

# Synthesis and Characterization of a New Oxynitride Catalyst: The ZrPON Solids

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## Abstract

*A new family of phosphate oxynitrides can be prepared by nitridation of X-ray amorphous zirconophosphate precursors under ammonia flow. By varying both nitridation time and temperature, ZrPON oxynitrides with different wt% nitrogen content were obtained. Acid-base characterizations have shown that the substitution of nitrogen for oxygen modifies their surface properties. It has thus been evidenced that the surface acidity sharply decreases with bulk nitrogen enrichment. The condensation rate in the Knoevenagel reaction also heavily depends on O/N ratio. © 1997 Elsevier Science Limited.*

## Résumé

*La nitruration sous flux d'ammoniac du phosphate de zirconium a permis de synthétiser une nouvelle famille d'oxynitride: les zirconophosphates 'ZrPON'. La substitution de l'oxygène par l'azote modifie les propriétés acido-basiques des ZrPON. En effet, l'acidité diminue fortement lorsque la teneur en azote dans les poudres augmente. Par ailleurs, la réaction de Knoevenagel, qui permet d'évaluer le caractère basique des oxynitrides, dépend également du rapport O/N.*

## 1 Introduction

Progressive substitution of nitrogen for oxygen in the anionic network of metal phosphate materials leads to the formation of a new family of solids: the oxynitride phosphates.<sup>1–3</sup> These high surface area oxynitrides are prepared according to a temperature-programmed activation under ammonia stream of metallophosphate precursors.<sup>4</sup> Nitrogen

atoms deeply influence the structural characteristics as well as the surface properties of the phosphate compounds. For example, it has been reported that the viscosity and chemical durability of nitrated phosphate glasses increase while their thermal expansion coefficient decreases with the nitrogen content.<sup>5</sup> In the catalytic field, nitrogen incorporation is an effective way to modify the acid-base properties of phosphate<sup>6</sup> and particularly to increase the number of basic surface sites, which is very promising since little is known about basic catalysis and since there is a large number of fine chemical processes which need strong basic sites.<sup>7</sup> Such activation of oxide compounds has been previously reported in particular preparation and characterization of silicon oxynitrides.<sup>8,9</sup> Various original catalytic systems have been prepared by nitridation processes: (i) aluminophosphate oxynitrides or 'AIPON';<sup>1,6</sup> (ii) aluminogallophosphate oxynitride systems called 'AlGaPON';<sup>2</sup> (iii) zirconophosphate oxynitrides, the 'ZrPON' solids.<sup>3</sup> The present study relates to the synthesis of these later catalysts which have been obtained by nitridation of high surface area amorphous zirconium phosphate precursors. The effects of various operating conditions on the stoichiometry of the products have been investigated. Moreover, the influence of substitution of nitrogen for oxygen on acid-base and surface properties has been evaluated.

## 2 Experimental

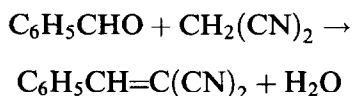
### 2.1 Analytical methods

The specific surface area was measured by the single point BET method ( $p - p_0 = 0.3$ ) in a Micromeritics Flowsorb 2000 apparatus. Samples were degassed for 1 h at 200°C under nitrogen flow before analysis at liquid nitrogen temperature.

The acid properties of the solids have been evidenced by ammonia chemisorption. These experiments were performed at different temperatures (35, 100 and 200°C) using a static volumetric apparatus (Micromeritics ASAP 2010C adsorption analyser). The samples (0.1 g) were firstly degassed at 400°C for 2 h at  $10^{-3}$  Torr (1 Torr = 133.3 N m<sup>2</sup>). In order to differentiate between ammonia physisorption and chemisorption, all analyses were repeated after the initial adsorption. The samples were degassed at the analyses temperatures for 0.5 h between the two experiments. In this work, only ammonia chemisorption results are presented.

## 2.2 Catalytic evaluation

The zirconophosphate oxynitride basicity was estimated by using the Knoevenagel reaction which consists of the condensation of benzaldehyde with malononitrile



First, 4 mmoles of each reactant and 30 ml of toluene as solvent were introduced in a 50 ml flask, equipped with a magnetic stirrer, at 323 K. Then 0.05 g of catalyst was added to the solution. Liquid samples were regularly withdrawn with a filtering syringe and analysed by a gas chromatograph (Intersmat Delsi Di 200), equipped with F.I.D. detector and using a capillary column (CPSil8CB–25 m) for separation of the products.

## 3 Results and Discussion

### 3.1 ZrPO precursors

In order to prepare high surface area, X-ray amorphous 'ZrPO' precursors, soft chemistry routes were used. For this study a ZrPO with Zr/PON=0.9 was obtained by the citrate method<sup>10</sup> and a ZrPO with Zr/PON=1 was synthesized using co-precipitation.<sup>11</sup>

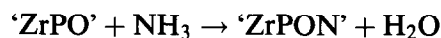
In the citrate method 20 g of ZrO(NO<sub>3</sub>)<sub>2</sub>, 3.4 H<sub>2</sub>O were dissolved by slight heating in 250 ml of distilled water and 20 ml of a 0.37M H<sub>3</sub>PO<sub>4</sub> solution was added. After stirring for 1 h, an excess of citric acid (55 g) was mixed in to the viscous and gelatinous precipitate. The resulting product was further stirred overnight. Water was then evaporated under reduced pressure and the precipitate was dried for 20 h at 120°C under vacuum (P = 50 mbar). After grinding, the sample was calcined for 16 h at 550°C.

In the co-precipitation route, 5 g of ZrOCl<sub>2</sub>, 8 H<sub>2</sub>O were dissolved in 50 ml of boiling 6M HCl.

The liquid was then cooled down to room temperature and a 2M H<sub>3</sub>PO<sub>4</sub> solution was slowly added. The obtained precipitate was filtered and washed with water and alcohol before being dried at 110°C for 16 h. The resulting solid was ground and calcined at 500°C. Powders prepared by both methods were X-ray amorphous with specific surface area values of the same kind, 240 and 290 m<sup>2</sup>g<sup>-1</sup> for solids issued from citrate and co-precipitation methods, respectively.

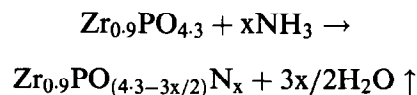
### 3.2 Nitridation study

Nitridation of these powders was performed in the isothermal region of a tube furnace. The thermal treatment including the temperature rise and step time was carried out in flowing NH<sub>3</sub> gas, whose flow was fixed at 30 l h<sup>-1</sup>. At the end of the nitridation, the samples were allowed to cool down to room temperature under pure nitrogen. This treatment led to new zirconophosphate oxynitrides according to the following reaction:



ZrPON oxynitrides with various nitrogen contents, depending on both nitridation temperature and time were prepared. For each composition, the wt% nitrogen content was determined by the Grekov method.<sup>4</sup>

The parameter which mainly influences the ZrPON composition is the nitridation temperature, as shown in Table 1 and Fig. 1. As in the AlPON system, two temperature ranges may be distinguished.<sup>12</sup> First, at low temperature — 550–800°C — the nitridation only involves an N/O substitution. The Zr/PON atomic ratio is the same in the nitrated zirconophosphate as in the ZrPO precursor, equal to 0.9 in the following example:



Second, when the nitridation temperature is higher than 800°C, ammonia reduces phosphorus P<sup>V</sup> with formation of volatile phosphine so that a increase

**Table 1.** Nitrogen content of ZrPON oxynitrides prepared by nitridation at different temperatures of a ZrPO precursor (Zr/PON = 0.9)

Sample	Nitridation temperature (°C)	wt% N
ZrPON 006	550	3.1
ZrPON 007	700	8.1
ZrPON 010	780	13.7
ZrPON 012	850	17.4
ZrPON 036	900	19.2
ZrPON 011	1000	17.0

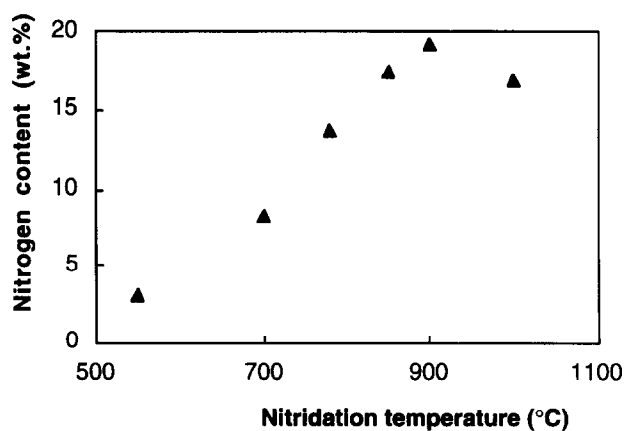
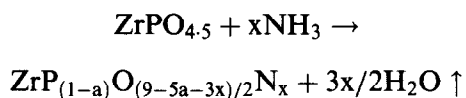


Fig. 1. Evolution of the wt% nitrogen content with the nitridation temperature.

in the Zr/P atomic ratio is observed. For example, starting from a  $\text{ZrPO}_{4.5}$  phosphate composition, the following reaction takes place:



The chemical analyses also show that at high temperature the phosphorus loss is accompanied by a decrease in the wt% nitrogen content.

Whatever the composition, the nitrided zirconophosphates are X-ray amorphous. Some crystalline compounds were only detected in powders nitrided in extreme conditions. The presence of ZrN and  $\text{Zr}_2\text{N}_2\text{O}$  were thus revealed by XRD in powders treated at 1300°C for a long nitridation time, which means that only a part of  $\text{Zr}^{\text{IV}}$  was reduced in  $\text{Zr}^{\text{III}}$  under these hard conditions. Absence of the ZrN phase below 1300°C indicates that no zirconium  $\text{Zr}^{\text{IV}}$  reduction occurs in the samples nitrided under mild conditions (700–800°C).

The second important parameter having an influence upon the zirconophosphate oxynitride composition is the nitridation time, at a given temperature. The main characteristics of samples obtained with various nitridation times at 780°C are collected in Table 2. These results clearly show that, whatever the Zr/PON atomic ratio, the nitrogen content increases with nitridation time. Moreover, as in the AlPON system,<sup>12</sup> the wt% nitrogen

Table 2. Nitrogen content and composition of ZrPON oxynitrides prepared at 780°C with various nitridation times

Sample	Nitridation time (h)	wt% N	Composition
ZrPON 016	0.5	5.5	$\text{Zr}_{0.9}\text{PO}_{3.27}\text{N}_{0.68}$
ZrPON 010	15.0	13.7	$\text{Zr}_{0.9}\text{PO}_{1.87}\text{N}_{1.62}$
ZrPON 031	263.0	19.9	$\text{Zr}_{0.9}\text{PO}_{1.01}\text{N}_{2.19}$
ZrPON 029	16.5	13.3	$\text{ZrPO}_{1.98}\text{N}_{1.68}$
ZrPON 034	40.0	15.3	$\text{ZrPO}_{1.63}\text{N}_{1.91}$

content tends towards a maximum. For instance, even after 11 days of treatment under ammonia, a ZrPON sample still contains a significant proportion of oxygen.

Whatever the nitridation time and temperature, the nitrided samples are characterized by lower specific surface areas (100–200  $\text{m}^2\text{g}^{-1}$ ) than those of the precursors (200–300  $\text{m}^2\text{g}^{-1}$ ). Figure 2 evidences that the lowering of surface area takes place mostly at the beginning of the nitridation process. This relative sintering is probably due to the presence of water at the ZrPO surface. Indeed, the ZrPO powders, as well as ZrPON, are moisture-sensitive — they absorb up to 10 wt% water — and rapid heating of the powders up to the nitridation temperature can induce a significant lowering of surface area. However, as shown in Fig. 2, the nitridation time itself, and therefore the nitrogen/oxygen substitution, does not significantly affect the surface area.

### 3.3 Surface properties of ZrPON oxynitrides

For evaluation of the surface properties, a series of ZrPON compositions with Zr/PON = 0.9 and various nitrogen contents were prepared. Their main characteristics are listed in Table 3.

The acid properties of the solids have been evidenced by ammonia chemisorption.<sup>13</sup> The results of these analyses show that the presence of nitrogen in the phosphate structure modifies the acidity of these solids. From the isotherms of ammonia adsorption (35, 100 and 200°C), it is possible to evaluate the number and the strength of acid sites. As can be seen in Fig. 3, the total number of acid sites corresponding to the chemisorbed ammonia at 35°C decreases when the nitrogen increases. Acidic strength can also be determined assuming that only strong sites are able to retain ammonia at 200°C while all sites (weak, medium and strong)

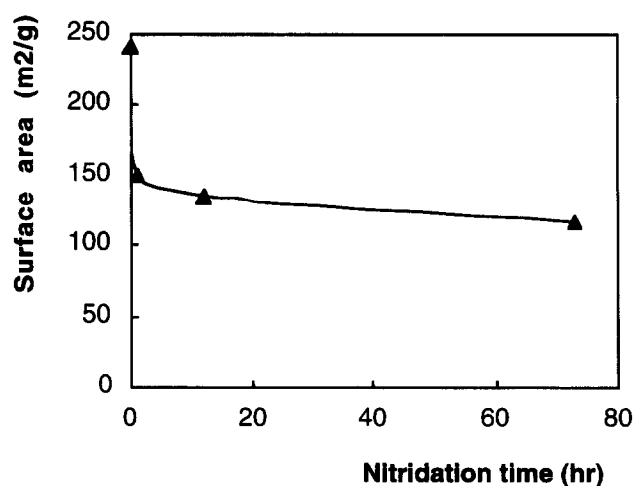


Fig. 2. Evolution of the surface area with nitridation time at 780°C.

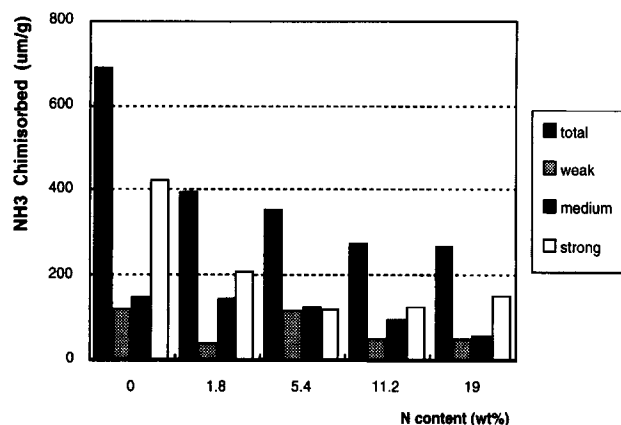
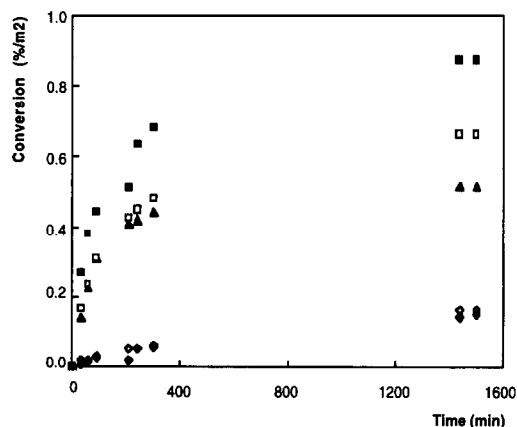
**Table 3.** Chemical composition of the precursor ZrPO and zirconophosphate oxynitrides ZrPON

Sample	N content (wt%)	Composition	Surface area ( $m^2 g^{-1}$ )
ZrPO	0	$Zr_{0.9}PO_{4.3}$	240
ZrPON1	1.8	$Zr_{0.9}PO_{3.95}N_{0.23}$	210
ZrPON2	5.4	$Zr_{0.9}PO_{3.29}N_{0.68}$	155
ZrPON3	8.2	$Zr_{0.9}PO_{2.79}N_{1.01}$	180
ZrPON4	11.2	$Zr_{0.9}PO_{2.28}N_{1.35}$	135
ZrPON5	19.0	$Zr_{0.9}PO_{1.04}N_{2.18}$	115

retain it at 35°C and medium and strong sites at 100°C. The different volumes corresponding to each strength can be found by suitable subtraction (Fig. 3). It appears that the number of strong sites sharply decreases as soon as nitrogen is present in the solids, while medium sites slightly decrease and the number of weak sites is more or less constant. However, it can be noticed that acid sites densities do not change significantly with increasing N content. The presence of 2 acid sites per 100 Å<sup>2</sup> was calculated on ZrPO precursor surface using the specific surface area data of Table 3 while 1.4 acid sites per 100 Å<sup>2</sup> were found for the more nitrated samples. Some microcalorimetry measurements with SO<sub>2</sub> adsorption show an increase of the

basicity of ZrPON solids with N/O ratio<sup>14</sup> (0.2 basic sites/100 Å<sup>2</sup> on ZrPO and 0.5 basic sites/100 Å<sup>2</sup> on ZrPON5).

In order to evaluate the basic properties of these new zirconophosphate oxynitrides, Knoevenagel condensation of benzaldehyde with malononitrile was performed. This type of reaction is well described in the literature as needing basic sites.<sup>15</sup> Fig. 4 shows the conversion rate of malononitrile versus the time of reaction for the ZrPON series. No activity was found for ZrPO tested under the conditions described above, while the same reaction performed with ZrPON5 results in 80% total conversion after 5 h. This figure also shows that the conversion is directly influenced by the nitrogen content which enhances basic sites. This correlation has already been shown by Lednor<sup>8,9</sup> on silicon oxynitride solids. It can be underlined that the rate of product formation (molecules s<sup>-1</sup> m<sup>-2</sup><sub>cata</sub>) are similar for these two catalysts: 3 10<sup>17</sup> for SiON and 1 10<sup>17</sup> for ZrPON. The strength of these sites is not yet estimated but a basicity range has been determined for AlPON solids by comparison to the conversion obtained among various liquid bases. Thus it has been shown that these oxynitride catalysts have basic sites in the range of 10.7 ≤ pK<sub>a</sub> ≤ 11.2.<sup>6</sup> The ZrPON solids present an activity comparable to that of AlPON so it can be assumed that their pK<sub>a</sub> are similar.

**Fig. 3.** Total, weak, medium and strong acid sites repartition measured by ammonia chemisorption with N content.**Fig. 4.** Knoevenagel condensation of benzaldehyde with malononitrile. ◇ 1.8%N; ◆ 5.4%N; ▲ 8.2%N; □ 11.2%N; ■ 19%N.

#### 4 Conclusion

A new family of X-ray amorphous and high surface area phosphate oxynitride catalysts has been prepared by nitridation of phosphate precursors ZrPO under ammonia flow. The nitrogen content of these zirconophosphates ZrPON can be controlled by varying both reaction time and temperature. This study also evidences that the nitrogen/oxygen substitution modifies the acid-base properties of the catalysts. Ammonia chemisorption analyses have thus shown that the surface acidity of the ZrPON solids decreases with the O/N ratio. The Knoevenagel condensation of benzaldehyde with malononitrile, which allows characterization of the basic properties, shows that the

condensation rate is directly linked to the nitrogen content. Thus, the adjustment of the O/N ratio during the synthesis allows the tuning of the ratio of basic/acid sites of these new solids and the production of valuable catalysts.

### Acknowledgements

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