Basic sites on mixed nitrided galloaluminophosphates "AlGaPON": infrared studies of SO_2 and $CDCl_3$ adsorption

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Received 18 November 1999; accepted 13 June 2000

The basic properties of nitrided galloaluminophosphate "AlGaPON" are documented by FTIR of sulphur dioxide and deuterated chloroform. To evidence the increase in the number of basic sites with nitrogen enrichment, we compared the spectra recorded after adsorption of $CDCl_3$ on the phosphate precursor "AlGaPO" and on four oxynitrides with increasing nitrogen contents. On the oxide, adsorption arises from $CDCl_3$ interacting with surface hydroxyl groups, on the oxynitrides basic sites are shown to be M–NH_2 groups. This interpretation is confirmed by FTIR of adsorbed SO_2.

Keywords: galloaluminophosphate oxynitrides AlGaPON, basic sites, SO_2 adsorption, $CDCl_3$ adsorption, FTIR

1. Introduction

In 15 years, the public opinion pressure for a better defence of our environment has strongly increased. The use of solid basic catalysts in a growing number of intermediate and fine chemistry production processes would not only allow higher profits but would also solve some of the environmental problems induced by the use of liquid bases: energetically costly separation of the catalyst from the reaction mixture, disposal of the used catalysts [1]. In that perspective we started to investigate the basic properties of several oxynitride systems, the aluminovanadate oxynitrides "VAlON" [2] or the nitrided phosphates, "ZrPON" [3,4] and "AlPON" [5,6].

More recently, we developed a new family of mixed nitrided galloaluminophosphates, the "AlGaPON". Those solids are synthesised by a solid–gas reaction, carried out at 750 °C between flowing pure ammonia and a high specific surface area mixed $Al_{0.5}Ga_{0.5}PO_4$ precursor. The control of the nitridation parameters – time, temperature and ammonia flow – allows us to choose the extent of the oxygen/nitrogen substitution and to obtain solids with nitrogen contents as high as 23.3 wt% [7,8].

Those solids present promising properties: their acidity decreases while their basicity increases with the nitrogen enrichment. The acidity decrease induced by nitridation is now fully understood. The replacement of acidic –OH by NH_x species decreases the surface Brønsted acidity, while the replacement of coordinatively unsaturated metals by M–NH_x species reduces the number of Lewis acidic sites [8].

The basicity increase with the nitrogen enrichment of the samples has been evidenced by means of a catalytic test: the Knoevenagel condensation between benzaldehyde and malononitrile, widely described in the literature [9] and typically catalysed by bases. The catalytic activity is much larger for the oxynitrides than for the corresponding oxide precursor, indicating a major influence of nitridation on the basic properties [8,10]. However, the nature of the basic sites appearing upon nitridation is still a subject of discussion:

- On "AlPON", Massinon et al. observed on a series of six samples with increasing nitrogen contents a good correlation between the catalytic activity and the amount of surface NH_x species ($1 \leqslant x \leqslant 4$) quantified by the Kjeldahl method. The authors suggest that those species are not the only active species and evoke an additional role of the nitride ions in the reaction [6]; on the other hand, Benitez et al. suggest hydroxyls linked to aluminium cations in the vicinity of terminal P–NH_2 groups as basic centers [11].
- On "ZrPON", basic sites are proposed to be nitride ions or non-bridging oxygen atoms appearing upon nitridation because of the complete reorganisation of the phosphate network [4].

This explanation, convincing on "ZrPON", cannot be transposed on "AlGaPON": indeed the removal of the less stable nitrogen molecules located at the surface under an helium flow strongly affects the condensation properties of those nitrided phosphates, which lead us to think that those hydrogenated species play a key role in the generation of basic sites on "AlGaPON", rather than the very stable nitrogen or oxygen framework atoms [10]. To refine this theory, we studied by IR spectroscopy the interactions of two acidic probe molecules, SO_2 and $CDCl_3$ with the "AlGaPO(N)".

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2. Experimental

The mixed galloaluminophosphate $Al_{0.5}Ga_{0.5}PO_4$ was synthesised by a process developed by Kearby [12] for aluminophosphates and adapted for the "(Al, Ga)PO" compositions [7]. The oxide precursor was then placed in the isothermal region of a tubular furnace and activated by NH_3 stream ($30\ \mathrm{l\,h^{-1}}$) at 750 °C. Four samples with 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 pure and dry nitrogen flow.

The surface areas of the samples were measured by the adsorption of nitrogen at liquid-nitrogen temperature by single-point BET method ($p/p_0 = 0.3$) after outgassing 20 min at 250 °C using a Micromeritics Flowsorb II 2300 equipment.

The total amount of nitrogen (bulk nitrogen of nitride-type and hydrogenated NH_x surface species) was determined by a method developed by Guyader and Grekov [13]: the ammonia produced by reaction of the nitride ions with melted potassium hydroxide at 400 °C is dissolved in water and titrated with sulphuric acid.

Deuterated chloroform spectra were recorded using a Brücker IFS88 spectrometer. The powders were pressed into self-supporting disks (20 mg, 13 mm in diameter), placed in an IR cell connected to a vacuum line. They were pre-treated under vacuum at 300 °C for 1 h before analysis. After the thermal treatment, the samples were cooled to room temperature and a spectrum of the powder was recorded. Deuterated chloroform was then adsorbed at a pressure of 10^4 Pa at RT for 8 min and an IR spectrum was immediately recorded.

Sulphur dioxide spectra were recorded using a Nicolet 710 spectrometer. The powders were pressed into self-supporting disks (15 mg, 16 mm in diameter), placed in an IR cell connected to a vacuum line. The wafers were degassed at 300 °C for 1 h before analysis. After cooling to room temperature, a spectrum of the powder was recorded. SO_2 was then adsorbed at a pressure of 6.7×10^3 Pa at RT for 5 min and an IR spectrum was immediately recorded.

3. Results and discussion

The compositions, nitrogen contents and surface areas of the studied samples are presented in table 1. All samples are X-ray amorphous white powders. The four oxynitrides used in this study are obtained by nitridation of the $Al_{0.5}Ga_{0.5}PO_4$ precursor at 750 °C. This reaction allows the progressive substitution of oxygen for nitrogen according to the equation

$$\begin{aligned} &Al_{0.5}Ga_{0.5}PO_4 + x\mathrm{NH_3} \rightarrow \\ &\quad Al_{0.5}Ga_{0.5}PO_{(4-3x/2)}N_x + (3x/2)H_2O\uparrow \qquad (1)\end{aligned}$$

As shown in table 1, the total nitrogen content of the samples increases with the nitridation time. It reaches a value of 23.3 wt% for the most nitrided sample. In spite of a slight decrease in surface area at the beginning of nitridation, high values are kept after synthesis.

The IR spectra recorded before $CDCl_3$ adsorption on the oxide (AG9) and on an oxynitride (AG9N6, 23.3 wt% N) are presented in figure 1. The assignments of the bands appearing in the "AlGaPON" vibrational spectra have been discussed in [14]. The comparison of the two spectra allows major changes induced by nitridation in the IR vibrational spectrum to be seen.

The substitution of various types of oxygen atoms by nitrogen atoms leads to

- the decrease of the superficial concentration of P–OH groups (ν(OH) in P–OH band at 3670 cm^{-1});
- the appearance of bridging M–NH–M groups: ν(NH) band at 3330 cm^{-1}; and of M–NH_2 groups (M = Al, Ga, P): δ(HNH) at 1560 cm^{-1}.

Figure 2 presents the IR spectra (2300–2200 cm^{-1}) of $CDCl_3$ adsorbed on the $Al_{0.5}Ga_{0.5}PO_4$ precursor and on two oxynitrides $Al_{0.5}Ga_{0.5}PO_xN_y$ (11.0 and 23.3 wt% N).

- On the oxide, the band at 2256 cm^{-1} arises from $CDCl_3$ interacting with surface hydroxyl groups, as can be deduced from the important changes in the ν(OH) region observed during adsorption. The ν(CD) frequency observed is intermediate between the values given by Paukshtis [15] at 2250 cm^{-1} for $CDCl_3$ interacting with a surface Me–OH group adjacent to an oxygen atom on alumina and 2265 cm^{-1} for a chlorine atom of chloroform interacting with a proton of a hydroxyl group on silica (SiOH$\cdots$Cl–$CDCl_2$). The tail of the peak towards the highest energies may indicate that both types of interactions occur on the $Al_{0.5}Ga_{0.5}PO_4$ surface.
- On the "AlGaPON" oxynitrides, the peak is shifted towards the lowest energies, indicating a stronger interaction between the probe molecule and the surface. Al-

Table 1

Characteristics of the studied oxide and oxynitride powders.

Sample	Composition	Nitridation		Total nitrogen content (wt%)	Specific surface area (m^2/g)
		Time (h)	Temp. (°C)		
AG9	$Al_{0.5}Ga_{0.5}PO_4$	–	–	–	240
AG9N2	$Al_{0.5}Ga_{0.5}PO_{3.22}N_{0.52}$	3	750	5.3	150
AG9N4	$Al_{0.5}Ga_{0.5}PO_{2.43}N_{1.04}$	8	750	11.0	160
AG9N5	$Al_{0.5}Ga_{0.5}PO_{1.81}N_{1.46}$	16	750	15.9	145
AG9N6	$Al_{0.5}Ga_{0.5}PO_{0.94}N_{2.04}$	89	750	23.3	170

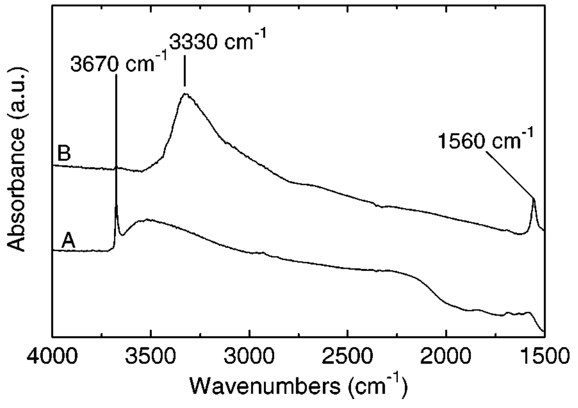


Figure 1. FTIR spectra of the "AlGaPO" precursor (A) and an "AlGaPON" oxynitride (23.3 wt% N) (B) evacuated at 300 °C.

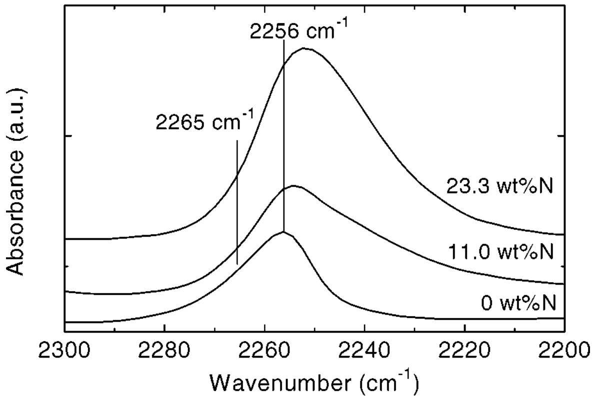


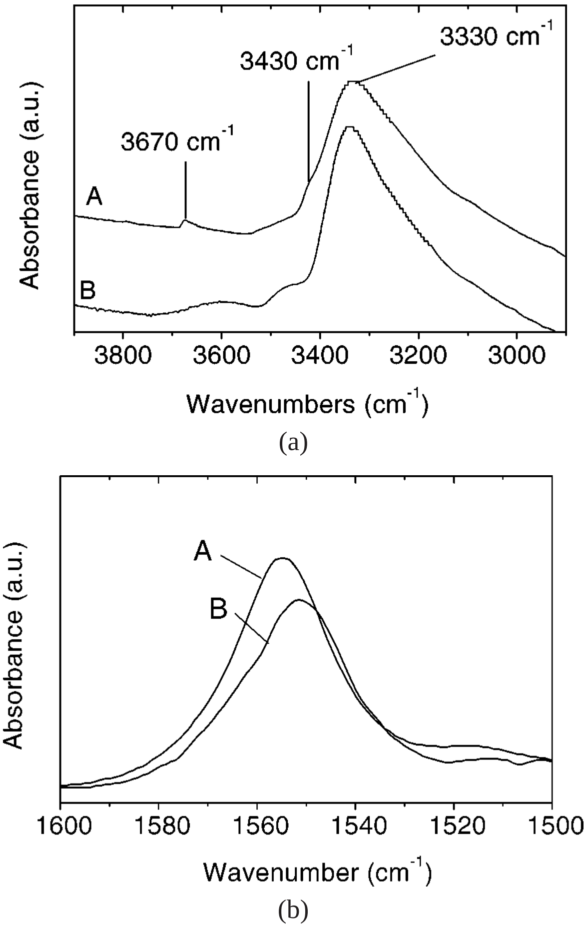
Figure 2. FTIR spectra of deuterated chloroform adsorption on the precursor "AlGaPO" and on two oxynitrides "AlGaPON" containing 11.0 and 23.3 wt% N, evacuated at 300 °C.

though the number of surface –OH groups decreases markedly upon nitridation (figure 1), substituting oxygen by nitrogen leads to a significant increase in the peak intensity and a modification of the peak shape. This broadening could be due to the appearance of a new type of basic surface sites.

To determine the nature of those new basic sites, we subtracted the IR spectrum recorded after $CDCl_3$ adsorption on the most nitrided sample (AG9N6, 23.3 wt% N) from the spectrum recorded before $CDCl_3$ adsorption. The spectra recorded before and after $CDCl_3$ adsorption are presented in figure 3, in the 3900–2900 and 1600–1500 cm^{-1} energy ranges. The difference spectrum is presented in figure 4.

In the 3900–2900 cm^{-1} energy range (figure 3(a)), IR bands at 3670 cm^{-1} (ν(OH) in P–OH) and 3430 cm^{-1} (ν(NH) in M–NH_2) are perturbed by $CDCl_3$ adsorption, while the ν(NH) in M–NH–M band around 3330 cm^{-1} is perturbed to a lesser extent by the probe.

In the 1600–1500 cm^{-1} energy range (figure 3(b)), the δ(HNH) in M–NH_2 band is shifted towards lower wavenumbers, while its intensity decreases upon adsorption.



(a)

(b)

Figure 3. Deuterated chloroform adsorption on an "AlGaPON" oxynitride (23.3 wt% N) evacuated at 300 °C: spectrum recorded before adsorption (A) and spectrum recorded after adsorption (B). Spectra are presented in the 3900–2900 (a) and 1600–1500 cm^{-1} (b) energy range.

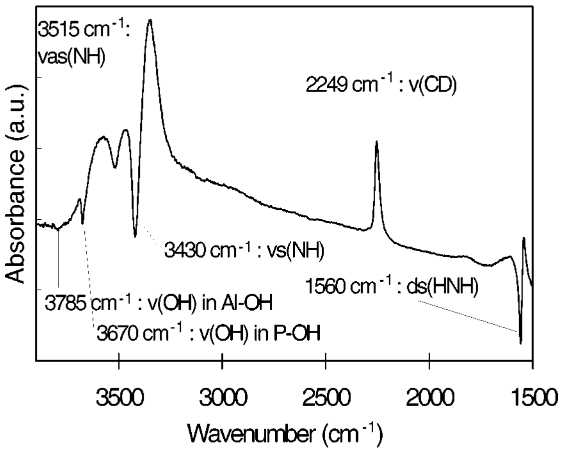


Figure 4. Difference spectrum obtained after $CDCl_3$ adsorption on an "AlGaPON" oxynitride (23.3 wt% N) evacuated at 300 °C: spectrum recorded after adsorption – reference spectrum recorded before adsorption.

The small shift towards lower wavenumbers of the stretching as well as the bending vibration bands of the NH_2 groups agrees well with their basic character. Indeed, literature reports that interaction of water (or alcohol) with

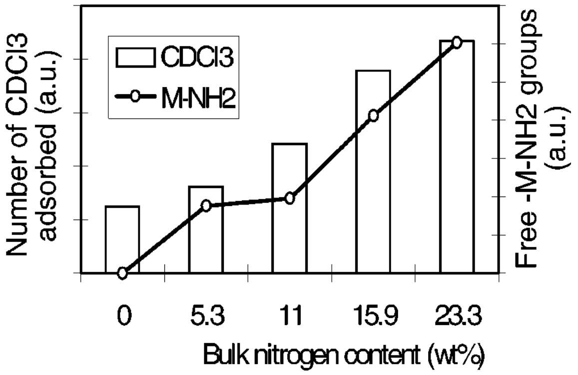


Figure 5. Evolution of the number of M–NH_2 species and of the number of $CDCl_3$ adsorbed with the total nitrogen content of “AlGaPON”.

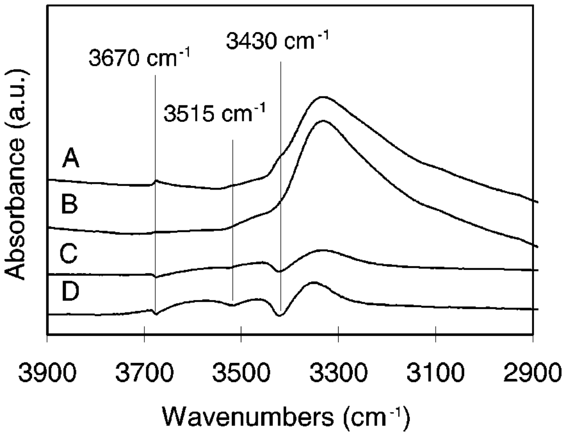


Figure 6. FTIR spectra of an “AlGaPON” oxynitride (23.3 wt% N), evacuated at 300 °C before (A), after (B) SO_2 adsorption and difference spectrum (C). Difference spectrum obtained after $CDCl_3$ adsorption on the same sample (D).

an acid leads to a small decrease of the wavenumbers of the ν(OH) and δ(ROH) bands while interaction with a base leads to a more pronounced decrease of the ν(OH) and a slight increase of the δ(ROH) wavenumbers [16–18].

Although perturbation of the δ(HNH) band upon $CDCl_3$ adsorption is clear (figure 3(B)) and reveals an interaction between $CDCl_3$ and M–NH_2 species, it is not very important, either because this band is weakly sensitive to perturbation by an acid (as observed for the δ(HOH) band of water interacting with acids [16]) either because only a fraction of the –NH_2 groups are sufficiently basic to interact with $CDCl_3$.

Changes induced by $CDCl_3$ adsorption on the IR spectrum are more clearly evidenced on the subtraction spectrum presented in figure 4. Next to the negative band at 3430 cm^{-1}, another negative band appears around 3515 cm^{-1}. Literature data indicate that it could be assigned to the antisymetric stretching frequency of –NH_2 groups [19,20].

If –NH_2 groups are mainly responsible for $CDCl_3$ adsorption (that is to say if we neglect the contribution of the remaining –OH groups), we should observe a good correlation between the area of the $\delta(NH_2)$ band in free M–NH_2 around 1560 cm^{-1} integrated before adsorption and the area of the ν(CD) band. Figure 5 shows that it is indeed the case on a series of five samples containing 0, 5.3, 11.0, 15.9 and 23.3 wt% N.

To confirm this interpretation, SO_2 was adsorbed on the “AlGaPON” oxynitride containing 23.3 wt% N. The difference spectrum obtained after SO_2 adsorption is similar to the one obtained for $CDCl_3$ (figure 6):

- The few –OH groups remaining after nitridation are shifted upon adsorption;
- SO_2 adsorption leads to a perturbation of all the bands characteristic of M–NH_2 groups.

Neither the SO_2, nor the $CDCl_3$ adsorption modifies in an important way the –NH– band at 3330 cm^{-1} (figures 3(a) and 6). We expected however that –NH– groups would interact to a great extent with the acidic probes. Indeed, Corma et al. have recently modelled the –NH– bridging groups substituting oxygen in aluminophosphates by $H_3AlNHPH_3$ clusters. By comparing the calculated proton affinities and HOMO energies of different systems, they determined that the –NH– bridging group should have a strong basic character [21]:

- A first explanation to this fact would be that the groups detected by IR are not all present on the surface, being mainly in the bulk and hence, not accessible to the probes. This explanation has in fact already been used by Busca et al. [22] studying the basicity of Si_3N_4 by probe adsorption to explain that the imido groups Si–NH–Si are perturbed only to a small extent by basic probe molecules.
- Another explanation would be that those –NH– groups are not basic. They are indeed available for isotopic exchange with deuterium and hence, we must not rule out the possibility that in “AlGaPON”, the –NH– groups being in an environment lowering the availability of the nitrogen’s lone pair for external donation are rather nonbasic.

4. Conclusions

To evidence the nature of the basic sites appearing upon nitridation on a mixed galloaluminophosphate $Al_{0.5}Ga_{0.5}PO_4$, we compared the IR spectra recorded before and after $CDCl_3$ and SO_2 adsorption on this precursor and on a series of four “AlGaPON” oxynitrides. On the oxide, adsorption arises from interaction between the probes and the surface hydroxyl groups. On the oxynitrides, we showed that the –NH_2 groups were able to interact with the acidic probes which reveals their basic character. We cannot rule out the presence of other basic sites. In particular, the role of surface chemisorbed ammonia should not be underestimated when “AlGaPON” are used not pre-treated as basic catalysts in the Knoevenagel condensation between benzaldehyde and malononitrile [8,10]. However, on samples pre-treated at 300 °C, the increase of superficial –NH_2

groups with nitridation time can, by itself, explain the good correlation obtained between the number of species that adsorb $CDCl_3$ and the bulk nitrogen content of the sample.

Acknowledgement

The authors are grateful to Jean Lamotte (Laboratoire de Catalyse et Spectrochimie, Caen, France) for the help provided in the recording and interpretation of the IR spectra. They would also like to thank the FNRS (Fonds National de la Recherche Scientifique, Belgium) for financial support.

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