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NMR Characterization of Synthetic and Modified Aluminum Orthophosphates

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^{31}P, ^{27}Al, and ^{1}H MAS-NMR spectra of aluminum phosphates (Al/P = 1), obtained from different salts (nitrate, chloride, and sulfate) have been analyzed. Thermal treatment of samples results in the transformation of amorphous into crystalline $AlPO_4$ samples (tridymite or α-cristobalite polymorphs). Structural changes induced by thermal treatments or incorporation of foreign ions (Li^+, F^-, or SO_4^{2-}) are also analyzed and related to the catalytic activity of these samples. In particular, the amount and nature of hydroxyls are important factors that determine the surface physicochemical properties of these catalysts.

INTRODUCTION

Many studies have been devoted to the investigation of the chemical and catalytic properties of metal phosphates, the most thorough review being that of Moffat (*1*). Perhaps $AlPO_4$ (Al/P = 1), used as catalysts or carriers, have been studied in more depth due to its structural similarity to SiO_2 and because they have a relatively large surface area and exhibit surface acid–base properties. Thus, $AlPO_4$ have been used as catalysts in such reactions as dehydration, isomerization, alkylation, rearrangement, cracking, retroaldolization, and condensation (*2–26*).

In all cases, surface concentration of acid–base and one-electron donor–acceptor sites, and hence catalytic activity, depends markedly on the precipitation medium used to synthesize $AlPO_4$ and on the activation temperature (*27–30*). When the solid is pretreated at 1273 K, the surface area and mesoporosity strongly decreases due to the transformation of amorphous into crystalline $AlPO_4$. Another factor that has influence on the surface chemistry and catalytic properties of $AlPO_4$ is the aluminum starting salt (*30*). Thus, when aqueous ammonia was used as precipitation agent, aluminum nitrate yielded materials with higher surface area and low activity for cyclohexene skeletal isomerization (CSI), while aluminum sulfate conferred higher acidity and catalytic activity for CSI, although the samples exhibited low surface areas. Aluminum chloride produces porous $AlPO_4$ catalysts with lower acidity. Likewise, the crystal structure of $AlPO_4$ calcined at 1073 and/or 1273 K depending on aluminum starting salt.

Another interesting factor that modifies the physicochemical surface properties of $AlPO_4$ is the incorporation of foreign ions, such as Li^+, Na^+, K^+, F^-, or SO_4^{2-} (*29, 31–35*). Thus, the modification with alkali cations increases surface basicity although the new basic sites formed do not have reducing properties (*31*); the $AlPO_4$ thus modified exhibits low activity in organocationic reactions like CSI (*32*). On the other hand, incorporation of increasing amounts of fluoride ions leads to a progressive decrease in the number of surface basic sites of a particular strength. Besides the complete elimination of reducing activity, fluorided $AlPO_4$ samples show a decrease in oxidizing activity and an increase in activity for CSI (*29*). In both types of modified samples any appreciable decrease in the textural proper-

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ties of the solids is observed. Finally, the impregnation of $AlPO_4$ with sulfate ions produces effects similar to that of fluoride incorporation although acidity and activity in CSI are higher (*34, 35*). However the mesoporosity of these samples is lost during the thermal treatment as a consequence of the complete crystallization.

The use of multinuclear high-resolution NMR techniques, including the CP-MAS method, permits analysis of the local environment of atoms in amorphous and well-crystallized phosphates (*36–38*). The great interest in $AlPO_4$ as catalyst led us to carry out a study of the ^{1}H, ^{27}Al, and ^{31}P NMR signals in $AlPO_4$ samples. This study includes samples obtained from different aluminum salts (nitrate, chloride, and sulfate) subjected to different thermal treatments. We especially focus on the nature of surface hydroxyls as well as on the structural changes induced by the foreign ions (Li^+, SO_4^{2-}, or F^-) at different temperatures. Likewise, we attempt to relate the Brønsted surface acidity (type and number of OH groups) of different $AlPO_4$ catalysts with their catalytic activity and selectivity in CSI.

EXPERIMENTAL

Materials

$AlPO_4$ catalysts (Al/P molar ratio = 1) were prepared from aqueous solutions of $AlCl_3 \cdot 6H_2O$ and H_3PO4 (85 wt%) by precipitation at 273 K with aqueous ammonia ($AlPO_4$-AC), ethylene oxide ($AlPO_4$-EC), or propylene oxide (AlP_4-PC). When we used aqueous ammonia, two new $AlPO_4$ catalysts were obtained from, respectively, $Al(NO_3)_3 \cdot 9H_2O$ ($AlPO_4$-AN) and $Al_2(SO_4)_3 \cdot 18H_2O$ ($AlPO_4$-AS). All solids were washed several times with 2-propanol, dried at 393 K for 24 h, screened at 200–250 mesh, calcined for 3 h at temperatures in the range 773–1273 K in an electric muffle furnace and stored in a desiccator.

The $AlPO_4$ catalysts containing foreign ions were prepared from $AlPO_4$-PC (calcined at 923 K for 3 h) by impregnation until incipient wetness with aqueous solutions of alkali (Li^+, Na^+, and K^+) hydroxides or aqueous solutions of ammonium fluoride (F^-) or ammonium sulfate (SO_4^{2-}). After impregnation, they were dried at 393 K for 24 h and calcined in air at temperatures in the range 573–773 K. The foreign ion content was in the range 1–5 wt%.

Pure $AlPO_4$ catalysts are designated by "$AlPO_4$" followed by two letters that indicate, respectively, the precipitation medium and the starting aluminum salt, and by the calcination temperature ($AlPO_4$-AC-923, $AlPO_4$-EC-1073, and so on). For modified $AlPO_4$-PC-923 catalysts, the nomenclature includes $AlPO_4$-PC followed by ion loading (wt%), the symbol of the element (Li, Na, K, or F) or the letter S (SO_4^{2-}), and by the temperature of the additional treatment ($AlPO_4$-PC-1Li-573, $AlPO_4$-PC-3F-573, $AlPO_4$-PC-5S-773, and so on).

To detect the possible segregation of Al_2O_3 during the synthesis of $AlPO_4$, the system $AlPO_4$–Al_2O_3 (75 : 25 wt%) was prepared by adding aluminum hydroxide, obtained by precipitation with aqueous ammonia from an aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$, to a reaction medium where the precipitation of $AlPO_4$, from $AlCl_3 \cdot 6H_2O$ and H_3PO4 (85 wt%) aqueous solutions, was initiated by the addition of aqueous ammonia. The total precipitation of $AlPO_4$ is then carried out by addition of aqueous ammonia. The sample was dried at 393 K for 24 h, screened at 200–250 mesh, and then calcined in air at 923 K for 3 h (APAl-A-923). A sample of aluminum hydroxide, obtained as above, was calcined for 3 h at 923 K (γ-Al_2O_3) or 1273 K (α-Al_2O_3).

Surface Properties

Specific surface areas were obtained by applying the BET method. Pore size analysis was made using the "corrected modelless" method developed for the analysis of mesopores (*39*).

Surface acidity (or basicity) at various acid (or basic) strengths was determined by adsorbing organic bases (or acids) with dif-

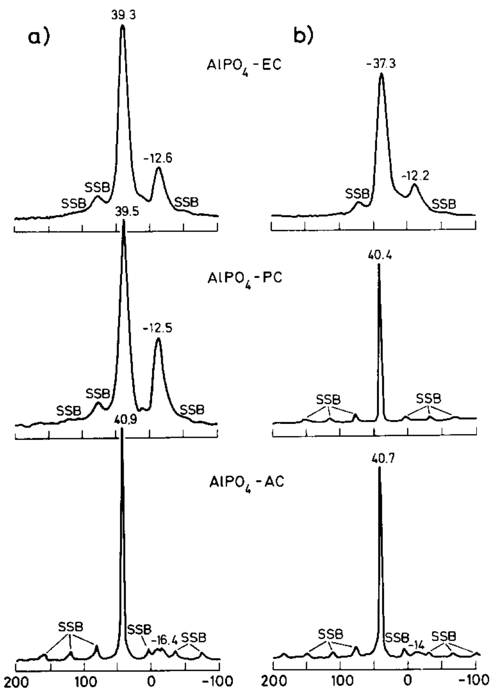

FIG. 1. ^{27}Al MAS-NMR spectra (104.26 MHz) of $AlPO_4$ catalysts prepared from aluminum chloride and ethylene oxide, propylene oxide, or aqueous ammonia as precipitation medium ($AlPO_4$-EC, $AlPO_4$-PC, and $AlPO_4$-AC). (a) Samples heated at 923 K. (b) Samples heated at 1073 K. SSB denotes spinning sidebands.

ferent pK_a values and steric hindrance following a spectrophotometric method described elsewhere (*27, 40, 41*). In addition, the surface acid properties were determined using a dynamic method that consists of determining the catalytic activity of $AlPO_4$ in CSI. This test reaction requires the presence of strong surface acid sites and it is one of the simplest reactions in studying stronger acid sites on solid catalysts (*42*).

Details on preparation as well as on the characterization of all the catalysts have been previously described (*28–35, 43*). In Table 1 are collected textural properties, crystallinity, and acidity of the different $AlPO_4$ samples. Acidity is expressed through the apparent rate constants (kK) and selectivity factors (σ) of the CSI process since these parameters are a function of the stronger acid site number. Thus, the larger the number of strong surface acid sites, the higher would kK and σ be expected to be. Moreover, the results compiled in Table 1 are part of a larger study on $AlPO_4$ characterization that we have recently conducted and whose results have been extensively described elsewhere (*26–35, 43*).

NMR Spectroscopy

^1H, ^{27}Al, and ^{31}P NMR spectra were recorded at 400.13, 104.26, and 161.98 MHz, respectively, with a Bruker MSL-400 spectrometer. The external magnetic field used was 9.4 T. All measurements were carried out at room temperature and the samples were spun about the magic angle (54° 44′ with respect to the magnetic field) in the range 4–4.5 kHz. ^1H and ^{31}P spectra were recorded after $\pi/2$ pulse excitation (3 and 2.6 μs, respectively) and the intervals between successive accumulations (3 and 6 s) were chosen to avoid saturation effects. ^{27}Al spectra were obtained after a 2-μs pulse (π/4 pulse) and a recycling time of 2 s. Cross-polarized proton-decoupled ^{31}P MAS-NMR spectra were obtained with a time contact of 2 ms, a decoupling time of 20 ms, and a recycle time of 6 s. TMS and solutions of H_3PO_4 and $Al(H_2O)_6^{3+}$ were used as external standard references for the proton, phosphorus, and aluminum chemical shifts. To preserve quantitative analysis no mathematical procedures of NMR signal treatment, such as multiplication by an exponential function, were used.

RESULTS

^{27}Al NMR Spectroscopy

^{27}Al MAS-NMR spectra of aluminum orthophosphates are formed by two major components at +40 and −12 ppm and a series of small bands (SSB components) associated with the spinning of the sample (Figs. 1–3).

Thermal treatment of the samples, in most cases, results in elimination of the −12-ppm component and narrowing of the +40-ppm component (Fig. 1). Most of orthophosphate samples, when heated at temperatures

TABLE 1

Textural Properties, Crystallinity, and Apparent Rate Constants (kK) at 673 K for Cyclohexene Skeletal Isomerization of $AlPO_4$ Catalysts

Catalysts	S_{BET} ($m^2 g^{-1}$)	V_P ($ml g^{-1}$)	r_P (nm)	Crystallinity[a]	$kK \times 10^6$ ($mol atm^{-1} g^{-1} s^{-1}$)	σ[b]
$AlPO_4$-PC-773	151	0.68	9.0	Amorphous	7.7	1.1
$AlPO_4$-PC-923	229	0.75	6.6	Amorphous	10.9	1.5
$AlPO_4$-PC-1073	11	—	—	Amorphous	—	—
$AlPO_4$-EC-923	242	0.52	4.3	Amorphous	23.3	1.9
$AlPO_4$-EC-1073	263	0.28	2.2	Amorphous	22.8	2.2
$AlPO_4$-AC-923	109	0.48	8.8	am + α-cri + tri	3.1	1.3
$AlPO_4$-AC-1073	81	0.46	11.4	am + α-cri + tri	2.0	1.1
$AlPO_4$-AN-773	196	0.76	7.7	Amorphous	6.8	1.7
$AlPO_4$-AN-923	183	0.74	8.0	Amorphous	6.3	1.5
$AlPO_4$-AN-1073	9	—	—	α-cri	6.7	1.5
$AlPO_4$-AS-773	37	0.12	6.6	tri	144.8	3.8
$AlPO_4$-AS-923	22	—	—	tri	81.6	3.0
$AlPO_4$-AS-1273	16	—	—	tri	0.7	1.0
$AlPO_4$-PC-3F-573	64	0.47	8.9	Amorphous	7.3	3.2
$AlPO_4$-PC-5Li-573	92	0.50	11.5	Amorphous	0.5	1.6
$AlPO_4$-PC-1S-573	60	0.32	10.6	Amorphous	14.3	2.5
$AlPO_4$-PC-3S-573	40	0.23	11.5	am + tri[c]	125.0	4.1
$AlPO_4$-PC-3S-673	46	0.30	13.0	am + tri[c]	66.7	3.6
$AlPO_4$-PC-3S-773	50	0.33	13.2	am + tri[c]	37.8	3.2
$AlPO_4$-PC-5S-573	16	0.05	5.1	tri	2.7	1.2
APAl-A-923	244	0.37	3.1	Amorphous	36.6	4.0

[a] am, amorphous; α-cri, α-cristobalite (Cu$K\alpha$, 2θ = 27°); tri, tridimite (Cu$K\alpha$, 2θ = 23.7°).
[b] Selectivity to 1-methylcyclopentene as the ratio of its fractional conversion to that of 3-methylcyclopentene.
[c] Scarcely found.

above 1073 K, crystallize into α-cristobalite or tridymite polymorphs; the relative proportions of both phases depend on the sample preparation and the aluminum starting salt (*28–31, 35*). ^{27}Al NMR spectra of samples in which each phase is preponderant comprise a single component at 40.6 or 39.2 ppm, respectively (Figs. 1 and 2). This permits the assignment of these components to tetrahedral aluminum sharing oxygens with four tetrahedra of phosphorus. The position of −12-ppm component is characteristic of octahedral aluminum. The strong upfield shift observed in both components with respect to other aluminum oxides is attributed by Muller *et al.* (*44*) to the influence of phosphorus atoms located in the second coordination sphere of aluminum.

In Fig. 2, ^{27}Al MAS-NMR spectra of to an $AlPO_4$-PC-923 sample impregnated with Li^+, F^-, and SO_4^{2-} ions and heated at different temperatures (*29, 31, 35*) are presented. For the same temperature of treatment, the octahedral aluminum increased with the amount of Li ions and decreased with the amount of SO_4^{2-} ions. Analysis of the relative intensity of tetrahedral and octahedral aluminum with the sample preparation and the temperature of thermal treatments will be discussed below (see Table 2).

In Fig. 3 are given ^{27}Al NMR spectra of γ-Al_2O_3 and α-Al_2O_3, obtained when aluminum hydroxide was calcined for 3 h at 923 and 1073 K, respectively, and the APAl-A-923 sample (75:25 wt% $AlPO_4$–Al_2O_3 system). From this figure, it can be observed that the positions of the

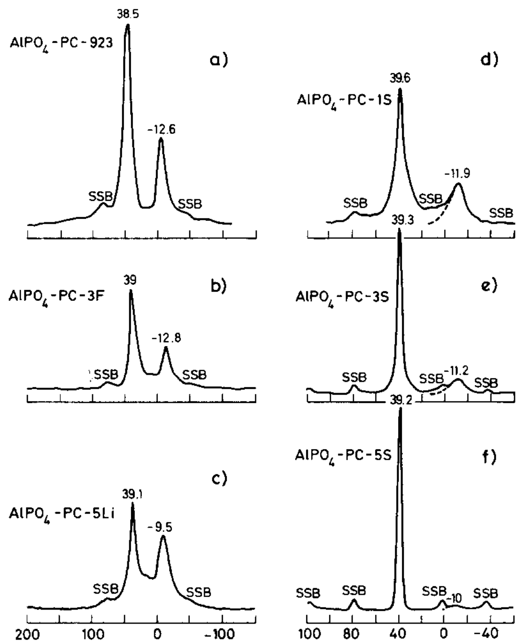

FIG. 2. ^{27}Al MAS-NMR spectra (104.26 MHz) of modified $AlPO_4$–PC catalysts. (a) $AlPO_4$–PC sample heated at 923 K. Separate $AlPO_4$–PC samples were impregnated with (b) 3 wt% F^- and (c) 5 wt% Li^+. (d, e, and f) Samples of $AlPO_4$–PC doped with 1, 3, and 5 wt% SO_4^{2-}. Impregnated samples were subsequently heated at 573 K.

octahedral and tetrahedral components of $AlPO_4$ do not correspond to those of the γ-Al_2O_3 and α-Al_2O_3 phases, showing that Al atoms occupy different sites in each type of sample.

^{31}*P NMR Spectroscopy*

^{31}P MAS-NMR spectra of aluminum orthophosphates comprise one component at −27 ppm and a symmetric set of spinning sidebands (SSB components) (Figs. 4–7). These components narrow during thermal treatment of samples and at 1073 K spectra are composed of two major components at −26.6 and −30 ppm (Fig. 4). The intensity of both components varies with the relative proportions of α-cristobalite and tridymite polymorphs (*44*). In general α-cristobalite phase content is higher; however, the tridymite phase is preponderant in $AlPO_4$-AS samples and in $AlPO_4$ doped with SO^{2-} ions ($AlPO_4$-PC-S) (Figs. 5 and 7). ^{31}P spectra of $AlPO_4$-PC-S and $AlPO_4$-PC-F samples are similar to those of nondoped samples; however, the spectra of the Li-doped sample ($AlPO_4$-PC-Li) present two new components at −18.5 and 10 ppm, indicating the formation of new phases with Li (Fig. 5). These new phases are not observed by XRD (*31*) for treatment temperatures in the range 573–773 K after lithium hydroxide impregnation.

To identify P atoms that bear OH groups, ^{31}P spectra were recorded with the CP-MAS technique. In this method, the transfer of polarization from the ^{1}H to the ^{31}P signal is produced by irradiation of two nuclei at their respective resonance frequencies with the Hartman–Hann condition (*45, 46*). Rotation of the sample and Irradiation of protons during ^{31}P signal acquisition reduce H–P dipolar interactions and narrow the phosphorus signal. Analysis of ^{31}P CP-MAS NMR spectra of orthophosphate samples treated at increasing temperatures shows a progressive decrease in intensity of the phosphorus signal during dehydroxylation of the sample (Figs. 6 and 7). In the case of $AlPO_4$-AS or

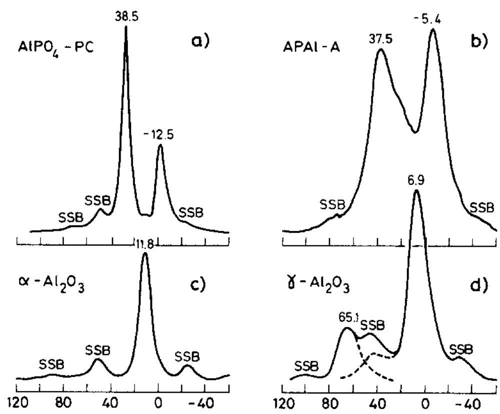

FIG. 3. ^{27}Al MAS-NMR spectra (104.26 MHz) of (a) $AlPO_4$–PC catalyst heated at 923 K and (b) the system $AlPO_4$–Al_2O_3 (75 : 25 wt%) prepared as indicated under Experimental. (c) α-Al_2O_3 and (d) γ-Al_2O_3 phases obtained after heating $Al(OH)_3$ at 1073 and 923 K.

TABLE 2

Chemical Shift Values, Ratio of Intensities Al_t/Al_0, and $P_{CP\text{-}MAS}/P_{MAS}$ Corresponding to ^{27}Al and ^{31}P NMR Signals of $AlPO_4$ Samples

Catalysts	d_{Al} (ppm)		Al_t/Al_0	d_P (ppm)	$P_{CP\text{-}MAS}/P_{MAS}$
$AlPO_4$-PC-773	+38.4	−13.3	2.3	−26.2	1.8
$AlPO_4$-PC-923	+39.5	−12.5	2.4	−27.4	1.6
$AlPO_4$-PC-1073	+40.4		>100	−26.5 −29.2	0.05
$AlPO_4$-EC-923	+39.3	−12.6	3.9	−26.4	1.7
$AlPO_4$-EC-1073	+37.3	−12.2	4.4	−26.4	1.1
$AlPO_4$-AC-923	+40.8	−16.4	20.5	−26.6 −29.8	0.2
$AlPO_4$-AC-1073	+40.7	−14.0	50.0	−26.6 −29.7	0.1
$AlPO_4$-AN-773	+39.5	−11.8	1.3	−26.3	1.6
$AlPO_4$-AN-923	+38.6	−13.6	3.0	−26.7	1.3
$AlPO_4$-AN-1073	+40.6		>100	−26.8 −29.8	0.0
$AlPO_4$-AS-773	+38.7		40.0	−30.4	0.1
$AlPO_4$-AS-923	+39.0		>100	−30.0	0.0
$AlPO_4$-AS-1273	+39.0		>100	−29.7	0.0
$AlPO_4$-PC-3F-573	+39.0	−12.8	2.4	−27.5	1.5
$AlPO_4$-PC-5Li-573	+39.1	− 9.5	1.4	+10.0 −18.2 −27.0	1.1
$AlPO_4$-PC-1S-573	+39.6	−11.7	3.2	−28.1	1.6
$AlPO_4$-PC-3S-573	+39.3	−11.2	10.0	−29.9	0.8
$AlPO_4$-PC-3S-673	+39.4	−10.9	11.0	−29.9	1.0
$AlPO_4$-PC-3S-773	+39.5	−11.5	13.0	−29.6	0.8
$AlPO_4$-PC-5S-573	+39.2	−10.0	57.0	−29.9	0.05
γ-Al_2O_3	+65.1	+ 6.9	0.3	—	—
α-Al_2O_3		+11.8	—	—	—
APAl-A-923	+37.5	− 5.4	0.9	−24.8	1.8

$AlPO_4$-PC-S samples a new component at −21 ppm is detected under these conditions (Fig. 7). The ratios of the intensity values of ^{31}P signal recorded with single-pulse and CP-MAS techniques are given in Table 2.

^1H NMR Spectroscopy

To analyze the amount and location of OH groups, ^1H spectra of aluminum orthophosphate samples were recorded after different thermal treatments. ^1H NMR spectra are composed of a principal component at +5.3 ppm and a series of small spinning sidebands (SSB in Figs. 6 and 7). During this treatment a progressive decrease in the intensity of the ^1H signal is observed with temperature of treatment (Figs. 6 and 7). In most spectra, only one component is detected at +5.3 ppm; however, in spectra of $AlPO_4$-AS or $AlPO_4$-PC-S samples, two components at +5.3 and −2.6 ppm were resolved, their relative intensities varying with the thermal treatment applied.

DISCUSSION

The analysis of ^{27}Al, ^{31}P, and ^1H spectra of aluminum orthophosphate samples has permitted us to show the influence that sample preparation has on the local structure of samples. In particular, $AlPO_4$-PC, $AlPO_4$-AN, and $AlPO_4$-EC samples present a considerable amount of OH and a low crystallinity. In contrast, for $AlPO_4$-AC and $AlPO_4$-AS samples, the amount of OH is smaller and the crystallinity higher. In the first group of samples, the crystallinity increases with the temperature of treatment. As reported for other aluminum phosphates by Blackwell and Patton, this fact parallels the elimination of the H_2O/OH groups and the octa-

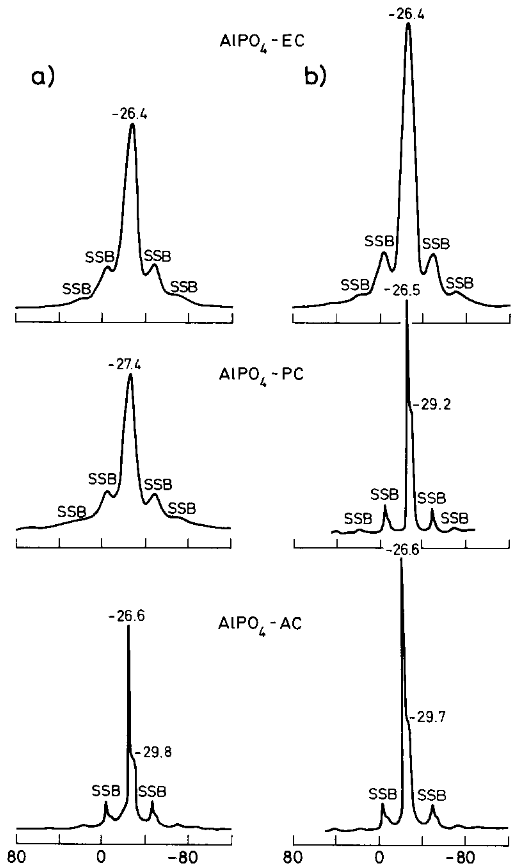

FIG. 4. ^{31}P MAS-NMR spectra (161.98 MHz) of $AlPO_4$ catalysts prepared from aluminum chloride and ethylene oxide, propylene oxide, or aqueous ammonia as precipitation medium ($AlPO_4$-EC, $AlPO_4$-PC, and $AlPO_4$-AC). (a) Samples heated at 923 K. (b) Samples heated at 1073 K.

hedral aluminum of the sample (*37*). In this process tetrahedral aluminum and phosphorus signals narrow considerably. However, in the case of $AlPO_4$ samples obtained with ethylene oxide, the amount of OH and octahedral aluminum at 1073 K is similar to that of the same sample heated at 923 K, indicating that the crystallization process is considerably delayed in this sample.

In samples heated at 1073 K, ^{31}P spectra comprise two components at -26.5 and -30 ppm, whose intensities vary with the relative proportions of α-cristobalite and tridymite polymorphs in the $AlPO_4$ samples. From the lack of variation in chemical shift values of ^{31}P and ^{27}Al signals during thermal treatment, it can be concluded that during crystallization, the coordination and cationic environment of phosphorus do not change appreciably and that eliminated OH groups are located mainly in the octahedra of aluminum. After dehydroxylation, each aluminum is surrounded by four phosphorus and the final structure of $AlPO_4$ is formed by the regular alternation of Al and P tetrahedra.

From a comparison of ^{27}Al spectra of $AlPO_4$ samples heated between 773 and 1073 K with spectra of γ-Al_2O_3, the positions of the tetrahedral and octahedral Al bands in γ-Al_2O_3 (+65 and +7 ppm) are observed to be very different from those detected in

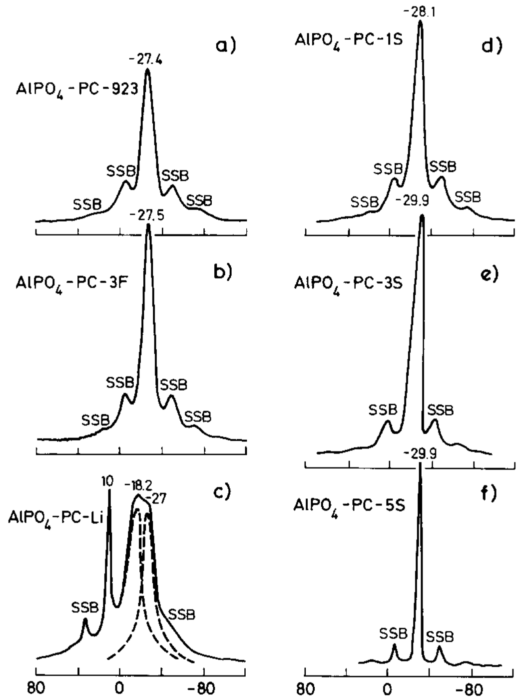

FIG. 5. ^{31}P MAS-NMR spectra (161.98 MHz) of modified $AlPO_4$–PC catalysts. (a) $AlPO_4$-PC sample heated at 923 K. Separated $AlPO_4$-PC-923 samples were impregnated with (b) 3 wt% F^- and (c) 5 wt% Li^+. (d, e, and f) Samples of $AlPO_4$-PC doped with 1, 3, and 5 wt% SO_4^{2-}. Impregnated samples were subsequently heated at 573 K.

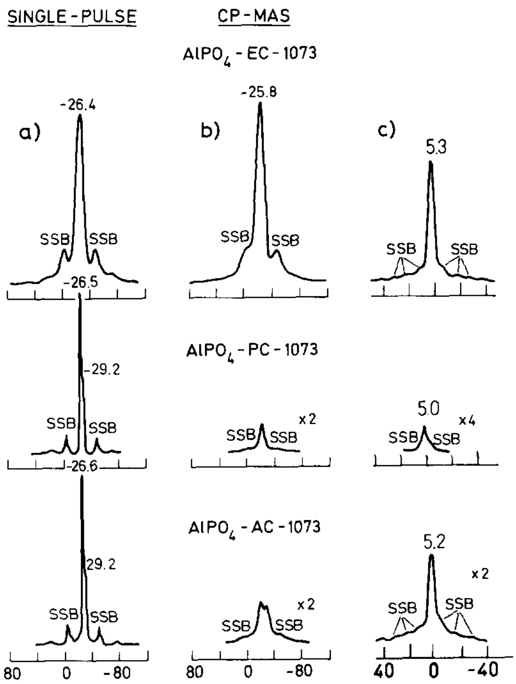

FIG. 6. ^{31}P (161.98 MHz) and ^{1}H (400.13 MHz) spectra of $AlPO_4$-EC, $AlPO_4$-PC, and $AlPO_4$-AC samples heated at 1073 K. (a) ^{31}P spectra recorded with MAS technique. (b) ^{31}P spectra recorded with CP-MAS technique. (c) ^{1}H spectra recorded with MAS technique.

$AlPO_4$ gels (+38 and −12 ppm). Moreover, thermal treatment of samples results in elimination of the octahedral component, and the positions of the tetrahedral Al do not change appreciably. Both facts are characteristic of $AlPO_4$ crystallization and permits one to conclude that Al is not segregated as Al_2O_3 during thermal treatment of $AlPO_4$ samples. Similar results concerning Al and P arrangement in amorphous compounds, obtained during coprecipitation of aluminophosphate catalysts with different P/Al ratios, have been reported by Cheung *et al.* (*47*).

To determine the influence of additives on the local structure of $AlPO_4$ samples different amounts of $(NH_4)_2SO_4$, NH_4F, and LiOH have been added to $AlPO_4$-PC sample heated at 923 K. Analysis of the spectra of samples heated between 573 and 773 K has permitted us to show that, for the same temperature, the amounts of OH and octahedral Al decrease considerably with the amount of SO_4^{2-} ions (Fig. 2). At the same time the position of the ^{31}P component moves from −26.4 in $AlPO_4$-PC-923, to −28.1 ppm in the $AlPO_4$-PC-1S-773 sample, to finally reach the value of −29.9 ppm characteristic of $AlPO_4$-AS samples in the $AlPO_4$-PC-5S-773 sample (Fig. 5). This process parallels the decrease in linewidths in the ^{31}P and ^{27}Al spectra, showing the influence that SO_4^{2-} ions have in crystallization and in determining the polymorph adopted (tridymite) by $AlPO_4$ samples.

Addition of 5 wt% Li to $AlPO_4$-PC-923 sample is responsible for the strong modifications produced in ^{31}P and ^{27}Al spectra of the sample $AlPO_4$-PC-5Li-573; in particular, the amount of octahedral Al increases considerably and two new lines at 10 and −18 ppm are detected in the ^{31}P signal (Fig. 5c). The position of the first line is characteristic of the Li_3PO_4 phase and the second must correspond to a gel with a composition intermediate between those of $AlPO_4$ and Li_3PO_4, in which P atoms share oxygens with Al and Li cations. Both observations demonstrate clearly that Li incorporation produces strong rearrangements in the local structure of aluminum orthophosphate sample during thermal treatments, producing first the segregation of P and Li in an amorphous Li_3PO_4 phase (no XRD patterns) and then the stabilization of the octahedral coordination of Al in the remaining phase. On the other hand, incorporation of F^- into $AlPO_4$-PC gels does not change the local structure of starting gels; the spectra of samples heated at 923 K are very similar to those obtained for nondoped samples and could indicate that F substitutes for OH groups in the octahedra of aluminum.

As concerns our understanding of catalytic activity, it is interesting to study OH distribution in different samples. In general, the samples with higher activity in CSI correspond to samples in which the concentration of strong acid sites is higher. Several authors claim that Brønsted and Lewis cen-

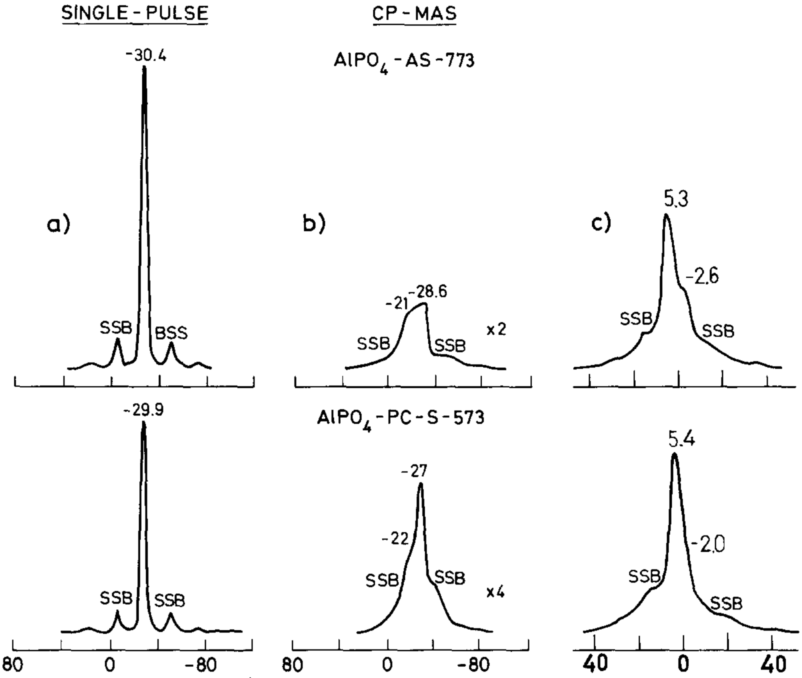

FIG. 7. ^{31}P (161.98 MHz) and ^{1}H (400.13 MHz) spectra of samples prepared from aluminum sulfate ($AlPO_4$-AS) and $AlPO_4$-PC samples doped with 3 wt% SO_4^{2-} ($AlPO_4$-PC-3S) after heating at 773 and 573 K, respectively. (a) ^{31}P spectra recorded with MAS technique. (b) ^{31}P spectra recorded with CP-MAS technique. (c) ^{1}H spectra recorded with MAS technique.

ters exist in these samples; in the case of Brønsted acidity it would be due to OH groups bonded to P atoms (*48*). Analysis of ^{1}H NMR spectra has permitted the identification of two components at +5.3 and −2.6 ppm. The first band is the most intense and decreases strongly with thermal treatment of the sample, which permits its assignment to OH groups associated with octahedra of aluminum (Fig. 6). In aluminum orthophosphates obtained from $Al_2(SO_4)_3$ ($AlPO_4$-AS samples) or those doped with $(NH_4)_2SO_4$ and subsequently heated between 573 and 773 K ($AlPO_4$-PC-S samples), detection of the second component is favored; at higher temperatures, the intensity of this band decreases but more slowly than that of +5.3 ppm, indicating for the latter a higher thermal stability (Fig. 7). On the basis of these observations, this component could be assigned to OH groups bonded to P atoms, in agreement with infrared data reported by Peri for the same system (*48*). Moreover, according to quantum-chemical theoretical investigation on acidic active sites on $AlPO_4$ catalysts, performed on both closed (*49, 50*) and opened (*51*) $AlPO_4$ clusters, the P–OH groups represent the most stable Brønsted acid sites on $AlPO_4$ surfaces. At the same time, P–OH–Al (bridged hydroxyl groups) exhibit the strongest acidity. However, their relative surface concentration with respect to P–OH is very low and, therefore, the Brønsted acidity of $AlPO_4$ is probably determined by P–OH sites. In addition, the proton abstraction energies for Al–OH groups indicate that these centers cannot be considered as strong Brønsted sites but, however, might enhance the Brønsted acidity of P–OH groups through H bonding (*51*).

In $AlPO_4$ samples with Al/P = 1, the amount of OH groups bonded to P atoms is very small (*36*); however, the presence of SO_4^{2-} ions during the synthesis or their incorporation, as $(NH_4)_2SO_4$, on subsequent treatments seems to increase the number of this type of OH group. To confirm this assignment, a study of the ^{31}P NMR signal has been carried out with CP-MAS technique. In this technique the detection of components due to P atoms coordinated with OH groups is enhanced in relation to P atoms surrounded by four Al. Analysis of ^{31}P spectra recorded with this technique, for different temperatures of treatment, shows a progressive decrease in intensity with dehydroxylation of the sample, indicating that the largest proportion of P tetrahedra are hydrogen bonded to OH coordinated with octahedral aluminum in starting gels. However, in $AlPO_4$-AS samples heated at 773 K, a new line of low intensity was detected in CP-MAS ^{31}P spectra, which supports the assignment of this component to P atoms bonded to OH groups (Fig. 7). The same observation has been reported in $AlPO_4$-5 samples, synthesized by Union Carbide (*38*), in which the acidity and catalytic activity is important. Samples doped with $(NH_4)_2SO_4$ ($AlPO_4$-PC-S) and heated between 573 and 773 K are an intermediate case. The location of these groups at the surface of the $AlPO_4$ sample would explain the catalytic activity for isomerization reactions in which acid character is required. Thus, samples with higher surface OH groups, and especially those on the P atom, correspond to samples with higher apparent rate constants and selectivities in CSI.

CONCLUSIONS

The use of multinuclear high-resolution NMR techniques, including the CP-MAS method, has permitted monitoring of the modifications produced in the local environment of atoms during thermal treatment of $AlPO_4$ samples.

Heating of samples between 773 and 1273 K results in dehydroxylation of the sample and progressive elimination of the octahedral aluminum. This is accompanied by the narrowing of ^{31}P and ^{27}Al signals which indicates the progressive transformation of amorphous into crystalline $AlPO_4$ samples. In these transformations, the chemical environment of P atoms does not change appreciably, suggesting that OH groups are coordinated mainly to Al atoms. From the analysis of ^{27}Al NMR spectra the formation of Al_2O_3 during thermal treatment of $AlPO_4$ gels has been also excluded.

The crystal structure adopted by $AlPO_4$ samples calcined at 1073 and/or 1273 K depends on the aluminum salt used in the synthesis and the foreign ions introduced by impregnation of the starting aluminum orthophosphates. In general, the α-cristobalite polymorph is preponderant; however, the tridymite phase is favored in $AlPO_4$-AS samples and in $AlPO_4$ doped with SO_4^{2-} ions ($AlPO_4$-PC-S). Incorporation of Li into $AlPO_4$ samples results in strong atomic rearrangements and the formation of amorphous Li_3PO_4 and an amorphous Li phase in which the octahedral coordination of aluminum is stabilized.

Comparative analysis of ^{31}P CP-MAS and ^{1}H spectra, recorded after different thermal treatments, has permitted the detection of two small bands in the ^{31}P and ^{1}H spectra of $AlPO_4$-AS samples that have been assigned to OH groups bonded to P atoms. The concentration of this OH type in the surface of these samples is low, but the OH groups are responsible for the acidic properties of these materials. Incorporation of $(NH_4)_2SO_4$, by the incipient wetness method, results in formation of this type of OH during thermal treatment of the sample, which modifies strongly the physico/chemical properties of these catalysts, thus increasing the catalytic activity for CSI. So, the catalytic activity of $AlPO_4$ catalysts in CSI can be relatively well interpreted in terms of the surface OH groups of the catalysts.

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