DRIFTS Study of Platinum Aluminophosphate Oxynitride Catalysts

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Diffuse reflectance infrared spectroscopy (DRIFTS) has been used to compare the surface structure and stability of fresh and reduced Pt-AlPON catalysts with that of AlPON support. DRIFTS reveals that surface PNH_2 species participate in the anchoring process of the platinum precursor; meanwhile, the metal-phase reduction process produces a deep decrease in the specific surface and total nitrogen content of the solid. On the other hand, the three solids undergo hydrolysis in the presence of gaseous water at concentration as low as 3 ppm. As a result of this hydrolysis reaction, part of the nitride ions are transformed into easily removable PNH_4^+ and NH surface species.

Introduction

Substitution of nitrogen by oxygen in the anionic network of amorphous aluminum phosphate (AlPO₄) solids leads to the formation of amorphous aluminophosphate oxynitrides (AlPON).1-3 These materials, prepared by nitridation with ammonia at high temperature, maintain the high specific surface area of the precursor and have been described as a new family of solid base catalysts^{2,4-6} showing a good activity in Knoevenagel condensation.⁷ The advantages of AlPON solids as basic catalysts are based on their high surface area and the possibility of tailoring their acid—base properties by adjusting the N/O ratio. The AlPON have also been used as a support to prepare polyfunctional catalysts with combined both basic and metallic sites. In this sense, Ni-AlPON has been revealed to be effective for the low-pressure, one-step methyl isobutyl ketone (MIBK) synthesis from acetone⁸ and Pt-AlPON to be a good catalyst in the dehydrogenation of isobutane to isobutene.^{9,10}

Diffuse reflectance infrared spectroscopy (DRIFTS) is a powerful technique to determine the surface and/or bulk structure of solids in real conditions, and it has been used to characterize AlPON catalysts.^{11–14}

In this work we present a DRIFTS study of surface stability of Pt-AlPON catalysts as compared with the AlPON support.

Experimental Section

High surface area amorphous aluminophosphate precursor AlPO₄ was synthesized by the citrate method. ¹⁵ Two aqueous solutions of Al(NO₃)₃•9H₂O (Merck) and (NH₄)H₂PO₄ (Merck), with the same molarity to obtain an Al/P ratio of 1, were mixed for 1 h at room temperature (RT) under stirring. Then, an excess of citric acid (Merck) was added, and the mixture was kept overnight under continuous stirring. After water evaporation under reduced pressure, the gel obtained was dried for 10 h at 100 °C in a vacuum oven (50 mbar). Finally, the solid was calcined for 16 h at 550 °C.

The AlPO₄ precursor was activated by dry NH₃ stream at 750 °C. The Pt—AlPON catalyst was prepared by impregnation of Pt(acac)₂ dissolved in 20 mL of acetone. The AlPON support, previously dehydrated for 48 h at 100 °C, was added to the Pt(acac)₂ solution and the slurry carried into dryness by continuous stirring at RT. The solid obtained was finally ovendried at 100 °C overnight.

For obtaining the metallic platinum, Pt–AlPON catalysts were treated under N_2 flow by increasing the temperature from RT to 500 °C at 2.5 °C/min, maintaining the solid at this temperature for 1 h, and then were reduced in pure H_2 flow for 2 h at that temperature.

The total nitrogen content of the AlPON and Pt-AlPON solids was determined by titration with a sulfuric acid solution of the ammonia liberated in alkaline digestion at 400 °C with melted KOH under a N₂ atmosphere following the reaction¹⁶

$$xN^{3-} + 3xKOH \rightarrow xNH_3 + (3x/2)K_2O + (3x/2)O^{2-}$$

The specific surface area was measured by the single-point BET method in a Micromeritics Flowsorb II 2300 apparatus. Before analysis, samples were degassed for 2 h at 200 °C under nitrogen flow

The amount of platinum was determined in a ICP-AES Philips PV8250 spectrometer.

Platinum dispersion was determined by H_2 chemisorption in a Micromeritics ASAP 2000 apparatus. Just before analysis, the sample was outgassed 30 min at 120 °C and 2 h at 420 °C. Then, it was cooled to 35 °C and reduced under pure H_2 (l'Air Liquide, 99,999%), 15 min at that temperature and 1 h at 450 °C. Finally, it was outgassed 2 h at 420 °C and later brought to 35 °C, the temperature of hydrogen chemisorption.

H₂ uptake was used to determine the metal dispersion by assuming that the hydrogen/platinum stoichiometry is one.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were collected with a Brucker IFS88 infrared spectrometer with KBr optics and a DTGS detector. The samples were placed without any treatment such as pressure or dilution inside a commercial controlled environmental chamber (Spectra-Tech 0030-103) attached to a diffuse reflectance accessory (Spectra-Tech collector). Samples were heated

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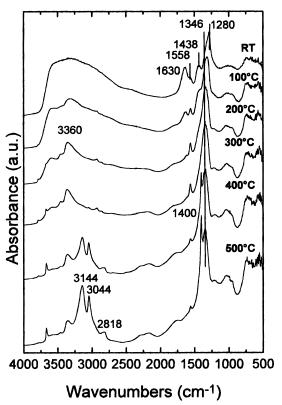


Figure 1. In situ DRIFTS spectra of AlPON support as a function of temperature.

TABLE 1: Physical Properties of the Catalysts

catalyst	S_{BET} (m ² g ⁻¹)	total N content (% w/w)		Pt dispersion (%)
AlPON support	200	4.3		
fresh Pt-AlPON	170	3.4	0.68	
reduced Pt-AlPON	17	0.8	0.60	7

from room temperature to 500 °C under a 30 mL min⁻¹ N_2 flow (l'Air Liquide, 99.999%). The spectra (200 scans, 4 cm⁻¹ resolution) were obtained every 100 °C after 30 min of stabilization. Then, the catalysts were cooled to RT under N_2 flow and kept under these conditions for 1 h. After that, they were heated again to 300 °C and cooled to RT. Finally, 30 mL min⁻¹ of a RT water-saturated N_2 flow was admitted into the DRIFTS cell, and spectra were obtained as function of time. An aluminum mirror was used as background, and data are presented in absorbance mode without any treatment. A commercial software (Brucker OPUS/IR 2.2) was used to calculate the area of the DRIFTS bands after baseline correction with a polynomial function.

Results

Catalysts. Table 1shows the physical properties of fresh and reduced Pt—AlPON catalysts. For comparative purpose, the values for the AlPON support are added.

The impregnation process produces a small decrease in the specific surface area and the total nitrogen content of the catalyst (around 20%). The reduction step induces a deep decrease of these parameters (around 85%).

DRIFTS Analysis. *Surface Thermal Stability.* Figures 1–3 show "in situ" DRIFTS spectra of the AlPON support, the fresh and the reduced Pt—AlPON catalysts, obtained at the different temperatures indicated in the figures.

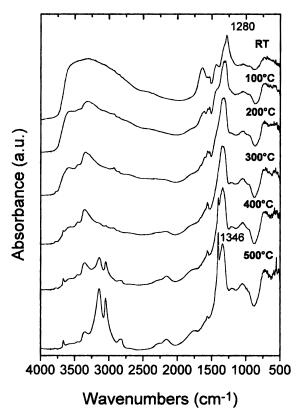
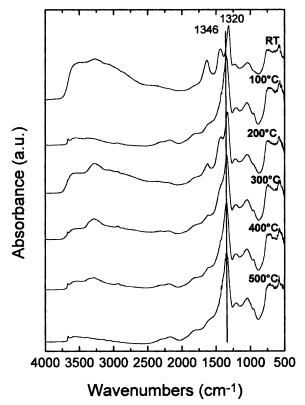


Figure 2. In situ DRIFTS spectra of fresh Pt-AlPON catalyst as a function of temperature.



 $\begin{tabular}{ll} \textbf{Figure 3.} & In situ DRIFTS spectra of reduced Pt-AlPON catalyst as a function of temperature. \end{tabular}$

Similar qualitative information can be obtained from the three solids at room temperature. The spectra are characterized by the presence of water adsorbed (ca. 3500 cm⁻¹, ν (OH); 1630 cm⁻¹, δ (HOH)), P-NH₂ species (1558 cm⁻¹, δ _{as}(NH₂)),¹⁷ and NH₃ adsorbed on acid Bronsted sites as NH₄⁺ (1438 cm⁻¹,

 $\delta_{as}(NH_4^+)$). The presence of NH₃ adsorbed on Lewis acid sites cannot be discarded since they appear at the same position as water adsorbed (ca. 1620 cm⁻¹).¹⁷ However, in the reduced catalysts the $\delta_{as}(NH_2)$ band is almost unobservable. In the framework region, the main feature is an intense and wide absorption due to the overlapped P=O, PO₂, -P=N, and -N= P-N= stretching vibrations bands of the solid. This broad band is centered at about 1280 cm⁻¹ in the AlPON and fresh Pt-AIPON solids and at 1320 cm⁻¹ in the reduced catalyst. Wide bands at 740 ($\nu_{\rm s}({\rm P-O-P})$) and 1000 cm⁻¹ ($\nu_{\rm as}({\rm P-O-P})$) are also observed. In addition, the fresh Pt-AlPON catalyst also presents a pair of bands at 1531 and 1606 cm⁻¹ characteristic of metal-coordinated acetylacetonate that remains on the catalysts surface after Pt impregnation. 18,19

Heating under N2 flow produces the desorption of adsorbed water and ammonia species from all three solids, as revealed by the elimination of bands at 1640–1630 and 1438 cm⁻¹, respectively, and by the broad band around 3500 cm⁻¹. Acetylacetonate bands disappear from the fresh Pt-AlPON catalyst surface at 200 °C. The elimination of the adsorbed species onto the catalyst surface causes the appearance of structural NH stretching (ca. 3360 cm⁻¹) as well as the hydroxyl vibrations. Three different bands are developed in that region at 3783, 3670, and 3582 cm⁻¹, being ascribed to hydroxyl groups bonded to tetrahedral aluminum (Al-OH)_t, tetrahedral phosphorus (P-OH)_t, and hydroxyl groups bridging aluminum cations, respectively. 12 Also, a band at 3460 cm⁻¹ is observed. It has been reported that this band is indicative of the presence of P-NH₂ groups.²⁰ In the same region, bands at 3144, 3044, and 2818 cm⁻¹, as well as another band at 1400 cm⁻¹, grow sharply above 300 °C in the support and fresh Pt-AlPON solid. These bands are characteristic of stretching and deformation vibrations of adsorbed NH₄⁺ ions.²¹ However, these NH₄⁺ ions are not adsorbed onto the catalysts surface but on the SeZn windows of the DRIFTS chamber. The removal of these bands after cleaning the windows (Figure 4) proves this assignation. The adsorption of ammonium ions on the windows indicates an intense desorption of nitrogen species as gaseous NH₃ from the catalysts surface during the heating.

In the framework region, a shift of the main band with temperature, from its position at RT to 1346 cm⁻¹, is observed for the three solids. This shift to higher wavenumbers is the consequence of the loss of the nitrogen species. The same behavior was observed when the nitrogen content in AIPON solids was modified and was ascribed to the replacing of nitrogen by oxygen (higher electronegativity). 12,22,23 According to this, the intensity of the bands at 1030, 946, 740, and 566 cm⁻¹ due to P-O and Al-O stretching vibrations^{14,17} is increased.

Another important feature is the appearance, when increasing the temperature, of bands at 2300 and 2170 cm⁻¹, previously assigned in AIPON solids to P-H bonds induced by the nitrogen loss. However, similar bands have been observed in other oxynitrides, some of them without phosphorus, as vanadiumaluminum-oxynitrides (VAION)²⁴ and AlN solids.^{25,26} In these studies, these two bands were assigned to the $\nu(N=N)$ stretching vibration of different metal dinitrogen species, although their assignation to hydride groups cannot be fully discarded.

To better evaluate the changes observed during the heat treatment, an integration of the DRIFTS bands were carried out as a function of temperature (Figure 5). At low temperatures, the presence of the water-adsorbed bands makes a good integration difficult.

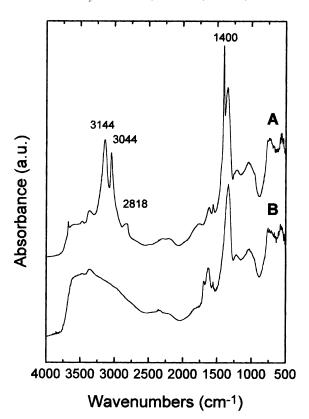


Figure 4. In situ DRIFTS spectra at RT of AlPON support treated at 500 °C, before (A) and after (B) cleaning of the ZnSe windows of the DRIFTS chamber.

The area of the $\delta_{as}(NH_4^+)$ DRIFTS band at 1440 cm⁻¹ presents almost the same values and trends for all the catalysts, decreasing continuously with temperature and disappearing at 300 °C. The $\delta_{as}(NH_2)$ (1560 cm⁻¹) and $\nu(NH)$ (3300 cm⁻¹) DRIFTS bands area pass through a maximum between 200 and 300 °C. Although the initial amounts of NH species are similar in all the catalysts, their loss during the heating process is quite different, showing that their thermal stability decreases in the sense AlPON support > fresh Pt-AlPON > reduced Pt-AlPON. It is important to note that, while NH and NH₄⁺ areas are similar for the AIPON solid and Pt-supported catalysts at low temperature, suggesting a similar concentration of such species, the area of the NH₂ band decreases strongly in the sense AlPON support > fresh Pt-AlPON > reduced Pt-AlPON. This observation tends to indicate a loss of a part of the initial P-NH₂ species during the impregnation and reducing processes and their participation in the anchoring process of the platinum precursor. Moreover, the temperature of the maximum of concentration of these species shifts from 250 °C for the support to 300 °C for the fresh Pt-AlPON catalyst, indicating the higher thermal stability of the NH₂ remaining in the supported catalysts after impregnation. In agreement with this proposal, one observes that the amount of NH₂ groups lost during the heating process is higher in the support than in the platinum AlPON catalysts.

The evolution of the 3783 cm⁻¹ ν (Al-OH)_t DRIFTS band area is similar to that observed for NH groups. They pass through a maximum between 200 and 300 °C, while the 3670 cm⁻¹ (P-OH)_t groups band intensity continuously increases with temperature. The difference observed between the AIPON support and the fresh Pt-AlPON catalysts in the area of the $\nu(Al-OH)_t$ DRIFTS band is not significant since it is in the order of the experimental error. We can thus consider that the amount of Al-OH groups does not change during the platinum impregnation process.

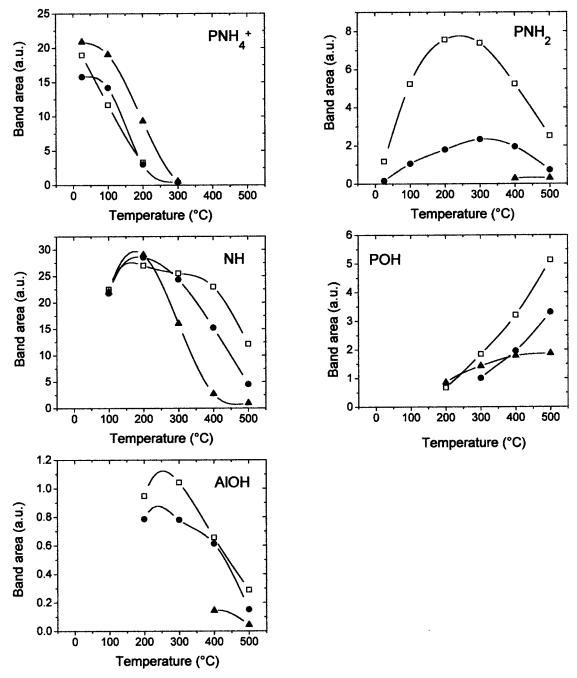


Figure 5. Evolution of the area of the DRIFTS bands with the in situ temperature treatment: AlPON support (\Box) , fresh Pt-AlPON (\bullet) , and reduced Pt-AlPON (\triangle) .

Surface Stability toward Hydrolysis. It has been reported that AIPON solids undergo hydrolysis when dispersed in pure water. In this process, the AIPON lose a quite important amount of N from the surface. To determine the stability of the surface of the catalysts in the atmosphere, where gaseous water is always present, we have analyzed the DRIFTS evolution during in situ water gas-phase treatment.

Figure 6 shows the evolution of the DRIFTS spectrum of the AlPON support as function of contact time with a 30 mL/min N_2 flow at RT, after the treatment at 500 °C. In such flow, the concentration of water is very low (<3 ppm). When increasing the time of exposure, bands due to adsorbed water (ca. 3500 and 1620 cm⁻¹) increase. An intense band at 1700 cm⁻¹ and a wide one at ca. 1440 cm⁻¹ also appear. These latter bands are due respectively to the symmetric and asymmetric deformation vibrations of NH_4^+ species formed on the AlPON

surface. Similar results are observed for Pt–AlPON catalysts (not reported). The presence of the $\delta_s({\rm NH_4}^+)$ DRIFTS band at 1700 cm⁻¹ is indicative of the existence of a perturbed ammonium ion since this mode of vibration is normally not IR-active.²⁷ To accelerate the hydrolysis reaction, a 30 mL/min N₂ flow saturated with water at RT was contacted with the reduced Pt–AlPON catalyst. In these conditions, the water concentration in the gas flow increases to 23 ppm. Figure 7 shows the DRIFTS spectra obtained as a function of time. The same behavior as that for low water concentrations is observed, but the hydrolysis reaction quickening. On the other hand, the NH₄+ band at 1700 cm⁻¹ is not visible, indicating that the ammonium groups are not perturbed.

The quantitative study (Figure 8) shows that, after the hydrolysis reaction over the AlPON support and the fresh Pt-AlPON catalyst, the concentration of NH₂, POH, and AlOH

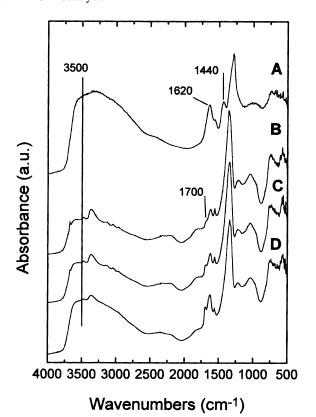


Figure 6. In situ DRIFTS analysis of hydrolysis reaction of AlPON support at RT, with 30 mL min⁻¹ N_2 flow: initial state (A), after treatment at 500 °C, 10 min (B), 30 min (C), and 1 h (D).

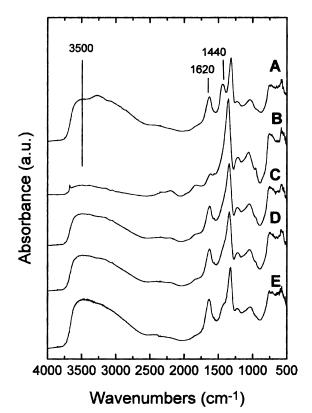


Figure 7. In situ DRIFTS analysis of hydrolysis reaction of reduced Pt—AlPON at RT, with water saturated 30 mL min⁻¹ N_2 flow: initial state (A), after treatment at 500 °C, 10 min (B), 1.5 h (C), 19 h (D), and 41 h (E).

groups does not change with respect to the values obtained at 500 °C, while the amount of NH species increases up to the

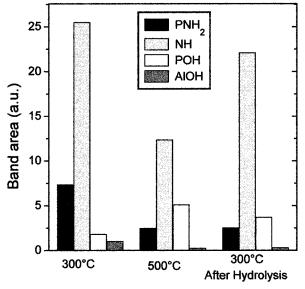


Figure 8. Comparison of the DRIFTS bands area of AlPON support before and after hydrolysis treatment.

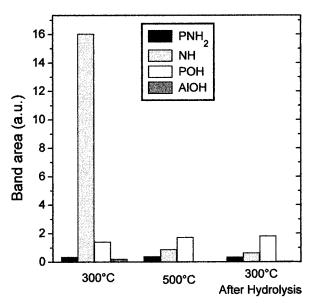


Figure 9. Comparison of the DRIFTS bands area of reduced Pt-AlPON catalyst before and after hydrolysis treatment.

value obtained before hydrolysis. This suggests that the NH groups are regenerated by the hydrolysis reaction. On the contrary, for the reduced catalyst (Figure 9), although NH₄⁺ groups are regenerated in the catalyst surface, the amount of PNH₂, NH, POH, and AlOH remains practically unchanged.

Discussion

DRIFTS reveals that the surface structures of AlPON and of fresh and reduced Pt—AlPON catalysts are qualitatively similar, showing the presence of PNH₄⁺, PNH₂, NH, AlOH, and POH functional groups. The evolution with temperature of the DRIFTS spectra of the three solids is also similar and can be easily explained.

The increase of the hydroxyls groups and NH and NH₂ observed on the three solids when heating from RT to 200–300 °C should be related to the surface cleaning due to water and ammonia desorption. The decrease of the 3783 cm⁻¹ (Al–OH)_t band area above 300 °C is a consequence of the condensation and dehydration of the hydrogen-bonding hy-

droxyls by a thermal effect. Moreover, the elimination of the PNH_2 groups above 300 °C has been ascribed to a hydrolysis reaction with the water coming from the hydroxyls condensation 12,13 following the reaction

$$PNH_2 + H_2O \rightarrow POH + NH_3(g)$$

This reaction explains the formation of the POH groups observed at high temperatures (Figure 5) and the observation of NH₄⁺ ions adsorbed over the ZnSe windows of the DRIFTS cell.

The same authors propose that the decrease of the PNH₂ bands can also be associated with the following reaction.

$$PNH_2 + O = P \rightarrow -P - NH - P - OH$$

However, if so, the -NH- band area should increase when PNH_2 decreases at 300 °C. We observed their decrease at such a temperature, so the contribution of this reaction to the PNH_2 decrease can be neglected.

The understanding of the influence of the impregnation and reduction processes in the final structure of the catalysts arises from the comparison between the quantitative DRIFTS analyses and the physical properties ($S_{\rm BET}$ and total N content) of the solids.

After the platinum impregnation process, the total nitrogen content of the catalyst decreases from 4.3 to 3.4%. The amount of PNH₂ present on the catalyst surface, determined by DRIFTS, also decreases. The remaining PNH2 groups show a thermal stability higher than those present in the AlPON support. From these observations, the participation of easily removable amido groups in the anchoring process of the Pt precursor can be established. Furthermore, the reduction of the Pt-AlPON catalyst produces a sharp decrease in the total nitrogen content as well as a large decrease of superficial NH2. The lower content of nitrogen species in the reduced catalyst is also induced by the shift of the main band in the framework region from 1280 cm⁻¹ for the support and the fresh catalyst to 1320 cm⁻¹ in the reduced one. The noncontamination of the ZnSe windows of the DRIFTS cell at high temperatures by NH₄⁺ is indicative of the lower production of gaseous NH3 during the heating. This decrease in the N content is probably explained by the prolonged heating treatment endured by the catalyst during the reduction step. Furthermore, since this step is carried out under high H₂ pressure, we can suspect that the reduction of the nitrogen species of the solid to form gaseous NH₃ can be produced:

$$N + (3/2)H_2 \rightarrow NH_3(g)^{\uparrow}$$

A suitable solid for catalytic purposes should be stable in working and storage conditions. The results show that all three catalysts are very sensitive to the presence of water in the atmosphere. They undergo hydrolysis even when the concentration of water in the gas flow is below 3 ppm. At this low concentration, a regeneration of the NH groups and the formation of highly perturbed NH₄⁺ groups are detected (Figure 8). The regeneration of NH and NH₄⁺ species must proceed via hydrolysis of the N3- ions, since no change in the concentration of the other nitrogen species is observed. In this sense, Benitez et al.11 have reported that, after the reaction with liquid water, the N 1s XPS peak at 397.2 eV, corresponding to N³⁻, which predominates in the untreated AlPON, is almost eliminated, while another peak at 398.8 eV ascribed to NH_X species shows up. Besides this, Mazur²⁸ observed that aging in air of an AlN film prepared by ion beam deposition results in the generation of a $\nu(NH)$ band at 3217 cm⁻¹ as a consequence of the hydrolysis of the AlN. However, hydroxyls or NH_2 groups are not regenerated. The nonregeneration of the PNH_2 groups after hydrolysis confirms that the observed decrease of the PNH_2 DRIFTS band area for the fresh Pt-AlPON catalysts as compared with the AlPON support (Figure 5) indicates the participation of such groups in the platinum impregnation process.

The synthesis of aluminophosphate oxynitrides solids, AlPON, from nitridation with NH₃ of the AlPO₄ precursor, proceeds by the substitution of the oxygen atoms by nitrogen atoms, following the reaction^{1,2}

$$AlPO_4 + xNH_3 \rightarrow AlPO_{4-3x/2}N_x + (3x/2)H_2O$$

In this process, water is formed. The reverse reaction can describe the AlPON hydrolysis. The liberation of NH_3 in this reaction can also explain the formation of NH_4^+ ions in the catalysts surface, since they can react with another water molecule

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

We have no evidence of the formation of OH groups on the catalyst surface after hydrolysis. However, the integration results of the hydroxyls bands is difficult since they are perturbed by the presence of the wide $\nu(\text{OH})$ vibration band of water at low temperatures, and they disappear at high temperatures by thermal effect. So, small changes in the area values are not easily observable. From XPS, DRIFTS, TG, and XANES data, Benitez et al. 11 described the resulting AlPON surface after liquid water reaction, as either AlPO or AlPON with a lower nitrogen content, in good agreement with this hydrolysis mechanism.

As seen above, the hydrolysis process implies a regeneration of the surface NH_4^+ and NH species from bulk N^{3-} ions. An important goal in the discussion is to determine whether this process can destroy the structure and catalytic properties of the AlPON support and of the Pt-AlPON catalysts.

It is clear that, after each step of impregnation, reduction, or heating of the catalysts, an hydrolysis reaction will take place on the catalyst surface, since in the aging process in atmosphere or in desiccator, the catalysts will be in contact with a water concentration above 3 ppm. Hydrolysis transforms part of the nitride ions in nitrogen species that are susceptible to be easily removed from the surface by heating. Because of this, the total nitrogen content of the catalysts continuously diminishes after treatment. The more the amount of N³- ions is low, the more the hydrolysis reaction and the surface regeneration process are low and slow, until the limiting case, if a sufficient number of heating processes were carried out, of the total transformation of the AIPON solid to an AIPO one.

Although Pt—AlPON catalysts hold the AlPON support structure, they present an important loss of specific surface area and N³- and PNH² species after reduction. As the basic properties of the AlPON catalysts increase with the nitrogen content,².5 the basicity of Pt—AlPON catalysts is expected to be lower than that of the AlPON support. However, as we can tailor the basic properties of the AlPON solids by adjusting the nitrogen concentration, the basic properties of the supported catalyst can be also tailored.

On the other hand, AlPONs are solids with micro- and mesoporosity having an average pores width close to 4 nm.²⁹ The specific surface area loss observed during the metal impregnation process has been associated with the microporosity

loss since no modifications of the average size of the mesopores have been observed.²⁹

All these considerations must be taken into account when measuring the catalytic properties of AlPON and Pt-AlPON solids. The nitrogen content and specific surface change during the catalytic activation process and, probably, are modified during the catalytic test itself. Such modifications in the physical properties of the solids can lead to a change in the catalyst activity which can be erroneously assigned to other factors as, for instance, catalytic deactivation processes.

Pt-AlPON solids with high nitrogen content have been described as good catalysts for isobutane dehydrogenation, 9,10 their activity being higher, for a constant platinum content, when the nitrogen content and the platinum dispersion are higher. The catalytic activity of the Pt-AlPON catalysts studied in this work has been tested in such a reaction. The activity of the solid is low and similar to that observed for Pt-AlPO₄.^{9,10} After reduction the Pt-AlPON catalyst presents a nitrogen content of 0.8%. As stated above, in reaction conditions this amount is expected to be lower. On the other hand, the platinum dispersion is very low (7%).

Conclusions

DRIFTS shows that the surface structure of Pt-AlPON catalysts is qualitatively similar to that of the AlPON support. Quantitative differences are nevertheless observed. In the Pt impregnation process, a decrease in the number of P-NH₂ groups with respect to the support is observed in the supported catalysts, indicating their participation in the process of anchoring of the platinum precursor. However the reduction process of the metallic phase leads to an important loss of specific surface area and total nitrogen content of the catalysts. On the other hand, both the support and the supported catalysts undergo hydrolysis in the presence of water, leading to a regeneration in the catalysts surface of the easily removable nitrogen species (NH and NH₄⁺) from N³⁻ ions. Thus, promising catalysts that combine the platinum and AlPON catalytic properties can be prepared.

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