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Continuous Dehydration and Hydrogenolysis of Glycerol over Non-Chromium Copper Catalyst: Laboratory-Scale Process Studies

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ABSTRACT: A non-chromium Cu:Al catalyst was developed for glycerol dehydration under N_2 atmosphere to acetol and hydrogenolysis to 1,2-propanediol (1,2-PDO). Among the various copper-based catalysts screened in this work, Cu:Al-1 catalyst showed the highest activity and acetol selectivity in water medium, whereas transfer hydrogenation in 2-propanol as the reaction medium led to the formation of 1,2-PDO (10−38%). The same catalyst was also found to catalyze the direct hydrogenolysis of glycerol to 1,2-PDO. Time on stream activity (TOS) of our Cu:Al-1 catalyst for both continuous dehydration and hydrogenolysis of glycerol was found to be 400 h with an average glycerol conversion of 90% and 65%, respectively. Maximum acetol selectivity was 55% while 1,2-PDO selectivity was 91% in dehydration and hydrogenolysis reactions separately. Effects of various reaction conditions on conversion, selectivity, and global rates of the two processes were also investigated.

1. INTRODUCTION

Most demandable biodiesel in the past decade, obtained by transesterification of vegetable oils and animal tallow helps to achieve two strategic goals viz. (i) the displacement of depleting fossil-based petroleum in favor of renewable domestic raw materials (an energy goal) and (ii) the establishment of a robust biorefinery (an economic goal) reducing the carbon footprint.[1] Today, nearly two-thirds of the world's glycerol production comes as a byproduct from biodiesel owing to the rapid increase in production of the latter from 1 million tons in 2000 (annual production capacity) to ~10 million tons in 2010.[2−4] The excess and consistent availability of glycerol in the market as well as its nontoxic and biodegradable nature has boosted the efforts for catalytic conversion of glycerol to value added chemicals.[5−8] Highly functionalized glycerol molecule can be converted into a variety of products in fine as well as commodity chemical sectors; however, 1,2-propanediol (1,2-PDO) via hydrogenolysis is being focused on commercially due to its high tonnage market demand. Archer Daniels Midland (ADM) has announced its first commercial plant of 0.1 million tons capacity of 1,2-PDO from glycerol, along with several other global players.[9] The global production of 1,2-PDO is about 1.4 million tons per year, and its increase in demand, @ 4% p.a., is due to its widespread applications as a functional fluid in polymer, cosmetics, and medicine and recently as a solvent replacement for toxic ethylene glycol.[10] Thus, a glycerol-based process for 1,2-PDO is a viable and sustainable alternative to the conventional fossil-fuel-derived propylene process associated with the generation of corrosive hydrochloric acid.[11]

Glycerol hydrogenolysis to 1,2-PDO proceeds through two distinct pathways, (i) glycerol dehydration to acetol (on acid sites) followed by its hydrogenation to 1,2-PDO (on metal sites) and (ii) through a dehydrogenation−dehydration−hydrogenation mechanism in the resence of a base (pathway A, Scheme 1).[12−17] In the first case, acetol is a first-step dehydration product, while in the other case, acetol is obtained in an indirect way from glyceraldehyde. Therefore, the first route via acetol to 1,2-PDO is generally preferred due to the use of acetol as a raw material for wide-range applications in cigarette filters, packaging, plastics, agriculture, pharmaceutical products, and consumer goods.[18] Second, acetol can be hydrogenated in a separate step with complete selectivity to 1,2-PDO. Catalyst systems reported for glycerol hydrogenolysis via acetol can be broadly classified into two types, viz. supported noble metals and other transition metals either supported or in their mixed oxide forms. Among noble metals Ru, Rh, Pt, and Au have been extensively studied and were found to be highly active in direct cleavage of both C−C and C−O bonds; thus, formation of ethylene glycol (EG) and methane are competing byproducts with 1,2-PDO.[19,20] As Cu catalysts are well-known for selective C−O bond hydrogenation, glycerol hydrogenolysis to 1,2-PDO is preferred over Cu in combination with other non-noble metals, particularly Cr, Zn, Ba, and Al.[21−24] Dasari et al. reported 20 wt % aqueous glycerol hydrogenolysis over various commercial copper chromite catalysts with 54.8% glycerol conversion and 85% selectivity to 1,2-PDO,[25] while copper chromite catalysts synthesized by template preparation resulted in enhancing 1,2-PDO selectivity to 96% using 40 wt % aqueous glycerol.[26] A systematic study of various promoters in Cu−Cr catalysts showed that the presence of Ba up to 30% in Cu−Cr gave higher activity and stability (>7-fold) as compared to Cu−Cr without any promoter. The better performance of Ba-promoted catalyst was found to be due to enhanced acidity and $BaCrO_4$ phase formation stabilizing the Cu^0 particle size at 69 nm.[27,28] However, toxicity associated with Cr in these catalysts necessitates the development of a new generation of catalysts. Among non-Cr catalysts, Cu−ZnO catalyst was first evaluated in the presence of a solid acid by Chaminand et al. to give 1,2-PDO selectivity >90% with a very low conversion of 20% in spite of longer reaction time (92 h).[29] Although a shorter

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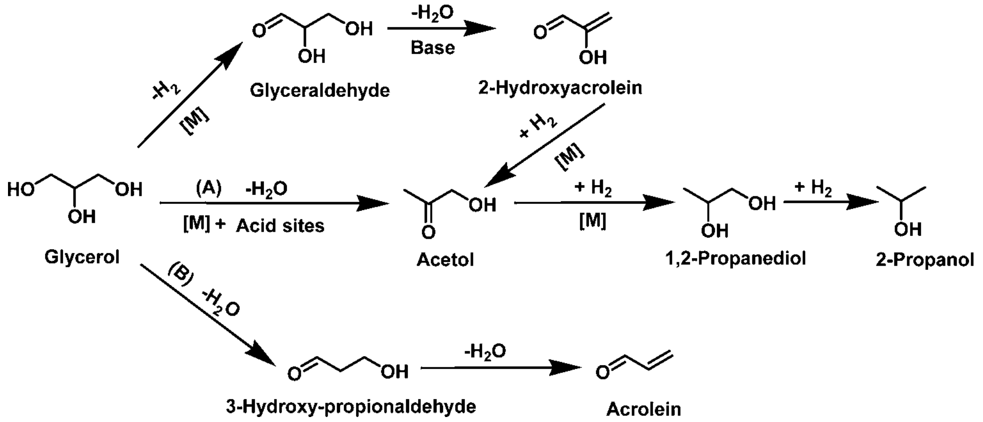
Scheme 1. Parallel and series reaction network in glycerol hydrogenolysis



reaction time (12 h) was reported by Wang and Liu for the Cu−ZnO catalyst, conversion was restricted to 22.5% with only 83.6% selectivity to 1,2-PDO.[30] As against this, incorporation of equimolar Al along with Cu prepared by a coprecipitation method caused a very high selectivity of 91% to 1,2 PDO at 47% glycerol conversion in only 5 h reaction time.[11] In spite of the fact that production of a high-volume product such as 1,2-PDO would be commercially viable with only continuous process, very few reports are available on process optimization. Some of these studies include gas-phase glycerol hydrogenolysis over Cu−Zn−Al catalysts and Cu−Al_2O_3 catalysts giving 96−100% glycerol conversion with 1,2-PDO selectivity >90%.[31,32] However, these studies were carried out under gas-phase conditions requiring a preheating step, at very low WHSV/LHSV conditions, and also the catalyst stability in terms of time on stream activity has not been specified. The main objective of this work was to investigate the activity performance of our Cu:Al catalysts for continuous dehydration of glycerol to acetol in an inert atmosphere and also for direct glycerol hydrogenolysis to 1,2-PDO, separately. This study is highly desirable from a process point of view since acetol can be first obtained and further hydrogenated over the same catalyst with complete selectivity to both the products. For this purpose, a detail study was carried out on comparison of performances of various copper catalysts with and without chromium for (i) dehydration and hydrogenolysis of glycerol to acetol and 1,2-PDO, respectively, in a batch reactor; (ii) effect of aqueous and organic solvents; (iii) performance study of the best non-chromium Cu:Al catalyst in a continuous process for both dehydration and hydrogenolysis of aqueous glycerol; (iv) comparison of product distribution in batch and continuous operations; (v) catalyst stability in terms of time on stream (TOS) activity of Cu:Al catalyst.

2. EXPERIMENTAL SECTION

2.1. Materials. Glycerol (99.9%) and EG were supplied by Merck Specialties, Mumbai, India, while acetol, 1,2-propanediol, and 2-propanol were obtained from Sigma-Aldrich, Bangalore, India. Copper nitrate, ammonium dichromate, aluminium nitrate, zinc nitrate, barium nitrate, potassium carbonate, and aq ammonia were purchased from Loba Chemie, Mumbai, India. Hydrogen and nitrogen of high purity (>99.99%) were obtained from Inox India and were used directly from the cylinders.

2.2. Catalyst Preparation. Copper chromite catalyst was prepared by a coprecipitation method. The required amounts of each of $Cu(NO_3)_2{\cdot}3H_2O$ and nitrate precursors of respective promoters, Al, Zn, or Ba were dissolved in deionized water. To this solution, the aqueous solution of ammonium chromate was added which was already prepared by dropwise addition of 30% aqueous ammonia to an aqueous solution of ammonium dichromate. The brown precipitate formed was then separated by filtration and washed with deionized water. The precipitate thus obtained was dried in a static air oven at 373 K for 8 h and calcined at 673 K for 3 h.

Cu:Al catalyst was prepared by co-precipitation involving simultaneous addition of an equimolar mixture of aq $Cu(NO_3)_2{\cdot}3H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, and 0.2 M aq K_2CO_3 at room temperature. Calcination was carried out as mentioned above. Following the same procedure Cu:Al catalysts with varying Cu:Al compositions were prepared, and these were designated as Cu:Al-1(50:50), Cu:Al-2 (70:30), and Cu:Al-3 (30:70). The prepared catalysts were pre-reduced under H_2 at 473 K for 12 h.

2.3. Activity Test. *Batch Operation.* Batch reactions were carried out in a Parr autoclave of 300 mL capacity. Typical hydrogenolysis conditions were the following: temperature, 493 K; glycerol concentration, 20 wt %; catalyst loading, 0.8 g; and hydrogen pressure, 35−70 bar. The dehydration experiments were carried out under the same conditions except that H_2 was replaced by N_2 atmosphere.

Continuous Operation. Continuous hydrogenolysis of glycerol was carried out in a bench-scale, high-pressure, fixed-bed reactor supplied by M/s Geomechanique, France. The details of the reactor setup are given in the literature.[28]

The powdered catalyst was pelletized in the form of pellets of 1×10^{-2} m diameter and cut into four pieces each having 2.5×10^{-3} m diameter (see Figure 1). Twenty grams of the pelletized catalyst was charged into the reactor. The specifications of the catalyst are given in Table 1. The section of 7×10^{-2} m above

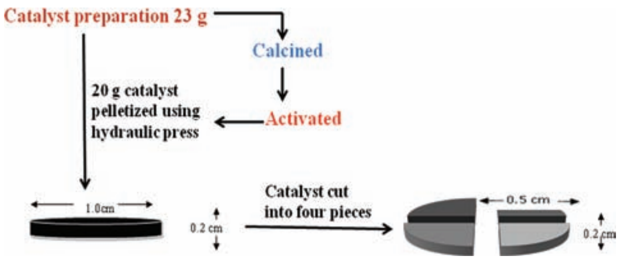


Figure 1. Schematic of Cu:Al-1 catalyst pellet preparation.

Table 1. Specifications of Cu:Al-1 catalyst

type	Cu:Al
form	pellets
size, m^2	0.005 × 0.002
surface area, m^2/g	31.37/56.63
bulk density, g/mL	1.05
Cu:Al composition	50:50

and 0.16 m below the catalyst bed was packed with carborundum as an inert packing, thus providing the catalyst bed of 0.13 m. Before starting the actual experiment the reactor was flushed thoroughly, first with N_2 and then with H_2 at room temperature. The liquid feed was "switched on" after attaining the desired temperature. The reactor was then pressurized with H_2 to the operating value that was maintained for 1 h to obtain the constant liquid flow rate. Liquid samples were withdrawn at regular intervals of time. 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).

Following this procedure, the experiments were carried out at different inlet conditions, the details of which are given in Table 2. Steady-state performance of the reactor was observed by analysis of the reactant and products in the exit stream. The dehydration experiments were carried out under the same conditions except that H_2 was replaced by N_2.

Table 2. Range of operating conditions

parameter	range	
	dehydration	hydrogenolysis
initial concentration of glycerol, wt %	10−40	20−60
solvent	water	water
temp., K	453−513	453−513
pressure, bar	20 N_2	21−62 H_2
catalyst wt, g	20	20
liquid velocity, LHSV, h^{-1}	0.3−2.7	0.3−2.7
gas velocity, GHSV, h^{-1}	500	500
catalyst packing length, m	0.13	0.13
particle diameter, d_p, m	0.005	0.005
density of the catalyst, kg/m^3	1050	1050

3. RESULTS AND DISCUSSION

3.1. Dehydration of Glycerol to Acetol.

Glycerol dehydration proceeds to give two different products viz. acetol and acrolein under liquid- and gas-phase conditions, respectively (pathways A and B, Scheme 1). Gas-phase dehydration is usually carried out under severe temperature and acidic conditions as compared to liquid-phase dehydration.[33] While gas-phase glycerol dehydration has been extensively studied, very few reports are available on liquid-phase dehydration of glycerol to acetol. More importantly, acetol formed via liquid-phase dehydration can be processed to cater to various applications and/or hydrogenated separately to produce 1,2-PDO. It is interesting to note that dehydration of glycerol takes place efficiently even in water; hence, the performance of the same catalyst was studied in both water and 2-propanol, the results of which are discussed below. All the dehydration experiments were carried out under N_2 atmosphere.

Table 3. Catalyst screening for dehydration of glycerol to acetol in aqueous medium under ambient conditions

catalysts[a]	composition	conversion, %	selectivity, % acetol	1,2-PDO	others
Cu:Al-1	50:50	17	93	7	0.0
Cu:Al-2	70:30	23	89	4	7
Cu:Al-3	30:70	26	92	2	6
NMT005	Cu, Cr, Ba	3	100	–	–
NMT006	Cu, Cr	<5	100	–	–
NMT008	Cu, Cr, Al Ba	8	100	–	–
NMT011	Cu, Cr, Zn	5	100	–	–

[a] Catalyst weight: 0.8 g, T = 493 K, P = N_2 ambient, 20 wt % glycerol, 3 h.

3.1.1. Batch Operation for Catalyst Screening. Catalyst Screening in Water. As shown in Table 3, Cu−Cr catalysts with and without promoters showed a low activity (3−8% conversion) with complete selectivity to acetol for glycerol dehydration in water, while in the case of Cu:Al catalysts activity and acetol selectivity were influenced by the Cu:Al composition. For Cu:Al composition of 30:70, the highest conversion of 26% was obtained; however, for both the lowest and the highest Cu contents, formation of other byproducts was observed. Since no byproduct formation was observed in the case of Cu:Al ratio = 50:50, this was chosen for further studies on glycerol dehydration. The better performance of Cu:Al-1 catalyst for the glycerol dehydration to acetol was mainly due to its highest surface acidity determined by NH_3-TPD (0.1873 mmol/g) as compared to Cu:Al-2 and Cu:Al-3 catalysts having acidity of 0.0533 mmol/g and 0.177 mmol/g, respectively. Nevertheless, formation of minor 1,2-PDO over Cu:Al catalysts in water medium could be due to an in situ hydrogenation reaction.

Catalyst Screening in 2-Propanol. Dehydration reaction involves the formation of water; hence, it is important to assess the role of water itself in the dehydration of glycerol. For this purpose, the catalysts screened for aqueous glycerol dehydration were also further evaluated under similar conditions in 2-propanol solvent, and the results are shown in Table 4. It was very interesting to note that several-fold increases in glycerol conversion were observed for both Cu−Cr and Cu:Al catalysts in 2-propanol solvent. Similar to the Cu:Al catalyst activity shown in dehydration in water, Cu:Al catalysts showed higher activity than Cu−Cr catalysts; however, with increasing Cu content from 30 to 70% (mole basis) glycerol conversion increased from 46 to 86%. For highest Cu content of 70 mol %, acetol selectivity was as low as 18% due to formation of byproduct up to 70% comprising mainly glycerol/acetol

Table 4. Catalyst screening for dehydration of glycerol to acetol in 2-propanol under ambient conditions

catalysts[a]	composition	conversion, %	selectivity, % acetol	1,2-PDO	EG	others
Cu:Al-1	50:50	70	54	38	8	–
Cu:Al-2	70:30	86	18	10	2	70
Cu:Al-3	30:70	46	50	29	3	17
NMT006	Cu, Cr	37	86	14	–	
NMT008	Cu, Cr, Al, Ba	34	90	8	2	–
NMT011	Cu, Cr, Zn	38	55	7	–	38

[a] Catalyst weight: 0.8 g, T = 493 K, P = N_2 ambient, 20 wt % glycerol, 3 h.

alkylation products. While in the case of Cu−Cr catalysts with and without the promoter, glycerol conversion remained constant in the range of 34−38%; however, the achieved acetol selectivity was as high as 90%. The lower selectivity to acetol over Cu:Al catalyst was due to formation of 1,2-PDO (10−38%) as a result of transfer hydrogenation of acetol in 2-propanol solvent.[34] It is clear from the above results that the Cu:Al catalyst system in water gave a very clean product distribution (acetol selectivity >90%). This was also confirmed by conducting the dehydration experiment in water for a longer period of 12 h (Figure 2), which also showed a consistent acetol selectivity of ∼95% with marginal increase in glycerol conversion of 17−20%. Hence, further studies on glycerol dehydration were carried out over Cu:Al-1catalyst in water medium.

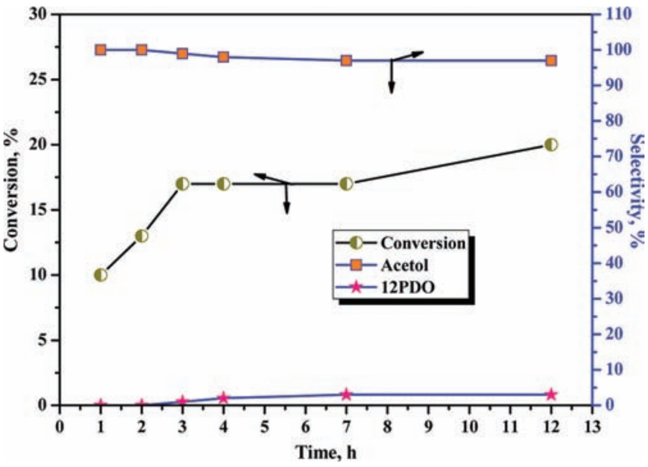


Figure 2. Conversion and selectivity vs time profile of aqueous glycerol dehydration in a batch reactor. Catalyst weight: 0.8 g, T = 493 K, P = N_2 ambient, 20 wt % aqueous glycerol, 12 h.

3.1.2. Continuous Operation. TOS activity of our Cu: Al-1 catalyst was also evaluated for continuous glycerol dehydration. Figure 3 shows a consistent performance of Cu:Al-1 catalyst for 400 h in water at 493 K under N_2 pressure of 20 bar with an average glycerol conversion of 92% and acetol selectivity in the range of 45−55%. However, unlike the product distribution in a batch operation (Figure 2) acetol selectivity was restricted to 54% in a continuous operation as shown in Figure 4. As can be seen from the conversion, selectivity vs time profile (Figure 4), the major byproduct formed was 1,2-PDO to the extent of 30% while others included propionic acid, acetic acid, acetaldehyde, propionaldehyde and 2-propanol formed up to 15%. The substantial formation of 1,2-PDO was due to in situ hydrogenation of acetol as the hydrogen availability was possible due to aqueous phase reforming (APR) of glycerol. The formation of 1,2-PDO and several other byproducts can be explained by C−C cleavage, isomerization of acetol, and excessive hydrogenation of 1,2-PDO as shown in Scheme 2. The effects of various reaction parameters on the global rate of glycerol dehydration, conversion, and selectivity pattern are discussed below. These studies were conducted in a single continuous run after establishing the TOS of the catalyst for more than 250 h. The effect of each parameter was continued for 24 h under steady-state conditions, and a standard run was conducted after every 24 h to ensure the original activity of the catalyst.

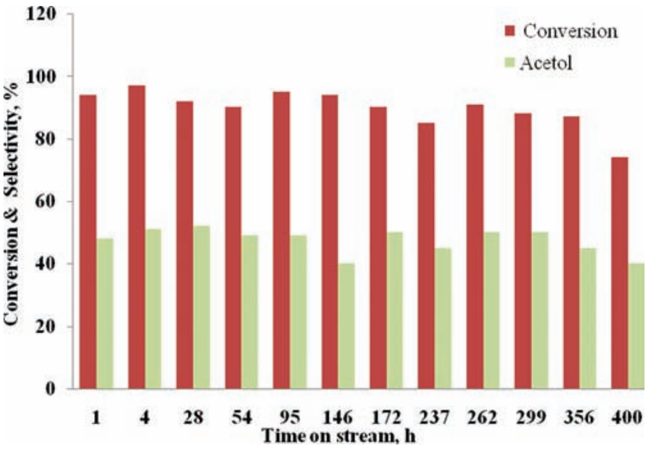


Figure 3. Time on stream (TOS)activity of Cu:Al-1 catalysts for dehydration of aqueous glycerol under inert atmosphere. Catalyst weight: 20 g, T = 493 K, P = 20 bar, 20 wt % aqueous glycerol, GHSV = 500 h^{-1}, LHSV = 1.53 h^{-1}, 400 h.

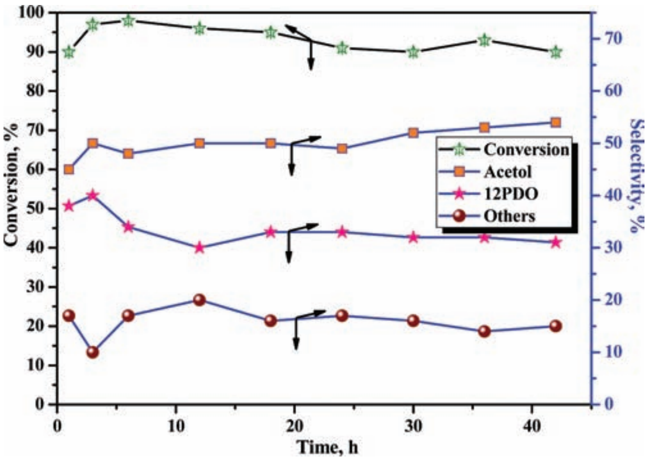
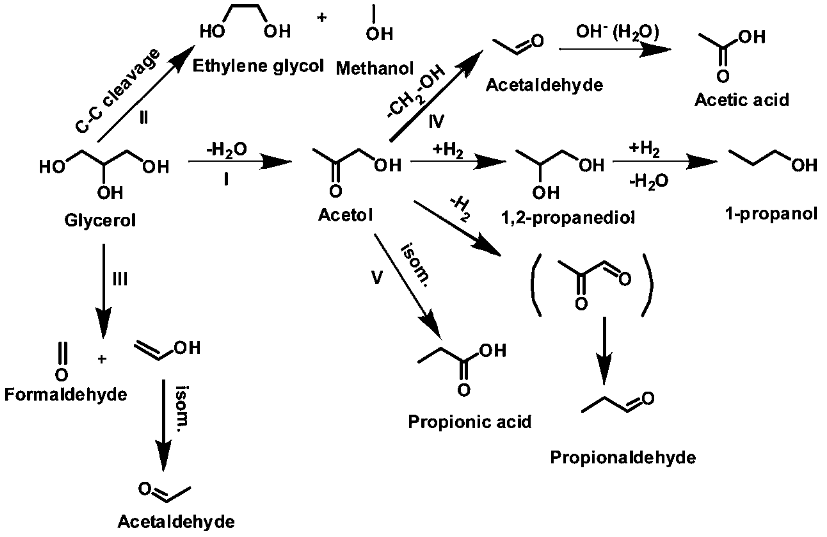


Figure 4. Conversion and selectivity vs time profile of aqueous glycerol dehydration in a continuous fixed bed reactor. Catalyst weight: 20 g, T = 493 K, P = 20 bar, 20 wt % aqueous glycerol, GHSV = 500 h^{-1}, LHSV = 1.53 h^{-1}.

Effect of Liquid Flow Rate. The effect of liquid flow rate on the global rate of dehydration, glycerol conversion, and the product selectivities was carried out in the range of 18−54 mL/h, and the results are shown in Figure 5. Initially, the global rate of dehydration increased by about 50% with an increase in the liquid flow rate from 18 to 30 mL/h, whereas with a further increase in liquid flow rate to 54 mL/h, a marginal increase in the overall dehydration rate was observed. The increase in liquid flow rate would wet more surface area of the catalyst particle resulting into a higher liquid−solid mass transfer coefficient, thus causing a higher overall rate of dehydration which is a liquid−solid reaction. More interestingly, the product distribution varied with the change in liquid flow rate as evidenced by an increase in acetol selectivity from 55 to 70% with an increase in flow rate by 3-fold (from 18 to 54 mL/h). 1,2-PDO selectivity initially increased from 22 to 30% with the increase in flow rate from 18 to 30 mL/h, beyond which it decreased to a minimum value of 15% at the highest flow rate of 54 mL/h. With the increase in liquid flow rate, contact time reduced; hence, the readsorption of acetol might not take place,

Scheme 2. C−O and C−C cleavage and isomerization products of glycerol over Cu:Al catalyst under dehydration conditions



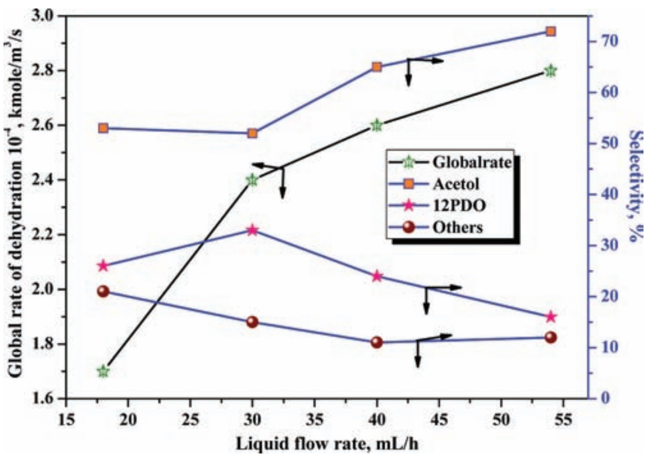


Figure 5. Effect of liquid flow rate on global rate of glycerol dehydration and product selectivity. Catalyst weight: 20 g, $T = 493$ K, $P = 20$ bar, 20 wt % aqueous glycerol, GHSV = 500 h^{-1}.

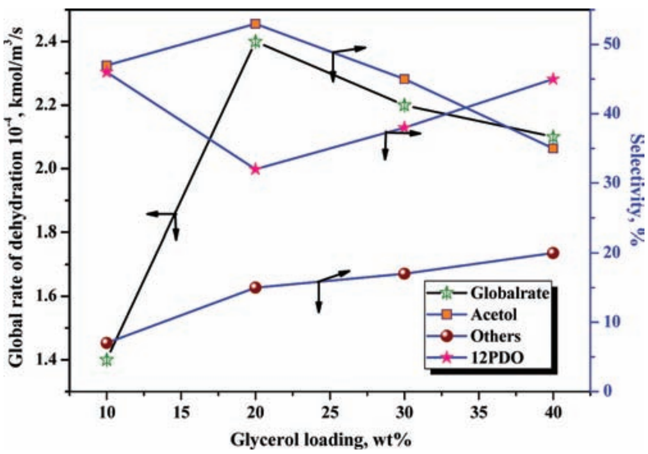


Figure 6. Effect of glycerol loading on global rate of aqueous glycerol dehydration and product selectivity. Catalyst weight: 20 g, $T = 493$ K, $P = 20$ bar, GHSV = 500 h^{-1}, LHSV = 1.53 h^{-1}.

thus retarding its further hydrogenation to 1,2-PDO. The selectivity to other byproducts also stabilized at a minimum value of 10% for the highest flow rate of 54 mL/h. The novel feature of this study was that the optimum selectivity to both acetol (55%) and 1,2-PDO (12%) could be achieved for a flow rate of 30 mL/h of 20% aqueous glycerol.

Effect of Glycerol Loading. Figure 6 shows the dependence of the overall rate of dehydration and the selectivity behaviour of acetol, 1,2-PDO, and other byproducts on glycerol loading. The overall rate of dehydration sharply increased (>70%) with initial increase in glycerol loading from 10 to 20 wt % while further increase in glycerol loading to 40 wt % decreased the rate of dehydration as well as acetol selectivity from 2.35 to 2.1 kmol/m^3/sec and from 55 to 35% respectively. The initial increase in glycerol loading to 20 wt % obviously caused the higher concentration of glyecrol on the catalyst surface leading to higher dehydration rate. Similarly, acetol selectivity first increased from 45 to 55% with increasing the glycerol loading from 10 to 20 wt % and then decreased to as low as 35% at the highest glycerol loading of 40 wt %. The lowering of acetol selectivity accompanied with increase in 1,2-PDO selectivity due to higher rate of glycerol APR at higher concentration of glycerol. Increase in glycerol loading also caused an increase in the selectivity to other byproducts. Hence the optimum glycerol loading was found to be 20 wt % for which highest selectivity to acetol achieved was 55%.

Effect of Temperature. The effect of temperature on both glycerol conversion and acetol selectivity was studied in the temperature range of 413−513 K for Cu:Al-1 catalyst. It was found that glycerol conversion remained almost constant (32−35%) for the temperature range of 453−473 K and then reached the maximum of 91% at 493 K. Acetol selectivity remained more or less contant at 52% up to 493 K, beyond which it slightly dropped down to 40% at 513 K due to the higher extent of formation of byproducts. The activation energy was found to be 38 kJ/mol/K as estimated from the Arrhenius plot for dehydration of glycerol over Cu:Al-1 catalyst.

3.2. Hydrogenolysis of Glycerol to 1,2-PDO. As our non-noble and non-chromium catalyst showed an excellent performance for dehydration in 2-propanol and also for reforming followed by in situ hydrogenation to 1,2-PDO in aqueous medium, it was thought appropriate to test it for direct hydrogenolysis of glycerol to 1,2-PDO.

3.2.1. Batch Operation for Catalyst Screening. The efficiency of Cu:Al catalyst could be observed by comparing its hydrogenolysis activity with various copper catalysts with and without chromium. The results of activity comparison in water and in 2-propanol are shown in Tables 5 and 6, respectively.

Table 5. Catalyst screening for hydrogenolysis of glycerol to 1,2-PDO in aqueous medium

			selectivity, %			
catalysts[a]	composition	conversion, %	1,2-PDO	acetol	EG	others
Cu:Al-1	50:50	38	91	4	5	–
Cu:Al-2	70:30	45	60	1	2	37
Cu:Al-3	30:70	51	85	6	3	5
NMT005	Cu, Cr, Ba	20	56	44	–	–
NMT006	Cu, Cr	6	55	45	–	–
NMT008	Cu, Cr, Al, Ba	8	65	35	–	–
NMT011	Cu, Cr, Zn	10	54	46	–	–

[a] Catalyst weight: 0.8 g, $T = 493$ K, $P = 69$ bar, 20 wt % glycerol, 5 h.

Table 6. Catalyst screening for hydrogenolysis of glycerol to 1,2-PDO in 2-propanol

			selectivity, %			
catalysts[a]	composition	conversion, %	1,2-PDO	acetol	EG	others
Cu:Al-1	50:50	47	88	7	5	
Cu:Al-2	70:30	69	90	4	4	2
Cu:Al-3	30:70	42	91	4	2	2
NMT005	Cu, Cr, Ba	34	84	3	5	8
NMT006	Cu, Cr	16	82	8	4	6
NMT008	Cu, Cr, Al, Ba	26	71	17	10	2
NMT011	Cu, Cr, Zn	29	77	19	1	3

[a] Catalyst weight: 0.8 g, $T = 493$ K, $P = 69$ bar, 20 wt % glycerol, 5 h.

Catalyst Screening in Water. As can be seen from Table 5, among various Cu–Cr catalysts screened for glycerol hydrogenolysis in water, only Cu–Cr with Ba as a promoter showed glycerol conversion of 20% with 56% selectivity to 1,2-PDO and 44% selectivity to acetol. Other Cu–Cr catalysts with and without promoters (NMT006–NMT011, Table 5) showed very poor hydrogenolysis activity (6–10% conversion, Table 5) in water. In the case of all Cu–Cr catalysts, the 1,2-PDO selectivity obtained was in the range of 54–65%, and the balance was acetol without any other byproducts. On the other hand, Cu:Al with varying compositions showed much higher hydrogenolysis activity in water in the order: Cu:Al-3 > Cu:Al-2 > Cu:Al-1. The lowest 1,2-PDO selectivity of 60% observed for Cu:Al-2 catalyst was due to formation of other byproducts to the extent of 37% which could be due to higher content of Cu, whereas the highest 1,2-PDO selectivity achieved was 91% with 38% glycerol conversion for a catalyst having an equimolar composition of Cu and Al (Cu:Al-1) with acetol and EG as the only byproducts. The reason for the best performance of Cu:Al-1 catalyst is due to the presence of both surface acidity and metal sites essential for the glycerol hydrogenolysis involving the first step of acid-catalyzed dehydration to acetol followed by its hydrogenation to 1,2-PDO. A detailed conversion and selectivity vs time profile (Figure 7) shows that with an increase in reaction time, 1,2-PDO selectivity increased from 75 to 91% within the first hour of reaction at the cost of acetol. This clearly indicates that acetol is the intermediate of glycerol hydrogenolysis to 1,2-PDO. Although a lower content of Cu (30 mol %) in Cu:Al-3 catalyst showed the highest glycerol conversion, 1,2-PDO selectivity obtained was less than that for Cu:Al-1 (Table 5). Hence, the Cu:Al-1 catalyst was chosen as the best catalyst for further studies on glycerol hydrogenolysis.

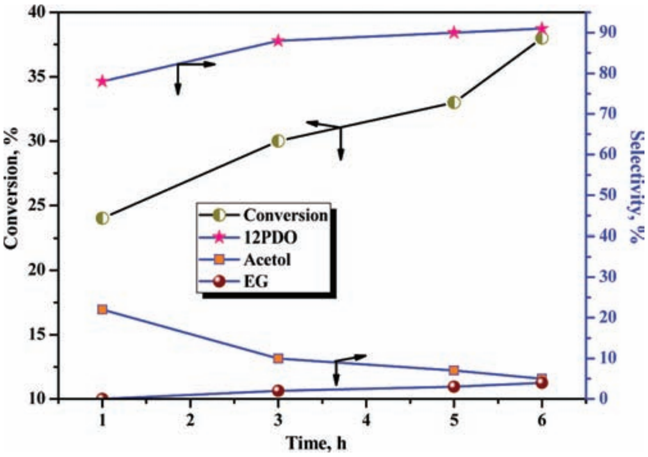


Figure 7. Conversion and selectivity vs time profile of aqueous glycerol hydrogenolysis in a batch reactor. Catalyst weight: 0.8 g, $T = 493$ K, $P = 69$ bar, 20 wt % aqueous glycerol, 6 h.

Catalyst Screening in 2-Propanol. As can be seen from Table 6, the catalyst activity for glycerol hydrogenolysis in 2-propanol solvent showed a trend of Cu:Al-2 > Cu:Al-1 > Cu:Al-3; however, in all cases higher conversions were observed. As high as 69% glycerol conversion was achieved over Cu:Al-2 catalyst having a maximum Cu content of 70 mol %. The selectivity to 1,2-PDO was in the range of 88–90% with slight variation due to either more accumulation of acetol or due to higher formation of byproducts, depending on the Cu content of the catalysts. Cu–Cr catalysts showed much higher hydrogenolysis activities in 2-propanol than those in water (Table 5); nevertheless, activities were lower than those of Cu:Al catalysts, the obvious reason being the higher hydrogen solubility in 2-propanol than in water. Among the Cu–Cr catalysts, the Ba-containing catalyst (NMT005) showed the highest activity (34% conversion) and 1,2-PDO selectivity (84%). NMT008 catalyst having Al in combination with Ba gave the highest EG selectivity, while NMT011 containing Zn gave the highest dehydration product acetol affecting the 1,2-PDO selectivity.

3.2.2. Continuous Operation. As water is supposed to be a green solvent and the Cu:Al-1 catalyst showed an optimum performance (Table 5), further studies on product distribution, TOS activity, and the effects of process parameters were carried out using this catalyst. A longer period of reaction for product distribution was necessary in order to ascertain if catalyst activity was constant in an acceptable range and if byproducts were accumulating which could be undesirable from a continuous process point of view. As can be seen from Figure 8, the initial glycerol conversion decreased from 85% to 65% after the first 30 h beyond which it remained constant at that value. The initial 1,2-PDO selectivity obtained was 92% which remained almost constant over the period of time as shown in Figure 8. Acetol selectivity obtained in the beginning of the continuous run was about 7% (Figure 8) as against much higher acetol selectivity of ~20% in a batch operation (Figure

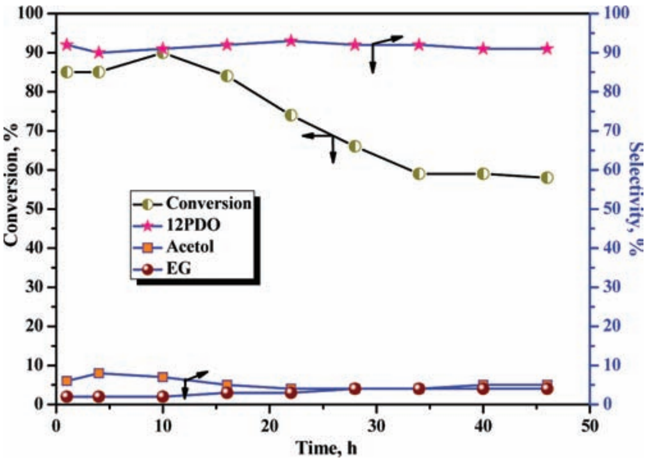


Figure 8. Conversion and selectivity vs time profile of aqueous glycerol hydrogenolysis in a continuous fixed bed reactor. Catalyst weight: 20 g, $T = 493$ K, $P = 40$ bar, 20 wt % aqueous glycerol, GHSV = 500 h^{-1}, LHSV = 1.5 h^{-1}.

7). TOS activity of this catalyst in Figure 9 shows the consistent performance of 60% glycerol conversion with 1,2-PDO selectivity of 90% for 400 h at 493 K and 40 bar H_2 pressure. Further studies on the effect of process parameters on glycerol conversion and 1,2-PDO selectivity are discussed below.

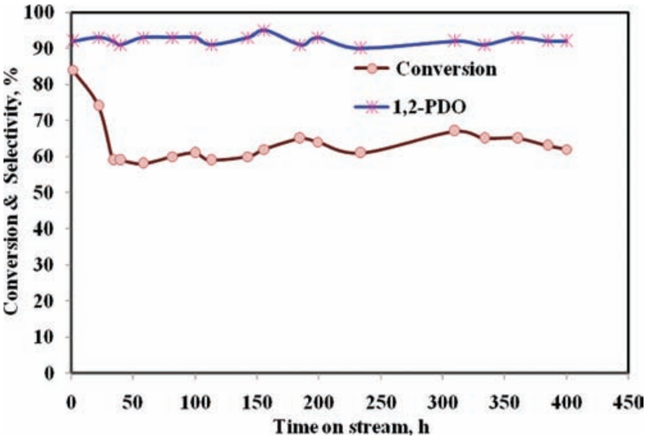


Figure 9. Time on stream activity of Cu:Al-1 catalysts for continuous hydrogenolysis of aqueous glycerol. Catalyst weight: 20 g, $T = 493$ K, $P = 40$ bar, 20 wt % aqueous glycerol, GHSV = 500 h^{-1}, LHSV = 1.5 h^{-1}.

Effect of H_2 Pressure. Figure 10 shows the effect of H_2 pressure at constant temperature of 493 K in the range of 20−62 bar on the global rate of reaction. It was observed that initially as the pressure increased (up to 42 bar) the rate of reaction also increased linearly to a maximum value and decreased sharply with further increase in H_2 pressure up to 62 bar. The initial increase in the rate of reaction up to 42 bar pressure indicates a first-order kinetics with respect to hydrogen. The enhancement of activity with higher H_2 pressure could also be due to in situ activation of the catalyst. Beyond 42 bar pressure, competitive hydrogen adsorption seems to be predominant; hence, a sharp decline in hydrogenation rate was observed. Glycerol conversion and selectivity dependence on H_2 pressure (Figure 11) shows that initially the conversion increased from 44 to 57% with increase in H_2 pressure from 20 to 40 bar, while it decreased again to 44% with further increase in H_2 pressure up to 62 bar. Selectivity to 1,2-PDO remained constant at 92% irrespective of H_2 pressure as the byproduct formation is strongly catalyst dependent rather than kinetic dependent. Acetol and EG were formed as major byproducts over the range of H_2 pressure studied in this work.

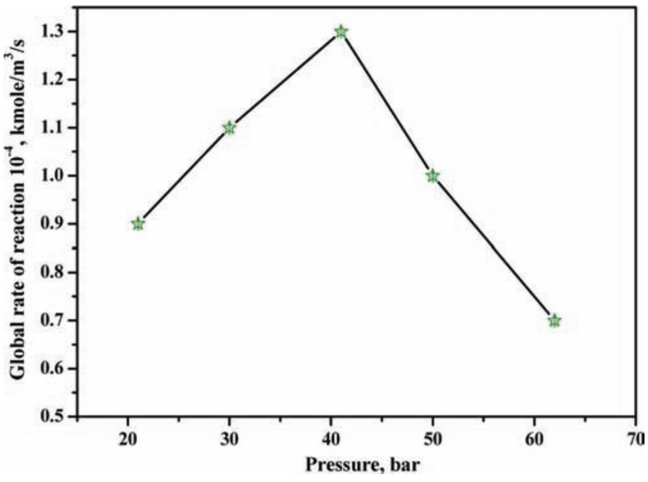


Figure 10. Effect of H_2 pressure on the global rate of aqueous glycerol hydrogenolysis. Catalyst weight: 20 g, $T = 493$ K, 20 wt % aqueous glycerol, GHSV = 500 h^{-1}, LHSV = 1.5 h^{-1}.

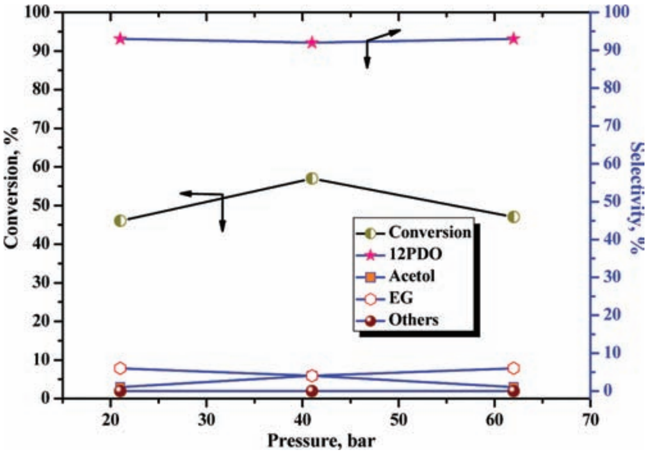


Figure 11. Effect of H_2 pressure on conversion and product selectivity in aqueous glycerol hydrogenolysis. Catalyst weight: 20 g, $T = 493$ K, 20 wt % aqueous glycerol, GHSV = 500 h^{-1}, LHSV = 1.5 h^{-1}.

Effect of Liquid Flow Rate. The effect of liquid flow rate on the rate of glycerol hydrogenolysis and product selectivity was studied in the range of 18−54 mL/h, keeping other reaction parameters constant. Figure 12 shows that an increase in the flow rate from 18 to 30 mL/h increased the rate of hydrogenolysis linearly from 0.74 to 1.3 × 10^{-4} kmol/m^3/s, while a further increase in liquid flow rate from 32 to 54 mL/h decreased the rate of hydrogenolysis. In the lower range of the liquid flow rate (18−30 mL/h), catalyst particles were partially wetted, resulting in a direct contact of gas-phase reactant and catalyst surface (already wetted internally due to capillary forces) which increased the reaction rate. An increase in the liquid flow rate beyond a certain value (>30 mL/h, in this case) causes complete wetting of the catalyst particle and thus is expected to retard the reaction rate due to enhanced liquid−solid resistance.[35,36] 1,2-PDO selectivity was found to remain

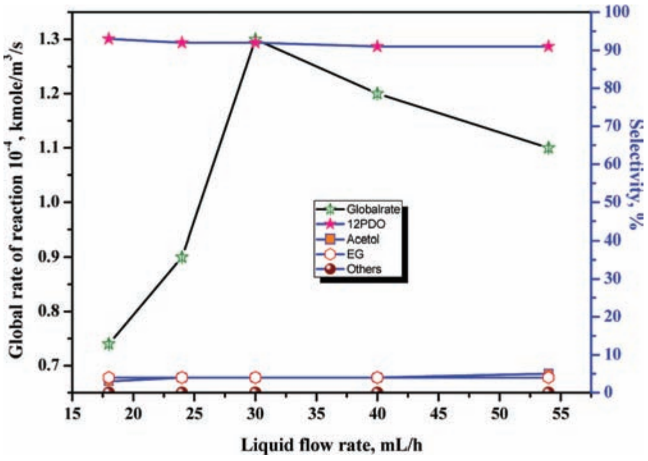


Figure 12. Effect of liquid flow rate on global rate and product selectivity in glycerol hydrogenolysis. Catalyst weight: 20 g, T = 493 K, P = 40 bar, 20 wt % aqueous glycerol, GHSV = 500 h^{-1}.

constant at 91% irrespective of the liquid flow rate. The effect of liquid flow rate in terms of contact time (W/F, h) on glycerol conversion was also studied, and the results are shown in Figure 13. It was found that conversion increased from 27 to 60% with an increase in contact time from 0.35 to 0.6 h beyond which it remained constant up to contact time of 1.07 h. On comparison of Figures 12 and 13, highest productivity of 1,2-PDO can be achieved at the optimum liquid flow rate of 30 mL/h.

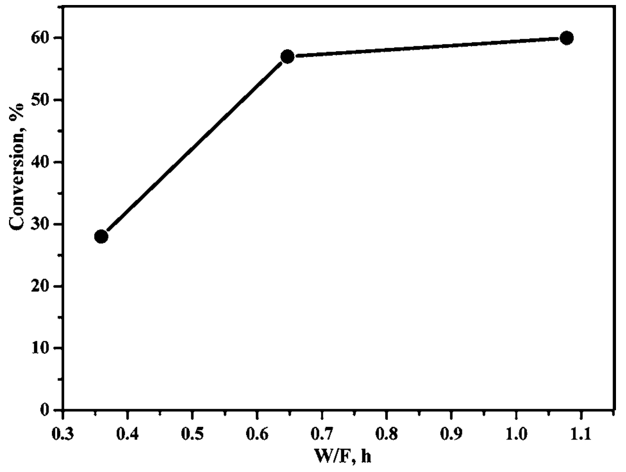


Figure 13. Effect of contact time W/F on glycerol conversion. Catalyst weight: 20 g, T = 493 K, P = 40 bar, 20 wt % aqueous glycerol, GHSV = 500 h^{-1}.

Effect of Glycerol Loading. Figure 14 shows the dependence of the rate of glycerol hydrogenolysis on glycerol loading in the range of 20–60 wt %, at 493 K and 40 bar H_2 pressure. Similar to the trend observed for the effect of hydrogen pressure, the rate of hydrogenolysis increased steeply by 3-fold with an increase in glycerol loading from 20 to 40 wt % while, it decreased dramatically for glycerol loading >40 wt %. This indicates that the substrate gets strongly adsorbed at higher concentration on the active sites and needs to be considered for design purposes. In order to achieve the maximum productivity, the effect of glycerol loading on conversion and product selectivity was also studied in the range of 20–60 wt %, the results of which are shown in Figure 15. Glycerol conversion increased from 53 to 67% with increase in glycerol loading up to 40 wt %, beyond which it decreased substantially (30%) while no appreciable change in product selectivities was observed.

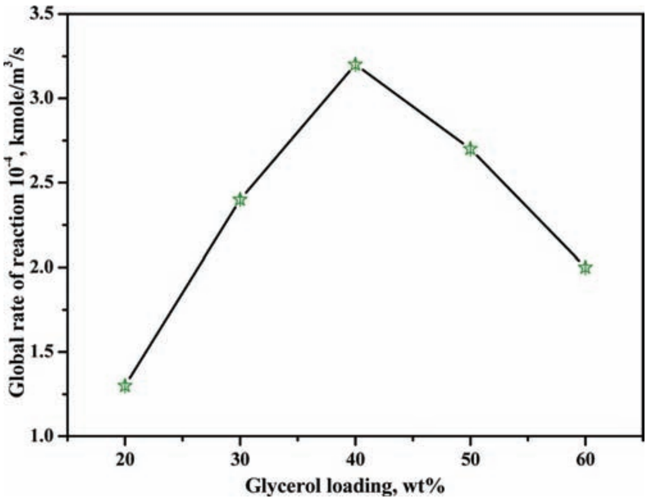


Figure 14. Effect of glycerol loading on global rate of aqueous glycerol hydrogenolysis. Catalyst weight: 20 g, T = 493 K, P = 40 bar, GHSV = 500 h^{-1}, LHSV = 1.5 h^{-1}.

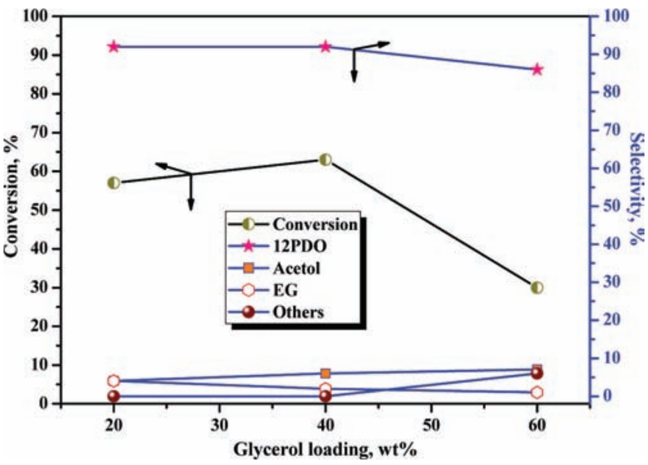


Figure 15. Effect of glycerol loading on conversion and product selectivity in aqueous glycerol hydrogenolysis. Catalyst weight: 20 g, T = 493 K, P = 40 bar, GHSV = 500 h^{-1}, LHSV = 1.5 h^{-1}.

Effect of Temperature. Figure 16 shows the effect of temperature on glycerol conversion and product selectivity, respectively. A significant increase in glycerol conversion from 20 to 84% was observed with an increase in temperature from 453 to 513K. Although 1,2-PDO slectivity remained constant (~93%) for the increase in glycerol conversion with an increase in temperature up to 493 K (Figure 16), it drastically decreased from 94 to 78% with a further increase in temperature to 513 K. This decrease in 1,2-PDO selectivity at highest temperature was due to increased acetol (4–10%), and other byproducts (0–11%). Other byproducts include acetaldehyde, formaldehyde, and 2-propanol formed from acetol and 1,2-PDO due to C–C clevage and excess hydrogenation, respectively. The increase in acetol selectivity at a higher temperature indicates glycerol dehydration is more favorable than acetol hydrogenation which

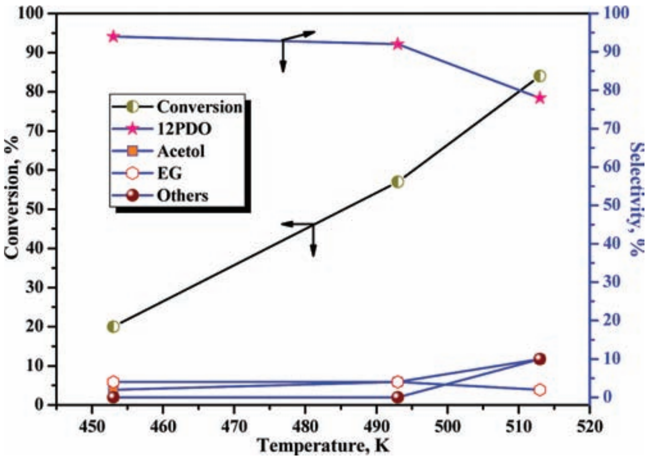


Figure 16. Effect of temperature on conversion and product selectivity in aqueous glycerol hydrogenolysis. Catalyst weight: 20 g, P = 40 bar, 20 wt % aqueous glycerol, GHSV = 500 h^{-1}, LHSV = 1.5 h^{-1}.

is also in accordance with the thermodynamic feasibility criteria.[37] The optimum temperature was found to be 493 K as the highest selectivity of 92% was achieved for 1,2-PDO with minium formation of acetol, EG, and other byproducts at that temperature. The activation energy evaluated from the Arrhenius plot was found to be 80 kJ/mol/K, indicating that the glycerol hydrogenolysis reaction over the present catalyst is kinetically controlled. It is also to be noted that for the same catalyst, activation energy for dehydration of glycerol (38 kJ/mol/K) was much less than that observed for the hydrogenolysis of glycerol, indicating that glycerol dehydration is much faster than the hydrogenolysis reaction.

4. CONCLUSIONS

Studies on the effect of process parameters on conversion−selectivity behaviour and global rates of continuous dehydration and hydrogenolysis of aqueous glycerol over a non-chromium copper catalyst were carried out. At an optimum glycerol loading of 20 wt % and 493 K, acetol selectivity in a continuous dehydration process under inert atmosphere increased from 55 to 70% with a 3-fold increase in the flow rate due to the decrease in the contact time. Activation energy evaluated from the Arrhenius plot of the dehydration reaction was found to be 38 kJ/mol/K. The same catalyst also gave a TOS activity of 400 h for continuous hydrogenolysis of glycerol with an average glycerol conversion of 65% and >90% selectivity to 1,2-PDO. A dramatic enhancement in glycerol conversion (>4-fold) was observed with a rise in temperature from 453 K to 513 K; however, 1,2-PDO selectivity dropped to 78% at the highest temperature. The activation energy of 80 kJ/mol/K for the hydrogenolysis reaction showed that hydrogenolysis is much slower than the dehydration reaction. Among other parameters, negative-order kinetics appeared to follow at higher H_2 pressure, while a higher feed flow rate decreased the glycerol conversion due to an enhanced liquid−solid mass transfer coefficient. Optimum glycerol loading for hydrogenolysis was found to be 40 wt % of glycerol, beyond which the conversion sharply declined from 67 to 30%.

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Notes

The authors declare no competing financial interest.

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