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Ammoxidation of 3-picoline over antimony promoted VPO catalysts and alumina supported Sb-VPO catalyst

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ABSTRACT

Ammoxidation of 3-picoline to nicotinonitrile was investigated on antimony promoted vanadium phosphorus oxide (Sb-VPO) catalysts and antimony promoted alumina supported vanadium phosphorus oxide (Sb-VPO/Al_2O_3) catalyst under atmospheric pressure and at 400 ^{0}C. The catalysts were characterized by means of X-ray diffraction, electron spin resonance, infrared, scanning electron microscopy, differential thermal analysis, ammonia chemisorption and BET surface area methods. The catalytic activity is correlated well with the physicochemical characteristics of the catalyst. Higher activity is observed for Sb-VPO-1 catalyst having lower surface area, lower oxidation state of vanadium and higher surface acidity. In supported system presence of VPO in highly dispersed state along with $AlSbO_4$ phase is responsible for higher activity and selectivity. A redox cycle between (V^{4+}) and (V^{5+}) species appears to be responsible for the ammoxidation activity of VPO catalyst.

Key words: 3-picoline; nicotinonitrile; antimony promoted vanadium phosphorus oxide; ammoxidation.

INTRODUCTION

Selective oxidation and ammoxidation in vapor phase is generally carried out over mixed oxide based catalysts [1, 2]. In the formulation of catalysts one of the elements from V, Mo, W, Sb, U will be present as main components and the more accepted mechanism is redox one. Nicotinic acid obtained by direct vapor phase air oxidation of 3-picoline over suitable heterogeneous catalyst the yield of nicotinic acid is limited through this process [3]. Nicotinic acid and nicotinamide which are essential constituents of vitamin B complex can be obtained by hydrolysis of nicotinonitrile [4]. Extensive studies of the ammoxidation of 3-picoline to nicotinonitrile were carried out on various catalyst system mainly composed of vanadium, molybdenum and antimony oxides supported on alumina or silica [5-10]. Andersson and Lundin [5] in their investigation found that V_6O_{13} is the most active and selective phase of the single phase oxides. Furthermore, they noted that presence of V_2O_5 along with V_6O_{13} is more active and selective than any of the single phase oxides. Baiker and Zollinger [11] found that VO_2 phase was active and non selective of the multiple phase oxides V_2O_5/V_4O_9 and V_4O_9/VO_2, it showed a selectivity comparable to the single phase oxides V_2O_5 and V_4O_9.

Supported vanadium oxide catalysts are used in oxidation/ammoxidation reactions because support provides higher surface area, mechanical strength and thermal stability when active component is dispersed on the support. Andersson and Lundin [12] reported the maximum activity for V-Ti-O catalyst which can be attributed to maximum contact between V_6O_{13} and the TiO_2 phases, which could result in weakening of the surface $(V{=}O)^{3+}$ bond. Andersson [13] found that in V_2O_5/SnO_2 catalyst the role of SnO_2 was to weaken the short V=O bonds. This can be due to incorporation of Sn^{4+}in to V_2O_5 lattice. The role of promoters in selective oxidation is related to history of modifications of the pure oxides of the main elements. Promoters which are present in relatively high amount will form well defined compound or solid solution but when present in small amount identification of their allocation on the surface and in the bulk becomes difficult.

Mixed antimony based oxides can be used in ammoxidation of olefins [14, 15]. A common and typical property of antimony based catalysts is the high activation temperature which is essential to obtain high selectivity in oxidation reaction. During high temperature treatment there is no formation of any compound, but of a solid solution of antimony oxide in SnO_2 [16]. Roginskaya et al [17] stated that the activity of mixed oxides is caused by the presence of Sb^{3+}. Free antimony oxide dispersed in mixed oxides exhibits a reduction rate higher than pure Sb-oxides.

Vanadium antimonite based catalysts have drawn considerable attention in recent years for their catalytic behavior in propane ammoxidation. A large number of patents have been filed claiming vanadium antimonite as the active phase, but only limited information is available in the literature about its characterization [18-20]. It is known that vanadium and antimony form a rutile $VSbO_4$ phase which is active and selective for propane ammoxidation when excess of antimony is present. Furthermore, it has been shown for vanadium antimonite samples with excess of vanadia that some vanadium oxide can also be present supported on $VSbO_4$ crystals [21]. V-Sb-O and VPO systems show the higher selectivity's in acrylonitrile formation from propane [22]. In this ammonia transforms (1) total oxidation sites to selective sites for acrylonitrile synthesis (2) reduces these sites due to its oxidation to nitrogen oxides.

Vanadium phosphorus oxide catalysts have been extensively studied because of their commercial success for selective oxidation of butane to maleic anhydride [23, 24]. VPO's are also reported to be active for selective ammoxidation of 3-picoline to nicotinonitrile [25, 26]. According to Hodnett [27] in VPO's the P: V ratio and reducing agent mainly determine the phase composition of the catalysts. It is well known that $(VO)_2P_2O_7$ is the active phase in VPO catalysts and $VOHPO_4$- $0.5H_2O$ is the precursor of this phase.

Hutchings [28] observed that the addition of promoter atom enhances the activity and selectivity of the VPO catalysts by preventing the formation of deleterious phases. Therefore, a systematic study is required in order to understand the role of promoter atoms on the phase composition and their catalytic properties. L. Forni [28] observed antimony as one of the active components in ammoxidation of 2-methylpyrazine to 2-cyanopyrazine. VPO's are used in oxidation of n-butane to maleic anhydride and V-Sb-O is used in ammoxidation of propane to acrylonitrile. Therefore, the primary objective of this investigation was to see the effect of various contents of antimony on the phase composition of VPO (P: V = 1:1.4 kept constant) and the activity or selectivity of the resulting phases for the ammoxidation of 3-picoline to nicotinonitrile. The preparation of Sb-VPO sample involves a two electron redox reaction in aqueous solution between Sb^{III} and V^{V} starting from Sb_2O_3 and NH_4VO_3, the formation of the mixed hydroxide containing V^{IV}.

EXPERIMENTAL SECTION

2.1. Catalysts

An aqueous medium was used for making of various samples. The P: V ratio was kept constant (1: 1.4) and antimony content was varied. In a typical experiment to obtain Sb-VPO-1 catalyst (3% Sb) 13.78 g of ammonium metavanadate and 14.96 g of antimony trioxide were suspended in 500 ml of distilled water. To the resulting suspension 15.81 g of O-H_3PO_4 was added and refluxed for 6 h and then excess water was evaporated slowly on water bath. The obtained light green paste was oven dried at 110 ^{o} C for 16 h and finally calcined at 750 ^{o} C for 4 h in an open air furnace. Similar procedure was used to obtain other catalysts Sb-VPO-2 (6% Sb) and Sb-VPO-3 (9% Sb) in which 13.78 g of ammonium metavanadate, 29.92 g and 44.98 g of antimony trioxide were suspended in 500 ml of distilled water. To the resulting suspension 15.81 g of O-H_3PO_4 was added and refluxed for 6 h and then excess water was evaporated slowly on water bath. The obtained light green paste was oven dried at 110 ^{o} C for 16 h and finally calcined at 750 ^{o} C for 4 h in an open air furnace.

To prepare alumina supported Sb-VPO catalyst, 24 g of ammonium metavanadate and 60 g of antimony trioxide were suspended in 500 ml water. To the resulting suspension, 23.8 g of 85% O-H_3PO_4 was added and refluxed for 2 h. To this 74 g of Al_2O_3 (SA = 174 m^2g^{-1}) fine powder was added as carrier and further heated to concentrate the suspension to obtain a paste, which was evaporated to dryness. The residue was calcined at 750 ^{o} C for 4 h in an open air furnace.

2.2. Characterization methods

The phase composition of the samples was determined by X-ray diffraction method. X-ray powder diffractograms were recorded on a Philips pw-1051diffractometer by using Ni-filtered CuK_{α} radiation. The decomposition patterns of oven dried catalyst samples before cacination were studied by differential thermal analysis technique. Thermo grams were recorded on a Leeds and Northap DTA unit with a heating rate of 6 ^{o}C min^{-1}. Average oxidation state of vanadium in various catalysts was determined by double titration with $KMnO_4$ solution [30]. The ESR spectra were obtained at liquid nitrogen temperature on a JEOL FE3X X-band spectrometer with 100 kHz modulation. Self supporting KBr pellets containing the catalyst samples were used to scan the IR spectra on a Perkin Elmer 283 B spectrometer at ambient condition.

Conventional static volumetric high vacuum system was used to determine the BET surface areas and ammonia uptake capacities of the samples. BET surface areas were estimated by N_2-physisorption at -196 ^{o} C and taking 0.162 nm^2 as the area of cross section of N_2-molecule. Ammonia gas chemisorption measured by double isotherm method at 150 ^{0}C temperature.

2.3. Catalytic tests

Ammoxidation of 3-picoline to nicotinonitrile was studied at 400 ^{0}C on a previously described fixed bed flow micro reactor operating under normal atmospheric pressure [31]. For each run about 3 g of catalyst sample was used and liquid products were collected after establishing steady state conditions (2-3 h). Liquid products were analyzed by gas chromatograph with a 10% OV-17 column on chromosorbG-AW (2m long) kept at 130 ^{0}C and with a flame ionization detector. The feed was consisting of 1: 5.45: 17.75: 15.44 mole percent of 3-picoline, steam, air and ammonia respectively was passed through the catalyst bed at a space velocity of 3976 h^{-1}.

In activity studies the optimum temperature observed for the maximum production of nicotinonitrile is 400 ^{0}C. Above this temperature formation of carbon oxides, tar and pyridine is observed. From the results obtained maximum conversion of 3-picoline is observed at mole ratio of ammonia to 3-picoline is 3.1and mole ratio of air to 3-picoline is 8.7. At a value higher than this the conversion of 3-picoline is decreased. At a space velocity higher than 3976 h^{-1} the conversion of 3-picoline decreases and selectivity to nicotinonitrile increases. At lower space velocities formation of tar and carbon oxide increases.

RESULTS AND DISCUSSION

3.1. XRD

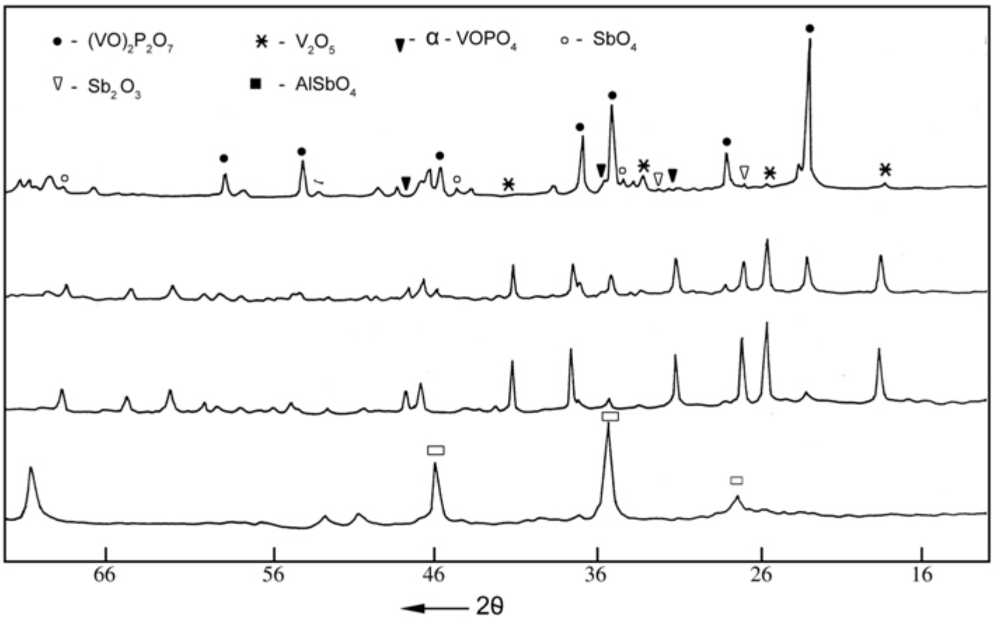


FIG. 1 - X-Ray Diffraction Patterns of Sb-VPO Catalysts

X-ray diffraction patterns of various samples are presented in figure 1. Various crystalline phases identified include $(VO)_2P_2O_7$, α-$VOPO_4$, $SbVO_4$, Sb_2O_3, and V_2O_5 respectively with varying intensities depending on the concentration of Sb_2O_3. In the case of Sb-VPO-1, Sb-VPO-2 and Sb-VPO-3 samples at lower antimony contents α-$VOPO_4$ and $(VO)_2P_2O_7$ are the major phases identified. As the antimony content increases the $(VO)_2P_2O_7$ phase dominates probably due to reduction of V^{+5} to V^{+4} by antimony. In supported system $AlSbO_4$ phase is observed and vanadium is present in highly dispersed state over the support surface.

3.2. IR

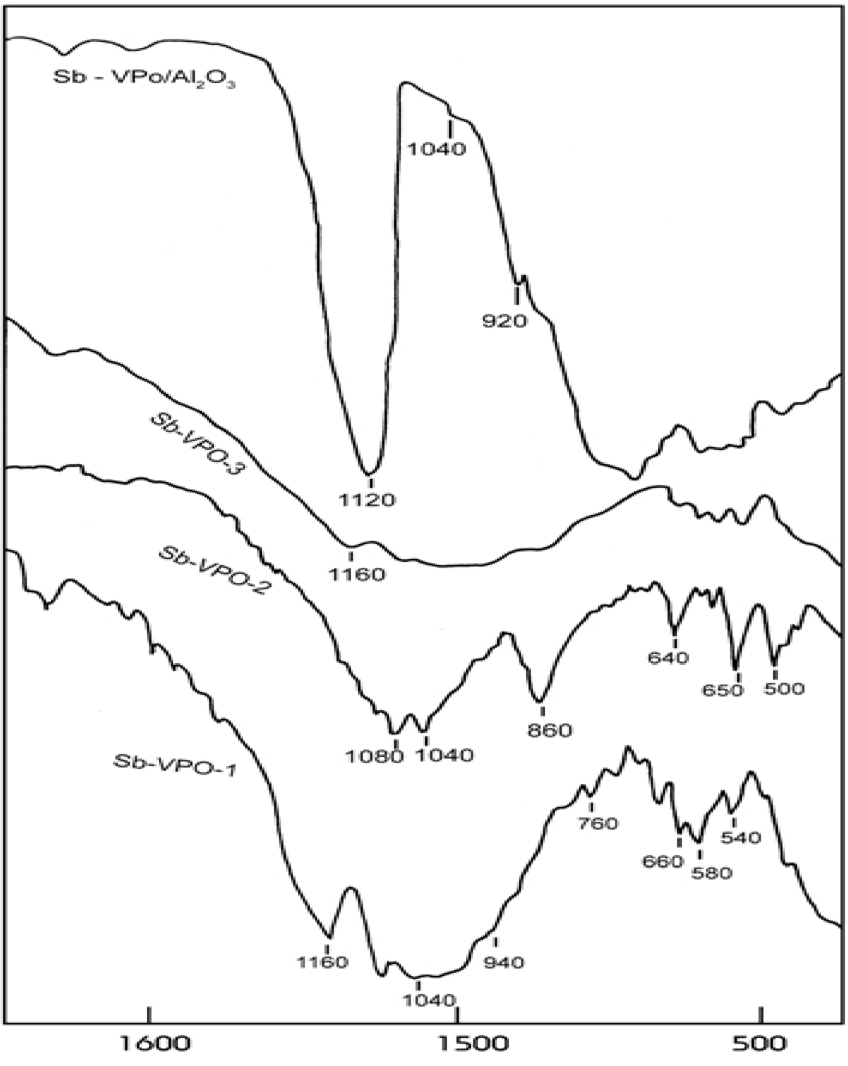


Fig. 2. FTIR Spectra of Sb-VPO Catalysts

Infrared spectra of Sb-VPO-1, Sb-VPO-2, Sb-VPO-3 and Sb-VPO/Al_2O_3 samples are recorded in the region 500-2000 $cm^{-1}$and given in the figure 2. Pure V_2O_5 shows two characteristic bands at 1020 $cm^{-1}$and 820cm^{-1} corresponding to V=O stretching and V-O-V deformation modes respectively. P-O stretching vibrations of orthophosphates fall in the region of 1000-1060 cm^{-1}, pyrophosphates in the region of 1060-1170 cm^{-1}, triphosphates in the region of 1085-1250 cm^{-1} and linear metaphosphates show absorption in the region 1265-1400cm^{-1}[32]. In Sb-VPO-1 sample an intense band is observed at 1120 and weak bands at 920, 725, 560 and 500 cm^{-1}. These values correspond to V-O, P-O stretching modes of $(VO)_2P_2O_7$ which is dominating phase along with weak bands corresponding to orthophosphates i.e. α-$VOPO_4$, β-$VOPO_4$ at 1040, 640 cm^{-1} are observed. In all other samples also peaks corresponding to V-O, P-O stretching of $(VO)_2P_2O_7$ and orthophosphates are observed. With the increase in antimony content a peak corresponding to Sb=O stretching is observed at 860 cm^{-1}.

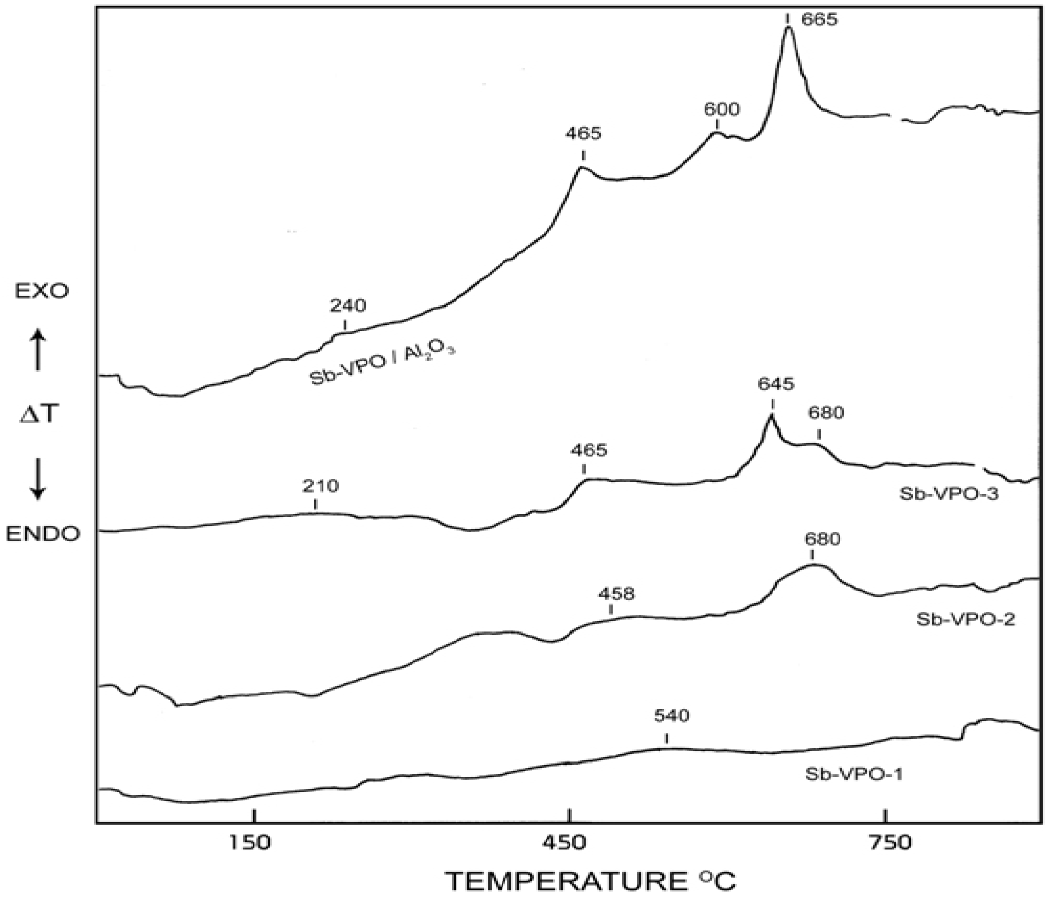


FIG. 3. Decomposition Patterns of Sb-VPO Catalysts

3.3. DTA

Differential thermal analysis helps to study phase composition and establish the temperature boundaries of existence of different compounds. For all the catalysts exothermic peaks are observed with the increase in antimony content the peaks have shifted towards lower temperature which can be seen in figure 3. Vanadium phosphorus oxides obtained from aqueous and organic media exhibit endothermic peaks at 420 ^{0}C. By addition of antimony a shift in thermal behavior from endothermic to exothermic is observed by the addition of promoter. In the preparation of VPO's $VOHPO_4.0.5\ H_2O$ is the precursor for obtaining vanadyl pyrophosphate and vanadyl phosphate phases. Upon heating $VOHPO_4.0.5\ H_2O$ transforms to various phases like α-$VOPO_4$, β-$VOPO_4$ and γ-$VOPO_4$. This change of phases can be seen in DTA results.

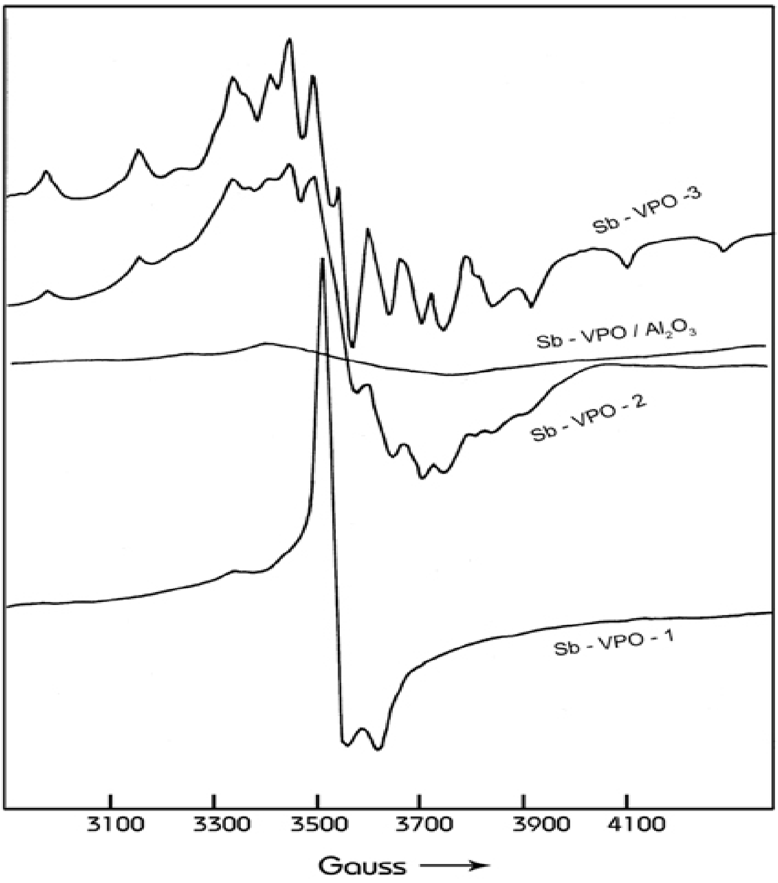
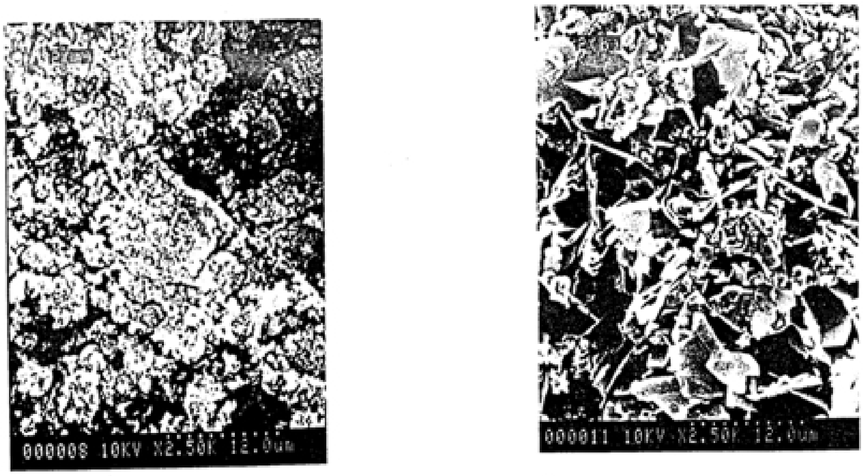


FIG. 4. ESR - Spectra of Sb-VPO Samples

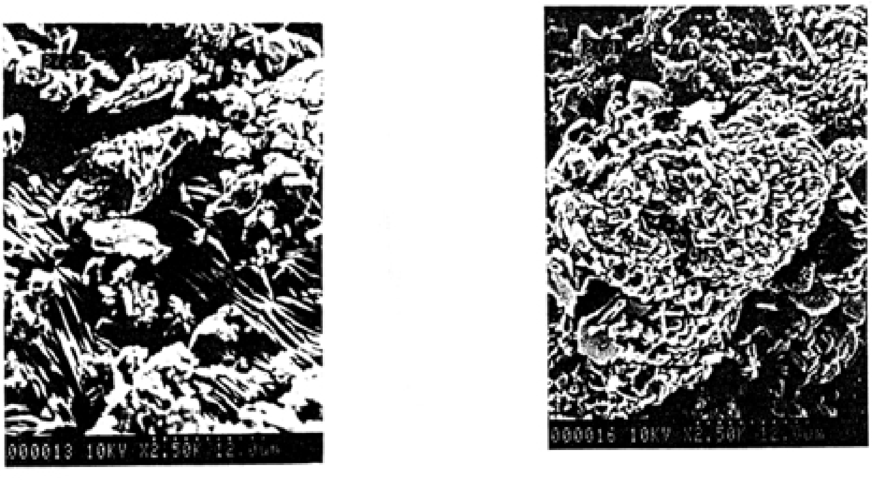
3.4. ESR

All the antimony promoted VPO catalysts have shown well resolved ESR spectrum with hyperfine splitting which can be seen in figure 4. This can be attributed to presence of ESR actives lower vanadium oxide V^{+4} in good quantity. The good resolution of this spectrum and the absence of exchange narrowed spectra indicate that $V^{4+}(VO^{2+})$ ions are sufficiently separated from each other and dispersed both on the surface and in the bulk of the VPO compound. For Sb-VPO-3 there is good hyperfine splitting and area under the curve is maximum which is proportional to number of unpaired electrons. g-values are calculated for various catalysts as reported in literature [34]. The g-values of the catalysts are given in table 2. The parameter $\Delta g_{II}/\Delta g_{\perp}$ is a measure of the overall distortion of an axial state. The larger $\Delta g_{II}/\Delta g_{\perp}$, the higher is the distortion, in other words , the shorter the V=O bond and the longer the V─O bonds in the basal plane of the VO^{2+} octahedron. The g and A parameters can be attributed to isolated sites connected via oxygen bridges to P. For Sb-VPO-1 $\Delta g_{II}/\Delta g_{\perp}$ is smallest.

3.5. SEM



Sb - VPo/Al$_2$ O$_3$ Sb - VPo - 1



Sb - VPO - 2 Sb - VPO - 3

Fig.5. Scanning Electron Micrographs of Sb-VPO Catalysts

Figure 5 gives scanning electron micrographs of the catalysts. Sb-VPO-1 has lower surface area and has plate like structure. In this the catalyst particle size is 12μm large enough compared to size of the particles in other catalysts. In Sb-VPO-3 presence of antimony particles over the surface of vanadium phosphate particles is observed. In Sb-VPO/Al_2O_3 sample agglomeration of antimony and VPO particles over the surface of γ- Al_2O_3 can be seen.

3.6. Catalytic activity

In oxidation/ammoxidation reactions catalytic activities are governed by acid-base properties of the catalyst and reactants. VPO's are solid acid catalysts having oxidizing power. Trifiro et al[35] reported that butane can be activated firstly by the coordinative unsaturated vanadium ion which is acidic situated on the (100) surface plane of $(VO)_2P_2O_7$ and then oxidized to maleic anhydride by the oxygen double bonded with the other paired V-ion on the cleavage plane of (100) crystal face of $(VO)_2P_2O_7$ are present. Pair of vanadium ions, each consisting of a V-ion double bonded with oxygen having oxidation property and a coordinative unsaturated V-ion and coordinative unsaturated phosphorus ions projecting from the surface plane. These coordinative unsaturated v-ion and P-ions are thought to provide acid sites in such a manner that V-ions act as Lewis acid and P-ions through taking water in them, as protonic acid (H^+).

Ammonia uptake measurements at 150 ^{0}C of various catalysts are given in table 1. Ammonia uptake at 150 ^{0}C is a measure of surface Bronsted acidity of the catalysts. Catalytic activity can be correlated with surface acidity. VPO/SiO_2 exhibits greater catalytic activity due to higher surface acidity [25, 26]. Incorporation of antimony into vanadium phosphorus oxides modifies their surface acidity. In Sb-VPO-1, Sb-VPO-2 and Sb-VPO-3 catalysts the P: V = 1:1.4 ratio is kept constant and content of antimony increased from 3 atom percent to 9 atom percent.

Table 1 Physico-chemical and catalytic properties of various Sb-VPO catalysts

Catalyst	BET surface area ($m^2 g^{-1}$)	Ammonia uptake(μ-moles g^{-1})	Average oxidation number	Conversion (percent)	Selectivity (percent)
Sb-VPO-1	2.0	33	4.5637	83	90
Sb-VPO-2	3.1	27	4.6472	80	90
Sb-VPO-3	6.2	16	4.7685	51	90
Sb-VPO/Al_2O_3	16	22	4.6374	89	93

Conversion =

$$\frac{\text{Number of moles of 3-picoline reacted}}{\text{Number of moles of 3-picoline introduced}} \times 100$$

Selectivity =

$$\frac{\text{Number of moles of nicotinonitrile produced}}{\text{Number of moles of 3-picoline reacted}} \times 100$$

Yield = Conversion % x Selectivity %

From the table 1 it can be seen that with the increase in antimony content surface acidity is decreasing. The oxidation activity for reactants like 3-picoline is controlled by the activation of –

CH_3 group and this is performed at the acidic sites of the catalyst. The greater catalytic activity is observed for Sb-VPO-1 which is having higher surface acidity in unsupported system.

Vanadium phosphorus oxides are characterized by low surface area. Incorporation of antimony has not shown appreciable change in surface areas of the catalysts. There is slight increase in surface area with the increase in the content of antimony which is almost negligible. The presence of vanadium in excess will increase surface vanadyl species their by catalytic activity. The increase in content of antimony causes dilution of vanadyl species on surface leading to decrease in catalytic activity.

Activity of catalyst depends on metal oxygen bond strength along with other reaction parameters. In vanadia based catalysts V=O species is active in oxidation/ammoxidation reaction. Addition of antimony weakens V=O bond strength thereby increases activity of the catalyst. In V_2O_5, V=O species are dispersed only on (010) plane and when vanadia is present in V^{+4} state the V=O species is dispersed on all other planes because of this vanadium is reduced from +5 to +4 state on addition of antimony and orthophosphoric acid. The active phase in n-butane oxidation is related to a surface layer of V^{+5} sites or to $VOPO_4$ islands on $(VO)_2P_2O_7$ matrix. Ye et al[35] have determined the number of surface V^{+5}=O species on the $(VO)_2P_2O_7$ surface using the NO-NH_3 rectangular pulse technique and fund that 50-70 percent of the surface vanadium ions on the (020) plane of vanadyl pyrophosphate are present as V^{+5} . This amount can be varied by doping with various elements but at the same time these elements induce the preferential exposure of the the (020) plane of vanadyl pyrophosphate. From Martin et al [36] V^{+5} phase along with V^{+4} phase is active in ammoxidation of 4-picoline. Bordes and Courtin [37] related the high selectivity to redox cycle between β-$VOPO_4$ and $(VO)_2P_2O_7$ phases.

In this series of Sb-VPO mixed oxide antimony exerts the reducing effect like solvent with the increase in antimony content the V^{+5} is reduced to lower vanadium oxide. Higher catalytic activity is observed for catalysts in which vanadium is present in +4 oxidation state along with optimum amount of V^{+5} species. From table 1 it can be observed that all the catalysts in this series have average oxidation number around +4. This is supported by hyperfine splitting observed in ESR spectra and g-values of the catalysts given in table 2. In Sb-VPO-1 catalyst presence of α-$VOPO_4$ and $(VO)_2P_2O_7$ phases can be seen from XRD and IR results. With the increase in antimony content α-$VOPO_4$ phase is disappearing slowly and $(VO)_2P_2O_7$ phase is dominating. For antimony rich sample Sb-VPO-3 in IR spectra a peak at 860 $cm^{-1}$is observed corresponding to Sb=O and rosette like structure is observed in SEM of the catalyst probably due to agglomeration of antimony particles over vanadium phosphate particles. Lowest activity for Sb-VPO-3 can be attributed to absence of α-$VOPO_4$ phase, lower surface acidity and higher average oxidation number.

Table 2 g-values of the catalysts

catalyst	g_{II}	$g_{\perp}$	A_{II}	$A_{\perp}$	g
V_2O_5	-	-	-	-	1.9749
Sb-VPO-1	2.0206	2.1003	93.5	70	-
Sb-VPO-2	1.9338	1.9721	185	53	-
Sb-VPO-3	1.9446	1.9721	187	51	-
Sb-VPO/Al_2O_3	-	-	-	-	1.9665

In oxidation/ammoxidation reactions redox mechanism plays an important role i.e. hydrocarbon consumes oxygen from the catalyst, which is then reoxidized by molecular oxygen. There exists equilibrium between V^{+4} and V^{+5} to provide rapid exchange of oxygen from surface to bulk and bulk to surface. Vanadium oxide gave certain amount of lower oxide by reduction of originally charged catalyst. In this series of Sb-VPO catalysts for ammoxidation of 3-picoline, catalyst showing high activity and selectivity consists of mixture of well crystallized $(VO)_2P_2O_7$ (V^{+4}) and amorphous phase (V^{+5}) i.e. redox cycle between V^{+4} and V^{+5} .

The active phase in propane ammoxidation is amorphous $VSbO_4$-Sb_2O_4 system [39] epitoxially grown on $AlSbO_4$ rutile whose formation is catalyzed by the presence of vanadium. This non-stoichiometric mixed metal oxide is supported on Al_2O_3. The greater activity and selectivity for Sb-VPO/ Al_2O_3 is observed because of presence of VPO in highly dispersed state and formation of $AlSbO_4$ phase. In SEM agglomeration of VPO particles over the surface of Al_2O_3 are observed

CONCLUSION

The investigations lead to the conclusion that maximum yield of nicotinonitrile can be obtained at the following reaction parameters.

Temperature	:	400 ^{0}C
Mole ratio of ammonia to 3-picoline	:	3.1
Mole ratio of air to 3-picoline	:	8.7
Space velocity	:	3976 h^{-1}

Addition of antimony reduces V^{+5} species to V^{+4} and weakens V=O bond strength allowing rapid exchange of oxygen. The redox cycle between V^{+4} and V^{+5} and higher surface acidity is responsible for higher activity of the catalyst. In supported system presence of VPO in highly dispersed state along with $AlSbO_4$ phase is responsible for higher activity and selectivity.

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