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Research Article

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Ammoxidation of 2-methylpyrazine to 2-cyanopyrazine over promoted VPO catalysts and alumina supported Sb-VPO catalyst

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ABSTRACT

Ammoxidation of 2-methylpyrazine to 2-cyanopyrazine was investigated on antimony, zirconia, cobalt, copper and manganese promoted vanadium phosphorus oxide (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 spectroscopy, scanning electron microscopy, 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. Sb-VPO/Al_2O_3 is active and selective in conversion of 2-methylpyrazine to 2-cyanopyrazine due to presence of VPO in highly dispersed state over Al_2O_3. Promoter antimony reduces V^{5+} to V^{4+} prevents the formation of deleterious phases and weakens V=O bond strength allowing rapid exchange of oxygen increasing selectivity towards 2-cyanopyrazine. Higher air to ammonia mole ratio enhances the activity and selectivity towards 2-cyanopyrazine. VPO catalyst showed better conversion and product selectivity than the zirconia, cobalt, copper and manganese promoted vanadium phosphorus oxide catalysts. Redox cycle between V^{4+} and V^{5+} and higher surface acidity favors formation of 2-cyanopyrazine.

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Key words: 2-methylpyrazine; 2-cyanopyrazine; promoted vanadium phosphorus oxide; ammoxidation

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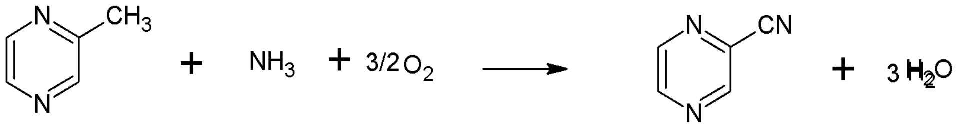
INTRODUCTION

In organic synthesis conversion of one functional group to other is very much important. By conventional methods conversion of a methyl group to nitrile involves more than one step and handling of hazardous chemicals like KCN and CuCN. Ammoxidation is a clean process by which a -CH_3 group can be converted into nitrile with the aid of air and ammonia over a suitable heterogeneous catalyst. Ammoxidation is nothing but a vapor phase partial oxidation with selective insertion of a nitrogen atom from gaseous ammonia into an inert or slightly activated –CH_3 group attached to an olefin, aromatic or N-heteroaromatic hydrocarbon to produce corresponding nitrile in large scale. Thus ammoxidation combines both oxidation and ammonolysis in a single step with the involvement of suitable heterogeneous catalyst. This process is clean one, gives high yield and purity of the products. The ammoxidation of organic substrate containing α- activated methyl group is an interesting reaction for production of fine chemicals. The cyano group constitutes a very versatile functional group susceptible for different kind of attacks such as hydrolysis or reduction for wide range of products. On the other hand they often by themselves valuable fine chemicals

Mixed oxide catalysts are generally used in selective oxidation and ammoxidation in vapor phase. 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 [1, 2].A large variety of vanadium antimony systems are developed for ammoxidation of propane [3]. Ammoxidation of heteroaromatic compounds yield intermediates and final products pertaining to the agrochemical and pharmaceutical area. Nicotinic acid and nicotinamide which are essential constituents of vitamin B complex can be obtained by hydrolysis of nicotinonitrile [4]. Pyrazinamide is a well known anti-tubercular drug. The ammoxidation of 2-methylpyrazine to 2-cyanopyrazine is the key step in the preparation of pyrazinamide. This reaction is intensively investigated by several research groups [5-10]. A large variety of catalyst system mainly composed of vanadium, molybdenum and antimony oxides supported on alumina, silica, HZSM-5 and modified clay are used in the ammoxidation of 3-picoline to nicotinonitrile [11-16].



2-methylpyrazine 2-cyanopyrazine

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 [17] 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 [18] 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 [19, 20]. 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 [21]. Roginskaya et al [22] 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 [23-25]. 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 [26]. V-Sb-O and VPO systems show the higher selectivity's in acrylonitrile formation from propane [27]. 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 [28, 29]. VPO's are also reported to be active for selective ammoxidation of 3-picoline to nicotinonitrile [30]. According to Hodnett [28] 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 [31] observed that the addition of promoter atom enhances the activity and selectivity of the VPO catalysts by preventing the formation of deleterious phases. Addition of zinc to $(VO)_2P_2O_7$ leads to increases the catalytic activity without effecting the selectivity as most of the zinc present on the surface of $(VO)_2P_2O_7$ and oxidizes vanadium to 5+ state [32]. Therefore, a systematic study is required in order to understand the role of promoter atoms on the phase composition and their catalytic properties. In view of the above reasons VPO and Cu, Zr, Mn and Co incorporated VPO catalysts were prepared and characterized by various physico-chemical techniques and evaluated for the title reaction. L. Forni [33] 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 2-methylpyrazine to 2-cyanopyrazine 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}. In this investigation an attempt is made to compare activity and selectivity of the VPO catalysts on addition of promoter atoms in micro quantities [Cu, Zr, Mn and Co] and macro quantities [Sb] for the title reaction.

EXPERIMENTAL SECTION

2.1. Catalysts

In aqueous method to prepare Sb-VPO-1 catalyst (3% Sb) 13.78 g of ammonium metavanadate and 14.96 g of antimony trioxide were added to 500 ml distilled water. To the resulting suspension 15.81 g of O-H_3PO_4 was added to maintain the P: V ratio at 1: 1.4 and refluxed for 6 h. The excess water was evaporated on water bath and green solid is obtained. The solid obtained 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 prepare Sb-VPO-2 (6% Sb) and Sb-VPO-3 (9% Sb) catalysts using requisite quantities of the precursors.

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.

In aqueous method 10% $NH_2OH.HCl$ solution is prepared first and to this 18 g of V_2O_5 is added and refluxed for 16 h until the color of the solution changes to dark blue. To the resulting solution requisite quantity of o-H_3PO_4 is added to maintain P: V ratio at 1.2: 1 and further refluxed for 6 h. The resulting light brown compound was filtered off and washed thoroughly with doubly distilled water several times until free from chloride ions. The obtained VPO precursor was oven dried at 110 ^{o} C for 12 h and calcined at 500 ^{o} C in presence of air. For the preparation of 0.2 atomic percent additive containing VPO catalysts the oven dried VPO precursor was suspended in distilled water and refluxed for 1 h. To this requisite quantities of $CuCl_2.2H_2O$ or $ZrOCl_2.6H_2O$ or $Mn(NO_3)_2.4H_2O$ or $Co(NO_3)_2.6H_2O$ were added and refluxed for 8 h. The resulting compound was filtered off, washed several times, oven dried at 110 ^{o} C for 12 h and calcined at 500 ^{o} C in presence of air.

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. Average oxidation state of vanadium in various catalysts was determined by double titration with $KMnO_4$ solution [34]. 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 2-methylpyrazine to 2-cyanopyrazine was studied at 400 ^{0}C on a previously described fixed bed flow micro reactor operating under normal atmospheric pressure [35]. 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: 5.5: 17.8: 15.4 mole percent of 2-methylpyrazine, steam, air and ammonia respectively was passed through the catalyst bed at a space velocity of 3974 h^{-1}.

In activity studies the optimum temperature observed for the maximum production of 2-cyanopyrazine is 400 ^{0}C. Above this temperature formation of carbon oxides, tar and pyrazine is observed. From the results obtained maximum conversion of 2-methylpyrazine is observed at mole ratio of ammonia to 2-methylpyrazine is 3.1and mole ratio of air to 2-methylpyrazine is 8.7. At a value higher than this the conversion of 2-methylpyrazine is decreased.

At a space velocity higher than 3974 h^{-1} there is decrease in the conversion of 2-methylpyrazine and selectivity to 2-cyanopyrazine increases. At lower space velocities formation of tar and carbon oxide increases.

RESULTS AND DISCUSSION

X-ray diffraction patterns and IR results suggest presence of various crystalline phases 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 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 IR spectra the values corresponding 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}.In supported system $AlSbO_4$ phase is observed and vanadium is present in highly dispersed state over the support surface [11].

X-ray powder diffractograms of VPO and additive incorporated VPO catalysts exhibit various crystalline phases $(VO)_2P_2O_7$, α-$VOPO_4$ and β-$VOPO_4$. The d-values observed are in agreement with literature values. There is no substantial difference between diffractograms of VPO and additive incorporated VPO catalysts. However, addition of an additive atom to VPO appears to increase the intensity of the peaks corresponding to α-$VOPO_4$ and β-$VOPO_4$ phases. This indicates an increase in the quantity of V^{5+} upon addition of the additive atom to VPO. IR spectra of VPO and additive containing VPO catalysts indicate the presence of $(VO)_2P_2O_7$ and β-$VOPO_4$. In the case of VPO catalysts intense bands are observed at 1120 and 970 cm^{-1} with some weak bands at 725, 680 and 560 cm^{-1}. These values correspond to V-O and P-O stretching vibrations of $(VO)_2P_2O_7$ which is dominating phase. In addition to this few weak and strong bands are observed at around 1160, 1040 and 640 cm^{-1} corresponding to β-$VOPO_4$ phase. However, in the case of additive containing VPO catalysts the latter phase is found to dominate over $(VO)_2P_2O_7$. Thus the IR results are in line with XRD observations.

All the antimony promoted VPO catalysts have shown well resolved ESR spectrum with hyperfine splitting. 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 [36]. The g-values of the catalysts are given in table 3. 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 parameter can be attributed to isolated sites connected via oxygen bridges to P. For Sb-VPO-1 $\Delta g_{II}/\Delta g_{\perp}$ is smallest.

In the case of VPO sample a well resolved ESR spectrum with hyperfine splitting is observed. This can be attributed to the presence of the ESR active lower oxidation state of vanadium (V^{4+}) in good quantity. In the case VPO-Zr sample a well resolved spectrum obtained may presumably be due to either preferential formation of X-ray amorphous $(VO)_2P_2O_7$ phase or dilution of this phase with Zr-oxide. In VPO-Cu sample spectrum of Cu^{2+} overlapping with the spectra of VPO. In VPO-Mn sample a broad signal is observed may be due to dipolar interaction of paramagnetic species. The g-values calculated are given in table 4.

Scanning electron micrographs of the promoted VPO catalysts show lower surface area and has plate like structure. In these catalysts particle size is uniformly12μm irrespective of the promoter used.

In oxidation/ammoxidation reactions activation of methyl group in N-hetero aromatic compounds depends on acid-base properties of the catalyst and reactants. VPO's are solid acid catalysts having oxidizing power. In N-hetero aromatic compounds methyl group 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 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^+). Then probably combines with ammonia forming corresponding nitrile.

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. 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 of 2-methylpyrazine (percent)	Selectivity to 2cyanopyrazine (percent)
Sb-VPO-1	2.0	33	4.5637	85	90
Sb-VPO-2	3.1	27	4.6472	82	90
Sb-VPO-3	6.2	16	4.7685	54	90
Sb-VPO/Al_2O_3	16	22	4.6374	92	93

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 2-methylpyrazine 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. Supported system has higher activity even though has lower acidity probably this may be due higher dispersion of VPO in amorphous state on support.

Table 2:Physico-chemical and catalytic properties of various promoted VPO catalysts

Catalyst	BET surface area (m^2 g^{-1})	Ammonia Uptake (μ-moles g^{-1})	Average oxidation number	Conversion of 2-methylpyrazine (percent)	Selectivity to 2-cyanopyrazine (percent)
VPO	9.51	256	3.849	90	90
VPO-Zr	2.81	168	4.042	85	92
VPO-Mn	4.31	135	3.943	81	90
VPO-Cuu	4.24	33	3.921	41	94
VPO-Coo	10.21	68	3.958	72	93

Conversion =
Number of moles of 2-methylpyrazine reacted
--- x 100
Number of moles of 2-methylpyrazine introduced

Selectivity =
Number of moles of 2-cyanopyrazine produced
--- x 100
Number of moles of 2-methylpyrazine reacted

Yield = Conversion % x Selectivity %

In the ammoxidation of 2-methylpyrazine the activation of C-H bond of methyl group is possible on acidic site of the catalyst. At P/V ratio of 1.0 and above all the surface cations act as surface functional groups i.e. all of the surface vanadium ions form V= O species having redox activity and all of the surface P-ions form P-OH species as Bronsted acid sites. Therefore, the PO_4 groups on the surface of $(VO)_2P_2O_7$ are believed to be responsible for the activation of 2-methylpyrazine molecule and should control the first step of the mechanism. Ammonia chemisorption at 150 ^{0}C is measure of Bronsted acidity of the catalyst since these acid centers chemisorb ammonia as NH^{4+}. As can be seen from table 2, there are more Bronsted acid sites on VPO catalyst compared to additive containing samples and same trend is observed in the total conversion of 2-methylpyrazine on various samples.

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. Supported system has higher surface area. A small decrease in surface area of zirconia, cobalt, copper and manganese promoted vanadium phosphorus oxide (VPO) catalysts observed compared to VPO catalyst, except the VPO-Co sample. It can be seen from the tables that catalytic activity increases with increase in surface area.

Several authors correlated the catalytic activity and selectivity of VPO catalysts to average oxidation number of vanadium [28, 29]. It was postulated that the activation of C-H bond takes place on the reduced surface of VPO [V^{4+}] and product is formed from oxidized surface. When the average oxidation state falls well below +4 selectivity to product decreases. The redox cycle between V^{4+} and V^{5+} phases is considered to be responsible for the selective formation of the product. 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[37] 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 [38] V^{+5} phase along with V^{+4} phase is active in ammoxidation of 4-picoline. Bordes and Courtin [39] 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 3.

Table 3:g-values of the catalysts

catalyst	g_{II}	$g_{\perp}$	g
V_2O_5	-	-	1.9749
Sb-VPO-1	2.0206	2.1003	-
Sb-VPO-2	1.9338	1.9721	-
Sb-VPO-3	1.9446	1.9721	-
Sb-VPO/Al_2O_3	-	-	1.9665

Table 4: g-values of the catalysts

catalyst	g_{II}	$g_{\perp}$	g
VPO	1.9780	2.0006	-
VPO-Zr	1.9838	2.0048	-
VPO-Co	1.9836	2.0476	-
VPO-Mn	-	-	2.0124
VPO-Cu	-	-	2.1512

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.

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 2-methylpyrazine, 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} .It is also well known in the case of supported transition metal oxidation catalyst that metal oxygen double bond groups are the reactive sites. The facile movement of electrons through the aggregated reduced structures facilitate dissociation of oxygen and formation of V = O active sites with vanadium in the +5 oxidation state during the course of the reaction. The active phase in propane ammoxidation is amorphous $VSbO_4$-Sb_2O_4 system [40] 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

The β-$VOPO_4$ (V^{+5}) phase can not be reduced to V^{+4} state as easily as α-$VOPO_4$. Therefore, the activities of the additive containing catalysts are less than the pure VPO catalysts. The preparation method adopted and the heating rates used for calcinations of the samples may probably be responsible for the greater quantity of β-$VOPO_4$ observed. Formation of any new phase between the dopent and VPO was not observed in this study. The present results show that the addition of cobalt to VPO significantly affects the activity of the catalyst. The N_2 BET surface area of the additive containing catalysts decreased upon addition of additive atoms. This observation clearly indicates that the additive atoms are not incorporated into the phosphate layers as originally expected. The additive atoms are present on the surface of pyrophosphate in the form of water soluble compounds. This is in agreement with ESR results. g-values calculated are given in table 4. The IR, ESR results and average oxidation number of vanadium in the catalyst suggests that vanadium is present in lower oxidation state along with some V^{+4}. The redox cycle between $(VO)_2P_2O_7$ (V^{+4}) and α-$VOPO_4$ (V^{+5}) phases appear to be responsible for the ammoxidation of 2-methylpyrazine to 2-cyanopyrazine[41,42].

CONCLUSION

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.

The undoped VPO is more active because of the higher surface area, higher surface acidity and lower oxidation number of vanadium. The activities of doped VPO catalysts are less, presumably due to spreading of additive atoms on the surface of active $(VO)_2P_2O_7$ phase and an increase in the quantity of β-$VOPO_4$ phase which can not be easily reduced to the V^{+4} state to produce redox couple.

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