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# **ARTICLE TYPE**

### Vapour phase dehydration of glycerol to acrolein over Vanadium Phosphorous Oxide (VPO) catalyst

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#### Abstract

Vanadium phosphorus oxide (VPO) catalysts were synthesized with the different P/V ratio in the range of 0.6-2.0. These catalysts were characterized by EDX analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), UV- diffuse reflectance spectroscopy, laser Raman spectroscopy (LRS), temperature programmed desorption of ammonia, temperature programmed reduction and X-ray photoelectron spectroscopy. The XRD results of the VPO samples suggest that the sample with P/V ratio less than unity possesses pure crystalline vanadia and  $\beta$ -VOPO<sub>4</sub> phases. However, the sample with the P/V ratio  $\geq 1.0$  contains various VOPO<sub>4</sub> and vanadyl pyrophosphate phases. The laser Raman spectroscopy and UV-DRS analysis of the samples also confirm above findings. The ammonia TPD analysis suggests that the acidity of the catalyst increases upto P/V ratio ~1.2 and further no significant change in the acidity was noticed. The catalytic performances of these samples were investigated for gas phase glycerol dehydration reaction. The results reveal that the conversion and selectivity depend on the P/V ratio of the VPO catalyst. The XRD pattern of the spent samples suggests that the VPO phase undergoes phase change

after the reaction. The XPS analysis result confirms the presence of higher amount of  $V^{4+}$  species in the  $_{20}$  spent samples than pure sample.

#### **1** Introduction

In the recent past, glycerol received particular attention as byproduct formed during biodiesel production. The extracted triglycerides can undergo transesterification with methanol, <sup>25</sup> yielding the methyl ester (biodiesel) and glycerol as by-product on a stoichiometric basis. The increasing production of biodiesel has resulted in a price decline of crude glycerol. This makes aqueous glycerol as an attractive compound for the synthesis of fine and crude chemicals. Catalytic conversion of glycerol to

- <sup>30</sup> acrolein by a double dehydration reaction could be an important route for the conversion of glycerol to value added commodity chemicals. However this process would provide a cost effective and sustainable alternative to the current commercial catalytic petrochemical process based on the oxidation of propylene over a
- <sup>35</sup> Bi/Mo mixed oxide catalyst. Acrolein is an important and versatile chemical intermediate and raw material for the production of acrylic acid esters, super absorber polymers, fiber treatment, detergents and production of other value-added derivatives.<sup>1-2</sup> Dehydration of glycerol has been extensively
   <sup>40</sup> studied using various solid acid catalysts such as zeolites,<sup>3</sup> metal oxides,<sup>4-5</sup> metal phosphates,<sup>6</sup> heteropoly acids on different supports,<sup>7-8</sup> tungsten oxide supported on different supports,<sup>9-10</sup> etc. The surface acidic property of the catalyst plays an important role in the glycerol dehydration reaction for obtaining good

<sup>45</sup> catalytic activities. From the literature, it is known that moderatestrong acidity of the catalyst is required in order to facilitate the double intra-molecular dehydration of the reactant. However the strong acidity is responsible for the formation of heavy compounds (coke) and also contributes to the catalyst <sup>50</sup> deactivation, since they accumulate on the catalyst surface. <sup>11,12</sup>

The metal phosphates are used as catalyst for various oxidation and oxidative dehydrogenation reactions as well as dehydration reaction because of the existence of acidic character.<sup>13,14</sup> Among them, vanadium phosphorus oxide (VPO) catalyst also used in 55 many solid acid catalysed reactions such as dehydration of fructose, dehydration of xylose,15 production of biodiesel,16 esterification of acetic acid<sup>17</sup> etc,. Vanadium phosphorus oxide (VPO) is well known as catalyst for an industrially important selective oxidation of n-butane to maleic anhydride.<sup>18</sup> The VPO 60 catalyst contains several VPO phases with vanadium in 5+ oxidation state ( $\alpha_{I}$ ,  $\alpha_{II}$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ - VOPO<sub>4</sub>), in 4+ oxidation state  $((VO)_2P_2O_7, VOHPO_4.0.5H_2O)$  and in 3+ oxidation state (VPO<sub>4</sub>). The VPO catalyst is prepared by a variety of methods, all of them eventually result in the formation of same active 65 phase vanadyl hydrogen phosphate hemihydrate, VOHPO<sub>4</sub>·0.5H<sub>2</sub>O. However, the most recent and common commercial formulations for the preparation of the precursor prefer organic compounds as solvents.<sup>19</sup> The thermal treatment of the above crystalline compound yield the well crystallized

vanadyl pyrophosphate phase.

The VPO catalyst with different pure VPO phases (uncalcined and calcined) was studied for glycerol dehydration reaction by Wang et. al <sup>20</sup> because it possesses strong acidic sites. They also <sup>5</sup> reported that the uncalcined sample (VOHPO<sub>4</sub>.0.5H<sub>2</sub>O) exhibits better catalytic activity (glycerol conversion 100% and acrolein selectivity 66%) than the calcined samples. Furthermore, they found that addition of molecular oxygen with glycerol feed greatly reduces the side product formation and maintains the

<sup>10</sup> glycerol conversion and acrolein yield. The same group also investigated the effect of calcination temperature on pure VPO catalyst (VOHPO<sub>4</sub>.0.5H<sub>2</sub>O) and found that calcination temperature affects the Lewis acidity of the catalyst.<sup>21</sup> The sample calcined at 800 °C was shown the best catalytic <sup>15</sup> performance (glycerol conversion 100% and acrolein selectivity

64%) in the glycerol dehydration reaction.

However, another important factor that affects the catalytic performance of VPO catalyst is the P/V atomic ratio used for catalyst preparation. There are several authors interested to study

<sup>20</sup> the relation between the P/V ratio and surface acidities of the catalyst. It is very hard to find out the relation between the acid site concentration of the VPO catalyst with different P/V ratio and the catalytic activity in the n-butane oxidation.<sup>22,23</sup> Hence, it is important to know that this parameter might affect the VPO <sup>25</sup> surface composition, the acidity and the catalytic application.

In the present wok, we prepared a series of VPO catalyst with various P/V ratios, and investigated the effects of P/V ratios on surface structure of the VPO catalyst and their catalytic activity during the gas phase dehydration of glycerol. These prepared

- <sup>30</sup> catalysts are well characterised by various spectroscopic and adsorption techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), UV- diffuse reflectance spectroscopy, laser Raman spectroscopy (LRS), temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD), temperature
- <sup>35</sup> programmed reduction analysis (TPR) and X-ray photoelectron spectroscopy to know the effect of modification on structure and surface properties. The purpose of this work is to examine the catalytic properties of VPO samples with different P/V ratio and also to find the relation between the surface structural properties

<sup>40</sup> of the different vanadium phosphorous oxide samples and catalytic functionalities during glycerol dehydration reaction.

#### **2** Experimental sections

#### 2.1 Preparation of the VPO catalyst

- The VPO precursors with different P/V ratios (P/V = 0.6-2.0) <sup>45</sup> were prepared through an organic route using isobutyl alcohol and benzyl alcohol as reducing agents. The required amount of vanadium pentoxide was first refluxed in a mixture of isobutyl alcohol and benzyl alcohol (volume ratio of 1:1, 21.2 ml of alcohol/g V<sub>2</sub>O<sub>5</sub>) at 140 °C for 5 h, after which the required
- <sup>50</sup> amount of phosphoric acid (85%) was added. After another 6 h of refluxing, the suspension was filtered and the solid was washed with isobutanol and acetone, respectively, then further dried in air at 120 °C for 24 h. The material thus obtained was the precursor of the vanadyl pyrophosphate. The dried precursor samples were
- <sup>55</sup> heated from room temperature (RT) to 550 °C at a rate of 5 °C/min in the muffle furnace and kept at this temperature for 4 h.

Similar method was employed to prepare other catalysts with P/V ratio of 0.6, 0.8, 1.0, 1.2, 1.5 and 2.0, and these are named as PV-0.6, PV-0.8, PV-1.0, PV-1.2, PV-1.5 and PV-2.0, respectively.

#### 60 2.2 Catalyst Characterization

X-ray diffraction (XRD) patterns were obtained on Rigaku miniflex diffractometer using graphite filtered Cu Ka (K = 0.15406 nm) radiation. The SEM analysis was obtained by mounting the sample on an aluminum support using a double 65 adhesive tape coated with gold and the micrographs were recorded Hitachi S-520 SEM unit. The specific surface area, pore size distribution studies of the prepared catalysts were estimated using N<sub>2</sub> adsorption isotherm at -196 °C by the multipoint BET method taking 0.0162 nm<sup>2</sup> as its cross-sectional area using 70 Autosorb 1 (Quanta chrome instruments). The Raman spectra of the catalyst samples were collected with a Horbia Jobin Yvon Lab Ram HR spectrometer equipped with a confocal microscope, 2400/900 grooves / mm gratings, and a notch filter. The Visible Laser excitation a 532 nm (visible/green) was supplied by a Yag 75 doubled diode pumped laser (20mW). The scattered photons were dried and focused on to a single stage monochromator and measured with a UV sensitive LN2 cooled CCD detector (Horbia Jobin Yvon CCD 3000V). The UV-Vis diffused reflectance spectra were recorded on a GBC UV-Visible Cintra 10e <sup>80</sup> spectrometer with an integrating sphere reflectance accessory. The spectra were recorded in air at room temperature and the data was transformed according the Kubelka-Munk equation f(R) = $(1-R_{\alpha})^{2}/2R_{\alpha}$ . TPD experiments were conducted on AutoChem 2910 instrument. In a typical experiment for TPD studies, the 85 sample was pretreated by passage of high purity helium (50 mL/min) at 200 °C for 1h. After pretreatment, the sample was saturated with high pure anhydrous ammonia (50 mL/min) with a mixture of 10% NH<sub>3</sub>-He at 80 °C for 1h and subsequently flushed with He flow (50 mL/min) at 120 °C for 1 h to remove 90 physisorbed ammonia. TPD analysis was carried out from ambient temperature to 600 °C at a heating rate of 10 °C/min. The amount of NH<sub>3</sub> desorbed is calculated using GRAMS/32 software. The X-ray photoelectron spectroscopy (XPS) spectra of catalysts were measured on a XPS spectrometer (Kratos-Axis 95 165) with Mg Kα radiation (1253.6 eV) at 75 W. The C 1s line at 284.6 eV was used as an internal standard for the correction of binding energies. The background pressure during the data acquisition was kept below 10<sup>-10</sup> bar. Temperature programmed reduction were conducted on AutoChem 2910 (Micromeritics, 100 USA) instrument. In a typical experiment, 100 mg of oven dried sample was taken in a U-shaped quartz sample tube. The catalyst was mounted on a quartz wool plug. Prior to TPR studies, the catalyst sample was pretreated by passing helium gas in a flow of 50 mL/min at 200 °C for 2 h. After pretreatment the sample was 105 cooled to ambient temperature and TPR analysis was carried out in a flow of 5% H<sub>2</sub>-Ar (50 mL/min) from ambient temperature to 800 °C at a heating rate of 10 °C/min. The H<sub>2</sub> consumption & T<sub>max</sub> positions are calculated using GRAMS/32 software.

#### 2.3 Catalytic activity studies

<sup>110</sup> The gas phase dehydration of glycerol was carried out under atmospheric pressure in a vertical fixed bed quartz reactor (40 cm length, 9 mm i.d.) using 0.2g of catalyst. Prior to the reaction, the catalysts were pretreated at 300 °C for 1 h in flowing dry N<sub>2</sub> (16 mL.min<sup>-1</sup>). An aqueous solution containing 20 wt% glycerol was fed into the reactor by a micro syringe pump at 0.5 mL/h (WHSV-2.6 h<sup>-1</sup>) and the reaction temperature was kept at 300 °C. The reaction products were condensed in an ice–water trap and s collected hourly for analysis on a gas chromatograph GC-2014

(shimadzu) equipped with a DB-wax 123-7033 (Agilent) capillary column (0.32 mm i.d., 30 m long) and equipped with flame ionization detector.

#### **10 3 Results and discussion:**

The concentrations of phosphorus (P) and vanadium (V) in the calcined catalyst were determined by using the EDX analysis. The results of P/V atomic ratio for each VPO catalyst was calculated by dividing the concentration of P to the concentration <sup>15</sup> of V and the results are reported in Table 1. As can be seen on Table 1 the P/V atomic ratio obtained via EDX analysis was lower than the calculated P/V ratio. The maximum P/V ratio in the pure VPO catalyst is 1.06 while the calculated P/V ratio is 2.0 but still this is higher than that of other VPO samples. This result <sup>20</sup> suggests that the added excess phosphorous might be leaching out

from the VPO samples during the filtration process.

Table 1: Results of textural properties, acidity and EDX analysis

S.No	P/V	P/V EDX		Surface Pore		Total
	ratio	results	area	volume	diameter	acidity
			$(m^2/g)$	(cc/g)	(Å)	(µmol/g)
1.	0.6	0.54	7.9	0.014	44.79	432
2.	0.8	0.75	9.9	0.019	46.27	1158
3.	1.0	0.96	17.8	0.021	47.70	1930
4.	1.2	1.03	20.6	0.026	49.50	2162
5.	1.5	1.04	28.3	0.035	50.11	2106
6.	2.0	1.06	20.7	0.029	55.52	2254
7.	1.2					844
	(spent)					

- Table 1 shows the results of BET surface area and pore volume of the different P/V ratio of the VPO catalysts. It can be seen from the Table 1 that the surface area and pore volume of the catalyst increases upto P/V ratio 1.5 and then they decreases. The maximum for those parameters is obtained at P/V ratio 1.5. The
- <sup>30</sup> increase in surface area and pore volume could be attributed to the complete formation of structurally arranged vanadium phosphate precursors during the preparation.

The XRD patterns of different P/V ratio of pure VPO catalysts are shown in Fig. 1. The X-ray diffraction pattern of the samples <sup>35</sup> with P/V ratio less than unity shows a different XRD pattern from the other samples. The P/V ratios  $\geq 1.0$  exhibits the X-ray diffraction peak at  $2\theta$ = 12.1°, 18.8°, 19.2°, 21.3°, 22.6°, 23.1°, 24.2°, 28.5°, 31.3°, 34.8°, 41°, 46.4° related to the VOPO<sub>4</sub>.H<sub>2</sub>O phase,  $\delta$ ,  $\gamma$ - VOPO<sub>4</sub> phase and vanadyl pyrophosphate phase.<sup>24</sup>

<sup>40</sup> Whereas the samples with P/V ratio less than unity shows the Xray diffraction peaks related to the pure crystalline vanadia phase and  $\beta$ -VOPO<sub>4</sub> phase.<sup>24</sup> Interestingly, the complete change in the XRD pattern is observed in the VPO sample of P/V ratio between

0.8-1.0 indicates that the small changes in the P/V ratio affects 45 the surface phase composition of the VPO samples. Cavani et al <sup>25</sup> studied the effect of the P/V atomic ratio in VPO catalyst for nbutane oxidation to maleic anhydride. It was found that the nature of the catalyst surface is affected by the P/V atomic ratio even in the case of small changes in this parameter between 1.0 - 1.2. 50 Though, the catalyst with the P/V ratios  $\geq 1.0$  exhibits the similar phases in the XRD pattern, the crystallinity of the P/V = 1.0 is higher than the other samples as shown in table 4. This result indicates that the excess phosphorous inhibits the formation of crystallinity of the samples. Moreover, there is no change in the 55 crystallinity and formed VPO phases in the samples of P/V ratio above 1.2. From the above results, it is found that the nature of the catalyst surface, the formed VPO phases and crystallinity of the VPO catalyst is affected by the P/V atomic ratio of the VPO samples. The detailed information about the different VPO

<sup>60</sup> phases present in the VPO samples and the characterised peaks are presented in table 2.



Fig. 1 X-ray diffraction patterns of various pure VPO samples



Fig. 2 SEM images of various pure VPO samples. SEM images of (a) PV-0.6 (b) PV-0.8 (c) PV-1.0 (d) PV-1.2 (e) PV-1.5 (f) PV-2.0

Sample name	Main Phases	Minor phases present in the sample
	present in the sample	
PV-0.6	β-VOPO <sub>4</sub>	
	XRD peaks (20) : 17.05, 19.28, 26.17, 29.09	
	Raman bands (cm <sup>-1</sup> ) : 318,367, 432, 599,653, 893, 1072	
	Crystalline V <sub>2</sub> O <sub>5</sub>	
	XRD peaks $(2\theta)$ : 15.2, 20.2, 21.6, 26.1	
	Raman bands (cm <sup>-1</sup> ): 287,307, 406, 482, 528, 699, 995	
PV-0.8	β-VOPO4	Crystalline V <sub>2</sub> O <sub>5</sub>
	XRD peaks (2θ) : 17.05, 19.28, 26.17, 29.09	XRD peaks (2θ) : 15.2, 20.2, 21.6, 26.1
	Raman bands (cm <sup>-1</sup> ): 318,367, 432, 599,653, 893, 1072	Raman bands (cm <sup>-1</sup> ): 287,307, 406, 482, 528, 704, 995
PV-1.0-PV-2.0	VOPO <sub>4</sub> .H <sub>2</sub> O XRD peaks (2θ) : 12.1, 18.8, 28.5, 31.3,46.4	δ- VOPO <sub>4</sub>
	Raman bands (cm <sup>-1</sup> ): 1042, 952, 542, 282, 302	XRD peaks (20) : 22.08, 24.2, 28.6, 34.8 Raman bands (cm <sup>-1</sup> ): 1070-1098, 1021, 586
	$\gamma$ -VOPO <sub>4</sub>	
	XRD peaks (20) : 18.1, 21.3, 22.6	
	Raman bands (cm <sup>-1</sup> ): 453, 408, 543, 582, 947, 1022, 103	8
	(VO) <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	
	XRD peaks $(2\theta)$ : 23.1, 28.5	
	Raman bands (cm <sup>-1</sup> ): 926 (more intense)	

**Table 2:** Detailed information about the different VPO phases present in the VPO samples

The morphology of the pure VPO samples with different P/V ratio was studied by SEM analysis and the respective SEM micrographs are shown in Fig. 2. It can be seen from the Fig. 2 that the PV-0.6 sample possesses the particles without any identified shape. As the P/V ratio increases the morphology of the VPO samples also changes. The PV-1.0 and 1.2 samples exhibit particles which are roughly spherical in shape. The PV-1.5 and 2.0 samples have rose like morphologies with uniform particle size distribution. The rosette type agglomerates are made up of agglomerates of (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> platelets that are preferentially

<sup>15</sup> expose (100) crystal planes.<sup>26, 27</sup> The Raman spectra of different P/V ratio of pure VPO catalyst are shown in Fig. 3. The Raman bands of the VPO catalyst with the P/V ratio less than unity shows different from the other catalyst. The VPO with low P/V ratio shows the Raman bands at

- $_{20}$  287, 307, 318, 367, 406, 432, 482, 528, 599, 653, 699, 893, 995, and 1072 cm  $^{-1}$ . These Raman bands are related to the  $\beta$ -vanadium orthophosphate phase (318, 367, 432, 599, 653, 893, 1072 cm  $^{-1}$ ) and pure crystalline vanadia phase (287, 307, 406, 482, 528, 699, 995 cm  $^{-1}$ ).  $^{28}$  With the increase of the P/V ratio of VPO catalyst
- <sup>25</sup> from 0.6-0.8, the intensity of the Raman band related to the vanadia phase decreases and the Raman bands related to the β-vanadium orthophosphate phase increases. The P/V ratio  $\geq 1.0$  show the major Raman bands at 926 cm<sup>-1</sup> can be attributed to v<sub>(as)</sub> P-O-P in P<sub>2</sub>O<sub>7</sub><sup>2-</sup> unit of vanadyl pyrophosphate which confirms <sup>30</sup> the formation of vanadyl pyrophosphate phase. However, the

Raman band at 926 cm<sup>-1</sup> exists as the broad type indicates the presence of vanadium orthophosphate phases ( $\delta$ ,  $\gamma$  - VOPO<sub>4</sub> phase) along with vanadium pyrophosphate phase.<sup>28</sup> The other Raman bands at 1022, 1038 cm<sup>-1</sup> further confirms the formation 35 of vanadium orthophosphate phases (VOPO<sub>4</sub>, H<sub>2</sub>O,  $\delta$ ,  $\gamma$ -VOPO<sub>4</sub> phase). These results suggests that the sample with P/V ratio  $\geq$ 1.0 show the Raman bands related to the vanadyl pyrophosphate phase and different types of vanadium orthophosphate phases. However, the catalyst with P/V ratios <1.0 possesses the  $_{40}$  vanadium in the form vanadium oxide phase. Though the V<sub>2</sub>O<sub>5</sub> was reduced in the alcohol medium at 140 °C, there is a possibility of oxidation of V<sup>4+</sup> to V<sup>5+</sup> phase under calcinations. However, the catalyst with P/V ratios  $\geq 1.0$  all the vanadium sites reacts with the added phosphorous leads to the formation 45 vanadium phosphate precursors because of the presence of equimolar phosphorous with vanadium content. Interestingly, there is no significant change in the Raman bands observed at higher P/V ratio of pure VPO catalyst except the intensity of the Raman bands of V5+ phases indicates that the addition of extra 50 phosphorous does not provide any change in the structure of the catalyst. As a whole, the Raman spectrum analysis result gives good supporting evidence to the results obtained from XRD analysis on the formation of different types of vanadium phosphate phases.

55



Fig. 3 Laser Raman spectra of various pure VPO samples

Besides the XRD patterns and Raman studies, UV-DRS analysis also used to find out the structural features of VPO s catalyst. The UV-DRS analysis of the VPO catalyst with varying P/V ratio is shown in Fig. 4. The shape of the charge transfer bands indicates the presence of different vanadium species on the surface of VPO samples. All spectra of VPO samples exhibit three major broad CTLM (charge transfer ligand-metal) band to centred at about 220 nm, 300 nm and 410 nm respectively. The first broad CTLM band centered at 220 nm is attributed to the

- charge transfer transition from  $O^{2-}$  to  $V^{4+}$  in the UV-DRS analysis. However, these charge transfer transition band is absent for samples with P/V ratio less than unity. This result suggests 15 that to stabilise the V<sup>4+</sup> over the surface of the catalyst, the
- equimolar or more than equimolar amount of phosphorous content is required. The other broad band centered at 300 nm is due to the charge transfer transition from O<sup>2-</sup> to V<sup>5+</sup> vanadium in tetrahedral coordination. However, another broad CTLM peak <sup>20</sup> centred at 410 nm that has been attributed to V<sup>5+</sup> species in <sup>29</sup> <sup>30</sup>.
- square-pyramidal coordination.<sup>29, 30</sup> In general, the UV-DRS analysis result is in good agreement with the XRD and Raman analysis results.

The XPS profiles of O 1s, V  $2p_{1/2}$  and V  $2p_{3/2}$  of fresh and <sup>25</sup> spent VPO samples with the P/V ratio 1.2 are shown in Fig. 5. The typical binding energy values of V  $2p_3/2$  peak of the VPO samples attributed to V<sup>4+</sup> and V<sup>5+</sup> phase are observed at 516.8 eV and 518.0 eV respectively.<sup>31, 32</sup> The typical binding energy value of V 2p peak of the fresh and the spent VPO samples is found to

- $_{30}$  be 517.8 eV and 517.3 eV respectively. Hence, the observed binding energy values of the VPO samples are closely related with the V  $^{5+}$  phase. However, the V 2p3/2 peak of both samples is relatively broad in the XPS profiles, exhibits the formation of V  $^{4+}$  phases also. The deconvolution of the V 2p3/2 peak revealed
- <sup>35</sup> the presence of two peaks with binding energies of 517.2 eV and 518.5 eV, confirms the presence of V<sup>4+</sup> and V<sup>5+</sup> in the VPO sample. The binding energy of P 2p (134.4 eV) is similar to that of the reported vanadyl pyrophosphate corresponding to a formal effective oxidation state of +5 is shown in Table. 3.<sup>33</sup> The binding
- <sup>40</sup> energy of the O 1s peak of the VPO sample is in the range of 532.3 eV. The deconvolution of the O 1s peak reveals the presence of two peaks with binding energies of 531.8 eV and 533.2 eV, respectively. The first peak corresponds to lattice

oxygen ions in the vanadium phosphate sample, whereas the <sup>45</sup> second peak is related to the presence of surface hydroxide ions and carbonates.<sup>34</sup>

The surface P/V ratio was calculated from the XPS analysis and the results are reported in Table 4. The results suggest that the surface P/V ratio of the sample increases with increase of <sup>50</sup> bulk P/V ratio and the highest ratio (2.33) were obtained for the VPO sample with P/V ratio 2.0. It is interesting to note that the surface P/V ratio of all samples is much higher than the bulk P/V ratio. However, the enrichment of phosphorous over the surface is a common phenomenon in the VPO samples.









Fig. 5 XPS profiles of various pure VPO samples

Table 3: XPS results of fresh and spent PV-1.2 samples									
S.No	Name of the	Binding energy (e.V)			$V^{4+}$ (%)	V <sup>5+</sup> (%)			
	samples	V2p	P2p	O1s					
1.	Fresh PV-1.2	517.8	134.4	532.3	57.5	42.5			
2.	Spent PV-1.2	517.3	134.4	532.3	66.6	33.4			

5 Table 4: Surface P/V ratio and crystallite size of various VPO

	samples		
S.No	Name of the	Surface	crystallite size
	samples	P/V ratio	(nm)
1.	PV-0.6	0.89	27.1
2.	PV-0.8	1.04	32.5
3.	PV-1.0	1.56	31.9
4.	PV-1.2	1.86	8.7
5.	PV-1.5	2.23	8.9
6.	PV-2.0	2.33	9.9

The NH<sub>3</sub>-TPD profiles of VPO samples with varying P/V ratio are presented in Fig. 6. The acidity of the VPO catalysts can be <sup>10</sup> attributed to the presence of surface P-OH groups and to the coordinatively unsaturated vanadium ions exposed on the surface coupled to V=O double bonds. According to Tanabe et al.<sup>35</sup> the strength of solid acid sites within TPD profiles can be classified by the temperature programmed desorption of NH<sub>3</sub> as weak

- <sup>15</sup> (120–300 °C), moderate (300–500 °C) and strong (500–600 °C). The NH<sub>3</sub> TPD profiles of the VPO samples with P/V ratio of 0.6 exhibit a broad and less intense peak in the weak acidic region and a sharp peak in the strong acidic region. The presence of strong acidic sites might be due to the presence of higher amount
- 20 of crystalline vanadia phase. As the increase of P/V ratio to 0.8 the intensity of the peak in the weak acidic region increases. However, further increase of phosphorous content to the VPO samples, the intensity of the peak in the weak acidic region increases and additionally, another new peak at moderate acidic
- <sup>25</sup> region is formed. However, these peaks get overlapped and form a new type of acidic sites region for the VPO sample with the P/V ratio of 1.2. The TPD profiles are shown in Fig. 6 clearly exhibits the changes in the peak shape upto P/V ratio of 1.2. This could be

due to the formation of different types of VPO phases in the VPO <sup>30</sup> samples of different P/V ratio.<sup>36</sup> Interestingly, the peak shape of the TPD profiles are similar with further increase of phosphorous content but there is no considerable changes in the amount of acidic values are observed. These acidic values are presented in the Table 1. As it can be seen from Table 1 that the acidity of the <sup>35</sup> catalyst increases upto P/V ratio 1.2 thereafter, there is no order in the acidity value of the catalyst.



Fig. 6 TPD of ammonia profiles of various pure VPO samples

The reduction behaviour of the pure VPO catalyst with different P/V ratio was examined by temperature programmed reduction and the TPR profiles are shown in Fig. 7. The results of TPR profiles of the VPO samples show that the reducibility of the VPO catalyst affected by the P/V ratio of the catalyst. This is 45 mainly because of the formation of different types of vanadium phosphate phases by varying the phosphorous content. The reduction profiles of VPO catalyst with P/V ratio of 0.6 was characterized by four reduction peaks at 490, 543, 650 and 780 °C. The first three peaks are related to the reduction of  $V^{5+}$  to  $V^{4+}$ 50 whereas the one at higher temperature peak is related to the reduction of  $V^{4+}$  to  $V^{3+37}$ . The reducible peak at lower temperature might be due to the different types of vanadium orthophosphate and crystalline vanadia species. As the increase of P/V ratio of VPO catalyst to 0.8, the number of peaks reduced 55 into two in the TPR profile. Again the increase of phosphorous

- content, the reducible peak shifts to lower temperature due to the formation of different types of VOPO<sub>4</sub> phase. Further increase of phosphorous content, did not change the reducibility of the  $V^{4+}$ . However, there is no order in the reducibility of  $V^{5+}$  species due
- to the formation of different types of vanadium orthophosphate species. It is known that a considerable excess of surface phosphorus prevents the oxidation of  $V^{4+}$  to  $V^{5+}$ . This is evidenced from the XPS analysis results (Table 4). The VPO samples with low phosphorous content possess more amounts of 65 reducible  $V^{5+}$  species than the VPO samples with high
- so reducible  $V^-$  species than the VPO samples with high phosphorous content due to stabilisation of  $V^{4+}$  over the surface.



Fig. 7 TPR profiles of various pure VPO samples

Table 5: Results of temperature programmed reduction analysis of various VPO samples

S.No	P/V ratio	T <sup>1</sup> (°C)	H <sub>2</sub> uptake	T <sup>2</sup> (°C)	H <sub>2</sub> uptake	Total H <sub>2</sub> uptake
			µmol/g		µmol/g	µmol/g
1.	0.6		7924	771	911	8835
2.	0.8	571	6102	755	3809	9911
3.	1.0		3177	735	3103	6280
4.	1.2	512	4150	738	3818	7968
5.	1.5	492	4230	740	3504	7734
6.	2.0		3371	741	4032	7403
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T<sup>1</sup>--Reduction temperature of V<sup>5+</sup> (below 700 °C) T<sup>2</sup>- Reduction temperature of V<sup>4+</sup> (above 700 °C)

- The catalytic results of dehydration of glycerol over VPO 10 catalyst with different P/V ratio by passing nitrogen (14ml/min) along with air (2ml/min) are reported in Table 6 (parenthesis outside). The catalytic results shown in the Table 6 are obtained at initial hour of the reaction (TOS = 1-2). As can be seen from
- 15 the Table 6 that the conversion of glycerol and acrolein selectivity increases with the increase of P/V ratio upto 1.2 thereafter both conversion and selectivity did not change appreciably with higher P/V ratio. In all the cases, the acrolein was obtained as main product accompanied with some other by-
- 20 products. The major by-products were acetic acid, hydroxy acetone and acetaldehyde at the initial time on stream. Moreover, at higher time on stream, the amounts of unidentified products (mainly from acetalisation product) become increases as a result the acrloein selectivity decreases. However the catalyst becomes
- 25 deactivates within 12 h of the reaction time because of the blockage of active sites by formed coke during the glycerol dehydration reaction.

In order to minimise the deactivation of the catalyst and to get 85

more insight into the influence of air flow on the dehydration of 30 glycerol, the catalytic experiments were additionally carried out by passing more amount of air flow (4 ml/min) along with N<sub>2</sub> flow (12 ml/min) and the obtained results are shown in Table 6 (in parenthesis). As can be seen the Table 6 that the acrolein selectivity increases with increase of P/V ratio upto 1.2 thereafter 35 there is no considerable change with higher P/V ratio. The conversion of glycerol is always maximum irrespective of the P/V ratio. Interestingly, the VPO samples with low P/V ratio (< 1.0) also show maximum conversion of glycerol. This result concludes that the redox property of the catalyst is crucial for the 40 conversion of glycerol. The major by-products were acetic acid and acetaldehyde at the initial time on stream. Hence, the sample with the P/V ratio of 1.2- 2.0 exhibits the total glycerol conversion with 65-67% of acrolein selectivity. These result showed that the sample PV-1.2-2.0 shows comparable activity to 45 the pure vanadyl pyrophosphate phase calcined at 800 °C and shows better catalytic activity than the respective pure VPO phases of vanadyl pyrophosphate (glycerol conversion 100% and acrolein selectivity 41%) and vanadium orthophosphate phase (glycerol conversion 100% and acrolein selectivity 56%).<sup>20,21</sup>

It is known that the amount and strength of acidic sites plays a significant role for the catalytic activity in the glycerol dehydration reaction. The inappropriate acidity of the catalyst may cause poor results, such as lowering the selectivity accompanied with severe coke deposition, and short catalyst 55 lifetime. In this case, the various performances of these prepared vanadium phosphate catalysts might arise from their different surface acidity. Volta et. al <sup>38</sup> also pointed out the effect of P/V ratio is related to the acidity of the VPO catalyst as an important property in maleic anhydride production. From Fig. 6, it is 60 observed that the total acidic sites increases up to P/V ratio of 1.2 thereafter there is no significant change in the acidic properties of the samples. The selectivity of the acrolein also follows the same order. This result suggests that the total acidic sites are necessary for the formation of acrolein.

65 The results of the product distribution of glycerol dehydration reaction at constant reaction conditions except the gas flow conditions are shown in the Table 6. The results clearly suggest that the increase of air to nitrogen gas flow ratio affects the product distribution during the glycerol dehydration reaction. The 70 major products of the glycerol dehydration over the VPO samples were acrolein, acetol, allylalcohol, acetic acid, acetaldehyde and acrylic acids. A product grouped under the label of other is some unidentified products. However, the significant change in the product distribution results is observed for the VPO samples with 75 low P/V ratio (<1.0) than the higher P/V ratio ( $\geq$ 1.0). This is due to the fact that the higher redox ability of the VPO samples with low P/V ratio which leads to the formation of higher amounts of oxidation products such as acetaldehyde, acetic acid and acrylic acid. However, in the case of the VPO samples with high P/V 80 ratio does not show much difference in the product distribution results due to the higher acidity of the catalyst. For the samples with low P/V ratio (<1.0), the formation of allyl alcohol and hydroxy acetone is higher than the high P/V ratio samples due to inappropriate acidity of the samples. However, as the increase of

S.No	Catalyst	Conversion	Selectivity (%)						
		(%)	acrolein	acetal dehyde	acetic acid	allyl alcohol	hydroxy acetone	acrylic acid	others
1.	PV-0.6	70 [100]	28 [38]	3 [9]	13 [31]	4 [-]	9 [-]	- [5]	43 [17]
2.	PV-0.8	86 [100]	42 [52]	2 [5]	12 [25]	2 [-]	4 [-]	- [3]	36 [15]
3	PV-1.0	100 [100]	56 [62]	2 [4]	10 [18]	1 [-]	2 [-]	- [1]	29 [15]
4	PV-1.2	100 [100]	60 [66]	1 [4]	11 [14]	1 [-]	1 [-]	- [2]	26 [14]
5	PV-1.5	100 [100]	60 [65]	1 [3]	10 [15]	1 [-]	- [-]	- [1]	28 [16]
6	PV-2.0	100 [100]	61 [67]	2 [4]	10 [15]	1 [-]	- [-]	- [1]	26 [13]

Table 6: Product distribution results of glycerol dehydration over various samples obtained in TOS (time on stream): 1–2 h

Reaction conditions: 0.2 g catalyst was used and diluted with 1.0 g of quartz. The aqueous glycerol (20% wt/wt) was fed at the speed of 0.5 g  $h^{-1}$  by syringe pump under N<sub>2</sub> and air atmosphere i.e. the reactant fed composition gly: H<sub>2</sub>O: N<sub>2</sub>: air was 1.37 : 50.0 : 37.47 :5.35 in molar ratio [N<sub>2</sub>-14 5 ml/min+air-2 ml/min] and reaction temperature was 300 °C. In parentheses, the same reaction condition except the reactant fed composition gly: H<sub>2</sub>O: N<sub>2</sub>: air was 1.37 : 50.0 : 32.12: 10.7 in molar ratio [N<sub>2</sub>-12 ml/min+air-4 ml/min].

air to nitrogen ratio in the reaction medium, restricts the formation of allyl alcohol and hydroxy acetone during the <sup>10</sup> reaction and enhances the formation of acetaldehyde and acetic acid. Interestingly, the small amount of acrylic acid is formed for the VPO sample with low P/V ratio indicates that these catalyst favours the oxidation of acrolein due to the presence of crystalline vanadia species which is more favourable for the <sup>15</sup> oxidation reaction. However, the selectivity of acetic acid decreases from 31 to 14% with the increase of P/V ratio of 0.6-1.2 catalyst. This could be due to the increase of acidity of the catalyst with the increase of P/V ratio which is more favourable for formation of acrolein. The formation of acetic acid could be

<sup>20</sup> attributed to the oxidation reaction of acetaldehyde with framework oxygen of the catalysts. However, the selectivity of unidentified products also decreases over the catalysts by changing the P/V ratio from 0.6 to 1.2.

The results with the time on stream of catalytic dehydration of 25 glycerol over the VPO samples with P/V ratio 1.2 and P/V ratio 0.6 by passing air and nitrogen are shown in Fig. 8. As can be seen from Fig. 8 that the glycerol conversion over PV-1.2 was 100% during the initial 6 h and then decreased to 86% at TOS = 11-12 h, whereas the VPO samples with P/V ratio 0.6 shows the

- <sup>30</sup> maximum glycerol conversion until TOS =11-12 h. However, in the case of PV- 1.2, the selectivity of acrolein at 1-2 and 11-12 h time-on-stream (66 and 48%, respectively) shows gradual decreases. Similarly, the PV- 0.6 sample shows a gradual decrease in the acrolein selectivity from 36% to 12% (TOS = 11–
- <sup>35</sup> 12 h) in spite of glycerol conversion being almost unchanged. These results concludes that the redox properties of the catalyst is crucial for the glycerol conversion and long life time of the catalyst and high acid site density is important for an initially high acrolein selectivity. Hence, the acidity and the redox ability
- <sup>40</sup> are important characteristic properties necessary to get better catalytic ability. In the case of VPO catalyst with the P/V ratio of 0.6, the formation of acetic acid is higher in the initial hour and it decreases with time on stream whereas the allyl alcohol formation increases. The allyl alcohol formation might be

- <sup>45</sup> proceeds via dehydration to acrolein and consecutive hydrogen transfer. This result suggests that because of the presence of crystalline vanadia species at PV 0.6 sample is particularly more favourable towards oxidation reaction instead of dehydration reaction. The same observations were reported earlier by the <sup>50</sup> Suprun et. al <sup>39</sup> for the VOx loaded aluminium phosphate catalyst. Hence, the catalyst with low P/V ratio is not suitable for the vapour phase dehydration of glycerol due to lower selectivity towards the acrolein. The VPO samples with high P/V ratio exhibits the decrease in the conversion of glycerol and acrolein <sup>55</sup> selectivity with time on stream. Hence, the spent sample was
- characterised by XRD, XPS analysis, CHNS elemental analysis and ammonia TPD analysis to find out the deactivation phenomena.



Fig. 8 Time on stream over Pure VPO samples of P/V-0.6 and P/V-1.2

The XRD pattern of the spent VPO catalyst after TOS of 11-12 h is shown in Fig. 1. Interestingly, the XRD pattern of the spent catalyst suggests that the PV - 1.2 sample is changed structurally

when compared to fresh VPO sample after the reaction. The XRD peaks noticed at  $2\theta = 12.1^{\circ}$  due to VOPO<sub>4</sub>. H<sub>2</sub>O is completely disappeared in the spent catalyst and the peak at 23.1° got intensified due to the formation of vanadyl pyrophosphate phase.

<sup>5</sup> This result indicates that the change of the VPO phases in the spent samples during the glycerol dehydration reaction leads to deactivation of the catalyst.

Furthermore, to find out the oxidation state of the spent samples, the XPS analysis were carried out and the results are 10 shown in Fig. 5. As can be seen by comparison of the spectra of fresh and spent samples of vanadium 2p3/2 peak, a slight shift by 0.5 eV to lower values was observed, thus suggesting a decrease of the average oxidation state in the sample. This result indicates that the vanadium ions of the VPO samples are getting reduced 15 during the course of the reaction. Moreover, in order to find out the percentage of the surface V<sup>4+</sup> and V<sup>5+</sup>, the V 2p3/2 peak is deconvoluted and the values are present in the Table 3. From the Table, it is observed that the spent VPO sample exhibits the higher amount of V<sup>4+</sup> than the pure VPO catalyst. There is no





Fig. 9 TPD of ammonia profiles of fresh and spent VPO samples

The ammonia TPD profiles of fresh and spent PV-1.2 samples <sup>25</sup> are shown in Fig. 9 and the results are given in Table 1. The TPD profile of spent sample shows that the moderate acidic peak disappears and the intensity of the weak acidic peak decreases. Hence, the total acidity of the spent sample is lesser than the fresh samples as a result the acrolein selectivity decreases considerably

<sup>30</sup> with time on stream. However, the peak position during TPD analysis also changed abruptly and the temperature maximum of weak acidic site peak also shifted to lower position.

The spent PV-1.2 sample was also analysed by CHNS elemental analysis and the result shows that there is the

<sup>35</sup> considerable amount of coke (carbon- 0.94%, H/C ratio 0.47) is formed over the catalytic surface. Hence, the coke formation and the changes of the VPO phases lead to the deactivation of the catalyst.

The spent PV-1.2 sample was activated at 400 °C for 2 hr by 40 passing air and the glycerol dehydration reaction was carried out at the same reaction condition (After activation the colour of the sample was changed from grey to yellowish green). The activated PV-1.2 sample gave 100% glycerol conversion and 63% acrolein selectivity. This result suggests that the simple activation <sup>45</sup> procedure is sufficient to regain the catalytic activity of the spent PV-1.2 sample.

#### 4. Conclusion

The VPO catalysts with varying P/V ratios were synthesized by using organic route and characterized by various spectroscopic 50 techniques. The information obtained by various spectroscopic techniques confirms that the VPO sample with P/V ratio less than 1.0 possesses mainly  $\beta$ -vanadium orthophosphate along with pure crystalline vanadia. Whereas, the samples with P/V ratio higher than 1.0 contain a mixture of vanadium orthophosphate phases 55 along with vanadyl pyrophosphate phase. The acidity and redox ability of the catalyst changes with the P/V ratio of the VPO samples. The catalytic activity of the VPO samples strongly depends on the acidity of the catalyst which is further related to the P/V ratio. This VPO sample gets deactivated with time during 60 the gas phase dehydration of glycerol. The results of XRD, XPS and CHNS elemental analysis reveals that the spent samples show  $V^{5+}$  phase of the VPO sample and it is reduces to  $V^{4+}$  phase and coke formation over the active sites leading to deactivation of the catalyst during the reaction.

#### 65 Notes and references

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