



Journal of Nanoscience and Nanotechnology Vol. 15, 5391–5402, 2015 www.aspbs.com/jnn

Vapor Phase Dehydration of Glycerol to Acrolein Over SBA-15 Supported Vanadium Substituted Phosphomolybdic Acid Catalyst

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Vapor phase dehydration of glycerol to acrolein was investigated over heteropolyacid (HPA) catalysts containing vanadium substituted phosphomolybdic acid (H₄PMo₁₁VO₄₀) supported on mesoporous SBA-15. A series of HPA catalysts with HPA loadings varying from 10-50 wt% were prepared by impregnation method on SBA-15 support. The catalysts were characterized by X-ray diffraction, Raman spectroscopy, Fourier Transform infrared spectroscopy, temperature-programmed desorption of NH₃, pyridine adsorbed FT-IR spectroscopy, scanning electron microscopy, pore size distribution and specific surface area measurements. The nature of acidic sites was examined by pyridine adsorbed FT-IR spectroscopy. XRD results suggest that the active phase containing HPA was highly dispersed at lower loadings on the support. FT-IR and Raman spectra results confirm that the presence of primary Keggin ion structure of HPA on the support and it was not affected during the preparation of catalysts. Pore size distribution results reveal that all the samples show unimodel pore size distribution with well depicted mesoporous structure. NH3-TPD results suggest that the acidity of catalysts increased with increase of HPA loading. The findings of acidity measurements by FT-IR spectra of pyridine adsorption reveals that the catalysts consist both the Brønsted and Lewis acidic sites and the amount of Brønsted acidic sites are increasing with HPA loading. SBA-15 supported vanadium substituted phosphomolybdic acid catalysts are found to be highly active during the dehydration reaction and exhibited 100% conversion of glycerol (10 wt% of glycerol) and the acrolein selectivity was appreciably changed with HPA active phase loading. The catalytic functionalities during glycerol dehydration are well correlated with surface acidity of the catalysts.

Keywords: Heteropolyacid, Acidity, Mesoporosity, Glycerol Dehydration, Acrolein.

1. INTRODUCTION

The conversion of glycerol to value-added chemical intermediates is a topic of enormous interest in the recent past because glycerol is a by-product formed in huge amounts during the production of biodiesel from renewable sources. Among several pathways to obtain valuable products from glycerol, the dehydration reaction of glycerol to acrolein is an interesting route using solid acid catalysts to achieve a total conversion of glycerol and also to obtain high acrolein selectivity. Acrolein is a value added and versatile chemical intermediate employed in many industrial applications.^{1–5} The dehydration of glycerol to acrolein is generally accompanied by side reactions leading to by-products such as hydroxypropanone, propanal, acetaldehyde, acetone and leads to the formation of coke deposits on the catalyst surface causing catalyst deactivation. The presence of these by-products with acrolein necessitates high recovery cost for separation and purification of acrolein. Various solid acid catalysts, including sulphates, phosphates, zeolites, heteropolyacids and solid phosphoric acid (SPA) have been investigated for the dehydration of glycerol in either gaseous or liquid phase under severe reaction conditions.^{6–17} The direct use of glycerol with water in the feed is advantageous over pure glycerol for the production of acrolein because of glycerol is usually produced as a mixture with water. It is a challenging task to achieve total conversion of glycerol with high acrolein selectivity and longer catalyst life. Therefore, a solid acid catalyst with better acidic and redox properties would be beneficial for complete conversion of glycerol

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to obtain high selectivity of acrolein and also to minimize the coke formation.

Glycerol dehydration was generally carried out in liquid phase using heteropolyacids as catalysts.¹⁴ However, it is difficult for product separation in liquid phase as the heteropolyacids tend to dissolve in polar solvents in homogeneous system. Comparing to liquid phase reactions using homogenous catalysts, the heterogeneous catalyzed reactions are more advantageous for the easier product separation and product recovery. Solid acids containing zeolites and heteropolyacids of phosphotungstic acid and phosphomolybdic acid are employed for glycerol dehydration reaction. However, the activity over above solid acid catalysts was found to be much lower and they can get deactivated easily during the course of reaction time.14-17 The heteropolyacid of vanadium containing phosphomolybdic acids are beneficial over the phophomolybdic acid, as the incorporated vanadium reduces or minimize the deactivation or decomposition of the catalyst. However, total conversions of glycerol and higher selectivity to acrolein are favoured with catalysts with tuneable Brønsted acidity coupled with larger pore size of mesoporous support. Therefore mesoporous silica SBA-15 supported heteropolyacid catalyst is advantageous for dehydration of glycerol to acrolein reaction.

There is a plethora of research work published in the recent past on nano and mesoporous materials¹⁸⁻²⁵ as these materials exhibited higher activity and selectivity for the synthesis of fine chemicals with stable activity. However, the non mesoporous materials exhibit lower activity with poor stability. This is mainly due to mesoporous materials have easy higher pore size and further easy diffusion of reactants to products for long time intervals. In above point of view, we have focused on mesoporous materials such SBA-15. In recent years mesoporous materials like SBA-15 and MCM-41 have been successfully employed as catalyst support in many catalytic applications apart from conventional oxides like Al₂O₃ and SiO₂. The advantage of these new class of mesoporous materials include high surface area and uniform pore structure. SBA-15 type of ordered mesoporous materials have larger pore diameter, high surface area, uniform tubular channels, high thermal stability and ordered pore structure. These mesoporous materials are generally prepared by using a tri-block copolymer as a template under strongly acidic conditions relative to MCM-41. This will allow an easier introduction of active components such as heteropolyacid. SBA-15 possesses well-ordered hexagonal arrays of mesopores with pore diameters between 5 and 30 nm.²⁶⁻²⁹ Supported heteropolyacids have high surface area, high thermal stability, especially when they are supported on mesoporous silica such as SBA-15. By varying the amount of HPA on the surface leads to an improvement of the catalytic performance.²⁸⁻³³ Bulk phosphomolybdic acid with primary Keggin ion unit is well recognized

as oxidation and acid catalyst in which the redox and acidic functionalities can be tuned by substitution of the added (vanadium) transition metal substituted Keggin units. The synthesis of vanadium containing Keggin ion units of phosphomolybdic acid is found to be promising heteropolyacid catalysts wherein the molybdenum metal is partially replaced by vanadium metal. In addition, the activities of the synthesized catalysts were evaluated in the dehydration of glycerol to acrolein. The vanadium containing phosphomolybdic acid possesses positive reduction potentials compared to pure phosphomolybdic acid and enhances the redox properties. Thus the incorporation of V into the structure of phosphomolybdic acid (PMA) enhances the catalytic performance (acid and redox catalysts).34 Vanadium containing HPAs showed excellent redox properties because substitution of vanadium stabilizes the LUMOs.³⁵ Vanadium containing HPA catalysts are the basic components of several oxidative and acidic reactions in homogenous and heterogeneous catalysis.³⁶⁻⁴²

In the present investigation, we report the dehydration of glycerol to acrolein over a series of HPA catalyst with active phase containing $H_4PMo_{11}VO_{40}$ supported on SBA-15. The aim of this investigation is to study the effect of HPA loading on SBA-15 during the vapor phase dehydration glycerol under mild reaction conditions. We also report the effect of porosity of the catalyst and catalytic performance during the reaction. The purpose of this work is to estimate acidity of vanadium substituted phosphomolybdic acid supported on SBA-15 as a function of HPA loading and to identify structural changes of HPA with increase of active phase loading and also to understand relation between selectivity and acidic sites. A comparison of catalytic performance is also made with non-mesoporous oxides such as Y-zeolite and alumina. The catalysts were characterized by XRD, Raman, SEM, TPD of NH₃, pyridine adsorbed FT-IR, BET surface area and pore size distribution (PSD) to obtain the structural information of materials of the active species and to correlate with catalytic functionalities during vapor phase dehydration of glycerol.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Catalyst

 V_2O_5 , TEOS, P123, CTAB are obtained from Aldrich, MoO₃ was supplied by Fluka chemie, H_3PO_4 Supplied by S.D Fine-Chem. Ltd. and protonated form of the Y-zeolite obtained from Conteka, The Netherlands and also Al₂O₃ obtained from Engelhard corporation.

SBA-15 silica was prepared according to procedure reported elsewhere^{28, 29} by using triblock copolymers based on poly(ethylene glycol)-poly(propylene glycol)poly(ethylene glycol) (P123, average molecular mass-5800, Aldrich) as a template. About 2 g of P123 copolymer was dissolved in a mixture of 15 g of water and 45 g of 2 M HCl under stirring at ambient condition followed

by the addition of 0.2 g of CTAB and 5.9 g of tetraethylorthosilicate (TEOS). The final molar ratio of mixture solution was 1TEOS:0.02CTMABr:3.1HCl:115H₂O:0.012 polymer. The synthesis mixture was introduced into a tefflon bottle, sealed and kept at 100 °C for 24 h. After cooling the contents were filtered and washed with deionised water and ethanol to remove the excess of template prior to calcination. The solid product was dried at 25 °C for 16 h and subsequently calcined in air at 500 °C for 5 h.

 $\rm H_4PMo_{11}VO_{40}$ (HPA) was prepared by adding requisite quantities of MoO₃, V₂O₅ and H₃PO₄ solutions to the distilled water in a 500 ml round bottom flask and refluxed at 100 °C. The resulting solid was dried at 60 °C for 16h. H₄PMo₁₁VO₄₀ was prepared according to the procedure described by Kanno et al. in literature.⁴¹ A series of H₄PMo₁₁VO₄₀ catalysts with H₄PMo₁₁VO₄₀ loadings ranging from 10–50 wt% supported on SBA-15 were prepared by the impregnation method. A requisite amount of HPA was dissolved in distilled water and SBA-15 support was added to it. The resultant solution was stirred at 25 °C for 5 h. The samples were dried at 110 °C for 10 h and subsequently calcined in air at 250 °C for 4 h. In similar method Al₂O₃ and Y-zeolite supported HPA are prepared.

2.2. X-Ray Diffraction Studies

X-ray powder diffraction patterns of the samples were obtained with a model: D8 Diffractometer (Advance, Bruker, Germany), using Cu K α radiation (1.5406 A°) at 40 kV and 30 mA. The measurements were recorded in steps of 0.045° with a count time of 0.5 s in the range of 2–40°.

2.3. Raman Spectroscopy

The Raman spectra of the catalyst samples were collected with a Horbia-Jobin Yvon LabRam-HR spectrometer equipped with a confocal microscope, 2400/900 grooves/ mm gratings, and a notch filter. The Visible Laser excitation at 532 nm (visible/green) was supplied by a Yag doubled diode pumped Laser (20 mW). The scattered photons were dried and focused on to a single-stage monochromator and measured with a UV-sensitive LN_2 -cooled CCD detector (Horbia-Jobin Yvon CCD-3000V).

2.4. SEM Analysis

Morphology of the catalyst samples were investigated by scanning electron microscopy (SEM) using a S-4800 (HITHACHI Co.) microscope.

2.5. Temperature Programmed Desorption of Ammonia

Temperature-programmed desorption (TPD) studies of NH₃ were conducted on Auto Chem 2910 (micromeritics, USA) instrument. In a typical experiment, ca. 100 mg of $H_4PMo_{11}VO_{40}/SBA-15$ calcined sample was taken in a U-shaped quartz cell. The catalyst sample was packed in

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one arm of the sample tube on a quartz wool bed. Prior to TPD studies, the catalyst sample was pre-treated by passing high purity helium (50 ml/min) at 200 °C for 2 h. After pre-treatment of the sample, it was saturated by passing (50 ml/min) high purity anhydrous ammonia at 80 °C for 1 h and subsequently flushed with He flow (50 ml/min) at 100 °C for 2 h to remove the physisorbed ammonia. TPD analysis was carried out from ambient temperature to 600 °C at a heating rate of 10 °C/min. The ammonia concentration in the effluent stream was monitored with the thermal conductivity detector, and the areas under the peaks were integrated using the software GRAMS/32 to determine the amount of desorbed ammonia during TPD.

2.6. FT-IR Spectroscopy

FT-IR spectra of the catalysts were recorded on a IR (Model: GC-FT-IR Nicolet 670) spectrometer by KBr disc method at room temperature. The *ex-situ* experiments of FT-IR spectra of pyridine adsorbed samples were carried out to find the nature of acidity (Brønsted and Lewis acid sites). Before the recording the IR spectra, samples preheated at 250 °C for 4 h and cooled to room temperature then pyridine adsorption experiments were carried out by placing a drop of pyridine on 10 mg of the HPA sample followed by evaporation in air for 1 h at room temperature to remove reversibly adsorbed pyridine molecules on the surface of the catalyst.⁴²

2.7. BET Surface Area and Pore Size Distribution

The specific surface area of catalysts was estimated using N_2 adsorption isotherms at -196 °C by the multipoint BET method taking 0.162 nm² as its cross-sectional area. The pore size distribution was measured by N₂ adsorptiondesorption isotherms using Autosorb 1 (Quantachrome instruments). Before performing N₂ gas sorption experiments, the samples were evacuated at 200 °C for 4 h under vacuum in order to remove the adsorbed moisture or impurities from surface of the sample. Degassing is often carried out by placing a sample in a quartz cell and heating it under vacuum or flowing helium gas. The experiments were carried out from relative nitrogen pressures (p/p_0) range of 0.05–0.9 by using nitrogen adsorption-desorption method. The resulting hysteresis leads to isotherm of the sample. The surface area was calculated from 5 adsorption isotherm points at relative nitrogen pressures (p/p_0) between 0.05 and 0.3. The pore size were calculated by BJH method.

2.8. Catalytic Activity Studies

The vapor phase dehydration reaction of glycerol was carried out at 225–250 °C under atmospheric pressure in a vertical fixed-bed Pyrex glass reactor of 36 cm length and 0.5 cm internal diameter with a catalyst bed set at the middle of reactor. The reactor was placed in an electrically Vapor Phase Dehydration of Glycerol to Acrolein Over SBA-15 Supported Vanadium

heated furnace. The temperature was controlled by a thermocouple which was located near to the catalyst bed and N₂ gas was used as a carrier gas. The glass reactor was packed with 0.3 g of catalyst and above the catalyst bed the reactor was packed with ceramic beads which serve as a pre-heater zone to increase evaporation of liquid glycerol feed before reaching the catalyst bed. The catalyst was pretreated with N2 gas at 60 ml/min at same reaction temperature for 1 h. A aqueous glycerol (10 wt%) solution (0.5 ml/h) was fed from the top of the reactor through inlet in a flow of N2 gas at 10 ml/min. The reaction products were collected in a cold trap for every hour and were analyzed by Gas Chromatograph (Shimadzu GC-2014) equipped with flame ionization detector, using DB-wax 123-7033 capillary column and methanol as an internal standard.

3. RESULTS AND DISCUSSION

3.1. X-Ray Diffraction and BET Surface Area

Low-angle powder X-ray diffraction patterns of SBA-15 and various heteropolyacid ($H_4PMo_{11}VO_{40}$) catalysts supported on SBA-15 are shown in Figure 1. An examination of XRD pattern reveals that the reflections appeared at 2θ angle 0.9°, 1.7° and 1.9° corresponds to the planes of (100), (110) and (200) and confirm the mesoporosity with hexagonal structure of pure SBA-15. The intensity of above XRD reflections decreases with $H_4PMo_{11}VO_{40}$ loading from 10 to 50 wt% on the SBA-15 support. Further the low-angle XRD results suggest that the existence of mesoporous nature of samples irrespective of HPA loading.

The powder X-ray diffraction patterns (Wide-angle) of SBA-15 and $H_4PMo_{11}VO_{40}$ supported catalysts are shown in Figure 2. The reflections of 2θ angle at 27.5° and



Figure 1. Low-angle X-ray diffraction patterns of various wt% of $H_4PMo_{11}VO_{40}/SBA-15$ catalysts (a) pure SBA-15, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50.



Figure 2. Wide-angle X-ray diffraction patterns of various wt% of $H_4PMo_{11}VO_{40}/SBA-15$ catalysts (a) pure SBA-15, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50.

33.5° are observed with increase of $H_4PMo_{11}VO_{40}$ loading on SBA-15 support. These reflections clearly suggest the crystallites of Keggin ion of heteropolyacid (HPA). The diffractograms also suggest that at low loadings the XRD peaks due to active phase of HPA are absent suggesting that HPA is well dispersed on the support. However, it cannot be ruled out for the presence of HPA crystallites having the size with less than 4 nm. This was beyond the detection limit of X-ray diffraction technique. These findings suggest that the active phase of HPA is well dispersed on SBA-15 surface at lower loadings and forms smaller crystallites that cannot be detected by XRD. These results are in agreement with the findings of BET surface area and scanning electron microscopy (SEM) studies of these materials (Fig. 5).

The BET surface area of pure SBA-15 and $H_4PMo_{11}VO_{40}/SBA-15$ catalysts are reported in Table I. The BET surface area of $H_4PMo_{11}VO_{40}/SBA-15$ catalyst decreases gradually with increase of active phase $H_4PMo_{11}VO_{40}$ loading on the support. This could be probably due to the partial filling of the mesoporous structure of SBA-15 silica support by the active phase and further leads to a decrease of BET surface area of the sample. These findings are in good agreement with previously discussed X-ray diffraction studies.

3.2. Raman Spectroscopy

The laser Raman spectra of pure $H_4PMo_{11}VO_{40}$ and various wt% HPA supported SBA-15 are shown in Figure 3. It can be seen from Figure 3, SBA-15 shows a symmetrical Si—O—Si and the Si—OH stretching mode of Raman bands around 500, 600, 800 cm⁻¹ respectively.⁴³ Raman spectroscopy is well explored to investigate the Keggin structure of heteropolyacid catalysts. The Raman spectrum for bulk $H_4PMo_{11}VO_{40}$ show bands at 1000, 842, 676 and 300 cm⁻¹ which are assigned to symmetric

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HPA loading (wt%)	BET surface area (m ² /g)	Total pore volume (mL/g)	Average pore diameter (nm)	NH ₃ uptake (mmol/g)			Total NH
				^a Weak	^b Moderate	^c Strong	uptake (mmol/g)
0	890	0.529	12.01	_	_	_	_
10	618	0.582	12.16	0.366	0.160	0.013	0.539
20	540	0.601	12.34	0.410	0.280	0.025	0.715
30	452	0.645	12.43	0.424	0.360	0.120	0.904
40	376	0.767	13.01	0.450	0.520	0.010	0.980
50	238	0.592	12.44	0.360	0.430	0.250	1.040

Notes: "Weak acidic sites (50 °C-150 °C); "Moderate acidic sites (150 °C-300 °C); "Strong acidic sites (450 °C-550 °C).

 (v_s) and asymmetric (v_{as}) vibrations of terminal oxygen v_s (Mo-O), v_{as} (Mo-O_t), edge shared bridged oxygen v_s (Mo-O_c-Mo) and oxygen in the central tetrahedron v_{s} (Mo–O_a). These catalysts have shown distinct changes in the Raman spectra with increasing the loading of active phase from 10-50 wt% of H₄PMo₁₁VO₄₀ on SBA-15 support. The sample with 40 wt% HPA showed clear characteristic Keggin ion band at 1000 cm⁻¹ and this band is shifted to 997 cm⁻¹ at higher loadings of active phase. The stretching frequencies of $v_{as}(Mo-O_t)$ were observed at 846 cm⁻¹ in higher loading of HPA. The Raman spectra of HPA/SBA-15 and bulk H₄PMo₁₁VO₄₀ suggest that the bands at 1000, 842, 676, 300 cm⁻¹ characteristic of Keggin ion of $[PMo_{11}VO_{40}]^{-4}$. Thus Raman spectra confirm that the Keggin structure of heteropolyacid remains intact in all the samples even after calcination of the supported catalysts. These findings are in good agreement with Raman spectra of H₄PMo₁₁VO₄₀/SiO₂ reported by Kanno et al.⁴¹ They have also reported that the characteristic band of Raman spectra appeared at 1000 cm⁻¹ and further confirms with FT-IR investigation.

3.3. Fourier Transform Infrared Spectroscopy

The FT-IR spectra of pure HPA and various H₄PMo₁₁VO₄₀ catalysts supported on SBA-15 recorded in the range



Figure 3. Raman spectra of pure H₄PMo₁₁VO₄₀ acid and various wt% of H₄PMo₁₁VO₄₀/SBA-15 catalysts (a) 10, (b) 20, (c) 30, (d) 40, (e) 50.

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1200–700 cm^{-1} are shown in the Figure 4. Vanadium substituted PMA on SBA-15 materials and H₄PMo₁₁VO₄₀ are also characterized by FT-IR spectroscopy to identify the primary Keggin ion structure. Figure 4 shows that all the samples exhibit four well-defined infrared bands in the range of 1200–700 cm⁻¹. The infrared spectra show various vibration bands of P-O, Mo-O, Mo-O_c-Mo $(O_c = \text{corner sharing oxygen})$ and $Mo - O_e - Mo$ (Oe =edge sharing oxygen) observed at 1,059 cm⁻¹, 950 cm⁻¹, 798 cm⁻¹ and 746 cm⁻¹ respectively. It can be seen from Figure 4 that the intensity of these four skeletal vibrations of Keggin ion are found to increase with HPA loading on SBA-15 support. At 40 wt% and at higher loadings, the presence of crystalline HPA phase on the surface of SBA-15 was observed. The characteristic bands of four skeletal vibrations observed in all materials suggests that the primary Keggin ion structure is retained on the support and these results well correlates with pure HPA as shown in Figure 4. The FTIR results confirm that all the materials possess primary Keggin ion structure.

3.4. Scanning Electron Microscopy

The morphology and distribution of active phase of HPA was investigated by scanning electron microscopy and the images are shown in Figure 5. The morphology of pure mesoporous silica containing SBA-15 shows a uniform



-Wave number (cm⁻¹)-

Figure 4. FT-IR spectra of various wt% of H₄PMo₁₁VO₄₀/SBA-15 catalysts (a) 10, (b) 20, (c) 30, (d) 40, (e) 50.

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Figure 5. SEM images of (a) pure $H_4PMo_{11}VO_{40}$ acid, (b) pure SBA-15, (c) 10, (d) 40, (e) 50 wt% of $H_4PMo_{11}VO_{40}/SBA-15$ catalysts.

hexagonal rod like structure. However, pure vanadium substituted heteropolyacid of $H_4PMo_{11}VO_{40}$ acid shows a cylindrical shape like morphology. Increase of the HPA loading from 10–40 wt% on SBA-15 support clearly exhibits uniform dispersion of active phase on the surface of the support. The morphology of pure $H_4PMo_{11}VO_{40}$ was observed beyond 40 wt% and at higher HPA loading, which is similar to the morphology of pure heteropolyacid. The present SEM findings are well supported with X-ray diffraction and Raman spectra of these catalysts.

3.5. Temperature-Programmed Desorption of Ammonia (TPDA)

Temperature-programmed desorption (TPD) profiles of ammonia for H₄PMo₁₁VO₄₀/SBA-15 with H₄PMo₁₁VO₄₀ loading ranging from 10 to 50 wt% are shown in Figure 6 and the amount of NH₃ desorbed is tabulated in Table I. TPD profiles suggest that a strong desorption peak appeared between 450 °C to 550 °C and a moderate desorption peak is noticed around 150 °C to 300 °C. The peak in the high temperature region of desorption is attributed to strong acidic sites of the catalyst and low temperature region desorption peaks are attributed due to moderate acidic sites of the catalyst. The strong acidic sites increased gradually from 10-30 wt% H₄PMo₁₁VO₄₀ supported SBA-15 and decreases considerably at 40 wt% HPA. It is interesting to note that the sample containing 50 wt% $H_4 PMo_{11} VO_{40}$ on SBA-15 show higher acidity (strong acid sites) than 40 wt% HPA sample. The TPD profiles have exhibited more number of strong acidic sites at higher loading. Whereas moderate acidic sites increased with increase of the HPA loading up to 40 wt% catalyst and decreased at higher loadings. The

temperature-programmed desorption of ammonia profile reveals that the 40 wt% of catalyst possesses fairly good number of moderate acidic sites compared to other loadings. Among all the catalysts analyzed for acidity measurements by TPD-NH₃, the sample containing 50 wt% loading of HPA has shown large number of these strong acidic sites.

3.6. Pyridine Adsorbed Fourier Transform Infrared Spectroscopy

The nature of Brønsted and Lewis acidic sites of HPA supported on SBA-15 is also examined by pyridine adsorption



Figure 6. TPD-NH₃ of various wt% of $H_4PMo_{11}VO_{40}/SBA-15$ catalysts (a) 10, (b) 20, (c) 30, (d) 40, (e) 50.

ex-situ FT-IR spectroscopy. The ex-situ pyridine FT-IR spectra of various wt% of H4PMo11VO40 on SBA-15 catalysts in the range 1600–1400 $\rm cm^{-1}$ are shown in the Figure 7. The spectrum shows IR bands in three regions. The vibration band appeared between 1542 and 1539 cm⁻¹ is attributed due to Brønsted acidic sites. The IR peak appeared at 1489-1487 cm⁻¹ is assigned to both Brønsted and Lewis (B + L) acidic sites. However, the vibration at 1447-1442 cm⁻¹ band is assigned exclusively to Lewis acidic sites. As can be seen from the Figure 7, the Brønsted acidic sites increased with increase of HPA loading up to 40 wt% and at higher loadings these acidic sites considerably decreased. The Lewis acidic sites increased gradually up to 30 wt% of HPA and decreases at higher loadings (> 40 wt% catalyst). The intensity of IR bands of both Brønsted and Lewis acidic sites in the region 1489–1487 cm⁻¹ increases with HPA loading up to 40 wt% and at higher loading the both the B+L acidic sites are decreased. These results are in good agreement with previously described acidity measurements by TPD-NH₃ method.

A comparison of acidity exhibited by 40 wt% HPA on SBA-15, Al_2O_3 and Y-zeolite are shown in Figure 8. The *ex-situ* pyridine FT-IR spectra in the range 1600–1400 cm⁻¹ for 40 wt% HPA of different supports is shown in the Figure 8. The spectra suggest that the IR bands at 1538 cm⁻¹ is assigned due to Brønsted acidic sites. The IR peak at 1488 cm⁻¹ is assigned to both Brønsted and Lewis (B+L) acidic sites and the vibration of 1444 cm⁻¹ is assigned exclusively to Lewis acidic sites. As can be shown from Figure 8, the intensity of IR peaks of B and B+L acidic sites of H₄PMo₁₁VO₄₀/SBA-15 was much higher compared to similar acidic sites of H₄PMo₁₁VO₄₀/SBA-15 was found to be less



Figure 7. Pyridine FTIR of various wt% of $H_4PMo_{11}VO_{40}/SBA-15$ catalysts (a) 10, (b) 20, (c) 30, (d) 40, (e) 50.

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Figure 8. Pyridine adsorbed FT-IR spectra of 40 wt% of catalysts with (a) SBA-15, (b) Al_2O_3 , (c) Y-zeolite.

compared to the L acidic sites of $H_4PMo_{11}VO_{40}/Al_2O_3$ and $H_4PMo_{11}VO_{40}/Y$ -zeolite. The above results clearly demonstrate that the presences of higher amount of Brønsted acidic sites are observed for $H_4PMo_{11}VO_{40}$ supported on SBA-15 than HPA supported on Al_2O_3 or Y-zeolite.

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3.7₆ N₂ Adsorption–Desorption Isotherms at – 196 °C The N₂ adsorption–desorption isotherms of the pure SBA-15 and H₄PMo₁₁VO₄₀/SBA-15 catalysts are shown in Figure 9 and the information derived is reported in Table I. The N₂ adsorption–desorption isotherms of all the samples show a typical type IV isotherm according to the IUPAC classification and exhibited a H1 hysteresis loop which is characteristic of mesoporous materials. The N₂



Figure 9. N_2 adsorption–desorption isotherms of various wt% $H_4PMo_{11}VO_{40}/SBA-15$ catalyst. (a) pure SBA-15, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50.

adsorption–desorption isotherm of the SBA-15 sample in the relative pressure of P/P_0 0.65–0.85 range have shown that all catalysts have exhibited uniform pore size distribution, which is a characteristic feature of a typical capillary condensation with uniform pores. As the loading of HPA increases on the SBA-15 support the shift of the position of capillary condensation is observed towards higher pressure range indicating that increase of the pore size. However, at higher loading (> 40 wt% HPA) shift in the position of the capillary condensation can be noticed towards lower pressure region and confirms that at higher loading of HPA on support, the pore size was decreased.

The pore size distributions measured by BJH method of various H₄PMo₁₁VO₄₀/SBA-15 catalysts are shown in Figure 10. All the samples have shown uniformed pore size distribution with majority of pores present in mesoporous range. As the loading of HPA increases on support from 10 to 50 wt%, the average pore diameter increases gradually from10 to 40 wt% HPA and decreased at higher loading (i.e., 50 wt% HPA). The decrease of pore size at higher loading is probably due to formation of crystalline phase of HPA supported on SBA-15. These results suggest that with increasing HPA loading the textural properties like pore volume and pore diameter increase up to 40 wt% and then decreased at higher loading. The decrease of these properties at higher loading is also probably due to blockage of pores by the crystalline phase formation of heteropolyacid on the SBA-15 support. The pore size

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Figure 10. BJH Pore size distribution of various wt% $H_4PMo_{11}VO_{40}/SBA-15$ catalysts (a) pure SBA-15, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50.



Figure 11. The conversion of aqueous glycerol/acrolein selectivity and wt% of $H_4PMo_{11}VO_{40}/SBA-15$ catalyst at 225 °C.

distribution results are good agreement with X-ray diffraction patterns of the different wt% of HPA on support.

A comparison study on pore size distribution (PSD) showed by 40 wt% HPA on SBA-15, Al₂O₃ and Y-zeolite are reported in Table IV. The PSD results for 40 wt% HPA of different supports was shown that the average pore diameter decreased with respect to support are following in the order HPA/SBA-15 > HPA/Al₂O₃ > HPA/zeolite. This was due to lower average pore diameter of Al₂O₃ and zeolite compare to SBA-15. When HPA impregnated on non-mesoporous support, the pores of support blocked by active component and it was located outside pores of support compare to SBA-15 support. Thus SBA-15 has more pore diameter than alumina and zeolite then HPA was highly dispersed and strongly interacts within the pores of SBA-15 support. The above results clearly reveal that higher average pore diameter observed for H₄PMo₁₁VO₄₀ supported on mesoporous SBA-15 than HPA supported on Al₂O₃ or Y-zeolite.

3.8. Dehydration of Glycerol

The catalytic properties of various wt% vanadium containing phosphomolybdic acid catalysts supported SBA-15 was investigated for the vapor phase dehydration of

Table II. Product distribution results of various $H_4PMo_{11}VO_{40}/SBA-15$ catalyst with 10 wt% aqueous glycerol solution at 225 °C^x.

UDA looding		Selectivity (%)						
(wt%)	${}^{a}\mathrm{C}_{\mathrm{gly}}$ (%)	^b Ac	^c Ace	^d Aceta	^y Other			
10	100	34	48	2	16			
20	100	41	42	2	15			
30	100	58	34	2	6			
40	100	74	17	4	5			
50	100	51	40	4	5			

Notes: ^xData on the conversion and selectivity of the mean values in the initial reaction period 4 h; Reaction conditions : catalyst weight = 0.3 g, feed= 0.5 mL h⁻¹, 10 mL min⁻¹ gas flow rate (N₂), 10 wt% aqueous glycerol solution, reaction temperature = 225 °C; ^yHydroxyacetone, acetone, other products; ^aConversion of glycerol; ^bAcrolein selectivity; ^cAcetic acid selectivity ^dAcetaldehyde selectivity.

glycerol at 225 °C under atmospheric pressure are shown in Figure 11 and the product distribution is reported in Table II. As can be seen from Figure 11, the results clearly demonstrate that acrolein selectivity during the glycerol dehydration depends on the HPA loading on mesoporous SBA-15 support. It was found that acrolein selectivity increased up to 40 wt% of HPA and then decreased at higher loading of H₄PMo₁₁VO₄₀ on SBA-15. TPD of ammonia results shows that moderate acidic sites are increased with increase in HPA loading and decreased at higher loading. The above results clearly suggested that acrolein selectivity depends on acidity of catalyst determined by TPD-NH₃. An evidence from FT-IR studies of pyridine adsorbed samples suggest that Brønsted acidic sites increases with HPA loading as shown in Figure 7. This result confirms that increase of acrolein selectivity is due to increase of Brønsted acidic sites in the catalyst. A considerable decrease of selectivity towards acrolein is noticed at 50 wt% HPA catalyst as this sample possesses more number of Lewis acidic sites (Fig. 7) and also less amount of moderate acidic sites (Table I). The 40 wt% HPA/SBA-15 exhibited 74% acrolein selectivity and it possesses large number of moderate acidic sites as determined by TPD of ammonia.

The acetic acid selectivity was decreased with increase of the HPA loading up to 40 wt% of HPA on support and further increased at higher loading of catalyst (Table II). This is probably due to the decrease of ratio of L/B acidic sites up to 40 wt% HPA loading. However the ratios of L/B acidic sites are increasing at higher HPA loading. As can be seen from Table II the conversion of glycerol did not appreciably change with HPA loading. The use of low wt% of glycerol in the fed minimises coke formation and also do not effect redox properties. However, the glycerol conversion decreases with high concentration of glycerol fed into the reactor (Table V). The presence of Lewis acidic sites favours the formation of hydroxy acetone, which is further converted to acetaldehyde and acetic acid by the solid acid catalysts. Thus catalytic activity results are well correlates with the nature of acidic sites and acidity of the catalyst.

Table III. Product distribution results of 40 wt% $H_4PMo_{11}VO_{40}$ on different supported catalysts with 10 wt% aqueous glycerol solution at 225 °C^x.

			Selectivity (%)					
HPA on support	(nm)	${}^{a}\mathrm{C}_{\mathrm{gly}}\ (\%)$	^b Ac	^c Ace	^d Aceta	^y Other		
SBA-15	13.01	100	74	17	4	5		
Al_2O_3	6.68	100	53	28	5	13		
Y-zeolite	2.61	100	46	36	3	15		

Notes: ^xData on the conversion and selectivity of the mean values in the initial reaction period 4 h; Reaction conditions : catalyst weight = 0.3 g, feed = 0.5 mL h⁻¹, 10 mL min⁻¹ gas flow rate (N₂), 10 wt% aqueous glycerol solution, reaction temperature= 225 °C; ^yHydroxyacetone, acetone, other products; ^aConversion of glycerol; ^bAcrolein selectivity; ^cAcetic acid selectivity; ^dAcetaldehyde selectivity.

J. Nanosci. Nanotechnol. 15, 5391-5402, 2015

Atia et al.⁷ reported that addition of alkaline metals like Li, K and Cs proved to be another tool to tune the properties of HPA on the support and to improve its performance in glycerol dehydration, in particular acrolein selectivity. But the added alkaline metal considerably decreases the activity. Garbay et al.¹⁰ have shown that ZrNbO catalysts improve the acrolein selectivity and prevent faster deactivation of the catalysts. Sancho et al.¹¹ discussed, the ZrNbO catalysts undergo deactivation easily in the dehydration of glycerol reaction. However, in the present work the glycerol dehydration was carried out with the vanadium incorporated or substituted phosphomolybdic acid catalyst, which exhibits excellent catalytic performance in the dehydration of glycerol to acrolein. Among all the catalysts examined the 40 wt% HPA has exhibited complete conversion of glycerol with 74% acrolein selectivity.

The superior catalytic functionalities of HPA/SBA-15 catalysts are compared with HPA supported on Al₂O₃ and Y-zeolite (Table III). The acrolein selectivity was found to be more in the case of SBA-15 support compare to other supports of Al₂O₃ and Y-zeolite. The enhanced selectivity of acrolein over HPA/SBA-15 was probably due to availability of large number of Brønsted acidic sites (Fig. 8). The acetic acid selectivity was higher in the case of Y-zeolite compared to other supports, HPA/Y-zeolite has more number of L acidic sites as shown in Figure 8. It is interesting to note that irrespective of support used in the reaction, the glycerol conversion has not changed appreciably due to the redox nature of HPA36-39, 41, 46-54 with 10 wt% of glycerol. However, the supports considerably affect the selectivity of acrolein and other products. The catalytic selectivities obtained over H₄PMo₁₁VO₄₀ on various supports is shown in Table III are well correlated with acidity of catalysts measured by pyridine adsorbed FTIR spectra (Fig. 8).

The textural properties or porosity of different supported HPA are reported in Table IV. The pore size of the support also influences the acrolein selectivity as it is decreased from 74% (HPA/SBA-15) to 46% (HPA/Y-zeolite) during the reaction. This could be due to decrease of pore size from 13.10 to 2.61 nm. The activity is same in all the

Table IV. Product distribution results of 40 wt% $H_4PMo_{11}VO_{40}/SBA-15$ 15 catalyst with 10 wt% aqueous glycerol solution at225 °C-250 °CX.

			Selectivity (%)					
Reaction temperature (°C)	^{<i>a</i>} C _{gly} (%)	^b Ac	^c Ace	^d Aceta	^y Other			
225	100	74	17	4	5			
250	100	48	23	14	15			

Notes: ^xData on the conversion and selectivity of the mean values in the initial reaction period 4 h; Reaction conditions: catalyst weight= 0.3 g, feed = 0.5 mL h⁻¹, 10 mL min⁻¹ gas flow rate (N₂), 10 wt% aqueous glycerol solution, reaction temperature = 225°-250 °C; ^yHydroxyacetone, acetone, other products; ^aConversion of glycerol; ^bAcrolein selectivity; ^cAcetic acid selectivity; ^dAcetaldehyde selectivity.

Vapor Phase Dehydration of Glycerol to Acrolein Over SBA-15 Supported Vanadium

catalysts but the acrolein selectivity is observed high in the case of SBA-15 supported HPA compared to zeolite supported HPA catalysts. This is probably due to decrease in pore diameter of HPA/Y-zeolite.

Several authors studied the vapor phase dehydration of glycerol to acrolein using different supported HPA catalysts.^{4,44,45} The influence of selected support materials on acrolein formation was studied under similar reaction conditions. The selectivity of acrolein on various HPA catalysts our present study follows the order SBA-15 > Al_2O_3 > Y-zeolite.

The effect of reaction temperature on the dehydration of glycerol was examined over 40 wt% HPA on SBA-15 and product distribution given in Table IV. From the Table IV it is observed that the selectivity of acrolein and acetic acid varies with reaction temperature. But the conversion of glycerol remains same with increase of reaction temperature from 225 °C–250 °C. This might be due to the oxidative property of vanadium containing heteropolyacids during the reaction.^{36–39,41,46–54} As the temperature increases from 225 °C to 250 °C, the acrolein selectivity decreases from 74 to 48% whereas acetic acid selectivity increases from 17 to 23% during reaction. The significant change in product selectivity is due to oxidation ability of vanadium containing phosphomolybdic anion at higher reaction temperature favours C—C bond cleavage.

Tao et al.⁶ reported that the gas-phase dehydration reaction of glycerol was carried out at 315 °C under atmospheric pressure. Kim et al.¹³ reported the vapour phase dehydration of glycerol to acrolein over H-zeolites carried out at 290 °C–340 °C temperature. However, in the present work the vapor-phase dehydration of glycerol to acrolein was carried out at mild reaction temperature (225 °C) under atmospheric pressure. Thus mild reaction temperature conditions are beneficial than the high reaction temperature in this vapor phase dehydration of glycerol reaction.

The effect of time on stream on catalytic properties during glycerol dehydration by using 40 wt% H₄PMo₁₁VO₄₀ on different supports are shown in Figure 12. As can be seen from Figure 12, HPA/SBA-15 exhibited complete conversion of glycerol with 74% acrolein selectivity (10 wt% aqueous glycerol solution) with stable activity for a period of 10 h of the continuous operation. However, HPA/Al₂O₃ shows stable activity up to 7 h and decreases gradually with time. Similarly, acrolein selectivity also decreases with time. In the case of HPA/zeolite the stable activity is noticed only up to 4 h and it was decreased later. The stable activity of SBA-15 supported catalysts compared to other supported catalysts can be explained based on the mesoporous nature of the SBA-15 support and also on the acidic and redox behaviour. However, the acrolein selectivity obtained in the case of HPA/SBA-15 stable during course of reaction compare to HPA/Al₂O₃ and HPA/Y-zeolite. Thus the mesoporous



Figure 12. Catalytic properties over 40 wt% HPA on SBA-15, Al_2O_3 and Y-zeolite supports at 225 °C.

materials as a catalyst supports are advantageous for glycerol dehydration reaction for obtaining high stable conversion and high selectivity of acrolein. The decrease of conversion and acrolein selectivity in HPA supported on Y-zeolite and alumina is might be due to significant deactivation of the catalysts or loss of Keggin ion structure of HPA.

Several authors reported that the activity of catalyst decreases because of coke formation on the surface of catalysts 13,15 However, the $H_4PMo_{11}VO_{40}$ show redox properties $^{36-39,46-54}$ to reduce the coke formation with time on stream up to 10 h. Hence the vanadium substituted PMA supported on SBA-15 has novel importance to the catalytic studies than alumina and zeolite under mild reaction conditions.

A comparison is made with other supported catalysts such as zirconia supported 12-tungstophosphoric acid (TPA) with the present results during glycerol dehydration. Chai et al.⁵⁵ reported that TPA/ZrO₂ catalysts have shown 67% conversion and 47% selectivity to acrolein. The above catalysts have shown rapid decrease in the glycerol conversion during the time on stream studies at TOS 9–10 h (35%). However, $H_4PMo_{11}VO_{40}/SBA-15$ catalysts employed in the present study exhibited total conversion of glycerol with 65% acrolein selectivity at TOS 9–10 h. The above findings suggest that $H_4PMo_{11}VO_{40}$ supported on SBA-15 exhibits better catalytic properties than TPA/ZrO₂. The stable activity shown by $H_4PMo_{11}VO_{40}/SBA-15$ during time on stream is probably due to the mesopores with higher pore size of SBA-15 support.

The vapor phase dehydration of glycerol reaction was carried out at 225 °C with 40 wt% HPA/SBA-15 by varying feed concentration of glycerol and the catalytic results are reported in Table V. The catalyst exhibited high activity on 10 wt% glycerol concentration amounting to 100% glycerol conversion at 74% acrolein selectivity. However, the conversion and acrolein selectivity decreased sharply with increase in concentration of glycerol feed. This is

Table V. Product distribution results of 40 wt% of $H_4PMo_{11}VO_{40}/SBA-15$ catalyst with 10–40 wt% aqueous glycerol solution at 225 °C^X.

Classeral		Selectivity (%)				
concentration (Wt%)	${}^{a}\mathrm{C}_{\mathrm{gly}}$ (%)	^b Ac	^c Ace	^d Aceta	^y other	
10	100	74	17	4	5	
20	96	66	24	2	8	
30	89	53	27	4	16	
40	78	38	32	8	22	

Notes: ^xData on the conversion and selectivity of the mean values in the initial reaction period 4 h; Reaction conditions : catalyst weight = 0.3 g, feed = 0.5 mL h⁻¹, 10 mL min⁻¹ gas flow rate (N₂), 10 wt% aqueous glycerol solution, reaction temperature = 225°C; ^yHydroxyacetone, acetone, other products; ^aConversion of glycerol; ^bAcrolein selectivity; ^cAcetic acid selectivity; ^dAcetaldehyde selectivity.

due to significant coke was deposited on the catalyst surface during the course of reaction and decreases available active sites with increase of glycerol concentration. Thus catalytic activity and acrolein selectivity decreases with increase in concentration of glycerol solution due to the fact that the number of available active sites of catalysts decreased due to deactivation of the catalysts caused by coke formation.

4. CONCLUSIONS

This work presents a comprehensive characterization, catalytic properties and investigation of the acidity and textural properties of H₄PMo₁₁VO₄₀ supported on mesoporous silica SBA-15. The vanadium substituted HPA supported on SBA-15 are found to be highly active for the vapor phase dehydration of glycerol to acrolein at moderate reaction temperature under normal atmospheric pressure. The XRD and SEM findings suggest that high dispersion of HPA on support was observed at lower loadings. The FT-IR and Raman spectral findings confirm the existence of primary Keggin ion structure of HPA and it was intact in all the prepared materials of HPA on SBA-15. TPD of ammonia results suggests that 40 wt% HPA has more number of moderate acidic sites and well correlates with pyridine adsorbed FT-IR results. The pore size distribution (PSD) results show that the pore size increased at lower wt% of HPA and decreased at higher loading and also mesoporous SBA-15 support exhibits large pore size than the Al₂O₃ and Y-zeolite. The pore size of the heteropolyacids supported on SBA-15 also influences the activity and selectivity.

The catalytic properties during the vapor phase glycerol dehydration reaction results are well correlated with acidic and textural properties of the catalysts. The vanadium containing HPA supported on SBA-15 has shown excellent catalytic performances during the dehydration reaction at 225 °C under atmospheric pressure than the other non mesoporous supported systems. The HPA catalysts supported on mesoporous SBA-15 exhibited higher and stable activity compared to HPA supported on alumina and Y-zeolite. It was found that incorporation of vanadium to

the phosphomolybdic acid shows tuneable redox and acid properties and improves catalyst stability to retard deactivation with high selectivity to acrolein. The catalyst shows better catalytic performance with 10 wt% glycerol solution than the other concentrations of glycerol. Mesoporous SBA-15 supported HPA with large average pore diameter was more efficient than the corresponding macroporous supported HPA and also the best acrolein selectivity was obtained with HPA supported on mesoporous SBA-15.

Acknowledgments: The authors Balaga Viswanadham, Vanama Pavan Kumar Thank CSIR, New Delhi for the award of Senior Research Fellowship and Amirineni Srikanth thanks Director, IICT for Project Assistant fellowship.

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