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Cu:Al Nano Catalyst for Selective Hydrogenolysis of Glycerol to 1,2-Propanediol

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Abstract Non-chromium Cu:Al nano catalyst prepared by simultaneous co-precipitation and digestion method without any template or stabilizer, showed three times higher activity than the bulk Cu–Cr catalyst for hydrogenolysis of glycerol in both isopropanol and water solvents, with the selectivity to 1,2-Propanediol (1,2-PDO) as high as 91% at 493 K and H_2 pressure of 7 MPa in 5 h. XRD pattern showed the presence of Cu^+ species in the activated Cu:Al nano catalyst. Although Cu^+ is catalytically inactive in glycerol hydrogenolysis reaction, the presence of Cu^+ helps to stabilize the particle size in a narrow range of 7–11 nm by inhibiting the sintering of copper particles under reaction conditions.

Keywords Cu:Al nano catalyst · Glycerol · Selective hydrogenolysis · 1,2-Propanediol

1 Introduction

Conversion of biomass to industrially important chemicals offers an attractive alternative to the consumption of petroleum based resources [1]. Large amount of glycerol is formed as a byproduct due to the rapid development of biodisel industries. Surplus amount of glycerol is currently being incinerated however, being a highly functionalized molecule glycerol can be converted into value added chemicals by various transformations and this will also significantly improve the biodisel production economics. Selective catalytic hydrogenolysis of glycerol represents a low cost and green route for 1,2-propanediol which is a major commodity chemical used in the production of antifreeze functional fluids, paints, humectants, and polyester resins [2–4]. The conventional route to produce 1,2-PDO involves the hydration of propylene oxide derived from propylene by chlorohydrin process or the hydro peroxide process [5–7]. Therefore, catalytic hydrogenolysis of glycerol to 1,2-PDO is a sustainable process based on renewable bio-feedstock.

Hydrogenolysis of glycerol is a two step process involving first step of either dehydration to acetol or dehydrogenation to glyceraldehyde depending on the acid or base catalysis respectively and subsequent hydrogenation to 1,2-PDO [8]. However, hydrogenolysis of glycerol via dehydration is a preferred (Scheme 1) route since [9–11] acetol is also an important intermediate in hydrogen production by catalytic steam reforming [12], pyruvaldehyde synthesis through oxidation [13] and as a starting material in various organic transformations [14, 15]. Catalyst systems involving various compositions of copper chromite as well as supported noble metals have been reported for the conversion of glycerol to 1,2-PDO in presence of a solvent under high pressure and temperature conditions [9, 16–18]. Among noble metals, Pd, Pt, Ru and Rh have been used on various supports for the hydrogenolysis of glycerol [19, 20]. Castle and Gomez first described glycerol hydrogenolysis using copper and zinc catalyst as well as sulfided Ru catalyst under very high pressure and temperature conditions (15 MPa; 513–545 K) with 75–85% selectivity to 1,2-PDO while >25% were cracked products such as EG, ethanol, methanol and lactic acid [21,

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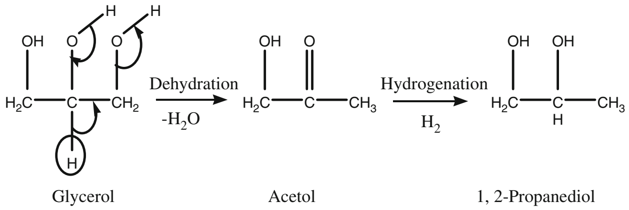
22]. Tomishige and co-workers developed Ru—solid acid bifunctional catalyst system for the hydrogenolysis of glycerol, however the highest selectivity to 1,2-PDO achieved was 82% with 40% conversion of glycerol [23–26]. The effect of sulphur addition to Ru/C catalyst was also investigated by Lahr et al. [27] in which the selectivity to 1,2-PDO linearly increased with sulphur loading nevertheless, maximum selectivity to 1,2-PDO obtained was up to 45%. It is clear from the literature that although Pt and Ru exhibited higher activity among the noble metal catalysts for the hydrogenolysis of glycerol, but Ru leads to C–C bond cleavage forming undesirable byproducts such as ethylene glycol and methane while Pt gives higher selectivity to lactate [8]. 1,2-PDO formation via glycerol hydrogenolysis involves selective cleavage of C–O bond without breaking C–C bond, for which Cu based catalysts are desirable. Dasari et al. [9] have reported copper chromite catalysts with the highest selectivity of 85% to 1,2-PDO with 55% glycerol conversion after 24 h at 473 K and 1.4 MPa H_2 pressure. Since the use of Cu–Cr catalysts is not favourable because of the toxicity associated with chromium, several researchers have focused their work on Cu–ZnO catalysts. Chaminand et al. [28] reported glycerol conversion of 20% with >90% selectivity to 1,2-PDO, using Cu–ZnO in presence of tungstic acid in 92 h. Wang and Liu proposed bifunctional Cu–ZnO catalysts and obtained 84% selectivity to 1,2-PDO with 23% glycerol conversion in 12 h [29]. Recently, highest selectivity of 93% to 1,2-PDO was achieved with 34% glycerol conversion for Cu–ZnO catalyst in 16 h reaction time [30]. Although, Cu–ZnO catalyst system could be acceptable due to elimination of chromium, but longer reaction times make it unpractical from process point view. Therefore, we aimed at developing highly efficient non-chromium nano (Cu:Al) catalysts by the reduction of cubic spinel-type phases, which contain excess copper ions that will exhibit good catalytic performance and do not require any promoter for the glycerol hydrogenolysis. As per the expectation, our non chromium Cu:Al nano catalyst (7–11 nm) exhibited greater than two fold activity as compared to the bulk Cu–Cr catalyst (>25 nm) with the highest selectivity of 91% to 1,2-PDO for aqueous phase hydrogenolysis of glycerol in a very short reaction time of 5 h. The catalyst was characterized for its physico-chemical properties based on which the observed activity results have been discussed. Effect of various reaction parameters on conversion of glycerol and selectivity to 1,2-PDO has also been reported for the nanostructured Cu:Al catalyst.



Scheme 1 Hydrogenolysis of glycerol to 1,2-Propanediol

2 Experimental

2.1 Materials

Glycerol (99%), ethylene glycol were purchased from Merck Specialities, Mumbai, India while acetol, 1,2-Propanediol, and iso-propanol were purchased from Sigma–Aldrich, Bangalore, India. Copper nitrate, aluminium nitrate were purchased from Loba Chemie, Mumbai, India. Hydrogen and nitrogen of high purity (>99.99%) were obtained from Inox-I.

2.2 Catalyst Preparation

The nanostructured Cu (Cu:Al) catalyst was prepared by coprecipitaion method. 0.05 M aqueous solution of each Cu $(NO_3)_2{\cdot}3H_2O$ and Al $(NO_3)_3{\cdot}9H_2O$ were taken and precipitated using 0.2 M aqueous potassium carbonate at room temperature. The precipitate was aged further for 6 h at room temperature. Then the precipitate was separated by filtration and washed with deionized water to remove the traces of potassium. The precipitate thus obtained was dried in static air oven at 373 K for 8 h and calcined at 673 K for 4 h.

Bulk copper chromite catalyst (Cu–Cr A) was prepared by a co precipitation method. First, aqueous ammonium chromate solution was prepared by drop wise addition of 19 mL of 30% aqueous ammonia to aqueous solution of ammonium dichromate. This solution was then added to an aqueous copper nitrate solution to give a reddish brown precipitate of copper chromate. This precipitate was then filtered, dried and calcined at 673 K for 5 h. Another bulk copper chromite catalyst (Cu–Cr B) was prepared following the patented procedure in which barium was used as an additive [31]. Copper content of Cu–Cr A and Cu–Cr B catalysts was 67 and 60%, respectively.

2.3 Characterisation

X-ray powder diffraction patterns were recorded on a Rigaku, D-Max III VC model, using nickel filtered CuKα radiation. The samples were scanned in the 2θ range of 1.5–80°. TPD measurements were carried out on a Quantachrome CHEMBET 3000 instrument. In order to evaluate acidity of the catalysts, ammonia TPD measurements were carried out by: (1) pre-treating the samples from room temperature to 473 K under nitrogen flow rate of 65 mL/min. (2) adsorption of ammonia at room temperature (3) desorption of adsorbed ammonia with a heating rate of 10 °C min^{-1} starting from the adsorption temperature to 973 K.

2.4 Catalyst Activity

Glycerol hydrogenolysis reactions were carried out in a 300 mL capacity autoclave (Parr Instruments Co., USA) at a stirring speed of 1,000 rpm. The typical hydrogenolysis conditions were: temperature, 493 K; glycerol concentration, 20 wt%; catalyst loading, 0.8 g; and hydrogen pressure 7–8 MPa. The catalysts were pre-reduced under H_2 at 1.4 MPa and 473 K for 12 h. Liquid samples were analyzed by GC (Varian 3600) equipped with a flame ionization detector and a capillary column (HP-FFAP 30 m, 0.53 mm, 1 μm). Conversion of glycerol was calculated as follows,

$$\mathrm{Conversion}(\%) = \frac{\text{moles of glycerol reacted}}{\text{initial moles of glycerol}} \times 100 \qquad (1)$$

The mass balance was also calculated in each experiment which was always >95%. Selectivity of various products was calculated as follows,

$$\mathrm{Selectivity}(\%) = \frac{\text{moles of a product formed}}{\sum \text{moles of all the product}} \times 100 \qquad (2)$$

Catalyst activity has been also expressed in terms of turn over frequency (TOF, h^{-1}) as given by eq. (3).

$$\mathrm{TOF}(\mathrm{h}^{-1}) = \frac{\text{Concn. of glycerol consumed}}{[\text{Concn. of catalyst (active metal)}](\mathrm{h})} \qquad (3)$$

3 Results and Discussion

3.1 Catalyst Characterisation

Figure 1 shows TEM image of the activated Cu:Al nano catalyst as an aggregation of the metal particles the size of which was estimated to be ~10 nm (Fig. 1a). Figure 1b shows the diffraction planes (110), (111), (311), (204) which correspond to acicular CuO nano particles [32]. TEM of bulk Cu–Cr (Fig. 2) clearly shows the higher extent of agglomeration of metal particles from which the particle size was found to be in the range of 25–30 nm.

Figure 3a, b show the XRD patterns of Cu:Al nano and the bulk Cu–Cr A catalysts respectively at various stages of preparation. The XRD patterns after calcination for both Cu-nano (A1 in Fig. 3a) as well as bulk Cu–Cr A catalysts (B1 in Fig. 3b) showed dominant peaks at 2 theta values of 35.46° and 38.7° corresponding to Cu^{2+} [29]. After reduction of Cu–Cr A in hydrogen, narrow well defined peaks appeared at 43.36°, 50.96°, and 74.5° which correspond to metallic Cu (B2 in Fig. 3b) [33]. While reduced nano catalyst shows broader peaks at 36.54° and 43.36° which could be assigned to Cu^{+} and metallic Cu respectively, indicating the inadequate reduction of Cu in nano catalyst. This also confirms that the Cu^{2+} in nano Cu:Al catalyst undergoes the sequential reduction as CuO first reduced to Cu_2O cubic phase as a stable intermediate and then to Cu° [32]. Using Scherrer–Warren equation, the crystallite sizes of fresh and used nano catalysts were found to be 7 and 11 nm while those of bulk catalysts were 24 and 42 nm, respectively. This shows that the extent of aggregation for nano Cu:Al catalyst was much less than that observed for the bulk catalyst under reaction conditions which could be due to the presence of Cu^{+} species in the nano catalyst.

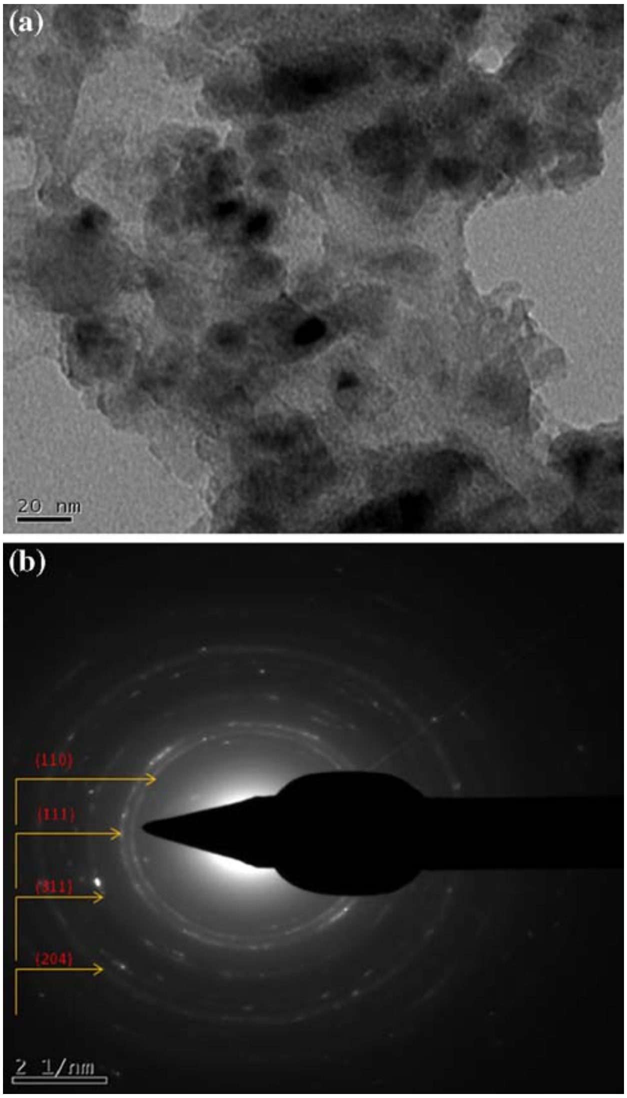


Fig. 1 **a** TEM image of nano catalyst **b** area of diffraction from the planes (110), (111), (311) and (204)

Since, the first step of glycerol hydrogenolysis involves its dehydration to acetol; the strength and nature of acid

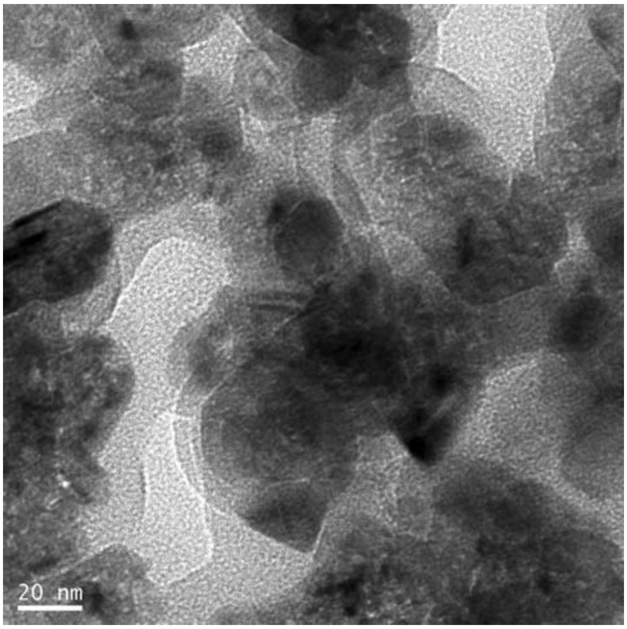


Fig. 2 TEM image of bulk Cu–Cr catalyst

sites of our catalysts were determined by NH_3-TPD. Table 1 shows the value of ammonia adsorbed and distribution of acidic sites of nano Cu:Al, Cu–Cr A and Cu–Cr B catalyst samples. The nano Cu:Al catalyst shows the highest total concentration of acidic sites as 1.567 mmol g^{-1} among all the three catalysts indicating that hydrogenolysis of glycerol proceeds through acetol via dehydration (Scheme 1) without needing a separate acidic catalyst.

The results of liquid phase glycerol hydrogenolysis in isopropanol at 493 K over different copper catalysts are presented in Table 2. Cu:Al nano catalyst showed the highest activity (TOF, 2.96 h^{-1}) with 88% selectivity to 1,2-PDO and 7% to acetol, while Cu–Cr A catalyst showed the lowest activity (TOF, 0.92 h^{-1}) with 74% selectivity to 1,2-PDO and 24% to acetol. Bulk catalysts (Cu–Cr A and Cu–Cr B) showed >20% selectivity to acetol due to lower rate of hydrogenation of acetol. The activity of Cu:Al nano catalyst was almost five fold higher than the bulk Cu–Cr catalysts reported in the literature [9, 29]. The novelty of our catalysts was that the formation of degradation product viz. ethylene glycol was much lower (≤5%) than that compared to bulk copper catalysts reported in the literature for which ethylene glycol along with methanol, propanols and gaseous products to the extent of >50% were formed [9, 29]. Also the major side product formed was only the acetol which eventually undergoes hydrogenation to give 1,2-PDO.

Table 3 shows the activity results of various catalysts for the hydrogenolysis of glycerol using water as a solvent. Cu:Al nano catalyst showed the highest (TOF, 2.63 h^{-1}) activity and selectivity (91%) to 1,2-PDO. Activity as well

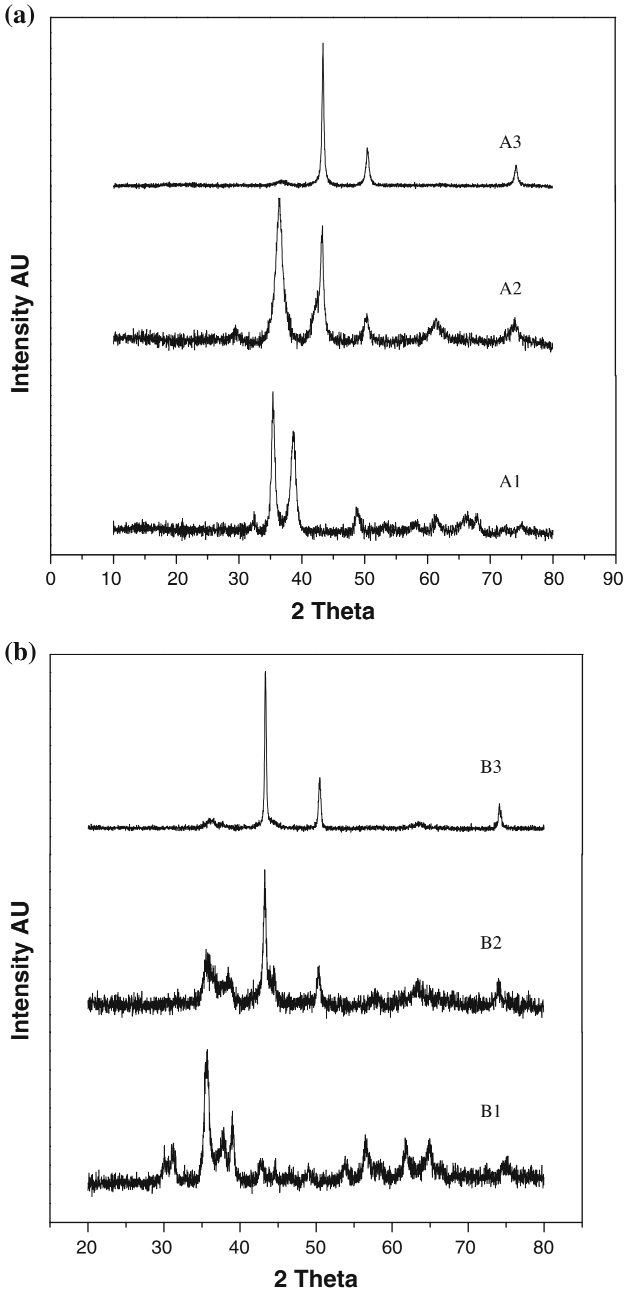


Fig. 3 **a** XRD pattern of nano catalyst (A1) calcined, (A2) reduced, (A3) after reaction. **b** XRD pattern of Cu–Cr A catalyst (B1) calcined, (B2) reduced, (B3) after reaction

Table 1 Ammonia TPD results of nano Cu-nano, Cu–Cr A and Cu–Cr B[31]

Catalysts	NH_3 adsorbed (mmol g^{-1})	Distribution of acidic sites	
		(85–200 °C)	(200–450 °C)
Nano Cu:Al	1.567	0.145	0.910
Cu–Cr A	0.482	0.0241	0.1713
Cu–Cr B	1.184	0.145	0.910

Table 2 Hydrogenolysis of glycerol in isopropanol

Catalysts	TOF h^{-1}	Conversion (%)	Selectivity (%)		
			1,2-PDO	Acetol	EG
Nano Cu:Al	2.96	47	88	7	5
Cu–Cr A	0.92	16	74	24	2
Cu–Cr B	1.26	24	63	32	5

Reaction conditions: 23 wt% glycerol aqueous solution (100 mL), 7 MPa H_2 pressure, 0.8 g catalyst, 493 K, 5 h

as selectivity to 1,2-PDO decreased drastically for bulk Cu–Cr catalysts in comparison with Cu:Al nano catalyst. The drop in selectivity to 1,2-PDO was mainly due to the accumulation of an intermediate, acetol indicating slower kinetics of acetol hydrogenation to 1,2-PDO over bulk Cu–Cr catalyst. The activity and selectivity exhibited by Cu:Al nano catalyst in water was almost comparable to that in isopropanol solvent indicated the better water tolerance of the Cu:Al nano catalyst hence, aqueous glycerol solution can be directly used as a feed for its selective hydrogenolysis to 1,2-PDO.

The highest activity of the Cu:Al nano catalyst for glycerol hydrogenolysis could be due to the following two reasons. (1) The higher acidic sites as shown by ammonia TPD results. As the glycerol hydrogenolysis is a two step process, the first step being dehydration of glycerol to acetol followed by the hydrogenation to give 1,2-PDO. Aluminium present in our nano catalyst gets converted to alumina during calcination step which is normally responsible for higher acidity leading to faster dehydration to form acetol. Sato et al. [34] proposed that alumina supported copper as well as pure copper were effective catalysts for the dehydration of glycerol to acetol under inert conditions, and (2) acetol thus formed undergoes probably a very fast hydrogenation to 1,2-PDO, catalyzed by nano size Cu°. The nano size Cu° is stabilized due to the inhibition of sintering by Cu^+, the presence of which is evidenced by the XRD pattern (Fig. 3a). Huang et al. [35] also have suggested that the Cu^+ formed during the reduction treatment, although catalytically inactive in glycerol reaction, helps to inhibit the sintering of copper particles during the reaction. While Cu–Cr A catalyst (Fig. 3b) consists of pure metallic copper phase i.e. Cu°, the Cu^+ species in Cu:Al nano catalyst formed due to alumina is responsible for the higher catalytic activity due to the stabilization of the catalyst by inhibiting the sintering of active species.

Table 3 Hydrogenolysis of glycerol in water

Catalysts	TOF h^{-1}	Conversion (%)	Selectivity (%)		
			1,2-PDO	Acetol	EG
Nano Cu:Al	2.63	38	91	4	5
Cu–Cr A	0.51	9	55	44	1
Cu–Cr B	0.94	18	38	62	<0.01

Reaction conditions: 20 wt% glycerol aqueous solution (100 mL), 7 MPa H_2 pressure, 0.8 g catalyst, 493 K, 5 h

3.2 Parameter Studies

3.2.1 Effect of Temperature

Figure 4 shows the influence of reaction temperature on conversion and selectivity pattern in glycerol hydrogenolysis over Cu:Al nano catalyst. Glycerol conversion increased from 29 to 76% with increase in temperature from 473 to 513 K. Maximum conversion of 76% was obtained at 513 K however, selectivity to 1,2-PDO decreased marginally from 93 to 89%, correspondingly increasing the selectivity to ethylene glycol from 6 to 10%, indicating that the higher temperature favoured degradation products due to C–C bond cleavage.

3.2.2 Effect of Catalyst Loading

Figure 5 shows the effect of catalyst loading on glycerol conversion and selectivity for hydrogenolysis of glycerol at 493 K. It was found that conversion of glycerol increased almost three fold with increase in catalyst loading from 0.4 to 1.6 g. The selectivity to 1,2-PDO slightly decreased at higher catalyst loading due to formation of degradation products. The increase in conversion with increase in catalyst loading could be due to more availability of the active sites on the catalyst surface for the reaction which also leads to excessive hydrogenation of 1,2-PDO to lower alcohols.

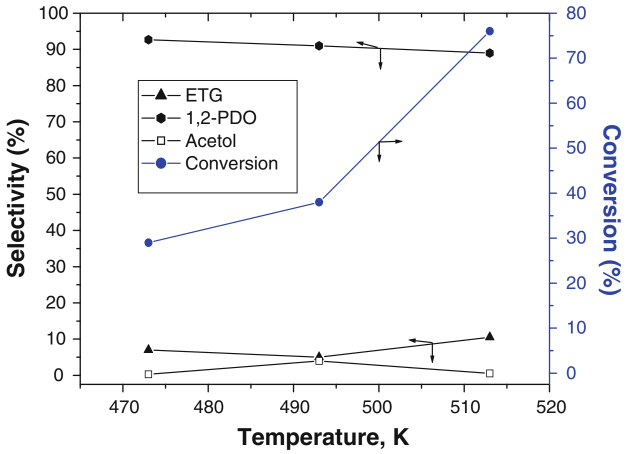


Fig. 4 Effect of temperature. Reaction conditions: 20 wt% glycerol aqueous solution (100 mL), 7 MPa H_2 pressure, 0.8 g catalyst, 5 h

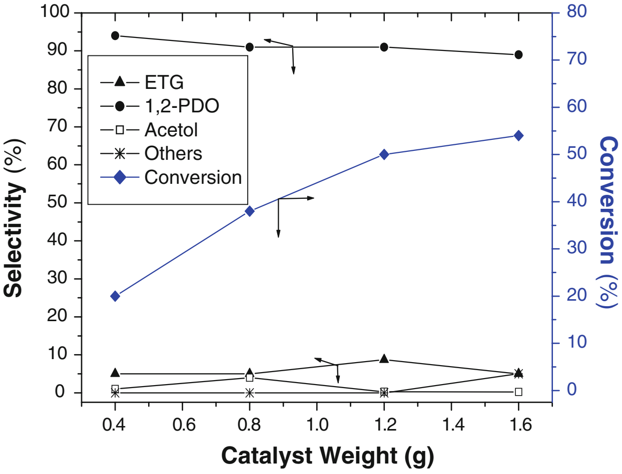


Fig. 5 Effect of catalyst loading. Reaction conditions: 20 wt% glycerol aqueous solution (100 mL), 7 MPa H_2 pressure, 493 K, 5 h

3.2.3 *Effect of Glycerol Concentration*

In order to achieve maximum productivity of 1,2-PDO, the effect of aqueous glycerol concentration on the conversion was also studied. Figure 6 shows that conversion of glycerol increased from 38 to 45% with increase in glycerol concentration up to 60 wt% beyond which it decreased drastically to 23%. This is because the limiting number of catalyst active sites was available since the catalyst concentration was constant. Substrate inhibited kinetics at higher glycerol concentration could be another explanation for decrease in conversion beyond 60% glycerol concentration. Similar observation was reported in case of butynediol hydrogenation also [36]. There was no significant effect of glycerol concentration on the selectivity pattern. For the highest glycerol loading of 60%, Cu:Al nano catalyst showed several fold (>10) higher activity (TOF, 10.2 h^{-1}) than the bulk copper catalysts [9, 29].

3.2.4 *Effect of Hydrogen Pressure*

The results of effect of H_2 pressure on glycerol hydrogenolysis studied at a constant temperature of 493 K are shown in Fig. 7. Glycerol conversion increased from 23 to 38% as the hydrogen pressure increased from 3.5 to 7 MPa. The increase in conversion was due to the higher availability of hydrogen at the catalyst surface at higher H_2 pressure. It is interesting to note that the selectivity to propanediol and acetol was not affected with change in H_2 pressure.

3.2.5 *Catalyst Recycle Study*

In order to establish the reusability of catalyst for glycerol hydrogenolysis reaction the catalyst was filtered after the first reaction and washed with a solvent. Then it was dried in oven at 383 K and regenerated under hydrogen and used for the subsequent hydrogenolysis of glycerol. This procedure was followed for two subsequent hydrogenolysis reactions and the results are shown in Fig. 8. Our Cu-nano catalyst showed significant activity even after the second recycle in terms of TOF. The turn over frequency of Cu-nano catalyst decreased from 2.96 to 2.27 which could be mainly due to the handling losses of the catalyst as well as metal sintering under reaction conditions of high temperature (493 K) for long time duration (5 h).

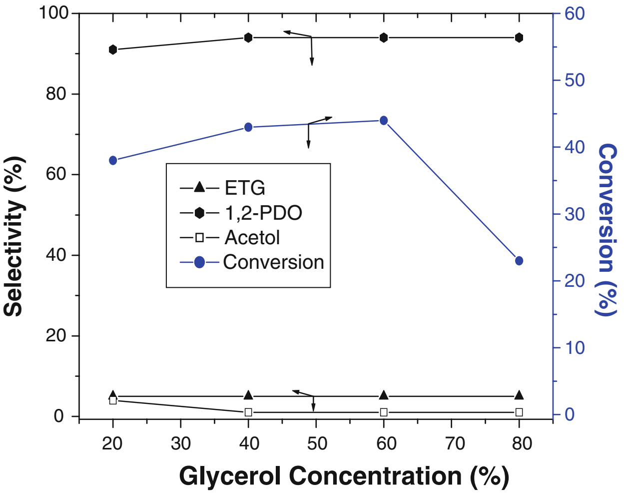


Fig. 6 Effect of glycerol concentration. Reaction conditions: 7 MPa H_2 pressure, 0.8 g catalyst, 493 K, 5 h

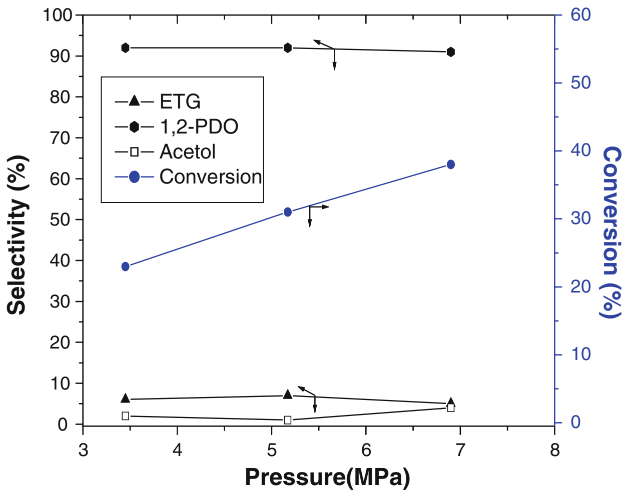


Fig. 7 Effect of hydrogen pressure. Reaction conditions: 20 wt% glycerol aqueous solution (100 mL), 0.8 g catalyst, 493 K, 5 h

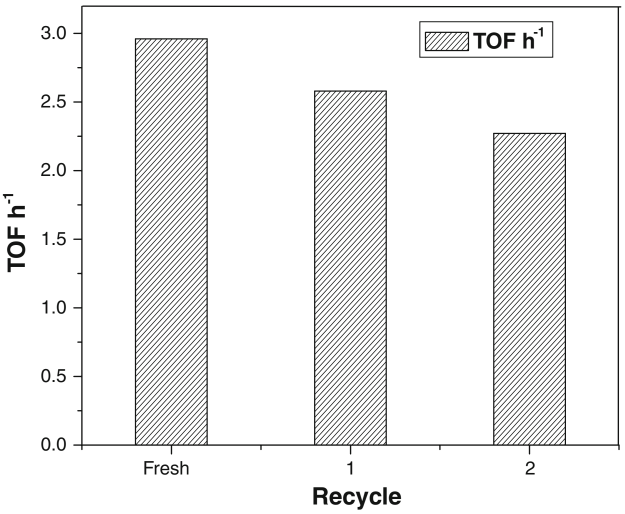


Fig. 8 Catalyst recycle study. Reaction conditions: 20 wt% glycerol aqueous solution (100 mL), 7 MPa H_2 pressure, 0.8 g catalyst, 493 K, 5 h

4 Conclusion

Highest TOF of 10.2 h^{-1} was achieved with Cu:Al nano (7–11 nm) non-chromium copper catalyst for the hydrogenolysis of aqueous glycerol (60 wt% in 100 mL). Major product formed was 1,2-Propanediol (91% selectivity) while the only degradation product formed was ethylene glycol (<5%). Presence of Cu^+ as evidenced by XRD, in the Cu-nano catalyst helps to inhibit the sintering of the active phase (Cu°) under reaction conditions leading to higher activity of the Cu-nano catalyst. Ammonia TPD results indicated higher acidity (1.567 mmol g^{-1}) of the non-chromium catalyst which is responsible for the hydrogenolysis of glycerol via dehydration pathway without using any acid catalyst. Glycerol conversion increased from 29 to 76% with increase in temperature from 473 to 513 K. Nano Cu:Al catalyst was also found to be active even after the second recycle indicating its excellent stability under reaction conditions.

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