Liquid phase conversion of Glycerol to Propanediol over highly active Copper/Magnesia catalysts

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Abstract. In this work, a series of Cu/MgO catalysts with different copper metal loading were prepared by the precipitation-deposition method. Their catalytic behaviour was investigated for glycerol hydrogenolysis to 1,2-propanediol (1,2-PDO). The physico-chemical properties of the catalysts were characterized by various techniques such as BET surface area, X-ray diffraction (XRD), temperature programmed reduction (TPR), NH₃-temperature programmed desorption (NH₃-TPD) and scanning electron microscopy (SEM) methods. The characterization results showed that the copper metal was well-dispersed over MgO support and a new phase Cu-MgO was also identified from XRD results after calcination. The 25Cu/MgO (Cu:25 wt%) catalyst exhibited the highest glycerol conversion of 88.7% and 1,2-PDO selectivity of 91.7% at 210°C, 4.5 MPa of hydrogen pressure after 12 h. The high glycerol conversion was mainly due to the Cu dispersion on MgO support and high acidic strength. Further, the effects of temperature, hydrogen pressure, catalyst loading and glycerol concentration were studied over 25Cu/MgO catalyst for optimization of reaction parameters. Kinetic study over highly active 25Cu/MgO catalyst showed that the reaction followed the pseudo second order rate with respect to glycerol and the apparent activation energy was found to be 28.7 ± 0.8 kcal/mol.

Keywords. Glycerol hydrogenolysis; 1,2-propanediol; Cu/MgO catalysts; kinetic study.

1. Introduction

There is a need to search for better sustainable and renewable energy resources to meet the energy demand for mankind. At present, biodiesel has proven to be one of the promising alternatives as a non-toxic and biodegradable energy resource. It is essentially a mixture of methyl esters of short chain alcohols such as methanol and ethanol derived from fatty acids obtained from renewable lipid sources via trans-esterification process. Crude glycerol is the principal by-product (10% in weight) of the biodiesel production process.¹ This increased production of biodiesel would lead to simultaneous increased production of glycerol which is expected to exceed the demand in near future.² Utilization of glycerol into value added products can help in reducing the overall cost of biodiesel production.

Currently propanediols are produced from petroleum derivatives via chemical catalytic routes. Their production from glycerol via catalytic hydrogenolysis could potentially offer great environmental benefits. Glycerol can be transformed into a number of value-added products namely propanediols, lactic acid, acrolein by

several processes. Among these processes, catalytic hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO) is a promising process. Some of the uses of 1,2-PDO are in the production of resins, unsaturated polyesters, cosmetics, anti-freeze agent, tobacco humectants, pharmaceuticals and paints. 1,3-propanediol (1,3-PDO) can also be used as the monomer with terephthalic acid for the production of polyesters.^{3,4}

Various heterogeneous catalysts such as supported Ru,^{5–9} Pt,^{6,7,10} Pd^{6,9} and Ir-Rh oxide¹¹ catalysts have been considered as highly active for the hydrogenolysis of glycerol. However, the selectivity towards 1,2-PDO is poor due to the propagation of C-C bond cleavage, which leads to the degradation products. Cu-based catalysts^{12–19} have been widely studied for glycerol hydrogenolysis to propanediols, mainly because of their high selectivity towards C-O bond hydro-dehydrogenation and poor activity towards C-C bond cleavage. Copper chromite, a conventional hydrogenation catalyst, showed good performance in the glycerol hydrogenolysis to 1,2-PDO (65% glycerol conversion with 90% 1,2-PDO selectivity)¹² Chaminand *et al.*¹³ reported 100% selectivity for 1,2-propanediol in the presence of CuO/ZnO catalysts under the conditions of 180°C and 8 MPa

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hydrogen pressure but the conversion was very low (17%) at longer reaction time of 90 h. Huang *et al.*¹⁴ reported 29% glycerol conversion and 99% 1,2-PDO selectivity over Cu/SiO₂ catalyst at 180°C and 9 MPa hydrogen pressure. Balaraju *et al.*¹⁵ achieved 49.3% conversion over Cu-MgO catalyst with 92% of selectivity for 1,2-PDO after 8 h at moderate reaction conditions (4 MPa 200°C). Guo *et al.*¹⁶ described Cu/Al₂O₃ catalyst showed 96.8% selectivity to propanediols with a glycerol conversion of 49.6% at 220°C, 1.5 MPa initial H₂ pressure after 10 h. More recently, mixed metal oxides such as Cu/Zn-Mg-Al,¹⁷ Cu/ZnO/ZnAl₂O₄¹⁸ and Cu-Zn-Cr-Zr¹⁹ were reported as highly active and achieved 80–100% glycerol conversions. Regardless of several investigations, the heterogeneous catalytic hydrogenolysis of glycerol is not fully commercialized because of the high reaction temperatures (250–350°C), high hydrogen pressures (6–30 MPa), poor catalyst stability and lower glycerol activity.

In the present study, highly active and selective MgO-supported copper metal catalysts have been employed for glycerol hydrogenolysis in aqueous phase, since alkaline supports are known to influence the dehydration of glycerol during hydrogenolysis reaction. Cu/MgO catalysts having different copper loadings were prepared and characterized. The effect of process parameters such as catalyst loading, reaction temperature, hydrogen pressure and glycerol concentration on the conversion of glycerol and product selectivity were examined. Also, for a better understanding of the reaction mechanism, kinetic study was undertaken.

2. Experimental

2.1 Catalyst synthesis

A metal supported composite catalyst was prepared by precipitation-deposition method. Firstly, calculated amount of Cu(NO₃)₂·3H₂O (Himedia chemicals, India, AR) and MgO (Thomas Baker, India, AR) were taken and precipitated with dropwise addition of 1 M aqueous sodium hydrogen carbonate solution until the pH of mixed solution reached to 8.0–8.25. The resulting slurry was stirred for 6 h at ambient temperature and aged for 12 h. The filtrate obtained was separated by vacuum filtration and washed thoroughly with distilled water to eliminate traces of any sodium ions. The obtained precipitate was dried overnight at 110°C in oven followed by calcination in air at 550°C for 4 h. The prepared catalysts are designated as 5Cu/MgO, 10Cu/MgO, 15Cu/MgO, 20Cu/MgO and 25Cu/MgO.

The numbers indicate the weight % of Cu on the MgO support.

2.2 Catalyst characterization

BET surface areas of prepared catalysts were determined by the Micromeritics Accelerated Surface Area and Porosimetry (ASAP-2020) system, employing nitrogen physisorption at liquid nitrogen temperature. Prior to the analysis, the catalyst samples were degassed at 300°C for 6 h. X-ray diffraction (XRD) of prepared catalysts were obtained in a Bruker diffractometer (Model AXS D8, Germany) using Ni filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with a scanning angle (2θ) of 10°–80°, a scanning speed of 0.02° with 3 s collection time. The identification of compounds in powder samples was attained by comparison of the peaks with data files provided by Joint Committee on Powder Diffraction Standards (JCPDS) using PCPDFWIN software. The average crystallite size was determined using the Scherrer equation, $D = 0.90\lambda/B \cos\theta$, where θ is the diffraction angle, B is the full width at half-maximum (FWHM). Temperature programmed reduction experiments with hydrogen (H₂-TPR) were studied using Micromeritics Chemsorb 2720 pulse chemisorption system. For each measurement, 25 mg of catalyst sample was placed in a quartz U-tube reactor. Before reduction, samples were pre-treated at 150°C in flowing argon for 2 h which helps to remove the physically adsorbed moisture. Then, 10% H₂/Ar flow of 20 mL/min was passed over the sample under heating at a rate of 10°C/min until temperature was raised up to 700°C. The hydrogen consumption was monitored by a thermal conductivity detector (TCD) by means of analyzed effluent gas with argon as reference. Temperature programmed desorption experiments with ammonia (NH₃-TPD) were carried out using same apparatus as above used for H₂-TPR. Prior to the measurements, about 80 mg of catalyst samples were degassed in flowing helium at 150°C. Then samples were cooled to room temperature and ammonia adsorption carried out by switching gas to 27% NH₃/He (30 mL/min) for 1 h. After saturated adsorption, samples were purged with helium (20 mL/min) for 1 h to remove any physisorbed ammonia on the surface. The ammonia desorption measurements were conducted in flowing helium (20 mL/min) from 30°C to 800°C at a heating rate of 15°C/min. The morphology of catalysts and metal distribution of catalysts were examined by scanning electron microscopy (SEM) on a microscope equipped with energy-dispersive X-ray analysis EDX used for estimation of local elemental composition. SEM images were collected using Quanta scanning

electron microscope (Model 200 FEG, USA) equipped with EDX.

2.3 Catalytic activity

Glycerol hydrogenolysis was carried out in a Teflon-lined stainless steel autoclave (250 mL) (Amar Equipments, India). The reactor was equipped with programmable temperature controller (PID), pressure gauge up to 10 MPa, stirrer (1–1450 rpm), a vent and a sample port for liquid sampling. Prior to the each run, catalyst samples were reduced in a tubular reactor under hydrogen flow of 50 mL/min at 350°C for 3 h. In a typical run, 100 mL of 20 wt% aqueous glycerol solution and 1.6 g of reduced Cu/MgO catalyst were fed into the reactor. Prior to reaction, the reactor was flushed with

nitrogen gas (0.5 MPa) for few times, further reactor was heated to reaction temperature of 210°C and pressurized the reactor by H₂ gas up to desired pressure of 4.5 MPa. The reaction was allowed to proceed under these conditions for 12 h at 700 rpm. After the reaction, liquid phase products were centrifuged (Heraeus Biofuge Stratos, Thermo Scientific) to separate any catalyst particles present in the sample. The reactant and products involved in this reaction were analyzed using a gas chromatograph (Model no: GC 6800 Newchrom Technologies, India) equipped with flame ionization detector (FID) and Chromosorb-101 packed column (1.52 m × 3.1 mm OD × 2 mm ID). n-butanol was used as an internal standard in analysis for the quantification of glycerol derived products. The following equations were used to calculate glycerol conversion and product selectivity:

$$\text{Conversion (\%)} = \frac{\text{Moles of glycerol in feed} - \text{Moles of glycerol in product}}{\text{Moles of glycerol in feed}} \times 100$$

$$\text{Selectivity of product X (\%)} = \left(\frac{\text{C-based moles of product X}}{\text{Total C-based moles of all products}} \right) \times 100$$

The error in reproducibility of experiments was within $\pm 3\%$ and carbon balance was $100 \pm 5\%$.

3. Results and Discussion

3.1 Catalyst characterization

The BET surface area and pore volume of Cu/MgO catalysts are summarized in table 1. The nitrogen adsorption-desorption isotherms represents typical mesoporous nature of type IV isotherms. The BET surface area was calculated from the relative pressure data (P/P_0) obtained in the range of 0.05–0.3. The surface area decreased sharply with increasing Cu loading from 70.3 m²/g (for 5Cu/MgO) to 24.5 m²/g (for 25Cu/MgO) probably due to the formation of CuO clusters on the MgO support which might be blocking the pores of MgO.¹⁵ Barret-Joyner-Halenda (BJH) method is applied to desorption branch of isotherms to calculate the pore volume. The pore volume of all catalysts is observed to be in the range of 0.13–0.03 (cm³/g).

XRD patterns of Cu/MgO catalysts having different metal loading (5 wt% to 25 wt %) is shown in figure 1. For pure MgO, the most intense peaks are observed at 2θ value of 42.9° and 62.2° corresponding to (200) and (220) planes, respectively (JCPDS: 78–0430). Three low intensity peaks are observed for MgO at the 2θ

value of 36.9°, 74.6° and 78.6° corresponds to (111), (311) and (222) planes.

The diffraction peaks corresponding to very high intensity CuO were not detected in any of the catalysts from 5Cu/MgO to 20Cu/MgO, whereas new diffraction appeared at 18.6° and 38.7°. This indicates the formation of new phase CuO-MgO between precursors. Previously, it was reported that the Cu-MgO phase can be easily generated on the interface of active Cu and MgO by the synergetic effect of Cu and MgO after the application of high temperature treatment to both mixtures.²⁰ While for 25Cu/MgO, high intense reflections are observed for monoclinic CuO (JCPDS: 80–1917) at $2\theta = 35.6^\circ$ and 38.9° correspond to (111) and (111) planes. For all Cu loaded catalysts, a low intensity diffraction peak is obtained at $2\theta = 58.8^\circ$ corresponding to CuO (202) plane. The low intensity or absence of CuO phases in some catalysts suggesting high dispersion of copper on the MgO surface.²¹ Previous studies also reported similar kind of Cu based catalysts with high dispersion on support and good metal-support interactions.^{22,23} The crystallite size of Cu/MgO were calculated based on the diffraction angle and X-ray line broadening using Scherrer equation are shown in table 1. The average crystallite size of MgO was calculated from the line widths of characteristic peaks at $2\theta = 42.9^\circ$, 62.2° and 78.6° corresponding to (200), (220) and (222) planes and the average crystallite size

Table 1. Physico-chemical properties of Cu/MgO catalysts.

Catalysts	BET Surface area (m ² /g)	Pore volume (cm ³ /g)	Acidity (mmol NH ₃ /g catalyst)	Average crystallite size (nm)			
				2 θ	CuO	2 θ	MgO
5Cu/MgO	70.3	0.13	2.21	58.8°	16.7	42.9°, 62.2°	19.6
10Cu/MgO	60.8	0.08	2.81	58.8°	18.0	42.9°, 62.2°, 78.6°	24.6
15Cu/MgO	31.6	0.04	3.47	58.8°	16.1	42.9°, 62.2°, 78.6°	15.1
20Cu/MgO	27.5	0.03	4.31	35.6°, 58.8°	19.1	42.9°, 62.2°, 78.6°	19.2
25Cu/MgO	24.5	0.03	4.89	35.6°, 38.9°, 58.8°	26.0	42.9°, 62.2°, 78.6°	24.1

Figure 1. X-ray diffraction patterns of calcined Cu/MgO catalysts on different loadings.

of CuO was determined from the line width of XRD peaks at $2\theta = 35.6^\circ$, 38.9° and 58.8° representing (111), (111) and (202) planes. The average crystallite size of CuO is observed in the range of 16.1–26 nm, whereas for MgO crystallite sizes are in the range of 15.1–24.6 nm.

TPR analysis was carried out to study the redox properties of catalysts. TPR profile for 25Cu/MgO catalyst is shown in figure 2. For 25Cu/MgO catalyst one high intensity broad reduction peak centered at 288°C is observed. Intense hydrogen consumption is noticed between 200– 350°C which may be attributed to the reduction of larger CuO particles to Cu. The broad reduction peak is might be due to assimilation of reduction peaks associated with dispersed and CuO cluster sites for high Cu metal loadings.^{15,21}

NH₃-TPD experiments were carried out to study the acidic characteristics of Cu/MgO catalysts. The quantitative estimation of acidic site distribution at different regions according to the desorbed amount of ammonia are summarized in table 1. For all the catalyst samples, the acidic sites distributed in three different regions at 80– 250°C , 250 – 500°C and 500 – 750°C (figure 3). According to previous literature, the first region should

Figure 2. Temperature programmed reduction profile of 25Cu/MgO catalyst. **Figure 3.** NH₃-Temperature programmed desorption profiles of Cu/MgO catalysts with different Cu loadings.

be attributed to ammonia desorption from weak acidic sites, the second region refers to moderate strength acidic sites and the third region represents desorption of ammonia from strong acidic sites.^{24,25}

Figure 4. SEM images of Cu/MgO catalysts. (a) 5 Cu/MgO, (b) 10 Cu/MgO, (c) 15 Cu/MgO, (d) 20 Cu/MgO, (e) 25 Cu/MgO.

The acidic strength of Cu/MgO catalysts increased from 2.21 to 4.89 mmol NH_3/g catalyst as the metal loading increases from 5% to 25%. Initially the weak and moderate acidic sites are more in case of lower metal loaded catalysts (5Cu/MgO and 10Cu/MgO). As the metal loading increased, the strength of weak acidic sites gets decreased and becomes moderate, and strong acidic sites become dominant in the catalysts (figure 3).

SEM images were used in order to observe the morphology of prepared catalysts. Figure 4 represents SEM images of Cu catalysts supported on MgO. All the catalysts supported on MgO are found as amorphous in nature. The particle morphology of all catalysts show similar to quasi spherical nanoparticles of 10–40 nm size. As the Cu loading increased, the coverage of the MgO surface by Cu particles is observed. At 5–25 wt% Cu loading, the agglomeration of the catalyst particles is noticed, which results in formation of big lumps.

The particle agglomeration maybe the reason for further decrease in surface area.

3.2 Catalytic activity measurements

3.2a Influence of Cu loading on MgO on glycerol hydrogenolysis: The glycerol conversion and 1,2-PDO selectivity obtained over different catalysts is tabulated in table 2. The results show that 39.4% conversion of glycerol, and 94.2% selectivity towards 1,2-PDO is achieved over 5Cu/MgO catalyst.

As the Cu metal loading increases from 10 to 25 wt%, the conversion of glycerol increased significantly from 39.4% to 88.7% and selectivity to 1, 2-PDO found to be in range of 90.5–94.2%. From the above results, it is observed that high Cu loading (25 wt%) on MgO showed high glycerol hydrogenolysis activity. Previous

Table 2. Conversion and selectivity of the products obtained for liquid phase hydrogenolysis.

Catalyst	Conversion (%)	Selectivity (%)			
		1,2-PDO	EG ^a	Acetol	Others ^b
5Cu/MgO	39.4	94.2	4.4	0.4	0.9
10Cu/MgO	69.2	92.0	5.0	0.7	2.2
15Cu/MgO	78.6	90.5	4.5	2.0	2.8
20Cu/MgO	85.0	92.9	4.6	0.5	1.9
25Cu/MgO	88.7	91.7	5.5	0.5	2.2

^a EG: Ethylene glycol, ^b Others: 1-propanol, 2-propanol, traces of ethanol and methanol

Reaction condition: 20 wt% glycerol concentration, Temperature = 210°C; Hydrogen pressure = 4.5 MPa, catalyst weight = 1.6 g, reaction time = 12 h.

literature has discussed about the development of various catalysts system for glycerol hydrogenolysis. However, the information regarding the Cu/MgO catalysts is limited. It is also reported in literature that high glycerol conversion was achieved over Cu-MgO catalysts.^{15,26} Yuan *et al.*²⁶ reported 72% glycerol conversion and 97.6% 1,2-PDO selectivity over Cu-15/MgO catalyst at 13.3% catalyst loading, 180°C, 3.0 MPa H₂ pressure after 20 h of reaction and when small amount of NaOH was added to the reaction mixture, the glycerol conversion and 1,2-PDO selectivity reached to 82% and 97.6%. Balaraju *et al.*¹⁵ observed 49.3% glycerol conversion and 92.3% 1,2-PDO selectivity over 20 CuMgO catalyst at 6% catalyst loading, 200°C, 4.0 MPa H₂ pressure after 8 h of reaction time. Yue *et al.*²⁰ achieved 36.2% glycerol conversion and 85% 1,2-PDO selectivity over Raney Cu/MgO catalyst at 2.5% catalyst loading, 180°C, 1.0 MPa H₂ pressure after 24 h. In the present study, maximum glycerol conversion of 88.7% was obtained over 25Cu/MgO catalyst with 91.7% selectivity to 1,2-PDO at 8% catalyst loading at 210°C, 4.5 MPa H₂ pressure. Comparison of the result reported in this study with the previous literature, it is clearly seen that the high glycerol conversion and 1,2-PDO selectivity are achieved at the mild reaction condition which is mainly due to the acidity of catalysts and bifunctional nature of Cu-MgO. As the acidic strength increases from 2.21 to 4.89 mmol NH₃/g catalyst, the glycerol conversion increased from 39.4% to 88.7%.

In published works, the role of acidic sites of catalysts was explained in different ways. Balaraju *et al.*⁸ found that solid acid (Niobia) as a co-catalyst with Ru/C could improve the glycerol activity and increasing the amount of Ru/C + solid acid led to a significant increase in both glycerol conversion and 1,2-PDO selectivity. Miyazawa *et al.*⁶ reported that the combi-

nation of Ru/C with solid acid (Amberlyst) enhanced the turn over frequency (TOF) of 1,2-PDO formation. Gandarias *et al.*¹⁰ suggested that Pt/ASA catalysts having acid sites are responsible for achieving higher glycerol conversions with maximum 1,2-PDO selectivity. Cu based catalysts such as Cu/Al₂O₃¹⁶ and Cu-Zn-Cr-Zr¹⁹ also suggested that increasing acidic strength of catalysts enhanced the rate of glycerol conversion. This indicates that dehydration of glycerol to acetol catalyzes by the acidic sites and subsequent hydrogenation on the metal catalyst results 1,2-PDO. Interestingly, Xia *et al.*¹⁷ reported that both acidic and/or basic sites are responsible for maximum activity over Cu_{0.4}/Zn_{0.6}Mg_{5.0}Al₂O_{8.6} layered double oxide catalysts. Earlier studies^{8,10,16,19} and the preceding discussion resolved that the activity of Cu/MgO catalysts reported in this study increased obviously with their acidity (table 1). The glycerol conversion of 88.7% with 81.3% yield to 1,2-PDO over 25Cu/MgO can be attributed to its stronger acidity (4.89 mmol NH₃/g catalyst). The activity and yield of the present study are comparable with published literature.^{8,10,16,19} Similar conclusions can be drawn from the XRD results, NH₃-TPD data and small particles of Cu observed from crystallite size and SEM that high dispersion of Cu and acidic strength of Cu/MgO catalysts improved the hydrogenolysis activity and 1,2-PDO yield.

3.2b Effect of reaction temperature: The effect of reaction temperature on the catalytic performance over 25Cu/MgO catalyst is shown in figure 5. The conversion of glycerol increased from 72% to 88% as the temperature increases from 190°C to 210°C and the selectivity of 1,2-PDO also increased from 88.7% to 91.7%. Further increase in temperature from 210°C to 225°C the conversion of glycerol slightly increased to 91.8% whereas the selectivity of 1,2-PDO is decreased from

Figure 5. Effect of reaction temperature on hydrogenolysis of glycerol over 25 Cu/MgO catalyst. Reaction conditions: 20 wt% glycerol solution, 1.6 g catalyst, H₂ pressure: 4.5 MPa, time: 12 h.

91% to 83% at high temperatures. EG selectivity is obtained in the range of 5–7%. This result indicates that at high reaction temperatures (>210°C), excessive hydrogenolysis of glycerol and 1,2-PDO is taking place which further yields byproducts like EG, propanol, methanol, ethanol and other gaseous products.¹² Hence reaction temperature of 210°C is identified as optimum temperature for hydrogenolysis of glycerol.

3.2c Effect of reaction pressure: The effect of reaction pressure on the catalytic performance over 25Cu/MgO catalyst is shown in figure 6. As the hydrogen pressure in reaction increases from 1.5 to 4.5 MPa,

Figure 6. Effect of reaction pressure on hydrogenolysis of glycerol over 25 Cu/MgO catalyst. Reaction conditions: 20 wt% glycerol solution, 1.6 g catalyst, reaction temperature: 210°C, time: 12 h.

the conversion of glycerol is increased from 49% to 88%. Further increase in pressure to 6 MPa, the conversion decreased to 81% indicating that at higher pressures hydrogen atoms compete with the readsorption of an intermediate product (acetol) for active catalyst sites resulting the decrease in glycerol conversion.^{15,27} However the selectivity of 1,2-PDO is decreased from 91% to 86% at higher pressure range of 4.5–6 MPa. The decrease in selectivity is due to formation EG. The selectivity of EG is found to be in range of 3–6%.

3.2d Effect of catalyst weight: The effect of catalyst weight on the catalytic performance over 25Cu/MgO catalyst is shown in figure 7. Catalyst weight was varied from 0.8 g (catalyst/glycerol = 4%) to 2 g (catalyst/glycerol = 10%). Results show that, glycerol conversion increased with increase in the catalyst amount. Glycerol conversion is found to be 56.7% at 0.8 g of catalyst loading. Further increase in catalyst loading up to 2 g, glycerol conversion is reached to 95%. The selectivity of 1,2-PDO obtained is in the range of 86–91% and the selectivity of EG is in the range of 5–7%. The increase in glycerol conversion with catalyst loading is due to the more availability of active catalytic sites for selective hydrogenolysis of glycerol.^{12,27}

3.2e Effect of glycerol concentration: The effect of glycerol concentration on the catalytic performance over 25Cu/MgO catalyst is shown in figure 8. It is observed that glycerol conversion decreased from 88% to 38% with increase in glycerol concentration from 10 wt% to 60 wt% which is likely due to the limited number of available Cu sites with respect to glycerol as

Figure 7. Effect of catalyst weight on hydrogenolysis of glycerol over 25 Cu/MgO catalyst. Reaction conditions: 20 wt% glycerol solution, H₂ pressure: 4.5 MPa, reaction temperature: 210°C, time: 12 h.

Figure 8. Effect of glycerol concentration on hydrogenolysis of glycerol over 25Cu/MgO catalyst. Reaction conditions: 1.6 g catalyst, H_2 pressure: 4.5 MPa, reaction temperature: 210°C, time: 12 h.

the catalyst weight is constant. The selectivity towards 1, 2-PDO decreased from 91% to 84% as the glycerol concentration increases from 10 wt% to 60 wt%, which is due to the formation of degradation reaction products. EG selectivity was obtained in the range of 3–5%. These results indicate that glycerol conversion depends on the concentration of glycerol in the reaction mixture.

The previous literature indicated that the glycerol activity depends upon Cu metal dispersion and basicity obtained from CO_2 -TPD in Cu-MgO catalysts prepared via co-precipitation method.¹⁵ It was reported that Raney Cu catalyst promotes the transformation of glycerol into hydroxyacetone (intermediate) by free radical process by removing the primary hydroxyl group in glycerol.²⁸ Thus, Cu is co-operated with MgO catalyzed glycerol to improve the selectivity to 1,2-PDO. Meanwhile, based on acid-base properties of MgO ,²⁹ very good catalytic dehydrogenation property of Cu-MgO,³⁰ and tendency to produce metastable acetol in thermody-

namics at low temperature,³¹ it is considered that glycerol dehydration is resulted by the combined effect of hydrogen spill over of Cu and acid-base property of MgO in Cu/MgO catalysts. Previously Sato *et al.*²⁸ proposed an analysis based on transition state of hydrogen effect on Cu surface and glycerol dehydrogenation, the secondary hydroxyl groups are removed under the effect of Mg^{2+} on Cu/MgO surface in free radical form under synergetic catalysis. Otherwise, it will produce aldehydes via dehydrogenation, followed by dehydration and hydrogenation to acetol. None of the acetalization products (cyclic compounds) are detected after reaction and enol is produced as intermediate by dehydration. Unstable enol is further converted to acetol by tautomerization followed by acetol to 1,2-PDO through catalytic hydrogenation on Cu surface (scheme 1). This result has been supported by other Cu based catalysts on hydrogenolysis of glycerol.^{20,32} Propanols are obtained by the over hydrogenolysis of 1,2-PDO and other products such as ethylene glycol, ethanol and methanol are generated by the other catalytic reactions. Nevertheless, further research and in-depth investigation are needed to affirm this hypothesis.

3.3 Kinetics of glycerol hydrogenolysis

Figure 9 shows the effect of time on glycerol hydrogenolysis over 25Cu/MgO catalyst at 190, 200, 210 and 225°C. The conversion of glycerol increased linearly at lower temperatures (190 and 200°C). The glycerol conversion is increased from 11.4% to 48.8% as the time increases from 1 h to 5 h at 190°C. At 220°C, the conversion of glycerol obtained from 20% to 67% with increase in time range of 1–5 h. The selectivity of 1, 2-PDO was found in the range of 86–88%. On the other hand at 210°C, the conversion of glycerol increased quickly from 41.5% (at 1 h) to 81.2% (at 5 h). The selectivity of 1,2-PDO was found in the range of 85–87%. Similarly for 225°C, the conversion of

Scheme 1. Reaction pathway scheme for glycerol hydrogenolysis to 1,2-PDO.

Figure 9. Effect of temperature with time on hydrogenolysis of glycerol over 25 Cu/MgO catalyst. Reaction conditions: 20 wt% glycerol solution, 1.6 g catalyst, H_2 pressure: 4.5 MPa, time: 12 h.

glycerol increased quickly to 68% in two hours and then increased slowly from 68% (after 2 h) to 87% (after 5 h).

It is observed from the results of time courses at different temperatures, the relation between $(X_G/1-X_G)$ and reaction time is found to be passing through origin (figure 10a), which confirms that the reaction is pseudo second order with respect to glycerol. The calculated reaction rate constants are 7.55, 17.53, 40.03 and $67.75 \text{ L mol}^{-1} \text{ h}^{-1}$ at 190, 200, 210 and 225°C , respectively. Arrhenius plot was made by plotting $\ln(k/\text{L mol}^{-1} \text{ h}^{-1})$ vs. $(1/T)$ (figure 10b). The calculated activation energy of glycerol hydrogenolysis over Cu/MgO catalyst in temperature range of $190\text{--}225^\circ\text{C}$ is found to be $28.7 \pm 0.8 \text{ kcal/mol}$, a value in agreement with that reported by Sharma *et al.*¹⁹ (31.5 kcal/mol) and Yadav *et al.*³³ (27.5 kcal/mol). This activation energy value also indicates that the hydrogenolysis reaction is intrinsically kinetically controlled.³³

From the current study it is observed that the MgO supported Cu catalysts increase the activity for hydrogenolysis of glycerol to produce 1,2-PDO in good yield. The increase in activity is due to the combined effects of metal dispersion over support and acidic strength which is confirmed by characterization results.

Figure 10. (a) Pseudo second order plot of $(X_G/1-X_G)$ vs. Time (h) to calculate rate constant. (b) Arrhenius plot to calculate energy of activation of glycerol hydrogenolysis to 1,2-PDO.

4. Conclusion

A series of Cu catalysts supported on MgO with different Cu metal loading were synthesized by precipitation-deposition method. The catalysts were characterized by various techniques and successfully evaluated for selective hydrogenolysis of glycerol.

The glycerol conversion was found to increase with increase in Cu metal loading and achieved maximum glycerol conversion of 88.7% over 25Cu/MgO catalyst with 91.7% selectivity to 1,2-PDO at 210°C , 4.5 MPa of hydrogen pressure after 12 h. Further, the effect of different reaction parameters such as temperature, pressure, catalyst amount and glycerol concentration was evaluated over 25Cu/MgO catalyst to maximize the glycerol conversion and 1,2-PDO selectivity. Effect of temperature study revealed that the glycerol conversion was increased from 72% to 92% with a rise in temperature from 190 to 225°C . The activity of glycerol conversion was tested at different catalyst weight and it was found that even at lower catalyst loading of 6% and 4%, the glycerol conversion was 67.5% and 56.7%, respectively and the 1,2-PDO selectivity was $\sim 91\%$ under same reaction condition.

The catalyst characterization results revealed that the combined effects of Cu metal dispersion over MgO support and acidic strength played a significant role to enhance the catalytic activity. Product distribution obtained over 25Cu/MgO catalyst suggested that the

hydrogenolysis reaction followed the tautomerization of unstable enol to acetol, followed by catalytic hydrogenation to 1,2-PDO. Kinetic results showed that the reaction is pseudo second order with respect to glycerol and the apparent activation energy was found to be 28.7 ± 0.8 kcal/mol.

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