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Study of the Stability of AlPON Catalysts in An Aqueous Environment

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Abstract

Aluminophosphate oxynitride (AlPON) stability is studied by dispersing the solid in pure water and analysing the product by X-ray photoelectron spectroscopy (XPS), diffuse reflectance infra-red spectra (DRIFTS), thermogravimetry (TG) and X-ray absorption near edge structure (XANES). The presence of phosphate ions and the absence of Al^{3+} cations in the aqueous phase indicates that no dissolution but real hydrolysis of AlPON occurs. Upon hydrolysis, AlPON loses a quite significant amount of P and N from surface. The result is a nitrogen-impoverished surface phase in which aluminum keeps its original first co-ordination sphere. This new surface phase may be ascribed to either AlPO or AlPON with a lower nitrogen content. A third possibility, phosphorous oxynitride (PON), may not be discarded due to the similarity between its P/N ratio and that of hydrolysed AlPON. © 1997 Elsevier Science Limited.

1 Introduction

Phosphates in general, and particularly aluminum orthophosphate ($AlPO_4$), have been widely employed either as supports or as high-surface catalysts in many catalytic reactions.[1] However, technical applications of phosphates have been conditioned by their lower durability compared with silicates.

$AlPO_4$ is also the basis of a new series of materials denominated as aluminophosphate oxynitrides (AlPON) in which oxygen has partially been replaced by nitrogen in a nitridation reaction. The introduction of nitrogen in the formulation of phosphate-based glasses increases their viscosity, life and resistance to lixiviation.[2] Regarding surface properties, oxygen substitution by nitrogen is proposed as a method to increase and control the surface Lewis basicity of materials,[3] a very important parameter, for instance, in catalyst design. Also, the combination of P and N fundamental chemistry opens a wide field of potential applications for aluminophosphate oxynitrides.

AlPON materials have been successfully tested as catalysts in Knoevenagel-type condensations[4] and in the synthesis of methyl isobutyl ketone.[5] Currently, AlPON is being investigated as a support for active metallic phases such as nickel.[6]

Catalyst preparation and metal loading implies calcination and impregnation with aqueous solutions. AlPON resistance to temperature is described in a previous paper.[7] In this article, we focus on the second aspect, the stability of AlPON samples exposed to water.

2 Experimental

2.1 Sample preparation

High surface and X-ray amorphous $AlPO_4$ precursor (AlPO) was prepared by co-precipitation by slowly mixing an ammonia solution (40%vol) to a well-stirred $Al(NO)_3.9H_20$ and H_3PO_4 mixture with a P/Al ratio equal to one. The solution was neutralized and the precipitate filtered, washed with water and 2-propanol, dried at 120°C and, finally, calcined at 800°C.

Aluminophosphate oxynitride (AlPON) was obtained after 10 days' nitridation under ammonia flow at 800°C. Hydrolysed (AlPON*) sample was prepared by dispersing AlPON in pure water and later filtering, washing with ethanol and drying the solid at 60°C. The resulting solution contains phosphate ions (detected by precipitation with

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Table 1. Bulk nitrogen content, Kjeldhal fraction, specific surface area and weight loss upon heating values for every sample. AlPON* designates the product of AlPON hydrolysis

Sample	N_{BULK} *wt(%)*	$N_{Kjeldhal}$ *wt(%)*	*Weight loss (%)*	S_{BET} $(m^2\ g^{-1})$
AlPO	0	0	19·1	150
AlPON	20	2·3	12·5	125
AlPON*	11	1	26·0	—

$AgNO_3$) but no Al^{3+} cations. Bulk nitrogen content is obtained by alkaline digestion with molten KOH. Residual surface nitrogen containing species are titrated by the Kjeldhal method.

2.2 Characterization techniques

XPS spectra were collected in a Vacuum Generator 210 spectrometer with a hemispherical analyser working at 20 eV constant pass energy. $Mg_{K\text{-alpha}}$ radiation at 240W is the excitation source and every spectrum is the co-addition of ten runs every 0·1 eV. Before acquisition, samples were evacuated at 10^{-7} torr overnight at room temperature (RT). C_{1s}, Al_{2s} Al_{2p}, P_{2s}, P_{2p}, O_{1s} and N_{1s} peaks were analysed and quantitative analysis was carried out using sensitivity factors provided by manufacturer. Peak position was assigned using C_{1s} binding energy (B.E.) at 284·6 eV as the reference.

Diffuse reflectance infra-red spectra (DRIFTS) were obtained in an FT Nicolet 510P spectrometer equipped with a deuterated trislicine sulphate (DTGS) detector working at 4-cm^{-1} resolution. Samples were placed in a controlled environment chamber (Spectra-Tech 0030-101) attached to a diffuse reflectance accessory (Spectra-Tech Collector). Specimen were purged under nitrogen flow (50 ml min^{-1}) at RT for several hours. Two hundred scans were accumulated in every case and data are presented in absorbance mode referred to powdered KBr.

Thermogravimetric diagrams are obtained from a Setaram thermobalance TG- DTA 92 using N_2 carrier at 26 ml min^{-1}. Temperature is raised at $5°C\ min^{-1}$ rate from RT to 500°C.

3 Results

Bulk nitrogen content, Kjeldhal fraction and weight loss of every sample are compiled in Table 1. It is important to notice the reduction in the $N_{Kjeldhal}$ content and the increase in the weight loss in the water-treated AlPON*.

Table 2 summarizes XPS peak positions and surface atomic composition of each specimen. Al_{2s} and Al_{2p} peaks are unaffected by exposure to water, but phosphorous and oxygen peaks shift to higher binding energy. N_{1s} spectra are made up of two contributions at 397·2 and 398·8 eV, (Fig. 1). In untreated AlPON predominates the low binding energy (B.E.) peak, which is almost eliminated after reaction with water.

P and N are effectively removed from the surface after exposure to water. However, Al concentration remains unmodified, Table 2. This is in good agreement with the presence of phosphate ions and with the lack of Al^{3+} cations in the solution. Consequently, AlPON is not partially dissolving in water; on the contrary, a hydrolysis reaction is occurring.

The DRIFTS spectra of AlPON and hydrolysed AlPON* in the 2000–500 cm^{-1} range is plotted in Fig. 2. The main peak is located around 1250 cm^{-1} and corresponds to (P–O) stretching.[8] The absorption at 1565 cm^{-1} was early assigned by Peri[9] to terminal $P\text{–}NH_2$ groups. Residual adsorbed water is responsible for the band at 1645 although some contribution coming from NH_3 adsorbed on Lewis sites may not be ruled out.[9] Upon exposure to water, weak bands at 1440, 1305 and 755 cm^{-1} are developed. The first one can be due to surface NH^{4+}, although phosphorous oynitride (PON) also shows a sharp peak in the 1475–1500 cm^{-1} range. Peaks at 1305 and 755 cm^{-1} are present in the precursion (AlPO) DRIFTS spectrum, the first due to (P–O) stretching and the second to the combination of (P–O) and (Al–O) modes.[8]

4 Discussion

From the surface composition in Table 2, and assuming the presence of hydrogen (undetectable

Table 2. Binding energy and surface composition obtained from XPS for every sample. PON values are included as reference.

	Binding energy (eV)						*Atomic percentage*			
Sample	Al_{2s}	Al_{2p}	P_{2s}	P_{2p}	O_{1s}	N_{1s}	*Al*	*P*	*O*	*N*
AlPO	119·6	74·8	191·5	134·2	532·3	—	14·2	15·1	70·7	—
AlPON	118·8	73·9	190·4	133·1	531·4	397·5	17·4	12·9	49·1	20·6
AlPON*	118·8	73·9	190·9	133·3	531·9	399·0	18·6	7·3	64·7	9·4
PON	—	—	192·4	135·1	534·4	398·8	—	28·1	46·4	25·5

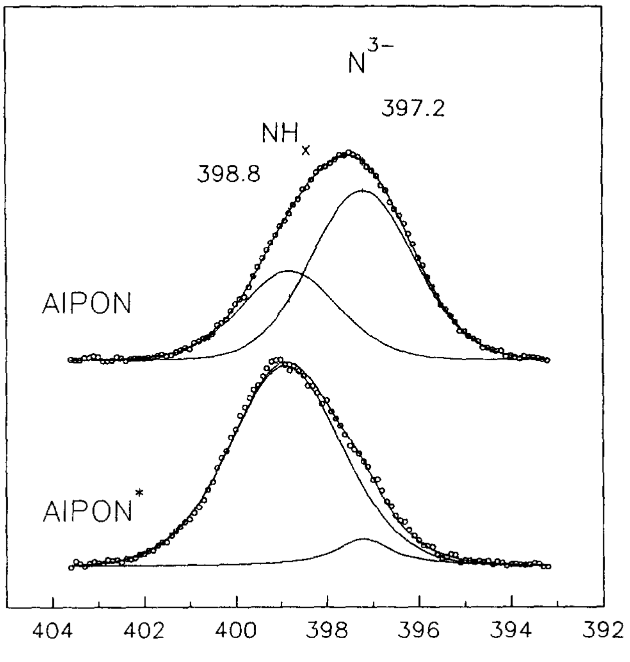

Fig. 1. N_{1s} XPS spectra for AlPON and AlPON hydrolysed (AlPON*) samples. Solid lines are the result of the best fit achieved with two components at 397·2 and 398·8 eV.

by XPS) to keep electrical neutrality, a surface formula can be obtained (Table 3). Furthermore, data included in this paper leads to the obtainment of a more elaborated surface composition. The procedure is as follows: the $N_{Kjeldhal}$ content allows us to distinguish between bulk structural nitrogen and surface nitrogenated species (in this case expressed as NH_3 adsorbed either on Brönsted or Lewis sites). Ammonia and adsorbed water are the only species detected in gas phase upon AlPON heating under vacuum below 500°C,[7] thus they are responsible for the weight loss observed by thermogravimetry. Once the amount of NH_3 is known through the Kjeldhal data, the fraction of adsorbed water is obtained by difference.

From early work on nitrided aluminophosphate,[10,11] –NH– groups were described as isolectronic with oxide ions and detected in AlPON structure by XPS. Also, terminal P-NH_2 are observable by DRIFTS, Fig. 2. A broad DRIFTS band corresponding to hydrogen-bonded hydroxyls groups prevents the characterization of

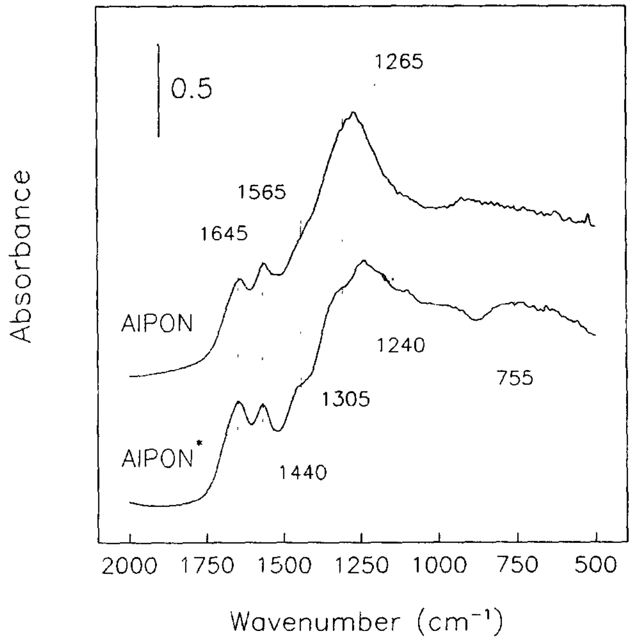

Fig. 2. DRIFTS spectra of AlPON and hydrolysed AlPON* at RT in the 2000–500 cm^{-1} range.

isolated (OH) groups although this is not enough to discard their existence in our samples. Thus, the remaining surface hydrogen (after NH_3 and H_2O quantification) should be distributed between–NH_x and–OH species.

Marchand *et al.*[11] and Day *et al.*[12] were able to resolve the contribution of –NH_2, –NH–, –N< and –N= to the overall N_{1s} spectrum. In our case, the resolution is not as good but, based on their results, we assign the peak at 398·8 eV, (Fig. 1), to NH_x species and the one at 397·2 eV to generic ions (N^{3-}). The ratio between N^{3-} and NH_x obtained by XPS is 2·0, while in hydrolysed AlPON* it is 0·08. Based on these ratios, structural nitrogen can be specified in the formulation assuming NH_x, as –NH–. Once the amount of –NH– species is calculated, the population of hydroxyl groups is obtained by computing the remaining amount of hydrogen. Formulae are compiled in Table 3.

Several aspects are of interest in analysing this formula. First, the higher coverage of adsorbed water in hydrolysed AlPON* is experimentally proved in the DRIFTS spectrum (Fig. 2). Second, essentially no hydroxyl groups or bulk N^{3-} are expected in AlPON*. Isolated hydroxyl groups are

Table 3. Bulk and surface compositions for AlPO, starting AlPON material and hydrolysed AlPON (AlPON*)

Sample	*Bulk composition*	*Surface composition (hydrogen corrected)*	*Surface composition (water and ammonia corrected)*
AlPO	$AlPO_4$	$AlP_{0.93}O_{4.79}H_{1.93}$	$AlPO_4(H_2O)_{0.88}$
AlPON	$AlPO_{1.71}N_{1.53}$	$AlP_{0.75}O_{2.83}N_{1.18}H_{2.45}$	$AlP_{0.75}O_{1.90}N_{0.66}(NH)_{0.33}(OH)_{0.31}(NH_3)_{0.19}(H_2O)_{0.62}$
AlPON*	$AlPO_{2.67}N_{0.89}$	$AlP_{0.39}O_{3.49}N_{0.51}H_{3.56}$	$AlP_{0.39}O_{2.03}N_{0.03}(NH)_{0.40}(OH)_{0.01}(NH_3)_{0.08}(H_2O)_{1.45}$

Bulk formulation is obtained assuming P/Al = 1 and with the nitrogen content found after alkaline digestion. Oxygen is adjusted to achieve charge neutrality.

not observed by DRIFTS (spectra not shown) due to broad hydrogen-bonded hydroxyl bands around 3550–3600 cm^{-1}. However, (N–H) stretching band is characterized around 3320 cm^{-1} in both samples.

It is interesting to notice that, despite the P and N loss upon hydrolysis, the P/N ratio is increased from 0·76 for untreated AlPON to 0·91 for the hydrolysed sample AlPON*. This introduces the hypothesis of the generation of a nitrogen-poor phase at the surface of AlPON after hydrolysis. Preliminary XANES analysis indicates that AlPON sample is basically made up of PO_2N_2 units. However, hydrolysed AlPON* shows a displacement towards higher energy and broadening of the phosphorous K-edge that is interpreted as an increasing contribution of a lower nitrogen containing PO_3N polyhedra. We have no conclusive proofs about the nature of such new surface nitrogen-poor phases. The increase of P/N ratio to almost one agrees either with the presence of PON-type or AlPON phases with a nitrogen content similar to hydrolysed AlPON*.[13] The increment of phosphorous, nitrogen and oxygen binding energy in hydrolysed AlPON* is also consistent with PON-type and nitrogen-poor AlPON phases, even with the presence of AlPO (Table 2). Besides, the constancy of Al peaks after hydrolysis was observed in a series of AlPON samples with an increasing amount of nitrogen[13] and can be explained by assuming that the aluminum first coordination sphere is essentially unmodified by exposure to water.

DRIFTS is also unable to resolve the product of AlPON hydrolysis. The shoulder at 1305 cm^{-1} in hydrolysed AlPON* is above the main peak in AlPON at 1265 cm^{-1}. (P–O) stretching was found to shift to higher frequency on reducing the nitrogen content in AlPON materials.[13] Furthermore, AlPO shows the main peak at 1302 cm^{-1}.[14] Finally, amorphous PON has an intense peak around 1475–1500 cm^{-1} that may explain the presence of the shoulder at 1440 cm^{-1}. Ascription of this shoulder to NH_4^+ seems to be unlikely since the $N_{Kjeldhal}$ content in hydrolysed AlPON* is smaller than in AlPON, (Table 1), and the overall weight loss is consistently explained by water removal.

Future efforts to properly assign the DRIFTS peaks at 1440 and 1305 cm^{-1} and to interpret XANES data seem to be the key to identify the surface phase resulting from AlPON hydrolysis.

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