

# Aluminovanadate Oxynitride Catalyst: Proposition for the Basic Site

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An aluminovanadate oxynitride (AIVON) catalyst is synthesized. This catalyst is active in the Knoevenagel condensation reaction between malononitrile and benzaldehyde, showing that it has basic sites. DRIFT characterization has evidenced the presence of ammonium ions due to the neutralization by ammonia of hydroxyl Brønsted acid sites. Since the catalyst loses its basic activity when the ammonium ions are removed by thermal treatment, the hypothesis of a negatively charged oxygen, generated by the neutralization of the Brønsted acid hydroxyls by ammonia, like  $V-O^- NH_4^+$ , is proposed as a basic center. This hypothesis is strengthened by three observations. (1) The inactive thermally treated AIVON recovers its catalytic activity when the ammonium ions are regenerated by gaseous ammonia adsorption. (2) When  $CDCl_3$  adsorption is carried out at increasing pretreatment temperature of the AIVON, a linear correlation is obtained between the amount of deuterated chloroform adsorbed and the ammonium ions staying after thermal desorption. This suggests that a relation can be expected between the ammonium ions and the basicity. (3) The oxide precursor that retains ammonium ions at the surface is active in the Knoevenagel condensation reaction. This provides evidence that the basic site is likely an oxygen atom rather than a nitrogenous species such as nitrides ( $N^{3-}$ ),  $-NH-$ , or  $-NH_2$  groups, since the oxide precursor has not been nitrified.

## Introduction

In oxide or modified oxide catalysts with basic or acid–base properties, the basic site is generally associated with an oxygen atom presenting high electron density. This is the case for alkaline earth oxides such as  $MgO$  or  $CaO$  (but also the rare earth oxides  $La_2O_3$  and  $CeO_2$  and the alkaline oxides  $Li_2O$ ,  $Na_2O$ , etc.) that show strong sites once degassed under vacuum.<sup>1,2</sup> On an  $Al_2O_3$  catalyst, the basic site is either an oxygen or a basic hydroxyl. The strength of the basic sites can be enhanced by incorporation of alkali ions,<sup>3</sup> or by deposition of alkali metals subsequently to  $NaOH$  treatment.<sup>4</sup> The strong basic sites thus generated are described as oxygens whose electron density are enriched. In other catalysts, such as zeolites (modified or not), the structural basic sites are the framework oxygens bearing the negative charge of the lattice, their basicity being affected by the chemical composition and the structure type of the zeolite. The basicity may be increased by addition of species that bring their own intrinsic basicity or interact with the framework oxygens increasing their charge.<sup>5,6</sup>

Recently, a new family of catalysts with basic character has been synthesized by nitridation of oxides. The nitridation of an oxide consists of substituting an oxygen atom by a nitrogen one. A common way to achieve this reaction is the thermal treatment of the oxide under a flow of ammonia for prolonged periods. A complete substitution leads to a solid called nitride; in the case of partial substitution an oxynitride is obtained. Recently, several nitride and oxynitride systems have been reported in the literature. Busca et al.<sup>7,8</sup> showed that the nitridation of amorphous silica leads to amorphous  $Si_3N_4$ , and they evidenced the presence of basic sites on the surface by IR spectroscopy of adsorbed probe molecules. Lednor et al.<sup>9</sup>

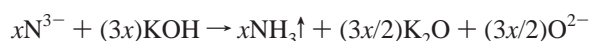
provided proofs of the basic properties of the silicon oxynitride by testing it in the Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate, a reaction generally catalyzed by amines, the degree of conversion is shown to be proportional to the nitrogen content present at the surface. More recently, Massinon et al.<sup>10</sup> and Grange et al.<sup>11,12</sup> pointed out the influence of the nitrogen content on the acid–base properties of aluminophosphate oxynitrides (AIPON). On AIPON, an increase in the bulk nitrogen content leads to a decrease of the acidity and to an augmentation of the catalytic conversion in the Knoevenagel condensation reaction, indicating that the surface exhibits more basic character. The same kind of trends have been observed by Fripiat et al.<sup>13,14</sup> and by Delsarte et al.<sup>15</sup> on the zirconophosphate oxynitrides and on aluminum gallium phosphate oxynitrides, where the degree of nitridation induces both the decrease of the number of acid sites and the creation of basic centers with increasing strength. On these non-oxide catalysts, the identification of the basic site is more controversial than in the case of the oxide ones, because several species present at the surface can act as a basic center. Among them, the nitride nitrogen ( $N^{3-}$ ), the  $-(NH)-$ , and the  $-NH_2$  groups could be candidates, but the oxygens and hydroxyls, whose charge would be modified by the vicinity of the less electronegative framework nitrogen, cannot be neglected. Finally, a cooperation between both a nitrogenous and an oxygenous species is also possible as indicated by Angeletti et al.<sup>16</sup> who proposed a concerted mechanism on a silica gel functionalized by amino groups where both silanol and amino groups are necessary for the Knoevenagel condensation reaction to proceed. In this paper, an aluminovanadate oxynitride (the term AIVON will be used in the text as an abbreviation for aluminovanadate oxynitride) has been synthesized and a proposition for its basic sites is presented.

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## Experimental Section

An AIVON is synthesized by nitridation of an oxide precursor (AIVO). The aluminovanadate oxide precursor powder, with an atomic ratio Al/V = 1.5 is obtained by coprecipitation of a solution of aluminum nitrate and ammonium metavanadate. A detailed procedure of the synthesis has been previously described.<sup>17</sup> Thermal nitridation of 1.5 g of powder is performed in a tubular furnace under a 500 mL/min pure ammonia flow. The heating rate was programmed at 1 K/min. Once the temperature of 873 K was reached, the sample was cooled to room temperature under N<sub>2</sub> flow.

**Nitrogen Content.** The total nitrogen content was determined using the method described by Guyader et al.<sup>18</sup> This method consists of measuring the ammonia produced by the reaction of molten potassium hydroxide with the nitrogenous species contained in the sample following the equation



A 0.020 g sample was introduced in an alumina crucible with an excess (approximately 1 g) of dry KOH. The mixture was heated to 673 K under a 50 mL/min flow of nitrogen (Air Liquide 99.8%). The output was connected to a trap containing distilled water. The ammonia produced was titrated by sulfuric acid 0.01 N.

**Specific Surface Area Measurement.** These determinations were performed on a Micromeritics Flow Sorb II 2300 using the single point ( $p/p_0 = 0.3$ ) method. The N<sub>2</sub> adsorbed on the surface at liquid nitrogen temperature was measured after degassing the solid for 1 h at 423 K.

**Catalytic Test: The Knoevenagel Condensation Reaction.** The condensation reaction of malononitrile with benzaldehyde was used to characterize the catalytic activity of the AIVON. In a three-neck batch reactor immersed in a thermostated bath at 323 K, 4 mmol of reagent diluted in 30 mL of toluene were brought into contact with 0.050 g of powder. The reactor was fitted with a reflux condenser that kept the mixture at atmospheric pressure and that prevented evaporation of the solvent. The temperature was controlled at  $\pm 0.5$  K by a thermometer placed in the liquid phase. The solution was stirred magnetically. Samples amounts of 0.25 mL were withdrawn before introducing the catalyst and after 5, 10, 20, 30, 60, 120, 240 min and 24 h. The sample was filtered removing the catalyst, and the solution was introduced in a cold (258 K) flask to stop the reaction before gas chromatography analysis.

**Diffuse Reflectance Infrared Fourier Transform Spectroscopy.** In situ DRIFT spectra were obtained on a Bruker IFS 88 spectrometer with a DTGS detector using a temperature- and environment-controlled chamber equipped with ZnSe windows (Spectra-Tech 00300). The spectra of the pure sample (without any dilution) were recorded (200 scans) in the 4000–400 cm<sup>−1</sup> range with 4 cm<sup>−1</sup> resolution. The spectra of an aluminum mirror were used as background. During the thermal treatment, a flow of 30 mL/min of helium (Air Liquide 99.995%) was passed through the samples. The temperature was increased manually at approximately 5 K/min from room temperature up to 373, 423, 473, 523, 573, 623, and 673 K. The sample was maintained for 30 min at each temperature before recording the spectrum.

The same equipment was used to study the adsorption of deuterated chloroform (CDCl<sub>3</sub>). An amount of 5 mL/min of helium was flowing through a saturator filled with CDCl<sub>3</sub> at room temperature. The saturated flow was passing through the sample for 30 min, then the flow was stopped and the chamber

**TABLE 1: Total Nitrogen Content, Chemical Composition, and Surface Area of the Oxide Precursor (AIVO)**

catalysts	Al/V (atomic)	nitridation temp (K)	nitrogen content (wt %)	composition	surface area (m <sup>2</sup> /g)
AIVO	1.5			AlV <sub>0.6</sub> O <sub>3</sub>	235
AIVON	1.5	873	3.1	AlV <sub>0.6</sub> O <sub>2.45</sub> N <sub>0.22</sub>	81

was isolated for 5 min before recording the spectrum. After that, the chamber was purged with 30 mL/min of pure helium for 15 min provoking the complete desorption of CDCl<sub>3</sub>. Then, the first pretreatment temperature was applied and maintained for 30 min before taking a spectrum. The sample was cooled and CDCl<sub>3</sub> was adsorbed again. Since CDCl<sub>3</sub> totally desorbed after 5 min under pure He flow and no decomposition was observed, the same sample was used for the adsorption of CDCl<sub>3</sub> at the different temperatures of the thermal treatment. Quantitative analyses of the bands were performed using an integration routine provided by the manufacturer.

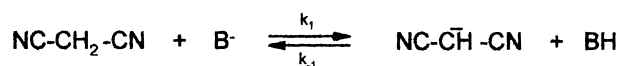
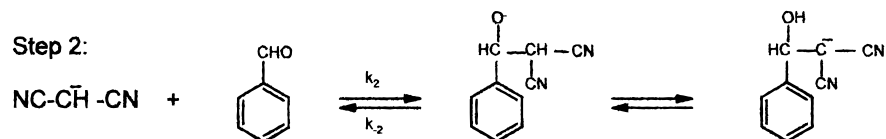
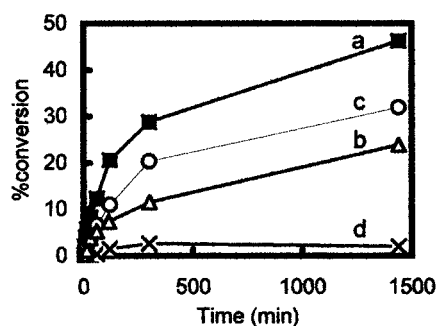
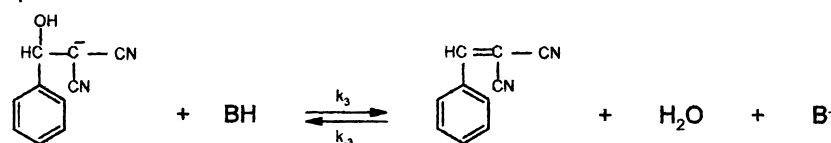
## Results and Discussion

Table 1 gives, for the oxide precursor (AIVO) and for the AIVON, the total nitrogen content, the global chemical formula based on chemical analysis, and the specific surface area. The nitrogen content of the oxide precursor was not measured since it was not nitrided and therefore supposed to be free of nitrogen species. The composition formula is then a theoretical one assuming the electroneutrality of the precursor and a charge of 3+ for Al and 5+ for V.

To characterize the catalytic basic activity of catalysts, condensation reactions have been often used. In this reaction an electron-donating component (methylenic compound activated by one or two electron-withdrawing substituents such as nitrile, acyl, or nitro) reacts with an electron accepting one (an aldehyde or a ketone for example) and forms a new carbon–carbon bond. This reaction is catalyzed by bases such as ammonia, amine (primary and secondary), or ammonium salt, and the first step is the removal of the acidic proton of the methylenic compound. Scheme 1 gives a detailed mechanism of the Knoevenagel condensation reaction between the malononitrile (electron-donating component) and the benzaldehyde (electron-accepting component) catalyzed by a base.

In Figure 1a, the conversion is plotted as a function of the time of reaction for the fresh AIVON catalyst. The selectivity in malononitrile benzylidene is 100%, no products of the Michael addition which would involve the reaction of another malononitrile with the double bond of the malononitrile benzylidene have been detected. This Michael addition is reported by Corma et al.<sup>19</sup> to require stronger basic sites than for Knoevenagel condensation. This is an indication that there is no strong basic sites at the surface of the AIVON.

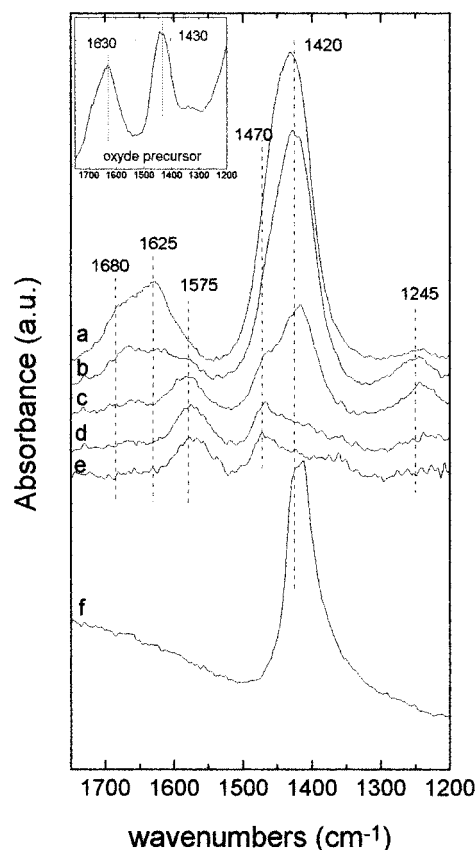
Since the AIVON is nitrided under a flow of ammonia and ammonia is known to catalyze the condensation reaction, additional proofs are necessary in order to ascertain that the reactivity observed is effectively due to the basic surface properties of the oxynitrides and not to physisorbed ammonia. First, Lednor et al.<sup>9,20</sup> have verified that gaseous ammonia (0.4 mmol) dissolved in toluene is slightly active in the condensation reaction between benzaldehyde and ethyl cyanoacetate; the reaction rate observed in the presence of the catalyst being much higher (the reaction temperature and the reagent concentration used by Lednor correspond exactly to the conditions followed in this work). Second, to ascertain that the water produced by the condensation reaction or the water present at the surface of

**SCHEME 1: Mechanism for the Knoevenagel Condensation Reaction between Malononitrile and Benzaldehyde When the Catalyst is a Base**
**Step 1:**

**Step 2:**

**Step 3:**


**Figure 1.** Conversion (%) in the Knoevenagel condensation reaction as a function of time for the (a) AIVON fresh catalyst, (b) AIVON aged in toluene for 12 h before starting the reaction, (c) AIVON pretreated up to 673 K under He followed by adsorption of  $\text{NH}_3$  at RT, and (d) AIVON pretreated up to 673 K under He (no hydrolysis of the surface before testing).

the fresh catalyst had no influence, an aqueous solution of ammonia, has been tested. A 4.5  $\mu\text{L}$  solution of 12.2 M was introduced in the reactor. This is equivalent to 0.055 mmol of ammonia. After 24 h, no condensation reaction was observed. Third, AIVON was stirred with toluene for 12 h at 323 K. The suspension was then filtered, and the reagents were added to the filtrate containing eventually the degradation product of the oxynitride (most likely ammonia). No conversion after 24 h of test at 323 K was observed with the filtrate. Nevertheless, the aging mentioned in this third experiment has partially degraded the catalyst since the catalyst removed after staying 12 h in toluene shows a decrease in activity when a new batch is started (Figure 1b) with this catalyst.

To understand these observations, in situ DRIFT analyses have been carried out. Figure 2 shows the evolution of the species present at the surface of AIVON during in situ DRIFT thermal treatment under He for the region 1200–1750  $\text{cm}^{-1}$ . The pure sample at RT (Figure 2a) exhibits vibrations characteristic of the asymmetric deformation of the ammonium species absorbing around 1430  $\text{cm}^{-1}$ . When the temperature is increased, the intensity of the large band at 1430  $\text{cm}^{-1}$  decreases drastically and two distinct vibrations at 1420 and 1470  $\text{cm}^{-1}$  (parts b–d of Figure 2) appear. In agreement with the literature,<sup>21–23</sup> the first band at 1420  $\text{cm}^{-1}$  is attributed to  $\delta_{\text{as}}(\text{NH}_4^+)$  ions coming from the neutralization by  $\text{NH}_3$  of an hydroxyl group bonded to a vanadium. This assignment is also supported by the DRIFT



**Figure 2.** DRIFT spectra for the pure (a) AIVON fresh catalyst at RT, (b) AIVON pretreated 30 min under He 30 mL/min at 373 K, (c) AIVON pretreated at 473 K, (d) pretreated at 573 K, (e) pretreated at 673 K, and (f) VN pure at RT. Frame: AIVO fresh catalyst at RT.

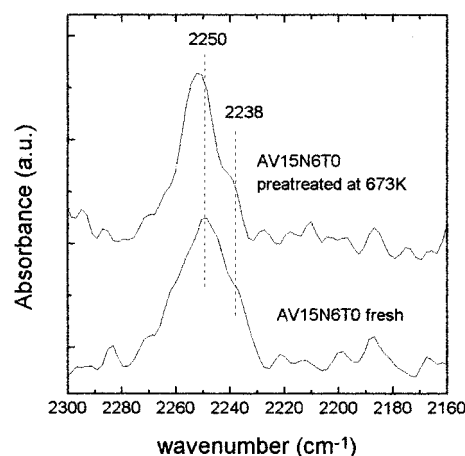
spectrum of commercial vanadium nitride (VN) (Figure 2f) which presents a large band at 1420  $\text{cm}^{-1}$  very close to that observed on the oxynitride. Its presence is also indicative of the hydrolysis of VN (see below). The other band at 1470  $\text{cm}^{-1}$  is attributed to  $\delta_{\text{as}}(\text{NH}_4^+)$  of  $\text{NH}_3$  bonded to an Al–OH hydroxyl group.<sup>22,24</sup> Furthermore, a small band at 1245  $\text{cm}^{-1}$  attributed to ammonia coordinatively bonded to a Lewis acid center<sup>21</sup> is observed. By increasing the temperature, the water (band at 1625  $\text{cm}^{-1}$ ) desorbs, the vibration at 1245  $\text{cm}^{-1}$  is better resolved, and a band at 1575  $\text{cm}^{-1}$  that corresponds to  $-\text{NH}_2$  groups is



rising. The region 4400–2500  $\text{cm}^{-1}$  is not presented here because, unfortunately, it does not present well-resolved species. It is characterized by a very broad band around 3500  $\text{cm}^{-1}$  due to  $\nu_{\text{O-H}}$  of adsorbed water and three shoulders at 2830, 3010, and 3150  $\text{cm}^{-1}$  corresponding to  $\nu_{\text{N-H}}$  of  $\text{NH}_4^+$ .<sup>25</sup> Increasing the temperature does not allow better definition of the bands. Nevertheless, the presence of strong IR absorption due to  $\text{NH}_4^+$  confirms the attributions made above in the region 1200–1600  $\text{cm}^{-1}$ . The presence of ammonium ions on the surface of the AIVON is explained by the hydrolysis of the nitrides ( $\text{N}^{3-}$ ) by atmospheric water. This is supported by the work of Centeno et al.<sup>25</sup> who studied by in situ DRIFT the hydrolysis of the AIPON and who showed that the oxynitrides react at room temperature with water, even at a concentration as low as 3 ppm in helium. The hydrolysis generates ammonium and  $-\text{NH}-$  groups at the expense of nitrides ( $\text{N}^{3-}$ ). The reaction corresponds to the reverse of nitridation and can be written in a general way as  $\text{MM}'\text{O}_{4-3x/2}\text{N}_x + (3x/2)\text{H}_2\text{O} \leftrightarrow \text{MM}'\text{O}_4 + x\text{NH}_3$  (where M and M' are for example Al and P or V). The ammonia then neutralizes the Brönsted acid hydroxyl group to produce the ammonium ions and a negatively charged oxygen:  $\text{M-OH} + \text{NH}_3 \rightarrow \text{M-O}^-\text{NH}_4^+$ . It should be pointed out that even 4 years after the synthesis of the AIVON the ammonia adsorbed on the surface corresponds to less than 10% of the total nitrogen content (mainly nitrides  $\text{N}^{3-}$ ). Could a hydroxyl neutralized by ammonia generating an oxygen with an increased electron density be the basic site? If such is the case, a correlation between the ammonium content and the activity in the condensation reaction should be observed. It could also explain the loss of activity observed when the AIVON has been degraded 12 h in toluene (see third point above), since we can assume that this treatment provokes the removal of ammonium ions. Furthermore, from DRIFT analysis, no nitrogenous species other than  $\text{NH}_4^+$  can be identified at RT, and they are easily removed by thermal treatment.

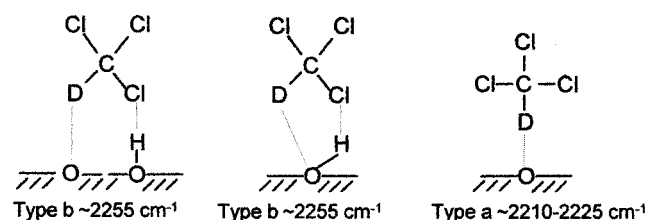
To verify if this hypothesis is realistic and to confirm that ammonia present at the surface of the catalyst is essential to the catalytic activity, two other experiments have been carried out. First, immediately before starting the reaction, the AIVON has been pretreated up to 673 K under He, cooled in a desiccator, and introduced in the batch reactor in order to measure its activity. Second the AIVON is pretreated under He up to 673 K, and cooled, like the previous one, but in this case 50 mL/min of ammonia is flowing through the catalyst for 5 min at RT. The excess of adsorbed gas is then purged with He, and then the reaction is started. The results of these experiments are illustrated by curves c and d of Figure 1. When the catalyst is pretreated under He up to 673 K, DRIFT experiment has shown that the largest part of ammonia is desorbed from the surface. Besides, since the time elapsed between the pretreatment and the beginning of the catalytic test is very short (less than 15 min) and that contact with ambient air is prevented, we can assume that hydrolysis of the surface is avoided. This catalyst is no more active (Figure 1d). In the second experiment, ammonia is readsorbed and the oxynitride recovers a fraction of its initial activity (Figure 1c). This indicates that ammonia adsorbed at the surface generates the active centers for the condensation reaction between malononitrile and benzaldehyde.

To verify this hypothesis and especially the decrease of basicity on heating the catalyst, the adsorption of  $\text{CDCl}_3$  has been carried out. This probe molecule has been chosen because it is a protonic acid able to form D complexes (H complexes in the case of  $\text{CHCl}_3$ ) with the basic center and because it is a weak base (Cl) which interacts very slightly with aprotic and



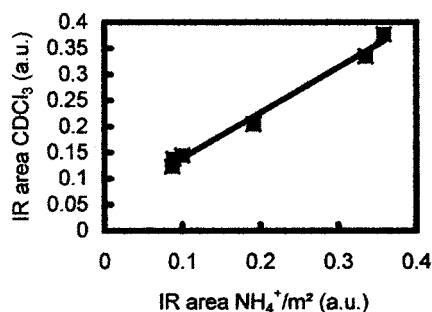
**Figure 3.** DRIFT spectra of the  $\nu_{\text{C-D}}$  vibration for  $\text{CDCl}_3$  adsorbed at RT on (a) AIVON fresh catalyst and (b) AIVON pretreated at 673 K under He 30 mL/min for 30 min.

**SCHEME 2: Modes of Adsorption of  $\text{CDCl}_3$  at the Surface of Oxides and the Corresponding Wavenumber of the  $\nu_{\text{C-D}}$  Vibration.**



proton acid sites.<sup>26–28</sup> The main modes of vibration of  $\text{CDCl}_3$  adsorbed on a basic oxygen and the corresponding wavenumber are presented in Scheme 2. These attributions are due to Paukshtis et al.<sup>29</sup> who adsorbed  $\text{CDCl}_3$  on different basic catalysts. These authors report that changing the basicity of the support gives rise to a change in the position of the maximum of the  $\nu_{\text{C-D}}$  band. For more basic catalysts, the vibration occurs at lower wavenumbers. Similar results are reported by Berteau et al.<sup>30</sup> who adsorbed  $\text{CDCl}_3$  on Na- or Mg-modified alumina and observed that a new band, as compared to nonmodified alumina, appeared at lower wavenumbers, which they attributed to more basic surface centers.

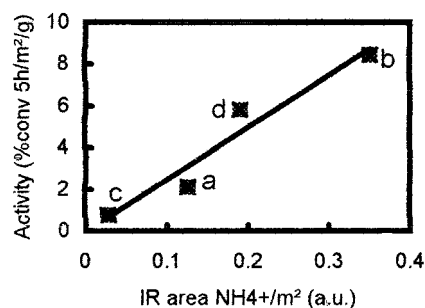
Figure 3 presents the vibration of  $\text{CDCl}_3$  adsorbed at RT on the fresh AIVON oxynitride catalyst and on the sample pretreated at 673 K. On the fresh catalyst, a band centered at 2250  $\text{cm}^{-1}$  with a shoulder at 2238  $\text{cm}^{-1}$  is visible, suggesting the presence of at least two distinct basic sites on the surface of the AIVON. According to the literature,<sup>29,31</sup> both bands can be assigned to  $\text{CDCl}_3$  adsorbed on b type sites, the basic sites being the oxygen of a hydroxyl group. The thermal treatment up to 673 K influences both the intensity and the position of the bands. The component at 2238  $\text{cm}^{-1}$  decreases, suggesting that the stronger basic sites are those removed during the thermal treatment (remember that the adsorption of  $\text{CDCl}_3$  is done at RT after thermal treatment). In Figure 4, the integrated area of the band of the adsorbed  $\text{CDCl}_3$  is plotted as a function of the area of the  $\text{NH}_4^+$  peak (1430  $\text{cm}^{-1}$ ) for the different temperatures of pretreatment studied. On this figure, the fresh AIVON has the largest amount of adsorbed species ( $\text{NH}_4^+$  and  $\text{CDCl}_3$ ). When the pretreatment temperature increases, both species decrease. This relation confirms that the basicity of the AIVON is directly proportional to the amount of ammonium ions present at the surface, strengthening the hypothesis that it generates a negatively charged oxygen that would be the basic active center.



**Figure 4.** Area of the DRIFT band at  $1430\text{ cm}^{-1}$  ( $\text{NH}_4^+$ ) of the AIVON catalyst at increasing pretreatment temperature versus the area of DRIFT band at  $2250\text{ cm}^{-1}$  ( $\text{CDCl}_3$  adsorbed at RT) for the corresponding temperature.

The site that catalyses the Knoevenagel condensation reaction on other oxynitride systems such as the aluminophosphate oxynitride has been attributed to amine or imine groups by analogy with the species active in homogeneous catalysis. Massinon et al.<sup>32</sup> have reported that on AIPON the catalytic activity is related to the Kjeldhal nitrogen, whereas Climent et al.,<sup>33</sup> on the same system have identified  $=\text{NH}$  and  $-\text{NH}_2$  groups as the active basic sites. On the ZrPON oxynitride catalyst,<sup>34</sup> the nitride  $\text{N}^{3-}$  is also reported as a potential candidate. In the case of AIVON, the argument that refutes a nitrogenous species as the active site is that amino  $-\text{NH}_2$  or imino  $=\text{NH}$  groups are not observed on the fresh oxynitride catalyst. On the other hand, the  $-\text{NH}_2$  groups appear significantly when the oxynitride is heated under He flow (DRIFT absorption at  $1575\text{ cm}^{-1}$ ), and their maximum concentration is reached when the pretreatment temperature is  $673\text{ K}$  (Figure 2, curves c–e), temperature for which the catalyst shows no activity. To reject the possibility of a nitride nitrogen as a candidate for the basic center, a last experiment has been carried out. If the hypothesis of an oxygen center is right, then it should be possible to generate it by neutralizing with ammonia the Brønsted acid sites present at the surface of the oxide precursor. Since it is not nitrified, it does not contain any nitride ( $\text{N}^{3-}$ ) species. So, if it is active in the Knoevenagel condensation reaction, it will be a strong argument in favor of a basic oxygen. In practice, it has not been necessary to neutralize the precursor with ammonia because its surface is already covered with ammonium ions (frame in Figure 2). Their origin is to be sought in the ammonium metavanadate used for the synthesis, since the precursor is dried at only  $60^\circ\text{C}$  without further calcination, their presence is logical.

The plot of the relation between the conversion in the Knoevenagel reaction after 5 h per unit surface area of catalysts and the area under the DRIFT band at  $1430\text{ cm}^{-1}$ , representative of the ammonium ions, for AIVO and AIVON fresh catalysts, AIVON pretreated at  $673\text{ K}$  and with subsequent readsorption of ammonia is given in Figure 5. This plot shows that the oxide precursor is active in the reaction of condensation between the malononitrile and the benzaldehyde. The fairly good correlation confirms that, if basic activity is expected, the presence of ammonium ions on the surface of the AIVON is necessary to generate the basic sites, strengthening the hypothesis of an oxygen whose electron density is increased. To further confirm the inductive effect of ammonia on the oxide precursor, it has been pretreated at  $673\text{ K}$  to remove the ammonia adsorbed and then tested in the same conditions. No conversion is observed. A similar kind of active species in solution has already been suggested by Lednor et al.<sup>9</sup> when measuring, for the Knoevenagel condensation reaction, the activity of gaseous ammonia dissolved in various solvents. When ammonia is



**Figure 5.** Conversion ( $\%/m^2/g$ ) after 5 h versus the area ( $\text{c.v.}/m^2$ ) of the DRIFT band at  $1430\text{ cm}^{-1}$  for AIVO (a) and AIVON (b) fresh catalyst, AIVON pretreated up to  $673\text{ K}$  under He without allowing hydrolysis of the surface (c), and AIVON pretreated up to  $673\text{ K}$  under He followed by adsorption of  $\text{NH}_3$  (d).

dissolved in toluene it is slightly active, but when ethanol is used, the activity is so high that it cannot be explained by intrinsic reactivity of ammonia. These authors interpret this result by proposing a new equilibrium where a small amount of ethanolate  $\text{C}_2\text{H}_5\text{O}^-\text{NH}_4^+$  (a much stronger base than ammonia) would be formed by reaction between ethanol and ammonia. This species can be compared directly with our interpretation. Finally, Delsarte et al.<sup>35</sup> have shown on the  $\text{AlGaPO}_4$ , an oxide calcined at  $923\text{ K}$  that is not active in the Knoevenagel condensation reaction, that, after chemisorption of ammonia at  $373\text{ K}$  and removal of the physisorbed species at the same temperature under an helium flow, the catalyst becomes very active. This proves that ammonia can increase the basicity of oxide anions.

## Conclusion

The basic site present on the surface of the aluminovanadate oxynitride catalysts is proposed to be a negatively charged oxygen. The high electron density carried by this oxygen is created by the neutralization of the acid hydroxyl group by ammonia, thus generating the ionic species  $\text{NH}_4^+\text{O}^-$ . This proposition is supported by the correlation between the catalytic activity in the Knoevenagel condensation reaction and the amount of ammonium ions measured by DRIFT at the surface of aluminovanadate catalysts studied. Furthermore, the relation between the adsorption of deuterated chloroform and the quantity of  $\text{NH}_4^+$  provides evidence that ammonium ions are involved in the generation of the basic sites.

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