



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



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## ABSTRACT

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 m<sup>2</sup>/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.

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## 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 dehydration 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 SiO<sub>2</sub> 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

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ZrO<sub>2</sub> made it a better support for HSiW. Alsalme et al., [20] revealed that interaction between HPAs and various supports decreased in the order of ZrO<sub>2</sub> > Nb<sub>2</sub>O<sub>5</sub> > TiO<sub>2</sub> > SiO<sub>2</sub>. 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 acidic 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-ZrO<sub>2</sub> 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 (H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>·14H<sub>2</sub>O (HSiW)), and zirconium (ZrO<sub>2</sub>) 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-ZrO<sub>2</sub> 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<sup>-1</sup> 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 (O<sub>2</sub>) 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 (NH<sub>3</sub>-TPD) using the Micrometrics Auto Chem II instrument. A specified amount of catalyst was dried at 200 °C for 1 h by saturation of NH<sub>3</sub> at 60 °C for 0.5 h before the physically adsorbed NH<sub>3</sub> 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 adsorbed NH<sub>3</sub>.

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 (N<sub>2</sub>) 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<sup>-1</sup>. 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

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