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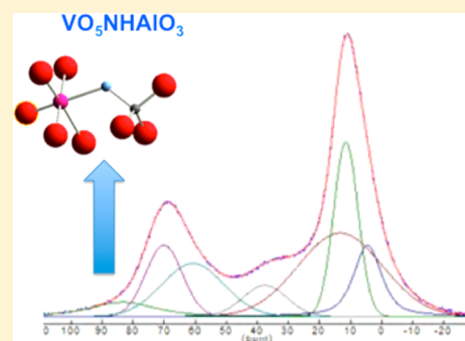
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ABSTRACT: Several techniques such as ²⁷Al 800-MHz NMR, X-ray diffraction (XRD; powder), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), Raman spectroscopy, and electrical conductivity measurements have been applied to characterize VAIO mixed oxides used in the selective ammoxidation of propane to acrylonitrile. The results confirmed that the catalysts were nitrated when exposed to ammoxidation conditions and that the nitridation occurred only for mixed oxides. The solids corresponding to poorly crystallized χ -alumina contained usual six-, five-, and four-coordinated aluminum and after testing, AlO_3N species in significant amount. These results are in line with those of XPS showing besides adsorbed nitrogenous species, the presence of NH^{2-} species allowing to propose $\text{AlO}_3(\text{NH})\text{VO}_{5.6}$ as active site for catalytic nitridation. On another side, the samples prepared by a new method allowing to better disperse vanadium in the mixed oxide as shown by EPR, were shown to be more active and selective. Based on these observations, it is proposed that most selective sites for propane activation correspond to monomeric isolated species or to low-size oligomeric vanadium oxide species, which is in line with any other study of vanadium containing catalysts used for light alkanes oxidation or ammoxidation. Finally, nitrogen substitution in the bulk was shown to greatly enhance the electrical conductivity, which should facilitate the complete catalytic redox cycling.



1. INTRODUCTION

Acrylonitrile is an important intermediate in the chemical industry for the synthesis of various polymers and coatings. It is currently produced by ammoxidation of costly and increasingly scarce propylene. There is a strong interest in developing novel catalysts allowing the use of cheaper and abundant propane, which is of economic potential and sustainability, since natural resources (gas and oil) can be more efficiently used. Despite much research in the past decade, propane-based processes have not been industrialized. Hence, totally novel routes to tailored catalysts should be developed.

The analysis of the literature shows that among the numerous catalysts proposed for the reaction, only three systems stand out by their efficiency or productivity.¹ They are constituted by combination of mixed metal oxides and correspond to molybdate or antimonate based systems such as $\text{MoVTe}(\text{Sb})\text{NbO}$, AlVSbWO , or to vanadium and aluminum oxy-nitride based systems. The two first catalytic systems are by far the most efficient in terms of yields but vanadium and aluminum oxy-nitride catalysts stand out from the others by a widely surpassing productivity. Furthermore, the development of molybdate and antimonate catalysts has reached a point where further modifications seem difficult and therefore, it is anticipated that they cannot be considerably improved

anymore. This is not the case of the third system, which has not been comparatively as much studied.

Vanadium aluminum oxy-nitrides are obtained by partial substitution of nitrogen for oxygen in the structure of the V–Al mixed oxides during a nitridation process.² The catalytic performances in propane ammoxidation of these catalysts strongly depend on the preparation parameters like the V/Al ratio, coprecipitation pH, V concentration in the solution, and nitridation conditions (temperature, nitridation mixture, time).^{3,4} The best catalysts are mixed oxides with V/Al of 0.25 prepared at pH 5.5 and with a V concentration of 0.020 $\text{mol}\cdot\text{L}^{-1}$. First studies of the VAIO system showed a propane conversion of 55% and an acrylonitrile selectivity of 60% in steady-state conditions at 500 °C and under an atmosphere of $\text{C}_3\text{H}_8/\text{O}_2/\text{NH}_3 = 1.25/3/1$ with a GSHV of 16.8 $\text{L}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$.^{5,6} A recent study confirmed the excellent results, however, with slightly lower conversion and selectivity and at higher ammonia partial pressure ($\text{C}_3\text{H}_8/\text{O}_2/\text{NH}_3 = 1.25/3.14/2.4$, GHSV=16.8 $\text{L}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$).⁷ In the later case, the best catalysts were characterized by a V/Al ratio around 0.30.

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Concerning the reaction mechanism, two pathways were proposed either through intermediate propene^{7,8} like for multielement based catalysts,⁹ or through a direct pathway.¹⁰ This later pathway was proposed since no propene was detected in the reaction byproducts, which is rather unexpected. The participation of the nitrogen from the lattice of a series of vanadium aluminum oxy-nitride catalysts was made evident by temporal analysis of products in the absence of NH_3 and O_2 , and a double Mars–van Krevelen mechanism, involving both oxygen and nitrogen from the lattice has been proposed.^{8,10}

The characterization of the vanadium aluminum oxy-nitrides is rather difficult since they are amorphous. Furthermore, after testing they may reoxidize when brought back at room temperature and expose to air. This makes understanding of relationships between structure, composition, and catalytic properties rather difficult. The local structure around the vanadium atoms in the oxide precursors and in the catalysts has been studied by EXAFS spectroscopy.¹¹ Their nitridation in NH_3 was followed with in situ characterization in the same study. It was shown that the oxide precursors have tetrahedrally coordinated vanadium, while after full nitridation octahedrons were found and a small decrease in vanadium oxidation state occurred. Thus, the catalysts used in the ammoxidation reaction contain a mixture of VO_4 tetrahedrons and VO_6 octahedrons. Later a study by in situ valence-to-core X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XANES) at the V K-edge confirmed the evolution during nitridation but showed that the reduction of vanadium was much more important.¹² Changes in formal oxidation state from +4.8 to $+3.8 \pm 0.1$, was evidenced. Exposure of the catalyst to pure NH_3 at 500 °C led to further reduction of vanadium. Valence-to-core XES also proved that the level of bulk nitridation of vanadium in the active catalyst was rather small. It has been concluded that activation of V/Al/O catalysts on-stream is mainly associated with reduction of vanadium in the bulk structure of the material and nitridation of vanadium atoms on the surface.

All the characterizations done so far do not provide a proper understanding of the complete reaction mechanism of paraffin ammoxidation on these catalysts, and the latter have to be further characterized to determine the exact functionalities of the vanadium and aluminum species, respectively. Such step is essential in trying to improve the catalysts on a scientific basis. In this paper we present the characterization of the vanadium aluminum oxy-nitride catalysts and their precursors by various techniques like ^{27}Al 800-MHz NMR, electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and electrical conductivity measurements. To better understand the evolution of the aluminum and vanadium oxide precursors during catalytic testing, nitridation of these precursors has also been performed ex situ under pure ammonia and several reference samples have been prepared and characterized. Catalysts prepared using a new method of preparation described in an earlier article have also been characterized.⁷

2. EXPERIMENTAL SECTION

2.1. Preparation of the Catalysts. The V/Al/O catalysts with different V/Al molar ratio have been prepared according to a published protocol, which has been shown to possibly be scaled up.^{10,13} The catalysts were synthesized by coprecipitation from solutions containing 0.01 M ammonium metavanadate and 0.01 M aluminum nitrate at 60 °C. Ammonium

metavanadate was dissolved in hot water (60 °C) under stirring and then nitric acid (50 wt %) was added until the pH reached 3.0. When the solution of aluminum nitrate was added to the mixture, the latter became red-orange with pH of 2.5. Then the pH was increased up to 5.5 by adding ammonium hydroxide solution (25 wt %) and the mixture was maintained under these conditions for 1 h. The yellow precipitate was washed with ethanol and dried in vacuum at 120 °C.

Catalysts have also been prepared using a technique developed previously.⁷ It comprises synthesizing first the mixed oxalate $(\text{NH}_4)_3[\text{Al}_x\text{V}_2(\text{C}_2\text{O}_4)_3] \cdot n\text{H}_2\text{O}$ followed by thermal decomposition. In the first step, appropriate quantities of oxalic acid and ammonium oxalate were dissolved in 200 mL of distilled water. Ammonium metavanadate was then added to the solution maintained under magnetic stirring at room temperature for 3 h. Oxalic acid, ammonium oxalate, and metallic aluminum were then added to the solution, which was maintained under stirring and reflux at 60 °C for 24 h. The mixed ammonium oxalate of vanadium and aluminum was separated by filtration and dried in ambient air. This method allowed preparing an oxide precursor with a V/Al ratio of 0.25. The obtained oxide precursor was finally fired at 180 °C under flowing ozone-air mixture (1.1 ppmv O_3) at 70 mL.min⁻¹ for 480 h.

The solids prepared using the standard method were either used directly as catalysts in the reaction conditions or prenitrided under ammonia at 500 °C for 5 h (ex situ nitridation). Both preparations (direct use or prenitridation) led to catalysts with comparable catalytic properties. When used directly, it took about 8 h on stream to obtain the best catalytic properties. The samples prepared using the mixed oxalate precursor method were always used directly as catalysts. The samples prepared using the standard method were referred to as VAIO-*a* with *a* being the V/Al ratio, whereas the samples prepared using the second method, which had always the same V/Al ratio equal to 0.25, were referred to as VAIO-OX.

2.2. NMR Spectroscopy. Magic angle spinning NMR experiments were performed on a Bruker Avance III 800 MHz SB spectrometer, equipped with a 2.5 mm double channel H/X CP-MAS at 18.8 T. A zirconia rotor of diameter 2.5 mm was spun at 30 kHz. ^{27}Al MAS NMR spectra were measured by a single $\pi/12$ pulse of 0.5 μs at a resonance frequency of 208.48 MHz, a recycle delay 1 s and a spectral width of 2400 ppm. This angle allowed recording quantitative NMR spectra. ^{27}Al chemical shifts were referenced to $\text{Al}(\text{NO}_3)_3$ aqueous solution, i.e., the resonance of $\text{Al}^{3+}(\text{H}_2\text{O})_6$ was set to 0 ppm. The experimental error of the shift was ± 0.5 ppm for ^{27}Al . An exponential broadening of 20 Hz was used during spectra processing.

Spectral decompositions have been done with DMFIT software of Massiot et al.¹⁴ The proposed fits for VAIO catalysts have been found by iteration to obtain a model applicable to all spectra and based on distributions of sites rather than on quadrupolar broadening. Indeed, using a high magnetic field allowed us to minimize the second order quadrupolar effect and not consider it. Because of the amorphous nature of the samples, large distributions of sites exist leading to spectra, which have to be decomposed considering distribution of Gaussian peaks.

2.3. EPR. EPR spectra in X-band were recorded on an EPR cw-spectrometer ELEXSYS 500-10/12 (Bruker) at a modulation frequency of 100 kHz and a modulation amplitude of 0.5 mT. The magnetic field was measured with respect to standard

2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH). Computer simulation of EPR spectra was performed with the program SIM14S of Lozos et al.¹⁵

2.4. X-ray Photoelectron Spectroscopy (XPS). XPS measurements were performed using a Kratos Axis Ultra DLD spectrometer. The base pressure in the analysis chamber was better than 5×10^{-8} Pa. XPS spectra of V2p, Al2p, O1s, and C1s levels were measured at 90° (normal angle with respect to the plane of the surface) using a monochromated Al K α X-ray source with a pass energy of 20 eV and a spot size aperture of 300 μm . Binding energies were corrected relative to the carbon 1s signal at 284.6 eV. The experimental precision of the quantitative analysis, after Shirley background, was considered to be around 10%.

2.5. Raman Spectroscopy. The Raman spectra were achieved with a LabRam HR spectrometer (Jobin Yvon) equipped with a CCD detector cooled at 77 K. The exciting line at 514.53 nm of an Ar⁺–Kr⁺ ion laser (Spectra Physics, Model 2018 RM) was focused on the solids with a X100 objective; the laser power was limited to 1 mW to avoid laser heating. The Raman spectrum of a silicon plate was previously achieved to adjust band positions. The wavenumbers reported in the following were accurate within 2 cm^{-1} .

2.6. Electrical Conductivity Measurements. The powdered oxides and oxy-nitrides were compressed at ca. 2.76×10^7 Pa using a Carver 4350.L pellet press to ensure good electrical contacts between the grains. The pellet was then placed in a horizontal quartz tube between two platinum electrodes. The flow rates of gases flowing over the sample were measured by capillary flow meters, and the temperature was controlled using thermocouples soldered to the electrodes that when short-circuited were used to determine the electrical conductivity. The electrical resistance was measured with a mega-ohmmeter (FLUKE 177 Digital Multimeter). Electrical conductivity σ of the samples can be expressed by the formula

$$\sigma = \frac{1}{R} \times \frac{t}{S} \quad (1)$$

where R is the electrical resistance and t/S is the geometrical factor of the pellet including the thickness t (ca. 3 mm) and the cross section area S of the pellet whose diameter was equal to 13 mm. Indeed, the electrical conductivity of semiconducting oxide powders can be written as

$$\sigma = An \quad (2)$$

where n is the concentration of the main charge carriers, and A is a coefficient of proportionality, which includes the mobility of the charge carriers and the elementary charge of the electron.

To compare the electrical conductivities of the samples, it is required that the solids have similar textures and surface states. This requirement was easily fulfilled since both samples had similar BET surface areas and were compressed at the same pressure and the electrical measurements were standardized. The common reference state for electrical conductivity (σ) determination has been chosen under air at atmospheric pressure and at 450°C . At this temperature, which was in the range used in the catalytic reactions, most of the ionically adsorbed species such as H_3O^+ , HO^- , which would produce an additional surface conductivity were eliminated. The solid was initially heated from room temperature to the desired temperature at a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$.

2.7. Other Techniques. Metal contents of the solids were determined by atomic absorption spectroscopy (inductively

coupled plasma (ICP)). The precisions of the chemical analyses have been evaluated and are considered to be 2%. The nitrogen content of the solids has been determined using a CHNS/Oxygen automatic elemental analyzer Thermo Scientific MAS 200R. The precision of the measurement was 0.3%. The simultaneous thermogravimetric and differential thermal analyses (TG-DTA) of the samples were conducted on a SETARAM TG92 apparatus with about 25 mg of solid under N_2 with a heating rate of 1 or $5^\circ\text{C}\cdot\text{min}^{-1}$. Surface areas of the catalysts were measured with a Micromeritics ASAP 2010 instrument. Samples were first degassed under vacuum at 250°C for 2 h. By using the adsorption–desorption isotherm at -196°C , surface areas were calculated by the Brunauer–Emmett–Teller (BET) method. Pore volumes were obtained using the Barret–Joiner–Halenda (BJH) adsorption curve. X-ray diffraction (XRD) patterns of the catalysts and of the catalysts precursors were obtained using a Bruker D 8 X-ray diffractometer. The X-ray source was Cu K α radiation. The 2θ diffraction angle was varied from 5 to 80° during the measurement. The International Center for Diffraction Data (ICDD) library was used for phase identification.

2.8. Catalysts Testing. The apparatus used for catalytic tests of the samples has been described elsewhere.⁷ The reaction was performed at 500°C and at atmospheric pressure. The catalyst amount was varied from 4 to 130 mg and was diluted with SiC (fraction between 106 and $180\text{ }\mu\text{m}$). The volume above the catalytic bed was filled by small pieces of quartz. The feedstock composition was $\text{C}_3\text{H}_8/\text{O}_2/\text{NH}_3/\text{N}_2 = 1.25/3.15/2.4/1.7$ with a total flow of $16.4\text{ mL}\cdot\text{min}^{-1}$. The gas products and reactants were analyzed on line by gas chromatograph using a Carboxen 1000 column. The organic substrates were condensed in water and analyzed off line using a capillary Nukol column and the FID method. Acrylonitrile (ACN) and acetonitrile (ACeN) were the two main products; traces of HCN have been detected but not considered for carbon balance calculations. The catalytic tests were conducted for at least 12 h and the catalysts were recovered after catalytic testing by cooling them under the reaction mixture to 120 – 150°C and then under a flow of nitrogen to room temperature. Under the reaction conditions and without catalyst propane conversion was very low and mainly CO_x and propene were formed.

3. RESULTS

The mixed V and Al oxides with V/Al ratios varying from 0 to 0.5, have been characterized by X-ray diffraction as synthesized, after heat treatment in air at 500°C and after use under ammoxidation conditions at the same temperature for 20 h. The patterns were in all cases similar and corresponded to poorly crystallized $\chi\text{-Al}_2\text{O}_3$ (ICDD 13-0373). To illustrate this, patterns obtained for the compound VAIO-0.25 are shown in Figure 1. After 40 h on stream no modification of the pattern was evidenced but after longer time, 80 h, small peaks corresponding to VO_2 could be evidenced. This occurred however without change in the catalytic properties of the catalysts. The elemental analysis data, determined by ICP for all the samples studied, are listed in Table 1 with their specific surface areas. The actual V/Al ratios are almost the same as in the initial synthesis mixture and the specific surface areas were all comparable with values ranging between 240 and $270\text{ m}^2\cdot\text{g}^{-1}$. The X-ray pattern of the VAIO-OX sample was similar to the other ones; its specific surface area was lower.

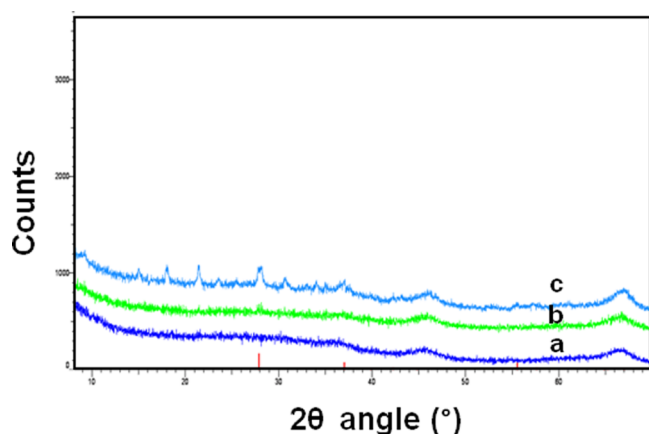


Figure 1. X-ray diffraction patterns of the VAIO-0.25 catalyst after (a) 5 h, (b) 40 h, (c) 80 h on stream (Red peaks: VO_2 , ICDD 73-2362).

Table 1. Specific Surface Area (SSA) Measured Using the BET Method, Chemical Composition Determined from Chemical Analysis

catalyst	V/(V+Al)	SSA ($\text{m}^2\cdot\text{g}^{-1}$)
VAIO-0.15	0.15	265
VAIO-0.25	0.25	255
VAIO-0.30	0.30	252
VAIO-0.35	0.35	240
VAIO-0.50	0.46	270
VAIO-OX	0.25	45

Before going into the details of the characterization results using different techniques, it is important to recall the best catalytic properties that have been observed with similarly prepared catalysts and which have been previously reported.⁷ The best catalytic properties were observed for samples characterized by a V/Al ratio around 0.30 close to the optimum proposed in the literature with 0.25.^{5,6} This latter ratio has, however, been the one chosen for the characterization of most of the catalysts and the study of the influence of various parameters. The catalytic properties of the VAIO mixed oxide catalysts were shown to depend strongly on the preparation method used (Table 2). The catalyst prepared using the mixed oxalate method (VAIO-OX) appeared more selective to ACN and much more active when propane rates at low conversion are compared. The same conclusion could be drawn at higher conversion, which ensured it (Table 3).

²⁷Al NMR Spectroscopy. Prior to the characterization of the vanadium and aluminum mixed oxides and oxy-nitrides, two reference phases corresponding to AlN and to a pure alumina sample prepared in the same way as the mixed vanadium and aluminum oxide have been studied. This latter sample has been characterized before and after nitridation in the conditions used for the mixed oxides (Figure 2). The spectrum of aluminum nitride is equal to that published in the literature with a major peak at 115 ppm corresponding to AlN_4 species.¹⁶ Small peaks at 111 and 103 ppm were observed that have been attributed to AlON_3 and AlO_2N_3 species. Their presence should certainly correspond to a surface passivation of the nitride.^{16,17} This surface oxidation was, however, limited and no strongly oxidized species like AlO_3N (86 ppm) or totally oxidized AlO_4 species (around 70 ppm) were detected. For the alumina sample tetrahedral and octahedral aluminum species, respectively, were observed between 77 and 60 and 11 and 3 ppm. An

Table 2. Catalytic Properties of VAIO Catalysts^a

catalyst	GHSV ($\text{L}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	conversion (%)	selectivity (%)			
			ACN	ACeN	propene	CO_x
VAIO-0.15	134	25	46	7	17	31
VAIO-0.25	134	30	53	10	16	24
VAIO-0.25 ^b	134	28	48	11	18	26
VAIO-0.30	134	34	52	8	15	26
VAIO-0.35	134	38	50	9	14	29
VAIO-0.50	134	40	46	13	14	30
VAIO-0.25	500	7.2	16.5	10.5	58	15
VAIO-OX ^c	670	6.4	24.5	5	68	2.5

^aGas feed composition $\text{C}_3\text{H}_8/\text{O}_2/\text{NH}_3/\text{He} = 1.25/3.14/2.4/1.75$; temperature: 500°C . ^bVAIO catalyst prenitrided with NH_3 at 500°C during 5 h. ^cVAIO catalyst prepared using the mixed oxalate method.

additional peak at ca. 35 ppm due to five-coordinated or highly distorted four-coordinated Al species was also observed (Table 4). The relative content of the different types of species was characteristic of $\chi\text{-Al}_2\text{O}_3$, which confirmed the X-ray diffraction data.¹⁸ After exposure to ammoxidation conditions at 500°C , the spectrum showed the same species in approximately the same ratios. No nitridation was detected. This result was confirmed by chemical analysis.

²⁷Al MAS NMR was then performed on as synthesized VAIO-0.25 samples, after calcination in air at 500°C and after exposure to ammoxidation conditions at the same temperature (Figure 3, Table 4). The spectrum before reaction displayed seven ²⁷Al NMR peaks. The peaks at 5, 12, and 14 ppm were attributed to AlO_6 sites, and the peaks at 61 and 70 to AlO_4 species. The low intensity peak in between at 38 ppm was assigned to five-coordinated sites. The peaks corresponding to the tetrahedral species were comparable to those of the pure alumina prepared similarly. Half-width and chemical shifts of the signals of pentahedral and octahedral Al species are different, due to the proximity of V cations. However, the relative content of the various species is still that of a χ alumina.

After nitridation a similar spectrum was obtained, the fit of which allowed identifying the same species with only one new peak at 87 ppm skewed to the high-shielding side of the tetrahedral peaks. It was assigned to AlO_3N sites.¹⁶ No other peaks at 115, 111, and 103 ppm corresponding to AlN_4 , AlN_3O , and AlN_2O_2 species were identified whatever conditions of nitridation were used. The comparison of the samples nitrided ex situ under ammonia flow and in situ under ammoxidation conditions showed that the samples were rather similar except that the sample nitrided in situ contained a larger amount of nitrogen. It should also be noted that the chemical shift of the N species (AlO_3N) in the sample nitrided in situ was systematically lower by a few parts per million than that in the sample nitrided ex situ, which indicates the formation of less electrophilic species.

The VAIO-OX sample has also been studied by ²⁷Al MAS NMR spectroscopy. The spectrum obtained was similar to those of the samples prepared using the standard method. Only

Table 3. Comparison of the Catalytic Properties of VAIO-0.25 and VAIO-OX Catalysts at High Conversion^a

catalyst	mass (mg)	SSA (m ² ·g ⁻¹)	conv. (%)	selectivities (%)				rate of propane conversion (μmol·s ⁻¹ ·m ⁻²)
				ACN	ACeN	propene	CO _x	
VAIO-0.25	40	170	53	46	7	13	35	0.27
VAIO-OX	28	45	49	55	5	12	30	1.35

^aGas feed composition C₃H₈/O₂/NH₃/He = 1.25/3.14/2.4/1.75; temperature: 500 °C; SSA: specific surface area.

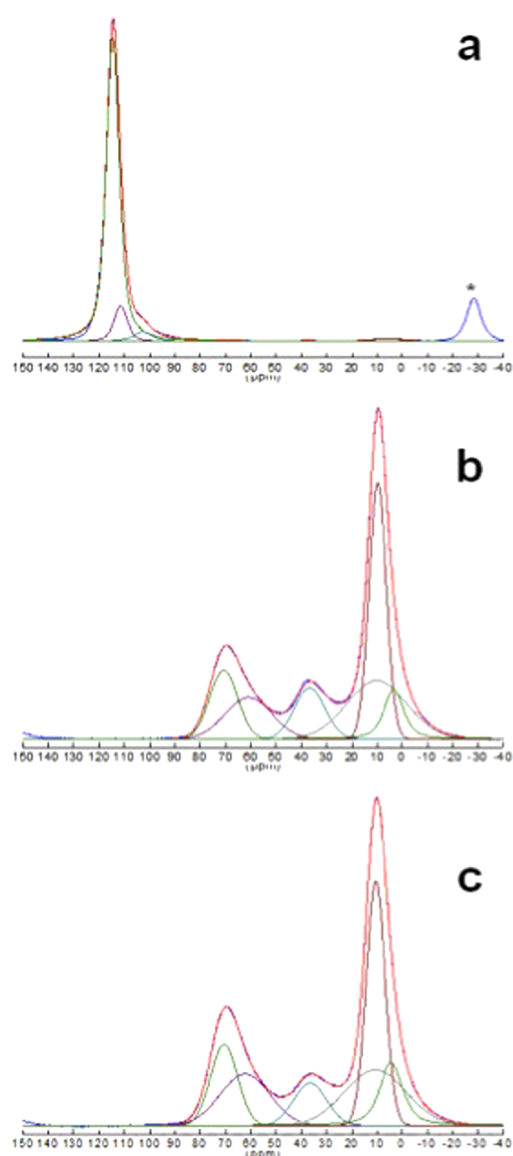


Figure 2. NMR spectra of an AlN sample (a) and of a sample of alumina prepared the same way as the mixed vanadium and aluminum oxide and calcined under air at 500 °C (b) and exposed to ammoxidation conditions at 500 °C (c).

some variations of the chemical shifts of octahedral aluminum and AlO₃N species were observed.

The influence of various parameters on the nitrogen content and the Al species distribution in the VAIO-0.25 sample has been studied. The results are presented in Figure 4. The influence of the type of nitridation (ex or in situ) has been studied comparing spectra of the same solid nitrided differently at 500 °C for 40h (Figure 4a). The relative content of AlO₃N species was higher in the solid exposed to ammoxidation conditions (5 instead of 2%). In the same time, the relative

Table 4. ²⁷Al 800-MHz MAS-NMR Spectral Decomposition of AlN, Al₂O₃ Co-precipitated and Calcined under Air at 500 °C and the VAIO-0.25 Mixed Oxide Calcined under Air, Nitrided ex Situ 40 h under Pure Ammonia or Nitrided in Situ in Catalytic Reaction Conditions at 500 °C

	aluminum coordination	total relative intensity (%)	chemical shift (ppm)	spectral width (ppm)	peak relative intensity (%)
AlN	AlN ₄	83.6	114.6	6.1	83.6
	AlN ₃ O	9.7	111.5	6.1	9.7
	AlN ₂ O ₂ /AlNO ₃	4.3	102.7	8.2	4.3
	AlO ₄	0.2	68.1	9.1	0.2
	AlO ₅	0.3	37.4	6.8	0.3
	AlO ₆	2.0	5.6	14.6	2.0
Al ₂ O ₃ calcined	AlO ₄	26.3	70.7	12.9	13.1
			60.9	21.6	13.2
	AlO ₅	10.6	36.7	14.6	10.6
			10.2	28.0	24.0
	AlO ₆	63.1	9.8	8.2	30.8
			3.4	9.2	8.3
VAIO-0.25 calcined	AlO ₄	20.9	70.1	13.0	7.0
			61.0	21.8	13.9
	AlO ₅	10.0	33.0	18.6	10.0
			10.4	5.8	9.6
VAIO-0.25 nitrided ex situ	AlO ₆	69.1	7.2	12.5	46.1
			4.2	21.1	13.4
	AlO ₃ N	2.4	86.3	26.3	2.4
	AlO ₄	23.5	70.1	14.3	9.2
			60.8	30.8	14.3
	AlO ₅	5.6	36.1	12.8	5.6
VAIO-0.25 nitrided in situ			12.4	31.0	32.0
	AlO ₆	68.5	9.1	9.7	27.3
			3.0	11.0	9.2
	AlO ₃ N	4.7	83.2	23.8	4.7
	AlO ₄	28.9	70.1	13.6	11.8
			60.8	23.1	17.1
	AlO ₅	5.6	38.0	16.7	5.6
			14.2	32.7	32.6
	AlO ₆	60.8	11.9	9.2	19.0
			5.1	11.1	9.2

content of tetrahedral species increased, whereas that of octahedral species decreased. When catalysts nitrided ex situ were tested, their composition evolved to that of the catalysts exposed to the ammoxidation feed mixture. This explained why similar catalytic properties were observed for both types of catalysts. In the same time, as their relative content increased in reaction conditions, their chemical shift decreased. Such decrease from 87 to 83 ppm was systematically observed after testing whatever the V/Al ratio.

The influence of nitridation time has been studied on solids nitrided ex situ in similar conditions (Figure 4b). When nitridation time increased, the contents of tetra and pentahedral

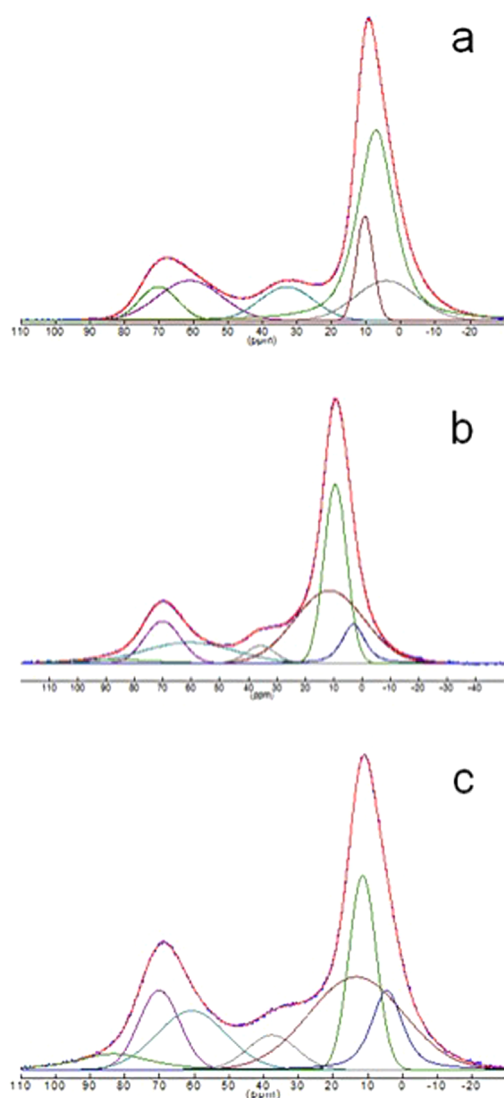


Figure 3. NMR spectra of (a) VAIO-0.25 calcined under air at 500 °C, (b) VAIO-0.25 nitrided under pure ammonia for 24h at 500 °C, (c) VAIO exposed to ammoxidation conditions.

species decreased to the benefit of the octahedral and AlO_3N species. The Al species distribution was rather similar after 24 or 40 h hours, showing that a limit of nitridation exists. The nitrogen level measured by chemical analysis was 0.5 wt % after 5 h and 1.9 and 2.5% after 24 and 40 h, which confirmed the results obtained by ^{27}Al MAS NMR. A limit of nitridation seemed to exist for long nitridation times in ammonia similar to the one under ammoxidation conditions. The influence of the V/Al ratio has also been studied (Figure 4c). Samples with V/Al ratios varying from 0.15 to 0.50 have been nitrided at 500 °C ex situ and analyzed. The relative content of AlO_3N species increased with the V/Al ratio. In parallel, the relative content of the pentahedral species increased, whereas the octahedral species one decreased, which could be related to an increase of structure defects with V insertion. Finally, XPS analysis of the samples, which is presented in the next section, has shown that some of the surface nitrogen species observed correspond only to adsorbed species. Most of these species have been removed by desorption at 300 °C under primary vacuum for 5 h. After desorption the relative content of octahedral species strongly decreased mainly to the benefit of the pentahedral species and

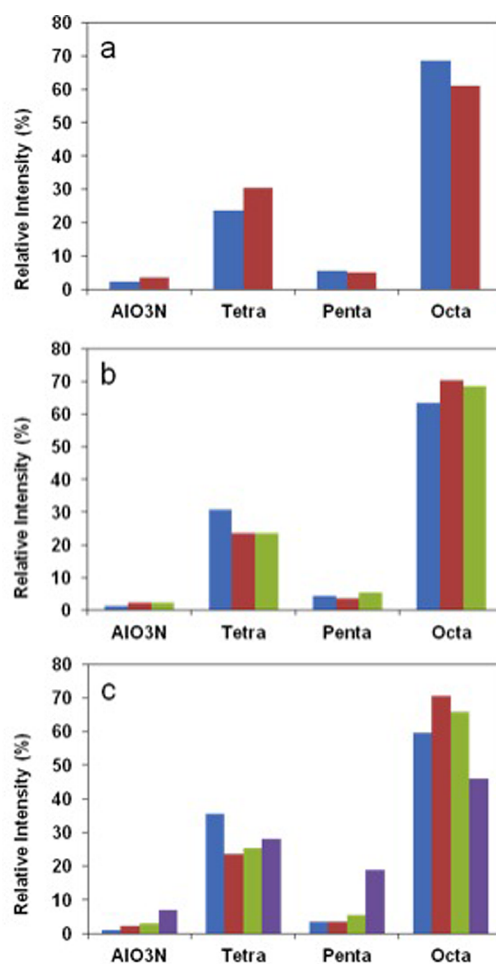


Figure 4. Comparison of aluminum sites composition by type (octahedral, pentahedral, tetrahedral and AlO_3N) determined by NMR ^{27}Al -MAS of (a) VAIO-0.25 nitrided ex situ (red) and in situ (blue), (b) VAIO-0.25 nitrided for different time (5 h: blue; 24 h: red; 40 h: green) and (c) in function of V/Al ratio (0.15: blue, 0.25: red, 0.35: green, 0.46: violet).

in a minor amount to the tetrahedral ones. The result may be explained by desorption of adsorbed nitrogen species like NH_x or dinitrogenous species. It leads to the conclusion that pentahedral species are the main adsorption sites for nitrogen species. This is in agreement with previous studies showing that these sites were preferential adsorbing and anchoring sites.¹⁹ Interestingly the AlO_3N bulk species content only slightly decreased and their chemical shift slightly increased.

XPS Spectroscopy. During the XPS measurements of catalysts after nitridation it appeared rather difficult to obtain rapidly the high vacuum necessary for spectra recording. This suggests that a large amount of adsorbed species was present on the catalyst surface. Consequently the catalysts have been heated under vacuum (10^{-2} Pa) at 300 °C for 5 h prior to analysis. The analysis of the spectra recorded for the same VAIO-0.25 catalyst nitrided ex situ for 24 h with NH_3 before and after desorption is presented in Table 4. First it can be seen that exposure of the VAIO-0.25 sample to ammonia at 500 °C for 24 h results in partial reduction of surface V, and insertion of nitrogen. The V 2p_{2/3} signal has been decomposed into three components at 515.2, 516.2, and 517.5 eV, respectively, attributed to V^{3+} , V^{4+} , and V^{5+} cations. The V^{3+} species were in all spectra in minor amount but always present. The nitrogen

signal was even more complex with four N 1s peaks identified at 396.8, 398.2, 400.3, and 402.6 eV. The peak at 396.9 eV could be attributed to N^{3-} , whereas those at 398.4 and 400.2 eV might be due to NH^{2-} and NH_x species.^{7,20–29} The last peak at 402.8 eV could correspond either to M–NO–M or M–NN–M species (with M = Al or V).^{20,23,24} The analysis of the O 1s region shows two peaks at 530.8 and 532.3 eV, respectively, attributed to O^{2-} species and to O^- , OH, or CO_3 species. Since the analysis of C 1s region only showed a very small peak that could correspond to carbonate, the two other species should be mainly considered for the second O1s peak attribution.

The V/Al ratio on the surface is always slightly lower than in the bulk. When the bulk V/Al ratio increased, the V surface content increased proportionally while the relative N^{3-} and NH^{2-} content increased to reach a maximum for V/Al = 0.25 (Figure 5). In the same time the V oxidation state remained almost unchanged.

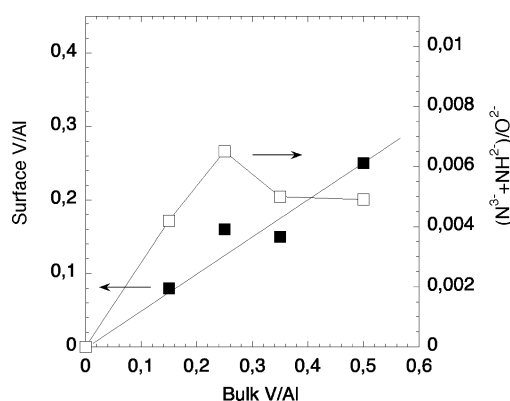


Figure 5. Variation of the surface V/Al ratio and of the N^{3-} and NH^{2-} relative content calculated from XPS data, as a function of the bulk V/Al ratio.

After desorption at 300 °C under primary vacuum for 5 h, a strong decrease of the nitrogen surface content is evident that reaches in certain cases 40% (Table 5). This decrease affected strongly the NH_x and M–NN–M species, which could be considered as adsorbed surface species. The NH^{2-} species were affected only in a minor manner and the N^{3-} species not at all. This agrees well with the negligible change of V oxidation state observed in parallel.

The surface compositions of a VAIO-0.25 catalyst nitrated ex situ and in situ have been investigated and compared after desorption (Table 6). The reduction of the vanadium surface is the same and the $V^{3+}/V^{4+}/V^{5+}$ ratios are comparable. The sample exposed to reaction conditions showed various carbon species probably due to reaction intermediates or products still adsorbed at the surface. The nitrogen relative content is much higher on this sample compared to the one nitrated ex situ. This result confirmed those obtained previously by Florea et al. by other techniques.²⁰ Moreover, it can be seen that the sample exposed to ammoxidation conditions does not contain any N^{3-} but only NH^{2-} species. This has been illustrated in Figure 6 showing the X-ray photoelectron spectra of both nitrated catalysts in the N1s region. This result was confirmed each time that a sample was analyzed after catalytic testing.

The surface composition of the VAIO-OX sample has also been studied by XPS (Table 7). Its surface composition appeared very close to that of the VAIO-0.25 sample; the relative V content was, however, higher (V/Al = 0.19 instead of 0.16), whereas the relative total nitrogen content appeared smaller.

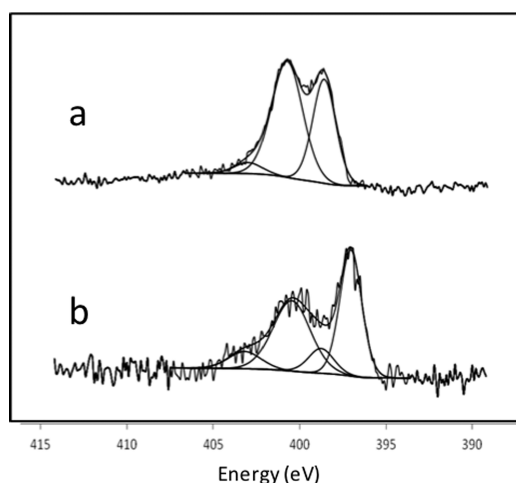
Raman Spectroscopy. The Raman spectrum of VAIO-0.25 sample dried at 120 °C has been recorded at room temperature (Figure 7). It exhibited intense band at 947 cm^{-1} and weaker bands at 525–590, 320–345, and 240 cm^{-1} attributed to $(VO_3)_n$ metavanadate species.^{25,27} Neither the bands of symmetrical $[VO_4]^{3-}$ tetrahedral species located at 826, 804, and 336 cm^{-1} nor the ones of V_2O_5 at 995, 700, 520, 404, 305,

Table 5. XPS Analysis of VAIO-0.25 Nitrated ex situ 5 h, under Pure NH_3 at 500 °C before and after Desorption

		binding energy (eV)	attribution	relative intensity (%)	V/Al	N/Al	N/V	N/O
VAIO-0.25 nitrided ex situ								
	Al2p	74.3	Al ³⁺	100	0.14	0.03	0.23	0.018
	V 2p3/2	515.2	V ³⁺	9				
		516.2	V ⁴⁺	20				
		517.5	V ⁵⁺	71				
		396.8	N ³⁻	28		0.008		
	N 1s	398.2	NH ²⁻ _x	14		0.004		
		400.3	NH _x	44		0.013		
		402.6	NO _x or M-NN-M	14		0.004		
		530.8	O ²⁻	86				
	O 1s	532.6	O ⁻ /OH/CO ₃	14				
VAIO-0.25 nitrided ex situ and desorbed								
	Al 2p	74.5	Al ³⁺	100	0.16	0.02	0.13	0.012
	V 2p3/2	515.2	V ³⁺	6				
		516.3	V ⁴⁺	20				
		517.7	V ⁵⁺	74				
		396.9	N ³⁻	40		0.008		
	N 1s	399.4	NH ²⁻	13		0.003		
		400.9	NH _x	33		0.004		
		402.4	NO _x ou M-NN-M	14		0.001		
		531.1	O ²⁻	71				
	O 1s	532.3	O ⁻ /OH/CO ₃	29				

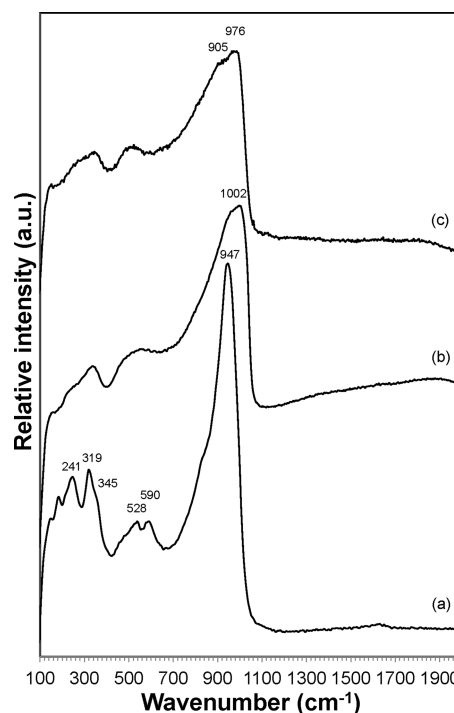
Table 6. XPS Analyses of VAIO-0.25 Mixed Oxide Nitrided ex Situ 40 h under Pure Ammonia or Exposed to Catalytic Ammoxidation Conditions (Nitridation in Situ) at 500 °C and Desorbed

		bonding energy (eV)	attribution	relative intensity (%)	V/Al	N/Al	N/V	N/O
VAION-0.25 nitrided ex situ	Al 2p	74.4	Al ³⁺	100	0.16	0.05	0.30	0.022
		515.2	V ³⁺	9				
	V 2p _{3/2}	516.3	V ⁴⁺	17				
		517.6	V ⁵⁺	74				
		397.0	N ³⁻	44				
		398.5	NH ²⁻	9				
	N 1s	400.5	NH _x	40				
		403.3	NO _x	7				
		530.8	O ²⁻	68				
		532.3	O ⁻ /OH/CO ₃	32				
VAION-0.25 nitrided in situ	Al 2p	74.5	Al ³⁺	100	0.16	0.11	0.68	0.063
		515.2	V ³⁺	6				
	V 2p _{3/2}	516.3	V ⁴⁺	18				
		517.7	V ⁵⁺	76				
		398.6	NH ²⁻	41				
		400.7	NH _x	53				
	N 1s	402.9	NO _x or M–NN–M	6				
		531.1	O ²⁻	84				
		532.4	O ⁻ /OH/CO ₃	16				

**Figure 6.** X-ray photoelectron spectra in the N1s region of the VAIO-0.25 Sample nitrided in situ in ammoxidation reaction conditions (a) and ex situ in ammonia (b).**Table 7.** XPS Analysis of VAIO-OX after Testing at 500 °C

compound	binding energy	energy (eV)	attribution	relative intensity (%)
VAIO-OX after testing	Al 2p	74.7	Al ³⁺	100
		516.4	V ⁴⁺	18
	V 2p _{3/2}	517.9	V ⁵⁺	82
		399.3	NH ²⁻	13
		401.0	NH _x	75
		402.8	NO _x or M–NN–M	12
	O 1s	531.3	O ²⁻	89
		532.8	O ⁻ /OH/CO ₃	11
	C 1s	284.7		70
		286.2		22
		288.8		8

258, and 145 cm⁻¹ were observed.^{26,27} The spectrum of VAIO-0.25 recorded at 500 °C under N₂ flow (Figure 7b)

**Figure 7.** Raman spectra of VAIO-0.25 precursor.

contained one band at 1002 cm⁻¹ in addition to those of (VO₃)_n species that were broadened. This band does not correspond to the (V=O) stretching vibrations of dehydrated single VO_x species supported on Al₂O₃, which are expected at 1008 cm⁻¹.²⁸ Instead, it is attributed to dehydrated polymeric surface VO_x species located with a stronger distorted tetrahedral environment caused by the removal of water molecules. The spectrum of VAIO-0.25 after ex situ nitridation recorded at room temperature exhibited very intense fluorescence. This, however, could be completely quenched by treatment in N₂ flow at 500 °C, after which Raman bands at 976, 905, 505, 344, and 275 cm⁻¹ could be observed (Figure

7c). The two main bands were located at much lower wavenumbers compared to the VAIO-0.25 precursor submitted to the same thermal treatment (Figure 7b). This can be explained by two effects: (i) a significant reduction of vanadium cations upon nitridation which leads to weaker interaction with anions and, thus, to vibrations at lower wavenumbers and (ii) by a change of the vanadium coordination from distorted tetrahedral to distorted octahedral or pentahedral as revealed by previous XANES/EXAFS data.^{11,12} For all the samples, the spectra recorded from different areas under the microscope were similar, revealing good homogeneity at the micrometer scale. After 40 h under ammoxidation conditions, no fluorescence was observed and Raman spectrum of the used VAIO-0.25 catalyst could be properly recorded in ambient air. Again, no significant differences were observed between spectra from 90 different areas, suggesting that the sample was homogeneous. The mean spectrum plotted in Figure 8

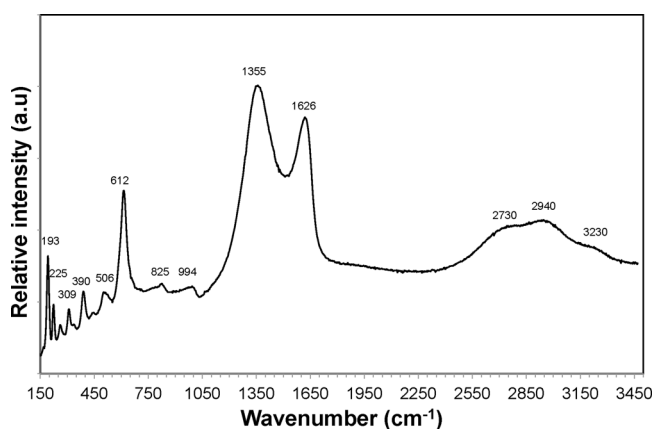


Figure 8. Raman spectrum of VAIO0.25 after testing at 500 °C in propane ammoxidation conditions.

contained a doublet 1355 and 1626 cm^{-1} typical of disordered graphite (coke).²⁹ The broad bands at 3230, 2730 cm^{-1} and 2930 cm^{-1} are attributed to overtones respectively to combinations of the first order bands at 1626 and 1355 cm^{-1} .³⁰ The band at 2940 cm^{-1} could also correspond to $\nu(\text{CH})$ stretching vibrations.³¹ The bands at 825, 612, 506, 390, 309, 225, and 193 cm^{-1} are typical for monoclinic VO_2 .³² The band at 994 cm^{-1} is attributed to the nitrided VAIO mixed oxide. Its higher position compared to the spectrum plotted in Figure 7c is due to the much lower temperature (room temperature vs 500 °C). The higher relative intensity of the VO_2 bands does not point to a high quantity since the scattering cross section of this crystalline phase is much higher than that of an amorphous phase.

EPR Spectroscopy. VAIO-0.25 and VAIO-OX catalysts appeared relatively similar when characterized by XRD, chemical analysis, XPS or NMR, and nothing could really account for the difference in catalytic properties. EPR spectra of these catalysts prepared using different methods have been recorded at room temperature after catalytic testing (Figure 9). Similar signals, yet with different intensity were identified in both spectra. A signal with hyperfine structure (hfs) due to the coupling of the electron spin of V^{4+} ($S = 1/2$) with the nuclear spin of vanadium ($I = 7/2$, natural abundance 99.76%), arises from isolated VO^{2+} species in square pyramidal or octahedral coordination. By spectra simulation, the following spin Hamiltonian parameters have been derived: $g_{\perp} = 1.976$, $g_{\parallel} =$

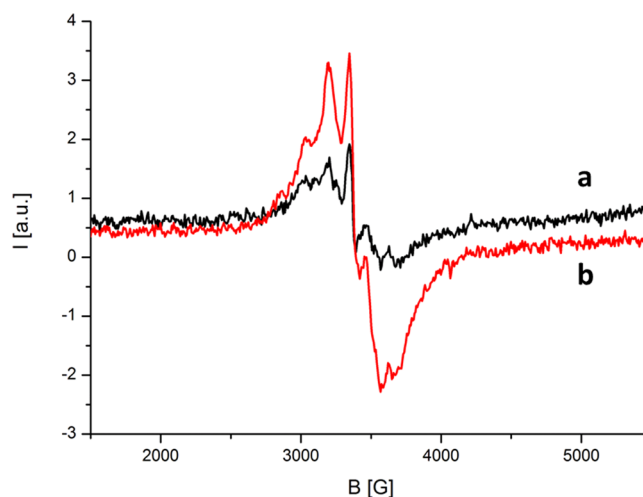


Figure 9. EPR spectra of VAIO-0.25 (a) and VAIO-OX (b) catalysts after catalytic testing.

1.925, $A_{\perp} = 65.3$ G, $A_{\parallel} = 195.4$ G for VAIO-OX and $g_{\perp} = 1.975$, $g_{\parallel} = 1.928$, $A_{\perp} = 59.3$ G, $A_{\parallel} = 196.0$ G for VAIO-0.25. The hfs signals are superimposed on a broad isotropic line caused by magnetically interacting VO^{2+} species within clusters. The double integral of the total EPR signal for VAIO-0.25 was 2.3 times smaller than that of VAIO-OX, indicating that the latter sample contained much more V^{4+} after use in propane ammoxidation. Moreover, the intensity ratio of the hfs signal was higher for sample VAIO-OX ($I_{\text{hfs}}/I_{\text{iso}} = 0.5$) compared to VAIO-0.25 ($I_{\text{hfs}}/I_{\text{iso}} = 0.1$), suggesting that the percentage of single VO^{2+} species is larger in the former sample.

Electrical Conductivity Measurements. The electrical conductivity of a VAIO-0.25 sample has been measured before and after nitridation as a function of temperature to determine the activation energy of conduction E_c under air at atmospheric pressure. The semilog plots [$\log \sigma = f(1/T)$] obtained are given in Figure 10. The linear variations observed showed that both solids behaved as semiconductors, the electrical conductivities of which varied exponentially with temperature. From the slopes of the semilog plots E_c values have been calculated (Table 8). The activation energy of conduction of the nitrided oxide was lower than that of the oxide. At the same time, its electrical conductivity was higher within the whole temperature range which means that the concentration of charge carriers increased after nitridation. The electrical conductivities of the catalysts have also been measured as a function of temperature under nitrogen at atmospheric pressure for determining the nature of the semiconductor type of the solid by applying the Hecksberg criterion.³³ The electrical conductivity was lower under air than under nitrogen for the nitrided compound and equal for the non nitrided one. This suggests that the first compound is a n -type semiconductor and the second an intrinsic semiconductor.

Variations of σ as a function of oxygen pressure at 450 °C in a log–log plot clearly showed that no dependence of σ on the oxygen pressure was observed for both samples (Figure 10). This would rather agree with the fact that these materials are intrinsic semiconductors ($\partial\sigma/\partial P_{\text{O}_2} = 0$). This is also suggested for the VAIO-0.25 sample by the Hecksberg criterion. If that was true, the theory would imply that the band gap energy E_G should be equal to twice the activation energy of conduction E_c ($E_G = 2E_c$). Consequently, E_G should be equal to 59.6 $\text{kJ}\cdot\text{mol}^{-1}$

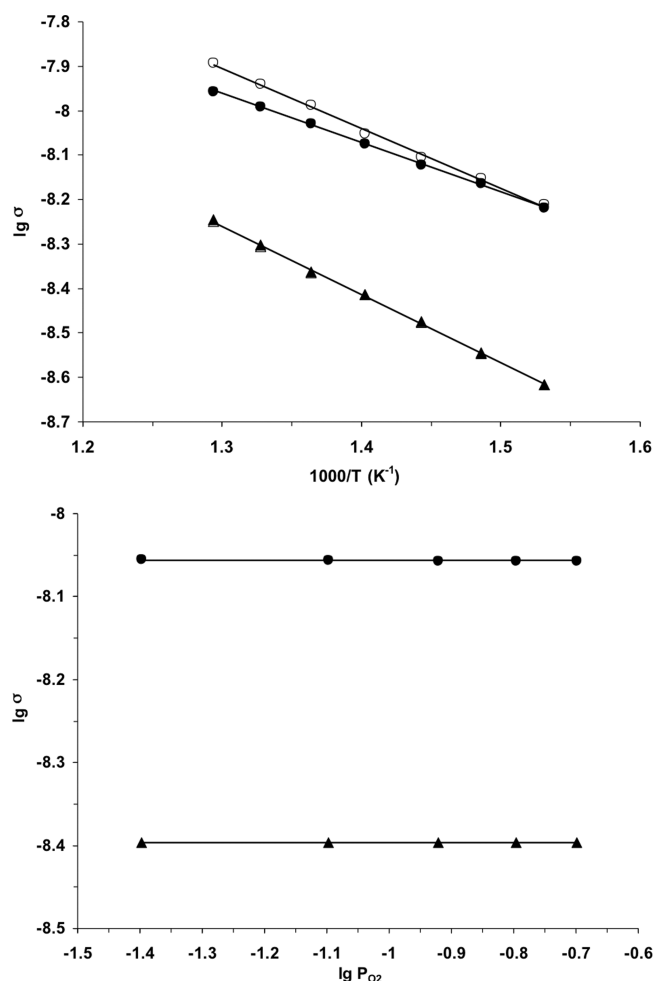


Figure 10. (a) Arrhenius plots for the electrical conductivity σ of the VAIO-0.25 sample before (\blacktriangle , \triangle) and after nitridation (\bullet , \circ) measured under air (filled symbols) and under nitrogen (open symbols) (σ in $\text{ohm}^{-1}\cdot\text{cm}^{-1}$); (b) Variation of σ as function of the oxygen pressure for the VAIO-0.25 sample before (\blacktriangle) and after nitridation (\bullet) at 450 °C (P_{O_2} in atm; σ in $\text{ohm}^{-1}\cdot\text{cm}^{-1}$).

Table 8. Energies of Conduction for VAIO-0.25 Samples before and after Nitridation, Obtained from Electrical Conductivity Measurements with Corresponding Theoretical Band-Gap Energies and Band-Gap Energies Calculated from UV Spectra

catalyst	E_c ($\text{KJ}\cdot\text{mol}^{-1}$)	theoretical E_G (eV)	experimental E_G (eV)
VAIO-0.25 before nitridation	29.3	0.62	3.18
VAIO-0.25 after nitridation	20.3	0.42	2.88

(0.62 eV) and 40.6 $\text{kJ}\cdot\text{mol}^{-1}$ (0.42 eV) for VAIO-0.25 before and after nitridation, respectively. However, the band gap energies determined from the UV spectra of the samples were equal to 3.18 and 2.88 eV, respectively (Table 8). These values are quite different from those calculated, and the solids cannot be considered as intrinsic but extrinsic semiconductors under our conditions with sources of electrical charge carriers independent of oxygen pressure. To get information on the solids under conditions as close as possible to those of catalysis, the electrical conductivity measurements were performed at

450 °C, i.e., within the reaction temperature range, during sequential periods under air, under nitrogen, under a propane–air mixture and under a propane–nitrogen mixture (Figure 11).

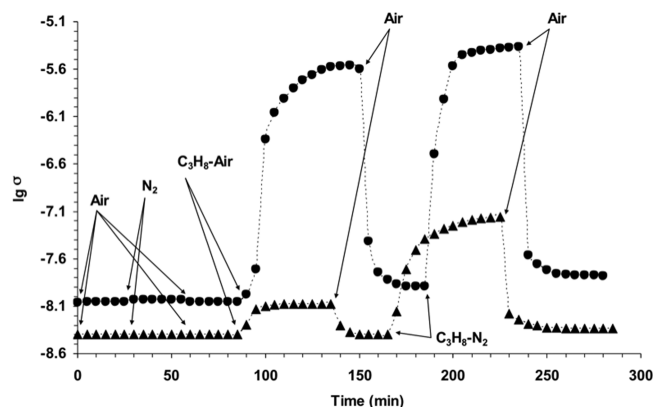


Figure 11. Variation of the electrical conductivity under sequential exposures to air, nitrogen, propane–air mixture and propane–nitrogen mixture for the VAIO-0.25 sample before (\blacktriangle) and after nitridation (\bullet) at 450 °C (σ in $\text{ohm}^{-1}\cdot\text{cm}^{-1}$).

The solids were heated from room temperature to 450 °C, at a heating rate of 5 °C $\cdot\text{min}^{-1}$ in air-flow at atmospheric pressure. After reaching the steady state, the atmosphere was switched to nitrogen. As expected, the electrical conductivity increased for the nitrided VAIO-0.25 sample and remained constant for the non-nitrided one. Then, nitrogen was again replaced by air and after reaching the steady-state, a propane–air mixture was passed over the samples. In the case of nitrided VAIO-0.25, the electrical conductivity immediately increased abruptly by 3.5 orders of magnitude. A sudden but markedly less pronounced increase was also observed for the non-nitrided sample. This different behavior arises from the *n*-type semiconducting character since, for oxide semiconductors, the *n*-type criterion is $\partial\sigma/\partial P_{\text{O}_2} < 0$ or $\partial\sigma/\partial P_{\text{C}_3\text{H}_8} > 0$, considering propane as a reductant. After reaching the steady state under the propane–air flow, pure air was again introduced. The electrical conductivity decreased immediately and reached a plateau for both samples confirming the *n*-type semiconducting character of the solids. After reaching again the steady state under air flow, the atmosphere was switched to a propane–nitrogen mixture before the air sequence was repeated for testing the reversibility of the phenomena. Again, the electric conductivity increased within 3.5 orders of magnitude for the nitrided sample and within 1 order of magnitude for not nitrided one. This corresponds to their *n*-type semiconductive character. Under air their electrical conductivities decreased immediately and reached a plateau confirming the reversibility of the phenomena observed.

4. DISCUSSION

It is widely accepted that the mechanism of ammoxidation of propane comprises three major steps: (1) activation of the propane molecule and its dehydrogenation to propene, (2) abstraction of hydrogen from propene and formation of a chemisorbed π -allylic intermediate, and (3) insertion of nitrogen into this intermediate. It is the purpose of this discussion to identify which characteristics of the catalysts are important for these steps and which sites could be the catalytically active.

We had previously shown by *operando* XES and XANES spectroscopy that the mean oxidation state of vanadium in the nitrated V/Al/O catalysts was close to +4.¹² The coordination of vanadium was shown to be 5 or 6. XPS spectroscopy data obtained in this study have shown that, although V³⁺ and V⁴⁺ species were present, V⁵⁺ were the main species at the surface of the catalysts. The relative content of the V³⁺, V⁴⁺, and V⁵⁺ cations was comparable for all the catalysts and did not vary with the total vanadium content and the amount of nitrogen introduced. Thus, no correlations exist between the nitrogen content and vanadium oxidation state. Determinant parameters may rather be the nature of the nitrogen species and the distribution of vanadium ones.

High-field ²⁷Al NMR spectroscopy showed that nitridation of the VAIO catalysts at 500 °C either in pure ammonia flow or under catalytic ammoxidation conditions led to the formation of AlO₃N species, while pure alumina could not be nitrated at 500 °C. This shows that vanadium is necessary to enable incorporation of nitrogen into the lattice of the mixed VAIO oxide and that only mixed oxides lead to stable oxy-nitrides under catalytic reaction conditions. With that respect a continuous increase of the N content after nitridation with increasing V content was observed. Comparison of XPS and NMR spectroscopic data showed that the nitridation occurred mainly in the near-surface region of the catalysts, in contrast to the reduction of vanadium. This conclusion confirmed previous results obtained by XES and XANES spectroscopy.⁷

XPS spectroscopy clearly showed that N³⁻ species were present in the nitrated catalyst when the nitridation was conducted *ex situ* but not *in situ*. Since no significant differences in the catalytic performance was observed for both types of nitrated catalysts it may be proposed that N³⁻ species do not play a key role in the catalytic reaction although they may contribute to the overall reduction state of vanadium and stability of the reduced active phase. From XPS data it could be concluded that the inserted nitrogen species are NH²⁻ moieties being located in the aluminum environment and forming AlO₃NH species. It is possible that the formation of the latter tetrahedral species involved an oxido-reduction of neighboring vanadium and the formation of AlO₃NHVO_x (*x* = 4 or 5) may be postulated. The nitridation of the solids would thus correspond to the general equation

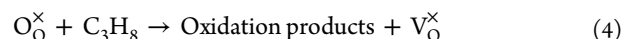


With that respect it is probable that the difference in the chemical shift observed in the ²⁷Al-NMR spectra of samples nitrated *ex situ* in NH₃ flow and exposed to ammoxidation conditions (Figure 3) arises from the formation of mainly AlO₃NHVO_x instead of AlO₃NVO_x species. In the oxide lattice, these NH²⁻ groups are nucleophilic species, and it is reasonable to think that they should be involved in the nitrogen insertion step as reported in conventional alkene ammoxidation pathways.^{34,35} Furthermore the ability of a vanadium containing catalyst to form V–N bonds during ammoxidation has recently been stressed as important to generate selective ammoxidation sites.³⁶

Insertion of NH²⁻ as well as formation of water molecules from abstracted hydrogen lead to anionic vacancies that should be replenished in a complete catalytic cycle. This can take place at sites physically separated from the active site including bulk migration of vacancies and charges to other sites at which dioxygen or ammonia are dissociated and incorporated as NH²⁻ and O²⁻. Study of desorbed mixed oxides by XPS and

²⁷Al NMR allowed showing that surface pentahedral Al species as well as coordinatively unsaturated vanadium sites are likely adsorption sites for nitrogen species. With that respect the *n*-type semiconductivity evidenced for the nitrated catalysts should be a critical material property. It is worth noting that the nitridation of the vanadium significantly improves the electronic conductivity of the oxide, which is beneficial for the overall catalytic process.

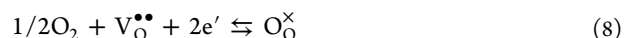
The reversible redox process observed for the fresh and nitrated samples during successive sequences under propane-air or propane-nitrogen mixtures and pure air can be explained in the same way as it has been done for *n*-butane oxidative dehydrogenation,³⁷ namely by the oxidation of propane by lattice oxygen anions on the catalyst surface, which leads to a partially reduced surface:



The increase of σ can be ascribed to the creation of anionic vacancies. It is followed by the spontaneous ionization of the anionic vacancies according to equations



where O_O[×] represents an oxygen anion of the solid in regular lattice positions, and V_O[×], V_O[•], and V_O^{••} are anionic vacancies either filled, singly ionized, or doubly ionized, respectively. The release of free electrons into the conduction band of the solid accounts for the observed increase in electrical conductivity. The subsequent exposure of the samples to air restores the initial value of σ indicating the refilling of the previously created anionic vacancies by dissociation of oxygen and capture of free electrons:



This behavior is in agreement with a Mars–van Krevelen type mechanism.³⁸

The last issue that has to be addressed is the determination of the site for activation of the initial C–H bond of propane, which is the rate-determining step in the overall process. This activation can unambiguously be attributed to vanadium species. In that respect, it can be noted that the activity of the catalysts increased in a constant manner as a function of the V/Al ratio. Monomeric, dimeric, or oligomeric vanadium species should coexist in the catalyst and could be active. The comparison of the VAIO and VAIO-OX catalysts by EPR study in relation with their catalytic data showed that the monomeric species (or low size oxide clusters like dimers) are as the most selective species. A general theoretical study of the mode of operation of such low size V sites has been carried out and is supported by various experimental data.³⁹ The higher activity of the VAIO-OX sample can be simply related to its higher surface vanadium content. Presumably, the V/Al ratio of 0.25–0.30 of the most active and selective catalysts corresponds to the stoichiometry for which a maximum of the monomeric species are present at the surface of the mixed oxide. It can be noted that an increase of the V content up to V/Al = 0.5 results in an increase of activity but to a decrease in selectivity to acrolein in favor of that to CO_x. At that point it is interesting to note that recent studies on other V containing mixed oxides used as catalysts for aromatics ammoxidation reached the conclusion

that V species in V_xO_y clusters are highly active but favor total oxidation to CO and CO_2 .³⁶ In this study, it can also be noted that the relative amount of monomeric species depends strongly upon the preparation method used but should not depend upon the conditions of activation at the beginning of the testing. Concerning the VAIO-OX sample, it is also possible that the better selectivity might be related to the higher reduction level of V that would help avoiding overoxidation of acrylonitrile or intermediate products.⁷ Furthermore, and in a general manner for these catalysts, the presence of reduced vanadium and of inserted nitrogen at the surface strongly weakens the surface acidity, which should be beneficial for the selectivity to partly oxidized or nitrated products.^{40,41}

With long time on stream, the formation of VO_2 in small amounts is observed, showing that a part of the vanadium species could be mobile subsurface species that slowly agglomerate. However, the no activity decrease was observed, which suggests that the surface content of the most active species is not changed. Finally the characterization by Raman spectroscopy of the catalysts after the catalytic test evidenced the presence of a small amount of coke. Its role is not known but it has been shown that in certain cases it can slightly modify the catalytic properties of an oxidation catalyst.⁴²

Except the first step of alkane dehydrogenation, the mechanism is a typical Mars–van Krevelen mechanism with two half reactions corresponding to the nitridation of propane and reoxidation and renitridation of the catalysts. With that respect the reaction mechanism occurring on the VAIO catalyst should in principle be rather similar to that recently described for $MoVTaNbO$ or $AlVSbWO$ catalysts, with NH^{2-} as nitriding species and V species as propane activation species.⁴³ The high efficiency of the VAIO catalyst should be related to the presence of a much larger number of highly active propane activating species at the surface of the solid. On the other hand the absence of elements like Te or Sb that have been shown to play a crucial role in the mechanism particularly in the selective dehydrogenation of the propene formed intermediately leads to less selective catalysts.

5. CONCLUSIONS

This study makes an effort to draw many characterization data into a consistent picture of a VAIO catalyst efficient for propane ammoxidation. The poor level of crystallinity with both nitrogen insertion and random distribution of vanadium oligomer species do not enable to have usual picture of catalyst structure. Furthermore the presence at the surface of carbonaceous or nitrogenous adsorbed species and the slow formation of VO_2 complicates the exercise. However in this study, the use of complementary techniques such as ^{27}Al 800-MHz NMR, XPS, EPR, Raman spectroscopy and electrical conductivity measurements, render possible the determination of the active site for catalytic nitridation and the identification of the most selective sites activating propane.

Nitrogen was shown to incorporate into the mixed oxide precursors under propane ammoxidation conditions, forming bulk N^{3-} and NH^{2-} species. The latter, which appeared as the nitriding species, were the major ones and their formation was linked to the presence of vanadium and AlO_3N species detected by ^{27}Al MAS-NMR spectroscopy. Therefore, in agreement with other characterization data, $AlO_3(NH)VO_{5.6}$ can be proposed as catalytic N-insertion site. The EPR spectroscopy study in relation with the testing of the catalysts prepared using different methods allowed to demonstrate that the dispersion of

vanadium in the mixed oxide was key for a high activity and selectivity. Whereas the activity seemed to be linked to the total vanadium surface content, the higher selectivity was attributed to the presence of mainly monomeric species or of low-size oligomeric vanadium oxide species. Finally, nitrogen substitution in the bulk was shown to greatly enhance the electrical conductivity of the catalysts, which should facilitate the complete catalytic redox cycling. It has to be noted that the numerous characterization data that bring a new and relatively complete picture of the VAIO catalysts, yielded results that are in line with those previously obtained on other vanadium based catalysts. At that point, a theoretical modeling would help completing the description of the surface vanadium oxo-clusters constituting the active sites and determining their mode of operation in the ammoxidation reaction.

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Notes

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