New class of catalysts for the propane ammoxidation process based on vanadium aluminum oxynitrides

M. Florea, R. Prada-Silvy, and P. Grange *

Université catholique de Louvain, Catalyse et chimie des matériaux divisés, Croix du Sud 2, boite 17,
B-1348 Louvain-la-Neuve, Belgium

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Amorphous high-surface-area vanadium aluminum oxynitrides (VAlON) prepared by nitridation of an amorphous oxide precursor exhibit a high acrylonitrile yield in propane ammoxidation at very low contact time, indicating the participation of ammonia dehydrogenated species in the ammoxidation of alkanes. The productivity of the VAlON catalysts (l of ACN/kg catalyst/h) was markedly improved as compared with known oxide systems.

KEY WORDS: vanadium aluminum oxynitride; nitrogen species; propane contact time; ammoxidation.

1. Introduction

Acrylonitrile (ACN) is an important intermediate product which is extensively used for the production of acrylic fibers, nitrile elastomers, rubbers, plastics and adiponitrile. Nowadays, about 95% of ACN production is obtained by the propylene ammoxidation process which gives ACN selectivities of more than 80% at 98% conversion per single pass [1].

Interest in the development of alternative processes using propane as a feed gas compound has increased in the last two decades. The main incentives are (i) the differences in price between alkanes and olefins, (ii) the increasing world demand for ACN and derived products and (iii) the risk of propylene shortage due to its increasing consumption. However, propane ammoxidation represents a technological challenge for research centers and catalyst companies due to the fact that alkane activation is a more difficult process and requires more severe operating conditions and very active and selective catalysts.

As ammoxidation products are more reactive than reactant molecules, they can be decomposed during the reaction, leading to the formation of undesired oxygenated compounds (CO_x, NO_x, organic acids, etc.), affecting in this manner the ACN yield.

Different catalyst formulations have been investigated in the literature and four catalytic systems have been proposed for propane ammoxidation:

(i) rutile structures with V, Sb, W and Al as key elements [2–5];
(ii) Bi–Mo–V scheelite structures [6–8];
(iii) vanadyl pyrophosphate catalysts [9–11];
(iv) Ga–antimonate pure or modified with W, Ni and P [12,13].

Most of these formulations contain vanadium oxides as the main cation due to its redox properties. Among these catalyst categories, V–Sb–W–Al oxide systems [14] and V–Mo mixed oxides modified with Nb and Te [15,16] have shown the best catalytic performance (ACN yields of 35–55%).

The acid–base properties of these catalysts are very important and several authors stressed their direct relation with the activity in propane ammoxidation. Osipova *et al.* [17] studied the activity behavior of a series of metallic oxide systems and observed that ACN formation is favored when the basicity of the catalyst increases.

Sokolovskii *et al.* [18] suggested that propane ammoxidation on catalysts such as V–Al_2O_3, V–Sb–Bi–O, V–TiO_2 and V–SiO_2 provides large amounts of ammonia dehydrogenated adsorbed species, such as $NH_2^{\sigma-}$ and $NH^{\sigma-}$ (NH_x^{σ}), which yield to the new strong nucleophilic (basic) active sites. These species could participate either in the processes of alkane activation with carbanion formation or in nitrogen insertion during the ammoxidation process. However, with acid catalysts (such as those containing V–Sb–O_x or V–Mo–O_x) the heterolytic activation of C–H bonds occurs on acid sites (V^{n+} sites) with carbocation formation, and propylene appears as an intermediate compound of the reaction.

Previous investigations carried out in our laboratory on the catalytic behavior of a family of oxynitride systems such as aluminophosphate oxynitrides [19], zirconophosphate oxynitrides [20,21], aluminogallophosphate oxynitrides [22] and vanadium aluminum

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* To whom correspondence should be addressed.
E-mail: grange@cata.ucl.ac.be

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oxynitrides (VAlON) [23,24] have shown that these catalytic materials exhibit basic properties. These were well evidenced by their activity in the Knoevenagel condensation between benzaldehyde and malonitrile and by different catalyst characterization techniques, such as TPD-MS and SO_2 and $CDCl_3$ adsorption [24]. The catalytic performances of the oxynitride systems are strongly affected by their composition and the nitridation conditions. In the particular case of the V–Al oxynitride system, it was demonstrated that the modification of (i) the V/Al atomic ratio in the oxide precursor, (ii) the degree of nitridation of the catalyst or (iii) the nature and distribution of the nitrogen species may cause important differences in the catalytic behavior [24].

The aim of this study was to extend the investigation of the catalytic behavior of VAlON in the ammoxidation of propane.

2. Experimental

A vanadium–aluminum oxynitride catalyst, with a V/Al = 0.25 atomic ratio, was prepared by thermal nitridation of a co-precipitated V–Al oxide precursor. Nitridation of the samples was carried out in a tubular rotating reactor under a flow of pure ammonia (30 l/h) at 773 K for 5 h. Starting from amorphous non-calcined precursor, the system was subsequently cooled to room temperature under a flow of pure nitrogen.

Catalytic tests were performed in a fixed-bed quartz micro-reactor at atmospheric pressure and a temperature of 773 K, with 0.1 g of catalyst and $W/F = 8$ g h/mol of C_3H_8. The feed composition was 1.25 : 3 : 1 of $C_3H_8 : O_2 : NH_3$. The activity results are reported after 24 h on stream. Feed and products were analyzed on-line using a gas chromatograph, equipped with FID and TCD detectors and an on-line mass spectrometer was used to check the NO_x formation.

The BET surface area corresponding to oxynitride catalysts before and after reaction was evaluated using a Micromeritics Flow Sorb II 2300 apparatus.

XRD lines were recorded using a Siemens D-5000 powder diffractometer equipped with Ni-filtered CuKα radiation ($\lambda = 1.5418$ Å).

The principle of the chemical analysis of nitrogen is based on the reaction of the nitride ion N^{3-} with a strong base, KOH, at 450 °C and the formation of ammonia which is then titrated [25]. In the Kjeldahl method, the alkaline attack occurs in the KOH solution at water vapor temperature. Bulk nitrogen does not react under these conditions. The ammonia titrated is evaluated from the superficial NH_x (NH and NH_2) species.

3. Results and discussion

Figure 1 shows the variation of propane conversion and the ACN, acetonitrile (AcCN) and CO_x ($CO_2 + CO$) selectivities as a function of the time on stream. The propane conversion remained stable at 59% after 4 h on stream. The VAlON catalyst shows an ACN selectivity and yield of about 50 and 29.5%, respectively. The selectivities to AcCN and CO_x are 3 and 38%, respectively.

No propylene, nitrogen, nitrogen oxides (NO_x), HCN or oxygenated hydrocarbons were detected during the catalytic reaction. The oxygen conversion was total even when the oxygen to propane ratio was higher than that of the stoichiometric reaction ($O_2 : C_3H_8 = 2 : 1$).

The XRD analysis indicated that both the co-precipitated V–Al oxide precursor and the V–Al oxynitride catalysts are amorphous.

Specific surface area, total nitrogen and surface nitrogen contents before and after the catalytic tests are presented in table 1. The surface area value corresponding to the V–Al oxide precursor was 250 m^2/g. After the nitridation process, the surface area of the solid decreased to 153 m^2/g, which represents a surface area loss of about 39%. After reaction, the surface area of the VAlON catalyst decreased by about 13%. Assuming that during the reaction a continuous replacement of the surface nitrogen by ammonia occurs, the slight decrease of surface may be explained. However, the nitrogen content of the samples before and after reaction remains almost the same. Evidence of nitrogen species on the vanadium aluminum oxynitrides has been reported elsewhere [26].

In the literature, different nitrogen species are proposed to be active in the ammoxidation reaction depending on

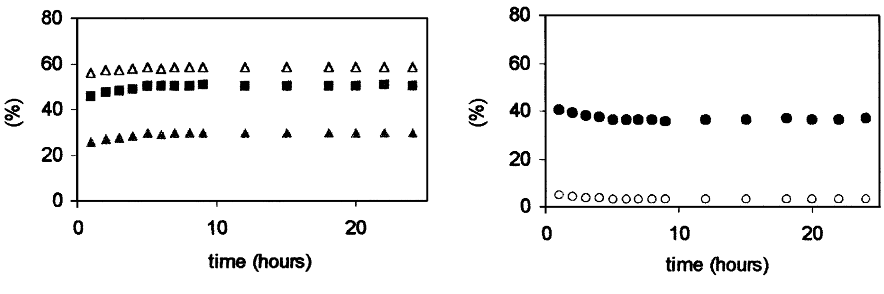

Figure 1. Time on stream behavior over VAlON catalyst (V/Al = 0.25): GHSV = 16 800 ml/g/h, propane : oxygen : ammonia = 1.25 : 3 : 1, $W/F = 8$ g h/mol C_3H_8; 773 K, 24 h (△, propane conversion; ■, selectivity to ACN; ▲, yield of ACN; ○, selectivity to AcCN; ●, selectivity to CO_x).

Table 1
Surface area and nitrogen content of VAlON catalyst (V/Al = 0.25)

VAlON	Surface area (m^2/g)	N_T [a] (wt%)	N_K [b] (wt%)	XRD
Before catalytic test	153	3.15	1.8	Amorphous
After catalytic test	133	3.05	2.1	Amorphous

[a] N_T = total nitrogen content.
[b] N_K = nitrogen determined by Kjeldahl method.

the nature of the catalyst. These nitrogen species have been identified on the catalyst surface during the catalytic reaction. NH_2^- groups would be active in nitrogen insertion on Ga–Sb oxides [17]. NH_4^+, NH_{3ads}, NH_2^- and NH groups are supposed to be active on vanadyl pyrophosphate [10]. If we compare the performance in propane ammoxidation of the vanadium aluminum oxynitride catalyst (ACN yield of 29.5%) with the catalytic results obtained on a vanadium aluminum oxide catalyst [27] (ACN yield of 1.5%), we can conclude that the catalytic activity is strongly related to the nitrogen species from the oxynitrides and that these species play a very important role in the ACN formation. Nevertheless, no nitrogen insertion was found for the vanadium aluminum oxide system [27] because once the oxide precursor is calcined and the $AlVO_4$ crystalline phase is formed, nitrogen insertion in the network is almost impossible [23].

The advantages of the VAlON system with respect to conventional oxide ammoxidation catalysts are not based on the level of ACN selectivity and yield. Some studies published in the literature showed ammoxidation catalysts that present, in some cases, an ACN selectivity up to 90% and yields between 35 and 45% [28].

In our case, ACN selectivity and yield are less than these values. However, the great difference is in the space time value (W/F), which is much smaller for the VAlON catalyst (8 g h/mol of C_3H_8) than for the conventional ammoxidation systems, as presented in table 2. We have estimated the ACN productivity (l of ACN/kg of catalyst per hour) from the W/F value and the ACN yield.

As indicated by the above results, the formation of propylene intermediate was not observed for the VAlON system. This observation, together with the fact that the VAlON system shows a high ACN selectivity at very low space time value, suggests a different reaction mechanism as compared with conventional metallic oxide ammoxidation systems. Presumably, alkane activation takes place via a carbanion, followed by allyl surface ion formation and subsequent transformation to ACN. In the case of VAlON, the activity behavior can be explained by a combination of different simultaneous effects: (i) a better efficiency in the activation of C–H bond in the alkane due to the basic character of the catalyst and a balanced redox capacity of vanadium species, (ii) a high NH_x surface concentration, which enhances the nitrogen insertion rate in the activated allyl surface species and (iii) an adequate texture of the catalyst.

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Table 2
Acrylonitrile productivity for different catalytic systems used in propane ammoxidation

Catalyst	Reaction temperature (°C)	Conv. C_3H_8 (%)	Select. ACN (%)	Yield ACN (%)	W/F (g h/mol C_3H_8)	Productivity (l ACN/kg/h)	Reference
Mo–V–Nb–Te–O	440	89.1	60.0	53.5	384.6	31.16	[29]
V–Sb–W–Al–O	500	77	48	37	53	164	[14]
V–Sb–O (Sb/V = 5)	425	30	26.6	8	2036	0.9	[5]
Fe–Sb–O (Fe : Sb = 1 : 2)	500	22	23	5	740	1.51	[30]
Ca–Bi–Mo	510	15	63	9.5	12	177	[31]
VAlON (V/Al = 0.25)	500	59	50	29.5	8	812	This work

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