

Preparation of Zeolite-like Pillared Metal(IV) Phosphate Materials

J. Santamaría González, A. Jiménez-López,¹ and María Martínez Lara

Departamento de Química Inorgánica, Cristalografía y Mineralogía, Facultad de Ciencias, Universidad de Málaga, 29071 Malaga, Spain

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It is possible to obtain mixed aminopropyl sil-aluminum sesquioxanes by simultaneous hydrolysis of (3-aminopropyl)triethoxysilane and aluminum (III) diisopropoxide-2,4-pentanedionate with the stoichiometric amount of water in methanol. These oligomers are intercalated in a *M(IV)*-phosphate in which the number of POH groups are controlled substituting POH groups by phenyl phosphonates. The zeolite-like pillared materials obtained after thermal treatment at 600°C have high surface areas (up to 126 m² g⁻¹) and high total acidity (up to 2.11 mmol of NH₃ desorbed between 100–500°C). XPS reveals that Al has tetrahedral coordination in these materials. © 1995

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INTRODUCTION

Pillared materials are recently developed layered solids, prepared by substitution of charge-compensating cations with polyhydroxocations of various elements. On heating, the cationic oligomers form oxide clusters that permanently prop apart the layers, originating a well-defined two-dimensional pore structure with high specific surface area. Pillared clays have been the materials largely prepared; the properties of these compounds have been recently reviewed (1, 2).

The use of α -metal(IV) layered phosphates as starting materials to prepare pillared materials offer hardness due to the high charge density of the phosphate layers. However, by using colloidal suspensions of these phosphates it is possible to obtain high expanded pillared materials of chromia, alumina, and mixed chromia-alumina (3, 5) with interesting catalytic activity.

A smart way to overcome the problem of the high charge density of α -zirconium phosphate is by using basic organometallic guest molecules. Thus, using (3-aminopropyl)triethoxysilane (APTEOSi), silica pillared α -*M(IV)* phosphates have been obtained. These materials present high interlayer distances and surface areas (6, 8).

Recently we employed these organometallic molecules for the preparation of porous material in a mixed Zr-Ti phosphate described elsewhere (9), but we used methylisobutyl ketone as solvent to favor the formation of octasilsesquioxane (10). Although this phosphate is less acidic than α -zirconium phosphate, stuffed structures of silica were obtained. A new strategy was adopted to reduce the number of guest molecules to intercalate, which consists of the substitution of POH groups by phenylphosphonate groups. In this way we have prepared a new family of silica pillared materials derived from this mixed phosphate [Zr_{0.75}Ti_{0.25}(HPO₄)₂] with surface area up to 150 m²/g and high acidity (1.1 to 1.6 mmol g⁻¹ of NH₃) (11, 12).

The acidity of a silica can be enhanced by introducing (AlO₄) tetrahedra unit into its framework to form a zeolite structure. The claim of this paper is to obtain a zeolite-like interlamellar structure by simultaneous hydrolysis of APTEOSi and aluminum(III) diisopropoxide-2,4-pentanedionate and to intercalate in two mixed phosphates-phosphonates, Zr_{0.75}Ti_{0.25}(HPO₄)_{1.5}(C₆H₅PO₃)_{0.5} and Zr_{0.5}Ti_{0.25}(HPO₄)_{1.1}(C₆H₅PO₃)_{0.9}.

EXPERIMENTAL

Preparation of Intercalates

The preparation of the two hosts, Zr_{0.75}Ti_{0.25}(HPO₄)_{1.5}(C₆H₅PO₃)_{0.5} and Zr_{0.75}Ti_{0.25}(HPO₄)_{1.1}(C₆H₅PO₃)_{0.9}, hereafter P_{1.5} and P_{1.1}, respectively, have been described elsewhere (12).

P_{1.5} or P_{1.1} (1.5 g) was suspended in methanol. To these suspensions was added a methanolic solution of (3-aminopropyl)triethoxysilane and aluminum(III) diisopropoxide-2,4-pentanedionate in such a way that the molar Si + Al/HPO₄ was 1.75. Then, water was added to achieve molar ratios H₂O/Al = 2 and H₂O/Si = 3. The resulting suspension was refluxed for 12 hr, and then the solid products were separated by centrifugation, washed with methanol, and dried at 60°C. Four different molar ratios of Al/Si were used for each host: 0.25, 0.50, 1.0, and 1.85.

¹ To whom correspondence should be addressed.

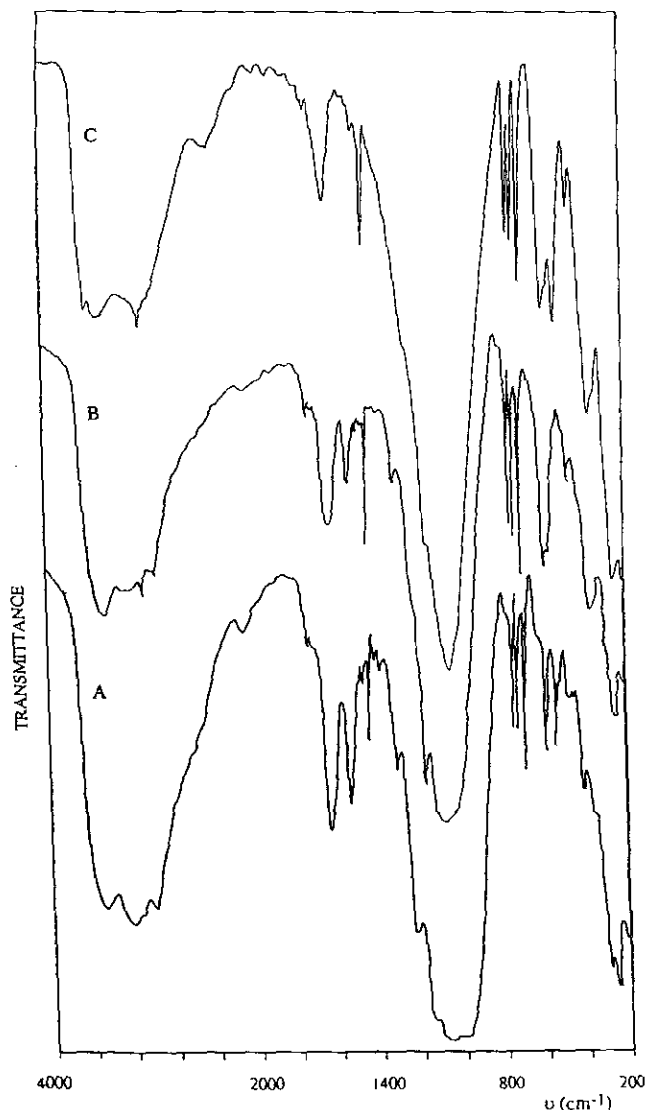


FIG. 1. Infrared spectra of: mixed oligomers (Al/Si = 1) in $P_{1.5}$ host (A), mixed oligomers (Al/Si = 1) in $P_{1.1}$ host (B), $P_{1.1}$ host (C).

Characterization

The P, Al, and Si contents were determined in the calcined solids (600°C, 6 hr) by electronic microscopy (Philips EM420) with a dispersive energy spectrometer Edax 9400. The counting time was 100 sec and the analysis surface was 20 nm, with a tilt angle of 30° and a takeoff angle of 50°.

X-ray diffraction spectra were measured with a Siemens D501 diffractometer using $\text{CuK}\alpha$ radiation. The infrared spectroscopy was run with a Perkin-Elmer 883 spectrometer. DTA-TG curves were obtained with a Rigaku-Thermoflex instrument at a heating rate of 10 K min^{-1} and with calcined alumina as reference. X-ray photoelectron spectra were determined with a Fisons Escalab 200R spectrometer equipped with an $\text{AlK}\alpha$ X-ray excitation source and hemi-

spherical electron analyzer. The residual pressure in the ion-pumped chamber during data acquisition was 10^{-9} Torr. The binding energies (B.E.) were determined (± 0.2 eV) by charge referencing with the adventitious C 1s peak at 284.9 eV.

Specific surface areas were determined (BET method) on a conventional volumetric apparatus at 77 K, degassing at 473 K (10^{-4} Torr overnight).

The thermo-programmed desorption of ammonia adsorbed at 373 K was determined between 373 and 773 K at 10 K min^{-1} and analyzed by on line gas chromatography

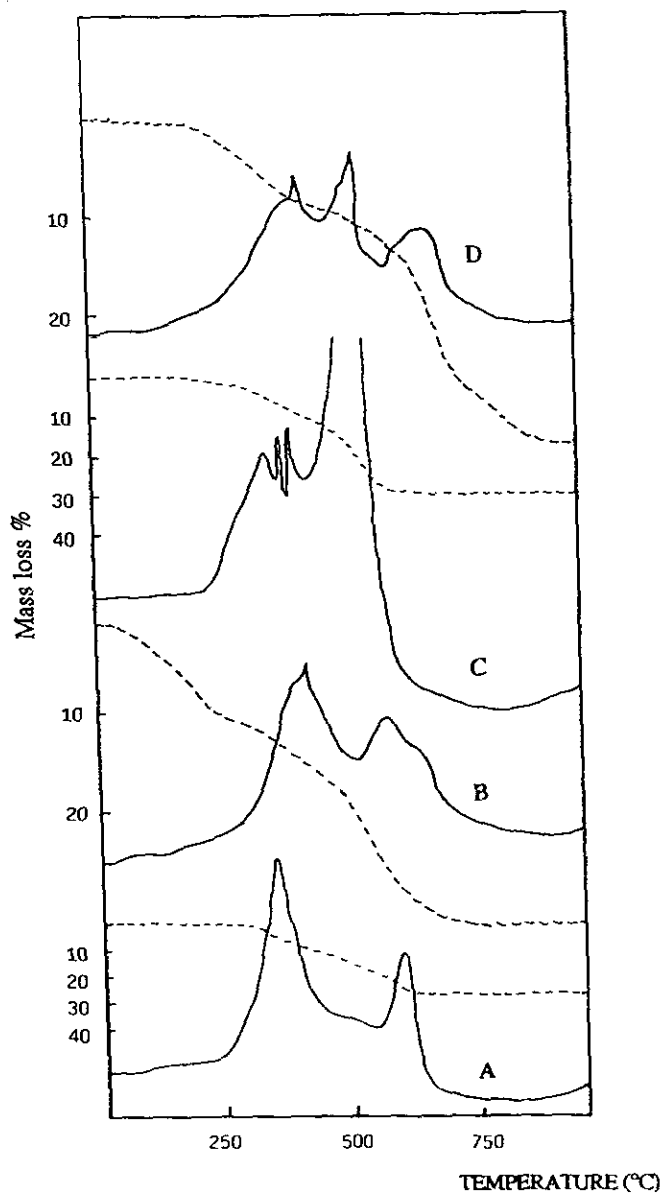


FIG. 2. DTA-TG curves of intercalates: polysilsesquioxane in $P_{1.5}$ host (A), mixed oligomers (Al/Si = 1.85) in $P_{1.5}$ host (B), polysilsesquioxane in $P_{1.1}$ host (C), mixed oligomers (Al/Si = 1.85) in $P_{1.1}$ host (D).

TABLE 1
Total Weight Loss at 600°C and Chemical Composition of Mixed Intercalates into P_{1.5} and P_{1.1} Hosts Calcined at 600°C

Host	Al/Si initial ratio	%P	%Si	%Al	Weight loss % at 600°C	Al/Si intercalated	Atomic ratios P:Si:Al
P _{1.5}	0.25	20.36	13.31	2.89	27.9	0.23	P ₂ Si _{1.44} Al _{0.32}
	0.50	20.52	11.66	4.28	28.4	0.38	P ₂ Si _{1.25} Al _{0.48}
	1.00	21.07	10.49	4.58	27.4	0.45	P ₂ Si _{1.1} Al _{0.5}
	1.85	21.84	7.49	5.88	28.3	0.83	P ₂ Si _{0.75} Al _{0.62}
P _{1.1}	0.25	23.11	9.33	2.27	32.8	0.25	P ₂ Si _{0.9} Al _{0.22}
	0.50	23.19	7.86	3.58	31.0	0.47	P ₂ Si _{0.75} Al _{0.35}
	1.00	22.79	6.36	4.66	30.6	0.76	P ₂ Si _{0.62} Al _{0.47}
	1.85	23.28	4.82	7.04	33.0	1.52	P ₂ Si _{0.46} Al _{0.7}

(Shimadzu GC-14A) provided with a thermal conductivity detector.

RESULTS AND DISCUSSION

It is known that when alkyltriethoxysilanes are hydrolyzed under controlled conditions, products with cage-like structure such as hexa- and octaalkylsilsesquioxanes are formed. In a similar way if a hydrolysis process was carried out in the presence of aluminum(III) diisopropoxide-2,4-pentanedionate, mixed aluminum-silsesquioxanes could be obtained. These polycyclic derivatives will be then intercalated into the phosphate hosts via acid-base reaction with the transference of protons from the layers to the amine group side arms located on the silicon atoms of the oligomers.

In Table 1 the Al/Si ratios found in both series of intercalated compounds are compiled. The comparison of these values with those of the initial solutions shows important differences. In general, the Al/Si ratios in the intercalates are lower for samples obtained with the P_{1.5} host. These

data indicate that the phosphate selectively intercalates different oligomers in each case; perhaps the P_{1.5} host with high exchange capacity takes up the oligomers with low aluminum content since only the silicon atoms are the carrier of basic groups. In the case of P_{1.1} intercalates the Al/Si ratios are closer to the initial ratio in solution, which indicates that this host has a low selectivity for the different oligomers.

The infrared spectra (Fig. 1) of the intercalates show three new bands characteristic of the oligomers. The first at 1312 cm⁻¹ is assignable to methyl groups (δCH_2) of pentanedionate ligands; their intensity increases with the content of aluminum in the samples. In the same way, the absorption band at 1530 cm⁻¹, corresponding to $\nu\text{C}=\text{C}$ of pentanedionate, also increases in intensity with the aluminum content. The bands that indicate the protonation of amine groups during the acid-base intercalation reaction are observed at 1475 cm⁻¹ ($\delta_s\text{NH}_3^+$) and at 3020 cm⁻¹ (νNH^+). The other bands in the IR spectra have previously been described (12).

The TG-DTA curves for mixed aluminum-silicon oligo-

TABLE 2
Basal Spacing Data of Mixed Intercalates into P_{1.5} and P_{1.1} at Different Temperatures

Host	Al/Si initial ratio	d_L (Å)					
		333 K	373 K	473 K	573 K	673 K	773 K
P _{1.5}	0.25	19.3-17.1	19.3-17.1	18.2-16.9	15.6	13.9	12.3
	0.50	18.9-16.9	18.2-16.9	17.4-16.2	15.4	~13.9	amorphous
	1.00	19.4-16.9	17.6-16.0	sh-16.0	15.2	~14	amorphous
	1.85	18.4-16.7	17.2-15.9	15.2	15.8	~14	amorphous
P _{1.1}	0.25	16.7	16.7	15.8	14.9	14	amorphous
	0.50	15.8	16.2	15.8	15.0	~14	amorphous
	1.00	16.5	14.7	15.4	14.7	~14	amorphous
	1.85	15.8	15.6	15.2	14.8	~14	amorphous

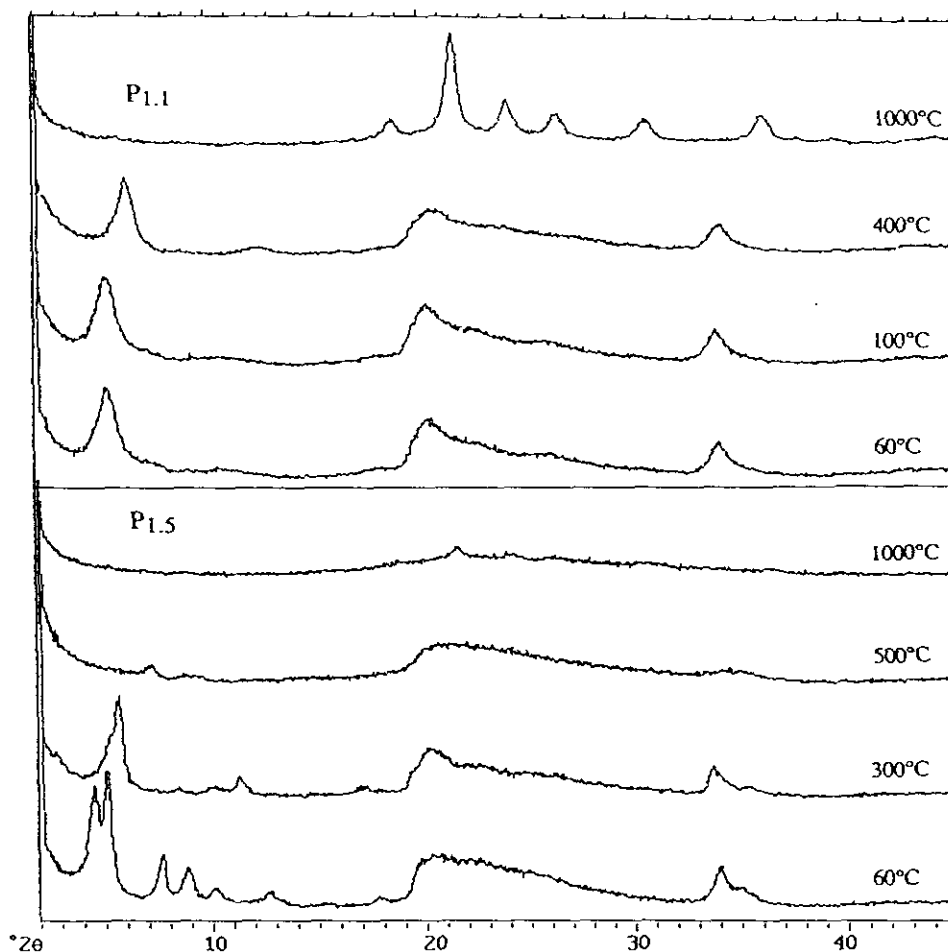


FIG. 3. XRD powder patterns of Al/Si mixed intercalates with initial ratio 0.25 in $P_{1.5}$ and $P_{1.1}$ hosts at different temperatures.

mers intercalates (Fig. 2) are, in general, quite similar, showing a continuous weight loss between 250 and 650°C. The most interesting feature is the occurrence of a new exothermal effect at 625°C after the two typical exothermal peaks observed in the polysilsesquioxane intercalates, one

at 350°C (combustion of aminepropyl sidearms) and another between 500–600°C (combustion of phenyl groups). This new peak is assigned to the combustion of pentanedionate groups coordinated to the aluminum cations.

The total weight loss at 600°C (6 hr) is compiled in Table 1. The empirical formula for these intercalates calcined at 600°C have been calculated from P, Al, and Si contents and are also included in this table. From this it can be seen that the total content $(\text{SiAl})\text{O}_2$ is almost constant for each series, but the aluminum content increases through both sets of samples according to the synthetic experimental conditions. It is noticeable that in both groups of compounds the total amount of mixed oxides intercalated are higher than in the simple parent silica pillaring materials (12). The incorporation of aluminum, with a lower hindrance of the pentanedionate groups and without protonable groups, to the oligomer decreases the total charge of the oligomers which may facilitate their intercalation.

On the other hand, for samples derived from $P_{1.5}$ the ratio Si + Al/P is in the range 0.88–0.69 decreasing with the charge of the oligomers. These ratios are very similar

TABLE 3
Kinetic Energies of Al 2p and Al_{KLL} and Modified Auger Parameter (α') of Al in Al/Si Oxide Pillared Materials Calcined at 500°C

Host	Al/Si initial ratio	KE Al 2p (eV)	KE Al _{KLL} (eV)	α' (eV)
$P_{1.5}$	0.25	1406.6	1380.4	1460.4
	0.50	1406.8	1380.5	1460.3
	1.00	1406.9	1380.6	1460.3
	1.85	1407.1	1381.1	1460.6
$P_{1.1}$	0.25	1406.9	1379.9	1459.6
	0.50	1406.3	1380.2	1460.5
	1.00	1406.8	1380.6	1460.4
	1.85	1406.8	1380.8	1460.6

TABLE 4
Binding Energies (eV) and Surface Chemical Composition of Al/Si Oxide Pillared Materials
Calcined at 500°C

Host	Al/Si initial ratio	O 2s ^a	Si 2p	Al 2p	P 2p	Ti 2p _{3/2}	Zr 3d _{5/2}	Al/Zr	Si/Zr	Al/Si
P _{1.5}	0.25	530.9 (59)	102.5	73.9	133.0	458.7	182.2	1.13	2.29	0.49
		532.0 (48)								
	0.50	530.8 (60)	102.4	73.9	133.0	458.7	182.2	1.47	1.82	0.81
		532.0 (40)								
1.00	530.8 (49)	102.4	73.8	133.0	458.6	182.2	1.28	1.34	0.96	
	531.8 (51)									
1.85	530.8 (67)	102.3	73.9	133.0	458.5	182.2	1.88	1.06	1.76	
	531.8 (33)									
P _{1.1}	0.25	530.9 (56)	102.7	73.9	132.9	459.0	182.2	0.40	1.07	0.37
		531.8 (44)								
	0.50	530.8 (76)	102.5	73.9	133.0	458.6	182.2	0.67	0.98	0.68
		532.0 (24)								
	1.00	530.9 (79)	102.5	74.0	133.0	458.7	182.2	1.18	0.70	1.68
532.2 (21)										
1.85	530.9 (53)	102.4	74.1	133.1	458.6	182.2	1.55	0.54	2.87	
	531.9 (47)									

^a Values between brackets indicate the percentage.

to those found by Roziere *et al.* (7) and Silvester *et al.* (8) for silica pillared α -ZrP prepared from aqueous aminepropyltriethoxysilane solutions. For samples prepared from P_{1.1} the ratio Si + Al/P is close to 0.55; this lesser value is due to the high content of phenyl groups of this host and thus to its lower number of superficial POH groups. According to these ratios, the percentage of POH groups neutralized ranged between 96–50% for P_{1.5} intercalates and between 81–42% for P_{1.1} derivatives. From this it is inferred that the incorporation of aluminum to the polycyclic-silsesquioxane does not notably reduce the trend to intercalate in the phosphate.

The intercalation of mixed Al–Si sesquioxane oligomers into the phosphate layers leads to expanded phases although the XRD patterns show low crystallinity (Table 2).

For intercalates obtained from the host P_{1.5} the basal spacing changed from 22.9 Å to two new values at about 19 and 17 Å, which could indicate the intercalation of two different oligomers (Fig. 3). But, taking into account that the basal spacing of this host phosphate-phosphonate is 22.9 Å due to the unit cell defined with two layers whose content of phenyl groups are different (11), the intercalation of oligomers into both different layers leads to the occurrence of these two basal spacings. However, after heating at 250°C both intercalates evolve to a single phase at about 15.5 Å. In general, the intercalates with mixed aluminum–silicon oligomers exhibit basal spacings lower than that of polysilsesquioxane in the same host (12) due to the lower hindrance of pentanedionate groups with respect to the side-arm propylamine groups of silicon.

In contrast, the intercalates obtained with the host P_{1.1} show a single phase with a basal spacing higher than the host (13.7 Å) and close to 16 Å (Fig. 3) and are also lower than that of polysilsesquioxane in this host (18.7 Å) (12).

After thermal treatment at 400°C (6 hr) all the samples became almost amorphous with a single and weak peak of about 14 Å. At 500°C (6 hr) nearly all the materials became amorphous; a weak peak at 12.5 Å was only observable in the samples derived from P_{1.1}. Because the thickness of the α -ZrP layers is 6.5 Å, the free height of the pillars is close to 12.5–6.5 = 6 Å. This should reveal that a monolayer of mixed Al–Si oligomer could be intercalated in all the cases and that after thermal removal of the organic groups and ligands there should appear [Si_{8-x}Al_xO₁₂] units linked to the layers through P–O–Si or P–O–Al bonds. At 500°C these mixed oxide pillared materials have similar basal spacing to those obtained in α -ZrP by intercalation of APTEOSi from ethanol–water solution (7) and aqueous solution (6). Another expanded material, but no single phase, is obtained (8) when this substance is intercalated from a colloidal solution of half-exchanged *n*-propylamine α -ZrP dispersion.

When the pillared materials are calcined at 1000°C, they show different behaviors depending upon the host. Thus, those derived from P_{1.5} remain amorphous but those derived from P_{1.1} decompose; in the XRD patterns appear the typical lines of mixed titanium–zirconium pyrophosphate. This differential behavior is due to the higher amounts of pillar props intercalated between the layers in the first case, which impedes the pyrophosphate formation. The

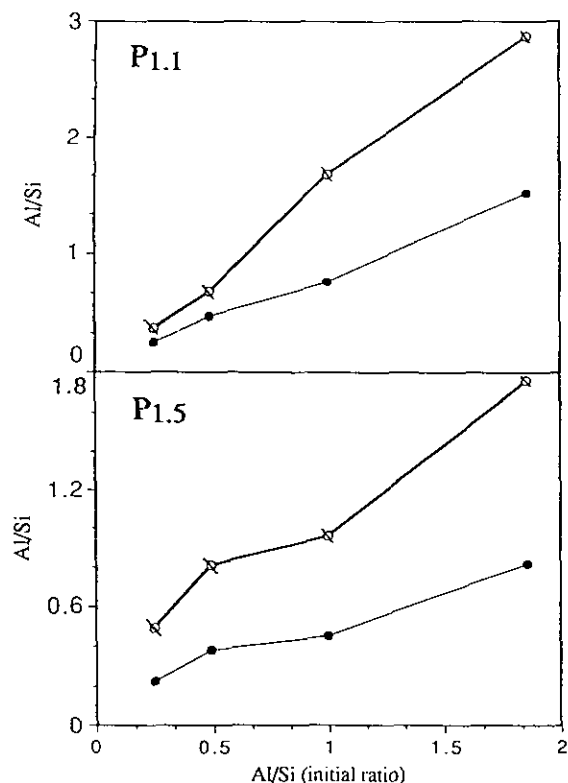


FIG. 4. Al/Si ratios from bulk (●) versus Al/Si ratios from XPS analysis (○) in P_{1.5} and P_{1.1} hosts at 600°C.

former also reveals the high thermal stability of these pillared materials and appears to be a rare case where no formation of pyrophosphate takes place at this temperature.

The XPS technique has been used to determine the binding energies and especially to determine the coordination environment of aluminum at the surface of pillared materials, which is very important for their catalytic activity.

The chemical environment of aluminum on the surface can be distinguished by using the modified Auger parameter (α') (13) obtained by the equation $\alpha' = 1486.6 + KE(\text{Al}_{\text{KLL}}) - KE(\text{Al } 2p)$, where $KE(\text{Al}_{\text{KLL}})$ is the kinetic energy of the Auger electron and $KE(\text{Al } 2p)$ is the kinetic energy of the photoelectron Al $2p$. The value 1486.6 eV is the energy of the AlK α excitation source. The values of α' reported for aluminum in tetrahedral coordination in zeolites are in the range 1460.3–1460.6 eV, and for aluminum in octahedral coordination in aluminosilicates varies between 1461.3–1461.5 eV (14). Taking these data into account, the values of α' obtained for the synthesized pillared materials (Table 3) indicate that aluminum has tetrahedral coordination and since under the experimental conditions, the formation of zeolite-like structure (AlSi)O₂ in the interlayer space takes place. Furthermore, the nonoccurrence of hexacoordinated

aluminum precludes any coprecipitation of Al₂O₃ on the external surface of phosphate.

Table 4 compiles the B.E. of O 1s, Si 2p, P 2p, Zr 3d_{5/2}, and Ti 2p_{3/2} and the atomic ratios Al/Zr, Si/Zr, and Al/Si. It is noticeable that the O 1s B.E.s appear split in two values, one at low energies (530.8 eV), which is very similar to that found in lamellar phosphates (15) and which is assigned to the phosphate layer, and another appearing at 0.9–1.3 eV higher in energy assigned to the oxidic silicon–aluminum interlamellar structure. The B.E. of P 2p is constant in all the materials and very similar to that of lamellar phosphates which indicates that layer framework is preserved after pillaring. The aluminum B.E. is constant and similar to that of Al₂O₃. In contrast, the B.E. of Si 2p shows a slight decreasing through both sets of compounds with the increasing of Al content, being parallel to that exhibited by the B.E. of Ti 2p_{3/2}. This could be interpreted that the incorporation of tetrahedral aluminum to the oxidic interlayer structure increases the number of linkage $\equiv\text{P}-\text{O}-\text{Al}(-)\equiv$ to the layer, thus affecting the core level of Si and Ti.

Finally, this technique has been used to determine the atomic ratio Al/Si on the surface of pillared materials. Figure 4 compares the Al/Si from bulk composition versus Al/Si ratios from XPS analysis. In general, the Al/Si superficial ratio is always higher than bulk ratios, clearly indicating the strong affinity of the Al³⁺ to coordinate with the lamellar phosphate groups. This high affinity has been observed in the preparation of alumina pillared materials, where generally stuffed structures are obtained with strong interaction of aluminum cation with the layers (16).

Surface Area and Acidity

The adsorption isotherms of N₂ on these pillared materials calcined at 500°C (6 hr) are in general type IV of BDDT classification (17), typical of mesoporous solids, and only

TABLE 5
Specific Surface Areas, Micropore Volumes and Total Acidity of Mixed Alumina–Silica Pillared Phosphate Materials

Host	Al/Si ratio	S _{BET} (m ² g ⁻¹)	V micropore (cm ³ g ⁻¹)	μ mole NH ₃ g ⁻¹
P _{1.5}	0.25	64	0.03	1344
	0.50	58	0.03	1250
	1.00	82	0.04	1233
	1.85	62	0.03	980
P _{1.1}	0.25	89	0.03	1849
	0.50	126	0.05	2115
	1.00	121	0.05	1636
	1.85	123	0.05	1688

in the case of the samples derived from P_{1.1} appears a moderate contribution of micropores, in agreement with their lower ratio Al + Si/P and thus with a higher accessibility of N₂ molecules to the intracrystalline structure. The specific surface areas are listed in Table 5 and are, for the first group of materials, in the range 58–82 m²/g, being lower than those of the simple silica pillared parent material. However, for the second group of samples the surface areas are, in general, higher than those of the homologous silica pillared materials, falling between 89 and 126 m²/g. The micropore volume is also included in Table 5.

The total acidity of the mixed oxide pillared materials have been determined by DTP of the adsorbed ammonia and in the range 100–500°C. In Table 5 is listed the total amount of ammonia desorbed. It is noticeable that in the P_{1.5} derivatives the total acidity is lower than the simple silica-pillared phosphate, in close agreement with the high Si + Al/P contents, which is possibly due to a more difficult access of NH₃ molecules to the intracrystalline structure. In contrast, the acidity of materials derived from P_{1.1} is enhanced in samples with low aluminum content. However, the total content Si + Al/P is also higher than that of the simple silica parent, which clearly indicates the occurrence of new acid sites due to the isomorphic substitution of silicon by aluminum in the nanostructures of the pillars. The total acidity of these materials is comparable to that of some zeolites (18, 19). Actually, experiments are being carried out to test the acidity of these materials in the decomposition of isopropylalcohol.

In conclusion, the simultaneous hydrolysis of (3-amino-propyl)triethoxysilane and aluminum(III) diisopropoxide-2,4-pentanedionate yields mixed aminopropylsil-aluminum sesquioxanes which by acid–base reaction are intercalated in M(IV) layered phosphates and by ulterior thermal decomposition yields aluminum–silicon oxide pillars with zeolite structure in the interlayer. Some of these compounds show high surface area and acidity with potential and interesting application as catalyst.

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REFERENCES

1. T. J. Pinnavaia, *Science* **220**, 365 (1993).
2. D. E. W. Vaughan, *Catal. Today* **2**, 187 (1988).
3. (a) P. Maireles-Torres, P. Olivera-Pastor, E. Rodríguez-Castellón, A. Jiménez-López, L. Alagna, and A. A. G. Tomlinson, *J. Mater. Chem.* **1**, 319 (1991); (b) P. Maireles-Torres, P. Olivera-Pastor, E. Rodríguez-Castellón, A. Jiménez-López, and A. A. G. Tomlinson, *J. Mater. Chem.* **1**, 739 (1991).
4. A. Guerrero, I. Rodríguez, J. L. G. Fierro, A. Jiménez-López, P. Olivera-Pastor, and P. Maireles-Torres, *Appl. Catal. Sect. A* **92**, 81 (1992).
5. P. Olivera-Pastor, J. Maza-Rodríguez, P. Maireles-Torres, E. Rodríguez-Castellón, and A. Jiménez-López, *J. Mater. Chem.* **4**, 179 (1994).
6. L. Li, X. Liu, Y. Ge, L. Li, and J. Klinowski, *J. Phys. Chem.* **95**, 5910 (1991).
7. J. Rozière, D. J. Jones, and T. Cassagneau, *J. Mater. Chem.* **1**, 1081 (1991).
8. P. Silvester, R. Cahill, and A. Clearfield, *Chem. Mater.* **6**, 1890 (1994).
9. E. M. Farfán, E. L. Sham, M. Martínez-Lara, and A. Jiménez-López, *Mater. Res. Bull.* **27**, 1255 (1992).
10. M. M. Sprung and F. O. Guenthe, *J. Am. Chem. Soc.* **77**, 3996 (1955).
11. E. M. Farfán, J. Maza-Rodríguez, M. Martínez-Lara, and A. Jiménez-López, *Solid State Ionics* **63**, 506 (1993).
12. M. Martínez-Lara, E. M. Farfán, J. Santamaría-González, and A. Jiménez-López, *Solid State Ionics* **73**, 189 (1994).
13. (a) C. D. Wagner, D. E. Passoja, H. F. Hilery, T. G. Kinisky, H. A. Six, W. T. Jansen, and J. A. Taylor, *J. Vac. Sci. Technol.* **21**, 933 (1982); (b) C. D. Wagner, in "Practical Surface Analysis" (E. D. Briggs and M. P. Seah, Eds.), Vol. 1, p. 595. Wiley, New York, 1990.
14. M. J. Remy, M. J. Genet, G. Poncelet, P. F. Lardinois, and P. Notte, *J. Phys. Chem.* **96**, 2614 (1992).
15. E. Paparazzo, E. Severini, A. Jiménez-López, P. Maireles-Torres, P. Olivera-Pastor, E. Rodríguez-Castellón, and A. A. G. Tomlinson, *J. Mater. Chem.* **2**, 1175 (1992).
16. E. Rodríguez-Castellón, P. Olivera-Pastor, P. Maireles-Torres, A. Jiménez-López, J. Sanz, and J. L. G. Fierro, *J. Phys. Chem.* **99**, 1493 (1995).
17. S. J. Gregg and K. S. W. Sing, "Adsorption Surface Area and Porosity," p. 98. Academic Press, London, 1982.
18. T. Hashiguchi and S. Sakai, in "Acid–Base Catalysis" (K. Tanabe, H. Hattori, T. Yamaguchi, and T. Tanaka, Eds.), p. 191. VCH, Tokyo, 1989.
19. K. Segawa, J. Sakaguchi, Y. Kurusu, S. Nakata, and S. Asaoka, "11th Reference Catalysts Forum," p. 35. Tokyo, 1987.