Selective Hydrogenolysis of Glycerol to 1,2-Propanediol over Highly Active and Stable Cu/MgO Catalyst in the Vapor Phase

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ABSTRACT: Highly active, selective, and stable Cu/MgO catalyst was developed for hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) in vapor phase. The effect of metal loading, temperature, pressure and weight hourly space velocity (WHSV) on glycerol conversion and 1,2-PDO yield was investigated in a down flow fixed bed tubular reactor. Catalytic results demonstrated that Cu/MgO catalyst promoted the selective hydrogenolysis of C–O bond and limited the cleavage of C–C bond which significantly reduced the selectivity of undesirable products. Very high yield (95.5%) of 1,2-PDO was obtained with 100% conversion of glycerol over 10 wt % Cu/MgO catalyst at very low WHSV of 1.2 h⁻¹, 220 °C, and 0.75 MPa pressure. The superior performance of 10 wt % Cu/MgO catalyst was attributed to the presence of bifunctional acidic-basic sites, small particle size, and synergetic interaction between copper nanoparticles and MgO support. Time-on-stream study and the characterization results of fresh and used catalyst confirmed the stability of the catalyst after prolonged contact under hydrogen environment, and the carbon deposition rate was almost negligible (∼0.6 mmol carbon g cat⁻¹ h⁻¹).

1. INTRODUCTION

Recently, the utilization of renewable biomass sources for the production of biofuels and valuable chemicals has received considerable attention due to the scarcity of fossil fuel reserves and environmental issues. Global biofuels production is expected to reach 139 billion liters in 2020.1 In this context, production of biodiesel has gained significant attention in the last two decades, and biodiesel has been regarded as a potential alternative of conventional fuels.2 The global biodiesel production is expected to be 33 billion liters by 2020.1 In the biodiesel production process, surplus glycerol (∼10 wt %) is obtained as a byproduct, and due to the rapid increase in biodiesel production worldwide, the cost of glycerol has reduced significantly.3 To make the economic viability of the biodiesel industry and biofuel supply chain, it is essential to find a way to convert this surplus glycerol to value added chemicals and fuel additives.4 Many glycerol conversion processes which includes hydrogenolysis to 1,2-propanediol (1,2-PDO), esterification to mono-, di-, and tri-acetyl glycerol, oxidation to glyceric acid, dehydration to acrolein, and etherification to others have been proposed in the current literature.5–9 Among all of these processes, selective hydrogenolysis of glycerol to 1,2-PDO has drawn a considerable attention due to the very high commercial value of 1,2-PDO.10–12 1,2-PDO is an important commodity chemical having major application as coolant, deicing agent, pharmaceuticals, cosmetics solvent, and raw materials for unsaturated polyester resin, and so forth.10,11 The global production of 1,2-PDO is about 1.4 million tons per year with the annual growth rate of 4%.11 Commercially, 1,2-PDO is produced by hydroylation of propylene oxide obtained from fossil resources through either chlorohydrin process or hydroperoxide process.12

In the last two decades, an extensive study is carried out on the liquid phase hydrogenolysis of glycerol to 1,2-PDO.10,13–24 Various noble metal and non-noble metal catalysts are developed, and their performances are evaluated in the liquid phase. However, liquid phase hydrogenolysis of glycerol has several disadvantages such as high operating pressure, separation of catalyst from the reaction mixture, catalyst stability and reusability, and so forth. As a result, vapor phase hydrogenolysis of glycerol to 1,2-PDO has received more attention nowadays. The literature information regarding the vapor phase hydrogenolysis of glycerol to 1,2-PDO is very limited.25–33 Cu/ZnO/Al₂O₃,33 Raney Cu,32 B₂O₃ promoted Cu/SiO₂,31 and Cu/SiO₂ catalyst has been reported as active for selective hydrogenolysis of glycerol to 1,2-PDO at higher pressure (>0.64 MPa) and higher hydrogen to glycerol molar ratio (>100) in the presence of aqueous glycerol (10–60 wt %) as feed. Complete glycerol conversion with 80% selectivity to 1,2-PDO is reported over Cu/Al₂O₃ catalyst at 210 °C and ambient pressure in the presence of very high hydrogen flow rate of 360 cm³ min⁻¹. It is also found that Cu/Al₂O₃ catalyst favored the dehydration of glycerol to hydroxyacetone (HA) at higher temperature (180–200 °C) and hydrogenation of HA to 1,2-PDO at lower temperature (145–160 °C).27,28,34 The effect of Ag on Cu/Al₂O₃ catalyst was investigated, and 100% conversion of glycerol with very high (>90%) selectivity to 1,2-PDO was achieved at 200 °C and 0.1 MPa in the presence of very high hydrogen to glycerol molar ratio of 700.35 It has been shown that 10% Ni/γ-Al₂O₃ catalyst was not selective to 1,2-PDO and the catalyst was deactivated due to the coke formation.36 Recently, it has been shown that nanostructured Ru/MCM-41 catalyst prepared by micro emulsion method is active for vapor phase hydrogenolysis of glycerol.26 It is also found that the catalyst preparation method, effect of support, and metal loading played an important role on glycerol conversion and 1,2-PDO selectivity. Maximum glycerol conversion of 62% with 38% selectivity to 1,2-PDO was achieved over 3 wt % Ru/MCM-41 catalyst at 230–280 °C and 0.1 MPa hydrogen pressure. Cu catalyst supported on SBA-15
were investigated, and this catalyst exhibited 90% conversion of glycerol with 84% selectivity to 1,2-PDO at 220 °C. It is also reported that dispersion of Cu metal and the acidity of the catalyst played an important role on 1,2-PDO selectivity. Recently, we also have developed an active and selective Cu–Ni/γ-Al2O3 catalyst, which showed very high yield (88%) of 1,2-PDO at 98.5% glycerol conversion at very low H2/glycerol mole ratio of 5.6 and at 220 °C and 0.75 MPa pressure.36 Previous studies indicated two-step glycerol hydrogenolysis processes. Initially, acetol is formed via dehydration of glycerol, and then acetol hydrogenated to 1,2-PDO. Dehydration reaction is favorable over the acidic and/or basic sites of the catalyst, whereas hydrogenation requires active metallic sites on the catalyst.27,28,37,38 Therefore, development of catalysts having bifunctional sites may be promising for selective conversion of glycerol to 1,2-PDO with higher yield. The primary objective of this work is to develop an active catalyst for selective conversion of glycerol to 1,2-PDO with higher yield at mild reaction condition. In this work, a highly selective, active, and stable Cu/MgO catalyst is developed, and the catalytic behavior is examined in the vapor phase. Effect of copper metal loading, temperature, pressure, and WHSV on the glycerol conversion and product selectivity are examined. Furthermore, the time-on-stream (TOS) study is performed to establish the stability characteristics of the catalyst which is described with the help of the characterization results obtained for fresh and used catalyst. The results obtained in this study established that Cu/MgO catalyst is very promising for commercial application.

2. EXPERIMENTAL SECTION

2.1. Materials. Copper(II) nitrate trihydrate (>99%, Himedia Chemicals, India) was used as metal precursors, and MgO light (Thomas Baker, India) was used as catalyst support. The standard chemicals such as glycerol (>99%, Merck Specialties, India), 1,2-PDO (>99%, Merck Specialties, India), acetal (95%, Alfa Aesar, India), 1-propanol (99%, Merck Specialties, India), 2-propanol (99.5%, Sigma-Aldrich, India), ethylene glycol (extra pure, Fluka analytical (Sigma-Aldrich), India), n-butanol (99.0%, Rankem, India), methanol (99%, Merck Specialties, India), and ethanol (99.999%, Merck Specialties, India) were used for calibration. The ultrahigh purity hydrogen (99.999%) and nitrogen (99.999%) were supplied by Sigma Gases, India and used directly without any further purification.

2.2. Catalyst Preparation and Characterization. Cu/MgO catalysts were prepared by precipitation–deposition method, and the metal loading was varied from 5 to 15 wt %. The catalysts were characterized by various techniques such as BET surface area measurement, H2 chemisorption, X-ray diffraction (XRD), temperature-programmed reduction (TPR), temperature-programmed desorption (TPD), transmission electron microscope (TEM), and so forth. The detailed catalyst preparation and characterization procedure is discussed in our previous study.39

2.3. Catalytic Test. Vapor-phase hydrogenolysis of glycerol was carried out in a continuous fixed bed down flow vertical tubular reactor (Chemito Technologies, India) consisting of a stainless steel tube 540 mm in length and 12.5 mm i.d. The schematic diagram of the flow reactor unit is shown in our previous work.36 The catalyst was placed on a quartz wool bed inside the reactor. The reactor was heated with the help of a tubular furnace equipped with a programmable temperature controller. The reactor was provided with mass flow controllers (AALBORG, model no. GFC17, Denmark) to control the feed gas flow, pressure indicators, and thermocouples to measure the temperature at inside and outside the reactor. Prior to an experiment, the catalyst was reduced in situ at 350 °C for 3 h under a hydrogen flow rate of 50 cc min⁻¹. Initially, the reactor was pressurized with the feed gas, and the aqueous feed was fed to the reactor with the help of liquid feed pump (Lab Alliance, USA, HPLC dosing type), when the reactor operating temperature and pressure were achieved. Feed (20 wt % aqueous glycerol) was vaporized in a preheater connected at the reactor inlet. Nitrogen which served as an inert was mixed with the hydrogen and the vaporized feed at the inlet of the reactor. The performance of the catalysts was investigated at different inlet conditions. Reaction temperature, pressure, and WHSV was varied in the range of 180–280 °C, 0.1–1.0 MPa, and 1.03–1.80 h⁻¹, respectively. A gas–liquid separator was connected at the other end of the reactor through a recirculating cooling bath (model no. FL 300, Julabo, Germany). The condensed product sample was collected in the gas liquid separator and analyzed by an offline gas chromatography (GC 6800, Newchrom Technologies, India) equipped with flame ionization detector (FID) and a Chromosorb-101 packed column (1.52 m × 3.1 mm O.D. × 2 mm I.D.). For calculating the product selectivity, n-butanol was used as an internal standard. The carbon balance of all the reported results agreed 100 ± 7%. The glycerol conversion, product selectivity, and yield are defined as follows:

![Table 1. Physiochemical Properties of Catalysts](image-url)
glycerol conversion(%) = \frac{\text{moles of glycerol converted}}{\text{moles of glycerol present in the feed}} \times 100 \quad (1)

product selectivity(%) = \frac{\text{moles of carbon present in the product}}{\text{total moles of carbon present in all the products}} \times 100 \quad (2)

product yield(%) = \frac{\text{glycerol conversion(%) \times product selectivity(%)}}{100} \quad (3)

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization. The physicochemical properties of catalysts obtained by \( \text{N}_2 \) adsorption–desorption isotherm are summarized in Table 1. The BET surface area of the pure \( \text{MgO} \) was 92 m\(^2\) g\(^{-1}\) and the surface areas of the catalysts were in the range of 57–70 m\(^2\) g\(^{-1}\). After addition of Cu metal, the surface area of the catalysts decreased about 24–38% due to the surface coverage of \( \text{MgO} \) by copper metal as well as the formation of copper metal clusters.\(^{20,40}\) Pore volume and pore diameter of the catalysts also decreased with increasing the metal loading due to the structural changes after metal impregnation followed by calcination.\(^{41}\) These values were in the range of 7.4 × 10\(^{-2}\) to 1.8 × 10\(^{-1}\) cm\(^3\) g\(^{-1}\) and 56–81 Å, respectively. Metal dispersion and metallic surface area obtained from \( \text{H}_2 \) chemisorption also decreased with increasing metal loading due to the formation of copper metal clusters. The obtained metal dispersion and metallic surface areas were in the range of 1.35–1.52% and 8.7–9.8 m\(^2\) g\(^{-1}\), respectively. The metal loading in the catalysts calculated by using inductively coupled plasma mass spectroscopy (ICP-MS) analysis method was almost close to the theoretically calculated values as shown in Table 1.

XRD patterns of the pure \( \text{MgO} \) and fresh calcined Cu/MgO catalysts are shown in Figure 1A. XRD pattern of pure \( \text{MgO} \) showed sharp reflection at the 2\( \theta \) value of 36.9\(^\circ\), 42.9\(^\circ\), 62.2\(^\circ\), 74.7\(^\circ\), and 78.6\(^\circ\), respectively, corresponding to the (111), (200), (220), (311), and (222) crystal planes of the typical cubic \( \text{MgO} \) phase (JCPDS: 78-0430). After addition of Cu metal on \( \text{MgO} \) support, additional peaks were detected at the 2\( \theta \) value of 32.8\(^\circ\), 50.9\(^\circ\), and 58.3\(^\circ\) corresponding to (111), (112), and (202) crystal planes of cubic CuO phase (JCPDS: 80-1917). Apart from this, combined peaks for CuO–\( \text{MgO} \) mixed oxide were also observed at the 2\( \theta \) value between 35.4–37.1\(^\circ\), 40.4–44.6\(^\circ\), and 61.4–62.4\(^\circ\), respectively, corresponding to (111), (200), and (220) crystal plane of cubic \( \text{MgO} \)–\( \text{CuO} \) mixed oxide phase (JCPDS: 77-2184). Formation of mixed metal oxide phase for Raney Cu on \( \text{MgO} \) catalysts are also reported in the previous literature.\(^{42}\) The intensity of the peaks corresponding to CuO and mixed oxide phases were found to be increased with increasing metal loading in the catalysts. Figure 1 (B) shows the XRD patterns of reduced Cu/MgO catalysts. As shown in Figure 1B, the XRD patterns of reduced Cu/MgO catalysts were very much similar to the fresh calcined catalyst. One additional diffraction peak was observed at the 2\( \theta \) value of 50.4\(^\circ\) corresponding to (200) crystal plane of metallic copper (JCPDS: 85-1326). The intensity of the peaks corresponding to the metallic copper as well as the mixed oxide phases were found to be increased with increasing copper metal loading in the catalysts.

The average crystallite sizes of CuO, \( \text{MgO} \), and CuO–\( \text{MgO} \) mixed oxide and the particle size of copper metal were calculated by using Scherrer’s equation from the line width of their respective XRD peaks, and the results obtained are summarized in Table 1. For calcined catalyst, the average crystallite size of CuO was estimated from the peaks corresponding to (110) and (112) crystal planes, and for MgO peaks corresponding to (111), (200), (220), (311), and (222) crystal planes, respectively. The calculated dimension of CuO and MgO crystallite size was in the range of 9.6–15.4 nm and 11.5–19.8 nm, respectively. The average crystallite size of CuO–\( \text{MgO} \) mixed oxide phase for calcined and reduced catalysts were estimated from the peaks corresponding to (111), (200), and (220) crystal planes, and the calculated dimension of mixed oxide in the calcined and reduced catalysts were in the range of 11.4–31.2 nm and 12.6–31.5 nm, respectively. For the reduced catalyst, the copper particle size was estimated from the line width of the peak corresponding to

Figure 1. XRD patterns of Cu/MgO catalysts. (A) Fresh calcined at 400 °C in air, time: 4 h, (B) fresh reduced at 350 °C, \( \text{H}_2 \) flow rate: 50 cc/min, time: 3 h.
(200) crystal plane of metallic copper, and the estimated dimension was in the range of 10.6−19.5 nm. As shown in Table 1, the particle size of copper and CuO−MgO mixed oxide was increased with increasing the metal loading due to the agglomeration of copper particles.

TPR profile of pure MgO and Cu/MgO catalysts with various copper metal loading is shown in Figure 2. The reduction profile of pure MgO showed two small broad reduction peaks at higher temperature of 612 and 706 °C, respectively, which suggested less reducibility of MgO at the applied reduction condition. Reduction profile of Cu/MgO catalysts showed one major reduction at 210 °C due to the partial reduction of CuO to Cu2O and a small reduction peak at higher temperature of 280 °C was due to the reduction of Cu2+ to Cu0. As shown in Figure 2, the reduction peaks were shifted toward the higher temperature side with increasing the metal loading (≥7 wt %), and a single broad reduction peak was detected at 263−294 °C. The broad reduction peak at higher temperature suggested direct reduction of CuO to metallic copper without the formation of intermediate copper oxide which is in agreement with the previous literature. The broadness of the peak at higher metal loading also attributed the formation of copper clusters and low metal dispersion which was in agreement with the XRD and H2-chemisorption results (Table 1). The calculated hydrogen consumption increased from 2.1 μmol g−1 cat for 5 wt % Cu/MgO to 9.3 μmol g−1 cat for 15 wt % Cu/MgO catalyst, and the degree of copper reduction decreased from 90.4% to 75.1% with increasing metal loading from 5 wt % to 15 wt % due to the agglomeration of copper particles.

The acidic and basic site strength of the catalysts were estimated with NH3-TPD and CO2-TPD analysis, respectively. The respective patterns obtained are shown in Figure 3. (A) NH3-TPD and (B) CO2-TPD.

The acidic and basic site strength of the catalysts were 2.8−4.5 mmol NH3 g cat−1 and 2.6−3.0 mmol CO2 g cat−1, respectively.

### 3.2. Catalytic Activity. 3.2.1. Vapor Phase Hydrogenolysis of Glycerol.

Initially, the performance of all the catalysts were evaluated at standard reaction conditions, i.e., at 220 °C and 0.75 MPa with WHSV of 1.2 h−1. After starting the liquid feed, the reaction was allowed to continue for 6 h to achieve the steady state. After achieving the steady state, the reaction data were started to collect after a regular time interval of 2 h. The variation of glycerol conversion obtained with time for all the catalysts at standard reaction conditions is shown in Figure 4. As shown in Figure 4, glycerol conversion was varied appreciably with time, and the variation was insignificant after a reaction time of 14 h. Therefore, all reaction data reported in this study were collected after a reaction time of 14 h.

Table 3 shows the catalytic performance of different catalysts having different copper metal loading at standard reaction condition. Glycerol conversion of 100% was obtained for all the catalysts at the reaction conditions used. For all of the catalysts, 1,2-PDO and acetol were the primary reaction product, and...
yield of 1,2-PDO slightly reduced (91.2%) due to the reduction of metallic surface area and metal dispersion. The yield of acetal also decreased with increasing the metal loading (5–10 wt %), and the yield of acetal increased slightly at the metal loading of 15 wt %. It is reported earlier that glycerol hydrogenolysis follows a two-step reaction process.46–49 Initially, glycerol converts to acetal as intermediate through dehydration on the basic and/or acidic sites of the catalysts, and further these intermediates convert to 1,2-PDO due to the hydrogenation reaction which is favorable over active metal sites of the catalysts.50 In the reduced catalysts, the presence of Cu⁺ and/or Cu²⁺ may be responsible for hydrogenation of acetal to 1,2-PDO.51 The product yield data obtained over Cu/MgO catalysts suggested that dehydration and hydrogenation both the reactions took place simultaneously and glycerol over-hydrogenolysis reaction was negligible. Very high yield of 1,2-PDO was due to the presence of high acidic strength (2.8−4.5 mmol NH₃ g cat⁻¹) on the catalyst. The high yield of 1,2-PDO can also be attributed to the presence of bifunctionality of the catalyst along with high metallic surface area (8.7–9.8 m² g⁻¹), small average copper crystallite size (10–20 nm), and high metal dispersion (1.35−1.52%). Formation of 1,2-PDO as the primary product also depicted that Cu/MgO catalysts selectively promoted the hydrogenolysis of C−O bond and limited the breakage of the C−C bond which significantly reduced the formation of degradation products. Maximum 1,2-PDO yield of 95.5% was obtained over 10 wt % Cu/MgO catalyst, and the yield of all other remaining products were 4.5%. It is reported earlier that dehydration–hydrogenation reaction require both acidic and basic sites of intermediate strength as well as synergetic effect between hydrogen spill over of copper and acidic–basic sites of MgO in Cu/MgO catalysts. 39,42–55 Previous literature also reported very low activity (~2.3−12.4%) and yield (0.7−1.3%) of 1,2-PDO in the presence of pure MgO.39,47 As shown in Table 2, the acidity of the catalysts increased with increasing the copper metal loading with simultaneously decreasing basicity in the catalysts. The acidity and basicity results obtained showed a direct correlation with the yield of 1,2-PDO. The yield of 1,2-PDO increased with increasing acidity. This results suggested that an appropriate combination of acidity and basicity in the catalyst is required for higher yield of 1,2-PDO which is in agreement with the previous results.39,52–55 The result obtained in this study is superior as compared to the results reported in the previous literature. Recently, 100% conversion of glycerol with 96.2% selectivity to 1,2-PDO is reported over Cu/Al₂O₃ catalyst at very high H₂ flow rate (360 cm³ min⁻¹) and at very high H₂/glycerol mole ratio of 700.59 3CuB/SiO₂ catalyst prepared by precipitation-gel method showed 100% conversion with 98% 

### Table 2. Summary of TPR and TPD Results of Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reduction peak (°C)</th>
<th>H₂ consumption (μmol g cat⁻¹)</th>
<th>Degree of reduction of Cu° (%)</th>
<th>Acidity (mmol NH₃ g cat⁻¹)</th>
<th>Basicity (mmol CO₂ g cat⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>612, 706</td>
<td>0.37</td>
<td>90.4</td>
<td>2.8</td>
<td>3.9</td>
</tr>
<tr>
<td>5 wt % Cu/MgO</td>
<td>210, 280, 422, 556</td>
<td>2.1</td>
<td>86.3</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>7 wt % Cu/MgO</td>
<td>263</td>
<td>3.7</td>
<td>82.0</td>
<td>3.9</td>
<td>3.0</td>
</tr>
<tr>
<td>10 wt % Cu/MgO</td>
<td>275</td>
<td>5.6</td>
<td>75.1</td>
<td>4.5</td>
<td>2.6</td>
</tr>
<tr>
<td>15 wt % Cu/MgO</td>
<td>278</td>
<td>9.3</td>
<td>60.0</td>
<td>7.4</td>
<td>6.5</td>
</tr>
</tbody>
</table>

°H₂ consumption calculated from TPR peaks. 1°Degree of reduction of Cu (%) = [(H₂ consumption theoretical − H₂ consumption from TPR peak)/H₂ consumption theoretical ] × 100. 2°Calculated from NH₃-TPD data.

### Table 3. Catalytic Performance

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>1,2-PDO Yield (%)</th>
<th>Acetol (%)</th>
<th>Others (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt % Cu/MgO</td>
<td>100</td>
<td>83.1</td>
<td>9.5</td>
<td>7.4</td>
</tr>
<tr>
<td>7 wt % Cu/MgO</td>
<td>100</td>
<td>85.6</td>
<td>3.2</td>
<td>11.5</td>
</tr>
<tr>
<td>10 wt % Cu/MgO</td>
<td>100</td>
<td>95.5</td>
<td>1.6</td>
<td>2.9</td>
</tr>
<tr>
<td>15 wt % Cu/MgO</td>
<td>100</td>
<td>91.2</td>
<td>2.3</td>
<td>6.5</td>
</tr>
</tbody>
</table>

°Reaction conditions: 20 wt % aqueous glycerol solution, temperature: 220 °C, pressure: 0.75 MPa, WHSV: 1.2 h⁻¹, H₂/glycerol mole ratio: 54.6, catalyst amount: 3 g.
selectivity to 1,2-PDO at 200 °C and at much higher pressure of 5 MPa.\textsuperscript{31} In this study, complete conversion of glycerol with 95.5% yield of 1,2-PDO is obtained at mild reaction conditions. Since the best result is obtained over 10 wt % Cu/MgO catalyst, therefore, this catalyst was selected further for a detailed reaction parameter and time-on-stream (TOS) study.

4. REACTION PARAMETER STUDY

To increase the 1,2-PDO yield, the effect of reaction parameters such as reaction temperature, pressure, and weight hourly space velocity (WHSV) was evaluated. The influence of these reaction parameters on glycerol conversion and 1,2-PDO yield are discussed in the following section.

4.1. Effect of Reaction Temperature. Effect of reaction temperature on glycerol conversion and product yield is shown in Figure 5A. Results showed that, with increasing temperature, glycerol conversion was increased and reached 100% at a temperature of 220 °C and higher. At lower temperature (<220 °C), glycerol conversion increased from 76.6% at 180 °C to 100% at 220 °C, the yield of 1,2-PDO also increased from 90% to 95.5% as temperature increased from 180 to 220 °C; the yield of acetol was unchanged (~1%), and the yield of others product decreased from 9% to ~4%. Further, the yield of 1,2-PDO decreased from 95.5% at 220 °C to 81.2% at 280 °C, and

Figure 5. Variation of glycerol conversion and products yield over 10 wt % Cu/MgO catalyst. (A) Effect of temperature at 0.75 MPa, WHSV: 1.2 h\textsuperscript{-1}, reaction time: 14 h, 20 wt % aqueous glycerol solution, H\textsubscript{2}/glycerol mole ratio: 54.6, catalyst amount: 3 g. (B) Effect of pressure at temperature: 220 °C, WHSV: 1.2 h\textsuperscript{-1}, reaction time: 14 h, 20 wt % aqueous glycerol solution, H\textsubscript{2}/glycerol mole ratio: 54.6, catalyst amount: 3 g. (C) Effect of WHSV at temperature: 220 °C, pressure: 0.75 MPa, reaction time: 14 h, 20 wt % aqueous glycerol solution, H\textsubscript{2}/glycerol mole ratio: 54.6.

Figure 6. Time-on-stream study. Others: EG, methanol, ethanol, 1-propanol, and 2-propanol. Reaction condition: 20 wt % aqueous glycerol solution, temperature: 220 °C, pressure: 0.75 MPa, WHSV: 1.2 h\textsuperscript{-1}, H\textsubscript{2}/glycerol mole ratio: 54.6, catalyst amount: 3 g.
the yield of acetol and other product increased from 1 to 9.4% and 3.9 to 9.3%, respectively. This results demonstrated that at higher temperature (>220 °C), overhydrogenolysis of 1,2-PDO favored which led to the breakage of C–C bond and produced higher concentration of undesirable products.27,28 Glycerol conversion and 1,2-PDO yield were found to be low at <220 °C and the overall yield of 1,2-PDO decreased from 95.5% to 81.2% with increasing temperature from 220 to 280 °C. This results suggested that the reaction temperature 220 °C was beneficial for high 1,2-PDO yield at complete conversion of glycerol.

4.2. Effect of Pressure. Results showed that the effect of pressure on glycerol conversion (100%) was insignificant (Figure. 5B) in the entire pressure range (0.01−1.0 MPa) studied. However, pressure had a significant effect on product yield. At lower pressure (0.01 MPa), the yield of 1,2-PDO and acetol was 28% and 70.6%, respectively, and a trace amounts (1.4%) of other products were also detected. Further increasing the pressure up to 0.75 MPa, the yield of 1,2-PDO increased significantly and reached the maximum value of 95.5%. With increasing pressure, the yield of acetol decreased drastically, and the yield of the other products increased to 3.9%. At a pressure higher than 0.75 MPa, the yield of 1,2-PDO decreased marginally, and at the same time the yield of acetol and other product increased to 2.7% and 5.5%, respectively. The product yield trend obtained suggested that, at lower pressure, acetol was formed as a primary reaction product via dehydration of glycerol, and with increasing the pressure, acetol converted to 1,2-PDO via hydrogenation. At higher pressure more active hydrogen species were available on catalysts surface, which increased the hydrogenation of acetol to 1,2-PDO.56 This results also suggested that dehydration of glycerol to acetol was favorable at low pressure and acetol hydrogenation to 1,2-PDO was favorable at high pressure. At higher pressure (>0.75 MPa), the yield of 1,2-PDO decreased with simultaneous increase in the yield of acetol and other undesirable products which suggested that, at higher pressure (>0.75 MPa), 1,2-PDO was further converted to undesirable products through the cleavage of C–C bond. The maximum 1,2-PDO yield of 95.5% was obtained at 0.75 MPa pressure, at 220 °C, and at WHSV of 1.2 h⁻¹.

4.3. Effect of WHSV. As shown in Figure. 5C, at WHSV of 1.03 h⁻¹, 100% glycerol conversion with 91.5% yield of 1,2-PDO was achieved. Further increase in WHSV from 1.2 to 1.8 h⁻¹, glycerol conversion, and 1,2-PDO yield decreased from 100% to 52% and 95.5% to 72.7%, respectively. The yield of acetol and other product increased from 1% to 19% and 3.9% to 8%, respectively. Decrease in space time with increasing WHSV may be the possible reason for decrease in glycerol conversion and 1,2-PDO yield. The product yield trend obtained suggested that, at higher H₂/glycerol mole ratio, the dehydration of glycerol to acetol was favorable and hydrogenation of acetol to 1,2-PDO was hindered due to low space time. The maximum 1,2-PDO yield of 95.5% achieved at WHSV of 1.2 h⁻¹.

4.4. Time-on-Stream (TOS) Study. A reaction parameter study showed that the maximum 1,2-PDO yield of 95.5% was achieved over 10 wt % Cu/MgO catalyst at 220 °C temperature, 0.75 MPa reaction pressure, and at WHSV of 1.2 h⁻¹. Therefore, this reaction condition was used to verify the time-on-stream stability of 10 wt % Cu/MgO catalyst. The reaction was performed for 42 h, and the results obtained are shown in Figure 6. As shown in Figure 6, after 14 h of reaction, 100% conversion of glycerol was achieved, and the yield of 1,2-PDO and other products were ~95.5% and ~4.5%, respectively. Further increase in reaction time, the glycerol conversion and product yield was almost unaffected up to 42 h. This results demonstrated that 10 wt % Cu/MgO catalyst was highly active, selective, and stable for conversion of glycerol to 1,2-PDO in vapor phase. The results obtained in this study is superior as compared to the results reported in the previous literature so far.25,26,30,57 Therefore, the catalyst developed in this study may be very promising for commercial application.

4.5. Characterization of Used Catalyst. To verify the stability of the 10 wt % Cu/MgO catalyst, characterization of fresh reduce and used catalyst was performed using different characterization techniques such as XRD, TPR, and TEM, respectively. Carbon hydrogen nitrogen sulfur (CHNS) elemental analysis was also performed to ensure the carbon deposited if any on the used catalyst after 42 h of reaction. The XRD patterns of the fresh reduced and used catalyst is shown in Figure 7A. Both the fresh and used samples represented similar XRD patterns, suggesting the structural stability of the catalyst after the reaction. The peaks corresponding to CuO-MgO
5. CONCLUSIONS

In this study, highly selective, active, and stable Cu/MgO catalysts were prepared for vapor phase hydrogenolysis of glycerol to 1,2-PDO. The performance of the catalyst was determined in a continuous fixed bed down-flow vertical tubular reactor. Catalytic results showed that the glycerol conversion was 100% for all the catalysts examined, and 1,2-PDO and acetol was obtained as the primary reaction products. However, small amounts of other products such as EG, 1-PO, 2-PO, methanol, and ethanol were also detected. The concentration of the products were varied with the copper metal loading in the catalyst. At higher metal loading (>10 wt%), the yield of 1,2-PDO decreased due to the reduction of metallic surface area and the metal dispersion due to agglomeration. The product yield data obtained suggested that Cu/MgO catalyst selectively promoted the hydrogenolysis of C−O bond rather than the breakage of C−C bond which significantly suppressed the formation of the side products. Complete glycerol conversion with maximum 95.5% yield of 1,2-PDO was obtained over 10 wt % Cu/MgO at 220 °C, 0.75 MPa at WHSV of 1.2 h⁻¹. The superior performance of the catalysts was obtained due to the presence of bifunctional acidic and/or basic sites and the presence of strong metal–support synergetic interaction. In addition, the higher yield of 1,2-PDO was obtained due to the high metallic surface area (9.5 m² g⁻¹), small average particle size (19.5 nm), and high metal dispersion (1.5%) in the catalyst. A reaction parameter study suggested that low reaction temperature (<220 °C), high pressure (>0.75 MPa), and low WHSV (<1.2 h⁻¹) was favorable for high yield of 1,2-PDO. Finally, a TOS study suggested that the 10 wt % Cu/MgO catalyst was highly selective, active, and stable for longer period of time (42 h) and showed consistent catalytic performance, and the carbon deposition rate over this catalyst was also insignificant (0.6 mmol carbon g cat⁻¹ h⁻¹). Therefore, 10 wt % Cu/MgO catalyst may be a very promising catalyst for...
selective conversion of glycerol to 1,2-PDO in commercial scale.

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**Notes**
The authors declare no competing financial interest.

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