

Synthesis and Characterisation of a Novel Aluminovanadate Oxynitride Basic Catalyst

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Abstract

The influence of the time and temperature of nitridation of aluminium vanadate oxide precursor prepared by the co-precipitation method is presented. The surface properties of one VAION containing 6.4 wt% of nitrogen are evaluated using two catalytic tests: the Knoevenagel condensation and the 1-butanol dehydrogenation/dehydration. This provides evidence that the substitution of oxygen by nitrogen induces basic catalytic properties. © 1997 Elsevier Science Limited.

1 Introduction

Recently we reported the synthesis of a high surface area catalyst obtained by nitridation of AlPO_4 amorphous oxide precursor. Nitridation, done under a flow of ammonia at 750°C , leads to the substitution of the anionic network oxygen by nitrogen, hereby changing the surface acid-base properties, for these aluminophosphate oxynitrides (AlPON) increase in the nitrogen content leads to the diminution of total surface acidity. Furthermore, AlPON's show an interesting catalytic activity for the condensation between malononitrile and benzaldehyde, a well-known based catalysed reaction, while the oxide precursor is not active.^{1–7} Other results obtained in our laboratory, on the zirconium phosphate oxynitrides family (ZrPON) allow us to correlate the catalytic activity in condensation with the amount of nitrogen incorporated, proving that it is possible to manage the acid-base properties controlling the nitridation step.⁸ That correlation has already been observed by Lednor and de Ruiter in silicon oxynitrides.^{9,10}

In this paper the synthesis and reactivity of aluminovanadate oxynitrides (VAION) is studied. The aluminovanadate oxide precursor is prepared by

soft chemistry routes.¹¹ The three ways of preparation are:

1. mineral: co-precipitation of aluminium nitrate and ammonium metavanadate;
2. organic: hydrolysis of aluminium butyroxide by ammonium metavanadate;
3. citrate: complexation by citric acid of aluminium and vanadium acetylacetonate solutions.

The mineral way of synthesis of the precursor and the influence of the temperature and time of nitridation of this precursor will be detailed here.

2 Synthesis and Characterisation

2.1 Synthesis of the precursor by co-precipitation method

First, 10^{-2} mole of ammonium metavanadate was dissolved in 100 ml of hot water and acidified with HNO_3 50% to $\text{pH}=3$, then 10^{-2} mole of aluminium nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 100 ml of water. The two solutions were mixed and heated to 70°C . An ammonia solution 1M was added slowly to the mixture until pH reached 7. A yellow precipitate rapidly occurs when the pH reaches a value higher than 5. The precipitate is then filtered and washed twice, first with ethanol then with propanol. The powder is then dried in an oven at 60°C . The colour of the powder turned green. The same procedure was applied for various V/Al ratios.

Depending on the pH and vanadium concentration, the aqueous solutions may contain numerous vanadate species. Acidification of Na_3VO_4 solution ($\text{pH}=13$) results in protonation and condensation through various vanadate to decavanadate intermediates $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ and VO_2^+ , both of which give yellow solutions.^{12,13} Nevertheless it seems that decavanadate species $\text{H}_x\text{V}_{10}\text{O}_{28}^{6-}$ are predominant between $\text{pH}=2.5$ and $\text{pH}=6$.¹⁴ The behaviour of the aluminium Al^{3+} cations is different

Table 1. Influence of the nitridation temperature on the VAIO-VAION₁₀ series

Sample	Nitridation time (h)	Nitridation temperature (°C)	V/Al	N content wt%	O content wt%	Specific area (m ² g ⁻¹)
VAIO	0	0	0.9	1.5	34.8	168
VAION ₂	3	250	0.9	2.9	40.1	119
VAION ₄	3	400	0.9	3.0	37.2	92
VAION ₆	3	600	0.9	5.9	34.5	80
VAION ₈	3	800	0.9	8.4	27.5	88
VAION ₁₀	3	1000	0.9	10.0	25.2	62

since precipitation of aluminium hydroxide occurs by pH elevation. The oxide precursor synthesis results in all probability from the co-precipitation of Al³⁺ cations and vanadate species, such as H_xV₁₀O₂₈⁶⁻. The precursor is X-ray amorphous and has a high specific surface area (~150 m² g⁻¹).

2.2 Nitridation of the precursor

In this section we will study the influence of temperature and time of nitridation. Thermal nitridation is performed in a tubular furnace under a flow of pure ammonia (45 dm³ h⁻¹). The heating rate was programmed at 1°C min⁻¹ and the plateau at maximum temperature is maintained during definite time.

2.2.1 Influence of nitridation temperature

Table 1 presents the evolution of the composition and texture of the oxynitride versus temperature of nitridation. The series studied has a V/Al ratio of 0.9. The temperature ranges from 250–1000°C and the reaction time at the plateau is maintained for 3 h.

A simplified reaction of nitridation can be written



It takes into account the electrical neutrality of the oxynitride, then substituting O without considering the reduction of vanadium that could occur. This substitution is confirmed by experimental data presented in Table 1 showing that the increase in the nitrogen content is accompanied by oxygen diminution.

We can observe that no nitridation occurs before 400°C and the samples nitrided at 250 and 400°C remained perfectly amorphous. The nitrogen encountered below this temperature is due to nitrogen present in the reactants used for preparation. Above 400°C the powders produced change colour from yellow-brown to black and an X-ray signal at $2\theta = 37^\circ$ and 44° appears. These signals could be attributed to a cubic vanadium nitride structure with very small crystallites, the higher the temperature, the sharper the signals. At 1000°C crystallisation of α -alumina begins and the N/V ratio is nearly 1, indicating that the nitridation occurs on vanadium atoms. Simultaneous to the substitution of oxygen by nitrogen, the increase in temperature provokes a decrease of the specific surface area. Since our goal is the synthesis of oxynitride catalysts with high surface area, the nitridation temperature will be maintained at 600°C in the following study. At this temperature the solid is still amorphous and presents a moderate surface area.

2.2.2 Influence of nitridation time

The effect of time of nitridation is presented in Table 2. The series studied has a ratio V/Al=0.5. The temperature is maintained at 600°C and nitridation time is increased from 1 to 11.5 h. The trend is characterised by a plateau up to which no nitrogen is incorporated, this can be seen in Fig. 1. Once the plateau is reached the N/V ratio does not change any more showing that temperature is a more critical parameter from this point of view. It should be noted that the kinetics of nitridation is high since 1 h at 600°C is enough to incorporate half the maximum nitrogen content. The surface

Table 2. Influence of nitridation time on the VAIO-VAIONe series

	Nitridation time (h)	Nitridation temperature (°C)	V/Al	N content wt%	Specific area (m ² g ⁻¹)
VAIO	—	—	0.5	—	141
VAION-a	1	600	0.5	2.4	116
VAION-b	2.0	600	0.5	3.0	113
VAION-c	5.0	600	0.5	4.8	120
VAION-d	7.5	600	0.5	5.8	113
VAION-e	11.5	600	0.5	6.4	84

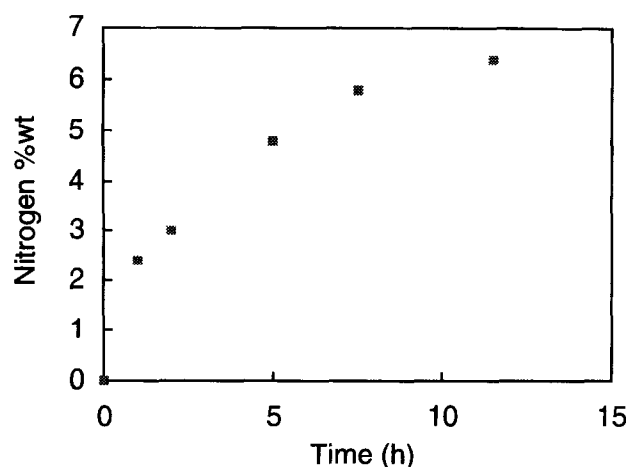


Fig. 1. Nitrogen content versus time of nitridation.

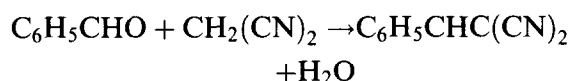
area is not influenced by the time of nitridation while temperature induces important loss.

3 Catalytic Evaluation

The aluminovanadate oxynitride containing 6.4 wt% of nitrogen (VAIONe) has been evaluated.

3.1 Knoevenagel condensation

The Knoevenagel condensation reaction can be written



This condensation between benzaldehyde and malononitrile is catalysed by bases¹⁵ and the first step of the reaction is the extraction of the hydrogen of the aldehydic group of benzaldehyde.

The catalytic test was performed in a liquid phase batch reactor at 50°C. Then $4 \cdot 10^{-3}$ mole of each reactant was introduced, diluted in 30 ml of toluene with $50 \cdot 10^{-3}$ g of catalyst. Figure 2 pre-

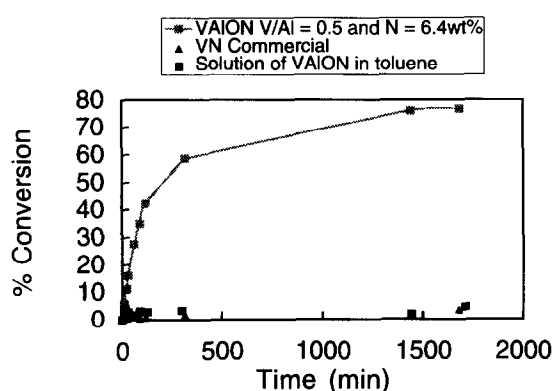


Fig. 2. Knoevenagel catalytic conversion versus time of reaction for VAIONe, filtrate from VAIONe in toluene and VN.

sents the activity in Knoevenagel for the VAIONe, for commercial VN (surface area = $1 \text{ m}^2 \text{ g}^{-1}$), and for VAIONe ageing in toluene for 12 h at 50°C under agitation. In this case the mixture is filtered before the test and the reaction is performed with the filtrate. This procedure is designed to extract eventual NH_3 species physically adsorbed on the VAION.

The conversion curves show that VAION is intrinsically active in condensation since no reaction was observed with the solvent in which the VAION was aged. Furthermore VN alone shows no conversion under these conditions of reaction. The oxide precursor of the VAIONe also tested in the Knoevenagel condensation is not active in these conditions. This indicates the presence of catalytic basic centres on the VAION and the important modifications generated by the nitridation.

3.2 Butanol dehydrogenation and dehydration

Depending on the type of sites present on the surface of the catalyst, butanol will give different products.¹⁶ The scheme of reaction can be written

1-butanol ($\text{C}_4\text{H}_9\text{OH}$)

–basic sites \rightarrow butyraldehyde($\text{C}_4\text{H}_8\text{O}$)
+ H_2

–weak acid sites \rightarrow 1-butene(C_4H_8) + H_2O

–twin acid sites \rightarrow dibutylether($\text{C}_4\text{H}_9\text{OC}_4\text{H}_9$)
+ H_2O

A catalytic test is performed in a fixed-bed reactor with 0.200 g of VAIONe using a flow of He (30 ml min^{-1}) saturated with butanol at 55°C.

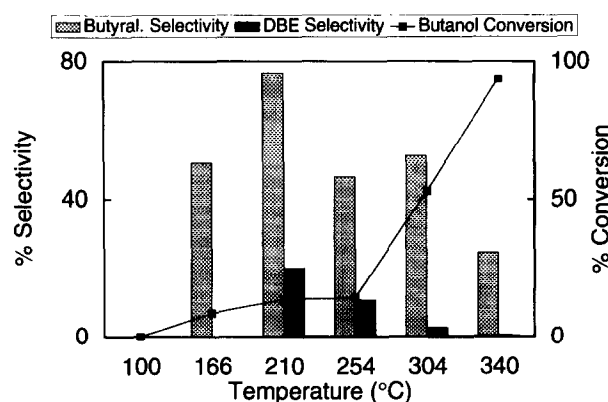


Fig. 3. Selectivity and conversion percentage versus temperature of reaction for the dehydrogenation and dehydration of 1-butanol

WHSV is equal to 1.4 h^{-1} . The temperature of reaction varies from 100 to 350°C . No problem of diffusion has been encountered in these conditions of reaction.

The results are presented in Fig. 3. Before 150°C no reaction occurs. Between 150 and 250°C the conversion of butanol is low but the selectivity in butyraldehyde is high (up to 75%). Increasing the temperature above 250°C does not improve selectivity even if the yield in butyraldehyde is better since conversion is higher. This reaction proves again that base catalysed reactions occur on the surface of the VAION.

4 Conclusions

The synthesis of a new family of oxynitrides was performed by nitriding aluminium vanadate oxide precursor leading to high surface area amorphous oxynitrides. These new compounds are very versatile materials since tuning of the V/Al ratio and N/O are possible, controlling the preparation conditions and the nitridation parameters. These oxynitrides have an interesting catalytic behaviour since they are able to catalyse well-known basic reactions such as condensation and dehydrogenation of 1-butanol.

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