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# Catalytic dehydration of glycerol to acrolein over $M_{2.5}H_{0.5}PW_{12}O_{40}$ (M = Cs, Rb and K) phosphotungstic acids: Effect of substituted alkali metals

Sharifah Bee Abd Hamid<sup>a,\*</sup> Nur Atiqah Daud,<sup>a</sup> Durga Devi Suppiah,<sup>a</sup> Wageeh Abdulhadi Yehya,<sup>a</sup> Putla Sudarsanam,<sup>b</sup> Suresh K. Bhargava<sup>b</sup> <sup>a</sup> Nanotechnology and Catalysis Research Centre (NANOCAT) University of Malaya, Kuala Lumpur, Malaysia <sup>b</sup> Centre for Advanced Materials and Industrial Chemistry (CAMIC), School of Science, RMIT University, Melbourne VIC 3001, Australia \**Corresponding Author E-mail: sharifahbee@um.edu.my* 

#### Abstract

Catalytic conversion of glycerol into value-added chemicals, particularly acrolein via acidcatalyzed dehydration route has received much attention due to the potential uses of acrolein. This work reports the synthesis of various alkaline metal substituted phosphotungstic acid  $(H_3PW_{12}O_{40}, HPW)$  catalysts, namely  $M_{2.5}H_{0.5}PW_{12}O_{40}$  (M = Cs, Rb and K) using a controlled precipitation method. A systematic structural, morphology, and chemical characterization were conducted using various analytical techniques. XRD studies revealed that the incorporation of alkaline metals in H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> leads to decreased crystallite size and enhanced lattice strain. N<sub>2</sub> adsorption-desorption studies show that the specific surface area of  $H_3PW_{12}O_{40}$  is significantly improved from 5 to 82 ( $K_{2.5}H_{0.5}PW_{12}O_{40}$ ), 103 ( $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ ), and 94 m<sup>2</sup>/g (Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub>). XRD, Raman, and FT-IR studies confirm the Keggin structure of all the alkaline metal substituted HPW catalysts. The acidity strengths estimated by NH<sub>3</sub>-TPD analysis were obtained in the following order: H<sub>3</sub>PW (2654.91  $\mu$ mole/g) > K<sub>2.5</sub>H<sub>0.5</sub>PW (1060.10  $\mu$ mole/g)  $> Rb_{2.5}H_{0.5}PW$  (762.08 µmole/g)  $> Cs_{2.5}H_{0.5}PW$  (461.81 µmole/g). Although alkaline metal substituted H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalysts exhibit higher specific surface area and smaller crystallite size compared to parent  $H_3PW_{12}O_{40}$  low glycerol conversions were found for substituted  $H_3PW_{12}O_{40}$ catalysts. As well, the parent  $H_3PW_{12}O_{40}$  catalyst shows an excellent acrolein selectivity (95%) which is much higher than that of Cs<sub>2.5</sub>H<sub>0.5</sub>PW (81.9%) and very close to the selectivities obtained over Rb<sub>2.5</sub>H<sub>0.5</sub>PW (95.1%) and K<sub>2.5</sub>H<sub>0.5</sub>PW (95.6%) catalysts. The catalytic performance of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and M<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> materials is directly proportional to their acidic

strengths, indicating that the catalyst acidity is a key factor for achieving better results in glycerol dehydration.

Keywords: Heteropolyacid catalyst; Alkali metal substitution; glycerol; dehydration; acrolein

#### 1. Introduction

The transformation of renewable energy feedstocks, especially biomass into valuable chemicals and fuels is currently a hot research topic due to the potentiality of biomass-derived products for replacing fossil fuel-derived products in chemical industry [1]. Glycerol is one of the most valuable biomass-derived molecules that can be largely obtained as the main by-product during biodiesel production via transesterification of vegetable oils and animal fats with ~10 wt% of the total biodiesel synthesized [2], [3]. Therefore, the surplus production of glycerol offers great opportunities for researchers to use glycerol as a bio-renewable source for the synthesis of value-added chemicals and fuels.

The dehydration of glycerol to acrolein is one of the most promising routes of glycerol valorization. Acrolein is an important intermediate for the production of acrylic acid, acrylic acid esters, adhesive, detergents, and polymers [1]. As well, it is a valuable ingredient in the production of quinoline, pentaerythritol, glutaraldehyde, 1,2,6-hexanetriol, and oil-well derivatives [4]. Acrolein is currently obtained from the partial oxidation of petrochemical-derived propene [5]. It is understandable that the production of acrolein from a cheap and abundant biomass-derived glycerol can provide a more economical and sustainable alternative route [1].

Various types of solid acid catalysts have been developed for the dehydration of glycerol to acrolein. The keggin type heteropolyacids (HPAs), which possess strong Brønsted acidity than the zeolites, metal oxides, and concentrated H<sub>2</sub>SO<sub>4</sub>, have been widely used in various acid-catalyzed reactions, including glycerol dehydration [6]. Their chemical composition is typically described as  $XM_{12}O_{40}^{x-8}$  where X is the central atom (Si<sup>4+</sup>, P<sup>5+</sup>, etc.), x is its oxidation state, and M is the metal ion (Mo<sup>6+</sup> or W<sup>6+</sup>). However, the application of HPAs is greatly limited in a number of acid-catalyzed reactions due to their various drawbacks, such as low surface area (<10 m<sup>2</sup>/g), low thermal stability and high polar solubility [1]. Various strategies have been developed to improve the physicochemical, acidic, and catalytic properties of HPAs, including exchange of

its protons (H<sup>+</sup>) with various metal ions and/or dispersing them on suitable supports [7, 8]. Particularly, the incorporation of alkaline metals (e.g., K, Rb, and Cs) into HPAs can improve the specific surface area, water-tolerance ability, and simultaneously adjust the acidity, resulting in enhanced catalytic performance and catalysts' stability [9]. It has been demonstrated that the synthesis of non-stoichiometric K<sup>+</sup> or Cs<sup>+</sup> salts of  $H_3PW_{12}O_{40}$  with a replacement ratio between two and three protons leads to improved specific surface areas. The highest activities in acidcatalyzed esterification of isoamyl alcohol were achieved upon substitution of 2.5 proton equivalents by Cs ion [5].

Therefore, this research work aims to investigate the potential of alkaline metals, such as K, Rb, and Cs to tune physicochemical, textural, and acidic properties of phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) which could replace the corrosive sulfuric acid in glycerol dehydration to acrolein. Various spectroscopic and non-spectroscopic analytical techniques, such as XRD, BET surface area, FT-IR, pyridine adsorbed FT-IR, SEM, NH<sub>3</sub>-TPD, and Raman were used to understand the properties of alkaline metal ion exchanged phosphotungstic acids. The catalytic application of developed acid catalysts was tested for the dehydration of glycerol under liquid-phase conditions.

#### 2. Experimental

#### 2.1 Catalyst synthesis

Various alkaline metal ion exchanged phosphotungstic acids  $(M_{2.5}H_{0.5}PW_{12}O_{40})$ , where M = K, Rb and Cs) were prepared by a controlled precipitation method that has been reported elsewhere [8, 10-12]. In a typical synthesis procedure, the predetermined amounts of aqueous solution of Cs<sub>2</sub>CO<sub>3</sub> (Cs<sup>+</sup>: 0.25 mol dm<sup>-3</sup>) or Rb<sub>2</sub>CO<sub>3</sub> (Rb<sup>+</sup>: 0.25 mol dm<sup>-3</sup>) or K<sub>2</sub>CO<sub>3</sub> (K<sup>+</sup>: 0.25 mol dm<sup>-3</sup>) are added to a 0.08 mol dm<sup>-3</sup> solution of H<sub>3</sub>PW at a rate of 1 mL min<sup>-1</sup> at 30 °C. The white precipitates formed in the solution were aged for 16 hours at 30 °C. The solutions were then filtered off and dried in the oven at 100 °C to remove access liquid. The solid precursor was then calcined at 350 °C for 4 hours under inert atmoshpere conditions.

#### 2.3 Catalyst characterization

The crystalline properties of the catalysts were analysed using powder X-ray diffraction (Bruker D8) theta/2theta goniometer (model D8) equipped with a Cu Kα monochromatized radiation

source and a scintillation counter detector. The data sets were collected in reflection geometry in the range of  $2^{\circ} \le 2\theta \le 80^{\circ}$  with a step size of  $\Delta 2\theta = 0.02^{\circ}$  analysed using High Score Plus software to determine the crystal phases and phase purity. The Keggin structure of the catalysts was confirmed by a Fourier transform infrared (FT-IR) spectroscopy (Bruker, Model IFS 66v/s) using KBr pellet technique with the resolution of 4 cm<sup>-1</sup>. Pyridine adsorbed FT-IR experiments were conducted using a Perkin Elmer spectrum 400. Approximately, 50 mg of catalyst was dried in an oven at 100 °C for 1 hour. Few drops of pyridine (~0.5 ml) were contacted directly with the sample. The sample was then dried in a vacuum oven at 120 °C for 1 hour. The sample was then stored in a desiccator and allowed to cool to room temperature prior to analysis. The spectra were recorded in the range of 1400-1900 cm<sup>-1</sup> using ATR method. Raman spectroscopic investigations were carried out with a Renishaw inVia Raman microscope using a 50x objective lens using 785 nm laser source with instrument grating 1200 1/mm.

The morphology of the catalysts was estimated using Hitachi S-520 scanning electron microscope (SEM) at an accelerated voltage of 5 kV. Specific surface area, pore volume, and pore size distribution of the catalysts were determined using N<sub>2</sub> adsorption-desorption analysis on Sorptometric 1990 instrument. The acidic properties of the catalysts were determined by ammonia temperature-programmed desorption analysis (NH<sub>3</sub>-TPD) using TPDRO 1100 series instrument (Thermo Finnigan). All the samples were pre-treated in nitrogen (30 min, 50 °C) followed by ammonia treatment (30 mL/min). The samples were the continued to be treated with nitrogen (30 min, 50 °C) followed by ammonia desorption from 30 to 900 °C under He flow.

#### 2.3 Catalyst activity test

The catalytic performance of alkaline metal ion exchanged phosphotungstic acids was conducted for the dehydration of glycerol using a 200 mL high-pressure autoclave reactor (Top Industries). For each experiment, 1 mol of glycerol (Friendienmann Schmidt,  $\geq$ 99.8%) and 0.1 g catalyst were loaded into the reactor. The sealed reactor was purged with pure N<sub>2</sub> at room temperature to evacuate air. The reactor was then pressurized with N<sub>2</sub> to 1 bar, followed by heating to the reaction temperature. After reaching the required reaction temperature, time and stirring (300 rpm) were initiated. After each reaction, the reactor was cooled to room temperature and liquid samples were collected for analysis.

Analysis of the products was done by Agilent GC 6890N equipped with two types of detector; flame ionization detector (FID) and thermal conductivity detector (TCD). Three different columns; 30 m x 0.53 mm x 5.00 µm DB1 column, 30 m x 0.32 mm x 20 µm HP-Plot Q and 30 m x 0.53 mm x 40 µm Molesieve (MS) column were used for product separation.

#### 3. Results and Discussion

#### 3.1 Structural Analysis



Figure 1: XRD diffractogram patterns for (a)  $H_3PW_{12}O_{40}$ , (b)  $K_{2.5}H_{0.5}PW_{12}O_{40}$ , (c)  $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ , and (d)  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  catalysts

The crystalline structure and phase integrity of pure HPW and alkaline metal ion exchanged  $(Cs^+, Rb^+, K^+)$  HPW catalysts were evaluated using XRD analysis. Figure 1 shows the characteristic reflections of the parent HPW acid at  $2\theta = 20.8^\circ$ ,  $23.3^\circ$ , 25.5,  $29.5^\circ$ ,  $34.7^\circ$  and  $37.9^\circ$ , which can be assigned to the (211), (220), (222), (400), (332) and (431) planes of face-centered cubic structured phosphotungstic acid, respectively (PDF-File 00-050-0304). Table 1 shows the main diffraction peaks with the corresponding d-spacings and relative intensities for the parent phosphotungstic acid.

No	2θ (°)	d-spacing (Å)	Intensity (%)	
1	20.8	4.27	40.7	
2	23.3	3.82	33.2	
3	25.5	3.51	100.0	
4	29.5	3.02	53.0	
5	34.7	2.58	72.8	
6	37.9	2.37	35.6	

**Table 1:** Main diffraction reflections, d-spacing and their relative intensity of the parent

 phosphotungstic acid (PDF-file: 00-050-0304)

The most intense peak observed at  $25.5^{\circ}$  (hkl 222) for the parent H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> acid has been marked as the signature peak representing the Keggin structure of phosphotungstic acid. This peak was also observed in the XRD patterns of all the alkaline metal substituted HPW catalysts; however it is shifted to higher angles (Fig. 1 and Table 2). Lattice strain and crystallite size of the catalysts were calculated using Scherrer equation [13] and the values were listed in Table 2. Substitution of protons by metal ions with different ionic radius causes a rearrangement of the secondary structure which also affects the crystallite size [14]. It was found that the replacement of protons with the alkaline metal ions leads to a significance decrease in the crystallite size of the phosphotungstic acid. This observation indicates that the exchanged alkaline metal ions played a crucial role in improving the thermal stability of the phosphotungstic acid. It is interesting to note from Table 2 that the crystallite size increases with the decrease of ionic radius of substituted alkaline metals:  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  (13.8 nm) <  $Rb_{2.5}H_{0.5}PW_{12}O_{40}$  (28.1 nm)  $< K_{2.5}H_{0.5}PW_{12}O_{40}$  (38.9 nm). It can be also noted from Table 2 that the prepared catalysts have different lattice strain values. As reported by Hanan Atia et al. the larger the size of metal cation, the higher the lattice strain of heteropolyacids [5]. Therefore, the percentage of the lattice strains and the size of d-spacing increases as the size of alkaline metal cation increases [15].

	22 2	Crystanne size	Lattice strain	d-spacing
	(20)	(nm)	(%)	(Å)
$H_{3}PW_{12}O_{40}$	25.517	43.6	0.360	3.51
$K_{2.5}H_{0.5}PW_{12}O_{40}\\$	26.601	38.9	0.388	3.34
$Rb_{2.5}H_{0.5}PW_{12}O_{40}$	26.423	28.1	0.539	3.37
Cs <sub>2.5</sub> H <sub>0.5</sub> PW <sub>12</sub> O <sub>40</sub>	26.059	13.8	1.112	3.42
		MA		

**Table 2**: Bragg angle, crystallite size, lattice strain, and d-spacing of the catalysts

#### 3.2 Surface area and porosity determination



Figure 2:  $N_2$  adsorption-desorption isotherms of (a)  $H_3PW_{12}O_{40}$ , (b)  $K_{2.5}H_{0.5}PW_{12}O_{40}$ , (c)  $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ , and (d)  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  catalysts.

Catalyst <sup>a</sup>	$\frac{S_{BET}}{(m^2g^{-1})}$	Micropore volume (cm <sup>3</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Mesopore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average pore diameter <sup>c</sup> (nm)	$S_{BETExt}^{d}$ (m <sup>2</sup> g <sup>-1</sup> )	
HPW	5	0.0121	0.0245	0.0124	98.6	4.6	
K <sub>2.5</sub> HPW	82	0.0106	0.0225	0.0119	22.9	71.5 [87.2%]	
Rb <sub>2.5</sub> HPW	103	0.1089	0.2229	0.1140	50.6	69.3 [67.3]	
Cs <sub>2.5</sub> HPW	94	0.0891	0.1897	0.1006	45.1	68.1 [72%]	

**Table 3**: BET surface area ( $S_{BET}$ ), pore volume, and pore size of the pure HPW and alkalinemetal ion exchanged HPW catalysts

<sup>a</sup> HPW=  $H_3PW_{12}O_{40}$ ,  $K_{2.5}HPW=K_{2.5}H_{0.5}PW_{12}O_{40}$ ,  $Rb_{2.5}HPW=Rb_{2.5}H_{0.5}PW_{12}O_{40}$ , and  $Cs_{2.5}HPW=Cs_{2.5}H_{0.5}PW_{12}O_{40}$ 

<sup>b</sup> DET surface area

<sup>b</sup>BET surface area

<sup>c</sup> Desorption average pore diameter

<sup>d</sup> External surface area from *t*-plot. The percentages in the square brackets show the fractions of external surface area to the total surface area.

The textural properties of pure HPW and alkaline metal ion exchanged HPW catalysts were investigated using N<sub>2</sub> adsorption-desorption analysis (Figure 2). As shown in Figure 2, the parent HPW (Figure 2a) exhibits a type II adsorption isotherm based on IUPAC classification which is usually observed for non-porous or macroporous materials. The structure of HPW indicates that it contains unrestricted monolayer and multilayer adsorption, where the monolayer coverage is completed at low relative pressure [16]. However, all the alkaline metal submitted  $M_{2.5}H_{0.5}PW_{12}O_{40}$  (M = K, Rb, and Cs) materials exhibit type IV isotherms with H2 hysteresis loop (Figure 2 (b), (c), (d)) which is usually observed for mesoporous materials in accordance to IUPAC classification [13]. The H2 hysteresis loop reveals the presence of slit-like pores in the synthesized  $M_{2.5}H_{0.5}PW_{12}O_{40}$  catalysts. This observation indicates that the incorporation of K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> into H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> altered its textural properties.

Table 3 summarizes the BET surface area, pore volume and pore size of the catalysts. The external surface areas were calculated from the obtained *t*-plot. It was found that the substitution of alkali metals in HPW leads to improved specific surface areas (Table 1). The specific surface areas of alkaline metal substituted HPW catalysts were in the range from 82 to 103 m<sup>2</sup> g<sup>-1</sup>. Among the synthesized  $M_{2.5}H_{0.5}PW_{12}O_{40}$  (M = K, Rb, and Cs) materials, the  $Rb_{2.5}H_{0.5}PW_{12}O_{40}$  catalyst has the highest specific surface area (103 m<sup>2</sup> g<sup>-1</sup>) and the highest pore volume (0.2229 cm<sup>3</sup>g<sup>-1</sup>). However, it was also noted that the external surface area of  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  and  $Rb_{2.5}H_{0.5}PW_{12}O_{40}$  were 72% and 67% of the total surface area, respectively. On the other hand, the fraction of external surface area of  $K_{2.5}H_{0.5}PW_{12}O_{40}$  catalyst has a greater adsorption capacity for large molecules because of great external surface area that can be seen in Table 3.

#### 3.3 Morphology analysis

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Figure 3 shows the SEM images of the catalysts. It can be clearly observed that by substituting the proton with alkali metal ions in  $H_3PW_{12}O_{40}$ , a more defined spherical structure was noticed. This observation supports the argument that the substitution of alkaline metal ions leads to distortion of the secondary Keggin structure of HPW acid, causing a reorganization of the polyoxometalate structure. The surface of parent HPW (Figure 3 (a)) appears to be smooth and 1-dimensional. Interestingly, the morphology and particle size of HPW is found to be highly dependent on the nature of the alkaline metal. The substitution of alkaline metal cation having a larger radius (Cs<sup>+</sup>) leads to the formation of smaller particles as shown in Figure 3 (d). In contrast, smaller sized K<sup>+</sup> substitution in HPW results in the larger particles (Figure 3 b).



Figure 3: SEM micrographs of a)  $H_3PW_{12}O_{40}$ , (b)  $K_{2.5}H_{0.5}PW_{12}O_{40}$ , (c)  $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ , and (d)  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  samples.

### **3.4 Spectroscopic analysis**

Figure 4(a) shows the FT-IR spectra of  $H_3PW_{12}O_{40}$ ,  $K_{2.5}H_{0.5}PW_{12}O_{40}$ ,  $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ , and  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  catalysts. The observed FT-IR bands in the range of 400-1200 cm<sup>-1</sup> confirm the Keggin structure of the materials (Figure 4b). The noticed IR band at ~1080 cm<sup>-1</sup> can be assigned

to the asymmetric stretching vibration of P-O in the central tetrahedron. The band at 980 cm<sup>-1</sup> corresponds to the stretching vibration of terminal  $W = O_t$  (O<sub>t</sub> is terminal oxygen in the Keggin structure), whereas the bands at 890 and 800 cm<sup>-1</sup> indicate W-O<sub>c</sub>-W and W-O<sub>e</sub>-W linkages, respectively [18]. These bands indicate the presence of PW<sub>12</sub>O<sub>40</sub> anion in the alkaline metal exchanged heteropolyacids. A low intensity band appeared at 552 cm<sup>-1</sup> is due to O-P-O and W-O-W linkages [19]. A broad band noticed in the range of 3000-3700 cm<sup>-1</sup> indicates hydroxyl groups from protonated water cluster (H<sub>5</sub>O<sub>2</sub><sup>+</sup>) [20] in catalysts, which can be further confirmed by bending vibration band at 1630 cm<sup>-1</sup>. It can be noted from Figure 4 (b) that the configuration of Keggin anion remains stable for all the catalysts. Therefore, it can be stated that despite the nature of substituted alkaline metal ion, all the samples possess a discrete unit of Keggin network which comparatively stable upon the substitution of alkaline metals.





**Figure 4: (a)** FT-IR spectra of pure  $H_3PW_{12}O_{40}$ ,  $K_{2.5}H_{0.5}PW_{12}O_{40}$ ,  $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ , and  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ , catalysts (4000 – 400 cm<sup>-1</sup>) and; (b) magnified FT-IR spectra of Keggin region (1300 – 400 cm<sup>-1</sup>).

Figure 5 shows Raman spectra of pure HPW and alkaline metal ion substituted HPW catalysts in the range of  $100 - 1100 \text{ cm}^{-1}$ . Raman spectroscopy was widely applied as a sensitive technique to study the chemical Keggin structure of the phosphotungstic acids. The H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> sample showed a strong band at 1004 cm<sup>-1</sup> with a shoulder at 993 cm<sup>-1</sup>, which can be attributed to the W=O stretch and W-O-W bending, respectively. A weak broad band is appeared at 904 cm<sup>-1</sup> which can be assigned to the bringing (W-O-W) stretching mode. The noticed weak band at 538 cm<sup>-1</sup> indicates O-Si-O bending, while those at 148, 213 and 235 are associated with W-O stretching mode and W-O-W bending modes [21]. There was no much difference in Raman spectrum of parent HPW catalyst upon the substitution of alkaline metal ions except around 100 – 200 cm<sup>-1</sup> region. This observation is due to the substitution of different sized alkaline metals into the Keggin structure of HPW acid, hence changes in W-O stretching mode and W-O-W bending modes [22].



Figure 5: Raman spectra of the (a)  $H_3PW_{12}O_{40}$ , (b)  $K_{2.5}H_{0.5}PW_{12}O_{40}$ , (c)  $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ , and (d)  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  catalysts

#### 3.5 Catalyst acidity determination

The NH<sub>3</sub>-TPD analysis was performed from 50 to 900 °C to estimate acidic strength of the catalysts (Figure 6). According to Tababe et al. [23] the strength of acidic sites can be classified by the temperature of desorbed NH<sub>3</sub> as weak (150–300 °C), moderate (300–500 °C) and strong acidic sites ( $\geq$ 500 °C). The estimated total acidic strength of the catalysts was presented in Table 4. Pure HPW sample shows two distinct peaks at low (194 °C) and high temperature (609 °C), indicating the presence of weak and strong acidic sites, respectively [24]. It can be noted from Fig. 6 and Table 4 that high concentration of strong acid sites is found in pure HPW sample compared to weak acidic sites. It is interesting to note that the peak at higher temperatures disappears after the replacement of H<sup>+</sup> ions with alkaline metal ions in HPW acid. As shown in Table 4, the parent HPW catalyst has high concentration of acidic sites and its acidic strength is

decreased with the substitution of alkaline metal cations in the order of  $K_{2.5}H_{0.5}PW_{12}O_{40} > Rb_{2.5}H_{0.5}PW_{12}O_{40} > Cs_{2.5}H_{0.5}PW_{12}O_{40}$ .



Figure 6: NH<sub>3</sub>-TPD profiles of (a)  $H_3PW_{12}O_{40}$ , (b)  $K_{2.5}H_{0.5}PW_{12}O_{40}$ , (c)  $Rb_{2.5}H_{0.5}PW_{12}O_{40}$ , and (d)  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  catalysts

Table 4: Acidity of the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> and alkaline metal ion substituted H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> catalysts

0 1	NH <sub>3</sub> -TPD peak position	Acid amounts	Total acidity	
Sample	(°C)	(µmole/g)	(µmole/g)	
$H_{3}PW_{12}O_{40}$	194	1062.42	2654.91	
0	609	1592.49		
$K_{2.5}H_{0.5}PW_{12}O_{40}$	183	1060.10	1060.10	
$Rb_{2.5}H_{0.5}PW_{12}O_{40}$	143	762.08	762.08	
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	168	461.81	461.81	



Fig. 7: Pyridine FTIR spectra of  $H_3PW_{12}O_{40}$  and  $M_{2.5}H_{0.5}PW_{12}O_{40}$  (M = Cs, Rb and K) samples: B – Brønsted, L – Lewis acidic sites and Pyr – Pysisorbed Pyridine

Fig. 7 shows pyridine adsorbed FT-IR spectra of the prepared catalysts. Various FT-IR peaks related to Brønsted and Lewis acid sites can be noticed in Fig. 7. The observed band at around 1637 cm<sup>-1</sup> can be assigned to the presence of Brønsted acidic sites in the catalysts. Though this peak was not obvious in  $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  catalyst due to low transmittance recorded, the peak appeared at 1556 cm<sup>-1</sup> proves the existence of Brønsted acidic sites. The FT-IR peak noticed at ~1487 cm<sup>-1</sup> indicates the existence of both Brønsted and Lewis acid sites in the catalysts [25]. The sharp IR band appeared at 1440 cm<sup>-1</sup> is attributed to the physisorbed pyridine [26]. It can be noticed from Fig. 7 that the parent  $H_3PW_{12}O_{40}$  catalyst exhibits high intensity FT-IR peaks, indicating high concentration of acid sites especially Brønsted acidity compared with that of alkaline metal substituted  $H_3PW_{12}O_{40}$  catalysts.

#### 3.6 Catalytic activity results

The liquid phase dehydration of glycerol to acrolein was performed using pure HPW and  $K_{2.5}$ ,  $Rb_{2.5}$  and  $Cs_{2.5}$  substituted HPW catalysts. The reaction was performed in a 200 mL autoclave reactor at 250 °C, and pressurized with 1 bar of  $N_2$  for 2 hours. The major product in the dehydration of glycerol over heteropolyacid catalysts was acrolein. In addition, various oxygenated products are possible in this reaction, which include hydroxyacetone, acetic acid, acetaldehyde, propanal and acrylic acid. The obtained results for glycerol dehydration over blank and various catalysts were presented in Table 5 and Figure 8.

 Table 5: Conversion of glycerol and products selectivity obtained from glycerol dehydration

 over blank and various catalysts at 250 °C for 2 hours

	Conversion	Selectivity (%)					
Catalyst	(%)	acrolein	crolein hydroxy- acetic acetalde-		nnononol	acrylic	
			acetone	acid	hyde	propanai	acid
Blank	65.8	18.5	47.1	5.2	6.7	2.8	19.7
HPW	96.3	95.0	3.9	0.1	0.0	0.1	1.0
Cs <sub>2.5</sub> HPW	88.6	81.9	16.0	0.2	0.6	0.1	1.1
Rb <sub>2.5</sub> HPW	91.2	95.1	3.6	0.1	0.0	0.1	1.0
K <sub>2.5</sub> HPW	91.3	95.6	3.2	0.1	0.1	0.1	0.9

A 65.8% of glycerol conversion was found under blank reaction conditions (Table 5). The parent HPW and the alkaline metal ion substituted HPW catalysts clearly exhibit higher glycerol conversion and superior acrolein selectivity compared to blank reaction. Among all the catalysts tested, the parent HPW catalyst exhibits the highest glycerol conversion (96.3%) in glycerol dehydration reaction. For alkaline metal ion exchanged HPW catalysts, the glycerol conversion increases with the decrease of ionic size of alkali metals;  $Cs_{2.5}HPW$  (88.6%) <  $Rb_{2.5}HPW$  (91.2%) <  $K_{2.5}HPW$  (91.3%). Figure 9 shows products distribution in glycerol dehydration obtained over blank, parent HPW, and alkaline metal ion substituted HPW catalysts. The  $K_{2.5}HPW$  catalyst not only gave the highest conversion of glycerol but also the highest selectivity towards acrolein compared to other alkaline metal substituted HPW catalysts (Table 5). The selectivity of hydroxyacetone however decreases with the decrease of the catalyst acidity (Table 5). Although alkaline metal substituted  $H_3PW_{12}O_{40}$  catalysts exhibit higher specific surface area

(Table 3) and smaller crystallite size (Table 2) compared to parent  $H_3PW_{12}O_{40}$  low glycerol conversions were found for substituted  $H_3PW_{12}O_{40}$  catalysts (Table 5). As well, the parent  $H_3PW_{12}O_{40}$  catalyst shows excellent acrolein selectivity (95%) which is much higher than that of  $Cs_{2.5}H_{0.5}PW$  (81.9%) and very close to the values obtained over  $Rb_{2.5}H_{0.5}PW$  (95.1%) and  $K_{2.5}H_{0.5}PW$  (95.6%) catalysts. It was found that the catalytic performance of  $H_3PW_{12}O_{40}$  and  $M_{2.5}H_{0.5}PW_{12}O_{40}$  materials is directly proportional to their acidic strengths (Table 4). This indicates that the catalyst acidity is a key factor for achieving better results in glycerol dehydration reaction [25]. Although direct comparisons with previous studies is quite difficult because of diversity in reactor type and reaction conditions used, however, the results of the present study show that the parent HPW and alkaline metal ion substituted HPW catalysts in liquid phase exhibit a comparable performance in dehydration of glycerol to acrolein compared to that of other type acid catalysts (e.g., zeolite and mixed oxides) and gas phase reaction reported in previous study [27-29].



**Figure 8:** Conversion of glycerol and selectivity and yield of acrolein for blank, HPW and alkaline metal ion substituted HPW catalysts.



Scheme 1: Reaction mechanism for glycerol dehydration over HPW-based catalysts



**Figure 9:** Products selectivity distribution over blank, HPW, and alkaline metal ion substituted HPW catalysts at 250 °C for 2 hours.

Scheme 1 shows the probable reaction mechanism for the dehydration of glycerol over HPWbased catalysts. The Bronsted acidic sites intiate the dehydration of glycerol, resulting in two enol intermediate formation. This enol rapidly changes to 1-hydroxyacetone and 3hydroxypropanal (3-HPA). The 3-HPA is highly unstable at higher reaction temperature, thus the

subsequent dehydration of 3-HPA gives acrolein [20]. It was obvious that the production of acrolein can be controlled by the intial dehydration step [20].

#### Conclusions

In this paper, the substitution of alkaline metals, such as K, Rb and Cs has proven to tune the properties of phosphotungstic acid (HPW). Particularly, the alkaline metal ion substituted HPW catalysts show smaller crystallite size and superior specific surface area compared to parent HPW acid. This observation indicates that alkaline metal ions enhance thermal stability of HPW acid. The Keggin structure of the synthesized alkaline metal ion substituted HPW catalysts is confirmed by XRD, Raman and FT-IR analyses. NH<sub>3</sub>-TPD studies reveal that the parent HPW catalyst exhibits the highest total acidity (2654.91  $\mu$ mol/g) compared to K<sub>2.5</sub>HPW (1060.10  $\mu$ mol/g), Rb<sub>2.5</sub>HPW (762.08  $\mu$ mol/g) and Cs<sub>2.5</sub>HPW (461.81  $\mu$ mol/g) catalysts. Among the catalysts tested, the parent HPW catalyst exhibits the best performance with a superior selectivity of acrolein (95.0 %) and glycerol conversion of 96.3% at 250 °C for 2 hours due to its superior acidic capacity.

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### Crystallize Size decreasing

