

# Synthesis and characterization of a novel zirconophosphate oxynitride catalyst

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**A high surface area zirconophosphate oxynitride is shown to have interesting basic properties which are influenced by the O/N ratio.**

Recently, a new family of phosphorus and aluminium oxynitrides, ALPON, have been prepared by a thermal treatment under  $\text{NH}_3$  of the aluminophosphate precursors.<sup>1-5</sup> The resulting ALPON solids show a very high specific surface area. This new method for catalyst preparation has been developed in the last decade using temperature-programmed nitridation of an oxide precursor.<sup>6,7</sup> The incorporation of nitrogen in the aluminophosphate anionic network seems to be an effective way to modify the surface acid-base properties of the aluminophosphates and particularly to decrease the number of acid sites and to increase the number of basic surface sites. This is very interesting, since little was known about basic catalysis and since there are a large number of fine chemicals processes that require strong basic sites.<sup>8</sup> This work reports the synthesis of a new system, the zirconium phosphate oxynitride ZrPON obtained by nitridation of a high surface area amorphous zirconium phosphate precursor. The influence of substitution of oxygen by nitrogen in the solid structure on acid-base and surface properties has been evaluated. Knoevenagel condensation of malononitrile with benzaldehyde has been used as a basic test reaction.

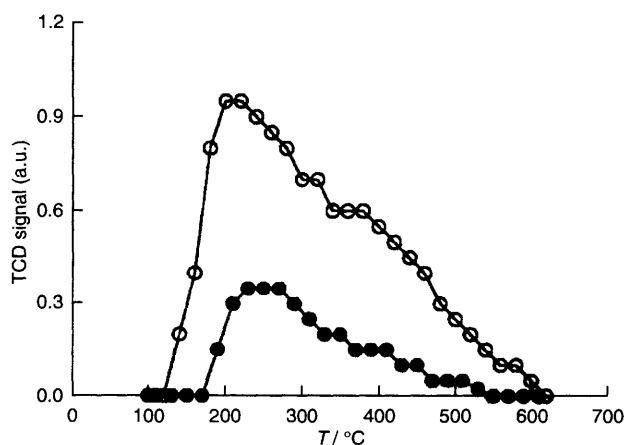
In order to prepare the high surface area amorphous phosphate precursor, the citrate method<sup>9</sup> was used. Nitridation of this powder was carried out under  $\text{N}_2\text{-NH}_3$ . This reaction was performed in a tubular quartz reactor with a coarse quartz fritted disk to contain the solid starting material. At the end of the activation process, the sample was allowed to cool to room temperature under a pure, dry nitrogen flow.

The oxynitride powder was obtained after nitridation of precursor for 7 h at 700 °C. The XRD pattern of this new solid, which contains 4.7 mass% of N, corresponds to an amorphous material. It is this lack of crystallinity of the precursor structure that permits low-temperature nitridation. Table 1 presents the chemical composition and the specific surface areas of the precursor (ZrPO) and of the zirconophosphate oxynitride (ZrPON). BET analysis shows a high specific surface area after nitridation.

The acid properties of the solids have been investigated by TPD and chemisorption of ammonia. The results of these analyses show that the presence of nitrogen in the phosphate structure modifies the number and strength of acid sites of these solid powders. Fig. 1 shows the results of the  $\text{NH}_3$  TPD experiments for both solids. The ammonia TPD experiments indicate that the total amount of desorbed  $\text{NH}_3$  which characterizes the number of acid sites is quite different for the two solids: 370 and 235  $\text{mmol g}^{-1}$  for ZrPO and ZrPON respectively. As can be seen, the temperature at which the

desorption curve maximum is observed and which is a measure of acid strength, is the same for the two solids. The nitridation process, however, modifies the acid-base properties of phosphate: the number of acid sites at the surface decreases when the nitrogen content increases in the solid while their strength does not change.

Chemisorption of ammonia is another way to evaluate the surface acidity of a sample.<sup>10</sup> The isotherms of ammonia chemisorption were carried out at three different temperatures (35, 100 and 200 °C). For a given pressure, each point of the isotherm at 35 °C lies above the corresponding one at 100 °C in turn lying above the corresponding one at 200 °C. This is in accord with thermodynamic expectations as ammonia chemisorption, an exothermic reaction, is less favoured at higher temperature. From the isotherms, it was possible to make rough comparisons between the solids in terms of the number of acid sites at a given pressure. The chemisorbed volume on the phosphate precursor is more important than that on the oxynitride at the same temperature (Table 2). This result means that the surface of the nitrated sample is less acidic than the oxidic precursor. The concentration (measured at 35 °C) gives the total acidity of ZrPO and ZrPON. Upon increasing the temperature, the chemisorbed ammonia concentration decreases and it decreases further when nitrogen is present in the phosphate structure, giving information about acid strength. At 200 °C, only stronger sites are able to retain ammonia, so the ammonia volume measured at this temperature corresponds to stronger surface acid sites, while volumes measured at 100 °C correspond to both stronger and medium sites and at 35 °C to all



**Fig. 1** Ammonia TPD analysis of the precursor (ZrPO) (○) and the zirconophosphate oxynitride (ZrPON) (●)

**Table 2** Chemisorbed ammonia concentration at 400 mmHg and at three temperatures (35, 100 and 200 °C)

Sample	35	100	200
	$\mu\text{mol NH}_3 \text{ g}^{-1}$	$\mu\text{mol NH}_3 \text{ g}^{-1}$	$\mu\text{mol NH}_3 \text{ g}^{-1}$
ZrPO	498	408	370
ZrPON	300	192	119

**Table 1** Chemical compositions and specific surface areas of the precursor (ZrPO) and the zirconophosphate oxynitride (ZrPON)

Sample	% Mass N	Composition	$S_{\text{BET}} / \text{m}^2 \text{ g}^{-1}$
ZrPO	0	$\text{Zr}_{0.9}\text{PO}_{4.3}$	140
ZrPON	4.7	$\text{Zr}_{0.9}\text{PO}_{3.4}\text{N}_{0.6}$	105

sites (weak, medium and strong sites). It is therefore possible to calculate the ratio between various strength sites and total surface-acid sites (Fig. 2). From this, it can be seen that when %N bulk increases, the number of weaker sites (35 °C) and medium sites increase and stronger sites decrease. The nitrogen incorporation, as already seen by TPD analysis, modifies the phosphate acidity properties. The global acidity of the precursor is important: many strong acid sites and only a few weaker sites have been found on its surface, while the opposite trend was found for the oxynitride surface.

In order to evaluate the basic properties of ZrPON, the Knoevenagel condensation of benzaldehyde with malononitrile was performed with 4 mmol of each reactant and 50 mg of catalyst at 50 °C in toluene in a batch reactor. Fig. 3 shows the

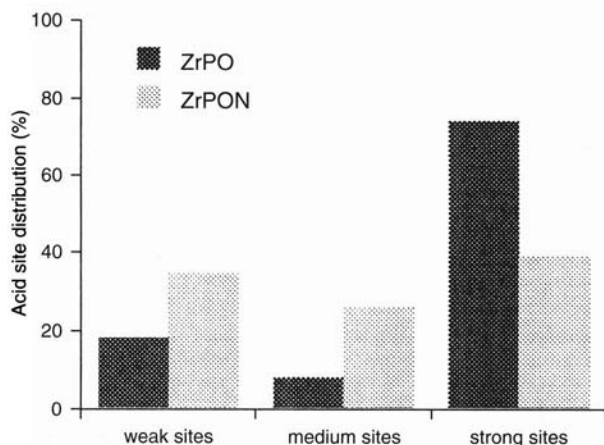


Fig. 2 Acid sites distribution determined by ammonia chemisorption

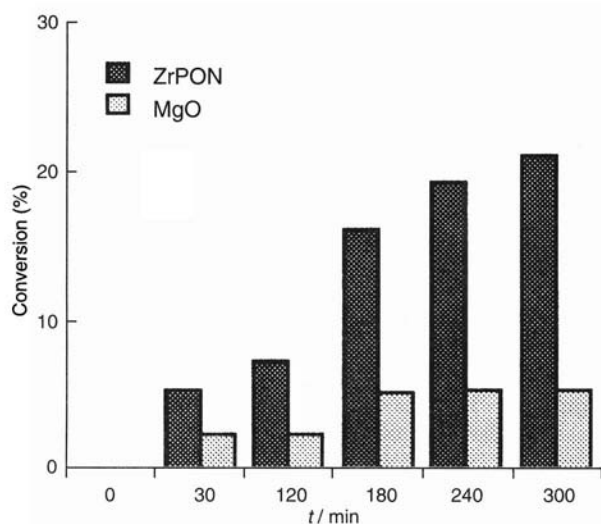


Fig. 3 Conversion of malonitrile and benzaldehyde vs. time of reaction in Knoevenagel condensation using ZrPON and MgO as catalyst

conversion of malonitrile and benzaldehyde with reaction time for ZrPON and for MgO (Janssen Chimica, p.a.) for comparison. This type of reaction is largely described in the literature as requiring strong basic sites.<sup>11</sup> No activity was found for ZrPO under the present conditions. The same reaction performed with ZrPON gives 21% conversion after 5 h while a commercial MgO catalyst with lower specific area and without pretreatment gives less than 5% conversion after the reaction time. The selectivity of the condensation product (malonitrile benzylidene) was 100% for the both catalysts. Experiments using recycled catalysts have not yet been performed; however, it should be underlined that comparable oxynitride solid (AlPON) shows almost the same activity in a second catalytic run which tends to indicate that at low temperature there is no modification of the surface (nitrogen loss or carbon deposition); additionally no change of colour of the solid due to coking occurred.

In conclusion, a new solid belonging to the oxynitride family has been synthesized by low-temperature nitridation of zirconium phosphate with a pure, dry gaseous  $N_2-NH_3$  mixture. The resulting powder, ZrPON, is amorphous and presents a high specific surface area. It was shown that nitrogen present in the anionic network of nitrated phosphate modifies the acid-base properties of this solid and enhances its basic activity: Knoevenagel condensation using ZrPON as catalyst gives a higher conversion than a commercial MgO catalyst. Under the same conditions, the phosphate precursor is not active.

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