

ARTICLES

Nitrogen Incorporation in an $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ Amorphous Solid Studied with ^{27}Al and ^{31}P NMRStéphanie Delsarte,^{*,†} Paul Grange,[†] Tiehong Chen,[‡] Piet Grobet,[‡] and Pierre Jacobs[‡]

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Amorphous nitrided galloaluminophosphate “AlGaPON” catalysts with nitrogen contents varying from 0 to 23.3 wt % were obtained by nitriding an $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ precursor under ammonia flow at 750 °C in a tubular furnace. Because these AlGaPON catalysts present very promising properties to the field of acid–base catalysis, an attempt was made to describe the structural changes induced by nitrogen incorporation in their structure so as to link their catalytic properties to their short-range structure. In this paper, we compare results previously obtained using X-ray absorption spectroscopy (XAS) and X-ray photoelectrons spectroscopy (XPS) on a series of five samples with increasing nitrogen content with new ^{31}P MAS NMR, ^{27}Al MAS, and ^{27}Al MQ(3Q) MAS results obtained on the same samples. ^{31}P NMR results confirmed our previous model, which indicated the formation of PO_3N units at the beginning of nitridation, followed by the apparition of PO_2N_2 units in the highly nitrided samples. ^{27}Al NMR results allow us to propose the substitution of oxygen atoms by nitrogen atoms in the first coordination sphere of aluminum, a result that is different from what is observed in nitrided aluminophosphates “AlPON”. This last result is further evidence of the particular influence of gallium atoms in the nitridation process.

Introduction

Solid catalysts obtained by reacting an oxide precursor with flowing ammonia have received increased attention in recent years. These include, not exhaustively, nitrided amorphous silica,^{1,2} nitrided amorphous phosphates (AlPON,^{3–5} AlGaPON,^{6–8} and ZrPON⁹), nitrided amorphous aluminovanadates,¹⁰ nitrided crystalline aluminosilicates,¹¹ and nitrided crystalline aluminophosphates.^{11,12} The role of the ammonia treatment is to prepare catalysts with basic properties due to the formation of terminal $-\text{NH}_2$ groups, bridging $-\text{NH}-$ groups, or $=\text{N}-$ nitride species or through an indirect effect of nitridation on the basicity of structural oxygen atoms or superficial $-\text{OH}$ groups. Nitridation of amorphous AlPO_4 ,^{3,4} $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$,^{7,8} and $\text{Zr}_{0.9}\text{PO}_{4.3}$,⁹ which are much more reactive toward ammonia than crystalline precursors, was possible with treatment at temperatures ranging from 500 to 800 °C. The resulting AlPON, AlGaPON, and ZrPON proved to be active for the Knoevenagel condensation between benzaldehyde and malonitrile, a reaction typically catalyzed by bases. The AlGaPON, which are at the center of this article, benefit from the ability of gallium to recombine hydrogen in the molecular form during dehydrogenation reactions,¹³ in addition to their basic properties.

To study the relation between the short-range structure of the nitrided phosphates and their catalytic properties, several attempts were made to describe the structural changes induced

by nitrogen incorporation in their structure. Those studies are complicated by the fact that classical X-ray diffraction cannot be used with amorphous solids. The first model was presented for AlPON in the late 1990s. Benitez et al.¹⁴ combined X-ray photoelectron spectroscopy (XPS) with mass spectrometry temperature-programmed desorption (TPD-MS) experiments to characterize amorphous AlPO_4 and six nitrided aluminophosphates AlPON and concluded that at the beginning of nitridation PO_3N tetrahedra were preferentially formed and then in a second nitridation stage PO_2N_2 units were formed. In the opinion of these authors, nitrogen cannot be incorporated in AlPON in the first coordination sphere of aluminum atoms, and nitridation induces the segregation of an Al_2O_3 -type phase.¹⁵

The structural changes of AlGaPON induced by nitridation in the first coordination sphere of Al, Ga, and P atoms were characterized previously¹⁶ by X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) on a series of samples with nitrogen content varying from 5.3 to 23.3 wt %. We also performed nitrogen-K ELNES analysis to get information on the type of bonding around nitrogen atoms in AlGaPON.¹⁶

In the present article, we characterized the same series of AlGaPON samples as the one studied in ref 16 by solid-state NMR, which is also a very valuable technique with which to study local arrangements of atoms in amorphous solids. First, we will present and discuss ^{31}P MAS NMR, ^{27}Al MAS, and ^{27}Al MQMAS spectra of AlGaPON as a function of their nitrogen content. As will be shown in the article, we failed to get valuable information on the environment of gallium atoms using ^{71}Ga MAS NMR. Then we will compare our NMR results

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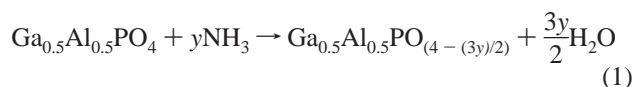
TABLE 1: Characteristics of the Oxide and Oxynitride $\text{AlGaPO}(\text{N})$ Powders

sample	composition	nitridation time (h)	weight nitrogen content (wt %)	atomic nitrogen content (%)	surface area (m^2/g)
AG9	$\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$				240
AG9N2	$\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_{3.22}\text{N}_{0.52}$	3	5.3	9.1	150
AG9N4	$\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_{2.43}\text{N}_{1.04}$	8	11.0	19.0	160
AG9N5	$\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_{1.81}\text{N}_{1.46}$	16	15.9	27.7	145
AG9N6	$\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_{0.94}\text{N}_{2.04}$	89	23.3	41.0	170

with the XPS and XAS experiments performed on the same samples. By comparison of our results with the structural model proposed for AlPON , we will discuss the influence of gallium atoms on the structural properties of AlGaPON .

Experimental Section

Materials. The high surface area, amorphous $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ precursor was synthesized by a process developed by Kearby¹⁷ for aluminophosphates and adapted for the $(\text{Al}, \text{Ga})\text{PO}$ compositions.⁶ A solution of adequate amounts of Ga^{3+} , Al^{3+} , and 2 M H_3PO_4 ($\text{P}/(\text{Ga} + \text{Al})$ and Ga/Al atomic ratios of 1) was cooled at 0 °C in a dry ice–alcohol bath. Then, a large excess of propylene oxide was slowly added under vigorous stirring. After a few hours at room temperature, a translucent gel was produced. The gel was washed with isopropanol and dried at 110 °C. The resulting powder was sieved ($\phi < 100 \mu\text{m}$) and calcined in air at 650 °C. The precursor, placed in the isothermal region of a tubular furnace, was activated under ammonia flow ($30 \text{ L}\cdot\text{h}^{-1}$) at 750 °C. This reaction allows the progressive substitution of oxygen by nitrogen according to eq 1.



Various nitrogen contents were obtained by modifying the time of nitridation from 3 to 89 h. At the end of the activation process, the samples were cooled to room temperature under a pure, dry nitrogen flow.

The total nitrogen content of the AlGaPON samples was determined by titration with a sulfuric acid solution of the ammonia liberated in alkaline digestion at 400 °C with melted KOH .¹⁸ The specific surface area was measured by the single-point BET method in a Micromeritics Flowsorb II 2300 apparatus after 20 min of degassing at 250 °C. The nitridation conditions and the main characteristics of the studied AlGaPON are presented in Table 1. The compositions of the nitrided samples presented in Table 1 were established from the total nitrogen content of the samples. Indeed, it has been shown that the Al/Ga and $(\text{Al} + \text{Ga})/\text{P}$ ratios were maintained during nitridation at this temperature and that the weight loss recorded during nitridation corresponds to the replacement of three oxygen atoms by two nitrogen atoms.⁶

Solid-State Nuclear Magnetic Resonance Experiments. ^{31}P MAS NMR experiments were performed on a Bruker AMX-300 spectrometer with a 4-mm ZrO_2 rotor spinning at 10 kHz. The repetition time is 30 s, and the ^{31}P chemical shift is referenced to 85% H_3PO_4 . A BRUKER DRX400 spectrometer (9.4 T) was used to record the ^{27}Al MAS NMR and MQMAS spectra. For the 1D ^{27}Al MAS NMR experiments, a 0.3- μs pulse with an rf field of around 150 kHz was applied. The repetition time was set to 0.2 s, and 3 000 scans were accumulated. An aqueous solution of $\text{Al}(\text{NO}_3)_3$ is used as the shift reference. The MAS frequency was 20 kHz for all of the aluminum measure-

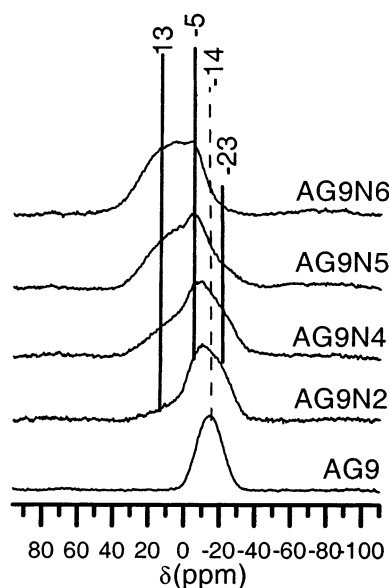
 ^{31}P 

Figure 1. ^{31}P MAS NMR spectra of AlGaPON oxynitrides as a function of nitrogen content.

ments. The ^{27}Al 2D MQ(3Q) MAS NMR spectra were obtained using the three-pulse, amplitude-modulated split- t_1 sequence.¹⁹ After each increment of t_1 , the phase of the first pulse was increased by 30°, and TPPI was applied in the 2D Fourier transformation. This pulse sequence directly provides a sheared spectrum that contains isotropic resolution along the F1 dimension. For the MQ measurements, 128 spectra were acquired in the F1 dimension. An increment of 5 μs between two successive spectra was used. The same BRUKER DRX400 spectrometer was used to record the ^{71}Ga MAS spectra. For the Bloch decay, a pulse of 0.3 μs with an rf field of 120 kHz was applied. The repetition was set to 0.3 s, and 5 000 scans were accumulated. An aqueous solution of $\text{Ga}(\text{NO}_3)_3$ was used as the shift reference. The MAS frequency was also 20 kHz.

Results

^{31}P MAS NMR Spectra. Figure 1 presents the ^{31}P MAS NMR spectra recorded on the AlGaPON series of samples with increasing nitrogen content. The characteristics are presented in Table 1. For the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ precursor (AG9), a single resonance signal is observed at -14 ppm.

As nitrogen is added to the precursor, the resonance signal at -14 ppm is shifted upfield (around -23 ppm), and its intensity decreases. Simultaneously, two other peaks appear, centered around -5 and 13 ppm. The positions of the three peaks, as well as their relative intensities, were obtained using the Bruker software 1D WINNMR and WINFIT programs. As an example, we present in Figure 2 the experimental and simulated MAS NMR spectra of the AG9N2 (5.3 wt % N) and AG9N6 (23.3 wt % N) samples.

The evolution of the relative intensities of the three peaks as a function of nitrogen enrichment is shown in Figure 3. The estimated error in the peak area resulting from the deconvolution is estimated to be less than 5%.

^{27}Al MAS NMR and MQMAS Spectra. Figure 4 presents the ^{27}Al MAS NMR spectra of the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ precursor (AG9) sample, which was exposed to air after synthesis without particular precautions, as well as the same sample dried for 2 h at 200 °C under nitrogen flow. To avoid rehydrating the sample

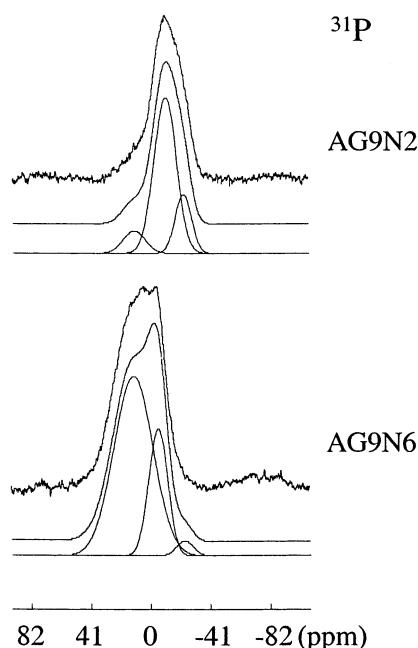


Figure 2. Simulated and experimental ^{31}P MAS NMR spectra of the AG9N2 (5.3 wt % N) and AG9N6 (23.3 wt % N) oxynitrides.

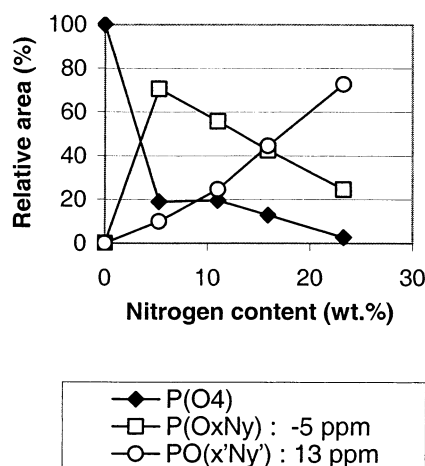


Figure 3. Evolution of the relative areas of the three peaks used to deconvolute the ^{31}P MAS NMR spectra of AlGaPON samples.

prior to analysis, the dehydrated sample was transferred into the MAS NMR rotor under dry nitrogen gas in a glovebox. This treatment has a major influence on the spectra. The fully hydrated sample shows three bands at 37, 9, and -14 ppm, and the band at -14 ppm is dominant. The spectrum of the dried sample is dominated by a band at 33 ppm and shows two shoulders at 5 and -18 ppm. Spectra recorded on the AlGaPON series of samples after drying at 200°C are shown in Figure 5 as a function of nitrogen content. Because the ^{27}Al isotope has a quadrupolar nucleus, the ^{27}Al MAS spectra were not used for quantitative evaluation because of the presence of invisible aluminum. On the sample nitrided for 3 h (AG9N2, 5.3 wt % N), the band at 35 ppm is still dominant, but the contribution of the two bands at 11 and -13 ppm are significantly greater than in the spectra of the precursor.

As the nitrogen content increases, the band at 35 ppm broadens progressively, but its position stays constant. Its height decreases as compared to that of the two bands at 11 and -13 ppm. For nitrogen contents higher than 15.9 wt % (AG9N5 sample), a fourth band appears at 62 ppm.

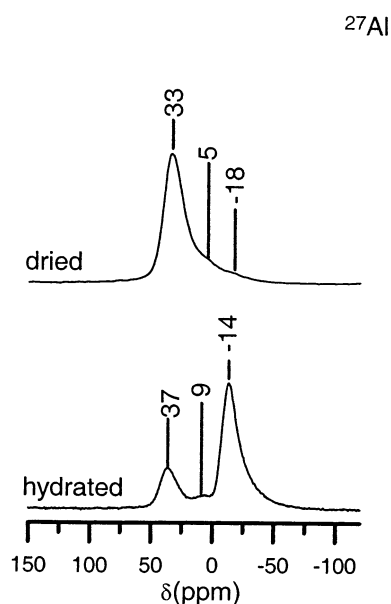


Figure 4. ^{27}Al MAS NMR spectra of the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ precursor prior to and after drying under nitrogen flow for 2 h at 200°C .

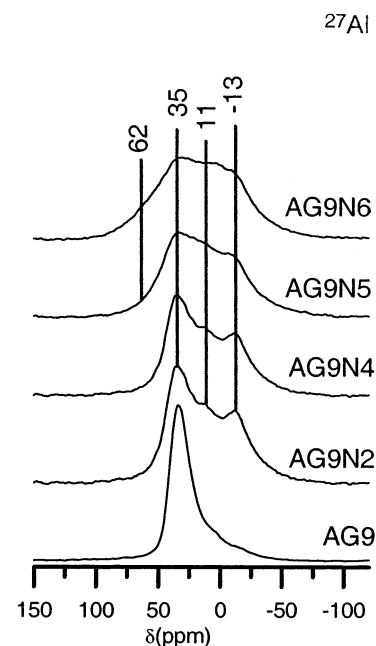


Figure 5. ^{27}Al MAS NMR spectra of AlGaPON oxynitrides as a function of nitrogen content.

The appearance of a new band in the 1D spectra is attested to by the ^{27}Al 2D MQ (3Q) MAS results presented in Figure 6, where signals A, B, and C correspond to the signals at -13 , 11, and 35 ppm of the ^{27}Al MAS NMR spectra (Figure 5), respectively. For the sample with a nitrogen content of 15.9 wt %, there emerged a separate signal D, providing evidence that the 62 ppm signal in the MAS spectra is from a newly formed Al species with increasing nitrogen content in the samples. When the nitrogen content increases to 23.3 wt %, signal D became more obvious; meanwhile, the line width of signals A, B, and C is broadened gradually.

^{71}Ga MAS NMR Spectra. Figure 7 presents the ^{71}Ga MAS NMR spectrum recorded on the hydrated $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ precursor (AG9). The spectrum is noisy, bands are very broad, and the chemical shift cannot be measured with accuracy from these experiments. Hence, we did not record ^{71}Ga MAS NMR spectra

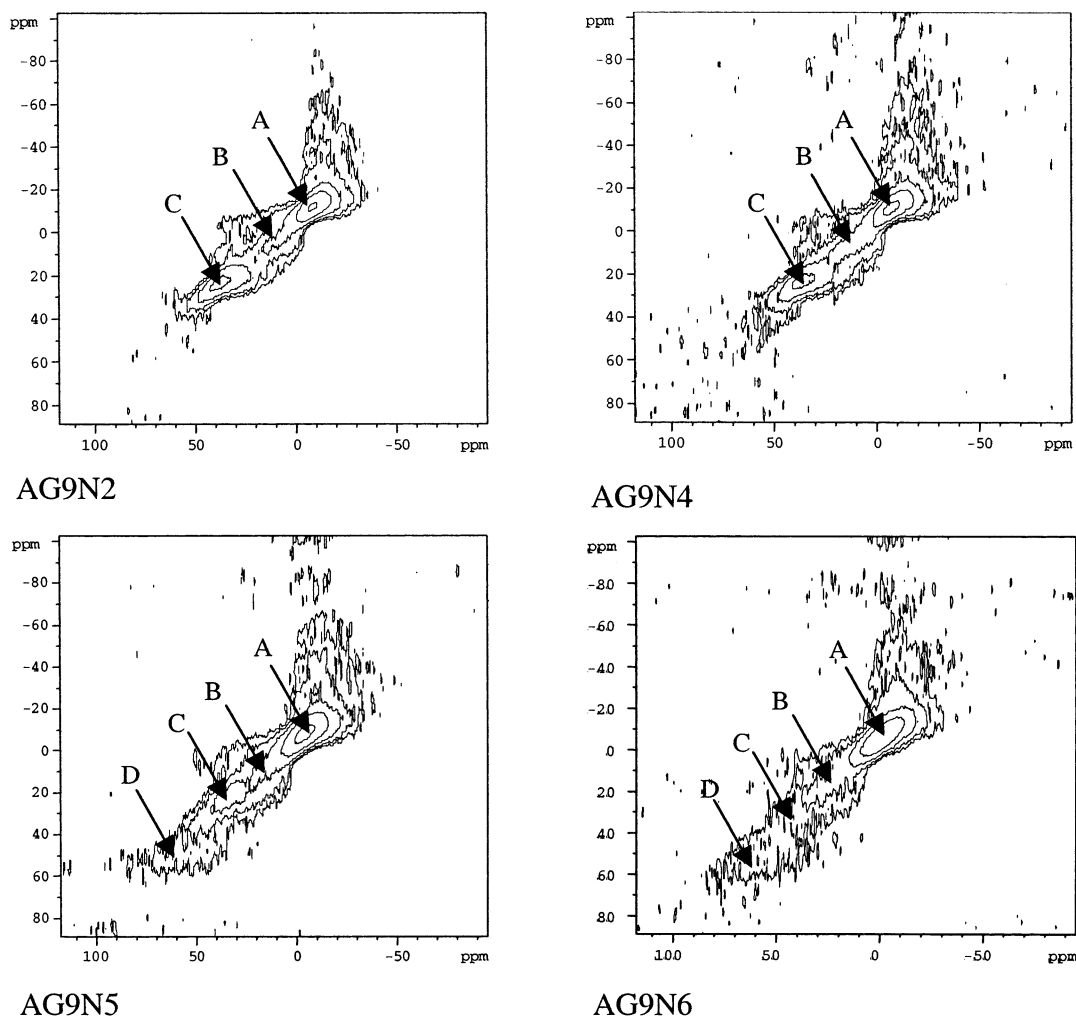


Figure 6. ^{27}Al 2D MQ(3Q) MAS NMR spectra of AlGaPON oxynitrides.

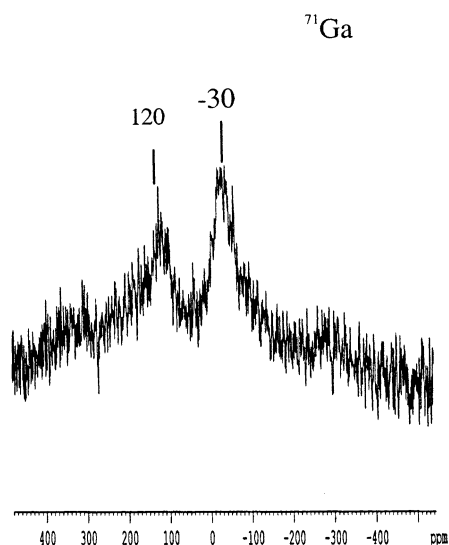


Figure 7. ^{71}Ga MAS NMR spectra of the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ precursor (AG9).

on nitrated samples. This is classical for ^{71}Ga MAS NMR²⁰ because of the strong quadrupolar coupling of the ^{71}Ga nuclei.

However, we can note that the ^{71}Ga MAS NMR spectrum is roughly similar to the ^{27}Al MAS NMR spectrum recorded on the same sample (Figure 4) and that it presents two bands around 120 and -30 ppm. The two observed bands surely correspond

to two different coordination states of Ga in the hydrated precursor, possibly $\text{Ga}(\text{O}_4)$ tetrahedra and $\text{Ga}(\text{O}_6)$ octahedra, respectively. For comparison, in oxide compounds, $\text{Ga}(\text{O}_4)$ groups give rise to a signal around 200 ppm, and $\text{Ga}(\text{O}_6)$ groups appear in the spectra around 0 ppm.²¹ Table 2 presents a summary of the MAS NMR results obtained on the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ precursor and on AlGaPON.

Discussion

1. Interpretation of the NMR Results. ^{31}P MAS NMR. The value of -14 ppm observed in the ^{31}P spectrum of the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ precursor (Figure 1) is intermediate between those described in the literature for $\text{P}(\text{OAl})_4$ in amorphous (ca. -25 ppm⁵) or crystalline (ca. -30 ppm¹²) AlPO_4 and for the tetrahedrally coordinated P atoms of $\text{P}(\text{OGa})_4$ in amorphous (ca. -8 ppm²²) or crystalline (ca. -11 ppm²³) GaPO_4 . In fact, as aluminum is replaced by gallium in the second coordination sphere of P atoms in phosphates, the ^{31}P signal progressively shifts downfield. This has been demonstrated by recording the ^{31}P signal in a series of seven $\text{Al}_x\text{Ga}_{(1-x)}\text{PO}_4$ samples with various Al/Ga ratios, synthesized according to the process developed by Kearby¹⁷ using propylene oxide as a gel-forming agent, as in the present article. In the latter study, a comparison of the width at medium height of the ^{31}P signal in AlPO_4 (~ 2.41 kHz) and GaPO_4 (~ 2.25 kHz) and in the mixed $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ (~ 2.82 kHz) revealed the presence of a randomized distribution of $\text{P}(\text{OAl}_{(4-x)}\text{Ga}_x)$ sites rather than a single $\text{P}(\text{OAl}_2\text{Ga}_2)$ type

TABLE 2: Summary of the ^{31}P ,^a ^{27}Al ,^b and ^{71}Ga ^b MAS NMR Results

sample	^{31}P	^{31}P	^{31}P	^{27}Al	^{27}Al	^{27}Al	^{27}Al	^{71}Ga	^{71}Ga
AlGaPO	-14			33	5	-18		120	-30
AlGaPON	-23	-5(9) ^c	13(27) ^c	35	11(22) ^d	-13(46) ^d	62(29) ^{d,e}		

^a Values given for ^{31}P NMR results from the simulation of the spectra using the Bruker software 1D WINNMR and WINFIT programs. ^b Values given for ^{27}Al and ^{71}Ga are unfitted chemical shifts. ^c Relative shift from the $\text{P}(\text{O}_4)$ resonance at -14 ppm in the precursor. ^d Relative shift from the $\text{Al}(\text{O}_4)$ resonance at 33 ppm in the precursor. ^e Resonance observed in the spectra when the nitrogen content reaches 15.9 wt %.

of site around phosphorus atoms in the mixed precursor.²² A deconvolution of the spectra recorded on the nitrided samples (Figure 2) reveals that the resonance signal observed at -14 ppm in the precursor is shifted upfield as nitrogen is incorporated into the network. We interpret this upfield shift as evidence that the phosphorus atoms bound to four oxygen atoms in AlGaPON contain a high proportion of aluminum atoms in their second coordination sphere rather than gallium. In a previous article, we proposed that Ga-N-P bonds preferentially replace Ga-O-P bonds rather than Al-O-P bonds.¹⁶ If this is correct, then one should observe a higher aluminum/gallium ratio in the second coordination sphere of the phosphorus atoms that remain bonded to four oxygen atoms in AlGaPON and hence a shift of the ^{31}P signal upfield. This is indeed in agreement with the observed shift of the $\text{P}(\text{O}_4)$ resonance from -14 to -23 ppm after nitridation.

After 3 h of nitridation, the signal corresponding to $\text{P}(\text{O}_4)$ tetrahedra is decreased by 80% (see Figure 3), and two new peaks develop around -5 and 13 ppm (Figures 1 and 2). At the early stage of nitridation, the peak at -5 ppm is by far the most intense. However, as the nitrogen content of the samples increases, the intensity of the peak at -5 ppm decreases, and the third peak at 13 ppm grows. Similar experimental results were obtained on a series of amorphous nitrided phosphates AIPON, with nitrogen contents ranging from 2.6 to 22.0 wt %. Those results were presented in detail in ref 5. Briefly, the authors observed in the parent AlPO_4 a signal with a chemical shift around -25 ppm corresponding to tetrahedral $\text{P}(\text{O}_4)$, and the intensity of this band decreases with increasing nitrogen loadings. At low nitrogen content, a second peak centered at a chemical shift of -2 ppm is visible, and for nitrogen contents higher than 15%, a third peak centered at a chemical shift of 10 ppm develops. To assign the peaks appearing upon nitridation, these authors used molecular cluster models to compute the relative shift expected in AIPON between the signal of the $\text{P}(\text{O}_4)$ coordination polyhedra and those of $\text{P}(\text{O}_3\text{N})$ and $\text{P}(\text{O}_2\text{N}_2)$. They calculated relative shifts of 21 and 28 ppm, respectively. They judged that those results agreed sufficiently with their experimental data to propose the replacement of $\text{P}(\text{O}_4)$ coordination polyhedra by $\text{P}(\text{O}_3\text{N})$ at the early stage of nitridation and then, at higher nitrogen content, the appearance of $\text{P}(\text{O}_2\text{N}_2)$ groups in the phosphate network.

Their model agrees quite well with the accepted picture of the changes induced in the first coordination sphere of phosphorus atoms during the ammonolysis of sodium phosphate glasses NaPO_3 . In those glasses, $\text{P}(\text{O}_4)$ tetrahedra appear at -20 ppm, $\text{P}(\text{O}_3\text{N})$ tetrahedra appear at -10 ppm, and $\text{P}(\text{O}_2\text{N}_2)$ tetrahedra appear at 0 ppm.²⁴

In our AlGaPON samples, the relative shifts between the $\text{P}(\text{O}_4)$ peak and the two peaks appearing upon nitridation are equal to 9 and 27 ppm (Table 2). Those values are close to the relative shifts observed experimentally in nitrided phosphate glasses between the signals of $\text{P}(\text{O}_4)$ and $\text{P}(\text{O}_3\text{N})$ coordination polyhedra (10 ppm) and between the signals of $\text{P}(\text{O}_4)$ and $\text{P}(\text{O}_2\text{N}_2)$ coordination polyhedra (20 ppm). Hence, we are tempted to assign the peak at -5 ppm in the ^{31}P NMR spectra

of AlGaPON to $\text{P}(\text{O}_3\text{N})$ tetrahedra and the one at 13 ppm to $\text{P}(\text{O}_2\text{N}_2)$ tetrahedra. From NMR experiments, we cannot elaborate on the nature of the P-N bonds formed by nitridation ($\text{P}-\text{NH}_2$, $\text{P}-\text{NH}-$, $\text{P}-\text{N}<$, or $\text{P}-\text{N}=\text{}$ bonds). Note that whereas the assignment of the peak at 13 ppm to $\text{P}(\text{O}_2\text{N}_2)$ tetrahedra is consistent with the theoretical calculations of Marquez et al., it is not satisfying for the assignment of $\text{P}(\text{O}_3\text{N})$ tetrahedra.

If we assign the first peak to $\text{P}(\text{O}_3\text{N})$ tetrahedra and the second one to $\text{P}(\text{O}_2\text{N}_2)$ tetrahedra, then we get the following picture: At the beginning of nitridation, the sample is composed of a randomized distribution of $\text{P}(\text{OAl}_{(4-x)}\text{Ga}_x)$ sites. After 3 h of nitridation, 70% of the $\text{P}(\text{O}_4)$ tetrahedra are replaced by $\text{P}(\text{O}_3\text{N})$ tetrahedra, and 10% are replaced by $\text{P}(\text{O}_2\text{N}_2)$ tetrahedra. The second coordination sphere of the P atoms that remain in a completely oxidized environment is rich in Al. As the nitrogen content of the sample increases, the remaining $\text{P}(\text{O}_4)$ as well as some $\text{P}(\text{O}_3\text{N})$ tetrahedra react further with ammonia, and $\text{P}(\text{O}_2\text{N}_2)$ groups, whose concentration increases with nitrogen content, are formed. For the highest nitrogen content under our nitridation conditions, almost all of the $\text{P}(\text{O}_4)$ groups have disappeared, and 70% of the phosphorus atoms contain two N atoms in their first coordination sphere.

This simplified picture of our system needs to be taken with caution, however, because we have neglected the contribution of ammonia molecules coordinated to Al (or Ga) in the proximity of phosphorus atoms or interacting with P-OH groups in the signal. Blasco et al.,²⁵ who reproduced the synthesis of AIPON samples, have shown by combining ^{31}P and ^1H MAS NMR spectra with IR results that those species could give rise to a peak centered around -10 ppm in the ^{31}P spectrum of an amorphous AlPO_4 sample heated under ammonia (i.e., a relative shift of 15 ppm with respect to the $\text{P}(\text{O}_4)$ signal). Hence, by assigning the ^{31}P NMR peak at -5 ppm in the spectra recorded on AlGaPON exclusively to $\text{P}(\text{O}_3\text{N})$ tetrahedra, we could overestimate the number of nitrogen atoms substituting for oxygen in the first coordination sphere of phosphorus atoms at the beginning of nitridation.

^{27}Al MAS NMR. ^{27}Al NMR spectra of crystalline AlPO_4 -*n* are greatly influenced by the treatment undergone by the sample prior to analysis. For instance, the work of I. Kustanovich and D. Goldfarb showed important differences between spectra recorded on "as synthesized", dehydrated, and calcined AlPO_4 -5 molecular sieves. Unlike the situation in the ^{27}Al spectrum, changes in the ^{31}P spectrum are reflected only in line-width increases.²⁶ The same applies to the amorphous $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ sample under study in this article: major changes are observed in the ^{27}Al NMR spectra recorded on the hydrated sample and on the sample dried for 2 h under nitrogen flow at 200 °C (Figure 4). The peak at 33 ppm, which dominates the ^{27}Al NMR spectrum of the sample dried at 200 °C, indicates an essentially tetrahedral environment for aluminum in this sample. Indeed, the value of 33 ppm is in the same range as that reported in the literature for $\text{Al}(\text{OP})_4$ tetrahedra in amorphous (~38 ppm,²⁵ ~45 ppm⁵) or crystalline (~39 ppm,²⁶ ~34 ppm¹²) AlPO_4 . The influence of gallium in the fourth coordination sphere of aluminum atoms has not been investigated.

In the sample that has been exposed to ambient air, the major resonance appears at -14 ppm. This resonance is characteristic of octahedral aluminum.^{25,26} It is due either to the coordination of aluminum atoms with two water molecules or to the reaction of the solid with atmospheric water leading to the formation of hydroxyl groups. The peak at 9 ppm could be attributed to aluminum atoms in a pentahedral environment. The two small high-field shoulders on the dried sample at 5 and -18 ppm probably result from residual coordinated water molecules or hydroxyl groups.

When the $\text{Al}_{0.5}\text{Ga}_{0.5}\text{PO}_4$ precursor is heated under ammonia flow at 750°C , the peak at 35 ppm associated with $\text{Al}(\text{OP})_4$ groups widens considerably (Figure 5). This can be explained either by greater structural disorder or by the substitution of oxygen for nitrogen beyond the first coordination sphere of aluminum atoms. Besides the broadening of the peak at 35 ppm, two peaks develop in the spectra around 11 and -13 ppm after treatment under ammonia flow. To assign these peaks, we will base our analysis on the work of Stein et al.,¹² who described the changes induced in the ^{27}Al NMR spectrum of an $\text{AlPO}_4\cdot 5$ phosphate after heating the molecular sieve under ammonia flow at various temperatures. Stein corroborated its assignments by ^1H and ^{15}N NMR. Stein et al. observed three resonances at 37 , 14 , and -13 ppm in the spectrum of an $\text{AlPO}_4\cdot 5$ phosphate heated to 200°C under ammonia. They attributed those resonances to 4 -, 5 - and 6 -fold coordinated Al, respectively (i.e., AlO_4^{5-} , $\text{AlO}_4(\text{NH}_3)^{5-}$, and $\text{AlO}_4(\text{NH}_3)_2^{5-}$ groups or the corresponding protonated forms). Blasco et al.²⁵ observed two new resonances at 11 and -13 ppm when treating an amorphous AlPO_4 sample at room temperature with NH_3 . They reached the same conclusions as Stein et al. and assigned the signals at 11 and -13 ppm to $\text{AlO}_4(\text{NH}_3)$ and $\text{AlO}_4(\text{NH}_3)_2$, respectively.

Concerning the resonance appearing downfield at 62 ppm, when the nitrogen content of the AlGaPON samples reaches 15.9 wt %, we think that this indicates the substitution of oxygen for nitrogen in the first coordination sphere of aluminum atoms. As already mentioned for ^{31}P NMR experiments, we cannot elaborate on the nature of the Al-N bonds formed.

The experimental relative shift from this new band at 62 ppm to the band characteristic of $\text{Al}(\text{OP})_4$ groups at 33 ppm in the precursor is equal to 29 ppm. According to the theoretical investigations of NMR chemical shieldings on AlPON catalysts,⁵ which were evoked here earlier for the assignment of ^{31}P NMR peaks, we expect a relative shift of 18 ppm when going from $\text{Al}(\text{O}_4)$ to $\text{Al}(\text{O}_3\text{N})$ and approximately twice that shift, 34 ppm, for $\text{Al}(\text{O}_2\text{N}_2)$. The experimental relative shift of 29 ppm that we observe in AlGaPON could imply the substitution of one or two oxygen atoms by nitrogen atoms in the first coordination sphere of aluminum when the global nitrogen content of the samples reaches 15.9 wt %.

For comparison, we can also cite positions observed for the $\text{Al}(\text{O}_4)$, $\text{Al}(\text{O}_3\text{N})$, $\text{Al}(\text{O}_2\text{N}_2)$, $\text{Al}(\text{ON}_3)$, and $\text{Al}(\text{N}_4)$ structural units in silicium aluminum oxynitride ceramics at 66 , 75 , 89 , 93 , and 112 ppm, respectively.²⁷

2. Comparison of the NMR Results with Previous XPS and XAS Results and Discussion of the Structural Model Proposed for AlPON .

2.1. Summary of Previously Obtained XPS and XAS Results.¹⁶ We have previously studied the modifications in the local environment of phosphorus atoms in AlGaPON as a function of their nitrogen content by P-K XANES experiments and P_{2p} XPS experiments on this series of samples. We observed the substitution of oxygen for nitrogen in the first coordination sphere of phosphorus atoms even at the early stage of nitridation.

By comparing the P-K XANES spectra recorded for AlGaPON and those recorded for $\text{Na}_3\text{AlP}_3\text{O}_9\text{N}$ (reference for PO_3N units) and PON (reference for PO_2N_2 units) crystalline references, we concluded that PO_3N tetrahedra were formed at the beginning of nitridation, followed by PO_2N_2 units, which dominate in the most nitrated sample AG9N6 (23.3 wt % N). By comparing Ga-K with Al-K XANES experiments and Ga_{3d} with Al_{2p} XPS experiments on AlGaPON , we concluded that the substitution of oxygen by nitrogen occurred in the first coordination sphere of gallium atoms at the beginning of nitridation, whereas the incorporation of nitrogen in the first atomic shell of aluminum was observed only when the nitrogen content reached 15.9 wt %.

Our main conclusion was that Ga-O-P bonds were replaced by Ga-N-P bonds preferentially to Al-O-P bonds.

2.2. Comparison of MAS NMR Results with the Model Proposed for AlPON . Concerning the modifications induced by nitridation in the first coordination sphere of phosphorus atoms, our conclusions were similar to those obtained on AlPON .¹⁴ Our present ^{31}P MAS NMR experiments confirm our hypothesis and even allow a rough quantification of the percentages of $\text{P}(\text{O}_4)$, $\text{P}(\text{O}_3\text{N})$, and $\text{P}(\text{O}_2\text{N}_2)$ units as a function of nitrogen content. This approach confirms our first hypothesis that $\text{P}(\text{O}_2\text{N}_2)$ tetrahedra are predominant in the most nitrated AG9N6 sample.

We also agreed with Benitez et al.¹⁵ and Marquez et al.,⁵ working on AlPON , that the incorporation in the first coordination sphere of aluminum atoms was difficult by the ammonolysis of a phosphate precursor. However, in AlGaPON , we observe that this substitution is feasible when the nitrogen content reaches 15.9 wt %. Indeed, we observe a new resonance at 62 ppm in the ^{27}Al MAS NMR spectra of the two most nitrated samples (Figure 5), which we assign to $\text{Al}(\text{O}_3\text{N})$ or $\text{Al}(\text{O}_2\text{N}_2)$ units. The existence of this new resonance is confirmed by the ^{27}Al 2D MQ (3Q) MAS results presented in Figure 6 (signal D).

Thus, it seems that gallium prevents the segregation of an Al_2O_3 phase and that nitrogen is observed in the first coordination sphere of aluminum atoms in AlGaPON . Additional experimental support of the influence of gallium would be needed prior to further elaboration on this result. However, our hypothesis is not irrational, and it is conceivable, for instance, that the formation of Ga-N-P bonds at the beginning of nitridation modifies the properties of the remaining Al-O-P bonds so as to facilitate their replacement by Al-N-P bonds.

In this context, we must also recall the favorable effect of gallium on nitridation.⁶

- The minimum nitridation temperature decreases when the gallium content of the sample increases. For instance, the minimum nitridation temperature of an AlPO_4 oxide is approximately 600°C , but the minimum nitridation temperature of a GaPO_4 oxide is approximately 400°C .

- The amount of nitrogen incorporated into the phosphate structure under fixed reaction conditions increases with gallium enrichment of the samples.

Conclusions

AlGaPON , obtained by reacting an amorphous mixed galloaluminumophosphate under ammonia flow at 750°C , constitute a new family of catalysts with tunable acid-base properties.^{7,8} The presence of gallium in their network leads to catalytic properties different than those observed in AlPON .¹³

To study the relation between the short-range structure of AlGaPON and their catalytic properties, we attempted to

describe the structural changes induced by nitridation on their structure. Because of the amorphous nature of the samples and the presence of five different types of atoms, we had to approach this structural investigation by combining several spectroscopies that are sensitive to local arrangements of atoms in solids. Previously, we characterized the changes induced by nitridation in the first coordination sphere of Al, Ga, and P atoms by XAS and XPS spectroscopies, and nitrogen-K ELNES was used to understand the type of bonding around nitrogen atoms.¹⁶

In the present work, we presented ³¹P and ²⁷Al MAS NMR results obtained on a series of five AlGaPON with various nitrogen content obtained by reacting the same mixed gallo-aluminophosphate precursor under ammonia flow for various periods of time. We propose the following model concerning the structural changes induced by nitridation:

The Al_{0.5}Ga_{0.5}PO₄ precursor consists of a randomized distribution of P(OAl_(4-x)Ga_x) tetrahedra. We know from DRIFTS investigations²⁸ that at the beginning of nitridation ammonia adsorbs on the surface by reacting with the Brönsted –OH acid groups and the Lewis acid sites.

Then, ammonia molecules substitute for the terminal hydroxyl groups to form –NH₂ groups. The formation of P–NH₂ and Ga–NH₂ species could explain the creation of P(O₃N) and Ga(O₃N) entities in the early stage of nitridation. The formation of Al–NH₂ groups is less probable but has not been ruled out. In a third step, imido –NH– species are formed. Finally, nitridation of the solid network occurs, nitrogen incorporation in the bulk phase being ensured by diffusion. P(O₂N₂) groups are formed because of the reaction of ammonia with the remaining P(O₄) groups or by the consumption of some of the P(O₃N) tetrahedra. P–O–Ga bonds were being preferentially replaced by P–N–Ga bonds. Once the sample reaches a nitrogen content of between 11 and 15 wt %, the substitution of some Al–O–P bonds by Al–N–P bonds becomes possible. We still need to confirm the role of gallium in the structural properties of the resulting AlGaPON, but it seems to have a considerable influence on the nitridation step.

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