



Metal–acid bifunctional catalysts for selective hydrogenolysis of glycerol under atmospheric pressure: A highly selective route to produce propanols



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ABSTRACT

Metal–acid bifunctional catalysts containing platinum and heteropolyacids (HPA) in supported on zirconia have been employed for the selective vapor phase hydrogenolysis of glycerol to propanols (1-propanol+2-propanol) under normal atmospheric pressure. The Pt–HPA/ZrO₂ catalysts (HPAs such as silicotungstic acid (STA), phosphotungstic acid (PTA), phosphomolybdic acid (PMA) and silicomolybdic acid (SMA)) were prepared by impregnation method and the calcined catalysts were characterized by means of X-ray powder diffraction, FTIR, Raman spectroscopy, BET surface area, CO chemisorption and NH₃-Temperature-programmed desorption methods. The characterization results reveal the presence of well dispersed Pt metallic phase and Keggin structure of HPAs on support. The catalytic performance during glycerol hydrogenolysis is well correlated with Pt dispersion and the acidic properties of catalysts. Among the tested catalysts, it was found that Pt–PTA/ZrO₂ exhibited excellent selectivity to propanols (98%) with total glycerol conversion at 230 °C. A detailed study was made on the effect of various reaction parameters such as the influence of reaction temperature, reduction temperature, glycerol concentration, hydrogen flow rate, feed flow rate and HPA loading to unveil the optimized reaction conditions. Reaction temperature was observed to have a significant effect on the glycerol conversion and product selectivity. The spent catalysts were also characterized by the X-ray diffraction, NH₃-TPD and SEM analysis to investigate the changes in catalytic performance and causes of catalyst deactivation.

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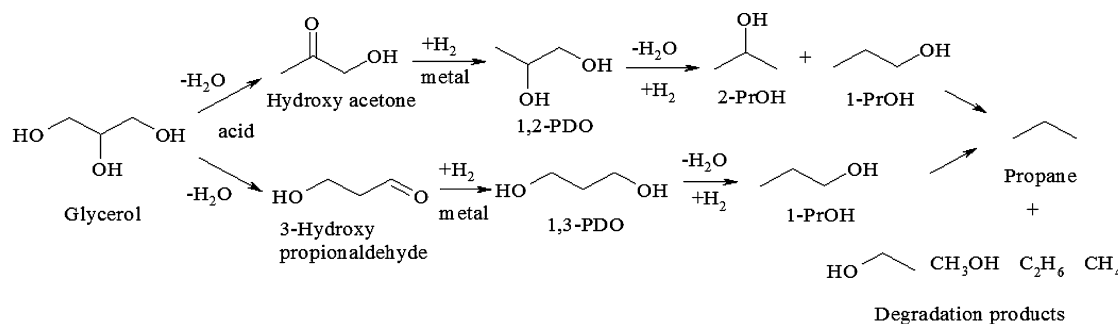
1. Introduction

Biodiesel production by transesterification of oils affords huge amounts of glycerol as a byproduct [1]. Since utilization or safe disposal of byproducts is a prime objective from the viewpoint of sustainable development, researchers focused on various transformations of bioglycerol, a renewable feedstock, into value added compounds and fine chemicals via oxidation, reduction, dehydration, hydrogenolysis, esterification, fermentation, pyrolysis, etherification and so on [2–4]. Production of 1,2-propanediol (PDO), 1,3-propanediol (1,3-PDO) and propanols by hydrogenolysis of bioglycerol over supported noble metal catalysts is one of such potential routes which has been extensively studied by several authors [5–8].

Propanediols, both 1,2-propanediol and 1,3-propanediol, are used as solvents and additives in many fields such as polymer, cosmetics and pharmaceuticals [9]. In comparison, propanols are also expensive commodity chemicals widely employed as industrial solvents and attracted much attention in recent years. Currently, 1-propanol is produced by hydroformylation of ethylene and is mainly used as printing ink or in production of n-propyl acetate [10]. 2-Propanol can be produced by the hydration of propylene and finds application in pharmaceuticals, as a disinfectant and a deicer [11]. However, routes to biopropanols [12–14] such as 1-propanol [7,15] and 2-propanol have been less discussed while abundant literature is available on conversion of glycerol to 1,2-PDO [16–24] and 1,3-PDO [25–35].

Tomishige and coworkers [36] conducted the hydrogenolysis of glycerol at 120 °C and 8.0 MPa in which the optimized Ru-added Ir-ReOx/SiO₂ catalyst gave high yields of propanols (84%). Previously reported processes describe a method of one step hydrogenolysis of glycerol to biopropanols over Pt–HSiW/ZrO₂ catalyst at a pressure

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Scheme 1. Hydrogenolysis of glycerol to various products.

of 5 MPa and 200 °C and achieved a combined selectivity of 90.9% toward propanols [12].

In spite of these research efforts, a major drawback is the fact that most research efforts to date have employed the use of high reaction pressure carried out in batch reactors, although few operated in continuous fixed bed reactors. Consequently, the energy consumption of the process is increased and in turn a decrease in the profitability of the process. Above all, the selectivities to propanols are still low and did not go beyond 91%. Therefore, there is tremendous interest to selectively convert glycerol to propanols under mild and most economical conditions.

In this context, developing proper fixed bed continuous flow reactors operated at desired temperature and atmospheric pressure for selective conversion of glycerol to propanols still remains an open challenge. The present investigation was undertaken considering the aforesaid background, evaluating metal–acid bifunctional catalysts for the vapor phase conversion of glycerol to propanols at normal atmospheric pressure. To the best of our knowledge, there is no report for the utilization of continuous fixed bed process under atmospheric pressure for the conversion of glycerol into propanols which is economically attractive.

The glycerol hydrogenolysis reaction involves dissociation of C–C and C–O with simultaneous addition of hydrogen. Since glycerol is rich in oxygen content, C–O hydrogenolysis is the most promising method in view point of biomass conversion to chemicals. The glycerol hydrogenolysis is generally believed to take place via the “dehydration–hydrogenation” mechanism [29,32,35]. In this view, “acid–metal” bifunctional catalysts are most effective for the hydrogenolysis of glycerol wherein the acid sites are responsible for the dehydration step and the metallic sites are responsible for the hydrogenation step, respectively (Scheme 1).

Noble metal based catalysts present good selectivity to propanols for hydrogenolysis of glycerol [12,13]. Heteropolyacids (HPAs) have high potential as catalyst. These materials offer the unique opportunity to replace the corrosive liquid acids currently used in many chemical conversion steps to provide “greener” processes. HPAs are typical strong Bronsted acids compared to conventional solid acid catalysts and catalyze a wide variety of homogeneous and heterogeneous reactions [37] offering a strong option for efficient and cleaner processing. Supported HPAs have been used in a variety of organic transformations such as acylation, alkylation, esterification, oxidation and hydrogenation. Zirconia based materials have attracted considerable interest in recent years for their potential use as catalyst supports [38] and often used to immobilize HPAs [39] as they present special characteristics such as high thermal stability, extreme hardness, and stability under reducing conditions.

In the present investigation, several zirconia supported Pt–HPAs (STA, PTA, PMA and SMA) bi-functional catalysts were prepared, characterized, and tested for glycerol hydrogenolysis. The main focus of this work was the evaluation of supported Pt–HPA catalysts

for the vapor phase hydrogenolysis of glycerol (Scheme 2) under atmospheric pressure with the aim to produce alcohols, in particular 1-propanol (1-PrOH) and 2-propanol (2-PrOH) with highest selectivities.

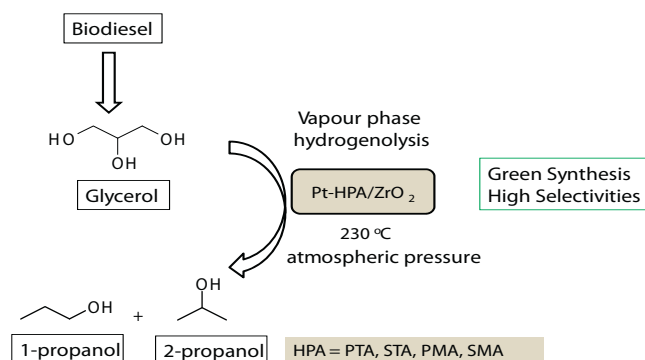
2. Experimental

2.1. Catalyst preparation

ZrO₂ support was obtained by hydrolyzing ZrOCl₂ with aqueous ammonia added until the solution reached pH 8.0, followed by washing and then drying at 110 °C for 24 h. The support was calcined at 500 °C for 3 h in air. The heteropolyacids (HPAs) such as phosphotungstic acid (PTA), phosphomolybdic acid (PMA), silicotungstic acid (STA), silicomolybdic acid (SMA) were used. The Pt–HPA/ZrO₂ catalysts employed in this investigation were prepared by sequential or step by step wet impregnation method. Initially, HPA/ZrO₂ was prepared by impregnation of ZrO₂ support with an aqueous solution of HPA. The impregnated sample was dried overnight at 110 °C and then calcined at 300 °C in static air for 3 h. The Pt–HPA/ZrO₂ catalysts were prepared by impregnation of HPA/ZrO₂ with aqueous solution of H₂PtCl₆·6H₂O. After impregnation, the sample was dried overnight at 110 °C and then calcined at 350 °C for 4 h. The optimum weight loadings of Pt metal and acid components (STA, PTA, PMA and SMA) in all the catalysts were confined to 2 wt% and 15 wt%, respectively. The catalysts will be hereinafter referred to as Pt–PTA/ZrO₂, Pt–STA/ZrO₂, Pt–PMA/ZrO₂ and Pt–SMA/ZrO₂.

2.2. Catalyst characterization

The calcined forms of catalysts were characterized by powder X-ray diffraction (XRD) analysis using a Rigaku miniflex X-ray diffractometer using Ni filtered Cu K α radiation ($\lambda = 0.15406$ nm)



Scheme 2. Hydrogenolysis of glycerol to propanols over Pt–HPA/ZrO₂ catalysts.

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