Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 118 (2006) 344–352
CATALYSIS TODAY
www.elsevier.com/locate/cattod

# Effect of nitridation on the electronic environment of vanadium in VAlO(N) powder catalysts, used for the ammoxidation of propane

G. Silversmit [a,*], H. Poelman [a], R. De Gryse [a], W. Bras [b], S. Nikitenko [c], M. Florea [d,1], P. Grange [d,✠], S. Delsarte [d]

[a] Ghent University, Department of Solid State Sciences, Surface Physics Division, Krijgslaan 281, S1, B-9000 Gent, Belgium
[b] Netherlands Organisation for Scientific Research (NWO), DUBBLE @ ESRF, BP 220, 38043 Grenoble Cedex 9, France
[c] Catholic University Leuven, DUBBLE @ ESRF, BP 220, 38043 Grenoble Cedex 9, France
[d] Université Catholique de Louvain, Unité de Catalyse et Chimie des Matériaux Divisés, 2/17 Croix du Sud, 1348 Louvain-la-Neuve, Belgium

Available online 1 September 2006

**Abstract**

VAlO(N) oxynitrides are promising novel catalysts for the ammoxidation of propane to acrylonitrile. These catalysts are obtained after nitridation of a VAlO oxide precursor in $NH_3$ or during the reaction in a $NH_3/C_3H_8/O_2$ mixture. The local structure around the vanadium atoms in the oxide precursor and in several catalysts that have been used in catalytic tests is studied by X-ray absorption spectroscopy (XAS). The nitridation in $NH_3$ was followed with in situ XAS. The oxide precursors have tetrahedral co-ordinated vanadium, while after full nitridation octahedrons are found and a small decrease in vanadium oxidation state occurs. The catalysts used in the ammoxidation reaction consist of a mixture of these tetrahedrons and octahedrons.


*Keywords:* Acrylonitrile; Ammoxidation; Catalyst; VAlON; Oxynitrides; V K-edge X-ray absorption spectroscopy

## 1. Introduction

Acrylonitrile (ACN) is a high volume intermediate for a wide range of products: acrylic fibers, Nylon (DuPont) and high-performance polymers like for instance acrylonitrile–butadiene–styrene (ABS). Acrylonitrile is mostly manufactured from the gas phase ammoxidation of propene. However, the feedstock of propene is expensive and it is therefore interesting to produce ACN from other base products, such as propane.

We have developed a novel amorphous mixed vanadium aluminium oxide ''VAlO'', which appears to have an advantage over other propane ammoxidation catalysts in acrylonitrile productivity, both in the time required for the manufacturing process as well as in the amount of catalyst required [1]. These VAlO catalysts are prepared by co-precipitation of $NH_4VO_3$ and $Al(NO_3)_3$. Four synthesis parameters appear to have an influence on their catalytic activity: the V/Al ratio in the co-precipitation solution [2], the drying temperature [3], the co-precipitation pH [4], and the metal concentration in the precipitation solution [4].

In a typical ammoxidation catalytic test, the VAlO is heated to 500 °C in a mixture of propane, oxygen and ammonia, and the course of the reaction is followed by GC analysis of the reaction gas over a period of 22 h. At the initial stage, the selectivity for ACN is low, but this increases markedly with time, until it reaches a steady-state after approximately 12 h [5]. The catalysts treated in this way are referred to as VAlON, because they have incorporated nitrogen in their anionic network during the tests.

To determine the electronic environment around vanadium in the amorphous VAlO(N) catalysts we performed V-K edge X-ray absorption spectroscopy (XAS) studies on two VAlO

* Corresponding author. Tel.: +32 9 264 43 71; fax: +32 9 264 49 96.
*E-mail address:* Geert.Silversmit@UGent.be (G. Silversmit).
[1] Present address: University of Bucharest, Department of Chemical Technology & Catalysis, B-dul R. Elisabeta 4–12, Bucharest 030016, Romania.
✠ Deceased July 2003.

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.07.013

precursors with different V/Al ratios (0.25 and 0.90) and on different catalysts used in a catalytic test to examine the influence of the drying temperature. The structural changes during nitridation were followed with in situ XAS.

## 2. Experimental

### 2.1. Preparation of catalysts

Two vanadium-aluminium oxide catalysts, with V/Al ratio of 0.25 and 0.90, respectively, were prepared by co-precipitation, at 60 °C, of solutions containing 0.01 M ammonium metavanadate and 0.01 M aluminium nitrate. The ammonium metavanadate solid was dissolved in hot water (60 °C) under stirring, after which nitric acid (50 wt.%) was added to reach a pH of 3.0. Subsequently, the aluminium nitrate solution was added to the vanadium containing solution. This solution had a red-orange colour and a pH 2.5. A solution of ammonium hydroxide (25 wt.%) was added progressively to the V-Al solution to reach a pH of 5.5. The system was kept at this condition for 1 h. The yellow precipitate formed was washed with ethanol and subsequently with propanol to eliminate water and $NO_3^-$ and $NH_4^+$ ions. The powder was dried in a vacuum oven at 60 or 120 °C under a pressure of 30 mbar. Except when stated otherwise, the samples were not calcined prior to the tests.

The labelling of the samples is based on the V/Al ratio in the co-precipitation solution, the drying temperature (60 or 120 °C) or calcination temperature (500 °C) and the nitridation conditions ($NH_3/O_2/C_3H_8$ for the catalysts nitrided during the catalytic tests, 5% $NH_3$/He for the samples heated under ammonia in the XAS "in situ" cell). For example VAlON (0.25; 60 °C; $NH_3/O_2/C_3H_8$) is the sample obtained from a VAlO precursor with a bulk V/Al ratio equal to 0.25, dried at 60 °C which has undergone a catalytic test under a mixture of ammonia, oxygen and propane.

### 2.2. XAS measurements

The transmission vanadium K-edge X-ray absorption spectroscopy (XAS) measurements were performed at the

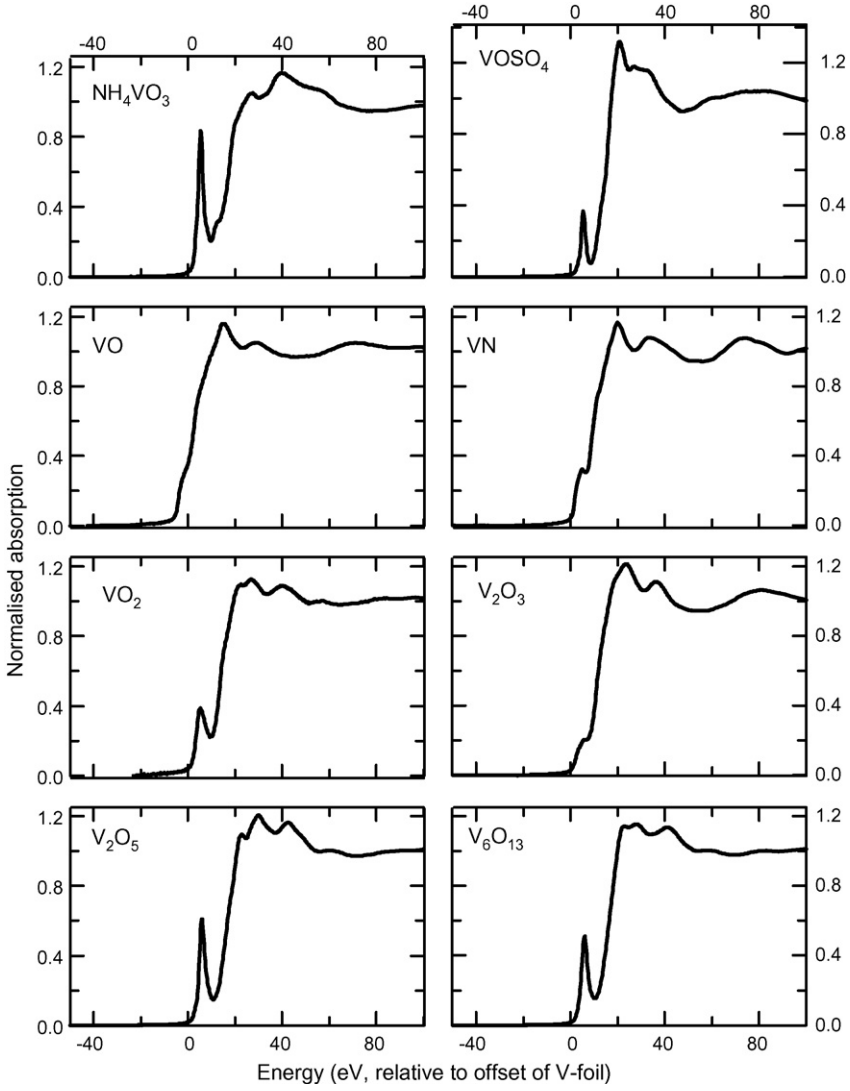


Fig. 1. Vanadium K-edge XANES spectra for different vanadium containing reference compounds.

DUBBLE beamline (BM26A) of the ESRF synchrotron. The beamline is equipped with a Si(1 1 1) double crystal monochromator and ionisation chambers filled with Ar/He mixtures. The higher harmonics of the primary energy that are also being transmitted by the monochromator were suppressed with the vertical focussing mirror after the monochromator.

The samples were pressed into self-supporting pellets in the hole of a stainless steel sample holder. The pellet thickness was chosen to give an absorption ($\mu x = \ln(I_0/I_t)$) of 2.5 at the vanadium K absorption edge in which $I_0$ is the intensity of the direct X-ray beam and $I_t$ of the transmitted beam. In a typical sample preparation, 12 mg of catalyst powder was pressed with 30 mg of BN, an inert and weakly absorbing binder. For in situ measurements, a stainless steel EXAFS chemical cell designed and built at the Ghent University was used. Kapton foils (25 μm) were used as X-ray transparent windows.

The XAS spectra of V foil, $V_2O_5$, $V_6O_{13}$, $VO_2$, $V_2O_3$, VO, $NH_4VO_3$, $VOSO_4{\cdot}3H_2O$ and VN were recorded at ambient temperature and pressure, for reference. A VAlO(0.25), VAlO(0.9) and three VAlON(0.25) samples with different drying/calcination temperatures (60, 120 and 500 °C) were also measured at ambient conditions. The nitridation of VAlO(0.25) and VAlO(0.9) was performed in situ on the beamline during which XAS spectra were obtained. For these in situ nitridations, the samples were heated from room temperature (RT) to 500 °C in an atmosphere of 5% $NH_3$ in He and kept at this temperature for 10 h. Spectra were recorded during heating and after 10 h nitridation time at 500 °C.

EXAFS data reduction and analysis were performed with the XDAP software [6]. The pre-edge background was subtracted using a modified Victoreen curve [7] whilst the atomic background, $\mu_0$, was subtracted using a cubic spline routine [8]. The spectra were normalised by division of the absorption data by the value of the edge step at 50 eV above the edge position. The fit parameters were determined by multiple shell fitting in *R*-space, by applying the difference file technique using Fourier Transformation [9]. Phase shifts and backscattering amplitudes, used to calculate the V-O contributions to the EXAFS signal, were obtained from $Na_3VO_4$, as described in Ref. [10]. The V-V contribution was calculated with FEFF 8.0 [11] utilising a vanadium cluster model with 7 Å radius with bcc crystalline structure. The accuracy of this procedure was checked by using the data from a measurement on a vanadium-foil. There was good agreement up to 15.6 $Å^{-1}$ and an EXAFS fit up to the 6th shell (6.3 Å) was possible. In all fits the $\Delta\sigma^2$ (a Debye–Waller type factor resembling the structural disorder) was confined between –0.005 and 0.005 $Å^2$ and $\Delta E_0$ between −5 and +5 eV.

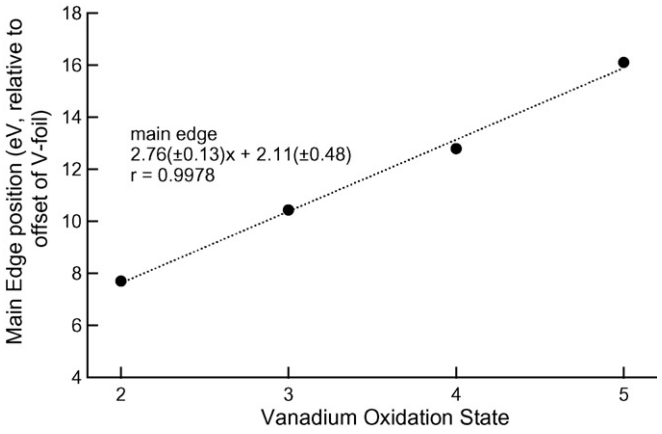


Fig. 2. 'Main edge' position as a function of vanadium oxidation state for the pure vanadium oxides $V_2O_5$, $VO_2$, $V_2O_3$ and VO.

## 3. Results

### 3.1. V-O reference XANES spectra

The XANES spectra of different reference compounds are shown in Fig. 1. Wong et al. [12] have shown that the position of the main-edge of vanadium compounds contains information about the valence of the vanadium cation whilst the pre-edge intensity contains information about the vanadium co-ordination. The position of the main-edge shifts towards higher energies with increasing vanadium cation valence. The energy shift in the main-edge for $V_2O_5$, $VO_2$, $V_2O_3$ and VO relative to the offset for vanadium-foil is given in Fig. 2. The data could very accurately be fitted with a linear function (correlation factor of 0.998). This linear relation between edge shift and the vanadium oxidation state can be used to estimate the oxidation state in the sample. With the data in Fig. 2 there is a ±0.6 error on the valence prediction.

Symmetrical vanadium-ligand co-ordinations with inversion symmetry, such as regular "$VO_6$" octahedrae, have only small pre-edge intensities, while co-ordinations without inversion symmetry, like distorted "$VO_6$" octahedrae or "$VO_4$" tetrahedrons, have significant to large pre-edge intensities. These relations are illustrated in the XANES spectra of the reference compounds. The XANES characteristics of the measured reference compounds are given in Table 1.

Table 1
XANES characteristics for selected V-O reference compounds

| Reference structure | 'Pre-edge' peak intensity | Absorption edge position, $E_m$ (eV) | V-O co-ordination | Valence |
|---|---|---|---|---|
| $V_2O_5$ | 1.78 | 16.1 | Distorted square pyramidal "$VO_5$" | 5+ |
| $VO_2$ | 1.51 | 12.8 | Distorted octahedral "$VO_6$" | 4+ |
| $V_2O_3$ | 0.49 | 10.4 | Regular octahedral "$VO_6$" | 3+ |
| VO | – | 7.7 | Regular octahedral "$VO_6$" | 2+ |
| VN | – | 8.9 | Regular octahedral "$VO_6$" | 3+ |
| $NH_4VO_3$ | 2.18 | 17.5 | Tetrahedral "$VO_4$" | 5+ |
| $VOSO_4{\cdot}3H_2O$ | 0.83 | 11.6 | Distorted octahedral "$VO_6$" | 4+ |

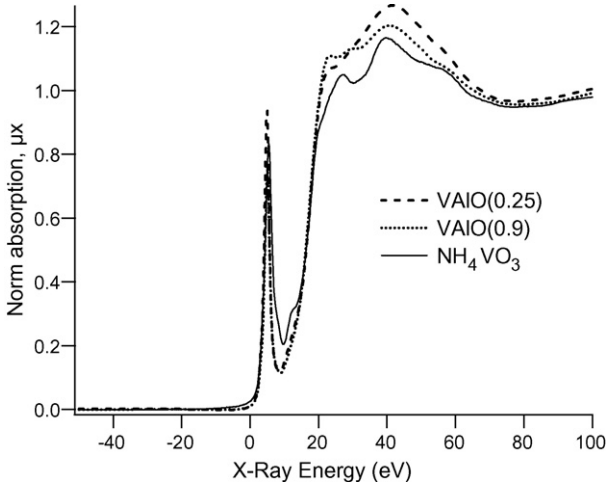


Fig. 3. V K-edge XANES spectra for VAlO(0.25) and VAlO(0.9) compared with the $NH_4VO_3$ reference sample spectrum.

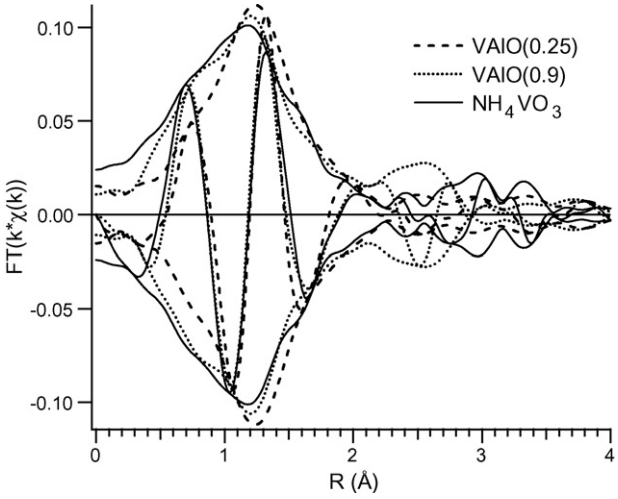


Fig. 4. $k^1$-Weighted Fourier Transformation of the experimental V K-edge EXAFS ($\chi(k)$) spectra for VAlO(0.25) and VAlO(0.9) compared with the $NH_4VO_3$ reference.

### 3.2. The VAlO oxide precursors

Fig. 3 shows the XANES spectra for VAlO(0.25) and VAlO(0.9) together with a spectrum of the $NH_4VO_3$ reference sample. From the position of the main-edge, the average vanadium cation valence is estimated at +5.5 (±0.6). A large pre-edge peak is observed, which is correlated to a tetrahedral "$VO_4$" co-ordination for these VAlO oxides (see Tables 1 and 2). There is good agreement with the XANES spectra for $NH_4VO_3$. This reference sample has a tetrahedral "$VO_4$" co-ordination with two V=O vanadyl bonds at 1.62 and 1.67 Å and two V–O bonds at 1.80 Å.

The $k^1$-weighted Fourier Transforms (FT) of the vanadium K-edge EXAFS signals for VAlO(0.25) and VAlO(0.9) are compared with $NH_4VO_3$ in Fig. 4. Again, there is a good agreement between the VAlO precursors and $NH_4VO_3$ spectra. Compared to VAlO(0.25), VAlO(0.9) shows an extra neighbour around 2.5 Å in the FT. This contribution is more pronounced in higher $k$-weighting, pointing to a neighbour with a relatively high $Z$-number like for instance vanadium or aluminium. Since this contribution appears in the spectra from the samples with the higher V/Al ratio, it is more likely originating from vanadium atoms. The $NH_4VO_3$ tetrahedron structure was used as the starting point in the

Table 2
XANES characteristics for VAlO(N) catalysts

| VAlO(N) catalysts | 'Pre-edge' peak intensity | Absorption edge position, $E_m$ (eV) | Estimated V-O(N) co-ordination | Estimated valence (±0.6) |
|---|---|---|---|---|
| VAlO(0.25) | 1.9 | 17.2 | Tetrahedral "$VO_4$" | 5.5+ |
| VAlO(0.9) | 1.7 | 17.2 | Tetrahedral "$VO_4$" | 5.5+ |
| VAlON(0.25; 60 °C; 5% $NH_3$/He) | 0.7 | 15.6 | Distorted octahedron | 4.9+ |
| VAlON(0.25; 120 °C; $NH_3/O_2/C_3H_8$) | 1.3 | 17.2 | Distorted octahedron | 5.5+ |
| VAlON(0.25; 60 °C; $NH_3/O_2/C_3H_8$) | 1.2 | 17.2 | Distorted octahedron | 5.5+ |
| VAlON(0.25; 500 °C; $NH_3/O_2/C_3H_8$) | 1.0 | 15.6 | Distorted octahedron | 4.9+ |

Table 3
EXAFS fit parameters for all samples

| Sample | Absorber–scatterer | $R$ (Å) | $N$ | $\Delta\sigma^2$ (Å$^2$) | $\Delta E_0$ (eV) | Fit details |
|---|---|---|---|---|---|---|
| VAlO(0.25) | V–O | 1.67 | 2[a] | −0.003 | −5.0 | $\Delta k$: 3.52–11.9 Å$^{-1}$; $\Delta R$: 0.5–2.5 Å |
| | V–O | 1.81 | 2[a] | 0.001 | 5.0 | 12 free parameters |
| | | | | | | $k^1$ variances: Im. part: 7.0%; Abs. part: 1.6% |
| VAlO(0.9) | V–O | 1.67 | 2[a] | 0.002 | −4.6 | $\Delta k$: 3.54–13.33 Å$^{-1}$; $\Delta R$: 0.5–3.0 Å |
| | V–O | 1.82 | 2[a] | 0.000 | 5.0 | 17 free parameters |
| | V–V | 3.17 | 0.5 | 0.003 | 1.6 | $k^1$ variances: Im. part: 4.3%; Abs. part: 0.7% |
| VAlON(0.25; 60 °C, 5% $NH_3$/He) | V–O | 1.68 | 0.8 | 0.005 | −5.0 | $\Delta k$: 2.76–12.35 Å$^{-1}$; $\Delta R$: 0.0–2.25 Å |
| | V–O | 1.96 | 3.9 | 0.005 | 5.0 | 15 free parameters |
| | V–O | 2.52 | 0.9 | 0.000 | 1.9 | $k^1$ variances: Im. part: 4.3%; Abs. part: 1.9% |

[a] Fixed parameter, based on XANES results.

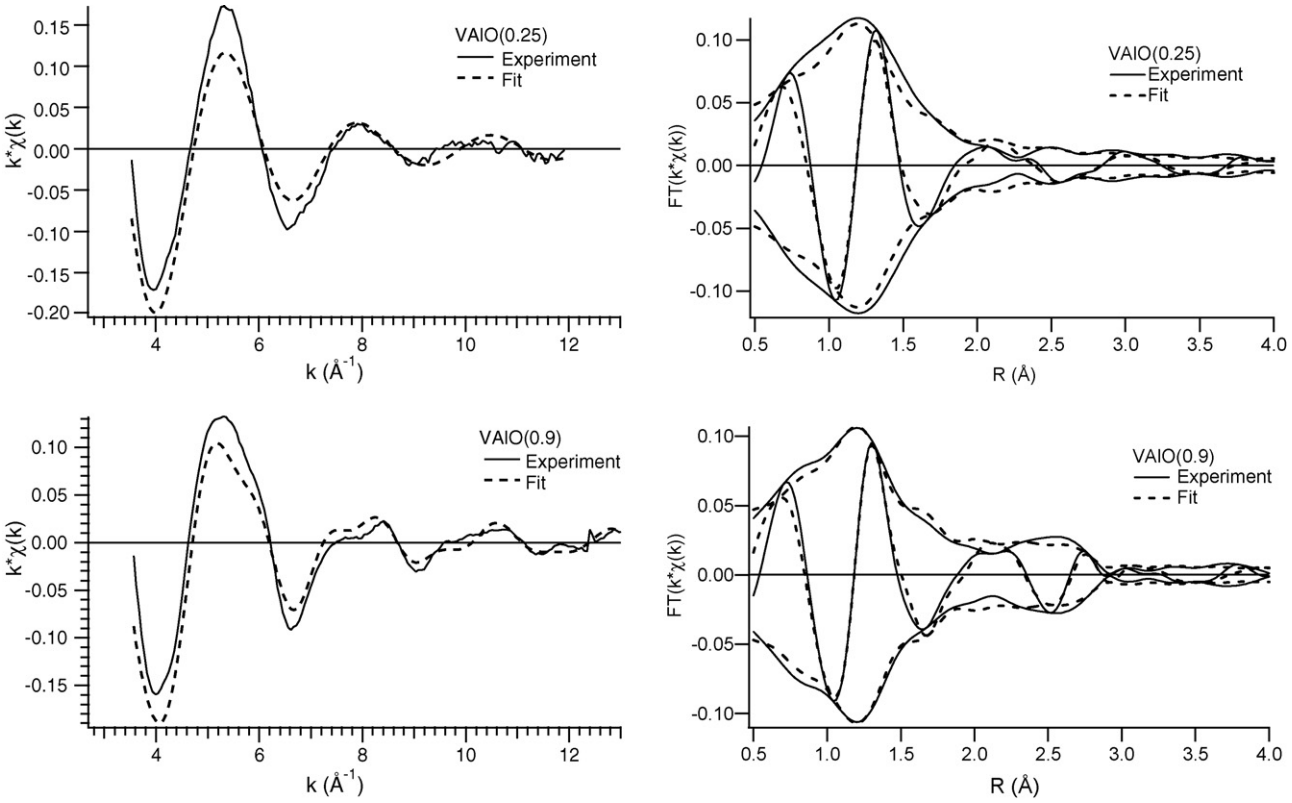


Fig. 5. Experimental (solid line) and fit (dashed line) $k^1 \times \chi(k)$ (left) and FT[$k^1 \times \chi(k)$] spectra (right) for VAlO(0.25) (top) and VAlO(0.9) (bottom).

EXAFS calculation. The $\chi(k)$ signal could be fitted with a ''$VO_4$'' tetrahedron with two V=O vanadyl bonds at 1.67 Å and two V–O bonds at 1.81 Å. The extra intensity around 2.5 Å in the FT contribution for VAlO(0.9) can be explained with a V-V contribution at 3.2 Å and a co-ordination number of ≈0.5. The fit details are given in Table 3 and Fig. 5.

### 3.3. The vanadium-environment in fully nitrided VAlON catalysts

The nitridation of a VAlO(0.25) and a VAlO(0.9) was followed with in situ XAS. The oxide precursor is first heated from room temperature to 500 °C in 5% $NH_3$/He and kept at

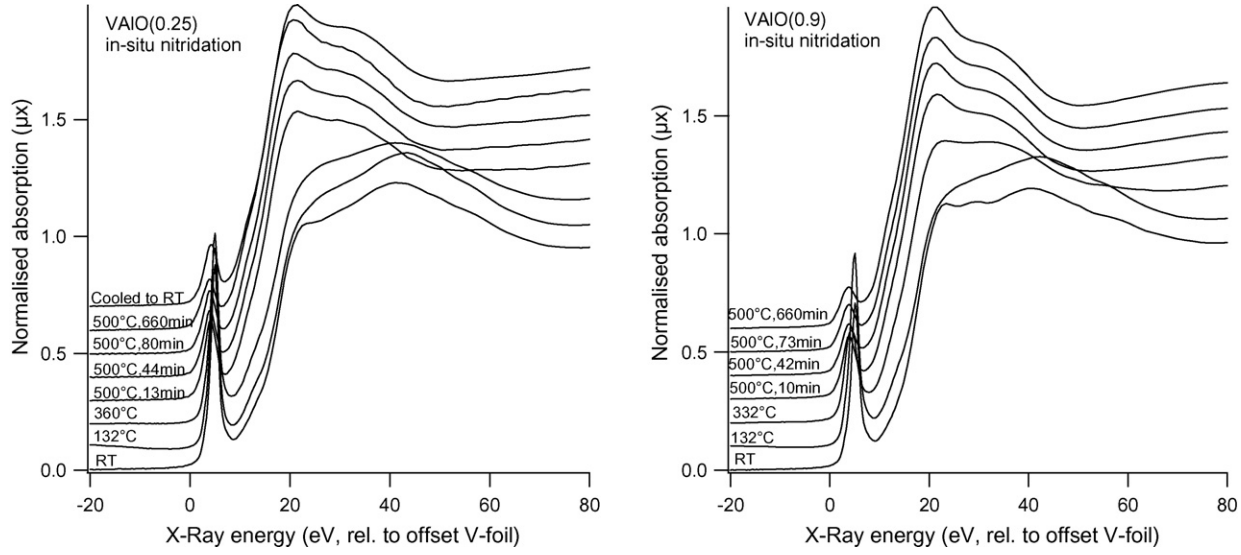


Fig. 6. V K-edge XANES spectra for VAlO(0.25) (left) and VAlO(0.9) (right) during heating in 5% $NH_3$/He and at 500 °C after different nitridation times. Temperatures and relevant times when each spectrum was started are indicated.

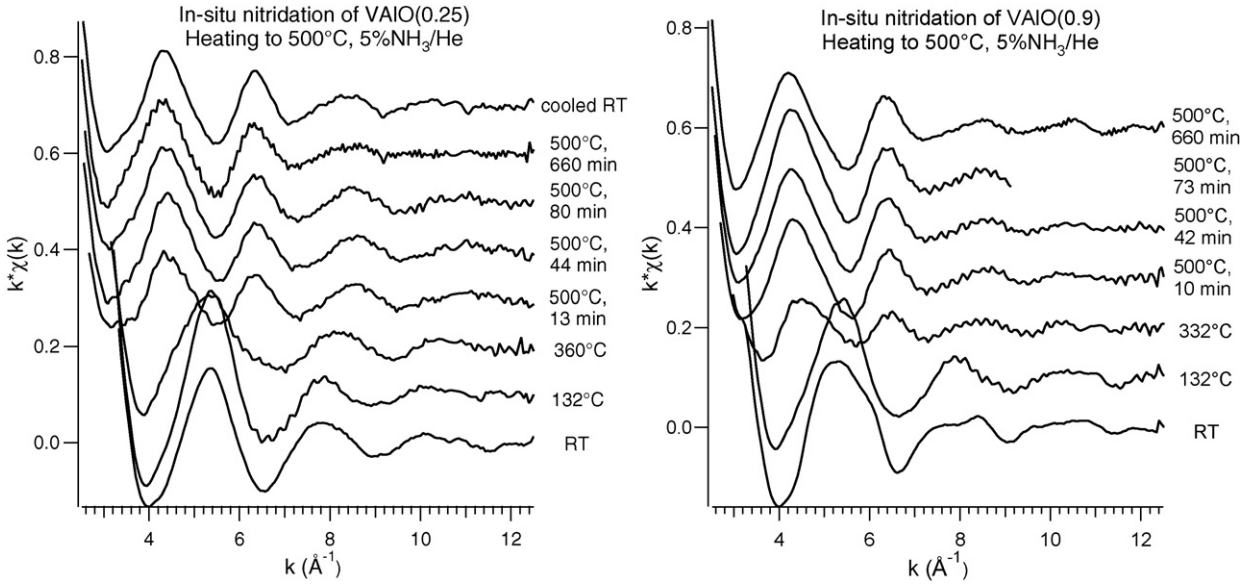


Fig. 7. V K-edge EXAFS spectra ($k^1 \times \chi(k)$) for VAlO(0.25) (left) and VAlO(0.9) (right) during heating in 5% $NH_3$/He. Temperatures and/or times when each spectrum was started are indicated.

this temperature for up to 10 h. The V K-edge XANES spectra taken during heating and isothermal at 500 °C, after different nitridation times for VAlO(0.25) and VAlO(0.9), are given in Fig. 6. These XANES spectra show that the pre-edge peak intensity diminishes strongly during nitridation. This indicates a transfer from a tetrahedral to an octahedral co-ordinated environment. The structural changes already begin during the initial heating and are nearly completed after 13 min at 500 °C. The in situ nitrided samples can be seen as fully nitrided VAlON catalysts. The XANES spectra now resemble more that of the VN reference sample rather than the $NH_4VO_3$. The position of the main-edge decreases during nitridation (Table 2), the estimated valence based on the relationship from Fig. 2 is 4.9+.

The EXAFS spectra during the nitridation of the VAlO(0.25) and VAlO(0.9) are given in Fig. 7. Identical spectra are eventually obtained for the two samples. EXAFS fits for the VAlO(0.25) after full nitridation and cooling to RT were performed. Based upon these results, the predicted model for the vanadium-environment is an octahedral co-ordination with one vanadyl V=O or V=N(H) bond at 1.68 Å, four V–O or V–N bonds at 1.96 Å and a sixth neighbour at 2.52 Å. The details of the fit are given in Fig. 8 and Table 3. The ligands in the octahedron are O or N. As the two atoms are neighbouring elements in the Periodic Table, they have similar X-ray scattering properties, which makes it difficult to differentiate between N and O in this case. The nature of the nitrogen-containing species (–$NH_2$, –NH– or –N<) bonded to vanadium atoms is not known at this stage.

### 3.4. The V-structure in different VAlON(0.25) catalysts

Fig. 9 shows the XANES spectra for three VAlON(0.25) catalysts obtained during the nitridation reaction in $NH_3/O_2/C_3H_8$ originating from oxide precursors dried at different temperatures (60, 120 or 500 °C). The features in these XANES spectra are between the positions observed in the spectra for the VAlO(0.25) oxide precursor and the fully nitrided VAlON(0.25,

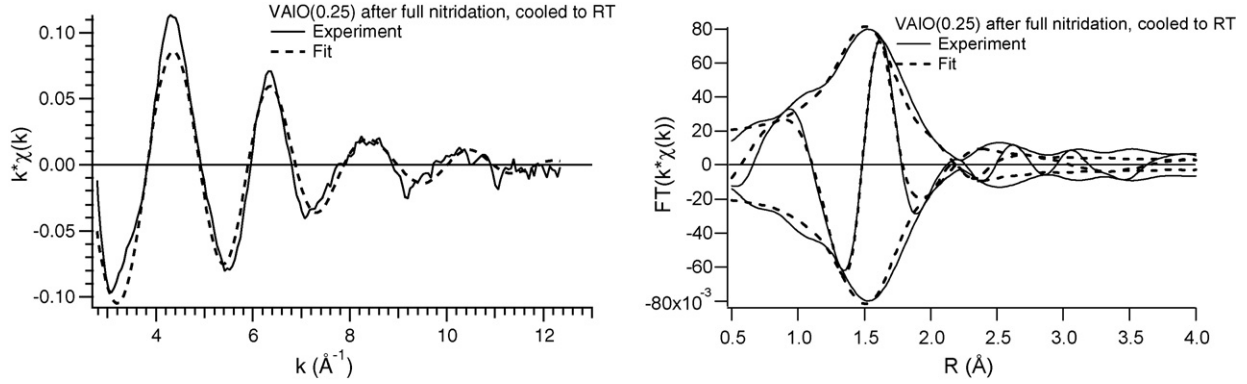


Fig. 8. Experimental (solid line) and fit (dashed line) $k^1 \times \chi(k)$ (left) and FT[$k^1 \times \chi(k)$] spectra (right) for VAlON(0.25; 60 °C; 5% $NH_3$/He) after 10 h at 500 °C in 5% $NH_3$/He and subsequent cooling to RT.

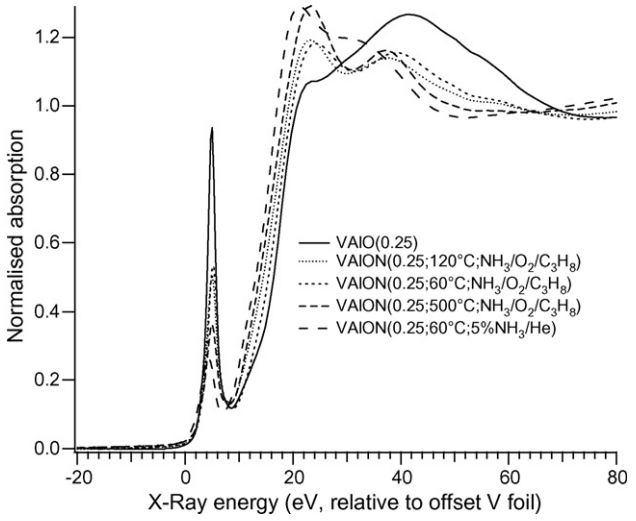


Fig. 9. V K-edge XANES spectra for different VAlON(0.25) catalysts compared with the oxide precursor VAlO(0.25) and the fully nitrided VAlON(0.25; 60 °C; 5% $NH_3$/He).

60 °C; 5% $NH_3$/He), which are added for comparison. The 'pre-edge' peak intensity, for example, decreases in the following order: oxide precursor > 120 °C > 60 °C > 500 °C > fully nitrided. Moreover, the EXAFS spectra can be seen as a linear combination of the EXAFS signals for the oxide precursor and the fully nitrided catalyst (see Fig. 10). The percentages indicate the relative contribution of the fully nitrided spectrum to the total spectrum.

## 4. Discussion

### 4.1. Catalytic properties of VAlO catalysts for propane ammoxidation

The catalytic properties of ''VAlO'' catalysts can be strongly influenced by the preparation conditions [1]. Optimal catalytic activity was reached at 500 °C, using a VAlO precursor prepared at pH 5.5, with a V/Al ratio equal to 0.25 [5]. The drying or calcination temperature of the VAlO precursor prior to the test also influences the acrylonitrile yield obtained when the process has reached a steady-state. Catalytic results, taken from Ref. [3] are reproduced in Table 4.

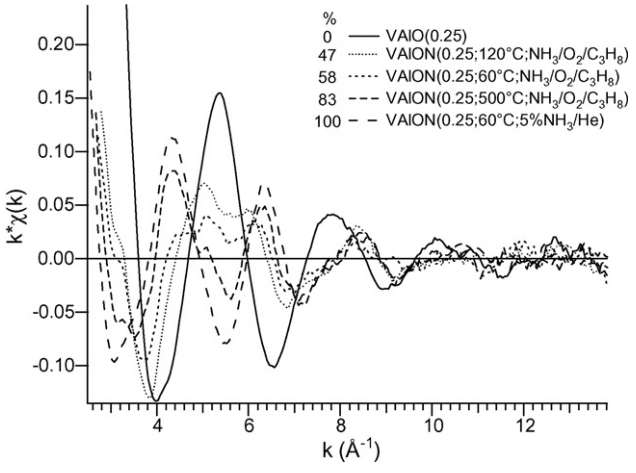


Fig. 10. V K-edge EXAFS spectra ($k^1 \times \chi(k)$) for different VAlON(0.25) catalysts. Spectra can be seen as a linear combination of the oxide precursor VAlO(0.25) and the fully nitrided VAlON(0.25; 60 °C; 5% $NH_3$/He) spectra. The percentages give the contribution of the fully nitrided sample.

Table 4
Catalytic results obtained at steady-state during propane ammoxidation over a VAlO(0.25) catalyst dried at 60 and 120 °C, as well as on one sample calcined at 500 °C (reaction temperature: 500 °C; $NH_3/O_2/C_3H_8$:1/3/1.25; GHSV = 16.8 l/g h)

| Sample | Propane conversion (%) | ACN selectivity (%) | ACN yield (%) |
|---|---|---|---|
| VAlON(0.25; 120 °C; $NH_3/O_2/C_3H_8$) | 59 | 46 | 27 |
| VAlON(0.25; 60 °C; $NH_3/O_2/C_3H_8$) | 61 | 57 | 35 |
| VAlON(0.25; 500 °C; $NH_3/O_2/C_3H_8$) | 56 | 38 | 21 |

During the 12 h activation period, the selectivity to acrylonitrile increases considerably, while the selectivity to acetonitrile (AcCN) and $CO_x$ decreases. Post mortem physico-chemical characterisations performed on the samples revealed that ammonia served as a reagent, thus enabling thermal nitridation of the VAlO precursor. The chemical analysis performed on the catalysts after 12 h of test indicated the incorporation of 3–5 wt.% nitrogen in the network. This amount remains constant once the steady-state is reached.

The participation of nitrogen, incorporated in the network, to the propane ammoxidation reaction was demonstrated recently using a transient analysis technique at low pressure [13]. Single pulses of propane were injected into a micro-reactor at 500 °C in order to react with a nitrided VAlON. The different compounds leaving the reactor were identified by mass spectrometry. The transformation of propane to acrylonitrile over VAlON, in the absence of any gaseous oxygen and ammonia, demonstrated the participation of the lattice nitrogen in the N-incorporation step.

### 4.2. Contribution of the present XAS study to the understanding of the VAlON catalytic activity

XAS spectroscopy was performed to study specifically the structural and electronic changes undergone by the vanadium atoms during nitrogen incorporation in the network. Two nitridation procedures were examined: with pure ammonia (in situ nitridation), or under a mixture of oxygen, ammonia and propane (post-test catalysts).

Nitrogen incorporation in the vanadium-aluminium oxide network changes the co-ordination of the vanadium atoms considerably, alters the chemical nature of the first ligands, and slightly reduces the vanadium oxidation state. Those modifications could explain the increase in time of the acrylonitrile yield during the catalytic process.

Changing the nitridation conditions influences the rate and the importance of the structural changes undergone by the vanadium species. The changes are more important and occur

more rapidly when using ammonia in helium than a mixture oxygen/ammonia/propane.

### 4.3. In situ nitridation

XAS analysis showed that vanadium atoms in two VAlO oxide precursors with different V/Al ratios (0.25 and 0.90) have a tetrahedral ''$VO_4$'' co-ordination, similar to their state in the $NH_4VO_3$ salt used for synthesis. In this structure, two V=O vanadyl pairs have an interdistance of 1.67 Å and two other V–O bonds have a length of 1.81 Å. During heating to 500 °C under 5% $NH_3$/He flow, the tetrahedral V co-ordination changes to an octahedral one. The resemblance of the XANES spectrum of the fully nitrided VAlON obtained after 10 h of nitridation to that of VN is larger than that of the starting $NH_4VO_3$ salt (Fig. 1).

It is well known that the substitution of oxygen atoms by nitrogen atoms in the first co-ordination sphere of transition metals, like vanadium, has a great influence on their chemical reactivities and hence on their catalytic properties [14,15].

It has been demonstrated in many studies that the catalytic properties of transition metal nitrides are similar to those of Pt-group metals (Pt, Pd, Ir, Rh and Ru). This is particularly true in catalytic reactions involving the transformation of C–H bonds to hydrocarbons, such as dehydrogenation, hydrogenation, hydrogenolysis and isomerisation reactions [16]. The activation of propane for ammoxidation necessitates the breaking of a carbon–hydrogen bond in the molecule. A partial substitution of oxygen by nitrogen in the first co-ordination sphere of vanadium atoms in VAlON could lead to structural and electronic modifications decreasing the activation energy of this reaction rate-limiting C–H bond activation step. The ''noble metal character of VAlON'' has already been used as hypothesis to explain that hydrogen transfer reactions were possible over VAlON catalysts during butan-1-ol dehydration/dehydrogenation reactions [14]. Our XAS study provides clear evidence that the electronic and structural properties of vanadium atoms in VAlON are affected by nitridation.

### 4.4. Post-mortem catalysts

When nitridation occurs under a mixture of propane, oxygen and ammonia (aged catalysts), we observe the same electronic and structural changes around vanadium atoms compared to those observed during ''in situ'' nitridation under pure ammonia, although to a smaller extent (Figs. 9 and 10). The EXAFS spectra of these aged catalysts can be seen as a linear combination of the spectra for the oxide precursor and the fully ''in situ'' nitrided catalyst (Fig. 10). The contribution of the fully nitrided spectrum to the signal depends on the drying (60 or 120 °C) or calcination (500 °C) temperature of the VAlO prior to the catalytic test as follows: 47% (drying temperature 120 °C) < 58% (drying temperature 60 °C) < 83% (calcination at 500 °C). However, there is no direct correlation between the catalytic activity (Table 4) and the importance of the electronic and structural changes induced by nitridation around vanadium atoms.

It should be underlined that XAS spectroscopy does not allow discriminating surface and bulk vanadium species, while the catalytic activity is mainly dependent on the catalyst surface properties. Most likely, another factor like for instance the catalyst superficial acido-basicity, also determines the activity of the samples. Indeed, many studies underline the important role of this factor for alkane ammoxidation (see for instance [17]), while others mention that nitrogen incorporation in mixed vanadium-aluminium amorphous oxides can lead to modified acid–base properties [15]. However, a confirmation of this interpretation could require further experimental evidence.

## 5. Conclusions

The local vanadium structure in mixed vanadium aluminium oxides (VAlO) powder catalysts used for propane ammoxidation was studied with V K-edge X-ray absorption spectroscopy. A tetrahedral vanadium co-ordination was found for the VAlO oxide precursors with a V/Al ratio of 0.25 and 0.90. The EXAFS analysis suggested two V=O vanadyl bonds with a length of 1.67 Å and two V–O bonds of 1.81 Å. The structural changes in the vanadium co-ordination for these two oxide precursors during nitridation in 5% $NH_3$/He was followed by in situ XAS. A distorted octahedron is observed for the fully nitrided catalysts and the vanadium oxidation state decreased slightly.

The VAlON catalysts studied ex situ after catalytic test in $NH_3/O_2/C_3H_8$ consist of a mixture of the octahedra found in the fully nitrited catalyst and the precursor tetrahedra. The degree of the change in the vanadium structure during the catalytic tests depends on the way the precursor was dried or calcined. The best catalytic results were obtained using a VAlO dried at 60 °C prior to the test. The contribution of the fully nitrided EXAFS spectrum to the spectrum of this post-test catalyst is equal to 58%, which may correspond to an optimum between the structural/electronic properties of vanadium atoms and the catalyst acid–base properties.

## Acknowledgements

The authors thank Ing. Nico De Roo (Department of Solid State Sciences, Surface Physics Division, Ghent University) for the development of the ''in situ'' XAS cell. They are grateful to Ing. Pierre Eloy and Ing. Fabrice Bertinchamp (Unité de Catalyse et Chimie des Matériaux Divisés, Université Catholique de Louvain) for the help provided in the recording of the XAS spectra, as well as all the DUBBLE staff.

They would also like to thank the Fonds National de la Recherche Scientifique (FNRS) for the fellowships awarded to Dr. Stéphanie Delsarte and the Fund for Scientific Research - Flanders (FWO-Vlaanderen) for making access available to the DUBBLE facility.

This work was supported by the Fund for Scientific Research – Flanders (FWO-Vlaanderen) and the Belgian Programme on Interuniversity Poles of Attraction initiated by the Belgian State, Prime Minister's Office, Science Policy Programming (IUAP-V/03). Its authors assume the scientific responsibility.

## References

[1] R.P. Silvy, M. Florea, N. Blangenois, P. Grange, AIChE J. 49 (8) (2003) 2228–2231.
[2] M. Florea, R. Prada Silvy, P. Grange, Silicates Ind. 69 (5–6) (2004) 53–59.
[3] M. Florea, Ph.D. Thesis, Université Catholique de Louvain, Belgium, 2003.
[4] R. Prada Silvy, N. Blangenois, M. Florea, L. Cadus, B. Barbero, P. Grange, Silicates Ind. 69 (5–6) (2004) 85–90.
[5] M. Florea, R. Prada Silvy, P. Grange, Appl. Catal. A 255 (2003) 289–300.
[6] M. Vaarkamp, J.C. Linders, D.C. Koningsberger, Physica B 208 and 209 (1995) 159–160.
[7] M. Vaarkamp, I. Dring, R.J. Oldman, E.A. Stern, D.C. Koningsberger, Phys. Rev. B 50 (1994) 7872–7883.
[8] J.W. Cook Jr., D.E. Sayers, J. Appl. Phys. 52 (1994) 5024–5031.
[9] D.C. Koningsberger, B.L. Mojet, G.E. van Dorsen, D.E. Ramaker, Top. Catal. 10 (2000) 143–155.
[10] E. Keller, F.M.F. de Groot, D.C. Koningsberger, B.M. Weckhuysen, J. Phys. Chem. B 109 (2005) 10223–10233.
[11] A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, Phys. Rev. B 58 (1998) 7565–7576.
[12] J. Wong, F.W. Lytle, R.P. Messmer, D.H. Maylotte, Phys. Rev. B 30 (1984) 5596–5610.
[13] M. Olea, M. Florea, I. Sack, R. Prada Silvy, E.M. Gaigneaux, G.B. Marin, P. Grange, J. Catal. 232 (2005) 152–160.
[14] H. Wiame, Ph.D.Thesis, Université Catholique de Louvain, Belgium, 2003.
[15] H. Wiame, C. Cellier, P. Grange, J. Catal. 190 (2000) 406–418.
[16] J.G. Chen, J. Eng Jr., S.P. Kelty, Catal. Today 43 (1998) 147–158.
[17] V.D. Sokolovskii, A.A. Davydov, O.Yu. Ovsitser, Catal. Rev. Sci. Eng. 37 (3) (1995) 425–459.