Intercalation of Amino Alcohols into α-$Zr(HPO_4)_2 \cdot H_2O$

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The formation of phases during the intercalation of amino alcohols (2-aminoethanol, 3-aminopropanol, 4-aminobutanol, 5-aminopentanol, and 6-aminohexanol) into α-$Zr(HPO_4)_2 \cdot H_2O$ was studied. The existence of three phases with general formula α-$Zr(HPO_4)_2 \cdot xNH_2(CH_2)_nOH \cdot zH_2O$ (x = 0.5, 1, 2; n = 2–6; z = 0.2–1.2) depends on the molar ratio of the starting compounds in the reaction mixture. The compounds α-$Zr(HPO_4)_2 \cdot 2NH_2(CH_2)_nOH \cdot 1.2H_2O$ (n = 5 and 6) lose water and one molecule of amino alcohol upon heating to about 200 °C, as observed by thermal X-ray diffraction measurements.

Introduction

α-$Zr(HPO_4)_2 \cdot H_2O$, hereafter α-ZrP, is a layered compound generated by the packing of two-dimensional macromolecular units that interact weakly with each other. Due to the presence of ionogenic P-OH groups on the surface of the layers, and to the easily accessible interlayer region, this compound is able to act as a host for cationic or molecular polar guest species. The host-guest chemistry of α-ZrP has been summarized in several reviews[1−3] and books.[4−6]

The intercalation of strong bases such as alkylamines is driven by the acid-base interaction between the amino group of the amine and the P-OH groups of the layer. The intercalation of aliphatic monoamines and diamines has been investigated by several groups.[7−12] The intercalation process usually occurs in well-defined steps, indicating the presence of two or more solid phases, and the final products contain one water and two monoamine molecules or one water and one diamine molecules per formula unit. The amine is usually protonated during the intercalation.

A homologous series of 1-alkanols or 1,ω-alkanediols with chain lengths ranging from 2 to 18, or 2 to 10 carbon atoms, respectively, was intercalated into α-ZrP, finely dispersed with the guest species, by exposing the reaction mixture to microwave radiation.[13] Thermogravimetric analysis showed that the intercalation compounds contain a maximum of two mols of alkanol or one mol of alkanediol per mol of zirconium phosphate.

The intercalation of amino alcohols was performed by titrating α-ZrP with their aqueous solution.[6] Fully intercalated products contain two molecules of amino alcohol per formula unit, forming a bilayer with the carbon chain axis almost perpendicular to the host layers. These compounds undergo thermal decomposition leading to phases with one and 0.6 amino alcohol molecules per formula unit.

This paper reports on the intercalation of amino alcohols into α-zirconium hydrogenphosphate. The work is focused on a study of phase formation as a function of reaction time and the ratio of the starting compounds (amino alcohol/α-ZrP, hereafter denoted as y).

Results and Discussion

Amino alcohol molecules enter between the host layers and the decrease of concentration of basic amino alcohol molecules in solution is accompanied by a decrease of pH, which can be observed. A plot of the pH value as a function of time is given in Figure 1. 3-Aminopropanol was added to an aqueous suspension of α-ZrP in an amount corresponding to the α-ZrP/aminopropanol ratios of 1:1 and 1:2 at time t = 2 min (see inset in Figure 1). The decrease in the amount of amino alcohol is indicated by an exponential decrease of pH. As is obvious from Figure 1, the decrease of pH proceeds for several hours. This means that a relatively long time is needed to reach equilibrium. This time increases with increasing length of the carbon chains.

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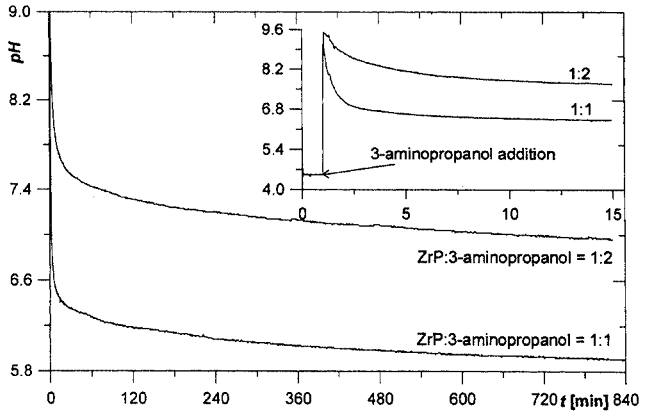

Figure 1. Time course of pH after addition of stoichiometric amount of 3-aminopropanol to an α-ZrP water suspension

For the titration of the aqueous suspensions of α-ZrP, a 100 min time interval between addition of 0.2 mL doses of amino alcohol was chosen, so that a constant pH value was reached (see Figure 2). For the 6-aminohexanol intercalations, 200 min intervals between 0.4 mL doses were used. Titration curves for the titration of α-ZrP with 2-aminoethanol, 3-aminopropanol, 4-aminobutanol, 5-aminopentanol, and 6-aminohexanol are given in Figure 3. In the case of 2-aminoethanol, the reaction occurs in well-resolved steps and plateaus, indicating the presence of three phases. Each step leads to the formation of the given intercalation compound with a characteristic value of the basal spacing that differs from the others in a higher amino alcohol content. The steps become less pronounced for longer amino alcohols.

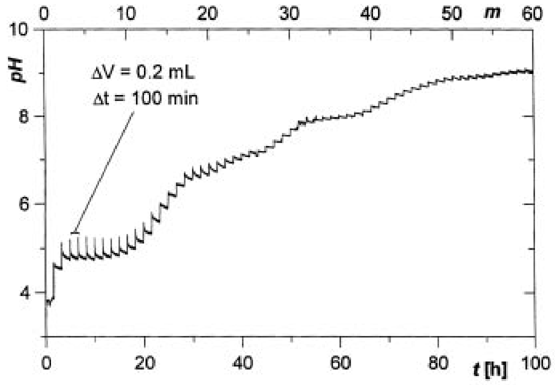

Figure 2. Time dependence of pH during potentiometric titration of an α-ZrP/water suspension with 2-aminoethanol solution; the number of additions of aminoethanol is given in the upper x axis

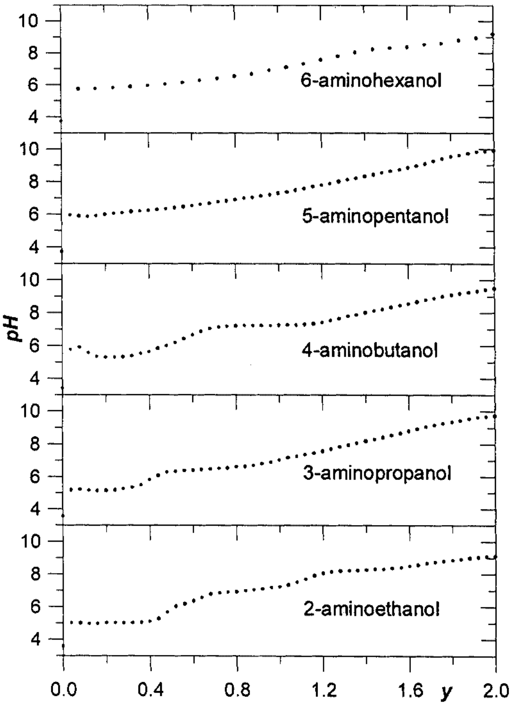

Figure 3. Potentiometric titration curves; y = amino alcohol:Zr ratio

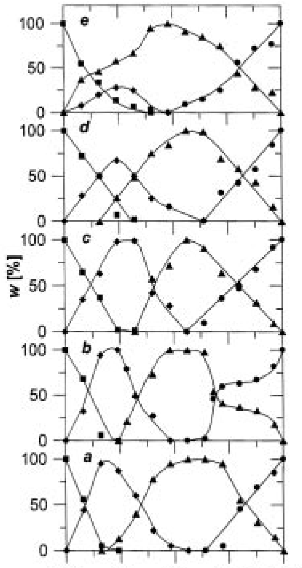

Figure 4. Dependence of relative phase content w on stoichiometric quotient y of: 2-aminoethanol (a), 3-aminopropanol (b), 4-aminobutanol (c), 5-aminopentanol (d), and 6-aminohexanol (e)

Three phases with different basal spacings were found in the samples during the intercalation (see Figure 4). They are formed consecutively, with a maximum relative ratio at amino alcohol contents x of 0.5, 1, and 2 (hereafter denoted as phases 0.5, 1, and 2). The 0.5 phase forms rapidly with amino alcohols having shorter chains (from 2-aminoethanol to 4-aminobutanol) and can be prepared in a pure form. In the case of 5-aminopentanol, this phase forms less readily, although it still represents a significant part of the reaction product. On the other hand, only a small amount of the 0.5 phase was observed in the intercalate with 6-aminohexanol, in which it accompanies the 1 phase. While a plateau corresponding to the 1.5 phase is observed on the titration curve for 2-aminoethanol, no such phase was observed for any amino alcohol in the diffraction spectra of the corresponding intercalates. A moderate consecutive change of the basal spacing of phases 1 and 2 is observed when the ratio of the starting compounds y is changed from 1 to 2. It can be presumed that the amino alcohol content x in these phases is variable within a certain range.

The pure phases $Zr(HPO_4)_2 \cdot xNH_2(CH_2)_nOH \cdot zH_2O$ were prepared by the reaction of α-ZrP with a stoichiometric amount of the corresponding amino alcohol. Their composition was determined by thermogravimetric and elemental analysis. The found compositions (Table 1) are in good agreement with the presumed values (x = 0.5, 1.0, and 2.0). The TG curves of all prepared pure intercalate phases of 4-aminobutanol are given in Figure 5. The intercalated water is released up to 200 °C, 4-aminobutanol is released at around 300 °C, and a slow weight decrease at 350−550 °C corresponds to the removal of condensation water and the formation of pyrophosphate ZrP_2O_7. A further slow decrease of the weight is given by the combustion of carbon formed by the decomposition of the amino alcohol. The final product of the heating to 1200 °C is gray and contains some residual carbon.

Table 1. Composition of intercalates $Zr(HPO_4)_2 \cdot xNH_2(CH_2)_nOH \cdot zH_2O$

n	Phase 0.5		Phase 1		Phase 2	
	x	z	x	z	x	z
2	0.46	0.7	0.91	0.4	2.00	1.2
3	0.45	0.9	0.94	1.0	2.00	0.8
4	0.45	1.0	0.86	0.3	1.91	0.7
5	–[a]	–	0.95	1.2	1.90	1.2
6	–[a]	–	0.90	0.2	1.93	1.2

[a] Pure compounds were not prepared.

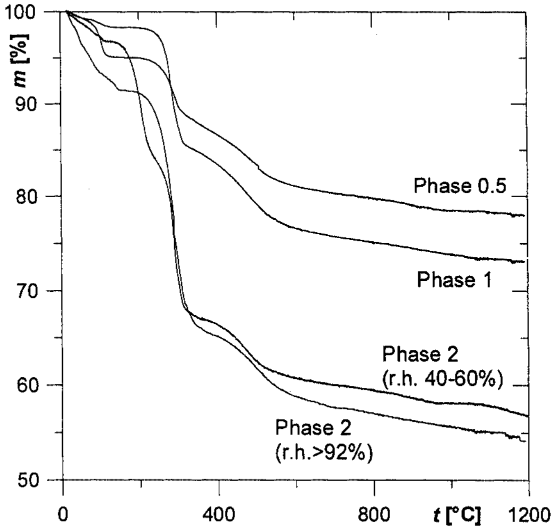

Figure 5. TGA of 4-aminobutanol intercalates

The dependence of the basal spacing of the intercalates prepared on the carbon chain length is given in Figure 6. This dependence is linear for the phases 0.5, with a slope of 0.407.

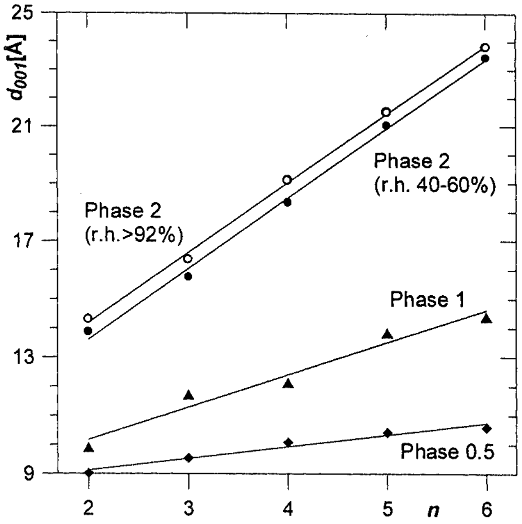

Figure 6. Dependence of the basal spacing d_{001} on the number of carbon atoms n in the amino alcohol chain

For the phases 1, the increment of the basal spacing alternates regularly when a homologous series of amino alcohols is used. The basal spacing increases by about 1.8 Å when going from an amino alcohol with an even number of carbon atoms to an amino alcohol with the chain one carbon atom longer. When we go from an amino alcohol with an odd number of carbon atoms to an amino alcohol with the chain one carbon atom longer, the increase of basal spacing is about 0.5 Å. This alternation can be explained by a different water content in the intercalates (see Table 1). The average increment of the basal spacing is 1.11 Å. As was found by XRD measurements at different relative humidities (*r.h.*), the basal spacing of the 2-aminoethanol, 4-aminobutanol, and 6-aminohexanol intercalates remains constant at *r.h.* > 92% and basal spacing of 3-aminopropanol and 5-aminopentanol intercalates does not change at *r.h.* < 11%. The water content in these intercalates does not depend on the relative humidity of ambient air, as was found by TG measurements.

On the other hand, the water content of the fully intercalated products (phases 2) does depend on the relative humidity. Under ambient conditions (*r.h.* = 40−60%), the intercalates contain about one water molecule per formula unit. The linear dependence of the basal spacing on n has a slope of 2.356. At high relative humidity (*r.h.* > 92%), these intercalates contain two water molecules and their basal spacings increase by about 0.62 Å, although the slope of the dependence of the basal spacing on n is practically the same as under ambient conditions.

The 5-aminopentanol and 6-aminohexanol intercalates (phases 2) were studied by thermal X-ray measurements. A small decrease of the basal spacing (about 0.25 Å) was observed at about 50 °C; this may be caused by water released from the interlayer space. Formation of phases 1 was observed at about 160 °C and the phases 2 disappeared at 200 °C. This is in good agreement with Costantino's results.[6] The temperatures of dehydration and loss of one molecule of amino alcohol determined by TG (79 and 220 °C for 6-aminohexanol) are higher than those determined by XRD. This difference is caused by the insensibility of TG to crystal structure changes which occur during the release of the guest from the interlayer space before its evaporation from the sample.

As follows from the calculated slopes, the molecules of amino alcohols in the interlayer space are less tilted relative to the host layers with an increasing degree of intercalation, so that they form a bimolecular film with chains tilted at an angle of 67° in the fully intercalated phases.

Experimental Section

Well-crystallized α-ZrP, of formula α-$Zr(HPO_4)_2 \cdot H_2O$, was obtained according to the method reported by Alberti and Torracca.[14] A clear solution was prepared by dissolving 10.1 g of $ZrOCl_2 \cdot 8H_2O$, 8 mL of hydrofluoric acid (40% w/w) and 92 mL of H_3PO_4 (85% w/w) in 160 mL of water. The solution was heated at 80 °C for 4 days, maintaining a constant volume by continuously adding water. The α-ZrP precipitate was washed with deionized water and dried in air.

Intercalation of 2-aminoethanol, 3-aminopropanol, 4-aminobutanol, 5-aminopentanol and 6-aminohexanol into α-ZrP was studied. Three types of experiment were carried out:
1) α-ZrP (0.25 g, 0.83 mmol) suspended in 50 mL of H_2O was titrated with a 0.166 M solution of the corresponding amino alcohol. In each step, 0.2 mL of amino alcohol was added at 100 min intervals. The pH values were followed as a function of time.
2) The successive formation of the phases was followed on the samples prepared by the reaction of the suspension of 0.125 g of α-ZrP in 50 mL of H_2O with 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 2.8, 3.2, 3.6, 4.0, 4.4, 4.8 and 5.0 mL of a 0.166 M solution of the corresponding amino alcohol. After the amino alcohol addition, the samples were stirred for 24 h and the solvents evaporated to dryness at 50 °C.
3) The pure phases $Zr(HPO_4)_2 \cdot xNH_2(CH_2)_nOH \cdot zH_2O$ ($x = 0.5$, 1.0 and 2.0; $z = 0.4-1.2$) were prepared by reaction of α-ZrP with a stoichiometric amount of corresponding amino alcohol. The basal spacing and content of water as a function of relative humidity of the atmosphere was followed.

X-ray powder diffraction (XRPD) patterns of the intercalates were obtained with an X-ray diffractometer (HZG-4, Germany) using Ni-filtered Cu-K_α radiation. The Cu-$K_{\alpha 2}$ intensities were removed from the original data. Silicon ($a = 5.43055$ Å) was used as internal standard. Diffraction angles were measured from $2\theta = 1.5°$ to $2\theta = 50°$. XRPD patterns at different temperatures, from 20 to 250 °C, were taken on samples heated on a sintered alumina ceramic plate equipped with a thermocouple.[15]

The compositions of the pure phases were calculated from thermogravimetry measurements (Stanton Redcroft STA-801, heating rate 5 °C/min, Pt crucible, Pt-Pt/Rh thermocouples, air flow) and elemental analysis. The weight of the gray residue obtained by heating to 1200 °C was corrected for the carbon remaining in the sample, which was determined by elemental analysis. The difference between the original weight of the sample and the corrected weight of the sample after heating is the weight of the organic substance, hydration water, and condensation water (water released by formation of pyrophosphate ZrP_2O_7). From the corrected weight of the heated sample, the amount of zirconium pyrophosphate was calculated and found to correspond to the amount of condensation water. The amount of hydration water corresponded to the weight loss observed to about 200 °C. The amount of the organic substance was calculated as the difference between the total weight loss and the amount of water. From the amount of the organic substance one can calculate the N, C, and H content of the sample and compare it with the results from elemental analysis. From these considerations the general formula of the intercalation compounds $Zr(HPO_4)_2 \cdot xNH_2(CH_2)_nOH \cdot zH_2O$ was determined.

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[1] G. Alberti, M. Casciola, U. Costantino, R. Vivani, *Adv. Mater.* **1996**, *8*, 291−303.
[2] G. Alberti, U. Costantino, *J. Mol. Catal.* **1984**, *27*, 235−250.
[3] A. Clearfield, *Chem. Rev.* **1988**, *88*, 125−148.
[4] G. Alberti, U. Costantino, in *Inclusion Compounds* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol), Oxford University Press, Oxford, 1991; Vol. 5, p 136−157.
[5] A. Clearfield, in *Progress in Intercalation Research* (Eds.: W. Müller-Warmuth, R. Schöllhorn) Kluwer Academic Publishers, Dordrecht, 1994; Vol. 17, p 240−252.
[6] A. Clearfield, U. Costantino, in *Comprehensive Supramolecular Chemistry* (Eds.: G. Alberti, T. Bein) Pergamon, Oxford, 1996; Vol 7, p 107−139.
[7] S. Yamanaka, Y. Horibe, M. Tanaka, *J. Inorg. Nucl. Chem.* **1976**, *38*, 323−326.
[8] A. Clearfield, R. M. Tindwa, *J. Inorg. Nucl. Chem.* **1979**, *41*, 871−878.
[9] J. P. Gupta, D. V. Nowell, *J. Chem. Soc., Dalton Trans.* **1979**, 1178−1182.
[10] G. Alberti, U. Costantino, *J. Mol. Catal.* **1984**, *27*, 235−250.
[11] R. M. Tindwa, D. K. Ellis, G.-Z. Peng, A. Clearfield, *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 545−552.
[12] M. Casciola, U. Costantino, L. Di Croce, F. Marmottini, *J. Incl. Phenom.* **1988**, *6*, 291−306.
[13] U. Costantino, R. Vivani, V. Zima, L. Beneš, K. Melánová, *Langmuir* **2002**, *18*, 1211−1217.
[14] G. Alberti, E. Torracca, *J. Inorg. Nucl. Chem.* **1968**, *30*, 317−318.
[15] L. Beneš, *Sci. Pap. Univ. Pardubice Ser. A* **1996**, *2*, 151−155; *Chem. Abstr.* **1997**, *126*, 310616v.

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