Journal of Thermal Analysis and Calorimetry, Vol. 76 (2004) 871–882

THERMAL BEHAVIOUR OF γ-ZIRCONIUM PHOSPHATE INTERCALATION COMPOUNDS WITH TEMPLATE SURFACTANTS
Synthesis and characterisation

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(Received November 16, 2003; in revised form March 16, 2004)

Abstract

Long chain alkylammonium cations can be exchanged into a preswelled phase of γ-zirconium phosphate, a layered inorganic ion-exchanger. The derived materials are used as templates to give organic-inorganic composite materials. The cationic exchange occurs very quickly. These intercalation compounds behave in a very similar way. They are still layered and exhibit an interlayer distance *d* notably greater than that of its precursor whose behavior depends on the chain length. By thermal and microanalyser characterizations it can be observed that the surfactant is lost in two stages, the second one as a result of the fragmentation of the chain. The layered structure with the expanded interlayer distance is maintained up to ~350°C.

Keywords: ion-exchanger, layered compounds, surfactants, thermal behavior, X-ray diffraction

Introduction

Acid salts of tetravalent metals with general formula $M^{IV}(HXO_4)_2 \cdot nH_2O$ (M=Zr, Ti,…; X=P, As,…; n=1,2,…) have been the object of growing interest for their particular ability both to exchange metal ions and to intercalate polar molecules [1–4]. Today it is widely recognized that both α- and γ-zirconium phosphates [α-$Zr(HPO_4)_2 \cdot H_2O$ and γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$] (α-ZrP; γ-ZrP) are excellent intercalating agents for many molecules belonging to different classes. Furthermore intercalation has been found to be an excellent tool both for preparing pillared derivatives and for application in fields such as heterogeneous catalysis. In particular γ-zirconium phosphate is one of the most extensively studied layered compounds. In continuing our studies on the intercalation of organic surfactants into inorganic ion-exchangers belonging to the class of

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1388–6150/2004/ $ 20.00

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Kluwer Academic Publishers, Dordrecht

zirconium phosphate [5, 6], a range of new surfactant intercalated has been synthesized by reacting the large chains of organic ionic surfactants and γ-zirconium phosphate, which is known to have a layered structure with interlayer distance d=12.30 Å. The cationic surfactants are trimethylammonium salts of general formula C_nTMABr (C_nTMA^+=C_n^+, n=12, 14, 16, 18). The H^+ cation of the POH groups of the γ-ZrP are exchanged with trimethylammonium cations ions. The general chemical formula of the derived materials is $\gamma\text{-}Zr(PO_4)(H_{2-x}PO_4)(C_n)_x \cdot mH_2O$ ($\gamma\text{-}ZrPC_n$). The aim of the work is to prepare layered materials with an increased interlayer distance, for specific use in selective catalysis. Usually the d of the derived materials increases after intercalation. The procedure of intercalation is in accordance with previous studies [7]. The synthesis of these γ-ZrP derivatives was carried out using two different methods: the batch (B) and hydrothermal methods (HM) with an aim to finding the best operating system and to discover differences if any in the same products resulting from the use of two different methods.

Experimental

Chemicals

Zirconyl chloride octahydrate, phosphoric acid 85%, C_nTMABr surfactants, were pure grade, marketed by Aldrich and they were used as solid without further purification.

Synthesis of materials

The γ-zirconium phosphate was prepared as reported in the literature [1].

The γ-zirconium phosphate surfactant materials were prepared using two methods: the batch method and the hydrothermal synthesis method. By using the batch method, 1 mmol of γ-ZrP preswelled with anhydrous EtOH [8] was contacted with 2 mmol of a $C_nTMACBr$ 0.2 M solution (1:1 water/ethanol) at 50°C, for varying lengths of time. This ratio was chosen to ensure a 100% of theoretic exchange between the H^+ of the POH groups and the cationic surfactant. After the synthesis, the C_n-materials were recuperated by filtration and carefully washed with a small quantity of ethanol and dried at room temperature (*r.t.*). A ‘small’ quantity of ethanol, ~7 mL of EtOH, was used to wash the materials, in order to eliminate the sorbed excess of surfactant C_n. The batch contact of the C_n-materials derived from HCl 0.1 M or H_3PO_4 0.1 M [9] gives, respectively, a partial or full C_n^+/H^+ exchange, so that the precursor can be regenerated. This behavior confirms the exchanging and layered properties of the derived surfactant materials.

By using the hydrothermal synthesis method 1 mmol of γ-ZrP was contacted with 2 mmol of a $C_nTMACBr$ 0.2 M solution (1:1 water/ethanol) at 120°C for two days. The derived materials were then recuperated by filtration, washed with a small quantity of ethanol and air-dried.

The materials derived with both methods needed to be powdered in a mortar for a better characterization in TG-DTA, XRDP. The cationic surfactants exchanged in the samples were determined by microanalysis measurements. An excess of surfactant solution and a 0.1 M surfactant solution (further diluted) to improve the exchange was also performed but without giving better results.

Physical measurements and chemical analysis

Manipulations were followed by X-ray diffraction powder (XRDP) on a Philips diffractometer (model PW 1130/00) using Ni-filtered CuK_α radiation (λ=1.541 Å) at 40 kV and 25 mA. The carbon, nitrogen and hydrogen contents in the materials were determined with a Fisions 1108 elemental microanalyser. The *P* content was determined colorimetrically [10]. Thermogravimetric (TG) and differential thermal analysis (DTA) were carried out under static conditions using a simultaneous Stanton Redcroft STA 1500 apparatus, at 10°C min^{-1} heating rate, from r.t. to 1100°C, in air or N_2 gas flow.

Results and discussion

Surfactant uptake

In the synthesis using the batch method, the kinetic uptake of all the surfactants over varying lengths of time (Table 1) was studied. The time of batch contact ranged from 5 min to 1 week (5 min; 6, 24 h, 7 days). The aim was to follow the surfactant content inside the γ-ZrP and its uptake rate over varying lengths of time, both in relation to the chain length. As written in Experimental (Synthesis of materials) the preswelling method was adopted to favor the surfactant uptake. The preswelling causes an increase of the *d* spacing with respect to that of the precursors. In this way the host matrix which gives poor intercalation with direct batch contact, can easily exchange the long chain of the cationic surfactants. In fact in both the methods where no preswelling took place, the uptake was less than ~20%. As shown in Table 1 the final uptake of all the surfactants is almost the same, independently of the chain length. At low batch contact time (e.g. 5 min) the longer the chain the greater the uptake [8], and the exchange occurs between ~65–90% of the total uptake. After one day of batch contact the exchange is almost complete. Prolonging the length of time of batch contact, for more than one week, the uptake increase is negligible. This fact shows the great affinity of the surfactant cation to exchange with the hydrogen of the POH groups of the γ-ZrP. Besides this it should be noted that the exchange of C_n^+ cations with the H^+ of the POH groups is ~23.50% of the theoretic exchange capacity of the γ-ZrP, of all the surfactants. So these derived compounds maintain acid POH groups both on the surface of γ-ZrP and between the layers. By varying the surfactant/exchanger molar ratio, (e.g. >100% of theoretic exchange) so as to obtain a more surfactant content, the uptake is increased by ~20%. By varying the surfactant/exchanger molar ratio, (e.g. ≤50%) the C_n^+ uptake decreases from 39 to 23% from γ-$ZrPC_{12}$ to γ-$ZrPC_{18}$, respectively. The shorter the chain the greater the decrease.

The materials derived using the hydrothermal method have a greater surfactant content with respect to those obtained using the batch method (Table 1). The water content of the derived materials is much the same for all the derived compounds and the complete chemical formula is reported in Table 1. Finally the surfactant deintercalates easily when the compounds are treated with HCl or H_3PO_4 (Experimental).

Table 1 Surfactant uptake at varying lengths of time, by batch (B) and by hydrothermal method (HM)

γ-ZrPC$_n$	5 min	6 h	24 h	168 h; 100%*; >100%*; 50%*	HM 100%*
γ-ZrPC$_{12}$	0.30	0.35	0.42	0.46 0.56 0.28	48
γ-ZrPC$_{14}$	0.30	0.37	0.43	0.47 0.57 0.31	0.51
γ-ZrPC$_{16}$	0.36	0.39	0.43	0.47 0.60 0.33	0.54
γ-ZrPC$_{18}$	0.42	0.44	0.48	0.51 0.65 0.39	0.57

*Theoretic exchange; Chemical formula for the γ-ZrPC$_n$; γ-Zr(PO$_4$)(H$_{1.54}$PO$_4$)C$_{12}$(0.46)·1.74H$_2$O; γ-Zr(PO$_4$)(H$_{1.53}$PO$_4$)C$_{14}$(0.47)·1.7H$_2$O; γ-Zr(PO$_4$)(H$_{1.53}$PO$_4$)C$_{16}$(0.47)·1.77H$_2$O; γ-Zr(PO$_4$)(H$_{1.49}$PO$_4$)C$_1$8(0.51)·1.80H$_2$O

Thermal behavior

Figure 1 shows the TG-DTA curves of the γ-ZrPC$_n$ materials derived using the batch method (one week of batch contact with the surfactant solutions) with respect to the precursor γ-ZrP. The thermal behavior of all the derived materials is similar. The TG curves show that between 25–150°C a loss occurs due to the hydration water. There is a plateau up to 220°C. Between 220–310°C a first surfactant loss occurs. At 310°C in the TG curve an inflection is evident due to a strong thermal effect. A more consistent loss, between 310–500°C, corresponds both to the surfactant combustion and also to the hydroxyl groups of the phosphate groups condensation, to give the pyrophosphate, related to the H^+/C_n^+ that had not been exchanged. The DTA curves are in accordance with the TG data: the endothermic peak corresponds to the loss of water. Then the two exothermic peaks of different intensity are evidently related to the decomposition and combustion of the surfactant. The second exothermic peak comprises the loss of water due to the condensation of hydroxyl groups (as seen before). In fact the stronger thermal effect of the surfactant combustion hides the endothermic peak usually present in the elimination of hydroxyl groups. The different decomposition temperature of the surfactant, marking the second stage of loss, is due to the fragmentation of the organic chain. This means that the cationic loss occurs with chain fragmentation where a partial chain in the amino group

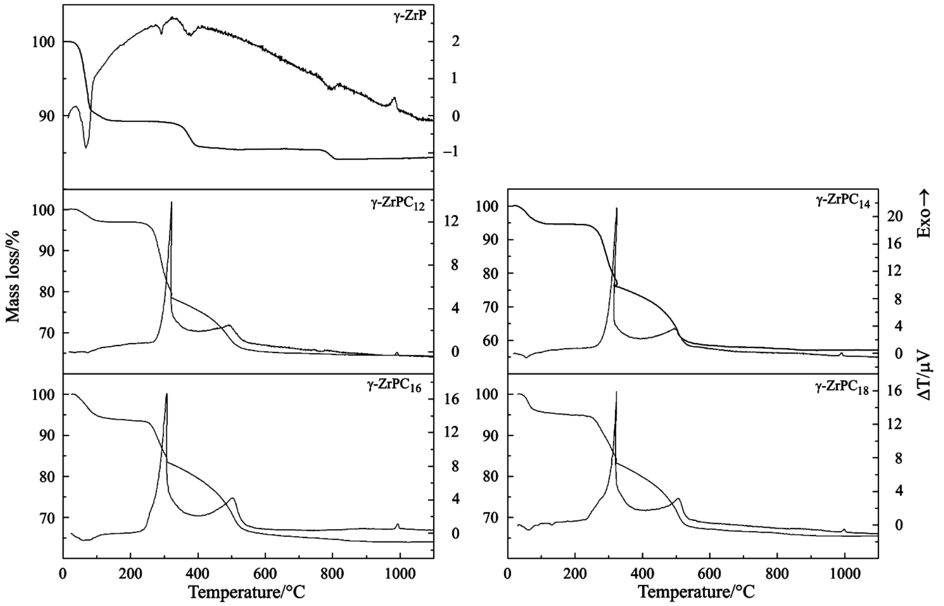

Fig. 1 TG-DTA curves of γ-ZrP and γ-ZrPC$_n$ intercalated materials for comparison

$-N(CH_3)_3^+$ (more strongly linked to the $-PO_4^{3-}$ groups) is lost at higher temperatures. As a result of microanalysis measurements of the intercalated materials, submitted to thermal treatment at 310°C (the end of the first mass loss) (Table 2) the loss is on average ~21% of the total content and could be related to the surfactant exchanged on the surface of the host matrix, which is weakly linked and more easily eliminated. At 420°C (the intermediate stage of the second loss) the N/C% ratio increases (Table 2) with respect to those at both *r.t.* and at 310°C. That means a decrease of

Table 2 %C and %N at surfactant loss temperatures

γ-ZrPC$_n$	*r.t.*		310°C		420°C	
	C	N	C	N	C	N
γ-ZrPC$_{12}$	21.73	1.72	18.33	1.48	9.8	1.24
	0.46		**0.38**			
γ-ZrPC$_{14}$	23.96	1.66	17.82	1.23	8.93	0.87
	0.47		**0.34**			
γ-ZrPC$_{16}$	26.0	1.63	18.25	1.14	10.66	0.91
	0.47		**0.35**			
γ-ZrPC$_{18}$	27.67	1.55	22.24	1.24	15.86	1.20
	0.51		**0.43**			

[*]dark number are C_n^+ mol present in the intercalated compounds at established temperatures

C%, as a result of CH_2 fragmentation; whereas the decrease of N% value at 420°C means an elimination of the chains linked differently to the host matrix. Besides this the TG curves between the first and the second stage of surfactant loss (at ~310°C) show an inflection, contrary to the case in $SGZrPC_n$ [6], where both the TG curve behavior and the microanalysis data confirm the fragmentation of the chain during heating. At ~980°C the exothermic effect, to which no mass loss is associated, corresponds to a structural transition from a *L*-pyrophosphate (*L*=layered) to cubic-pyrophosphate of the $-PO_4^{3-}$ groups as identified by X-ray diffraction [12]. In the case of all the surfactants at low contact time, from 5 min up to 24 h, the inflection in the TG curves is not evident. In this time range the surfactant combustion between 220 and 310°C occurs in two stages (TG curves) and an exothermic peak with a shoulder in the DTA curves (Fig. 2) is evident.

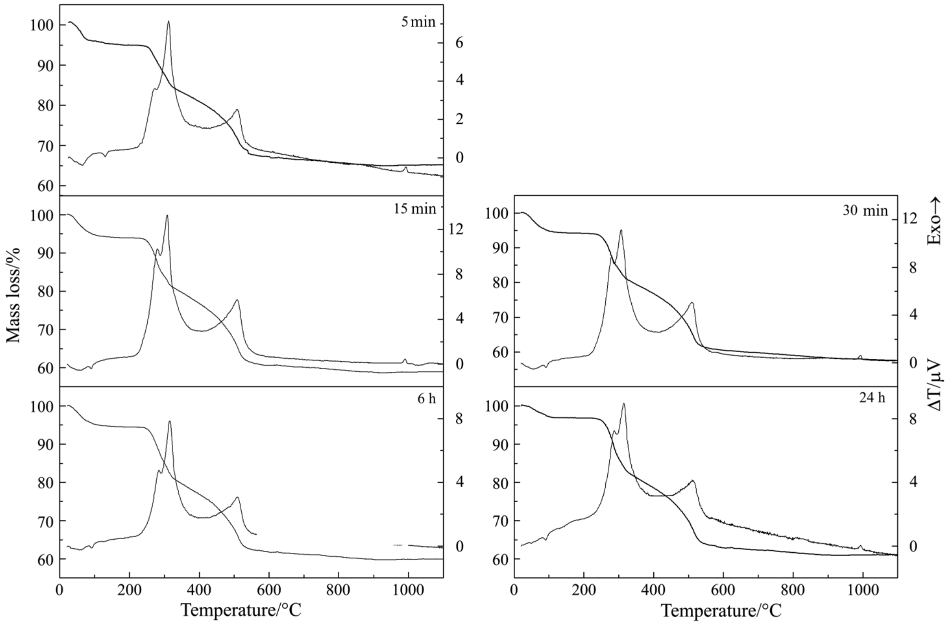

Fig. 2 TG-DTA curves of γ-$ZrPC_{18}$ at various sets of contact time (5 min–15 min–30 min–6 h–24 h)

The materials obtained with the hydrothermal methods are very similar to those obtained in batch (after a week) and they are also very similar to each other. The only difference is the less sharp exothermic peak at 310°C for all the surfactants. The materials obtained with the molar ratio surfactant/exchanger ≤50% show TG-DTA curves similar to each other and to those of the materials with molar ratio 100% or by (HM). The only difference being a decrease in the total surfactant loss.

Note that the good thermal stability of all the intercalate materials contrasts with their poor chemical stability when treated with acid solution. The materials contacted in batch for 3 days with a solution of alcohol and HCl 0.1 M show in the TG curves a decrease in surfactant loss and an even bigger evidence of loss between 310–600°C, related to the presence of water due to condensation of the phosphate groups to give pyrophosphates (Fig. 3). At ~800°C the pyrophosphate temperature is notably increased with respect to that of γ-ZrP (Fig. 1). The DTA curves are in accordance with the TG data. The exothermic peak due to the first stage of surfactant loss is lower and broader and the second exothermic peak at 500°C is almost absent. The peak at 800°C is higher due to the cubic-pyrophosphate formation. This fact is clearly due to the ion-exchange between the C_n^+ and the H^+ of the HCl that has taken place. The surfactant elution is ~80%. As far as the material γ-ZrPC$_{18}$ is concerned the elution is less than with the other materials.

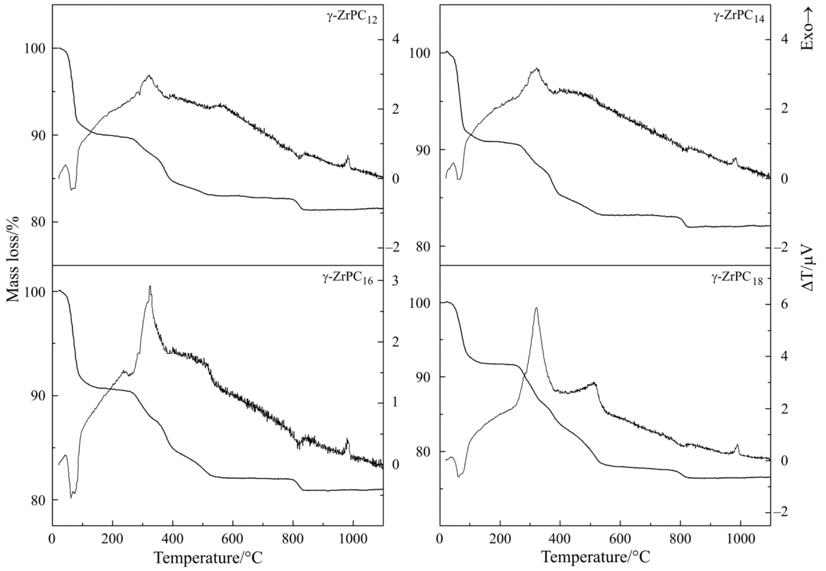

Fig. 3 TG-DTA curves of γ-ZrPC$_n$ after elution with HCl

The furnace atmosphere of the simultaneous TG-DTA apparatus is particularly important in the examination of organic-inorganic materials. Under static-atmosphere conditions it is sometimes difficult to distinguish those thermal effects that are due to oxidation. In vacuum all oxidation reactions except auto-oxidation are suppressed. So it is normal practice to examine organic compounds in either an oxidizing atmosphere to enable the burning characteristics to be determined or in an inert atmosphere to suppress oxidation and so bring about another reaction e.g. the bonds of the molecules break. When the thermal characterization of the γ-ZrPC$_n$ is performed in N_2 gas (Fig. 4) the combustion of the surfactant does not occur. Between 220–500°C the endothermic peaks are evidently related to the surfactant loss. The transition related to the cubic-pyrophosphates formation occurs at a lower temperature, at ~920°C instead of 980°C (Figs 1 and 4).

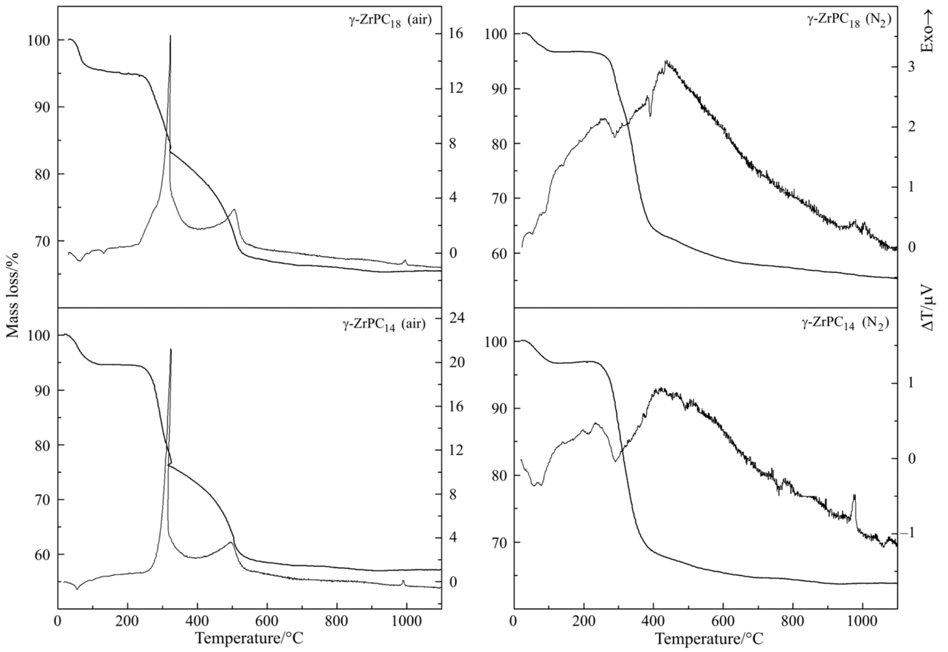

Fig. 4 TG-DTA curves of γ-$ZrPC_{18}$ and γ-$ZrPC_{14}$ materials submitted to thermal treatment in N_2 and in air gas flow

XRD

Figure 5 shows the XRD patterns of the γ-$ZrPC_n$ materials obtained after 1 week of batch contact, with respect to their precursor γ-ZrP. Table 3 reports the *d* values obtained by varying the length of time of batch contact and those obtained with the hydrothermal method. In the case of all the materials obtained with the (B) synthesis, utilizing 100% of theoretic exchange, the coordination between the layer of the host matrix is almost complete after just one day of batch contact and the starting γ-ZrP phase was converted into a monolayer derivative. The materials show a single diffraction peak corresponding to a *d*-spacing and a few broad reflections of low intensity between 2θ=14–17; 27–34. It should be noted that a cationic exchange H^+/C_n^+ equal to a quarter of total exchange capacity of the γ-ZrP is sufficient to give a pure new structure. The new structure is formed even after a short time of batch contact (e.g. 5 s) together with the *d*=12.30 Å reflection of the γ-ZrP. Only in the case of the γ-$ZrPC_{12}$ and γ-$ZrPC_{18}$ does the 12.30 Å reflection disappear after just one day of batch contact. The same can be said of all the materials obtained with the hydrothermal method. They have one single phase, and the first reflection is less in intensity. The diffractograms of the intercalated materials are typical of the other intercalated materials [5, 6]. The *d* value is much higher with respect to that of the host. The increase ranges from 12.24 up to 18.74 Å depending on the chain length:

Table 3 *d*(Å) of the γ-ZrPC$_n$ obtained by batch (B) and by hydrothermal methods (HM); C_n^+/exch=100% of theoretic exchange (after a week)

γ-ZrPC$_n$	5 min	6 h	24 h	7 days	HM
γ-ZrPC$_{12}$	25–12.30	24.54–12.30	25.95	24.54	25.25 fh=16.25
γ-ZrPC$_{14}$	26–12.30	25.24–12.30	27–12.30	26.50	29.00 fh=20
γ-ZrPC$_{16}$	28.50–12.30	26.77–12.30	29–12.30	28.50	31 fh=22
γ-ZrPC$_{18}$	30–12.30	28.49–12.30	31	31	31.55 fh=22.55

fh=free height (Å) as deduced from [γ-ZrPC$_n$ (*d* interlayer distance Å)]– [γ-ZrP (9 Å thickness)]

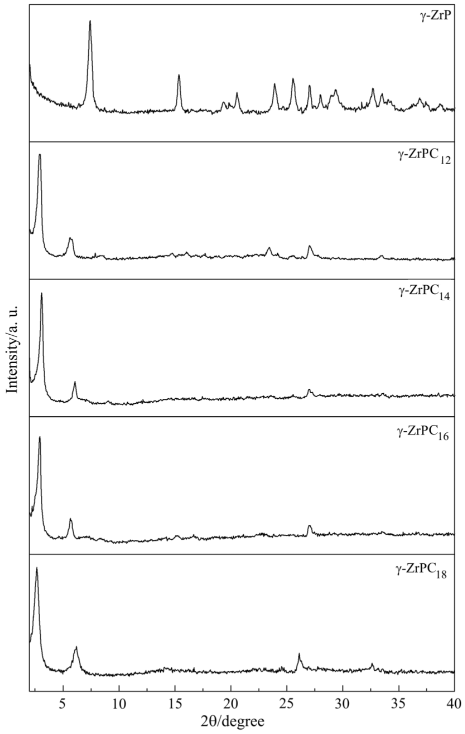

Fig. 5 XRDP of γ-ZrPC$_n$ materials in comparison with γ-ZrP

the longer the chain the more evident is the *d* increase. The intense and sharp reflection at low angle indicates an ordered structure. Considering that the 'free height' for γ-ZrPC$_n$ reported in Table 3 and the fact that in the chain surfactants the C–C distance is ~1.40 Å, it can be deduced that the C$_n$ chains are monolayer [11], positioned between the layers of the host matrix almost perpendicular or a little tilted in an extended form (paraffin-type) or stretched [13, 14]. When the batch contact refers to the theoretic exchange at >100% only for the γ-$ZrPC_{12}$ is obtained a single pure phase. In the case of the other materials the diffractograms are similar to the previous ones, the only difference being a double reflection for *d* or a single one peak with a shoulder (Table 4). That means a disorder results in the lodge. In the case of the materials obtained with the theoretic exchange ≤50% (Table 5) the diffractograms show both *d*-spacing, the new one and that of γ-ZrP in the case of γ-$ZrPC_{14}$ and γ-$ZrPC_{16}$. As far as γ-$ZrPC_{12}$ and γ-$ZrPC_{18}$ materials are concerned only one *d*-spacing is present. When the materials are contacted with a solution of HCl and alcohol the initial γ-ZrP phase is obtained of all the surfactants, except γ-$ZrPC_{18}$. In fact this shows the reflections of both γ-ZrP and γ-$ZrPC_{18}$ (of very low intensity).

Table 4 *d*(Å) of the γ-$ZrPC_n$ obtained by batch (B) by hydrothermal methods (HM); C_n^+/exch>100% of theoretic exchange (after a week)

γ-$ZrPC_n$	5 min	6 h	24 h	7 days	HM
γ-$ZrPC_{12}$	26.80	25.50	25.50	24	25.20
γ-$ZrPC_{14}$	27.80–25	29.44–25.24	29–25.24	29.45–26.77	33.5–27.80
γ-$ZrPC_{16}$	30.46–25.95	31.55–26	31.55–26	31.55–26.77	27–25.24
γ-$ZrPC_{18}$	31–27.80	29.45–26.00	32.70–27.80	30.46–26.50	29.45–26.50

Table 5 *d*(Å) of the γ-$ZrPC_n$ obtained by batch method; C_n^+/exch≤50% of theoretic exchange (after a week)

γ-$ZrPC_n$	*d*/Å
γ-$ZrPC_{12}$	25.95
γ-$ZrPC_{14}$	26.77–12.30
γ-$ZrPC_{16}$	28.50–12.30
γ-$ZrPC_{18}$	29.45

XRD thermal characterization

The XRD patterns of the derived materials were studied at various temperatures, related to the dehydration or surfactant combustion to determine the variation of the crystallinity of the materials. In Fig. 6 the XRD patterns of γ-$ZrPC_{18}$ material, which underwent thermal treatment, are reported. After dehydration at 150°C, the *d*=38.40 Å shows an increase of ~5 Å with respect to that recorded at *r.t.* At 250°C when the partial surfactant loss occurs the *d* value decreases to 23.25 Å. At 350 and 450°C the diffractograms become quite amorphous with *d*=19.20 and 10.91 Å, respectively. Note that the layered structure is maintained up to 350°C. From 500 up to 950°C the diffractogram is amorphous. At 1000°C the cubic zirconium pyrophosphate is evident. The increase of *d* in the material heated from 50 up to 200°C is in accordance with that reported by Alberti *et al*. [15] for the intercalation processes

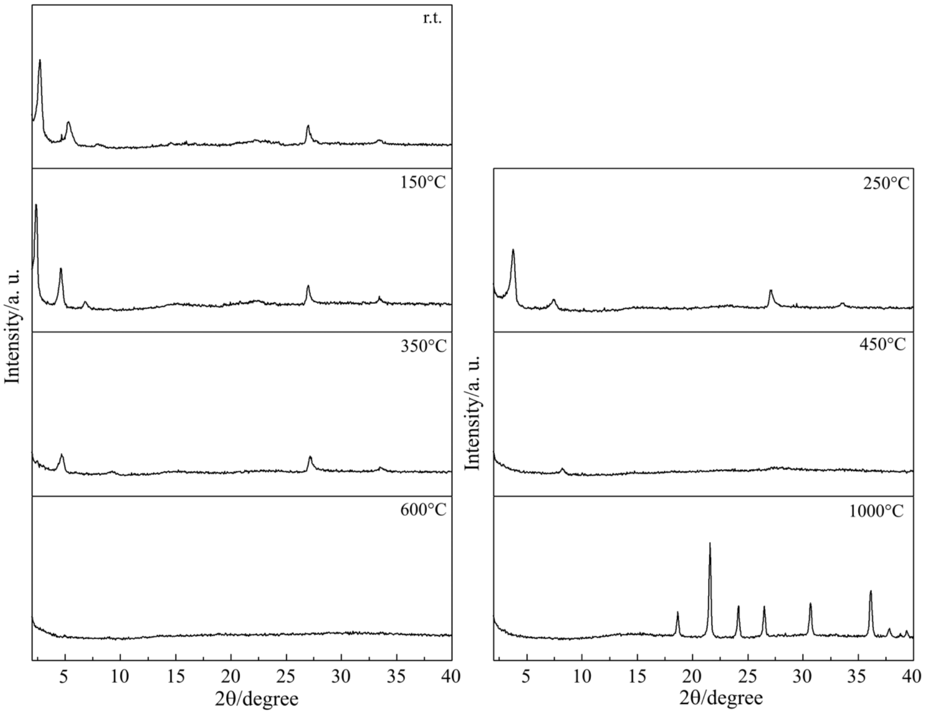

Fig. 6 XRDP of γ-$ZrPC_{18}$ heated at various temperature

of *n*-alkyl monoamines in γ-ZrP. So the hypothesis of a reversible conformational change of the alkyl chains is possible.

Conclusions

γ-Zirconium phosphate intercalated with alkyl chains such as trimethylammonium salts may be prepared by using two different methods, batch or hydrothermal synthesis. The surfactant uptake is ~23.50% of the theoretic exchange capacity of the exchanger γ-ZrP. The derived materials, still layered, have an increased distance with respect to the precursor γ-ZrP due to the chain length. In the derivatives the ‘free height’ can vary from 16.25 to 22.55 Å. By considering these values it is clear that the chains are arranged almost perpendicular between the host layer as a monolayer. By varying the surfactant/exchanger molar ratio so as to obtain a more cationic exchange it creates a ‘disorder’ with a double reflection *d* in the XRD patterns. As regards the materials with low surfactant content the XRDP shows two reflections: *d*=12.30 Å of γ-ZrP and of γ-$ZrPC_n$. The materials obtained with (HM) have similar XRDP to those synthesized with (B), but in the XRPD it is evident that a low kinetic is better for the crystallinity of the materials. All the intercalated materials show also a similar thermal behavior: the surfactant loss occurs in two stages, the second one resulting from the fragmentation of the cationic chain during heating. Their stability is maintained up to 220°C when the surfactant loss occurs, whereas at this temperature *d* decreases to 23.55 Å.

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The authors wish to thank MURST (protocollo 2003039774/03) for partial financial support.

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