CO_2 adsorption and surface basicity evaluation of aluminophosphate oxynitride (AlPON) catalysts

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Aluminophosphate oxynitrides (AlPON) are new catalysts obtained by nitridation of $AlPO_4$ showing a high surface area and an enhanced surface basicity. In this article, surface basicity is evaluated by CO_2 adsorption and related to the nitrogen content. CO_2 simultaneously adsorbs linearly and as bidentate carbonate and bicarbonate species on AlPON surface. Particularly strong basic centers involving hydroxyls linked to Al cations and in the vicinity of terminal $–PNH_2$ groups are identified. However, the influence of nitrogen content on surface basicity of AlPON is mostly through the change in the number of sites rather than on the modification of their strength. Activity results obtained for AlPON in base-catalyzed reactions are related with their capability of adsorbing CO_2.

Keywords: aluminophosphate oxynitrides (AlPON), surface basicity, CO_2 adsorption

1. Introduction

Nitridation of $AlPO_4$ to obtain aluminophosphate oxynitrides (AlPON) has been recently proposed as a method to obtain solid catalytic systems maintaining the high specific surface area of the precursor and showing an enhanced surface basicity that can be adjusted by the modification of the nitrogen content [1–3]. Indeed, catalytic performances of AlPON, either as a catalyst or as a support for active metallic phases, have been successfully tested in base-catalyzed reactions such as the Knoevenagel condensation and the synthesis of methyl isobutyl ketone from acetone [4–6]. Such a behavior has been explained by the replacement of O^{2-} and OH^- by new N^{3-}, –NH–, $–NH_2$ and N-modified hydroxyls upon nitridation [7]. The diminishment of surface acidity of AlPON upon increasing N/O ratio has been characterized by ammonia adsorption [2] and by analyzing spontaneous surface hydrolysis products [3]. However, and up to now, no surface basicity evaluation on AlPON has been published. Carbon dioxide is the most widely used probe molecule to evaluate basic sites, however, early attempts of characterization and quantification by CO_2 adsorption on AlPON have failed [2,8]. Two reasons may lay behind this failure, the small amount of CO_2 retained and surface conditions. Once surface stability of AlPON has been analyzed in detail [9–11], conclusions obtained are used as the base to study CO_2 adsorption on these systems. This paper provides for the first time ever direct evaluation of surface basicity of a set of aluminophosphate oxynitrides (AlPON) with a nitrogen content ranging from 0 up to 20% N (w/w) by CO_2 adsorption using mass spectrometry thermoprogrammed desorption (MS-TPD) and diffuse reflectance infrared spectroscopy (DRIFTS).

2. Experimental

Amorphous aluminophosphate oxynitride (AlPON) catalysts are obtained by nitridation of $AlPO_4$ precursors in a tubular furnace by flowing dry NH_3 at 800 °C. Nitridation times of 3, 8, 40, 65, 120 and 200 h yield a nitrogen content of 2.8, 3.6, 7.2, 11, 17.5 and saturation 20% N by mass, respectively. Nitrogen analysis was done by alkaline digestion with molten KOH at 400 °C and resulting NH_3 titration with H_2SO_4. Both $AlPO_4$ precursors and AlPON solids obtained were XRD amorphous.

$AlPO_4$ precursors were previously prepared by mixing, at room temperature, two aqueous solutions of $AlNO_3$ and $(NH_4)H_2PO_4$ 0.66 M each and adding an excess of citric acid. The mixture was stirred overnight. Later, water was removed in an evaporating dish at 40 °C and the resulting solid oven-dried at 105 °C for 10 h and calcined at 550 °C for 16 h.

Temperature-programmed desorption (MS-TPD) experiments were carried out in a stainless steel high vacuum chamber (base pressure 6.5×10^{-5} Pa) equipped with a Leybold (QUADRUVAC Q-100) quadrupole detector. Samples (approximately 20 mg) are treated inside a quartz reactor connected to the chamber. Before any experiment, samples are pumped overnight at room temperature. Pure CO_2 is adsorbed at 1 atm and RT after 30 min static exposure. The excess of CO_2 is eliminated by evacuation until a base pressure of 1.3×10^{-4} Pa is achieved. Temperature is raised at 5 °C/min from RT to 450 °C. When specified, and before

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CO_2 adsorption, samples are pre-cleaned by outgassing at 200 °C for 2 h.

DRIFTS spectra were obtained in a FT Nicolet 510P infrared spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector working at 4 cm^{-1} resolution. The sample was analyzed inside a controlled environment chamber (Spectra-Tech 0030-101) attached to a diffuse reflectance accessory (Spectra-Tech collector). Undiluted samples were used and treated *in situ* following a similar procedure as described for MS-TPD. Now, adsorption is from a pure CO_2 stream (30 ml min^{-1}) and evacuation is replaced by N_2 purge at 50 ml min^{-1}. Spectra are collected at RT, 200 and 400 °C under continuous N_2 flow and after increasing the temperature at 5 °C min^{-1} and 1 h stabilization period. One hundred scans are accumulated in every case and data are shown in absorbance mode and after a 9 points–3 passes smoothing. Powered KBr is used as background.

3. Results

The thermal stability of aluminophosphate oxynitrides (AlPON) has been analyzed in detail in previous papers [9–11]. However, in order to design adsorption experiments, basic results should be mentioned here. Adsorbed water and ammonia, resulting from surface partial hydrolysis, are removed from AlPON upon heating below 200 °C. This removal is accompanied by the definition of an infrared band, corresponding to terminal $-PNH_2$ groups, at 1560 cm^{-1}, figure 1. Such groups are due to –P–O–P– bond breaking by nitridation of $AlPO_4$. Simultaneously, a hydroxyl peak develops at 3745 cm^{-1} (trace B–A in figure 1). In a first approach this peak can be assigned to hydroxyls bonded to aluminum cations in a pentahedral coordination [12]. However, it is also possible to assign it to bridging hydroxyls [13] or even to Al–OH suffering neighboring perturbation [14]. Parallel developing of the 1560 and 3745 cm^{-1} peaks can be explained by the desorption of a molecule of water bridging such Al–OH and $-PNH_2$ groups.

Heating AlPON above 200 °C causes $-PNH_2$ to react, figure 1. Thus, 200 °C is the temperature at which sites involving adjacent Al–OH and $-PNH_2$ are available for adsorption before undergoing reaction.

Freshly prepared AlPON samples readily adsorb CO_2 from the atmosphere as deduced from the very broad desorption peak around 130 °C in figure 2(A). The adsorption is more intense if exposed to pure CO_2 at RT, besides, some structure on the lower temperature side (90–100 °C) is observed. However, AlPON samples calcined at 450 °C almost lose their capability of adsorbing CO_2 and only the

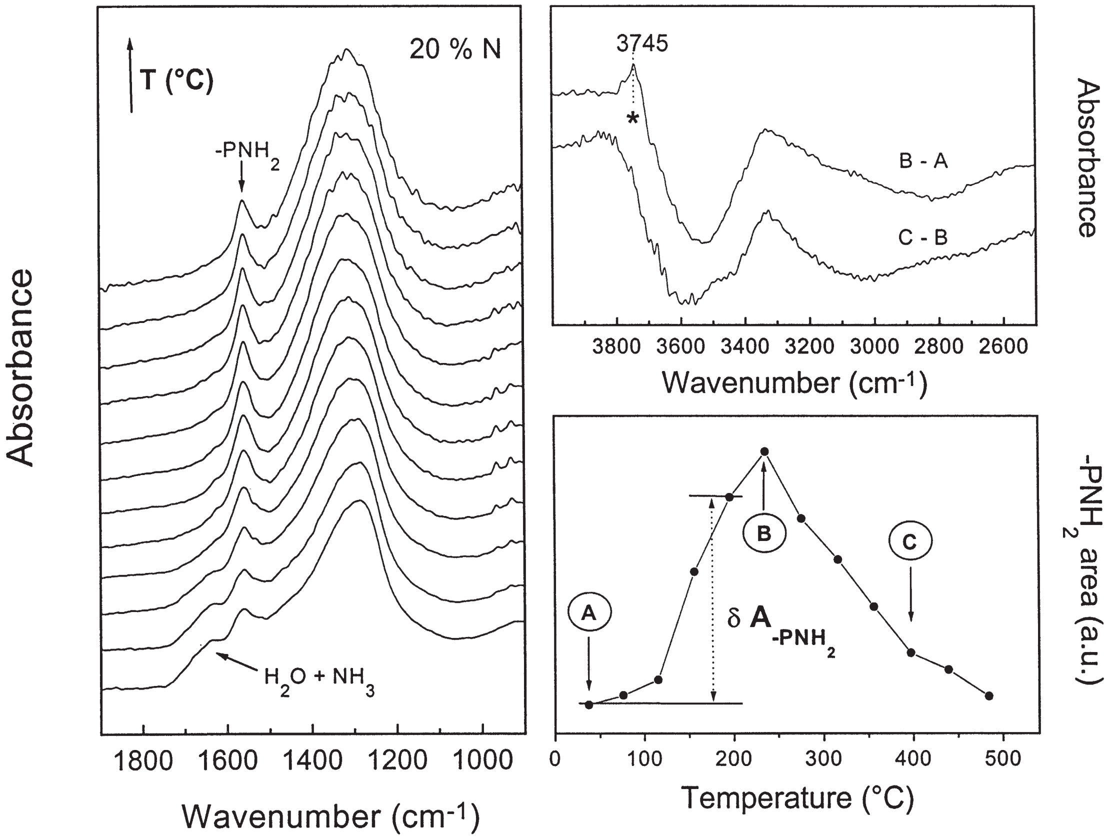

Figure 1. Thermal modification of DRIFTS spectra in the 1900–900 cm^{-1} and 3900–2500 cm^{-1} regions showing the evolution of the $-PNH_2$ band versus temperature and spectral changes observed upon heating from RT to 240 °C (B–A) and from 240 to 400 °C (C–B). Spectra are collected starting at RT and every 40 °C under N_2 flow for AlPON (20% N (w/w)).

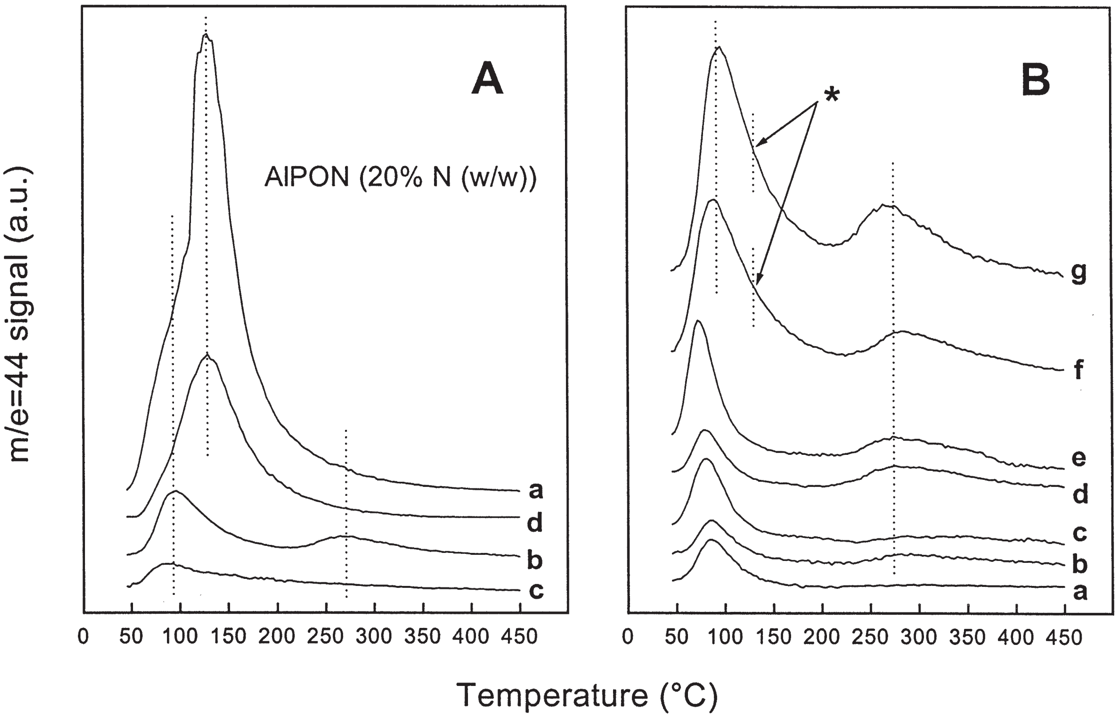

Figure 2. Mass spectrometry thermoprogrammed desorption of CO_2 as a function of (A) surface pretreatment of AlPON (20% N (w/w)); (a) untreated, (b) outgassed at 200 °C, (c) outgassed at 450 °C, and (d) untreated AlPON exposed to atmospheric CO_2. (B) Nitrogen content (after outgassing at 200 °C) (a) 0, (b) 2.8, (c) 3.6, (d) 7.2, (e) 11, (f) 17.5, and (g) 20% N (w/w). Curves are corrected by weight and specific surface areas.

low temperature peak (90–100 °C) develops. If the sample is previously outgassed at 200 °C, besides an intense desorption at 90–100 °C with some contribution on the high temperature side, a new desorption peak appears at 270 °C. The intensity of this new feature grows with the nitrogen content (figure 2(B)) and it is absent from the precursor $AlPO_4$. From these results at least three CO_2 desorption stages at 95, 130 and 270 °C can be detected in AlPON.

Spectroscopic characterization of adsorbed species has been carried out by DRIFTS over AlPON samples previously purged at 200 °C. Due to the low intensity of their peaks and to the contribution of other species such as residual adsorbed water (1640 cm^{-1}), ammonia (NH_3 (1620 cm^{-1}) and/or NH_4^+ (1440 cm^{-1})) and intense structural bands corresponding to terminal $-PNH_2$ groups (1560 cm^{-1}) and P–O bonds (1310–1350 cm^{-1}), direct identification of adsorbed carbonates from the DRIFTS spectrum in absorbance mode is very difficult. We have subtracted DRIFTS spectra before and after adsorption/desorption experiments in order to minimize such contributions and remark the presence or absence of adsorption products, figure 3. Thus, physisorbed CO_2 molecules are characterized by the intense peak at 2343 cm^{-1} and their concentration grows with nitrogen content. Linearly physisorbed CO_2 molecules are probably interacting with hydroxyl groups as suggested by Busca [15] and as indicated by negative peaks corresponding to Al–OH (3790 cm^{-1}) and P–OH (3675 cm^{-1}) [16]. On the $AlPO_4$ precursor, and in the 1800–1200 cm^{-1} region, a peak at 1620 cm^{-1} is observable, which is assigned to adsorbed bidentate carbonate [15,17–19]. The second feature characterizing this species (~1290 cm^{-1}) falls over the very intense P–O stretching making difficult any identification (although some perturbation is presumed from the first-derivative shaped peak around 1340 cm^{-1} in figure 3). Adsorbed bidentate carbonates are also observed in AlPON samples although they overlap with the more intense bands at 1660 and 1480 cm^{-1}, which are assigned to adsorbed bicarbonate resulting from CO_2 reaction with hydroxyl groups [20–23]. The presence of a broad band around 3590 cm^{-1} also supports this assignation. It is interesting to note that the presence of adsorbed bicarbonate is accompanied by the elimination of hydroxyl groups at 3745 cm^{-1}.

Heating at 200 °C under nitrogen flow causes the elimination of both physisorbed and chemisorbed (either bidentate carbonate or bicarbonate) CO_2 and the restoration of the hydroxyl structure, figure 3. However, mass spectrometry shows a second CO_2 desorption peak above 200 °C, figure 2(B). At this temperature most of adsorbed CO_2 has already been desorbed so spectroscopic identification of the residue becomes even more difficult. In figure 4, the 4000–3400 cm^{-1} and 1800–1200 cm^{-1} regions of the DRIFTS spectra are displayed for AlPON purged at 200 °C (trace a), after adsorbing CO_2 at RT and purging at 200 °C (trace b) and finally, spectrum b heated at 400 °C. CO_2 adsorption at RT and further heating at 200 °C causes very weak bands at 1625, 1450 and 1430 cm^{-1} to appear (trace b versus trace a). They are assigned to ν_a(C–O) and to ν_s(C–O) modes in adsorbed bicarbonate, respectively. The enhancement of the (O–H) stretching mode at 3600 cm^{-1} reinforces

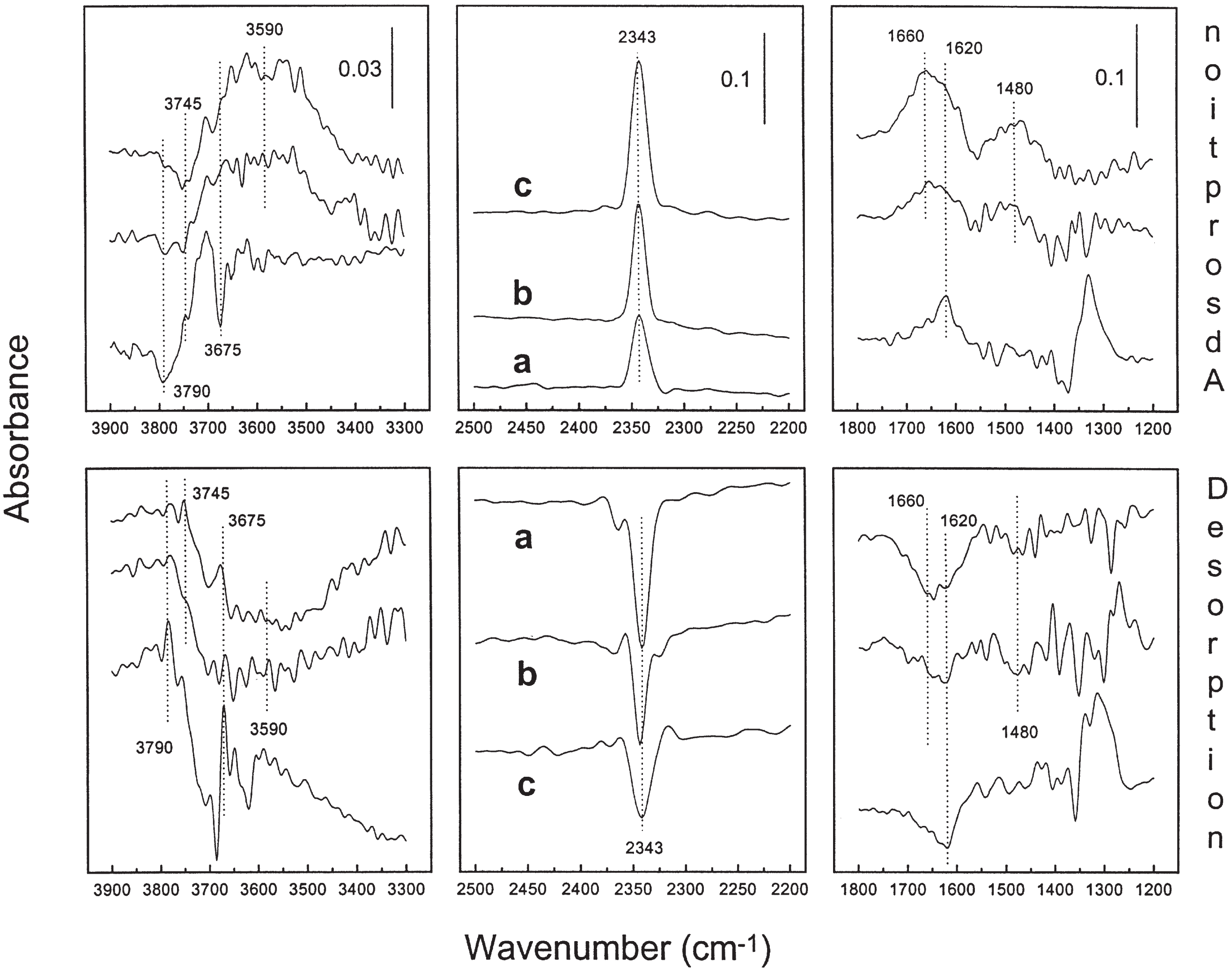

Figure 3. DRIFTS spectrum changes occurring upon CO_2 adsorption at RT (up) and desorption at 200 °C (down) for AlPON samples containing (a) 0, (b) 11, and (c) 20% N (w/w) and previously cleaned at 200 °C.

this assignation. Such a residual adsorbed bicarbonate is removed at 400 °C from an absorption site involving hydroxyls linked to Al and in the vicinity of $-PNH_2$ groups, as indicated from the reversible evolution of bands at 3745 and 1560 cm^{-1} in figure 4.

4. Discussion

CO_2 adsorption on aluminophosphate oxynitrides (AlPON) depends on their nitrogen content and surface conditions. Linearly physisorbed, bidentate carbonate and bicarbonate species are detected on both partially hydrolyzed and clean AlPON surfaces, although their adsorption stages cannot be isolated from our experiments. However, some aspects can be discussed by the combination of MS-TPD and DRIFTS results. Thus, linearly adsorbed and bidentate carbonates are responsible for the single MS-TPD desorption peak observed for the unnitrided sample at 90 °C. If we assume that bidentate carbonates are the result of CO_2 adsorption on surface O^{2-} centers, the disappearance of hydroxyl groups, figure 3, has to be the consequence of their interaction (either as Al–OH or P–OH) with linear CO_2 molecules. Linearly adsorbed CO_2 bands below the frequency corresponding to the asymmetric stretching mode in gaseous CO_2 (2349 cm^{-1}) are associated to electron donating centers [15]. Hydroxyl groups in the AlPON surface are then acting as weak Lewis basic sites. The amount of those sites increases with nitrogen content as deduced from the evolution of the intensity of the 2343 cm^{-1} band in figure 3. However, no modification in their strength is expected because no band shift is observed as the nitrogen content changes.

Adsorbed bidentate carbonates and bicarbonates are the consequence of CO_2 adsorption on O^{2-} and OH^- basic sites, respectively. In this case no particularized estimation of their concentration versus nitrogen percentage can be made because of the overlapping between desorptions. However, the displacement of the lower temperature MS-TPD peak towards higher temperature observed for highly nitrided AlPON, figure 2(B), and the growing intensities of 1660 and 1480 cm^{-1} DRIFTS peaks are due to the increasing presence of bicarbonate species. Besides, the broaden-

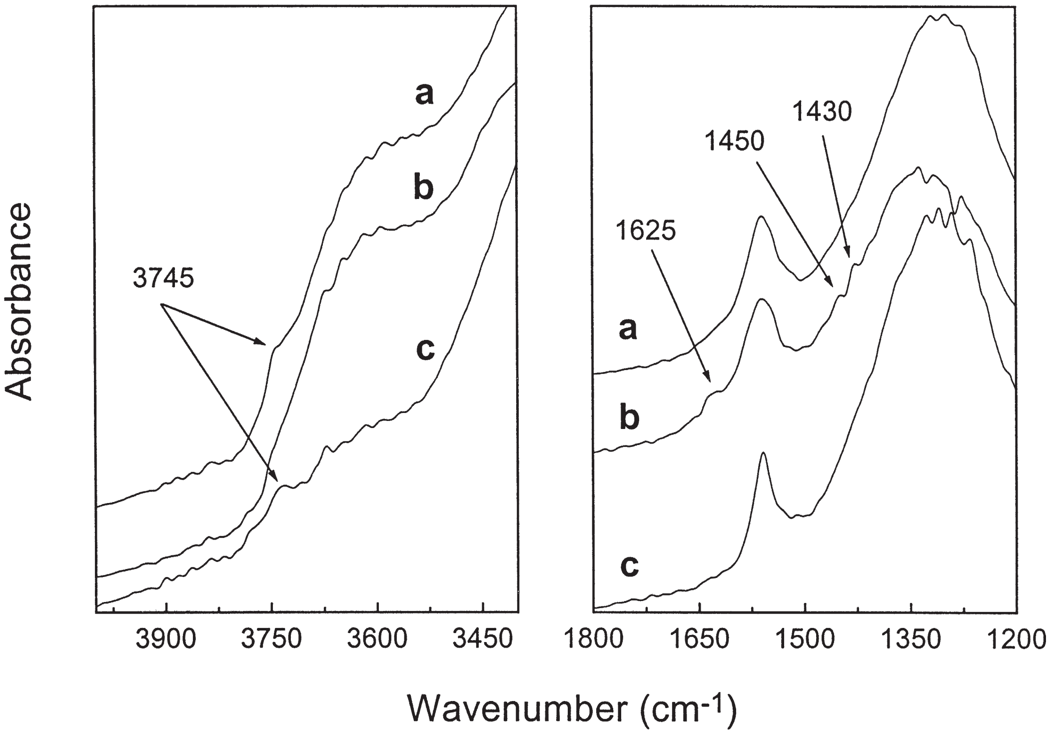

Figure 4. DRIFTS spectra in the 4000–3400 and 1800–1200 cm^{-1} regions of AlPON (20% N (w/w)) after (a) purging under N_2 at 200 °C, (b) previous sample after adsorption of CO_2 at RT and purging again at 200 °C, and (c) previously purged at 400 °C.

ing on the high temperature side of the MS-TPD peak at 90 °C is interpreted as the development of a more heterogeneous distribution of adsorption centers on highly nitrided AlPON. Such a bicarbonate adsorption mode can be associated to the presence of residual surface NH_4^+ cations, as deduced from the strong enhancement of the MS-TPD peak at 130 °C experienced by untreated (partially hydrolyzed) AlPON, figure 2(A).

In any case, and despite the variety of adsorption centers, the fact is that CO_2 adsorption directly reveals a growing surface basicity of AlPON upon nitridation.

A second important aspect about CO_2 adsorption on aluminophosphate oxynitrides is the presence of a second desorption peak around 270 °C after outgassing at 200 °C, figure 2(B). AlPON activation at 200 °C is accompanied by spectroscopic changes indicating that adsorbed water molecules bridging $–PNH_2$ and Al–OH groups are removed. CO_2 adsorbs on these new centers forming bicarbonate species by interaction with the hydroxyl group, as deduced from weak bands at 1625, 1450, 1430 and 3600 cm^{-1} and a parallel diminishment of $–PNH_2$ and Al–OH peaks, figure 4. This assignation of the high-temperature MS-TPD peak to CO_2 adsorption on new sites involving Al–OH and $–PNH_2$ groups after water removal is supported by the linear relationship found when plotting the area of the CO_2 MS-TPD at 270 °C and the amount of sites created (δA_{-PNH_2}) estimated from the modification in the $–PNH_2$ peak area upon heating from RT to 200 °C, figure 5. Despite their lower concentration and based on the desorption temperature, the basicity of these new sites is the highest found in AlPON catalysts. Consequently they should be taken into account when analyzing the activity of aluminophosphate oxynitrides in reactions requesting strong basic sites.

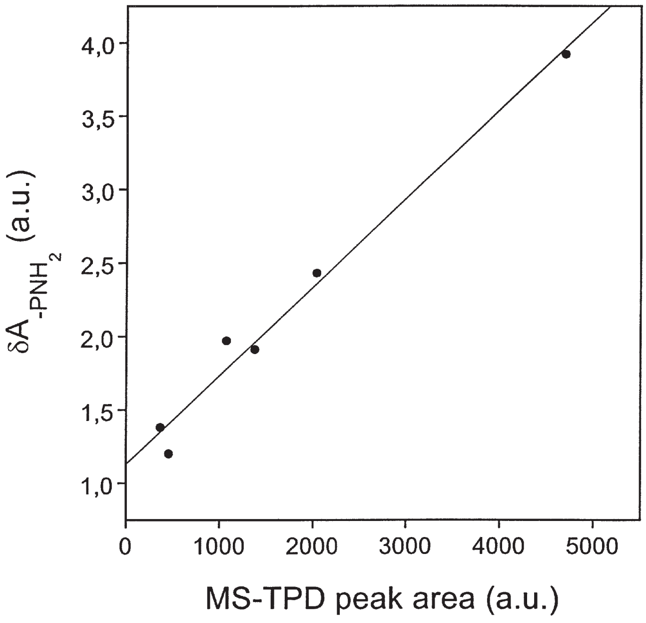

Figure 5. Relationship between changes in $–PNH_2$ band area (δA_{-PNH_2}) upon heating from RT to 200 °C and the area of the CO_2 MS-TPD peak at ∼270 °C in AlPON series.

In previous papers we have found an empirical relationship between the activity of AlPON catalysts and the frequency of the P–O stretching mode in base-catalyzed processes such as the Knoevenagel reaction [3] and the syn-

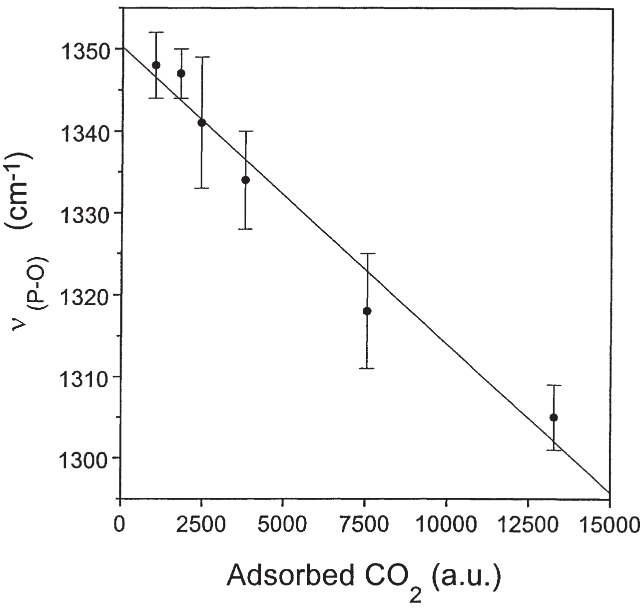

Figure 6. Relationship between the frequency of P–O stretching mode and the amount CO_2 adsorbed (estimated from the area of MS-TPD profiles) in AlPON series. Error bars account for the thermal drift observed in peak position.

thesis of methyl isobutyl ketone from acetone (MIBK) [6]. This empirical relationship is now justified in terms of surface basicity by the linear trend found when plotting the P–O stretching frequency and the amount of CO_2 adsorbed evaluated by the area of MS-TPD peaks, figure 6.

5. Conclusions

CO_2 adsorbs on basic sites of aluminophosphate oxynitrides (AlPON) catalysts originating bidentate carbonate and bicarbonate species as well as linearly physisorbed molecules. The amount of CO_2 adsorbed is a growing function of nitrogen content in AlPON and, therefore, the concentration of nitrogen is a parameter controlling the basicity of these catalysts. The influence of nitrogen on the surface basicity of AlPON is based on the modification of sites concentration rather than on the alteration of their basic strength. However, particularly stronger basic centers are identified after careful surface cleaning and adsorption of CO_2 as bicarbonates. Their structure involves neighboring Al–OH and $-PNH_2$ groups. The activity of AlPON in base-catalyzed reactions such as the Knoevenagel condensation and the synthesis of methyl isobutyl ketone from acetone is explained in terms of surface basicity estimated from CO_2 adsorption.

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