Synthesis, Characterization and Catalytic Dehydration of Glycerol to Acrolein Over Phosphotungstic Acid Supported Y-Zeolite Catalysts

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Abstract

Vapour phase catalytic dehydration of glycerol to acrolein was studied over phosphotungstic acid (PTA) supported (with different loadings of PTA) on Y-zeolite catalysts. The active component PTA was varied between 10 and 40% w/w on the support Y-zeolite and was synthesized by the wet impregnation method. The physico-chemical characterization of the catalyst samples was investigated by X-ray diffraction (XRD), FT-IR, Raman and by the gas adsorption measurements. The XRD results showed that active component PTA is highly dispersed in an amorphous form at lower loadings of PTA and attained a crystalline state beyond 20 wt% of PTA. Both Raman and FT-IR spectra indicated that the Keggin ion structure of PTA was present in a highly dispersed state in the supported PTA/zeolite catalysts as compared to the bulk form of PTA. Temperature programmed desorption (TPD) of ammonia and FT-IR spectra of pyridine adsorption were used to determine the acidic properties of the PTA catalysts. The TPD of ammonia showed the presence of moderate acidity on the catalyst surface. The total acidity increased with raise in PTA loading up to 20 wt% and beyond this, it had decreased. The FT-IR results suggested the presence of Brønsted acidity. The Pore size increased with PTA loading until 20 wt%. Finally, the PTA/zeolite catalysts were tested for the gas phase dehydration of glycerol in a fixed-bed, micro-reactor in the temperature range between 250 and 300 °C. Among all the catalysts tested, PTA (20 wt%)/zeolite showed a total conversion of 100% glycerol and a selectivity of 79% for acrolein. These results are correlated with surface acidity, textural and structural properties of the PTA/zeolite catalysts.

Graphical Abstract

Glycerol dehydration products over Lewis and Bronsted acidic sites.



Keywords Glycerol dehydration · Acrolein · Heteropolyacid · Zeolite · Brønsted acidity · Porosity

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1 Introduction

Biomass is renewable and relatively environmentally clean source of energy. With increasing demand on energy security, the focus is more on the renewable sources of energy to produce clean fuels, and chemicals. Hence, there is an intensive surge to work on biomass. The conversion of biomass to fuels and other related chemicals are well known. Biodiesel is an attractive alternative fuel produced from renewable oil sources like palm, canola, soya bean and rape seeds. Glycerol is the most important by-product produced from biodiesel. The availability of a cheaper feed stock like glycerol, and converting them into value added chemicals would be more challenging in near future. Various catalytic routes for converting glycerol to other value added chemicals, such as dehydration, hydrogenolysis, acetylation etc., have been investigated [1-3]. Among them, dehydration of glycerol is a very challenging one.

Acrolein, as a chemical intermediate is used in many industrial applications. It is a well-known intermediate used in the production of acrylic acid, acrylic acid ester, glutaraldehyde and methionine [1-3]. The commercial process for making acrolein involves the partial oxidation of propylene over mixed metal oxides catalytic system, consisting of Bi–Mo (W)–O phase [4]. However, the title reaction, viz., the dehydration of glycerol to acrolein is an inexpensive benign process. Several authors have studied this reaction in the liquid phase on various kinds of solid acid catalysts such as sulfuric acid, solid phosphoric acid, zeolites and metal oxides [5-19]. Most of the catalysts used had shown a poor catalytic performance in terms of conversion and selectivity for acrolein.

The catalytic functionalities of the active phase can be strongly influenced by the nature of the support material and by its dispersion on the support. Some of the supports used for this reaction are alumina, titania and zirconia. However, protonic form of zeolites used as solid catalysts have shown better results [20]. The superior catalytic results of zeolites is predominantly due to its acidity function of the bridged hydroxyl groups present in the Si-(OH)-Al units and due to its shape selectivity linked with the well-defined pore size of the material [21]. Though, zeolites have higher acidic sites, but shows a lower Brønsted acidic sites available on the surface and hence lower acrolein selectivity [11, 22]. Therefore, one way to enhance the selectivity for acrolein is to increase the number of Brønsted acid sites on the surface of the catalysts [5–19]. The challenge lies in increasing the acidic property of zeolite by surface alteration through promotion of strong Brønsted acid species such as phosphotungstic acid (PTA), with Keggin ion structure either on the surface or within the inner channels or pores of the

zeolites [23, 24]. This would enhance the Brønsted acid sites quantitatively. It is reported that the dehydration reaction of glycerol to acrolein over supported heteropolyacids depends on the acid strength and the textural parameters of the catalysts [5, 11–15]. This is further supported by the work of Katryniok et al. [2] who had identified that the two properties, high surface acidity and pore structure, are needed for higher conversion of glycerol and acrolein selectivity. Recently, few researchers reported oxidation and acid catalytic performance of heteropolyacid catalysts during Knoevenagel and toluene oxidation reactions over pronounced Brønsted and Lewis acidic sites in the heteropolyacid catalyst enhance the catalytic activity [25–27].

The present investigation reports on the vapour phase dehydration reaction of glycerol to acrolein over a series of PTA, with different loadings of PTA, supported on Y-zeolite catalysts. The objective of the study is mainly to draw a correlation between the structural composition and high acidity of the active phase, PTA on the catalyst surface and the overall catalytic activity, selectivity and stability of the catalyst.

2 Experimental

2.1 Catalyst Preparation

A series of PTA catalysts with 10–40 wt% of $H_3PW_{12}O_{40}$ loading on Y-zeolite (Si/Al ratio = 30, Conteka, The Netherlands) support was synthesized by wet impregnation method. A known quantity of PTA (Sigma-Aldrich) was dissolved in a double distilled water and the support, Y-zeolite was added to the above solution. The resultant mixture was stirred at 25 °C for 5 h and subsequently dried at 100 °C for 10 h and calcined in air for 4 h at 400 °C.

2.2 Catalyst Characterization

The XRD analysis of the samples was carried out using Bruker D8 Diffractometer, using Cu K α radiation (1.5406 Å). The diffraction profiles were collected with an X-ray gun operated at 40 kV and 30 mA. The measurements were recorded in steps of 0.0450 with a count time of 0.5 s in the scanning range of 2°–62°.

Raman spectra of the catalyst samples were studied with the micro-Raman attachment of a Horbia-Jobin Yvon Raman spectrometer equipped with a confocal microscope, 2400/900 grooves/mm gratings, and a notch filter. Visible laser excitation at 532 nm (visible/green) is supplied by a Yag doubled diode pumped Laser (20 mW). 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-3000 V).

Surface acidity was determined by Temperature programmed desorption (TPD) of NH₃ using Auto Chem 2910 (micromeritics, USA) instrument. In a typical experiment, ca. 100 mg of calcined sample was taken in a U-shaped quartz cell. The catalyst sample was packed in one arm of the sample tube on a quartz wool bed. Prior to TPD-NH₃ studies, the catalyst sample was pre-treated by passing high purity helium (50 ml/min) at 200 °C for 1 h. After pre-treatment the sample 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 150 °C for 1 h to remove physically adsorbed ammonia from the surface of the catalyst samples. The TPD analysis was carried out from room temperature to 600 °C at a heating rate of 10 °C/min. The ammonia concentration in the effluent stream was monitored with thermal conductivity detector, and the area underneath the peak was integrated using the software GRAMS/32, to determine the desorbed amount of ammonia.

The FT-IR spectra of the catalysts were recorded on IR (Model: GC-FT-IR Nicolet 670) spectrometer using KBr disc at room temperature. The ex-situ analysis of FT-IR spectra of pyridine adsorbed samples were usually studied to determine the nature of acidity (Brønsted and Lewis acid sites) [28]. Prior to recording the IR spectra, the pyridine adsorption experiments were carried out by placing a drop of pyridine on a 10 mg of the HPA sample followed by evacuation for 1 h at room temperature to remove the reversibly adsorbed pyridine on the surface of the catalyst.

The specific surface area of the catalysts was determined by the physical adsorption of nitrogen gas (cross-sectional area = 0.162 nm^2) at -195 °C from BET adsorption measurements using an Autosorb-1 (Quantachrome) instrument. Before performing the adsorption experiments, the samples were evacuated at 200 °C for 4 h under vacuum in order to remove moisture or impurities from the surface of the sample. Degassing was 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°) in the range of 0.05–0.9, using nitrogen adsorption–desorption method. The pore size distribution was calculated from the BJH method.

2.3 Catalyst Testing

The gas phase dehydration of glycerol reaction was studied at 250–300 °C under normal atmospheric pressure in a vertical down ward fixed-bed micro glass reactor of length 36 cm and 0.5 cm id with a catalyst bed at the middle of reactor. The reactor was positioned in an electrically heated furnace and the temperature was monitored by a thermocouple which is set near to the catalyst bed and nitrogen was used as a carrier gas. The glass reactor was filled with 0.3 g of the catalyst and was filled above with ceramic beads. This is mainly to vaporize the feed, glycerol, before reaching the catalyst bed. The catalyst was pretreated with nitrogen gas at 60 ml/min at similar reaction temperature for 1 h. An aqueous glycerol (10–40 wt%) solution (0.5 ml/h), was fed from the top of the reactor through the inlet in a flow of N_2 gas at 10 ml/min. The reaction products were, collected periodically and analyzed by means of a GC which was equipped with a flame ionization detector and a packed capillary column (DB-wax 123-7033).

3 Results and Discussion

3.1 Characterization Techniques

3.1.1 X-Ray Diffraction (XRD)

The X-ray diffraction (XRD) patterns of fresh Y-zeolite and different loadings of PTA on Y-zeolite are shown in Fig. 1. The diffractograms of pure zeolite shows intense reflections at $2\Theta = 6.4^{\circ}$, 10.0° , 12.0° , 16.7° , 18.9° , 20.8° , 24.0° and 27.5°. The XRD patterns of all the samples of PTA/zeolite show reflections similar to the diffractogram of the pure zeolite. However, as the PTA loading increased from 10 to 40 wt% on the support, the reflections due to PTA has also increased. This indicates that the zeolite framework is not affected by the impregnation of PTA. The peaks corresponding to PTA were noticed at $2\Theta = 10.5^{\circ}$, 20.7° , 26.1° , 35.4° , $38.9^{\circ}, 43.5^{\circ}, 55.4^{\circ}$ and 62.0° and their intensity increased with increase in PTA loading on the support. These peaks are contributed due to the crystallites of PTA having Keggin ion structure [29]. At lower PTA loadings, the above said peaks were absent suggesting that PTA is well dispersed on the surface of the zeolite support. The presence of smaller crystallites of PTA (<4 nm) cannot be ruled out, since they are beyond the detection limit of powder XRD technique.

3.1.2 Fourier Transform Infrared Spectroscopy

FT-IR spectra of various PTA/zeolite catalysts in the range 1200–700 cm⁻¹ are shown in Fig. 2. The catalysts show four well-defined IR bands at 1080, 983, 890 and 796 cm⁻¹. These bands are attributed to P–O, W–O, W–O_b–W and W–O_c–W phases, respectively. These four skeletal vibrations of Keggin ion intensity increases with increasing PTA loading on the support. At higher loading, the IR band of W–O_b–W is distinctly observed indicating the formation of bulk PTA on the surface of the support. The SiO₂ asymmetric and Si–O–Si symmetric stretching vibration bands are located, at ca. 1080 and 800 cm⁻¹, respectively [30] and these bands are formed due to the complete overlap of the two fingerprint vibrations of the [PW₁₂O₄₀]⁻³. The WO₃ stretching vibration band at 981 cm⁻¹ is observed



Fig. 1 A X-ray diffraction patterns of various wt% of $H_3PW_{12}O_{40}/Y$ -zeolite: (*a*) pure Y-zeolite (*b*) 10, (*c*) 20, (*d*) 30, (*e*) 40. **B** X-ray diffraction profile of $H_3PW_{12}O_{40}$ catalyst

only at the higher loading of PTA. In otherwords, the IR spectra indicate that the intensity of primary Keggin ion of $[PW_{12}O_{40}]^{-3}$ increases with increase in PTA loading on the support, Y-zeolite [31].

3.1.3 Raman Spectroscopy

Raman spectra was used to investigate the primary structure of Keggin ion of the heteropolyacid catalysts. Laser Raman spectra of bulk $H_3PW_{12}O_{40}$ and different loading of PTA on Y-zeolite catalysts, are shown in Fig. 3. The Raman spectrum of the bulk $H_3PW_{12}O_{40}$ showed bands at 1014, 994, and 241 cm⁻¹ which are assigned to $vs(W-O_t)$ (vs-symmetric), $vas(W-O_t)$ (vas-asymmetric) and $vs(W-O_a)$ respectively. As loading of PTA increases from 10 to 40 wt% on the Y-zeolite support, the intensity of Raman bands also



Fig. 2 FT-IR spectra of various wt% of $H_3PW_{12}O_{40}$ /Y-zeolite: (*a*) pure Y-zeolite, (*b*) 10, (*c*) 20, (*d*) 30, (*e*) 40



Fig. 3 Raman spectra of various wt% of $H_3PW_{12}O_{40}$ /Y-zeolite: (a) 10, (b) 20, (c) 30, (d) 40

increases. This suggests that the primary Keggin structure of PTA was observed only at higher loadings of PTA on the support Y-zeolite. However, the intensity of the stretching frequency of $vs(W-O_t)$ at 1010 cm⁻¹ has increased dramatically at higher PTA loadings (40 wt%) suggesting the presence of bulk or crystalline phase of PTA on the surface of the zeolite support. Raman spectra of PTA/zeolite catalysts and bulk H₃PW₁₂O₄₀ spectra suggest that intensive band at ~1010 cm⁻¹ is characteristic Raman band of Keggin ion of [PW12O40]⁻³. These results are in good agreement with

Caliman et al. [32]. These findings further confirm that at lower PTA loading, the Keggin ion of PTA, are well dispersed on the zeolite support as compared to the higher PTA loadings and bulk PTA (Fig. 3).

3.1.4 Temperature-Programmed Desorption of Ammonia

The TPD profiles of pure Y-zeolite and PTA/Y-zeolite catalysts are shown in Fig. 4 and the corresponding amount of NH₃ desorbed are reported in Table 1. The peaks appeared around 150–300 and 450–600 °C are due to the weak acidic and moderate acidic sites present on the PTA/Yzeolite catalysts, respectively. The fact that the two desorption peaks have appeared suggest the presence of two types of acidic sites (weak and moderate) present on the surface of the Y-zeolite. It is interesting to observe that



Fig. 4 TPD of ammonia profile of various wt% of $H_3PW_{12}O_{40}/Y$ -zeolite: (*a*) pure Y-zeolite, (*b*) 10, (*c*) 20, (*d*) 30, (*e*) 40

Table 1Results of texturalproperties and TPD-NH3measurements of various $H_3PW_{12}O_{40}/Y$ -zeolite catalysts

the moderate acidic sites have increased gradually from 10 to 20 wt% of PTA on the surface of the support while decreases gradually with further increase in PTA loading. Whereas the weak acidic sites observed in the case of pure zeolite has decreased significantly with increase in PTA loading. The decrease in acidity at higher PTA loadings may be due to the formation of crystalline form of PTA (bulk like) and must have lower surface area at higher loadings leading to a decrease in the acidity [17]. Among all the catalysts studied for acidity measurements, the 20 wt% PTA on zeolite, has shown higher amount of acidity than the rest of the catalysts.

3.1.5 Pyridine Adsorbed Fourier Transform Infrared Spectroscopy

The Brønsted and Lewis acidic sites of PTA supported on zeolite catalysts were studied by ex-situ pyridine adsorbed FT-IR spectroscopy. These FT-IR spectra results of various wt% of H₃PW₁₂O₄₀ on zeolite catalysts in the range of 1600–1400 cm⁻¹ are shown in Fig. 5. The IR bands appeared at 1544, 1489 and 1443 cm^{-1} are attributed to the Brønsted, both Brønsted and Lewis (B+L) and to the Lewis acidic sites, respectively. As shown in Fig. 5, both Brønsted as well as the Lewis acidic sites, increase with increase in PTA loadings up to 20 wt%, and start decreasing with further increase in PTA loading. Intensity of IR bands, of both Brønsted and Lewis acidic sites at 1486 cm⁻¹ increases with increase in PTA loading up to 20 wt% and decreased at higher loading. The above findings are well correlated with the TPD of ammonia analysis. We also studied the B/L acidic sites ratio from pyridines IR spectra based on peak area of catalysts. These results are reflecting more number of Brønsted acidic sites was observed in 20 wt% catalysts compared to higher and lower PTA loadings as well as pure zeolite support.

H ₃ PW ₁₂ O ₄₀ loading (wt%)	S_{BET}^{a} (m ² /g)	$V_P^{\ b}(cc/g)$	$D_{p}^{c}(nm)$) NH ₃ uptake (mmol/g)		Total NH ₃ uptake ^f	B/L ratio
				Weak ^d	Moderate ^e	(mmol/g)	
0	720	0.45	2.61	0.82	0.40	1.20	0.17
10	635	0.42	2.68	0.36	1.12	1.48	0.22
20	582	0.39	2.79	_	2.46	2.46	0.35
30	522	0.36	2.54	-	1.97	1.97	0.29
40	496	0.31	2.26	-	1.68	1.68	0.26

^aSpecific surface area estimated by using BET method

^{b,c}Pore volume and pore diameter estimated from BJH method

^dWeak acidic sites = 150-300 °C

^eModerate acidic sites = 450–600 °C

^fAcidity measured by NH₃-TPD analysis



Fig. 5 Pyridine adsorbed FT-IR spectra of various wt% of $H_3PW_{12}O_{40}$ Y-zeolite: (*a*) pure Y-zeolite, (*b*) 10, (*c*) 20, (*d*) 30, (*e*) 40

3.1.6 N₂ Adsorption–Desorption Studies

The N2 adsorption-desorption isotherms of the pure Y-zeolite and various wt% of PTA on Y-zeolite is shown in Fig. 6. The PTA/Y-Zeolite catalysts showed type-I isotherms, which is characteristic of micro-porous material. The N2 uptake quickly increased to lower P/P⁰ values by adsorbing inside the micro pores as well as on the external surface of the catalyst. The N₂ uptake remained almost constant and a small hysteresis loop was observed at a higher relative pressure (P/ P^{0}) in the isotherm curves suggesting few narrow meso pores on the catalysts [33]. The BET surface area, pore volume and pore size of pure Y-zeolite and calcined PTA/Y-zeolite catalysts are given in Table 1. The surface area of pure Y-zeolite is 720 m²/g. The surface area of PTA on Y-zeolite catalyst decreased with increase in PTA loading on Y-zeolite. The decrease in surface area of the catalyst with increasing PTA loading is due to the blocking the pores of the support, Y-zeolite by the PTA crystallites. It can be seen from Table 1, the pore size of pure zeolite and PTA supported on Y-zeolite show a single peak at 2.2–2.8 nm. It is evident from the Table 1, that pore volume and the specific surface area of the PTA/Y-zeolite catalysts are much lower as compared to the pure Y-zeolite. As the loading of PTA increases on the support from 10 to 40 wt%, the average pore diameter



Fig.6 N_2 adsorption–desorption isotherms of various wt% of $H_3PW_{12}O_{40}/Y$ -zeolite catalysts: (*a*) Y-zeolite, (*b*) 10, (*c*) 20, (*d*) 30, (*e*) 40

initially increases from 10 to 20 wt% PTA and decreased with further increase of PTA loadings. The initial increase in pore size of Y-zeolite is probably due to the expansion of pores but at higher PTA loading, the decrease of pore size is due to blockage of pores of the support.

3.2 Catalytic Activity Studies

3.2.1 Effect of PTA Loading

Catalytic performance of various PTA supported on Y-zeolite catalysts for the title reaction is reported in Table 2. The results suggest that pure Y-zeolite showed a glycerol conversion of 67% and increased significantly with glycerol conversion to 100% at 20 wt% PTA/ Y-zeolite catalysts. However, at higher PTA loadings (>20 wt% PTA), a drop in conversion was noted. This is in direct correlation with the total acidity of the catalysts which showed an increase in acidity with rise in PTA loading up to 20 wt% and thereafter decreases at higher loading of PTA on the Y-zeolite support (Table 1). Similarly, the pure Y-zeolite, showed a selectivity of 37% for acrolein and increased from 58 to 79% in with PTA/Y-zeolite catalysts along with increase in PTA loading from 10 to 20 wt% PTA on Y-zeolite support. However acrolein selectivity decreases to 65% at higher PTA loadings. This may be due to the changes in moderate acidity of the PTA/Y-zeolite catalyst [17]. The general schematic pathway of dehydration of glycerol is shown in Scheme 1.

The Brønsted acidic sites are mostly accountable for the acrolein formation [34]. However, this does not preclude the contribution of Lewis acid sites in forming acrolein. As

Table 2Product distributionand glycerol conversion resultsof various wt% of $H_3PW_{12}O_{40}/$ Y-zeolite catalyst at 275 °C

H ₃ PW ₁₂ O ₄₀ Load- ing (wt%)	C _{gly} (%) ^a	Selectivity (mol%)							
		$\overline{S_{Ac}}^{b}$	S _{Aceti} ^c	$\mathbf{S}_{\mathrm{Acta}}^{d}$	S _{HA} ^e	$S_{Act}^{\ \ f}$	Other ^g		
0	67	37	14	16	9	3	21		
10	82	58	10	8	6	4	14		
20	100	79	3	6	3	2	7		
30	95	72	8	3	5	6	6		
40	89	65	6	4	7	10	8		

Data on the conversion and selectivity at TOS 3 h. Reaction conditions: catalyst weight=0.3 g, feed=0.5 ml/h, 10 ml/min gas flow rate (N₂), 10 wt% aqueous glycerol solution, reaction temperature=275 °C

^aConversion of glycerol

^bAcrolein selectivity

^cAcetic acid selectivity

^dAcetaldehyde selectivity

^eHydroxy acetone selectivity

^fAcetone selectivity

^gAllylalchol and other products



Scheme 1 Dehydration of glycerol to acrolein over PTA $(H_3PW_{12}O_{40})/Y$ -zeolite catalyst

seen in Fig. 5, that Brønsted acidic sites are inclining up to 20 wt% of PTA loading and beyond which it is decreasing. These results confirm that the increase in acrolein selectivity is due to the pronounced Brønsted acidic sites. A considerable decrease in selectivity to acrolein is noticed at higher PTA loadings on the support Y-zeolite. This is mainly due to the presence of more number of Lewis acidic sites and lesser amount of moderate acidic sites (Table 1). This suggests that the Brønsted acidic sites play a dynamic role in the formation of acrolein. This result strongly inclined with B/L acidic site ratio and 20 wt% catalysts possess more number of B acidic sites (with respect to B/L ratio) provides higher selectivity towards acrolein. The fact that catalytic activity decreased at higher loadings is probably due to bulk formation of crystalline phase of PTA on zeolite support and leads to a minor destruction of the Keggin ion of PTA. The results are in good agreement with the findings of Chai et al. [35] where they had observed the decomposition of Keggin structure of PTA at higher loadings of the active phase. It is also evident from the previously described results of XRD, FT-IR and Raman spectra that bulk PTA was observed at higher PTA loadings. Among various PTA loadings, 20 wt% PTA/Y-zeolite catalysts show a conversion of glycerol with 79% acrolein selectivity. The above results clearly suggest that catalytic functionalities during the glycerol dehydration depend on the PTA loading on Y-zeolite. However, the hydroxy acetone selectivity changed with PTA loadings on the zeolite support. The as-received Y-zeolite showed 9% hydroxy acetone or acetol selectivity and decreased from 6 to 3% with increase in PTA loading up to 20 wt% PTA and again increases to 7% at higher PTA loading on zeolite support. This might be due to the change of intensity of Brønsted/Lewis acidic sites ratio with active phase loading (Fig. 5).

3.2.2 Effect of Pore Size

Enhancement of acrolein selectivity can also be elucidated, in terms of textural parameters of the catalysts. The selectivity towards acrolein for various wt% of PTA supported on Y-zeolite catalysts is reported in Table 2, and the pore sizes of these materials are reported in Table 1. These findings show that the acrolein selectivity increased from 37 to 79% with increase in PTA loading from 0 to 20 wt% and decreases to 65% at higher PTA loading. A similar trend is noticed as the pore size increased from 2.61 to 2.79 nm with increase in PTA loading from 0 to 20 wt% PTA and decreases to 2.26 nm at higher PTA loading on the support Y-zeolite. At higher PTA loadings decrease of acrolein selectivity is noticed due to decrease of the pore size of the catalyst. If the pore size is very less, it hinders the diffusion of the reactants and products leading to the side reactions instead of dehydration reaction causing a decrease in the overall activity of the catalysts. Thus 20 wt% PTA on zeolite has higher pore size and easily allows the diffusion of the reactants and products during the course of reaction as compared to the rest of the other loadings of PTA over Y-zeolite catalysts.

3.2.3 Effect of Reaction Temperature

The effect of reaction temperature on glycerol dehydration was observed over 20 wt% PTA on Y-zeolite catalyst and the product distribution results are given in Table 3. It is noticed that glycerol conversion and acrolein selectivity changed with reaction temperature. Glycerol conversion increased from 75 to 100% with rise in reaction temperature from 250 to 275 °C and dropped to 94% at 300 °C. The decrease in conversion at higher reaction temperature is possibly due to the deactivation of catalyst. This is because of more coke deposited on the surface of the catalyst which further leads to the decrease of available active sites on the surface of the catalyst. As temperature increases from 250 to 300 °C, acrolein selectivity increases from 46 to 79% and decrease to 62% at 300 °C. This may be due to the blocking of the Brønsted acidic sites by coke deposition on the surface of the catalysts. These findings suggest that the catalyst exhibit better catalytic performance at the reaction temperature 275 °C.

3.2.4 Effect of Glycerol Concentration

Table 3Product distributionresults of 20 wt% of $H_3PW_{12}O_{40}$ /zeolite catalyst atdifferent reaction temperatures

Catalytic results of glycerol dehydration at $275 \,^{\circ}$ C over 20 wt% PTA on zeolite support was explored by varying the feed, glycerol concentration. The product distribution of this reaction is shown in Fig. 7. It is observed that the glycerol conversion and the acrolein selectivity dropped



Fig. 7 Effect of glycerol concentration on glycerol conversion and acrolein selectivity over 20 wt% PTA/zeolite. Reaction conditions: 0.3 g catalyst, glycerol concentration (10–40 wt%), fed=0.5 ml/h, N₂ Flow=10 ml/min

with change in feed glycerol concentration (10–40 wt% of glycerol). This decline in catalytic activity with rise in the glycerol concentration is perhaps due to the decrease in the available active sites on the catalyst surface which further leads to the reduction in dehydration activity. Therefore, the increase of glycerol concentration in the feed favours coke formation and subsequently drops the catalytic performance of the reaction.

3.2.5 Effect of Time on Stream

The effect of time-on-stream (TOS) up to 10 h was investigated over 20 wt% PTA on Y-zeolite and the results are shown in Fig. 8. A 100% glycerol conversion with acrolein selectivity of 79% was observed at 3 h and decreased

Reaction tempera- ture (°C)	C _{gly} (%) ^a	Selectivity (mol%)						
		$\overline{S_{Ac}}^{b}$	S _{Aceti} ^c	S _{Acta} ^d	S _{HA} ^e	$\mathbf{S}_{\mathrm{Act}}^{\mathrm{f}}$	otherg	
250	75	46	2	4	2	6	40	
275	100	79	3	6	3	5	4	
300	94	62	4	8	6	10	10	

Data on the conversion and selectivity at TOS 3 h. Reaction conditions: catalyst weight=0.3 g, feed=0.5 ml/h, 10 ml/min gas flow rate (N₂), 10 wt% aqueous glycerol solution, reaction temperature=250-300 °C

^aConversion of glycerol

- ^bAcrolein selectivity
- ^cAcetic acid selectivity
- ^dAcetaldehyde selectivity
- ^eHydroxyacetone selectivity
- fAcetone selectivity
- ^gMethanol, allylalchol products



Fig. 8 Effect of time on stream on glycerol conversion and acrolein selectivity over 20 wt% PTA/zeolite. Reaction conditions: 0.3 g catalyst, glycerol concentration (10 wt%), fed=0.5 ml/h, N₂ flow=10 ml/min

significantly beyond this time period. The fall in activity is possibly due to the coke deposition on the catalyst which further leads to the blocking of pores and hence the unavailability of the active sites.

4 Conclusions

The present investigation describes the PTA modified over Y-zeolite catalysts for the vapour phase dehydration of glycerol to acrolein. The XRD, FT-IR and Raman spectra results show that the active phase, PTA is highly dispersed at lower loadings of PTA on the surface of the support. The FT-IR and Raman spectra results show that the primary structure of Keggin unit remains intact during the impregnation of PTA over the zeolite support. The Pore size distribution results show that large pore size is observed at lower PTA loading and decreases as PTA increases to a higher loading. The TPD of ammonia profile shows that 20 wt% of PTA on the zeolite support possess higher amount of acidity than the rest of the PTA loadings. The FT-IR spectra of adsorbed pyridine catalysts show that 20 wt% of PTA on zeolite show higher amount of Brønsted acidity. In summary, it is observed that the PTA catalysts supported on Y-zeolite are highly active and selective for the title reaction. Among the several catalysts studied, the 20 wt% PTA supported on Y-zeolite show a total conversion of glycerol with 79% acrolein selectivity at 275 °C under normal atmospheric pressure.

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