

Effect of Crystallinity on the Intercalation of Monoamine in α -Zirconium Phosphate Layer Structure

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Crystalline α -zirconium phosphate (α -ZrP), $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, has been extensively studied for its intercalation chemistry,^{1–8} ion exchange properties,^{2–6,9} catalytic properties,^{2,5–7,10} proton conductivity,^{2,5} and related applications since it was first discovered in 1964 by Clearfield and Stynes.¹¹ The intercalation chemistry of α -ZrP turns out to be especially important because many of its applications cannot be realized until it is intercalated or exfoliated. The intercalation chemistry of α -ZrP stems from the presence of medium strong P–OH Brønsted acid groups in its interlayer region. Therefore, compounds with a functional group which can accept protons, such as amines, are the preferred guests. The intercalation chemistry is, thus, often driven by an acid–base reaction. However, with special procedures, guests with very low basic strength, such as alkanols, glycols, ketones, and amides, are also possible to insert into interlayers.^{12,13} In addition, oxidation–reduction and esterification reactions can be used to drive the intercalation of guest molecules into α -ZrP.¹⁴ Several factors have been reported to affect the arrangement of guest compounds within the layers, including their dimensions, their stoichi-

ometry ratios, and the presence of co-intercalated solvent (generally water).⁴ The progress of intercalation can also be considered as an ion exchange process, through which the guest compounds are distributed within each layer from the border of the crystallites toward the center.

In the past few years, a growing interest has been paid to the intercalation of guest species with special functionalities in the fields of photochemistry and photophysics,^{15–17} molecular and chiral recognition,^{18,19} biocatalysis,^{20,21} and so forth. Recently, a new application of α -ZrP as a nanofiller in polymer matrices to prepare polymer nanocomposites has also been explored and reported.^{22,23} Such nanocomposites not only show excellent mechanical and barrier properties but also may possess proton conductivity when a proper matrix is selected.^{24–26} These proton conductive nanocomposites may find great applications in the fuel cell field.

However, some fundamental aspects of the intercalation chemistry of α -ZrP still need to be elucidated. A better understanding of the intercalation chemistry may facilitate the manipulation of the intercalation process, as a result improve the quality of final intercalation compounds, and moreover, benefit its following applications such as the preparation of nanocomposites. Owing to this, a simple polyoxyalkyleneamine, Jeffamine M715 (Huntsman Chemicals, hereafter referred to as M715) with a reported average molecular weight of 715, was adopted here to study the intercalation chemistry of α -ZrP.

α -ZrP with different crystallinities was prepared by refluxing $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in phosphoric acid of different concentrations. The detailed chemistry and procedures for the preparation of α -ZrP can be found in the literature.^{27,28} Figure 1 shows the X-ray powder diffraction (XRD) patterns of α -ZrP prepared from 3 and 6 M H_3PO_4 [hereafter referred to as ZrP(3M) and ZrP(6M), respectively]. The wide and unseparated peaks of ZrP(3M) indicate that ZrP(3M) is of low crystallinity, while ZrP(6M) is of higher crystallinity.

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- (1) Clearfield, A. *J. Mol. Catal.* **1984**, *27*, 251–262.
- (2) Clearfield, A. *Annu. Rev. Mater. Sci.* **1984**, *14*, 205–229.
- (3) Clearfield, A. In *Progress in Intercalation Research*; Müller-Warmuth, W., Schollhorn, R., Eds.; Kluwer: Dordrecht, 1994; pp 240–263.
- (4) Clearfield, A.; Costantino, U. In *Comprehensive Supramolecular Chemistry*; Alberti, G., Bein, T., Eds.; Elsevier: Oxford, U.K., 1996; Vol. 7, pp 107–149.
- (5) Alberti, G.; Casciola, M.; Costantino, U.; Vivani, R. *Adv. Mater.* **1996**, *8*, 291–303.
- (6) Kumar, C. V.; Bhambhani, A.; Hnatiuk, N. In *Handbook of Layered Materials*; Auerbach, S. M., Carrado, K. A., Dutta, P. K., Eds.; Marcel Dekker: New York, NY, 2004; pp 313–372.
- (7) Alberti, G.; Costantino, U. *J. Mol. Catal.* **1984**, *27*, 235–250.
- (8) Alberti, G. *Acc. Chem. Res.* **1978**, *11*, 163–170.
- (9) Clearfield, A., Ed. *Inorganic Ion Exchange Materials*; CRC Press: Boca Raton, FL, 1982.
- (10) Curini, M.; Rosati, O.; Costantino, U. *Curr. Org. Chem.* **2004**, *8*, 591–606.
- (11) Clearfield, A.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1964**, *26*, 117–129.
- (12) Costantino, U. *J. Chem. Soc., Dalton Trans.* **1979**, 402–405.
- (13) Costantino, U.; Vivani, R.; Zima, V.; Benes, L.; Melanova, K. *Langmuir* **2002**, *18*, 1211–1217.
- (14) Johnson, J. W. *J. Chem. Soc., Chem. Commun.* **1980**, 263–265.

- (15) Colon, J. L.; Yang, C. Y.; Clearfield, A.; Martin, C. R. *J. Phys. Chem.* **1990**, *94*, 874–882.
- (16) Marti, A. A.; Colon, J. L. *Inorg. Chem.* **2003**, *42*, 2830–2832.
- (17) Hoppe, R.; Alberti, G.; Costantino, U.; Dionigi, C.; Schulz-Ekloff, G.; Vivani, R. *Langmuir* **1997**, *13*, 7252–7257.
- (18) Cao, G.; Garcia, M. E.; Alcalá, M.; Burgess, L. F.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 7574–7575.
- (19) Mallouk, T. E.; Gavin, J. A. *Acc. Chem. Res.* **1998**, *31*, 209–217.
- (20) Kumar, C. V.; Chaudhari, A. *J. Am. Chem. Soc.* **2000**, *122*, 830–837.
- (21) Kumar, C. V.; Chaudhari, A. *Microporous Mesoporous Mater.* **2003**, *57*, 181–190.
- (22) Sue, H.-J.; Gam, K. T.; Bestaoui, N.; Spurr, N.; Clearfield, A. *Chem. Mater.* **2004**, *16*, 242–249.
- (23) Sue, H.-J.; Gam, K. T.; Bestaoui, N.; Clearfield, A.; Miyamoto, M.; Miyatake, N. *Acta Mater.* **2004**, *52*, 2239–2250.
- (24) Costamagna, P.; Yang, C.; Bocarsly, A. B.; Srinivasan, S. *Electrochim. Acta* **2002**, *47*, 1023–1033.
- (25) Vaivars, G.; Furlani, M.; Mellander, B. E.; Granqvist, C. G. *J. Solid State Electrochem.* **2003**, *7*, 724–728.
- (26) Yang, C.; Srinivasan, S.; Bocarsly, A. B.; Tulyani, S.; Benziger, J. B. *J. Membr. Sci.* **2004**, *237*, 145–161.
- (27) Clearfield, A.; Duax, W. L.; Medina, A. S.; Smith, G. D.; Thomas, J. R. *J. Phys. Chem.* **1969**, *73*, 3424–3430.
- (28) Clearfield, A.; Oskarsson, A.; Oskarsson, C. *Ion Exch. Membr.* **1972**, *1*, 91–107.

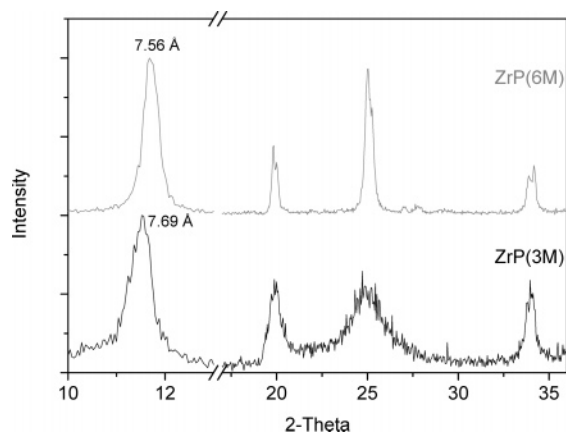


Figure 1. XRD patterns of ZrP(3M) and ZrP(6M).

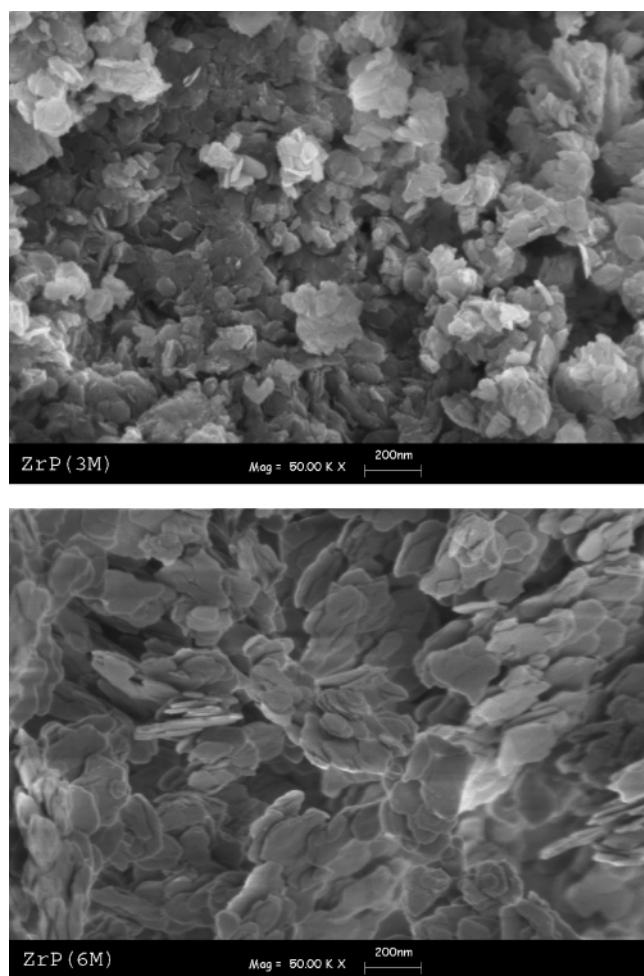


Figure 2. SEM images of ZrP(3M) and ZrP(6M).

While the 002 peak of ZrP(6M) locates exactly at the same position as that of the reported refined crystal structure of α -ZrP,²⁹ the 002 peak of ZrP(3M) shifts to a lower degree, which means that its interlayer distance is slightly larger than that of ZrP(6M). The larger interlayer distance results from extra co-intercalated H_2O .²⁸ Their difference in crystallinity is also shown in their scanning electron microscopy (SEM) images in Figure 2. ZrP(6M) clearly shows a platelike structure, although the round edge of the sheets indicates that its crystallinity is still not very high. Compared with

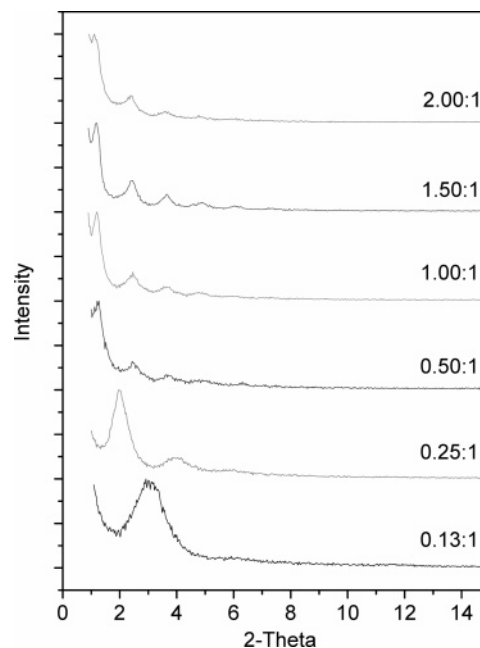


Figure 3. XRD patterns of ZrP(3M) intercalated by M715 at different molar ratios.

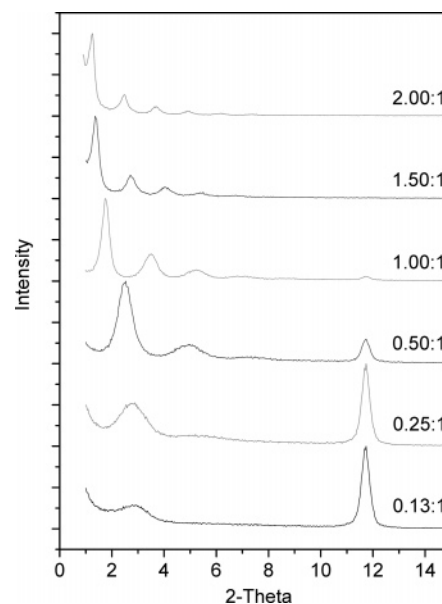


Figure 4. XRD patterns of ZrP(6M) intercalated by M715 at different molar ratios.

ZrP(6M), ZrP(3M) shows a much less regular structure, which consists of the aggregates of both sheets and spherical particles. However, their dimensions are close to each other.

Both ZrP(3M) and ZrP(6M) were intercalated by M715 very slowly in an acetone dispersion system with different molar ratios of M715 to α -ZrP from 0.13 to 2.00 followed by 0.5 h of sonication in a sonication bath. The XRD patterns of intercalated ZrP(3M) and ZrP(6M) are shown in Figures 3 and 4, respectively. Because of the severe preferred orientation exhibited by the M715 intercalate resulting from its layered structure, only the (00 l) reflections are present in the XRD patterns. It is interesting that for all the intercalation compounds prepared from ZrP(3M), even at a very low intercalation ratio of 0.13, the original α -ZrP peaks disappeared completely, which indicates that the original layer

(29) Troup, J. M.; Clearfield, A. *Inorg. Chem.* **1977**, *16*, 3311–3314.

Table 1. Composition of Intercalation Compounds from ZrP(3M) Determined by C, N, H Analysis

formulation (M715/ α -ZrP)	composition determined by C, N, H, elemental analysis
0.13	Zr(HPO ₄) ₂ (M715) _{0.08} ·H ₂ O
0.25	Zr(HPO ₄) ₂ (M715) _{0.12} ·H ₂ O
0.50	Zr(HPO ₄) ₂ (M715) _{0.45} ·H ₂ O
1.00	Zr(HPO ₄) ₂ (M715) _{0.60} ·H ₂ O
1.50	Zr(HPO ₄) ₂ (M715) _{0.76} ·H ₂ O
2.00	Zr(HPO ₄) ₂ (M715) _{0.90} ·H ₂ O

stacking of α -ZrP has been destroyed. At the lowest intercalation ratio of 0.13, the interlayer distance after interaction is about 29 Å. With the increase of the intercalation ratio, the peaks shift to lower 2θ . However, for ZrP(6M), the original α -ZrP peak at about 11.70° does not completely disappear until the intercalation ratio is increased to 1.50. When the intercalation ratio is below this value, the peaks from both the intercalation compound and the original α -ZrP exist in the XRD patterns. With an increase of the intercalation ratio, the intensity of the original α -ZrP peak decreases gradually, while the peaks from intercalation compounds turn out to be more intense and also shift to lower 2θ .

The elemental analysis of carbon, nitrogen, and hydrogen was performed (via Robertson Microlit Laboratories, Inc., Madison, NJ) to determine how much M715 did enter the interlayer of α -ZrP. While the intercalated compounds based on ZrP(3M) contain a one-component composition, most of the interacted compounds based on ZrP(6M) contain two components: intercalated α -ZrP and unintercalated α -ZrP. It is extremely difficult to determine the exact percentage for each of them. Consequently, the elemental analysis was performed on M715 and on the intercalated compounds from ZrP(3M) only. The results (Table 1) show that only part of M715 entered the interlayers, and with an increase in intercalation ratio, more M715 molecules are intercalated into the interlayers of α -ZrP.

The above XRD results indicate that ZrP(3M) is much easier to be intercalated by M715 than ZrP(6M). Considering that the crystal size of ZrP(3M) is close to that of ZrP(6M), the above results can be explained by the difference in crystallinity of ZrP(3M) and ZrP(6M) and the characteristics of the intercalation chemistry of α -ZrP. It is assumed that the intercalation occurred through two steps: (1) the guest molecules enter at the edges of the layer structure of the crystallites, and (2) the guest molecules diffuse from the edge toward the center of the crystallites region. Usually, the energy required for the diffusion of guest molecules at the second step is supplied by the formation of new bonds through the uptaking of additional guest molecules and sonication post-treatment. It is a relatively slow process, and sometimes the XRD pattern shows the simultaneous presence of two or more different phases if the rate of the addition of the guest is faster than the diffusion of the guest molecules.⁴ The incomplete intercalation of ZrP(6M) indicates that, for the case of ZrP(6M), the second step requires a higher activation energy than sonication can provide. However, for ZrP(3M), because its crystallinity is low, which means there are some distortions or even some defects on its layered structure, plus the slightly larger interlayer distance and, thus,

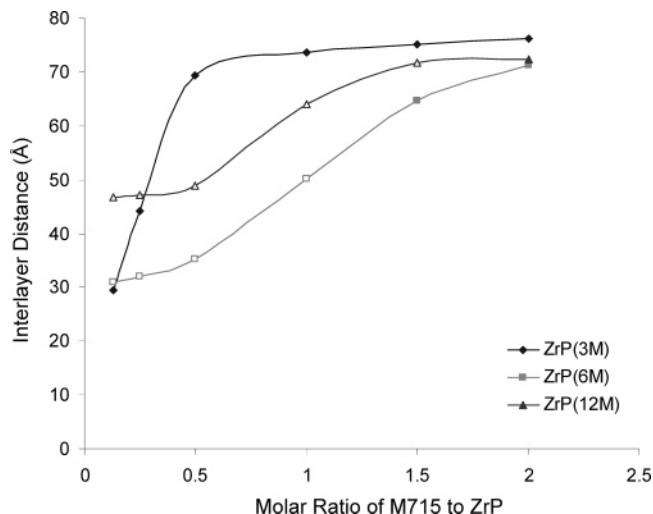


Figure 5. Interlayer distance of intercalated α -ZrP versus intercalation molar ratio. In the figure, the solid symbols represent a complete removal of the original α -ZrP peak; the open symbols represent an intercalation with the original α -ZrP peak still partially maintained.

weaker van der Waals forces between the layers, the activation energy required for second step diffusion becomes lower. Therefore, during the slow intercalation process carried out here, the M715 molecules can not only open the edges of the ZrP(3M) layers but also diffuse into the center of the gallery space easily. The following sonication process facilitates M715 to diffuse throughout the entire layer and spread the layers apart even without the further uptake of additional guest molecules. For ZrP(6M), which has a high degree of crystallinity and less distortions and defects within its layered structure, the first step of edge opening can still go smoothly driven by the reaction between M715 and α -ZrP, but the second step of further diffusion turns out to be much more difficult. Even with the help of sonication, it is hard to drive the diffusion of the intercalant uniformly throughout the gallery space. Compared with ZrP(3M), this step of the reaction occurred at a much slower rate and to a lower degree. Without further uptake of guest molecules, it cannot overcome the activation energy. Thus, this step of intercalation ended when all the M715 molecules were inserted into the layer edges. So finally, there may be a small amount of M715 molecules that reached deeper into ZrP(6M) layers, but most of them were packed within the layer regions near the edge. The un-intercalated area results in the presence of the original α -ZrP peak. This is in conformity to the mechanism proposed by Alberti.⁸ With the increasing intercalation ratio, more and more M715 molecules diffused toward the center of α -ZrP layers because the exothermic reaction of amines and α -ZrP is able to overcome the activation energy for this process. Until the intercalation ratio reaches 1.50, the M715 molecules finally are able to spread throughout the entire interlayer space.

The relationship of interlayer distance versus initial intercalation ratio of both ZrP(3M) and ZrP(6M) was plotted and is shown in Figure 5. It is clear that, for ZrP(3M), the interlayer distance of its intercalation compound increases quickly when the intercalation ratio is below 0.50. When the intercalation ratio rises to 0.50, the interlayer distance is already about 69 Å, which is about 90% of the interlayer

distance of the intercalation compound from the intercalation ratio of 2.00. After that, the increase of interlayer distance slows down, and finally, at a molar ratio of 2.00, the interlayer distance reaches its maximum of about 76 Å. However, for ZrP(6M), the interlayer distance of its intercalation compound increases slowly below the molar ratio of 0.50. After that the interlayer distance increase speeds up until the molar ratio reaches 1.50 and then slows down again. On the whole, it shows an “S” shaped curve.

Such different interlayer distance changing trends can also be explained by the intercalation mechanism generated above. For ZrP(3M), during the intercalation process, the increasing intercalation molar ratio corresponds to an increasing degree of packing density within the layers. With the increase of packing density, M715 chains turn to tilt toward the direction normal to the layers.³⁰ It is reasonable that, during the early period of tilt, it can result in a more significant increase in interlayer distance, while later on, the changes turn out to be less and less. Another reason is that when the packing density reaches a certain degree, its influence on the chain tilt will be less significant than the beginning period.

For ZrP(6M), as discussed above, its intercalation process at the beginning period is the guest molecules diffusion process, although the packing density should also increase correspondingly but not appreciably. Therefore, during this period, its interlayer distance increase is limited. Note that, at the low molar ratio of 0.13, the interlayer distance of the intercalation compound of ZrP(6M) is even higher than that of ZrP(3M). This is because, at that point, the same amount of guest molecules are accumulated within a smaller region in the layers of ZrP(6M) than in ZrP(3M), which results in a higher packing density. When the intercalation molar ratio reaches 0.50, the guest molecules have diffused to most areas within the layers; thus, the interlayer distance increase begins to speed up because, from this point on, the M715 chains begin to pack and tilt more than diffuse. When the intercalation ratio reaches 1.50, the M715 molecules have almost diffused throughout all the layers, and they have reached a high degree of pack and tilt. Therefore, the interlayer distance increase slows down again.

ZrP(12M) (α -ZrP prepared from 12 M H_3PO_4) was also prepared and intercalated with M715 at different molar ratios.

The crystallinity of ZrP(12M) is even higher than that of ZrP(6M). During the intercalation, the original α -ZrP peaks did not disappear completely until the intercalation ratio reached 2.00. The interlayer distance versus intercalation ratio is also shown in Figure 5 to make a comparison. As expected, the curve also shows an “S” shape but lies above the curve of ZrP(6M). This is because, at low intercalation ratios, M715 molecules accumulated within an even smaller region in the layers of ZrP(12M) than in ZrP(6M) because of the relatively higher van der Waals forces between ZrP(12M) layers. Thus, the higher packing density of M715 in ZrP(12M) layers gives rise to a higher interlayer distance. This happens until the two samples are intercalated with M715 at 1:2 molar ratio, when their interlayer distances are very close to each other.

In summary, a model of intercalation of α -ZrP was suggested that explains the experimental data very well. The results also indicate that, for intercalation purposes and probably for ion exchange purposes too, it is not necessary to prepare highly crystallized materials. This model may be applied to the intercalation of other layered compounds. Therefore, when preparing layered-compound-based nanocomposites, both the crystallinity and the intercalation ratio can be used to control the properties so that the final products can match different requirements. Another significant implication from this result for the preparation of polymer nanocomposites is that the amount of organic modifier for the layered compound intercalation, which may seriously impair the thermal properties of polymer nanocomposites,^{22,31} can be greatly reduced. Corresponding computer modeling research is ongoing.

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Supporting Information Available: XRD patterns of ZrP(12M) and ZrP(12M) intercalated by M715 at different molar ratios. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(30) Clearfield, A.; Tindwa, R. M. *J. Inorg. Nucl. Chem.* **1979**, *41*, 871–878.

(31) Triantafillidis, C. S.; LeBaron, P. C.; Pinnavaia, T. J. *Chem. Mater.* **2002**, *14*, 4088–4095.