Gas phase selective conversion of glycerol to acrolein over supported silicotungstic acid catalyst

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Gas phase dehydration of glycerol to acrolein over a series of supported HSiW on ZrO_2 and nano-sized γ-Al_2O_3 catalyst has been investigated. The characterization results revealed that impregnation of γ-Al_2O_3 nanoparticles increased the specific surface area, pore diameter, and thermal stability of the supported catalysts. The highest acrolein selectivity of 88.5% at 97.0% glycerol conversion was achieved over 0.5 g 30HZ-20A catalyst in 3 h at glycerol feed concentration of 10 wt%, temperature = 300 ?C and TOF = 136 h^{-1}. The coke deposition has no significant effect on the activity of 30HZ-20A catalyst. Indeed, the catalyst was stable even after 40 h.

Introduction

The catalytic conversion of renewable feedstock for synthesis of value-added chemicals has attracted much attention in the last two decades to compensate various environmental concerns and excessive demand for fossil fuel consumption [1]. The production of biodiesel worldwide has caused surplus of glycerol, the main by product. In accordance to the global surge, over 1.54 million tones of glycerol are anticipated in 2015 and beyond. Hence, enormous availability of glycerol has drastically decreased the price of glycerol from 1.2 USD/kg in 2001 to 0.3 USD/kg in 2015 [2].

Industrial application of glycerol as a bio-renewable feedstock has been increasing not only because of the rapid surge in glycerol capacity, but also because glycerol is bio-sustainable, non-toxic, and bio-degradable. Furthermore, the multi-functional structure and physico-chemical characteristics of glycerol make it as one of the top 12 most important bio-based chemicals in the world [3]. Value-added chemicals such as acrolein, ethylene glycol, propanediol, and lactic acid are produced by catalytic dehydration, oxidation, reforming, hydrogenolysis, esterification, and oligomerization of glycerol [4,5].

Acrolein is also known as 2-propenal or acrylic aldehyde, the simplest unsaturated aldehyde. Moreover, acrolein is one of the most significant intermediates in the chemical industry for production of acrylic acid and methionine. For instance, superabsorbent polymers from acrylic acid are being used in the hygienic products due to the extreme absorbance of liquids (more than 500 times their weight).

The conventional method for production of acrolein is selective oxidation of propylene in presence of complex $BiMoO_x$ based catalyst with approximately 85% acrolein selectivity at 95% propylene conversion. However, petrochemical exhaustion is foreseen in the near future. Therefore, the notion to produce significant industrial materials like acrolein from sustainable and renewable resources is more prevalent recently. The renewable route for acrolein production is through glycerol dehydration over various acid catalysts such as mineral acids, zeolites, heteropoly acids, and metal oxides in gas [6–9] or liquid [10] phases.

Among several types of catalysts for glycerol conversion, heteropoly acids (HPAs) have attracted much attention because of its strong and easily tunable acidity as well as uniform acidic sites. Acidic active sites are the most important factor for higher catalytic activity and acrolein yield. The main advantage of HPAs is the unique Keggin structures favorable for acrolein production due to high Bronsted acid strength [11]. The disadvantages are its low thermal stability and surface area. In order to overcome these problems, HPAs are often supported on acidic or natural carriers such as zirconia (ZrO_2), alumina (Al_2O_3), and silica (SiO_2).

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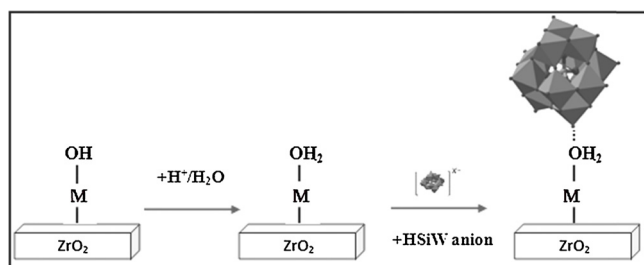 E-mail addresses: amin.talebian63@gmail.com, noraishah@cheme.utm.my
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Fig. 1. Electronic interaction between HSiW and ZrO₂ support.

Mixing ZrO_2 with other oxides can easily adjust its acid-base characteristics. In addition, the supported HPAs species on ZrO_2 could lead to full disappearance of the surface anions, and emergence of very strong Bronsted acidic sites [12]. ZrO_2 support increases the long-term [13] and thermal stability of the HPA supported catalysts, even better than silica supported catalysts [11]. The main reason for higher thermal stability and activity of supported HSiW on ZrO_2 and Al_2O_3 catalysts is the strong interaction between HSiW and the supports. In fact, the hydroxyl groups on the surface of support are protonated in contact with water during the impregnation process to produce $Zr-OH_2^+$ species. The support and the negatively charged heteropoly anions have strong electronic interaction [14,15] as described in Fig. 1.

Cs-HPW catalyst displayed the highest ever reported acrolein selectivity of 98% at 100% glycerol conversion, but the catalyst was stable only for a few hours and deactivated quickly [16]. The main reason for fast deactivation is coke deposition on the catalyst surface. Therefore, the large scale production of acrolein by glycerol dehydration depends on circumventing the fast deactivation problem. Small pore diameters, low surface acidity, and even very strong acidic sites on the catalyst surface are known to aggravate coke formation [17].

Co-feeding of hydrogen or oxygen is one of the common methods intended for eliminating or slowing down coke deposition on catalyst surface. However, this method may increase the possibility of explosive conditions or oxidation of products, finally decreasing the acrolein selectivity. Otherwise, large pore structure and high surface acidity are the two key catalyst properties for higher acrolein production. The effects of these two characteristics have been studied elsewhere [18]. As reported by Stosic et al. [12] the catalyst activity is dependent on the total acidity of catalyst as well as the nature of acid sites on the catalyst surface. Thus, the current study proposes the catalyst long-term stability can be enhanced without gas co-feeding or any noble metals application and it would be possible only by improving the textural characteristics of the catalyst such as acidity, thermal stability, and particularly pore size during the catalyst preparation step.

Among the HPAs (HSiW, HPW, and HPMo), HSiW was chosen due to several reasons including strong acidic sites (Bronsted) and higher water tolerance abilities. According to several literatures, ZrO_2 is one of the best supports for HPAs because ZrO_2 increases the long-life and thermal stability of catalyst. Since both ZrO_2 and HSiW have low surface areas, γ-Al_2O_3 nanoparticle was added as the third component to the catalyst in order to increase the surface area and pore diameter.

The main objective of this study is to prepare a series of thermally stable, high surface acidity, large surface area, and large pore diameter catalysts for gas phase glycerol conversion to acrolein. The catalysts were characterized to elucidate the textural characteristics. After determining the best catalyst with the highest selectivity to acrolein, the effects of various reaction temperatures (280–320 ?C), prolonged time, and Keggin anion density on the catalyst activity were also evaluated.

Experimental

Materials

Glycerol (purity > 99%), silicotungstic acid ($H_4SiW_{12}O_{40} \cdot 14H_2O$ (HSiW)), aluminum oxide (Al_2O_3) nanoparticle, zirconium oxide (ZrO_2), acetic acid, allyl alcohol, hydroxyacetone, acetone, propanal, ethanal at reagent grade were supplied by Sigma Aldrich (Malaysia). Acrolein at reagent grade was purchased from Scientific Trends (M) Sdn. Bhd.

Catalyst preparation

In the initial step, a series of catalysts with various HSiW loadings (10, 20, 30, and 40 wt%) on ZrO_2 were prepared by the incipient-wetness impregnation method. In this method, aqueous HSiW solutions were added drop-wise to the ZrO_2 support. The slurries were rigorously stirred for 12 h followed by drying at 110 ?C for 18 h. The HSiW-ZrO_2 supported catalysts were denoted as 10HZ, 20HZ, 30HZ, and 40HZ for 10, 20, 30 and 40 wt% of HSiW loading, respectively.

Next, the second series of catalysts were prepared by impregnation of Al_2O_3 nanoparticles with different weight percentages (10–30 wt%) on the 30HZ sample. Initially, 30HZ suspension was prepared while the nanoparticle alumina was mixed with water to form slurry. Finally, the 30HZ suspension was added drop-wise to the alumina slurry under continuous stirring for at least 20 h followed by drying at 120 ?C for 18 h. The synthesized catalysts were denoted to as 30HZ-10A, 30HZ-20A, and 30HZ-30A. The 70Z-30A sample was similarly prepared, but without HSiW to evaluate the effect of ZrO_2 and Al_2O_3 combination on the catalyst activity.

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 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.

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 $CuK\alpha$ radiation (40 keV, 40 mA). The patterns were scanned in the 2θ range of 10–80? (step width 0.05?, 1 s per step). The crystalline size of Al_2O_3 in supported 30HZ catalyst with 10–30 wt% Al_2O_3 samples is calculated using Scherrer 's equation [19,20], $D_P = (0.94 \times \lambda / \beta \times \cos\theta)$, where D_p, λ, β, and θ are average crystalline size, X-ray wavelength, line broadening (Peak half-width) in radius, and diffraction angle, respectively.

The total acidity of the prepared catalysts was determined by temperature programmed desorption of ammonia (NH_3–TPD) using the Micrometrics Auto Chem II instrument. A specific amount of catalyst was dried at 200 ?C for 1 h by saturation of NH_3 at 60 ?C for 0.5 h before the physically adsorbed NH_3 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 NH_3.

Thermogravimetric analysis (TG) of prepared catalyst was performed using a THERMO TGA instrument in a temperature range of 30 to 800 ?C with a ramp rate of 10 K/min under nitrogen flow. The Fourier Transform Infrared Spectroscopy (FTIR) spectra of the freshly prepared catalysts were performed by Perkin Spectrum One FTIR spectrometer with a spectral resolution of 2 cm^{-1} and scan time of 1 s using KBr disc method.