Formation of silica interlayers in α-zirconium-titanium mixed phosphate and phosphonate

E.M. Farfan-Torres 1, J. Maza-Rodriguez, M. Martinez-Lara and A. Jimenez-Lopez
Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Málaga, Apartado 59, 29071 Málaga, Spain

Intercalation of a mixed zirconium-titanium hydrogen phosphate and a phosphate-phosphonate with 3-[ (triethoxy)silyl]-1-propylamine, NH2(CH2)3Si(OC2H5)3, was investigated. Heating the intercalated solids at about 400 °C produces the formation of silica-like species between the interlayers, resulting in a basal space of ~ 15 Å, in both cases. However, only for the intercalated phosphate-phosphonate an increase of the original surface area was obtained, showing that a pillared solid was formed in this case.

1. Introduction

Layered compounds such as clays, oxides and phosphates may be intercalated with inorganic polycations. After thermal treatment two-dimensional microporous solid materials may be formed. The resulting structures can be finely “tuned” by changing the size, shape and concentration of the intercalating species. But, in the case of metal (IV) hydrogen phosphates of the α form, the formation of porous derivatives using inorganic pillaring agents is quite difficult, due to the high charge density of the layer phosphates. However, the synthesis of highly porous pillared tin and zirconium phosphates, using simple colloidal methods, have recently been reported [1,2]. Another alternative method proposed for the forming of pillared phosphates consist in the derivation of the phosphate groups [3].

The use of basic organometallic guest molecules with bulky organic groups removable by thermal treatment, could also allow the obtainment of porous solids [4,5]. We have studied the intercalation of aminopropyltriethoxysilane NH2(CH2)3Si(OC2H5)3 (APTEOSi) oligomeric derivatives into a mixed phosphate, Zr0.75Ti0.25(HPO4)2·H2O (α-ZrTiP), and a mixed phosphate-phosphonate Zr0.75Ti0.25(HPO4)1.5(C6H5PO3)0.5 (α-ZrTiPPh). A multiplicity of complex polysiloxanes, polysiloxanols, alkoxy polysiloxanes and alkoxy polysiloxanols are encountered in the hydrolysis produces of trifunctional organosilanes [6–8]. Sprung et al. [9] have shown that under controlled total hydrolysis, products have “cage-like” structures, and the most probable structures are those of hexa-(alkylsilsesquioxane) or octa-(silsesquioxane). To favour the formation of octa-(silsesquioxane), methyl-isobutyl-ketone (MIBK) was chosen as solvent and water as catalyst for the hydrolysis of APTEOSi [9].

2. Experimental

Two different kinds of host solids were used in the preparation of silica intercalated materials: a mixed zirconium-titanium phosphate Zr0.75Ti0.25(HPO4)2·H2O and a mixed phosphate-phosphonate Zr0.75Ti0.25(HPO4)1.5(C6H5PO3)0.5. The first one was prepared as described elsewhere [10]. The α-ZrTiPPh was prepared in the same way but a mixture of 1 M H3PO4 and 1 M C6H5PO3H2 in n-propanol was used in the first step of hydrolysis, with a molar ratio H3PO4/C6H5PO3H2=1. Also a mixture of concentrated H3PO4 (85%) and C6H5PO3H2 instead of pure concentrated phos-
phoric acid was used before refluxing the gel with a molar ratio of H$_3$PO$_4$/C$_6$H$_5$PO$_3$H = 9. All the other steps have not been modified.

To favour the formation of polycyclic polysiloxanes, methyl-isobutyl-ketone (MIBK) was chosen as solvent and water as catalyst for the hydrolysis of APTEOSi. The intercalation procedure was as follows: α-ZrTiP and α-ZrTiPPh were suspended in MIBK, a solution of APTEOSi (0.1–0.2 M) in MIBK and water (molar ratio Si:H$_2$O = 1:3) were then added. The resulting mixture was refluxed for 12–24 h. Then the solid product was separated by centrifugation, washed with acetone and air-dried at 60 °C. Five different preparations (hereafter ZrTiPSi) were carried out with molar ratios Si/P of: 1.0, 1.5, 2.0, 3.0 and 4.0 in the case of α-ZrTiP. In order to study the effect of partial blockage of the exchanging sites a mixture of APTEOSi and hexylamine with a molar ratio Si/P=1.0 was also used (HAZrTiPSi). In the case of α-ZrTiPPh only an intercalation with a molar ratio Si/P=1.30 was prepared. The different solids were prepared and the preparation parameters are given in table 1.

These materials were characterized by XRD (Siemens D-501 diffractometer using monochromatic Cu Kα radiation), simultaneous DTA–TG analysis (Rigaku Thermoflex apparatus at a heating rate of 10 K min$^{-1}$), IR (Perkin-Elmer 883), specific surface area (S–N$_2$, BET), and NH$_3$ Thermo Programmed Desorption (NH$_3$–TPD). Thermostability of samples was studied by calcination during at least three hours at temperatures between 100 and 700 °C.

Table 1
Experimental conditions for the intercalation of poly-(silsesquioxanes) in α-ZrTiP and α-ZrTiPPh.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Host material</th>
<th>Initial molar Si/P ratio (%)</th>
<th>(w/w) Si uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrTiPSi1</td>
<td>α-ZrTiP</td>
<td>1.0</td>
<td>7.6</td>
</tr>
<tr>
<td>ZrTiPSi1.5</td>
<td>α-ZrTiP</td>
<td>1.5</td>
<td>10.0</td>
</tr>
<tr>
<td>ZrTiPSi2</td>
<td>α-ZrTiP</td>
<td>2.0</td>
<td>11.0</td>
</tr>
<tr>
<td>ZrTiPSi3</td>
<td>α-ZrTiP</td>
<td>3.0</td>
<td>10.5</td>
</tr>
<tr>
<td>ZrTiPSi4</td>
<td>α-ZrTiP</td>
<td>4.0</td>
<td>11.1</td>
</tr>
<tr>
<td>HAZrTiPSi</td>
<td>α-ZrTiP</td>
<td>1.0</td>
<td>7.2</td>
</tr>
<tr>
<td>ZrTiPPhSi</td>
<td>α-ZrTiPPh</td>
<td>1.3</td>
<td>7.0</td>
</tr>
</tbody>
</table>

* Sample prepared using hexylamine as competing agent with a molar ratio of Si/P = 1.0.

The silicon uptake by the intercalated solids reached a maximum for an initial molar Si/P ratio of 2.0, and then remained constant even though higher concentrations of APTEOSi were used (fig. 1). That is to say that saturation is achieved only when all the exchange sites are occupied, corresponding to the neutralization of the acid sites by the amine groups present in the hydrolyzed APTEOSi (11.0% w/w of Si in the intercalated solid), which correspond to a composition of one $\equiv$Si–C$_3$H$_7$–NH$_2$ per P–OH group. The formation of the NH$_3^+$ groups was confirmed by the presence of NH$_3^+$ vibration in the IR spectra (bands at 3177, 1475 cm$^{-1}$) [4].

The XRD patterns indicate that intercalation of polycyclic species produced from APTEOSi hydrolysis do not alter the layer structure of the α-ZrTiP, producing an interlayer swelling. Only one crystalline phase corresponding to a basal spacing of ≈20 Å was observed for Si/P > 2.0 initial ratios. For lower initial concentrations, the 7.6 Å line, corresponding...
to the unexpanded host material, was also present (fig. 2).

According to the DTA–TG data for ZrTiPSi2 there was a 8% weight loss during the exothermic peak at 300°C and a 17% weight loss during the two less intense exothermic peaks at 380 and 540°C. At temperatures higher than 640°C, no further weight loss occurred. All these changes are related with the transformation of the octa-(silsesquioxane) in a silica-like structure.

Evolution of the basal space $d_{002}$, when samples were heated in air at different temperatures is presented in fig. 3. It can be seen that only slight changes were detected at temperatures between 60 and 200°C. At higher temperatures and, concurring with the beginning of the combustion of the organic groups present in the intercalated poly(silsesquioxane), an important decrease in the interlayer space took place, and after 700°C the intercalated structure was destroyed.

Although the intercalated materials presented a high interlayer space ($d_{002} = 15$ Å, at 400°C), the specific surface area of α-ZrTiP derivatives was almost the same as that of the starting metal phosphate (37 m² g⁻¹), and therefore, these materials cannot be considered as pillared solids. These results agree with the fact of total occupation of the exchange sites, determined by the silicon uptake analysis, and confirm that the interlayer region was crowded.

In order to overcome this problem, an attempt was made to produce a partial blockage of the exchange sites with an organic molecule which latter could be removed by heating, competing in the intercalation with octa-(silsesquioxane). For this purpose the hexylamine was chosen, because of its length very similar to the silicon derivative. In this way, the HAZrTiP sample was prepared, which present a single $d_{002}$ diffraction line at ≈ 20 Å at 60°C, falling at 12.6 Å after calcination at 500°C. However, the specific surface area was only slightly increased up to 50 m² g⁻¹, showing that the blockage of the exchange sites by the amine was not effective. This result was confirmed by the chemical analysis, which showed that the %Si uptake was almost the same as when compared with a sample prepared with the same molar Si/P ratio and without the presence of amine.

In view of these results, another strategy was chosen, and it was decided to work with a α-ZrTiPPh derivative which presented a 25% less of the –OH groups than the corresponding α-ZrTiP, as consequence of it having a lower exchange capacity.

3.2. APTEOSi intercalation into $\text{Zr}_{0.75}\text{Ti}_{0.25}(\text{HPO}_4)_{1.5}(\text{C}_6\text{H}_5\text{PO}_3)_{0.5}$

The formation by the sol–gel method of a crystalline mixed phosphate-phosphonate with formula $\text{Zr}_{0.75}\text{Ti}_{0.25}(\text{HPO}_4)_{1.5}(\text{C}_6\text{H}_5\text{PO}_3)_{0.5}$, was confirmed by XRD and chemical analysis. As shown in fig. 4,
XRD patterns of this layer compound presented a first diffraction line at near 22.9 Å, and two more at 11.6 Å and 7.6 Å. The presence of the first line is not in agreement with the data reported in literature for the pure Zr phenylphosphonates, which present the $d_{002}$ line at 14.7 Å. But, since in our case, we have only a partial substitution of randomly distributed $-\text{OH}$ groups by phenyl radicals in the layer, structures such as those schematically represented in fig. 5 are formed. Then, because all the layers are not equivalent, at least two of them are necessary to represent the unit cell, resulting in a total basal space of 22.9 Å. The presence of a interstrafied of two phases, one of pure metal phosphonate and other of pure metal phosphate is precluded, because the first one could not be intercalated with APTEOSi. (This fact was confirmed during intercalation of solids, where any diffraction line at 14.7 Å was never detected.)

The IR spectra of $\alpha$-ZrTiPPh, showed the presence of the band at 1440 cm$^{-1}$ corresponding to the stretch of Ph–P and the band at 1250 cm$^{-1}$ related to the stretching of P–OH groups (fig. 6) [10].

The DTA–TG curves of $\text{Zr}_{0.75}\text{Ti}_{0.25}(\text{HPO}_4)_{1.5}$ ($\text{C}_6\text{H}_5\text{PO}_3)_{0.5}$, presented in fig. 7 show that there was a first step with a weight loss of 6% corresponding to the endothermic loss of crystallization water. A second endothermic process at 250°C without mass loss.

---

**Fig. 4.** X-ray powder diffraction patterns of $\alpha$-ZrTiPPh heated in air at: (a) 60°C, (b) 200°C, (c) 400°C and (d) 500°C. (Position of the diffraction lines in the figure are given in Å.)

**Fig. 5.** Schematic structure proposed for the distribution of phenyl radicals and $-\text{OH}$ groups in the $\text{Zr}_{0.75}\text{Ti}_{0.25}(\text{HPO}_4)_{1.5}$ ($\text{C}_6\text{H}_5\text{PO}_3)_{0.5}$ material.

**Fig. 6.** IR spectra of: (a) $\text{Zr}_{0.75}\text{Ti}_{0.25}(\text{HPO}_4)_{1.5}$, (b) $\text{Zr}_{0.75}\text{Ti}_{0.25}$ ($\text{HPO}_4)_{1.5}$ ($\text{C}_6\text{H}_5\text{PO}_3)_{0.5}$ and (c) $\text{Zr}_{0.75}\text{Ti}_{0.25}$ ($\text{C}_6\text{H}_5\text{PO}_3)_{2}$ materials.

**Fig. 7.** DTA–TG curves of $\text{Zr}_{0.75}\text{Ti}_{0.25}(\text{HPO}_4)_{1.5}$ ($\text{C}_6\text{H}_5\text{PO}_3)_{0.5}$.
corresponding to the $(\alpha' \rightarrow \alpha''$) phase transformation, was then observed. The combustion of the organic matter, accompanied by an exothermic peak, was detected at near 575°C, leading to the formation of the corresponding layered pyrophosphate [11]. The crystallisation of the cubic pyrophosphate is then observed at 900°C [11]. These results were confirmed by XRD patterns obtained after calcination during four hours at different temperatures, which showed the $d_{002}$ line at 22.9 Å shift to 21.0 Å after heating at 200°C. No more changes were detected up to 500°C when an amorphous structure is formed, and finally at near 900°C the corresponding cubic pyrophosphate is formed [10].

Intercalation of polycyclic derivatives of AP-TEOSi in Zr$_{0.75}$Ti$_{0.25}$ (HPO$_4$)$_{1.5}$ (C$_6$H$_5$PO$_3$)$_{0.5}$ lead to the formation of an expanded solid with a $d_{002}$ line at 19.5 Å ($d_{004}=9.8$ Å) (fig. 8). The remaining diffraction line at 12.0 Å, showed that there was a steric hindrance for the introduction of poly-(silsesquioxane) into the layers with a high degree of substitution of phenyl groups (fig. 5). Heating the intercalated samples at different temperatures resulted in the decrease of the basal interlayer space to 15.0 Å at 400°C, because the octa-(silsesquioxane) was transformed to a silica-like pillar. The intercalated solid calcined at 600°C is already amorphous.

The formation of porous solids was confirmed by the increase of the specific surface area. In table 2, the variation of $S$–N$_2$ as a function of the calcination temperature is presented. Here we can see that when organic matter is removed a material with 102 m$^2$ g$^{-1}$ specific surface area is obtained, which corresponds to an increase of $\approx$ 40% as compared with the α-ZrTiPPh host material.

The acid sites concentration evaluated from NH$_3$-TPD spectra, shows that the introduction of silica-like intercalated species produces an increase of the active acid sites due to cooperation effect between the layer phosphate and the silica interlayer. This effect was detected even in the case of low surfaces solids ZrTiPPhSi. When hexylamine was used, the formation of coke particles on the external surface of the solids produced a decrease on the acid activity (fig. 9). For ZrTiPPhSi the acid sites concentration was also enhanced up to 2100 µmol NH$_3$ g$^{-1}$ for the

### Table 2

Specific surface area ($S$–N$_2$) for silica-pillared α-ZrTiPPh at different calcination temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcination temp. (°C)</th>
<th>Specific surface area ($\text{m}^2 \text{g}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-ZrTiPPh</td>
<td>500</td>
<td>74</td>
</tr>
<tr>
<td>ZrTiPPhSi</td>
<td>200</td>
<td>83</td>
</tr>
<tr>
<td>ZrTiPPhSi</td>
<td>400</td>
<td>102</td>
</tr>
<tr>
<td>ZrTiPPhSi</td>
<td>600</td>
<td>66</td>
</tr>
</tbody>
</table>

![Fig. 8. X-ray powder diffraction patterns of (a) α-ZrTiPPh at 60°C and ZrTiPPhSi heated in air at: (b) 60°C, (c) 200°C, (d) 400°C and (e) 600°C. (Position of the diffraction lines in the figure are given in Å.)](image)

![Fig. 9. Amount of NH$_3$ desorbed from 100 to 400°C for solids calcined at 500°C.](image)
pillared material calcined at 500°C from 700 μmol NH₃ g⁻¹ for the α-ZrTiPPh. These results confirmed that enhancement of the acid activity was due not only to the internal surface accessibility achieved with the formation of pillars, but also to a cooperative synergic effect of phosphate-silica interaction.

4. Conclusions

Using adequate strategy for the intercalation of layered phosphates, allows the formation of pillared porous materials, which are stable up to 600°C of heating temperatures. The introduction of silica-like pillars results also in the enhancement of the acid sites concentration and activity, providing in this way a solid material that could be applied in catalysis.

Acknowledgement

The authors wish to express their grateful acknowledgement to CICYT (Spain) MAT 90/298 for financial support. E.M. Farfan Torres also thanks the Ministerio de Educación y Ciencia (Spain) for the provision of a Research Fellowship.

References