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Porous zirconium phosphate supported tungsten oxide solid acid catalysts for the vapour phase dehydration of glycerol

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ABSTRACT

Solid acid catalysts containing WO_x/ZrP with varying the active component loading (5–40 wt%) on porous ZrP support have been investigated for the vapour phase dehydration of glycerol to acrolein. The catalyst containing 30 wt% WO_x/ZrP has shown high selectivity to acrolein (about 82%) with a total conversion of glycerol at 300 °C in the presence of water. The calcined catalysts were characterized by X-ray diffraction, pore size distribution, FT-IR, UV-DRS, pyridine absorbed FT-IR and NH_3-temperature programmed desorption to elucidate the structural and acidic properties of the catalysts. The XRD results suggest that WO_x is found to be present in a highly dispersed state at lower loadings (<30 wt%) and crystalline WO_x at higher loadings. NH_3-TPD and FT-IR results of adsorbed pyridine suggest that the total acidity and number of Brønsted acidic sites are found to increase with WO_3 loading on the support. Further, there is no significant change of acidity was noticed at higher loadings. The conversion of glycerol and the selectivity toward acrolein mainly depend on the fraction of moderate acidic sites and Brønsted acidic sites. The Glycerol dehydration functionalities are explained in terms of the acidity and structural properties of WO_x/ZrP catalysts. In addition, the positive effect due to addition of air to N_2 feed flow suppresses the coke formation on the surface of catalyst was also investigated during dehydration reaction.

1. Introduction

Renewable biomass resources are promising alternatives for the sustainable synthesis of chemical intermediates and liquid fuels [1]. The by-product produced in bio-diesel synthesis is glycerol and its effective utilization will be a key issue to promote the bio-diesel commercialization. Therefore, new uses of glycerol need to be explored for its valorization. The crude glycerol can be converted to acrolein, which is an important chemical intermediate for the production of acrylic acid, acrylic acid esters, super absorbers and polymers [2,3]. Acrolein is also used for the manufacture of methionine, 1,3-propanediol, glutaraldehyde, pyridines, flavors, and fragrances [4]. Compared to the petroleum-based processes [5], the dehydration of glycerol to acrolein has received a great deal of attention in the recent past as a significant route by virtue of its being an environmentally benign process.

The dehydration of glycerol in gas phase on acidic catalysts is a typical example of double dehydration reaction proceeds via the formation of 3-hydroxypropionaldehyde and 1-hydroxyacetone [6] (Scheme 1). The highest selectivity to acrolein reported so far in both the vapour phase and liquid phase dehydration process is 65–90%. It was found that a solid acid with Hammet acidity (H_o) between −10 and −16 is the most suitable catalyst for the dehydration of glycerol than the catalysts having lower acidity with H_0 between −2 and −6 [7]. However, such strong acidic catalysts are known to deactivate rapidly due to deposition of carbonaceous species on the catalyst surface [8]. The acidic properties in combination with textural properties of the catalysts in the presence of large number of micro pores also play an important role in determining the catalytic performance [9–13]. The selectivity and deactivation during glycerol dehydration will be strongly affected by diffusion constraints due to coke formation.

The dehydration of glycerol to acrolein in the gaseous phase over a solid acid catalyst leads to a sufficiently high dehydration activity. However the catalyst deactivation is a major concern due to severe reaction conditions, coke formation [8,14–16], sintering or leaching of active phase in the reaction media [17] and formation of large amount of by-products.

Among various solid acid catalysts reported, WO_3/ZrO_2 catalysts represent one of the highly active catalysts for vapour

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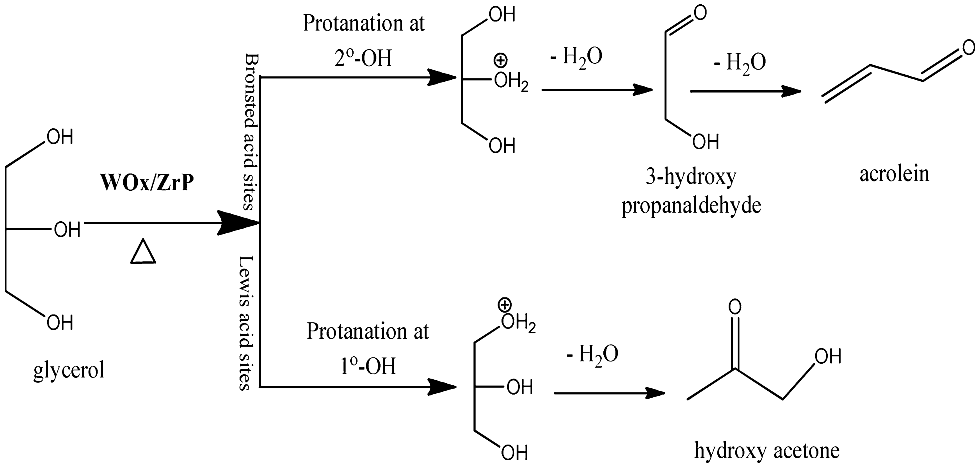

Scheme 1. Schematic representation of the dehydration of glycerol to acrolein and acetol.

phase dehydration of glycerol, as they exhibit show unique catalytic performance in the dehydration of glycerol [18–20]. Ulgen and Hoelderich [18] have evaluated the catalytic performance of WO_3/ZrO_2 catalysts with various WO_3 loadings and noticed an increase of acrolein selectivity in 73% with 19 wt% catalyst. Similar acrolein selectivity was also reported at 300 °C with total conversion using a commercial WO_3/ZrO_2 catalyst [19]. On the other hand improvement of tungstated zirconia catalyst with SiO_2 doping, exhibited better acrolein selectivity (80%) with long catalyst life and thermal stability to the catalyst [20]. There are many investigations reported on the structural and acidic properties of WO_x/ZrO_2 solid acids for glycerol dehydration reaction. However, not many studies reported so far on the interaction of WO_x with porous zirconium phosphate support for the gas phase glycerol dehydration reaction.

In the present study we report the synthesis, characterization and application of porous zirconium phosphate (ZrP) supported WO_x catalysts for the dehydration of glycerol to acrolein. Our results provide mainly a basis for correlating the catalyst acidity by varying the tungsten oxide content and the effect of reaction temperature in glycerol dehydration. In addition, we also report the positive effect due to addition of air to reactant flow in the gas phase dehydration of glycerol.

2. Experimental

Porous zirconium phosphate support was prepared from zirconium n-propoxide precursor and 85% phosphoric acid following the procedure described elsewhere [21]. About 0.01 mol of zirconium n-propoxide, (70 wt% solution in 1-propanol, Aldrich) was added drop wise to a 60 mL solution of H_3PO_4 (0.1 mol L^{-1}) under stirring. After 2 h of stirring at room temperature, the obtained mixture was transferred into a teflon lined autoclave and aged statically at 80 °C for 24 h. The final material was filtered, dried and calcined at 400 °C for 5 h. A series of WO_x/ZrP catalysts with WO_x loadings ranging from 5 to 40 wt% supported on ZrP were prepared by impregnation method by adding aquous solution of ammonium metatungstate to the calcined ZrP support. The catalysts were subsequently dried at 100 °C for 12 h and calcined in a muffle furnace at 400 °C for 5 h.

X-ray powder diffraction patterns of the samples were obtained by a model: D8 Diffract meter (Advance, Bruker, Germany), using Cu Kα radiation (1.5406 Å) at 40 kV and 30 mA. The measurements were recorded in steps of 0.045° with a count time of 0.5 s in the range of 2–40°.

Pore size distribution measurements were performed on Autosorb-1 instrument (Qunta chrome, USA) using by nitrogen physisorption.

The UV–vis diffused reflectance spectra were recorded on a GBC UV–visible Cintra 10e spectrometer with an integrating sphere reflectance accessory. The spectra were recorded in air at room temperature and the data was transformed according the Kubelka–Munk equation $f(R) = (1 - R\alpha)\ 2/2r\alpha$.

NH_3-TPD experiments were conducted on the AutoChem 2910 (Micromeritics) instrument. Prior to TPD analysis the sample was pretreated by passing high purity (99.999%) helium (50 ml/min) at 300 °C for 1 h. After pretreatment, the sample was saturated with 10% NH_3 balance He mixture (75 ml/min) at 80 °C for 1 h and subsequently flushed at 150 °C for 1 h to remove the physisorbed ammonia. TPD analysis was carried out from ambient temperature to 700 °C at a heating rate 10 °C/min. The amount of NH_3 desorbed is calculated using GRAMS/32 software.

The ex situ experiments of FT-IR spectra of pyridine adsorbed samples were carried out to find the Brønsted and Lewis acid sites. Pyridine was adsorbed on the activated catalysts at 200 °C until saturation. Prior to adsorption experiments the catalysts were activated in N_2 flow at 300 °C for 1 h to remove adsorbed water in the samples. After such activation, the samples were cooled to room temperature. The IR spectra were recorded using IR (Model: GC-FT-IR Nicolet 670) spectrometer by KBr disk method at room temperature. FT-IR spectra of the catalysts were recorded on IR (Model: GC-FT-IR Nicolet 670) spectrometer by KBr disk method at room temperature.

Thermogravimetry analysis (Shimadzu TGA-51) was measured at a heating rate of 10 °C/min from 25 °C up to 800 °C under the flow of air.

The gas-phase dehydration of glycerol was conducted in the reaction temperature ranging from 280 to 340 °C under atmospheric pressure in a vertical fixed-bed quartz reactor (400 mm length, 9 mm i.d.) using 0.2 g of catalyst. Before the reaction, the catalyst was pretreated at 320 °C for 1 h in flow of dry N_2 (30 mL min^{-1}). An aqueous solution containing 20 wt% glycerol was fed into the reactor by a micro-syringe pump at a flow rate of 0.5 mL/h (WHSV-2.6 h^{-1}). The reaction products were condensed in an ice–water trap and collected hourly for the analysis using a gas chromatograph GC-2014 (Shimadzu) equipped with a DB-wax 123-7033 (Agilent) capillary column (0.32 mm i.d., 30 m long) and a flame ionization detector (FID). The oven temperature was set from 56 °C to 119 °C (heating rate 5 °C/min, isothermal step at 119 °C, 3 min), then from 119 °C to 240 °C (heating rate 15 °C/min, final isothermal step at 240 °C, 6 min).