

Synthesis and Characterization of Expanded Layer-Spacing Zirconium Phosphate by Ion-Exchange and Intercalation Processes

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Abstract

In a previous work [1], we prepared α -Zr(HPO₄)₂·2H₂O (ZrP) by direct precipitation, reflux, and by sol-gel method. The results of characterization indicated that the properties of the resultant ZrP samples depended on the method and conditions of preparation as well as on the nature of precursor used. As an important factor governing the use of such layered phosphates, various modifications were done to enlarge the interlayer spacing of α -ZrP (7.6 Å) to be suitable for exchange of large cations. This work aims to modify the interlayer spacing of α -ZrP prepared from zirconium acetylacetonate complex and phosphoric acid. Two routes were used to achieve this goal; the first is by intercalation of acid α -ZrP with n-butyl amine in its vapor-saturated atmosphere. The second route is by performing ion-exchange of the α -ZrP protons by different cations.

Introduction

The previous works on layered zirconium phosphates reveal the wide variety of compounds that can be prepared, as well as, their possible and promising applications such as ion-exchangers and gas sensors.

The smaller basal spacing of α -zirconium phosphate (7.6 Å) makes it less satisfactory for exchange of large cations and complexes, though it has good accessibility to small molecules and ions.

Many modifications have been made in various attempts to enlarge the interlayer spacing of α -ZrP to be suitable for exchange of large cations [2]. One of these attempts to exchange large cations on α -ZrP is by using the highly hydrated dihydrogen form of zirconium phosphate, Zr(HPO₄)₂·8H₂O, which has an interlayer distance of 10.4 Å as previously reported by Alberti [3].

Large cations can also be taken up on α -ZrP by using base or buffered media. Under the influence of the OH⁻ ions, the layers move apart [4]. Hydroxide ion can diffuse to the exchange sites and neutralize the protons. The negative charge would thus accumulate and force the layers apart so that

the hydrated ions may be accommodated. This process continues until all of the OH⁻ ions are consumed [2]. However, the hydroxides of many cations are insoluble in neutral or alkaline solutions which serve as a limitation to their use. This limitation may be overcome by first expanding the layers of α -ZrP to provide suitable spacing for large guest cations like Cs⁺. The exchange of Cs⁺ ions for the protons of α -ZrP, (7.6 Å), is obstructed because of their size. Compared to α -ZrP, (7.6 Å), the more expanded form ZrHNa(PO₄)₂·5H₂O, (11.8 Å), was used as a precursor [5], its larger basal distance allows the exchange of the interlayer POH or PO⁻Na⁺ sites for Cs⁺.

Another (and more generalized) way to achieve this goal is the intercalation of large molecules (like amines) into the spaces between the layers of α -ZrP. This, in general, widens the applications of α -ZrP as catalysts support and as highly selective ion-exchangers [6].

Layered α -zirconium phosphates provide a fertile starting point for chemists to engineer compounds to achieve desired chemical and physical properties by controlling its basal distance. Layered α -zirconium phosphates that are prepared by using the methods proposed by Clearfield [7] and Alberti [8], have been intensively studied and a great number of papers have been published.

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Despite this active research, some crystalline α -ZrP products obtained by decomposition of zirconium complexes, other than zirconium-fluoro complexes [8], are, as yet, not fully elucidated.

It seemed of interest to investigate the different phases that can be obtained by partial or total exchange of the protons of the α -ZrP layers, prepared by decomposition of zirconium acetylacetonate complex [1], with other cations, as well as by the intercalation of amine molecules in the interlayer region.

Materials and methods

Reagents. All chemicals were of reagent grade (Merck) and were used without further purification.

Preparation of the parent α -Zirconium Phosphate. (L_C sample)

α -ZrP samples were prepared by sol-gel method as previously described¹. By adding acetylacetonate to zirconium isopropoxide, $Zr(OPr^{iso})_4$ under nitrogen atmosphere, a complex is formed. The formed zirconium acetylacetonate complex was slowly added to 1M phosphoric acid solution, the Zr/P molar ratio was kept at 1:2. The mixture was then refluxed and the formed precipitate was filtered, washed, and dried. This sample is denoted as sample L_C .

Ion-exchange Procedure

The ion-exchange runs were performed by first equilibrating the parent ZrP powder (L_C sample) with an aqueous solution of the respective metal ions at a constant temperature for some long time before the suspension was titrated against the hydroxide solution of the same metal [2, 5, 7, 9]. So, in each experiment, 1 gram of dry L_C sample was suspended, with overnight magnetic stirring, in 100 ml 0.1 N solution of the metal chloride at 25°C. The suspension was then titrated against a 0.1 N hydroxide solution of the same metal where the pH of the mixture was measured and recorded using a Ross 1120 pH Electrode on an Orion SA 720 pH/ISE Direct Readout Meter.

Intercalation Procedure. (L_C -BA sample)

The *n*-butylamine–intercalated α -ZrP compounds were obtained by maintaining the vapor-phase equilibration of an amine vapor-

saturated atmosphere with α -ZrP: A 5 g sample of the dry solid ZrP was put into a 50 ml beaker with a small Teflon-coated magnet for occasional stirring. 30 ml of *n*-butyl amine was put into another 50 ml beaker and both beakers were then carefully introduced, side by side, into a large Teflon jar and the jar was covered for 7 days at room temperature with occasional stirring every day. This sample is denoted as sample L_C -BA.

Characterization

The prepared samples were identified through their interlayer distance by XRD Powder pattern at conditions described earlier [1].

Information on the thermal stability was obtained by using Perkin Elmer Thermogravimetric Analyzer TG A7. Differential thermal analysis (DTA) was also performed using a Shimadzu DTA-50 machine. The heating rate in all runs was 10°C/min.

FT-IR absorption spectra of products were examined in the frequency range of 400-4000 cm^{-1} using a Nexus 670 FTIR spectrophotometer (Nicolet-USA) using the KBr pellet technique.

The morphology of crystalline samples was scanned by a JEOL JXA-840A Electron Probe Microanalyzer.

High-resolution ^{31}P MAS-NMR spectra were collected at a frequency of 161.98 MHz on a Bruker AMX400WB spectrometer with a 9.4 tesla magnet. ^{31}P spectra were obtained by averaging over 16 scans, with a recycle time of 60 s and a 90° pulse of 9 μs . They were referenced to 85% H_3PO_4 solution.

Results and discussion

The possible routes of synthesis of crystalline zirconium phosphate were tried as described before [1] where the best results have been obtained by decomposition of zirconium complexes. This was ascribed to the gradual decomposition of the zirconium complexes that enabled a slow precipitation of zirconium phosphate to produce very large and well-formed crystals [1, 10].

Characterization of the parent α -ZrP

The L_C samples prepared in the current study were first characterized by XRD, SEM, TG, DTA, and ^{31}P MAS-NMR analysis.

As shown by their XRD pattern in figure 1, the prepared sample presents some better tendency for crystallization with reflux at 90 °C in its mother liquor. Slow and well-controlled hydrolysis of zirconium propoxide, after being complexed with the acetylacetonate, seems to have occurred that favored the formation of crystalline α -zirconium phosphate on reflux for only two days.

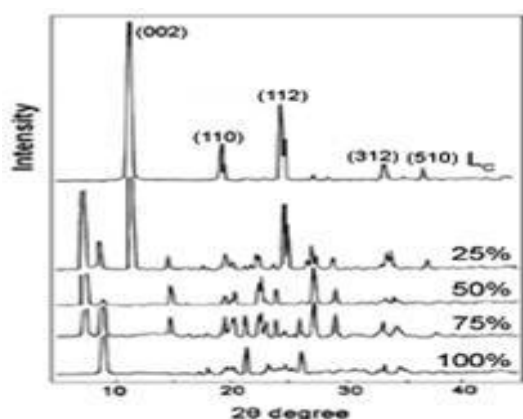


Fig. 1. X-ray diffraction patterns of α -ZrP (LC samples) at various degree of conversion to sodium form

This may be due to a slower decomposition of the zirconium precursor (zirconium acetylacetonate complex) during reaction with phosphate anion to form crystalline product. However, its degree of crystallinity is not as much good as that obtained by decomposition of zirconium-fluoro complexes as reported before [1].

Compared with several α -ZrP samples obtained from zirconium-fluoro complexes in our previous study [1], the thermal behavior of the current samples (L_C sample) behaves nearly in the same manner as shown in Figures 2 and 3.

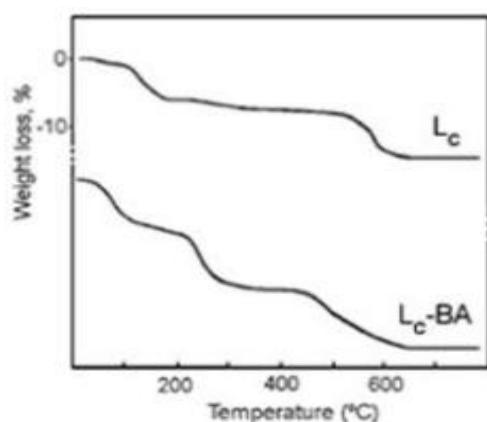


Fig. 2. TG curves of sample L_C and its n-butylamine-intercalation product (L_C -BA)

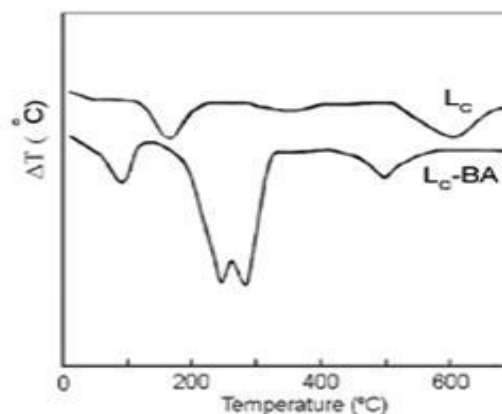


Fig. 3. DTA curves of sample L_C and its n-butylamine-intercalation product (L_C -BA)

Figure 4 shows the SEM micrograph of the synthesized zirconium phosphate as aggregations of hexagonal platelets (typical of α -ZrP).

Magic angle spinning-nuclear magnetic resonance is a powerful tool to investigate both the identity and purity of ZrP powders. The ^{31}P MAS-NMR spectra of sample L_C is shown in figure 5 where the chemical shifts are referenced to 85% phosphoric acid with an experimental error of ± 0.2 ppm. The main peak is observed at -19.2 ppm while two other very small peaks appear at -65.4 and +47.0 ppm corresponding to rotation bands [11]. The single sharp peak at -19.2 ppm is characteristic of the highly crystalline α -Zr(HPO_4) $_2 \cdot \text{H}_2\text{O}$ phase. It corresponds to a phosphate group HPO_4^{2-} triply bound to three different zirconium atoms [11, 12]. This figure shows that all phosphorus atoms in the prepared L_C sample are of the same nature concerning their local chemical and electronic environments indicating a highly pure product.

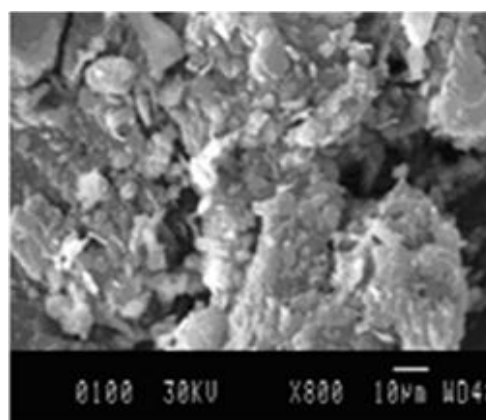


Fig. 4 SEM of sample L_C

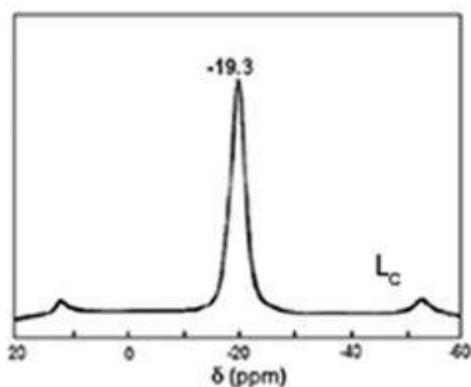


Fig. 5. ^{31}P MAS-NMR spectrum of sample L_C

Modified or exchanged zirconium phosphate in various ionic forms

The structure of α -ZrP is a layered one with an interlayer distance of 7.6 Å. The good ion-exchange characteristics of the ionic forms of layered zirconium phosphate having a large interlayer distance appreciably enable potential applications of this exchanger [2, 5]. For this reason, it seemed interesting to carry out some investigations on some ionic forms of the parent L_C samples (7.6 Å). The compact layered structure of the parent samples (7.6 Å), can be enlarged by replacing one or both of the protons with other counterions.

Sodium ion exchange on α -ZrP

In parallel with the x-ray diffraction patterns, the sodium ion titration curves are used to follow up the extent of crystallization as well as ion exchange properties of the prepared samples.

Figure 1 shows the x-ray diffraction patterns of the parent α -ZrP (L_C sample) at various degrees of conversion to the sodium form while Figure 6 shows its $\text{Na}^+ \rightarrow \text{H}^+$ exchange titration curve using 0.1 M-NaOH as titrant and its backward titration curve using 0.1 M-HCl solution. X-Ray patterns (figure 1) obtained for samples titrated to 25%, 50%, 75%, and 100% replacement of hydrogen ion with sodium ion (figure 6). This range corresponds to that of the titration curve from zero exchange to the second inflection point in the forward titration curve.

The titration curve shows two plateaus (one at low pH and the other at high pH) and an intermediate region with a steep pH-rise. XRD-patterns, taken at different points of the abscissa, show plateaus that correspond to coexistence of two different phases. The presence of coexisting phases

suggests that ion-exchange starts at the surface of the crystals and then diffuses toward their centers, with advancing phase boundary, until the new phase is completely obtained [6].

At low pH values, two diffraction maxima are observed on the x-ray diffractograms, corresponding to the inter-layer distance of the original (pure α -ZrP) and the new phase (the half-exchanged phase, $\text{Na}^+.5\text{H}_2\text{O}$). Initially, the cations displace the hydrogen from the P-OH groups, which are hydrogen bonded to the water molecule. The protons form hydronium ions with the lattice water molecules and these diffuse out of the lattice under the influence of the incoming cations. The cations then occupy the positions in the lattice vacated by the water molecules. Therefore, no appreciable enlargement of the interlayer space takes place. Thus, the reflection at 7.56Å, which is thought to represent the distance between adjacent zirconium phosphate layers, is not shifted to lower angles at this stage of the exchange because the hydrogen bonds between the layers are undisturbed [7].

During the conversion, the intensity of x-ray peaks of the pure α -ZrP decreases while, that of the 50% exchanged phase increases, as if two phases, one transforming into the other, were co-existent.

In the XRD pattern of 25%-exchanged sample, it is observed that a fully exchanged sodium phase was initially formed when NaOH + NaCl was added to crystalline α -ZrP. Because of the low pH of the first plateau, this high sodium-containing phase will convert to a more stable phase (a half-exchanged phase).

In the steep region of the titration curve, only the 50% exchanged phase is present. At this region, all the cavities contain one cation. These cations attract more water and re-hydrate giving rise to a layer expansion. Attention will be devoted to this monosodium form of crystalline zirconium phosphate (the 50% exchanged phase, $\overline{\text{NaH}}$), since it possesses an interlayer distance (11.8 Å) which is much larger than that of α -ZrP. Thus, it seemed interesting to investigate exchange of large cations, such as Cs^+ , using $\overline{\text{NaH}}$ as an exchanger.

On further exchange of sodium ion, a second two-phase region was obtained. The two phases are the half-exchanged phase ($\text{Na}^+.5\text{H}_2\text{O}$) and a fully exchanged phase ($2\text{Na}^+.3\text{H}_2\text{O}$). The two-phase region extended from just beyond the first inflection point or half-exchange point to the second end point. This second stage of the exchange process occurs when one mole of cation

per mole of zirconium phosphate has been exchanged. This is thought to involve the breaking of the hydrogen bonds between the layers causing a gradual spreading apart of the layers as cations are inserted between them. The intensity of the x-ray reflections of the fully exchanged phase increased while those of the half-exchanged phase ($\text{Na}^+.5\text{H}_2\text{O}$) decreased steadily with increasing sodium ion uptake. As the amount of Na^+ exchanged approached saturation, the two diffraction maxima merged into a single reflexion and, finally, at saturation, attained an inter-planar spacing of 10.0 \AA [7].

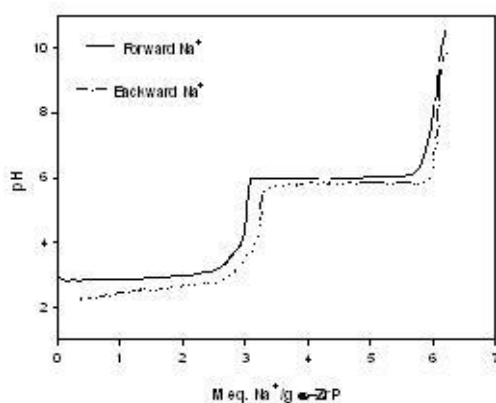


Fig. 6. Sodium ion titration curve of L_C -sample using 0.1 N-NaOH and its backward titration curve using 0.1 M-HCl

In the reverse titration, (shown in Figure 6), the first portion of this curve, up to 50% replacement of sodium ions with hydrogen ions, is almost identical with that of the forward curve. Furthermore, the same two phases, phase ($\text{Na}^+.5\text{H}_2\text{O}$) and phase ($2\text{Na}^+.3\text{H}_2\text{O}$), which were obtained in the forward titration are also observed in the back-titration. Thus, the exchange reaction, over the range of 50% to 100% sodium ion content of the solid, must be a reversible process. The observed slight difference in pH probably arises from slightly different hydrolysis behaviors during the two titrations.

On further replacement of sodium ion (below 50%) with protons, the titration curve is seen to markedly deviate from that obtained when sodium ions replace protons.

Exchange of cesium ion

Large cations, (such as Cs), which are not appreciably or too slowly exchanged by $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, due to steric hindrance, can be quickly, and even selectively, taken up by the

monosodium form, $\text{ZrHNa}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ which has an interlayer distance of 11.8 \AA [3].

Figure 7 shows the variation of pH with the amount of cesium hydroxide added for $\text{Cs}^+ \text{-H}^+$ exchange on both parent L_C sample (crystalline α -ZrP or $\overline{\text{HH}}$) and its 50% Na^+ -exchanged product ($\overline{\text{NaH}}$ product) as shown by curves (1) and (2) respectively.

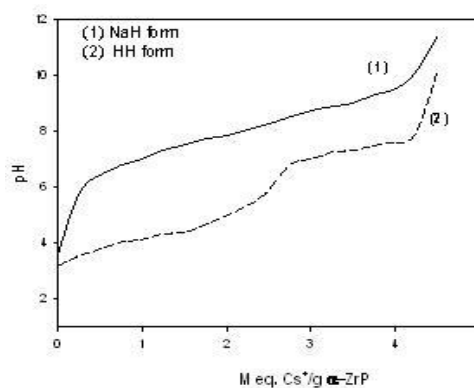


Fig. 7 Titration curves of cesium ion exchange on both samples L_C , (α -ZrP, $\overline{\text{HH}}$), and its 50% Na^+ -exchanged product ($\overline{\text{NaH}}$ product) as shown by curves (1) and (2) respectively

Curve (1) appears relatively smooth (with one plateau) if compared to the more complex one obtained in a previous investigation [13]. The difference between the two cases may arise from the fact that the present study adopted the continuous titration while the previous one used the batch-procedure. The later procedure enables the reacting species to attain equilibrium for long periods of time using a fresh exchanger sample for each reading point on the curve. The present study, however, checked the response of the pH to the fast and continuously changing or increasing additions of Cs^+ to both the unexchanged $\overline{\text{HH}}$ form and the 50% Na^+ -exchanged one in a comparative way.

However, the exchange process on the $\overline{\text{HH}}$ form is shown by curve (1) to have started only at high pH values. The pH abruptly increased from the first drop of addition of CsOH solution and the plateau appeared only after a pH value of 7. This is in a good agreement with the previous studies [13].

It should be noted here that $\text{Cs}^+ \text{-H}^+$ exchange is complicated [13] where two phase transitions were found in the range 50-100 percent of conversion. At alkaline pH values, it is possible to exchange about two thirds of the H^+ ions with Cs^+ [14], although this is accompanied by a strong hydrolysis of phosphate groups of the exchanger [15].

Cs^+ ion can be easily exchanged on $\text{ZrHNa}(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$, $(\overline{\text{NaH}} \cdot 5\text{H}_2\text{O})$,⁵. Where only $\text{Cs}^+ \rightarrow \text{Na}^+$ exchange occurs and anhydrous half-exchanged Cs^+ form is obtained. The two plateaus shown by curve (2) in figure 7 may be summarized by the $\text{Cs}^+ \rightarrow \text{Na}^+$ exchange and the subsequent conversion from mono- to dicesium form [13]. This curve shows that crystalline ZrP can be easily converted into the monocesium form even in acid medium or low pH values if some Na^+ ions are previously added.

Modified zirconium phosphate intercalates

ZrP is able to intercalate many neutral and polar molecules. Amines are of special interest [6] as they represent Brönsted bases and display a high affinity for the Brönsted acid POH groups of ZrP. The insertion of amines into the spaces between the layers of α -ZrP results in a controlled enlargement of the interlayer distance. This controlled enlargement makes the interlayer distance as a modifiable parameter that can be directed by the amount and type of amine.

In the present study, the intercalation of the parent α -ZrP with n-butylamine in the vapor phase was examined using XRD, FT-IR, and ^{31}P MAS-NMR analysis.

Figure 8 shows that the interlayer spacing in α -ZrP can be increased to about 18.7\AA using n-butylamine as a host during the intercalation process. This maximum interlayer spacing of 18.7\AA is reached when the amine loading goes up to about 6.7 mmole of the n-butylamine per gram of α -ZrP [16, 17]. Lower values of interlayer spacing can thus be controlled depending on the extent of loading below this saturation capacity.

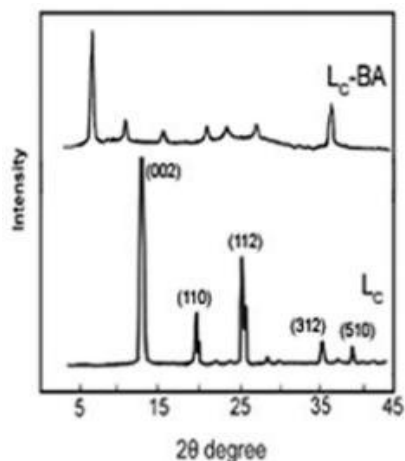


Fig. 8. XRD patterns of sample L_C , and its n-butylamine-intercalation product (L_C -BA)

Figure 2 shows the TG curves of sample L_C and its n-butylamine intercalation product (L_C -BA). The two endothermic changes of sample L_C at 150 and 200 °C are due to the dehydration or elimination of crystallization water [17] while the endothermic peak at about 590 °C is due to the dehydroxylation of structural water forming pyrophosphate. These two endothermic changes correspond to a single step of weight loss in the same temperature range on the corresponding TG curve.

The TG curve of the L_C -BA intercalation product shows two weight losses in the temperature ranges of 30-165 °C and 150-400 °C that correspond to the dehydration and the desorption of the amine respectively and a third weight loss above 400 °C that corresponds to the dehydroxylation or condensation to pyrophosphate [16].

The large exothermic change at about 295 °C, shown by the DTA curve (Figure 3) of the intercalation product L_C -BA, shows the decomposition of the intercalation product L_C -BA at this temperature. It can be noted that dehydration of the L_C -BA intercalates occur at lower temperatures than for pure α -ZrP [16]. This is due to the fact that crystallization water in α -ZrP undergoes H-bonding with the neighboring P-OH groups and is situated in a fixed position that results in a high dehydration temperature (≈ 165 °C). Intercalation of the amine removes this water.

Figure 9 shows the solid-state ^{31}P magic angle spinning-nuclear magnetic resonance (MAS-NMR) spectra of the L_C -BA intercalation product. A comparison with figure 5 reveals the effect of the n-butylamine, introduced into the interlayer spaces, on the overall chemical environment of the phosphorus atoms. This figure confirms the binding state between the n-butylamine and the phosphate groups [16, 18-19].

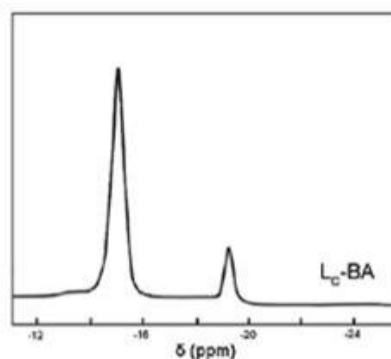


Fig. 9. Solid-state ^{31}P MAS-NMR spectra of the L_C -BA intercalation product

The peak at -15.0 pm can be assigned to a BA intercalation compound with a bilayer phosphate structure as confirmed by x-ray diffraction in other investigations [16]. The peak at about -20 ppm might be due to the phosphate of the monolayer structure [17, 20].

The FT-IR spectra of the n-butylamine intercalation product of sample L_C at maximum loading, L_C-BA, is shown in figure 10. All peaks characteristic of α-ZrP are found [1]. In addition, other characteristic peaks for butylamine are also found. So, the strong peak at 3600-3000 cm⁻¹ region, connected with extra H₂O and isolate OH and is also with a strong peak of C₄-NH₂ bond, appears at 1650 cm⁻¹ [21-22].

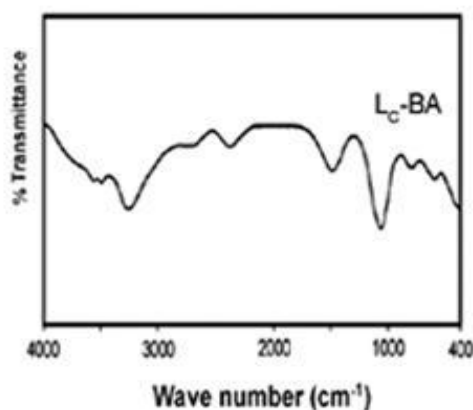


Fig 10. FT-IR absorption spectra of L_C-BA (n-butylamine intercalation product at maximum loading)

The strong peak at 630 cm⁻¹ corresponds to the OH group bond and the strong one at 1200 cm⁻¹ is assigned to the H-bonding [21-22].

Conclusion

α-ZrP prepared by decomposition of zirconium acetylacetonate complex is found to have a good degree of crystallinity. The interlayer distance of such layered α-ZrP is a modifiable parameter. Several distinct crystalline phases of ion exchange modification of the parent α-ZrP were obtained. The most important, is the monosodium form which possesses an interlayer distance larger than that of α-ZrP and show a good ion exchange properties for large cations. The maximum interlayer spacing of 18.7Å is reached by intercalation of α-ZrP with n-butylamine in the vapor phase. Controlling the interlayer distance of α-ZrP widens its applications.

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