



## Influence of solid acids as co-catalysts on glycerol hydrogenolysis to propylene glycol over Ru/C catalysts

M. Balaraju<sup>a</sup>, V. Rekha<sup>a</sup>, P.S. Sai Prasad<sup>a</sup>, B.L.A. Prabhavathi Devi<sup>b</sup>, R.B.N. Prasad<sup>b</sup>, N. Lingaiah<sup>a,\*</sup>

<sup>a</sup> Catalysis Laboratory, I&PC Division, Indian Institute of Chemical Technology, Hyderabad 500607, India

<sup>b</sup> Lipid Science & Technology Division, Indian Institute of Chemical Technology, Hyderabad 500607, India

### ARTICLE INFO

#### Article history:

Received 8 September 2008

Received in revised form 12 November 2008

Accepted 13 November 2008

Available online 21 November 2008

#### Keywords:

Glycerol

Niobia

Ruthenium

Hydrogenolysis

Propanediol

Ethylene glycol

### ABSTRACT

Glycerol hydrogenolysis to propane diols was carried out over Ru/C catalysts using different solid acids as co-catalysts. Solid acids such as niobia, 12-tungstophosphoric acid (TPA) supported on zirconia, cesium salt of TPA and cesium salt of TPA supported on zirconia were used. The acidities of the solid acid catalysts were measured by temperature programmed desorption of ammonia. The conversion of glycerol depends on the total acidity of the catalysts and there exists a linear correlation between conversion and acidity. The selectivity towards 1,2-propanediol and the glycerol conversion varied with the change in the concentrations of both Ru/C and solid acid catalysts, suggesting a synergetic effect of the reaction. This reaction requires minimum amount of both acid and metal sites to obtain reasonable activity. Different reaction parameters were studied and optimized reaction conditions were established.

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### 1. Introduction

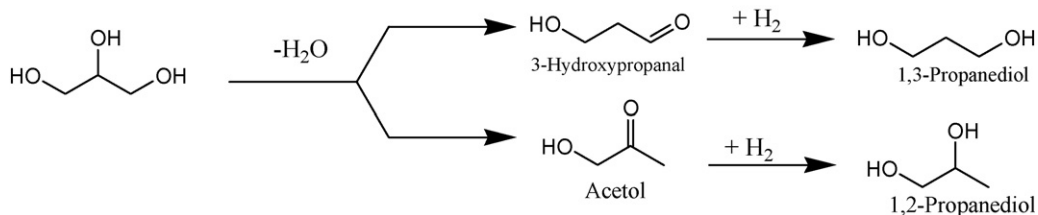
Glycerol, a by-product in biodiesel production has been identified as one of the top building blocks in the biorefinery feed stocks in this decade [1,2]. Large amounts of glycerol will be produced in biodiesel industry as by-products during transesterification of oils [3–5]. Biodiesel production will soon look into new applications to convert its by-product glycerol to value-added products to make the biodiesel industry economically more attractive. A broad overview of the chemistry of glycerol and its conversion to new products are presented in a recent review [6]. Among possible chemicals derived from glycerol, propylene glycol and ethylene glycol are important. These glycols are used widely in the syntheses of pharmaceuticals, polymers, agricultural adjuvants, plastics and transportation fuel [7–10]. The commercial route to produce propylene glycol or ethylene glycol is by the hydration of propylene oxide or ethylene oxide derived from propylene or ethylene [11]. The production of glycols by the catalytic hydrogenolysis of glycerol is a green process, as the existing methods use petroleum-derived products (fossil resources) [11,12]. Hydrogenolysis of glycerol is generally carried out in liquid phase under high H<sub>2</sub> pressures. Hydrogenolysis of

glycerol leads to the formation of 1,2-propanediol (1,2-PD) and 1,3-propanediol (1,3-PDO) and ethylene glycol (EG) as main products.

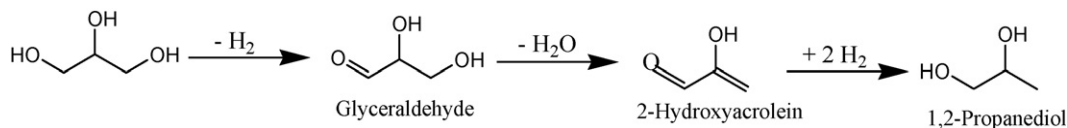
Supported Pt, Ru, Rh and Pd catalysts are used for glycerol hydrogenolysis [13–15]. Among these catalysts, supported Ru catalysts are more active for this reaction than other catalysts [13–16]. This reaction is carried out batch wise at elevated H<sub>2</sub> pressure in the temperature range of 110–220 °C. Acid additives promote the hydrogenolysis of glycerol over noble metal catalysts. Addition of solid acid catalysts to supported noble metal catalysts enhances the conversion and selectivity in hydrogenolysis of glycerol more than the values obtained for supported noble metal catalyst alone [8,9]. Previous research shows that hydrogenolysis of glycerol to propane diols proceed via dehydration of glycerol to acetol on acid catalysts and consecutive hydrogenation over metal catalysts [7,13–15]. This mechanism is supported by identification of acetol in the reaction mixture (Scheme 1) [17,18]. On other hand, dehydrogenation of glycerol to glyceraldehyde is followed by dehydration to 2-hydroxyacrolein and subsequent hydrogenation to 1,2-propylene glycol as suggested by Montassier et al. (Scheme 2) [19]. Thus, a hydrogenolysis reaction is known as a bifunctional reaction. It requires catalysts both for dehydration and for hydrogenation functionality. According to the above mechanisms, acid catalysts play an important role in hydrogenolysis reactions. Different solid acid catalysts such as zeolites, sulfated zirconia, tungstic acid and ion exchange resin have been studied as acid

\* Corresponding author. Tel.: +91 40 2719 3163; fax: +91 40 2716 0921.

E-mail address: [nakkalingaiah@iict.res.in](mailto:nakkalingaiah@iict.res.in) (N. Lingaiah).



**Scheme 1.** Glycerol hydrogenolysis pathways.



**Scheme 2.** Glycerol hydrogenolysis pathway to prepare 1,2-propanediol.

catalysts [4]. Miyazawa et al. used Ru/C metal catalyst with Amberlyst 15 as acid catalyst for hydrogenolysis reaction, their results showed 21% conversion and 55% selectivity towards 1,2-PD [8]. In the case of ion exchange resins, the reaction temperature range is limited as they are not thermally stable. An ion exchange resin like Amberlyst 15 decomposition starts at about 120 °C [1]. Increase in reaction temperature leads to low glycerol conversion due to the deactivation of Amberlyst catalysts [8,20].

Even though there are a few reports using solid acid as co-catalyst during glycerol hydrogenolysis over supported Ru catalysts, there are no details about the influence of acidity on the reaction. Most of the studies are focused on using ion exchange resins and are not stable under reaction conditions used for hydrogenolysis. In some cases, zeolites are used as acid catalyst. However, the glycerol conversion is very low [4]. In the present study, glycerol hydrogenolysis is carried out over Ru/C catalysts using different solid acid catalysts. The influence of acidity of the catalysts on glycerol conversion and selectivity is studied in detail. The catalysts are further studied at different reaction parameters to optimize the reaction conditions for selective formation of propylene glycol.

## 2. Experimental

All the chemicals used in this study were of analytical grade. Commercially available 5%Ru/C (Sigma–Aldrich) and Nb<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O (CBMM Brazil) are used. All other catalysts are prepared in the laboratory.

### 2.1. Catalyst preparation

#### 2.1.1. Preparation of TPA/ZrO<sub>2</sub>

ZrO<sub>2</sub> supported TPA (15%) catalyst was prepared by an impregnation method. Firstly, zirconium hydroxide was prepared by hydrolysis of zirconium oxychloride (0.5 M) by the dropwise addition of aqueous NH<sub>3</sub> (10%) solution until the solution reaches a pH of 10. The precipitate thus obtained was filtered and washed with deionized water until it was free from chloride ions as determined by the silver nitrate test. Zirconium hydroxide thus obtained was dried at 120 °C for 12 h, powdered well and dried for another 12 h. This is used as a support. The required quantity of TPA is dissolved in methanol (4 ml of methanol was used per gram of solid support) and this solution is added to the support while stirring. The excess of methanol was removed on a rota evaporator. The resulting solid was dried at 120 °C overnight and finally calcined in air at 300 °C for 2 h. This catalyst is denoted as TPA/ZrO<sub>2</sub>.

#### 2.1.2. Preparation of CsTPA

Cs exchanged TPA catalysts were prepared by adding the required quantities of CsNO<sub>3</sub> drop wise to the TPA solution at room temperature. During the addition of CsNO<sub>3</sub>, formation of a white precipitate took place. This solution was kept for ageing overnight. After ageing, excess water was removed slowly on a water bath. The dried samples were dried further in an oven at 120 °C for 12 h and finally calcined at 300 °C for 2 h. Two hydrogen atoms were replaced by cesium atoms in TPA; this is designated as Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub>.

#### 2.1.3. Preparation of Cs/TPA ZrO<sub>2</sub>

This catalyst was prepared by exchanging the protons of the TPA of TPA/ZrO<sub>2</sub> catalyst. The required quantity of CsNO<sub>3</sub> was exchanged with TPA/ZrO<sub>2</sub>. TPA/ZrO<sub>2</sub> thus prepared as reported above was used to exchange the proton of TPA with cesium. The final catalyst was obtained after calcinations at 300 °C for 2 h.

The presence of intact Keggin ion after the ion exchange and supporting was confirmed by the FT-IR and XRD analyses.

## 2.2. Characterization

Temperature programmed desorption of ammonia (TPD) was carried out on a laboratory-built apparatus equipped with a gas chromatograph using a TCD detector. In a typical experiment about 0.05 g of the oven dried sample was taken in a quartz tube. Prior to TPDA studies, the catalyst sample was treated at 300 °C for 1 h by passing pure helium (99.9%, 50 ml/min) over it. After pretreatment, the sample was saturated with anhydrous ammonia (10% NH<sub>3</sub>) at 100 °C at a flow rate of 50 ml/min for 1 h and was subsequently flushed with He at the same temperature to remove physisorbed ammonia. The process was continued until a stabilized base line was obtained in the gas chromatograph. Then the TPD analysis was carried out from ambient temperature to 700 °C at a heating rate of 10 °C/min. The amount of NH<sub>3</sub> evolved was calculated from the peak area of the already calibrated TCD signal.

## 2.3. Activity measurements

Hydrogenolysis of glycerol was carried out in a 100-ml haste alloy PARR autoclave. Required quantities of glycerol diluted in deionized water and of catalysts were introduced to the autoclave. The reactant and catalysts were put into the autoclave and this reactor was purged three times with H<sub>2</sub>. After the third purge, the reactor was heated to the reaction temperature by maintaining the required H<sub>2</sub> pressure. During the reaction, a decrease in hydrogen pressure was observed. After the reaction, the gas phase products

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