Selective Hydrogenolysis of Glycerol to 1,2-Propanediol: Comparison of Batch and Continuous Process Operations[†]

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Abstract:

The screening of copper chromite catalysts with various promoters such as Al, Zn, and Ba for glycerol hydrogenolysis to 1,2-propanediol (1,2-PDO) in a batch reaction showed that Cu−Cr (Ba) catalyst gave the highest conversion of 34% and selectivity of 84% to 1,2-PDO. In a continuous operation (23 g catalyst bed) the same catalyst showed higher conversion of glycerol and selectivity for 1,2-PDO of 65% and >90%, respectively, with an on-stream activity of ∼800 h. Better performance in a continuous operation could be due to the in situ activation of the catalyst, suppression of glycerol cracking to ethylene glycol, as well as excessive hydrogenation of 1,2-PDO to 2-propanol due to lower contact time of 1.3 h as compared to that in a batch operation (5 h). Effects of various process parameters on conversion and selectivity also have been compared for batch and continuous operations.

Introduction

Catalytic production of propylene glycols is one of the most attractive downstream applications of glycerol which is a main byproduct of biodiesel formation.[1] Propylene glycol is an industrially important chemical which is used in unsaturated polyester resins, functional fluids (antifreeze, de-icing, and heat transfer), foods, cosmetics, pharmaceuticals, liquid detergents, flavors and fragrances, tobacco humectants, paints, etc. The use of propylene glycol in functional fluids is growing because of the toxicity associated with ethylene glycol-based products to human and animals. The commercial route for propylene glycol involves the hydration of petroleum-based propylene oxide derived by either chlorohydrin process or the hydroperoxide process.[2] Hence, catalytic hydrogenolysis of glycerol to 1,2-PDO is a sustainable process utilizing a renewable feedstock as well as substantially improving the process economics of the biodiesel manufacture.

Consequently, glycerol hydrogenolysis has been studied using various catalyst systems involving both noble metals such as Rh, Ru, Pt, Pd as well as other transition metals, mainly copper, chromium, and zinc in combination with each other or supported on active carbon, SiO_2, or Al_2O_3.[3] Among noble metals, ruthenium on carbon in the presence of amberlyst resin gave glycerol conversion of 79% with the highest selectivity of 82% to 1,2- propanediol at 393 K and 80 bar initial H_2 pressure for 10 h.[4] However, higher reaction pressure, longer reaction time, and the formation of byproducts such as ethylene glycol due to C−C bond cleavage favored by Ru make this catalyst system unviable from a process point of view. Although sulfur addition to Ru/C catalyst increased the selectivity to 1,2-PDO, the glycerol conversion was limited to only 45%.[4] In the case of Pt catalyst, in spite of its higher activity for the glycerol hydrogenolysis, it gave higher selectivity to lactate.[5] Since, copper is responsible for selective cleavage of the C−O bond without affecting the C−C bond and also it is much cheaper than Ru or Pt, more attention has been focused on copper-based catalysts for glycerol hydrogenolysis. Glycerol hydrogenolysis was first reported using copper and zinc catalysts under very high pressure and temperature conditions (150 bar; 513−545 K) with 75−85% selectivity to 1,2-PDO while >25% were cracked products such as EG, ethanol, methanol and lactic acid.[6] Chaminand et al.[7] reported glycerol conversion of 20% with >90% selectivity to 1,2-PDO, using Cu−ZnO in the presence of tungstic acid in 92 h. Bifunctional Cu−ZnO catalysts were also proposed to obtain 84% selectivity to 1,2-PDO with 23% glycerol conversion in 12 h.[8] Sato et al.[9] showed that hydrogen pretreated Cu/Al_2O_3 materials could effectively catalyze the dehydration of glycerol to produce hydroxyacetone where 1,2-propanediol was formed as a byproduct. Schuster and Eggers-dorfer, and Cameron et al.[10] reported a catalyst system comprising cobalt, manganese, molybdenum, along with copper and an inorganic polyacid for achieving a 95% yield of

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[†] This paper is dedicated to the memory of my father Vasant V. Rode who passed away on 28th August 2010.

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propanediol under severe conditions of 250 bar pressure and 523 K for glycerol hydrogenolysis.

Copper along with chromium forms a copper chromite system which is also well studied for hydrogenation as well as for the decomposition or dehydration of alcohols.[11,12] After the first report of copper chromite catalyst by Fleckenstein et al.[13] for glycerol hydrogenolysis at very high pressure (250 bar), several reports have appeared using various types of copper chromite catalysts.[14−16] Commercial as well as proprietary copper chromite systems are also reported for which the reaction conditions could be much milder, such as 473 K and 14 bar H_2 pressure.[13,17] Another possibility with this catalyst system is that, by altering the composition and reaction conditions, very high selectivity to intermediate acetol (80%) with 86% glycerol conversion can be achieved. Recently, a nonchromium Cu/Al nano-structured catalyst system has been reported for the hydrogenolysis of glycerol under relatively milder conditions, giving >47% glycerol conversion in 5 h.[18]

However, it is evident from the literature that most of the work on various catalyst systems including promising ones such as copper chromite has been carried out using a batch reactor operation. Although few reports describe the continuous dehydration/hydrogenolysis of glycerol, reaction conditions are very harsh, and/or the major product formed was acetol along with considerable formation of unidentified side products. Continuous process for the production of a commodity product such as 1,2-PDO will be highly desirable from a commercialization point of view. However, performance of the same catalyst would differ considerably in a continuous operation from that in a batch mode. Therefore, the main objectives of our work were: (i) to study the product distribution and a systematic comparison of batch and continuous process for glycerol hydrogenolysis over copper chromite catalyst of a specific composition prepared in our own laboratory; (ii) to optimize the process conditions for a continuous operation; (iii) to study the catalyst life. For this purpose, copper chromite catalysts of different compositions were prepared with promoters such as Al, Zn, and Ba by the coprecipitation method. These catalysts were then screened for glycerol hydrogenolysis in a batch reaction. Among these catalysts, Cu−Cr with barium as a promoter showed the highest glycerol conversion of 34% with 84% selectivity to 1, 2 propanediol. Hence this catalyst was used to carry out further studies on effect of reaction parameters in both batch and continuous operations. Our catalyst showed an excellent performance (65% conversion with selectivity >90% to 1,2-PDO)

and stability up to 800 h for continuous hydrogenolysis of glycerol in a fixed bed reactor.

Experimental Section

Materials. Glycerol (99.9%) was supplied by Merck Specialties, Mumbai, India, and acetol, 1,2-propanediol, and 2-propanol were obtained from Sigma-Aldrich, Bangalore, India. Copper nitrate, ammonium dichromate, aluminium nitrate, zinc nitrate, and barium nitrate 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.

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 4 h.

Procedure. *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, 1 g; and hydrogen pressure, 35−70 bar. The prepared catalysts were pre-reduced under H_2 at 473 K for 12 h.

Continuous Operation. Continuous hydrogenolysis of glycerol was carried out in a bench scale, high-pressure, fixed-bed reactor supplied by M/s Geomechanique, France. A schematic of the reactor setup is shown in Figure 1. This reactor set up consisted of a stainless steel single tube of 0.34 m length and 1.5×10^{-2} m inner diameter. The reactor was heated by two tubular furnaces whose zones (TIC1 and TIC2) were independently controlled at the desired bed temperature. The reactor was provided with mass flow controllers, pressure indicator, and controller (PIC) devices and two thermocouples to measure the temperature at two different points. A storage tank was connected to the HPLC pump through a volumetric buret to measure the liquid flow rate. The pump had a maximum capacity of 3×10^{-4} m³/h under a pressure of 100 bar. The gas−liquid separator was connected to other end of the reactor through a condenser.

The powdered catalyst was pelletized in the form of pellets of 1×10^{-2} m diameter and cut into 4 pieces each having 2.5 $\times 10^{-3}$ m diameter. Twenty-three g of the pelletized catalyst was charged in to the reactor. The section of 7×10^{-2} m above and 0.16 m below the catalyst bed was packed with carborundum as an inert packing, thus providing the catalyst bed of 0.11 m. Before starting the actual experiment the reactor was flushed thoroughly, first with N_2 and then with H_2 at room temperature. Then the reactor was pressurized with H_2 after attaining the desired temperature. The liquid feed was "switched on" after the reactor reached the operating pressure and was kept at that value 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

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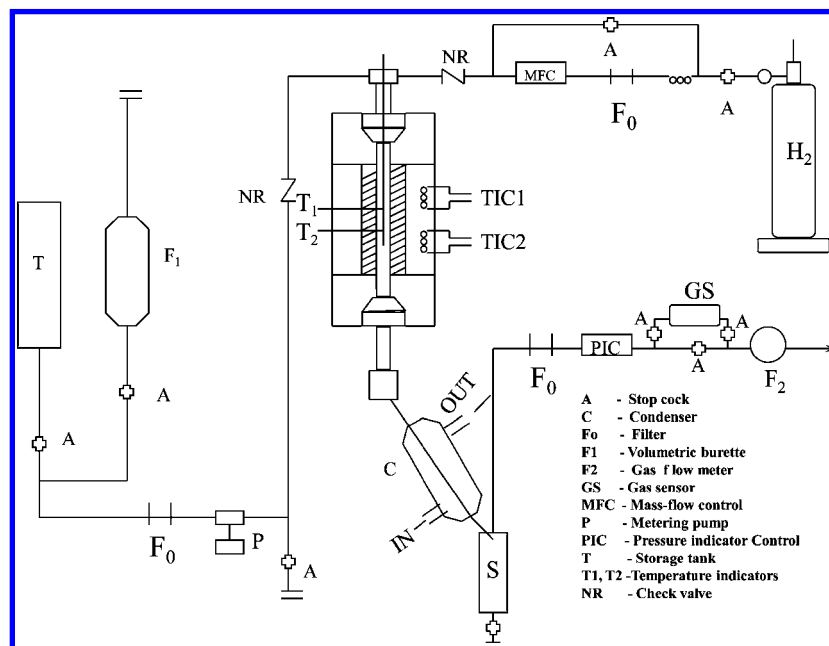
Figure 1. A schematic of the fixed-bed reactor setup.

Table 1. Specifications of copper chromite catalyst

type	Cu/Cr
Form	pellets
size, m	0.005 × 0.002
surface area, m²/g	54.24
bulk density, g/mL	1.35
promoters, 30%	Al, Ba, and Zn

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 of liquid and gas flow rates. The reactor was operated in the temperature and pressure ranges of 453−513 K and 20−60 bar, respectively. Steady-state performance of the reactor was observed by analysis of the reactant and products in the exit stream.

Results and Discussion

Major objectives of this work were (i) screening of several Cu−Cr systems and studying the product distribution for glycerol hydrogenolysis in a batch reactor; (ii) evaluating time of on-stream activity and product distribution of the best catalyst for continuous glycerol hydrogenolysis; (iii) optimizing reaction conditions for the best catalyst in both batch and continuous hydrogenolysis of glycerol and to compare their performances. For this purpose, Cu−Cr catalysts were prepared with various promoters and the specifications of these catalysts are given in Table 1. The effects of temperature, H_2 pressure, liquid and gas flow rates and glycerol concentration on the conversion of glycerol and the product selectivities were also investigated. The range of reaction conditions used for this study is given in Table 2. In all the experiments, concentrations of the reactant and products in the reactor effluent were determined quantitatively by GC on the basis of which the conversion of glycerol and product selectivities were calculated. Reproducibility of the rate, conversion, and selectivity measurements were found to be within 3−4% error as indicated by a few repeated experiments.

Table 2. Range of operating conditions

parameter	Range batch	Range continuous
Initial concentration of glycerol, wt%	20−60	20−60
solvent	2-propanol	2-propanol
temperature, K	453−513	453−513
H_2 pressure, bar	35−70	20−60
catalyst wt, g	0.8 − 2 g	23 g
liquid velocity, U_l LHSV, h^{-1}		0.78−2.34
gas velocity, U_g GHSV, h^{-1}		434−1304
catalyst packing length, m		0.11
particle diameter, d_p, m		0.004
density of the catalyst, kg/m³		1685

Table 3. Catalyst screening in a batch reactor[a]

catalyst	components	% conversion	% selectivity 1, 2-PDO	acetol	EG	2-propanol	methanol
NMT 002	Cu, Cr (Al)	31	81	5	3	9	2
NMT 005	Cu, Cr (Ba)	34	84	3	4	6	3
NMT 006	Cu, Cr	16	82	6	3	6	3
NMT 011	Cu, Cr (Zn)	29	77	19	1	3	−

[a] Reaction conditions: temperature, 220°C; 20 wt % glycerol; pH₂, 52 bar; solvent, 2-propanol; catalyst, 0.01 g/mL; reaction time, 5 h.

The results on catalyst screening in a batch reactor are summarized in Table 3, in which various promoters used in Cu−Cr catalysts are shown in the parentheses. As can be seen from this Table, Cu−Cr catalyst without any promoter gave the lowest glycerol conversion of 16%, while Cu−Cr catalysts with Al and Zn promoters gave almost similar glycerol conversions of 31 and 29% respectively. Al and Zn promoters were chosen mainly due to their Lewis acid characteristics that were expected to play an important role in the glycerol hydrogenolysis, since it involves the first step of dehydration of glycerol to acetol which is an acid-catalyzed reaction. However, Cu−Cr with a barium promoter was found to give the highest glycerol conversion of 34% with >84% selectivity to 1,2-propanediol. Probably, the stability of Cu−Cr catalyst
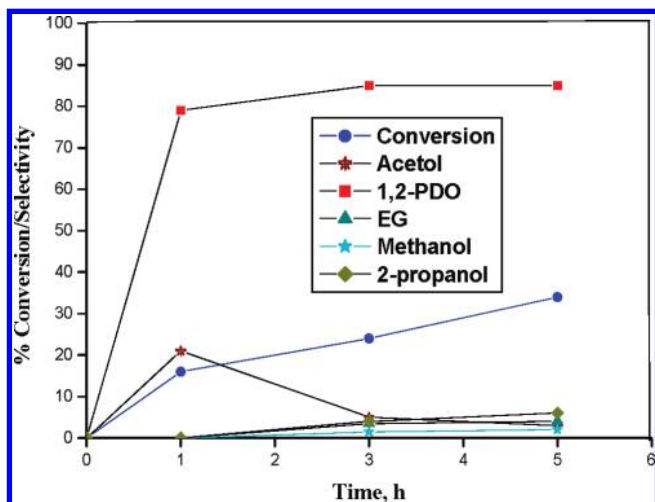
Figure 2. Concentration vs time profile of glycerol hydrogenolysis in a batch reaction Reaction conditions: temperature, 493 K; 20 wt % glycerol; pH_2, 52 bar; solvent, 2-propanol; catalyst, 0.01 g/mL; reaction time, 5 h.

Figure 3. Concentration vs time profile of glycerol hydrogenolysis in batch reaction using *n*-butanol solvent. Reaction conditions: temperature, 493 K; 20 wt % glycerol; pH_2, 52 bar; solvent, 1-butanol; catalyst, 0.01 g/mL; reaction time, 5 h.

against sintering imparted by barium seems to be more important than the acidity in enhancing the activity of these catalysts in hydrogenolysis of glycerol.[19] This was also evidenced by the consistent activity of Cu—Cr (Ba) catalyst for about 800 h for continuous glycerol hydrogenolysis. Therefore, all the further studies for both batch and continuous glycerol hydrogenolysis were carried out using Cu—Cr (Ba) catalyst.

Batch Reactor Performance. *Product Distribution.* Figure 2 shows the conversion, selectivity vs time profile for liquid-phase glycerol hydrogenolysis over Cu—Cr (Ba) catalyst in 2-propanol at 493 K, pH_2 of 52 bar for 5 h. Glycerol conversion increased from 10 to 34% with increase in reaction time from 1 to 5 h, beyond which no effect of reaction time was observed on the conversion levels. For Cu—Cr catalysts, usually very long reaction times of >12 h are reported;[14] however, our catalyst gave a maximum conversion of 34% within a very short reaction time of 5 h. Another novelty of our catalyst was that the highest selectivity of >84% to 1,2-PDO was achieved, and from the beginning of the reaction it was ∼>4 times higher than that of the intermediate dehydration product, acetol, indicating that the hydrogenation of acetol to 1,2-PDO is a very fast reaction. The highest selectivity of acetol formed was ∼15% in one h, after which it started decreasing and was stable at ∼5%. The only side products formed under the conditions of the present work were ethylene glycol, methanol, and 2-propanol. Two separate hydrogenolysis experiments starting with 1,2-PDO and glycerol were carried out using *n*-butanol as a solvent, in order to confirm the pathway of formation of 2-propanol and ethylene glycol. In case of hydrogenolysis of 1,2-PDO, the only product formed was 2-propanol, confirming that 2-propoanol was a product of further hydrogenolysis of primary —OH, and no cleavage products were formed from 1,2-PDO. As shown in Figure 3, glycerol hydrogenolysis gave 2-propanol, ethylene glycol, and methanol along with acetol (minor) and 1,2-PDO as a major product. It was interesting to note (Figure 3) that the selectivity to 1,2-PDO reached a
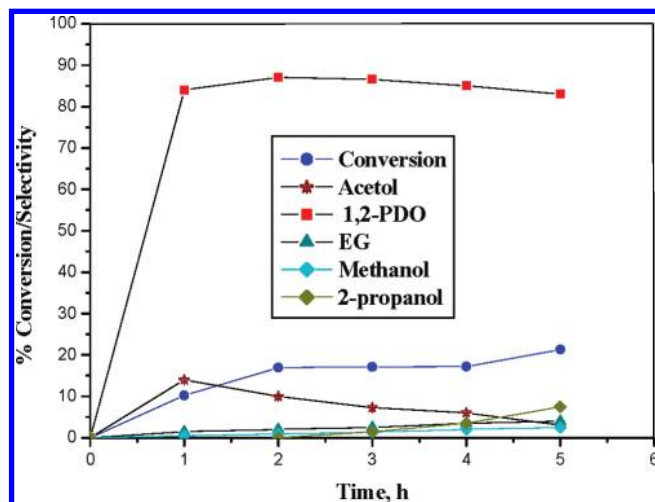
maximum value of 86% in about 2 h, after which it marginally decreased to 84% due to the onset of formation of 2-propanol. This indicates that after a certain critical concentration of 1,2-PDO was reached, with a longer contact time its further hydrogenation to 2-propanol started. Also the formation of ethylene glycol was due to cleavage of C—C bond directly from glycerol and not from the 1,2-PDO, while 2-propanol was formed at the cost of excessive hydrogenolysis of 1,2-PDO.[20] As expected, methanol formation was also observed due to the hydrogenation of formaldehyde formed during C—C bond cleavage to give ethylene glycol. These results as well as no formation of the gaseous product, viz. methane, justify the reaction pathway for the hydrogenolysis of glycerol shown in Scheme 1.

Effect of Temperature. The effect of temperature on both glycerol conversion and 1,2-PDO selectivity was studied in the temperature range of 453−513 K for Cu—Cr (Ba) catalyst, and the results are shown in Figure 4. Glycerol conversion increased from 18 to 43% with increase in temperature from 453 to 513 K. As expected, the selectivity to 1,2-PDO decreased from 86 to 78% due to the excessive hydrogenation of 1,2-PDO favored at higher temperature to give 2-propanol. Also the selectivities to ethylene glycol and methanol increased from 0 to 6%, and 0 to 4%, respectively, indicating that the degradation due to C—C cleavage of glycerol was more facile at high temperature. An Arrhenius plot was also obtained as shown in Figure 5, from which the activation energy was estimated to be 147.5 kJ mol^{-1}.

Effect of Pressure. The results of the effect of hydrogen pressure on glycerol hydrogenolysis studied at a constant temperature of 493 K are shown in Figure 6. Glycerol conversion decreased marginally from 34% to 28% with an increase in H_2 pressure from 35 to 67 bar, indicating that the hydrogen atoms at a higher pressure compete with the readsorption of an intermediate, acetol for the active catalyst sites causing the decrease in conversion. Increase in hydrogen pressure in the higher range from 50 to 67 bar resulted in

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Scheme 1. Reaction pathway for hydrogenolysis of glycerol
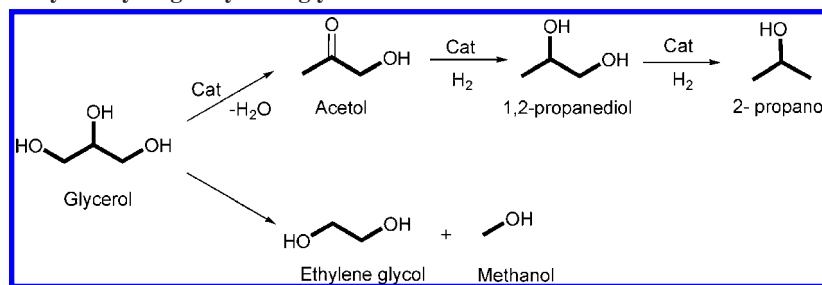
decreasing the selectivity to 1,2-PDO from 84 to 77% due to enhanced further hydrogenation of 1,2-PDO to 2-propanol. It is interesting to note that an increase in H₂ pressure did not affect the selectivity to the degradation product EG because copper is responsible for selective cleavage of C−O bond without affecting C−C bond. This was also confirmed by the study of catalyst loading effect discussed below.

Effect of Catalyst Loading. The effect of catalyst loading on the hydrogenolysis reaction was studied in the range of 0.8−2.0 g at 493 K and 52 bar of hydrogen pressure, and the results are presented in Figure 7. It was observed that the conversion of glycerol increased from 31 to 47% with increase in catalyst weight from 0.8 to 2 g. Selectivity to 1,2-PDO initially increased from 81 to 84% for an increase in catalyst

weight from 0.8 to 1 g, while at the same time acetol selectivity decreased, indicating that the rate of hydrogenation of acetol to 1,2-PDO increased at higher catalyst loading. The selectivity to the degradation product EG remained constant, irrespective of the catalyst loading, confirming that a copper-based catalyst does not favor C−C bond cleavage.

Effect of Glycerol Loading. The effect of glycerol concentrations on the conversion of glycerol and selectivity pattern was also studied in the range of 20−60 wt % glycerol, and the results are shown in Figure 8. The conversion of glycerol decreased drastically from 34 to 11%, while the selectivity to 1,2-PDO marginally decreased from 84 to 82% with increase in glycerol loading from 20−60 wt %. Interestingly, ethylene glycol selectivity increased by twice (from 3 to 6%), while that
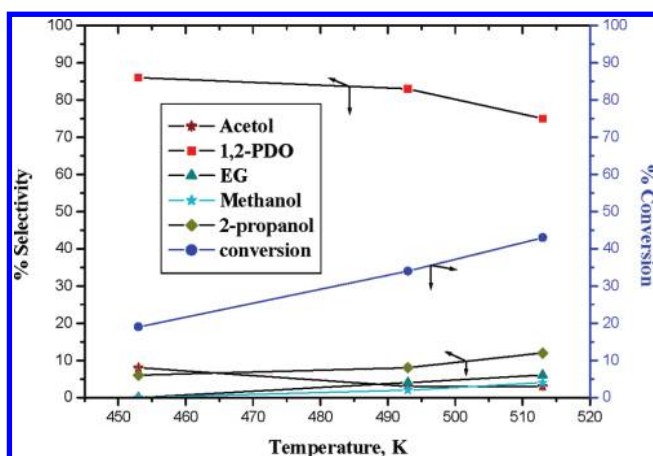

Figure 4. Effect of temperature on conversion and selectivity Reaction conditions: glycerol, 20 wt %; pH₂, 52 bar; solvent, 2-propanol; catalyst, 0.01 g/mL; reaction time, 5 h.
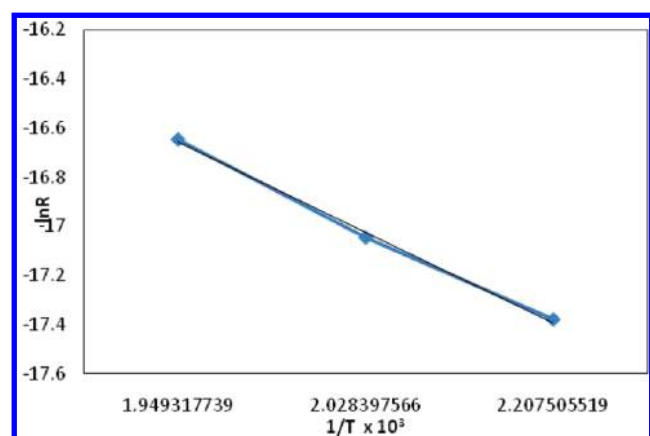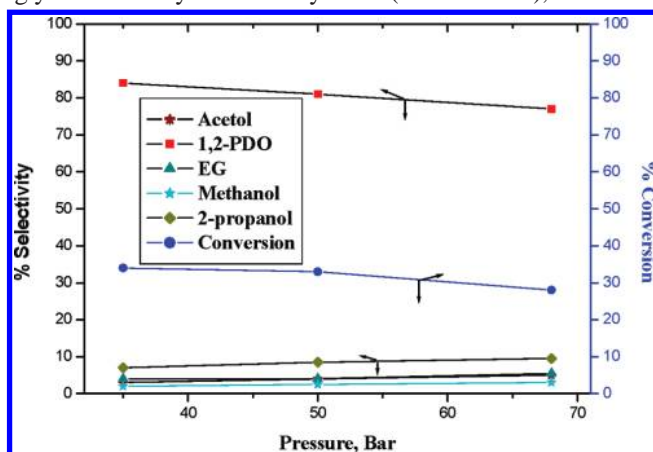

Figure 6. Effect of H₂ pressure. Reaction conditions: glycerol, 20 wt %; temperature, 493 K; solvent, 2-propanol; catalyst, 0.01 g/mL; reaction time, 5 h.
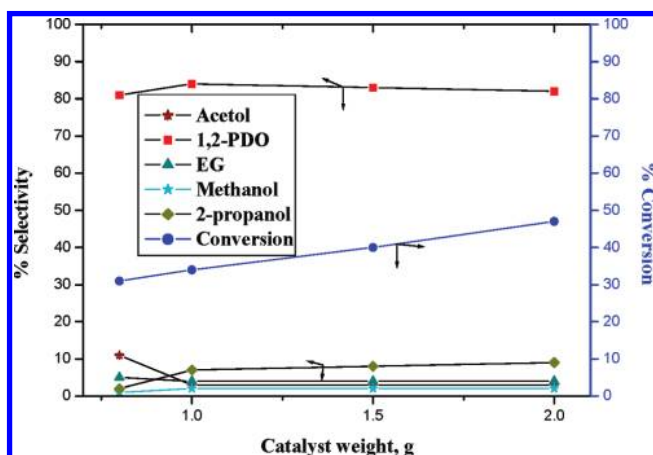

Figure 5. Plot of ln *R* vs 1/*T*. Reaction conditions: glycerol, 20 wt %; pH₂, 52 bar; solvent, 2- propanol; catalyst, 0.01 g/mL; reaction time, 5 h.

Figure 7. Effect of catalyst loading. Reaction conditions: glycerol, 20 wt %; temperature, 493 K; pH₂, 52 bar; solvent, 2-propanol; reaction time, 5 h.
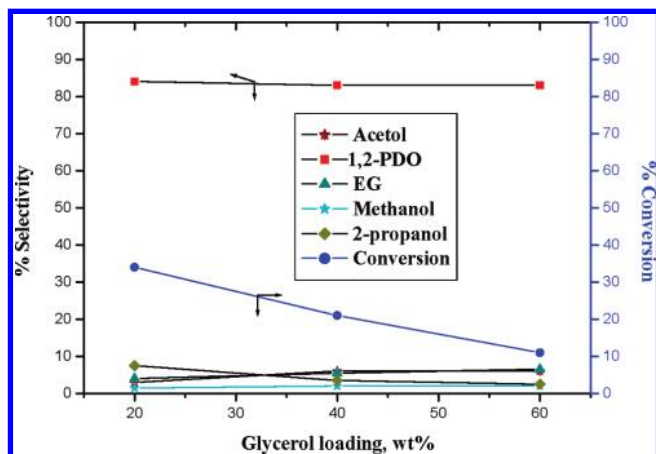
Figure 8. Effect of glycerol loading. Reaction conditions: temperature, 493 K; pH_2, 52 bar; catalyst, 0.01 g/mL; solvent, 2-propanol; reaction time, 5 h.
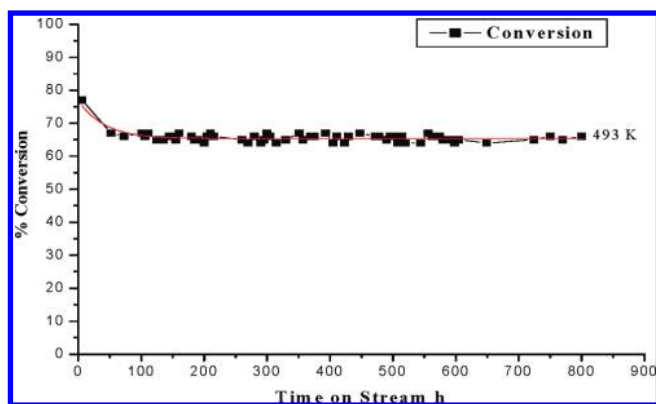

Figure 9. Time on stream activity for continuous glycerol hydrogenolysis. Reaction conditions: catalyst wt, 23 g; solvent, 2-propanol; 20 wt % glycerol; feed flow rate, 30 mL/h; H_2 flow rate, 10 NL/h; pressure, 40 bar; temperature, 493 K.

Figure 10. Concentration vs time profile for continuous glycerol hydrogenolysis. Reaction conditions: catalyst wt, 23 g; solvent, 2-propanol; 20 wt % glycerol; feed flow rate, 30 mL/h; H_2 flow rate, 10 NL/h; pressure, 30 bar; temperature, 493 K.

Figure 11. Concentration vs time profile for continuous glycerol hydrogenolysis in *n*-butanol Reaction conditions: catalyst wt, 20 g; solvent, *n*-butanol; 20 wt % glycerol; feed flow rate, 30 mL/h; H_2 flow rate, 10 NL/h; pressure, 30 bar; temperature, 493 K.

of 2-propanol decreased substantially from 7 to 3% as the concentration of glycerol increased from 20−60 wt %. Hence, 20 wt % of glycerol was found to be the optimum glycerol concentration. The substantial decrease in glycerol conversion could be due to the limiting number of catalytic sites at higher glycerol concentration. Miyazawa et al. also reported a high glycerol conversion at lower glycerol concentration of 10%.[4a]

Continuous Reactor Performance. As mentioned above, our Cu−Cr (Ba) catalyst was found to be the best catalyst during screening in a batch operation; hence, its time on stream activity was also evaluated for the continuous hydrogenolysis of glycerol. Figure 9 shows that this catalyst gave an excellent performance for 800 h for continuous operation in 2-propanol under 493 K, and 40 bar hydrogen pressure conditions, with an average glycerol conversion of ∼65% and >91% selectivity to 1,2-PDO. The product distribution pattern studied in 2-propanol solvent is shown in Figure 10. The consistent performance of the catalyst was without any deactivation-reactivation cycle indicating that the activity of the catalyst was being maintained by *in situ* activation in a continuous flow of hydrogen and also resulted in higher activity (>65% conversion) as compared to that in a batch operation (34% conversion). As shown by a concentration vs time profile in Figure 11 formation of 2-propanol was again confirmed by a separate glycerol hydrogenolysis experiment in butanol solvent. Interestingly, much
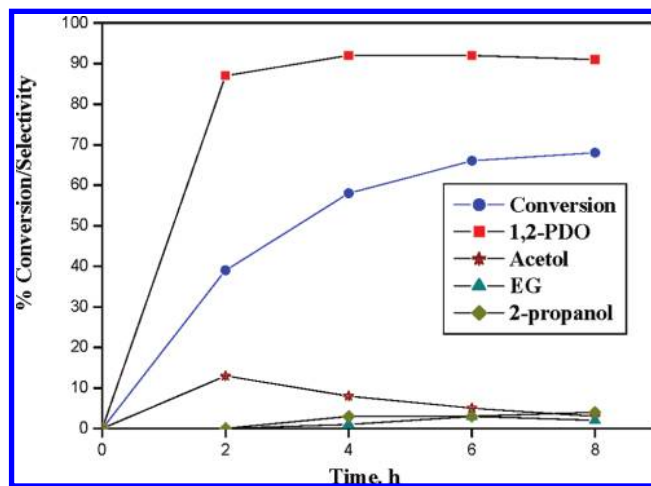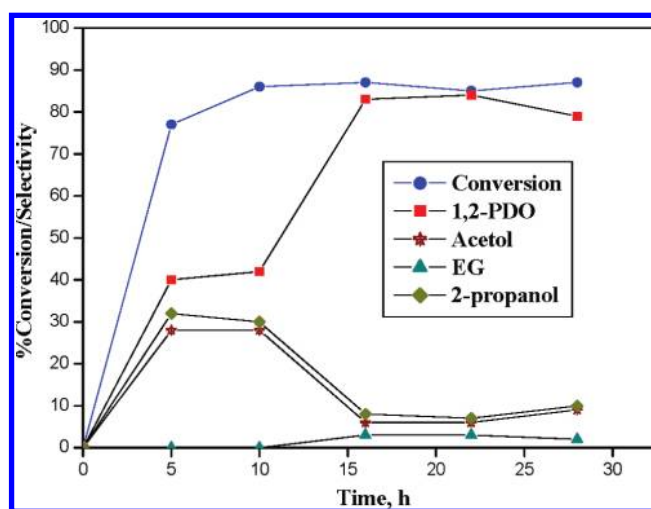
less (<2%) formation of EG was observed in the continuous glycerol hydrogenolysis due the lower contact time (1.3 h) as compared to that in the case of a batch operation (5 h). The lower EG formation also led to a very negligible (<0.8%) formation of methanol in the continuous operation and hence could not be shown in concentration vs time profiles. The effects of various reaction parameters on glycerol conversion and the selectivity pattern are discussed below.

Effect of Liquid Flow Rate. The effect of liquid flow rate on conversion of glycerol was studied in the range of 18−54 mL/h, under constant temperature, H_2 pressure, and gas flow rate conditions, and the results are shown in Figure 12. With increase in liquid flow rate from 18 to 54 mL/h, glycerol conversion decreased proportionately. The reason for this decrease in conversion is the reduction in residence time of glycerol in the reactor with an increase in the liquid flow rate. Therefore, less time was available for the intimate contact of H_2 with liquid glycerol and the catalyst pellets, thus inhibiting the substrate diffusion. At lower liquid flow rate, catalyst
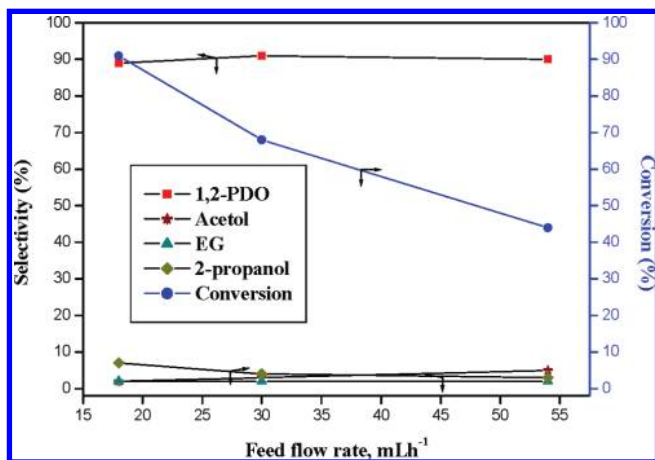
Figure 12. Effect of liquid flow rate. Reaction conditions: catalyst wt, 23 g; solvent, 2-propanol; 20 wt % glycerol; H_2 flow rate, 10 NL/h; pressure, 40 bar; temperature, 493 K.
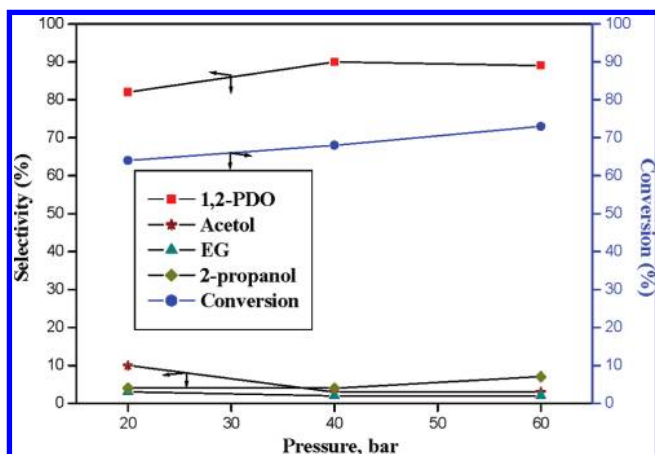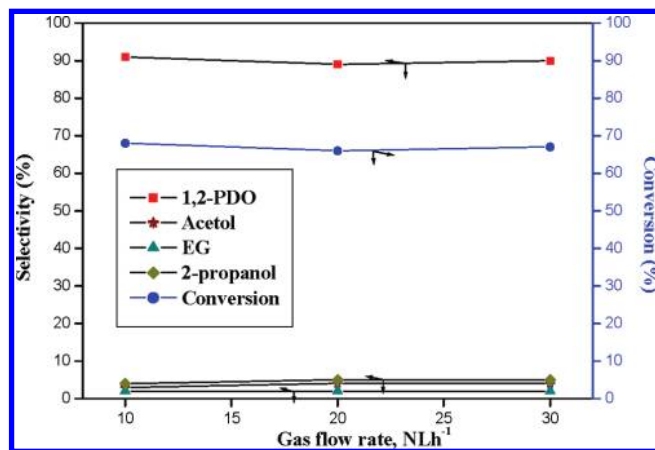

Figure 14. Effect of hydrogen flow rate. Reaction conditions: catalyst wt, 23 g; solvent 2-propanol; 20 wt % glycerol; feed flow rate, 30 mL/h; pressure, 40 bar; temperature, 493 K.
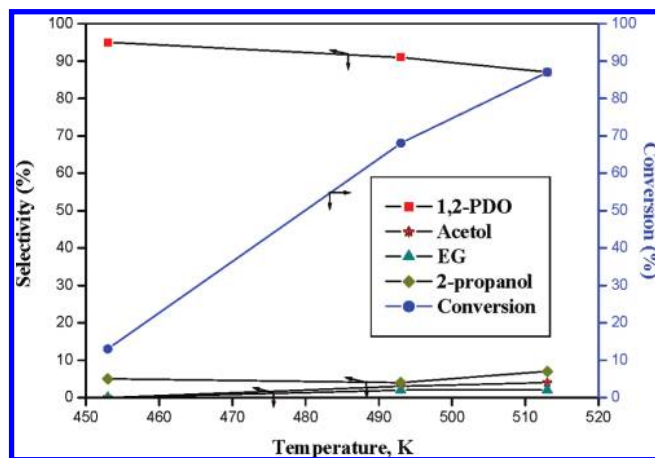

Figure 13. Effect of hydrogen pressure. Reaction conditions: catalyst wt, 23 g; solvent, 2-propanol; 20 wt % glycerol; feed flow rate, 30 mL/h; H_2 flow rate, 10 NL/h; temperature, 493 K.

Figure 15. Effect of temperature. Reaction conditions: catalyst wt, 23 g; solvent 2-propanol; 20 wt % glycerol; feed flow rate, 30 mL/h; H_2 flow rate, 10 NL/h; H_2 pressure, 40 bar.

particles were partially wetted; therefore, there would be direct contact of gas-phase reactant and catalyst surface which increases the reaction rate. Subsequently at higher liquid flow rate, the increased wetted fractions of catalyst surface would slow down the reaction rate. A similar observation was reported for continuous hydrogenation of 2-butyne−1,4-diol by Rode et al.[21]

Effect of H_2 Pressure. The effect of H_2 pressure was studied at constant temperature of 493 K in the range of 20−60 bar H_2 pressure, and the results are shown in Figure 13. Unlike the results in a batch operation, (Figure 6), glycerol conversion increased from 64 to 74% with an increase in H_2 partial pressure from 20 to 60 bar, in a continuous operation. At higher H_2 pressure, in situ reactivation of the catalyst could be more efficient, leading to higher glycerol conversion. 1, 2-Propanediol selectivity initially increased from 82 to 91%, while the selectivity to acetol decreased from 10 to 3% with an increase in H_2 pressure from 20 to 40 bar, indicating a higher hydrogenation rate at higher H_2 pressure.

Effect of Gas Flow Rate. Effect of hydrogen gas flow rate on glycerol hydrogenolysis was studied in the range of 10 −30

NL/h under constant temperature and pressure conditions. From Figure 14, it was observed that there was not any effect of gas flow rate on glycerol conversion. The product selectivities also remained constant since the change in gas flow rate did not affect the reaction rate to a considerable extent.

Effect of Temperature. The effect of temperature was studied over the range of 453 to 513 K by keeping other parameters constant. It was observed from Figure 15 that reaction temperature had a considerable effect on the conversion of glycerol. However, as compared to that of the batch operation, the effect of temperature on the glycerol conversion was highly predominant in a continuous operation as evidenced by about more than 6 times increase in glycerol conversion (from 13 to 87%) as temperature increased from 453−513 K, while the selectivity to 1,2-propanediol decreased marginally from 95 to 86%, correspondingly increasing the selectivity to the cracking product such as ethylene glycol.

Effect of Glycerol Concentration. Effect of glycerol concentration was also studied by varying the wt % of glycerol from 20 to 60% in liquid feed, and the results are shown in Figure 16. Although similar to that of the batch operation where glycerol conversion initially decreased from 68 to 40% with an increase in concentration from 20 to 40 wt %, it remained constant for further increase in glycerol loading up to 60 wt %.

(21) Rode, C. V.; Tayade, P. R.; Nadgeri, J. M.; Jaganathan, R.; Chaudhari, R. V. *Org. Process Res. Dev.* **2006**, *10*, 278.
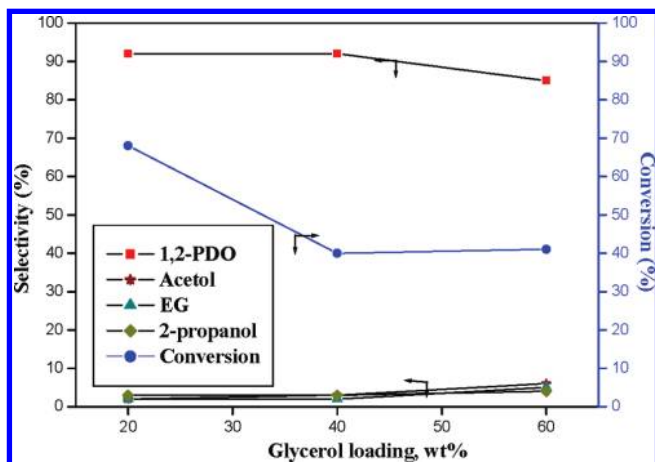
Figure 16. Effect of glycerol loading. Reaction conditions: catalyst wt, 23 g; solvent, 2-propanol; feed flow rate, 30 mL/h; H_2 flow rate, 10 NL/h; H_2 pressure, 40 bar; temperature, 493 K.

Thus, the effect of glycerol loading on the catalyst activity was much milder in a continuous operation, which could be due to the fact that the continuous flow of hydrogen leads to the catalyst surface renewal inhibiting the strong adsorption of the substrate. Another observation different from that in the batch operation was that the selectivity to 1,2-PDO remained constant at 90% with initial increase in glycerol loading from 20 to 40% and then decreased to 85% with further increase in glycerol loading up to 60%. At this glycerol loading, corresponding formation ($\sim$10%) of other side products was observed.

Conclusions

Glycerol hydrogenolysis over Cu−Cr (Ba) catalyst in a continuous operation was carried out for a total period of 800 h without any deactivation−activation cycle, which also showed better performance than that in a batch operation. Product distribution studies in a batch operation confirmed that 2-propanol was formed due to excessive hydrogenation of 1,2-PDO, while the C−C bond cleavage in glycerol led to the formation of ethylene glycol and methanol. Selectivity of >90% to 1,2-PDO was achieved in a continuous operation higher than that in a batch operation (84%) due to elimination of the formation of ethylene glycol. A study of the effect of process conditions in a continuous operation revealed that glycerol conversion and selectivity to 1,2-PDO increased from 65 to 74% and from 82 to 91%, respectively, with an increase in H_2 partial pressure from 20 to 60 bar, while the selectivity to acetol decreased from 10 to 3%, indicating a higher hydrogenation rate at higher H_2 pressure.