Selective Hydrogenolysis of Glycerol to 1, 2 Propanediol Over Cu–ZnO Catalysts

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Abstract A series of Cu–ZnO catalysts with varying Cu to Zn weight ratio are prepared by co-precipitation method. The catalysts were characterized by surface area, XRD, TPR and N_2O chemisorption to measure Cu metal area. These catalysts were evaluated for hydrogenolysis of glycerol. The catalyst with Cu to Zn ratio of 50:50 is highly active under relatively low H_2 pressure. The catalysts are highly selective towards 1,2 propanediol (>93%). The glycerol conversion depends upon the bifunctional nature of catalyst where it requires both acidic sites and metal surface. The presence of sufficient amount with small particle size of ZnO and Cu are required for high conversion of glycerol and selectivity to 1,2 propanediol. Different reaction parameters are studied in order to optimize the reaction conditions.

Keywords Glycerol · Copper oxide · Zinc oxide · Hydrogenolysis · 1,2 Propanediol

1 Introduction

A large amount of glycerol will be produced from the biodiesel industry as by product in next decades. About 10% of crude glycerol will be formed during the synthesis of biodiesel from triglycerides [1–3]. It is required a new technology for conversion of glycerol into valuable chemicals to make biodiesel production a cost effective process. Products derived from glycerol can be used in pharmaceuticals, food, agricultural adjuvants, polymer, resins functional fluids, cosmetics, plastics etc Transportation fuel industries that are now derived from fossil resources might be producible in future biorefineries from renewable resources [4–9].

The hydrogenolysis of higher polyols gives propylene glycol and ethylene glycols. These glycols obtained by catalytic conversion of glycerol are environmentally and economically attractive compared to their production from petroleum derivatives [9–12]. Supported metal catalysts are used for hydrogenolysis of glycerol. Supported Pt, Ru, Rh and Pd catalysts are studied for this reaction [13–15]. Addition of solid acid to metal catalysts enhances the conversion and selectivity of reaction [1, 5, 16]. Hydrogenolysis is two step reaction; in first step dehydration takes place and followed by hydrogenation in next step. Previous results showed that conversion of glycerol to 1,2 propanediol proceeds by combination of dehydration over acid catalysts and subsequent hydrogenation over metal catalysts [5, 6]. Solid acid catalyst plays a major role in conversion of glycerol hydrogenolysis. It is found that Ru based catalysts exhibit better activity than other metals for this reaction [15–18]. Unfortunately, Ru promotes excessive C–C bond cleavage, which leads to degradative products as ethylene glycol and methane [13, 14].

It requires selective cleavages of C–O bond without cleavage of C–C bond in hydrogenolysis of glycerol to get 1,2 propanediol [20]. In this direction Cu based catalysts are better catalysts compared to supported transition metal catalysts. Moreover, the Cu based catalysts are active under mild reaction conditions and does not require a separate solid acid catalyst [20]. Dasari et al. reported that copper chromite catalyst showing good conversion and selectivity

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towards propylene glycol under mild reaction conditions particularly at low H_2 pressures [4]. Chaminand et al. proved that Cu–ZnO catalyst along with H_2WO_4 as additive exhibited about 20% glycerol conversion at a reaction temperature of 180 °C. However, the reaction time is very high (92 h) [9]. Wang and Liu reported 23% of glycerol conversion with 83% selectivity to 1,2 propanediol at 200 °C with 42 bar of H_2 pressure for 12 h [20]. Copper chromite catalyst showed better activity and selectivity under mild reaction conditions compared to Cu–ZnO catalyst [4]. Due to toxicity of chromium, copper chromite based catalysts are undesirable due to environmental aspects [20]. Recently, glycerol hydrogenolysis is studied using Cu–ZnO relatively at high pressures compared to copper chromate catalysts [4, 20]. There is no detailed study about the catalyst characterization to understand the observed catalytic activities.

In the present study hydrogenolysis of glycerol is carried over a series Cu–ZnO catalysts with varying Cu to Zn ratio at low H_2 pressures. The physico-chemical characteristics of the catalysts are correlated to explain the observed catalytic activity. The catalysts are studied at different reaction parameter to optimize the reaction conditions for selective formation of propylene glycol.

2 Experimental

2.1 Catalyst Preparation

Cu–Zn oxide catalysts were prepared by co-precipitation method [21]. Calculated amounts of aqueous solutions of Cu $(NO_3)_2$ $3H_2O$ and Zn $(NO_3)_2$ $6H_2O$ were taken and precipitated with sodium carbonate. The concentrations of Cu^{2+} and Zn^{2+} in the solutions were varied to change the Cu/Zn weight ratio. During the precipitation the solutions were maintained at 70 °C to form precipitate. The precipitate was aged further at the same temperature for 3 h. After cooling the precipitate was separated by filtration and washed thoroughly with deionized water to remove traces of sodium. Thus obtained precipitate was dried overnight at 120 °C and finally calcinated at 400 °C for 3 h. The catalysts prepared are designated as Cu: Zn-40: 60, Cu: Zn-50: 50, Cu: Zn-60: 40, Cu: Zn-70: 30. The numerical numbers indicate the weight percentage of Cu and Zn respectively.

2.2 Catalysts Characterization

X-ray powder diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex (M/s. Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu Kα radiation (λ = 1.5406 Å) with a scan speed of 2 min^{-1} and a scan range of 2–80 at 30 kV and 15 mA. Particle sizes of

Cu and Zn oxides were calculated from XRD patterns by using Debye–Scherrer equation.

The BET surface areas of the catalyst samples were calculated from N_2 adsorption–desorption data acquired on an autosorb-1 instrument (Quantachrome, USA) at liquid N_2 temperature.

Temperature programmed reduction (TPR) of the catalysts was carried out in a flow of 10% H_2/Ar mixture gas at a flow rate of 30 mL/min with a temperature ramp of 10 °C/min. Before the TPR run the catalysts were pretreated with argon at 300 °C for 2 h. The hydrogen consumption was monitored using a thermal conductivity detector.

In order to determine the copper surface exposed and the dispersion in the reduced samples, the nitrous oxide chemisorption was used as described in literature [22, 23]. For the analysis, a Autochem 2910 (Micrometrics, USA) was employed. In a typical experiment, pre-reduction of the CuO phase to Cu (0) was performed at 300 °C for 2 h with 5% H_2/Ar mixture. Then the sample which is in the form of Cu (0) phase exposed to N_2O to oxidize Cu to Cu_2O by adsorptive decomposition of N_2O at 80 °C by a continuous N_2O flow for 0.5 h. Then, the TPR was carried out on the freshly oxidized Cu_2O surface in order to reduce Cu_2O to Cu. and a thermal conductivity detector (TCD) was used to measure the amount of H_2-uptake with a heating rates of 10 °C/min.

Copper dispersion (D), defined as the ratio of Cu exposed at the surface to total Cu, was calculated from the amount of H_2 consumed in the TPR analysis. Cu metal surface area (S) was calculated as: $S(m^2/g_{Cu})$ = 100 $MolH_2$ SF N_A/C_M W_{Cu}, where $MolH_2$, SF, N_A, C_M, and W_{Cu} are moles of hydrogen experimentally consumed per unit mass of catalyst ($MolH_2$/g_{cat}), stoichiometric factor, Avogadro's number (6.022 × 10^{23}), number of surface Cu atoms per unit surface area (1.47 × 10^{19} atoms m^{-2}) and Cu content (wt.%), respectively. Average copper particle size was calculated as: $d_{v.s}$ (nm) = 10^7 SK C_M W_{Cu}/$MolH_2$ SF N_A ρ_{Cu}, where SK is a constant depending on Cu particle shape (six or five) and ρ_{Cu} is the density of copper (8.92 g/cm^3).

2.3 Catalytic Activity Measurement

Glycerol hydrogenolysis reactions were carried our in a haste alloy autoclave (200 mL) at a stirring speed of 500 rpm. Required quantity of glycerol (99% pure, Qualigens Chemicals, India) diluted in deioninzed water and catalysts were introduced to the autoclave. Unless specifically stated, Cu–ZnO samples are pre-reduced at 300 °C for 3 h by H_2 stream (60 mL/min) were used as the catalysts in this work. The autoclave after it was flushed with H_2 was pressurized with H_2 to desired pressure by maintaining at stated reaction temperatures. During the reaction it

observed a decrease in hydrogen pressure and the total decrease in hydrogen pressure was, at most, 1/10 of the initial pressure. After the reaction, the gas phase products were collected in a gasbag and the liquid phase products were separated from the catalyst by filtration. These products were analyzed using a gas chromatograph (shimadzu) equipped with a flame ionization detector (FID). A TC-WAX capillary column (diameter 0.25 mm, length 30 m) was used for separation of products. Products were identified on GC-MS (GCMS-QP5050, column Stabilwax; Shimadzu Corp.) and the products detected were: 1,2-propanediol (1,2-PD), 1-propanol (1-PO), and 2-propanol (2-PO) as hydrogenolysis products, and ethylene glycol (EG), ethanol, methanol and methane as degradation products. Conversion of the reactants in all reaction tests were calculated on the basis of the following equation:

Conversion (%)
$$= \frac{\text{Sum of C} - \text{based mol of all products}}{\text{Sum of C - based mol of reactant}} \times 100.$$

The selectivity of the products was calculated on carbon basis.

3 Results and Discussion

Initially the Cu–Zn catalysts with varying Cu to Zn ratio are studied to optimize the catalyst composition for the glycerol hydrogenolysis. The results obtained over these catalysts are presented in Table 1. The results suggests that with increasing the Cu content the glycerol conversion is increased up to 50% of Cu and there after the activity is decreased with further increase in Cu composition. The optimum conversion is recorded for the catalyst with Cu to Zn ratio of 1. The decrease in conversion at higher Cu content might be due to the insufficient amount of ZnO. The presence of ZnO is essential as it catalyze the dehydration step to yield acetol from glycerol, which further undergoes hydrogenation on Cu sites to yield propylene glycol. The dehydration step will determine the over all

conversion of glycerol. The product distributions over the Cu–ZnO catalysts presented in Table 1 suggests that the selectivity towards the formation of acetol decreased with increase in Cu content (or decrease in ZnO content). It is important to note that the selectivity toward 1,2-propane diol is almost constant irrespective of the Cu to Zn ratio. This suggests that the catalysts are possessing sufficient amount of Cu to hydrogenate the acetol intermediate to propylene glycol. These results endorse that the content of Zn is important in the conversion of glycerol. During glycerol hydrogenolysis Cu to Zn ratio plays an important role in glycerol conversion and propylene glycol formation.

In order to understand the reasons for high activity of Cu–ZnO catalysts with particular Cu/Zn ratio these catalysts are characterized by different techniques such as copper metal area by N_2O chemisorption, XRD, temperature programmed reduction (TPR) etc.

XRD patterns of the catalysts are presented in Fig. 1. The XRD patterns related to the crystallite phases of ZnO and CuO. There is no formation of any mixed oxide phases. The crystallite sizes of these catalysts are calculated from the XRD patterns obtained for the catalysts after reduction and are shown in Table 2 along with other physico-chemical properties. The Cu crystallite size is increasing with increase in Cu content and similar behavior is noticed with the crystallite sizes of ZnO. The catalyst with Cu/Zn ratio of 40:60 and 50:50 contains relatively small crystallite sizes compared to other catalysts. The high activity of these catalysts might be due to the presence of well-dispersed smaller Cu particles on ZnO. The low glycerol conversion of the catalysts with high Cu content might be due to non-availability of sufficient amount of ZnO. In glycerol hydrogenolysis, ZnO initiates the reaction by dehydrating the glycerol and further hydrogenolysis takes place on Cu sites.

Table 1 Effect of Cu/Zn ratio on the glycerol hydrogenolysis activity

Catalyst	Conversion (%)	Selectivity (%)			
		Acetol	1,2 PDO	EG	Others
Cu–Zn 40:60	30	5.5	91.0	1.7	1.8
Cu–Zn 50:50	37	3.4	92.0	3.0	1.6
Cu–Zn 60:40	24	3.4	92.2	2.5	1.9
Cu–Zn 70:30	15	2.9	92.0	2.8	2.3

Reaction conditions: 100 mL of 20 wt.% glycerol aqueous solution; H_2 pressure: 20 bar; reaction time: 16 h; catalyst weight: 1.2 g (6%); reaction temperature: 200 °C

Fig. 1 X-ray diffraction patterns of the Cu–ZnO catalysts (*) Cu (#) ZnO phases

Table 2 Physico-chemical properties of Cu–ZnO catalysts

| Catalyst	Molar ratio (Cu/Zn)	Metal surface area (m^2/g)	Dispersion (%)	H$_2$ uptake from TPR ($\times 10^{-4}$ moles/g)	After reduction crystal size (nm)	
					Cu	ZnO
Cu–Zn 40:60	0.68	90.6	29.5	74.8	33.4	32.7
Cu–Zn 50:50	1.03	142.1	22.0	93.3	33.4	30.9
Cu–Zn 60:40	1.54	140.0	20.7	102.5	35.6	37.3
Cu–Zn 70:30	2.40	120.6	18.6	133.8	38.1	40.0

The copper metal area and the dispersion shown in Table 2 suggest that there exists a relationship with Cu dispersion and glycerol conversion. It is reported that smaller ZnO and Cu domains lead to higher glycerol conversions and propylene glycol selectivities respectively [20].

The TPR patterns of Cu–ZnO catalysts are shown in Fig. 2. The TPR patterns contain a major peak around 325 °C along with two shoulder peaks at 250 and 350 °C. The major peak corresponds to the reduction of CuO to metallic copper. The low temperature shoulder peak is assigned to the reduction of CuO to Cu$^+$ and the high temperature shoulder peak is assigned to the reduction of Cu$^+$ to metallic copper [24, 25]. With increase in the Cu content the reduction temperature is marginally shifted towards higher temperature. The catalyst with maximum amount of Cu showed a high temperature shoulder peak, which corresponds to reduction of Cu^{+1}. The catalyst with Cu/Zn ratio of 1 showed maximum activity and this catalyst is easily reduced to metallic copper under reaction conditions. The low glycerol conversion for the catalysts with high Cu content might be due to the presence of some amount of Cu^{+1} species that are not easily reduced under reaction conditions.

3.1 Effect of Reaction Temperature

In the glycerol hydrogenolysis, reaction temperature has a significant effect on over all conversion of glycerol. The effect of reaction temperature was studied over Cu/Zn catalysts and the results are presented in Fig. 3. As the temperature of the reaction increased from 120 to 200 °C a drastic increase in glycerol conversion is observed. At low reaction temperature the over all conversion is very low up to 160 °C. The conversion is high at a reaction temperature of 220 °C. Further increase in temperature may increase the conversion. However, the selectivity towards the 1,2
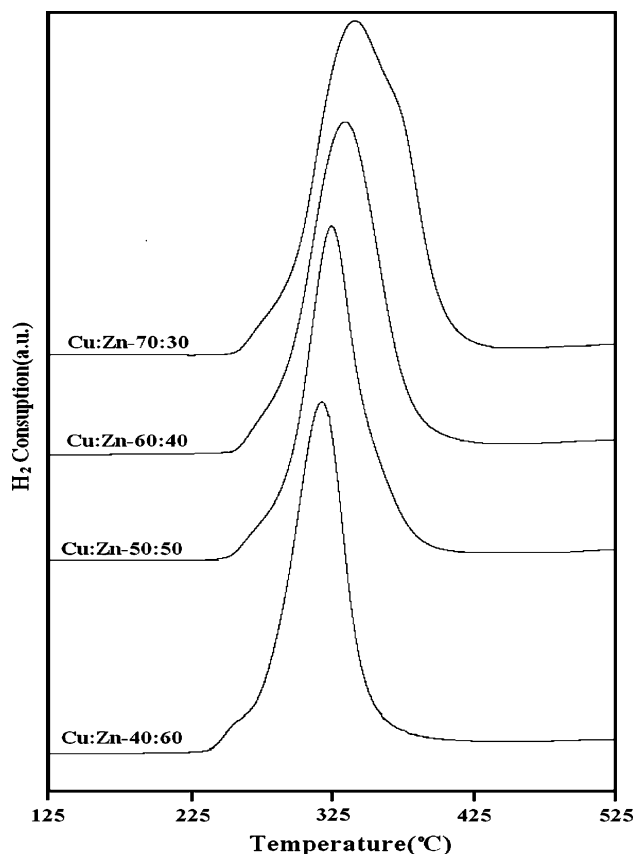
Fig. 2 Temperature programmed reduction profiles of Cu–ZnO catalysts
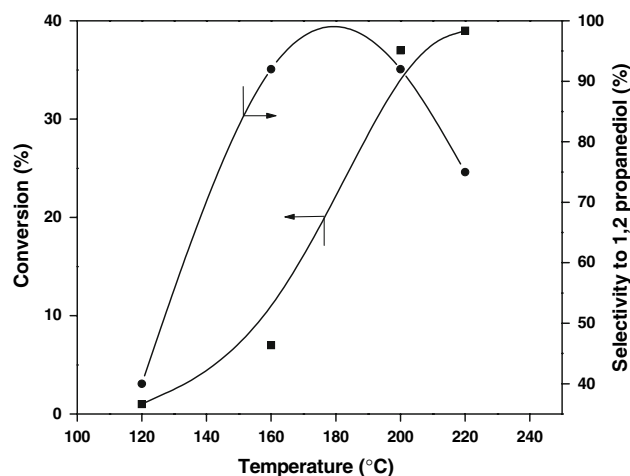
Fig. 3 Effect of reaction temperature during the glycerol hydrogenolysis over Cu–Zn . 50:50 catalyst. Reaction conditions: 100 mL 20 wt.% glycerol aqueous solution; H$_2$ pressure: 20 bar; reaction time: 16 h; catalyst weight: 1.2 g (6%)

propanediol is decreased at high temperatures. It is reported that at above 200 °C the reaction lead to excessive hydrogenolysis converting the propylene glycols into lower alcohols [4, 6, 20].

## 3.2 Effect of Glycerol Concentration

The effect of glycerol concentration or water content on hydrogenolysis was studied and the results are tabulated in Table 3. The glycerol conversion is increased with increase in glycerol concentration up to 20% and there after a decrease in conversion is noticed. The decrease in conversion at higher glycerol concentration is due to the less number of available active sites of the catalyst as the catalysts concentration is constant in all reactions. The catalyst showed considerable conversion even at high glycerol concentration without any variation in selectivity to desired propylene glycol. However, others reported a decrease in selectivity at higher glycerol concentration as degradation of reaction product takes place by polymerization [4].

3.3 Effect of Reaction Time

The change in conversion with reaction time is studied and the results are shown in Fig. 4. As expected the glycerol conversion increased from 25 to 45% with increase in reaction time from 4 to 24 h. Most of the reported catalysts showed reasonable conversion at longer reaction times usually at 24 h. The present catalyst exhibited about 20% conversion within 8 h. The catalyst is selective in forming propylene glycol with more than 90% irrespective of reaction time. These results suggest that the products are not decomposed during the long reaction time.

3.4 Influence of Hydrogen Pressure

The influence of hydrogen pressure on the hydrogenolysis of glycerol over Cu/Zn catalyst is studied at constant reaction temperature of 200 °C. The conversion is increased from 9 to 37% when H_2 pressure is varied from 10 to 20 bar. There after there is no considerable variation in conversion with further increase in H_2 pressure up 40
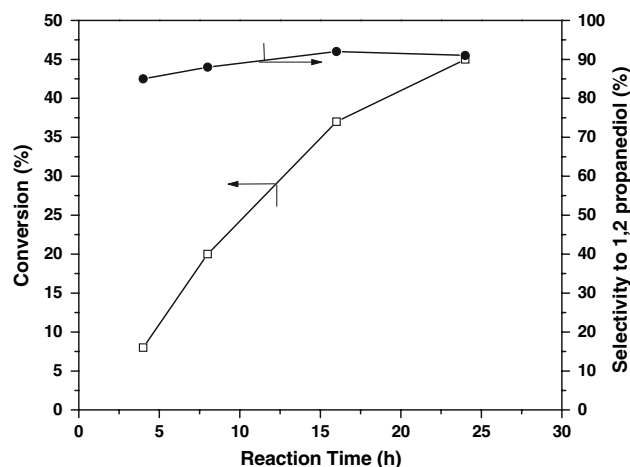
Fig. 4 Effect of reaction times during the glycerol hydrogenolysis over Cu–Zn 50:50 catalyst. Reaction conditions: 100 mL 20 wt.% Glycerol aqueous solution; H_2 pressure: 20 bar; catalyst weight: 1.2 g (6%); reaction temperature: 200 °C

and 60 bar. Cu–ZnO catalysts are active for glycerol hydrogenolysis at lower H_2 pressures compared to noble metal catalysts.

3.5 Effect of Catalyst Weight

Figure 5 shows the variation in conversion and selectivity with increase in the catalyst weight during glycerol hydrogenolysis. The glycerol conversion increased with increase in catalyst weight. With increase in catalysts weight more surface area is available for the hydrogenolysis reaction to takes place. It is interesting to see that there is no change in selectivity with increase in glycerol conversion. At higher catalyst concentration excessive hydrogenolysis takes place and propylene glycol converts to lower alcohols [4]. The results suggest that the Cu–ZnO catalysts are highly selective during glycerol hydrogenolysis.

3.6 Characterization of Used Catalyst

The active Cu/Zn catalyst after the glycerol hydrogenolysis reaction is characterized by XRD to see any structural changes during the reaction. The XRD patterns of the used

Table 3 Effect of glycerol concentration in the hydrogenolysis of glycerol over Cu–Zn 50:50 catalyst

Catalyst (%)	Concentration (%)	Conversion	Selectivity (%)			
			Acetol	1,2 PDO	EG	Others
Cu–Zn 50:50	10	34	2.0	93	2.4	2.6
Cu–Zn 50:50	20	37	3.4	92	3.0	1.6
Cu–Zn 50:50	40	25	3.2	92	2.8	2.0

Reaction conditions: catalyst weight: 1.2 g (6%); H_2 pressure: 20 bar; reaction time: 16 h; reaction temperature: 200 °C
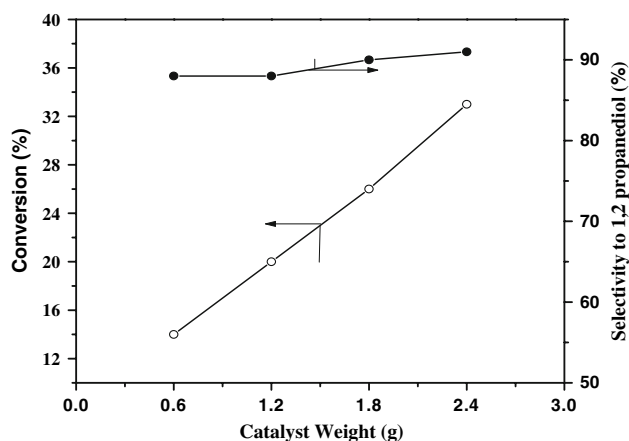
Fig. 5 Influence of catalyst weights on glycerol hydrogenolysis over Cu–Zn 50:50 catalyst. Reaction conditions: 100 mL 20 wt.% glycerol aqueous solution; H_2 pressure: 20 bar; reaction time: 8 h; reaction temperature: 200 °C
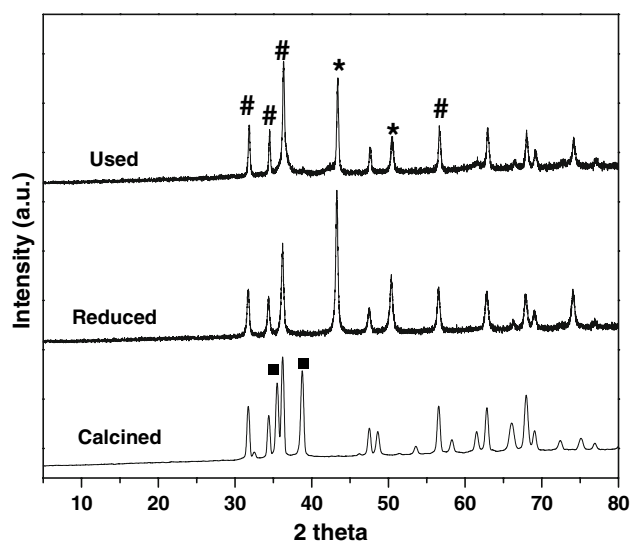
Fig. 6 X-ray diffraction patterns of the used Cu–ZnO catalysts (*) Cu (#) ZnO (■) CuO phases

catalyst are shown in Fig. 6 along with its fresh and reducing forms. The catalysts shown similar XRD patterns related to the reduced form of the catalyst, as it is pre-reduced before reaction. These results suggest the structural stability of the catalyst under the glycerol hydrogeloysis conditions. The stability of the catalyst might be one of the reasons for the high activity of the catalysts under different reaction conditions.

4 Conclusions

Selective formation of 1,2 propanediol by glycerol hydrogenolysis is achieved at low hydrogen pressures using Cu–ZnO based catalysts. High conversion and selectivity is obtained for the catalyst with Cu to Zn weight ratio of 50:50. The presence of small Cu and ZnO particles are required for better activity in glycerol hydrogenolysis. Sufficient amount of ZnO is needed for high conversion of glycerol. The catalysts are highly stable under reaction conditions. The conversion of glycerol and selectivity to 1,2 propanediol depends on the reaction temperature and glycerol concentration.

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