Propane Ammoxidation Catalyst Based on Vanadium-Aluminum Oxynitride

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Upgrading of alkane to high-value products for the chemical industry 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 (C_3) ammoxidation process. This chemical intermediate is used extensively in the production of nitriles, acrylic fibers, resins, rubbers, and other specialties. About 95% of the worldwide ACN production is obtained through the propylene ($C_3^=$) ammoxidation process which was developed by the Standard Oil Company of Ohio (Sohio) in the 1960s (Petzny and Mainusch, 2000).

The idea of replacing olefins by alkane in the ammoxidation process dates back of the early 1970s. The advantages are essentially the lower price of propane with respect to propylene, and managing the risk of a propylene shortage due to its increasing consumption in the polymerization process and the increasing worldwide demand of ACN, plastics, synthetic fibers, and other derived products. However, two fundamental problems arise in the transformation processes of alkanes. On the one hand, alkane activation is difficult and requires severe operating conditions ($T = 460$–550°C, contact times = 8–60 s) and very active, selective, and stable catalysts. On the other hand, the reaction products are generally less stable than the reactants, therefore they can be easily decomposed during the process conditions leading to the formation of undesirable oxygenated carbon and nitrogen compounds (Bowswell, 1999).

The main reaction route of propane ammoxidation to ACN over conventional metallooxide catalysts was found to be intermediate propylene formation. The propane-based process scheme is similar to that of the propylene process design due to the similarity in reaction mechanisms (Petzny and Mainusch, 2000; Chauvel and Lefebvre, 1989). However, a key difference between these two catalytic processes is the necessity to recycle unconverted propane. The conversion level of propane per pass should be between 40 and 60%, in order to keep ACN selectivity and yield up.

Several companies, among them BP, Asahi Chemical, Mitsubishi-BOC, Nitto, BASF, and Rhodia, are independently developing new catalysts and processes for the alkane ammoxidation route. For instance, BP has recently scaled up the propane process to a semicommercial demonstration, while the other companies are operating at pilot, bench, or lab scale.

The main identified factors for obtaining cost benefits over current propylene technology are the following:

(1) Maintain propane vs. propylene cost advantages higher than 50%.

(2) Productivity levels comparable to those obtained with propylene, to enable retrofitting of existing process units or at least of their separation units.

(3) Operation temperatures no higher than 500°C to lower byproduct formation (acrolein, acrylic acid, and CO_x) and minimize problems related to reactor materials.

(4) Maximize the production of coproducts such as acetonitrile (ACCN) and hydrogen cyanide (HCN), which have a high value in the chemical market.

According to Chem System, the propane ammoxidation process promises variable cost savings of up to $380 per metric ton of ACN over the conventional propylene technology (Bowswell, 1999).

It is, thus, clear that the key to successful commercialization of propane 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 coproducts of commercial interest.

With that in mind, 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 (Wiame et al., 1997, 2000; Massinon et al., 1996; Fripiat et al., 1997; Delsarte et al., 1998). These bifunctional catalytic systems are essentially constituted of metallic "redox" sites and basic sites

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Table 1. Propane Ammoxidation Catalyst Systems and Reaction Conditions

Reference	Catalyst System	Feed-Gas Composition $C_3:NH_3:O_2$	T (°C)	LHSV (h^{-1})	ACN Productivity ($V_{ACN}/V_{cata} \cdot h$)
Ushikubo et al. (1993)	$MoV_{0.3}Te_{0.23}Nb_{0.15}\ O_x$	1.0:1.5:3.2	410	1200	34
Hinago and Komada (2000)	$MoV_{0.33}Te_{0.40}Nb_{0.11}O_x$	1.0:1.2:3.0	420	7200*	221**
Guttmann et al. (1988)	$VSb_5W_{0.5}Te_{0.5}Sn_{0.5}O_x/SiO_2\text{-}Al_2O_3$	1.0:2.0:1.5	500	800	24
Albonetti et al. (2000)	$VSb_{12.5}Fe_5O_x$	2.5: 1.0:2.0	470	7200	144
Prada Silvy et al. (2001)	VAlON	1.25:1.0:3.0	500	5600	360
	VAlON	1.25:1.0:3.0	500	16.800*	1103**

* mL/h · g of catalyst.

** $v_{ACN}/w_{cata} \cdot h$.

with different-strength distribution that allow the activation of the alkane molecules and the subsequent nitrogen insertion reaction at relatively moderate reaction temperatures. In this communication, we show the competitive advantage of vanadium aluminum oxynitride catalysts (VAlON) in ACN production, as compared with propane ammoxidation systems reported in the patent literature.

Experimental Studies

Preparation of VAlON catalyst

Vanadium aluminum oxide, V/Al atomic ratio of 0.25, was prepared by coprecipitation of ammonium metavanadate and aluminum nitrate solutions followed by a drying step (60°C, 4 h and 120°C overnight). The oxide precursor was submitted to nitridation pretreatment in NH_3 flow = 5 mL/min at 500°C for 4 h. The V/Al oxynitride catalyst showed an amorphous character, a specific surface area of 154 m^2/g, and a total nitrogen content of 3.1 wt. %. More specific details about the catalyst preparation procedure have been reported elsewhere (Prada Silvy et al., 2001).

Catalytic activity measurements

The activity for the propane ammoxidation reaction was determined using a fixed-bed catalytic reactor under the following experimental conditions: catalyst weight = 0.1 g; feed composition = 5:12:4:7 mL/min of $C_3:O_2:NH_3:He$, respectively; reaction temperature = 500°C; and a total pressure of 10^5 Pa. A gas chromatograph equipped with both TCD and FID detectors was used for the analysis of ACN, ACCN, HCN, propylene, carbon, and nitrogen oxide products and unconverted reactants. The activity results are reported at steady-state conditions obtained after 12 h on stream.

Results

Typical propane ammoxidation catalysts are essentially constituted by a combination of metallic mixed oxides. In the literature, these catalysts have been classified according to two main categories:

(1) Vanadium–molybdate catalysts, represented by $VMo_xM_yO_z$ where "M" is most often Bi or Te. Most of the vanadium molybdate compounds present a scheelite-type structure, while others possess complex structures. Among these vanadium–molybdate systems, the highest ACN yields are claimed for catalysts combining the $V_yMoNb_wTe_zO_x$ elements (Ushikubo et al., 1993; Hinago and Komada, 2000).

(2) Vanadium–antimonates, which possess a rutile-type structure represented by the $VSb_xM_yO_z$ formula, where "M" are elements used as a promoter such as W, Te, Nb, Sn, Bi,

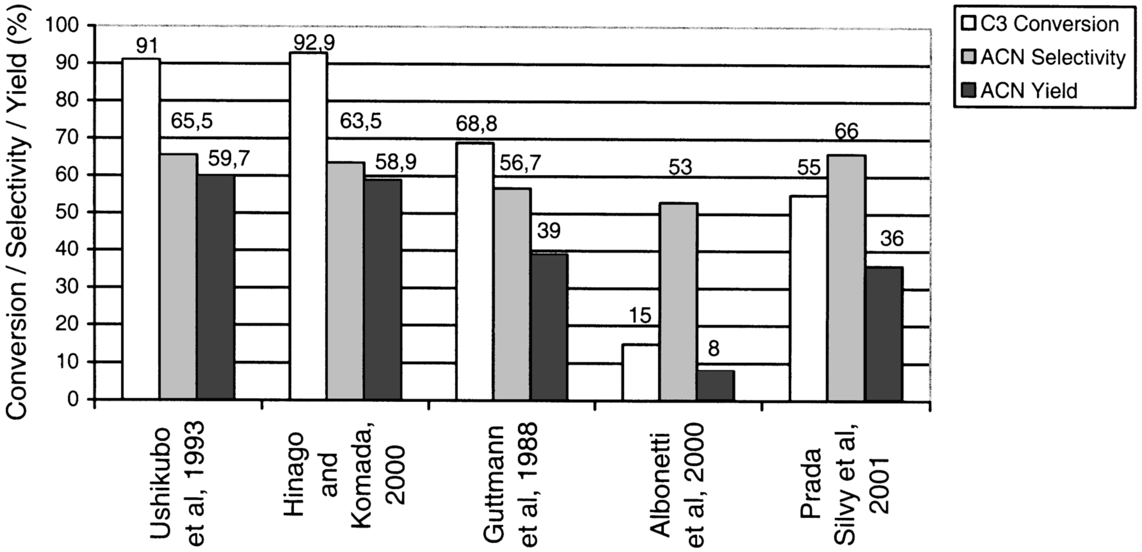

Figure 1. Activity results corresponding to different propane ammoxidation catalysts.

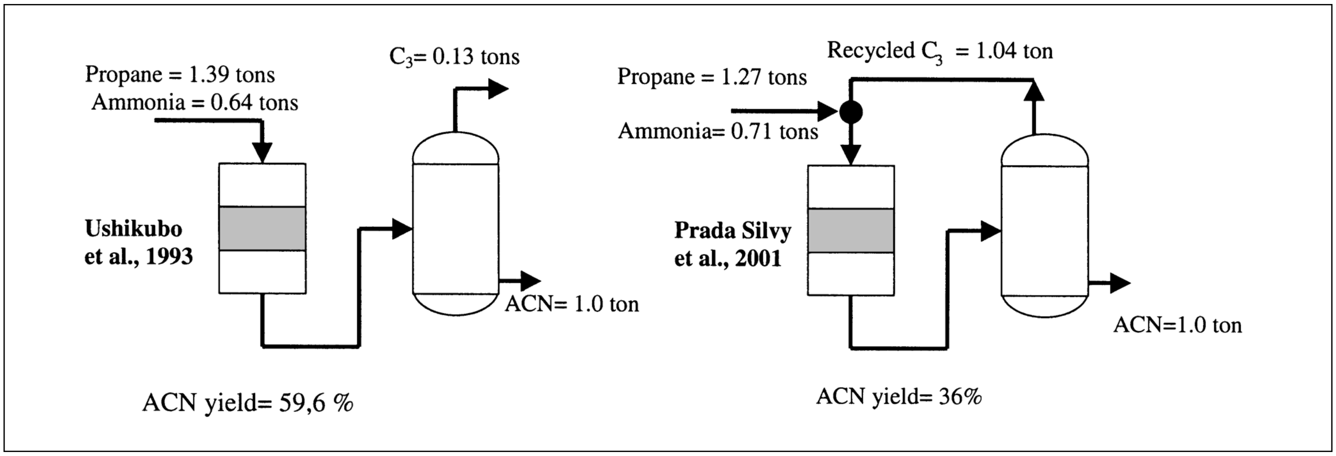

Figure 2. Comparison between propane ammoxidation processes.

Cu, Al, or Ti (Grasselli, 1999; Guttmann et al., 1988; Albonetti et al., 2000).

Other catalytic systems based on Ga-Sb oxides modified with W, Ni, and P as well as vanadyl pyrophosphates were also investigated. However, they were not so promising for the propane ammoxidation reaction.

Comparative catalytic test conditions and activity results corresponding to the best-performing ammoxidation catalysts vs. the VAlON system published in the patent literature are shown in Table 1 and Figure 1, respectively.

The main observations are:

(1) All catalysts show differences in feed-gas composition, reaction temperature, and space velocity for achieving optimal ACN yield.

(2) The vanadium–molybdates system exhibits higher propane conversion and ACN yield at a lower reaction temperature than the $VSb_xM_yO_z$ and VAlON systems. However, VAlON catalyst shows slightly higher ACN selectivity than $VMo_xM_yO_z$ systems.

(3) ACN productivity, expressed as the volume of ACN produced per hour and per volume or weight of catalyst, is higher for the VAlON system than that obtained for the different $VMo_xM_yO_z$ (11.0 and 5.2 times, respectively) and $VSb_xM_yO_z$ (16.0 and 2.5 times, respectively) catalyst formulations. The differences in productivity would be higher if a process scheme with propane recycle were considered.

(4) Propylene formation was reported for all $VMo_xM_yO_z$ and $VSb_xM_yO_z$ catalyst formulations. However, this intermediate was not detected during catalytic reaction with the VAlON system.

The catalytic behavior observed for the VAlON system is the result of an optimal balance between the basic character generated by the activated nitrogen surface species and bulk species ($NH_x^{\delta-}$,N^{3-}) and the electrophilicity degree of the V^{+n} species. Characterization of the VAlON system conducted using different techniques (XPS, XRD, DRIFT, RAMAN, TAP, nitrogen content analysis) point in this direction and the results will be published elsewhere (Florea et al., 2003).

Table 2. Raw Material Cost and Product Price

Raw Material	Cost ($/m·ton)	Product	Price ($/m·ton)
Propane	131	Acrylonitrile	860
Ammonia	220	Ammonium sulfate	105
Sulfuric acid	65		

Comparison between ammoxidation process with recycle of unconverted propane vs. single-step process

We compared propane ammoxidation processes with and without unconverted propane recycle steps, taking the following considerations into account:

(1) Fixed bed catalytic reactor;

(2) Production of 1 metric ton of ACN;

(3) Single-step propane ammoxidation process: propane conversion, ACN selectivity corresponding to $MoV_{0,3}Te_{0,23}Nb_{0,15}O_x$ catalyst reported in Table 1 (Ushikubo et al., 1993), C_3/NH_3 molar ratio of 0.83;

(4) Ammoxidation process scheme with propane recycling: propane conversion and product selectivity corresponding to the VAlON catalyst reported in Table 1, C_3/NH_3 molar ratio of 1.25;

(5) Consumed H_2SO_4 and produced ammonium sulfate were estimated from the unreacted NH_3 (0.92 metric ton for $MoV_{0,3}Te_{0,23}Nb_{0,15}O_x$ catalyst and 1.11 metric ton for VAlON catalyst.

Product prices and raw material costs are those reported in Table 2 (Chem. Market Reporter 2001, 2002; *Chem. Week*, 2002; Van Savage, 2002). Figure 2 shows the consumption of raw materials and product yield for both ammoxidation processes, while Table 3 reports the product price estimated from the preceding yield and raw materials cost deduced from consumption data and the margin between total price and cost.

The results clearly illustrate that propane ammoxidation, using a VAlON catalyst system in a process scheme with recycling, provides a cost margin similar to that of the single-step ammoxidation process. It is also clear that the strategy to increase the production of coproducts would have a positive impact on the profit margin. In fact, VAlON catalyst shows an acetonitrile selectivity of 5% (around 0.12 metric ton). This represents an increase of about $172 product price per metric ton of ACN produced. However, the impact of

Table 3. Product Price, Raw Material Cost, and Gross Margin Estimation

Process	Product	Est. Value	Total Value [1]	Raw Material	Est. Cost	Total Cost [2]	Margin [1]–[2]
Single-step ammoxidation process	Acrylonitrile	$860		Propane	$182		
	Ammonium sulfate	$130	$990	Ammonia	$141	$383	607
				Sulfuric acid	$60		
Scheme with propane recycling	Acrylonitrile	$860		Propane	$166		
	Ammonium sulfate	$159	$1,019	Ammonia	$156	$395	624
				Sulfuric acid	$73		

propane recycling and energy costs must be considered for a better perspective of production costs between these two ammoxidation scheme processes.

The competitive advantage between VAlON and the other propane ammoxidation catalysts would be higher if the space velocities and the coproducts yields (such as HCN and ACCN) were considered in the global economical balance.

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 competitive advantages in acrylonitrile productivity per time and per amount of catalyst as compared with conventional vanadium–molybdates and vanadium–antimonates propane ammoxidation catalysts.

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