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Identification of the Basic Site on the Aluminovanadate Oxynitride Catalysts

H. Wiame, C. Cellier, and P. Grange

Unité de catalyse et de chimie des matériaux divisés, Université catholique de Louvain, Place Croix du Sud 2 bte 17 B-1348 Louvain-la-Neuve, Belgium

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A series of aluminovanadate oxynitride (VAlON) catalysts with increasing nitrogen content was synthesized by thermal nitridation of an oxide precursor with a fixed Al/V atomic ratio of 1.5. The surface of these oxynitrides is characterized by TPD-MS, DRIFT, XPS, and DRIFT of the adsorbed $CDCl_3$. TPD results show that NH_3 desorb from all the VAlON samples when they are heated from RT to 673 K under a flow of pure helium. XPS and DRIFT analysis revealed that on the surface of the fresh catalysts, ammonia is adsorbed on Brønsted acid sites, giving two XPS N1s binding energy peaks at 400 and 401.8 eV and two DRIFT absorption bands of $\delta_{as}(NH_4^+)$ at 1425 and 1480 cm^{-1}. The VAlON catalysts present basic properties as evidenced by the activity in the Knoevenagel condensation reaction between benzaldehyde and malononitrile. It is shown that the catalytic activity is directly correlated with the amount of ammonium ions measured by DRIFT. This relationship between the basic character and the amount of NH_4^+ is further confirmed by the adsorption of $CDCl_3$, a weak acid probe, for which the intensity of the ν(C–D) vibration between 2250 and 2238 cm^{-1} is proportional to the amount of NH_4^+ remaining after thermal treatment. Since NH_4^+ is not a basic species, it is proposed that the oxygen of an hydroxyl group whose negative charge is increased by ammonia interaction is the active basic center. The basic center can be described as $V–O^- \ ^+H_4N$, with the hydroxyls bonded to vanadium atoms. This basic site is thermally unstable and presents a strength similar to that of alumina with a $pK_a \cong 7$. To explain the high rate of reaction observed, a concerted mechanism with activation of the benzaldehyde by the acid sites of the catalysts and/or the retention by the surface of the water produced by the reaction is proposed. © 2000 Academic Press

Key Words: **oxynitrides; aluminovanadate; basic catalysts; basic oxygen; Knoevenagel condensation; IR of $CDCl_3$; ammonia adsorption.**

1. INTRODUCTION

Solid basic catalysts are becoming extensively studied these past years and the scientific literature on the subject is becoming more and more abundant. The main goal of all these works is the replacement, in the future, of the liquid bases used industrially in reactions such as alkylation, condensation, and isomerization with heterogeneous catalysts (1, 2). At present, several classes of basic catalysts can be distinguished according to how they synthesize. A first class would group unmodified oxide solids, i.e., intrinsically basic oxides, namely the alkaline earth oxides like MgO or CaO (but also the rare earth oxides La_2O_3, CeO_2, and the alkaline oxides Li_2O, Na_2O, etc.), that present strong sites once degassed under vacuum, and Al_2O_3 or ZrO_2 that have both acid and basic centers. The basic site of these solids is either an oxygen or a basic hydroxyl. A second group of basic solids could be the modified oxide solids. For example, the basic properties of alumina are enhanced by incorporation of alkali ions (3) or by deposition of alkali metals subsequently to NaOH treatment (4). In these solids strong basic sites, described as an oxygen whose electron density is enriched, are generated. Other catalysts that could be classified in this second group are the zeolites (modified or not), where the structural basic sites are the framework oxygens bearing the negative charge of the lattice; their basicity is affected by the chemical composition and the structure type of the zeolite (5). The basicity may be increased by addition of species that bring their own intrinsic basicity or interact with the framework oxygens increasing their charge. For more details, a complete review concerning basic zeolites has been written by Barthomeuf (6).

Another way of modifying the acid–base properties of solids can be the nitridation of oxides. In our arbitrary classification, these new solids would represent a third group reassembling the non oxide solids. The nitridation of an oxide consists in substituting of an oxygen atom by a nitrogen atom. A common way of achieving this reaction is the thermal treatment of the oxide under a flow of ammonia for a prolonged time. If the substitution is complete the solid is called a nitride; in the case of partial substitution it is an oxynitride. Recently, several nitride and oxynitride systems have been reported in the literature. Busca *et al.* (7) have shown that the nitridation of amorphous silica led to amorphous Si_3N_4 and evidenced the presence of basic surface sites by IR spectroscopy of adsorbed probe molecules. Lednor *et al.* (8) provided proofs of the basic catalytic properties of the silicon oxynitride by testing it in the Knoevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate, a reaction generally catalyzed

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TABLE 1

Nitridation Conditions of the Aluminovanadate Oxide Precursor (AV15ox), Total Nitrogen Content, Chemical Composition, and Surface Area of the Oxynitrides

Serie AV15	Al/V (atomic)	Nitridation temp. (K)	Nitridation time (hours)	Nitrogen content (wt%)	Composition	Surf. area (m^2/g)
AV15ox	1.5	—	—	n.d.	$AlV_{0.6}O_3$	235
AV15N4	1.5	673	3	0.8	$AlV_{0.6}O_{2.85}N_{0.06}$	107
AV15N5	1.5	773	3	1.2	$AlV_{0.6}O_{2.78}N_{0.09}$	95
AV15N6T0	1.5	873	0	3.1	$AlV_{0.6}O_{2.45}N_{0.22}$	81
AV15N6T2	1.5	873	2	3.2	$AlV_{0.6}O_{2.44}N_{0.23}$	79
AV15N6T10	1.5	873	10	4.1	$AlV_{0.6}O_{2.27}N_{0.29}$	84
AV15N7	1.5	973	3	2.8	$AlV_{0.6}O_{2.50}N_{0.20}$	92
AV15N8	1.5	1073	3	6.5	$AlV_{0.6}O_{1.84}N_{0.46}$	65

by amines, and showing that the conversion is proportional to the nitrogen content at the surface. More recently, Massinon *et al.* (9) and Grange *et al.* (10, 11) pointed out the influence of the nitrogen content on the acid–base properties of aluminophosphate oxynitrides (AlPON). On AlPON, an increase in the bulk nitrogen content leads to a decrease in the acidity and to an augmentation in the catalytic conversion in the Knoevenagel condensation reaction, indicating that the surface exhibits a more basic character. The same kind of trends have been presented by Fripiat *et al.* (12, 13) and by Delsarte *et al.* (14) on the zirconophosphate oxynitrides and on the aluminium gallium phosphate oxynitrides, where the degree of nitridation induces both a decrease of the number of acid sites and the creation of basic centers with increasing strength. On these nonoxide catalysts the identification of the basic site is more difficult than in oxide ones, because several species present at the surface can act as basic centers. Among them the nitride nitrogen (N^{3-}), the –(NH)–, and the $-NH_2$ group could be candidates, but the oxygen and the hydroxyl 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 a oxygenous species is also possible as indicated by Angeletti *et al.* (15), who proposed a concerted mechanism on a silica gel functionalized by amino groups where both these latter and silanol groups are necessary for the Knoevenagel condensation reaction to proceed.

In this paper the basic properties of an aluminovanadate oxynitride series are tested in the Knoevenagel condensation reaction and a proposition of the active site based on TPD and XPS analyses, as well as on the infrared study of adsorbed deuterated chloroform used as probe molecule, is presented.

2. EXPERIMENTAL

2.1. Materials

The aluminovanadate oxynitrides (the term VAlON will be used in the text as an abbreviation for aluminovanadate oxynitride containing varying nitrogen contents) are synthesized by nitridation of an oxide precursor. The aluminovanadate oxide precursor powder, with an Al/V = 1.5 atomic ratio, is obtained by coprecipitation of a solution of aluminum nitrate and ammonium metavanadate. A detailed procedure of the synthesis has been previously described (16, 17). Thermal nitridation of 1.5 g of powder is performed in a tubular furnace under a 500 ml/min flow of pure ammonia. The heating rate was programmed at 1 K/min and the maximum temperature was maintained for a determined time. The samples were cooled down to room temperature under N_2. The temperature, the time, the total nitrogen content, the global chemical formula based on chemical analysis, as well as the surface area, are presented in Table 1. The labeling of the samples is as follows: AV15 means a series of aluminovanadates with an aluminum to vanadium ratio of 1.5. When N4, N5, etc., is added it means that the compound is nitrided at 400°C, 500°C, etc., for 3 h. The oxide precursor is labeled AV15ox because it is not nitrided. Moreover, T0, T2, etc., is added if the time of nitridation is different from 3 h. So, AV15N6T0 is an aluminovanadate (Al/V = 1.5) nitrided up to 600°C at 1 K/min; 0 h means that the sample is cooled down once attaining that maximum temperature. No special care was taken during storage and several months passed between the synthesis and the characterization. One comment must be made about Table 1. The nitrogen content of the oxide precursor was not measured since it was not nitrided and, therefore, supposedly contained no nitrogen species. The composition formula is a theoretical one that assumes the electroneutrality of the precursor and a charge of 3+ for Al and 5+ for V. We will see that this supposition is not correct and that the oxide precursor still contains adsorbed nitrogenous species from the synthesis.

2.2. Methods

2.2.1. Nitrogen content. The total nitrogen content was determined using the method described by Guyader *et al.* (18). This method consists of measuring the ammonia produced by the reaction between molten potassium hydroxide and a nitrogenous species contained in the sample, following the reaction

$$x\mathrm{N}^{3-} + 3x\,\mathrm{KOH} \rightarrow x\mathrm{NH}_3\uparrow + 3x/2\,\mathrm{K}_2\mathrm{O} + 3x/2\,\mathrm{O}^{2-}.$$

Some (0.020 g) sample was introduced in an alumina crucible with an excess (approximately 1 g) of dry KOH. The mixture was heated up 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.

2.2.2. Specific surface area measurement. These analyses were performed on a Micromeritics Flow Sorb II 2300 using the single point ($p/p_0 = 0.3$) method. The N_2 adsorbed on the surface at liquid nitrogen temperature was determined after degassing the solid for 1 h at 423 K.

2.2.3. Thermo-programmed-desorption on line with a mass-spectrometer. TPD-MS was used to study the stability and the nature of the species desorbed from the VAlON during a thermal treatment under a flow of inert gas. TPD-MS experiments were achieved in a U-shaped reactor on 0.075 g of sample, under a 50 ml/min flow of He (Air Liquide 99.999%). The heating rate was programmed at 10 K/min from room temperature to 1073 K. The mass spectrometer (Hewlett Packard 1800-A) was connected on line to the TPD apparatus. The flow entering in the MS was split, 1% being directed into the capillary column (empty silica tube without retention phase), and analyzed from m/e 10 to 200 in scanning mode; the rest flowed out and was trapped in a solution composed of 20 ml boric acid (10 g/L) and 100 ml distilled water. This device trapped the NH_3 desorbed by the catalyst. At the end of the thermal treatment NH_3 was titrated by sulfuric acid 0.01 N. Data from the titration are used without further correction. From MS data, ammonia desorption is analyzed; for that, $m/e = 17$ is followed once corrected by the theoretical fraction (21.2%) of m/e 17 coming from the water ($NH_3 = m/e\ 17 – 0.212 \times m/e\ 18$).

2.2.4. Diffuse reflectance infrared Fourier transformed spectroscopy. In situ DRIFT spectra were obtained from a Bruker IFS 88 spectrometer with a DTGS detector by using a temperature- and environment-controlled chamber equipped with ZnSe windows (Spectra-Tech 00300). The spectra were recorded (200 scans) in the 4000–400 cm^{-1} range with 4 cm^{-1} resolution. For quantitative analysis, fresh catalysts analyzed at room temperature were diluted in KBr (1/20). In this case, the spectra of KBr was used as background. For the thermal treatment or the adsorption of $CDCl_3$, the pure samples were placed in the DRIFT cell and the spectra of an aluminium mirror was used as background. In order to simulate the TPD experiment a 30 ml/min flow of He (Air Liquide 99.995%) was passed through the samples during the whole thermal treatment. The temperature was increased manually at approximately 5 K/min from room temperature up to 373, 473, 573, and 673 K, remaining 30 min at each step before recording the spectrum.

The same equipment was used to study the adsorption of the deuterated chloroform ($CDCl_3$). Helium (10 ml/min) was flowed through a saturator filled with $CDCl_3$ at room temperature. The saturated flow was passed through the sample for 30 min, and then the flow was stopped and the chamber 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. This produces the complete desorption of $CDCl_3$. Then the first pretreatment temperature was reached and maintained for 30 min before taking a spectrum. The sample was cooled down and $CDCl_3$ was adsorbed again. Since $CDCl_3$ totally desorbed after 5 min under pure He flow and since no decomposition was observed, the same sample was used for the adsorption of $CDCl_3$ at the different temperatures of the thermal treatment. Quantitative analysis of the bands was made using an integration routine provided by the manufacturer.

2.2.5. X-ray photoelectron spectroscopy. The XPS analysis was performed with an SSI X-Probe (SSX-100/206) photoelectron spectrometer (Fisons), equipped with a monochromatized microfocus Al X-ray source, a 30° solid angle acceptance lens, a hemispherical analyzer, and a position-sensitive detector. The powder samples pressed in small stainless steel troughs of 4 mm diameter were placed on an alumina plateau (some samples are semiconductors) and introduced in the pretreatment chamber attached to the analysis chamber. The samples were heated at 393 K three times for 15 min under vacuum, the heating periods being separated by 30 min of outgassing. The samples were then outgassed overnight under vacuum (10^{-4} Pa) and then introduced into the analysis chamber, where the pressure was around 10^{-7} Pa. The angle between the surface normal and the axis of the analyzer lens was 55°. The spot size was approximately 1.4 mm^2 and the pass energy was set at 50 eV; under these conditions the resolution determined by full width at half maximum (FWHM) of the $\mathrm{Au}_{4f7/2}$ peak of a standard gold sample was around 1.1 eV. An energy flood gun set at 10 eV and an Ni grid placed at 3 mm above the sample were used to compensate for charging. The following sequence of spectra was recorded: $\mathrm{V}2p_{3/2}$–O1*s*, C1*s*, N1*s*, C1*s*, Al2*p*, C1*s*. Since the number of scan for the N1*s* region is high, multiple C1*s* spectra are recorded in order to check the absence of modification of the sample during analysis. The binding energies was calculated with respect to the C–(C,H) component of the C1*s* adventitious carbon fixed at 284.8 eV. The spectra were decomposed with the least squares fitting routine provided by the manufacturer with a Gaussian/Lorentzian ratio of 85/15 and after subtraction of a calculated baseline. The atomic ratio concentration was calculated using peak areas normalized on the basis of acquisition parameters and of sensitivity factors provided by the manufacturer (mean free path varying according to the

0.7th power of the photoelectron kinetic energy; Scofield cross sections; transmission function assumed to be constant). In this paper the nitrogen region will be shown for the oxynitride series. The spectra will be discussed qualitatively in order to understand the evolution of the nature of the nitrogenous species at increasing nitrogen content. Details of the other regions are beyond the scope of this paper and will be presented elsewhere. A detailed XPS analysis for another VAlON series is presented in (16).

2.2.6. Catalytic test: The Knoevenagel condensation reaction. The reaction of the condensation between malononitrile and benzaldehyde was used to characterize the catalytic activity of the VAlON. Four millimoles of reagent diluted in 30 ml of toluene was introduced into a three-neck batch reactor immersed in a thermostated bath at 323 K. 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 ±0.5 K by a thermometer placed in the liquid phase. The solution was stirred magnetically. A 0.25-ml sample was withdrawn before introducing the catalyst and after 5, 10, 20, 30, 60, 120, and 240 min and 24 h of contact with the catalyst. The sample was filtered removing the catalyst and the solution was introduced into a cold (258 K) flask to stop the reaction before chromatography analysis. The catalytic activity of the different oxynitrides catalysts were compared based on the initial rate of reaction and the conversion after 300 min run.

3. RESULTS

Characterisation of the VAlON by TPD, DRIFT, and XPS

The two main species detected, up to 673 K, by mass spectrometry during the thermal treatment under He flow are water and ammonia. Figure 1 plots the NH_3 released during the TPD experiment for the AV15ox, AV15N4, AV15N5, AV15N6T0, and AV15N8. These results indicate that all the fresh oxynitrides, even the oxide precursor, desorbed ammonia between 320 and 670 K. The relatively large area found for AV15ox is explained by the fact that the precursor still contains large amounts of ammonium from the synthesis, because it is not calcined. Nevertheless, since we have not found a good correlation between the area of MS peak and the amount of NH_3 obtained by titration, the curves of Fig. 1 are presented for qualitative characterization of the NH_3 desorption. The amount of NH_3 (titrated) desorbed by TPD is presented in Fig. 2, as well as the total nitrogen content for the series. This plot shows that the NH_3 desorbed during TPD represents only a small fraction of the total nitrogen and increases regularly with the percentage of nitrogen incorporated during nitridation, except for the most nitrided sample (AV15N8). Ammonia desorbed by the oxide precursor AV15ox was not measured but the XPS N1*s* percentage is 1.7 at.% and is the lowest of the series (AV15N4 = 2.3 at.%, AV15N8 = 7.9 at.%).

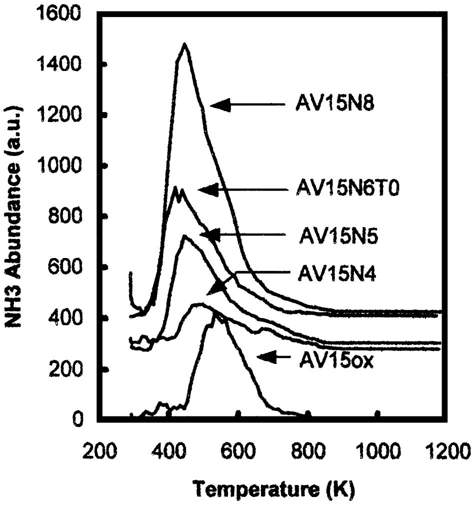


FIG. 1. NH_3 desorbed by TPD under He up to 1073 K ($r = 10$ K/min) of the AV15ox and AV15Nx series.

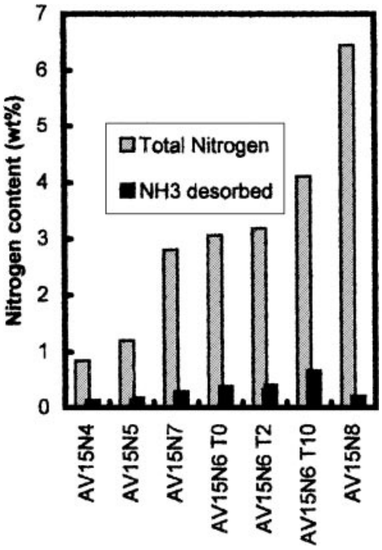


FIG. 2. Comparison between the NH_3 desorbed during the thermal treatment under He up to 1073 K (black column) and the total nitrogen content determined by the Grekov method for the AV15Nx series.

Figure 3 shows the evolution of the species present at the surface of AV15N6T0 oxynitride during *in situ* DRIFT thermal treatment under He. This sample is representative of all the VAlON of the series. The pure sample at RT (Fig. 3a) shows a band at 1430 cm^{-1} characteristic of $\delta_{as}(NH_4^+)$. When the temperature is raised, the intensity of this large band decreases drastically and two distinct vibrations at 1425 and 1470 cm^{-1} (Figs. 3c and 3d) appear. In agreement with the literature (19–21), the first band at 1425 cm^{-1} is attributed to $\delta_{as}(NH_4^+)$ in $V–O^-NH_4^+$. This assignment is supported by the DRIFT spectrum of commercial vanadium nitride (VN) (Fig. 3f) which presents a large band at 1420 cm^{-1} very close to that observed at 1425 cm^{-1} on the oxynitride. Its presence is also indicative of the

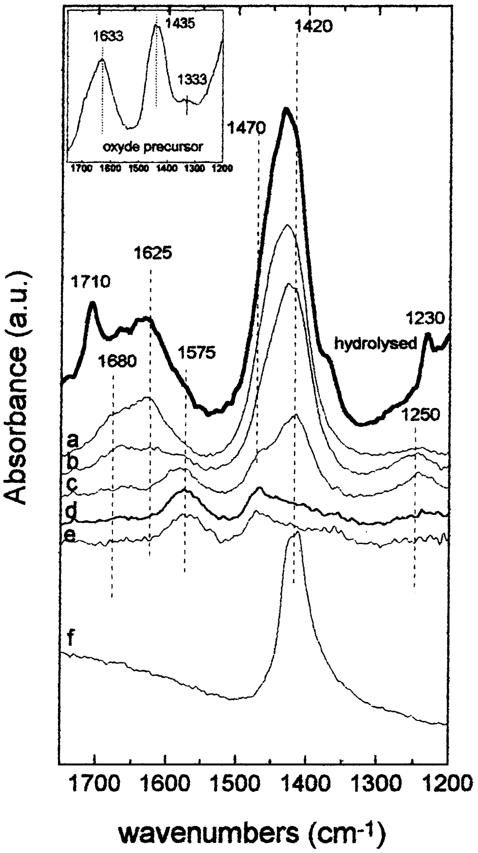


FIG. 3. DRIFT spectra for the pure (a) AV15N6T0 fresh catalyst at RT, (b) pretreated 30 min under He 30 ml/min at 373 K, (c) at 473 K, (d) at 573 K, (e) at 673 K, (f) VN pure at RT. AV15N6T0 hydrolyzed at RT for 30 min in a flow of He saturated with water at 293 K (bold). (Insert) Pure AV15ox in He 30 ml/min at RT.

hydrolysis of VN. The other band at 1470 cm^{-1} is attributed to $\delta_{as}(NH_4^+)$ of NH_3 bonded to an Al–OH hydroxyl group (20, 22). Furthermore, a small band at 1250 cm^{-1} characteristic of $\delta_s(NH_3)$ coordinatively bonded to a Lewis acid center is better resolved when the sample is pretreated due to the desorption of water (band at 1630 cm^{-1}) (19). From 473 K, a band at 1575 cm^{-1} corresponding to $\delta_s(NH_2)$ rises. In the inset, the spectrum of pure AV15ox at RT is shown. It is characterized by absorptions at 1333, 1435, 1633, and 1700 cm^{-1} that are ascribed, respectively, to adsorbed nitrate species, $\delta_{as}(NH_4^+)$, $\delta(HOH)$ of adsorbed water, and $\delta_s(NH_4^+)$. The presence of these species at the surface of the oxide precursor is explained by the use of ammonium metavanadate and aluminum nitrate as reagents for the synthesis and the absence of calcination of the precursor before the nitridation process. No calcination was made before nitridation because when the precursor is heated under air it crystallizes at 550°C in $AlVO_4$ and the surface area drops to 0.1 m^2/g (17). Furthermore we have experienced that no nitrogen can be incorporated at low temperature (between 773 and 873 K) once the crystallization has occurred. These results suggest that all VAlON catalysts contain Brønsted acid sites that adsorb ammonia. This is confirmed by the good correlation, presented in Fig. 4, between the integrated area of the $\nu_{as}(NH_4^+)$ measured in DRIFT for the fresh catalysts series and the NH_3 desorbed by TPD-He.

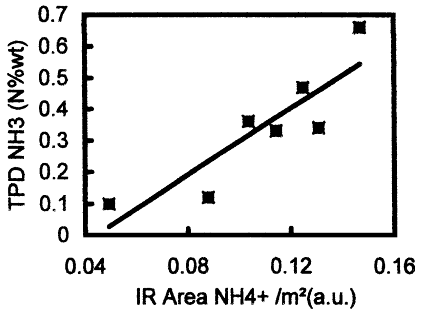


FIG. 4. Ammonia trapped during the TPD up to 1073 K under 50 ml/min of He as a function of the area of the DRIFT $\nu_{as}(NH_4^+)$ band at 1430 cm^{-1} measured at RT on the fresh VAlON catalysts for samples diluted in KBr (1/20) (from AV15N4 to AV15N8).

The XPS spectra of the N1*s* region for AV15ox, AV15N4, AV15N5, AV15N6T0, and AV15N8 are illustrated in Fig. 5.

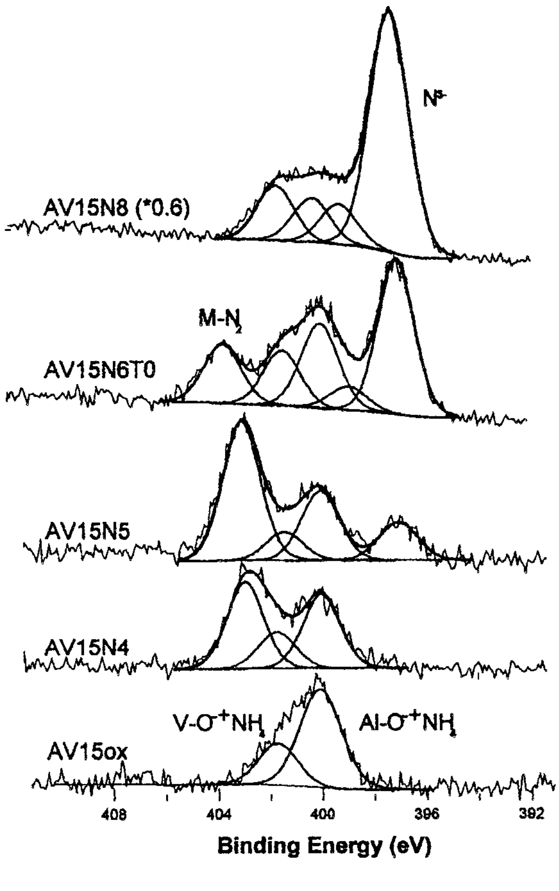


FIG. 5. XPS spectra of the nitrogen N1*s* region for the AV15 series. Samples are heated three times for 15 min at 393 K under vacuum (10^{-4} Pa) and then evacuated overnight.

The oxide precursor contains two well defined nitrogen species with a binding energy maximum at 400 and 401.8 eV that can be attributed to ammonium ions adsorbed on Al and V, respectively (23). This attribution is supported by the DRIFT results where the main species present at the surface of the oxide precursor are the ammonium ion (Fig. 3, inset). However, a contribution to the 400-eV peak from ammonia coordinatively bonded to a Lewis acid center cannot be totally excluded. When the nitridation temperature reaches 673 K (AV15N4), in addition to the two ammonium species a new peak appears at 403 eV. It has been ascribed to a metal dinitrogen species *M*–NN–*M*. A detailed discussion of this XPS peak at 403 eV and the species to which it corresponds can be found in (24, 25); let us just recall that in the literature this kind of fingerprints at high binding energy is observed when nitride or oxynitride compounds are oxidized. During the thermal oxidation of AlN (26) or TiN (27), for example, the nitride species (N^{3-}), characterized by an XPS N1*s* binding energy of 398.5 and 397.2 eV, respectively, progressively decreases while a new species revealed by a peak at 403 and 402.8 eV is emerging. This species is stable up to high temperatures (1100 K in the case of AlN) and is attributed to dinitrogen (N_2) in strong interaction with the solid that would stabilize the structure before complete oxidation of the nitride (28). In the case of VAlON, a species with a similar binding energy are observed during the nitridation (not the oxidation as in examples above) and are most likely explained by the oxidation of ammonia at the surface of the VAlON at the beginning of the nitridation process. Indeed, vanadium oxide based catalysts are very active in oxidation reactions and V_2O_5 is known to catalyze the oxidation of ammonia into N_2, N_2O, and NO (29–32). The oxidation of ammonia in the first step of the nitridation process is accompanied by the reduction of vanadium and by the formation of nitrogenous species that are successively chemisorbed at the surface. Depending on the degree of nitridation of the catalyst and the thermal stability of the chemisorbed nitrogenous species, H–*M*–NN would be first present, followed by the more stable *M*–NN or *M*–NN–*M* (where *M* is Al or V). The presence of azides cannot be ruled out, but their thermal instability make them bad candidates at temperatures as high as 873 K (Fig. 4, AV15N6T0) (24). When the temperature of nitridation is increased up to 773 K (AV15N5) the peaks characteristic of the ammonium ions are still present and another peak at 397 eV is detected, ascribed to nitride N^{3-} (16). Its intensity increases for higher nitridation temperatures where it is associated to a peak at about 399 eV that corresponds to NH_x groups ($x = 1$ or 2). So XPS shows the presence of at least five different nitrogenous species the nitrides being present from 773 K. Their presence helps to explain why ammonium ions are detected on high-temperature nitrided catalysts. Indeed, Centeno *et al.* (33) have studied the hydrolysis of AlPON by *in situ* DRIFT and have shown that the oxynitrides react at room temperature with water generating ammonium and –NH– groups at the expense of nitrides (N^{3-}). The reaction that corresponds to the reverse of nitridation can be written in a general way:

$$MM'O_4 + x\mathrm{NH}_3 \leftrightarrow MM'O_{4-3x/2}N_x + 3x/2\,\mathrm{H_2O}$$

(where *M*, *M*′ are, for example, Al and P in the case of Centeno work). The ammonia then reacts with a hydroxyl group (presence of water) to produce the ammonium ions:

$$M\text{–OH} + \mathrm{NH}_3 \rightarrow M\text{–O}^-\mathrm{NH}_4^+$$

This reaction explains why the samples with high total nitrogen content exhibit high ammonia adsorption capacity, since the hydrolysis generates more ammonia and then more neutralized Brønsted acid sites. At low reaction temperature the ammonium ions are coming from the synthesis.

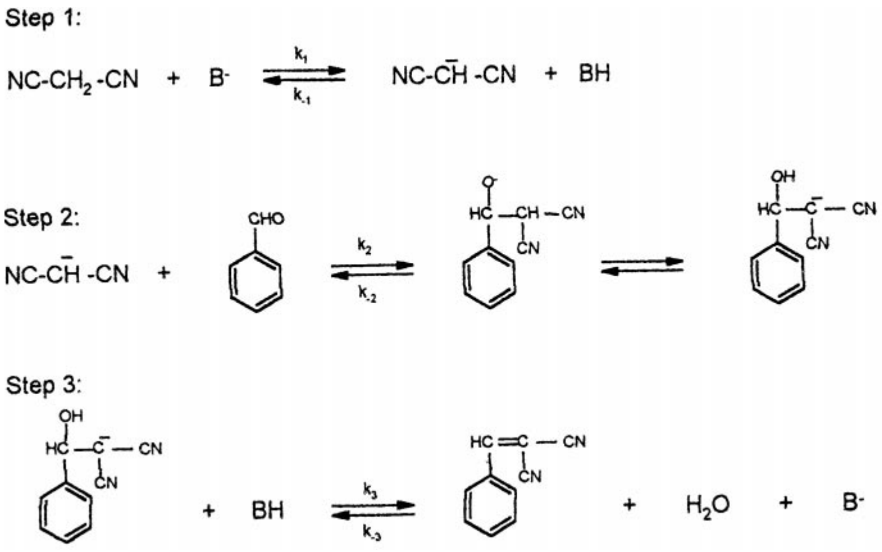
Reactivity of the VAlON in the Knoevenagel Condensation Reaction

In order to characterize the basicity of catalysts, condensation reactions have often been 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 keton for example) and forms a new carbon–carbon bond. When the reaction is catalyzed by a base such as ammonia, amine (primary and secondary) or an ammonium salt, 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 malononitrile (electron donating component) and benzaldehyde (electron accepting component) catalyzed by a base.

However, the reaction can also be catalyzed by acids (34–36). In homogeneous catalysis boron trifluoride, aluminum chloride, and acetic or perchloric acid (however, the yields with these two last acids are much lower than with basic catalysts (35)) are known to be good catalysts for the condensation reactions. In this case, the first step is the activation of the electron-accepting component (the benzaldehyde) by the acid to form a carbocation due to the ionization of the C=O through the formation of a coordination complex like for example, $\mathrm{R{-}HC^{\delta+}{=}O \rightarrow BF_3}$. The yields in this case are also dependent on the reactivity of the electron donating component (malononitrile) itself. Since, with malononitrile the proton ionization is activated by two nitrile groups, it is important to verify that the Knoevenagel condensation reaction is not catalyzed by the acid properties of the oxynitrides.

Is the Acidity Responsible of the Activity?

On AlPON (9, 37), ZrPON (13), and AlGaPON (14), which all contain acid sites as revealed by ammonia chemisorption, the authors have shown that the oxide



SCHEME 1. Mechanism for the Knoevenagel condensation reaction between malononitrile and benzaldehyde.

precursor, calcined between 923 and 1023 K, is the most acid catalyst of the series and is not active in the reaction of Knoevenagel condensation. Once the oxide is nitrided, the oxynitride becomes less acid and sufficiently basic to catalyze the Knoevenagel condensation reaction. This proves that the Knoevenagel condensation reaction is not catalyzed by the acidity of the surface and that the use of this test to characterize the basic character of their oxynitrides is fully justified. In our case the possible contribution of the acidity in the Knoevenagel condensation reaction has also been controlled by oxidizing a VAlON (AV15N6T0) at 673 K for 30 min and by testing it under the same conditions of reaction as used for the VAlON series. The surface characterization of this catalyst compared to that of the AV15N6T0 fresh one is summarized in Table 2. As revealed by XPS, its surface nitrogen content is very low and its acidity is much higher than that of the fresh oxynitride as indicated by the area under the IR band at 1430 cm^{-1} after NH_3 adsorption at RT. This oxidized VAlON does not catalyze the condensation reaction, suggesting that the Knoevenagel reaction is also an appropriate test to control the basicity of VAlON.

TABLE 2

Characteristics of the AV15N6T0 and the AV15N6T0 Oxidized at 673 K in a Mixture O_2/He (5%/95%)

Catalyst	AV15N6T0	AV15N6T0 oxidized at 673 K
Surface area (m^2/g)	81	81
Acidity (NH_4^+ area 1430 cm^{-1}/m^2)	0.19[a]	0.58
Activity (%conv 5 h/50 mg)	26	0
XPS nitrogen (at.%)	3.7	1.5

Note. The activity is measured for the Knoevenagel condensation reaction.

[a] The catalyst is pretreated at 673 K under He before adsorption of NH_3 for the measurment of acidity.

Is NH_3 Desorbed from the Oxynitride Responsible for the Catalytic Activity?

When the catalytic activity of the VAlON series is tested, all the catalysts convert benzaldehyde and malononitrile into benzylidene malononitrile. The selectivity in the first condensation product is 100% and the Michael addition, which would involve the reaction of another malonate carbanion with the double bond of the benzylidene malononitrile, is not observed. In Fig. 6 the initial rate of reaction (black squares), and the number of mole converted after 300 min (circles) are plotted as a function of the integrated area of the $\nu_{as}(NH_4^+)$ band observed in DRIFT for the oxynitride series. Surprisingly a correlation exists meaning

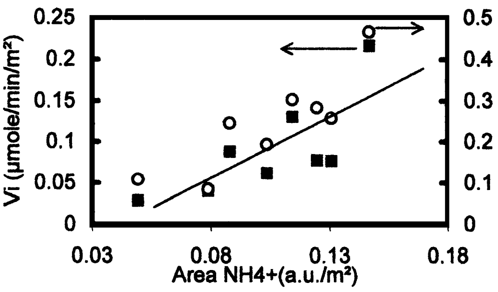


FIG. 6. Initial rate of reaction (μmole/min/m^2) in the Knoevenagel condensation reaction (the line fits those points) and number of mole of malononitrile converted after 300 min (10^{-3} mol/m^2) as a function of the area of the DRIFT $\nu_{as}(NH_4^+)$ band at 1430 cm^{-1} measured on the fresh VAlON catalysts at RT for samples diluted in KBr (1/20) (from AV15ox to AV15N8).

that there could be a relation between an acid species (NH_4^+) and a basic activity. Two hypotheses can be drawn from these results in order to explain the basic catalytic activity. First, since the ammonia present at the surface of the oxynitride catalyst is not thermally stable and since the catalytic test is performed at 323 K in toluene, some of the ammonia desorbed from the surface during the test and this ammonia in solution would be responsible for the catalytic activity. Another explanation would be that the neutralization of the hydroxyls by ammonia can be responsible for the catalytic activity. In other words, the formation of ammonium ions would generate a negatively charged oxygen, the "conjugated base" of the acid M–O–H, that would be the basic active center.

The first hypothesis which suggests that the ammonia in solution would be the active species is invalidated by several experiments. First, Lednor *et al.* (8, 38) have verified that gaseous ammonia dissolved in toluene is slightly active in the condensation reaction between benzaldehyde and ethyl cyanoacetate, but cannot explain the rate of the reaction observed when the catalyst is present (the reaction temperature and the reagent concentration used by Lednor correspond exactly to the conditions followed in this work). Furthermore, the amount of ammonia introduced by Lednor is 0.4 mmol, a value to be compared with the 0.005 to 0.024 mmol of ammonia liberated by 50 mg for the series of VAlON catalysts during the TPD. Second, in order to ascertain that the water produced by the condensation reaction, or the water present at the surface of the fresh catalyst, had no influence, an aqueous solution of ammonia was tested. A 12.2 M solution (4.5 μL) was introduced into the reactor. This is equivalent to 0.055 mmol of ammonia or three times the amount of ammonia desorbed by the AV15N6T0 in TPD. After 24 h no condensation reaction was observed. Third, AV15N6T0 was stirred with toluene for 12 h at 323 K. The suspension was then filtered and the reagents were added to the filtrate that could contain ammonia generated by the degradation of the oxynitride. No conversion after 24 h of test at 323 K was observed with the filtrate. The conclusion is clear: even if all the amount of ammonia present at the surface of the fresh oxynitride would desorb during the test, it cannot explain the conversion observed for the fresh catalyst. Nevertheless, the aging for 12 h in toluene mentioned in the third experiment partially degraded the catalyst, since when a new batch is started with it, the activity decreases (Fig. 7c). This result underlines the importance of the presence of ammonia in equilibrium with the surface to have an effective catalytic cycle. Finally, when the AV15N6T0 catalyst is aged 18 h in toluene before starting the test in this batch without changing anything, the catalyst converts the same percentage of reagents after 5 h as the one obtained in the third point. This shows that it is not ammonia in solution in contact with the catalyst that catalyzed the reaction, but ammonia adsorbed at the surface of the oxynitride since here ammonia desorbed from the AV15N6T0 is still present in the solvent when the test is started. The deactivation is the same after 12 (starting a new batch) or 18 h in toluene at 323 K. This suggests that once the catalyst has slowly lost some NH_3, an equilibrium is reached and afterward there is no more deactivation. This slow degradation is confirmed by the results presented in Fig. 6 where the same trend is obtained for initial rate and after 300 min of reaction. This confirms that the activity of the catalysts is controlled by the amount of NH_3 present at the surface and that poor reusability of the catalysts is expected without reactivation of the surface.

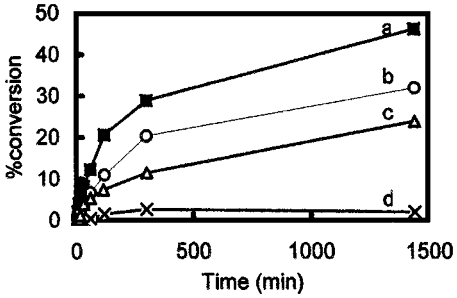


FIG. 7. Conversion (%) in the Knoevenagel condensation reaction in function of time for the (a) AV15N6T0 fresh catalyst, (b) AV15N6T0 pretreated up to 673 K under He followed by adsorption of NH_3, (c) AV15N6T0 aged in toluene 12 h before starting the reaction, and (d) AV15N6T0 pretreated up to 673 K under He without allowing hydrolysis of the surface.

So the results presented here show that ammonia desorbed from the VAlON during the catalytic test causing catalysts degradation but that dissolved NH_3 in toluene is not the basic species active in the condensation reaction.

Is the Conjugated Base of M–OH the Basic Species?

In order to verify if the second hypothesis is realistic, and to confirm that ammonia adsorbed on the surface of the catalyst is essential to the catalytic activity, two other experiments were carried out. First, immediately before starting the reaction, the AV15N6T0 was pretreated up to 673 K under He, cooled down in a desiccator, and introduced into the batch reactor in order to measure its activity. Second, the AV15N6T0 was pretreated under He up to 673 K and cooled down, like the previous one, but in this case 50 ml/min of ammonia was flowed through the catalyst for 5 min at RT; the excess of adsorbed gas was then purged with He and the reaction was started. The results of these experiments are illustrated in Fig. 7, curves b and d. When the catalyst was pretreated under He up to 673 K and since the time elapsed between the pretreatment and the beginning of the catalytic test was very short (less then 15 min), the contact with ambient air was minimum and the hydrolysis of the surface was avoided. Then the catalyst was not active. In the second experiment ammonia was readsorbed

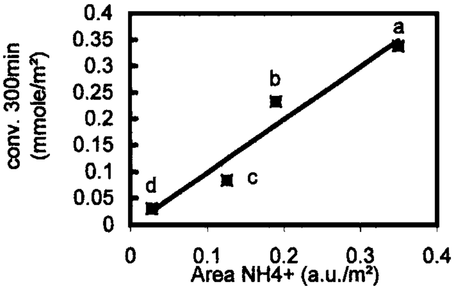
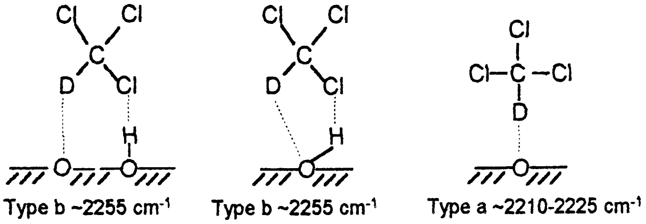


FIG. 8. Millimoles of malononitrile converted after 300 min versus the area of the DRIFT $\delta_{as}(NH_4^+)$ band at 1430 cm^{-1} of pure AV15ox (c) and AV15N6T0 catalyst obtained as specified in Fig. 7, curves a, b, and d.

and the oxynitride recovers a fraction of its initial activity. This is an evidence that ammonia adsorbed at the surface generates the active center for the reaction of condensation between malononitrile and benzaldehyde. The plot of the relation between the conversion in the Knoevenagel reaction and the area of the DRIFT band of $\delta_{as}(NH_4^+)$ at 1430 cm^{-1}, for pure AV15ox, AV15N6T0 fresh catalysts, AV15N6T0 pretreated at 673 K, and with subsequent readsorption of ammonia is given in Fig. 8. The good correlation confirms the previous trend observed for diluted samples in KBr (Fig. 6) and underlines that, if basic activity is expected, the presence of ammonium ions on the surface of the VAlON is necessary.

Characterization of the Basic Site by $CDCl_3$ Adsorption

In order to characterize the basic sites and especially the decrease of basicity that the catalyst experiences during the pretreatment, the adsorption of $CDCl_3$ was carried out. This probe molecule was chosen because it is a protonic acid able to form D complexes (H complexes in the case of $CHCl_3$) with the basic center, and because it is a weak base (Cl) that interacts very slightly with aprotic and proton acid sites (39–41). Moreover, the vibration of interest is the ν(C–D) situated between 2250 and 2180 cm^{-1} and corresponds to an IR region of the spectra of the catalyst particularly free of perturbation. The main modes of vibration of $CDCl_3$ adsorbed on a basic oxygen and the corresponding wavenumbers are presented in Scheme 2. These results are taken from the work of Paukshtis *et al.* (42) who adsorbed this molecule on different basic catalysts. These authors reported that changing the basicity of the support leads to a change in the position of the maximum of the ν(C–D) band. For more basic catalysts the vibration occurs at lower wavenumbers. The same results are reported by Berteau *et al.* (43) who adsorbed $CDCl_3$ on Na or Mg modified alumina. A new band at lower wavenumbers compared to nonmodified alumina appeared and was attributed to a more basic surface center. Gordymova *et al.* (44) and Davydov *et al.* (45, 46) mentioned that chloroform can be decomposed or irreversibly adsorbed at the surface of some oxides like alumina or magnesium oxide, thus modifying the acid–base properties of the support under analysis. In our case, no evidence of decomposition of $CDCl_3$ such as irreversible perturbation of the hydroxyls, appearance of bands at 1360–1390 and 1600 cm^{-1} due to formiate species, has been noticed. This is probably due to the very short contact time (15 min) used here between the adsorption and the analysis, as compared to up to 60 h necessary in the work of Gordymova to observe the decomposition. So $CDCl_3$ is well adapted for the characterization of the basicity of the VAlON.



SCHEME 2. Mode of adsorption of $CDCl_3$ at the surface of oxides and the corresponding wavenumbers of the νC–D vibration.

Figure 9 presents the vibration of $CDCl_3$ adsorbed at RT on the fresh AV15N6T0 oxynitride catalyst and on the sample pretreated at 673 K. On the fresh catalyst a band centered at 2250 cm^{-1} with a shoulder at 2238 cm^{-1} is visible, suggesting the presence of at least two distinct basic sites at the surface of VAlON. According to the literature (42–47) both bands can be assigned to $CDCl_3$ adsorbed on b-type sites. The thermal treatment up to 673 K influences both the quantity and the position of the bands. The component at 2238 cm^{-1} decreases, suggesting that the stronger basic sites are those removed during the thermal treatment

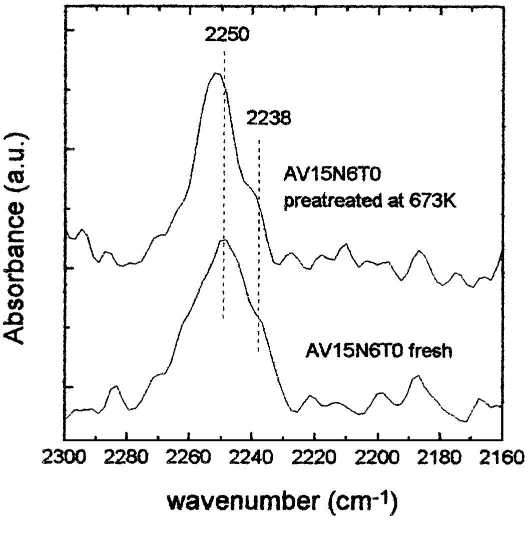


FIG. 9. DRIFT spectra of the νC–D vibration for $CDCl_3$ adsorbed at RT on AV15N6T0 fresh catalyst and on AV15N6T0 pretreated at 673 K under He 30 ml/min for 30 min.

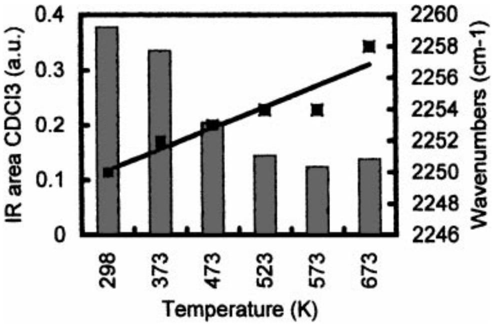


FIG. 10. Area (bars) and shift (black dots-right) of DRIFT ν(C–D) band of adsorbed $CDCl_3$ on AV15N6T0 at RT versus the pretreatment temperature.

(remember that the adsorption is done at RT after thermal treatment). The plot of the position of the maximum of the ν(C–D) band, as well as the area under the peak, as a function of the pretreatment temperature is presented in Fig. 10. The position of the ν(C–D) shifts to higher wavenumbers when the catalyst is pretreated at increasing temperatures. This can be explained by a decrease in the basic strength of the sites and corresponds to a weaker interaction between the D atom and the surface. In Fig. 11 the area of the $\nu_{\mathrm{C-D}}$ peak of the adsorbed $CDCl_3$ as a function of that of $\delta_{\mathrm{as}}(\mathrm{NH}_4^+)$ for the different temperatures of pretreatment studied is plotted. This relation confirms that the basicity of the VAlON is directly proportional to the amount of ammonium ions present at the surface, strengthening the hypothesis that they generate a negatively charged oxygen that would be the basic active center. However, it was shown that when NH_4^+ ions are removed by pretreatment at 673 K, the VAlON are no more active, but at that temperature they still adsorb $CDCl_3$. This indicates that the second site titrated by chloroform and characterized by a maximum at 2258 cm^{-1} is a weaker one not active in the condensation reaction. According to the literature that reports ν(C–D) for $CDCl_3$ interacting with hydroxyls at 2250 cm^{-1} on γ-alumina (44, 47), at 2251 cm^{-1} on gallium oxide (50), or at 2245 cm^{-1} on MgO (45), the band at 2250–2258 cm^{-1} can be attributed to an interaction with neutral hydroxyls present at the surface of the VAlON.

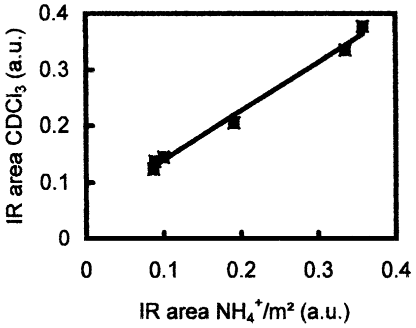


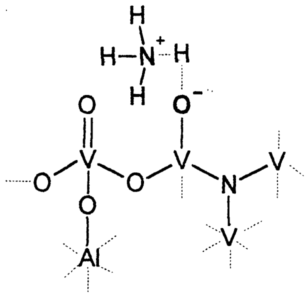
FIG. 11. Area of the DRIFT $\nu_{\mathrm{as}}(\mathrm{NH}_4^+)$ band at 1430 cm^{-1} of the AV15N6T0 catalyst at increasing pretreatment temperature versus the area of the corresponding ν(C–D) band at 2250 cm^{-1} of adsorbed $CDCl_3$.

4. DISCUSSION

A proposition for the basic site active in the Knoevenagel condensation reaction is attempted in Scheme 3 where the active site is an O^- generated by the neutralisation of an acid V–OH by ammonia. A similar kind of active species in solution has already been suggested by Lednor *et al.* (8) when they measured the activity, in the Knoevenagel condensation reaction, of gaseous ammonia dissolved in various solvents. When ammonia is dissolved in toluene it is slightly active but when ethanol is used, the activity is so high that it cannot be explained by the intrinsic reactivity of ammonia. To interpret this result, these authors proposed the formation of the ethanolate $C_2H_5O^-NH_4^+$, the conjugated base of the weak acid ethanol, a much stronger base than ammonia.

Could Amino or Imino Groups Be the Basic Center?

The site that catalyzes the Knoevenagel condensation reaction on other oxynitride systems such as SiON or aluminophosphate oxynitride has been attributed to surface nitrogenous species by analogy with the amine or imine active in homogenous catalysis (8, 38, 48). Massinon *et al.* (48) reported that on AlPON the catalytic activity is related to the Kjeldhal nitrogen and Climent *et al.* (49), on the same system, have identified =NH and $-NH_2$ as the active basic sites. On the ZrPON oxynitride catalyst, the nitride N^{3-} group is also a candidate (50). In the case of VAlON, the arguments that refute a nitrogenous species as the active site are, first, that amino $-NH_2$ or imino =NH groups are not observed on the fresh oxynitride catalysts, second, that the $-NH_2$ groups appear significantly when the oxynitrides are heated above 523 K under He (DRIFT absorption at 1575 cm^{-1}) and their maximum concentration is reached when the pretreatment temperature is 673 K (Fig. 3, curves c–e), temperature for which the catalyst shows no activity. Furthermore, here the oxide precursor AV15ox is active in



SCHEME 3. Proposition for the basic site present on the aluminovanadate oxynitride catalysts.

the Knoevenagel condensation reaction. This strongly suggests that the active site is an oxygen and not a nitrogenous species like N^{3-}, $=NH$, or $-NH_2$, since AV15ox has not been nitrided and that the main nitrogenous species present on its surface are NH_4^+.

Is the Basic Site a Neutralized V–OH or Al–OH?

In Scheme 3, the hydroxyl that is neutralized by ammonia is bonded to a vanadium atom. This is inferred from the analysis of both the thermal stability of the ammonium species at the surface of AV15N6T0 and the amount of $CDCl_3$ adsorbed at the corresponding pretreatment temperature. Indeed, at the beginning of the thermal treatment (from RT to 523 K) the main ammonium species that diminishes is characterized by a vibration at 1425 cm^{-1} (Fig. 3) and has been assigned to the $\delta_{as}(NH_4^+)$ in $V–O^-\ NH_4^+$ groups. A decrease is also observed for the amount of D-chloroform (Figs. 10 and 11) adsorbed in this range of temperature. From 523 to 673 K, the quantity of ammonium ions and the number of adsorbed $CDCl_3$ are stable, the former being characterized mainly by a vibration at 1480 cm^{-1} assigned to $\delta_{as}(NH_4^+)$ in $Al–O^-NH_4^+$. The parallel evolution between the ammonium ion $V–O^-NH_4^+$ and the chloroform adsorbed strongly suggests that the basic center active in the condensation reaction is the oxygen associated to the $V–O^-NH_4^+$ center and that the ν(C–D) at 2238 cm^{-1} can be attributed to the interaction between the D-chloroform and this site, since this band is the most affected by the thermal treatment.

Another argument that strengthens the hypothesis that the electron density of the oxygen atom of the $V–O^-\ NH_4^+$ species would be higher than in the $Al–O^-\ NH_4^+$ case arises from the comparison of the mobility of the proton in an Al–O–H and in the V–O–H, i.e., the relative acidity of both groups. It has been reported (20) that when ammonia is adsorbed on these groups the position of the $\delta_{as}(NH_4^+)$ band can be related to the mobility of the proton. The lower the wavenumber the higher the mobility, a stronger acidity corresponding to a more mobile proton and to better separated positive and negative charges. Since $V–O^-\ NH_4^+$ groups adsorb at a lower frequency than $Al–O^-\ NH_4^+$, it is then a stronger Brønsted acid and its neutralization by ammonia will generate more ionic species then the latter. This means that the negative charge on the oxygen atom will also be denser in this case, corresponding to a more basic species.

What Is the Strength of the Basic Site?

In the Knoevenagel condensation reaction catalyzed by bases the first step is the abstraction of a proton from the malononitrile and the formation of a carbanion (Scheme 1). The basic strength required to realize this step could be estimated by knowing the pK_a of the malononitrile since it represents the tendency of this molecule to lose a proton. This approach to characterise the force of the sites, using methilenic components of various pK_a, has been used by Corma *et al.* on several systems such as exchanged zeolites (51) or sepiolites (52) and by Grange *et al.* (11) to evidence the strength of the basic site of the AlPON catalyst. This method helps to understand the results of Lednor *et al.* (8) who observe a slight conversion between ethylcyanoacetate and benzaldehyde using ammonia as catalyst and no conversion when malononitrile is used as the methylenic compound. Indeed, since the malonitrile is a very weak acid with a $pK_a = 11.2$, therefore, the pK_b of the basic site for the reaction to occur must be lower than 2.8, otherwise the equilibrium will not be displaced in the direction of product formation. Since the pK_b of ammonia is 4.74 no reaction occurs. On the contrary, when using ethylcyanoacetate ($pK_a = 9$) the pK_b of the base necessary to displace the equilibrium is 5 and then a slight conversion is expected using NH_3 as catalyst. Using this approach the strength of the basic site on VAlON can be estimated to have a $pK_b \leq 2.8$.

Another way to characterize the basic strength of the center is to use the $\Delta\nu$(C–D) in cm^{-1} between gaseous D-chloroform (2265 cm^{-1}) and the position for the adsorbed probe (39–42). Paukshtis *et al.* indicated that this shift is correlated to the proton affinity (PA, kJ/mol) and to the pK_a of the base. The dependence is described by the equation: $\log \Delta\nu(C–D) = 0.0057.PA - 3.54$. A strong basic catalyst such as MgO has a PA of 925 kJ/mol and a pK_a value estimated to +10. This value means that the basic center is able to abstract the proton of a weak acid molecule whose pK_a is +10. Using this method the strength of the strongest basic sites encountered on the VAlON has a PA of 872 kJ/mol. By comparison, the strongest basic site encountered on γ-alumina has a PA of 895 kJ/mol and its pK_a is about +7 (41, 42). So the basic strength is very much the same as that found on alumina. Then, if we assume a maximum value of 7 for the pK_a of the VAlON, it corresponds to a basic strength very different from that estimated by the pK_a of the malononitrile. This much weaker basic site should be inactive in the proton abstraction of the malononitrile.

Proposition of a Mechanism of Reaction

The contradiction between the strength and the reactivity can be explained assuming that, at the surface of the VAlON, another mechanism requiring weaker sites is active. Indeed, if the appropriate strength of the active site is one of the keys in a catalytic cycle, another important step is the stabilization of the transition complex or of the intermediates of the reaction. This argument is used by Climent *et al.* (49) to explain the higher activity of malononitrile ($pK_a = 11.2$) with respect to that of ethyl cyanoacetate ($pK_a = 9$) on AlPON when condensed with benzaldehyde, indicating that a particular interaction between the substrate and the catalyst can be critical for the final reactivity. Furthermore, kinetic studies (51, 52) have revealed that the reaction rate depends on both the acid–base characteristics of the catalysts and the nature of the carbonylic component (benzaldehyde). Hence, if the rate limiting step on VAlON, like on other catalysts, is the attack of the carbonyl group by the carbanion to form a C–C bond (step 2 in Scheme 1), and not the formation of the carbanion (step 1 in Scheme 1), the activation of benzaldehyde on acid sites (A), i.e., the formation of $R–C^{\delta+}=O \rightarrow A$, is likely to be a favorable factor in this reaction. This would also mean that the carbanion is quite stable, this being compatible with the description of the basic site made here. The O^- pulls the proton of malononitrile, but there is also the positive charge of the ammonium that can favor this abstraction by stabilizing the resulting carbanion. The carbanion then reacts with the benzaldehyde activated on an acid site that can be either a Brønsted as in the mechanism proposed by Angeletti *et al.* (15) or a Lewis acid sites as described earlier. Thus we are most likely faced with a concerted mechanism that takes into account both the acid and the basic properties of the VAlON surface. This means that the strength of the basic site measured by the pK_a of the methilenic compounds is not appropriate in our case. Finally, the VAlON are very hygroscopic and water reacts readily with the nitride at room temperature. This characteristic can also explain the particularly high reactivity of VAlON in the Knoevenagel condensation reaction since the water produced by the reaction is probably adsorbed on the surface of the oxynitrides displacing the equilibrium toward the formation of the products. This is supported by DRIFT analysis of AV15N6T0 submitted to a flow of He saturated with water at room temperature (Fig. 3, hydrolyzed), which evidences the reaction of water with the surface of the fresh catalysts (bands at 1630 cm^{-1} $\delta(HOH)$ and 1710 $\delta s(NH_4^+)$).

5. CONCLUSION

The basic site present at the surface of aluminovanadate oxynitride catalysts is an oxygen negatively charged bonded to a vanadium atom. The high electron density carried by this oxygen is created by the neutralization of the acid hydroxyl group by ammonia, that generates the ionic species $NH_4^+O^-$. This proposition is supported by the correlation between the catalytic activity in the Knoevenagel condensation reaction and the amount of ammonium ions at the surface of the series of aluminovanadate catalysts observed by DRIFT; moreover, the relation between the adsorption of deuterated chloroform and the quantity of NH_4^+ provides evidence that ammonium ions are involved in the generation of the basic sites. Nevertheless, the low value of the pK_a obtained for this center cannot explain the high rate of reaction observed. Other factors, such as a concerted mechanism with activation of the benzaldehyde by the acid sites of the catalysts and/or the retention by the surface, of the water produced by the reaction, are to be taken into account in order to understand the reactivity of those oxynitrides.

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