

Calorimetric Study of Amine Adsorption on α - and γ -Titanium Phosphate

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Using a microcalorimetric technique, we have determined the differential heat of adsorption of ethyl- and *n*-butylamine over α - and γ -titanium phosphate phases. The recorded data were compared with those obtained by using N₂/77 K adsorption–desorption isotherms, X-ray diffraction peak broadening studies, and scanning electron microscopy. At low coverage, the measured heat of adsorption decreases with increasing coverage, which means the solids have superficial heterogeneity. The γ -phase external surface is more energetic than the α -one. The average heats of adsorption in the interlamellar region of the α -titanium phosphate at 298 K (ethylamine, 95 kJ mol⁻¹; *n*-butylamine, 110 kJ mol⁻¹) are in good agreement with gas-phase proton affinities data.

Introduction

Layered titanium(IV) phosphates are interesting as ion exchangers and precursors of molecular sieves and pillaring materials.^{1,2} These metal phosphates are also versatile solids amenable to structural design by modulation of both their ionic frameworks and organic constituents.^{3,4} The textural characterization of these materials should be studied in depth in order to determine their possible applications.^{5,6}

Most studies about titanium(IV) phosphate reactivity have been carried out over layered microcrystalline phases which show low external surface and high internal arrangement,^{7,8} as can be expected from the systematic correlation between surface area and crystallinity in this type of material.⁹ Taking into account the fact that most experimentation has been performed in equilibrium conditions,^{10–12} the results obtained have been explained as a function of the nature of the interlayer region and the external surfaces of the solids have been forgotten.^{13–15} This oversight is not amazing because only around 1–2% of all solid active centers are located on the external surface. Despite that, it must be acknowledged that the surface of the solids is the door to their reactivity and has a great influence on the reaction mechanism and kinetics. Calorimetry has been used for a number of years to examine the distribution of acid-site strengths in zeolitic materials.^{16–18} This technique provides a direct method for measuring the enthalpy of the acid–base interactions in acid solids. In this study, the textural and microcalorimetric characterizations of Ti(HPO₄)₂·H₂O (α -TiP) and Ti(H₂PO₄)(PO₄)·2H₂O (γ -TiP) are described. We have measured the heat of adsorption of two amines (ethylamine and *n*-butylamine) in these materials.

Experimental Section

Reagents. All chemicals used were of reagent grade. α -TiP was prepared using 10 M H₃PO₄ and a reflux time of 50 h.¹⁹ γ -TiP was prepared using 17 M H₃PO₄ and a reflux time of 10

days.²⁰ Both solids were washed with water until all chloride was eliminated (tested with AgNO₃), were dried at 323 K, and were ground to a particle size of less than 0.03 mm.

Instrument Techniques. A heat-flow microcalorimeter of the Tian-Calvet type (Model BT, Setaram) was used to determine differential heats of adsorption. For this purpose, the calorimeter cells form part of a conventional volumetric apparatus, which allows the simultaneous determination of volumetric and calorimetric isotherms. A capacitance manometer (Baratron 310, MKS) was used. Dead volumes were carefully calibrated, either by mercury weighing or by helium expansions. The reproducibility of the amounts adsorbed was always better than 0.2 μ mol. The system was calibrated by special cells based on the Joule effect. The limit of detection of the microcalorimeter is about 0.2 mJ or 2 μ W. The correction for the heat involved in gas compression was previously determined with helium; typical correction values of 25 mJ were calculated for the maximum pressure increment used. Experiments were made at 298 and 353 K. Previously, samples were outgassed at 378 K.

N₂ adsorption–desorption isotherms were recorded at 77 K by using an automatic volumetric system equipped with a turbomolecular pump ($\sim 10^{-5}$ Torr) Micromeritics ASAP 2000 instrument. The measurement of the vapor pressure of the liquid nitrogen bath was made each hour for the N₂ adsorption branch.

X-ray powder diffraction (XRD) measurements have been carried out in a Philips diffractometer, Model PW 1729/1720 (step-scan method 0.125–3° min⁻¹, Cu K α radiation, λ = 1.5418 Å).

Scanning electron micrographs have been performed by using a JEOL JSM 6100 electron microscope, operating at 20 kV.

Results and Discussion

For a polycrystalline material consisting of sufficiently large and strain-free crystallites, diffraction theory predicts that the lines of the powder pattern will be exceedingly sharp. The experimental breadth of the diffraction lines is due to the combined effect of a number of instrumental and physical factors.²¹ Of more fundamental importance to the present work

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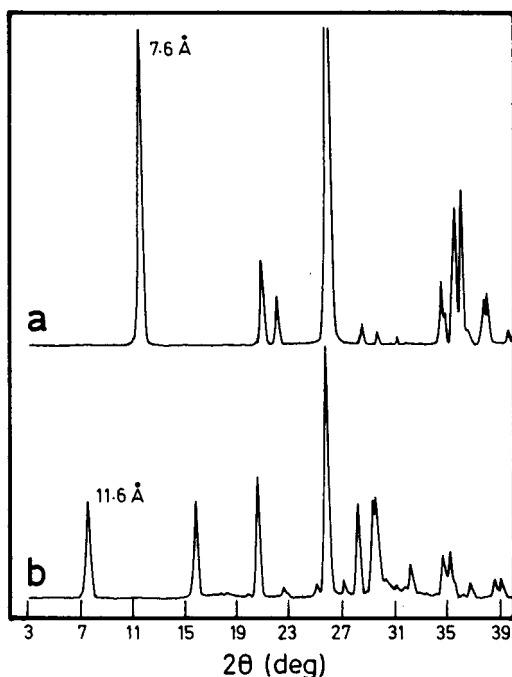


Figure 1. X-ray powder diffraction patterns of (a) α -TiP and (b) γ -TiP.

is the fact that the shape and breadth of the diffraction bands are determined both by the mean crystallite size and by the particular imperfections in the crystalline lattice.

Figure 1 shows powder XRD patterns of α - and γ -TiP layered phases; their interlayer distances can be seen at 7.6 and 11.6 Å, respectively. The XRD peak profile study allows us to calculate the crystallite size of both solids, by means of the Sherrer equation.²¹ For the determination of the entire line profile, the half-maximum width is used, and the NaCl (d_{200} reflection) is used as a reference. Typical interlaminar XRD reflections have been used in the study of both phases; therefore the obtained data are related with the average thickness of the layered microcrystalline plates, which results in values of 1850 Å for α -TiP and 3050 Å for γ -TiP. Due to the limitations of the

method used, the results obtained must be considered as approximate.

α -TiP and γ -TiP samples were outgassed at 413 K during 16 h over a dynamic vacuum in order to perform N_2 adsorption–desorption measurements. This thermal treatment did not change the α -TiP chemical composition; however, when performed with the γ -TiP sample, dehydration occurred, yielding $Ti(H_2PO_4)(PO_4)$ (β -TiP) ($d_{001} = 9.2$ Å). The dehydration process is reversible and takes place without reorganization of the layer structure,^{20,22} from which the γ -TiP textural nature remains unchanged. The N_2 adsorption–desorption isotherm shape of both samples (Figure 2) at 77 K corresponds to the type II of the BDDT classification,²³ which indicates that the adsorption process takes place in a mono-multilayer with negligible porosity. The BET method application over the adsorption branches gives rise to values of $S_{BET} = 15.3$ m² g^{−1} for α -TiP and $S_{BET} = 13.1$ m² g^{−1} for γ -TiP.

SEM micrographs obtained from titanium phosphates can be seen from Figure 3. The α -TiP phase shows hexagonal plates, and γ -TiP shows irregular rectangular plates. Scanning electronic microscopy allows semiquantitative determination of the average size of the particles. Statistical studies over the crystals' dimensions indicate that the average surfaces of the plates are 5000×5000 Å² and 3500×5500 Å² for α -TiP and γ -TiP, respectively. The plate thicknesses are more difficult to calculate using this method because the layered nature of the solids gives a preferential arrangement. The solid layers are placed parallel to the sample carrier, hence perpendicular to the optic axis. The semiquantitative knowledge of the shape and average size of the crystallites allows calculation of the approximate specific surface area of these materials. In the α -TiP case, the average crystallite external area is 87×10^6 Å² and the average crystallite volume is 45×10^9 Å³. Since α -TiP has got four formula units per unit cell, which has a volume of 656 Å³,¹⁵ the calculated specific surface area of this phosphate results in 7.4 m² g^{−1}. In the γ -TiP case,¹⁴ with a ratio area–volume (93.4×10^6 to 58.7×10^9 Å³) and with the following facts being taken into account, namely, that the unit cell contents are just two formula units and its volume is 383 Å³,¹⁴ the calculated

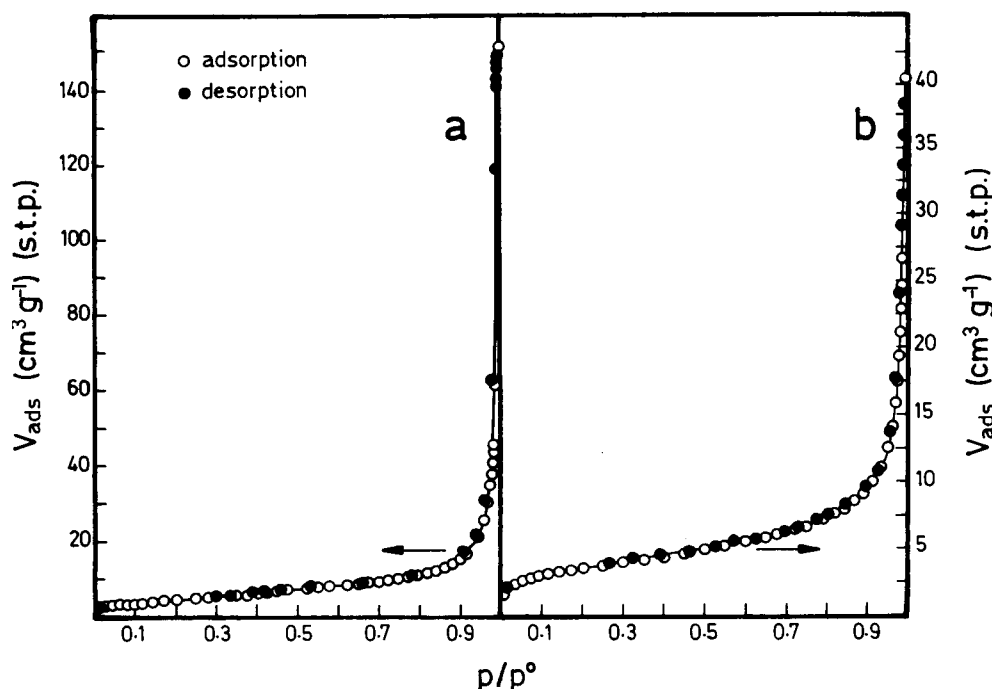


Figure 2. N_2 /77K adsorption–desorption isotherms of (a) α -TiP and (b) γ -TiP.

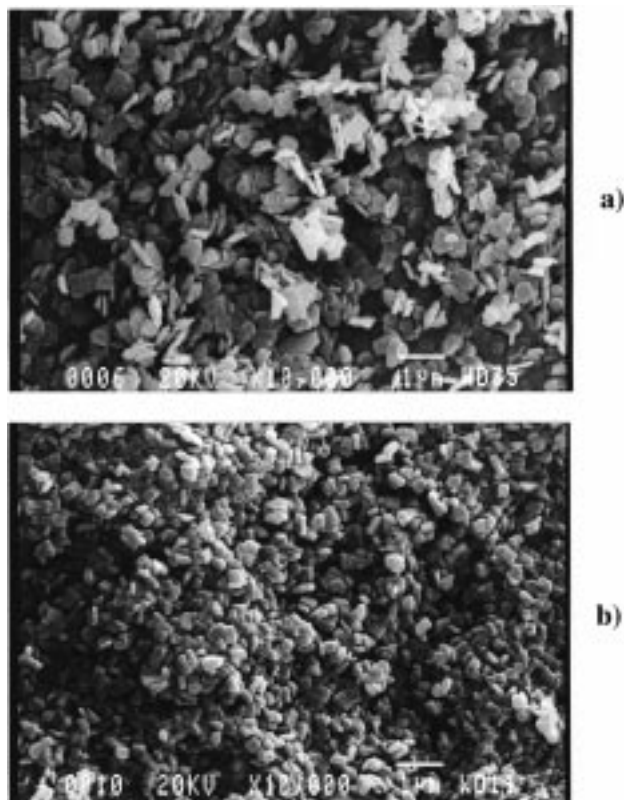


Figure 3. SEM images of (a) α -TiP and (b) γ -TiP.

specific surface area is $6.7 \text{ m}^2 \text{ g}^{-1}$. Although there is not a big difference, in absolute numbers, these values are lower than the experimental data obtained by using a volumetric method. The main reasons must be due to both the limitations of the method used to measure the crystallite size and the supposition taken that the crystallites are regular and roughness-free.

In attempting to have information about the energetics of the amine intercalation process, ethylamine and *n*-butylamine vapors were submitted for interaction with the inorganic matrix and the enthalpy values were measured from the reaction. The calorimetric isotherms of the α -TiP intercalation process recorded at 298 K have got a similar shape for both studied amines (Figures 4 and 5), even though *n*-butylamine intercalation takes place with higher heat of adsorption values than ethylamine does, as is expected from the higher *n*-butylamine gas-phase proton affinity value.^{17,24} From the ethylamine isotherm trace it can be seen how first there is a strong decrease of the heat of adsorption values (referred to 1 mol of adsorbed amine), which concludes when 0.12 mmol of amine/(g of α -TiP) are adsorbed. This amount of intercalated amine corresponds to the value 0.115 mmol of H on the external surface/(g of α -TiP) (assuming that the α -TiP specific surface area is $15.3 \text{ m}^2 \text{ g}^{-1}$). Hence, this stage can be associated with the adsorption taking place over the external surface of the particles, meaning that the solid shows high superficial heterogeneity.

When the amount of adsorbed amine is higher than 0.12 mmol g^{-1} , a plateau can be seen in the isotherm traces at 95 and 110 kJ mol^{-1} for ethylamine and *n*-butylamine, respectively, which corresponds with an adsorption process taking place into the interlayer space. These stable values agree with the high energetic homogeneity of the α -TiP interlaminar sites.

The isotherms recorded at 353 K from both guests show at the low-adsorption region a pattern similar to the ones performed at 298 K. However, at 353 K, the plateau associated with the amine intercalation into the interlayer space is quite short,

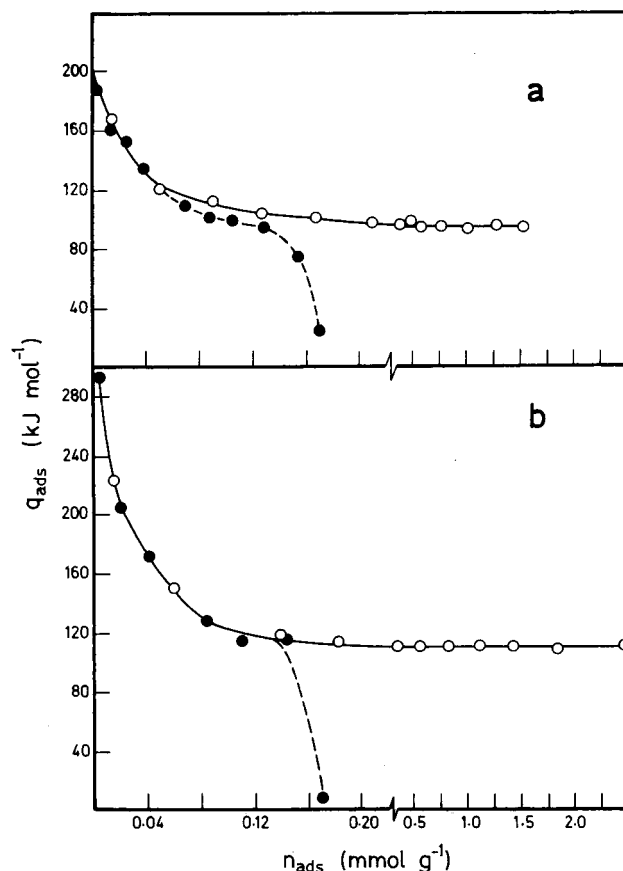


Figure 4. Calorimetric adsorption isotherms at 298 (○) and 353 K (●) of amines in α -TiP: (a) ethylamine; (b) *n*-butylamine.

dropping the adsorption values to practically zero. This indicates that at this temperature the interaction solid–vapor takes place just on the solid external surface and the intercalation equilibrium moves to the desorption process.

In the γ -TiP case, it must be pointed out that the adsorption process takes place just on the plates surface; intercalation was not detected (XRD). The amine adsorption isotherm traces at 298 K are very similar for both amines (Figure 5) but different from the ones shown by α -TiP. At the beginning of the process, a smooth decrease in the differential heat of adsorption when the amount of adsorbed amine is increased can be seen. This is followed by a strong decrease in the recorded values until 20 kJ mol^{-1} . This step takes place in the range 0.053 to 0.073 mmol of adsorbed *n*-butylamine/(g of α -TiP) and from 0.065 to 0.10 mmol of ethylamine/(g of α -TiP). The number of superficial active centers of γ -TiP, H atoms, can be deduced from its BET surface ($13.1 \text{ m}^2 \text{ g}^{-1}$) and cell parameters¹⁴ as 0.132 mmol of H/(g of α -TiP). Hence, the guest molecules do not take all acid centers of γ -TiP plates. This fact can be easily explained by considering steric factors. The OH groups in γ -TiP structure are closely placed, and the external area associated with each group is 16.4 \AA^2 ,²⁵ which is smaller than the cross-section of an alkyl chain, 18.6 \AA^2 .²⁶ Thus, the simultaneous interaction of two amine molecules with two OH groups binding to the same phosphorus atom is not possible (a maximum amount of 66% of the OH groups of the γ -TiP phase has been proven to be achieved by lineal amines).²⁵ Assuming this percentage also as a maximum for the studied interaction, the adsorption may reach 0.088 mmol of amine/(g of α -TiP). This amount of intercalated amine is in the range in which the differential heat of adsorption shows a strong decrease. This step begins at 0.065, corresponding with the occupancy of 50%

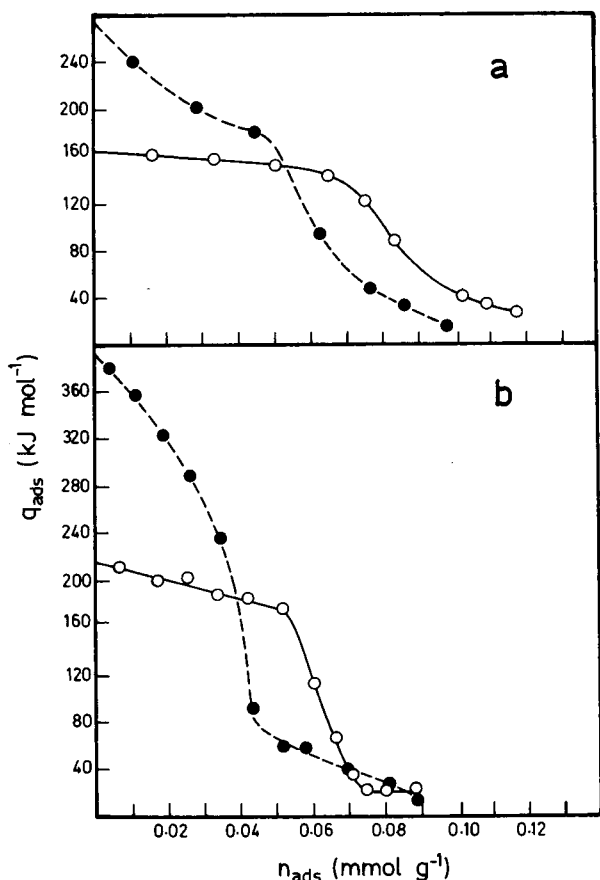


Figure 5. Calorimetric adsorption isotherms at 298 (○) and 353 K (●) of amines in γ -TiP: (a) ethylamine; (b) *n*-butylamine.

of γ -TiP superficial active centers. When the external amine pressure increases, all accessible centers (66%) are occupied, with a noteworthy decrease of the recorded heat of adsorption. The *n*-butylamine behavior is slightly different because not all γ -TiP geometrically accessible centers are saturated. It could be due to the *n*-butylamine molecules larger size that tends to arrange the molecules parallel to the layer. The smaller ethylamine molecules can be placed in an approximately perpendicular disposition to the phosphate plane, allowing access to more molecules.

The amine adsorption isotherm shape recorded at 353 K is different from the ones recorded at 298 K. The intercalation equilibrium is displaced toward desorption with the increasing temperature recorded for α -TiP also being seen in the γ -TiP isotherms. In this way, a decrease of the heat of adsorption takes place for even a lesser amount of adsorbed amine (0.049 mmol ethylamine g^{-1} , 0.043 mmol of *n*-butylamine g^{-1}) than at 298 K (0.065 mmol of ethylamine g^{-1} , 0.053 mmol of *n*-butylamine g^{-1}).

Most important differences between γ -TiP isotherms at 298 and 353 K are in the low-adsorption region. Whereas at 298 K the heat of adsorption is practically constant in this isotherm area, meaning superficial uniformity, at 353 K the behavior is the opposite manner, what can be related to superficial heterogeneity. The molecule kinetic energy at 353 K is enough to have an efficient sweep over the solid surface. However, at 298 K, the molecule kinetic energy is not enough, making the measurement performed in the nonequilibrium situation and the obtained adsorption heat values give an average information of the solid superficial characteristics.

γ -TiP initially adds amine to the first proton of the dihydrogenphosphate groups and continues to do so along the surface for two reasons. The first proton has a much lower $\text{p}K_a$ and by putting a second amine molecule on the adjacent OH group would be steric crowding. The $\text{p}K_a$ of γ -TiP ($-\text{H}_2\text{PO}_4$ groups) is also lower than the α -TiP one ($=\text{HPO}_4$ groups), and it explains why the differential heats of adsorption for γ -TiP are higher than the α -TiP one, when the amount of adsorbed amine is low.

Conclusions

Calorimetric measurements provide important information on the nature of the active sites in solid materials. The temperature working conditions are a critical factor; it must be high enough to give molecules mobility so that each pulse can interrogate all of the available adsorption sites. Nevertheless, higher temperatures do not allow study of the interlamellar region since the intercalation equilibrium moves toward the desorption process.

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