Mechanism of the Topotactic Formation of γ-Zirconium Phosphate Covalently Pillared with Diphosphonate Groups

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The topotactic reaction of γ-$ZrPO_4[O_2P(OH)_2]\cdot 2H_2O$ (γ-ZrP) with benzenediphosphonic acid was examined in water and in acetone−water mixtures. This reaction was found to take place in water only on the external surface of the microcrystals, and pillared compounds were never obtained, even after very long reaction times. On the contrary, covalently pillared compounds were quickly obtained in acetone−water mixtures. The mechanism of the latter topotactic reaction was investigated by determining the rate of the phosphate groups released and the rate of the benzenediphosphonates taken up by γ-ZrP over a long time (50 days). These data showed that pillared derivatives of γ-ZrP can be obtained because colloidal dispersions of exfoliated lamellae are formed in acetone−water mixtures. The diphosphonate group acts initially as a monovalent species, replacing only one dihydrogen phosphate group on the surface of the exfoliated γ-lamellae. The colloidal and partially derivatized lamellae thus formed can interact with each other by forming polylamellar pillared systems. When the number of pillared lamellae exceeds a given value (usually 5−6), flocculation of the colloidal γ-ZrP takes place. Topotactic reactions between packets of pillared lamellae may also continue in the flocculated system. Therefore, the average number of the pillared lamellae slowly increases over time.

Introduction

Covalently pillared α- and γ-zirconium phosphates can be obtained by joining adjacent layers of these lamellar solids with diphosphonate groups.[1−5] In contrast to α-type zirconium diphosphonates, which have only been obtained by direct reaction between a Zr^{IV} salt and a diphosphonic acid,[1−3] γ-Zirconium phosphate diphosphonate pillared compounds have only been prepared by topotactic reactions in water−acetone mixtures in which the original $O_2P(OH)_2^-$ groups of γ-$ZrPO_4[O_2P(OH)_2]\cdot 2H_2O$ (hereafter γ-ZrP) are replaced with diphosphonate groups.[4,5] From a practical point of view, this kind of preparation is important because pillared solids are obtained with soft reactions and with an almost quantitative yield.[5] Furthermore, the lateral distance between adjacent pillars can be easily modulated just by choosing the appropriate amount of the diphosphonic acid in the reaction. Since the distance between adjacent layers may also be modulated by choosing the length of the pillar, the topotactic reaction of γ-ZrP with diphosphonate acids permits the preparation of tailor-made microporous compounds.[1,2,5]

The topotactic reaction between γ-ZrP and monophosphonic acids has been largely used for the preparartion of γ-organic derivatives,[1,2,6] and the mechanism has been recently investigated both in water and in water−acetone mixtures.[7] However, the mechanism with diphosphonic acids must be more complicated because each diphosphonate group has to replace two $O_2P(OH)_2^-$ ligands attached to the external part of two different γ-lamellae. Knowledge of the multistep mechanism of this substitution could be of interest not only from a fundamental point of view but also for choosing the best experimental conditions for the preparation of microporous compounds of this type. Therefore, the topotactic reaction with 1,4-benzenediphosphonic acid, already used for the preparation of the first pillared γ-ZrP,[4] was further investigated. An amount of this acid corresponding to the replacement of 50% of the original dihydrogenphosphate groups was chosen, and the rate of the phosphate groups released and the rate of the benzenediphosphonates taken up by γ-ZrP over a long time (50 days) were determined both in water and in 1:1 acetone−water mixtures at 80 °C.

Experimental Section

Reagents and Materials. All of the chemicals were C. Erba RPE grade except zirconyl chloride octahydrate (Merck). The 1,4-benzenediphosphonic acid was prepared as reported in ref 8.

γ-Zirconium phosphate was prepared according to the method described in ref 4, slightly modified to minimize the presence of

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fluorides in the final product: 640 mL of 2 M $(NH_4)_2HPO_4$ aqueous solution was mixed, in a plastic bottle, with 10 mL of a solution containing 4.95 mL of HF and 7.5 g of $ZrOCl_2{\cdot}8H_2O$. The resulting solution was maintained at 80 °C for 24 h on a water bath. A diammonium form of γ-ZrP, of composition γ-$ZrPO_4[O_2P(ONH_4)_2]_{0.88}(FH_2O)_{0.12}$, was obtained. A large part of the fluorides was then replaced by contacting this form three times with 20 mL of 0.5 M $(NH_4)_2HPO_4$ at 80 °C, for about 3 h. The solid was then washed 6 times with a solution 1 M in HCl and 0.5 M in H_3PO_4. After these treatments, a very crystalline form of γ-ZrP with a negligible amount of fluorides (less than 2×10^{-2} mol per formula weight (hereafter fw) of γ-ZrP) was obtained. The interlayer distance, obtained from the X-ray powder diffraction (XRD) pattern, was 1.22 nm.

Instrumental Details, Analytical and Methods. Ion Chromatography. The amount of $H_2PO_4^-$ groups released into the mother liquors of the exchange reaction was analyzed by ion chromatography with a DIONEX series 2000 I/sp, AS4A column, and 1.7×10^{-3} M $NaHCO_3/1.8 \times 10^{-3}$ M Na_2CO_3 solution as eluent.

NMR Measurements. The relative proportions of phosphonates to phosphates in the solids were obtained by quantitative ^{31}P liquid NMR analysis with a Bruker AC200 spectrometer after dissolution of weighed amounts of the sample (30 mg) in 1 mL of 4 M HF acid and deuterated dimethyl sulfoxide as solvent. The shifts of the signals of 1,4-benzenediphosphonic and phosphoric acids were 17.5 and 2.9 ppm, respectively. The shifts are relative to 85% D_3PO_4 in D_2O.

X-ray Powder Diffraction Measurements. XRD patterns were recorded according to the step-scanning procedure (step size 0.02°) with the help of a computerized Philips PW1710 diffractometer using Cu Kα radiation, PW 1820 goniometer supplied with a bent graphite monochromator in the diffracted beam.

Procedure for the Topotactic Reaction. Water Solution. Various portions of 0.25 g of γ-ZrP were contacted at 80 °C, with shaking, with 50 mL of a 3.9×10^{-3} M solution of benzenediphosphonic acid. At fixed reaction times, the samples were rapidly cooled to room temperature in an ice−NaCl bath (2 min). The solids were then quickly separated from the solutions by centrifugation (3 min). Therefore, 5 min was the shortest time (in the following indicated as t_1) in which analytical data of the separated solutions and solids could be collected.

Water−Acetone Mixture. Various portions of 0.25 g of γ-ZrP were dispersed in 35 mL of a 1:1 acetone−water mixture with shaking at 80 °C for about 15−20 min to allow the formation of good colloidal dispersions.[9] To avoid acetone evaporation, bottles with hermetic seals were used. To each dispersion was quickly added 15 mL of a 1.3×10^{-2} M benzenediphosphonic acid solution (previously heated at 80 °C), with shaking. The samples were cooled and separated as described above for the reaction in water.

Determination of the Degree of Pillaring. The x value in derivatives of general formula $ZrPO_4[O_2P(OH)_2]_{1-2x}[O_2P(OH)C_6H_4(OH)PO_2]_x$ (corresponding to the pillaring degree) was calculated as the average value obtained from the amount of diphosphonates in the solids (NMR analyses) and from the amount of phosphates released by γ-ZrP (ion chromatography analyses). The percentage of substitution (or pillaring percentage) can be directly obtained from the x value multiplied by 100.

Results and Discussion

Topotactic Reaction in Water. In a previous paper[7] it was found that the substitution of the original $O_2P(OH)_2^-$ groups of γ-ZrP with monophosphonates takes place in aqueous solutions through a slow interdiffusion of phosphoric and monophosphonic acids in the interlayer region of the lamellar compound. To see if a similar mechanism is also possible for diphosphonic acids, the topotactic reaction with benzenediphosphonic acid was first studied in water at 80 °C. The diphosphonates taken up and the phosphate groups released were determined over a long period (25 days). The results of these preliminary experiments are shown in Figure 1. Unlike monophosphonates, it is evident that, in the case of diphosphonates, the topotactic reaction does not proceed in aqueous solution. Since no change was observed in the XRD pattern of γ-ZrP, the small amount of diphosphonate groups taken up can be attributed to the topotactic reaction occurring on the surface of γ-ZrP microcrystals. It can be concluded that the pillaring of γ-ZrP by topotactic reaction with diphosphonic acids cannot be performed in aqueous solution.

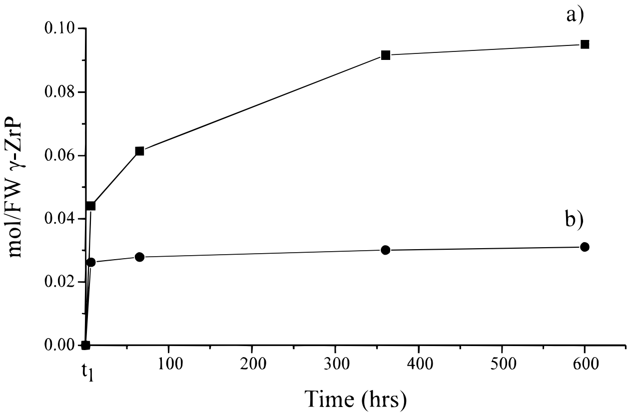

Figure 1. Phosphate groups released (curve a) and diphosphonate groups taken up by γ-ZrP (curve b), as a function of time, when the topotactic reaction is carried out in water at 80 °C. t_1 is defined in the Experimental Section.

Another interesting aspect of this experiment was the unexpected slow release of a small amount of phosphates without the corresponding uptake of the diphosphonate groups. Taking into account the charge balance and the fact that no other anions are present in the initial solution, this phenomenon was attributed to a slow replacement in the interlayer region of $O_2P(OH)_2^-$ bidentate ligands by OH^- and H_2O. Due to the high affinity of the OH^- for zirconium, an appreciable hydrolysis (7−10%) can be reached after several days of contact. Thus, unlike α-ZrP, where hydrolytic reactions are practically limited only to the surface of microcrystals,[10] in γ-ZrP the hydrolytic reactions can also take place in the bulk of the crystal. This is probably due to the relatively higher diffusion of the dihydrogen phosphate groups in the interlayer region of γ-ZrP.[7]

Topotactic Reaction in Acetone−Water Mixture. It was previously reported that when γ-ZrP is contacted with 1,4-benzenediphosphonic acid in 1:1 acetone−water mixtures at 80 °C, γ-ZrP derivatives with a high percentage of pillaring are obtained.[4] However, no kinetic studies nor hypotheses on the mechanism of the topotactic reaction were made. After the discovery that exfoliation of γ-ZrP takes place in 1:1 acetone−water mixtures at 80 °C,[9] it became evident that the formation of pillared compounds was possible only because the topotactic replacement occurred on the surface of the exfoliated lamellae.[7]

Nevertheless, the mechanism of the topotactic reaction with diphosphonic acids to give pillared compounds was expected to be more complicated than that observed for monophosphonic acids since each diphosphonate group must replace two $O_2P(OH)_2^-$ groups belonging to two different γ-lamellae. The reaction should therefore take place through a multistep process. Furthermore, a drastic reduction of the rate of the substitution reaction should occur after an initial formation of the partially pillared compound because the rate of diffusion of the diphosphonic acid in the pillared interlayer region was expected to be very low. In contrast to this expectation, preliminary experi-

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Table 1. Phosphate Released and Diphosphonate Groups Taken Up by γ-ZrP at Various Times

time[a] (min)	phosphate released (mol/fw γ-ZrP)	diphosphonate taken up (mol/fw γ-ZrP)	R[b]	n_L[c]
t_1[d]	0.04	0.04	1.08	1
5	0.19	0.14	1.36	1−2
10	0.27	0.18	1.46	1−2
15	0.28	0.19	1.48	2
25	0.31	0.20	1.53	2
35	0.33	0.21	1.56	2−3
45	0.35	0.22	1.60	3
60	0.37	0.23	1.63	3
120	0.40	0.24	1.70	3
180	0.43	0.25	1.75	4
360	0.44	0.25	1.78	4−5
600	0.45	0.25	1.82	5
955[e]	0.45	0.25	1.84	6
1 440	0.46	0.25	1.88	9
10 080	0.47	0.25	1.92	13
28 800	0.48	0.25	1.94	15
72 000	0.49	0.25	1.99	77

[a] The reaction time elapsed between the contact of γ-ZrP with the diphosphonate acid solution and the initial time in which the solution is rapidly cooled at room temperature. [b] Moles of phosphate released/moles of diphosphonate taken up. [c] Average number of pillared lamellae calculated by the relation $n_L = 1/(2 - R)$. [d] t_1 is defined in the text. [e] An appreciable flocculation of pillared γ-ZrP was only observed after this time.

ments performed in acetone−water mixtures showed that even compounds with a high pillaring degree were obtained in relatively short times. To obtain information on the mechanism of the topotactic reaction, investigations of the gradual formation of pillared compounds were carried out.

To establish the time necessary to reach equilibrium, the phosphates released were first determined every 10 h, over a long time (50 days). It was found that about 74% of the final equilibrium was reached in about 10 min, while more than 96% was already reached in the first 10 h. Then the release slowed down considerably, and the final equilibrium was attained only after about 45 days. It was also observed that an appreciable flocculation of the colloidal dispersion took place after only about 15 h of reaction. Since the very low rate of the phosphate release in the range 0.6−45 days of reaction could be related to the very slow diffusion rate of these species in the flocculated phase, many data were then collected in the first 10 h (i.e., before flocculation). Furthermore, the diphosphonate groups taken up by γ-ZrP were also determined to control the stoichiometry of the replacement.

Experimental data are reported in Table 1, while Figure 2 shows the kinetic curves of the leaving phosphate and entering diphosphonate groups (curves a and b, respectively). The dotted lines represent the respective equilibrium values previously determined after 50 days of reaction. The final uptake was almost quantitative, confirming that the selectivity coefficient of γ-ZrP for the diphosphonate groups is very high.

Note that the diphosphonate uptake is much faster than the phosphate release and that all the diphosphonate groups used for the topotactic reaction (0.25 mol/fw of γ-ZrP) were taken up in less than 3 h. Thus, to clarify this point, the ratios R = *moles of phosphates released/moles of diphosphonates taken up* were calculated (see Table 1).

Note that R is near to 1 in the first measured points. This means that each diphosphonate group behaves initially as a monovalent anionic ligand replacing only one dihydrogenphosphate anion on the surface of γ-ZrP according to the process

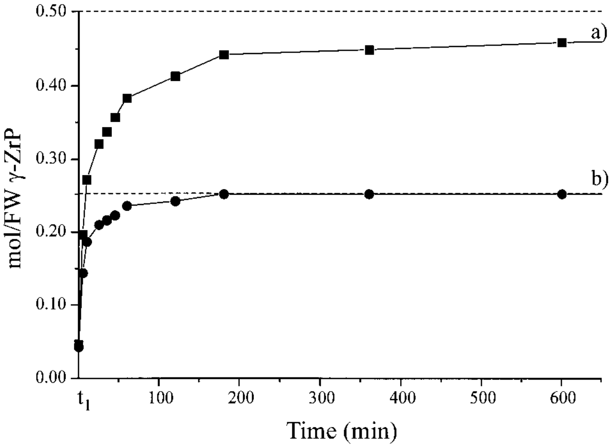

Figure 2. Phosphate groups released (curve a) and diphosphonate groups taken up by γ-ZrP (curve b), as a function of time, when the topotactic reaction is carried out in a 1:1 acetone−water mixture at 80 °C. The dashed lines indicate the equilibrium of the reaction after 50 days. t_1 is defined in the Experimental Section.

$$\mathrm{ZrPO_4[O_2P(OH)_2]} + x\mathrm{[O_2P(OH)C_6H_4PO_3H_2]^-} \rightleftharpoons \mathrm{ZrPO_4[O_2P(OH)_2]_{1-x}[O_2P(OH)C_6H_4PO_3H_2]_x} + x\mathrm{[O_2P(OH)_2]^-} \quad (1)$$

It is of interest to point out that process 1 takes places in exfoliated lamellae since flocculation was not observed (see Table 1). Furthermore, since the diphosphonate groups are taken up as monovalent anionic ligands, considerations similar to those already discussed for the topotactic reaction with phenylmonophosphonate[7] can be made. There is, however, an important difference. In the case of phenylphosphonic acid, due to the hydrophobicity of the phenyl groups, flocculation of the exfoliated lamellae takes place before the equilibrium of substitution of the dihydrogenphosphate groups is completed. Thus, the final equilibrium is reached slowly through a slow interdiffusion of phosphate−phosphonate groups in the interlayer region.[7] In the case of diphosphonic acids, the partially derivatized lamellae, probably due to the presence of free PO_3H_2 groups, remain in colloidal dispersion for sufficient time to allow attainment of a large part of the equilibrium (eq 1). This explains the fast uptake of the diphosphonate groups shown in Figure 2, curve a, without a corresponding fast release of a double number of phosphate moles.

The partially derivatized lamellae with monovalent anionic diphosphonate groups, once formed, begin to interact with each other. The acid $O_2(OH)PC_6H_4PO_3H_2$ groups of one lamella can thus substitute the $O_2P(OH)_2$ groups of another lamella so forming a bilamellar pillared system (packet), as schematically shown in Figure 3. Note that 50% of the diphosphonate groups behave as bivalent anionic ligands (inner pillars) while the remaining 50% are attached as monovalent anionic ligands in the external part of this packet. The average value of R is therefore 1.5. This bilamellar packet can react with another lamella or with another bilamellar packet, giving trilamellar or tetralamellar pillared packets and so on.

The total reaction between partially derivatized single lamellae to give a poly-lamellar-pillared compound can be written as

$$n\mathrm{ZrPO_4[O_2P(OH)_2]_{1-x}[O_2P(OH)C_6H_4PO_3H_2]_x} \rightarrow \mathrm{\{ZrPO_4[O_2P(OH)_2]_{1-2x}[O_2P(OH)C_6H_4(OH)PO_2]_x\}_n} + nx\mathrm{H_3PO_4} \quad (2)$$

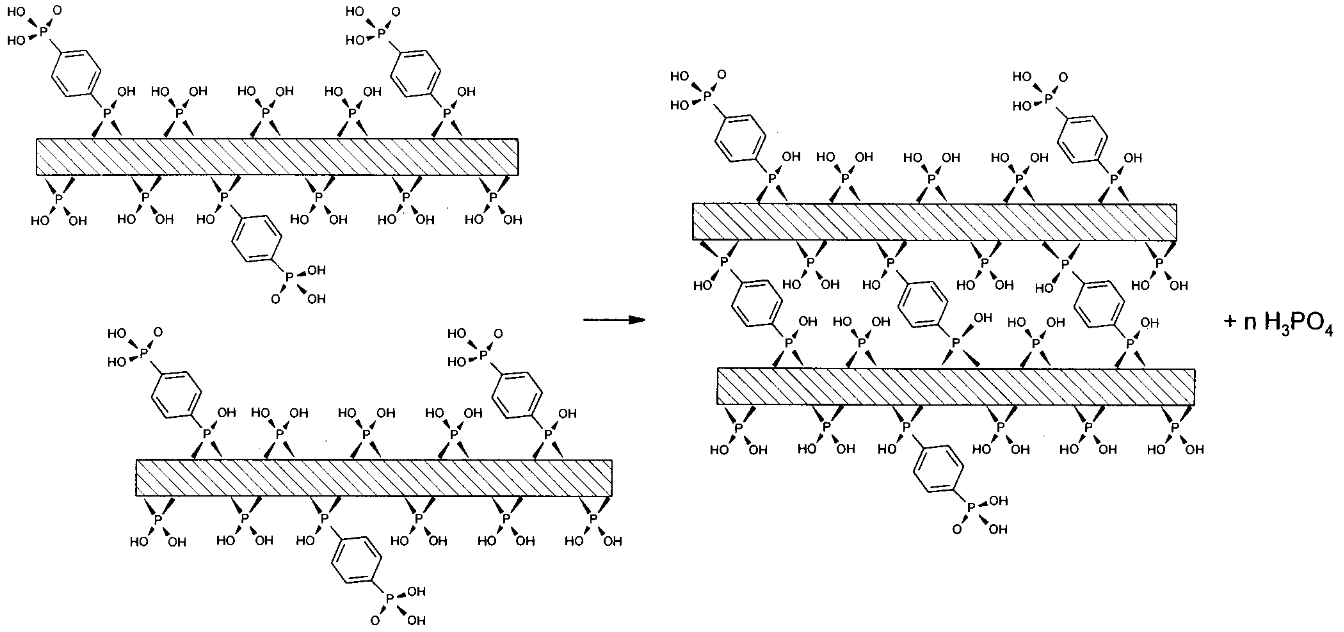

Figure 3. Reaction between two partially derivatized lamellae with diphosphonate groups behaving as monovalent anionic bidentate ligands. A bilamellar pillared packet is formed in which $R = 1.5$ (see text).

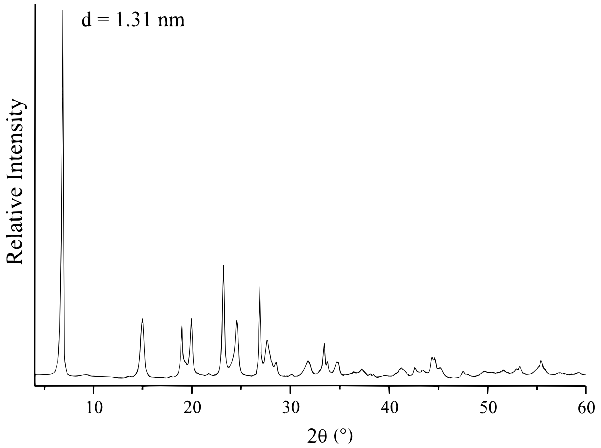

Figure 4. XRD pattern of a sample of γ-ZrP with 50% pillaring, obtained after 15 days of topotactic reaction and then recrystallized in hydrothermal bomb at 250 °C for 3 days.

This reaction (eq 2) may start before (eq 1) is completed. This can explain the relatively high R values observed in the first hours of the reaction. The R values can be used to obtain a rough estimate of the average number of pillared lamellae, n_L, by the relation $R = (2n_L - 1)/n_L$. The estimated n_L values at the established times of the reaction are therefore reported in Table 1. Note also that the average number of pillared lamellae in each packet increases slowly over time. Thus, although more than 90% of the topotactic reaction is completed in a few hours, the reaction must be continued for many days if samples with a good degree of crystallinity are desired.

Note also that R values very near 2 are only obtained after very long reaction times. Thus, taking also into account the recently elucidated structure of zirconium butanediphosphonate,[11] the greater part of the pillars in these samples behave as bivalent tetradentate ligands bridging adjacent layers.

XRD patterns of the samples taken after their flocculation always gave the same interlayer distance (1.31 nm when conditioned at 75−90% of relative humidity). Only the degree of crystallinity was found to appreciably increase over reaction time. A further increase may be obtained by treating the samples in a hydrothermal bomb. The XRD pattern of a sample after 15 days of reaction and then treated in a hydrothermal bomb at 250 °C for 3 days is shown in Figure 4.

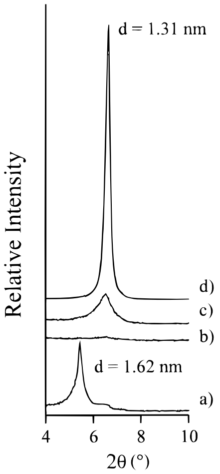

Figure 5. Evolution of the XRD pattern of a sample, flocculated by the cooling procedure, after 1 h of topotactic reaction: (a) sample just flocculated, (b) the same sample washed with 10 mL of water and then measured after 10 min, (c) 2 h, (d) 2 days.

The increase of the crystalline degree over time can be related to the reaction between packets of pillared lamellae which leads to the formation of new packets in which the number of pillared lamellae is considerably increased.

Samples obtained after short reaction times and forced to flocculate by cooling always showed a very low degree of crystallinity. However, when these samples were conditioned over $BaCl_2$ or maintained in water, their degree of crystallinity increased rapidly. It must be concluded that the reaction between packets of lamellae may also occur in flocculated systems, even at room temperature.

In agreement with previous results,[4] the pillared zirconium benzenediphosphonate conditioned at 90% of relative humidity and then dehydrated at 110 °C was found to lose 2 mol of

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interpillar water per fw of pillared derivative. After dehydration the interlayer distance was found to decrease to 1.13 nm. This decrease can be attributed to a variation of the slope of the pillars with the loss of the intrapillar solvent. After rehydration, the interlayer distance of 1.32 nm was again obtained.

It was also found that a semicrystalline phase with an interlayer distance of 1.62 nm was always initially present. However, when the acetone was eliminated (e.g., by heating at 60 °C or by washing with water), this peak disappeared. Figure 5 shows the time evolution of the XRD pattern of a sample just flocculated after 1 h of reaction and then maintained in water at room temperature.

Taking as 0.65 nm the distance between the centers of the two phosphorus atoms in the pillar $O_2P(OH)C_6H_4(OH)PO_2$, and considering that the thickness of the γ-layer in different compounds, taken between the centers of the external phosphorus atoms, may range from 0.74 to 0.79 nm, the maximum interlayer distance cannot exceed 1.44 nm, even when the pillars are perpendicular to the layers. Thus, the semicrystalline phase with an interlayer distance of 1.62 nm cannot be attributed to a pillared γ-ZrP phase. In our opinion, since the peak at 1.62 nm disappeared when acetone was removed, the presence of this peak could be due to a small amount of a γ-ZrP−acetone intercalated phase, stabilized by the presence of some diphosphonate groups.[7]

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