Supported silicotungstic acid on zirconia catalyst for gas phase dehydration of glycerol to acrolein

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A B S T R A C T

The gas phase dehydration of glycerol to acrolein over a series of supported silicotungstic acid (HSiW) on zirconia (10HZ, 20HZ, 30HZ and 40HZ) has been investigated. The catalysts were characterized by temperature programmed desorption, nitrogen adsorption–desorption, thermogravimetric analysis, Fourier transform infrared spectroscopy, X-ray diffraction, field-emission scanning electron microscopy and energy dispersive X-ray techniques. The large pore diameters (>19 nm) of the prepared catalysts alleviated the coke deposition effect. Also, the specific surface area and acidity of the samples surged from 18 to 22 m²/g and 0.38 to 1.24 mmol/g cat, respectively by varying HSiW loadings from 10 to 40 wt% on zirconia. The highest acrolein yield achieved was 63.75% at 92% glycerol conversion over 30HZ catalyst for 10 wt% glycerol feed concentration and 300 °C reaction temperature in 3 h. The combined physico-chemical characteristics of 30HZ made it more superior compared with other samples in the current study.

1. Introduction

Relentless environmental concerns, steep hike in fossil fuel price, and increasing demand for non-renewable fossil fuels consumption have led to dramatic surge in the global search for alternative energy, particularly biodiesel [1–3]. It is estimated that global biodiesel production will reach 37 billion gallons by 2016 [4] largely because of the outstanding biodiesel characteristics: environmental friendly, technically feasible, and biodegradable [5].

The huge amount of biodiesel production worldwide directly affects glycerol availability, since 10% of the total transesterification process is glycerol [6]. The surplus offers great opportunities for researchers to use glycerol as a bio-renewable source for value-added chemical production. According to recent studies, glycerol was acknowledged as one of the top 12 most important bio-based chemicals in the world [7] and it will become the major chemical for future bio-refineries. Indeed, the application of glycerol for production of more than 2000 products was reported recently [8]. The three most important value-added chemicals that can be produced from glycerol are 1,3-propanediol, hydrogen, and acrolein by fermentation, thermal reforming, and dehydration processes, respectively.

Acrolein is an important and versatile intermediate in the chemical industries. It can be used in the production of acrylic acid, superabsorbent polymers (SAP) and methionine, which is widely used in manufacturing of plastics, coatings, adhesives, diapers, and even animal food. Acrolein can be produced by petroleum-based (oxidation of propylene) or bio-based (dehydration of glycerol) routes, but the bio-based method attracted much attention as petrochemical exhaustion is foreseen in the near future. Glycerol dehydrogenation to acrolein is commonly performed over acid catalysts. Thus, applications of various types of solid acid catalysts have been reported in gas or liquid phase dehydration of glycerol to acrolein such as supported heteropoly acids [9–11], zeolites [12–14], and metal oxides [15–17].

Heteropoly acids (HSiW, HPW, and HPMo) catalysts are widely investigated in glycerol dehydration studies to acrolein since heteropoly acids (HPAs) have strong acidity (Bronsted acidic sites), uniform acidic sites, and easily tunable acidity. However, low thermal stability, low surface area, and easy leaching in polar solvents are the main disadvantages of HPAs. To overcome the disadvantages, HPAs are often supported over acidic or natural carriers such as alumina, titanium, zirconia, and silica. The main benefits related to each of these supports are reported in various studies. For instance, large surface metal oxides prevent damage to HPAs structure even at temperatures >500 °C [18]. Zhu et al., [19] reported that zirconia exhibited better results compared to SiO₂ and it enhanced the Keggin structure stability of HPW up to 750 °C. In fact, strong interaction between the catalyst active sites (Keggin anions) and
ZrO₂ made it a better support for HSiW. Alsaleme et al. [20] revealed that interaction between HPAs and various supports decreased in the order of ZrO₂ > Nb₂O₅ > TiO₂ > SiO₂. Also, zirconia improved the stability of HSiW supported on SBA-15 catalyst and 20%HSiW-SBA-20%Zr gave 88% acrolein selectivity even after 25 h at 78% glycerol conversion [21].

The main drawback for commercialization of bio-based glycerol dehydration to acrolein over different solid acid catalysts in gas phase is coke deposition. Coking on the catalyst surface substantially reduces the catalyst activity. Cs-HPW catalyst displayed the highest ever reported catalyst selectivity of 98% at complete glycerol conversion, but it deactivated very fast (stable for a few hours only) due to excessive coke deposition [22]. Indeed, small pore diameters (steric limitation) and low or highly strong catalyst acidity favored coking [23]. In addition, high reaction temperature is another factor which increases the probability of coke deposition.

Previously, other researchers have proposed four methods to reduce coking on catalyst surface: co-feeding of oxygen or hydrogen, periodic regeneration of catalyst or pulse injection, moving bed reactor for circulation of catalyst, and recently application of noble metals in catalysts. However, each method has its own disadvantages such as explosive condition or oxidation of reaction products, loss of productivity, serious technical difficulties, and high costs, respectively. Yun et al. [24] recently demonstrated that high acidity and large pore size directly affected coke deposition on catalyst surface. Therefore, in this research we suggest that improvement of catalyst textural properties such as pore size, acidity, and thermal stability during the catalyst preparation step can enhance the long-term stability of the catalyst.

Among various HPAs, silicotungstic acid (HSiW) was chosen due to its strong acid sites (Bronsted) and higher water tolerance. Meanwhile, zirconia was selected as a support to increase long-term and thermal stabilities. The loadings of HSiW in the HSiW-ZrO₂ catalysts were varied from 10 to 40 wt%. The objective of this study is to prepare and test a group of catalysts with high surface acidity, high thermal stability, and particularly large pore diameter to significantly reduce the effect of coke deposition on the catalyst surface during the gas phase dehydration of glycerol to acrolein. After the optimal catalyst for glycerol dehydration to acrolein was determined, effect of different reaction temperatures (280–320 °C), long-term catalyst stability, and Keggin anion density on the catalyst activity was investigated.

2. Materials and methods

Glycerol (purity >99%), silicotungstic acid (H₄SiW₁₂O₄0·14H₂O (HSiW)), and zirconium (ZrO₂) were purchased from Sigma–Aldrich (Malaysia). Other chemicals including acetic acid, allyl alcohol, hydroxyacetone, acetone, propanal, ethanal at reagent grade were also supplied by Sigma–Aldrich (Malaysia). Acrolein at reagent grade was purchased from Scientific Trends (M) Sdn. Bhd.

2.1. Catalyst preparation

A series of catalysts with different HSiW loadings (10, 20, 30, and 40 wt%) on zirconia were prepared by the incipient-wetness impregnation method. In this method, aqueous HSiW was added drop wise to the zirconia support. The suspension was rigorously stirred for 12 h followed by drying at 110 °C for 18 h. The HSiW-ZrO₂ supported catalysts were denoted as 10HZ, 20HZ, 30HZ, and 40HZ for 10, 20, 30 and 40 wt% of HSiW loading, respectively.

2.2. Catalyst characterization

Nitrogen adsorption/desorption at −196 °C was employed to determine the BET surface area, pore volume, and average pore diameter (Thermo Scientific, SURFAR). Prior to each analysis, the sample was degassed under vacuum at 200 °C for 4 h to ensure complete removal of adsorbed moisture. The BJH method was used for average pore diameter calculation.

Thermogravimetric analysis (TG) of the prepared catalyst was performed using a THERMO TGA instrument in a temperature range of 30–800 °C with a ramp rate of 10 °C/min under nitrogen flow. The Fourier Transform Infrared Spectroscopy (FTIR) spectra of the freshly prepared catalysts were performed by a Perkin Spectrum One FTIR spectrometer with a spectral resolution of 2 cm⁻¹ and scan time of 1 s. Before the curves were recorded, approximately 1 wt% of each sample was dissolved in KBr.

The morphology of the samples was observed by Field Emission Scanning Electron Microscopy (FESEM, HITACHI, SU-8000) with STEM detector. All samples were coated with gold under vacuum condition in an argon atmosphere ionization chamber. Energy dispersive X-ray (EDX) analysis was carried out with the same equipment.

The elemental characterization of the used catalysts substances in terms of coke content was determined by Thermo Scientific Flash 2000 instrument. First, each sample was weighed in a tin capsule and then placed in the combustion reactor. The reaction was performed in a furnace at 900–1000 °C. Small volume of oxygen (O₂) was added to the system to burn the inorganic or organic materials. As a result, the sample was converted to simple elemental gases. Finally, a TCD detector with separation column was used to determine the coke content.

The total acidity of the prepared catalysts was determined by temperature programmed desorption of ammonia (NH₃–TPD) using the Micrometrics Auto Chem II instrument. A specified amount of catalyst was dried at 200 °C for 1 h by saturation of NH₃ at 60 °C for 0.5 h before the physically adsorbed NH₃ was removed by helium purging at 60 °C for 0.5 h. The temperature was ramped at a heating rate of 20 °C/min to 700 °C to desorb the chemically absorbed NH₃.

X-ray diffraction (XRD) was used to determine the structure of the prepared catalysts and to evaluate the degree of crystallinity. The XRD patterns were obtained by D5000 Siemens instrument using CuKα radiation (40 keV, 40 mA). The patterns were scanned in the 2θ range of 10–80° (step width 0.05°, 1 s per step).

2.3. Catalytic reaction

The gas phase glycerol dehydration was conducted at atmospheric pressure in a vertical fixed bed quartz reactor (30 cm length, 11 mm i.d.) using 0.5 g catalyst sandwiched between plugs of glass wool. Prior to reaction, the catalyst was pretreated at reaction temperature (300 °C) under nitrogen (N₂) flow (1200 ml/h) for 1 h. Aqueous glycerol (10 wt%), pre-heated to 300 °C for complete vaporization, was swept into the reactor by a syringe pump at 2 ml/h flow rate. Gas hourly speed velocity (GHSV) of the inert carrier gas was 1200 h⁻¹. After 3 h, the products and unconverted glycerol were condensed in a water–ice salt bath (−5 °C) and collected hourly for analysis. n-Butanol was added to the condensed products as internal standard. The final solution was analyzed by a gas chromatograph (GC) equipped with a capillary column (DB wax; 30 m × 0.53 mm × 0.25 μm) and FID detector. To achieve effective product separation, the column was held at 40 °C for 4 min before the temperature was ramped up to 200 °C at a rate of 12 °C/min and remained there for 23 min. The glycerol
conversion, product selectivities and yields are defined by equations (1)–(3):

\[
\text{Glycerol conversion(\%) = } \frac{\text{Moles of reacted glycerol}}{\text{Moles of glycerol in the feed}} \times 100\%
\]

(1)

\[
\text{Product selectivity(\%) = } \frac{\text{Moles of each product}}{\text{Moles of reacted glycerol}} \times 100\%
\]

(2)

\[
\text{Product yield(\%) = } \frac{\text{Moles of each product}}{\text{Moles of glycerol in feed}} \times 100\%
\]

(3)

3. Results and discussions

3.1. Adsorption isotherm, surface area, pore structure analysis

The summary of surface area (S\text{BET}), pore volume (V\text{p}), average pore diameter (P\text{d}), and pore area (P\text{a}) of 10HZ, 20HZ, 30HZ, and 40HZ supported silicotungstic acid on zirconium oxide, derived from nitrogen physisorption isotherms, is presented in Table 1. The specific surface areas of pure HSiW and ZrO\text{2} were 8.20 and 14.00 m\text{2}/g, respectively. By increasing the amount of HSiW from 10 to 40 wt% on the ZrO\text{2} support, the surface areas of the prepared catalysts increased dramatically from 18.00 to 22.00 m\text{2}/g. Indeed, the surface area of 40HZ sample exhibited 50% enlargement compared with bulk ZrO\text{2}. Chai et al., [25] reported similar results with the addition of 5–15 wt% phosphotungstic acid (HPW) on zirconia. Theoretically, there should be some plugging after HSiW was added to the support. However, the larger surface areas were attributed to the porous characteristics of ZrO\text{2}, which enhanced its own surface area after combining with HSiW [21]. Large size metal cations increased the interstitial volume among Keggin anions forming new pores. Consequently, surface areas which were blocked by plugging were renewed [18].

Impregnation of silicotungstic acid on ZrO\text{2} had no effect on supported catalyst pore volumes (V\text{p}=0.65 cm\text{3}/g) except for 10HZ. The pore volume of 10HZ was twice the volume of pure zirconium oxide. However, the average pore diameter registered proportional reduction from 39.50 to 19.00 nm with increasing HSiW. In fact, the pore diameter for 40HZ exhibited 50% reduction compared to the bare zirconia. Pore plugging is the main reason for the reduction in pore diameters as HSiW Keggin anion size (D = 1.2 nm) is small enough to enter the micropores of zirconia [19,21].

3.2. Catalyst acidity

The NH\text{3}-TPD profile and acidity strength of the prepared catalysts are exhibited in Fig. 1 and Table 2. The strength of the acidic sites is calculated by the TPD peak position [26]. The acid sites are divided into three groups: weak, medium, and strong based on the temperature of the TPD peak position. The total acidity of pure zirconia and HSiW are 0.19 and 1.62 mmol/g, respectively. The total acidity of the supported HSiW catalysts increased from 0.38 to 1.24 mmol/g with HSiW loading on zirconia. All samples displayed three peaks: the first two peaks were in the weak acidic strength (100–300 °C) and the third was in the strong acidic strength (>450 °C). It was also observed the TPD peaks related to the strong acid strength shifted to higher temperatures from 481 to 516 °C when the HSiW loading increased (Fig. 1). Indeed, the acid site strength increased with higher HSiW loading. The main reason for the shift of the TPD peak position is attributed to the hydroxyl groups on the ZrO\text{2} surface, which were protonated with water during the impregnation process. Consequently, with addition of HSiW an electronic interaction occurred between HSiW and ZrO\text{2}, which caused stronger bonding between HSiW and ZrO\text{2} [12,27].

3.3. FTIR spectroscopy

Fig. 2 exhibits the FTIR spectra for HSiW, ZrO\text{2} and supported HSiW (10–40 wt%) on zirconium oxide. The pure HSiW spectra rendered three major absorption peaks at 874, 931, and 981 cm\text{−1}. These three peaks are assigned to W=O (981 cm\text{−1}), Si–O (931 cm\text{−1}), and W–O–W (874 cm\text{−1}) silicotungstic anions, respectively [28,29]. All the supported catalysts (10–40HZ) exhibit absorption peaks of 874, 931, and 981 cm\text{−1} to consolidate the presence of the Keggin structure. In fact, the spectra are able to confirm the structural stability of the HSiW even after impregnation [30].

3.4. Morphological analysis

The field emission scanning electronic micrograph (FESEM) of the fresh and used 30HZ catalyst, which exhibited the highest catalytic activity in this study, is presented in Fig. 3. Pure ZrO\text{2} has plate like morphology [31–33]. HSiW particles are regular in shape and are dispersed uniformly on the external surface of the ZrO\text{2} (Fig. 3a–b), which reflects the surge of the specific surface area and porosity according to the BET results. Indeed, the surface area of pure ZrO\text{2} was 14.01 m\text{2}/g, but supported 30HZ sample registered more than 40% surface area increment to 19.76 m\text{2}/g. Most importantly, no dramatic change on the catalyst surface morphology was seen after the dehydration reaction (Fig. 3c–d). Indeed, FESEM image reveals that the catalyst morphological characteristics remain unaffected during the reaction due to the good hydrothermal stability of zirconia (confirmed by TGA results). Similar results were also reported elsewhere [34–36].

The EDX analysis was performed at higher magnification for the 30HZ sample (Fig. 3e). EDX mapping confirmed an extremely homogenous distribution of zirconium (Zr) and tungsten (W) elements throughout the 30HZ catalyst (Fig. 3f–g). In addition, the EDX results indicated 29.9 and 70.8 wt% of HSiW and ZrO\text{2} in the catalyst sample conforming to the theoretical values of 30 and 70 wt%, respectively. These results can strongly assure the precision of the preparation method and strongly supports our earlier claim on the stability of the catalyst structure under dehydration reaction conditions. Fig. 3h exhibits the EDX spectra of W and Zr elements of fresh 30HZ catalyst.

3.5. Thermal stability

The thermal stability of supported HSiW on ZrO\text{2} was determined by thermogravimetric analysis (TGA) under nitrogen flow (Fig. 4). The thermal decomposition of the bulk HSiW is reported at 445 °C in the literature [37]. The thermal degradation profile of HSiW displays three weight-loss steps from room temperature to 800 °C, maximized at 85, 200, and 480 °C. The first two decrements of 9% and 3% at 85 and 200 °C respectively, are attributed to the loss of crystallization water [38–40]. The third weight loss (1%) at 480 °C indicates the decomposition of the HSiW Keggin units [23,41]. In addition, pure ZrO\text{2} only sample registered weight loss during heating from ambient temperature to 800 °C due to loss of physically adsorbed water. More notably, 30HZ catalyst exhibited a characteristic loss of only 1% of crystalline water between 30 and 150 °C, above which the prepared catalyst did not exhibit any weight loss. Most possibly it is attributed to the high stability of the catalyst compared to pure HSiW owing to the electronic interaction between HSiW and zirconia. In fact, the protonated hydroxyl groups on the surface of zirconia metal oxide are in contact with water during the reaction and produces Zr–OH\text{2}⁺ species. The latter species and negatively charged heteropoly anions have strong interaction with electronic effect [12,27]. The electronic interaction between HSiW and zirconia is higher, even stronger than silica [21,30]. Thus,
Table 1

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>( \text{Pv} ) (cm³/g)</th>
<th>( \text{Pd} ) (nm)</th>
<th>( \text{Pa} ) (m²/g)</th>
<th>Keggin-anion density (HSiW nm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSiW</td>
<td>8.20</td>
<td>0.02</td>
<td>10.30</td>
<td>11.20</td>
<td>25.57</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>14.00</td>
<td>0.06</td>
<td>37.00</td>
<td>13.50</td>
<td>0</td>
</tr>
<tr>
<td>10HZ</td>
<td>18.00</td>
<td>0.12</td>
<td>39.50</td>
<td>14.00</td>
<td>1.18</td>
</tr>
<tr>
<td>20HZ</td>
<td>18.40</td>
<td>0.05</td>
<td>27.00</td>
<td>16.50</td>
<td>2.28</td>
</tr>
<tr>
<td>30HZ</td>
<td>20.00</td>
<td>0.05</td>
<td>22.40</td>
<td>18.40</td>
<td>3.20</td>
</tr>
<tr>
<td>40HZ</td>
<td>22.00</td>
<td>0.05</td>
<td>19.00</td>
<td>21.00</td>
<td>3.83</td>
</tr>
</tbody>
</table>

Fig. 1. NH₃-TPD profiles of supported catalysts (10HZ, 20HZ, 30HZ, and 40HZ).

3.6. X-ray diffraction (XRD)

Fig. 5 illustrates the XRD patterns of bulk HSiW, ZrO₂ and supported HSiW (10–40 wt%) on ZrO₂ catalysts. The XRD spectrum of bulk HSiW exhibits characteristic crystalline peaks at 10.9°, 25.5°, and 34.7° related to the Keggin anions [28]. In addition, pure ZrO₂ depicts characteristic peaks attributed to the monoclinic phases at 24.05°, 28.2°, 31.5°, 34.25°, and 50.15°. The XRD patterns related to 10–40 wt% HSiW impregnated on ZrO₂ did not correspond to the peaks of HSiW Keggin structure inferring high dispersion of HSiW on ZrO₂ support [44]. One of the main reasons that prevent HSiW crystallization on ZrO₂ support is the surface coverage of zirconia by HSiW, which is attributed to the large Keggin anion size \( (D = 1.2 \text{ nm}) \) and low ZrO₂ surface area \( (14.0 \text{ m²/g}) \) [19]. The most important advantage of surface HSiW coverage is the strong interaction between support (ZrO₂) and active phase (HSiW) to enhance the thermal stability of catalyst and also to avoid leaching of HSiW during reaction [19,20,23].

The surface coverage of HSiW on ZrO₂ surface is calculated by equation (4):

\[
\text{Surface coverage of HSiW } \left( \frac{\mu \text{mol}}{\text{m²}} \right) = \frac{X(\text{wt} \%)}{\text{MW}_{\text{HSiW}} \times S_{\text{BET}}} \tag{4}
\]

where, X referred to the weight percent (wt%) of HSiW loading on zirconia, MW_{HSiW} is the molecular weight of HSiW (g/mol) and \( S_{\text{BET}} \) is the surface area of the catalyst sample (m²/g).

Table 2

| NH₃-TPD results (acidity) for pure and supported silicotungstic acid catalysts. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Catalyst       | Weak (100–300 °C) | Medium (300–450 °C) | Strong (>450 °C) | Total acidity (mmol/g cat) |
|                 | NH₃ peak position (°C) | Acid amounts (NH₃/Cat, mmol/g) | NH₃ peak position (°C) | Acid amounts (NH₃/Cat, mmol/g) | NH₃ peak position (°C) | Acid amounts (NH₃/Cat, mmol/g) | |
| HSiW            | 131 and 250      | 0.02             | –                | –                | 545             | 1.60             | 1.62 |
| ZrO₂            | 127 and 279      | 0.14             | 414             | 0.05             | –                | –                | 0.19 |
| 10HZ            | 125 and 293      | 0.22             | –                | –                | 481             | 0.16             | 0.38 |
| 20HZ            | 122 and 292      | 0.27             | –                | –                | 501             | 0.42             | 0.69 |
| 30HZ            | 133 and 244      | 0.31             | –                | –                | 520             | 0.66             | 0.97 |
| 40HZ            | 129 and 240      | 0.38             | –                | –                | 516             | 0.86             | 1.24 |
The theoretical HSiW surface coverage on zirconia are 1.71, 3.29, 4.59, and 5.52 μmol/m² for 10–40 wt% loading of HSiW on zirconia. Less surface coverage showed better dispersion. Thus 30HZ showed better dispersion compared with 40HZ sample due to surface coverage of 4.59 and 5.52 (μmol/m²), respectively [23]. The inverse relation between molecular weight and surface coverage indicated that HSiW acid has a higher dispersion among HPAs due to its higher molecular weight than HPW and HPMo catalysts [23].

3.7. Catalytic performance

The gas phase dehydration of glycerol to acrolein over ZrO₂ supported HSiW (10–40 wt%) catalysts was investigated at different temperatures: 280, 300, and 320 °C in 3 h reaction time. The results in Table 3 indicate that increasing the HSiW loading from 10 to 30 wt% led to a surge in glycerol conversion from 84 to 92% at 300 °C reaction temperature. In addition, acrolein selectivity registered significant increases from 55.5% for 10HZ to 63.9% for 30HZ catalyst. Well-dispersed HSiW on the ZrO₂ surface enhanced the accessibility of glycerol molecules to the catalytically active protons on the supported catalyst, thus increasing the glycerol conversion [23]. The numbers in brackets in Table 3 represent the glycerol conversion and acrolein selectivity for different catalysts at 300 °C after 1 h of reaction time.

Theoretically, a catalyst should be more active when the acidity of catalyst increases with higher HSiW loading. 10HZ, 20HZ, and 30HZ catalyst samples exhibited a slight reduction (only 1–2%) in glycerol conversion and acrolein selectivity after 3 h compared to the first hour of reaction. However, 40HZ sample displayed high activity (92% glycerol conversion and 69% acrolein selectivity) only
during the first hour of the experiment. The 40HZ sample suddenly exhibited a dramatic drop in acrolein selectivity from 69% to 56.34% after 3 h. As the HSiW loading increased (>30 wt%) huge amount of active protons deposited on ZrO₂ and increased the number of acid sites. Consequently, the coke formation on the catalyst surface increased and the catalyst deactivated faster [45, 46].

Similar results have also been reported elsewhere [9, 43, 47]. Haider et al. [9] reported lower acrolein selectivity (78%) for 50STA-1 catalyst compared to the 30STA-1 sample at 80%. Liu et al. [43] reported better activity for 50HPW/Ca-SBA catalyst compared with 70HPW/Ca-SBA sample due to lower Keggin anion layers or better dispersion of HPW on support. Also, Liu et al. [47] reported a 20% reduction in acrolein selectivity by increasing the CsPW loading from 20 to 60 wt% on support. In fact, the effect of multiple layers of Keggin anions was reported as the main reason for reduction of acrolein selectivity. The 30HZ catalyst displayed the best performance with the highest acrolein selectivity of 69.3% and 92% glycerol conversion at 300 °C after 3 h. Increasing the reaction
temperature from 280 to 320 °C steadily surged the glycerol conversion from 84% to 93% over 30HZ catalysts. The main byproducts were ethanol, propanal, and acetone with 3.62%, 3.95%, and 2.49% selectivities, respectively.

The nature of acidic sites on the catalyst surface exerted great influence on glycerol conversion and acrolein selectivity summarized in Table 3 [48,49]. In fact, HSiW loading on ZrO2 formed significant Bronsted acidic sites on the catalyst surface [50,51]. The increase in HSiW supported catalyst’s activity is related to the acidity and hydrolytic stability of these catalysts [52]. Also, it is reported that HSiW is more active than other HPAs in dehydration of glycerol to acrolein due to higher Bronsted acid strength [46]. Some selectivities in Table 3 were undetermined due to unknown minor peaks in GC analysis and deposits on the catalyst surface such as glycerol oligomers and polymers from acrolein.

The strong interaction between HSiW and zirconia is required for long-term catalyst activity [52]. In fact, strong interaction leads to higher stability during the reaction at higher temperatures. The profile of TG-DTA demonstrates the strong binding between HSiW and zirconia. Furthermore, all the prepared catalysts have large pore diameters (>19 nm), which is one of the main reasons for high catalyst stability. Indeed, pore size larger than 4 nm formed a more effective catalyst by providing the required space for Keggin anions (D = 1.2 nm) at the surface and enhanced the interaction between adsorbed glycerol molecules and Keggin anions [23]. Also, large pore diameter considerably reduced the impact of internal mass transfer limitations [46,53]. The FESEM results of used 30HZ catalyst also indicated no differences compared to the fresh ones inferring the catalyst still remained highly active even after reaction due to the large pore diameter.

The glycerol conversion related to all the prepared catalysts decreased steadily during 12 h reaction time. However, 30HZ recorded the least conversion reduction among all the tested samples (Fig. 6a). The acrolein selectivities for all four samples (10HZ, 20HZ, 30HZ, and 40HZ) are exhibited in Fig. 6b. All samples exhibit rapid reduction in acrolein selectivity except for the most active and stable catalyst, 30HZ, which registered a difference of only 9.1% from 70 to 60.9%. The 30HZ sample has a higher total acidity compared to 10HZ and 20HZ samples. Similarly, the 30HZ sample possessed stronger acidic sites compared to 10HZ and 20HZ due to a significant shift of TPD peaks from 481 to 520 °C. The stronger acidity of 30HZ sample compared to 40HZ is attributed to the shift of its TPD peak to 520 °C compared with 40HZ where the TPD peak shifted lower to 516 °C. The number of acid sites (Total acidity (NH3 – TPD)/Surface area (BET)) (mmol/m2) for 30HZ sample was higher compared to the 10HZ and 20HZ samples. In fact, the number of acid sites surged from 0.02 to 0.05 mmol/m2 by increasing the HSiW loading from 10 to 30 wt%. The 40HZ sample registered slightly higher number of acid sites (0.056 mmol/m2) compared with 30HZ sample.

Table 3
Catalytic performance for glycerol dehydration to acrolein at 300 °C, 2 ml/h glycerol feed, 20 ml/min carrier gas flow rate in 3 h reaction time.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T (°C)</th>
<th>X (%)</th>
<th>Y (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Acrolein</td>
</tr>
<tr>
<td>Blank</td>
<td>300</td>
<td>56</td>
<td>11.58</td>
<td>20.68</td>
</tr>
<tr>
<td>ZrO2</td>
<td>300</td>
<td>80</td>
<td>24.69</td>
<td>30.87</td>
</tr>
<tr>
<td>HSiW</td>
<td>300</td>
<td>85</td>
<td>32.37</td>
<td>38.08</td>
</tr>
<tr>
<td>10HZ</td>
<td></td>
<td></td>
<td></td>
<td>41.04</td>
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<td></td>
<td>280</td>
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<td>41.04</td>
<td>63.87</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>86 [86]</td>
<td>46.62</td>
<td>55.50 [57]</td>
</tr>
<tr>
<td>20HZ</td>
<td></td>
<td></td>
<td></td>
<td>41.05</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>82</td>
<td>49.10</td>
<td>69.88</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>86 [88]</td>
<td>55.05</td>
<td>64.01 [65]</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>90</td>
<td>52.50</td>
<td>58.30</td>
</tr>
<tr>
<td>30HZ</td>
<td></td>
<td></td>
<td></td>
<td>55.03</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>84</td>
<td>63.75</td>
<td>69.30 [70]</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>92 [93]</td>
<td>58.23</td>
<td>62.61</td>
</tr>
<tr>
<td>40HZ</td>
<td></td>
<td></td>
<td></td>
<td>41.33</td>
</tr>
<tr>
<td></td>
<td>280</td>
<td>83</td>
<td>50.14</td>
<td>56.34 [69]</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>89 [92]</td>
<td>53.11</td>
<td>54.75</td>
</tr>
</tbody>
</table>

a Acrolein yield.

b Glycerol conversion after 1 h reaction time.

c Acrolein selectivity after 1 h reaction time.
Fig. 6. (a) Glycerol conversion versus time and (b) acrolein selectivity versus time for all supported catalysts (10HZ, 20HZ, 30HZ, and 40HZ) at 300 °C, 12 h reaction time, 2 ml/h glycerol feed, and 20 ml/min carrier gas flow (c) acrolein selectivity versus glycerol conversion only for the most stable and active sample of 30HZ, and (d) overall selectivity versus conversion related to the 30HZ sample (e) long-term catalyst stability investigation of 30HZ sample.

![Graphs of glycerol conversion and acrolein selectivity](image)

**Table 4** Coke content on used catalyst surface.

<table>
<thead>
<tr>
<th>Used catalyst</th>
<th>Coke (wt%)</th>
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<tbody>
<tr>
<td>HSiW</td>
<td>0.21</td>
</tr>
<tr>
<td>ZrO2</td>
<td>0.72</td>
</tr>
<tr>
<td>10HZ</td>
<td>1.01</td>
</tr>
<tr>
<td>20HZ</td>
<td>1.46</td>
</tr>
<tr>
<td>30HZ</td>
<td>1.75 [2.10]*</td>
</tr>
<tr>
<td>40HZ</td>
<td>1.95</td>
</tr>
</tbody>
</table>

* Reaction condition: 300 °C reaction temperature, 2 ml/h glycerol feed, and 20 ml/min carrier gas flow, 3 h reaction time.

**Fig. 7.** Comparison of acrolein yields among this study and other reported work.

The selectivity of acrolein for 40HZ sample was initially high, but as more coke was deposited on the catalyst surface, the selectivity dwindled during 12 h of reaction time. Consequently, the optimum amount of HSiW loading was found to be 30 wt%. For above 30 wt% HSiW loading, the catalyst activity remained stable in the first hour of reaction, but then its activity and acrolein selectivity declined dramatically (Fig. 6a–b).

Fig. 6c exhibits glycerol conversion versus acrolein selectivity related to the 30HZ sample during 12 h reaction time. It can clearly be seen that selectivity and conversion are directly related to each other. With decreasing glycerol conversion from 93 to 71% the acrolein selectivity also dropped steadily from 70 to 60.9%. Also, Fig. 6d presents the catalyst performance of 30HZ is indeed in the fourth quadrant confirming the remarkable performance of 30HZ catalyst with above 60% and 70% acrolein selectivity and glycerol conversion, respectively. Fig. 6e exhibits long-term stability of 30HZ catalyst during 30 h reaction time. The stability of 30HZ sample with 60% acrolein selectivity at 67% glycerol conversion prevailed up to 30 h.

**Fig. 7** compares the acrolein yields of previous published research over supported heteropoly acid catalysts with the 30HZ catalyst in this study. The red, pink, and blue colors mark the acrolein yields less than 50, 60, and 70%, respectively [18,23,25,30,45,46,54,55]. Very low glycerol conversion with less than 25% and 70% in dehydration reaction was the main reason for low acrolein yields over 5%HPW/α-Al2O3, SiO2–Al2O3, and 40HZ catalysts, respectively. HSiW/AS5 and Q6-PW-30 catalysts reported only 2 and 1.2% higher acrolein yields, respectively, compared with 30HZ catalyst (63.7%). Thus, the results listed in **Table 4** indicated the 30HZ catalyst in the current study was highly selective for acrolein production with 92% glycerol conversion, 69.3% acrolein selectivity, and 63.7% yield. Indeed, the 30HZ catalyst exhibited promising results since the catalyst did not require regeneration methods (oxygen co-feeding) to remain active for a long time.

### 3.8. Coke deposition

**Table 4** summarizes the coke contents of used catalysts determined by CHNS-elemental analyzer. Pure HSiW and ZrO2 registered the lowest amount of coke content among the used catalysts with 0.21 and 0.89 wt%, respectively. However, increasing the HSiW loading from 10 to 40 wt% surged the coke content from 1.01 to 1.95 wt% during 3 h reaction time. The total coke content on the optimal 30HZ catalyst surface was measured to be 2.10 wt% after 12 h. Generally, catalysts can tolerate about 6–10 wt% coke content with limited amount of activity loss, particularly when coke is
deposited on inactive sites [4,56]. The coke deposition on 30HZ catalyst surface after 12 h in this study was much lower than 6–10 wt%. Thus, the elemental analysis confirmed the other characterization results which showed only limited amount of coke was deposited on the used 30HZ catalyst surface, but still retained its high activity and stability.

3.9. Effect of Keggin anion density

The loadings of HSiW in the HSiW-Zr catalysts were varied from 10 to 40 wt% to determine the optimal amount of the HSiW loading over the zirconia support. Fig. 8a illustrates the interaction between HSiW loading and catalyst specific surface area or HSiW atom surface density. According to the BET results, increasing the HSiW loading increased the surface area. In addition, the relation between HSiW loading and Keggin anion density is illustrated in Fig. 8b. The Keggin anion density is calculated by equation (5):

$$\text{Keggin anion density (HSiW nm}^{-2}\text{)} = \frac{\text{HSiW Loading (wt%)/100 × (6.02 × 10}^5\text{)}}{\text{BET surface area of catalyst (m}^2/\text{g) × (2878.2 g/mol)}}$$

Fig. 8c depicts the effect of 10–40 wt% HSiW loading on the glycerol conversion and acrolein selectivity. Pure zirconia and bulk HSiW are denoted as 0HZ and 100HZ catalysts, respectively. Higher acrolein selectivity was achieved by increasing HSiW up to 30 wt% on zirconia with a maximum value of 69.3% in 3 h. However, the acrolein selectivity declined to 56.3% when HSiW loading increased to 40 wt%. The glycerol conversion also registered a similar trend.

Finally, Fig. 8d exhibits the relationship between the acrolein selectivity and Keggin anion density of HSiW atoms. Acrolein selectivity reached optimum 69.3% with increasing Keggin density of HSiW atoms up to 3.20 HSiW nm$^{-2}$, but decreased to 56% with larger HSiW density (3.83 HSiW nm$^{-2}$). The effect of multiple layers of Keggin anions was reported as the main reason for the decline in acrolein selectivity [43,47]. The high acidity of HSiW, originates from its Keggin structure properties and decomposition or destruction of Keggin anions, lead to a significant drop in the acidity and finally decreases the catalyst activity [57,58].

4. Conclusions

Supported HSiW (10–40 wt%) on zirconia catalysts were prepared and tested in gas phase glycerol dehydration to acrolein at different temperatures (280, 300, and 320 °C). All the prepared catalysts with large pore diameters defied the coke deposition effect. The most active and stable catalyst, 30HZ, registered 69.3% acrolein selectivity with 92% glycerol conversion at 300 °C in 3 h. The characterization results proved that the 30HZ sample was thermally stable (TG-DTA) with the Keggin structure remained intact even at high temperatures. Meanwhile, the 30HZ sample possessed the strongest interaction between Keggin-anions and zirconia support. In addition, the 30HZ sample exhibited remarkable stability (60% acrolein selectivity at 67% glycerol conversion) even after 30 h of reaction time. Generally, the optimal catalyst, 30HZ, has particular characteristics in this study such as higher surface area and total acidity compared with 10HZ and 20HZ samples and also stronger acidic sites and lower coke content compared to 40HZ sample.

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References
