Synthesis and Characterization of Novel Alumina-Pillared \(\gamma\)-Zirconium Phosphates

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The preparation of alumina-pillared \(\gamma\)-zirconium phosphate materials was carried out for the first time by thermal hydrotreatment at 473 K of stable aqueous colloid suspensions of \(\gamma\)-zirconium phosphate and alumina in nonaqueous solutions. The nature of the resulting porous materials depends on the delamination processes used. \(^{31}\)P MAS NMR data suggest the existence of \(\gamma\)-zirconium phosphate materials was carried out for the first time, to the best of our knowledge.

Introduction

In the past years, layered phosphates of tetravalent metal (Zr, Ti, Sn) have attracted considerable attention because of their application in catalysis, ion-exchange, ion conduction, and adsorption. \(^1\) However, they have low surface area because they do not have permanent porosity. To overcome this, chemical moieties (stable pillars) can be introduced between the inorganic layers in order to expand the interlayer spacing and ultimately facilitate the control of the pore dimensions after thermal treatment. Thus, the synthesis, characterization, and properties of \(\alpha\)-zirconium phosphate pillared with alumina, chromia, silica, and mixed oxides of Al−Cr, Fe−Cr, and Ga−Cr\(^5\)−\(^\)−\(^\)⁵⁴ as well as \(\alpha\)-tin pillared with alumina and mixed oxide Ga−Al\(^5\) have been reported. These materials are essentially mesoporous, but with a certain contribution of micropores (sometimes \(V_{\text{mic}} \geq 0.1 \text{ cm}^3 \text{ g}^{-1}\) and exhibit high specific surface areas, thermal stability, and interesting catalytic properties. The microporosity of these materials originates from the space between the pillars, whereas the mesoporosity is created principally by edge−edge and edge−face interactions of the platelets. However, pure microporous solids were obtained only by covalent pillaring of the inorganic layers with diphosphonic groups. \(^1\)−\(^\)⁶\(^\)−\(^\)⁷

Research is now addressed to the use of other layered phosphates having a higher layer rigidity such as \(\gamma\)-zirconium phosphate, \(\gamma\)-ZrPO\(_4\)H\(_2\)PO\(_4\)\(\cdot\)2H\(_2\)O (\(\gamma\)-ZrP), to be able to tune the porous nature of the resulting metal oxide pillared solids. This lamellar phosphate has a basal spacing of 12.2 Å and more rigid layers owing to its structure made up of dihydrogenphosphate groups linked through the layers by phosphate groups. \(^1\)−\(^\)⁷−\(^\)⁸ to the best of our knowledge.

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Experimental Section

Materials: Alumina-Pillared γ-Zirconium Phosphates.

Two different solids designed as Al-γ-ZrP(1)-673 and Al-γ-ZrP(2)-673 were prepared as follows:

(i) Al-γ-ZrP(1)-673. A solution containing polyhydroxy-aluminum oligomers, of formula \( [Al_{x}O_{y}OH]_n \), was heated at 473 K in a Teflon-lined autoclave for 1 day. After this treatment, the solid was separated by centrifugation, washed with water, air-dried at 333 K (sample Al-γ-ZrP(1)-673), and finally calcined in air at 673 K (sample Al-γ-ZrP(1)).

(ii) Al-γ-ZrP(2)-673. In this case, 50 mL of an aqueous solution of trimethylaluminum hydroxide (0.1 M), with its pH previously adjusted to 6.0 with 0.1 M phosphoric acid solution, was added dropwise to 15.1 mL of the aluminum oligomeric solution \( [Al_{x}O_{y}OH]_n \), prepared as described before, up to a pH of 4.6. On the other hand, a colloidal suspension of γ-ZrP was obtained by first exposing 1 g of γ-ZrP to propylene vapors and then putting the expanded solid in contact with 67 mL of 0.025 M phosphoric acid solution \( (pH = 4.4) \). Under these conditions, the acidic groups of γ-ZrP are neutralized by the amine to about 80% of the cation exchange capacity.

Finally, the aluminum oligomeric solution was added to this colloidal suspension, and the mixture was set in a Teflon-lined autoclave at 473 K for 1 day. After separation of the solid by centrifugation, the solid was washed with water, air-dried at 333 K (sample Al-γ-ZrP(2)-673), and finally calcined at 673 K (sample Al-γ-ZrP(2)).

Instrumental Techniques. Elemental chemical analyses were carried out by atomic absorption spectrometry (Al, Zr), UV–vis spectrophotometry (P), CHN, and thermogravimetry, after dissolving the samples in a HF aqueous solution. X-ray diffraction patterns of the different samples were obtained on cast films dissolving the samples in a HF aqueous solution. X-ray diffraction was carried out using a Siemens D-5000 instrument using graphite-monochromatized Cu Kα radiation. 29 NMR experiments were performed on a Bruker AMX 400WB spectrometer operating at 161.9 MHz. 2D-5Q MQMAS NMR spectra were collected using the reported parameters of the different measured elements core levels. Atomic concentration data analysis. A Shirley type background was subtracted from the XPS data. The energy scale was calibrated using Cu 2p3/2, Ag 3d5/2, and Au 4f7/2 lines. The pressure in the analysis chamber was maintained lower than 10⁻⁹ Torr. A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian-Lorentz curves in order to determine more accurately the binding energy of the different element core levels. Atomic concentration percentages of samples were determined taking into account the corresponding area sensitivity factor for the different measured spectral regions.

Thermogravimetric–differential thermal analysis (TG–DTA) was performed in air by use of a Stanton Redcroft thermal analyzer STA781 at a heating rate of 5 K min⁻¹. N₂ adsorption–desorption isotherms at 77 K were obtained by using a Micromeritics ASAP 2010 instrument. The micropore volumes were calculated by using the Dubinin method. 25 Total acidity of the samples was determined by ammonia (NH₃-TPD). Before the adsorption of ammonia at 373 K, the samples were heated at 673 K in a He flow. The NH₃-TPD was performed between 373 and 673 K, with a heating rate of 10 K min⁻¹, and analyzed by an on-line gas chromatograph (Shimadzu GC-14) provided with a thermal conductivity detector. IR spectra of adsorbed pyridine were recorded on a Perkin–Elmer 883 spectrometer. Self-supporting wafers of the samples with a weight/surface ratio of 12 mg cm⁻² were mounted in a vacuum cell with greaseless stopcocks and CaF₂ windows. The samples were evacuated at 623 K and 10⁻⁴ Torr overnight, exposed to pyridine vapors for 15 min, and then degassed at different temperatures. IR spectra of pyridine interacting with Bronsted and Lewis acid centers exhibit the characteristic vibration bands at 1550 cm⁻¹ (pyridinium ion) and 1450 cm⁻¹, respectively. The conversion of both types of acid sites is estimated from the integrated absorption at 1550 and 1450 cm⁻¹ using the extinction coefficients obtained by Datka et al. 26 E₀ = 0.73 cm⁻¹ mol⁻¹ and E₁ = 1.11 cm⁻¹ mol⁻¹ for Bronsted and Lewis sites, respectively.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the solids obtained by the method denominated after different treatments. The as-prepared solid exhibits a basal spacing of 30.1 Å, but after washing with water, this value lowered to 24.4 Å and, interestingly, high order harmonics at 11.9 and 8.0 Å are found, indicating the existence of long-range order of the platelet stacking. However, a reflection line at 16.8 Å was also observed, probably because of the presence of a small amount of n-propylammonium-γ-ZrP phase. After heating at 673 K, the order dramatically decreases and a reflection line at 20.0 Å is observed together with a high order harmonic at 9.8 Å. The empirical formula of Al-γ-ZrP(1), deduced from the chemical analysis, is \( ZrH_{0.55}[Al_{1.02}O_{1.54}](OH)_{0.49}F_{0.06}(H_{2}O)_{0.08}(PO_{4})_{0.7}H_{2}O \). Its TG curve (Figure 2) shows several well-defined weight loss steps; the first one between 343 and 573 K (weight
The loss of 9.1% corresponds to the loss of water of hydration and coordinated water of the oligomeric cations and appears associated to an endothermic effect in the DTA curve. A pronounced second step is observed between 573 and 693 K (weight loss of 8.6%) also corresponding to loss of water of coordination plus mainly water evolved from the dehydroxylation process, associated to the very sharp endothermic peak centered at 623 K in the DTA curve. Finally, a small third step is observed between 873 and 1073 K that is assigned to the formation of pyrophosphate, bringing the total weight loss to 23.5%. The shape of this TG curve is very similar to that of the acetate-hydroxide of Cr(III) intercalated into $\gamma$-ZrP, but in the case of the Al-$\gamma$-ZrP(1) sample, the condensation reaction of hydroxo ligands occurs at a higher temperature. Figure 2 shows the TG curve for sample Al-$\gamma$-ZrP(1)-673. In this case, the weight loss is due to adsorbed water and pyrophosphate formation.

The use of method ii leads to an intercalation compound with different characteristics. The diffractogram of the n-propylamine-$\gamma$-ZrP intercalation compound shows a basal spacing $d_{001} = 17.4$ Å, which increases up to 34.5 Å after the intercalation of polyhydroxy-aluminum oligomers under hydrothermal conditions (Figure 3). If this precursor is rinsed with water, the value shifts to 28.8 Å and a weak peak appears at 9.5 Å, assigned to the dehydrated $\gamma$-ZrP phase. The thermal treatment at 673 K gives rise to a more crystalline solid than that obtained with method i, and a very well-defined reflection line at 23.2 Å, corresponding to the interlayer distance, was observed together with other high order harmonics at 11.5 and 7.7 Å. This long-range order was not observed with the analogous alumina-pillared $\alpha$-zirconium phosphates. This behavior can be attributed to the higher rigidity of the $\gamma$-ZrP layers. Furthermore, the amount of aluminum oligomers intercalated in the case of Al-$\gamma$-ZrP(2) is higher than in the case of Al-$\gamma$-ZrP(1). The empirical formula of Al-$\gamma$-ZrP(2), also estimated from chemical analysis and TGA, is Zr-$\{Al_{2.0}(OH)_{3.6}(H_2O)_{2.2}\}^{0.20}(PO_4)_{2}$. In this case, the TG curve (Figure 4) is different showing a continuous weight loss without defined steps; the DTA curve shows three endothermic effects centered at 418, 474, and 715 K that are assigned to dehydration, loss of coordination water, and water loss from the condensation reaction of hydroxo ligands, respectively. The total weight loss was 23.8%. The TG curve of the Al-$\gamma$-ZrP(2)-673 sample (Figure 4) exhibits a weight loss lower than Al-$\gamma$-ZrP(1)-673 indicating a lesser capacity to adsorb water.

The high basal spacings of the precursors prepared by both methods i and ii clearly indicate that oligomeric
species with a high nuclearity, such as Al_{24}^{10+}, are indeed intercalated. However, after calcination at 673 K the resulting basal spacings are strongly reduced giving values of 20 and 23 Å, respectively. Taking into account that the layer thickness of γ-ZrP is 8.6 Å, the free gallery heights in both materials are 11.4 and 14.6 Å for Al-γ-ZrP(1)-673 and Al-γ-ZrP(2)-673, respectively. These values are in good agreement with the total amount of aluminum oxide inserted in both cases in the interlayer space of γ-ZrP.

Solid-state NMR is a valuable tool in the investigation of the pillaring process, being particularly sensitive to short- and medium-range geometries. For this reason, we have used 31P and 27Al MAS NMR to shed light on the nature of the pillars and the alumina-layer interaction. 31P MAS NMR spectra of fresh and calcined samples are shown in Figure 5. In the spectra of Al-γ-ZrP(1) and Al-γ-ZrP(2), two resonances at high field, at ca. −16 or −19 ppm and −26 ppm, are observed. The last signal is typical of PO₄ groups in γ-ZrP, whereas the resonance ranging between −16 and −18 ppm may be assigned to phosphate groups interacting with the aluminum oligomers (P–O–Al). This interaction always causes a shift of the 31P resonance toward high field. Furthermore, the amount of Al–O–P linkages in Al-γ-ZrP(1) is smaller than in Al-γ-ZrP(2), as expected from the amount of polyhydroxyaluminum oligomers retained in each case. The spectra of both calcined solids show only a large and asymmetric peak with a maximum at −26 ppm, revealing different interactions of PO₄ groups with the alumina pillars.

Concerning the 27Al MAS NMR spectra of the fresh and calcined samples (Figure 6), they are quite different from that of the aluminum Keggin ion (Al₁₃) with resonances at 62.9 and 11.8 ppm for tetra- and hexacoordinated aluminum, respectively. Furthermore, these spectra differ from that of the oligomer (Al₁₃^{10+}) presumed to be present in the pillaring solution used, which shows two characteristic signals at 70.2 and 10 ppm for AlO₄ and AlO₅ environments, respectively. Thus, the spectra of the fresh samples display the resonance signal corresponding to octahedral aluminum between −6 and +6 ppm, but the most significant feature is the appearance of a signal between 39 and 65 ppm, which is more intense for Al-γ-ZrP(2). This signal could correspond to either tetrahedral aluminum in a distorted environment or pentacoordinated aluminum, as was established from different studies in aluminum silicates and aluminum phosphates. On the other hand, it is well-known that Al₂₄ clusters exhibit a strong tendency to form pentacoordinated aluminum after thermal decomposition. After calcination of the samples, a new peak at 65 ppm, typical of tetrahedral aluminum, is observed, but only in the AI-

Figure 5. 31P MAS NMR spectra of samples (a) Al-γ-ZrP(1), (b) Al-γ-ZrP(2), (c) Al-γ-ZrP(1)-673, and (d) Al-γ-ZrP(2)-673.

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Figure 7. 27Al MAS and 2D-5Q MQMAS NMR spectrum of sample Al-γ-ZrP(1).


γ-ZrP(1)-673 sample. However, in both samples the intensity of the signal centered at ca. 44 ppm increases upon calcination to the detriment of the octahedral signal, which means that this resonance could be related to the formation of P–O–Al linkages. Furthermore, this signal is more intense for Al-γ-ZrP(2)-673, confirming the existence of a higher degree of connectivity between the aluminum oligomers and the POH groups of the layers. This fact was expected because fluoride ions were added in preparation method i, which are incorporated into the polyhydroxy-aluminum oligomers by substitution of OH groups, and their presence seems to reduce the number of Al–O–P linkages. These results indicate that in Al-γ-ZrP(2)-673 the alumina pillars could be more spread out in the interlayer region.

The resolution of the 27Al MAS NMR spectra can be considerably improved by using the 2D-5Q MQMAS technique, developed by Frydman et al.30 for the study of quadrupolar nuclei. This method provides enhanced resolution compared to conventional MAS spectra because common sources of spectral broadening, such as the second-order quadrupolar broadening and the chemical shift distribution due to structural disorder, are dispersed over two dimensions. It was then possible, by using this technique, to resolve different aluminum sites. Figures 7–10 display the 2D-5Q MQMAS NMR spectra for the fresh and calcined samples. In the 2D-5Q spectra of the fresh samples, octahedral aluminum at 6 and −5 ppm can be observed together with a resonance signal between 42 and 55 ppm, which is more pronounced for Al-γ-ZrP(2), thus indicating the existence of two types of aluminum species. Given that both samples were prepared by using the same polyhydroxy-aluminum oligomer solution, this latter signal would reveal the existence of Al–O–P linkages, where the aluminum ions exhibit distorted tetrahedral or pentahedral coordination. In fact, Caldarelli et al. have found in aluminum phosphates several signals between 37 and 44 ppm, assigned to different aluminum species with tetrahedral coordination.31 After calcination, whereas the Al-γ-ZrP(2)-673 spectrum (Figure 10) showed only an increment in the signal at 44 ppm, the spectrum of Al-γ-ZrP(1)-673 (Figure 9) exhibits a new signal at 60 ppm corresponding to several tetrahedral aluminum species, possibly located on the external surface of the alumina oxide pillars. At the same time, an important increase of the signal at ca. 44 ppm takes place, pointing to the formation of additional chemical bonds with the layers. The high concentration of tetrahedral and pentacoordinated aluminum in the Al-γ-ZrP(1)-673 sample will be very interesting from the point of view of surface acidity and catalytic activity.

Table 1. Binding Energies (eV) and Modified Auger Parameter of Aluminum in γ-Zirconium Phosphate Materials

<table>
<thead>
<tr>
<th>sample</th>
<th>Zr 3d_{5/2}</th>
<th>O 1s</th>
<th>P 2p</th>
<th>Al 2p</th>
<th>$\alpha'_{Al}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-ZrP-673</td>
<td>183.4</td>
<td>531.6</td>
<td>134.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-γ-ZrP(1)-673</td>
<td>183.5</td>
<td>532.0</td>
<td>134.1</td>
<td>75.0</td>
<td>1460.9</td>
</tr>
<tr>
<td>Al-γ-ZrP(2)-673</td>
<td>183.1</td>
<td>531.8</td>
<td>134.0</td>
<td>74.8</td>
<td>1460.9</td>
</tr>
</tbody>
</table>

XPS has also been employed to get complementary insights about the structural characteristics of the calcined materials. The binding energy values corresponding to the different atoms present in the solids and the modified Auger parameters of aluminum (\( \alpha' \)) are compiled in Table 1. The Zr and P binding energies are similar to those of \( \gamma \)-ZrP heated at 673 K, indicating that the phosphate structure is preserved during the pillaring process. The Al 2p binding energy is higher than those values observed in other pillared phosphates\(^{32} \) and aluminas\(^{32} \), which could reveal a strong interaction of aluminum ions with the layers.

The modified Auger parameter of Al (\( \alpha' \)) was calculated by using the following equation:

\[
\alpha' = 1486.6 + \text{KE(Al}_{\text{KLL})} - \text{KE(Al 2p)}
\]

where KE(Al\(_{\text{KLL}}\)) and KE(Al 2p) are the kinetic energies of the KLL Auger transition and the Al 2p photoelectron, respectively.\(^{33} \)

The value deduced for both samples is 1460.9 eV, which is intermediate between those corresponding to tetrahedral and hexacoordinated aluminum, thus revealing the presence of Al species in different environments.\(^{34} \)

The differences between the calcined samples have been also found in the study of their textural characteristics. N\(_2\) adsorption–desorption isotherms at 77 K reveal that the Al–\( \gamma \)-ZrP(1)-673 (Figure 11) is a micro/mesoporous solid with a Brunauer–Emmett–Teller (BET) surface area of 116 m\(^2\) g\(^{-1}\) and a micropore volume of 0.043 cm\(^3\) g\(^{-1}\), whereas Al–\( \gamma \)-ZrP(2)-673, showing a similar BET surface (119 m\(^2\) g\(^{-1}\)), is essentially a mesoporous solid (see Table 2). By use of \( \gamma \)-ZrP as the host and two different preswelling methods but similar pillaring solutions, two materials with different porosity were obtained. Taking into account that Al–\( \gamma \)-ZrP(1)-673 was prepared using a pillaring solution containing F\(^-\) ions, more stable pillars were obtained because of the partial substitution of such ions by OH\(^-\). Under such experimental conditions, a solid containing micropores is obtained. In contrast, the preparation of Al–\( \gamma \)-ZrP(2)-673 without F\(^-\) ions favors the intercalation of a larger amount of aluminum oligomers, which spread out in the interlayer space upon calcination, giving rise to a filled-up structure. Consequently, micropores are absent and because the

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Table 2. Textural and Acidic Characteristics of the Alumina-Pillared \( \gamma \)-Zirconium Phosphates

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m(^2) g(^{-1}))</th>
<th>( V_{\text{microp}} ) (cm(^3) g(^{-1}))</th>
<th>( V_{\text{mesop}} ) (cm(^3) g(^{-1}))</th>
<th>( C_L ) (( \mu \text{mol g}^{-1}))</th>
<th>373 K</th>
<th>493 K</th>
<th>Total acidity (( \mu \text{mol NH}_3) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–( \gamma )-ZrP(1)-673</td>
<td>116</td>
<td>0.043</td>
<td>0.061</td>
<td>185</td>
<td>67</td>
<td>591</td>
<td>54</td>
</tr>
<tr>
<td>Al–( \gamma )-ZrP(2)-673</td>
<td>119</td>
<td>0.010</td>
<td>0.160</td>
<td>54</td>
<td>0</td>
<td>480</td>
<td></td>
</tr>
</tbody>
</table>

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The delamination obtained with propylamine is better than in the case of acetone/water, a mesoporous solid is isolated. The pore size distribution of Al-$\gamma$-ZrP(1)-673, determined by the MP (micropore analysis) method\(^{35}\), indicates that most of the pores have a hydraulic radius between 4.5 and 6.0 Å (Figure 12), which is consistent with the observed basal spacing of this solid (20 Å).

The determination of the mesoporous volume was made from the desorption data. The pore volume in the 20–100 Å radius range is 0.061 cm\(^3\) g\(^{-1}\) for Al-$\gamma$-ZrP(1)-673 and 0.11 cm\(^3\) g\(^{-1}\) for Al-$\gamma$-ZrP(2)-673. Therefore, these experimental data confirmed the presence of both micro- and mesopores in Al-$\gamma$-ZrP(1)-673 and the mesoporous nature of the Al-$\gamma$-ZrP(2)-673.

The total acidity of the calcined samples was determined by using NH\(_3\)-TPD. The value found for the Al-$\gamma$-ZrP(1)-673 sample (591 µmol NH\(_3\) g\(^{-1}\)) is higher than that for Al-$\gamma$-ZrP(2)-673 (480 µmol NH\(_3\) g\(^{-1}\)). The nature of these acid sites was determined by pyridine adsorption coupled to IR spectroscopy. The spectra obtained after evacuation at different temperatures (Figure 13) show only the typical absorption band at 1450 cm\(^{-1}\) of pyridine coordinated to Lewis acid sites. From the area integration of this peak and use of the extinction coefficient given by Datka et al.,\(^{26}\) the number of acid sites per gram has been calculated. The results obtained (Table 2) corroborate the higher acidity of the Al-$\gamma$-ZrP(1)-673 sample. However, only 17% of such acidity remained after outgassing at 493 K. This higher acidity is expected by taking into account the larger amount of aluminum ions with low coordination found by the \(^{27}\)Al MAS NMR studies. Moreover, the microporous nature of this sample facilitates the access of both basic probe molecules to the acid sites located on the surface of the alumina pillars.

Conclusions

A new hydrothermal method is proposed for the preparation of porous alumina-pillared $\gamma$-zirconium phosphates with specific surface areas higher than 100 m\(^2\) g\(^{-1}\). \(^{27}\)Al MAS NMR analysis with the help of the 2D-5Q MQMAS technique reveal the coexistence, in both calcined materials, of octahedral, tetrahedral, and pentacoordinate aluminum species. The higher acidity of Al-$\gamma$-ZrP(1)-673 samples in comparison with that of Al-$\gamma$-ZrP(2)-673 can be explained by the existence of a larger amount of aluminum ions with low coordination, as found by \(^{27}\)Al NMR studies.

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**Figure 13.** IR spectra of Al-$\gamma$-ZrP(1)-673 and Al-$\gamma$-ZrP(2)-673 exposed to pyridine vapors after evacuation at (a) room temperature, (b) 373 K, and (c) 493 K.

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