Evidence for the participation of lattice nitrogen from vanadium aluminum oxynitrides in propane ammoxidation

M. Olea [a], M. Florea [b], I. Sack [a], R. Prada Silvy [b], E.M. Gaigneaux [b,*], G.B. Marin [a], P. Grange [b]

[a] *Laboratorium voor Petrochemische Techniek, Department of Chemical Engineering, Ghent University, Krijgslaan 281-S5, B-9000 Ghent, Belgium*
[b] *Unité de catalyse et chimie des matériaux divisés, Catholic University of Louvain, Croix du Sud 2/17, B-1348, Louvain-la-Neuve, Belgium*

Abstract

The participation of the nitrogen from the lattice of a series of vanadium aluminum oxynitride catalysts (VAlONs) during propane ammoxidation to acrylonitrile was made evident by temporal analysis of products (TAP) at 773 K in the absence of NH_3 and O_2. Moreover, the influence of the presence of gaseous oxygen and/or gaseous ammonia on the catalytic performance of this new catalytic material was studied. Propane conversion increases in the presence of O_2, but it is not affected by NH_3. Propene and acrolein are also formed from propane in the absence of O_2 and are intermediates towards acrylonitrile. In the absence of NH_3 and O_2, the acrylonitrile yield increases with nitrogen content for the same V/Al ratio and decreases with increasing V/Al ratio at constant nitrogen content. Propene yield decreases with nitrogen content and with increasing V/Al ratio. Almost no influence of either nitrogen content or V/Al ratio on the CO_2 yield is observed. The presence of oxygen increases the CO_2 yield at the expense of acrylonitrile and, even more so, of propene. Ammonia does not influence the product distribution in the absence of O_2. The amount of acrolein formed is almost constant, regardless of nitrogen content, V/Al ratio, and reactant mixture, but vanishes when mixed oxides rather then oxynitrides are used. Single-pulse experiments performed with labeled ammonia confirmed the participation of lattice nitrogen in the ammoxidation.

1. Introduction

The direct conversion of alkanes to high-value products for the chemical industry constitutes an arduous and stimulating scientific and technological challenge. Among the most significant industrial applications in this field is the production of acrylonitrile (ACN) through the propane ammoxidation process. This chemical intermediate is used extensively in the production of nitriles, acrylic fibers, resins, rubbers, and other specialized substances. However, until now, about 95% of worldwide ACN production, which is estimated to about 5 million metric tons per year, is obtained through the propene ammoxidation process [1].

The idea of replacing olefins with alkanes in the ammoxidation process dates back to the early 1970s. The advantages are essentially (i) the price of propane as a raw material is about 50–65% lower than that of propene (PE); (ii) the lower risk of a propene shortage due to its increasing consumption in polymerization processes; and (iii) the increasing worldwide demand for ACN, plastics, synthetic fibers, and other derived products.

However, two fundamental problems arise in the transformation of alkanes: (i) alkane activation is more difficult, requiring severe operating conditions and very active, selective, and stable catalysts; and (ii) reaction products are generally less stable than the reactants, such that they can be decomposed during the reaction, leading to the formation of undesirable oxygenated compounds, such as acrylamide, acrylic acid, carbon and nitrogen oxides, etc.

To surpass the first problem, many catalysts have been proposed. According to the literature, they can be classified into two main categories: (i) vanadium-antimonates, $VSb_xM_yO_z$, where M is elements used as promoters, such as W, Te, Nb, Sn, Bi, Al, and Ti [2,3]; and (ii) vanadium-molybdates, $VMo_xM_yO_z$, where M is most often Bi or Te [4]. Other catalytic systems based on Ga–Sb oxides modified with W, Ni, or P and vanadyl pyrophosphates [5,6] were studied, but they were not so promising for the ammoxidation of alkanes, especially of propane.

A promising new catalytic material consists of vanadium aluminum oxynitrides. VAlONs are obtained by partial substitution of nitrogen for oxygen in the structure of the V–Al mixed oxides during a nitridation process [7]. These materials are amorphous and behave as bifunctional catalysts. Their active sites are essentially made up of redox sites (V^{n+}) and basic sites (NH_x^-, NH_4^+, N^{3-}) with different strength distributions. It was found that the catalytic performances in propane ammoxidation of these new materials strongly depend on the V/Al ratio, coprecipitation pH, V concentration in the solution, and the nitridation protocol (temperature, nitridation mixture, time) [8,9]. The VAlON system shows a propane conversion of 55% and an acrylonitrile selectivity of 60% in steady-state conditions for a V/Al of 0.25 prepared at pH 5.5 and a V concentration in solution of 0.020 mol/l.

Despite this promising behavior, the selectivity of VAlONs for acrylonitrile from propane is still lower than that obtained with propene. Therefore, further improvement of the catalyst formulation is necessary. To realize this objective, knowledge of the details of the reaction mechanism and the nature of the active sites can be very helpful. Until now many conflicting mechanisms have been proposed for ammoxidation catalysts, involving different intermediates. On $VSb_xM_yO_z$ catalysts, ACN formation is suggested to occur sequentially via propene and acrolein (ACO) as intermediates [10–12]. For the $(VO)_2P_2O_7$ catalysts, Centi and Perathoner [13] proposed the formation of propylamine or acrylate species as intermediates. Direct propane-to-ACN transformation was observed with the use of vanadium aluminum oxynitride catalysts [8].

However, the most controversial aspect was the nature of the N-insertion species. Data from the literature indicate that different nitrogen species are active in ammoxidation, depending on the nature of the catalyst. NH_2^- groups are reported to be active in nitrogen insertion on Ga–Sb oxides [14], and NH_4^+, NH_{3ads}, NH_2^-, and NH groups are suggested to be active on vanadyl pyrophosphate [5]. NH_{3ads} and NH_4^+ have been suggested by Zanthoff et al. [15] as the N species to be inserted, and amido- and imido-like species have been proposed by Centi and Perathoner [13]. Martin et al. [16] reported isotopic pulse experiments indicating the participation of ammonium ions in the N-insertion step during benzonitrile formation from toluene over alpha-$(^{14}NH_4)_2[(VO)_3(P_2O_7)_2]$.

The aim of this study is to investigate the role of ammonia and oxygen in the reaction mechanism of the ammoxidation of propane on VAlONs. Labeled ammonia, $^{15}NH_3$, was used to distinguish between adsorbed ammonia and lattice nitrogen. The influence of the V/Al ratio and nitrogen content on catalytic performance was investigated. A transient technique at low pressure, temporal analysis of products (TAP) [17], was used to minimize the influence of homogeneous gas-phase reactions, which are well known to influence ammoxidation pathways [1].

2. Experimental

2.1. Catalyst preparation

V–Al oxide precursors with two different V/Al ratios were prepared by coprecipitation of aluminum nitrate and ammonium meta-vanadate solutions at a pH of 5.5, constant vanadium concentration (0.062 M), and variable aluminum concentration (0.250 M for V/Al ratio = 0.25, and 0.083 M for V/Al ratio = 0.7). These two samples are referred to here as VAlO025 and VAlO07. The ammonium meta-vanadate salt was dissolved in hot water (333 K) with stirring, and then nitric acid was added progressively to reach a final pH of 3.0. Subsequently, the aluminum nitrate solution was added to the vanadium solution. The resulting solution was red-orange, and the final pH was 2.5. A solution containing ammonium hydroxide (10% v/v) was added progressively to the V–Al solution until a final pH of 5.5 was reached. After 1 h, a pH between 2.8 and 3.0 was reached and a deep yellow precipitate was formed. The slurry was subsequently filtered, and the solid was washed several times with hot water to remove nitrates and ammonia ions before drying at 333 K overnight. The nitridation of a batch amorphous non-calcined vanadium aluminum oxide precursor was carried out in a tubular rotating reactor under a flow of pure ammonia (30 Nl/h) for 5 h, either at 673 K or at 773 K. The batch was cooled to room temperature under a flow of pure nitrogen. The degree of nitridation and the nature and bulk and surface distribution of the nitrogen species were strongly influenced by the V/Al ratio [18].

The samples tested in the present work were one oxide precursor, VAlO025, and the following oxynitrides: VAlON07773, VAlON025773, and VAlON025673, all nitridated ex situ at 773 and 673 K, respectively; VAlO025 nitridated in situ during the TAP experiments at 773 K; and VAlON025773 equilibrated catalyst (i.e., kept for 15 h at 773 K in a flow of $C_3H_8/O_2/NH_3$ (= 1.25:3:1) at GHSV = 16.8 Nl/(g h), which corresponds to a space time of 4.48 kg/(mol s)).

2.2. TAP setup and procedure

The experiments were carried out in an original TAP setup [17]. The TAP reactor consists of three vacuum cham-

bers in line. The first chamber is the reactor chamber, which contains a micro-reactor in quartz, 45 mm long and 5 mm in diameter. The entrance of this reactor is connected via a small inlet volume with two high-speed pulse valves and two continuous-feed valves. The pulse time is less than 110 µs. The background pressure in the reactor chamber is about 10^{-4} to 10^{-5} Pa and consists mainly of N_2 and H_2O. The second chamber is the differential chamber. This chamber also acts as a pre-vacuum chamber for the analysis chamber. The pressure in the differential chamber is about 10^{-6} Pa. The responses of the reactant and of the products at the exit of the reactor are measured with a UTI 100C quadrupole mass spectrometer located in the analysis chamber. The pressure in the analysis chamber is 10^{-7} Pa. This ensures that the signal detected with the mass spectrometer is proportional to the flow at the outlet of the reactor. The time resolution at which the evolution of the flow at the outlet of the reactor can be measured is far less than 1 ms.

The TAP strategy is to operate in the Knudsen diffusion regime, in which transport is well defined and the outlet pulse shape is independent of pulse intensity. Before we carried out the experiments over the VAlON catalysts, experiments over an inert bed consisting of quartz particles were performed to calibrate the mass spectrometer and to verify the Knudsen regime. An input pulse intensity of approximately 8×10^{14} molecules/pulse was used. For each experiment, the mass of catalyst loaded to the micro-reactor was adapted as a function of the BET specific surface area to have the same surface area of 10.5 m². Moreover, the catalyst, packed between two layers of quartz, was diluted with quartz in a 1:1 weight ratio, to maintain isothermal conditions. The catalyst particle size and the quartz particle size were in the range of 250–500 µm. The number of reactant molecules in a pulse was at least 10^5 times smaller than the number of active sites in the reactor.

Two types of TAP experiments were performed at 773 K over the tested samples: single-pulse experiments and alternating pulse experiments. To increase the signal-to-noise ratio in the response, a train of 25 reactant pulses was injected into the reactor, and the average was taken for each atomic mass unit (AMU).

Alternating pulse experiments were performed to examine the influence of short-lived catalyst surface species on the reaction. Therefore, a pulse of pure oxygen or ammonia (5%) in helium was alternated with a pulse of pure propane (or vice versa), and the time interval between the two pulses was varied from 0.03 to 0.1 s.

The catalyst was charged to the micro-reactor, which was subsequently evacuated and heated to the reaction temperature at a rate of 5 K/min. During the heating, the desorption of water, ammonia, and small amounts of NO and N_2O from the catalyst surface could be observed in the case of oxynitride catalysts. In the case of VAlO025 only water and a small amount of ammonia and nitrogen were observed. The latter is attributed to the use of ammonium meta-vanadate during the catalyst preparation.

For mass spectroscopic identification of the different compounds leaving the TAP reactor, the following AMUs were chosen, based on sensitivity and specificity for each component: 14 for dinitrogen, 16 for nitrous oxide, 17 for ammonia, 18 for water, 30 for nitrogen oxide, 32 for oxygen, 41 for propene, 43 for propane, 44 for carbon dioxide, 46 for nitrogen dioxide, 53 for acrylonitrile, and 56 for acrolein. The fragmentation patterns for propane, propene, and CO_2 were experimentally determined, whereas for the others, data were taken from the literature to calculate the contribution of different compounds to a measured AMU signal and to analyze the experimental data.

For a quantitative interpretation of the pulse responses, the absolute calibration factors of propane, propene, Ar, O_2, CO_2, and NH_3 were experimentally determined. Calibration factors for acrolein and acrylonitrile were taken to be equal to that of propane. For all inorganic N compounds calibration factors were taken to be equal to that of NH_3. For each experiment, the conversion and yields were calculated according to the following equations:

$$X_{C_3H_8} = \frac{n_{in,C_3H_8} - n_{out,C_3H_8}}{n_{in,C_3H_8}}, \tag{1}$$

$$Y_i = \frac{n_{out,i}}{n_{in,C_3H_8}}, \tag{2}$$

where n is the total number of moles (mol), X is the conversion (mol/mol), and Y_i is the yield for component i (mol/mol). The subscript "in" means introduced into the reactor, and the subscript "out" means detected at the reactor outlet.

Further details on the reaction conditions of the experiments are given in Section 3.

2.3. Catalyst characterization

The VAlON catalysts were extensively characterized by surface area measurement, XPS, XRD, DRIFT, Raman spectroscopy, and TPR [8,9,18].

Specific surface area measurements were performed on a Micromeritics Flow Sorb II 2300 with the single-point ($p/p_0 = 0.3$) method. The XPS spectra were recorded at room temperature under a vacuum of 1.33 mPa on a SSX-100 model 206 Surface Science Instrument spectrometer with monochromatized Al-K_α radiation. An X-ray diffractometer (Kristalloflex Siemens D5000) with Cu-K_α radiation was used to obtain XRD patterns for the catalyst in the 2θ range of 2°–65°, with a scan step size of 0.03°. IR investigations were performed in a DRIFTS configuration with a Brucker IF S88 spectrometer equipped with a DTGS detector and a commercial chamber Spectra-Tech 0030-103. The spectra were recorded (200 scans) in the 4000–400 cm^{-1} range with 4 cm^{-1} resolution. Raman spectroscopy was performed with a Dilor–Jobin Yvon–Spex spectrometer, interfaced with an optical microscope (Olympus DX-40) and equipped with a He–Ne ($\lambda = 632.8$ nm) laser. The spectra

were recorded in the 200–1600 cm^{-1} range. The redox behavior of the catalyst was investigated by a TPR technique with a ChemBET 3000 (Quanta Chrome Corporation) equipment.

The total nitrogen content (N_T) was determined with the Grekov method. The superficial nitrogen species (N_S) were quantified by the Kjeldahl method. A detailed description of these two methods can be found in [19].

3. Results

The vanadium aluminum oxide precursors are totally amorphous according to XRD and have a BET surface area of 225 m^2/g in the case of VAlO07 and 250 m^2/g for VAlO025. After the nitridation process, the surface area of the solids decreased by 40%. The BET specific surface area, total nitrogen, and surface nitrogen content after nitridation are presented in Table 1.

Before each experiment, we pretreated non-nitridated catalysts by pulsing oxygen at reaction temperature to create a completely oxidized state.

No influence on the catalytic activity was found when the catalysts were kept for one night under vacuum.

3.1. Interaction of propane with the VAlO025 precursor

The results of single-pulse experiments with a C_3H_8/Ar = 2:1 reaction mixture are shown in Fig. 1. Propene, CO_2, and water were observed as reaction products. No acrolein was observed. The response of water was very broad and therefore could not be quantified on the time scale of this

experiment. However, the formation of water was shown by a comparison of the background scan taken before and after the single-pulse experiment. The propane conversion amounted to 44%. The mean residence times of the products increase in the following order: nonconverted propane < propene < CO_2. Based on this, one can assume that CO_2 either desorbs more slowly than propene or is formed consecutively. The order of the peaks' appearance was the same: the time of peak maximum was 0.024 s for propane, 0.029 s for propene, and 0.031 s for CO_2. The propene curve decayed more rapidly than the CO_2 curve. This is an indication of the conversion of propene to CO_2, but the direct formation from propane cannot be ruled out. The relative importance of the two CO_2 formation pathways was studied with alternating pulse experiments. Oxygen was pulsed first, followed by a pulse of propane after a time interval of 0.5 s to study the interaction of the gaseous propane with preadsorbed oxygen.

Table 1
Some characteristics of the investigated catalysts

Catalysts	V/Al ratio	BET surface area (m^2/g)	N_T[a] (wt%)	N_S[b] (wt%)	XRD
VAlO025	0.25	250	–	–	Amorphous
VAlON07$_{773}$	0.7	122	1.99	0.3	Amorphous
VAlON025$_{773}$	0.25	153	3.15	1.8	Amorphous
VAlON025$_{673}$	0.25	175	2.03	–	Amorphous
VAlON025$_{773}$ equilibrated catalyst	0.25	153	4.04	–	Amorphous
VAlO025 nitridated in situ	0.25	250	1.45 (by interpolation)	–	Amorphous

[a] N_T = total nitrogen content determined by Grekov method.
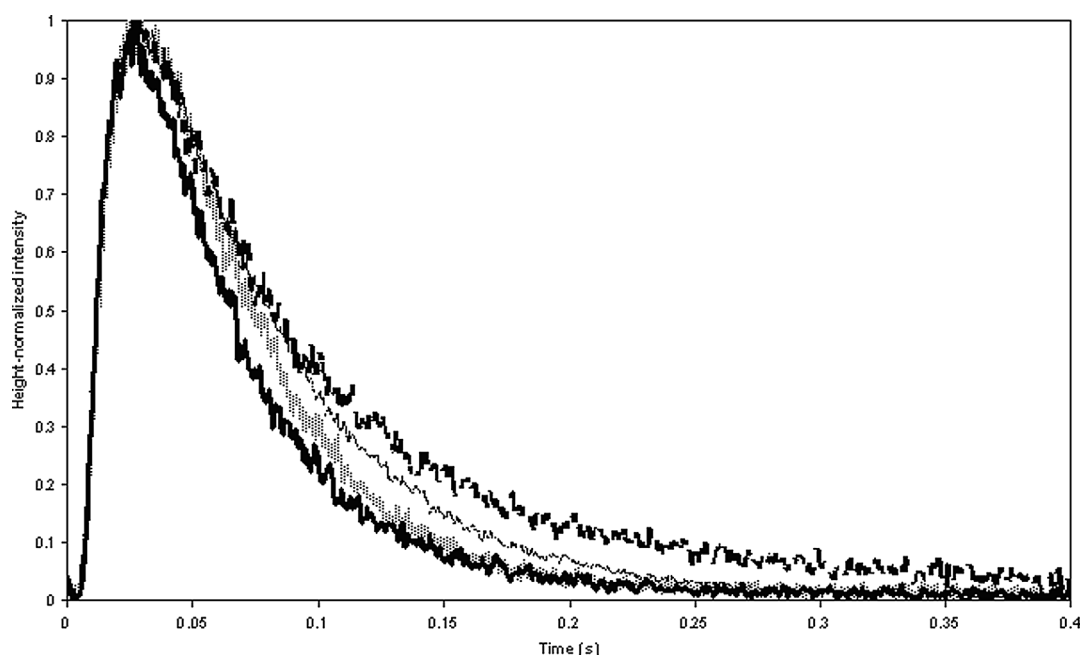[b] N_S = surface nitrogen content determined by Kjeldahl method.

Fig. 1. Height-normalized responses of propane, propene, carbon dioxide and argon as a function of time at 773 K. Single-pulse experiments of propane/Ar = 2/1, over 0.095 g of VAlO025, with a pulse intensity of 8×10^{14} molecules. Propane (—), propene (—), carbon dioxide (- - -), argon (—).
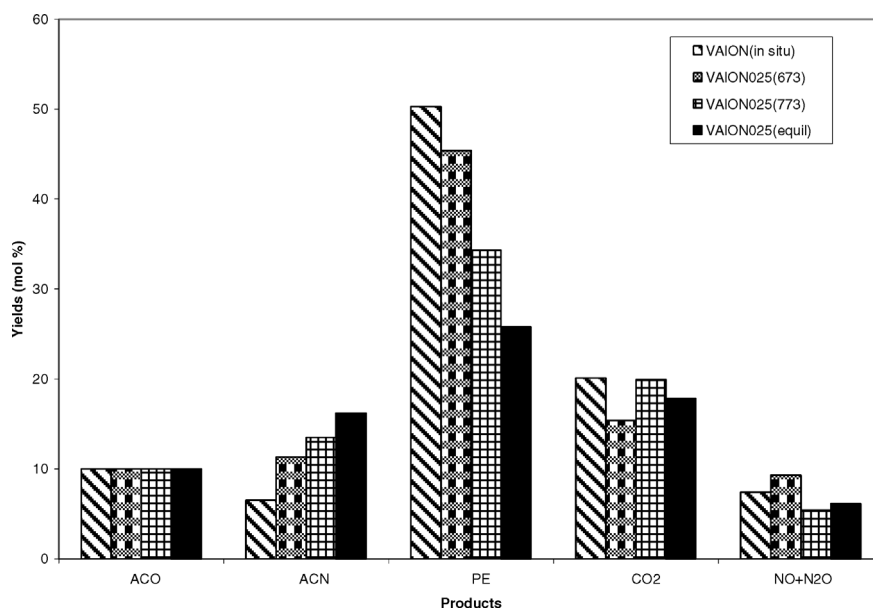
Fig. 2. The influence of the nitrogen content on product yields. Single-pulse experiments of propane/Ar = 2/1, with a pulse intensity of 8×10^{14} molecules.

To study the interaction of gaseous oxygen with preadsorbed propane, we switched the sequence of the two pulses, but the time interval between the two pulses was kept constant. The reaction products were obtained only on the propane pulse regardless of the sequence of the pulses and with a distribution that was independent of the sequence of pulses: propene/CO_2 = 1:2.5. Moreover, the same distribution of reaction products was found during single-pulse experiments with propane. It can be concluded that the oxidative reaction of propane on the VAlO025 precursor does not require adsorbed oxygen species, but proceeds through the involvement of lattice oxygen: a Mars–van Krevelen mechanism is operational. The lifetime of the surface oxygen was less than 0.5 s. No long-lived surface carbonaceous species were deposited during the propane pulse.

3.2. Interaction of propane with the VAlON catalysts

TAP experiments were performed to study the influence of the V/Al ratio and of the nitrogen content on the activity and selectivity of these catalysts toward the ammoxidation of propane.

A C_3H_8/Ar = 2:1 reaction mixture was used for the single-pulse experiments over VAlON catalysts. The propane conversion amounted to 10%, much lower than that obtained over the VAlO025 oxide catalyst. The yields of propene (PE), acrolein (ACO), acrylonitrile (ACN), CO_2, water, and NO + N_2O are shown in Figs. 2 and 3. Whereas the acrolein yield was constant irrespective of the V/Al ratio and nitrogen content, the distribution of the other reaction products varied with the V/Al ratio and nitrogen content. The yield towards acrylonitrile increases with increasing nitrogen content and decreases slightly with increasing V/Al ratio. The propene yield decreases with increasing nitrogen content and

V/Al ratio. Almost no influence of either nitrogen content or V/Al ratio on the CO_2 yield is observed. For all samples the mean residence times of the products increase in the following order: nonconverted propane = PE < CO_2 < ACO = ACN. The formation of acrolein and acrylonitrile in the absence of any gaseous oxygen and ammonia is an indication of the participation of lattice oxygen and nitrogen in the O-insertion step and N-insertion step, respectively.

3.3. Interaction of propane/dioxygen mixture with the VAlON catalysts

Single-pulse experiments with a C_3H_8/O_2 = 1:3 mixture over the oxynitride samples showed similar effects of nitrogen content and V/Al ratio compared with experiments in the absence of dioxygen. Figs. 4 and 5 show that (i) the acrylonitrile formation diminishes slightly and (ii) the production of propene diminishes considerably. The CO_2 production increases strongly with nitrogen content and decreases with the V/Al ratio (not shown). The direct oxidation of propane becomes more important in the presence of dioxygen and at high nitrogen content. In these conditions, the ACO/CO_2 ratio was, for example, 1:5.3 for the VAlON025₇₇₃ equilibrated catalyst, whereas in the absence of dioxygen the ratio was 1:1.8 for the same sample. Alternating pulse experiments in which dioxygen was pulsed first, followed by a propane pulse at different time intervals (Δt = 0.03, 0.05, and 0.1 s), show a maximum of the amount of CO_2 formed at about a Δt = 0.05 s for all samples (Table 2). Moreover, the amount of propene showed a minimum at this time interval (results not shown). This indicates that weakly adsorbed oxygen species are involved in the total oxidation of propane and propene on VAlON. The amount of acrolein decreased
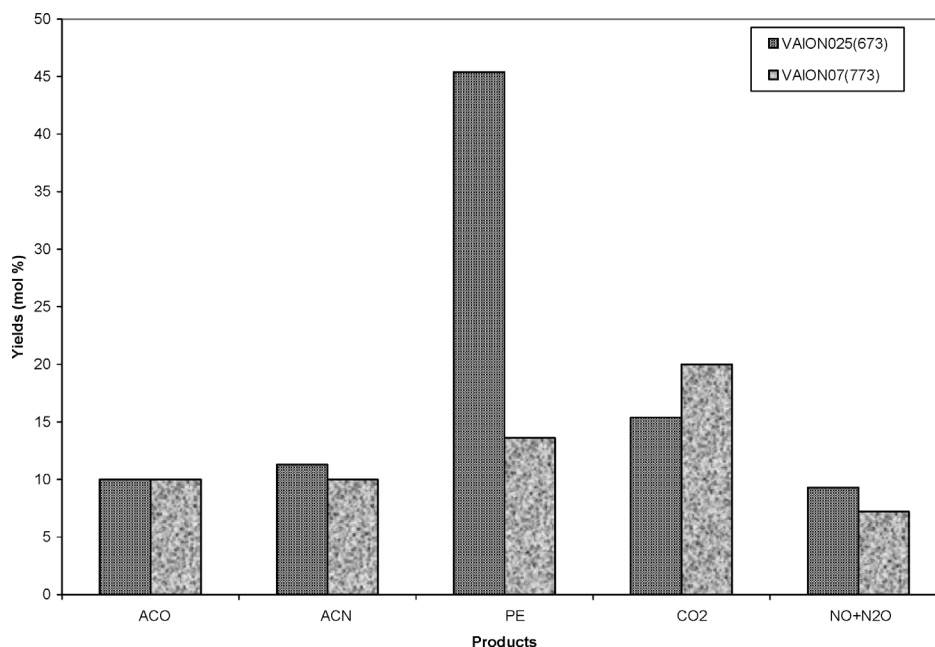
Fig. 3. The influence of V/Al ratio on product yields. Single-pulse experiments of propane/Ar $= 2/1$, with a pulse intensity of 8×10^{14} molecules.
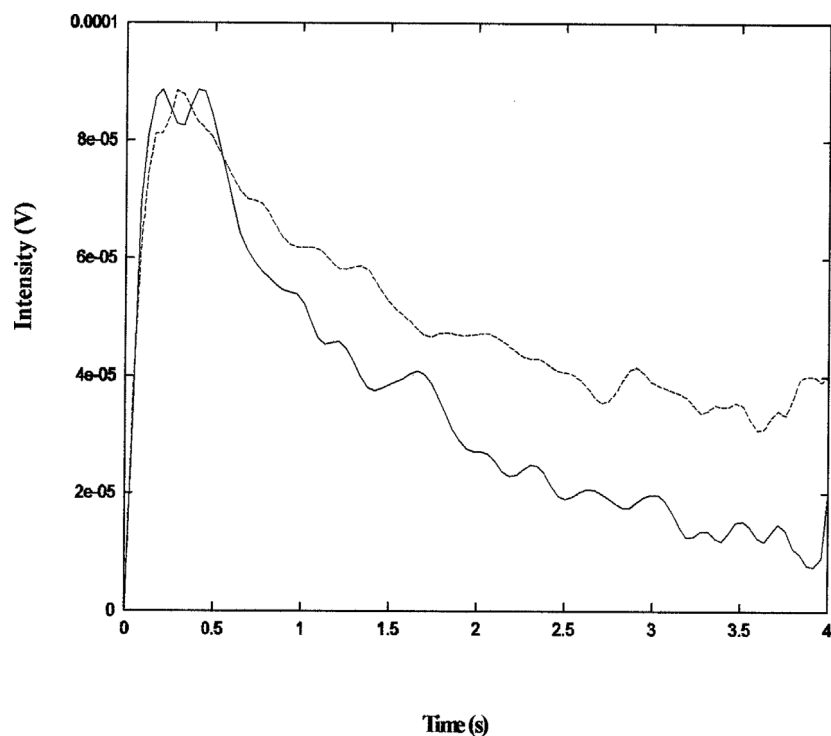

Fig. 4. Acrylonitrile response as a function of time at 773 K. Single-pulse experiments of propane/Ar $= 2/1$ (—), and propane/oxygen $= 1/3$ (- - -) over VAlON025$_{773}$, with a pulse intensity of 8×10^{14} molecules.

with an increasing time interval, suggesting that there also is a direct route from propane to acrolein with weakly adsorbed oxygen participating (results not shown). Dioxygen was totally consumed, and the propane conversion was about 22%. Finally, single-pulse experiments with dioxygen over VAlONs showed that the adsorbed oxygen did not react with lattice nitrogen to form NO and/or N_2O.

3.4. Interaction of propane/ammonia mixture with the VAlON catalysts

In a single-pulse experiment a mixture of propane and ammonia (5%) in helium ($C_3H_8/NH_3/He = 33:1:16$) was pulsed over the oxynitride samples. The product distribution was identical to that obtained with the pulse of propane
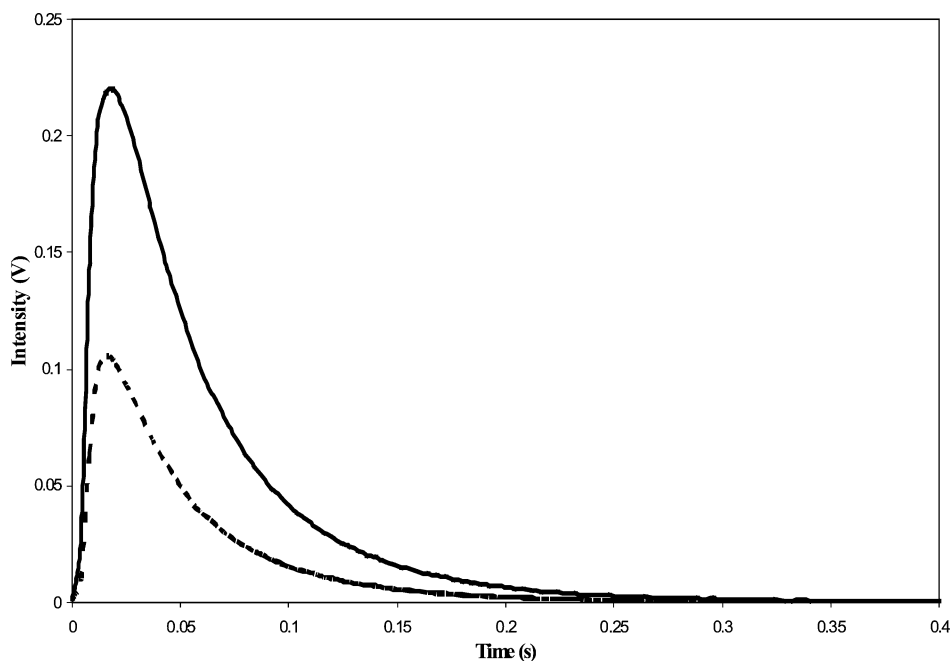
Fig. 5. Propene response as a function of time at 773 K. Single-pulse experiments of propane/Ar = 2/1 (—), and propane/oxygen = 1/3 (- - -), over VAlON025$_{773}$, with a pulse intensity of 8×10^{14} molecules.

Table 2
CO$_2$ yields over investigated catalysts by performing alternating pulse experiments at different time intervals between the successive pulses of oxygen and propane

Catalyst	CO$_2$ yield (a.u.)		
	Time interval (s)		
	0.03	0.05	0.1
VAlON07$_{773}$	0.88	0.89	0.84
VAlON025$_{773}$	2.35	2.80	2.64
VAlON025$_{673}$	0.91	0.93	0.90
VAlON025$_{773}$ equilibrated catalyst	3.20	3.30	3.25
VAlO025 nitridated in situ	0.81	0.90	0.64

alone. In particular the acrylonitrile yield is not dependent on the presence of ammonia, confirming the importance of the participation of the nitrogen species from vanadium aluminum oxynitrides in propane ammoxidation. Conversion of propane (about 10%) was not affected by NH$_3$, while the later was totally consumed. To investigate the reaction of ammonia with the catalyst, a mixture of ammonia (5%) in helium was then pulsed over the VAlON07$_{773}$ catalyst. Reaction with lattice oxygen occurred, and N$_2$, NO, N$_2$O, and H$_2$O were detected as products. This can be considered a nonselective reaction pathway during the ammoxidation of propane. However, the nitrogen mass balance reveals that not all reacted ammonia was transformed into oxidation products. Therefore, part of the adsorbed ammonia is converted to more stable surface NH$_x$ species.

Alternating pulse experiments in which ammonia (5%) in helium was pulsed first followed by a pulse of propane at different time intervals ($\Delta t = 0.03$, 0.05, and 0.1 s) show acrylonitrile as a product in response to the propane pulse. The amount of acrylonitrile formed was independent of the time interval between the two pulses, as shown in Fig. 6. Again, this indicates the participation of the nitrogen species from the lattice only in the N-insertion step. As expected, the amount of acrolein formed in response to the propane pulse was also independent of the time interval. The nonselective oxidation products of ammonia were observed in the response to the ammonia pulse only, and their yields decreased slightly with increasing time interval.

To finally conclude about the role of ammonia, a single-pulse experiment was performed with labeled ammonia, ^{15}NH$_3$, in a mixture with propane and argon (C$_3$H$_8$/^{15}NH$_3$/ Ar = 2:1:10) over VAlON025$_{773}$. Both acrylonitrile isotopes were formed in a 1:1.5 ratio (labeled to unlabeled), but the total yield did not change with respect to the corresponding unlabeled experiment. If only unlabeled ACN would have been formed, the conclusion would have been much more clear-cut: in the N-insertion step only the lattice nitrogen is involved. But the labeled ACN came 0.05 s later than the unlabeled one. Moreover, as previous experiments had shown, when ammonia is pulsed over a surface on which the ammoxidation reaction has already occurred, part of the adsorbed ammonia is converted to more stable surface species, leading to the renitridation of the surface. These species are responsible for the formation of the labeled ACN isotope. That the total ACN yield did not change means that the total number of N-active species on the surface is constant. This suggests indeed that the renitridation process occurred.

To summarize, the above results sustain the assumption that in the N-insertion step only the lattice nitrogen is in-
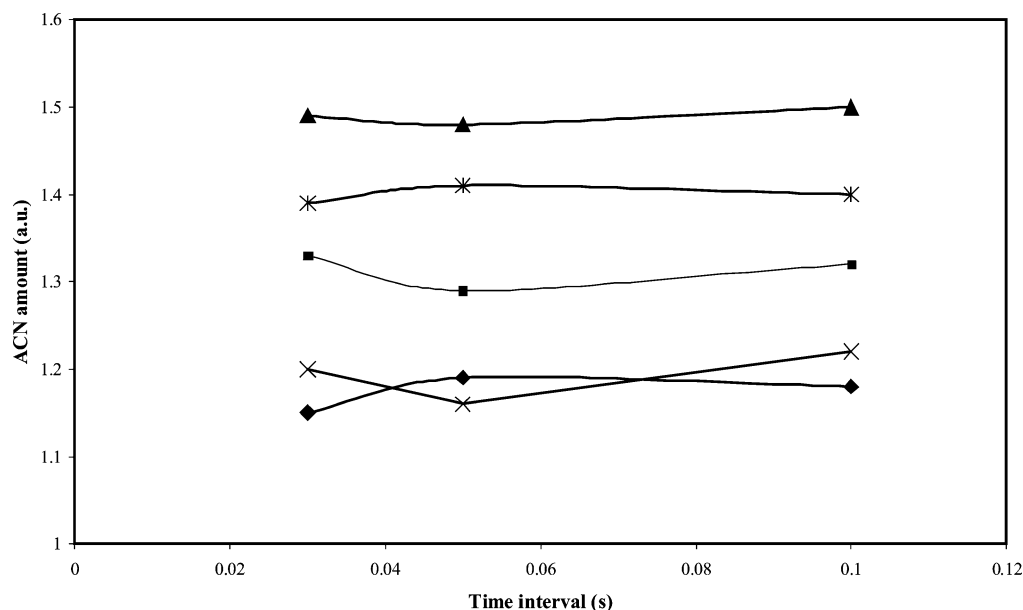
Fig. 6. ACN yield as a function of pump–probe time interval. VAlON025 nitridated in TAP (◆), VAlON025$_{673}$ (■), VAlON025$_{773}$ (▲), VAlON025$_{773}$ equilibrated catalyst (×), and VAlON07$_{773}$ (✳).

volved. During the ammoxidation process, ammonia participates in a nonselective reaction pathway that leads to the formation of ammonia oxidation products, and in a selective one as well, possible because of its stronger adsorption, which leads to more stable NH$_x$ species belonging to the lattice of the oxynitrides and involved in the further N-insertion step.

4. Discussion

The VAlO025 precursor behaves as an active (propane conversion amounted to 44%) and relatively selective catalyst for the oxidative dehydrogenation of propane. It was reported that its activity is controlled by the redox capacity of V ions while the selectivity is achieved by site isolation (due to the presence of alumina) [18]. XPS measurements revealed a high $V^{5+}/(V^{4+} + V^{5+})$ ratio (0.83) and a low V/Al surface ratio of 0.14 [8,18], which, indeed, explains the relatively high activity and selectivity. Moreover, Raman spectroscopy indicated the presence of $[(VO_3)_n]^{n-}$ meta-vanadate species (intense band at 940 cm^{-1}) in high concentration and some isolated monomers, VO$_x$, with one terminal V=O bond and three Raman inactive V–O–Al bonds (the band at 1050 cm^{-1}) [8]. There is a consensus in the literature about vanadia-based catalysts that the vanadia phase is more easily reduced at low loadings, that is, when the existence of isolated monomers or meta-vanadate species on the surface is favored. Therefore, the relatively high activity of the precursor is due to the high concentration of meta-vanadate species revealed by Raman spectra.

The activity of VAlONs catalysts was much lower than that of oxide precursors and was constant irrespective of the V/Al ratio and nitrogen content. This means that the number of active sites for propane activation is constant. If we admit, as most other studies did [20], that the activation of propane occurs on V^{5+} and V^{4+} centers, a lower and almost constant $V^{5+}/(V^{4+} + V^{5+})$ ratio of VAlONs compared with that of VAlOs would explain the VAlONs lower activity. Indeed, XPS measurements show an average value for the $V^{5+}/(V^{4+} + V^{5+})$ ratio of 0.78 for all VAlON025 catalysts, whereas for VAlON07 the found ratio was 0.80. Moreover, steady-state experiments performed over these VAlONs catalysts, with a propane/oxygen/ammonia mixture = 1.25:3:1, revealed that for $V^{5+}/(V^{4+} + V^{5+})$ ratios between 0.76 and 0.81, the conversion of propane was nearly constant [8].

DRIFT spectra [8,18] show that the nitridation by ammonia (as used for all VAlONs studied) leads to the formation of coordinated NH$_3$ (by adsorption of ammonia on the Lewis acid sites), NH$_x$ species ($x = 1$ or 2) and M–NH$_4^+$ species (by neutralization of the Brønsted acid sites by ammonia) (where M is V or Al), which are all stable on the surface at reaction temperature. Their relative ratio depends on the V/Al ratio. With increasing nitrogen content, at the same V/Al ratio, only the amount of NH$_x$ species increases. As the highest amount of ACN is obtained on the catalyst with the highest nitrogen content (VAlON025$_{773}$ equilibrated catalyst), we can conclude that the NH$_x$ species are more probably involved in the N-insertion step. At this stage, one can try to further envisage the mechanism through which these NH$_x$ species are involved in the formation of ACN. Our proposal is that the formation of ACN on oxynitride catalysts can be related to the presence of basic sites on the surface, on which propene, once formed by oxidative dehydrogenation of propane on acidic sites, can readsorb and react further. A first argument in favor of this hypothesis is the fact that the ACN mean residence time is higher than that of propene. An additional argument comes from the formation of ACO
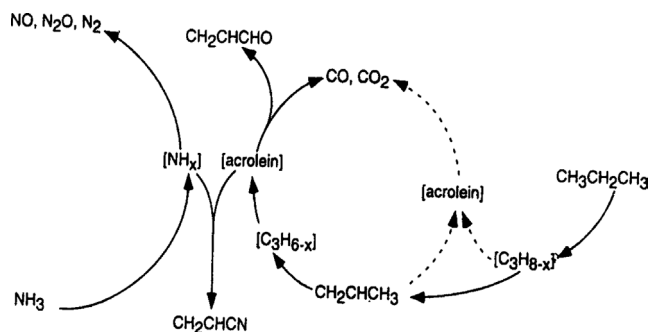
Scheme 1. Reaction mechanism for propane ammoxidation over VAlON catalysts as derived from TAP experiments. Solid lines indicate reaction paths involving lattice oxygen, and dashed lines denote pathways with adsorbed oxygen. Square brackets are used to symbolize surface intermediates.

only on the oxynitrides, suggesting that ACO can only form in the presence of basic sites, which suggests that selective O-insertion can only proceed on PE adsorbed on basic sites. A similar mechanism can be envisaged for N-insertion.

Taking into account all TAP results on propane ammoxidation over the VAlONs catalysts, we assume a double Mars–van Krevelen redox mechanism, involving both lattice oxygen and surface N species, as shown in Scheme 1. This was indicated by the formation of acrolein and acrylonitrile in the absence of dioxygen and gaseous ammonia, by the consumption of dioxygen to reoxidize, and by the consumption of ammonia to renitridate the surface. Direct participation of dioxygen and gaseous ammonia in the reaction with propane leads only to nonselective side reactions.

5. Conclusions

Lattice NH_x species ($x = 1$ or 2), formed most probably by irreversible reaction of NH_3 with the catalysts, are involved in the formation of ACN, whereas coordinated NH_3 or $M–NH_4^+$, formed by weak adsorption of ammonia on the surface, is involved in the nonselective pathway. Oxygen adsorbed species are involved in the nonselective reactions catalyzed by the surface. A double Mars–van Krevelen mechanism, involving both oxygen and nitrogen from the lattice, is proposed. ACN is formed consecutively via propene and ACO. However, the parallel pathway, the direct formation of ACN, cannot be ruled out.

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