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A Review of the Catalysts Used in Propane Ammoxidation Reaction to Produce Acrylonitrile

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Abstract: Background: Various catalysts were studied to synthesize acrylonitrile via propane ammoxidation. The catalysts used for this process can be categorized as antimony-based catalysts, molybdenum-based catalysts, zeolites, nitride material catalysts, and other catalysts. The catalyst which was proved to be an efficient catalyst among all other catalysts is the mixed metal oxide catalyst MoVNbTe due to its high selectivity and yield.

Methods: This review discusses different categories of catalysts and their performance for propane ammoxidation. The parameters discussed to examine the performance of the catalysts are selectivity, yield, and conversion. The review discusses the nature and composition of the phases present in different catalysts, the supports, and additives incorporated into these catalysts, the effect of catalyst preparation methods, and the effect of catalysts on the selectivity and yield of acrylonitrile.

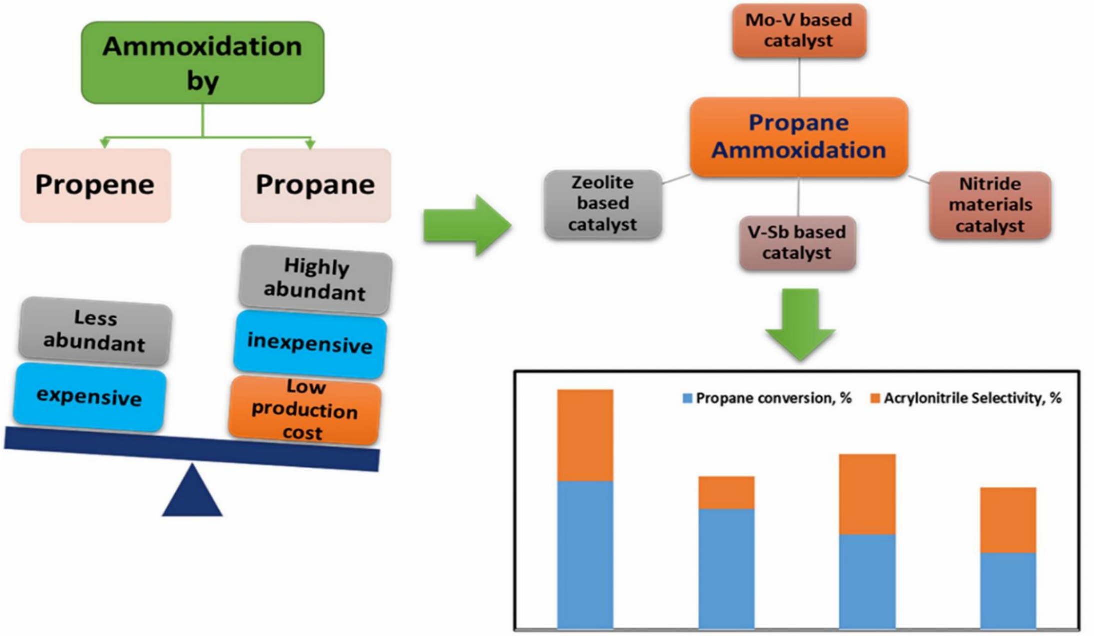
Significant findings: MoVNbTe mixed metal oxide catalyst is proved to be the most efficient catalyst among other catalysts for propane ammoxidation reactions. It consists of M1 and M2 phases; both have different active sites. The M1 phase has an orthorhombic structure and is active for propane activation, while the M2 phase has a pseudohexagonal structure and is active in converting propene intermediate into acrylonitrile.

Keywords: Ammoxidation, Acrylonitrile, Mo-V-Nb-Te, Propane, Propene, Acetonitrile

HIGHLIGHTS

- V/Sb/O oxides generally contain several phases like $VSbO_4$ rutile phase, Sb_2O_4 and V_2O_5
- Hydrothermal method for synthesizing MoVNbTe oxide catalyst gives better activity and higher surface area
- It was observed that the MoVNbTe catalyst possesses two main phases, namely M1 and M2
- The $MoV_{0.4}Nb_{0.1}Te_{0.2}$ gave good results when calcined in the range of 800-970K in the presence of N_2 flow for two hours.

GRAPHICAL ABSTRACT



I. INTRODUCTION

Acrylonitrile (ACN) is an organic monomer with the molecular formula CH_2-CH-CN. It is a colorless, volatile, and toxic liquid compound. It is formed as an intermediate in producing synthetic fibers, rubbers, nitriles, resins (ABS, SAN), and other polymer products. Acrylonitrile is mainly used as a monomer in synthetic polymers, such as polyacrylonitrile (PAN). Moreover, adiponitrile is formed by the dimerization of acrylonitrile, which is used in producing Nylons. BASF (Germany's chemical company) is one of the three adiponitrile producers that use the ACN-based process. Currently, 90% of acrylonitrile is produced by the ammoxidation of propene using Bi–Fe–Ni–Co molybdates as catalysts, by the process called a SOHIO (Standard Oil of Ohio) process. For the first time in the 1950s, SOHIO invented this technology and started the production of acrylonitrile commercially. In 1987, SOHIO became a subsidiary of The British Petroleum (BP) company, and now SOHIO is a part of INEOS [1–3]. Due to the widening price gap, research has recently turned its attention from propene to propane. Even though propene ammoxidation yields acrylonitrile with a higher selectivity and conversion rate, propane ammoxidation is now preferred due to the affordability and availability of propane. Asahi Kasei Chemical Corporation started the commercialization of the process of acrylonitrile production from propane by rejuvenating an old plant [4,5]. Several industries are also considering substituting propene with alkanes, mainly propane, by trying different reaction conditions and catalytic systems.

However, there are some challenges in using the propane ammoxidation process, such as the reaction conditions require high energy to activate the C–H bond in propane, which reduces the selectivity. Thus, the C-H bond activation is the slowest step; hence it is the rate-determining step [6]. It is necessary to accelerate the rate-determining step to improve both the catalyst selectivity and activity. Furthermore, the propane ammoxidation process is very exothermic, with a reaction heat of $\Delta H_{\circ}$= -629 kJ/mol, roughly 22% higher than the propylene-based approach [7]. To avoid the creation of hot spots locally and to limit the bulk oxidation of acrylonitrile and propene, which converts to carbon oxides, efficient heat propagation and precise temperature control of the reaction are essential.

In the literature, two primary catalytic systems have been proposed thus far. They are made up of rutile V-antimonates or multi-component molybdates (Mo/V/Nb/Te/O). According to the reports, V/Sb/Al/W/O system showed the highest acrylonitrile yield among the antimonates [8]. The Mo/V/Nb/Te/O system discovered by Mitsubishi Kasei [9] has been proven active and selective and gave the highest acrylonitrile yields. Asahi [5] altered the Mitsubishi catalyst's composition by substituting Sb in place of Te in one of the catalyst phases, resulting in a more stable catalyst with a longer catalyst lifetime but not as efficient as Mo/V/Nb/Te/O catalytic system.

This study focuses on the catalysts used for propane ammoxidation over the last two decades. The catalysts categorized here are as follows (i) V-Sb-based catalysts [10,11], (ii) V-Mo-based catalysts [12,13], (iii) Zeolite materials doped with different metals [14,15]. (iv) Nitride materials (VAlON, nickel molybdenum mixed nitrides) [16,17].

II. VANADIUM-ANTIMONY BASED CATALYSTS

Several catalysts were introduced for direct selective acrylonitrile formation from propane. The well-known catalysts are V-Sb due to extensive research on the preparation procedure, catalytic performance, and characterization. V/Sb/O oxides generally contain several phases like $VSbO_4$ rutile phase, Sb_2O_4, V_2O_5, and amorphous V and Sb oxides, depending on the conditions applied during calcination, e.g., the reaction environment, Sb/V ratio, and preparation procedure [18]. It is known that a cation-deficient rutile $VSbO_4$ and α-Sb_2O_4 are the crucial phases for an efficient catalyst [19]. However, for ACN formation, the pure phase is neither active nor selective, but the performance is improved if the Sb/V atomic ratio is higher than one [18,20].

According to Centi et al. [21], one of the most exciting catalytic systems for propane ammoxidation is V/Sb/O, and the excess of antimony in the catalyst decreases the activity and also increases the acrylonitrile and propene selectivity. The high antimony content quickens the conversion of the intermediate propene to acrylonitrile. In contrast, an increase in vanadium content not only increases the activity but also decreases the acrylonitrile selectivity due to increased production of carbon oxides (CO_x) and propene. Olga et al. [22] reported a mechanism for propane ammoxidation over alumina-supported V-Sb-O catalyst using rapid scan FTIR coupled with a mass spectrometer. The FTIR-MS analysis revealed that the first step during the propane ammoxidation process is propane dehydrogenation from propylene. The second step is the conversion of propylene to acrylonitrile. The latter was the slowest step and hence the rate-determining step.

A. Addition of Different Elements to the V/Sb System

Propane ammoxidation over metal oxide catalyst contains various reaction steps, including adsorption of propane, hydrogen abstraction, nitrogen insertion, etc. therefore, it is beneficial for the catalyst to contain different types of cations to create required functionalities.

Therefore, several studies were focused on substituting vanadium in the $SbVO_4$ phase with other elements like Aluminium, titanium, tungsten, iron, niobium, chromium, etc. Andersson et al. indicated that the replacement causes the isolation and dilution of the vanadium sites, which was selective for acrylonitrile, although the activity was decreased [23].

Catalysts synthesized by substituting elements in the V/Sb system were proved to be efficient catalysts for acrylonitrile production through the propane ammoxidation process. These catalysts were mainly synthesized by the co-precipitation method, mainly used for synthesizing SnO_2-based rutile systems [24]. These systems have properties that arise from the following features:

- The components in the mixed oxide catalyst, some of which are essential for paraffin activation (i.e., V, Fe, Cr, Ti), and some are active in the oxygen/nitrogen insertion in the allylic intermediate, their structures are similar and can cooperate in the alkane transformation and
- These components can disperse antimony oxide on the surface and provide new active sites efficient in transforming propane to acrylonitrile. The surplus antimony oxide dispersed on the surface and formed a layer above quasi-$VSbO_4$, giving better acrylonitrile selectivity [8,25].

1) Effect of tin incorporation in V/Sb system

The tin-antimony system has been widely studied as an active catalyst in ammoxidation. The catalyst performance depends mainly on the Sn/Sb ratio, the calcination temperature, and the preparation method. The co-precipitation method to prepare these types of catalysts gives better performance. This method consists of co-precipitation of Sn^{4+}, V^{4+}, and Sb^{5+} from a homogeneous ethanol solution and a thermal treatment at 700 °C in the presence of air. Propane ammoxidation is a highly exothermic reaction, so for the effective removal of produced heat, it is suggested to use a fluid-bed reactor [26]. The mixed catalyst of Sn/V/Sb of atomic ratio = 1.0:0.2:1.0 has been synthesized and optimized. Albonetti and co-workers conducted experiments to optimize the original preparation technique of fluid bed catalyst. The silica-based catalyst was not very active, the propane conversion reached 16% only, and the selectivity of acrylonitrile was 22% at 490 °C. The acrylonitrile selectivity was 41% at 8% propane conversion at 450 °C. However, the alumina-based catalyst is more active and reached 27% conversion with low acrylonitrile selectivity (14%) due to the production of carbon oxides. Thus, it can be concluded that the number of active phases in the catalyst was low, and the catalyst was separated into different single oxides (V_2O_5, SnO_2, Sb_2O_4), resulting in high activity and low acrylonitrile selectivity [27].

2) Effect of iron incorporation in V/Sb system

Iron (Fe) was incorporated in the VSbO4 phase due to its specific properties. It has a similar structure to V in $VSbO_4$, and the Fe^{3+} has a cationic radius similar to V^{3+}. The catalysts of composition $V_{1-x}Fe_xSbO_4$ have been prepared using two methods which depend on their relative composition in iron and vanadium, such as V-rich compounds (x<0.5) as described by Nilsson et al. [18] and Fe-rich compounds (x>0:6) as described by Allen et al. [28].

The vanadium substitution by a small amount of iron increases the activity of the catalyst, but the acrylonitrile selectivity decreases while propene selectivity increases. At low loading of Fe, the iron substitutes V^{4+} not V^{3+}, in the cation-deficient structures of $VSbO_4$ as expected. This structure had active sites of high efficiency, which could activate propane but were less selective to acrylonitrile, as shown in Table 1.

At high loading of Fe, Fe substitutes V^{3+} where there is less number of vacancies. It shows low activity, but the acrylonitrile selectivity was high, maybe because of isolating active V-sites [29].

Table 1: Catalytic properties of $V_{1-x}Fe_xSbO_4$ in propane ammoxidation at 753K.

Catalyst	Surface area(m^2/g)	Propane conversion, %	Selectivity, %			Ref.
			Acrylonitrile	propene	CO_2	
$VSbO_4$	3.3	16	24	33	10	[29]
$FeSbO_4$	10.7	22	11	14	67	
$Fe_{0.8}V_{0.2}SbO_4$	6.6	19	38	11	15	
$Fe_{0.2}V_{08}SbO_4$	16	19	15	51	7	

3) Effect of Chromium incorporation in V/Sb system

Chromium (Cr) is proven to be an effective catalyst for the dehydrogenation of low mol. wt. Paraffin. Therefore, Cr may also be used for propane ammoxidation, and $CrSbO_4$ is also isostructural with $VSbO_4$. So, compared to single metal antimonates, the presence of chromium along with vanadium and antimony might lead to the modification of catalytic properties [30].

The considerable difference between single metal antimonates like CrSbO4 and VSbO4 is the reactivity. The reactivity of $VSbO_4$ was mainly affected by the V/Sb atomic ratio. As the ratio decreases from 1/0.8 to 1/2, the acrylonitrile selectivity increases from 15 to 60%; propene selectivity decreases from 55 to 20%; and carbon oxides from 20 to 15%. The combustion of ammonia to nitrogen also decreases from 70 to 20% [31]. Thus, it seems that the catalyst works as a dual-component system. The rutile vanadium plays the role of propane activation and the dispersed Sb_2O_3 acts as a vital component in the transformation of propene to acrylonitrile. While in the case of CrSbO4 catalysts, the reactivity decreases with a decrease in Cr/Sb ratio. The excess antimony oxide formation favors the acrylonitrile formation directly from propane, and propene selectivity was less than 10% [32].

The co-precipitation technique prepared the mixed metal catalysts consisting of chromium, vanadium, and antimony. Cr/V/Sb/O catalysts (Rutile type) were active in propane ammoxidation. A synergetic effect of Cr/V/Sb/O catalysts was suggested to elucidate the high activity compared with V/Sb and Cr/Sb. This effect was maybe due to the generation of V^{4+} instead of V^{3+} in the presence of chromium and (Cr+V)/Sb ratio >1. The acrylonitrile selectivity depends on this ratio. The 35% selectivity was obtained for samples of the lowest ratio of (Cr+V)/Sb. In all cases, the selectivity of propene is very low except where propane conversion is low. This behavior was due to the inherent multifunctionality of the Cr/V/Sb/O catalysts. The excess antimony on the surface helped the catalyst convert the unsaturated intermediates to acrylonitrile for catalyst samples where the (Cr + V)/Sb ratio was 0.5 to 1. Excess antimony oxide favors increased acrylonitrile selectivity due to decreased carbon oxides even for (Cr + V)/Sb ratio < 0.5.

Table 2: (Cr + V)/Sb atomic ratio versus selectivity

(Cr + V)/Sb (at. ratio)	Selectivity (%)			Ref.
	ACN	CO_2	propene	
>1	<20	60-80	10-30	[32]
0.5-1	20-30	55-70	<10	
>0.5	25-35	50-60	<5	

4) Effect of titanium incorporation in V/Sb system

The possibility of titanium incorporation was good since rutile type TiO_2 exists, and the crystal radii of Ti^{4+} are similar to V^{4+}, V^{3+}, and Sb^{5+}, i.e., ~0.61A°. The objective of Ti incorporation in $VSbO_4$ was to substitute vanadium and then achieve isolation and dispersion of V sites on the material surface. The catalyst was prepared with a composition $Sb_{0.9}V_{0.2}Ti_{0.6}O_y$. This catalyst's best performance was 53% ACN selectivity at 25% propane conversion, which was reasonable compared to 12% ACN selectivity at 15% propane conversion for non-substituted $VSbO_4$, as shown in Table 5. The reason behind improved selectivity was maybe lesser bridging of V-O-V moieties that are active for combustion and degradation of propane and the intermittently formed propene [11].

5) Effect of Ti, Ga, Fe, and Nb incorporation in V/Sb system

Another catalyst system formulated for the ammoxidation of propane is the MoV(Nb,Ta)(Te,Sb)O system giving the ACN yield of up to 62% [9,33]. Next is the modified V/Sb system, which gives an ACN yield of up to 40% [8]**,** in which the $SbVO_4$ was a crucial catalyst phase. However, the pure $SbVO_4$ phase had cation deficiency [25] and low activity and selectivity for acrylonitrile [18]. Thus, selectivity improvement could be attained by replacing some of the V and Sb atoms from the crystal structure. Considering the cations valencies, the replacement can be done by other metals of the same size. Hence the ionic radii of Fe^{3+}, Ga^{3+}, Ti^{4+} Nb^{5+} are similar to V^{3+}, V^{4+}, Sb^{5+}, all are approx. 0.6Å [66]. The substitution in a $SbVO_4$ was made with V^{3+} replaced by Ga^{3+} and Fe^{3+}, and Nb5+ replaced Sb^{5+}, while Ti^{4+} substituted both V^{4+} and V^{3+}/Sb^{5+} pairs. The same procedure prepared this type of catalyst reported elsewhere to prepare the pure $SbVO_4$ with the nominal composition $Sb_{0.9}V_{0.9-x}M_xO_y$where M was Fe, Ti, or Ga.

The catalytic performance of the samples prepared was observed. It was revealed that as compared to pure $SbVO_4$, Fe, Ti, Ga, substitution gives low activity but high acrylonitrile selectivity at the same conversion of propane, such as the catalyst with metal atom ratio Sb:V: Ti=9:5:4 gives 44% acrylonitrile selectivity and 11% yield at 25% propane conversion and 480 °C. In contrast, niobium substitution gives very low acrylonitrile selectivity [34].

6) *Effect of Aluminium and Niobium Support on V/Sb system*

The catalysts containing V/Sb oxides on niobium and aluminum support exhibit different structural characteristics that reflect in catalyst behavior during the propane ammoxidation reaction. It has been observed that alumina had weak interaction with the supported oxides, due to which it was described as good support. Hence structural changes may occur only on the dispersed species on the alumina-supported V/Sb surface, named “horizontal interactions.” While niobium’s behavior as a support is intriguing, since it is acidic, it promotes the interaction of ammonia with the catalyst. Niobium oxide possesses similar features as vanadium oxide, and the control over side reactions such as ammonia elimination may become more accessible due to its lower reducibility [35].

Niobia-supported V/Sb oxides show another kind of dependence on V + Sb coverage. The catalysts were more selective towards acrylonitrile below monolayer coverage and obtained high yields than alumina-supported catalysts, as shown in Table 3. Therefore, the presence of niobium must be responsible for forming new catalytic sites[36].

7) *Effect of Tungsten on alumina supported V/Sb system*

Tungsten is considered an active material, while alumina is considered a suitable catalyst. The catalyst incorporating tungsten and alumina on the V/Sb system was prepared by the slurry method. At 610 °C, the Al/Sb/V/W oxide catalyst was calcined in air, and the propane ammoxidation reaction took place at 480 °C. Due to the influence of the reaction medium, an active and selective catalyst structure was formed. From XPS measurements, it was observed that during activation, the amount of Sb was decreased on the surface, while the W and V amount increased. The continuous increase of acrylonitrile selectivity could be due to the introduction of W^{4+} in the rutile-type structure. The tetrahedral and octahedral tungsten oxides attached to alumina were present in the system. The only active phase in this system was $Sb_{0.9}V_{0.9-x}W_xO_4$, where $0.3<x<0.6$, obtained by solid solution between $Sb_{0.9}V_{0.9}O_4$ and WO_2, which is selective and active to acrylonitrile formation [8].

Table 3: Supported V/Sb oxides dependence on V + Sb coverage

Catalyst (Sb+V)	Below monolayer coverage (e.g., $0.5Sb_5V/Al$)	At monolayer (e.g., $1Sb_5V/Al$)	Above monolayer coverage (e.g., $2Sb_5V/Al$)	Ref.
Alumina supported	Not Selective because the main products are CO_x and propylene	Selectivity towards acrylonitrile	High acrylonitrile selectivity and high propylene production	[8]
Niobia supported	More selective than alumina. The main products are acrylonitrile and propylene, and high yield	Low selectivity	High acrylonitrile selectivity and high CO_x production, and low propylene	

The performance of the catalysts $(Sb,V,Ti)O_4$, $Sb(V,Al)O_4/Al_2O_3$, and $Sb(V,W)O_4/\ Al_2O_3$ were compared based on propane conversion. The propene selectivity decreases as the propane conversion increases, and simultaneously the acrylonitrile selectivity increases and goes through a maximum. Over $(Sb,V,Ti)O_4$ catalyst, at 25% propane conversion, the acrylonitrile selectivity reaches 53%. In contrast, over $Sb(V,Al)O_4/Al_2O_3$ catalyst, the acrylonitrile selectivity reaches 45% at 30% propane conversion, and for $Sb(V,W)O_4/\ Al_2O_3$ catalyst, the selectivity reaches 50% at 55% propane conversion. At 40–50% propane conversion, the acrylonitrile yield was around 20% over the catalysts with Al and Ti. W substitution is the most effective, and the acrylonitrile selectivity and yield were 47% and 38% over an $Sb(V,Al)O_4/Al_2O_3$ catalyst at 80% propane conversion, as shown in Table 4. The reaction was carried out at 480 °C in a glass-made plug–flow reactor. The composition of the inlet stream was 35.7 % nitrogen, 14.3% propane, 14.3% ammonia, 28.6% oxygen, and 7.1% water vapor [23].

Table 4: Catalytic performance of titanium or tungsten-modified V/Sb system

Catalyst	Propane conversion, %	ACN selectivity, %	ACN yield, %	Ref.
$(Sb,V,Ti)O_4$ Sb :V : Ti = 9 : 3 :6	25	53	13	[23]
$Sb(V,Al)O_4/Al_2O_3$ Al : Sb :V = 21: 5 : 1	50	39	20	
$Sb\ (V,\ W)\ O_4/\ Al_2O_3$ Al : Sb :V:W = 21 : 5 : 1 : 1	80	47	38	

8) *Effect of Magnesium on alumina supported V/Sb system*

The effect of magnesium as a dopant on alumina-supported V-Sb mixed oxides catalyst was studied here. The unmodified catalyst sample was loaded with an appropriate amount of magnesia (Mg/Al= 0.1) [37]. The loading was the same in all samples with Sb/V= 1. The magnesia-alumina supported catalyst was prepared by impregnation at room temperature for 2 h with the solutions of ammonium metavanadate (NH_4VO_3), antimony chloride ($SbCl_3$), and tartaric acid. The tartaric acid completely dissolves the antimony and enables better involvement of Sb sites than the catalyst samples prepared by the slurry method [38]. The specific surface area of catalyst samples decreases with an increase in Mg amount. This behavior may be due to the formation of magnesium vanadate phases. Therefore, small amounts of Mg were used in catalyst preparation. The XRD patterns for $MgAl_6O_{10}$ and Al_2O_3 are almost the same. Thus, the presence of $MgAl_6O_{10}$ in the V–SbO/Mg–Al catalyst cannot be neglected. A peak was obtained, which may represent both $VSbO_4$ and Sb_2O_3. Since Sb_2O_3 possess strong RAMAN bands, which were not observed in catalyst samples, thus, these diffraction patterns must represent the $VSbO_4$ phase.

Since Mg has a high affinity for vanadium, it was observed that due to the interaction of vanadium with magnesium, a high fraction of vanadium detached from the $VSbO_4$ phase, increasing cationic vacancies. The high intensities of RAMAN bands of cationic vacancies in the VSbO4 structure backed this up. Also, Mg reduces the acidic sites on the catalyst surface. It reduces the undesired oxidation of propene intermediate to form carbon oxides, which in turn eases the insertion of nitrogen to form acrylonitrile. Therefore, the Mg-containing samples at low propane conversion give higher selectivity of acrylonitrile and low selectivity to carbon oxides, as shown in Table 5. It was also observed that both catalyst samples were stable during the time on stream for at least eight hours [39].

Table 5: Catalytic performance of magnesium incorporated alumina supported V/Sb system

Catalyst	Surface area (m_2/g)	Propane conversion, %	Selectivity, %			Ref.
			ACN	Propylene	CO_x	
VSb/Al	87	42	48	12	22	[39]
VSb/MgAl	67	30	60	20	16	

9) *Effect of Molybdenum Incorporation in V/Sb System*

Mo-based mixed metal catalysts are well known for converting alkene by oxidation into an oxygenated compound. Adding molybdenum is believed to take part in NH insertion in the allylic intermediate. Apart from V/Sb systems, another category of catalysts used in propane ammoxidation, which are active and selective, are Mo/V/ Nb/Sb(Te) mixed oxides, developed first by Mitsubishi [40]. However, Mo incorporated in the V/Sb system has a very different catalyst composition from the Mitsubishi catalysts. Here the co-precipitation method was used for catalyst preparation.

The presence of molybdenum in the structure boosts catalytic activity while lowering acrylonitrile selectivity. This behavior was owing to increased propane combustion and ammonia oxidation to molecular nitrogen. Since Lewis acidity is enhanced, the interaction of the catalyst with NH_3 increases. For Mo-containing samples (Mo/V/Sb atomic ratio= 0.4/2/1), the maximum in the acrylonitrile selectivity was not observed. This behavior was not expected from the Mo-containing catalyst; no new sites were generated, while carbon oxides and ammonia yields were enhanced [41].

On the contrary, Shishido et al. [42] prepared Mo/V/Sb catalyst by slurry method with different catalyst compositions, as shown in Table 6. and found that the addition of Mo increases the acrylonitrile selectivity. At the same time, the propane conversion was not affected very much. It indicates that the propene formed was quickly converted to acrylonitrile. The phases detected by XRD were highly dispersed MoO_3 along with $VSbO_4$ and Sb_2O_3. Since the surface of bulk MoO_3 is acidic, a large amount of dispersed MoO_3 on a metal oxide support results in a higher local acid concentration on the surface. Thus, due to large crystallites of MoO_3 in $Mo_{10}V_1Sb_{10}O_x$ than $Mo_1V_{10}Sb_{10}O_x$, cracking reactions like C-C bond cleavage occurs. With the cracking reaction, it is likely that non-selective oxidation may occur over the $Mo_{10}V_1Sb_{10}O_x$ and decreases the acrylonitrile selectivity. The acrylonitrile selectivity also depends on the V/Mo ratio.

Table 6: Catalytic performance of molybdenum incorporated V/Sb system

Catalyst	Propane Conversion, %	Selectivity, %				Ref.
		Propene	Acrylonitrile	Acetonitrile	CO_x	
$V_1Sb_{10}O_x$	8.5	33.7	42.4	5.8	18.1	[42]
$Mo_1\ V_1Sb_{10}O_x$	7.4	11.5	61.3	3.7	21.7	
$Mo_{10}\ V_1Sb_{10}O_x$	9.7	18.5	42.2	16.8	22.5	

10) Effect of Molybdenum and niobium incorporation in the V/Sb system

Mo and Nb introduction in the V/Sb system improves the catalyst performance for the ammoxidation of propane individually [35,42]. Perez and co-workers studied the effect of these compounds when they are employed together in the V/Sb system. The catalyst preparation procedure dramatically affects the nature of the phases present in the catalyst samples. A reference catalyst ($SbVO_4$) and different catalyst samples of variable Nb/Mo, Sb/Mo, and V/Mo were prepared. The catalyst having enough α-MoO3 gives low ACN selectivity and yield, while the presence of the $SbVO_4$ phase showed high activity and high ACN selectivity. Sb appears as a critical component in the catalyst for the ammoxidation of propane and prevents the oxidation of propane to acrylic acid.

At moderate loading, adding Mo had a good effect, but it shifted the reaction towards acetonitrile at high loading. The catalysts possessing large α-MoO3 crystallites were less selective towards acrylonitrile. Due to the low content of Nb, the Nb-containing phases were not detected by XRD. However, the reference catalyst ($SbVO_4$) obtained a high acrylonitrile yield among other catalyst samples. The second-best yield was obtained by MoVSbNbO (V/Mo=1, Sb/Mo=1, Nb/Mo=0.1), as shown in Table 7. The high performance of the reference catalyst was not entirely due to the high surface area but the presence of a small amount of α-Sb_2O_4. The excess of α-Sb_2O_4 increases the catalytic properties [43].

Table 7: Catalytic properties of molybdenum and niobium incorporated V/Sb system

Catalyst	BET area (m^2/g)	Phases detected by XRD	Propane conversion, %	Selectivity, %	Yield, %	Ref
$SbVO_4$ (reference catalyst)	55.1	$SbVO_4$ (V_2O_5, α -Sb_2O_4)	84	47	39	[43]
$Mo_1V_1Sb_1Nb_{0.1}O$	6.4	$SbVO_4$, Sb_2MoO_6	58	42	24.3	
$Mo_1V_{0.33}Sb_{0.22}Nb_{0.07}/SiO_2$	-	-	50	56.4	28.7	[44]

11) Effect of different catalyst preparation methods for V/Sb system

The mixed-metal oxide catalysts are prepared mainly by slurry and co-precipitation methods. In comparison, the co-precipitation method has a higher surface area than the slurry method [24].

The co-precipitation method for V/Sb catalyst of atomic ratio=1 involved the dissolution of vanadyl acetylacetonate ($VO(acac)_2$) and $SbCl_5$ (V/Sb atomic ratio=1) in ethanol; this solution was mixed into a buffered aqueous solution at pH=7. The precipitate formed was removed from the residual liquid. The samples were dried overnight at 140 °C and then treated in the presence of air at temperatures from 140 °C to 300, 450, 550, and 700 °C. The highest surface area (34 m^2/g) was achieved when the sample was gone through the thermal treatment at 550 °C.

But the co-precipitation method has certain disadvantages:

- During the thermal treatment of the catalyst sample, harmful compounds may release into the gas phase.
- The solution used for catalyst preparation by this method contains cations and anions in the waste stream, which requires further treatment for their removal.

Another V/Sb mixed oxide catalyst preparation technique advantageous over other methods is solid-state synthesis, also known as mechano-chemical synthesis. This method may change the texture or morphology but can initiate solid solution formation. It is appropriate for nanocrystalline materials. This method has been used to prepare several catalysts such as V/Sb/Ti/O [45], V/P/O either supported or bulk [46].

In the mechano-chemical method to prepare the V/Sb catalyst, $V_2O_{5,}$ and Sb_2O_3 were mixed in the appropriate ratio and kept in a vessel with stainless steel spheres (metal oxides/spheres weight ratio= 0.05).

Then the solids were kept for 70h under pulverizing conditions. The uncalcined sample had a surface area of 18m^2/g. The surface area was decreased after calcination. The calcination at 700 °C led to a higher number of cationic vacancies in vanadium antimonite than the corresponding sample synthesized by the co-precipitation method. It resulted in higher activity but lower acrylonitrile selectivity. It was due to the excess amount of oxidized V sites which increases the combustion of ammonia and propane [47].

III. MOLYBDENUM-VANADIUM BASED CATALYSTS

Various Mo-V-based catalysts have also been proposed for the propane ammoxidation process to produce acrylonitrile. The Mo/V system alone was insufficient to give proper activity for the propane ammoxidation process. Hence it was necessary to incorporate other elements into the system to play their roles toward increasing the catalyst performance.

For a comparative study, five single-phase samples (Mo-V-O, Mo-V-Sb-O, Mo-V-Te-O, Mo-V-Sb-Nb-O, and Mo-V-Te-Nb-O) were prepared by the hydrothermal method. For the Mo-V-Sb-Nb-O catalyst, it is evident that when the drying method is used, both two phases were formed. Thus, to remove the pseudo-hexagonal phase (M2), the calcined samples in which both phases were present underwent treatment in a 15% H_2O_2 at ambient temperature. It was reported that in the case of Mo-V-O, Mo-V-Sb-O, Mo-V-Te-O, and Mo-V-Te-Nb-O catalysts, it was possible to synthesize only the orthorhombic phase when the catalysts were prepared by hydrothermal synthesis. It was indicated that Nb is not responsible for orthorhombic phase formation. Niobium is considered to inhibit crystallization during synthesis. The molar ratio of Sb/Mo and Te/Mo of Mo-V-Sb-Nb-O and Mo-V-Te-Nb-O were increased due to the introduction of Nb. The catalysts synthesized above were all active for the ammoxidation of propane. In the case of Te-containing catalysts, the propane conversion was slightly higher than catalysts containing Sb. All catalysts showed similar activities of 20-30% for converting ammonia. Thus, it can be deduced that the presence of Mo and V was the common factor that largely contributed to active site creation for propane activation in propane ammoxidation. It was observed that the formation of nitrogen decreased in the following manner Mo-V- O> Mo-V-Te- O = Mo-V-Sb- O = Mo-V-Sb-Nb-O > Mo-V-Te-Nb-O. This ammonia conversion to nitrogen molecule was worst in the Mo-V-Te-Nb-O catalyst, which means that most ammonia was utilized in the reaction when Te and niobium were present in the catalyst. The introduction of Te or Sb exhibits a crucial role in the allylic oxidation of the propene intermediate, improving acrylonitrile selectivity. Also, the oxidative decomposition was reduced by Sb or Te. Niobium had a dilution effect on vanadium already present in the phase, thus increasing acrylonitrile's selectivity, resulting in the highest acrylonitrile yield for the Mo-V-Te-Nb-O catalyst [48].

A. Effect of Te addition over alumina-supported Mo-V-O catalysts

These supported catalysts were prepared by the wetness impregnation method. The supported catalyst was labeled as $Mo_aV_bTe_c$-(N) or (O), depending on the activation environment, whether in nitrogen or air. After BET characterization, it was observed that tellurium does not have a significant impact on the surface area, but when calcined in the presence of air, the surface area of the samples decreased five times when calcined. When the Mo-V-Te oxide catalyst was supported on alumina support, small nanoaggregates of the oxides were obtained, increasing the surface-to-volume ratio and allowing a better understanding of active sites. For the Te-containing catalyst, at temperatures (<400 °C), propene was the main product, but at higher temperatures (>425 °C), acrylonitrile was the main product. For oxygen-calcined samples, the conversion of propane decreases, and for nitrogen-calcined samples, propene and acrylonitrile yields were around 5% and 8% at 425 °C. The acrylonitrile yield obtained in any case for this catalyst system was not relatively high. High yields were achieved when Sb/Nb was added to the Mo-V-Te catalyst system. Although, tellurium and high concentration of molybdenum favor the presence of V^{4+} species and prevent the generation of molybdenum-based poly acids [49].

B. Mesostructured Mo-V-Nb-O catalyst

Mesostructured Mo-V-Nb mixed oxide catalysts were synthesized by the reaction of metal precursors in the presence of anionic, cationic, and alkyl amine surfactants. Surfactant-assisted catalyst is an emerging method for developing novel catalytic phases with particular structural, morphological, and compositional properties. The surfactants employed in the preparation procedure were alkyl trimethyl ammonium bromides, do-decyl sodium sulfate salt, and primary alkyl amines. The XRD patterns of these mesostructured oxide catalysts exhibit the peaks representing the lamellar phase, and Mo, V, Nb species coexisted as polyanionic species in the catalyst synthesis at a solution pH of 5.8. The SEM images of the catalysts have shown the plate-like morphology of the observed lamellar phase, indicating the mesostructured formation as large aggregate particles (~15-20 µm) with a layered structure. This behavior was determined in terms of the surfactant packing parameter called 'g' and $g = V/a_o l$, where 'V' was the total volume of the surfactant and any molecules between the chains, 'a_o' was the surfactant headgroup area at the interface and 'l' was the surfactant length. For 1/3 <g<1/2, the formation of hexagonal phases was favored; for 1/2<g<2/3, the cubic phases were favored, and for g=1, the lamellar phases were favored. The mesostructured catalyst prepared by employing octadecyl amine calcined at 400 °C gives 26% acrylonitrile selectivity and 49% acetonitrile selectivity at 66% propane conversion and 480 °C [50].

C. Use of Mo-V-P-O_y/Al_2O_3 catalysts

Mo-V-P mixed oxide catalysts supported on Al_2O_3 were prepared by the impregnation method with the varied phosphorus content. The prepared catalysts were denoted as 18.1Mo1.9VXP/Al where X= 0, 0.6, 1.2, 2.3, 3.5 is the weight percentages of phosphorus. The Mo and V loading in total was fixed at 20% by weight in all catalyst samples. All the catalysts had high surface area, large pore diameter, and large pore volume, indicating well-developed mesopores existence. It was observed that the pore diameter and volume decrease with an increase in phosphorus content, possibly due to the pore's blockage by phosphorus. The XRD pattern indicated the presence of γ-alumina and MoO_2 in all samples, but the peaks associated with phosphorus and vanadium were not observed.

The atomic ratio of P/Al increased with an increase in P content, and the (Mo+V)/Al surface atomic ratio of 18.1Mo1.9VXP/Al catalysts was higher than that of 18.1Mo1.9V/Al. It means phosphorus weakened the interaction between Mo-V oxide and alumina and helped transfer Mo and V to the alumina surface. Most of the molybdenum existed as Mo6+ in phosphorus-containing samples.

The catalyst sample in which X= 0.6 gives the highest acrylonitrile selectivity and yield (29%). It was also observed that acrylonitrile yield increases with the decrease in the binding energy of Mo $3d^{5/2}$ of the samples. It was because polymeric molybdenum species were more advantageous for the ammoxidation of propane [51].

D. Orthorhombic Mo-V-Sb-O catalyst

Inukai et al. synthesized this type of catalyst by introducing Sb into the Tri-MoVO structure by dispersing Tri-MoVO in the solution of $Sb_2O_{3,}$ and Sb was entered into the system through a redox process and deposited at the heptagonal channel and gets connected in the form of infinite $[O-Sb(=O)-]_\infty$ chains. Surprisingly, when this structure underwent heat treatment, structural transformation of the Tri-MoVSbO sample to the Ortho-MoVSbO sample was observed. Sb was found to be located at the hexagonal channel of the Ortho-MoVSbO sample as dimers of trigonal pyramids. This Ortho-MoVSbO catalyst showed considerable catalytic activity for propane ammoxidation but was not as good as other MoVSb catalytic systems. The propane conversion was 56%, and acrylonitrile selectivity was 55.4%. However, the results of structural transformations can be quite valuable in gaining a better knowledge of the crystallization process of orthorhombic MoVTe(Sb)NbO catalyst for propane ammoxidation if prepared for industrial use [52].

E. Mixed metal Mo-V-Nb-Te oxide catalyst

Firstly, Ushikubo and co-workers synthesized this new catalyst [9,40,53], and it was found that the catalyst shows high acrylonitrile selectivity at high propane conversion in comparison with other catalyst systems and can operate at relatively low temperatures (693-723K) [6]. From XRD, it was observed that this catalyst possesses two main phases, M1 and M2, described below in detail. Over the past years, various modifications have been done to this mixed metal oxide catalyst, like a supported catalyst, doped catalyst, promoted catalyst, and use of additives with a catalyst to further improve the catalyst performance.

Later, Asakura et al. reported the kinetic study of the ammoxidation of propane on MoVNbTe catalyst and observed that the activation energy in the case of propane conversion for propane ammoxidation was lower than for propene ammoxidation. Some parameters which affect the propane ammoxidation process were also examined, like optimum preparation conditions for the active catalyst, calcination temperature, and environment and drying process. It was observed that the $MoV_{0.4}Nb_{0.1}Te_{0.2}$ gave good results when calcined in the range of 800-970K in the presence of N_2 flow for two hours. The catalyst showed 87% propane conversion and 55% acrylonitrile selectivity at 693K under the flow conditions 6/7/17/70% ($C_3H_8/NH_3/O_2$/He) [13], as shown in Table 8.

Table 8. Performance of multicomponent oxide catalysts

Catalyst	Flow conditions,%	Temp, K	Propane conversion	ACN selectivity	Ref.
$MoV_{0.4}Nb_{0.1}Te_{0.2}O_x$	$C_3H_8/NH_3/O_2$/He =6/7/17/70	693	87	55	[13]
$MoV_{0.32}Nb_{0.13}Te_{0.2}O_n$	$C_3H_8/NH_3/O_2$ =1/1.2/15	693	92.7	57.5	[53]
$VSbO_x$	$C_3H_8/NH_3/O_2$ =1.2/15.3/15.2	773	75	20	[54]
AgBiVMoO	$C_3H_8/NH_3/O_2$ =44/15/41	788	15.8	64.9	[55]
$VSbWP/Al_2O_3$	$C_3H_8/NH_3/O_2/H_2O$ =1/2/3/6	773	85	37	[56]

It was suggested that this multi-component catalyst have the following features:

- Isolation of active Mo and V sites
- Low valence states stabilization (V, Mo)
- Over reduction prevention
- Acidity enhancement
- Active site formation [13].

The catalyst is acidic due to the high electronegativity of the elements of the MoVNbTe oxide catalyst. Introducing additives with strong different acid-base properties affects the acidity of surface-active sites and changes the catalytic process [57].

1) M1 and M2 phase

The M1 phase has an orthorhombic structure and is active for propane activation, while the M2 phase has a pseudo-hexagonal structure and is active in converting propene intermediate into acrylonitrile. It is suggested that the elemental composition and peculiar structure of these catalysts were closely related to the catalytic ability [58].

The elemental composition of M1 is $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$, and M2 is $Mo_{4.67}V_{1.33}Te_{1.82}O_{19.82}$ [59]. It was reported that the $Mo_{0.6}V_{0.187}Nb_{0.085}Te_{0.14}O$ catalyst comprises 60% M1 phase and approx. 40% M2 phase and a trace of monoclinic $TeMo_5O_{16}$, a maximum activity of acrylonitrile can be achieved [7].

The M1 phase is responsible for paraffin activation due to the presence of V^{5+} centers. However, it is also efficient in transforming propane directly to acrylonitrile since it contains the remaining key ammoxidation elements at the active center and within bonding distance. The M2 phase (missing V^{5+}centres) is incapable of converting paraffins, but it is a suitable olefin ammoxidation catalyst. Thus, they can work together when the two phases are in proximity under reaction conditions. The M1 phase primarily converts the propane directly to acrylonitrile, while the M2 phase converts any unconverted propylene produced on the phase into acrylonitrile. And so forth, the M2 phase, also called the mop-up phase, is the co-catalyst assisting the phase [7], performing a clean-up operation transforming free intermediates like propene into the desired end products such as acrylic acid or acrylonitrile [59,60].

M1 phase comprises metals of different oxidation states like V^{4+}, V^{5+}, Mo^{6+}, Mo^{5+}, Te^{4+}, Nb^{5+} and M2 phase containsV^{4+}, Mo^{6+}, $Te^{4+}$and might some Nb^{5+} [7]. The main difference between the M1 and M2 phases is that the M1 phase contains V^{5+} centers. Thus, the M1 phase is capable of activating paraffins. Another difference is that the M1 phase had niobium, while the M2 phase had traces of Nb. Niobium plays crucial roles in the M1 phase, which are as follows:

- It segregates the active catalytic centers from one another and is responsible for the high selectivity of the M1 phase to produce acrylonitrile
- It is also responsible for overall catalyst structure stabilization [61].

2) Mechanism of propane ammoxidation over MoVNbTe catalyst

Graselli et al. proposed that in the orthorhombic M1 phase, the active catalytic center is a multi-metallic, multifunctional assembly containing all the key elements ($2V^{5+}/Mo^{6+}$, $1V^{4+}/Mo^{5+}$, $2Mo^{6+}/Mo^{5+}$, $2Te^{4+}$) that are needed for the conversion of propane into acrylonitrile. These centers are stabilized by four Nb^{5+} centers which spatially isolate the active centers from each other, hence leading to high acrylonitrile selectivity. Each Nb^{5+} center is surrounded by Mo octahedra. In mild reaction conditions, the M1 phase is sufficient as a catalyst for propane ammoxidation, but in demanding conditions, the synergetic effect of M1 and M2 is required [62]. The whole mechanism of acrylonitrile formation through propane ammoxidation reaction over the M1 phase of MoVNbTe catalyst involves the following steps:

- Initially, the propane activation occurs by methylene (-CH2-)-H abstraction on a V^{5+} center located on the active site of the catalyst, as shown in sketch 2 of figure 1. The abstraction occurs at the methylene position to produce the secondary propyl radical, which is more stable.
- The propyl radical then loses methyl hydrogen, which attaches with the oxygen of an adjacent, Te^{4+} forming a propylene molecule as shown in sketch 3.
- The π-electrons of the propylene molecule coordinate with the Mo^{6+} center, and the neighboring Te^{4+} abstracts another H from the allyl intermediate, as shown in sketch 5.
- For this abstraction, regeneration of tellurium from +3 to +4 oxidation state was required, which was done by reaction of supplied oxygen with the hydrogen associated as O-H to Te, which was removed as half water molecule regenerates tellurium as shown in sketches 4 and 6.

- The NH associated with Mo^{6+} inserts into the allyl radical reducesMo^{6+} to Mo^{5+}, with the support of the spectator oxo group (Mo^{6+}=O) as shown in sketch seven, and the hydrogen transfers from N to adjacent O as (Mo^{5+}-OH) as shown in sketch 8.
- The remaining transformations occur, like removing two hydrogens, one from Mo^{5+} and one from Te^{3+}, as shown in sketch 8.
- Another hydrogen abstraction takes place by tellurium, as done in earlier steps, and the dissociation of the Mo^{5+}-N bond also takes place, resulting in the formation of acrylonitrile, as shown in sketch 9.
- Further addition of ammonia results in removing the water molecule and inserting NH as Mo^{4+}=NH, as shown in sketch 10.

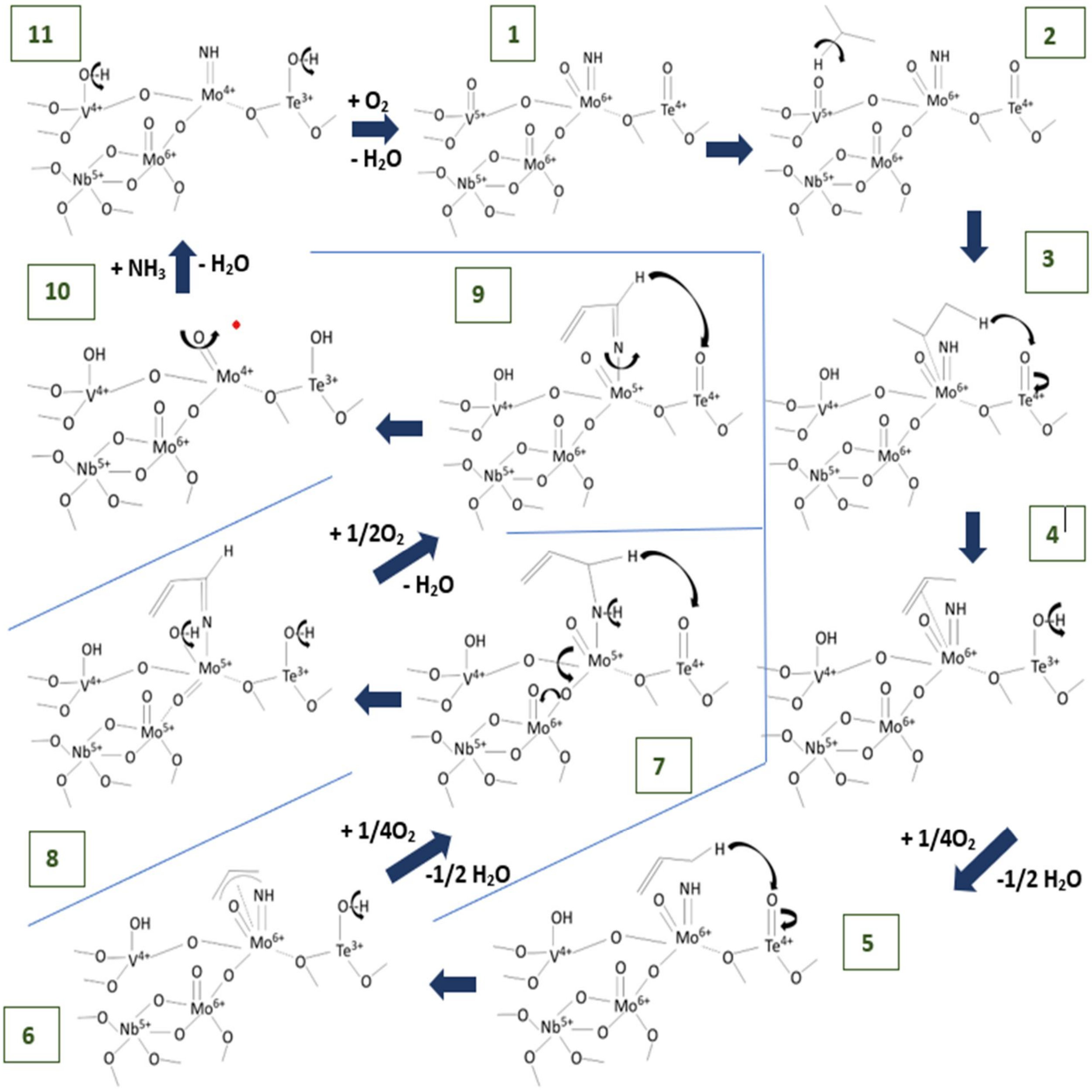


Fig. 1 Proposed mechanism of propane ammoxidation reaction over MoVNbTe catalyst

3) The function of each element in the MoVNbTe catalyst

The paraffin-activating element is almost always vanadium. It is also in its highest oxidation state (e.g., V^{5+}), giving an intensely radical nature to its oxygen, capable of attacking the methylene-hydrogen of paraffin and abstracting it as an H-free radical. The olefin chemisorbing an O or NH inserting element must have a covalent character, be unsaturated, and reside in its highest oxidation state (e.g., Mo^{5+}, Sb^{3+}, Te^{4+}).

When other redox elements are present in the catalyst, they have a redox potential higher than the O or NH-inserting elements of the active center (e.g., V^{5+}).In general, the α-hydrogen abstracting site of the olefin ammoxidation catalyst is an element having a lone pair of electrons (e.g., Te^{4+},) giving a partial radical nature to the oxygen associated with it, hence causing the abstraction of the α-H as an H free radical. The active catalytic centers must be isolated from each other to function efficiently, so site isolation is necessary for optimum selectivity. To achieve the optimum activity, they must be adjacent to or in close contact with re-oxidation sites so they can communicate with each other. V^{5+} species act as active sites on the surface of MoVTeNbO in propane activation [62]. The Nb^{5+} introduction favors the M1 phase with higher thermal stability and low acid sites on the catalyst surface, improving the yield of acrylonitrile during propane ammoxidation [63].

4) *Effect of catalyst preparation methods*

The first method used to prepare this catalyst is the slurry method, also called the dry-up method. The catalyst synthesized by the slurry method shows high acrylonitrile selectivity (>50%) at high propane conversion (>85%) in comparison with other catalyst systems, and it can be operated at relatively low temperatures with respect to other catalysts [12].

The calcination procedure for this catalyst has been optimized, and higher or lower above that temperature gives fewer active catalysts. Also, when the oxygen contamination in helium flow during calcination exceeds 1000 ppm, propane conversion decreases abruptly. The peak intensities in the patent decreased, and the new peaks were generated, corresponding to the MoO_3 phase [53]. No peaks were observed that correspond to Nb_2O_5 and V_2O_5, even under the presence of oxygen during calcination.

It was reported that the low calcination temperature of 673K was necessary for the amorphous phase of the catalyst, and Nb plays a crucial role in stabilizing the amorphous phase. But in this catalyst, at 773 K, the activity starts appearing, and crystalline phases are observed. The active phases were present only in the crystalline phases [64].

In the early years of this field research, the mixed metal oxide catalyst was synthesized by the slurry or dry-up method. Then later, Watanabe et al. suggested that the hydrothermal method for preparation of MoVNbTe mixed metal oxide catalyst gives better activity and higher surface area in propane ammoxidation to acrylonitrile than the dry-up method [65]. Table 2 shows the surface area of this catalyst prepared by hydrothermal (HTT) and dry-up methods (DRU). Reaction conditions: feed inlet gas molar ratio, propane/ammonia/air = 1.0/1.2/15.0, reaction temperature 693 K.

Suppose a catalyst of composition $Mo_aV_bNb_cTe_dO_x$ is to be prepared. In that case, b, c, and d are atomic ratios based on the molybdenum of atoms ‘a’. and ‘x’ is the value corresponding to the highest oxidized state of Mo, V, Nb, Te. It is especially preferred that a =1, b=0.1 to 0.6, c=0.01 to 0.6, and d=0.05 to 0.4.

a) *Slurry method or dry-up method (DRU)*

In the patented method, complex oxide $Mo_1V_{0.4}Nb_{0.1}Te_{0.2}$ was prepared as follows:

Ammonium metavanadate (4.21 g) was dissolved in 117 mL of hot water to make solution 1, then telluric acid (4.13 g) and ammonium heptamolybdate (15.89 g) was added to solution 1 to make solution 2. Then, to make a slurry, ammonium niobium oxalate (3.99 g) was dissolved in 17.9 ml water and added to solution 2. The resulting slurry is dried by evaporating at 150°C until complete dryness. The dry powder was then calcined for 2 hours in a nitrogen environment at 873K [9].

b) *Hydrothermal Method (HTT)*

The complex oxide $Mo_1V_{0.3}Nb_{0.12}Te_{0.17}$ was prepared as follows:

According to the literature, 6.6 mmol of heteropoly anion was dissolved in 40 ml of hot water heated to 353K, and 16 mmol of vanadium-containing 10 ml of aqueous $VOSO_4$, 4.8 mmol Nb_2O_5, and 16.7 mmol oxalic acid was mixed successively to generate a blue solution. The solution was agitated for 10 minutes at 80°C before being placed in the autoclave and heated for 48 hours at 448°K. The product was then filtered and washed with DI water before being dried at 353K for 12 hours and then calcined in nitrogen at 873K for 2 hours.

c) *Solid State Reaction Method (SSR)*

The complex oxide $Mo_1V_{0.3}Nb_{0.12}Te_{0.17}$ was prepared as follows:

MoO_3 (5.76 g), V_2O_5 (1.09 g), TeO_2 (1.06 g), Nb_2O_5 sol (4.8 mmol Nb), and 12.0 mmol oxalic acid were sequentially added to 50 ml of hot water at 353 K to produce a slurry. The resulting slurry was heated to 353°C and then dried to 473°C, yielding a black solid. The solid was heated for 48 hours at 448 degrees Fahrenheit, then calcined for two hours at 873 degrees Fahrenheit in a nitrogen stream [65].

The hydrothermal method showed good activity and high acrylonitrile yield. The maximum acrylonitrile yield of 52% was obtained at 91% propane conversion, as shown in Table 9. But the yield was almost the same as the dry-up method. Although at the same reaction temperature, the activity was much higher, even for low catalyst amounts. The sample prepared by the hydrothermal method has the same morphology as those of the dry-up method, but the average size of particles was less than those prepared by the dry-up method.

Table 9: Comparison of catalyst performance made by different methods

Method	Catalyst weight, g	GHSV, h^{-1}	Surface area(m^2/g)	Propane conversion, %	Selectivity %	Yield %	Ref.
HT($MoV_{0.3}Nb_{0.12}Te_{0.17}O_x$)	0.30	1800	19.1	91.1	56.8	51.7	[65]
DRU ($MoV_{0.4}Nb_{0.1}Te_{0.2}Ox$)	0.55	1000	9.9	62	63	50	
SSR($MoV_{0.3}Nb_{0.12}Te_{0.17}O_x$)	0.55	1000	1.1	4	18.8	0.8	

It was observed that the production rate for HTT catalyst was nearly twice that for DRU catalyst when the relative rate of acrylonitrile formation is described as g-AN/kg-cat/h. Furthermore, the HTT catalyst production rate was slightly smaller than the value obtained by DRU method when described as a function of surface area (mg-AN/m^2-cat/h), as shown in Table 10.

Table 10: Rate of formation of acrylonitrile at 683K based on catalyst weight and area

Method	(g Propane/)	GHSV, h^{-1}	Conversion, %	ACN Selectivity, %	Rate per weight	Rate per area	Ref.
HTT	1.14	7900	27	70.9	270	14.1	[65]
DRU	1.14	7900	18.5	66.5	170	17.2	
SSR	1.14	7900	0.2	45.6	1.3	1.2	

In each preparation method, the metal oxide structure depends on the average oxidation states and the composition of elements. Conclusively because of its larger surface area, the catalyst synthesized using the HTT technique demonstrated a high production rate for propane ammoxidation [65].

d) Citrate method

In this method, the catalyst was prepared by hydrothermal treatment in the presence of cetyl trimethyl ammonium bromide, CTAB (a cationic surfactant). It was used in synthesizing mesoporous materials as a structure-directing agent. This approach uses the same aqueous precursor solution as other methods but adds citric acid for complete cation complexation. After vigorous stirring, the resultant solution was evaporated, and a gel-like liquid was formed. By dry-up approach, a catalyst with a molar ratio of Mo/V/Te/Nb = 1/0.30/0.20/0.15 was synthesized for comparison. For both routes, cationic surfactant was added by two procedures:

- Directly in the precursor solution for the dry-up method, i.e., before the drying step, and for the citrate method, it was added to the gel.
- After the drying step, i.e., suspending the obtained dried powder for the dry-up method and suspending the crushed spongy ‘citrate’ solid in CTAB for the citrate route.

The resulting solution was hydrothermally treated at 373K for four days. The product was dried and calcined for five hours at 773K in the presence of air. The use of cationic surfactant led to a significant increase in surface area, as shown in Table 11. According to SEM images, the sample RO5 had fibrous morphology, while the sample by dry-up method corresponds to plates.

The specific activity (conversion/surface area) of all citrate-prepared catalysts was nearly identical. However, the catalyst generated by the dry-up approach had the highest specific activity among the other samples. It could be due to the addition of cationic surfactants to enhance surface area increases the number of accessible sites, but the density (number of sites per unit area) was lower than the catalysts generated using the dry-up approach. Because of $TeMo_5O_{16}$, which was active in the total oxidation of propane, the acrylonitrile selectivity for citrate route samples was higher than that of dry-up method catalysts [66].

Table 11: Comparison of catalyst performance prepared by citrate and dry-up method

Catalyst	Preparation method	Surface area (m_2/g)	Propane Conversion, %	Specific activity $(\%g/m^2)$	Selectivity, %				Ref.
					ACN	AcCN	Propylene	CO_x	[66]
RO1	Citrate	98	46.8	0.47	29.7	15.4	13.2	32.7	
RO2	Citrate+ surfactant(gel)	110	48.2	0.43	31.8	9.5	12.2	36.8	
RO3	Citrate+ surfactant(powder)	53	18.5	0.34	32.2	8.5	10.0	42.4	
RO4	Dry-up	17	29.8	1.75	17.8	12.6	19.3	46.6	
RO5	Dry-up+ surfactant(gel)	239	36.3	0.15	28.2	8.2	12.6	40.4	
RO6	Dry-up+ surfactant(powder)	66	23.4	0.35	24.8	13.4	16.6	39.8	

5) *Effect of supports on MoVNbTe catalyst*

MoVNbTe catalyst has been proven to be an efficient catalyst for propane ammoxidation. Still, it is not sufficient for this catalyst to be commercialized, so various studies are focussed on this to improve the performance of this catalyst system further. One way to improve the performance is by increasing the dispersion of the active material, which can be done by using supports. Therefore, Al_2O_3, SiO_2, and TiO_2 sols were used to support this propane ammoxidation catalyst. The catalyst involving the supports were prepared by the precursor method as described, and their performance was observed. The composition of sols in the final catalyst samples was 30 wt.%. Considering the catalyst's activity per unit surface area and acrylonitrile selectivity for propane ammoxidation, the best catalysts contain neat M1 and M1/M2 in the proper ratio. They give a total selectivity of 65% in pure M1 and 59% in M1/M2 at 50% propane conversion. Then comes the second-best catalyst system in which the MoVNbTe catalyst is diluted with SiO_2 with total selectivity of 50%. The phases observed by XRD in these prepared samples are shown in Table 12. From the phases, it was observed that silica was the most inert material with respect to the formation of M1 and M2. At the same time, alumina is the least inert material used as support due to its reaction with Mo and V [67].

Table 12: Catalyst properties on different supports

Catalyst	Surface Area (m^2/g)	Support	Phases observed by XRD	Ref.
$Mo_1V_{0.20}Nb_{0.13}Te_{0.11}$	6.1	-	M1	[67]
$Mo_1V_{0.5}Te_{0.5}$	2.5	-	M2	
$Mo_1V_{0.33}Nb_{0.11}Te_{0.22}$	5.2	-	M1, M2	
$Mo_1V_{0.33}Nb_{0.11}Te_{0.22}$	10.3	Al_2O_3	$Al_2(MoO4)_3$, $AlVO_4$, $TeMo_5O_{16}$, Nb_2O_5	
$Mo_1V_{0.33}Nb_{0.11}Te_{0.22}$	7.7	SiO_2	M1, M2	
$Mo_1V_{0.33}Nb_{0.11}Te_{0.22}$	2.4	TiO_2	M1, M2, TiO_2 (anatase)	

Ramli et al. [68] prepared the supported catalysts using Al_2O_3, SiO_2, and MgO via the wetness impregnation method, and 10% of MoVNbTe was loaded on each support. The SEM images of the catalysts showed agglomerate morphology. The unsupported catalyst had an image of aggregates of small cylinder-shaped crystallites, while supported catalysts had an image of variable sizes and shapes of the crystallites. The SEM image of SiO2 supported catalyst was observed to have an image consisting of many small crystallites that looked like a honeycomb structure. The surface areas of the support were significantly reduced when MoVNbTe was loaded in the support. It means that the surface deposition of metal oxide occurred onto the surface.

Support introduction with the catalyst improves the surface area. It increases the conversion of propane, but the development of crystalline phases essential for propane ammoxidation was also hampered by these supports. as shown in Table 13. Thus reduces the acrylonitrile selectivity in the case of supported catalysts.

Table 13: Catalyst properties on different supports

Catalyst	Surface Area (m^2g^{-1})	Phases observed by XRD	Selectivity ACN	Ref.
MoVNbTe/MgO	25.42	$(Nb_{0.09}Mo_{0.91})O_{0.28}$, $TeMo_5O_{16}$	40%	[68]
MoVNbTe/ SiO_2	13.31	$(Nb_{0.09}Mo_{0.91})O_{0.28}$ nano crystallites	Low, due to the phase	
MoVNbTe/Al_2O_3	76.61	No crystalline phase	Low, only 10%	
MgO	39.21	MgO		
SiO_2	213.70	Amorphous material		
Al_2O_3	176.60	No crystalline phase		

6) *Effect of modifications on MoVNbTe catalyst*

Mixed metal oxide catalysts with the atomic ratio of Mo:V:Nb:Te =1:0.3:0.12:0.23 were modified with Ce, Zr, Ga, Ge, Bi, Ca, Sb, P, and K. The starting materials for additives were nitrates of Ga, Bi, Ca, Ge, Ce, Sb_2O_4, ZrO_2, H_3PO_4, and KVO_3. The ratio of M1 / M2 phases was 3/1 in the reference catalyst, with an additive content of less than 0.1. Acrylonitrile and Acrylic acid form through an intermediate propylene, as evidenced by increased selectivity and a reduction in propylene selectivity along the propane conversion. The maximum yield of acrylonitrile on the reference catalyst is 51% at a conversion of 79.6%. Among the promoted samples, the highest yield (54-55%) is observed on the Ca, Zr, and Bi modified samples. These catalysts are more active than the un-promoted ones. The overall activity of catalysts decreases after introducing a higher concentration of additives with the production of the M2 phase. The amount of M2 phase was significant (>35%) with increasing additive more than 0.1 (0.15Ca, 0.15 Zr) and 0.05Bi. In propylene and propane oxidation, it is observed that the M2 phase is less active than the M1 phase. In addition, the M1 phase possesses less weakly bound reactive oxygen than the M2 phase [69]. Only samples modified by Ca, Zr, and Bi show incomplete conversion of ammonia. Thus, these additives mitigate the acidity or reduce the active sites that activate ammonia. It reduces ammonia combustion and increases its concentration in the feed mixture at high propane conversion, thus providing the occurrence of the primary reaction and decreasing selectivity to propane oxidation products [57].

7) *Effect of Gold and Ruthenium on MoVNbTe catalyst*

This study investigates the behavior of the M1 phase of MoVNbTe catalysts doped with 5% by weight of ruthenium and gold for the propane ammoxidation reaction. The MoVNbTe catalyst was prepared by hydrothermal method, and gold and ruthenium were added by the incipient wetness impregnation method. According to XRD analysis, the real MoVNbTe catalyst promoted the formation of the M1 phase. In contrast, the XRD patterns of modified catalysts revealed that the inclusion of gold and ruthenium significantly impacted the structure of the M1 phase. At 360–445 °C and 1 atm pressure, the reaction was carried out in a tubular fixed bed micro-reactor with a catalyst. The catalytic activity of ruthenium and gold-doped MoVNbTe catalysts was lower than that of unmodified MoVNbTe catalysts. Even though the modified catalysts were highly active in the oxidative dehydrogenation of propane at a low temperature (400 °C), the selectivity to propylene was 85% for the ruthenium-doped catalysts and 73% for the gold-doped catalysts in the oxidative dehydrogenation of propane at a relatively low temperature (400 °C). Including iconic ruthenium and gold or gold nanoparticles could explain the vigorous propane oxidative dehydrogenation activity.

The ruthenium-doped catalyst was significantly less active for propane ammoxidation. When incorporated into the MoVNbTe M1 catalyst, Ruthenium distorts and destabilizes the M1 structure. At high temperatures, the propylene selectivity again increased, possibly due to ruthenium oxide on the catalyst surface [70].

8) *Effect of slurry pH*

This study concentrates on the effect of slurry pH on the formation of active phases of MoVNbTe catalyst for propane ammoxidation. The catalysts were synthesized by the slurry method, as reported earlier. In 300 ml of water, 34.267g of ammonium heptamolybdate, 6.811g of ammonium metavanadate, and 10.247g of telluric acid were dissolved and stirred at 80°C to obtain a uniform aqueous solution of pH=6. Then at 30 °C, 50.7 ml of niobium oxalate solution is added to the resulting mixture, and a bright orange gel of pH=3 forms. The resultant solution was spray cooled and calcined for 2 hours at 320°C in air and 600°C in helium flow. Adding HNO_3 or NH_4OH to the catalyst slurry changed the pH from 1 to 4. The samples were characterized by XRD, IR, RAMAN, AAS, HTEM, and DD (differential dissolution) techniques. At pH=4, the $(NH_4)_6TeMo_6O_{24}$ (heteropoly anion) phase is detected by FTIR and XRD. After heat treatment at 320 °C, the heteropoly anion destruction occurs, and nano-size particles with structures like M1 and M2 phases formed. The maximum amount of M1 phase, maximum surface area, and maximum activity and acrylonitrile selectivity is obtained at pH=3 [71].

9) *Effect of SiC foam-supported MoVNbTe catalysts*

The silicon carbide (carborundum) foam supported MoVNbTe catalysts formed by dip coating and slurry method for propane ammoxidation. The coating analysis showed that single-layer coating contained only the M2 phase, while two-layer coating contained a significant amount of the M1 phase. Thus, this two-layer catalyst shows high activity between 380 °C and 420 °C. But compared with the powdered pure M1 phase catalyst, the coated foam catalyst appeared less active due to low concentration in the M1 phase. The silicon carbide foam was cut into thin rectangular pieces and underwent surface oxidation at 750 °C. The pieces were used as a substrate to support the catalyst, made by dip coating. The SEM images of the single-layer catalyst led to a uniform envelope with morphology-like thin mud cracks. From XRD plots, it was observed that the deposit contains the M2 phase in a large amount.

On the other hand, for two-layer deposits, the major phases were M1 and M2. The SEM image of the two-layer sample showed the same type of morphology but fewer uniform cracks but more significant than the previous. The catalytic microreactor was tested, and results were gained at different temperatures and contact times. Acrylonitrile selectivity and activity increased with increasing temperature and then almost remained constant at 58% at propane conversion of 64% at 430 °C, as shown in Table 13. The reactor's selectivity was the same as powdered catalysts, but activity was lower. The decrease in activity may result from low concentration in the M1 phase [72].

10) *Effect of cerium incorporation in MoVNbTe catalyst*

Cerium incorporation was done by co-precipitation method on MoVNbTe metal oxides with different amounts of cerium for the ammoxidation of propane to form acrylonitrile. CeO_2 has a high capacity for storing oxygen and high redox property. It also possesses a Ce^{3+}/ Ce^{4+} redox pair of ions to increase the transfer of lattice oxygen in the mixed metal oxide catalysts. Catalysts were prepared by dissolving appropriate amounts of required precursor salts in specific ratios. The resulting mixed solution was kept for 3 hours at 70 °C and dried at 90 °C. Then it was calcined at 600 °C under nitrogen for 2 hours and cooled at 25 °C. This $MoV_{0.31}Nb_{0.24}Te_{0.23}Ce_x$ is denoted as $MCe_{x,}$ where 'x' is the mole ratio of Ce/Mo in the catalyst. The catalyst performance was evaluated, and it was found that the Co_x selectivity increases and propylene selectivity decrease with increasing reaction temperature. While at a temperature less than 420 °C, acrylonitrile selectivity and propane conversion increase with temperature, and above 420 °C, acrylonitrile selectivity decreases, and propane conversion slightly increases. Hence, the optimum reaction temperature must be 420 °C for this catalyst. It is observed that the activity of the catalyst reaches a maximum when the molar ratio of Ce/Mo=0.05, propane conversion reaches 68%, and ACN selectivity is 67%. The selectivity of Co_x dropped to 16%, as shown in Table 13. The catalyst was characterized by XPS, XRD, H_2-TPR, and low-temperature N_2 adsorption techniques. All catalyst samples approached surface areas in the 2.5-3.1 m^2/g. XRD results show that the diffraction peak at 27.1o of the MCe0.05 is more prominent than MCe0.03, suggesting that the M1 phase concentration was increased with a higher concentration of cerium and $MCe_{0.05}$ catalyst possessing the most substantial peaks of both M1 and M2 phases. The reduction peak areas of $MCe_{0.05}$ are higher than $MCe_{0.03,}$ indicating that it has a strong reducing ability and the amount of M1 phase in it is higher than $MCe_{0.03.}$ Therefore, it can be concluded that the presence of cerium in the mixed metal oxide catalyst can improve the catalyst performance, increases the acrylonitrile selectivity for propane ammoxidation, sufficient V content on the catalyst surface, and more M1 and M2 active phases and the catalyst $MCe_{0.05}$ possesses higher Te^{4+} concentration [73].

11) *Effect of Bi as a promoter over MoVNbTe catalyst*

Bismuth is a more electro-positive element as compared to other elements of the MoVNbTe catalyst. It is because catalyst centers with little acidity favor partial oxidation, and firm acidity favors deep oxidation. Thus, the strong acidity leads to side product formation. Lowering the acidity of active centers using an electro-positive element must help decrease the acrylonitrile's bond strength, inhibiting the oxidative scission and oxidation of surface material. The catalyst was synthesized by the slurry method according to the patented procedure, and then the catalyst was mixed with Bi_2O_3. At high propane conversion (>90%), the acrylonitrile selectivity of Bi modified catalysts sample is much higher (57%), as shown in Table 14, than non-modified catalysts. Still, introducing a large amount of bismuth (Bi/Mo=0.05) leads to decreased activity and selectivity due to the rich abundance of the M2 phase. It was pointed out that the propene transformation was not affected by the introduction of bismuth in the catalyst. The reason for this is the low basicity of Bi, due to which the acidity of propene-binding active sites did not reduce.

XPS found similar surface and bulk bismuth concentrations in the promoted sample. Incorporating bismuth also leads to a reduction in tellurium concentration, an increase in vanadium concentration, and no change in niobium concentration on the promoted sample surface only. The MoVNbTe oxide catalysts are composed of highly electronegative elements. Thus, promoting these catalysts decreases the active sites acidity due to incorporating less electronegative bismuth and incapacitates the acrylonitrile binding with active centers, decreasing its oxidation and degradation. Concurrently, the acetonitrile selectivity reduced, and the formation of HCN was due to the reduction of the strength of acid sites accountable for oxy-hydrative scission. Another advantage of bismuth introduction is the low catalyst activity for oxidizing ammonia [57].

Table 14: MoVNbTe catalyst performance after adding different promoters

Catalyst	Catalyst weight, g	T °C	Propane conversion, %	Selectivity, %			Yield, %	Ref.
				ACN	Propene	CO_x		
$MoV_{0.31}Te_{0.23}Nb_{0.24}Ce_{0.05}$	2	420	68	67	13	16	46	[20]
$MoV_{0.4}Nb_{0.1}Te_{0.2}Ox$-SiC	1	430	67	57	8	34	38	[32]
$Mo_1V_{0.28}Te_{0.18}Nb_{0.11}Bi_{0.01}$	-	420	94.9	56.9	3.5	36.5	54	[33]

12) Nanoscale alumina supported MoVNbTe catalysts

It is suggested that the nanoscale alumina-supported catalyst lowers the required concentration of active phase to form an equal amount of acrylonitrile, as in the case of bulk MoVNbTe catalysts. A Nanoscale alumina-supported MoVNbTe catalyst was prepared by the slurry method. High-performance catalysts show an intense RAMAN band of vanadium alkoxide species (990-1030 cm^{-1}, characteristics of V=O, Mo=O bonds) during the reaction, and the higher vanadium content results in higher acrylonitrile yield and propane conversion. The band around 380 $cm^{-1,}$ shown in all the samples, represents the Mo-V-O phase. The band at 440 cm^{-1} showed the presence of the M2 phase, which is hardly be seen in some samples. The rutile-type structure is shown by a band at approximately 820 cm^{-1}. The stretching mode of bridging Mo-O M(M=Mo, V) bonds of severely distorted $Te_2M_{20}O_{57}$ can be attributed to the band around 880-890 cm^{-1}. The area obtained by the BET method for catalyst calcined in the air is relatively low compared to catalyst calcined in an inert environment, which could indicate that over the support, a porous oxide layer was developed in the case of an inert environment. XPS analysis showed that the Mo^{4+}, Mo^{5+}, and Mo^{6+} were present in N_2-calcined catalysts, and only Mo^{6+} and Mo^{5+} were present in air-calcined catalysts; the amount of Mo^{5+} species is very low. The propane conversion and acrylonitrile selectivity increased as the reaction temperature increased and passed through a maximum of 450 °C. The acrylonitrile yield is higher for catalyst calcined inertly. CO, CO_2, propylene, and acetonitrile with a minimal concentration of acetic acid and acrolein were also detected. It is also observed that higher vanadium content leads to higher acrylonitrile yield and propane conversion. According to previous research, molecularly distributed vanadium oxide is the essential site for hydrocarbon transformation into propylene. The nanoscale-supported catalyst outperforms typical bulk catalysts with a substantially lower amount of mixed metal oxide active phase. It means that in the case of a nanoscale-supported catalyst, the amount of acrylonitrile produced per gram of active phase is more than in the case of a bulk catalyst **[23]**.

IV. USE OF ZEOLITES AS CATALYSTS FOR PROPANE AMMOXIDATION

A. Gallium-modified MFI zeolites

The MFI zeolites, also known as ZSM-5, Zeolite Socony Mobil–5 (framework type MFI), an aluminosilicate zeolite, belong to the pentasil zeolites family.

Ga-modified MFI zeolites were used as a catalyst for the direct ammoxidation of propane, and it was first reported that bronsted sites acted in cooperation with redox sites. Two catalyst samples with gallium loading of 0.3 and 2% by weight were prepared by ion exchange of MFI with Si/Al ratios of 33 and 150. Fully protonated H-MFI catalysts were obtained by NH^{4+} ion-exchange and calcination, and then the gallium was loaded; the whole catalyst preparation procedure is described elsewhere.

It was observed that as the temperature increases to 773K, acrylonitrile selectivity decreases. However, on increasing the ammonia propane ratio from 2 to 4, the selectivity increases, and both the propane conversion and the acrylonitrile selectivity increase by increasing the oxygen propane ratio from 0.3 to 2. These catalysts were proved to be efficient for propane ammoxidation. The highest selectivity of 40% was obtained at 48% propane conversion with a very low yield of carbon oxides, as shown in Table 15. Thus, a new pathway leading to the formation of acrylonitrile was suggested, and the proposed transition states were protonated cyclopropane (PCP) and protonated pseudo cyclopropane (PPCP) species **[89]**.

B. *Fe-silicalite zeolites*

This catalytic system involves the direct ammoxidation of propane over steam-activated Fe-silicalite using O_2 and N_2O as oxidizing agent. It was indicated that the presence of Bronsted sites in synergy with redox sites in Ga-modified MFI zeolites was responsible for their performance in the propane ammoxidation to acrylonitrile with oxygen. The catalytic tests showed 40% acrylonitrile selectivity at 50% propane conversion and carbon oxides yield less than 1% at 773K. These performances could be compared well with conventional multicomponent mixed oxide catalysts. The proposed transition states resulting from the activation of propane through a bi-functional reaction step were a protonated pseudo-cyclopropane and a protonated cyclopropane species **[89]**. In N_2O and O_2 environment 10.5% acrylonitrile (ACN) yield and 13.4% acetonitrile (AcCN) yield were obtained. At 823K, the ammonia conversion in N_2O +O_2 was 45% which is lower than both, 60% for N_2O as oxidant and 72% for O_2 as oxidant. According to Table 14. the acrylonitrile productivity (35 mol $h^{-1}kgcat^{-1}$) over iron silicalite in N_2O and O_2 was higher than over other catalysts and comparable to V-Al oxynitrides. Different oxidation states of the active iron sites can be tried to achieve higher acrylonitrile and acetonitrile yields **[51]**.

Table 15: Performance of different catalysts for propane ammoxidation

Catalyst	Oxidant	T, °C	W/F	X	Selectivity, %		Yield, %		Productivity		Reference
					ACN	AcCN	ACN	AcCN	ACN	AcCN	
Fe- silicalite	N_2O+ O_2	823	6	42	25	32	10.5	13.4	35	45	[51]
Ga-ZSM-5	O_2	773	163	48	40	-	19.2	-	1.2	-	[89]
V-Sb-O	O_2	698	2036	30	26.6	10	8	3	0.04	0.01	[90]
Fe-Sb-O	O_2	773	740	22	23	-	5	-	0.07	-	[74]
V-Sb-Al-W-O	O_2	773	53	77	48	13	37	9.2	7	1.7	[47]
Ca-Bi-Mo-O	O_2	783	12	15	63	7	9.5	1	7.9	0.9	[91]
Mo-V-Nb-Te	O_2	713	31.2	89.1	60	Ns	53.5	-	1.4	-	[7]
VAlON		773	8	59	50	5	29.5	2.9	37	3.7	[49]

V. NITRIDE MATERIAL CATALYTIC SYSTEMS FOR PROPANE AMMOXIDATION

A. *V-Al oxynitrides catalysts (VAlON)*

Most of the catalyst studied for propane ammoxidation process contains vanadium as the key component due to its redox properties. The acid base properties of these catalysts are very important and various authors suggested the direct relation of these properties with the activity of catalyst. Osipova and co-workers observed that the activity behaviour of catalysts and found that if the basicity of catalyst increases the acrylonitrile formation was favoured [92]. A new catalytic system (V- Al oxynitrides) exhibits basic properties [93]. It was reported that the catalytic behaviour depends significantly on the V/Al atomic ratio, the nature and distribution of nitrogen species and the degree of nitridation. The catalyst when synthesized by thermal nitridation of a co-precipitated V-Al oxide precursor showed and acrylonitrile selectivity 50% and yield 29.5% with acetonitrile and carbon oxides selectivity of 3% and 38% as shown in Table 12. No other by products were detected during the reaction. The surface area of the V-Al oxide precursor was 250 m^2/g and after the nitridation process, the surface area decreased to $153m^2/g$. After the reaction the surface area decreases to $133m^2/g$. The advantages of the VAlON catalyst over other catalysts was the difference in the space time value (W/F), which is much smaller as compared to other systems, but acrylonitrile selectivity and yield were relatively low. However, no propylene intermediate was observed for this system. This finding, together with good selectivity at such a short time scale, suggests a distinct mechanism than previous known systems. [49].

B. *Ni-Mo nitride catalysts*

Zhang and co-workers were first reported the Ni-Mo mixed nitride catalysts for propane ammoxidation. It was observed that mixed nitrides give high acrylonitrile selectivity and high catalyst activity, and best catalytic performance was obtained when Ni/Mo atomic ratio = 1. In these types of catalysts first the precursors were prepared by preparation methods like co-precipitation and then the final catalysts were prepared by temperature-controlled nitration of the precursors. The XRD patterns of the precursors exhibited mainly the peaks of MoO_3 and $NiMoO_4$. The acrylonitrile yield reached maximum to 28.5% at Ni/Mo=1-1.2. the acrylonitrile selectivity gradually decreases with time on stream. Therefore, further research was required to study the stability of the Ni/Mo catalysts [22].

Later Fan and co-workers prepared Ni-Mo nitride catalysts by five different methods such as co-precipitation (CP), rotary evaporation-microwave drying (RM), sol-gel (SG), mechanical mixing (MM) and impregnation (IMP) with Ni/Mo atomic ratio of 1. According to XRD, some peaks detected in all samples indicating the formation of Ni_2Mo_3N. The catalysts prepared by impregnation, mechanical mixing and co-precipitation showed peaks which indicate the formation of γ-Mo_2N and MoO_3. The γ -Mo_2N sample had the largest surface area (59.8 m^2/g) among other samples. The surface area of Ni-Mo nitride catalyst (47.8 m^2/g) prepared by co-precipitation method was the largest among other nitride samples. Due to pyrophoric nature of these catalysts, passivation was necessary to avoid bulk oxidation on contact with air. This passivation layer is important because it offers and O species at the start of the reaction.

The Ni-Mo nitride catalysts prepared by IMP, MM and CP showed low catalytic activity of less than 10% at 693K but at 793K exhibited much higher activity (>65%). The differences catalytic activities indicated that the mobility of oxygen specie and redox properties of nitride catalysts played crucial role in improving the catalytic activity. It was observed that the acrylonitrile selectivity gradually increases as the temperature increases from 713 to 753K. Among other samples, sample prepared by co-precipitation method gives the highest acrylonitrile selectivity of 35.4% at 753K **[94]**.

C. Fe-silicalite catalyst activated by gas reduction-nitridation (GRN)

The nitridation of zeolites is the process in which nitrogen atom is inserted into the zeolites structure to substitute oxygen atom at elevated temperature to synthesize solid basic catalysts. Nitridation increases the Lewis basicity of the structure due to lower electronegativity of nitrogen than oxygen. This substitution is generally achieved by high temperature treatment of the original material under ammonia flow for a long time. It was previously known that for the propane ammoxidation reaction catalysed by zeolites, formation of acrylonitrile was favoured by the non-appearance of strong acid sites **[101]**. It had also observed that increased basicity of metallic oxide catalyst favoured the acrylonitrile formation **[92]**. Therefore, this catalytic system can be better than other catalytic system due to the increased basicity of the nitrided catalysts.

The performance of these catalysts was observed for propane ammoxidation using oxygen as oxidizing agent and it was found that the Fe-silicalite preserves Fe^{3+} cations due to the presence of bronsted acid sites. These sites were responsible for the decomposition of acrylonitrile to acetonitrile. At zero hour of nitridation catalyst were not active but after one hour of nitridation the catalyst showed some activity. After further increase in time of nitridation, propane conversion and acrylonitrile selectivity increases. The maximum acrylonitrile selectivity of 44% was obtained after 5 hours of GRN but maximum conversion of 31% reached after 7 hours of GRN. Further increase in time does not increase the activity or selectivity due to total conversion of oxygen and for longer time of nitridation carbon oxides were formed instead of acrylonitrile.

Even though these catalysts were not active as compared to other catalysts, the productivity obtained by Fe-silicalite activated by GRN was better than other catalysts. Some advantages of these catalysts over other are mild conditions of pre-treatment, required less time for activation (5h) and low ammonia flow rate with propane resulted in selective and active catalyst with 25% propane conversion and 44% acrylonitrile selectivity as shown in Table 16.

Table 16: Catalyst performances based on activation environment

Catalyst	Activation	Oxidizing agent	T (°C)	W/F Propane, kg.h/mol	Propane conversion %	ACN Selectivity %	Productivity, mol/kg.h	Ref.
FE-Silicalite-HT	30 vol.% H_2O in N_2 (30ml/min), 873 K, 5 h	N_2O+O_2	550	0.006	42	25	17.5	[51]
FE-Silicalite GRN	5 vol.% C_3H_8 + 5 vol.% NH_3 in He (100 ml/min), 813 K, 5 h	O_2	540	0.012	25	44	9.3	[2]

GaZSM5	Calcination, N2, 723 K; air, 823 K	O_2	500	0.16	48	40	12	[89]
VAlON	30 l/h NH3, 773 K, 5 h	O_2	500	0.008	59	50	36.9	[49]
$Mo_1V_{0.33}Nb_{0.11}Te_{0.22}O_n/SiO_2$	Calcination, inert gas, 773–873 K, 1–3 h	O_2		0.37	91	56	1.5	[100]

VI. OTHER CATALYSTS USED FOR PROPANE AMMOXIDATION

A. $V/Al_{0.5}Ga_{0.5}PO_4$ as catalyst

$Al_{0.5}Ga_{0.5}PO_4$ was proved to be a good support because of its large surface area. In the dehydrogenation of isobutene, it was used as support for platinum as a catalyst **[95]**. The presence of V_2O_5 crystals on $Al_{0.5}Ga_{0.5}PO_4$ support seemed to play a crucial role in ammoxidation of propane. This mixed metal support originally amorphous, crystallizes in the presence of vanadium. It was observed that a cooperation between takes place during the reaction.

The$Al_{0.5}Ga_{0.5}PO_4$ support was prepared by the process developed by Kearby **[96]**. The catalyst containing vanadium (5wt. %) was synthesized by impregnation of support with an aqueous ammonium metavanadate (NH_4VO_3). It was observed that the impregnation of vanadium on the support leads to a reduction in surface area as well as pore volume and an enhancement in average pore diameter. According to XRD, the $Al_{0.5}Ga_{0.5}PO_4$support was amorphous and after vanadium impregnation the calcined sample exhibits the peaks of V_2O_5 but for uncalcined sample, no peaks were observed.

The$Al_{0.5}Ga_{0.5}PO_4$ support individually was not selective to acrylonitrile but the acrylonitrile selectivity improves with the impregnation of vanadium as $5V/Al_{0.5}Ga_{0.5}PO_4$ catalyst. The selectivity reached a maximum of 27% at 530 °C and at 46% conversion and decreases with further increase temperature. The main products obtained in the presence of catalyst for propane ammoxidation reaction were acrylonitrile, propylene, acetonitrile, carbon oxides, ethylene, N_2O and N_2**[97]**.

B. Fe-Bi nano-catalyst with silica Support

The capability of silica supported Fe-Bi nanoparticles obtained from Fe-Bi carbonyl cluster complexes to catalyse the propane ammoxidation reaction was examined because the ternary Fe-Bi-P oxide systems was reported to be an effective catalyst for propene ammoxidation [98].

The catalyst was prepared from the bimetallic salts and the final weight of the catalyst is 5.25 g and metal loading of 5% denoted as Fe_3BiO_x/SiO_2. For comparison, the Fe-Bi/SiO_2 was prepared with Fe/Bi molar ratio 3 by co-impregnation and yielded supported catalyst 1.05g with 5% of metal loading.

The activity of theFe_3BiO_x/SiO_2catalyst was limited below 450 °C, primarily due to the oxidation of propane and formation of carbon dioxide as main product. However, as the temperature rises, so does propane conversion and selectivity for various products. At 500 °C and GHSV of 1360 h^{-1}, the maximum propane conversion of 36% and acrylonitrile selectivity of 49% were reached. When the space velocities were lowered to 408h^{-1} propane conversion increases to 59% and yield increases to a maximum of 29%, while selectivity remains unchanged at 48% at 500 °C.

When the oxygen propane ratio lowered from 5.5 to 2.5, propane conversion decreases from 59 to 47% and acrylonitrile selectivity goes higher (from 48% to 59%) while the yield remains same.

The results for Fe-Bi/SiO_2 catalyst at the same reaction conditions was observed and it was found that the catalyst exhibits much lower catalytic activity and propane conversion. No acrylonitrile or acetonitrile was detected in the product stream. Although low content of propene and CO_2 was observed **[12]**.

The particles formed on the surface of the catalysts under operating conditions was almost uniform with 2nm average size. Measurements through XPS and EDS indicated that these particles accommodate both iron and bismuth compounds in oxidation state of +3 with atomic ratio of 3:1 in the active material. The cluster derived catalyst sample performed better than Fe-Sb catalysts ammoxidation of propane **[10,16]**, but not better than MoV(Nb,Ta)(Te,Sb)O catalysts **[30,45]**.

C. Vanadium-phosphorus oxide (VPO) catalyst on alumina support

Vanadium-Phosphorus catalysts are attractive due to their eco-friendly nature, less expensive and are being used for several selective oxidation processes [36]. These catalysts contain many crystalline phases like $VOPO_4$, $(VO)_2P_2O_7$, α_I, α_{II}, β, γ, δ, metastable ω and disordered phases **[37,38,44]**. It has been studied that an active surface prepared by polyphosphoric acid and vanadium oxide formed on VPO catalysts of ratio P/V > 1.0 while at ratio <1.0 catalyst become unselective but active **[40]**. The role of P/V ratio was not known therefore there was need to explore ratios above and below 1:1.

The structure of these catalysts depends on reaction conditions and affects by the existence of hydrocarbon, water, and ammonia in the supplied feed. For propane oxidation reaction, addition of steam improves acrylic acid selectivity but decreases the propane conversion because of increase in crystallinity and loss of acidic sites on the surface of the catalyst.

The VPO catalysts for propane ammoxidation were prepared by incipient wetness impregnation method with different P/V ratios. According to XPS, V^{5+} and V^{4+} species existed on the surface of the supported catalyst. TPR and UV-VIS analysis also confirmed the V^{4+} ions in catalyst and V^{5+} ions on alumina supported catalysts. The XRD patterns of used catalyst exhibited peaks of phases containing V^{4+} which means that V^{5+} ions reduced on stream.

Use of Supported 8V8.8P/Aland 8V8P/Al catalysts increases the acrylonitrile yield at temperature less than the temperature for bulk catalysts. It was observed that the alumina supported V was selective to acetonitrile but when the phosphorus was added, selectivity shift towards acrylonitrile. This change must be caused by V-P interaction and maybe at high reaction temperatures stabilization of V^{4+} occurred. From the catalytic activity, it was observed that both the bulk and supported catalysts were selective and active for ammoxidation of propane with acrylonitrile yield of 48% for supported catalyst and 42% for bulk catalyst respectively as shown in Table 17. **[21]**.

Table 17: VPO catalytic performance

Sample	T °C	Propane conversion, %	Selectivity (ACN), %	Yield (ACN), %	Selectivity (Propylene), %	Yield (Propylene), %	S.A., m^2/g	Ref
8V8.8P/Al	400	13	4	1	67	9	135	[21]
	450	43	30	13	31	13		
	500	82	58	48	9	7		
VPO	400	9	1	0	70	6	37	
	450	19	15	3	55	10		
	500	59	72	42	9	5		

VII. CONCLUSION

Various catalysts were used for propane ammoxidation in last two decades in which MoV(Te,Sb)Nb catalytic system were proved to be an efficient catalyst for propane ammoxidation. Several other catalysts were also used like vanadium antimony based catalytic system; this is the second-best catalyst system for propane ammoxidation. Both these systems were studied extensively, and many modifications were also done in these systems to improve the performance of MoVNbTe catalyst. It was observed that V/Sb system includes $SbVO_4$ phase with some other phases, but this phase is crucial for propane ammoxidation however, pure $SbVO_4$ is not active for ammoxidation of propane. In MoVNbTe catalyst system it was found out that this catalyst contains M1 and M2 phases, where M1 phase is responsible for conversion of propane to acrylonitrile and M2 phase is responsible for conversion of propylene formed on M1 phase into acrylonitrile. Hence these two phases act in cooperation. Other catalysts like nitrided materials or zeolites were also proved to be active and selective for propane ammoxidation but not as much efficient as MoVNb(Te,Sb) system. Furthermore, the hydrothermal method for catalyst preparation gives better catalyst activity and surface are in the case of MoVNbTe catalyst.

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