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Synthesis and characterization of microporous pillared α-zirconium phosphate–biphenylenebis(phosphonate)

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Nanocrystalline, microporous pillared zirconium phosphate–biphenylenebis(phosphonate) materials were obtained by a sol–gel route involving the reaction of the 4,4′-biphenylenebis(phosphonic acid) and phosphoric acid with tetra-*n*-propoxyzirconium, followed by a mild hydrothermal crystallization treatment. The variation of the micropore volume with the pillar fraction demonstrated that the micropores were of interlamellar origin; the pore size distributions showed the presence of well defined micropores along with a broad distribution of meso- and macro-pores. However, it was not possible to control the micropore volume and the micropore size by varying the pillar fraction.

Introduction

Pillared zirconium bisphosphonates, $Zr(O_3PRPO_3)$, are built of inorganic layers connected by the organic spacer R groups bonded to the phosphorus atoms.[1–3] These compounds are usually prepared by reacting an aqueous solution of a Zr(IV) salt (in most cases $ZrOCl_2$) with a bis(phosphonic) acid; synthesis in the presence of HF leads to significantly increased crystallinity in the final product. When all of the pillaring R groups are identical, they occupy practically all of the interlayer space. Hence, pure pillared compounds are not intrinsically microporous. By contrast, mixed compounds $Zr(O_3PRPO_3)_x(R'PO_3)_{2-2x}$ containing both organic pillars and short pendent groups R′ (R′ = H, Me, OH, *etc.*) should exhibit interlayer microporosity (Fig. 1). In such materials, the dimension of the micropores should depend on the pillaring fraction and on the length of the pillars and pendent groups. This idea, which was originally proposed by Dines *et al.*,[4] gave rise to several studies[5–9] which have been recently reviewed.[10,11] It appears that the synthesis of pillared α-zirconium phosphonates with interlayer microporosity by simple coprecipitation of the pillaring and pendent groups with a Zr(IV) salt is not straightforward, and very few clear examples of such compounds are found in the literature. Indeed, interlayer micropores are found only if an homogeneous mixed phase is formed, with both pillars and pendent groups distributed in the same layers. Unfortunately, such phases appear thermodynamically unstable, and segregation often took place when the synthesis was carried out in the presence of HF to obtain crystalline samples.[4,5,12,13] Recent attempts to prepare microporous mixed zinc phosphate–biphenylenebis(phosphonate) derivatives, which do not require the presence of HF to crystallize, proved unsuccessful.[14] A wide range of compositions could be obtained for low crystallinity zirconium compounds, prepared in the absence of HF from 4,4′-biphenylenebis(phosphonic acid) and phosphoric acid.[4,10] These compounds exhibited high surface areas, but the origin of their porosity was difficult to assess: a wide range of pore diameters was found, not only for the mixed samples but for the pure pillared compound as well,[8] and the texture of the samples largely depended on the solvent used.[8,15,16] The tendency to segregation has been overcome by Alberti *et al.* who used pillars with broad bases, namely 4,4′-(3,3′,5,5′-tetramethylbiphenyl) diphosphonate, to force the incorporation of small phosphite groups.[6,9] Using this strategy, they obtained a fairly crystalline, α-layered pillared phosphonate, with a high surface area (405 $m^2\ g^{-1}$), negligible mesoporosity, a micropore volume of 0.16 $cm^3\ g^{-1}$ and a micropore size around 5 Å.

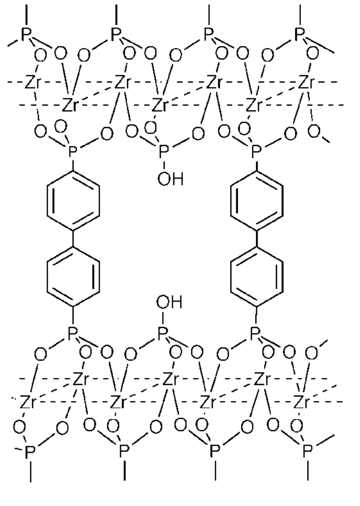


Fig. 1 Idealized representation of a pillared α-zirconium phosphate–biphenylenebis(phosphonate).

In this work we chose a different approach to obtain α-zirconium phosphate–biphenylenebis(phosphonate) materials with interlayer microporosity. First, a sol–gel route based on the non-hydrolytic condensation of Zr–OPr^n and P–OH groups[17,18] was used. Second, the crystallinity of the samples was improved by a mild hydrothermal treatment in order to avoid segregation. Depending on the synthetic conditions, even pure pillared phosphonates may exhibit significant microporosity.[8,15] Accordingly, we prepared samples with a degree of pillaring ranging from 1 to 0, and the evolution of the micropore volume with the degree of pillaring was studied to ascribe the origin of the microporosity in the mixed samples.

Experimental

Reagents

$Zr(O)Cl_2{\cdot}8H_2O$, $Zr(OPr^n)_4$ (70 wt% solution in *n*-propanol), phosphoric acid (85 wt% aqueous solution or crystalline solid) were purchased from Aldrich and used without further purification. The other reagents and solvents were of reagent grade and were distilled prior to use. 4,4′-Biphenylenebis(phosphonic acid) (BPBPA) was prepared by reaction of 4,4′-dibromobiphenyl with diethyl phosphite (Aldrich) in toluene in the presence of triethylamine, catalyzed by tetrakis(triphenylphosphine)palladium (yield: 62%, δ_P 14.8);[19] the P–OEt groups were converted to P–OH groups by treatment with Me_3SiBr followed by hydrolysis.[20]

Synthesis of mixed compounds $Zr(O_3PC_6H_4C_6H_4PO_3)_x(HPO_4)_{2-2x}$

A typical procedure ($x=0.4$, samples **d** and **e**) is as follows: period; 185 mg (2.7 mmol) of H_3PO_4 (85 wt% aqueous solution) diluted in *n*-propanol (4.5 mL) was added to a suspension of BPBPA (283 mg, 0.9 mmol) in *n*-propanol (18.0 mL) and 1.045 g (2.26 mmol) of $Zr(OPr^n)_4$ was added under vigorous stirring to this suspension. The reaction mixture was stirred for 15 min at room temperature, then transferred into a 60 mL high-pressure glass tube which was sealed under vacuum after freezing in liquid nitrogen. The sealed tube was heated in an oven at 110 °C for 7 days. The resulting precipitate was washed with ethanol and acetone, then dried at 150 °C under vacuum (1 Torr) for 12 h, to give 741 mg of sample **d**.

214 mg of **d** in 21.5 mL of deionized water was transferred into a 60 mL high-pressure glass tube which was sealed under vacuum after freezing in liquid nitrogen. The sealed tube was heated in an oven at 110 °C for 7 days. The resulting precipitate was then washed with ethanol and acetone, and dried at 150 °C under vacuum (1 Torr) for 12 h, to give 206 mg of sample **e**.

Characterization

Solid-state ^{31}P NMR spectra were recorded on a Bruker ASX 400 spectrometer, with a 4 mm MAS NMR probe, using high-power proton decoupling, π/4 pulses and 10 s recycle delays. Solution ^{31}P NMR spectra were recorded on a Bruker Advance DPX200 spectrometer. 85 wt% aqueous H_3PO_4 was used as a reference. Adsorption–desorption isotherms of nitrogen at 77.35 K were recorded on a Micromeritics ASAP 2010 instrument. X-Ray powder diffraction (XRD) patterns were recorded with Cu-Kα radiation on a Seifert MZIV diffractometer. FTIR spectra were recorded on a Perkin-Elmer 1600 Series instrument using the KBr pellet technique. Transmission electron microscopy (TEM) imaging was performed using a JEOL 200CX microscope operating at 120 kV. The Zr/P ratios were obtained by energy dispersive X-ray analysis (EDX) with a Cambridge Stereoscan 360 scanning electron microscope equipped with a Link AN 10000 probe.

Results and discussion

Choice of synthetic conditions

In preliminary experiments, we attempted to prepare an α-zirconium phosphate–4,4′-biphenylenebis(phosphonate) sample with 0.4 pillars per zirconium by conventional aqueous routes, using $ZrOCl_2{\cdot}8H_2O$ as a zirconium source (Scheme 1).

The solid-state ^{31}P NMR spectrum of sample **a** (Fig. 2) showed two broad resonances, typical of amorphous materials, centered at δ_P 5 and −25, corresponding to the biphenylenebis(phosphonate) and phosphate units, respectively. The broadness of the signals can be ascribed to a distribution in the connectivity of the RPO_3 and PO_4 units, and/or to distortion of the O–P–O angles.[17] In addition, a sharp peak at δ_P 15.2 indicated that *ca.* 20% of the PO_3H_2 groups bonded to the biphenylene units remained unreacted [the ^{31}P signal of the starting biphenylenebis(phosphonic acid) occurs at δ_P 15.3]. This result suggests that the reaction rates of the bis(phosphonic) and phosphoric acids are quite different which is not favourable for the formation of a homogeneous mixed compound. When the reaction was performed in the presence of HF to obtain a well condensed, crystalline sample (sample **b**), the ^{31}P NMR spectrum showed two main sharp resonances at δ_P 5.5 and −21.9, characteristic of biphenylenebis(phosphonate) units[8] and phosphate units[12], respectively, in a well ordered material, in agreement with the X-ray powder diffraction pattern. However, the integration of these signals indicated that only a small amount of phosphate units (0.18 per zirconium *cf.* 1.2). were retained in the material, as already reported.[10]

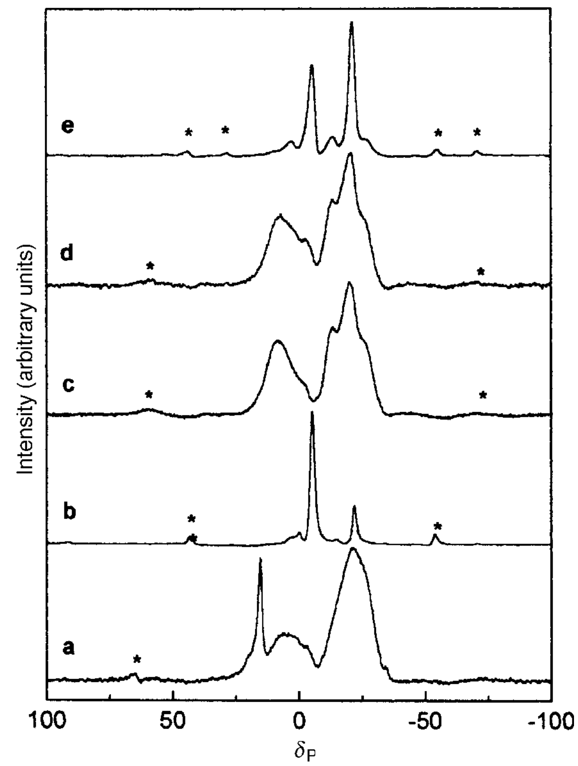
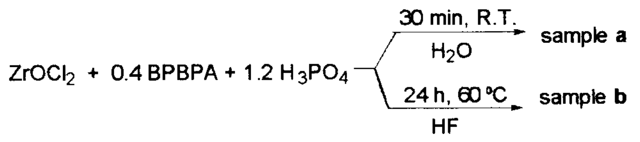


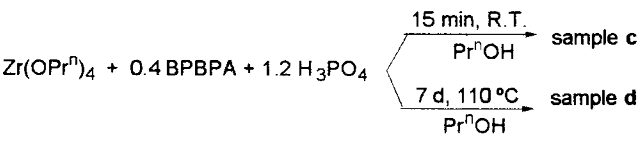
Fig. 2 Solid-state ^{31}P NMR spectra of mixed zirconium phosphate–biphenylenebis(phosphonate) samples **a**–**e**.

In subsequent experiments, we employed the non-hydrolytic condensation between $Zr(OPr^n)$ and P–OH groups,[17,18] according to Scheme 2. According to the literature, P–OH groups condense faster and at a lower temperature with Zr–OPr^n groups than with Zr–OH groups[17] and a signal at δ_P 15.2 (P–OH) was not present in the ^{31}P NMR spectrum of samples **c** or **d** (Fig. 2). Both samples appeared amorphous to X-ray diffraction. Note that very similar results were obtained independently of the source of phosphoric acid: 85% aqueous solution or anhydrous (strictly non-hydrolytic condensation).

To improve the crystallinity of sample **d** without decreasing



Scheme 1



Scheme 2

$$\text{sample } \mathbf{d} \xrightarrow[\text{H}_2\text{O}]{\text{7d, 110 °C}} \text{sample } \mathbf{e}$$

Scheme 3

the phosphate content, a mild hydrothermal treatment in the absence of HF was used (Scheme 3).

The ^{31}P NMR spectrum of sample **e** showed a significant decrease of the peak widths and an increase in the intensity of the signals at δ_P −5.5 and −21.3 characteristic of biphenylenebis(phosphonate) units and phosphate units, respectively, in a layered material. The X-ray powder diffraction pattern of sample **e** showed a major, broad reflection of *ca.* 14 Å and a second order reflection of *ca.* 7 Å, indicating an interlayer spacing of *ca.* 14 Å in good agreement with the spacing expected for biphenylenebis(phosphonate) pillars.[4,8] Dark field TEM confirmed that **e** was nanocrystalline, with crystallite sizes around 100–200 Å. In addition, elemental analyses and ^{31}P NMR indicated that the composition of **e** corresponded within experimental error with the theoretical composition $Zr(O_3PC_6H_4C_6H_4PO_3)_{0.4}(O_3POH)_{1.2}$: the P/Zr ratio determined by EDX was 2.1 ± 0.2 and the pillar fraction derived from the integration of the ^{31}P NMR spectrum was 0.39.

The synthesis used for **e** appeared adequate, since mixed layered phosphate–phosphonate samples with a controlled composition could be obtained. The same experimental procedure was used to prepare α-zirconium phosphate–biphenylenebis(phosphonate) samples with a pillaring degree ranging from 1 to 0, according to Scheme 4.

Characterization of $Zr(O_3PC_6H_4C_6H_4PO_3)_x(O_3POH)_{2-2x}$ samples

The solid-state ^{31}P NMR spectra of the samples (Fig. 3) showed signals corresponding to bis(phosphonate) (from δ_P 18 to −7) and phosphate units (from δ_P −7 to −30). Integration of these signals indicated that in all cases the pillar fraction was close to the theoretical value; in the same way, EDX indicated P/Zr ratios close to 2 (Table 1). For samples with a low pillar fraction (up to $x = 0.6$), the main signals were sharp peaks at δ_P *ca.* −5 and −21, characteristic of biphenylenebis(phosphonate) and phosphate units in a layered compound. The intensity of these sharp signals was significantly lower in the spectra of the samples with a high pillar fraction ($x = 0.8$ and 1), although dark-field TEM indicated that these samples also were nanocrystalline.

The texture of all the samples was investigated using nitrogen adsorption–desorption (Table 1). The adsorption–desorption isotherms of all the samples (Fig. 4) were of type II according to the BDDT classification.[21] In addition, the isotherms of the mixed samples ($x = 0.2$, 0.4 and 0.6) showed a steep increase at low relative pressure indicating the presence of micropores (Fig. 4). Indeed, analysis of the data by the t-plot method[22] (using α-zirconium phosphate as a reference) revealed the presence in these samples of micropores accounting for surface areas of *ca.* 130 m^2 g^{-1}. The remainder of the surface area was located in meso- and macro-pores, with pore diameters ranging from 50 to >2000 Å, according to the BJH method.[22] The micropore volume ranged between 0.07 and 0.13 cm^3 g^{-1} depending on the calculation method: t-plot, Saito–Folley[23] or Horvath–Kawazoe method.[24]

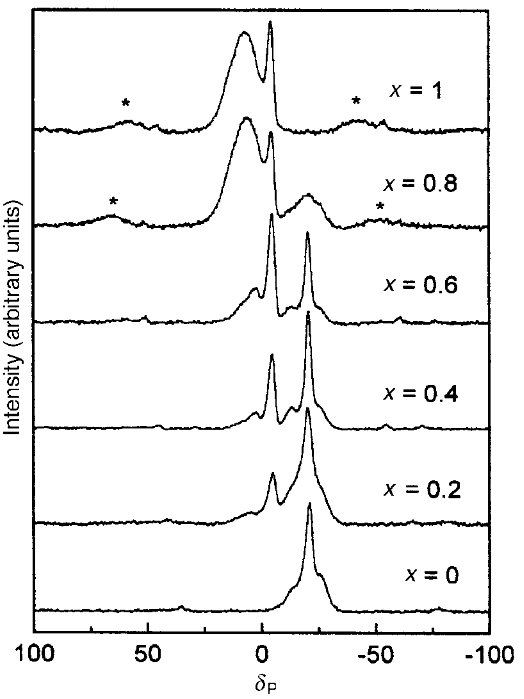


Fig. 3 Solid-state ^{31}P NMR spectra of $Zr(O_3PC_6H_4C_6H_4PO_3)_x(O_3POH)_{2-2x}$ samples ($x = 0$–1) (after hydrothermal treatment).

As pure pillared phosphonates may exhibit significant microporosity depending on the preparation conditions,[8,15] it is important to note that, under our conditions, the pure pillared sample ($x = 1$) as well as the phosphate sample ($x = 0$) showed very low microporosity. Thus the microporosity in the mixed samples should mainly result from interlayer micropores.

The variation of the BET surface area and the micropore volume with the pillaring fraction is shown in Fig. 5. Note that both curves are very similar, which demonstrates that the high

$$Zr(OPr^n)_4 + x\text{BPBPA} + (2\text{-}2x)H_3PO_4 \xrightarrow[\text{2) 7 d, 110 °C, H}_2\text{O}]{\text{1) 7 d, 110 °C, Pr}^n\text{OH}} Zr(O_3PC_6H_4C_6H_4PO_3)_x(HPO_4)_{2\text{-}2x}$$

Scheme 4 $x = 0$, 0.2, 0.4 (sample **e**), 0.6, 0.8 and 1.

Table 1 Characterization of mixed α-zirconium phosphate-4,4′-biphenylenebis(phosphonate) samples

Sample (x)	P/Zr[a]	Pillar fraction x[b]	S_{BET}[c]/m^2 g^{-1}	V_{micro} (t-plot)[d]/cm^3 g^{-1}	S_{micro} (t-plot)[d]/m^2 g^{-1}	V_{micro} (HK)[e]/cm^3 g^{-1}	V_{micro} (SF)[f]/cm^3 g^{-1}
0	2.0	0.00	31	0.004	8	0.012	0.007
0.2	2.1	0.23	262	0.065	127	0.112	0.080
0.4	2.1	0.39	304	0.070	124	0.125	0.083
0.6	1.9	0.61	307	0.070	134	0.132	0.092
0.8	2.2	0.84	99	0.014	16	0.048	0.033
1.0	2.1	1.00	91	0	0	0.034	0.022

[a]From EDX measurements. [b]From the integration of ^{31}P NMR spectra, assuming P/Zr = 2. [c]Total specific surface area determined using the BET method. [d]External surface area and micropore volume determined using the t-plot method. [e]Micropore volume determined using the Horvath–Kawazoe method (lamellar pore geometry). [f]Micropore volume determined using the Saito–Folley modification of the Horvath–Kawazoe method (cylinder pore geometry).

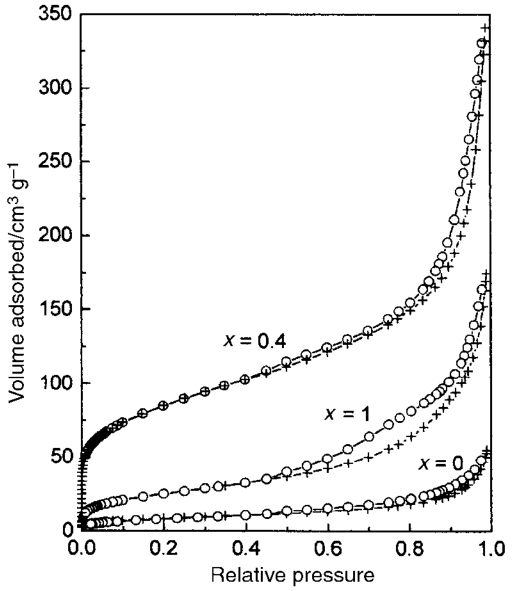


Fig. 4 N_2 adsorption–desorption isotherms at 77 K of Zr (O$_3$PC$_6$H$_4$C$_6$H$_4$PO$_3$)$_x$(O$_3$POH)$_{2-2x}$ samples with $x = 0$, 0.4 and 1. (+): adsorption; (○): desorption.

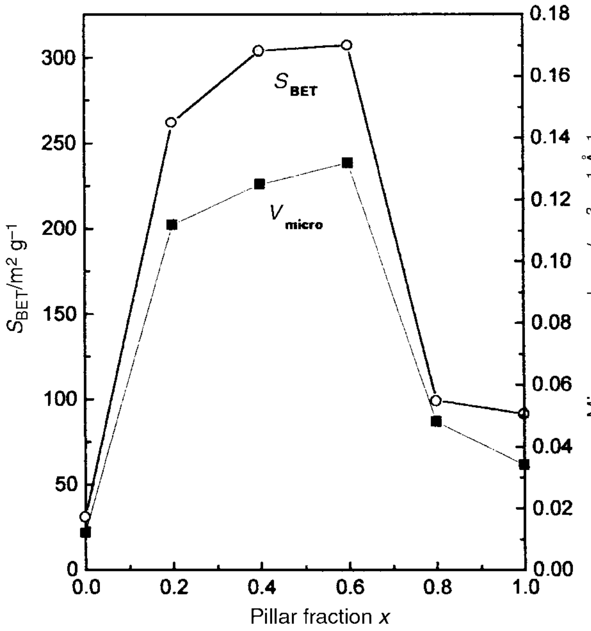


Fig. 5 Specific surface area, S_{BET} (○) and micropore volume (■) of Zr(O$_3$PC$_6$H$_4$C$_6$H$_4$PO$_3$)$_x$(O$_3$POH)$_{2-2x}$ samples as a function of the pillar fraction x.

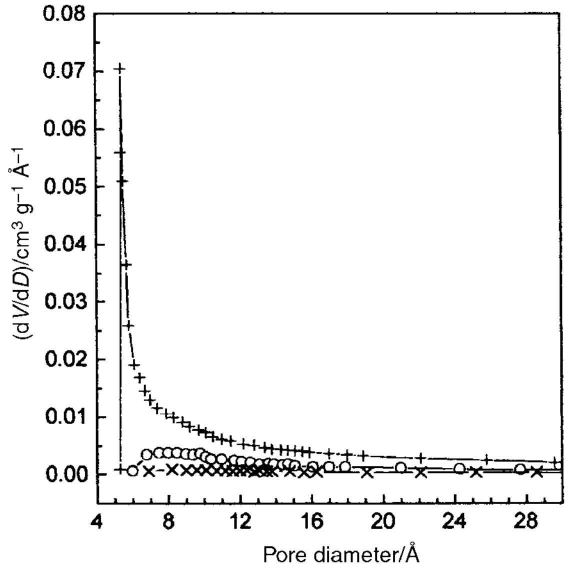


Fig. 6 N_2 adsorption–desorption isotherms at 77 K of Zr(O$_3$PC$_6$H$_4$C$_6$H$_4$PO$_3$)$_x$(O$_3$POH)$_{2-2x}$ samples with $x = 0$ (×), 0.4 (+) and 1 (○).

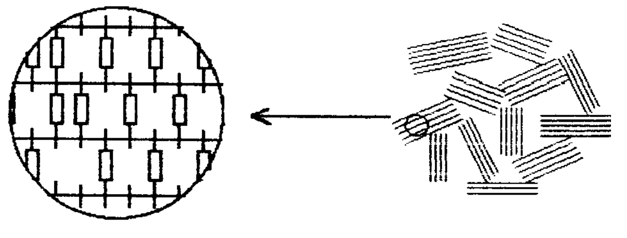


Fig. 7 Schematic representation of the texture of a nanocrystalline pillared zirconium phosphate–bis(phosphonate).

surface area of the mixed samples arises mainly from the presence of micropores. These curves are similar to those reported for covalently pillared γ-zirconium phosphate–biphenylenebis(phosphonates).[25] Ideally, the microporosity should be a maximum at low pillar fraction, then decrease with increasing pillar fraction. The variation observed, with a nearly constant micropore volume between $x = 0.2$ and 0.6, suggests that the layers are not stable at low pillar fractions. The very low microporosity of the sample with $x = 0.8$ may be ascribed to the high probability of forming closed micropores at such a high pillar fraction.

The micropore distribution curves (Fig. 6) (obtained by the Horvath–Kawazoe method) of the pure phosphate ($x = 0$) and bis(phosphonate) ($x = 1$) samples confirmed that they contained very few micropores. On the other hand, the distribution curves of the mixed samples ($x = 0.2$, 0.4 and 0.6) showed the presence of micropores with diameters ranging from *ca.* 5 to 15 Å, with a maximum at *ca.* 6 Å, whatever the pillar fraction. It is of note that the micropore distribution observed, for instance for $x = 0.4$, is very similar to those reported by Alberti *et al.* for mixed pillared α- and γ-zirconium bis(phosphonates).[6,9,25] The main difference, from the textural point of view, between our mixed samples and those reported by Alberti *et al.* is the presence in our case of a significant amount of meso- and macro-pores. This significant external porosity has to be related to the very small crystallite size in our samples. From TEM and nitrogen adsorption data our mixed samples can be described as loose submicronic aggregates built of *microporous* lamellar nanoparticles (*ca.* 10–20 nm diameter). In this model, the microporosity results from the alternation in the interlamellar space of biphenylene pillars and short pendent OH groups, and the meso- and macro-pores result from the disordered stacking of the nanoparticles and of the aggregates (Fig. 7).

The interlayer micropore volume that would be created by replacing a fraction of the biphenylenebis(phosphonate) pillars by phosphate groups may be estimated using a simple model. In a mixed zirconium phosphate–biphenylenebis(phosphonate), the area available per phosphorus atoms is *ca.* 24 Å^2, and the distance between two phosphate groups is *ca.* 5.7 Å. Accordingly, each replacement of one pillar by two phosphate groups should lead to the formation of an interlayer pore volume of *ca.* 140 Å^3. For a sample with a pillar fraction of 0.4, with composition Zr(O$_3$PC$_6$H$_4$C$_6$H$_4$PO$_3$)$_{0.4}$(O$_3$POH)$_{1.2}$ ($M_w = 331$ g mol^{-1}), 60% of the pillars are replaced by phosphate groups, and the interlayer micropore volume expected would be: $(6.023 \times 10^{23} \times 0.6 \times 140 \times 10^{-24}/331) \cong 0.15$ cm^3 g^{-1}. Comparison of this value with the experimental values measured for our sample with $x = 0.4$ (0.07–0.13 cm^3 g^{-1}) shows that the microporosity created in this sample is far from negligible.

For pillaring fractions $x = 0.2$ and 0.6, the expected interlayer micropore volumes would be 0.22 and 0.10 $cm^3 g^{-1}$, respectively. Thus, a large variation in micropore volume would be expected for samples with a pillar fraction ranging from 0.2 to 0.6; experimentally, however, similar micropore volumes were found for the samples with pillar fractions of 0.2, 0.4 and 0.6. In conclusion, our results show that although α-zirconium phosphate–bis(phosphonate) samples with a significant, well defined microporosity could be prepared, it was not possible to control the micropore volume and the micropore size by varying the pillar fraction.

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References

1 G. Alberti, M. Casciola, U. Costantino and R. Vivani, *Adv. Mater.*, 1996, **8**, 291.

2 A. Clearfield, *Curr. Opin. Solid State Mater. Sci.*, 1996, **1**, 268.

3 A. Clearfield, *Prog. Inorg. Chem.*, 1998, **47**, 371.

4 M. D. Dines, P. M. Digiacomo, K. P. Callahan, P. C. Griffith, R. H. Lane and R. E. Cooksey, in *Chemically Modified Surfaces in Catalysis and Electrocatalysis*, ed. J. S. Miller, *ACS Symp. Ser.*, American Chemical Society, Washington, DC, 1982, p. 223.

5 A. Clearfield, in *Design of New Materials, 4th Symposium, College Station*, ed. A. Clearfield and B. L. Cocke, Plenum, New York, 1987, p. 121.

6 G. Alberti, U. Costantino, F. Marmottini, R. Vivani and P. Zappelli, *Angew. Chem., Int. Ed. Engl.*, 1992, **32**, 1357.

7 H. Byrd, A. Clearfield, D. Poojary, K. P. Reis and M. E. Thompson, *Chem. Mater.*, 1996, **8**, 2239.

8 A. Clearfield, J. D. Wang, Y. Tian, F. L. Campbell III and G. Z. Peng, in *Materials Synthesis and Characterization*, ed. D. Perry, Plenum Press, New York, 1997, p. 103.

9 G. Alberti, U. Costantino, F. Marmottini, R. Vivani and P. Zappelli, *Microporous Mater.*, 1998, **21**, 297.

10 A. Clearfield, *Chem. Mater.*, 1998, **10**, 2801.

11 G. Alberti, R. Vivani, F. Marmottini and P. Zappelli, *J. Porous Mater.*, 1998, **5**, 205.

12 J. D. Wang, A. Clearfield and G.-Z. Peng, *Mater. Chem. Phys.*, 1993, **35**, 208.

13 G. Alberti, U. Costantino, R. Vivani and P. Zappelli, in *Mater. Res. Soc. Symp. Proc.*, Materials Research Society, Pittsburgh, PA, 1991, p. 101.

14 B. Zhang, D. M. Poojary and A. Clearfield, *Inorg. Chem.*, 1998, **37**, 1844.

15 G. Alberti, U. Costantino, F. Marmottini, R. Vivani and P. Zappelli, in *Mater. Res. Soc. Symp. Proc.*, Materials Research Society, Pittsburgh, PA, 1991, p. 105.

16 G. Alberti, F. Marmottini, R. Vivani and P. Zappelli, *J. Porous Mater.*, 1998, **5**, 221.

17 H. Benhamza, P. Barboux, A. Bouhaouss, F.-A. Josien and J. Livage, *J. Mater. Chem.*, 1991, **1**, 681.

18 P. H. Mutin, C. Delenne, D. Medoukali, R. Corriu and A. Vioux, in *Mater. Res. Soc. Symp. Proc.*, ed. R. M. Laine, C. Sanchez, C. J. Brinker and E. Giannelis, Materials Research Society, Warrendale, PA, 1998, p. 345.

19 T. Hirao, T. Masunaga, Y. Ohshiro and T. Agawa, *Synthesis*, 1981, 56.

20 C. E. McKenna, M. T. Higa, N. H. Cheung and M.-C. McKenna, *Tetrahedron Lett.*, 1977, **2**, 155.

21 S. Brunauer, L. S. Deming, W. E. Deming and E. Teller, *J. Am. Chem. Soc.*, 1940, **62**, 1723.

22 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, New York, 1982.

23 A. Saito and H. C. Folley, *AIChE J.*, 1991, **37**, 429.

24 G. Horvath and K. Kawazoe, *J. Chem. Eng. Jpn.*, 1983, **16**, 470.

25 G. Alberti, F. Marmottini, S. Murciamascaros and R. Vivani, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1594.

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