

## VANADIUM-BASED CATALYSTS FOR PROPANE AMMOXIDATION REACTION

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

### Introduction

Alkane transformation to high value chemical products constitutes an arduous and stimulating scientific and technological challenge. Among the most significant examples of industrial application in this field is the production of acrylonitrile (ACN) through the propane ammoxidation process. The advantages for replacing olefins by alkanes in the current ammoxidation process are essentially: the lower price of propane with respect to propylene, the risk of propylene shortage due to its increasing consumption and the increasing worldwide demand of nitriles and other derived products. However, two fundamental problems arise in the transformation processes of alkanes. i) alkane activation is difficult and requires severe operating conditions and very active, selective and stable catalysts and ii) products are generally less stable than reactants and they can be easily decomposed during the reaction leading to the formation of undesirable oxygenated C and N compounds [1].

Companies and research centers are independently developing new catalysts for the alkane ammoxidation process. The main identified factors for obtaining advantages over current propylene technology are i) maintain propane versus propylene cost advantages higher than 50%, ii) productivity levels comparable to those obtained with propylene, iii) operation temperatures no higher than 500°C and iv) maximize co-products formation, such as acetonitrile (AcCN) and hydrogen cyanide (HCN), which have a high value in the chemical market. It is thus clear that the key to successful commercialization of propane

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ammoxidation technology is the development of a new generation of catalysts capable of activating alkane molecules under moderate reaction conditions and promoting the production of other co-products of commercial interest.

The type of catalyst support and its acid–base character has a marked influence on the vanadium phase structure, surface dispersion, reducibility and catalytic properties. In fact, basic or amphoteric supports promote the formation of bidimensional vanadate surface dispersion, whereas acidic supports lead to the formation of tri-dimensional  $V_2O_5$  species.

Lemonidou and co-workers [2] studied the effect of different catalyst supports on the vanadium reducibility and catalytic properties for the propane oxidative dehydrogenation (ODH) reaction. They observed that a  $V_2O_5/TiO_2$  catalyst is the most active of the studied series of catalysts, while  $V_2O_5/Al_2O_3$  is most selective in propylene formation. The authors also observed that the reduction temperature corresponding to the different V-supported catalysts varies according to the following sequence:  $V/ZrO_2 < V/TiO_2 < V/Al_2O_3 < V/MgO$ . The addition of basic promoters to the V-supported catalysts hinders the reducibility of the metal and enhances the catalytic activity. Other researchers have observed selective propylene formation over V-based catalysts supported on basic or amphoteric oxides rather than on acidic supports [3-6].

Typical propane ammoxidation catalysts are essentially constituted by combination of metallic mixed oxides. These catalysts have been classified according to two main categories i) Vanadium-molybdate catalysts, represented by  $VMo_xM_yO_z$  where “M” is most often Bi or Te, with scheelite-type structure [7,8] and ii) Vanadium-antimonates which possess a rutile-type structure represented by the  $VSb_xM_yO_z$  formula, where “M” are elements used as promoter such as W, Te, Nb, Sn, Bi, Cu, Al or Ti [9,10]. Other catalytic systems based on Ga-Sb oxides as well as vanadyl pyrophosphates were also investigated [11]. However, they were not so promising for the propane ammoxidation reaction.

Thus, we have been working on the development of new catalytic systems for alkane activation reactions. Metallic oxynitrides are materials that have shown excellent catalytic properties for different types of reactions [12,13]. These bi-functional catalytic systems are essentially constituted of metallic «redox» sites and basic sites with different strength distribution, which allow the activation of the alkane molecules and the subsequent nitrogen insertion reaction at relatively moderate reaction temperatures. In this article, we show the catalytic behavior of vanadium aluminum oxynitride catalysts (VAION in the following) in the ACN production, as compared with metallic oxide propane ammoxidation catalysts reported in the literature.

## Experimental

Vanadium aluminum oxide, V/Al atomic ratio of 0.25, was prepared by co-precipitation of ammonium vanadate and aluminum nitrate solutions followed by steps of drying (60°C-120°C) and calcination (500°C). The oxide precursor was submitted to nitridation treatment in  $NH_3$  flow = 5 ml/min at 500 °C for 5hr. The system was subsequently cooled down to room temperature under a flow of pure nitrogen. More specific details about the catalyst preparation procedure have been reported elsewhere [13].

The principle of the chemical analysis of total nitrogen content is based on the reaction of the nitrogen species from the catalyst with a strong base (KOH) at 450°C and the formation of ammonia which is then titrated with a standard solution of sulphuric acid 10<sup>-2</sup> N (Grekov method). The superficial nitrogen species were quantified by the Kjeldahl method. The alkaline attack was realized using a KOH saturated solution at 100°C. The titrated ammonia corresponds to the superficial NH<sub>x</sub> (NH and NH<sub>2</sub>) species. Bulk nitrogen does not react under these conditions.

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 a Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ).

Catalytic tests were performed in a fixed bed quartz micro-reactor at atmospheric pressure and temperature of 500 °C, 0.1 g of catalyst and W/F= 8 g.h/mol of C<sub>3</sub>H<sub>8</sub>. Feed composition was 1.25:3:1 of C<sub>3</sub>H<sub>8</sub>: O<sub>2</sub>: NH<sub>3</sub>. The activity results are reported after 24 hours on stream. Feed and products were analysed on-line using a gas chromatograph, equipped with FID and TCD detectors and an on-line mass spectrometer was used to check the NO<sub>x</sub> formation. The principal reaction products were: acrylonitrile (ACN), acetonitrile (AcCN) and carbon oxides (CO<sub>x</sub>). Propane conversion is defined as the % ratio between the mole of propane consumed per mole of propane in the feed; the ACN selectivity as mole of ACN in the product per mole of propane consumed; and the ACN yield as mole of ACN in the product per mole of propane in the feed.

## Results and discussions

Sample with V/Al atomic ratio of 0.25 was prepared by the co-precipitation method followed by nitridation in the presence of ammonia at 500°C for 5 hours. The sample is X-ray amorphous before and after the catalytic test. Table 1 compiles the values of the surface areas and the nitrogen content of the oxynitride powders before and after propane ammoxidation. A specific surface area of 154 m<sup>2</sup>/g and the total nitrogen content of 3.1 wt% was obtained for the oxynitride sample after the nitridation process.

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

VAION	Surface area (m <sup>2</sup> /g)	N <sub>T</sub> <sup>*</sup> (wt%)	N <sub>K</sub> <sup>*</sup> (wt%)	XRD
before the catalytic test	154	3.15	1.8	Amorphous
after the catalytic test	133	3.05	2.1	Amorphous

\*N<sub>T</sub> = total nitrogen content

\*N<sub>K</sub> = nitrogen determined by Kjeldahl method.

The surface area value corresponding to the V-Al oxide precursor was 250 m<sup>2</sup>/g. After the nitridation process, the surface area of the solid decreased to 154 m<sup>2</sup>/g, which represents a surface area loss of about 39%. After reaction, the surface area of the VAION catalyst

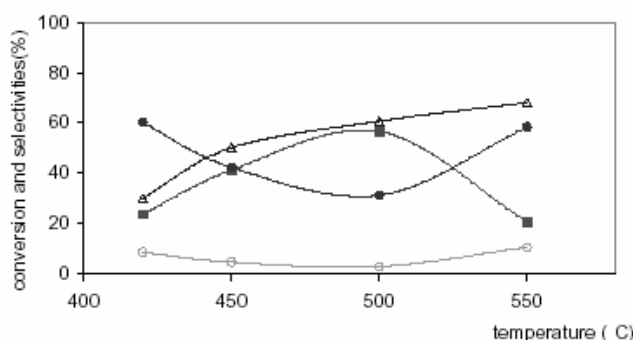
decreased by about 13%. Assuming that during the reaction a continuous replacement of the surface nitrogen by ammonia exists, the slight decrease of surface may be explained. However, the nitrogen content of the samples before and after reaction remains almost the same. Evidence of nitrogen species on the vanadium aluminium oxynitrides was reported elsewhere [12].

In the literature, different nitrogen species are discussed to be active in the ammoxidation reaction depending on the nature of the catalyst. These nitrogen species have been identified on the catalyst surface during the catalytic reaction.  $\text{NH}_2^-$  groups would be active in nitrogen insertion on Ga-Sb oxides [14].  $\text{NH}_4^+$ ,  $\text{NH}_{3\text{ads}}$ ,  $\text{NH}_2^-$  and  $\text{NH}$  groups are discussed to be active on vanadyl pyrophosphate [15]. If we compare the performance in propane ammoxidation of the vanadium aluminium oxynitride catalyst (acrylonitrile yield of 29.5%) with the catalytic results obtained on the vanadium aluminium oxide catalyst (acrylonitrile yield of 1.5% [16]), 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 acrylonitrile formation.

Nevertheless, no nitrogen insertion was found in [16] for the vanadium aluminium oxide system because once the oxide precursor is calcined and the  $\text{AlVO}_4$  crystalline phase is formed, the nitrogen insertion in the network is almost impossible [12].

The effect of the reaction temperature and of the feed composition on the activity properties of VAION system is shown in Figures 1 and 2. Optimal catalytic activity is achieved when the  $\text{C}_3\text{H}_8:\text{O}_2:\text{NH}_3$  molar ratio in the feed is 1.25:3.0:1.0, respectively, and the reaction temperature is 500°C.

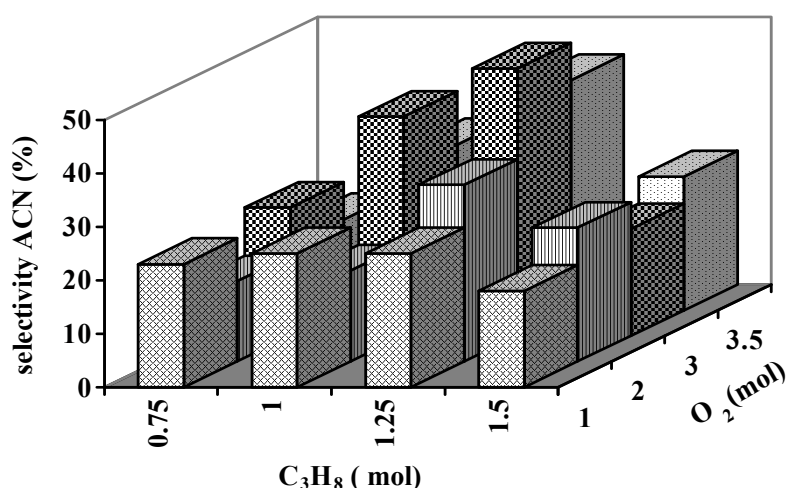
For the formation of unsaturated nitriles, such as acrylonitrile from propane, the hydrocarbon activation is an important step, which proceeds at rather high temperatures compared with the formation of acrylonitrile from propylene. In order to identify the optimal range of temperature for propane ammoxidation over vanadium–aluminium oxynitrides, catalytic tests were carried out in the range of 400–550°C.



**Fig. 1.** Catalytic behavior over VAION catalyst ( $V:Al = 0.25$ ) as function of the reaction temperature:  $GHSV = 16.800 \text{ m l/g h}$ ,  $\text{C}_3\text{H}_8:\text{O}_2:\text{NH}_3 = 1.25:3:1$  (△) propane conversion; (■) ACN selectivity; (○) AcCN selectivity; and (●)  $\text{CO}_x$  selectivity

Figure 1 shows the conversion of propane and product selectivities as a function of the reaction temperature over the vanadium–aluminium-based catalyst. The conversion of propane increased continuously with reaction temperature, while the selectivity to acrylonitrile increased with the temperature up to 500 °C and then decreased. Under these conditions, the maximum in selectivity to acrylonitrile corresponding to 55% was obtained at 500 °C. The selectivity to CO<sub>x</sub> exhibited an opposite variation, namely, it progressively decreased up to 500 °C, while above this temperature most of the propane was oxidized. After 500 °C, traces of heavier products such as butanedinitrile were also detected.

The influence of the gas feed composition on propane ammoxidation was investigated under reaction conditions in which the catalyst showed the highest ACN selectivity value ( $T = 500\text{ °C}$ ,  $GHSV = 16.800\text{ ml/g h}$ ). The results are depicted in Figure 2.



**Fig. 2.** Catalytic behaviour over VAION catalyst ( $V:Al = 0.25$ ) as function of propane and oxygen molar ratio:  $GHSV = 16800\text{ ml/g h}$ ,  $C_3H_8:O_2:NH_3 = X:Y:1$

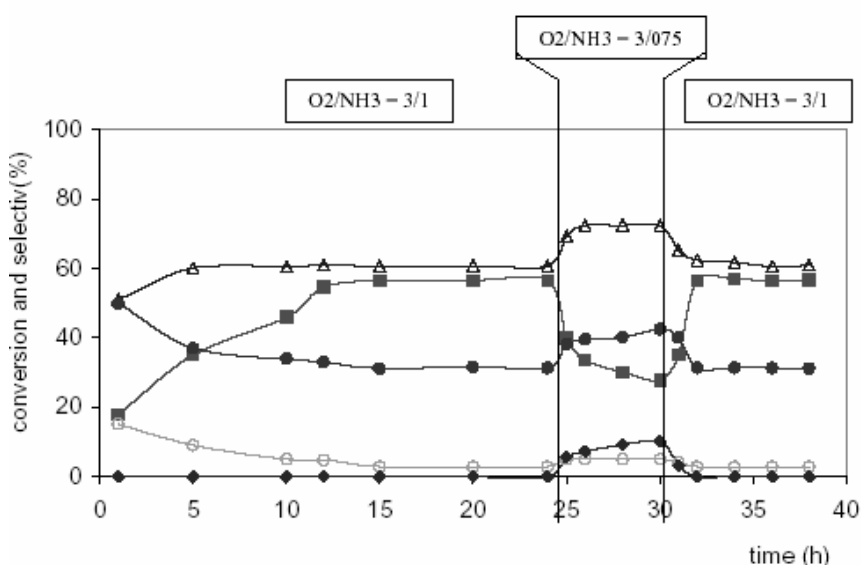
The catalytic tests were performed by changing the contact time of one reactant and keeping the others constant. The total flow and the space velocity were kept constant by changing correspondingly the flow of helium used as diluent gas. These variations allowed the optimization of the gas composition of the mixtures subjected to the reaction.

Higher oxygen contents favor the oxidation of ammonia and under these conditions the V–NH<sub>x</sub> species are transformed into V–O electrophilic ones, as already suggested [15]. However, a contact time of oxygen up to 3 mol of oxygen led to a large coverage of the catalyst surface with NH<sub>x</sub> species, and for this value, the nitrogen content on the corresponding catalyst is about 3.2%. Under these conditions, the selectivity to acrylonitrile achieved 46.5%. It worth to note that even at higher contact time of oxygen, the formation of propylene was not observed.

Propane can also be a limiting reagent in the propane ammoxidation over VAION catalysts and it seems that the propane:oxygen and propane:ammonia ratios have a significant influence on the catalyst selectivity. When very low contact times of propane are employed propylene is formed. Under these conditions, the conversion of propane reached 75% and the main reaction products were carbon oxides.

Thus, a proper feed composition provides a correct equilibrium between the active nitrogen and oxygen species. However, the activity of the VAION catalyst is maximal when the molar ratio among  $C_3H_8:O_2:NH_3$  reactants is 1.25:3:1. This optimal molar ratio corresponds to a space time (W/F) of 7.69 g h/mol  $C_3H_8$ , 3.11 g h/mol of  $O_2$  and 10.2 g h/mol  $NH_3$ .

A series of transient experiments were conducted varying the  $O_2:NH_3$  ratio in order to investigate the effect of the oxidation/reduction reaction environment on the catalytic activity of the VAION system. The results are presented in Figure 3.



**Fig. 3.** Catalytic behavior over VAION catalyst ( $V:Al = 0.25$ ) function of time on stream and function of  $O_2:NH_3$  ratio:  $GHSV = 16800$  ml/g h;  $C_3H_8:O_2:NH_3 = 1.25:3:X$  ( $X = 0.75$  and  $1$ ),  $500^\circ C$  ( $\Delta$ ) propane conversion; ( $\blacksquare$ ) ACN selectivity; ( $\circ$ ) AcCN selectivity; and ( $\bullet$ )  $CO_x$  selectivity, and ( $\blacklozenge$ ) propylene selectivity).

After 24 h on stream, the  $O_2:NH_3$  ratio was varied from 3:1 to 3:0.75 for 5 h. Subsequently, the reaction conditions used were the same as initially. Under these conditions, decreasing the  $O_2:NH_3$  molar ratio had the following effects: (i) propane conversion increased, (ii) ACN selectivity decreased, (iii)  $CO_x$  selectivity increased, (iv) AcCN selectivity underwent a slight increase, and (v) propylene formation was detected. By changing the  $O_2:NH_3$  ratio and returning to the initial conditions, the catalyst recovered the same catalytic activity and

selectivity, leading to the same selectivity to acrylonitrile, namely 56%. At the same time, propylene disappeared from the reaction products. Thus, a proper feed composition provides a correct equilibrium between the active nitrogen and oxygen species. These data obtained from transient experiments, clearly demonstrate that the catalytic behavior of the surface does not only depend on the presence of a particular surface species, but also depends on the nature of the changes in the surface reactivity induced by the adsorption of the reactants. It is also necessary to pay a special attention to the surface restructuring phenomena during the catalytic.

Comparative test conditions and activity results corresponding to the best performing propane ammoxidation catalysts vs VAION system are shown in Table 2. Main observations are: i) all catalysts show differences in feed gas composition, reaction temperature and space velocity for achieving optimal ACN yield, ii) vanadium-molybdates system exhibits higher propane conversion at lower reaction temperature than V-Sb-W-Al-O and VAION systems whereas, VAION catalyst shows slightly higher ACN selectivity than Mo-V-Nb-Te-O systems, iii) ACN productivity is higher for the VAION system than that obtained for Mo-V-Nb-Te-O (26 times) and for the V-Sb-W-Al-O (4 times) catalyst formulations and iv) propylene and HCN formation were reported for all Mo-V-Nb-Te-O and V-Sb-W-Al-O catalyst formulations. These products were not detected during catalytic reaction with the VAION system, which suggests differences in reaction mechanism.

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

Catalyst	Conv C <sub>3</sub> H <sub>8</sub> (%)	select ACN (%)	Yield ACN (%)	W/F (g.h/moles C <sub>3</sub> H <sub>8</sub> )	Productivity (l ACN/kg.h)
Mo-V-Nb-Te-O	89.1	60.0	53.5	384.6	31.16
V-Sb-W-Al-O	77	48	37	53	164
V-Sb-O	30	26.6	8	2036	0.9
Fe-Sb-O	22	23	5	740	1.51
Ca-Bi-Mo	15	63	9.5	12	177
VAION	59	50	29.5	8	812

## Conclusion

In conclusion, the results of this work allow us to propose a new category of highly active catalysts for the alkane ammoxidation process based on metallo oxynitride materials. This novel catalytic system shows high ACN yield and competitive advantages in acrylonitrile productivity per amount of catalyst and per time as compared with conventional vanadium-molybdates and vanadium-antimonates propane ammoxidation catalysts.

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