds to 5.67 mmol of –OH groups per gram of lamellar phosphate. The procedure of calculation was used to obtain the set of values for the other compounds. The complete set of calculated results are presented in Table 1.

Table 1 Numbers of acidic Brönsted sites calculated via thermogravimetric data *a*; and obtained by potentiometric titration *b*, from literature data [5]. For thermogravimetric determinations, m_i is the initial mass, $\%m$ is the percentage mass loss due to the release of water of crystallization and ΔT is the temperature range considered for each calculation

Compound	m_i/mg	m/%	ΔT/°C	a/ mmol g^{-1}	b/ mmol g^{-1}
α-$Ti(HPO_4)_2\cdot H_2O$	8.85	7.03	295–800	7.81	7.76
γ-$Ti(PO_4)(H_2PO_4)\cdot 2H_2O$	5.76	5.10	300–800	5.67	7.25
α-$Zr(HPO_4)_2\cdot H_2O$	15.5	5.70	440–850	6.33	6.64
γ-$Zr(PO_4)(H_2PO_4)\cdot 2H_2O$	12.37	5.01	200–800	5.56	6.27

The results in Table 1 demonstrate that, for the crystalline α-lamellar hydrogenphosphates, the values calculated from the thermogravimetric data are very close to the reported values [5], obtained by potentiometric titration. On the other hand, the thermogravimetric values for the γ-lamellar hydrogenphosphates demonstrate only poor agreement, as may be seen in Table 1. However, on the basis of three independently reported thermogravimetric data [13–15], the ion-exchange capacity of the γ-lamellar titanium hydrogenphosphate can be calculated as 8.89, 7.66 and 5.92 mmol H^+ g^{-1}. The first two values and particularly the second one, are in good agreement with the non-thermogravimetric value.

Thermogravimetric curves for such compounds are generally well behaved and the temperature range due to –OH condensation is well determined. Hence, differences in thermogravimetric values can be attributed to the diverse synthetic routes used [5]. This argument is supported by the fact that different experimental procedures result in distinct ion-exchange capacities for the obtained matrices [5]. On the other hand, previous treatment of the sample, before the thermogravimetric curve is recorded, could be another significant factor which could affect the thermogravimetric values. As observed for silica samples [6], the thermogravimetric technique

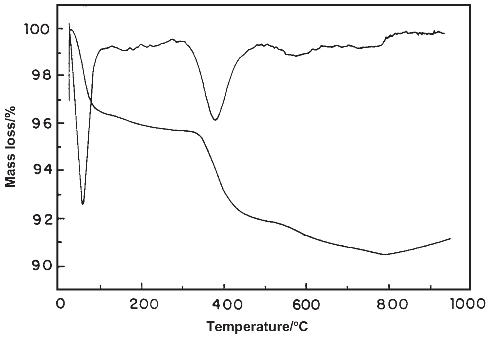


Fig. 1 Thermogravimetric curve of γ-$Ti(PO_4)(H_2PO_4)\cdot 2H_2O$, obtained under an argon atmosphere

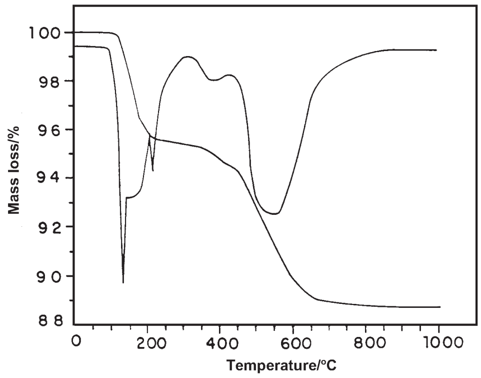


Fig. 2 Thermogravimetric curve of α-$Zr(HPO_4)_2\cdot 2H_2O$, obtained under an argon atmosphere

provides a more specific value for a given sample, as obtained here for γ-lamellar titanium hydrogenphosphate.

Conclusions

The results obtained demonstrate convincingly that thermogravimetry can be used successfully as a very simple and reliable analytical tool to calculate the number of acidic Brönsted sites, which represent the ion-exchange capacity of lamellar hydrogenphosphates.

The clear advantage of thermogravimetry as compared with other techniques is related to the quick and simple analysis procedures, with a minimal sample amount to assay. Another advantage is that this kind of analysis is carried out directly on the solid sample, without any previous preparation which could introduce some chemical interference. These properties associated with thermogravimetry make it a very useful analytical technique for determination of the compositions of solid inorganic materials. The present results are in agreement with those obtained on silica gel samples [6], which demonstrates the potential of the determination of –OH groups distributed on an inorganic support.

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