Journal of Thermal Analysis and Calorimetry, Vol. 71 (2003) 1023–1033

SYNTHESIS AND CHARACTERIZATION OF SOL-GEL ZIRCONIUM PHOSPHATE WITH TEMPLATE SURFACTANTS BY DIFFERENT METHODS

C. Ferragina[*], *P. Cafarelli, A. De Stefanis, R. Di Rocco and L. Petrilli*

CNR, IMIP-ISM-ISMN, Via Salaria Km 29.300, 00016 Monterotondo (Roma), Italy

Abstract

Long chain trimethylammonium salts can be successfully used as guest molecules to produce mesoporous layered materials when intercalated in sol-gel zirconium phosphate, an inorganic ion-exchanger. The obtained materials are very similar independently of the chain length and the synthesis method batch (B) or direct intercalation (DI). They show a good thermal stability, and a very high interlayer distance if compared with their precursor. By the thermal characterization it can be observed that the surfactant is lost in two or three steps depending on its position in the host. The layered structure with the expanded interlayer distance is maintained up to 300°C. From the IR spectra the different surfactant release models for (B) and (DI) are confirmed.

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

Introduction

In the last years [1] the synthesis of materials as mesoporous molecular sieves has been of great interest for selective catalysis [2] and other applications [3]. The goal is to obtain framework with large pore diameters so to use the obtained materials as hosts for inclusion compounds.

The synthesis of these materials are obtained by reacting ionic surfactants with two- or three-dimensional structures as layered solids or zeolites to give ordered mesostructures [4].

The organic species can be carefully chosen to synthesize stabilized zeotype structures. In this way it is possible to prepare derivatives with predicted properties [5] by choosing the appropriate molecules to be intercalated in host matrices. Layered solids as group IV phosphates, inorganic ion-exchangers, have been intensely studied for this purpose [6]. In this work we describe two approaches for the synthesis of non-rigid pillar containing sol-gel (SG) zirconium bis (monohydrogen orthophosphate) $[Zr(HPO_4)_2 \cdot H_2O]$, SGZrP, and its characterization. The SGZrP is an inorganic ion-exchanger with the two hydrogens of the phosphate groups exchangeable with

---

[*] Author for correspondence: E-mail: carla.ferragina@mlib.cnr.it

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

cations. The cationic surfactants used for the synthesized materials are trimethylammonium salts of general formula C_nTMACl ($C_nTMA=C_n$, with n= 12, 14, 16, 18). The general formula of the obtained materials is $SGZr(H_{2-x}P_2O_8)(Cn)_x{\cdot}mH_2O$ [$SGZrPC_n$]. The synthesis has been performed with two different methods: batch (B) and direct intercalation (DI). The aim was to find the best operating system and to disclose the possible differences in the same products obtained with different methods and the possible connections with the chain length.

SGZrP layers are negatively charged and separated by an interlayer region containing H^+ exchangeable cations. The exchange of these hydrogen ions by alkylammonium ions is the predicted reaction.

Experimental

Chemicals

Zirconyl propoxide, phosphoric acid 85%, 1-propanol alcohol, CnTMACl surfactants were pure grade, commercially available from Aldrich and they were used as received.

Materials

The SG zirconium phosphate was prepared as reported in the literature [7].

In the synthesis with the (B) method, 1 mmol of SGZrP preswelled with anhydrous EtOH [8] and 10 mmol of a C_nTMACl 0.2 M aqueous solution, were contacted in an oven at 50°C, for different sets of time. The obtained materials were then recovered by filtration, washed with a small quantity of ethanol and dried in air. The powders needed to be powdered in a mortar for a better characterization in TG-DTA and XRPD analyses.

In the synthesis by direct intercalation (DI) the materials preparation was the one reported in literature [9] using the appropriate surfactants. The P:Zr molar ratio was 2, whereas the P:C_n^+ was 1.

Physical measurements and chemical analysis

Manipulations were followed by XRPD 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]. Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) were carried out under static conditions using a Stanton Redcroft STA 1500 instrument at 10°C min^{-1} heating rate, from room temperature to 1100°C.

The IR spectra (resolution 2 cm^{-1}) have been registered on a Perkin-Elmer 16F PC instrument. The materials were prepared as KBr disks: 3 mg of sample with 300 mg of KBr at 2 ton per square centimeter for 3’. Samples were heated in air and left at temperature for 10’; they were used for the KBr disk preparation at 60°C to avoid possible rehydration.

Results and discussion

Surfactants uptake

In the synthesis with the (B) method, the uptake by the SGZrP host is quite similar for all the surfactants. The kinetic uptake was studied for all the surfactants as a function of time. The time of batch contact was ranging from 2 h to 1 month (2, 6, 24 h and 3, 7, 30 days). The aim was to follow the surfactant content inside the SGZrP and its uptake rate with time, both to be related with the chain length. Table 1 shows the C_n^+ uptake at various batch contact time. The cation surfactant exchange is almost complete (≥90%) within one day of batch contact. The behavior is similar for all the surfactants and the uptake amount is related with the chain length: the longer the chain, the larger the quantity uptake in the same time. After 2 h of batch contact the exchange is already almost complete, showing the great affinity of the surfactant cation to exchange with the hydrogen of the POH groups in the phosphate. With respect to the two exchangeable hydrogens of the POH groups in 1 mmole of the SGZrP (100% of exchange), after 1 month of batch contact the C_{12}^+ has exchanged ~18.5% of the hydrogen; the C_{14}^+ ~20%; the C_{16}^+ ~25%; the C_{18}^+~30%. The chemical analysis of the products obtained with the (DI) method gave in all the four cases a P:Zr molar ratio very close to 2 and variable contents of surfactants and water. The obtained products are the same as those reported in literature [9]. It was impossible to have an uptake kinetic as for the (B) materials. The surfactant uptake is higher than that of the (B) method. There is a difference of >10% for the C_{18}^+; >28% for the C_{16}^+ and >35% for C_{14}^+ and C_{12}^+ between the two methods.

Table 1 Surfactant uptake at various batch contact time

Time	2 h	6 h	24 h	3 days	7 days	1 month
SGZrPC$_{12}$	0.30	0.32	0.33	0.35	0.37	0.37
SGZrPC$_{14}$	0.33	0.35	0.38	0.40	0.40	0.40
SGZrPC$_{16}$	0.43	0.43	0.45	0.48	0.50	0.50
SGZrPC$_{18}$	0.55	0.57	0.58	0.61	0.61	0.61

0.n (n=0.3–0.61)=mol C_n^+/mol exchanger

In Table 2 the C_n^+ content for the materials obtained with the (B) and (DI) synthesis is reported, with their respective chemical formula.

Table 2 Chemical formula of the materials obtained by batch (B) and direct intercalation (DI) method

(B)	(DI)
$SGZr(H_{0.81}PO_4)_2(C_{12})_{0.37}\cdot 1.51H_2O$	$SGZr(H_{0.64}PO_4)_2(C_{12})_{0.71}\cdot 1.75H_2O$
$SGZr(H_{0.80}PO_4)_2(C_{14})_{0.40}\cdot 1.62H_2O$	$SGZr(H_{0.60}PO_4)_2(C_{14})_{0.80}\cdot 1.70H_2O$
$SGZr(H_{0.75}PO_4)_2(C_{16})_{0.50}\cdot 1.75H_2O$	$SGZr(H_{0.55}PO_4)_2(C_{16})_{0.89}\cdot 1.83H_2O$
$SGZr(H_{0.69}PO_4)_2(C_{18})_{0.61}\cdot 1.78H_2O$	$SGZr(H_{0.54}PO_4)_2(C_{18})_{0.91}\cdot 1.92H_2O$

Thermal behavior

Figures 1 and 2 show the TG-DTA curves of the SGZrP precursor and of the $SGZrPC_n$ materials obtained with the two synthesis methods.

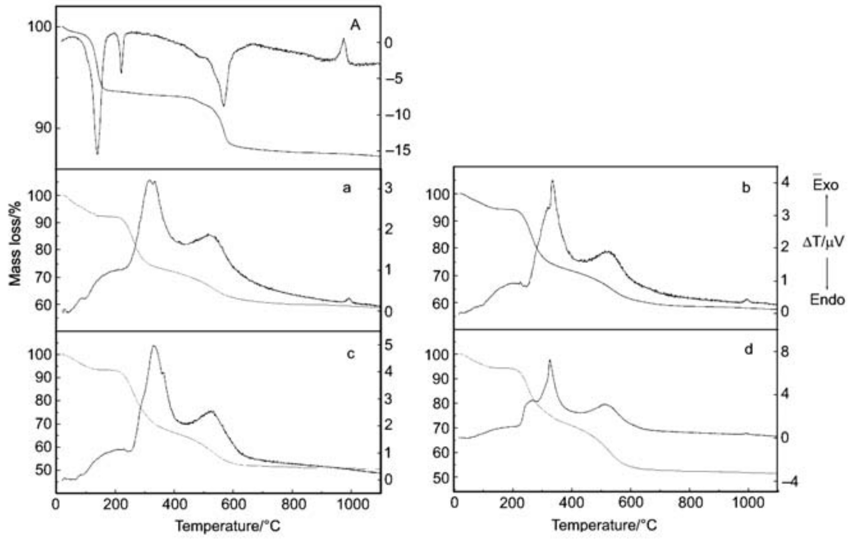

Fig. 1 TG-DTA curves of the $SGZrPC_n$ (B) obtained materials, in comparison with the SGZrP precursor (A): a – $SGZrPC_{12}$; b – $SGZrPC_{14}$; c – $SGZrPC_{16}$; d – $SGZrPC_{18}$

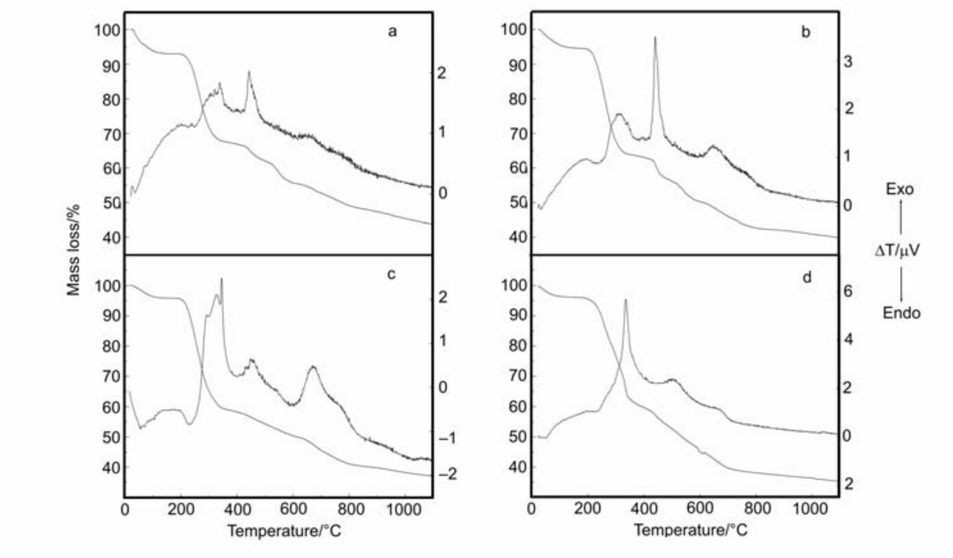

Fig. 2 TG-DTA curves of the $SGZrPC_n$ (DI) obtained materials: a – $SGZrPC_{12}$; b – $SGZrPC_{14}$; c – $SGZrPC_{16}$; d – $SGZrPC_{18}$

For the materials obtained with the (B) method (Fig 1; after 1 day of batch contact between SGZrP and the surfactant solution), between 25–200°C the loss of their hydration water is evident. In the TG curves, after dehydration, between 200–380°C the materials show a first surfactant loss; the second surfactant loss between 420–600°C corresponds mainly to the decomposition and combustion of the surfactant, and also to the hydroxyl groups condensation related to the not exchanged hydrogens. The different decomposition temperature of the surfactant can be attributed to the different POH groups of the SGZrP, on the surface or between the layers position. After the exchange with the SGZrP, the strength of surfactant interaction depends on the position and needs different energy for decomposition. Between 200–380°C the surfactant loss is bigger and faster than that between 380–600° C (2/3 *vs.* 1/3). Water deriving from the phosphates condensation to pyrophosphates is included in the second loss. The DTA curves confirm the TG data showing endothermic (dehydration) or exothermic (combustion) peaks corresponding to the mass losses.

When the SGZrP:C_n^+ratio for the batch contact is 1:5, the surfactant uptake is ranging between 0.15–0.10 mol mol^{-1} exchanger and the TG-DTA curves show that there is only one step for the surfactant elimination between 200–380°C (Fig. 3). This confirms that the surfactant is differently intercalated in the SGZrP host: the ion–exchange occurs first on the surface and then between the layers. At ~1000°C the exothermic effect, to which no mass loss is associated, corresponds to a structural transition to pyrophosphate of the POH groups. This is particularly evident when the cation surfactant exchange in the SGZrP host is ≤0.40 mol mol^{-1} exchanger (Fig. 3).

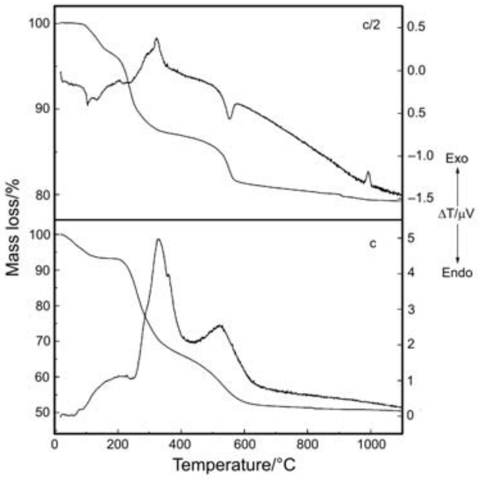

Fig. 3 TG-DTA curves of the SGZrPC$_{16}$ (c) and SGZrPC$_{16}$ c/2 (obtained with 1:5 molar ratio) (B method)

For the materials obtained with (DI) (Fig. 2) the TG-DTA curves are more complex. Three separated surfactant losses at temperatures between 200–380°C; 380–600°C; 600–800°C with corresponding exothermic peaks are evident. From the TG curves the surfactant loss quantity, between 200–380°C, is quite similar to that of the corresponding material synthesized with the (B) method. The exothermic peak at ~1000°C, related to the pyrophosphate, is not present in any of the obtained materials. Finally it can be stated that the good thermal stability of all the intercalated materials contrasts with their poor chemical stability: the surfactant easily deintercalates when the compounds are washed with EtOH, or when treated with HCl.

Table 3 Microanalysis values of the obtained materials, calculated at various temperatures

SGZrPC$_n$	C	N	H	C	N	H	C	N	H
	200°C			380°C			600°C		
SGZrPC$_{12}$ (B)	19.80	1.42	4.62	8.00	0.71	1.45	7.42	0.48	0.58
(DI)	28.66	2.24	6.31	20.22	1.65	3.85			
SGZrPC$_{14}$ (B)	20.23	1.48	4.64	9.23	0.67	1.52	7.24	0.34	0.78
(DI)	33.40	2.32	7.08	24.46	1.54	4.76			
SGZrPC$_{16}$ (B)	26.91	1.58	5.74	12.95	0.99	1.50	9.80	0.44	1.26
(DI)	38.01	2.35	7.72	26.86	1.46	3.72			
SGZrPC$_{18}$ (B)	32.39	1.66	6.69	13.36	0.78	1.45	7.50	0.28	0.60
(DI)	38.86	2.41	7.89	26.32	1.43	3.64			

C_n^+ content in the SGZrPC$_n$ materials at rt., 380 and 600°C as deduced by the Table 3 data.
%C_n^+ mass loss at 380 and 600°C

Table 4 Surfactant contents in the SGZrPC$_n$ materials at various temperatures

SGZrPC$_n$	rt.	380°C	600°C
SGZrPC$_{12}$ (B)	0.37	0.14	
SGZrPC$_{14}$ (B)	0.40	0.14	
SGZrPC$_{16}$ (B)	0.50	0.19	
SGZrPC$_{18}$ (B)	0.61	0.18	
SGZrPC$_{12}$ (DI)	0.71	0.43	0.13
SGZrPC$_{14}$ (DI)	0.80	0.49	0.11
SGZrPC$_{16}$ (DI)	0.89	0.50	0.13
SGZrPC$_{18}$ (DI)	0.91	0.49	0.09

C, H, N, experimental quantities mass% of the materials heated at 200°C (dehydration); at 380°C (after first surfactant loss); at 600°C (after second surfactant loss). In Table 3 the microanalysis (MA) values of the obtained materials are reported. The experimental values refer to the materials at 200°C (after dehydration); at 380°C (after the first surfactant loss); at 600°C (after the second surfactant loss, only for the (DI) materials). In Table 4 the surfactant contents, calculated from the Table 3 data, are reported.

XRPD

Figure 4 shows the XRPD of the SGZrP precursor and of the SGZrPC$_{16}$ (B) material. All the SGZrPC$_n$ derivatives have similar diffractograms so only the SGZrPC$_{16}$ (B) material is shown as an example. The SGZrPC$_{16}$ material has an interlayer distance *d* (35.2 Å) remarkably increased with respect to its precursor SGZrP (7.6 Å). This increase is ~27.6 Å, similar to the one for the materials derived from the classic α-zirconium phosphate phase [11b]. Already after 2 h of batch contact the diffractogram shows the first reflection at 35.2 Å, intense and sharp, indicating an ordered structure and a quick insertion inside the SGZrP layers. There are no other reflections in the X-ray diffraction pattern at low angle. The other reflections are broad and of low intensity and appear at 2θ=20, 25, 34 (4.43, 3.54, 2.63 Å, respectively). These diffractograms are typical of these intercalated materials [11a]. The high value of *d* spacing and the free height (29 Å) [11a] suggest that the C$_n$ chain is arranged within the interlayer region of the SGZrP in a lengthwise configuration a little tilted, as a paraffin–type monolayer [6a]. The C$_{12}$ derivatives are less crystalline as deduced by the X-ray diffraction pattern which show a broad pattern for the first reflection and its armonic at 2θ=2.7, 5.8 (32.70, 15.23 Å). When the materials are subject to the dehydration at 200°C the *d* interlayer distance is only slightly reduced (30.5 Å). After one day on air, the materials rehydrate, the *d* value is again back to 35.20 Å and this reflection appears more sharp.

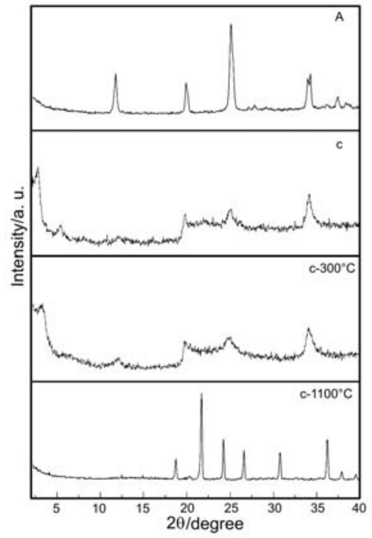

Fig. 4 XRPD of the precursor SGZrP (A) and of the SGZrPC$_{16}$ recorded at rt. (c), 300°C (c-300°C); 1100°C (c-1100°C) (B method)

The layered structure is maintained up to 300°C (Fig. 4 c-300°C) with *d*=26.7 Å. At 1100°C the pyrophosphate pattern is present as for the α-zirconium phosphate [12] or SGZrP [13] at the same temperature. When the surfactant content inside the

SGZrP is ≤0.3 mol mol^{-1} exchanger (B method) the diffractograms of the obtained materials are similar to that of the SGZrP host.

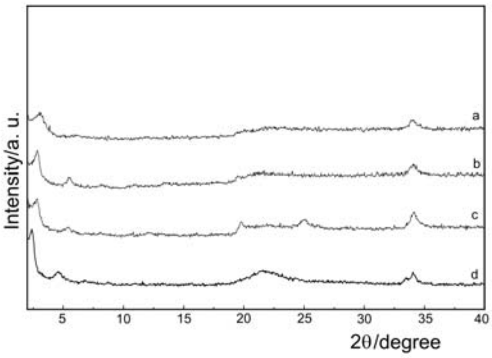

Fig. 5 XRPD of the a – SGZrPC$_{12}$; b – SGZrPC$_{14}$; c – SGZrPC$_{16}$; d – SGZrPC$_{18}$ (DI) obtained materials

Figure 5 shows the X-ray of the materials (DI). The diffractograms are very similar to one each other and with respect to those obtained with (B) method.

IR measurements

The IR spectra of both series of surfactant intercalated (B) and (DI) have been recorded and compared with the parent phosphate one (Fig. 6). In another set of spectra (Fig. 7) the SGZrPC$_{16}$ (B) and (DI) materials have been heated at various temperatures to follow the surfactant with respect to its intercalation in the phosphate. The two temperatures chosen represent each one a particular step in the TG curve of this material: 200°C the complete dehydration and 380° the end of the first step in the surfactant release.

There are two major intervals of interest in the spectra of Fig 6. The first is at 3600–3150 cm^{-1}. The bands of the OH stretching which are present in the parent phosphate [14] at 3591 and 3511 cm^{-1} disappear for all the intercalated products and are substituted by a very broad one at ~3480 cm^{-1} indicating that the surfactant is now bound to the phosphate. The broad band at 3151 cm^{-1} for the crystallization water of the phosphate is also shifted and overlaps with the previous ones. The pattern is the same for both the (B) and (DI) series.

In the second interval between 1250 and 950 cm^{-1} the $\nu_3(PO_4)$ bands either disappear or are shifted to lower frequencies indicating the presence of H-bonds between the P–OH of the phosphate and the :N of the surfactant. Again this is the case for both series.

In Fig. 7 for the SGZrPC$_{16}$ (DI) material there is a noteworthy change in the IR recorded after treatment at 380°C: the sharp band at 1248 cm^{-1}, previously disappeared in the broad one at 1230 cm^{-1} after the intercalation, reappears slightly shifted at 1257 cm^{-1}. This pattern can be explained with the surfactant partial release from at least one of the two bonding positions. This is further confirmed by the reappearing of the bands at 2952,

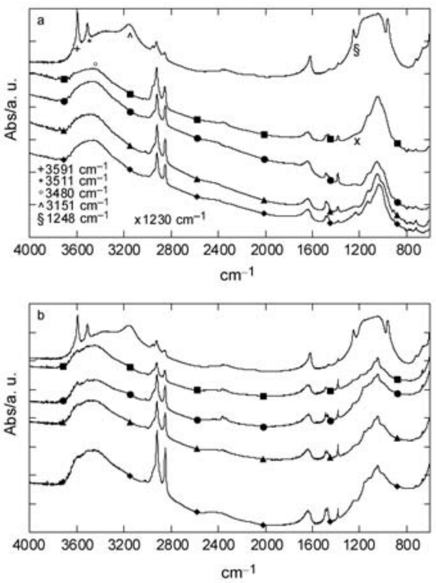

Fig. 6 IR spectra of a – (DI) materials; b – (B) materials. —— : parent material SGZrP; ■ – SGZrPC$_{12}$; ● – SGZrPC$_{14}$; ▲ – SGZrPC$_{16}$; ◆ – SGZrPC$_{18}$

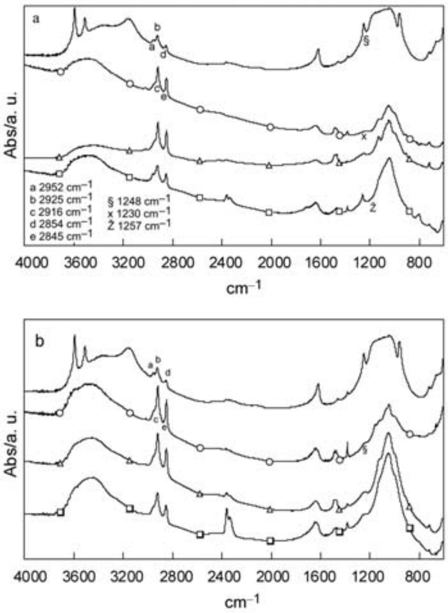

Fig. 7 IR spectra of a – (DI) materials; b – (B) materials —— – parent material SGZrP; ○ – SGZrPC$_{16}$ at room temperature; ▽ – SGZrPC$_{16}$ after treatment at 200°C; □ – SGZrPC$_{16}$ after treatment at 380°C

2925 and 2854 cm^{-1} of the phosphate itself and the disappearing of those at 2916 and 2845 cm^{-1} relative to the $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ of the amine chains, respectively. For the $SGZrPC_{16}$ (B) the pattern is less defined: a small broad band remains visible at 1248 cm^{-1} after intercalation and it is slightly enhanced by both water loss (at 200°C) and surfactant loss (at 380°C). To further confirm this picture, among the three bands at 2952, 2925 and 2854 cm^{-1} only the last two reappear after treatment at 380°C, with the first one still covered by the shoulder of the $\nu_{as}(CH_2)$ band relative to the amine chain.

Conclusions

It has been demonstrated that intercalated materials derived from long chain surfactants and sol-gel zirconium phosphate could be synthesized using two methods. These materials have a lamellar structure and higher interlayer distance with respect the precursor showing a packed monolayer inside the phosphate interlayer region. These intercalated materials have similar X-ray diffractograms. Compounds with low surfactant content show both surface exchange (only one decomposition temperature in the TG curve) and only the SGZrP reflections in the XRPD. In the TG-DTA curves the mass loss for the dehydration and surfactant combustion process are evident. Due to the different surfactant combustion temperatures, it is also evident that the chains are differently linked in the SGZrP.

The IR pattern for all the intercalated materials is the same showing as main feature the :N bonded to the OH, as expected. The IR recorded at various temperature are in agreement with the models as derived from the two TG curves: in particular the difference between (B) and (DI) materials is confirmed.

* * *

The authors are grateful to Mrs. Gisella Menichelli for her great help in the bibliographical research (CNR, IMIP) and Miss Beatrice Pagliari (CNR, ICMAT) for her technical assistance.

References

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and P. Beck, Nature, 359 (1992) 710.
2 P. T. Tanev, M. Chibwe and T. J. Pinnavaia, Nature, 368 (1994) 321.
3 T. J. Bein and C. G. Wu, Science, 264 (1994) 1757.
4 Q. Huo, D. I. Margolese, P. Feng, T. E. Gier, P. Sieger, G. D. Stucky, R. Leon, P. Petroff, V. Ciesla and T. H. F. Schu, Nature, 368 (1994) 317.
5 G. Alberti, U. Costantino, S. Murcia-Mascaros and R. Vivani, Supramolecular Chem., 11 (1995) 1.
6 a) G. Lagaly, Solid State Ionics, 22 (1986) 43; b) Y. Kanzaki et al., Bull. Chem. Soc. Japan, 64 (1991) 1846; c) Y. Ma et al., Microporous Mesoporous Mater., 37 (2000) 24.
7 J. Livage, H. Benhamza, P. Barboux, A. Bouhaouss and F. A. Josien, J. Mater. Chem., 1 (1991) 681.
8 U. Costantino, J. Chem. Soc. Dalton Trans., (1979) 402.

9 a) J. Jimenez-Jimenez, P. Maireles-Torres, P. Olivera Pastor, E. Rodriguez-Castellon and A. Jimenez-Lopez, Langmuir, 13 (1997) 2857; b) D. J. Jones and J. Roziere, Adv. Mater. Comm., 10 (1998) 812.

10 G. Alberti, U. Costantino and E. Torracca, J. Inorg. Nuclear Chem., 28 (1966) 225.

11 a) C. Ferragina, A. De Stefanis and A. A. G. Tomlinson, P. A. Jacobs, R. Maggi, J. A. Martens, P. Grange and G. Poncelet, Studies in Surface Science and Catalysis, 118 Preparation of Catalysts VII, Eds B. Delmon, 921 (1998); b) C. Ferragina, P. Cafarelli, A. De Stefanis, R. Di Rocco and P. Giannoccaro, Mater. Res. Bull., 36 (2001) 1799.

12 U. Costantino and A. La Ginestra, Thermochim. Acta, 58 (1982) 179.

13 C. Ferragina, P. Cafarelli and R. Di Rocco, J. Therm. Anal. Cal., 63 (2001) 709.

14 N. J. Clayden, J. Chem. Soc. Dalton Trans., (1987) 1877.