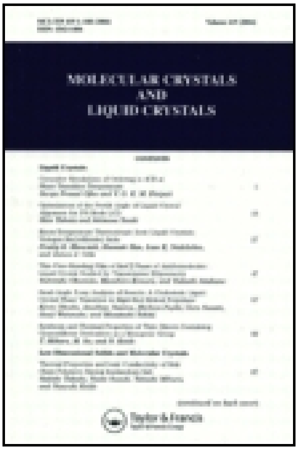

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Intercalation and Thermal Decomposition of Urea in Layered Zirconium Phosphates of α- and γ-Type

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Intercalation and Thermal Decomposition of Urea in Layered Zirconium Phosphates of α- and γ- Type.

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The intercalation of urea in α- and γ- zirconium phosphates was achieved by equilibrating the propanolic form of the two layered hosts with saturated aqueous solutions of urea at room temperature. C, N and H elemental analysis and thermogravimetric determination of α- and γ- intercalates, conditioned at room temperature and 75% relative humidity, give the compositions α-$Zr(HPO_4)_2 \cdot 0.9\ CO(NH_2)_2 \cdot 1.6\ H_2O$ and γ-$ZrPO_4(H_2PO_4) \cdot 1.2\ CO(NH_2)_2 \cdot 0.6\ H_2O$; the interlayer distances of the samples were 1.09 nm and 1.38 nm respectively. FT-IR absorption spectra, analytical data and computer models gave evidence that urea is arranged in the interlayer region as a monolayer. In the 120-220° C temperature range the thermal decomposition of urea in a constrained system gives rise to the formation of the monoammonium form of zirconium phosphates and the elimination of a compound with N/C molar ratio equal to 1.

keywords: layered zirconium phosphates, urea intercalation, urea decomposition.

INTRODUCTION

It is now well known that the names α- and γ-zirconium phosphate refer to two different layered compounds having the formulae α-$Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP) and γ-$ZrPO_4(H_2PO_4) \cdot 2H_2O$ (γ-ZrP) respectively. The ability of the two hosts to exchange cations and to insert polar molecules (including alkanols, glycols, aliphatic and aromatic amines and aminoacids) has led to a growing interest in their use as matrices for the preparation of a large number of intercalation compounds and for the design and synthesis of nanocomposites and pillared layered structures with potential application as catalysts, ionic conductors, ionic and molecular receptors, etc.[1]. It is however surprising that very little information is available on the intercalation of urea in such inorganic hosts. In a pioneering work[2] Behrendt, Beneke and Lagaly reported the formation of urea intercalation compounds when the hosts are dispersed in a saturated urea solution at 60°C for several days. The interlayer distances of the compounds obtained (0.94 nm and 13.6 nm respectively[2]) are very similar to those of the intercalation compounds with the ammonia, that could be formed in the urea-hydrolysis reaction. It seemed thus of interest to obtain urea-zirconium phosphates intercalation compounds with a different procedure and this paper reports the preparation, a preliminary chemical and structural characterisation and the thermal decomposition of urea α and γ-ZrP intercalation compounds.

EXPERIMENTAL

Batches of α-$Zr(HPO_4)_2 \cdot H_2O$ (hereafter α-ZrP: interlayer distance 0.76 nm, maximum exchange capacity 6.64 meq/g) and of γ-$ZrPO_4(H_2PO_4) \cdot 2H_2O$ (hereafter γ-ZrP: interlayer distance 1.22 nm, maximum exchange capacity 6.27 meq/g) were prepared by thermal decomposition of zirconium fluorocomplexes[1]. The propanolic form of α-zirconium phosphate was prepared by dispersing 1 g of the ethanolic form of α-ZrP[3] in 50 mL of pure propanol at room temperature for one day. The interlayer distance of the α-$ZrP \cdot xCH_3CH_2CH_2OH$ (x~2) obtained is 1.6 nm. The propanolic form of γ-zirconium phosphate was prepared by dispersing 1 g of γ-ZrP in 50 mL of pure propanol at room temperature for one day (interlayer distance 2.02 nm). The X-ray powder diffraction (XRPD) patterns were taken with a computer-controlled Philips PW1710 diffractometersupplied with an A. Paar H.T.K. attachment for XRPD patterns at high temperature, using Cu K_α radiation (40 KV, 20 mA). TG-DTA coupled analyses were performed with a Stanton STA thermoanalyzer with a heating rate of 5°C/min in air flow. FT-IR absorption spectra were obtained with a Jasco FT/IR-410 spectrometer equipped for solids. KBr was used as reference.

RESULTS AND DISCUSSION

Urea is a very weak base (pK_b=13.8), highly soluble in water, where it hydrolyses to give ammonium carbonate. The rate of the reaction is very slow at room temperature, but becomes fast at higher temperatures increasing by about 200 times when the temperature increases from 60 °C to 100 °C[4]. The subsequent hydrolysis of ammonium to ammonia and carbonate to hydrogen carbonate determines a pH of about 9, a value at which both α and γ-ZrP are converted into their ammonium forms. In order to prevent the formation of the ammonium forms it is necessary to avoid water as solvent or to perform the reaction at low temperatures and short reaction times in aqueous media. Attempts to obtain the intercalation compounds starting from solutions of urea dissolved in different solvents (ethanol, methanol, acetonitrile) failed. It was decided to use the so called "propping on" mechanism, that is a displacement reaction where the urea displaces a weakly bounded guest that maintains a gallery height much higher than the urea dimension and is intercalated in zirconium phosphates. The propanolic forms of α- and γ-zirconium phosphates were used as precursors to achieve urea intercalation. After equilibration with urea saturated aqueous

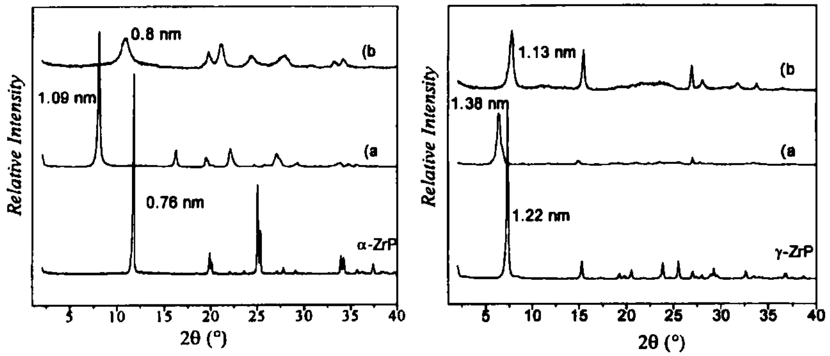

FIGURE 1 XRDP patterns of urea intercalates of (left) α-ZrP a) at r.t. and 75% R.H., b) after heating at 135 °C ; (right) γ-ZrP a) at r.t. and 75% R.H., b) after heating at 120 °C

solution at room temperature, for one day, the XRPD pattern of the sample, washed several times with acetonitrile (extensive washing with water produces deintercalation), revealed (Fig. 1) the disappearance of the diffraction maxima corresponding to the propanol intercalates and the presence of a single phase with interlayer distance 1.09 and 13.8 nm for α-ZrP(urea) and γ-ZrP(urea) compounds respectively.

Table I: Elemental analysis results

Sample	%N	%C	N/C
α-ZrP(urea) r.t.	6.74	3.00	1.93
α-ZrP(urea) 135 °C	5.89	2.29	2.20
γ-ZrP(urea) r.t.	8.70	4.55	1.91
γ-ZrP(urea) 120 °C	5.87	2.13	2.36

Thermogravimetric (Fig. 2) and N, C elemental analysis (Table I) of α- and γ- intercalates, at room temperature (r.t.) and 75% relative humidity (R.H.), give the compositions α-$Zr(HPO_4)2\cdot 0.9CO(NH_2)_2\cdot 1.6\ H_2O$ and γ-$ZrPO_4(H_2PO_4)\cdot 1.2CO(NH_2)_2\cdot 0.6\ H_2O$. IR analysis confirm the presence of urea interacting with α- and γ- layer. Fig. 3a shows the FT-IR absorption spectra of α-ZrP(urea) intercalate at r.t. and 75% R.H.. Similar results were obtained for the γ- compound. The bands 1 and 2 may be assigned to ν(N-H) while the δ_{as} and $\delta_s(NH_3^+)$ (see bands 4 and 5) indicate some proton transfer to $-NH_2$. In addition, the shoulder at 1661 cm^{-1} of bands 3 probably represents the ν(C=O); its down shift in frequency could indicate some interactions with the layers through the carbonyl oxygen. This further implies that proton transfer is probably limited to only one of the $-NH_2$ groups, and this is consistent with the strong absorption of the band 3 given by $\delta_s(NH_2)$ and $\delta_s(H_2O)$. These observations, as well as the composition and interlayer distance data, allowed the design of a molecular model with the "Hyperchem" program. This model, shown in Fig. 4, indicates that both amino and carbonyl groups belonging to the guest molecules, can easily interact with the acidic -POH sites of the layers. When the α-ZrP(urea) and γ-ZrP(urea) samples are dried at 50 °C and 60°C respectively, the interlayer distances decrease to 0.99 nm for α and 1.28 nm for γ intercalates as a

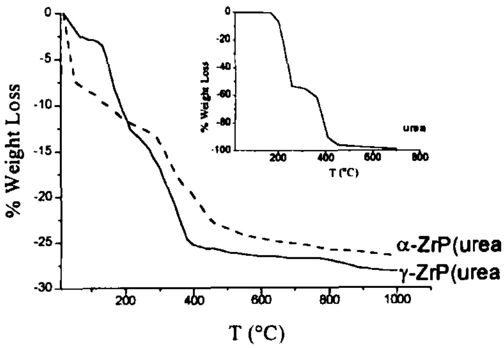

FIGURE 2 weight loss of the α-Zrp and γ-ZrP urea intercalates. The weight loss of the urea is shown as reference.

consequence of water loss. Interlayer distance remains practically unchanged up to 120°C for α and 135°C for γ, temperatures at which the urea decomposition starts (Fig. 2).

When both urea intercalates are kept at these temperatures, they change into the corresponding mono ammonium forms as confirmed by XRPD patterns (Fig. 1) and IR analysis (Fig. 3). After heating, IR spectra show the appearance of $\delta_s(NH_3^+)$ (Fig. 3, curve b, band 8), the disappearance of ν(N-H) of urea (Fig. 3, curve a, bands 1 and 2). Furthermore, the presence of the ν(CN) (Fig. 3, curve b, band 6), suggests that the thermal decomposition in a interlamellar constrained system is similar to that occurring in acid solutions[4] with the formation of cyanic acid and ammonia. Consequently, ammonium

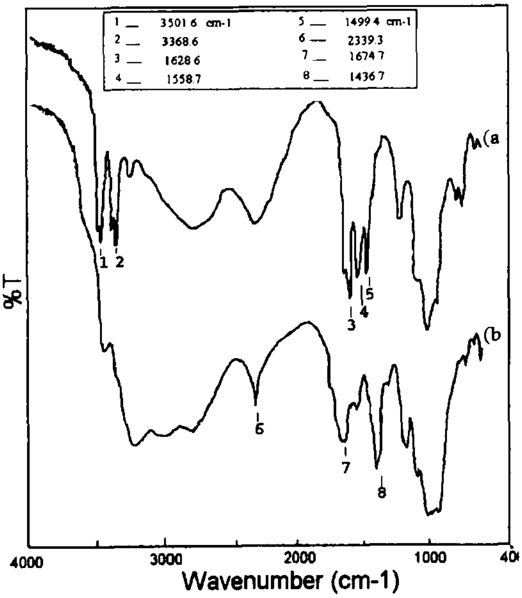

FIGURE 3 IR spectra of α-ZrP urea intercalates:a) at r.t. and 75% R.H.;b)after heating at 135°C

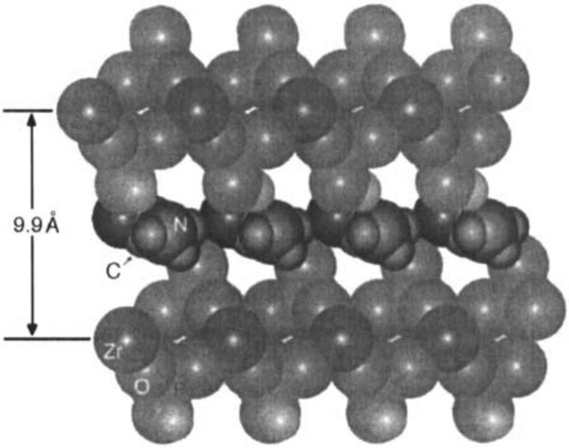

FIGURE 4: Structural model obtained for α-ZrP(urea).

intercalation compounds can be formed, and the cyanic acid probably remains partially trapped in the interlayer region. Elemental analysis (Table I) shows that, during thermal treatment, the molar ratio N/C increases and an equal number of C and N mol is lost. We think that a species with a C/N ratio equal to 1 (possibly the cyanic acid) is lost. Note that the increase of N/C molar ratio with the temperature is higher for γ- than for α-intercalate, even though the thermal treatment was performed at a lower temperature. It is as if the γ-ZrP(urea) decomposition occurs at lower temperatures and /or the diffusion of the decomposition products is faster in the γ than in the α- interlayer region.

Acnowledgments

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