Catalytic properties of nitrided V/Al/O-mixed oxides in the ammoxidation of propane and new efficient preparation method for the catalysts

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ABSTRACT

V/Al/O oxides have been prepared and tested as catalysts for the ammoxidation of propane into acrilonitrile at 500 °C. The high efficiency of these catalysts, which were partially nitrided under catalytic reaction conditions, is confirmed. The best catalysts characterized by a V/Al ratio around 0.30, exhibited selectivity to acrilonitrile of 51% at 58% conversion. Testing at low conversion showed that propene was the main primary product from propane ammoxidation and that the reaction pathway on these catalysts was similar to that on other efficient catalytic systems. A new method of synthesis based upon the decomposition at low temperature of a mixed ammonium aluminum–vanadium oxalate was developed. It leads to highly active catalysts, which displayed increased selectivity to acrylonitrile. The gain in activity and selectivity was attributed to a better dispersion of vanadium with a higher concentration of isolated vanadium species in the bulk and presumably at the surface of the catalysts.

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1. Introduction

V/Al/O amorphous mixed oxide is one of the best catalysts for the selective ammoxidation of propane to acrylonitrile (ACN) [1]. Since its discovery, it has been studied extensively [2–8]. It was demonstrated that these oxides were partially nitrided under reaction conditions and that such nitridation was crucial in their high catalytic performance [3]. The nitridation could also be obtained prior to the catalytic testing under annealing in NH_3 at high temperatures. Maximal concentration of nitrogen observed in the catalysts was 3–5 wt.% [6]. Contrarily to other efficient catalysts V/Al/O mixed oxide catalysts do not contain element with specific role in NH insertion such as Mo, Sb, or Te; their absence is balanced by the ability of the structure to stabilize nitrogen species substituted to oxygen, proposed to be involved in the ammoxidation reaction through a Mars and van Krevelen type mechanism [4]. It was also demonstrated that catalytic performances of these materials strongly depend on synthesis parameters [5]. In a previous work, we have shown using valence-to-core X-ray emission spectroscopy that the level of nitridation of the active catalyst was rather small and limited to the surface and that vanadium was strongly reduced in the bulk [9]. *In situ* studies showed that acrylonitrile production started when vanadium in the bulk structure of the oxide material

changes its formal oxidation state from +4.8 to +3.8 ± 0.1. This mean oxidation state reached even 3.5 ± 0.1 under pure ammonia. These results led us to reconsider the true nature of the active phase and to investigate a new preparation protocol that could lead to more efficient catalysts.

In this paper we present a study of a V/Al/O catalyst for propane ammoxidation at low and high conversion level in order to better understand the effect of some parameters related to the catalyst composition or catalytic reaction conditions. While the study was not designed to be exhaustive, it allowed drawing general conclusions on the reaction pathway and trends on optimum reaction conditions. In a second part, we describe a new preparation protocol of V/Al/O catalysts based upon the synthesis of a mixed aluminum and vanadium precursor with the desired cationic ratio and containing vanadium already reduced, with formal oxidation state III.

2. Experimental

### 2.1. Preparation of V/Al/O mixed oxides

Several ways to prepare V/Al/O mixed oxides like the co-precipitation of aluminum nitrate and ammonium metavanadate, the hydrolysis of aluminum butoxide by ammonium metavanadate or the complexation by citric acid of aluminum and vanadium acetylacetonate solutions, have been developed and patented [10]. In this study V/Al/O mixed oxides have been prepared using the

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method commonly used, which is by co-precipitation [2]. This method has recently been proved to be extrapolatable to at pilot-scale [7]. Ammonium metavanadate salt was dissolved in water (0.03 M) at 60 °C under stirring, and then nitric acid was added progressively to reach a pH of 3.0. An aluminum nitrate solution (0.08 M) was then added to the vanadium solution (V/Al = 0.15, 0.25, 0.30, 0.35 and 0.50). A solution containing ammonium hydroxide (10%, v/v) was finally added progressively to the V–Al solution until a final pH of 5.5 was reached. The pH was kept at pH of 5.5 for 1 h and a precipitate was formed. The obtained solid was recovered by filtration, washed several times with hot water and dried at 60 °C overnight. The prepared samples were referred to as VAlO-x with x being the V/Al ratio.

A new method has been used to prepare the V/Al/O mixed oxides. This new synthesis method consisted in first of preparing a mixed ammonium vanadium and aluminum oxalate that was further be transformed to the mixed oxide. To prepare the mixed ammonium vanadium and aluminum oxalate, the ammonium and vanadium oxalate was first synthesized. The reduction of pentavalent vanadium in tetravalent vanadium by oxalic acid is completed, as follows:

$$2VO_3^- + 5C_2O_4^{2-} + 8H^+ \rightarrow 2[VO(C_2O_4)_2]^{2-} + 2CO_2 + 4H_2O \qquad (1)$$
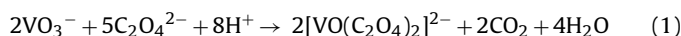
$(NH_4)_2VO(C_2O_4)_2 \cdot 2H_2O$ is easily obtained by reaction between ammonium metavanadate NH_4VO_3 and oxalic acid, in quantity calculated from the equation:

$$2NH_4VO_3 + 4H_2C_2O_4 + (NH_4)_2C_2O_4$$
$$\rightarrow 2(NH_4)_2[VO(C_2O_4)_2] + 2CO_2 + 4H_2O \qquad (2)$$
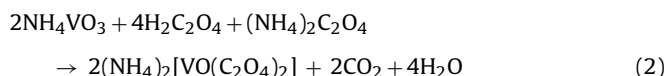
In a balloon, appropriate quantities of oxalic acid and ammonium oxalate are then dissolved in 200 mL of distilled water. Ammonium metavanadate is added to the solution maintained under magnetic stirring at room temperature for 3 h. The ammonium salt is totally stable under air atmosphere, in solid form or in water solution. To synthesize the $(NH_4)_3[Al_xV_z(C_2O_4)_3]\cdot nH_2O$, the first solution is to do a syncrystallisation of the trioxalic salts:$(NH_4)_3[Al(C_2O_4)_3]\cdot 2H_2O$ and $(NH_4)_3[V(C_2O_4)_3]\cdot 3H_2O$. The trioxalic salt of aluminum is easily obtained, but the Vanadium (III) salt requires an electrolytic reduction on mercury-cathode of the vanadium (IV) salt. To avoid this operation, the reduction proprieties of metallic aluminum (which is a reactant in our case) is used to reduce the dioxalato-vandate (IV) $[VO(C_2O_4)_2]^{2-}$ ion in trioxalato-vanadate (III), $[V(C_2O_4)_3]^{3-}$. The reaction is complete in oxalic condition, following the next equation:

$$2[VO(C_2O_4)_2]^{2-} + Al^0 + 6C_2O_4^{2-} + 6H^+$$
$$\rightarrow [Al(C_2O_4)_3]^{3-} + 3[V(C_2O_4)_3]^{3-} + 3H_2O \qquad (3)$$
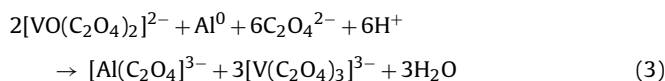
In a balloon, the previous vanadate ammonium oxalate complex was first solubilized, in water then appropriate quantities of oxalic acid, ammonium oxalate and metallic aluminum were added. The solution was maintained under stirring and reflux at 60 °C for 24 h. The solid obtained was separated by filtration and dried in ambient air. This method allows preparing mixed oxide of vanadium (III) and aluminum (III):$(NH_4)_3[Al_xV_z(C_2O_4)_3]$, in which the ratio V per Al is lower than 3. The samples prepared using this method had all a V/Al ratio equal to 0.25, they were referred to as VAlO-OX.

The catalysts were either used directly as catalyst in the reaction conditions or pre-nitrided under ammonia at 500 °C for 5 h. Both preparations (direct use or pre-nitridation) lead to catalysts with comparable catalytic properties. When used directly, it took about 8 h on stream to obtain the best catalytic properties.

2.2. Characterization techniques

Metal contents of the solids were determined by atomic absorption (ICP-AES). 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 measure 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 air with a heating rate of 1 or 5 °C/min. Surface areas of the catalysts were measured with a Micromeritics ASAP 2020 instrument. Samples were first degassed under vacuum at 300 °C for 5 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 D8 X-ray diffractometer equipped with a 9-sample holder. The X-ray source was Cu Kα radiation. 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. The unit cell of the crystallized phase was refined using Bruker Topas P program.

EPR spectra were recorded on an EPR cw-spectrometer ELEXSYS 500-10/12 (Bruker) at a modulation frequency of 100 kHz and modulation amplitude of 0.5 mT. The magnetic field was measured with respect to the standard 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH). Computer simulation of EPR spectra was performed with the program SIM14S of Lozos et al. [11].

2.3. Catalysts testing

The ammoxidation of propane was performed at 500 °C in a fixed bed reactor operating at atmospheric pressure. The reaction was conducted in down flow mode using Pyrex fixed bed reactor placed in a tubular furnace. The catalytic properties were determined between 460 and 520 °C with a catalyst amount varying from 4 to 130 mg diluted into SiC (fraction between 106 and 180 μm). The volume above the catalytic bed was minimized by adding pieces of quartz (2 mm). The feedstock composition was $C_3H_8/O_2/NH_3/N_2 = 1.25/3.15/2.4/1.7$ with a total flow of 33 mL/min. The gas products and reactants were analyzed on line by gas chromatograph using a Carboxen 1010 column. The organic substrates were condensed in water and analyzed off line using a capillary Nukol column and FID detection. 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 data given in the results section were those obtained after between 12 and 48 h on stream. No deactivation was observed during this period of time. Blank tests have shown that without catalyst and under the used reaction conditions, the propane conversion was very low and that mainly CO_x and propene were formed. After catalytic testing all the catalysts were recovered in the same way. The temperature was decreased to 120–150 °C then the reaction gas flow was shifted to a pure N_2 flow and the temperature further decreased to room temperature.

3. Results and discussion

3.1. Study of V/Al/O catalysts prepared by co-precipitation

The VAlO-0.25 catalyst prepared by co-precipitation has been nitrided *ex situ* under ammonia (100 mL/min) at 500 °C for different times or directly tested as catalyst at the same temperature. The

Table 1
Nitrogen content of the VAlO-0.25 catalyst after treatment under ammonia and after testing.

Treatment at 500 °C under NH₃ (h)	N content (wt%)	N content after testing[a] (wt%)
0	0.0	1.9
5	0.5	1.8
24	1.6	1.9
40	2.4	1.9

[a] Reaction temperature: 500 °C, GHSV = 20.1 L g⁻¹ h⁻¹, composition of the flow: $C_3H_8/O_2/NH_3/N_2 = 1.25/3.15/2.4/1.7$.

Table 2
Comparison of the catalytic properties of the VAlO-0.25 catalyst prepared in this study with the ones of a catalyst from the literature prepared similarly. Reaction conditions 500 °C, WGSH = 16.4 L g⁻¹ h⁻¹.

Sample	$C_3H_8/O_2/NH_3$	Conversion (%)	Selectivity (%)				Ref.
			ACN	ACeN	C_3H_6	CO_x	
VAlO-0.25	1.25/3.15/2.4	57	51	5	11	34	This study
VAlO-REF	1.25/3/1	60	56	4	0	34	[2]

ACN, acrylonitrile; ACeN, acetonitrile.

solids, which were all amorphous to X-rays diffraction, exhibited nitrogen contents increasing with the duration of the treatment under ammonia (Table 1). These nitrogen contents were the same after catalytic testing (at least 48 h on stream), showing that nitridation of the catalyst was reversible and can be regarded as a consequence of an equilibration of the catalyst under reaction conditions. The catalysts had similar catalytic properties and appeared almost as efficient as the catalysts described in literature tested at the same temperature (Table 2) [2]. However a higher ammonia to propane ratio was required to obtain the best catalytic properties and nevertheless propene was always detected as a by-product. The variation of the propane conversion and the selectivity as a function of the contact time is shown in Fig. 1. At low contact time, the selectivity to propene strongly increased proving that propene is the major primary product of propane on the V/Al/O catalysts. This result shows that ACN should mainly be formed through intermediate propene as proposed by Olea et al. [3] rather than through a direct pathway [2]. This last hypothesis cannot be ruled out and there might be two pathways for ACN formation with a total propane ammoxidation mechanism rather similar to that proposed on multi-element based catalysts [12]. At high conversion, the selectivity to acrylonitrile decreased to the benefit of that to CO_x showing that acrylonitrile can be further oxidized and that CO_x could be formed from nitriles and not only from propane or propene. It is noteworthy that the direct oxidation of ammonia
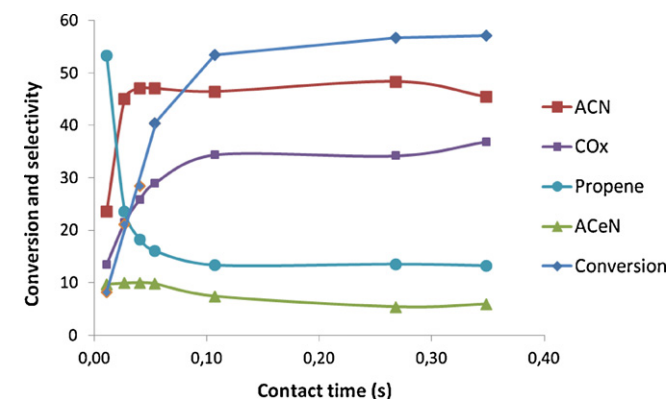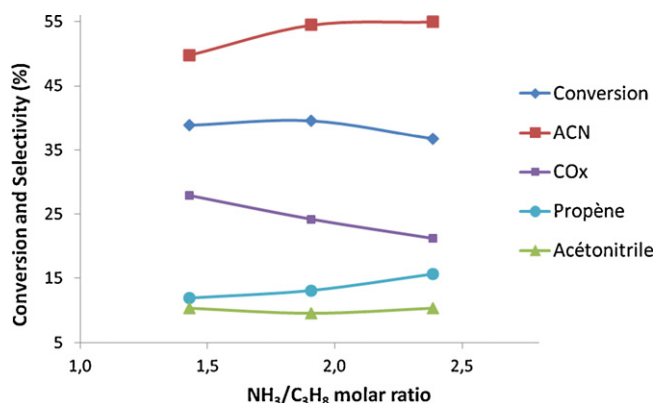

Fig. 2. Propane conversion and selectivity to acrylonitrile, propene, acetonitrile and CO_x on VAlO-0.25 as a function of the NH_3/C_3H_8 ratio; reaction temperature: 500 °C, WGSH = 20.1 L g⁻¹ h⁻¹ and $C_3H_8/O_2/N_2 = 1.25/3.15/1.7$).

always took place as a side reaction; this oxidation lead systematically to N_2O and N_2 was never detected.

While the exhaustive reaction kinetic study is not presented, the influences of the ammonia and oxygen to propane ratios on the catalytic properties of the VAlO-0.25 catalyst are reported in Figs. 2 and 3. Propane conversion showed a maximum for an ammonia to propane ratio around 2 and selectivity to acrylonitrile increased continuously in the tested range whereas propane conversion increase continuously with the oxygen to propane ratio with a maximum of selectivity to acrylonitrile for a ratio around 2.5. The two maxima have been used to establish the reaction conditions used for the study. They might be explained by competitions of propane and ammonia adsorption on one hand, and oxygen and ammonia on the other, on two different sites.

Although the contact times used with V/Al/O catalyst were much lower than those used with other efficient multi-component catalysts, the relative ammonia consumption (i.e. not selectively inserted in the acrylonitrile molecules) was of in the same order, 80% for V/Al/O catalyst against 81% for vanadium antimonate type catalysts at the same temperature [13].

Additionally, V/Al/O catalysts with different V/Al ratios have been prepared by co-precipitation. Their main characteristics are given in Table 3. These solids were amorphous and remained amorphous after catalytic testing. Their surface areas of the compounds are comparable before and after testing with around 230 and 160 m²/g respectively. The co-precipitated V/Al/O samples have been tested as catalysts at low contact time under standard conditions (Fig. 4); the activity of the catalysts increased monotonously
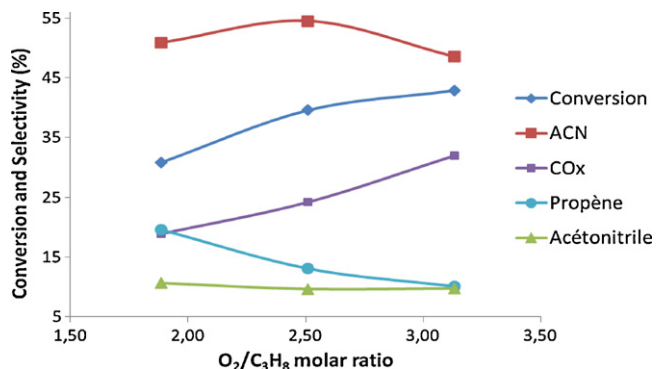

Fig. 1. Variation of the rate of propane conversion and selectivity, as a function of the contact time on VAlO-0.25; reaction temperature: 500 °C and $C_3H_8/O_2/NH_3/N_2 = 1.25/3.15/2.14/1.7$).

Fig. 3. Propane conversion and selectivity to acrylonitrile, propene, acetonitrile and CO_x on VAlO-0.25 as a function of the O_2/C_3H_8 ratio; reaction temperature: 500 °C, WGSH = 20.1 L g⁻¹ h⁻¹ and $C_3H_8/NH_3/N_2 = 1.25/2.14/1.7$.

Table 3
Physico-chemical characteristics of the different V/Al/O catalysts prepared using the co-precipitation method; SSA: specific surface area.

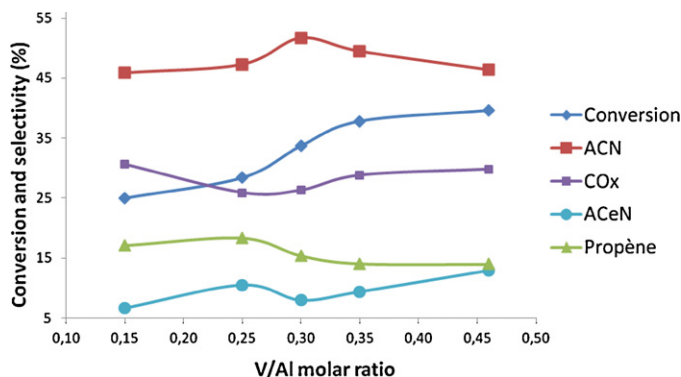| Compound	Chem. anal. V/Al	XRD	SSA (m^2/g^1)
VAlO-0.15	0.15	Amorphous	265
.VAlO-0.25	0.25	Amorphous	255
VAlO-0.30	0.30	Amorphous	n.m.
VAlO-0.35	0.35	Amorphous	240
VAlO-0.50	0.46	Amorphous	270

n.m.: not measured.

Fig. 4. Variation of the rate of propane conversion and selectivity, as a function of the V/Al ratio of the V/Al/O catalysts; reaction temperature: 500 °C, WGSH = 20.1 L g^{-1} h^{-1} and C$_3$H$_8$/O$_2$/NH$_3$/N$_2$ = 1.25/3.15/2.14/1.7.
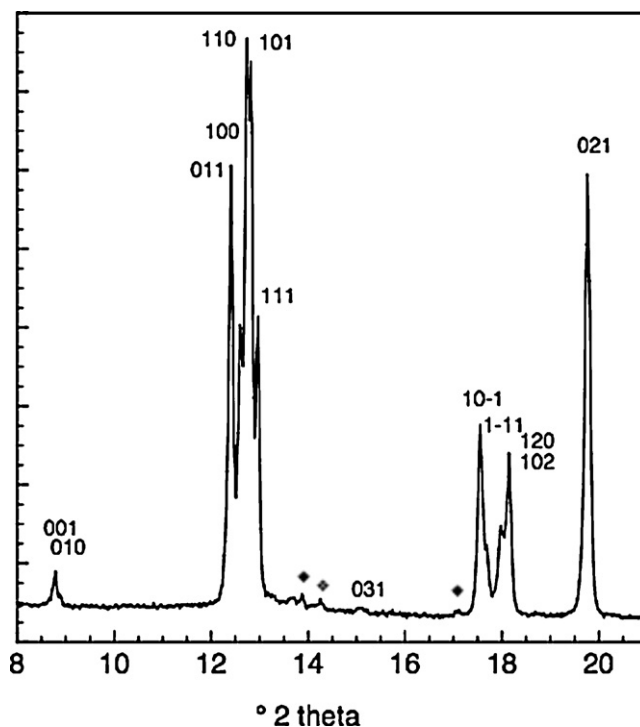

Fig. 5. Indexed X-ray diffraction pattern of the synthesized mixed ammonium aluminum–vanadium oxalate, full and empty rhombus correspond respectively to ammonium oxalate and ammonium hydrogeno–oxalate.

with the V/Al ratio and the selectivity to ACN showed a maximum for the VAlO-0.30 catalyst. The best ACN yields were obtained with the VAlO-0.35 catalyst. For compounds with V/Al ratios varying from 0.15 to 0.30, the apparent activation energies were equal to 32 ± 2 kJ/mol whereas for compounds with higher ratios they decreased up to about 25 ± 3 kJ/mol.

Since the rate of propane conversion initially increased continuously with the V/Al ratio, but remained almost constant at V/Al ratios > 0.35, it can be concluded that at low V content the catalysts sites remained identical in their nature and increased only in their number by rising the V/Al ratio. At higher V content we assume that the sites changed in nature while their total number remained more or less constant. Since the nitrogen content of the catalysts after catalytic testing did not vary with the V/Al ratio, it could be hypothesized that the change of the sites might be related to the nuclearity of the vanadium species and that the most active and selective sites correspond to isolated V species, which should mainly be present at low V content.

3.2. Study of V/Al/O catalysts prepared by mixed ammonium oxalates decomposition

The mixed aluminum and vanadium ammonium oxalate has been compared to the pure aluminum and vanadium ammonium oxalates. The X-ray diffraction patterns of the pure compounds correspond to those referenced in the literature (ICDD 00-049-1188 and ICDD 01-075-7080). The X-ray diffraction pattern of the mixed vanadium–aluminum oxalate correspond well to that of the pure aluminum ammonium oxalate which is in agreement with the expected substitution of Al^{3+} by V^{3+} (Fig. 5). Peaks attributed to ammonium oxalate (ICDD 00-011-0515) and ammonium hydrogeno-oxalate (ICDD 00-014-0754) have been identified but remained very small. Cell parameters of the mixed aluminum and vanadium ammonium oxalate have been calculated from X-ray powder pattern: $a = 0.77853(7)$, $b = 1.9804(1)$, $c = 1.0443(1)$ nm and $\beta = 106.966(4)°$. They are almost similar to those of the pure

aluminum ammonium oxalate [14]. This observation was expected since Al^{3+} and V^{3+} have similar cationic radii.

The TG curve of the mixed vanadium–aluminum oxalate is also similar to that obtained with the pure ammonium aluminum oxalate (Fig. 6, Table 4). The analyses using a heating rate of 5 °C/min showed a crystal water loss of 1.7 mol per metallic cation instead of two in the theoretical compound. The oxalate decomposition occurred between 140 and 380 °C and a difference was observed between the corresponding experimental and theoretical weight losses. It is attributed to the deposition of carbon formed during this
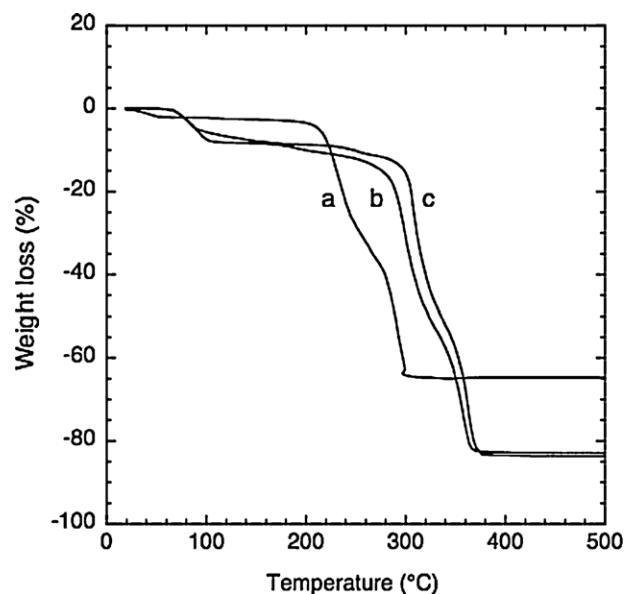

Fig. 6. TG analysis curves of the synthesized ammonium vanadium (a), ammonium aluminum (b) and ammonium aluminum-vanadium oxalate (c) recorded in air (10 mL/min) recorded at 5 °C/min.

Table 4
Thermal and thermogravimetric analyses data of the ammonium oxalates precursors under air (60 mL/min) from 25 to 600 °C using various heating rate.

Sample	Heating rate (°C/min)	Water departures			Oxalate decomposition		
		T (°C)	m (wt%)	$\frac{H_2O}{(Al+V)}$	T (°C)	m (wt%)	[a]$C_{residual}$ (wt%)
$(NH_4)_2VO(C_2O_4)_2 \cdot xH_2O$	5	25–160	2.69	0.4	150–310	62.11	9.8
$(NH_4)_3Al(C_2O_4)_3 \cdot xH_2O$	5	60–215	8.85	1.8	180–380	75.06	16.2
$(NH_4)_3AlV(C_2O_4)_3 \cdot xH_2O$	5	55–140	8.29	1.7	150–380	74.83	8.4
$(NH_4)_3AlV(C_2O_4)_3 \cdot xH_2O$	1	25–105	10.29	2.1	120–335	74.25	2.1

[a] Residual content in carbon after total decomposition.

decomposition in the remaining amorphous oxide. The observed amount of carbon depended strongly upon the conditions of thermal analysis and it could be minimized when a heating rate of 1 °C/min was applied (Fig. 6, Table 4). Furthermore in the later case the departure of hydration water took place in two steps at 40 and 80 °C with the expected total water loss of 2 mol per metallic cation. Presumably in the analysis with a higher heating rate, the first low temperature water departures were not observed because they took place during the time when the solids were maintained under the air flow for stabilization of the balance without recording and which was skipped in the case of the slow heating. The presence of carbon in the catalyst was further confirmed by the XPS analysis of the solid after nitridation with pure ammonia.
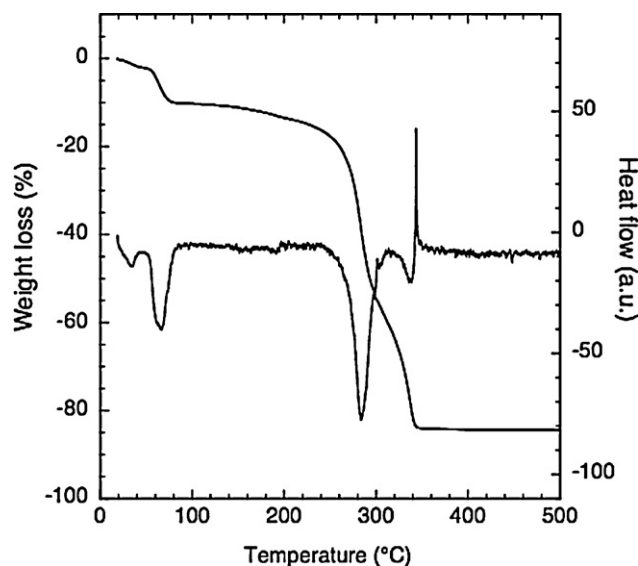
The mixed oxalate has been tested as catalysts in standard conditions (Table 5). The results showed a rather low activity with selectivity to acrylonitrile, which did not exceed 28%. Obviously the presence of bulk and/or surface carbon in the catalyst significantly modified the catalytic properties of the V/Al/O catalysts. It has to be removed in order to retain high catalytic efficiency.

To remove the carbon residue formed during the decomposition of the oxalates two different treatments have been applied to the solids prior to their testing. The first one corresponds to a heat treatment under flowing air (100 mL/min) for 12 h at 300 °C (Treatment 1). The temperature must to be high enough to burn the carbon residue and on the other hand low enough to avoid the crystallization of the mixed oxide occurring at 339 °C as shown on the DTA curve (Fig. 7). Results presented in Table 5 show that such treatment improved the acrylonitrile's selectivity but not the conversion; the catalyst remained much less efficient than those prepared by the conventional preparation method. The solid after treatment 1 and before catalytic testing still exhibits a light grey color indicating that carbon remained at the surface, which might explain the catalytic results. Furthermore characterization of the catalysts by XRD showed small peaks corresponding to V_2O_5 that could have been formed during the treatment 1.

The second treatment consisted in firing the solid at 180 °C under flowing ozone–air mixture (1.1 ppmv O_3) at 70 mL/min for 3 weeks (Treatment 2). After such treatment the obtained solid was completely amorphous and but with a lower specific surface area i.e. 45 m^2/g. Further experiments showed that the same effect could be reached with ozone–air mixture richer in ozone for shorter time. The catalytic testing of the solid showed a more active than the catalyst prepared by the conventional method and a slightly higher

Fig. 7. TG and DTA analysis curves of the mixed ammonium aluminum–vanadium oxalate recorded in air (10 mL/min) at 1 °C/min.

selectivity to acrylonitrile (Table 5). Such increase in activity and selectivity has been confirmed at low conversion (Table 6). In order to explain why the catalyst prepared using the oxalate method and treatment 2 was more active and selective than the one prepared using conventional method, both catalysts have been studied by EPR spectroscopy after catalytic testing. The spectra recorded at room temperature are presented in Fig. 8. Spectra simulations showed, that both EPR spectra consist of two superimposed signals. The first signal was characterized by a hyperfine structure (hfs) multiplet, which arises from isolated VO^{2+} species in square-pyramidal or octahedral coordination due to the coupling of the electron spin of V^{4+} ($S = 1/2$) with the nuclear spin of vanadium ($I = 7/2, S = 1/2$, natural abundance of nuclear spin = 99.76%). This hfs signal was superimposed for both EPR spectra by a broad isotropic line caused by cluster-like magnetically interacting VO^{2+} species. Moreover, it was found by spectra simulation that the spin Hamiltonian parameters of the isolated VO^{2+} sites are almost equal for the two catalysts, meaning that for both preparation routes the structure of isolated vanadyl sites is almost identical ($g_\perp =1.976$, $g_{II} = 1.925, A_\perp =65.3$ and $A_{II} = 195.4$ for oxalate method and $g_\perp =1.975$, $g_{II} = 1.928, A_\perp =59.3$ and $A_{II} = 196.0$ for the conventional method).

Table 5
Catalytic properties of the VAlO-OX catalyst after different heat treatments. Reaction temperature: 500 °C, WGSH = 20.1 L g^{-1} h^{-1}, C$_3$H$_8$/O$_2$/NH$_3$/N$_2$ = 1.25/3.15/2.4/1.7.

Sample	Conversion (%)	Selectivity (%)			
		ACN	ACeN	C$_3$H$_6$	CO$_x$
Without treatment	58	28	5	8	62
After treatment 1[a]	50	40	3	11	48
After treatment 2[b]	58	54	4	12	31

[a] Treatment 1: 12 h at 300 °C in flowing air at 100 mL/min.
[b] Treatment 2: 3 weeks at 180 °C under flowing ozone–air mixture (1.1 ppmv O$_3$) at 70 mL/min.

Table 6
Comparison of the catalytic properties of VAlO-OX after treatment with ozone air mixture and of the VAlO-0.25 at iso-conversion, reaction temperature: 500 °C, and C$_3$H$_8$/O$_2$/NH$_3$/N$_2$ = 1.25/3.15/2.4/1.7.

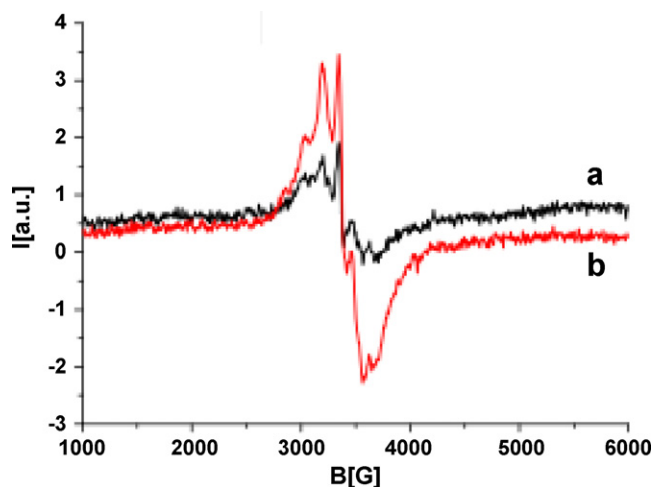| Sample	Conversion (%)	Selectivity (%)			
		ACN	ACeN	C$_3$H$_6$	CO$_x$
VAlO-0.25	7.2	16.5	10.5	58	15
VAlO-OX after treatment 2	6.4	24.5	5	68	2.5

Fig. 8. ESR spectra at 298 °C of the VAlO-0.25 (a) and VAlO-OX (b) catalysts after catalytic testing.

However, the double integral of the EPR signal for the catalyst prepared *via* the oxalate method I_{oxa} is much more higher than the double integral of the EPR signal for the sample prepared by co-precipitation I_{pre}, indicating that the latter sample contained less amount of V^{4+} after use in propane ammoxidation ($I_{oxa}/I_{pre} = 2.3$). The relative areas of the two superimposed signals, I_{iso} and I_{poly}, showed that proportionally the sample prepared by the oxalate method contained more isolated species than the sample prepared *via* precipitation ($I_{iso}/I_{poly} = 0.50$ for the oxalate method and $I_{iso}/I_{poly} = 0.11$ for the co-precipitated sample).

If we postulate that the isolation of vanadium sites are key for a high selectivity to acrylonitrile, these results would explain why the solid prepared with oxalate method was more selective than the one prepared using the precipitation method. This assumes however that the surface and bulk composition are the same but we have shown in a previous study that surface composition determined from XPS data corresponded relatively well to the bulk composition for these catalysts [7]. It is also possible that the better selectivity might be related to the higher reduction level of V that would help avoiding over-oxidation of acrylonitrile or intermediate products.

4. Conclusion

The results described in this paper confirm the high efficiency of the V/Al/O catalysts for propane ammoxidation. The catalysts characterized by a V/Al around 0.30–0.35 were the most efficient. We speculate at present time that it corresponds to the higher vanadium surface content of isolated or low nuclearity clusters of vanadyl species. We confirm that the mixed oxides are nitrided in the reaction conditions. This nitridation seems to be crucial for their efficiency although it mainly depends on the reaction conditions and not of the catalyst composition. Propene was shown to be the main primary product from propane ammoxidation on the V/Al/O catalysts. It is further transformed to acrylonitrile and/or acetonitrile. CO and CO_2 should be formed from propene but also in minor amount from propane and/or nitriles. This leads to a reaction pathway rather similar to that observed for multi-component catalysts either based on antimonates or molybdates.

In addition we have shown that the V/Al/O catalysts can be prepared by decomposition of mixed vanadium and aluminum ammonium oxalates. A traditional calcination of these oxalates in air at 300 °C results in solids with high specific surface area nevertheless these solids appeared to be poorly efficient as catalysts. Presumably this is due to the formation of carbon trapped in the

catalysts particles during the decomposition process. However, when the decomposition was conducted at low temperature in air–ozone mixture, the formation of carbon was avoided and active and selective catalysts were obtained. This preparation technique should be applicable to other preparation of oxide materials from oxalate precursors and even other precursors like acetylacetonate or acetate and open new preparation routes for catalysts. The increased activity and selectivity to ACN observed for the catalyst prepared with this new method has been ascribed to the synthesis of a catalyst with a higher content of isolated vanadium species in the bulk as shown by EPR that may also be present at the surface and to a higher reduction level of the vanadium species.

With the co-precipitation method at pH 5.5 it has been reported that V/Al/O mixed phase was formed by a condensation reaction of tetrahedral polymeric species $[VO_x]_n^{n-}$ and the aluminum hydroxide ions ($[Al_2(OH)_2(OH_2)_4]^{4+}$ [8]. A study by X-ray absorption spectroscopy (XAS) of the same type of catalysts showed that a part of the V cations changed in reaction conditions their coordination to octahedral but no data was reported on the isolation or polymerization of such species [5]. The change in coordination was confirmed later by a study combining of valence-to-core X-rays emission spectroscopy and XAS, which proposed that V cations had a mixed octahedral or square pyramidal oxygen local environment in the activated catalysts [9]. However none of the studies reported on the nuclearity of the V species in the catalysts, which is shown in this study to be important both for the activity and the selectivity of the catalysts

To conclude, theses catalysts are promising due to their outstanding high productivity. However compared to other catalytic systems working under propane-lean conditions, the obtained ACN yield is lower and the reaction temperature and ammonia to propane ratio needed for an optimum productivity are high. The catalysts consume as much ammonia as the other multi-component efficient catalysts and therefore no cost reduction can be established; furthermore under the conditions of catalysis used, the by-product formed is N_2O and no N_2, which requires further treatment. Further improvements of the catalystic performance might be possible in particular by modifying the catalyst composition and maybe by modifying the reaction conditions with propane rich feeds.

Acknowledgment

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