Journal of Chemical and Pharmaceutical Research



J. Chem. Pharm. Res., 2011, 3(4):357-369

# Ammoxidation of methyl N-heteroaromatic compounds over vanadium phosphorus oxide based catalysts

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# ABSTRACT

Ammoxidation of methyl N-heteroaromatic compounds was investigated on non-conventional vanadium phosphorus oxides of different origin and supported vanadium phosphorus oxide catalyst under atmospheric pressure at 400  $^{\circ}$ C. Conventional V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was studied for comparison under similar conditions. 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 for SiO<sub>2</sub> supported VPO catalyst compared to conventional catalyst V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and vanadium phosphorus oxides of different origin can be attributed to high active surface area, lower oxidation state of vanadium and higher surface acidity. A redox cycle between (V<sup>4+</sup>) and (V<sup>5+</sup>) species appears to be responsible for the ammoxidation activity of VPO catalyst.

**Key words**: vanadium phosphorus oxide; VPO/SiO<sub>2</sub>; ammoxidation of methyl N-heteroaromatic compounds; selectivity to nitrile.

## **INTRODUCTION**

Nitrile group is susceptible to different kinds of attack like hydrolysis and reduction which yield commercially important intermediates. Ammoxidation is a process in which -CH<sub>3</sub> group is converted into nitrile over a suitable heterogeneous catalyst. Ammoxidation is vapor phase partial oxidation with selective insertion of nitrogen from gaseous ammonia in to inert or slightly activated CH<sub>3</sub> group attached to olefin, aromatic and N-heteroaromatic compounds.



The resulting nitrile are valuable intermediates for the production of dyestuffs, pesticides, pharmaceuticals and other chemical products [1]. In most of the oxidation or ammoxidation reactions supported and promoted vanadium oxide based catalyst is used because of its ability to transfer oxygen from bulk to surface and then to the reactant molecules. The reduced surface gets oxidized by the supply of molecular oxygen [2].  $V_6O_{13}$  is active and selective for ammoxidation of 3-picoline among all single oxide phases and combination of  $V_2O_5$  and  $V_6O_{13}$  more selective than single phase oxide [3]. Selective ammoxidation of 3-picoline and 2-methylpyrazine to their corresponding nitriles was investigated on various catalyst systems composed mainly of vanadium, molybdenum and antimony oxides supported on alumina or silica [4-8].

Vanadium phosphate compounds are important industrial catalysts used in the conversion of nbutane to maleic anhydride. This reaction requires the presence of both  $V^{5+}$  and  $V^{4+}$  in close proximity [9, 10]. Recent studies reveal that VPO catalysts with some promoter atoms and/or support materials are also active for ammoxidation reactions of commercial importance [11, 12]. Influence of support and promoter on the ammoxidation activity of VPO catalysts in conversion of 2, 6- dichloro toluene to 2, 6- dichloro benzonitrile has been evaluated. Higher activity and selectivity is achieved over TiO<sub>2</sub> anatase supported VPO catalyst and promoted VPO catalyst [13, 14]. The choice of P/V ratio, acidity and redox properties play important role in enhancing catalytic activity [15]. Catalyst supported on H<sub>3</sub>PO<sub>4</sub> treated ZrO<sub>2</sub> is highly active for n-butane oxidation. The change in VPO loading is found to have effect on catalyst efficiency. The best performance achieved on 36% VPO/H<sub>3</sub>PO<sub>4</sub> treated ZrO<sub>2</sub> catalyst [16]. VPO/SiO<sub>2</sub> showed low activity and high selectivity due to well dispersed VPO phase on SiO<sub>2</sub> and VPO/TiO<sub>2</sub> (anatase) shows higher activity due to interaction of VPO with TiO<sub>2</sub> increases number as well as the activity of active sites [17].

Ammoxidation of 3-picoline to nicotinonitrile and 2-methylpyrazine to 2-cyanopyrazine are very important reactions in the pharmaceutical industry. Niacin and nicotinamide are constituents of vitamin B-complex derived from nicotinonitrile hydrolysis. Pyrazinamide is one of the anti-TB drugs obtained by hydrolysis of 2-cyanopyrazine. Recent investigations have shown that the VPO systems are much more superior than the conventional vanadium pentoxide based catalysts in catalyzing the above reactions. Therefore, a systematic study was undertaken in order to develop efficient catalysts for the above ammoxidation reactions. In this study, both conventional vanadia based catalyst and non-conventional VPO systems are prepared, characterized and the physicochemical characterstics of VPO's which effect the conversion and selectivity of the above reactions is evaluated and compared with the conventional catalyst.

#### **EXPERIMENTAL SECTION**

## **Preparation of VPO catalysts**

The investigated VPO catalysts with atomic ratio V: P = 1: 1.2 were prepared by different methods involving aqueous and organic media [18]. In aqueous method,  $V_2O_5$  (20g) was dissolved in 37% aqueous HCl solution (300 cm<sup>3</sup>) to which 85% ortho phosphoric acid (30 cm<sup>3</sup>) was added under reflux. The dark green precipitate obtained was filtered off and washed several times with doubly distilled water to remove chloride ions. Then it was dried at 120  $^{0}$ C for 8 h and calcined at 450  $^{0}$ C for 6 h in air. In other aqueous method 10% NH<sub>2</sub>OH.HCl solution was prepared first and then 20 g of V<sub>2</sub>O<sub>5</sub>(Loba chemie, GR grade) was added 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 resulting VPO precursor was oven-dried at 120  $^{0}$ C for 12 h and then calcined at 500  $^{0}$ C in presence of dry air. In organic method, V<sub>2</sub>O<sub>5</sub> (20g) was suspended in a mixture of isobutyl alcohol (360 cm<sup>3</sup>) and benzyl alcohol (40 cm<sup>3</sup>) and reduced under reflux for 16 h. Then stoichiometric amount of 85 percent ortho phosphoric acid was added. The resulting precipitate was filtered off, dried at 120  $^{0}$ C for 8h and calcined in air at 450  $^{0}$ C for 6 h. For another sample isobutyl alcohol alone was used as reducing agent.

In preparation of 20 weight percent SiO<sub>2</sub> supported VPO catalyst (VPO/SiO<sub>2</sub>), the support was impregnated with organic slurry of VPO. This suspension was dried at 120  $^{0}$ C for 8 h and calcined at 450  $^{0}$ C for 6 h. (Sb-VPO/Al<sub>2</sub>O<sub>3</sub>) alumina supported and antimony promoted VPO catalyst (V:P:Sb:Al = 1.4:1:3.3;10) was prepared by deposition precipitation method. The requisite quantities of ammonium metavanadate (Fluka, AR grade) and antimony trioxide (Loba chemie, AR grade) were suspended in deionized water, to which a stoichiometric 85% orthophosphoric acid was added and refluxed for 6 h. To the resulting light green slurry suspension the desired quantity of gamma alumina (ACC, India, surface area 104 m<sup>2</sup>g<sup>-1</sup>) fine powder was added and heated further to concentrate the suspension to obtain a paste. The paste was then oven dried at 120  $^{0}$ C for 16 h and calcined at 800  $^{0}$ C for 4h. The V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst containing 7.5 wt% V<sub>2</sub>O<sub>5</sub> and 7.5 wt% MoO<sub>3</sub> was prepared by aqueous co impregnation of gamma alumina support (Harshaw, USA, surface area 146 m<sup>2</sup>g<sup>-1</sup>) with ammonium metavanadate (Fluka, AR grade) and ammonium heptamolybdate (JT Baker, USA). The impregnated catalyst was oven dried 120  $^{0}$ C for 16 h and calcined at 500  $^{0}$ C for 6 h.

#### **Catalyst characterization**

The phase composition of calcined samples was determined by X-ray powder diffraction method. X-ray diffractograms were recorded on a Philips PW 1051 diffractometer by using monochromatic FeK<sub> $\alpha$ </sub> radiation. The decomposition patterns of oven dried catalyst samples (before calcination) were studied by differential thermal analysis technique. Thermo grams were recorded on a Leeds and Northap DAT unit with a heating rate of 6<sup>o</sup>C per minute. Average oxidation state of vanadium in various catalysts was determined by double titration with KMnO<sub>4</sub> solution [19]. The ESR spectra were obtained at liquid nitrogen temperature on a JOEL FE-3X X-band spectrometer with 100 KHz modulation. Self supporting KBr pellets containing the catalyst samples were used to scan the IR spectra on a Nicolet 740 FTIR spectrometer at ambient conditions. SEM investigations were made on a Hitachi model S-520 scanning electron microscopy at an applied voltage of 19 KV.

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A conventional static volumetric high vacuum system was used to determine the BET surface areas and ammonia uptake capacities of various samples. BET surface areas were estimated by nitrogen physisorption at -196  $^{0}$ C and by taking 0.162nm<sup>2</sup> as the cross-section of the nitrogen molecule. Ammonia gas chemisorption was measured by a double isotherm method at 150  $^{0}$ C following the procedure described elsewhere [20].

## **Activity studies**

Ammoxidation of 3-picoline to nicotinonitrile and 2-methylpyrazine to 2-cyanopyrazine was studied at 400  $^{0}$ C on a fixed bed flow micro reactor at atmospheric pressure. For each run about 2 g of catalyst sample was used and liquid products were collected after establishing steady state conditions (2-3h). Liquid products were analyzed by GLC with a 10 percent OV-17 column (2 m) on chromosorb G-AW kept at 130  $^{0}$ C and with a flame ionization detector. The feed mixture consisting of 1:10:10:16 mole percent of 3-picoline / 2-methylpyrazine, steam, air and ammonia respectively was passed through the catalyst bed at a space velocity of 3946 h<sup>-1</sup>.



Fig 1.Powder X-ray diffraction patterns of VPO catalysts obtained from different origins

 $\star$  (VO)<sub>2</sub> P<sub>2</sub>O<sub>7</sub> $\Box$  AlSbO<sub>4</sub> $\P$   $\alpha$  - VO(H<sub>2</sub>.PO4)<sub>2</sub> $\circ$   $\beta$  - VOPO<sub>4</sub> $\nabla$   $\alpha$  - VOPO<sub>4</sub> $\Delta$   $\alpha$  - VOPO<sub>4</sub>.2H<sub>2</sub>O

## **RESULTS AND DISCUSSION**

X-ray powder diffraction patterns of VPO catalysts and promoted and supported VPO catalysts are shown in fig 1. The various crystalline phases identified are  $(VO)_2P_2O_7$ ,  $\alpha$  -VOPO<sub>4</sub> and  $\beta$ -VOPO<sub>4</sub> with some other minor unidentified phases in varying intensities. The d-values obtained are in agreement with literature values [21]. In silica supported VPO system V<sup>4+</sup>species  $(VO_2P_2O_7 \text{ phase})$  is assumed to be present in amorphous state and V<sup>5+</sup> species ( $\beta$ -VOPO<sub>4</sub>) is present in crystalline state which unequivocally shows that active component is in a highly dispersed state. The XRD patterns of  $V_2O_5$ -MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited the presence of broad diffraction lines due to Al<sub>2</sub>O<sub>3</sub> support only. The active phases are apparently in a highly

dispersed and amorphous state. In Al<sub>2</sub>O<sub>3</sub> supported and antimony promoted VPO catalyst AlSbO<sub>4</sub> phase is observed and VPO is present in highly dispersed state over the support surface.



The FTIR spectra of VPO and supported VPO catalysts are given in fig 2. The V—O and P—O stretching modes fall in the region 800-1200cm<sup>-1</sup>. Band at 1020cm<sup>-1</sup> corresponds to V = O stretching and 820cm<sup>-1</sup> to V-O-V deformation. The IR spectra of all the investigated VPO samples are almost similar. In VPO catalysts intense bands are observed at 1160, 1120, 1040, 975, 920 and 680 cm<sup>-1</sup>. In VPO/SiO<sub>2</sub> an intense band at 1120 and weak band 825 cm<sup>-1</sup> are observed. These bands correspond to V-O and P-O stretching vibrations of VO<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and β-VOPO<sub>4</sub>. Thus, the IR results are in line with XRD observations. The IR bands observed in all samples at 1610 - 1640 cm<sup>-1</sup> can be related to ammonia formed during preparation, which remains adsorbed on the catalyst surface even after evacuation [23].

The ESR spectra of various catalysts are presented in fig 3. A single line ESR signal with undetectable hyperfine structure was obtained for all the catalysts except for VPO (NH<sub>2</sub>OH.HCl) indicating the interaction between  $V^{4+}$  ions. However, signal intensities, known to be proportional to spin concentration, are different for various methods of preparations. A broad signal at g = 1.96 and a weak hyperfine structure is observed. The broad band was similar to that of reduced  $V_2O_5$ , indicating that  $V^{4+}$  ions are localized in the  $V_2O_5$  matrix. At P/V > 1 the hyperfine structure became obscure and narrow signal was observed ascribed to the hyperfine structure of  $V^{4+}$ ions dispersed in the bulk and narrow band to  $V^{4+}$  ions in phosphate compounds. The broad signal is ascribed to  $V^{4+}$ ions in  $V_2O_5$  which dissolves a small amount of  $P_2O_5$ . In the case of the VPO (NH<sub>2</sub>OH.HCl) sample a well resolved ESR spectrum with hyperfine splitting is observed. This can be attributed mainly due to the presence of the ESR active lower oxidation state of vanadium  $V^{4+}$  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 [23, 24].





Fig 4. Scanning electron micrographs of VPO catalysts obtained from different origins

In differential thermal analysis (DTA) substance is subjected to programmed heating along with thermally inert material  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Thermo grams recorded for all the VPO catalysts before calcinations. The temperature difference  $\Delta T$  is plotted on the ordinate and temperature of the sample on abscissa. Sample obtained from isobutanol-benzyl alcohol mixture exhibited endothermic peaks at 430°C, 675°C, and 765°C and sample obtained from aqueous media exhibited endothermic peaks at 430°C degree cateratic peaks at 430°C. Silica supported system exhibited exothermic peak at 375°C and 350°C. Silica supported system exhibited exothermic peak at 375°C and Sb-VPO/Al<sub>2</sub>O<sub>3</sub> exhibited exothermic peaks at 105°C can be attributed to desorption of water. This is not observed in samples obtained from organic medium. The remaining peaks can be attributed to topotactic transformation of precursor VOHPO<sub>4</sub>.0.5 H<sub>2</sub>O to corresponding VO<sub>2</sub>P<sub>2</sub>O<sub>7</sub>,  $\alpha$ -VOPO<sub>4</sub> and  $\beta$ -VOPO<sub>4</sub> phases. Exothermic phase in supported system may be due to change in physico-chemical properties of the active component when dispersed on the support [25].

Figure 4 provides scanning electron micrographs of VPO catalysts. The catalysts obtained from organic medium exhibited platelet structure and the size of the particles observed for these catalysts is small as compared to aqueous ones. The platelets are irregular shaped and randomly clustered. For HCl reduced sample rosette like structure is observed with fairly uniform size of 30µm. In supported system aggregation and uniform distribution of VPO particles is observed with fairly uniform size of 6µm. VPO catalysts obtained from organic media have well formed morphology with fairly uniform size of 6µm.

BET face area and ammonia uptake

The BET surface area, ammonia uptake and average oxidation state of vanadium is given table 1. Surface area of catalysts obtained from aqueous media is higher than the catalysts obtained from organic medium.

Catalyst	BET surface are	Ammonia	Average oxidation number
	$(m^2 g^{-1})$	uptake(µ-moles g <sup>-1</sup> )	
VPO(HCl)	6.58	236	4.83
VPO(NH <sub>2</sub> OH.HCl)	9.8	255	3.88
VPO(I)	3	169	4.5
VPO(IBa)	5.6	213	4.25
VPO/SiO <sub>2</sub>	49.8	582	4.11
Sb-VPO/Al <sub>2</sub> O <sub>3</sub>	20	30	4.6
V-Mo/Al <sub>2</sub> O <sub>3</sub>	152	427	-

Table 1 Physico-chemical properties of various VPO catalysts

In supported system higher surface area is observed for VPO/SiO<sub>2</sub> compared to other supported systems. Similarly ammonia uptake capacity at 150  $^{0}$ C for catalysts obtained from aqueous media is higher than the catalysts obtained from organic medium. However, the highest uptake of ammonia was observed on the VPO/SiO<sub>2</sub> sample followed by for V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>. The average oxidation state of vanadium was lower for the catalysts obtained from organic medium and for VPO (NH<sub>2</sub>OH.HCl) and VPO/SiO<sub>2</sub> sample.

x 100

#### Correlation of physico-chemical properties with that of Catalytic activity

An activity and selectivity result of various catalysts for ammoxidation of methyl Nheteroaromatics is shown in table 2. The preparation method, average oxidation number and physical treatment determine the phase composition. The calcination temperature, heating rate and atmosphere in which calcination is carried out greatly effect the structure of the formed catalyst. Shimoda et al [26] observed at high heating rate  $\beta$ -VOPO<sub>4</sub> and at low heating rate  $\alpha$ -VOPO<sub>4</sub> phases. The calcination of the samples containing vanadium (IV) in air or oxygen yielded mixed oxide phases. The content of VO<sub>2</sub>P<sub>2</sub>O<sub>7</sub> tended to increase as the calcination temperature increased or heating rate is increased and calcination is carried out in nitrogen atmosphere.

 Table 2 conversion of methyl N- heteroaromatic compounds and selectivity to corresponding nitriles with different VPO catalysts

catalyst	Conversion%	Conversion%	Selectivity%	Selectivity%	yield (nicotino	yield (2-cyano
	(5 preonine)	pyrazine)	nitrile)	pyrazine)	nitrile)	(2 cyano pyrazine))
VPO(HCl)	44	62	80	70	35.2	43.4
VPO(NH <sub>2</sub> OH.HCl)	80	90	90	90	72	81
VPO(I)	58	64	80	80	46.4	61.2
VPO(IBa)	65	71	90	82	58.5	58.2
VPO/SiO <sub>2</sub>	89	92	92	93	81.9	85.6
Sb-VPO/Al <sub>2</sub> O <sub>3</sub>	76	82	93	92	70.7	75.4
V-Mo/ Al <sub>2</sub> O <sub>3</sub>	68	72	70	73	47.6	52.6

Conversion =

Number of moles of 3-picoline/2-methylpyrazine reacted

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number of moles of 3-picoline/2-methylpyrazine introduced

Selectivity =

Number of moles of nictinonitrile/2-cyanopyrazine produced	
	x 100

no of moles of 3-picoline/2-methy pyrazine reacted

Yield = Conversion % x Selectivity % x 100

All the VPO catalysts prepared are calcined at 450  $^{0}$ C in presence of air at the rate of 10 $^{0}$ C/minute. XRD results revealed the formation of  $\alpha$ -VOPO<sub>4</sub> or  $\beta$ -VOPO<sub>4</sub> along with VO<sub>2</sub>P<sub>2</sub>O<sub>7</sub> phase mostly in amorphous state for VPO catalysts which is in agreement with the literature data [27].

In the ammoxidation of methyl N- heteroaromatic compounds the activation of C-H bond of the methyl group is a crucial step. This is possible on acidic sites of the catalysts as per the published literature [28]. At the P/V ratio of 1.0 and above all the surface cations act as 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. The activation methyl group of methyl N-heteroaromatic compound takes place on the  $PO_4$  groups on the surface of  $VO_2P_2O_7$  and

should control the first step of mechanism. Ammonia chemisorption, when conducted at 150  $^{0}$ C, is the measure of Bronsted acidity of the catalyst since these acid centers chemisorbed ammonia as NH<sub>4</sub><sup>+</sup>. It can be seen from the results given in table 1 that there are more Bronsted acid sites on VPO (NH<sub>2</sub>OH.HCl) than the equivalent organic ones. The same trend is observed in the total conversion of methyl N-heteroaromatic compounds exception being VPO (HCl).

In oxidation or ammoxidation reaction V=O species is proposed to be active. V=O species are dispersed only on (010) plane when vanadium is present in +5 state but reduction using organic and aqueous medium to  $V^{4+}$  state leads the dispersion of V=O species over all other phases. The VPO catalyst obtained from organic medium and VPO (NH<sub>2</sub>OH.HCl) exhibited higher activity because of smaller size and uniform distribution of particles as observed from SEM figures and greater reducibility leading to lower oxidation states which can be observed from table 1. Reducing agent provides V<sup>4+</sup> species and stabilization of the species takes place when phosphorus is present in excess of P: V > 1.2. At low P: V ratio vanadium becomes pentavalent, while both  $V^{4+}$  and  $V^{5+}$  are present for P: V > 1.2. The higher P: V superficial ratio observed by XPS lead to think that owing to their acidity, the PO<sub>4</sub> groups on the surface of VO<sub>2</sub>P<sub>2</sub>O<sub>7</sub> should be responsible for the activation of C-H bond of butane and thus should control the first step of mechanism. Further steps involving the O-insertion could be controlled by the presence of  $VOPO_4$  entities [29]. It may be envisaged that during testing at higher temperatures excess of phosphorus plays important role of maintaining the core of the catalyst in reduced state while allowing free moment of lattice oxygen through the near surface layers. Trifiro et al [30] concluded that butane can be activated first by the coordinative unsaturated V-ion which is acidic, situated on the (100) surface phase of VO<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and oxidized to maleic anhydride by the oxygen double bonded with the other paired V-ions. VO<sub>2</sub>P<sub>2</sub>O<sub>7</sub> thus can be said a solid acid catalyst having oxidative power. On the cleavage phase of (100) crystal phase of  $VO_2P_2O_7$  are present pair of vanadium ions, each consisting of V-ion doubly bonded with oxygen having oxidation property and coordinative unsaturated P-ions projecting from the surface plane. The coordinative unsaturated V-ions and P-ions thought to provide acidic sites in such a manner that V-ion act as Lewis acid and p-ions, through taking water, as protonic acid. Catalysts having higher acidity exhibit higher activity in total conversion of methyl N- heteroaromatic compounds can be observed in table 2 exception being Sb-VPO/Al<sub>2</sub>O<sub>3</sub>. The VPO/SiO<sub>2</sub> sample shows better catalytic performance than the unsupported VPO. The increase in activity and selectivity of the VPO/SiO<sub>2</sub> catalyst may presumably arise from an increase in the exposed area of the active component on the support surface. Ammonia uptake, BET surface area, XRD and other results support this assumption.

Physicochemical properties of various catalysts are given in table 1 and activity and selectivity results are presented in table 2. Activity and selectivity of various catalysts were studied at different temperatures, at various contact times and air to ammonia mole ratios. An increase in the conversion with the increase in temperature is noted on all the samples and at temperature 430  $^{\circ}$ C and above total conversion of methyl N- heteroaromatic compounds with more than 95 percent selectivity to nitrile was observed on VPO(NH<sub>2</sub>OH.HCl), VPO/SiO<sub>2</sub> and other organic origin samples. Air to ammonia had marked effect on these products. VPO catalysts are more selective towards the desired nitrile products at more air and less ammonia concentration while the V-Mo/Al<sub>2</sub>O<sub>3</sub> was more selective under reverse condition. It is observed that the reactivity of 2-methylpyrazine is greater than 3-picoline under identical reaction conditions. This can be

attributed to higher basicity of 2-methylpyrazine because of presence of two nitrogen atoms with their lone pair of electrons which in turn facilitate relatively strong adsorption of this molecule on the acidic VPO catalyst.

Several authors have correlated the catalytic activity and selectivity of VPO catalysts to the average oxidation number of vanadium [31, 9]. The average oxidation number of vanadium appears to depend on the type of solvent/reducing agent used and shows a marked effect on the activity and selectivity of the catalyst. Lowest average oxidation number of vanadium was observed in the case of VPO (NH<sub>2</sub>OH.HCl), VPO/SiO<sub>2</sub> and other organic origin samples on which maximum activity and selectivity is obtained. In the case of VPO (NH<sub>2</sub>OH.HCl) sample a well resolved ESR spectrum with hyperfine splitting is observed. This can be attributed mainly due to the presence of the ESR active lower oxidation state of vanadium  $V^{4+}$  in good quantity. The good resolution of the spectrum and absence of exchange narrowed spectra indicate that ions are sufficiently separated from each other and dispersed both on the surface and bulk of the VPO compound. In other samples a single line ESR signal with undetectable hyperfine structure was obtained for the catalysts indicating the interaction between V (IV) spin concentration are different for various preparations in agreement with average oxidation number results given in table 1. XRD and IR results of the catalysts indicated the presence of various vanadium phosphorus oxide crystalline phases like  $\alpha$ -VOPO<sub>4</sub>,  $\beta$ -VOPO<sub>4</sub> and VO<sub>2</sub>P<sub>2</sub>O<sub>7</sub> with varying intensities. DTA curves of the corresponding precursors also show that the nature of the medium mainly determines the type of precursor and which in turn related to the resulting calcined catalyst.

The VPO (NH<sub>2</sub>OH.HCl) and VPO/SiO<sub>2</sub> catalysts had a better performance than either the equivalent aqueous/organic sample or the conventional catalyst. A similar high activity for VPO catalyst of organic origin was also noted for butane oxidation [18]. This was considered to be owing to the formation of a crystalline VO<sub>2</sub>P<sub>2</sub>O<sub>7</sub> phase with a preferential exposition of the surface of the (020) phase. Nakamura et al [19] related the yield of maleic anhydride over amorphous VPO catalyst to the very high mobility of electron present in the reduced vanadium oxide structure which has segregated. The optimum average value was close to +4. These workers postulated that facile movement of electrons through this segregated reduced structures facilitated the dissociation of oxygen and formation of V=O bonds as active sites with vanadium in +5 oxidation state.

According to Centi et al [32] a mixture of B-phase and  $\alpha$ -VOPO<sub>4</sub> is best in transformation of nbutane to maleic anhydride. The increase in activity of the VPO/SiO<sub>2</sub> catalyst may presumably arise from an increase in the exposed area of the active component on the support area. XRD, IR and other results suggest that VO<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is the major observable phase along with  $\alpha$ -VOPO<sub>4</sub>, or  $\beta$ -VOPO<sub>4</sub> on the freshly obtained VPO catalyst irrespective of their method of preparation. However on silica support no such phase was observed which unequivocally shows that the active component is in a highly dispersed state. The average oxidation state of vanadium is almost same in VPO (NH<sub>2</sub>OH.HCl), VPO/SiO<sub>2</sub> and VPO (org) catalysts. The working catalyst contains a mixture of well crystallized VO<sub>2</sub>P<sub>2</sub>O<sub>7</sub> (V<sup>4+</sup>) and amorphous VPO phase (V<sup>5+</sup>) and a redox cycle between V<sup>4+</sup> and V<sup>5+</sup> species is known to be responsible for the steady state activity of the catalyst in accordance with classical Mars and Vankrevelen mechanism [33]. Thus

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VPO/SiO<sub>2</sub> is efficient catalysts for the conversion of methyl N- heteroaromatic compounds to corresponding nitrile.

## CONCLUSION

The VPO/SiO<sub>2</sub> and VPO (NH<sub>2</sub>OH.HCl) catalysts are more active and selective than the conventional catalyst V-Mo/ Al<sub>2</sub>O<sub>3</sub> because of higher surface area, higher surface acidity and lower oxidation number of vanadium. The VPO/SiO<sub>2</sub> is still more active because of increase in exposed area of the active component on the support which is in highly dispersed state. A redox cycle between (V<sup>4+</sup>) and (V<sup>5+</sup>) species is responsible for the steady state activity of the catalyst.

## Acknowledgements

Thanks are due to Dr. B. Mahipal Reddy, Deputy Director, Indian Institute of Technology, Hyderabad for his constant encouragement and support in carrying out this work. Author thanks university grants commission for the financial assistance.

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