

Cadmium ions and cadmium sulphide particles in γ -titanium dihydrogen phosphate. Synthesis, thermal behaviour and X-ray characterization.

Research Article

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Abstract: Layered compounds with CdS particles supported on the ion-exchanger, γ -titanium dihydrogen phosphate, were prepared by the stepwise reaction of the ion-exchanger and cadmium solution, followed by reaction with H₂S gas. The CdS content on the ion-exchanger is dependent on the timeframe of the H₂S gas flow. The materials obtained were layered, as shown by the X-ray measurements that exhibit both precursor and CdS diffraction peaks. The thermal treatment of the material obtained gives evidence of its stability ($\leq 320^\circ\text{C}$) before the CdS decomposition, which occurs in a single step.

Keywords: Composite materials • X-ray technique • Thermal properties

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1. Introduction

CdS is an important semiconducting material used in different applications in optoelectronics and photonics [1] or as hydrotreating catalysts [2]. Colloidal methods provide effective routes of preparation for semiconductor nanocrystals or for encapsulating them in zeolites [3,4] due to the three-dimensional structure of the host matrix. Over the last few years the inorganic ion-exchangers of the class of tetravalent elements (Zr, Ti, Sn, Ge...), with a layered structure, have proved their potential not only as ion-exchangers, [5] but also useful intercalating support [6,7]. The gamma phase of titanium dihydrogen phosphate [γ -TiPO₄(H₂PO₄)₂·2H₂O, γ -TiP], one of the most studied ion-exchangers, together with the analogue gamma phase of zirconium phosphate, have renewed researchers' interest in supporting non polar molecules [8-11] due to their chemical and thermal stability. The insertion of non polar molecules into a two dimensional structure such as layered γ -TiP is of increasing importance as a way of controlling the structure of chemical reactions, caused by the homogeneity and stability of the host matrix.

2. Experimental Procedures

Crystalline γ -TiP was prepared and stored as previously described [12]. The cadmium material was prepared by ion-exchange. The cadmium sulphide γ -TiP material was obtained by flowing anhydrous H₂S [7,13] over the anhydrous cadmium material, for several days. Cadmium ions were analyzed on a GBC 903 A.A. spectrophotometer by studying the concentration changes which took place in the supernatant solutions before and after contact with the exchanger. The phosphate content was determined by the colour method [14]. The water content and the thermal behaviour were determined with a simultaneous TG-DTA Stanton Redcroft 1500 thermoanalyzer, Pt crucibles, heating rate 10°C min⁻¹, heated up to 1100°C to constant weight in an air or nitrogen flow. An X-ray powder diffractometer (XRPD) was used to study phase changes in the materials. This was done by monitoring the *d* reflection and its harmonics. A Philips diffractometer (model PW 1130/00) was used with Ni-filtered CuK_α radiation ($\lambda = 1.541 \text{ \AA}$). The content of sulphur in the materials was determined using a Fisons 1108 elemental microanalyser.

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3. Results and discussion

A sample of 1 mmol of γ -TiP, previously enlarged with EtOH, was immersed in 200 mL, 5 mmol dm⁻³ solution of cadmium acetate to obtain the fully exchanged cadmium titanium phosphate phase. The pre-intercalation of molar molecules, such as alcohol, allows the interlayer separation d , to be expanded [15,16]. A fully exchanged compound was not obtained by prolonging the time of batch contact between the exchanger and cadmium solution (3 weeks). So a renewed contact with 50 mL of Cd²⁺ solution, every third day, for five times, was done until a fully exchanged form was obtained, $[\gamma\text{-TiCd}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}]$; γ -TiPCd. Thermal analyses of the γ -TiPCd material were performed to study its stability and thermal behaviour.

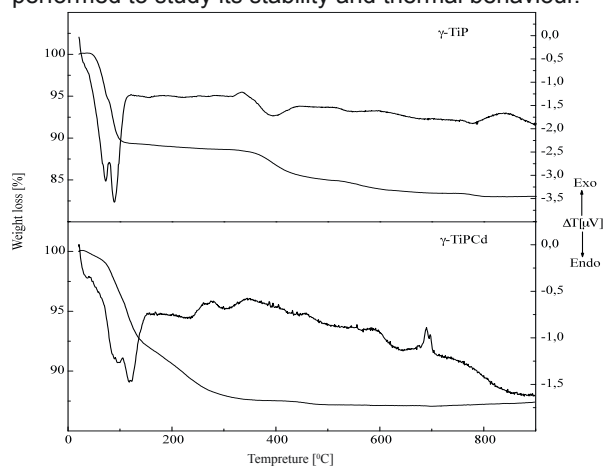


Figure 1. TG-DTA curves of the material obtained, compared with those of the precursor γ -TiP

In Fig. 1 the TG-DTA curves of the material obtained, compared with those of the precursor γ -TiP, are reported. The γ -TiPCd shows losses between 25 and 350°C, due to the coordination water at three different steps (25 - 120°C; 120 - 200°C; 200 - 350°C). Between 25 - 200°C two subsequent losses occur. The last loss which takes place between 200 - 350°C occurs more slowly. The DTA curve shows corresponding, endothermic peaks, confirming the TG data. Between 650 - 750°C the DTA curve shows an exothermic reaction, without weight loss in the TG curve. This is due to the anhydrous phase $\gamma\text{-TiCd}(\text{PO}_4)_2$ which rearranges to form cadmium titanium double phosphate, $\text{CdTi}(\text{PO}_4)_2$ [9,17]. Fig. 2 shows the diffractograms of the material obtained (a. γ -TiPCdS) compared with that of the precursor (b. γ -TiP).

The integrity of the layered structure appears to be maintained during the exchange even if the cadmium materials are less crystalline than the γ -TiP precursor. The d has noticeably decreased (6.28 Å vs. 11.60 Å) and evidence of a little amorphization has occurred. In Scheme 1 the dehydration steps and variations in the d reflection for γ -TiPCd are reported. For the synthesis of cadmium sulphide γ -TiP material, anhydrous H₂S gas was passed at room temperature (r.t.) over a sample of 1 mmol of fully dehydrated (350°C) γ -TiPCd. When the gas flowed over the white powder, the colour changed to yellow and the longer the flow of H₂S the more intense the colour grew. Different CdS values were obtained depending on the length of time of the H₂S gas flow. As reported in Table 1, four days of continuous gas flow gave optimum yields for the CdS content.

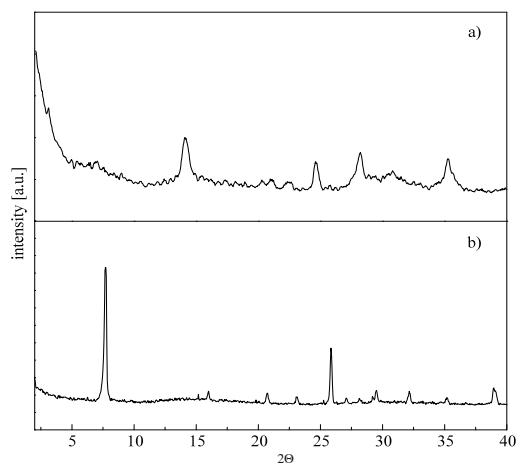
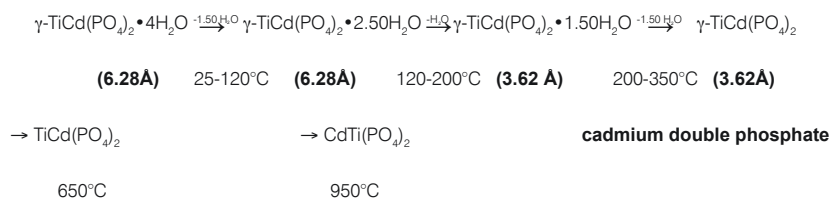


Figure 2. XRD patterns of the material obtained (a. γ -TiPCdS) compared with that of the precursor (b. γ -TiP)

Table 1. Results of microanalysis measurements

Materials	Days of H ₂ S flow	% S r.t.	% S 400°C	% S 600°C
γ -TiPCd	2	3.51 (0.35)	1.83 (0.15)	abs
γ -TiPCd	3	5.61 (0.56)	3.01 (0.25)	abs
γ -TiPCd	4	7.67 (0.85)	2.26 (0.19)	abs
γ -TiPCd	7	7.64 (0.85)	2.45 (0.21)	abs

*In the brackets the CdS content: at room temperature (r.t.) and at 400°C and 600°C (of the obtained materials)



Scheme 1. Dehydration steps and variation in the d of γ -TiPCd

The CdS formation was achieved by flowing H_2S gas over the cadmium titanium phosphate material and combining the S^{2-} ions with the cadmium ions already exchanged in γ -TiP, to give CdS particles. However the free charge left by the Cd^{2+} can be replaced by the H^+ ions of the H_2S gas. The chemical composition of the cadmium sulphide titanium phosphate obtained was $\gamma\text{-TiCdS}_{0.85}(\text{Cd}_{0.15}\text{H}_{1.20}\text{P}_2\text{O}_8) \cdot 3.70\text{H}_2\text{O}$, (γ -TiPCdS). It should be noted that not all the cadmium ions present in the fully exchanged form combine with the H_2S . Only about $\sim 85\%$ of the Cd^{2+} ions in the ion-exchanger are involved in the CdS formation. In Fig. 3, the TG-DTA curves of the γ -TiPCdS are reported. The TG curve losses are present between 25 - 270°C and between 270 - 450°C. The former losses are related to dehydration and they occur at two subsequent steps between 25 - 75°C and 75 - 270°C; there is a step where the CdS particles stay stable, intercalated in the γ -TiP host by weak Van der Waal's forces, but strong enough up to 320°C. The second loss between 320 - 450°C is due to sulphur elimination.

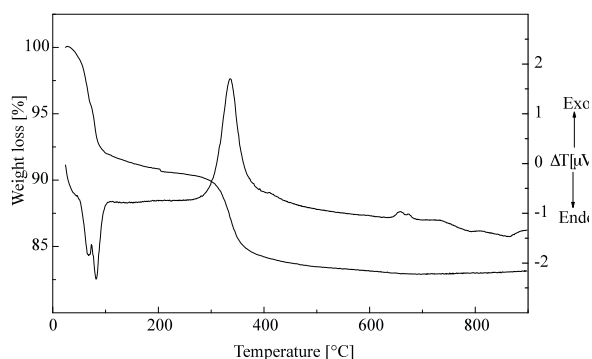


Figure 3. TG-DTA curves of the γ -TiPCdS

In the DTA curve endothermic peaks (dehydration) and exothermic peaks at 350°C and at 680°C (CdS decomposition, cadmium double phosphate formation, respectively) are shown. This behaviour is confirmed by the microanalysis measurements, which

showed decreasing sulphur content in the γ -TiPCdS materials calcined at 400°C and 600°C (Table 1). It is evident from these data that, on average 75% of the CdS is decomposed at 400°C. In fact this is reflected by the strong orange colour of the calcined materials at 300°C and colour change to white at 500°C. In Fig. 4 diffractograms of the γ -TiPCdS (a) and CdS (b, from Aldrich) are reported.

Both the γ -TiP first reflection (Fig. 2b) and the CdS phases (between $2\theta = 23 - 32$ as wurtzite hexagonal or greenockite [18] very similar to the X-ray diffractograms reported in the literature [19,20]) are observed in (a). The presence of the γ -TiP phase is a consequence of when H_2S flows over γ -TiPCd it reverts back to the starting host γ -TiP form. In fact, the S^{2-} ions combine with Cd^{2+} present to give CdS particles in the ion-exchanger and H^+ of the H_2S gas replaces the free charge left from the Cd^{2+} (as reported in the material synthesis).

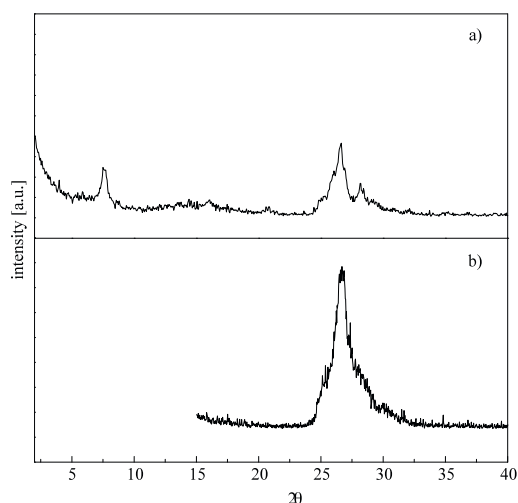


Figure 4. XRD patterns of the γ -TiPCdS (a) and CdS (b)

4. Conclusion

Cd^{2+} ions can be exchanged between the layers of γ -TiP by batch synthesis. This material was then submitted to thermal treatment, up to 350°C resulting in the loss of coordination water. The XRPD of the material obtained reveals a decrease in d (6.28 \AA vs. 11.60 \AA) with respect to the starting γ -TiP. When anhydrous H_2S is flowed over the white γ -TiPCd, its colour suddenly changes to orange due to the formation of CdS particles. The CdS decomposition occurs between $320 - 450^\circ\text{C}$, in one step. The XRPD of γ -TiPCdS demonstrates a layered structure with the γ -TiP phase and CdS particles.

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