

Influence of the nitridation parameters on the stoichiometry, structure and specific surface area of zirconium phosphate oxynitride catalysts

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Oxygen can be exchanged by nitrogen atom in high surface specific and amorphous zirconium phosphate solids thank to nitridation process. Various nitridation parameters influence the O/N substitution. A minimum temperature of 550 °C is required for efficient nitridation whereas temperature higher than 850 and 1300 °C induces reduction of phosphorus and zirconium atoms respectively. In intermediate temperature range, O/N exchange increases with temperature as well as with time of nitridation. In these conditions, the ZrPON solids obtained are X-ray amorphous and a slight decrease of precursor specific surface area is observed (110–210 m² g⁻¹). © 1999 Kluwer Academic Publishers

1. Introduction

An approach to the development of high strength materials is to replace all or a part of the oxygen content of suitable ceramics by a non-oxide element such as nitrogen or carbon. The incorporation of nitrogen into glasses for example, influences their properties significantly, essentially as a result of the nitrogen producing a more highly bonded glass structure [1, 2]. Density, viscosity, glass transition temperature, refractive index, microhardness and Young's modules all increase with increasing nitrogen content [3–5], whereas the thermal expansion of the glass decreases [6].

Until recently, non-oxide materials received relatively little attention in heterogeneous catalysis, although the properties of these materials compared to oxides or metals may lead to catalytic performances not attained with the latter. During the last decade, many papers have been published on the subject. Lednor *et al.* [7] have used high area silicon oxynitrides as basic catalysts in the Knoevenagel condensation. They have also tested the silicon oxynitrides in the isomerisation reactions of butene-1 [8]. Oyama *et al.* [9] have also described the use of molybdenum nitrides Mo₂N in the synthesis of ammonia (described earlier by other authors [10, 11], in the hydrogenation of carbon monoxide and in the processing of coal liquids. Mo₂N may also be used as a hydrodenitrogenation catalyst [12–15]. Volpe and Boudart prepared Mo₂N and W₂N with surface areas of 220 and 91 m² g⁻¹, respectively, for the synthesis of ammonia [16, 17].

Recently, it has been shown that progressive substitution of nitrogen for oxygen in the anionic network of metal phosphate materials leads to the formation of a new family of catalysts: the oxynitride phosphates [18–23]. These high area oxynitrides are prepared

according to a temperature programmed activation under ammonia stream of metallophosphate precursors [24]. Nitrogen atoms deeply influence the structural characteristics as well as the surface properties of the phosphate compounds. Indeed, nitrogen incorporation is an effective way to modify the acid-base properties of the surface and particularly to increase the number of basic sites. Such activation of the oxide precursor has been previously reported in the preparation and characterisation of silicon oxynitrides [7, 8], titanium oxynitrides [25] and molybdenum oxynitrides [16]. Various original catalytic systems have been prepared by nitridation processes: (i) aluminophosphate oxynitrides or "AlPON" [18, 26], (ii) aluminogallophosphate oxynitride systems called "AlGaPON" [19, 27, 28], (iii) zirconophosphate oxynitrides, the "ZrPON" solids [20–22] and (iv) aluminium vanadate oxynitrides "AlVON" [29, 30]. The composition of these solids is laid down during the synthetic step, as the control of the nitridation parameters allows the tuning of the O/N ratio.

The present study relates to the synthesis of ZrPON oxynitrides obtained by nitridation of high surface area amorphous zirconium phosphate precursors. The effects of various operating conditions on the stoichiometry, the specific surface area and the structure of the products are presented.

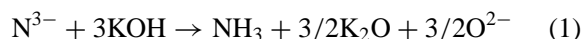
2. Experimental

2.1. Materials

The synthesis of the zirconophosphate used as precursor for the preparation of oxynitrides has already been described in a previous paper [22]. Two chemical methods were used to establish the nitrogen content of the

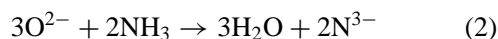
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samples. (i) The total nitrogen content was determined by displacement reaction of nitride ions N^{3-} induced by an excess of strong solid base which leads to the formation of ammonia [31]:



The reaction mixture (20 mg sample and ≈ 6 g of potassium hydroxide) is heated to 400 °C. The released ammonia, which is carried away by a nitrogen flow, is neutralised by 0.01 N sulphuric acid. (ii) The surface nitrogen (NH_x) species concentration was measured by a Kjeldahl type method: The ZrPON sample (75 mg) was suspended in 10 ml of saturated KOH solution to which 30 ml of distilled water were added. The liberated ammonia was then carried to a receiving flask by steam distillation, condensed and collected in a boric acid solution (10 g dm^{-3}) with mix indicator methylene blue-methyl red. This solution was titrated by sulphuric acid 0.01 N.

The nitrogen content may also be indirectly determined by measuring the weight variation of the precursor sample which has been transformed into oxynitride by heating under ammonia flow. If it is assumed that 3 oxygen atoms are exchanged for 2 nitrogen following



the production of a mole of water corresponds to the fixation of 2/3 mol of nitrogen. As a result, there is a weight loss of about 7 g/mol of released water.

2.2. Powder X-ray diffraction

Structural characterisation of the precursor and oxynitrides was done by X-ray diffraction (XRD). Patterns were obtained with a $CuK\alpha$ radiation on a Philips model PW 3710.

2.3. Surface measurements

The specific surface areas were measured by the single point BET method ($p/p_0 = 0.3$) in a Micromeritics Flowsorb II 2300 apparatus. Samples were degassed for 1 h at 120, 220 and 300 °C (20 minutes at each temperature) under helium/nitrogen flow before analysis at liquid nitrogen temperature.

2.4. Nitridation process

Reactions with ammonia were carried out in an alumina tube containing an alumina boat with precursor powder. The tube was heated by an electric tubular furnace whose temperature was monitored with a programmable linear rate temperature controller. The extremities of the system were cooled down with water.

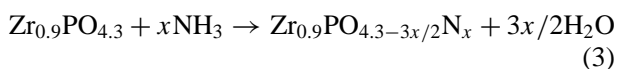
During an experiment, 0.3 to 3 g of zirconophosphate were nitrided at atmospheric pressure in a $30 \text{ dm}^3 \text{ h}^{-1}$ ammonia stream. The gases employed for the activation of the oxide precursors were NH_3 (Air Liquide, industrial grade) and N_2 (Air Liquide, custom grade, 99.5%). Different temperatures and nitriding times were used. After the heat treatment, the reactor was cooled in flowing N_2 .

3. Results and discussion

3.1. Nitridation generalities

The nitridation of the zirconophosphate oxynitrides was carried out under ammonia flow in a large temperature range (500–1300 °C). During the thermal treatment, the oxygen atoms in the anionic network of the phosphate precursor are replaced by nitrogen atoms of the ammonia (Equation 2). The oxygen for nitrogen substitution is controlled by the nitridation parameters: ammonia flow, mass of precursor to be nitrided, temperature and nitridation time. The adjustment of these parameters allows the tuning of the O/N exchange and thus the synthesis of ZrPON with various nitrogen contents. For each composition, the wt % nitrogen content was determined by two chemical quantitative determinations as described in the experimental section. The first one allows to measure the total of nitrogen amount (N_T) which consist in nitrided anions in bulk solids (N^{3-}) as well as NH_x ($1 \leq x \leq 4$) surface species [31]. The second method gives only access to these NH_x species, named N_K for the Kjeldahl principle on which it is based.

Taking into consideration the large possible composition field of ZrPON oxynitrides, Equation 2 can be written as



In this equation, the possible modifications in the cationic network are not considered. Nevertheless, the ammonia, in addition to being a good nitriding agent, can also act as a reductor. Indeed in the preparation of zirconium nitrides, ZrN, it has been reported that at very high temperature (> 2000 °C) the oxidation stage of the zirconium is reduced from IV to III under ammonia flow [32]:



The ammonia is also able to reduce the phosphorus P^V in P^{III} during the nitridation. In this case, volatile phosphine species with a typical orange colour are observed at the end of the reactor when nitridation is carried out above 800 °C.

3.2. Nitridation parameters

As already explained, four parameters influence the nitridation rate of the oxide precursor (coefficient x in Equation 3): (i) the ammonia flow, (ii) the mass of precursor to be nitrided, (iii) the temperature and (iv) the nitridation time. Their control is of crucial importance in the synthesis of ZrPON catalysts as it allows the adjustment of their acid-base properties. Indeed, it has been shown that the acidity and the basicity of ZrPON, as for AlPON solids [26], are directly correlated to the O/N ratio [21].

3.2.1. The ammonia flow

In the following study, the ammonia flow has been fixed at $30 \text{ dm}^3 \text{ h}^{-1}$. This high value ensures a rapid kinetic of nitridation and allows the elimination of water vapour produced during the reaction. In a study on aluminophosphate nitridation, it has been established that higher flows are not required as no further increase

TABLE I Influence of the mass of the precursor to be nitrated on the composition of ZrPON oxynitride powders (temperature of nitridation = 780 °C, ammonia flow = 30 dm³ h⁻¹)

Test no.	ZrPO weight (g)	Nitridation time (h)	Total N content (wt %)
1	3.049	16	8.1
2	0.304	15	13.7

of the nitrogen content is observed when increasing the ammonia flow [33]. Indeed, the larger flow results in the cooling of the reaction media and, the nitridation being an endothermic process, the Equation 3 is not favoured any more.

3.2.2. The mass of precursor

The second parameter influencing nitridation is the quantity of precursor to be heated. Table I shows the difference in nitrogen content for two zirconophosphates nitrated in the same conditions. As it is observed, the weight of the precursor to be nitrated influences the nitridation result: after 15 h under ammonia flow at 780 °C and when decreasing the loading from 3 to 0.3 g, the nitrogen weight content increases from 8 to 14%. This observation is explained by limitations encountered in the gas diffusion between particles for larger precursor bed in the reactor. In further experiments this weight has been fixed to 300 mg and, to counteract diffusion effects, the nitridation is interrupted at regular intervals and the precursor powder homogenised before resuming the heat treatment.

3.2.3. The nitridation temperature

The temperature at which the reaction is carried out is probably the main parameter affecting the composition of the zirconophosphate oxynitrides. As for the aluminophosphate oxynitrides AIPON, several temperature ranges may be distinguished [34] (Fig. 1 and Table II).

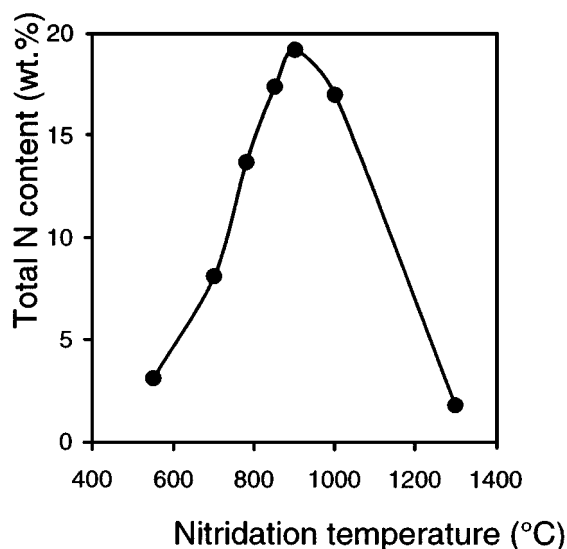


Figure 1 Evolution of the total nitrogen content with the nitridation temperature ($t = 15$ h, precursor loading = 0.3 g, NH₃ flow = 30 dm³ h⁻¹).

TABLE II Influence of the nitridation temperature on the composition of ZrPON oxynitride powders (precursor loading = 0.3 g, time of nitridation = 15 h, ammonia flow = 30 dm³ h⁻¹)

Test no.	Nitridation temperature (°C)	Total N content (wt %)	Oxynitride formulation
3	550	3.1	Zr _{0.9} PO _{3.7} N _{0.4}
4	700	8.1	Zr _{0.9} PO _{2.8} N _{1.0}
2	780	13.7	Zr _{0.9} PO _{1.9} N _{1.6}
5	850	17.4	Zr _{0.9} PO _{1.3} N _{2.0}
6	900	19.2	Zr _{0.9} PO _{1.0} N _{2.2}
7	1000	17.0	Zr _{0.9} P _{0.7} O _{0.8} N _{1.8}
8	1300	1.8	ZrO ₂ + Zr ₇ N ₄ O ₈

At temperature lower than 550 °C, there is no formation of oxynitride phases, as the values of total and Kjeldhal quantitative nitrogen determination are the same: all the nitrogen atoms are confined on the solid surface. Therefore the oxygen for the nitrogen substitution in the bulk is not effective at this temperature yet. Only ammonia adsorption on Brönsted or Lewis acid sites which are present on the surface [21] occurs, leading to the formation of NH₄⁺ or adsorbed NH₃. The substitution of hydroxyl groups (Zr-OH and P-OH) by NH₂ (amine) or NH (imine) entities could also be considered (Fig. 2).

It has been already established that the ammonia dissociation temperature must be reached in order to succeed in the nitridation of some oxide precursors. At 550 °C, the ammonia is decomposed to nitrogen and hydrogen [35, 36] and the oxygen for nitrogen exchange is not possible at this temperature.

Fig. 1 shows the evolution of total nitrogen content with the nitridation temperature when the length of the nitridation process and the mass of precursor are kept constant. From this figure, two trends are observed:

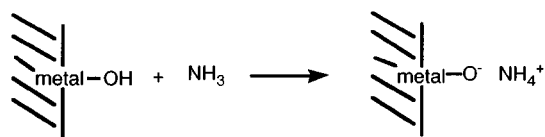
- At low temperature, in the range of 550 to 800 °C, the nitridation only involves a 2 nitrogen for 3 oxygen atoms substitution as described in Equation 3 and the initial Zr/P atomic ratio is maintained at 0.9. The nitrogen content increases from 3 to 17 wt % after 15 h under ammonia flow when the temperature is raised from 550 to 850 °C.
- Beyond 800 °C, a decrease of nitrogen content is observed. This decrease is explained by the reduction of phosphorus P^V to P^{III} under the ammonia atmosphere, with removal of volatile phosphine compound. The experimental weight loss confirms the removal of phosphorus in such compounds represented by the general formula Zr_{0.9}P_{1-a}O_{(3.6+5(1-a)-3x)/2}N_x. Indeed, the measured weight losses are higher than the ones calculated on the basis of the O/N substitution.

When the phosphate precursor is heated under NH₃ flow up to 1300 °C the phosphorus is completely removed and the resulting powder shows some X-ray diffraction signals while the nitrated zirconophosphates obtained previously are X-ray amorphous. Two phases, ZrO₂ and Zr₇N₄O₈, were detected (Fig. 3). Crystalline zirconium nitride ZrN mixed with Zr₂N₂O oxynitride appears after prolonged nitridation, indicating that in

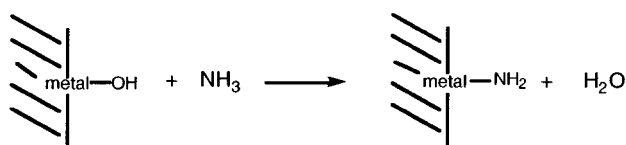
TABLE III Influence of the nitridation time on the composition of ZrPON oxynitride powders (precursor loading = 0.3 g, ammonia flow = 30 dm³ h⁻¹)

Temperature (°C)	Test no.	Nitridation time (h)	Total N content (wt %)	Kjeldhal N content (wt %)	RX analysis	Oxynitride formulation
550	3	15	3.1	1.6	Amorphous	Zr _{0.9} PO _{3.7} N _{0.4}
	9	53	3.2	1.5	Amorphous	Zr _{0.9} PO _{3.6} N _{0.45}
	10	65	3.0	1.5	Amorphous	Zr _{0.9} PO _{3.8} N _{0.4}
	11	88	2.8	1.4	Amorphous	Zr _{0.9} PO _{3.8} N _{0.35}
	12	184	3.1	1.4	Amorphous	Zr _{0.9} PO _{3.7} N _{0.4}
780	13	0.5	5.5	0.3	Amorphous	Zr _{0.9} PO _{3.3} N _{0.7}
	2	15	13.7	2.2	Amorphous	Zr _{0.9} PO _{1.9} N _{1.6}
	14	263	19.9	5.3	Amorphous	Zr _{0.9} PO _{1.0} N _{2.2}
900	6	15	19.2	4.5	Amorphous	Zr _{0.9} PO _{1.0} N _{2.2}
	15	64	21.8	5.4	Amorphous	Zr _{0.9} PO _{0.6} N _{2.4}
	16	280	18.3	5.8	Amorphous	Zr _{0.9} P _{0.7} O _{0.5} N _{2.0}
1000	7	15	17.0	5.6	Amorphous	Zr _{0.9} P _{0.7} O _{0.7} N _{1.8}
	17	64	13.7	6.2	Amorphous	Zr _{0.9} P _{0.5} O _{1.1} N _{1.4}
	18	287	11.0	6.0	Zr ₂ N ₂ O	Zr _{0.9} P _{0.15} O _{0.9} N _{0.8}

• Brönsted acidity



• Hydroxyl substitution



• Lewis acidity

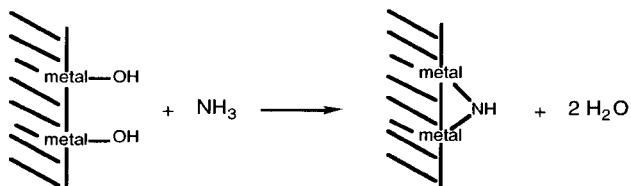
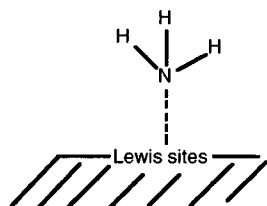


Figure 2 Reactivity of ammonia with ZrPON surface.

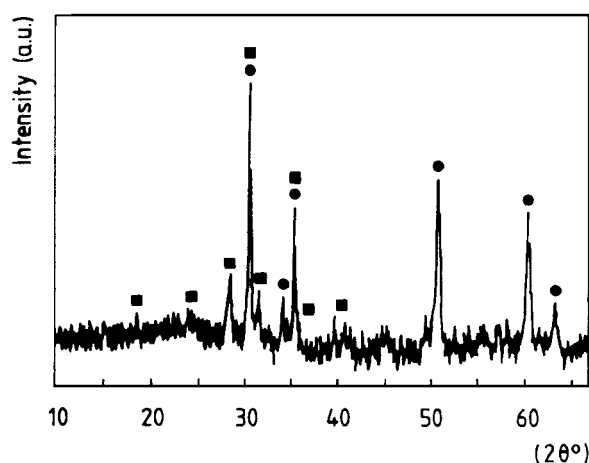


Figure 3 XRD pattern of the biphasic system ZrO₂ (●) and Zr₇N₄O₈ (■) for the oxynitride powder obtained at 1300 °C ($t = 15$ h, precursor loading = 0.3 g, NH₃ flow = 30 dm³ h⁻¹).

spite of this high temperature, only a part of Zr^{IV} is reduced to Zr^{III}. The absence of the ZrN phase below 1300 °C indicates that no zirconium Zr^{IV} reduction occurs in the samples nitrided at 700–800 °C (Table II).

3.2.4. Time of nitridation

The last parameter that can be adjusted during the nitrides synthesis is the time of the thermal treatment. Various observations are made depending on the temperature (Table III).

- At 550 °C, for example, the total nitrogen contents are systematically higher than the corresponding Kjeldhal values (Table III). The formation of oxynitride phases is then really effective while the observations made at 500 °C indicate only nitrogen adsorption at the solid surface. Furthermore, both surface and total nitrogen contents are kept constant even for long nitridation times. Various oxygenous functions may be found in the ZrPO structure. Indeed, in addition to bridging oxygen between the metal cations, the presence of other species such as double bonded oxygen and hydroxyl groups bonded either to zirconium or phosphorus atoms has been proved by IR spectroscopy [21]. It could perhaps be assumed that only one type of these oxygens is involved in the oxygen for nitrogen substitution at 550 °C. The constant value (3 wt %) of total nitrogen content could then agree

with the concentration of these oxygens. Once the surface is saturated, further substitution would no longer be possible.

- At 780 °C, the nitrogen content increases with the nitridation time (Table III). Moreover, as in AIPON systems, the wt % nitrogen content tends towards a maximum: after 11 days of heat treatment under ammonia, the ZrPON solids of test 14 still contain a significant proportion of oxygen atoms. It does not seem possible to exceed the value of 20 wt % N while the hypothetical composition of $Zr_{0.9}PN_{2.9}$ in which all the oxygen are replaced corresponds to 26 wt % N. The total substitution of oxygen for nitrogen atoms is frequently reported in the synthesis of ceramic powders as AlN or ZrN but these solids are prepared at higher temperatures (>1200 °C). The soft conditions of ZrPON preparation do not supply sufficient activation energy for the overall oxygen exchange. Moreover, the difference of coordination between bivalent oxygen and trivalent nitrogen involves some major modifications in the initial phosphate organisation. The higher degree of cross-linking would provide excessive tension which could prevent the total oxygen exchange.
- At 900 °C, the departure of the phosphorus, as described in the previous paragraph, is observed for the long nitridation time (test 16, Table III). Knowing that phosphorus is not reduced when the ZrPO precursor is nitrided at 850 °C during 300 h, it can be concluded that the temperature limit of sublimation of this element lies between 850 and 900 °C.
- At 1000 °C, a loss of phosphorus is observed for all the solids whatever the nitridation time, and the nitrogen content decreases in the same way. After 287 h, a crystalline phase corresponding to the Zr_2N_2O composition appears. However the chemical analysis reveals that some phosphorus still remains in the solids.

Moreover when the samples deficient in phosphorus are calcined under air at 1000 °C, the XRD data shows the presence of 2 phases: zirconium pyrophosphate ZrP_2O_7 and zirconia ZrO_2 while the calcination of the phosphate precursor led to the formation of $Zr_2P_2O_9$ and ZrP_2O_7 (Fig. 4).

3.3. Influence of the nitridation on the physico-chemical properties of ZrPON solids

All the powders synthesised during this study are X-ray amorphous except for the solids nitrided in extreme conditions. Indeed, four different crystalline phases have been identified when nitridation is carried out above 900 °C, i.e., ZrO_2 , ZrN, $Zr_7N_4O_8$ and Zr_2N_2O (Tables II and III, Fig. 3). These phases are distinguished by the absence of phosphorus and are characterised by various nitrogen weight contents ranging from 0% in ZrO_2 to 13% in ZrN.

Fig. 5 shows the evolution of the ZrPON specific surface area with the nitrogen content: the nitrided samples are characterised by a lower specific surface area than that of the precursor. Indeed, during the nitridation, the initial specific surface area of the precursor

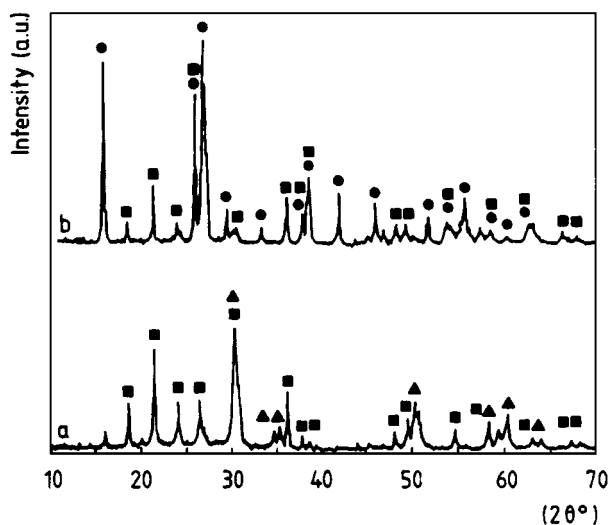


Figure 4 XRD pattern of obtained after the calcination at 1000 °C of (a) samples deficient in phosphorus leading to ZrP_2O_7 (■) and ZrO_2 (▲) biphasic system and (b) zirconophosphate precursor leading to ZrP_2O_7 (■) and $Zr_2P_2O_9$ (●) biphasic system.

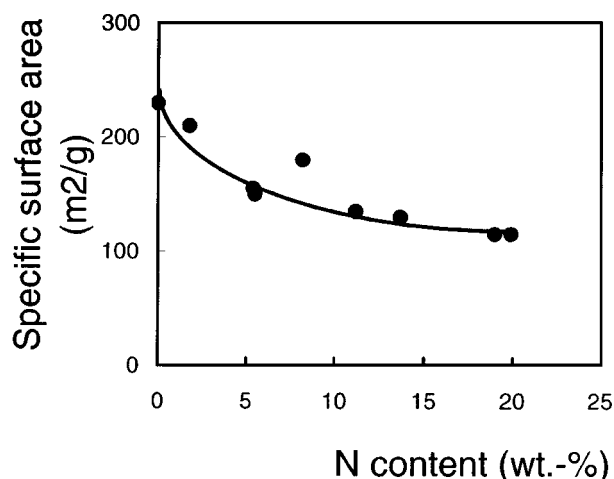


Figure 5 Evolution of the specific surface area with the nitrogen content in ZrPON solids.

progressively decreases from 230 $m^2 g^{-1}$ to approximately 115 $m^2 g^{-1}$ in the more nitrided ZrPON. It has been shown in the previous paragraph that the nitrogen for oxygen substitution is ruled either by temperature or time of nitridation. Thus, the variation of the specific surface area is also dependent on these parameters (Fig. 6 and Table IV): the increase of the nitridation temperature from 590 to 780 °C results in a decrease of the surface from 210 to 150 $m^2 g^{-1}$ (Table IV). Fig. 6 evidences that this lowering takes place mostly at the beginning of the process. This relative sintering is due to the heating in presence of water. Indeed, the ZrPO

TABLE IV Influence of the time and temperature of nitridation on specific surface area of ZrPON

Test no.	Nitridation time (h)	Nitridation temperature (°C)	Specific surface area ($m^2 g^{-1}$)
19	0.75	590	210
20	0.5	780	155
2	15	780	130
21	73	780	115

TABLE V Effect of calcination temperature on the precursor specific surface area

Sample	Temperature (°C)	Specific surface area (m ² g ⁻¹)
ZrPO	500 ^a	230
ZrPO	780 ^a	130
ZrPON	780 ^b	150

^aCalcination temperature.

^bNitridation temperature.

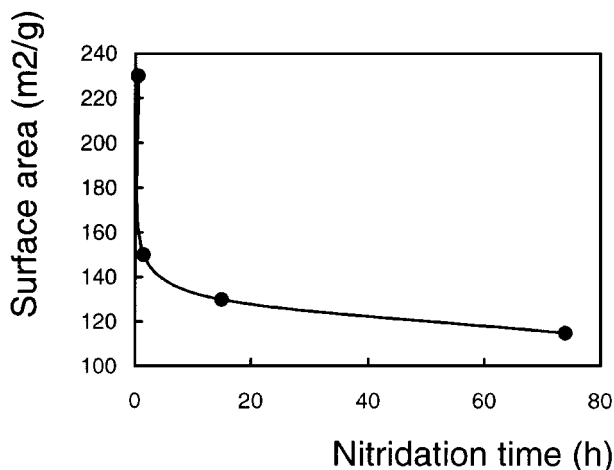


Figure 6 Evolution of the specific surface area with the nitridation time ($T = 780^{\circ}\text{C}$, precursor loading = 0.3 g, NH_3 flow = $30\text{ dm}^3\text{ h}^{-1}$).

precursor, as the ZrPON solids, is moisture sensitive and it contains up to 10 wt % of water before the nitridation. Furthermore, water is produced during the nitridation reaction as expressed in Equation 3.

Before its nitridation, the ZrPO precursor ($230\text{ m}^2\text{ g}^{-1}$) was calcined at 500°C but the surface area of ZrPO calcined at the nitridation temperature (i.e., 780°C) is similar to that of the corresponding ZrPON (Table V). It can be then concluded that N/O substitution does not significantly affect the surface area, compared to the influence of the high temperature treatment responsible for precursor powder sintering.

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 zirconophosphate oxynitrides ZrPON may be controlled by varying both temperature and reaction time of the heat treatment. The adjustment of these parameters allows the exploration of a large composition range in the Zr-P-O-N system. It has been shown that progressive substitution of oxygen for nitrogen in the anionic network of the zirconophosphates takes place at temperatures higher than 550°C , which correspond to decomposition of ammonia. When the temperature is raised above 950°C , some modifications appear in the cationic network: reduction with loss of phosphorus at 900°C and reduction of zirconium at 1300°C . The ZrPON obtained are X-ray amorphous except for a few solids nitrided in extreme conditions. The sintering of the powder during the

nitridation induces a slight decrease of the precursor surface area. Nevertheless ZrPON may still be presented as divided solids ($110\text{--}210\text{ m}^2\text{ g}^{-1}$) which allows them to be used as valuable acid-base catalysts. Indeed, the accurate control of nitridation parameters allows the tuning of the oxygen/nitrogen atomic ratio which is directly correlated to their acid-base properties.

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