Ni on Ce:Mg Oxides (9:1) as Catalyst for the Selective Catalytic Thermochemical Conversion of Glycerol to 1,2 Propanediol and Ethanol

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Authorization to Submit Thesis

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Abstract

A supported Ni catalyst was developed for the selective production of ethanol and 1,2 propanediol (1,2 PDO) from glycerol hydrogenolysis. Screening of various supports showed that Ni/ CeO2 has the best potential and was improved by addition of promoters. Adding Mg at a Ce:Mg molar ratio of 80:20 provided the best improvement for the combined selectivity of ethanol and 1,2 PDO. Ethanol selectivity was further improved to 15.28% by varying Ce:Mg molar ratio to 90:10. The catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared via deposition precipation showed higher activity as compared to the catalyst prepared by impregnation. Catalyst calcined at 350˚C showed better selecitivies of ethanol and 1,2 PDO at 15.61% and 67.3%, respectively. The effects of reaction temperature, initial water content, initial hydrogen pressure, and extension of reaction time were also investigated. The catalyst 25 wt% Ni/Ce:Mg (9:1) showed a better potential as compared to the commercial Raney® Ni catalyst.

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Chapter 1

Introduction

Biodiesel, considered as the main renewable alternative of diesel fuel [1], is made up of long chain fatty acid alkyl esters [2]. It is commonly produced using vegetable oil or animal fats reacted as feedstock, which are composed of a variety of long chain fatty acids free or attached to glycerol as mono-, di-, or tri- glycerides. The oils and fats are reacted with an alcohol with the help a suitable catalyst usually via the transesterification reaction producing biodiesel and glycerol (Fig. 1.1) [1, 3]. The most commonly used alcohol for the reaction is methanol and the products formed by transesterification with oils and fats are termed fatty acid methyl esters (FAME) [1, 3-4]. In the transesterification using methanol, about 100 kg of oil reacts with 10 kg of alcohol in the presence of a catalyst to produce about 100 kg of biodiesel and 10 kg of glycerol (Fig. 1.1) [4].

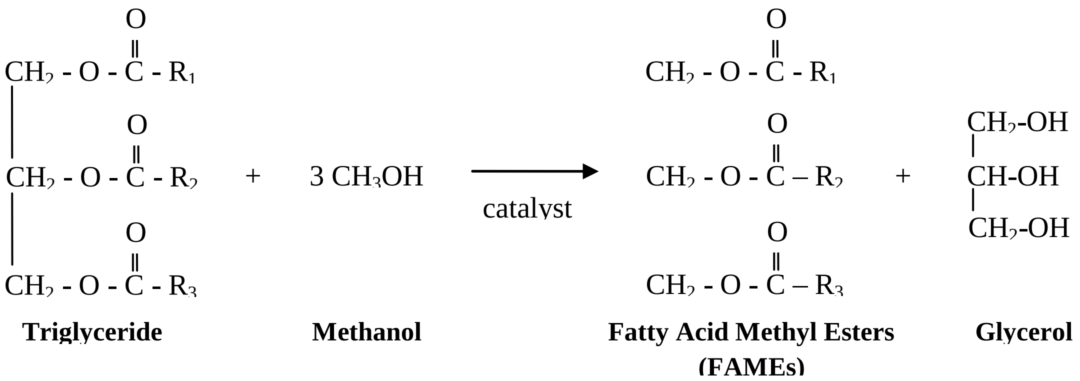

Figure 1.1 Biodiesel and glycerol production via transesterification reaction

In commercial and large scale biodiesel production, an alkali catalyst is used and the biodiesel production process is carried out in a series of steps [5]. First, the oil, methanol, and catalyst are mixed and heated to 60˚C producing a double layered product with one portion containing most of the biodiesel and the other glycerol [6]. These two major products are separated by settling or centrifugation. The biodiesel rich fraction is further purified through removal of excess methanol, neutralization and washing, and drying. On the other hand, the glycerol fraction is treated with acid to recover the fatty acids present as soaps and followed by methanol removal through evaporation to produce a crude glycerol fraction. Crude glycerol contains impurities such as methanol, salts, residual fatty acids, protein, carbohydrates, and ash with quantities depending on the feedstock [7, 8].

Currently, biodiesel is more expensive than petroleum-based diesel and various factors affect its cost of production such as the capacity of the production plant, feedstock and its quality, processing technology, net energy balance, nature of purification, and its storage [4]. Of these, two main factors that affect the production cost are the costs of feedstock and processing into biodiesel. Feedstock accounts for 75-88% of biodiesel overall cost [4, 9]. Processing costd include transesterification and the byproduct (glycerol) recovery [4]. In a process model by M.J. Haas et al. [9], the production cost of biodiesel varies inversely and linearly with variations in the market value of glycerol, where US$ 0.022/kg reduction in glycerol value would increase biodiesel cost by US$0.0022/L. Biodiesel production rose from 8 million liters in year 2000 to 1.2 billion liters in 2010 [8], while the global market is estimated to reach 37 billion gallons along with about 4 billion gallons of crude glycerol produced in 2016 [10]. However, the increase in biodiesel production resulted in a huge surplus of glycerol which caused a significant drop in glycerol price for both the crude and purified forms [11-12]. In 2007, refined glycerol dropped from $1.32-$1.98/kg to $0.66/kg, while crude glycerol price dropped from $0.55/kg to $0.11/kg [11-12]. Refining of crude glycerol is approximately $0.33/kg [12] making purification uneconomical [8]. Aside from crude glycerol refining, other options for glycerol utilization have been considered like its use as a boiler fuel, supplement in animal feed, and conversion into value-added products. Conversion of crude glycerol into value-added products presents a variety of options for glycerol utilization that could be carried out through chemical, biochemical, or thermochemical conversions [11-13].

Thermochemical conversion has shown to be a promising route for glycerol conversions into value added chemicals. Depending on the process conditions and catalyst employed, glycerol can undergo various types of modification or reactions such as pyrolysis, gasification, oxidation, dehydration, and hydrogenolysis [13]. Oxidation of glycerol could lead to a variety of products including glyceraldehyde, dihydroxyacetone, glyceric acid, hydroxypyruvinic acid, tartronic acid, glycolic acid, mesoxalic acid, dihydroxymalonic acid, lactic acid, oxalic acid, acetic acid, and formic acid [14]. Dehydration of glycerol produces acetol [15] or acrolein [16] upon a further removal of another water molecule. Hydrogenolysis, which involves chemical bond dissociation and simultaneous addition of hydrogen to the resulting molecular fragments [17], converts glycerol into 1,3 propanediol (1,3 propylene glycol), 1,2 propanediol (1,2 propylene glycol), propanol, isopropanol, ethylene glycol, ethanol, and methanol [17-18]. The products obtained from glycerol hydrogenolysis have a wide range of industrial applications for food, cosmetics, and specialty chemicals (e.g. polymers, anti-freezing agent, etc.) [17-19]. Propylene glycol (1,2 propanediol) finds use as a humectants, antifreezing agent, brake fluid, or as a component of polyesters and alkyd resins [19] and sold at around $ 0.97-2.2/kg [20]. On the other hand, 1,3 propylene glycol, used as a monomer for poly-propanediol terephthalate (PPT fibre)[19], sells at around $ 1.76/kg [21]. The propanols n-propanol and isopropanol are widely used as a solvent and sell at $1.14/kg and $0.62-1.08/kg, respectively [20]. Ethylene glycol is used as an antifreezing agent and raw material for polyethylene terepthalate and has a market value of around $ 0.99/kg [17].

Various catalysts have been investigated for the conversion of glycerol to value added chemicals via hydrogenolysis which could be categorized as noble metal-based catalysts and non-noble metal-based catalysts [17]. Noble metal based catalysts make use of ruthenium (Ru), rhenium (Re), rhodium (Rh), molybedenum (Mo), iridium (Ir), gold (Au), platinum (Pt), or combinations of these metals as the active component [17]. The non-noble metal based catalysts that usually employ nickel (Ni) and copper (Cu) as the active component have shown to be promising alternatives for hydrogenolysis of glycerol, especially for 1,2 PDO production [22-86].

Cu in combination with or supported by Cr, SiO_2, ZnO, MgO, Al_2O_3, ZnO- Al_2O_3, MgO-Al_2O_3, and ZrO_2 has been shown to produce 1,2 PDO with 90% selectivity from glycerol hydrogenolysis [22-69]. Catalyst activity is affected by the catalyst's composition, metal to support ratio, addition of promoters, catalyst preparation (method, calcination conditions, and reduction conditions), and process conditions which in turn affect the catalyst structure, acidic/basic nature, metal dispersion, size of Cu species, active Cu area, and state of Cu species. Higher acidity/basicity, dispersion, and active Cu area, smaller size of Cu species, and higher amounts of Cu in Cu(O) and Cu(I) states result in superior catalyst activity. Process conditions such as temperature, hydrogen pressure, glycerol concentration, catalyst loading, reaction time, agitation rate, and choice of solvent have been shown to be important for catalyst activity as well. In general, glycerol conversion is favored at higher temperatures, hydrogen pressure, catalyst loading, and reaction time. On the other hand, selectivity for 1,2 PDO usually has an optimal value depending on the catalyst with optimal temperature in the range of 180˚C-240˚C. Catalyst deactivation may be caused by Cu sintering, leaching, and coking. Ni catalysts have also shown some promise for the selective hydrogenolysis of glycerol to 1,2 PDO with a few of them able to achieve a 1,2 PDO selectivity of over 90%, including Raney Ni, Ni on SiO_2 (with P), SiO_2-Al_2O_3, and Ni/Al_2O_3-CuCr [72-79].

Further hydrogenolysis of glycerol has been shown to produce ethylene glycol [69-70, 83-85], propanols [26-27, 46, 53, 69, 73], and ethanol [46, 57, 73-74] in high levels. Mostly, Cu based catalysts produced higher levels of EG and propanols, while Ni catalysts dominate for ethanol production. Favorable conditions for EG production depend on the particular catalyst used where higher selectivity for EG being observed at low temperatures for catalysts of Cu-Cr on γ-Al_2O_3, while higher temperatures favored EG production with catalysts of Cu-Zn-Ti combination. Propanol production is favored with higher catalyst acidity, reaction temperature, hydrogen pressure, and reaction time. Higher temperatures enhanced ethanol production due to further hydrogenolysis.

Investigations in catalyst development of Ni- and Cu-based catalysts for hydrogenolysis of glycerol focus on 1, 2 PDO and so far none has reported catalyst development specifically targeting ethanol. This study aims to utilize glycerol as the feedstock to produce 1,2 PDO and ethanol through catalytic thermochemical conversion. Specifically, it aims to develop a Ni based catalyst suitable for 1, 2 PDO and ethanol production from glycerol. In order to achieve the aim of this study, it will investigate the effects of:

1. Metal support on Ni for glycerol hydrogenolysis

2. Various bi-metal support combinations/promoters (based on potential supports identified)

3. Preparation methods on the selectivity and activity of the potential catalyst developed

4. Process conditions temperature, pressure, water content, and time on the selectivity and activity of the potential catalyst developed

It is expected out of this study that a new metal based combination heterogeneous catalyst will be developed that has a satisfactory potential for the conversion of glycerol into 1, 2 PDO and ethanol.

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Chapter 2

Literature Review

Hydrogenolysis of Glycerol into Value Added Products using Supported Nickel and Copper Catalysts

Abstract

Glycerol, a by-product from biodiesel production, is considered as an inexpensive feedstock for a variety of valuable chemicals. Catalytic thermochemical conversion presents a promising route for glycerol conversion into valuable chemicals. One promising option for this route is the glycerol hydrogenolysis pathway that leads to the production of alcohols such as 1,2 propanediol, 1,3 propanediol, ethylene glycol, n-propanol, isopropanol, ethanol, and methanol. The choice of catalyst is essential to attain a high level of selectivity for a desired product and has been a subject of interest for a number of studies. Aside from noble metal catalysts, supported Ni and Cu catalysts have been shown to have great potential for application in glycerol hydrogenolysis. In this review, reports of promising supported Ni and Cu catalysts are presented. How the catalyst activity is affected for a specific hydrogenolysis product by factors such as catalyst preparation and reaction conditions are also discussed.

2.1 Introduction

Glycerol (Fig. 2.1), 1,2,3 propanetriol, is a water-soluble, clear, almost odorless, viscous, hygroscopic liquid with a high boiling point (Table 2.1) [1-2]. It can be obtained through synthetic or natural means [3]. In the synthetic route, propene is used as the starting material and converted to glycerol via the allyl chloride-epichlorohydrin, acrolein-allyl alcohol-glycidol, or propylene oxide-ally alcbohol-glycidol pathway [3]. Naturally, it can be generated upon liberation from fats and oils and achieved through high pressure splitting, saponification, enzymatic hydrolysis, or transesterification [3].

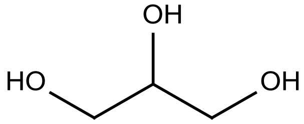

Figure 2.1 Chemical structure of glycerol (1,2,3 propanetriol)

Table 2.1 Physicochemical properties of glycerol.

Chemical formula	$C_3H_5(OH)_3$
Molecular mass	92.09382 g/mol
Desnsity	1.261 g/cm^3 (20˚C)^a
Viscosity	1.5 Pa.s (20˚C)^a
Surface tension	64.00 mN/m(20˚C)^a
Melting point	18.2˚C^a
Boiling point	290˚C (760 mm Hg)^b
Freezing point	-46.5 ˚C (66.7% glycerol)^b
Flash point	177˚C (99% glycerol)^b
Fire point	204˚C (99% glycerol)^b
Autoignition	523˚C (on platinum)^b
	429˚C (on glass)^b
Heat of Combustion	397.0 cal/mol^b
Food Energy Value	4.32 kcal/g^b
Sound transmission	1923 m/s (2k0˚C)^b
Coefficient of thermal expansion	0.0006115 (15-25˚C)^b
Thermal conductivity	0.000691 cal cm ˚C /s (0˚C)^b
Molar Heat of solution	1381 cal^b
Dissociation constant	0.07 x10$^{-12\ b}$
Dielectric Constant	42.48 (25˚C;current frequency=0.57x10 6 cycles/s)^b
Specific Conductivity	5.6x10^{-8} /ohms^b
Compressibility	21.1x10-6 cm^3/atm (28.5˚C)^b

a - Ref. [1], b- Ref. [2]

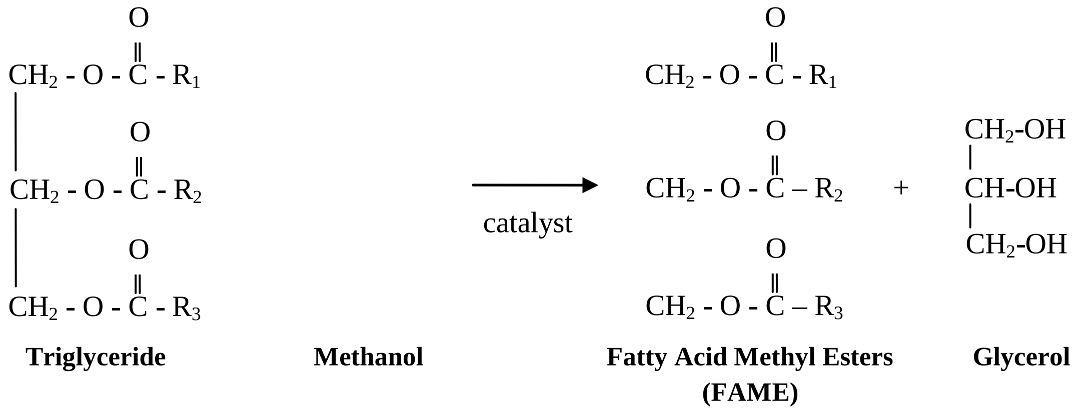

Figure 2.2 Transesterification reaction to produce fatty acid methyl Esters (FAME or Biodiesel) and glycerol.

Transesterification is typically used to produce biodiesel from fats and oils upon reaction with an alcohol (Fig. 2.2), usually methanol, with the help of a suitable catalyst [4]. Generally when producing about 100 kg of Fatty Acid Methyl Esters (FAME), 10 kg of glycerol is co-produced [5]. Biodiesel production in the U.S. has largely increased from 8 million liters in year 2000 to 1.2 billion liters in 2010 [6], while the global market is estimated to reach 140 billion liters along with about 15.1 billion liters of glycerol byproduct in 2016 [7]. Depending on the process and feedstock used, the glycerol fraction from biodiesel production may contain varying amounts of impurities such as methanol, salts, residual fatty acid, mono-, di-, and triglycerides, methyl esters, protein, carbohydrates, and ash [6, 8-9]. The crude glycerol obtained from biodiesel production is typically 80-95% pure [10-11]. Glycerol from biodiesel production can be sold as is or can be refined further to 99.5-99.7% glycerol using vacuum distillation or ion exchange processes [8, 11]. However, the huge surplus in glycerol supply due to the recent surge in biodiesel production and its projected increase in production caused a significant drop in glycerol price for both crude and purified forms. In 2007, refined glycerol dropped from \$1.32-1.98/kg to \$0.66/kg, while the crude glycerol price dropped from \$0.55/kg to \$0.11/kg [12-13] with cost of refining the crude glycerol approximately \$0.33/kg [13]. This development is seen as an opportunity to utilize glycerol as an inexpensive feedstock for the production of value-added chemicals [1]. A variety of options for the conversion of glycerol into value added chemicals are available which can be carried out through chemical, biochemical, or thermochemical routes [12, 13, 8].

Thermochemical conversion has been shown to be a promising route for glycerol conversions into value added chemicals. Depending on the process conditions and catalyst employed, glycerol can undergo various types of modification or reactions such as pyrolysis, gasification, oxidation, dehydration, and hydrogenolysis. Oxidation of glycerol could lead to a variety of products including glyceraldehyde, dihydroxyacetone, glyceric acid, hydroxypyruvinic acid, tartronic acid, glycolic acid, mesoxalic acid, dihydroxymalonic acid, lactic acid, oxalic acid, acetic acid, and formic acid [14]. Dehydration of glycerol produces acetol [15] and acrolein upon further removal of another water molecule from acetol [16]. Hydrogenolysis, which involves chemical bond dissociation and simultaneous addition of hydrogen to the resulting molecular fragments [17], lead to the conversion of glycerol into 1,3 propanediol (1,3 propylene glycol), 1,2 propanediol (1,2 propylene glycol), propanol, isopropanol, ethylene glycol, ethanol, and methanol [17-18].

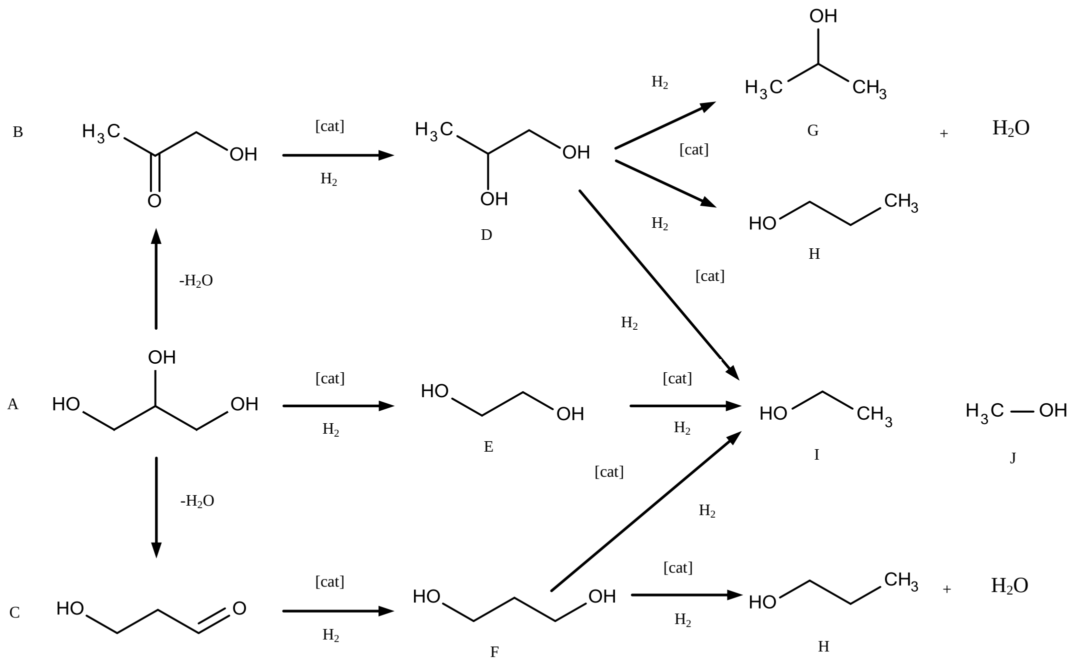

Figure 2.3 Schematic diagram of hydrogenolysis pathway of glycerol (A) acetol, (**B**) 3-hydroxypropionaldehyde (**C**), 1,2-propanediol (**D**), ethyleneglycol (**E**), 1,3-propanediol (**F**), isopropanol (**G**) 1-propanol (**H**), ethanol (**I**), methanol (**J**) [17,19]

Catalyst application plays a very important role in glycerol conversion to value-added products via chemical and/ or thermochemical routes. Various catalysts have been investigated for the conversion of glycerol to value added chemicals via hydrogenolysis using noble metal based catalysts and non-noble metal based catalysts. Noble metal based catalysts make use of ruthenium (Ru), rhenium (Re), rhodium (Rh), molybedenum (Mo), iridium (Ir), gold (Au), platinum (Pt), or combinations of these metals as the active component [17]. The non-noble metal based catalysts usually employ nickel (Ni) and copper (Cu) as the active component and have shown to be promising for glycerol conversion via hydrogenolysis [17]. In this work, we present a review on supported nickel and copper catalysts used for conversion of glycerol into value-added chemicals via the hydrogenolysis pathway (Fig. 2.3).

2.2 Products of Glycerol Hydrogenolysis and Their Preparation

Hydrogenolysis, which involves chemical bond dissociation and simultaneous addition of hydrogen to the resulting molecular fragments [17], leads to the conversion of glycerol into 1,3 propanediol (1,3 propylene glycol), 1,2 propanediol (1,2 propylene glycol), propanol, isopropanol, ethylene glycol, ethanol, and methanol [17-18]. The products obtained from glycerol hydrogenolysis have a wide range of industrial applications for food, cosmetics, and specialty chemicals (e.g. polymers, anti-freezing agent, etc.) [17-19].

2.2.1 1,2 Propanediol

Propylene glycol (1,2 PDO) finds use as a humectant, antifreezing agent, brake fluid, or as a component of polyesters and alkyd resins [20]. It has a market volume of around 1.18-1.58 million tonnes per year [21] and sold at about $0.97-2.2/kg [13]. It was traditionally manufactured via hydrogenolysis of sugars using metal catalysts and is presently produced through hydration of propylene oxide. Enantiomerically pure 1, 2 PDO may be produced by catalytic hydrogenation of lactic acid, bioreduction of acetol, or resolution of racemic 1,2 PDO [22].

The production of 1,2 PDO from glycerol via hydrogenolysis using various supported copper and nickel catalysts is also an alternative way. The focus of many researchers is the selection of catalysts, which is mainly reviewed in this section as shown below.

2.2.1.1 Cu-Cr

One of the earlier copper based catalysts that showed potential for the conversion of glycerol to 1,2 PDO is the Cu-Cr combination (Table 2.2). Commercial Raney® Cu and Cr-Cu tested for hydrogenolysis of 80 wt% glycerol in a continuous trickle bed reactor at 205˚C both gave 100% glycerol conversion with a 1,2 PDO selectivity of 94% and 87%, respectively. The lower selectivity for Raney® Cr-Cu was attributed to interference of Cr with Cu metal in the hydrogenation step [23]. Raney® Copper (a commercial copper and copper-chromite catalyst from Sud-Chemie impregnated on activated carbon) was tested in a batch reactor at 200 psi, 200˚C, 80 wt% glycerol for 24 hours with Cu-Cr giving 54.8% conversion and 85.0% selectivity towards 1,2 PDO and was used further to investigate the effect of catalyst concentration, temperature, pressure and initial water content. The increase in hydrogen pressure improved glycerol conversion and selectivity towards 1,2 PDO, while the decrease in initial water content enhanced the selectivity towards 1,2 PDO but decreased glycerol conversion. The best conditions were found to be 5.0 wt% catalyst, 200 ˚C, 20 wt% water, and 2.1 MPa (300 psi) of hydrogen which resulted to a glycerol conversion and selectivity towards 1,2 PDO of 65.3 % and 89.6 %, respectively [24].

A variation of the Cu to Cr ratio revealed that a 1:2 Cu:Cr ratio results in the best activity for catalysts prepared via the co-precipitation [25] and impregnation method [26]. While, a 4:1 Cu:Cr ratio was favorable for a sol-gel route prepared catalyst [27]. Formation of a $CuCr_2O_4$ spinel structure was observed at a 2:1 ratio and resulted in a significant increase in its acidic property (for dehydration step) and hydrogen occluding property (for hydrogenation step) [25]. At a 2:1 Cu:Cr ratio, the catalyst prepared by co-precipitation performed better than the catalyst prepared via impregnation [26] where a 1,2 PDO selectivity of 84% at around 80% conversion was achieved by the former. The difference in activity was attributed to the difference in their structure. The Cu-Cr formed via impregnation resulted in two separate oxide phases with chromium oxide as the support, while the Cu-Cr formed via co-precipitation had a single spinel phase which allowed complete reduction of Cu in the former and partial reduction of Cu in the latter.

In the sol-gel prepared 4:1 Cu:Cr catalyst, 1,2 PDO formation was favored at higher glycerol concentrations and agitation rates as well as lower reaction time, reaction temperature, and hydrogen pressure. A 1,2 PDO selectivity up to 98.5% was achieved at a 85.9% glycerol conversion [27]. Xerogels of Cu-Cr prepared by an epoxide-assisted method were calcined at different conditions with the environment (gas) and calcination temperature varied. Among them, the Cu-Cr xerogel calcined at 500˚C under 20% oxygen and 80% Ar gave the best activity and resulted in glycerol conversion 32% and a 1,2 PDO selectivity of 54%. The observed change in the catalyst performance with variation in calcinations conditions was due to the difference in the phase composition and pore structure [28]. Reduction of a commercially and co-precipitation prepared $CuCr_2O_4$ catalyst improved the selectivity for 1,2 PDO. The increment in the reduction time slightly lowered glycerol conversion, but improved the 1,2 PDO selectivity. The 1,2 PDO selecitivity improved further to 70% when the catalyst was reduced for 24 hours. The loss in catalytic activity was caused by Cu sintering or the destruction of epitaxial bond between metallic Cu and oxide [29].

The addition of promoters, such as Zn, Al, and Ba, to Cu-Cr enhanced the catalyst activity. Among them the addition of Ba gave the best activity due to an increase in catalyst acidity which resulted in a glycerol conversion and 1,2 PDO selectivity of 34% and 85%, respectively [30]. A change in Ba concentration from 15% to 40% showed 30% Ba as the optimal concentration due to the combination of raised acidity but not too much to affect the hydrogenating capability of the catalyst. The Ba promoted Cu-Cr catalysts were also used in a continuous mode of reaction in which the effect of liquid feed flow rate, hydrogen gas flow rate, temperature, pressure, and glycerol concentration were investigated [31]. The raise in feed flow rate (18-54 mL/h) declined glycerol conversion but maintained 1,2 PDO selectivity, while the variation in gas flow rate (10-30 NL/h) did not seem to affect the conversion and selectivity. Temperature increase from 180˚C to 240˚C improved the conversion of glycerol, while highest the 1,2 PDO selectivity was observed at 220 ˚C. Hydrogen pressure increase from 2.0 MPa to 6.0 MPa improved both glycerol conversion and 1,2 PDO selectivity. A reduction in both glycerol conversion and 1,2 PDO selectivity occurred with the increase in glycerol concentration. The best conditions (Table 2.2) resulted in a 91% 1,2 PDO selectivity at a 74% glycerol conversion.

Table 2.2 List of Cu-Cr catalysts investigations for conversion of glycerol to 1,2 PDO

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
T= 205 ˚C P= 1.5 MPa H_2 Cglycerol= 80.0 wt% Vcat= 14 mL $\text{Frate}_{\text{glycerol}}$= 0.05 mL/min Frate_{H2} = 375 mL/min TOS = 120 h Continuous reactor	Raney® Cu Raney® Cr–Cu Cu chromite (Commercial)	100 100 100	94 87 85	[23]
T= 200˚C P = 1.38 MPa Cglycerol = 80 wt% t = 24 h Batch	Raney Cu Copper (Sud-Chemie) Copper-chromite (Sud-Chemie)	48.9 53.0 54.8	69.1 39.8 85.0	[24]
	Impregnated on Activated Carbon Cu-Cr Wt% 1 , 2.5, 5,10, 15, 20, 5 (P= 2.07 MPa)	28.3, 33.5, 54.8, 58, 70.1,78.5,65.3	63.3,78.2,85.0,77.6 ,64.5,62.0,89.6	
	Temperature (˚C) 150, 180, 200, 230, 260	7.20, 28, 54.80, 72, 87	2.3,9.8, 46.6,35.1, 7.7	
	Pressure (psi) 50, 100, 150, 200, 300	25, 37, 44, 54.8, 65.3	36.4, 42.4, 50.7, 85.0, 89.6	
T= 220˚C P= 8.0 MPa H_2	CuCr Cu:Cr = 1:0 (CuCr-1)	27	62	[25]

Cglycerol= 90 wt% msoln. = 50 g mcat = 1.0 g t= 12 h Batch	Cu:Cr = 1:1 (CuCr-0.5) Cu:Cr = 1:2 (CuCr-0.33) Cu:Cr = 1:3 (CuCr-0.25) Cu:Cr = 0:1 (CuCr-0) prepared by a co-precipitation method	63 80.3 63 8	73 83.9 82 0	
T= 220˚C P= 8.0 MPa H_2 mcat = 1 g Cglycerol = 90 wt% msoln. = 50 g Batch	CuCr (Cu : Cr=1 : 10 prepare by impregnation) (Cu : Cr=1 : 2, prepared by impregnation) (Cu : Cr=1 : 2, prepared by precipitaion)	~26 ~34 ~80	~32 ~41 ~84	[26]
T= 210˚C P= 4.1 MPa H_2 $V_{soln.}$ = 60 mL m_{cat} = 5 wt% (based on glycerol) $C_{glycerol}$= 60 wt% Agitation = 150 rpm t= 10 h batch	Cu-Cr (Cu/Cr molar ratio) 0, 0.5, 2, 4, 6 Cu/Cr =4 Reaction time (h) 3, 5, 7, 10, 17 Reaction temperature (˚C) 180, 195, 210, 230 Hydrogen Pressure (MPa) 2,3, 4.1, 5 Glycerol Concentration (%) 20, 40, 60, 80, 100 Agitation (rpm) 150, 300, 600, 900 Synthesized by sol-gel route	~0, 28, 43, 45, 43 ~44, 47, 50, 53, 56 ~8, 24, 47, 64 ~32, 45, 47, 58 ~32, 38, 46, 78, 92 49.2, 73.4, 78.7, 85.9	~0, 53, 58, 59, 54 ~83, 75, 73, 68, 42 ~93, 82, 75, 45 ~84, 80, 75, 43 ~10, 28, 75, 82, 84 59.7, 84.6, 90.6, 98.5	[27]
T= 210˚C P= 4.1 MPa m_{cat}= 5wt% $C_{glycerol}$= 60 wt% t= 10 h Agitation = 150 rpm Batch Prepared by an epoxide-assisted procedure	Cu-Cr-OH(500) Calcined in 20% O_2/Ar at 500˚C(surface area 230 m^2) Cu-Cr-OH(400) Calcined in 20% O2/Ar at 400˚C(surface area 230 m^2) Cu-Cr-OL(400) Calcined in 20% O2/Ar at 400˚C(surface area 94 m^2) Cu-Cr-Ar(400) Calcined in Ar at 400˚C (surface area 230 m^2)	32 20 11 6	54 39 40 56	[28]
T= 200˚C P= 3.0 MPa H_2 $C_{glycerol}$= 80 wt% $V_{soln.}$ = 20 mL Agitation = 100 rpm t= 24 h batch	$CuCr_2O_4$ Commercial Unreduced Reduced Prepared by co-precipitation Unreduced Reduced Reduction time (h) 0, 4, 8, 10, 16, 24	30.2 33.5 31.1 30.6 ~30,30,30,29,27,25	35.3 55.8 18.2 58.8 ~18,59,67,68,70,70	[29]
T= 220˚C P = 5.2 MPa H_2 $C_{glycerol}$ = 20 wt% in 2-propanol C_{cat} = 0.01 g/mL t = 5 h Batch	Cu, Cr (Al) Cu, Cr (Ba) Cu, Cr Cu, Cr (Zn) prepared by the co-precipitation method	31 34 16 29	81 84 82 77	[30]
T = 220 ˚C P= 4.0 MPa F_{rate} glycerol = 30 mL/h F_{rate} H_2 = 10 N/ h mcat = 23 g Continuous	Cu, Cr (Ba) Prepared by a co-precipitation method	74	91	[31]

2.2.1.2 Cu/SiO_2

Silica as a support for Cu-based catalysts has also been investigated and developed for selective hydrogenolysis of glycerol to 1,2 PDO (Table 2.3). Comparison of the catalyst silica supported Cu prepared by impregnation and the catalyst prepared by precipitation-gel (PG) methods revealed that 1,2 PDO selectivity is not significantly affected by the preparation method. A superior catalytic activity was achieved with the catalyst prepared via PG method due to higher dispersion and smaller particle size of Cu species. The PG method prepared catalyst was able to achieve a 1,2 PDO selectivity of 93.4% at a glycerol conversion of 73.4%[32]. Mesoporous silica (SBA-15) supported Cu catalysts prepared by ion-exchange method gave a higher selectivity towards 1,2 PDO, but a slightly lower glycerol conversion as compared to the silica supported Cu catalyst [33]. A glycerol conversion of 96% and 1,2 PDO selectivity of 92.4% were achieved with 1% Cu on mesoporous silica, which also showed superior stability. The ordered mesoporous channels and large specific area of SBA-15 were thought to play an important role to enhance catalyst activity and stability [33].

In a similar study, hexagonal mesoporous silica (HMS) was used instead of SBA-15 and the catalyst was prepared by impregnation [34]. The increase in Cu loading from 5% to 20% improved glycerol conversion both for silica supported Cu catalyst from 10% to 16% and HMS supported Cu catalyst from 28.5% to 42.5%. The 1,2 PDO selectivity improved from 83.6% to about 97% for silica supported Cu catalyst but slightly dropped from 93.2% to 91% for HMS supported Cu catalyst. The combination of Ru with the catalyst of Cu on silica resulted in a better catalyst activity and achieved a 1,2 PDO selectivity of 85.9% at 39.2% glycerol conversion. After the HMS supported Cu catalyst was used for three times, the catalyst activity dropped by more than 50% from 42.5% to 20.8% but maintained 1,2 PDO selectivity. The improved catalytic activity of HMS supported Cu catalyst was linked to the higher active Cu metal area, while the drop in catalytic activity after reuse of the catalyst was attributed to partial collapse of the mesoporous structure and agglomeration of active metal particles [34].

Silica-gel and SBA-15 supported Cu catalysts calcined at 350˚C under flowing 1% NO-N_2 or air gave similar catalytic activity in terms of glycerol conversion and 1,2 PDO selectivity. A raise in calcination temperature to 900˚C for the SBA-15 supported Cu catalyst resulted in a drop of the glycerol conversion from about 50% to 37.4% and 20.3% when calcined with 1% NO-N_2 and air, respectively. It also resulted in a decline of the 1,2 PDO selectivity from 96.2% to 92.4% for the catalyst calcined with air, while 1,2 PDO selectivity was maintained with the catalyst calcined with 1% NO-N_2. It was found that SBA-15 supported Cu catalyst was the most stable among the catalysts prepared with an increasing stability in the order of Cu/SG(NO) < Cu/SBA(NO) <Cu/SG(stag) < Cu/SBA900C(NO) < Cu/SBA(air) < Cu/SG(air) < Cu/SBA900C(air) (Table 2.3). Stability loss of the silica-gel and SBA-15 supported Cu catalyst was correlated to the loss in the active Cu area available [35].

Table 2.3 Summary of Cu supported on SiO_2 catalyst investigations for glycerol conversion to 1,2 PDO.

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
T= 200˚C	Cu	1.6	78.6	[32]
P= 9.0 MPa H_2	SiO_2	-	-	
$C_{glycerol}$= 80 wt%	Cu/SiO_2			
$m_{soln.}$ = 80 g	precipitation gel method			
m_{cat} = 4.0 g	calcined, reduced	52.7, 73.4	93.1, 94.3	
t= 12 h	impregnation method			
batch	calcined, reduced	22.9, 25.6	94.5, 95.2	
T= 250˚C	1.0% Cu/SBA-15	96.0	92.4	[33]
P= 4.0 MPa H_2	5.0% Cu/SBA-15	96.0	86.0	
$C_{glycerol}$= 80 %	1.0% Cu/SiO_2	99.6	86.4	
LHSV = 0.8 $h^{/}$	5.0% Cu/SiO_2	96.4	84.3	
m_{cat} = 1.5 g	Prepared by ion-exchange			
$m_{H2}/m_{glycerol}$ = 15	method			
TOS= 6-7 h				
T= 240˚C	5% Cu/SiO_2	10	83.6	[34]
P= 8.0 MPa H_2	20% Cu/SiO_2	16	~97	
$V_{soln.}$ = 120 mL	5% Ru-Cu/SiO_2	39.2	85.9	
m_{cat} = 0.9 g	5% Cu/HMS	28.5	93.2	
$C_{glycerol}$= 100 wt%	20% Cu/HMS (1st use)	43	91.1	
Agitation = 1000 rpm	20% Cu/HMS (3rd use)	20.8	92.4	
t= 5 h	prepared using the wet			
batch	impregnation method			
T= 240˚C	Cu/Support			[35]
P= 8.0 MPa H_2	(Calcination atmosphere)	1st use, 2nd use		
mcat/mglycerol= 0.006	Cu/SG(stagnant air)	32.7, 19.4	94.3	
t= 5 h	Cu/SG(NO)	50.7, 20.6	95.4	
	Cu/SG(air)	51.9, 47.7	96.6	
	Cu/SBA(NO)	48.8, 28.4	95.9	
Silica Gel (SG)	Cu/SBA(air)	52.0, 40.2	96.2	
SBA-15 (SBA)	Cu/SBA			
Prepared by impregnation method	(T= 900˚C NO)	37.4, 25.7	95.6	
	Cu/SBA900			
	(T= 900˚C NO)	20.3, 17.4	92.4	
T= 180˚C	CuO/SiO_2 with Na			[36]
P = 9.0 MPa H_2	wt% Na			
$C_{glycerol}$ = 80 wt%	4.50, 2.49, 0.54, 0.14,	15.4, 21.6, 27.2,	94.4, 96.7, 98.5,	
$m_{soln.}$ = 40 g	< 0.01	32.7, 28.6	98.7, 99.0	
m_{cat} = 2.0 g	Prepared by precipitation gel			
t = 12 h	method			

An increase in sodium (Na) content of a silica supported Cu catalyst prepared by precipitation-gel method lessened the glycerol conversion in general. The highest glycerol conversion was attained at a Na content of 0.14% and resulted in a glycerol conversion of 32.7% glycerol with a 1,2 PDO selectivity of 98.7%. The presence of sodium diminished the Cu surface area and caused the decline in glycerol conversion. The optimal activity observed in the presence of small amounts of Na was thought to arise from the leaching of Na instead of Cu into solution which prevented the loss and inhibition of catalyst activity [36].

2.2.1.3 Cu/ZnO

Zinc oxide has also been reported as one of the promising supports for Cu-based catalysts in the selective hydrogenolysis of glycerol towards 1,2 PDO (Table 2.4). In one of the earlier studies, ZnO-supported Cu catalyst prepared by a co-precipitation method without pre-reduction was used to investigate the effect of Cu/Zn molar ratio, pre-reduction of the catalyst, initial pH and temperature using 20% glycerol-water mixture. The increase in Cu/Zn ratio from 0.6 to 2.0 caused a decline in glycerol conversion from 22.5% to 7.8%, while the 1,2 PDO selectivity was improved from 20.4% to 76.8%. This was also extended to CuO without ZnO and ZnO without CuO, which exhibited very low activities leading to a glycerol conversion of 4.0% and 3.6%, respectively. A superior selectivity towards 1,2 PDO was observed for CuO at 76.8%, while ZnO exhibited no preference for 1,2 PDO which indicates that CuO is the active component for the selective hydrogenolysis of glycerol to 1,2 PDO and ZnO only contributes to the dehydration of glycerol [37].

Table 2.4 Summary of Cu supported on ZnO catalyst investigations for glycerol conversion to 1,2 PDO.

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
T= 200˚C	Catalyst			[37]
P = 4.20 MPa H_2	(Cu/Zn mol. ratio)			
$C_{glycerol}$ = 20 wt%	Cu–ZnO (0.6)	22.5	20.4	
n_{Cu} = 7.5 mmol	Cu–ZnO (1.0)	17.2	29.4	
$m_{soln.}$ = 80 g	Cu–ZnO (2.0)	7.8	51.3	
t = 12 h	CuO	4.0	76.8	
batch	ZnO	3.6	-	
	Cu–ZnO (1.0)			
	Initial pH			
	2	10.4	27.90	
prepared by co-precipitation	7 (no pre-reduction)	21.1	29.4	
no-prereduction unless stated	7 (with pre-reduction)	22.5	83.6	
	12	33.9	77.5	

	At initial pH = 7 Temperature (˚C) 180, 200, 220, 240	~10.3, 21.1,35.5, 55.7	~16.5, 29, 81.4, 59	
T= 200˚C P = 6.0 MPa H_2 $C_{glycerol}$ = 20 wt% $v_{soln.}$ = 50 mL t = 6 h Prepared by homogeneous co-precipitation method (pre-reduced)	Cu/ZnO Cu:ZnO (mol ratio) 2:1 1:1 0.4:1 1:0 0:1 Cu+ZnO (1:1) Hydrogen Pressure(MPa) 2, 4, 6, 8 Glycerol Conctration (%) 20, 40, 60, 80 Temperature (˚C) 180, 200, 220, 240	Conversion %, TOF (10^{-3} $s^{/}$) ~25%, 1.2 ~25%, 2.6 ~25%, 1.7 ~25%, 0.4 0,0 ~25%, 0.6 TOF (10^{-3} $s^{/}$) ~1, 1.7, 2.55, 3.25 ~2.5, 3.2, 5.5, 9.0 ~0.4, 2.6, 5.9, 9.7	93.9 93.9 93.5 86.3 - 89.0 ~88, 91, 93, 94 ~92, 95, 96, 97 ~93, 92, 91, 88	[38]
T= 200˚C P = 2.00 MPa H_2 $C_{glycerol}$ = 20 wt% m_{cat} = 1.2 g (6 wt%) t = 16 h prepared by co-precipitation method	Catalyst (Cu:Zn wt ratio) 40:60, 50:50, 60:40, 70:30 Cu–Zn (50:50) Temperature (˚C) 160, 200, 220 Glycerol Concentration (wt%) 10, 20, 40 t= 24 h	30, 37, 24, 15 ~7, 37, 39 34, 37, 25 44	91, 92, 92.2, 92.0 ~92, 92, 75 93, 92, 92 90	[39]
T= 200˚C P= 5.0 MPa H_2 $C_{glycerol}$= 100 % $V_{soln.}$ = 140 mL m_{cat} = 3.0 g t= 7 h co-precipitation method (CP) oxalate gel co-precipitation method (OG)	CuO/ZnO Prepared by CP OG Temperature (˚C) 190, 200, 210, 215, 225 OG (50% glycerol) in 1,2 butanediol in water	17 46 ~10, 46, 36, 60, 78 55 5	87 90 ~92, 90, 88, 92, 83 86 87	[40]
T= 220˚C P = 5.0 MPa H_2 m_{feed} = 177 g t= 7 h (m_{cat} = 3.0 g, $C_{glycerol}$ = 50 wt%) (m_{cat} = 3.0 g, $C_{glycerol}$ = 100%) (m_{cat} = 7.0 g, $C_{glycerol}$ = 100%, t = 5.5 h) (m_{cat} = 2.8 g, $C_{glycerol}$ = 90 wt%) (m_{cat} = 0.3 g, $C_{glycerol}$ = 90 wt%, T=200˚C, t = 5.0 h)	CuO/ZnO CuO/ZnO/Ga_2O_3 CuO/ZnO/Ga_2O_3 CuO/ZnO/Ga_2O_3 CuO/ZnO CuO/ZnO/Ga_2O_3 T=200˚C CuO/ZnO CuO/ZnO/Ga_2O_3 Cu/ZnO/Ga_2O_3 prepared by coprecipitation	12 36 60 99 84 96 Run 1, 2 55, 38 43,41 Run 1,2,3,4 57,53,57,52	71 85 81 80 81 82 Run 1, 2 82,79 88,84 Run 1,2,3,4 80,82,83,85	[41]

Variation of the initial pH from 2 to 12 (Cu/Zn = 10) enhanced both the glycerol conversion and 1,2 PDO selectivity from 10.4% to 33.9% and 27.9% to 77.5%, respectively. A reduction in ZnO and Cu particle sizes were also observed with the increase in initial pH, which caused the enhancement in catalyst performance and allowed increase in surface potentials and prevention of aggregation. The use of pre-reduced Cu on ZnO (Cu/ZnO) slightly improved the glycerol conversion from 21.1% to 22.5%, while it vastly enhanced 1,2 PDO selectivity from 29.4% to 83.6% which was again linked to the reduction in Cu size. Meanwhile, a raise in the reaction temperature from 180˚C to 240˚C improved the glycerol conversion from 10.3% to 55.7%. A similar pattern was observed for 1,2 PDO selectivity with the increase in temperature from 180˚C to 220˚C, which went from 16.5% to 81.4% but declined to 59% as the reaction temperature was increased further to 240˚C [37].

The variation of Cu:Zn ratios at 2:1, 1:1, and 0.4:1 in a pre-reduced catalyst appeared to have no effect on the selectivity towards 1,2 PDO but affected the turnover frequencies (TOF, 10^{-3}/s). The TOF improved from 1.2 to 2.6 upon the decrease in Zn:Cu ratio from 2:1 to 1:1 but declined to 1.7 with the reduction of the Cu:Zn ratio to 0.4:1. This behavior was attributed to a favorable formation of strained Cu particles at a Cu:Zn ratio of 1:1 [38]. An increase in hydrogen pressure from 2.0 to 8.0 MPa enhanced both the TOF and 1,2 PDO selectivity from 87.7% to 94.3%. The same trend was observed upon increase in glycerol concentration from 20% to 80% with a slight increase of 1,2 PDO selectivity from 92.8% to 96.4%. While, a raise in the reaction temperature from 180˚C to 240˚C improved the TOF, but reduced the 1,2 PDO selectivity from 93.5% to 87.5%. In a similar study, the Cu-Zn combinations have been investigated for the effects of Cu:Zn ratios, temperature, pressure, glycerol concentration, time, and catalyst concentration [39]. Similar results were obtained for the effects of Cu:Zn ratio, temperature, and pressure with a favorable activity at 50:50 wt% Cu:Zn ratio, which is close to the 1:1 molar ratio due to the proximity of molecular mass of Cu (63.546 g/mol) and Zn (65.38 g/mol). A favorable temperature for the selective production of 1,2 PDO was observed at 200˚C. However, there is a contrast in the effect of glycerol concentration. In the previous study [38], glycerol conversion (in terms of TOF) and 1,2 PDO selectivity were enhanced with the increase in glycerol concentration. In this case, glycerol conversion deteriorated with the increase in glycerol concentration but maintained 1,2 PDO selectivity [39]. Both increase in time and catalyst concentration showed no effect on 1,2 PDO selectivity, while the increased glycerol conversion indicated that 1,2 PDO is not considerably decomposed along the reaction completion.

Oxalate gel co-precipitation method (OG) and co-precipitation method (CP) were used to prepare the catalyst of Cu on ZnO to investigate its activity for the selective conversion of glycerol to 1,2 PDO [40]. The catalyst prepared via OG gave a slightly better 1,2 PDO selectivity at 90% as compared to 87% for the catalyst prepared by CP and a superior glycerol conversion at 46% for the former as compared to 17% for the latter. The superior activity for the OG prepared catalyst was attributed to its greater surface area and a smaller diameter of the active Cu. The choice of solvent for glycerol also affected the catalyst activity. A higher glycerol conversion was achieved at 55% with glycerol in 1,2 butanediol as compared to 5% with glycerol in water, while similar 1,2 PDO selectivities were achieved in both. A greater increase in the size of Cu was observed with the catalyst used for glycerol conversion in water as compared to the catalyst used for glycerol conversion in 1,2 butanediol, thus explaining the difference in the catalyst activity [40]. An inconsistency in glycerol conversion was observed with the variation in the reaction temperature. Improvement in the glycerol conversion was observed with a raise in the reaction temperature from 190˚C to 200˚C but declined with its increase from 200˚C to 210˚C. However, it rose again with further increase of the reaction temperature from 210˚C to 230˚C. The 1,2 PDO selectivity remained relatively constant at this range temperature range (84-92%). The unusual behavior was perceived as a consequence of the difference in the dependence of the rate constant and reactants' adsorption constants [40].

The incorporation of Ga_2O_3 into the catalyst of Cu on ZnO improved the glycerol conversion at 220 ˚C, while the 1,2 PDO selectivity was retained. A lower glycerol conversion and a slightly better 1,2 PDO selectivity was observed at 200˚C for the catalyst with Ga_2O_3, indicating temperature dependence of the catalyst performance relative to the other. An increase in glycerol concentration, enhanced glycerol conversion but maintained 1,2 PDO selectivity. Aside from glycerol conversion, the addition of Ga_2O_3 to the catalyst of Cu on ZnO improved the catalyst stability through the separation and isolation of individual particles which prevented their sintering during its utilization at high temperatures [41].

2.2.1.4 Cu/MgO

Another promising support for the selective hydrogenolysis of glycerol towards 1, 2 PDO is MgO (Table 2.5). Three different copper loadings and two different preparation methods were tested and reported [42]. An enhancement in glycerol conversion was observed with the increase in the catalyst's Cu loading from 10 wt% to 15 wt%. However, it declined upon the further increase of the catalyst's Cu loading from 15 wt% to 20 wt%. The observed trend in the catalyst activity was thought to arise from the increase in the active Cu from 10 wt% to 15 wt%, while raising the Cu content further to 20 wt% promoted the sintering of the copper sites. Catalyst of Cu on MgO prepared by co-precipitation gave a higher glycerol conversion and slightly better 1,2 PDO selectivity as compared to the catalts prepared by impregnation. It was observed from catalyst characterization that the catalyst of Cu on MgO prepared by co-precipitation had smaller metal particles and greater surface area. Addition of small amounts of NaOH into the glycerol phase promoted glycerol conversion but slightly reduced the1,2 PDO selectivity.

In another work with Cu catalyst on MgO prepared by co-precipitation, the effects of copper content, temperature, hydrogen pressure, reaction time, catalyst concentration, glycerol content, and use of crude glycerol were investigated [43]. An increase in Cu loading from 10% to 20% enhanced glycerol conversion, but its further increase led to a decline in glycerol conversion, while attaining a relatively constant 1,2 PDO selectivity (~88-92%). This behavior was attributed to the effect of the basic property of MgO and enough Cu metal surface to provide the favorable conversion of glycerol and 1, 2 PDO selectivity, while not blocking the MgO sites. Glycerol conversion improved with increase in reaction temperature, while the highest 1,2 PDO selectivity was observed at 200˚C and gradually declined with further increase in reaction temperature. This trend was linked to the excessive hydrogenation at temperatures higher than 200˚C, which leads to the formation of lower alcohols and degradation products. Glycerol conversion was enhanced with increase in initial hydrogen pressure until 6.0 MPa (60 bar), but declined as the intial hydrogen pressure was further increased. The selectivity stayed at a similar level (~90-92%) throughout the range of 2.0-8.0 MPa of hydrogen. Both increases in reaction time and catalyst concentration improved glycerol conversion, but didn’t have much effect on the 1,2 PDO selectivity. Only a marginal loss in glycerol conversion was observed when crude glycerol was used instead of purified glycerol, while a similar 1,2 PDO selectivity was achieved for both [43].

Table 2.5 Summary of Cu supported on MgO catalyst investigations for glycerol conversion to 1,2 PDO.

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
T= 180°C P = 3.0 MPa H_2 $C_{glycerol}$ = 75 wt% $V_{soln.}$ = 8.0 mL m_{cat} = 1.0 g t = 20 h Prepared by Coprecipitation (CP) or Impregnation (IM) method	10 wt%CuO/MgO-CP	48.6	97.4	[42]
	15 wt%CuO/MgO-CP	72.0	97.6	
	20 wt% CuO/MgO-CP	58.4	96.8	
	15 wt% CuO/MgO-CP +NaOH (0.125 g)	82.0	95.8	
	10 wt% CuO/MgO-IM	22.0	86.7	
	15 wt%CuO/MgO-IM	30.0	92.8	
	20 wt% CuO/MgO-IM	25.6	93.2	
T= 200°C P= 4.0 MPa H_2 $V_{soln.}$ = 50 mL m_{cat} =0.1 g $C_{glycerol}$= 20 wt% t=8 h	Cu/MgO (% Cu) 10, 20, 40, 60, 80	30.2, 49.3, 36.6, 18.0, 6.1	92.4, 92.3, 90.3, 90.0, 87.6	[43]
	20% Cu/MgO Temperature (°C) 160, 180, 200, 220	~4, 15, 49.3, 75	~89, 91, 92.3, 73	
	Pressure (MPa) 2.0, 4.0, 6.0, 8.0	~45, 49.3, 52, 27	~90, 92.3, 90, 90	
	Gycerol Conc. (wt%) 10, 40, 60, 80	~62, 44, 28, 22	~87, 92, 90, 87	
	Reaction Time (h) 4, 6, 8, 10	~32, 48, 49, 53	~86, 90, 93, 92	
	Catalyst Conc. (wt%) 4, 6, 8, 10	~32, 48, 55, 60	~85, 92, 92, 90	
	crude glycerol	44.5	92	

2.2.1.5 Cu/Al_2O_3

One of the more studied supports for Cu-based catalysts in the selective hydrogenolysis of glycerol into 1,2 PDO is Al_2O_3 (Table 2.6). In a continuous mode of reaction, a commercial catalyst containing 55% CuO on Al_2O_3 was used to investigate the effects of temperature, hydrogen gas feed rate, glycerol concentration, temperature gradients on the hydrogenolysis of glycerol to 1,2 PDO [44-45]. Glycerol conversion improved with increase in temperature from 170°C to 190°C and remained at 100% with further increase. The 1,2 PDO selectivity improved with increase in reaction temperature from 170°C to 190°C and reached 82%, but declined thereon. The application of temperature gradient enhanced the 1,2 PDO selectivity and as high as 96.9% was achieved with a top to bottom temperature gradient of 200°C and 100°C with 100% of the glycerol converted. Hydrogen flow rate increase to 360 cm^3/ min improved the 1,2 PDO selectivity but no further improvement beyond that flow rate. Variation in the glycerol concentration had no effect on glycerol conversion and 1,2 PDO selectivity. The observed enhancement in the 1, 2 PDO selectivity with application of the temperature gradients was attributed to the efficient dehydration of glycerol to hydroxyacetone at higher temperatures and hydrogenation which was favored at lower temperatures.

Table 2.6 Summary of Cu supported on Al_2O_3 catalysts investigations for conversion of glycerol to 1,2 PDO.

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
PH_2= ambient $C_{glycerol}$ = 30 wt% $Frate_{glycerol}$ = 1.8 cm^3/h $Frate_{H2}$ = 360 cm^3/min m_{cat} = 2.9 g (2.4 cm^3)	(N242) 55wt% Cu/Al_2O_3 Temperature (˚C) 170, 180, 190, 200, 210, 230, 250	~67, 93, 100, 100, 100, 100, 100	~60, 65, 82, 77, 72, 53, 39	[44]
m_{cat}=8.7 g (7.2 cm^3)	Gradient Temperature (˚C) Top:Bottom 210:170, 200:160, 180:145, 170:135 Commercial catalyst	100, 100, 100, 100	81.9, 91.7, 93.7, 92.3	
T= 200˚C P = 20.0 MPa H_2 $C_{glycerol}$ = 30 wt% $Frate_{glycerol}$ = 1.8 cm^3/ h $Frate_{H2}$ = 360 cm^3/min H_2/glycerol =141 V_{cat} = 2.4 mL TOS= 2-5 h	2.9 g 55.1 wt % CuO/Al_2O_3 (N-242, commercial)	100	78.2	[45]
	2.0 14.9wt%CuO/Al_2O_3 (T-317, commercial)	100	75.0	
	55.1wt %CuO/Al_2O_3- Top T = 200˚C, mcat = 8.7 g Bottom T: (˚C) 173, 160, 150, 130, 120	100, 100, 100, 100, 100	91.2, 92.6, 94.3, 96.1, 96.9	
Top T = 200˚C Bottom T = 160 ˚C m_{cat} = 8.7 g	55.1wt%CuO/Al_2O_3 Glycerol concentration (wt%) 30, 60, 80, 94	100, 100, 100, 100	96.1, 95.4, 95.5, 95.2	
T= 200˚C P = 3.6 MPa H_2 $C_{glycerol}$ = 50 wt% Agitation = 400 rpm t = 10 h	Cu/γ-Al_2O_3 (mmol Cu/g) 0:100, 0.75:100, 1.5:100, 2.25:100, 3:100, 3.75:100, 4.5:100	0, 8.0, 20.3, 26.4, 34.6, 26.0, 18.1	0, 90.6, 95.8, 94.4, 93.9, 93.0, 93.0	[46]
	3:100 Reduction Temperature (˚C) 200, 300, 400	23.3, 34.6, 24.6	98.3, 93.9, 98.1	
synthesized using an incipient wetness impregnation method	Reaction Temperature (˚C) 180, 200, 220, 240	~10, 34.6, 50, 52	~95, 95, 95, 72	
	Glycerol Concentration (wt%) 100, 80, 50, 20	41.9, 39.8, 34.6, 17.7	93.3, 96.5, 93.9, 95.6	
	Reuse of Catalyst Fresh	34.6	93.9	
	Used and Washed	20.2	92.1	
	Used, washed, and reduced	24.7	93.3	
T= 240˚C P= 6.0 MPa H_2 m_{cat} = 4.0 g $C_{glycerol}$= 10 wt% LHSV = 0.9 h	Cu/γ-Al_2O_3 % Cu 5, 10, 20, 30 50	60.58, 76.04, 85.05 57.95, 40.52	85.2, 86.66, 85.71, 86.65, 86.39	[47]
	Temperature (˚C) 180, 210, 240, 270 prepared by means of incipient wetness impregnation method	8.25, 31.15, 85.05, 95.55	87.64, 86.04, 85.71, 35.65	

T= 200˚C P= 2.0 MPa H_2 $C_{glycerol}$= 80 wt% m_{cat} = 6 wt% Agitation = 100 rpm t= 24 h Prepared by a modified co-precipitation method calcined at 400˚C for 4 h	Cu/Al_2O_3 Pressure (MPa) 3.5, 4.1,5.5,8.0,8.7 Temperature (˚C) 150, 160, 170, 180, 190, 200, 210, 220, 230 Glycerol Concentration (wt%) 20, 40, 50, 60, 70, 80, 90, 100 Catalyst (wt%) 2, 3, 4, 5, 6, 7, 8, 9 Agitation (rpm) 100,200,300,400,500,700,100, 1250 Time (h) 16,24,30,48 Fresh 3rd reuse.	~58, 62, 67, 71, 73 ~ 15, 20, 28, 38, 48, 63, 73, 82, 93 ~53, 54, 55, 58, 59, 62 ,68, 73 ~47, 53, 58, 61, 62, 64, 73 ~62, 65, 68, 72, 76, 82, 90, 96 ~66,76, 82, 98 75.7 70.5	~78, 90, 91, 93, 94 ~15, 25, 41, 58, 77, 91, 87, 48, 34 ~54, 72, 83, 87, 89, 91, 67, 45 ~73, 79, 86, 92, 91, 83, 68, 55 ~92,92,93,94, 95,83, 67,58 ~83, 96, 80,51 95.8 88.3	[48]
T= 200˚C P= 3.0 MPa H_2 $C_{glycerol}$= 80 wt% $V_{soln.}$ = 20 mL Agitation = 100 rpm t= 24 h Prepared by a modified co-precipitation method calcined at 300˚C for 6 h and reduced by hydrogen at 300˚C	Cu/Al_2O_3 Commercial Unreduced Reduced Prepared by co-precipitation Reduction time (h) 0, 4, 8, 10, 16, 24	30.6 34.0 35.4 50.3, 55.4, 59.0, 55.2, 39.7, 30.1	58.8 36.5 41.1 ~37,62,77,70, 66, 58	[29]
Batch: T= 220˚C P= 6.9 MPa H_2 m_{cat} = 0.8 g $C_{glycerol}$= 20 wt% t= 5 h Continuous Hydrogenolysis T= 220˚C P= 4.0 MPa H_2 m_{cat} = 20 g $C_{glycerol}$= 20 wt% in H_2O GHSV = 500 h LHSV = 1.5 h	In H_2O Cu:Al 30:70, 50:50, 70:30 In 2-Propanol Cu:Al 30:70, 50:50, 70:30 Cu:Al (50:50) In H_2O batch Continuous TOS = 1h (46-400 h) Pressure (MPa) 2.2, 4.2, 6.2 Glycerol Concentration (wt%) 20, 40, 60 Temperature (˚C) 180, 220, 240	51, 38, 45 42, 47, 69 ~85 (~60) ~ 45, 57, 47 ~57,63,30 ~20, 56, 84	85, 91, 60 91, 88, 90 ~90 (~90) ~93,92,93 ~92, 92, 90 ~94, 92, 78	[49]
T= 180˚C P= 0.1 MPa H_2 V_{cat}= 5 mL $C_{glycerol}$= 16.67 wt% $Frate_{glycerol}$ = 4.2 mL h $Frate_{H2}$ = 250 mL min t= 1 h	Catalyst (mass ratio), Total Acidity: mmol NH3 g_{cat} T= 180˚C, 210˚C, 240˚C CuO/Al_2O_3 (5:95), 2.18 CuO/Al_2O_3 (10:90), 1.99 CuO/Al_2O_3 (20:80), 1.59	100 100 100	~79, 68, 50 ~85, 70, 53 ~88, 73, 52	[50]
T= 220˚C P= 5.2 MPa m_{cat}= 1.0 g $C_{glycerol}$= 20 wt% $V_{soln.}$ = 100 mL t = 5h Cu/Al Preparation method, P or F (precipitating agent) Preparation Co-precipitatio (P) Solid State Fusion (F)	CAP (K_2CO_3) CAP (K_2CO_3F) CAP (K_2CO_3) CAP (Na_2CO_3) + NaOH (0.9 M) CAP (Na_2CO_3R) CAP (KOH) CAP (NaOH) CAF (KOH) CAF (NaOH) CAF (KNO3)	38 36 38 62 63 58 51 5 39 15	91 87 88 88 88 88 87 74 88 84	[51]

T= 220˚C P = 5.0 MPa H_2 m_{cat} = 1.0 g $C_{glycerol}$= 99.9 wt% $M_{glycerol}$ = 50 g t= 12 h	$CuAl_2O_4$ Calcination Temperature (˚C) 400, 500, 600, 700, 800 Prepared by sol-gel method	61,72, 55, 76, 90	13, 38, 65, 84, 91	[52]
T= 200 ˚C P= 1.5 MPa H_2 $C_{glycerol}$= 50 wt% $m_{soln.}$ = 65 g n_{cat}= 3:100 (Metal:Glycerol) Agitation = 400 rpm t=10 h Prepared by incipient wetness impregnation	$CuAg/Al_2O_3$(2.7)(7 : 3)	27	96	[53]
	$CuZn/Al_2O_3$(2.7)(7 : 3)	6	94	
	$CuCr/Al_2O_3$(2.7)(7 : 3)	1	92	
	Cu/Al_2O_3(1.9), Metal:Glycerol(2.1:100)	2	83	
	Ag/Al_2O_3(0.8), Metal:Glycerol(0.9:100)	8	94	
	Cu/Al_2O_3(1.9) +Ag/Al_2O_3(0.8)	20	94	
	Cu/Al_2O_3(2.7)			
	$CuAg/Al_2O_3$(2.7)			
	Cu:Ag 100:0, 95:5, 85:15, 70:30, 50:50, 30:70, 15:85, 5:95, 0:100	3, 21, 25, 27, 24, 25, 23, 23, 21	84, 99, 97, 96, 96 95, 94, 93, 93	
	CuAg (7:3)/Al_2O_3(2.7) Impregnation sequence Cu First, Ag First, Simultaneous	20, 18, 27	93, 93, 96	
	Calcination temperature (˚C) 200, 300, 350, 400, 450, 500	~2,17,22,27,22,18	~77,93,94,96,94,96	
T= 240˚C P= 6.0 MPa H_2 $C_{glycerol}$= 10 wt% m_{cat} = 4.0 g LHSV= 0.9 h	Cu-STA/ Al_2O_3 Cu: STA 5:0, 5:3, 5:5, 5:15, 5:30, 0:5	60.6, 77.6, 90.1, 41.9, 8.6, 3.7	85.2, 87.8, 89.7, 91.6, 92.1, -	[54]
	5Cu-5STA/Al_2O_3 Temperature (˚C) 180, 210, 240, 270	2.5, 31.2, 90.1, 97.4	97.3, 95.4, 89.7, 37.7	
	Space Velocity (h) 1.8, 0.9, 0.45 prepared by incipient wetness impregnation	81.2, 90.1, 95.7	95.1, 89.7, 70.5	
T= 220˚C P= 4.5 MPa H_2 $V_{soln.}$ = 135 mL $C_{glycerol}$= 4 wt% $Frate_{formicacid}$ = 3.6 mmol g_{cat} h Agitation = 550 rpm t= 24 h	0Ni35Cu /Al_2O_3	29.2	75.5	[55]
	7Ni28Cu /Al_2O_3	40.9	82.2	
	13Ni22Cu /Al_2O_3	47.5	78.1	
	20Ni15Cu /Al_2O_3	49.3	75.4	
	28Ni7Cu /Al_2O_3	47.7	74.3	
	35Ni0Cu /Al_2O_3	53.0	42.0	
	prepared by the sol–gel method			
T= 220˚C P= 4.5 MPa H_2 m_{cat} = 0.166 g/ g glycerol $C_{glycerol}$= 4 wt% $V_{soln.}$ = 41 mL t = 24 h	Catalyst (activation T) Cu/Al_2O_3 (320˚C)			[56]
	in H_2 and H_2O	32.9	90.1	
	in N_2 and 2-Propanol (glycerol:2-Propanol=1:1)	14.6	40.5	
	Ni/Al_2O_3 (320˚C)			
	in H_2 and H_2O	5.2	73.7	
	in N_2 and 2-Propanol (glycerol:2-Propanol=1:1)	2.0	7.5	
	$Ni-Cu/Al_2O_3$ (320˚C)			
	in H_2 and H_2O	31.0	84.7	
	in N_2 and 2-Propanol (glycerol:2-Propanol=1:1)	41.2	48.3	
	Cu/Al_2O_3 (450˚C)			
	in H_2 and H_2O	57.0	72.8	
	in N_2 and 2-Propanol (glycerol:2-Propanol=1:1)	39.1	59.4	
	Ni/Al_2O_3 (450˚C)			
	in H_2 and H_2O	69.0	61.3	

	in N_2 and 2-Propanol (glycerol:2-Propanol=1:1)	31.8	50.4	
	Ni-Cu/Al_2O_3 (450˚C)			
	in H_2 and H_2O	70.5	66.9	
	in N_2 and 2-Propanol (glycerol:2-Propanol=1:1)	57.3	62.1	
	in N_2 and 2-Propanol (glycerol:2-Propanol=1:1.5)	60.4	64.6	
	Prepared by a sol-gel method			
T= 220˚C P= 3.0 MPa H_2 H_2/glycerol = 20 molar ratio SV= 2.0 /h	Cu/P-Al_2O_3 (% P) 0, 1, 2, 4, 6 prepared by the successive impregnation method	~17, 78, 92, 94, 95	~84, 94, 96, 97, 97	[57]

In a γ-Al_2O_3 supported Cu catalyst prepared via impregnation, glycerol conversion improved with the increase in Cu loading from 0 to 3:100 mmol Cu/ g catalyst. Further increase in Cu loading caused a drop in glycerol conversion. The 1,2 PDO selecitivity was maintained allthrough out the various Cu loading [46-47]. The copper particles were observed to be highly dispersed at lower copper loading. But as copper loading was increased the dispersion of the active metal deteriorated, blocked the pores of the support, and increased Cu crystallites size and caused a dip in glycerol conversion [46]. Glycerol conversion improved with increase in reaction temperature. The 1, 2 PDO selectivity was maintained (~95) until 220˚C [46] to 240˚C [47] but declined upon further increase due to the formation of lower alcohols like methanol and ethanol. The variation of glycerol concentration exhibited different outcomes from separate investigations. In one of them, the increase in glycerol content slightly improved glycerol conversion, while sustaining the selectivity for 1,2 PDO (93-96%)[46]. In the other work, a decline in glycerol conversion was observed with increase in glycerol content and the 1,2 PDO selectivity was not affected as well [47]. A drop in glycerol conversion occurred when the catalyst was reused in a batch reaction signifying catalyst deactivation [46]. A co-precipitation prepared Cu catalyst on Al_2O_3 performance was tested by varying several parameters and gave similar trends with those observed from the impregnation prepared Cu catalyst on γ-Al_2O_3 and just having differences in some optimal values [46-48]. In this case, an optimal 1,2 PDO selectivity occurred at 200˚C, while a favorable selectivity for 1, 2 PDO happened at 80 wt% glycerol and dropped after further increase in glycerol concentration [48]. The 1,2 PDO selectivity was found to be optimal at a

5 wt% catalyst loading, stirring speed of 500 rpm, and reaction time of 24 hours. Further increase in each of the parameters lowered the 1,2 PDO selectivity due to further hydrogenolysis. Pre-reduction of a commercial and co-precipitation prepared Cu catalyst on Al_2O_3 enhanced the 1,2 PDO selectivity. The extent of reduction was optimal at 8 hours, which declined with longer exposure to reducing environment. The presence of both Cu metal and Cu^+ being was observed the greatest at the optimal reduction time compared to shorter and longer reduction times [29].

Similarly, a Cu catalyst on Al_2O_3 prepared by co-precipitation was tested for the continuous production of 1,2 PDO via glycerol hydrogenolysis. The effects of Cu loading, solvent, reaction temperature, hydrogen pressure, glycerol concentration, and feed flow rate were studied [49]. The effect of Cu loading on glycerol conversion and 1,2 PDO selectivity was dependent on the choice of solvent. As the Cu loading was increased from 30% to 50% and 70%, glycerol conversion in water was observed to drop from 51% to 38% and 45%, respectively. The 1,2 PDO selectivity improved from 85% to 91% then dropped to 60% with the increase in Cu loading from 30%, 50%, and 70%, respectively. Glycerol conversion in 2-propanol was enhanced from 42% to 69% with the increase in Cu loading from 30% to 70% and the 1,2 PDO selectivity was steady at 88-91%. Catalyst performance deteriorated with the increase of time on stream (TOS) to 46 hours as the glycerol conversion dropped from about 85% to 60% but no further decrease in glycerol conversion was observed from there on, while 1,2 PDO selectivity was maintained. The increase in hydrogen pressure from 2.2 to 4.2 MPa slightly improved glycerol conversion. But further increase to 6.2 MPa caused a drop in glycerol conversion. Glycerol concentration increase from 20 wt% to 40 wt% slightly improved glycerol conversion with the 1,2 PDO selectivity maintained at around 90%. Both glycerol conversion and 1,2 PDO selectivity declined with further increase in glycerol concentration to 60 wt%. An improvement in glycerol conversion was observed with increase in reaction temperature from 180˚C to 240˚C. A drop in the 1,2 PDO selectivity occurred from 92% to 78% with the increase of temperature from 220˚C to 240˚C.

A catalyst of Cu on Al_2O_3 prepared via incipient wetness impregnation has also been used for gas phase continuous hydrogenolysis of glycerol. It was found that the increase in Cu loading from 5 to 20 wt% slightly improves the 1,2 PDO selectivity. A drop in the 1,2 PDO selectivity was observed with the increase in reaction temperature from 180˚C onwards. The response of the catalyst performance with the increase in Cu loading can be linked with the observed reduction in specific surface area and total acidity and the increase in the crystallite size of Cu with the increase in Cu loading [50].

The activity of Cu catalyst on Al_2O_3 prepared by co-precipitation was found to be affected by the choice of precipitating agent. Among the various precipitation agents tested, Na_2CO_3 gave the highest glycerol conversion at 62-63%. Meanwhile, the 1,2 PDO selectivity (87-91%) was relatively independent on the precipitating agent [51]. Catalyst characterization revealed that the Cu catalyst on Al_2O_3 prepared with Na_2CO_3 as the precipitating agent produced a catalyst with a defined spherical morphology without any aggregation, smaller crystallite size, and high acidity which translated to a higher catalyst activity. The same catalyst prepared by solid-state fusion exhibited a lower glycerol conversion, but a similar 1,2 PDO activity [51]. The raise in calcination temperature enhanced the glycerol conversion and the 1,2 PDO selectivity of the catalysts prepared by sol-gel method. Both glycerol conversion and 1,2 PDO selectivity reached at least 90% for the catalyst calcined at 800˚C, which was due to the decrease in CuO formation and the increase in crystalline $CuAl_2O_4$ spinel structure formation [52].

Incorporation of Zn, Cr, and Ag to the Cu catalyst on Al_2O_3 improved the 1,2 PDO selectivity from 83% to 92-96% [53]. The Cu catalyst on Al_2O_3 with Ag gave the highest 1,2 PDO selectivity at 96%. Variation in the ratios of Ag and Cu had minimal effects on the glycerol conversion and 1,2 PDO selectivity. A 1,2 PDO selectivity of 99% was attained at a Cu:Ag ratio of 95:5 with 21% of the glycerol converted. The addition in small amounts of Ag improved the dispersion of CuO, which led to the enhanced catalyst activity. A superior catalyst activity resulted from the simultaneous impregnation of Cu and Ag onto Al_2O_3 as compared to the impregnation of each metal in any sequence due to uniform mixing in the former. The optimal calcination temperature was at 400˚C due to the formation of Cu(O) or Cu (I) in the majority of Cu species. The catalysts calcined at other temperatures contained higher proportions of Cu(II) after reduction [53].

Addition of $H_4SiW_{12}O_{40}$ (STA) to Cu catalyst on Al_2O_3 at lower to medium levels improved the glycerol conversion and 1,2 PDO selectivity. An optimal glycerol conversion of 90.1% was achieved at 5:5 Cu to STA ratio. Further increase in STA caused a decline in glycerol conversion, but slightly improved the 1,2 PDO selectivity [54]. The enhancement in the catalyst activity was attributed to the additional acid sites necessary for dehydration. However, beyond the optimal ratio, the catalyst activity declined due to the excess acidity and may have caused the catalyst deactivation from coking. Glycerol conversion improved with increase in the reaction temperature, but the 1,2 PDO selectivity dropped as the temperature was raised due to the increased formation of byproducts. A similar trend was observed with the decrease in space velocity as the glycerol conversion increased and 1,2 PDO selectivity declined due to the increase in other hydrogenolysis products [54]. The incorporation of Ni to Cu catalyst on Al_2O_3 prepared via sol-gel method, with formic acid as the hydrogen, enhanced the catalyst activity. Glycerol conversion improved with the increase in Ni content. The 1,2 PDO selectivity peaked when Ni:Cu ratio was at 7:28 and reached 82.2% with 40.9% of the glycerol converted [55]. The use of 2-propanol as the solvent and the hydrogen donor did not yield a favorable outcome. A lower glycerol conversion and 1,2 PDO selectivity were observed as compared to the use of water and hydrogen gas as the solvent and the hydrogen donor, respectively [56].

Various modifications to the Cu catalyst on Al_2O_3 have also been carried out to enhance the catalyst activity [57-69]. The addition of phosphorous enhanced both glycerol conversion and 1,2 PDO selectivity. Up to 95% glycerol conversion and 97% 1,2 PDO selectivity were achieved with the addition of 6% phosphorous. It was assumed that the increased catalyst acidity as well the strong interaction between Cu and P species caused the promotion effect of phosphorous [57].

2.2.1.6 Cu/ZnO-Al_2O_3

The combination of Cu, ZnO, and Al_2O_3 as catalyst for glycerol hydrogenolysis has been covered in a number of studies [58-63]. However, a definite trend on the Zn:Al ratio has not been reached with these studies. In a continuous mode of reaction, the increase in reaction temperature from 180˚C to 210˚C and hydrogen pressure from 0.1 MPa to 0.64 MPa H_2

improved both glycerol conversion and the 1,2 PDO selectivity of the catalyst prepared by impregnation method. A 1,2 PDO selectivity of up to 96.66% at a glycerol conversion of 92.2% was achieved at 200˚C and 0.64 MPa [58]. On the other hand, the activity of a Cu/Zn/Al_2O_3 (4/2/4) catalyst prepared by co-precipitation was not affected by hydrogen pressure increase from 3 to 5 MPa, but declined with further increase to 6 MPa. As high as 99.0% 1,2 PDO selectivity was observed at 92.5% glycerol conversion. Glycerol conversion improved with the extension of the reaction time, while the 1, 2 PDO selectivity was sustained at similar levels [59].

Higher glycerol conversion and 1,2 PDO selectivity were achieved with lower Zn/Al ratios for the catalyst prepared by co-precipitation method [60]. The 1,2 PDO selectivity reached 93.8% at a 52% glycerol conversion for the catalyst Cu-Zn-Al combination with a Zn to Al ratio of 0.5 [60]. Glycerol conversion improved with the increase in catalyst application rate and the 1,2 PDO selectivity was optimal at 5 wt% catalyst. Higher rate of catalysts application favored further hydrogenolysis which caused the observed decline in 1,2 PDO selectivity. Likewise, glycerol conversion and 1,2 PDO selectivity improved with the increased in initial hydrogen pressure and glycerol concentration until 1.38 MPa and 80% glycerol. At these conditions, 1,2 PDO selectivity reached 93.9% with 48.0% of the glycerol converted. Almost half of the catalyst activity was lost after reuse, but it retained a similar 1,2 PDO selectivity. Purity of the feed did not affect the catalyst activity and 1,2 PDO selectivity [60].

A catalyst of Cu/Zn/Al combination prepared by co-precipitation at a 1:1:0.5 Cu:Zn:Al ratio used in a continuous reactor achieved optimal results of 81.5% and 93.4% glycerol conversion and 1,2 PDO selectivity, respectively at 220˚C [61]. A variation in catalyst preparation method used generated contrasting results. In one report, the catalyst prepared by impregnation showed a superior activity in terms of glycerol conversion, 1,2 PDO selectivity, and stability [62], while another work on the catalyst Cu/Zn/Al (5:1:1) combination prepared by co-precipitation featured a better catalyst activity [63]. The former links the poor activity of catalyst prepared by the other methods to some leaching, coking, and sintering of Cu metal [62], while the latter cites a better dispersion of the catalysts prepared by co-precipitation [63].

Table 2.7 Summary of Cu supported on ZnO-Al_2O_3 catalyst investigations for glycerol conversion to 1,2 PDO.

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
Batch: T= 200˚C P = 5.0 MPa H_2 $C_{glycerol}$ = 60 wt% m_{cat} = 1.8 g $m_{soln.}$ = 60 g Agitation = 1000 rpm t = 10 h Continuous: WHSV = 0.08/ h P = 0.1 MPa H_2 H_2/glycerol = 140:1 molar ratio	32.3 wt% Cu /ZnO/Al_2O_3 Batch Continuous Temperature (˚C) 180, 190, 200, 210 Pressure (MPa) 0.1, 0.23, 0.36, 0.52, 0.64 Prepared by impregnation (Incipient wetness Technique)	20.4 90.4,93.0, 96.8, 100 93.0, 93.9, 95.3, 95.7, 96.2	80.1 50.4, 65.3, 73.4, 77.4 65.3, 77.2, 84.3, 90.8, 92.2	[58]
T= 180˚C P= 3.0 MPa H_2 $C_{glycerol}$= 10 wt% t= 12 h Prepared by co-precipitation method	Cu/Zn/Al_2O_3 (4/2/4) Time (h) 4, 8, 12, 20 Pressure (MPa) 3, 4, 5, 6	31.4, 65.6, 92.5, 94.0 92.5, 94.1, 95.2, 66.0	98.5, 94.4, 99.0, 97.0 99.0, 98.1, 96.6, 94.6	[59]
T= 200˚C P = 200 psig H_2 $C_{glycerol}$ = 80 wt% m_{cat} = 5.0 wt% t = 24 h Prepared using co-precipitation method	Cu/Zn/Al (M2+/M3+) 0.5, 1.0, 1.5, 2.0, 2.13, 2.5 3.0 Cu/Zn/Al (1:1:4) Catalyst concentration 1, 3, 5, 7, 10 Hydrogen Pressure (psig) 0, 100, 200, 300 Glycerol Concentration (%) 100, 80, 50 Catalyst Recyle Fresh, Spent Glycerol Feedstock Purified, Crude	52, 44.3, 41.9, 37.9, 32.8, 33.2, 30.6 12.3, 37.1, 48.0, 57.6, 70.5 15.0, 25.0, 48.0, 47.8 57.0, 48.0, 35.4 48, 25.60 39.2, 38.4	93.8, 73.8, 66.2, 44.5, 63.0, 64, 64.5 45.5, 78.0, 93.9, 89.4, 75.0 0, 50.50, 93.9, 90.0 59.5, 93.9, 75.0 93.9, 92.7 75.6, 76.6	[60]
T= 220˚C P= 4.0 MPa H_2 $C_{glycerol}$= 80 % LHSV = 4.6 h m_{cat} = 3.0 g H_2:glycerol = 5:1(molar ratio)	Cu:ZnO:Al_2O_3 2:1:0.67, 2:1:1.5, 2:1:3, 2:1:6, 1:1:0.25, 1:1:0.5, 1:1:1, 1:1:2, 1:2:0.5 prepared using the co-precipitation method	33.2, 65.1, 78.8, 38.3, 70.0, 81.5, 75.5, 73.3, 69.7	93.9, 85.4, 87.4, 71.9, 90.8, 93.4, 91.5, 90.5, 84.5	[61]
T= 250˚C P= 3.2 MPa m_{cat} = 2.0 g H_2:Glycerol = 4:1 $C_{glycerol}$= 80 wt% WHSV= 2.8 h TOS = 1h (10 h)	Cu-ZnO/Al_2O_3 Preparation method incipient wetness Impregnation Fresh Regenerated co-precipitation Fresh Regenerated 1h (6h) sol-gel method Fresh Regenerated	~100 (100) ~100 (75) ~100 (26) ~100 (16) ~100 (80) ~100 (62)	~90 (90) ~90 (90) ~90 (74) ~90 (70) ~90 (85) ~90 (72)	[62]
T= 250˚C P= 0.1 MPa H_2 m_{cat}= 5.0 g $C_{glycerol}$= 80 wt% WHSV = 0.05 h H_2/glycerol = 150:1 mole ratio	Cu/Zn/Al (Cu:Zn:Al molar ratio of 5:1:1) Prepared by: Co-precipitation (TOS = 48.5, 96.5 h) Impregnation (TOS = 46.5, 97.0 h) Cu/Al_2O_3	85.5, 85.3 63.7, 58.0	83.7, 82.5 68.4, 63.7	[63]

	(Cu:Al molar ratio of 5:1) Co precipitated (TOS= 49.5, 97.5)	48.2, 44.5	75.8, 74.6	

2.2.1.7 Cu/MgO-Al$_2$O$_3$

The combination of Cu, MgO, and Al$_2$O$_3$ has also been explored in fair detail and has proved to be one of the most promising combinations for the selective hydrogenolysis of glycerol to 1,2 PDO (Table 2.8). In a test of Cu/Mg (Al)O catalyst prepared by co-precipitation, temperature increase from 180˚C to 230˚C improved the glycerol conversion, but reduced the 1,2 PDO selectivity. An increase in the hydrogen pressure from 2 to 7 MPa enhanced the glycerol conversion, but further increase did not lead to any improvement. Meanwhile, the 1,2 PDO selectivity improved with the increase in hydrogen pressure from 2 to 9 MPa, but declined upon further increase to 11 MPa. Glycerol conversion also improved with the increase in glycerol concentration. The 1,2 PDO selectivity was sustained until a glycerol concentration of 80%, but dropped from 95% to 88% upon further increas. After being used for 8 times, the catalyst retained its activity but took a slight drop in the 1,2 PDO selectivity [64].

The 1,2 PDO selectivity of a catalyst prepared by impregnation with ethanol as the solvent for glycerol was not affected by a variation in Mg to Al ratio and was maintained at around 93%. A drop in glycerol conversion with a constant 1,2 PDO selectivity of 93% was experienced upon the increase in Cu loading from 2 to 6 wt% [65]. A superior activity was achieved with the catalyst combination Cu$_{0.4}$ on Mg$_{5.6}$Al$_2$O$_{8.6}$ prepared via co-precipitation as compared to the ones prepared by ion exchange or impregnation. Homogeneous dispersion of Cu species in the catalyst prepared via co-precipitation resulted in a selectivity of up to 98.2% at 80% glycerol conversion [66].

Small amounts of rhodium (Rh) added into the catalyst of Cu$_{0.4}$ on Mg$_{5.6}$Al$_2$O$_{8.6}$ enhanced the catalyst activity. The use of methanol or ethanol as the solvent for glycerol improved both glycerol conversion and 1,2 PDO selectivity. A 1,2 PDO selectivity of 98.7% was observed at 91.0% glycerol conversion with ethanol as the solvent. A decline in catalytic activity was observed upon reuse of the catalysts, while the 1,2 PDO selectivity was retained [67]. Addition of Palladium (Pd) into the catalyst of Cu$_{0.4}$ on Mg$_{5.6}$Al$_2$O$_{8.6}$ improved the glycerol conversion and maintained the 1,2 PDO selectivity. At a catalyst composition of $Pd_{0.04}Cu_{0.4}$ on $Mg_{5.56}Al_2O_{8.56}$, the highest glycerol conversion was achieved along with a 1,2 PDO selectivity of 97.2% [68]. The temperature dependence of the catalyst from 120˚C to 200˚C was only evident in the increase of glycerol conversion as the 1,2 PDO selectivity was unaffected [68]. The promoter effect of the small amounts of Rh and Pd were both attributed to the synergistic effects of Cu catalyst and the promoter (Rh or Pd). The use of ethanol as solvent for glycerol was beneficial, since it does not adsorb to the catalyst as strongly as water. Therefore, it did not hinder in the the glycerol hydrogenolysis [67-68]. An improvement in the catalytic activity was also observed with the addition of Zn to the catalyst of $Cu_{0.4}$ on $Mg_{5.6}Al_2O_{8.6}$ in small amounts. The optimal composition was found to be $Cu_{0.4}$ on $Zn_{0.6}Mg_{5.0}Al_2O_{8.6}$, which resulted in a 1,2 PDO selectivity of 99.3% with 78.2% of the glycerol converted [69].The enhancement in the catalyst performance was linked to stronger basicity of the catalyst and hydrogen spillover from Cu to ZnO.

Table 2.8 Summary of Cu supported on $MgO-Al_2O_3$ catalyst investigations for glycerol conversion to 1,2 PDO.

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
T= 210˚C	Cu/Mg(Al)O			[64]
P= 9.0 MPa H_2	Temperature (˚C)			
$C_{glycerol}$= 100 wt%	180, 200, 210, 230	~26, 77, 95, 98	~85, 75, 76, 54	
$V_{glycerol}$ = 15 mL	Hydrogen Pressure (MPa)			
m_{cat} = 6 wt%	2, 4,7, 9, 11	~88, 95, 99, 98, 99	~40, 75, 83, 90, 84	
Agitation = 500 rpm	Glycerol Concentration (%)			
t= 24 h	20, 40, 60, 80, 100	~50, 63, 74, 82, 92	~97, 95, 89, 95, 83	
standard aqueous co-precipitation method	Catalyst Recycle			
	1st use, 8th use	~95, 95	~88, 72	
T= 200 ˚C		Conversion rate (mol/mol surface Cu-s)		[65]
P= 6.0 MPa H_2	$Cu/MgO-Al_2O_3$			
$C_{glycerol}$= 20 wt% in dioxane	Mg:Al			
$V_{soln.}$ = 50 mL	0:1, 1:1, 3:1, 4:1, 1:0	0.1, 1.6, 2.2, 2.2, 2.4	90.1, 93.7, 93.2, 93.2, 90.2	
t = 3 h				
	Cu/Al_2O_3+ $MgO-Al_2O_3$ (3/1)	0.1	90.0	
Prepared by impregnation with ethanol as solvent	$Cu/MgO-Al_2O_3$(3/1)			
	Cu loading (wt%)			
	2, 3, 4, 6	~2.8,2.3, 2.2, 1.7	~93, 93, 93, 93	
	4 wt% Cu/MgO- Al_2O_3 (3/1)			
	Run number	Conversion (%)		
	1, 2, 3, 4	~24, 20, 19, 22	~93, 93, 93, 93	
T= 180˚C	$Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$-CP	80.0	98.2	[66]
P = 3.0 MPa H_2	$Cu_{0.8}/Mg_{5.2}Al_2O_{8.2}$-CP	51.8	97.2	
$C_{glycerol}$ = 75 wt%	$Cu_{1.5}/Mg_{4.5}Al_2O_{7.5}$-CP 2	29.6	98.6	
V_{soln}. = 8.0 mL	Cu–Mg–Al-IE	52.9	95.4	
m_{cat} = 1.0 g	Cu–Mg–Al-IM	22.6	95.3	
t = 20 h	$Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$-CP + NaOH (0.5 g)	85.0	96.2	
Prepared by Coprecipitation (CP), Impregnation (IM), or Ion Exchange (IE) method	$Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$-CP + NaOH (1.0 g)	91.2	95.5	
	$Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$-CP Glycerol Concentration			

	(wt%) 15, 30, 45, 60, 75	41.2, 58.1, 73.0, 77.9, 80.0	98.0, 97.3, 98.5, 97.0, 98.2	
	Temperature (˚C) 150, 180, 200, 220	35.0, 80.0, 93.0, 99.1	98.0, 97.3, 98.5, 97.0	
T= 180˚C	$Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$	56.7	97.1	[67]
P= 2.0 MPa H_2	$Rh_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$	74.1	96.1	
m_{cat} = 1.0 g	$Rh_{0.02}/Mg_{5.6}Al_{1.98}O_{8.57}$	1.0	82.1	
$C_{glycerol}$ = 75 wt% $m_{soln.}$ = 8.0 g	$Rh_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ (in CH_3OH)	95.2	98.7	
t = 10 h	$Rh_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ (in C_2H_5OH)	91.0	98.7	
	$Rh_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ (0.5 g_{cat} in C_2H_5OH)	47.8	98.3	
	$Rh_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.94}O_{8.51}$ (0.5 g_{cat} in C_2H_5OH)	48.5	98.2	
prepared by co-precipitation	$Rh_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.90}O_{8.45}$ (0.5 g_{cat} in C_2H_5OH)	49.3	98.1	
	$Rh_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ (0.4 g_{cat} in C_2H_5OH, T=200 ˚C)	66.1	98.4	
	$Rh_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ (0.3 g_{cat} in C_2H_5OH, T=220 ˚C)	91.7	98.3	
	Water content in bioethanol (wt%) 0, 10, 20, 30, 40	91.0, 84.0, 81.8, 77.8, 69.3	98.7, 99.2, 99.3, 99.3, 98.5	
	Reuse (in 75% ethanol) 1,2,3,4	91.0, 63.6, 56.7, 53.6	98.7, 96.3, 95.9, 96.0	
T= 180˚C	$Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$	56.7	97.1	[68]
P= 2.0 MPa H_2	$Pd_{0.008}Cu_{0.4}/Mg_{5.592}Al_2O_{8.592}$	59.1	96.8	
m_{cat} = 1.0 g	$Pd_{0.024}Cu_{0.4}/Mg_{5.576}Al_2O_{8.576}$	70.5	97.9	
$C_{glycerol}$= 75 wt%	$Pd_{0.04}Cu_{0.4}/Mg_{5.56}Al_2O_{8.56}$	76.9	97.2	
$M_{glycerol}$ = 8.0 g	$Pd_{0.08}Cu_{0.4}/Mg_{5.52}Al_2O_{8.52}$	66.6	97.5	
t= 10 h	$Pd_{0.04}/Mg_{5.56}Al_2O_{8.56}$	1.2	79.9	
	$Pd_{0.04}Cu_{0.4}/Mg_{5.56}Al_2O_{8.56}$ (in CH_3OH)	89.5	98.2	
prepared by co-precipitation	$Pd_{0.04}Cu_{0.4}/Mg_{5.56}Al_2O_{8.56}$ (in C_2H_5OH)	88.0	99.6	
	$Pd_{0.04}Cu_{0.4}/Mg_{5.56}Al_2O_{8.56}$ in H_2O, mcat (g) 0.25, 0.5, 1.0, 1.5	24.7, 48.7, 76.9, 91.2	97.8, 97.6, 97.2, 97.0	
	Temperature (˚C) 120, 150, 180, 200	10.4, 30.8, 76.9, 95.0	96.0, 99.3, 97.2, 96.1, 97.9	
	Recycle 5th use	50	97.9	
T= 180˚C	$Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$	56.7	97.1	[69]
P= 2.0 MPa H_2	$Cu_{0.4}/Zn_{0.3}Mg_{5.3}Al_2O_{8.6}$	60.3	99.4	
m_{cat} = 1.0 g	$Cu_{0.4}/Zn_{0.6}Mg_{5.0}Al_2O_{8.6}$	78.2	99.3	
$C_{glycerol}$= 75 wt%	$Cu_{0.4}/Zn_{1.9}Mg_{3.7}Al_2O_{8.6}$	64.3	99.2	
$m_{soln.}$ = 8.0 g	$Cu_{0.4}/Zn_{2.8}Mg_{2.8}Al_2O_{8.6}$	29.6	98.1	
t= 10 h	$Cu_{0.4}/Zn_{3.7}Mg_{1.9}Al_2O_{8.6}$	18.9	99.4	
	$Cu_{0.4}/Zn_{5.6}Al_2O_{8.6}$	14.1	98.9	
	$Cu_{0.4}/Zn_{0.6}Mg_{5.0}Al_2O_{8.6}$	85.5	98.6	
	Catalyst weight (g) 0.2, 0.4, 0.6, 0.8, 1.0	22.6, 39.7, 55.7, 65.7, 78.2	99.5, 99.6, 99.3, 99.2, 99.3	
P= 2.0 MPa H_2 mcat = 0.4 g mglycerol = 6.0 g	Glycerol Concentration (wt%) 50, 60, 75, 85	11.5, 24.6, 39.7, 29.4	99.4, 99.5, 99.6, 98.6	
t= 10 h Prepared by co-precipitation	Temperature (˚C) 160, 180, 200	12.8, 39.7, 85.5	99.6, 99.4, 98.6	

2.2.1.8 Cu on ZrO_2

Zirconia (ZrO_2) as support for copper has also been investigated. A 1,2 PDO selectivity of 99.6% was observed for the liquid product at 28.0% glycerol conversion. Addition of Ru at 8:10 Cu:Ru ratio improved glycerol conversion to 50.60%, while it retained the 1,2 PDO in the liquid product. The increase in Ru content in the catalyst of Cu on ZrO_2 improved glycerol conversion, but reduced the 1,2 PDO selectivity. The improvement in catalytic activity was attributed to the synergistic effect of Cu-Ru combination. A raise in reaction temperature from 120˚C to 180˚C improved both glycerol conversion and 1,2 PDO selectivity. However, further increase in temperature caused a decline in both glycerol conversion and 1,2 PDO selectivity. Glycerol conversion was enhanced with increase in hydrogen pressure from 1 to 4 MPa, but further increase did not affect the catalyst activity [70].

Table 2.9 Summary of Cu supported on ZrO_2 catalyst investigation for glycerol conversion to 1,2 PDO.

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
T= 180˚C P= 10.0 MPa H_2 $C_{glycerol}$= 60 wt% $V_{soln.}$ = 0.5 mL m_{cat} = 0.05g (Cu/Ru = 1/10 mol/mol) $Frate_{glycerol}$ = 0.5 mL/ h $Frate_{H2}$ = 10 mL/ min t = 24 h	Cu–Ru/ZrO_2 Cu:Ru (atom:atom) 0:1, 1:10, 3:10, 5:10, 8:10, 1:0	100, 100, 90.2, 77.6, 50.60, 28.0	1,2 PDO (Liquid-products) 47.7(38.7), 84.0(87.0), 89.4(88.0), 94.0(92.4), 99.6(97.6), 99.6 (97.0)	[70]
	1:10 Temperature (˚C) 120, 150, 180, 200	47.2, 87.6, 100, 75.6	76.4(89.2), 77.3(83.6), 87.0(100), 75.6(100)	
	Hydrogen Pressure (MPa) 1, 4, 8 10 prepared by incipient wetness co-impregnation	15.2, 100, 100, 100	85.0(92.0), 81.0(80.9), 83.5(94.0), 84.0(87.0)	

2.2.1.9 Ni Catalysts

Nickel catalysts for selective hydrogenolysis of glycerol to 1,2 PDO have also been reported (Table 2.10) with Raney® Ni used as the catalyst in earlier investigations [71-73]. The raise in reaction temperature and amount of catalyst used enhanced glycerol conversion, but had an opposite effect on the 1,2 PDO selectivity [71-72]. As high as 93% 1,2 PDO selectivity was achieved at 150˚C with 12% of the glycerol converted [71]. The increase in hydrogen pressure from 2.0-4.0 MPa lowered the glycerol conversion, while 1,2 PDO selectivity improved. However, further increase in hydrogen pressure did not affect both glycerol conversion and 1,2 PDO selectivity [72]. A reduction in both glycerol conversion and 1,2 PDO selectivity was observed with the increase in glycerol concentration. A lower glycerol conversion was achieved with biodiesel derived glycerol as feedstock. A similar 1,2 PDO selectivity was attained for both purified and biodiesel derived glycerol [72]. The addition of Bu_4PBr lowered both the glycerol conversion and 1,2 PDO selectivity. On the other hand, the addition of $(C_6H_{13})_3C_{14}H_{29}PCl$ slightly improved 1,2 PDO selectivity, but reduced the glycerol conversion [71]. Production of 1,2 PDO under nitrogen environment has also been achieved with Raney Ni through in situ hydrogen generation from the aqueous glycerol feed. Glycerol conversion improved with time. However, the 1,2 PDO selectivity declined with time due to further hydrogenolysis to other products such as methanol and ethanol. A Change in water concentration from 70 wt% to 50 wt% improved the 1, 2 PDO selectivity from 24% to 33%, but declined to 16% with further reduction of water concentration to 30 wt% [73].

In a study of working with a commercial catalyst of Ni on SiO_2, a raise in the reaction temperature from 230˚C to 320˚C improved the glycerol conversion. However, 1,2 PDO selectivity declined from 70.6% to 4.6% due to the increase in by-products. Hydrogen pressure increase from 4.0 to 7.5 MPa reduced both the glycerol conversion and 1,2 PDO selectivity [74]. The addition of Ce to an SBA-15 supported Ni catalyst prepared by impregnation enhanced both glycerol conversion and 1,2 PDO selectivity. At 7.5% Ce, 1,2 PDO selectivity and glycerol conversion reached 29% and 50%, respectively.[75]. The extension of the reaction time from 8 to 10 hours improved glycerol conversion, but caused a drop in 1,2 PDO selectivity due to its partial decomposition. An increase in hydrogen pressure from 3 MPa to 4.6 MPa slightly improved glycerol conversion and the 1,2 PDO selectivity from ~50% and 29% to ~55% and 32%, respectively. The incorporation of phosphorous to the Ni catalyst on SiO_2 enhanced glycerol conversion and 1,2 PDO selectivity. A 1,2 PDO selectivity of up to 92% was achieved with 55% of the glycerol converted at 220˚C and 3.0 MPa of H_2 [75].

The Ni catalyst on Al_2O_3 or its combinations have also been shown to be effective for the selective hydrogenolysis of glycerol to 1,2 PDO [74, 76-78]. The use of a commercial Ni on

Al_2O_3 catalyst was investigated in a continuous reactor [74]. The raise in reaction temperature from 230˚C to 320˚C improved glycerol conversion, but the 1,2 PDO selectivity declined. The highest 1,2 PDO selectivity reached 79.9% with 15.9% of the glycerol converted at 230˚C. The increase in reaction temperature from 170˚C to 250˚C also improved glycerol conversion using the Ni catalyst on Al_2O_3-SiO_2 [76]. The favorable temperature for 1,2 PDO selectivity was at 200˚C. The increase in the amount of catalyst used from 2.5 wt% to 5.0 wt% improved glycerol conversion and 1,2 PDO selectivity. A decline in both glycerol conversion and 1,2 PDO selectivity was observed with further increase in catalyst amount to 5.5 wt%. The increase in hydrogen pressure from 0.8 MPa to 2.5 MPa enhanced both glycerol conversion and 1,2 PDO selectivity from 7% to 30% and 46% to 98%, respectively [76]. The catalyst of Ni/Al_2O_3-CuCr combination gave a better catalytic performance when used and prepared as a single catalyst as compared to a combination of physically mixed catalysts [77]. A Ni to Cu ratio of 0.03:1 gave the best 1,2 PDO selectivity and glycerol conversion at 94% and 32%, respectively. The re-use of the catalyst caused a drop in both glycerol conversion and 1,2 PDO selectivity. Retention of the catalytiv activity was observed to be dependent on the solvent used for washing the catalyst. The catalyst washed with methanol gave the best retention of the catalyst activity [77].

Various types of zeolite were tested as the support for Ni based catalysts prepared via impregnation for the selective hydrogenolysis of glycerol to 1,2 PDO [78]. Among them, Ni on NaX showed the best 1,2 PDO yield. A decrease in Na content from 9.49 wt% to 3.21 wt% improved the glycerol conversion. The highest selectivity was achieved at a Na content of 9.32 wt%. The observed trend in the activity of the activity was attributed to the surface acidity of the zeolite support. The increase in reaction temperature from 140˚C to 220˚C improved the glycerol conversion, but lowered the 1,2 PDO selectivity of the catalyst Ni catalyst supported on zeolite with 8.78 wt% of Na. As high as 88% 1,2 PDO selectivity was observed with 22% of the glycerol converted. Both glycerol conversion and 1,2 PDO selectivity improved with the increase in hydrogen pressure from 3 to 6 MPa. However, further increase in hydrogen pressure restuled in a drop of the 1,2 PDO selectivity. Glycerol conversion improved with extension of reaction time. A similar 1,2 PDO selectivity was maintained until 8 hours of reaction, but declined afterwards [78].

The Ni catalyst in combination with Ce, Cu, Co, Sn, Zn, Al, and Fe, supported on activated carbon (AC) were tested for its catalytic activity for the hydrogenolysis of glycerol to 1,2 PDO [80]. The Ni-Co combination gave the highest 1,2 PDO selectivity at 82.1% with 35.31% of the glycerol converted. However, the highest glycerol conversion was achieved using the catalyst of Ni-Ce on AC combination. Up to 90.4% of glycerol was converted, but the 1,2 PDO selectivity only reached 65.7%. An improvement in glycerol conversion was observed with the increase in temperature (160˚C to 200˚C), water content (25 wt% to 75 wt%), hydrogen pressure, and reaction time (2 to 8 h), while the selectivity was not affected using the catalyst of Ni-Ce on AC [80].

Table 2.10 Summary of various Ni catalyst investigations for glycerol conversion to 1, 2 PDO.

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
P= 1.01 MPa H_2 $m_{glycerol}$ = 8.0 g m_{cat} = 2.0 g	Raney® Ni Temperature (˚C):time(h) 150:20, 190:8, 190:20, 190:44, 210:20	12, 32, 63, 97, 91	93, 79, 77, 71,48	[71]
	RaneyNi + Bu_4PBr (2.0 g) 190, 20	49	68	
	RaneyNi +2.0 g $(C_6H_{13})_3C_{14}H_{29}PCl$ 190,20	47	81	
T= 230˚C P= 4.0 MPa H_2 $V_{soln.}$ = 80 mL $C_{glycerol}$= 20 wt% C_{cat} = 21 g L Agitation = 400 rpm t= 9 h	Raney® Ni Pure glycerol (Biodiesel Derived Glycerol)			[72]
	Agitation (rpm) 200, 300, 400	~52(31), 52(37), 48 (46)	~23(25), 28(34), 33(26)	
	Temperature (˚C) 200, 210, 220, 230, 240	~25(18), 36(21), 43 (33), 49(46), 64 (48)	~36(38), 38 (40), 32 (40), 35(25), 27(30)	
	Hydrogen Pressure (MPa) 2.0, 4.0, 6.0	~56(49), 47(45), 46(41)	~28(24), 36(26), 35 (35)	
	Catalyst Amount (g/L) 7, 21, 35	~(23)5, 48(46), 80(74)	~54(50), 33(25), 23(23)	
	Glycerol content (%) 10, 20, 30	~57(59), 48(46), 42(30)	~36(41), 34(25), 28(38)	
T=230˚C Water:Glycerol =1:1 (mass ratio) t= 0.75 h	Raney® Ni Reaction time (min) 15, 45, 75, 105	91.1, 98.6, 99.6, 99.9	~33, 29, 23, 17	[73]
	Water: Glycerol (mass) 7:3, 3:7	99.9, 95.3	~24, 16	
T= 230˚C P= 6.0 MPa H_2 $V_{soln.}$ = 60 mL V_{cat} = 5 mL $C_{glycerol}$= 100 wt%	Ni/SiO2, TA= 2.175 Temperature (˚C) 230, 250, 275, 300, 320	16.2,34.9, 69.3, 99.8, 99.9	70.6, 69.1, 47.8, 19.0, 4.6	[18]
	Pressure (MPa)			

H2:Glycerol = 2:1 (molar ratio) GHSV= 1060/ h LHSV = 3.0/ h	4.0, 6.0, 7.5	14.5, 16.2, 13.0	77.9, 70.6, 67.8	
	Ni/Al_2O_3, TA = 1.924 Temperature (˚C) 230, 250, 275, 300, 320	15.9, 25.6, 39.3, 83.7, 96.1	79.9, 70.2, 36.7, 12.1, 1.8	
T= 200˚C P= 2.4 MPa H_2 m_{cat} = 0.6 g $C_{glycerol}$= 80 wt% $m_{soln.}$ = 25.0 g Agitation = 500 rpm t= 8 h	Ni-Ce/SBA % Ce 0, 2.5, 5.0, 7.5 10	~26,33,43,50,45	~2,5,28,29, 14	[74]
	7.5% Ce-Ni-SBA time (h) 6, 8, 10	~47, 50, 52	~23, 29,17	
	Pressure (MPa) 3, 4.6	~50, 56	~29, 32.5	
	impregnated by the incipient wetness method			
T= 220˚C P= 3.0 MPa H_2 $C_{glycerol}$= 60 wt% WHSV = 1.13/ h H_2/glycerol = 20	Ni/SiO_2 Ni_2P/SiO_2	73.2	49.9	[75]
	Pressure (MPa) 2, 3, 4	~92, 95, 88	~88, 86, 80	
	WHSV=1.73 h Temperature (˚C) 220, 230,240	~55, 88, 97	~92, 84, 77	
	Prepared by impregnation method			
T= 200˚C $C_{glycerol}$ = 100 wt% m_{cat} = 5 wt% t= 8h	$Ni/Al_2O_3–SiO_2$ pH_2= 1.5 MPa Temperature (˚C) 170, 180, 190, 200, 210, 220, 230, 240, 250	~3,10,16,18,24,29, 54, 67, 76	~48, 56, 60, 84, 76, 64, 26, 18, 10	[76]
	pH_2= 2.0 MPa catalyst content (wt%) 2.5, 2.75, 3.0, 3.5, 4.0, 4.25, 4.5, 5.0, 5.5	~9, 10, 12, 14, 17, 18, 18, 24, 18	~66, 72, 73, 77, 78, 80, 86, 91, 80	
	Hydrogen Pressure (MPa) 0.8, 1.5, 2.0, 2.5	~7, 21, 24, 30	~46, 80, 92, 98	
T= 200˚C P = 2.5 MPa H_2 $C_{glycerol}$ = 100 wt% m_{cat} = 5 wt% t= 8h	$Ni/Al_2O_3–CuCr$ Physically mixed catalyst combination Ni/Cu (mass ratio) 0.03, 0.05, 0.08, 0.17, 0.44, 0.94	~22, 22,21, 20, 17, 16	~ 87, 87, 84, 81,78, 78	[77]
	Single catalyst Ni/Cu (mass ratio) 0.03, 0.05, 0.08, 0.17, 0.44, 0.94	~32, 28, 26, 24, 22, 17	~94,88, 87, 84, 83, 79	
	Reaction time (h) 4, 8, 12, 16, 20 (Ni/Cu = 0.03 mass ratio)	~21, 32, 35, 42, 46	~85, 94, 96, 97, 96	
	Catalyst Reuse Fresh	32.11	94.05	
	Reused, washing solvent Water, methanol, ethanol, 2-propanol	17.1, 30.2, 21.0, 15.3	53.3, 82.3,75.9, 78.7	
	prepared impregnation technique			
T= 200˚C P= 6.0 MPa H_2 m_{cat} = 2.0 g $m_{soln.}$ = 160.0 g Agitation = 500 rpm t = 10 h	Ni/NaMOR	14.0	56.7	[78]
	Ni/NaZSM-5	47.8	9.4	
	Ni/NaA	65.3	46.8	
	Ni/NaX	94.5	72.1	
	Ni/SiO_2	56.9	44.4	
	$Ni/\gamma\text{-}Al_2O_3$	97.1	44.2	
	Ni/NaX Na+ content (wt%)	79.8, 86.6, 94.5,	72.1, 80.4, 72.1,	

	9.49, 9.32, 8.78, 3.21	96.8	64.9	
	Ni/NaX (8.78% Na)			
	Temperature (˚C)	~22, 55, 78, 94, 96	~88, 83, 77, 72, 40	
	140, 160, 180, 200, 220			
	H_2 Pressure (MPa)	~54, 82, 86, 93, 93	~45,50, 58, 72,64	
	3, 4, 5, 6,7			
	Reaction time (hr)	~24, 42, 58, 71, 94	~84, 84, 86, 84, 72	
	2, 4, 6, 8 ,10			
	Prepared by incipient impregnation			
T= 200˚C	Ni–Ce/AC	90.4	65.7	[79]
P = 5.0 MPa H_2	Ni–Cu/AC	57.5	77.9	
$C_{glycerol}$ = 25 wt%	Ni–Co/AC	35.3	82.1	
$V_{soln.}$ = 150 mL	Ni–Sn/AC	34.1	63.4	
m_{cat} = 6.95 g	Ni–Zn/AC	65.6	73.5	
t = 6 h	Ni–Al/AC	73.2	70.3	
	Ni–Fe/AC	68.1	70.4	
	Ni-Ce/AC			
	Temperature (˚C)			
prepared by incipient wetness	160, 180, 200	~63, 88, 95	~63, 68, 63	
impregnation followed	Pressure (MPa H_2)			
by the process of carbothermal	3 (8 h), 5, 7	~68, 90, 92	~68, 66, 66	
reduction and KBH4 treating	Glycerol concentration (wt%)			
	25, 50, 75	~90, 75, 69	~66, 68, 63	
	Time (h)			
	2, 4, 6, 8	~63, 83, 90, 95	~73, 67, 65, 62	

2.2.2 Ethylene Glycol

Ethylene glycol (EG), a clear, colorless, odorless and sweet tasting liquid, which finds its use as an antifreezing agent, raw material for polyester fibers (i.e., polyethylene terepthalate), plasticizer, solvent, hydraulic fluid, and solvent [81], has a market value of approximately $ 0.99/ kg [17]. Currently, EG is produced via the hydrolysis of ethylene oxide. Alternately, it can be produced by direct catalytic oxidation of ethylene and the catalytic conversion of synthesis gas [81]. EG has also been produced as one of the products from hydrogenolysis of carbohydrates [82-83]. Ethylene glycol can also be obtained from the hydrogenolysis of glycerol, but usually not as the main product.

In this section we present some works on the hydrogenolysis of glycerol when EG is a co/by-product using either Cu or Ni catalyst with a selectivity of at least 30% (Table 2.11).

In a gas phase hydrogenolysis of glycerol, various catalysts of Cu on Zn:Al:Ti:Zr combinations were tested [84]. Among them, the catalyst of Cu on Zn-Ti combination prepared via co-precipitation produced the most EG. Temperature greatly influenced the dominant product formed and its increase from 240˚C to 280˚ improved the EG selectivity. The highest EG selectivity was observed with the catalyst of Cu:Zn:Ti ratio of 1:2:1 at 37%

with 100% glycerol conversion. The observed catalyst activity and EG selectivity resulted from the presence of weak to mild acid sites and small-sized metallic Cu in the catalyst of Cu-Zn-Ti combination [84]. The catalyst of Cu-Cr on γ-Al_2O_3 prepared by impregnation was found to produce EG under the hydrogen or CO_2 environment. In general, hydrogenolysis in CO_2 environment, lower gas flow rate, and lower temperature resulted in a higher EG selectivity. The highest EG selectivity observed was 64.8% with 85% of the glycerol converted under hydrogen environment at 150˚C and a Cu:Cr ratio of 9:1 [85].

A Cu-Ru bimetallic catalyst on various supports prepared by incipient wetness co-impregnation was investigated for its glycerol hydrogenolysis activity. Among the supports tested, the catalyst of Cu-Ru on SiO_2 gave the highest EG selectivity. The EG produced accounted for 43.4% of the liquid product at 12.5% glycerol conversion with 70.3% of the glycerol converted going to the liquid products [70]. In another work using the catalyst of Cu-Ru combination, various ratios of Cu:Ru were supported by a 1,1,3,3- tetramethyl-guanidinium lactate (TMGL) modified bentonite [86]. The catalyst with a Cu:Ru ratio of 0.5:3 gave the highest EG selectivity in the liquid product at 37.3% with 71.9% of the glycerol converted and 34.4% of the glycerol converted going to the liquid products. A Ni catalyst on SiO_2 also exhibited high EG production potential from glycerol hydrogenolysis, which attained an EG selectivity of 30.4% at a glycerol conversion of 73.2% [75].

Table 2.11 Summary of various Cu and Ni catalysts investigations for conversion of glycerol to EG

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
T= 280˚C P= 0.1 MPa H_2 V_{cat}= 5 mL $C_{glycerol}$= 16.67 wt% $Frate_{glycerol}$ = 4.2 mL/ h $Frate_{H2}$ = 25 mL/ min t= 1 h	Cu:Zn:Al:Ti:Zr ; TA (mmol NH_3/gcat); Temperature (˚C) 1 : 2 : 0 : 1 : 0 ; 1.27; 240, 260, 280, 300 1 : 2 : 0 : 2 : 0; 2.25; 240, 260, 280, 300 2 : 2 : 0 : 1 : 0 ; 1.21; 240, 260, 280, 300 prepared by a continuous coprecipitation method	~100, 100, 100, 100 ~100, 100, 100, 100 ~100, 100, 100, 100	~8, 21, 37, 36 ~6, 19, 33, 32 ~6, ~16, 32, 31	[83]
T= 150˚C m_{cat}= 5 g $C_{glycerol}$= 50 wt% $Frate_{glycerol}$ = 1 mL/ h $Frate_{H2}$= 30 mL/ h	10 wt % Cu /γ-Al_2O_3 Glycerol Flowrate (mL/ h) 0.5, 1, 1.5, 2 Gas Type CO_2 (mL/ h) 30, 60, 120 H_2 (mL/h)	 97.3, 98.7, 87.8, 74.8 94.6, 77.8, 55.7	 44.5, 48.5, 42.1, 48.4 60.2, 55.1, 48.1	[84]

	30, 60, 120 Cu-Cr/γ-Al_2O_3 Cu:Cr (wt%) 10:0 Temperature (˚C) 150, 160, 170, 180, 190 5:5 Temperature (˚C) 150, 160, 170, 180, 190 3:7 Temperature (˚C) 150, 160, 170, 180, 190 7:3 Temperature (˚C) 150, 160, 170, 180, 190 9:1 Temperature (˚C) 150, 160, 170, 180, 190 prepared by wet impregnation	98.7, 95.3, 96.7 98.7, 99.1, 98.9, 98.4, 99.2 97.4, 98.1, 95.8, 97.0, 98.5 92.5, 94.2, 94.4, 93.8, 95.3 94.8, 96.2, 94.9, 96.1, 96.9 85.0, 83.2, 83.8, 79.4, 81.60	48.5, 29.4, 38.9 48.5, 37.9, 31.0, 27.1, 24.7 44.1, 38.1, 27.2, 21.5, 23.1 45.5, 37.1, 25.3, 23.2, 21.2 52.2, 37.1, 20.3, 24.3, 19.2 64.8, 47.7, 25.2, 21.4, 20.5	
T= 180˚C P= 10.0 MPa H_2 $C_{glycerol}$= 60 wt% $V_{soln.}$ = 0.5 mL m_{cat} = 0.05g (Cu/Ru = 1/10 mol/mol) $Frate_{glycerol}$ = 0.5 mL/ h $Frate_{H2}$ = 10 mL/ min t = 24 h	Ru–Cu/SiO_2 Ru–Cu/TiO_2 Ru–Cu/ZrO_2 Ru–Cu/Al_2O_3 Ru–Cu/HY Ru–Cu/NaY prepared by incipient wetness co-impregnation	12.5 78.6 100 68.0 47.3 32.3	Liquid, EG 70.3, 43.4 78.0, 21.1 87.0, 9.3 74.8, 20.1 59.4, 0 32.1, 8.4	[70]
T= 195˚C P= 10.0 MPa H_2 V_{water} = 1.0 mL $n_{glycerol}$= 5 mmol C_{cat} = 0.6 mol. % Agitation = 400 rpm t= 18 h Prepared via impregnation TMG-BEN 1,1,3,3-tetramethyl-guanidinium lactate (TMGL) modified Bentonite (58.98% SiO_2, 19.82% Al_2O_3, 3.73% MgO, 5.18% Na_2O, 0.42% K_2O, 0.87% CaO, 1.31% Fe_2O_3, 0.10% TiO_2, 0.74% P_2O_5, and 0.08% FeO)	Ru-Cu/TMG-BEN (3 wt% Ru) Ru/Cu = 3/0 Ru/Cu = 3/0.5 Ru/Cu = 3/1 Ru/Cu = 3/2 Ru/Cu = 3/3 Ru/Cu = 3/4 Ru/Cu =3/9 Ru/Cu = 0/3 Ru/Cu = 3/1 (T=210˚C) Ru/Cu = 3/1 (T=230˚C)	90.7 71.9 70.9 66.1 64.4 41.7 27.0 26.5 71.4 100.0	Liquid, EG 27.4, 32.7 34.4, 37.3 46.1, 23.6 40.4, 24.8 30.6,28.6 23.4,23.7 22.0, 17.9 59.1, 11.6 65.0, 14.7 98.5, 9.4	[85]
T= 220˚C P= 3.0 MPa $C_{glycerol}$= 60 wt% WHSV = 1.13/h H_2/glycerol = 20	Ni/SiO_2 Prepared by impregnation method	73.2	30.4	[74]

2.2.3 Propanols

The 1-propanol and 2-propanol are sold approximately at \$1.14/ kg and \$0.62-1.1/ kg, respectively [13]. Aside from being used as a solvent, 1-propanol also finds its use as a raw material for the production of propylamines, glycol ethers, and n-propyl propionate; while 2-propanol also finds applications as an antiseptic, raw material for production of acetone, monoisopropylamine (herbicide and pesticide production), isopropyl acetate, fuel blends (octane enhancement), and carburetor anti-icing additive.

Table 2.12 Summary of Cu and Ni catalyst investigations for glycerol conversion to propanols

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
T= 210˚C P= 4.1 MPa H_2 $V_{soln.}$ = 60 mL m_{cat} = 5 wt% (based on glycerol) $C_{glycerol}$= 60 wt% Agitation = 150 rpm t= 10 h	Cu-Cr (Cu/Cr molar ratio) 0, 0.5, 2, 4, 6	~0, 28, 43, 45, 43	1-Propanol (2-Propanol) ~0 (0), 36(3), 34 (2), 34(1), 39(1)	[27]
	Cu/Cr =4 Reaction time (h) 3, 5, 7, 10, 17	~44, 47, 50, 53, 56	~11(1), 9(1), 23(1), 29(1), 55(1)	
	Reaction temperature (˚C) 180, 195, 210, 230	~8, 24, 47, 64	~2(4), 11(2), 20(0), 48 (1)	
	Hydrogen Pressure (MPa) 2,3, 4.1, 5	32, 45, 47, 58	3(2), 10 (1), 19(1), 53(1)	
	Glycerol Concentration (%) 20, 40, 60, 80, 100	~32, 38, 46, 78, 92	~88(1), 67(2), 20(0), 13 (0), 5(0)	
	Agitation (rpm) 150, 300, 600, 900 Synthesized by sol-gel route	49.2, 73.4, 78.7, 85.9	34.9 (0.7), 2.7(0.2), 7.5 (0.2), 1.1(0)	
T= 210˚C P= 4.1 MPa m_{cat}= 5wt% $C_{glycerol}$= 60 wt% t= 10 h Agitation = 150 rpm Batch Prepared by an epoxide-assisted procedure	Cu-Cr-OH(500) Calcined in 20% O_2/Ar at 500˚C (surface area 230 m^2)	32	1-Propanol, 2-Propanol 36, 2	[28]
	Cu-Cr-OH(400) Calcined in 20% O_2/Ar at 400˚C (surface area 230 m^2)	20	50, 3	
	Cu-Cr-OL(400) Calcined in 20% O_2/Ar at 400˚C (surface area 94 m^2)	11	49, 3	
	Cu-Cr-Ar(400) Calcined in Ar at 400˚C (surface area 230 m^2)	6	32, 7	
T= 260 ˚C P= 6.0 MPa H_2 $C_{glycerol}$= 10 wt% m_{cat} = 4.0 g LHSV= 0.9/ h	5Cu-5STA/Al_2O_3 Temperature (˚C) 180, 210, 240, 270	2.5, 31.2, 90.1, 97.4	1- Propanol 0, 1.6, 1.5, 49.5	[54]
T= 240˚C P= 6.0 MPa H_2 m_{cat} = 4.0 g $C_{glycerol}$= 10 wt% LHSV = 0.9/ h prepared by means of incipient wetness impregnation method	5Cu/ZrO_2	37.79	1-Propanol 41.56	[47]
	20 Cu/γ-Al_2O_3 Temperature (˚C) 180, 210, 240, 270	8.25, 31.15, 85.05, 95.55	0, 1.07, 0.52, 40.46	
T= 180˚C P= 10.0 MPa H_2 $C_{glycerol}$= 60 wt% $V_{soln.}$ = 0.5 mL m_{cat} = 0.05g (Cu/Ru = 1/10 mol/mol) $Frate_{glycerol}$ = 0.5 mL/ h $Frate_{H2}$ = 10 mL/ min t = 24 h prepared by incipient wetness co-impregnation	Ru–Cu/SiO_2	12.5	Liquid, 2-Propanol, 1- Propanol 70.3, 1.1, 8.3	[70]
	Ru–Cu/TiO_2	78.6	78.0, 1.0, 10.6	
	Ru–Cu/ZrO_2	100	87.0, 0.1, 6.4	
	Ru–Cu/Al_2O_3	68.0	74.8,1.5, 31.3	
	Ru–Cu/HY	47.3	59.4, 0, 62.3	
	Ru–Cu/NaY	32.3	32.1, 4.0, 87.5	
T= 230-320 ˚C P= 6.0 MPa H_2 $V_{soln.}$ = 60 mL V_{cat} = 5 mL $C_{glycerol}$= 100 wt% H_2:Glycerol = 2:1 (molar ratio) GHSV= 1060/ h LHSV = 3.0/ h	Ni/SiO_2, TA= 2.175 Temperature (˚C) 230, 250, 275, 300, 320	16.2, 34.9, 69.3, 99.8, 99.9	1- Propanol 0.6,6.3, 14.2, 36.6, 42.8	[18]
	Ni/Al_2O_3, TA = 1.924 Temperature (˚C) 230, 250, 275, 300, 320	15.9, 25.6, 39.3, 83.7, 96.1	0.5, 2.4, 12.1, 24.4, 35.3	

Production of 1-propanol can be through hydrogenation of propanal via the hydroformylation of ethylene, propylene oxide isomerization and hydrogenation, catalytic conversion of a synthesis gas, methanol, and the Guerbet reaction. The 2-propanol can be produced via direct or indirect hydration of propene, and hydrogenation of acetone [87].

Propanols were observed to be produced from the hydrogenolysis of glycerol using Cu-Cr catalyst with 1-propanol production higher than 2-propanol [27-28]. Propanol production was favored by higher Cu to Cr ratio, reaction time, hydrogen pressure, and a lower glycerol concentration and rate of agitation. A 1-propanol selectivity of up to 55% was achieved with 56% of the glycerol converted at a Cu to Cr ratio of 4, 210˚C, and 4.1 MPa of hydrogen [27]. Variation of the calcination conditions also affected the catalyst activity and selectivity for propanol. The Cu-Cr catalyst calcined with 20% O_2 and 80% Ar at 400˚C achieved a selectivity of 50% for 1-propanol at 20% glycerol conversion. Up to 7% 2-propanol selectivity was achieved with the catalyst calcined under Ar environment at 400˚C [28]. The catalysts of Cu [47] and 5Cu-5STA [54] on Al_2O_3 were also able to produce 1-propanol at high levels. At 270˚C, the 1-propanol selectivity reached 40.46% and 49.5% for the catalysts Cu on Al_2O_3 and 5Cu-5STA, respectively. The Cu catalyst on ZrO_2 achieved a1-propanol selectivity of 41.56% at 37.79% glycerol conversion [54].

The use of the catalyst of Ru-Cu combination on several supports allowed production of 1-propanol and 2-propanols at high levels, especially for 1-propanol with zeolites as the support [70]. The high 1-propanol selectivity was attributed to the acidic nature of zeolite. Up to 87.5% 1-propanol selectivity was achieved at 32.3% glycerol conversion. However, only 32.1% of the glycerol converted went to the production of liquid products with NaY as the support [70]. The Ni catalysts supported on SiO_2 and Al_2O_3 also produced 1-propanol at high levels. Higher temperatures favored the 1-propanol production. Silica supported Ni catalyst gave a better 1-propanol selectivity at 42.8% with 99.9% of the glycerol converted at 320˚C[74].

2.2.4 Ethanol

Ethyl alcohol (CH_3CH_2OH), also known as ethanol, is used for alcoholic beverage, solvent, raw material in chemical synthesis (e.g., acetaldehyde, butadiene, diethyl ether, ethyl acetate, ethylamines, ethylene, glycol ethers, acetic acid and, etc.), and fuel. It is produced chemically via direct and indirect catalytic hydration of ethylene, homologation of methanol, carbonylation of methanol and methyl acetate, synthesis gas conversion, and fermentation of sugars [88]. Ethanol has been observed to be produced as a by-product from glycerol hydrogenolysis. In this section, studies regarding glycerol hydrogenolysis where at least 10% selectivity for ethanol was observed using Ni or Cu catalysts are presented (Table 2.13).

Table 2.13 List of various Ni and Cu catalysts investigations for conversion of glycerol to ethanol

Conditions	Catalyst (Preparation)	Conversion (%)	Selectivity (%)	Reference
P= 1.01 MPa H_2 $m_{glycerol}$ = 8.0 g mcat = 2.0 g	Raney Ni Temperature (˚C):time(h) 150:20, 190:8, 190:20, 190:44, 210:20 RaneyNi + Bu_4PBr (2.0 g) 190, 20 RaneyNi +2.0 g $(C_6H_{13})_3C_{14}H_{29}PCl$ 190,20	12, 32, 63, 97, 91 49 47	1, 18, 15, 19, 40 26 13	[71].
T= 230-320 ˚C P= 6.0 MPa H_2 Vsoln. = 60 mL Vcat = 5 mL Cglycerol= 100 wt% H2:Glycerol = 2:1 (molar ratio) GHSV= 1060/h LHSV = 3.0/h	Ni/SiO2, TA= 2.175 Temperature (˚C) 230, 250, 275, 300, 320 Ni/Al_2O_3, TA = 1.924 Temperature (˚C) 230, 250, 275, 300, 320	16.2, 34.9, 69.3, 99.8, 99.9 15.9, 25.6, 39.3, 83.7, 96.1	5.4, 6.6, 12.4, 16.9, 20.2 9.0, 8.4, 10.6, 11.4, 16.8	[18]
T= 220˚C P= 3.0 MPa Cglycerol= 60 wt% WHSV = 1.13/h H_2/glycerol = 20	Ni/SiO_2 Prepared by impregnation method	73.2	12.4	[75]
T= 240˚C P= 6.0 MPa H_2 mcat = 4.0 g Cglycerol= 10 wt% LHSV = 0.9/h	5 Cu/HZSM-5 prepared by means of incipient wetness impregnation method	2.1	20.68	[47]

Hydrogenolysis of glycerol using Raney® Ni produced ethanol in high quantities along with 1,2 PDO. An ethanol selectivity of 40% was observed with 91% of the glycerol converted at 210˚C under 1.01 MPa of hydrogen [71]. The increase in reaction temperature and time improved both glycerol conversion and ethanol selectivity. The addition of addition of Bu_4PBr and $(C_6H_{13})_3C_{14}H_{29}PCl$ caused a decline in the glycerol conversion, while the ethanol selectivity was improved by the addition of the former but declined upon addition of the latter. The Ni catalyst supported on SiO_2 [74, 58] and Al_2O_3 [74] were also observed to produce ethanol from glycerol hydrogenolysis. Ethanol production improved with the increase in the reaction temperature due to the increase in degradation products. At 320˚C, ethanol selectivity of 20.2% and 16.8% were observed for the Ni catalyst on SiO_2 and Al_2O_3, respectively [74]. The Cu catalyst supported on zeolite HZSM-5 gave 20.68% ethanol selectivity but only 2.1% of the glycerol was converted [47].

2.3 Summary and Outlook

The recent trend of the increase in biodiesel production and the drop in market price of glycerol serves as an opportunity to utilize glycerol as a cheap valuable feedstock for the production of value added chemicals for various applications. Options for conversion of glycerol include chemical, biochemical, and thermochemical routes. The thermochemical conversions include processes such as pyrolysis, gasification, oxidation, dehydration, and hydrogenolysis. Hydrogenolysis can be used to convert glycerol into valuable chemicals like 1, 3 propanediol, 1, 2 propanediol, ethylene glycol, propanols, and ethanol. The choice of catalyst is crucial for the selective hydrogenolysis of glycerol into a desired product. Typically, the noble and non-noble based catalysts are the top choices. The non-noble based catalysts comprised of Ni and Cu have been shown to be the promising alternatives for hydrogenolysis of glycerol, especially for 1,2 PDO production.

The Cu catalyst in combination with or supported by Cr, SiO_2, ZnO, MgO, Al_2O_3, ZnO-Al_2O_3, MgO- Al_2O_3, and ZrO_2 has shown to produce 1,2 PDO with at least 90% selectivity from glycerol hydrogenolysis. Catalyst activity is affected by the catalyst’s composition, metal to support ratio, addition of promoters, way of preparation (method, calcination conditions, and reduction conditions), and process conditions, which in turn affect the catalyst structure, acidic/basic nature, metal dispersion, size of Cu species, active Cu area, and state of Cu species. Higher acidity/basicity, dispersion, and active Cu area, smaller size of Cu species, and higher amounts of Cu in Cu(O) and Cu(I) states resulted in superior catalyst activity. Process conditions such as temperature, hydrogen pressure, glycerol concentration, catalyst loading, reaction time, agitation rate, and choice of solvent have been shown to be important to the catalyst performance. In general, glycerol conversion is favored at higher temperatures, hydrogen pressure, catalyst loading, and reaction time. On the other hand, the 1,2 PDO selectivity usually has an optimal value depending on the catalyst used. The optimal temperature is usually in the range of 180˚C-240˚C. Catalyst deactivation may be caused by Cu sintering, leaching, and coking. Ni catalysts have also shown some promise for the selective hydrogenolysis of glycerol to 1,2 PDO with a few of them able to achieve a 1,2 PDO selectivity of over 90%, including Raney® Ni catalyst, Ni catalyst on SiO_2 (with P), SiO_2-Al_2O_3, and the catalyst of Ni/Al_2O_3-CuCr.

Further hydrogenolysis of glycerol will produce ethylene glycol, propanols, and ethanol. Mostly, Cu based catalysts produced higher levels of EG and propanols, while Ni catalysts dominated for ethanol production. Favorable conditions for EG production depend on the particular catalyst used. Higher EG selectivity were observed at low temperatures for the catalysts of Cu-Cr on γ-Al_2O_3, but higher temperatures favored EG production with the Cu-Zn-Ti combination. Propanol production is favored by higher catalyst acidity, reaction temperature, hydrogen pressure, and reaction time. On the other hand, ethanol production is enhanced at higher reaction temperatures due to further hydrogenolysis.

The hydrogenolysis of glycerol to value added chemicals using Ni and Cu catalysts presents a promising utilization and valorization of a low value feedstock. This is especially true with the selective hydrogenolysis of glycerol to 1,2 PDO, where up to 99% selectivity is achieved using the Cu catalyst on ZnO-Al_2O_3, MgO-Al_2O_3, and ZrO_2. Continuous production, especially with the use of gradient temperature [45], further promotes the potential of glycerol conversion to 1,2 PDO. Hydrogen generation for the hydrogenolysis of glycerol to occur may be one of the challenges of the process, which may be addressed via a two stage hydrogen generation from a variety of sources or one-stage in situ hydrogen generation and hydrogenolysis of glycerol [73].

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Chapter 3

Improved Ethanol and 1,2 PDO Selectivity for Thermocatalytic Conversion of Glycerol via Hydrogenolysis using Ni/Ce-Mg Catalyst

Abstract

Glycerol, a by-product from biodiesel production, is a cheap and renewable alternative feedstock for the production of valuable chemicals. Its hydrogenolysis allows the production of ethanol and 1,2 propanediol (1,2 PDO) with the help of catalysts. So far, only commercial Ni-based catalysts have been reported to produce high levels of ethanol along with 1,2 PDO. In this work, a supported Ni catalyst was developed for the selective production of ethanol and 1,2 propanediol (1,2 PDO) from glycerol hydrogenolysis. Various supports were screened with Ni catalyst on CeO_2 showing the highest potential for the selective production of ethanol and 1,2 PDO. A raise in the reaction temperature (215-245 ˚C) and Ni (15-50 wt%) content improved glycerol conversion, but reduced 1,2 PDO selectivity. An improvement in 1,2 PDO selectivity was attained with the addition of Al, Si, Zn , or Mg as promoters to the Ni catalyst on CeO_2. However, ethanol selectivity only improved with the addition of Si or Mg. Overall, the catalyst of 25 wt% Ni/Ce:Mg (4:1 mol:mol) achieved better combined selectivity for 1,2 PDO and ethanol at 73.10% and 8.0%, respectively. A variation in the Mg content showed that the 1,2 PDO selectivity is favored at higher Mg content, while the highest ethanol selectivity occurrs at 10% Mg.

3.1 Introduction

Concerns for limited oil reserves and the environmental impact of its use has stirred great interests in utilizing renewable bio-resources as an alternative feedstock for the production of fuel and other valuable chemicals [1-3]. Glycerol, a by-product from biodiesel production, is recently seen as a potential alternative renewable feedstock with its selling price dropping due to the surge and projected increase in biodiesel production [4]. A variety of valuable chemicals have been reported to be produced from glycerol via the chemical, biochemical, or thermochemical route [3, 5-6]. Ethanol, the most widely used transportation liquid biofuel [7] which also finds its use as a solvent, raw material in chemical synthesis (e.g. acetaldehyde, butadiene, diethyl ether, ethyl acetate, ethylamines, ethylene, glycol ethers, acetic acid and, etc.), and as beverage [8], has also been targeted to be produced from glycerol.

Naturally occurring microorganisms such as *Escherichia coli* [9-10], *Enterobacter aerogenes* [11], and *Klebsiella planticola* [12] have been reported to produce ethanol with glycerol as the carbon source, while *E. coli* [13] and *Enterobacter aerogenes* [14] ability to produce ethanol from glycerol were improved through metabolic engineering and adaptive evolution, respectively. Up to 26.5 g/L of ethanol were produced starting with 70 g/L glycerol after 72 hours of fermentation with yields greater than 1 mole ethanol per mole glycerol upon optimization of culture conditions [15]. Although glycerol is converted to ethanol efficiently by the microorganisms, the ethanol concentration achieved and initial feed concentration utilized are still below those of the industrial fermentation which usually produces 8-11% v/v ethanol within 6-11 hours using as much as 20% w/v of sugar [16].

Another approach could be the thermochemical catalytic conversion of glycerol, as ethanol is also observed to be produced during glycerol hydrogenolysis using Ni catalysts [17-19]. Hydrogenolysis of glycerol using Raney® Ni catalyst produced ethanol in high quantities along with 1,2 PDO with a selectivity of up to 40% and 48%, respectively for 91% glycerol conversion at 210˚C under hydrogen environment [17]. The increase in reaction temperature and time improved both glycerol conversion and ethanol selectivity. Addition of Bu_4PBr and $(C_6H_{13})_3C_{14}H_{29}PCl$ caused a decline in glycerol conversion, while the selectivity for ethanol was improved by the former but dropped upon addition of the latter. The Ni catalyst supported on SiO_2 [18-19] and Al_2O_3 [18] were also observed to produce ethanol from glycerol hydrogenolysis, which increased with increase in reaction temperature. At 320˚C, a selectivity of 16.8% and 20.2% for ethanol was observed for the Ni catalyst on Al_2O_3 and SiO_2, respectively [18]. At the same conditions, 1,2 PDO and propanol were also produced at a selectivity of 1.8% and 35.3% for the Ni catalyst on Al_2O_3 and 4.6% and 42.8% for the Ni catalyst on SiO_2 [18].

Aside from ethanol, glycerol hydrogenolysis can also lead to the formation of 1,3 propanediol (1,3 propylene glycol), 1,2 propanediol (1,2 propylene glycol), propanol, isopropanol, ethylene glycol, ethanol, and methanol (Fig. 3.1) [20-21].

In a proposed glycerol hydrogenolysis pathway [18, 20], ethanol can be produced from glycerol after its conversion to 1, 3 propanediol, ethylene glycol, or 1,2 propanediol. Based on the proposed pathway, to produce ethanol from glycerol, the catalyst must have the ability to convert glycerol to 1, 3 propanediol, ethylene glycol, or 1,2 propanediol and utilize these precursors to product ethanol. The catalysts reported to produce ethanol from glycerol [17-19] were commercial and may have been prepared or developed for other purposes and not specifically for ethanol production from glycerol hydrogenolysis. Aside from that, selectivity is much higher for other products like propanol [18] and most of the catalysts developed for glycerol hydrogenolysis focus on the selective production of 1,2 PDO from glycerol [20]. In that regard, we aim to develop a novel supported Ni catalyst for ethanol production from glycerol hydrogenolysis. In this work, we present the catalyst od Ni on Ce-Mg combination with an improved selectivity towards 1,2 propanediol and ethanol.

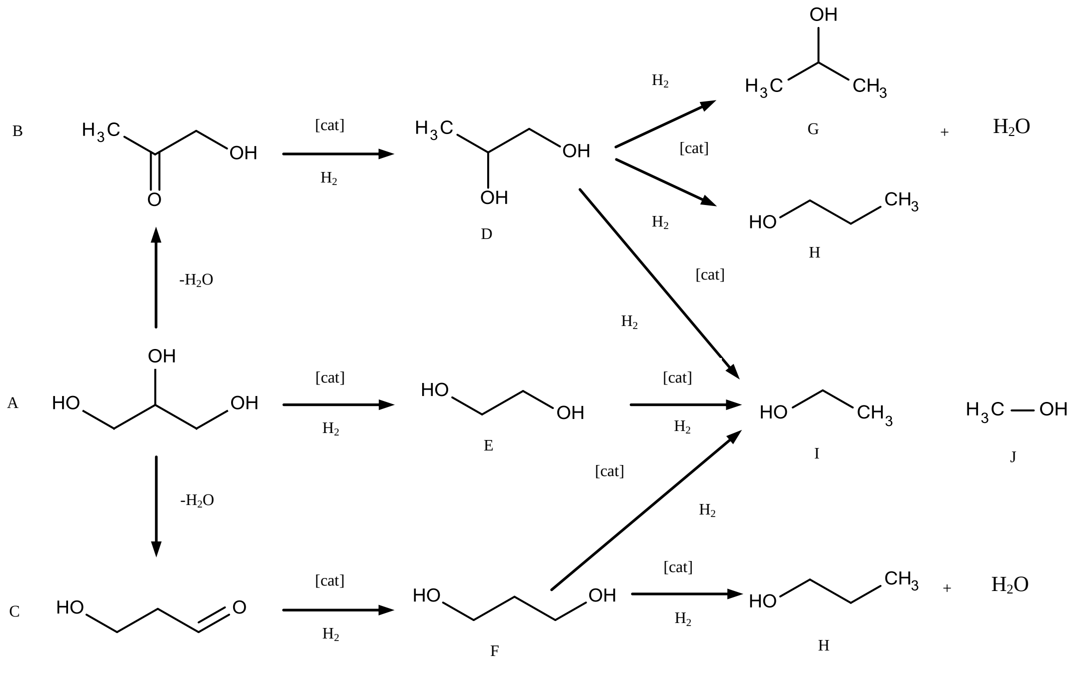

Figure 3.1 Schematic diagram of hydrogenolysis pathway of glycerol (A) acetol, (**B**) 3-hydroxypropionaldehyde (**C**), 1,2-propanediol (**D**), ethyleneglycol (**E**), 1,3-propanediol (**F**), isopropanol (**G**) 1-propanol (**H**), ethanol (**I**), methanol (**J**) [18,20].

3.2 Materials and Methods

3.2.1 Materials

In this work, glycerol (<99.5%) obtained from Macron chemicals and D.I. water were used as the mixed reactant for the aqueous phase reaction. The precursors $Ni(NO_3)_2 \cdot 6H_2O$(98%) from Alfa Aesar, $Mg(NO_3)_2 \cdot 6H_2O$ from Ward's Science, and CeO_2 from Acros Organics were used for preparing the catalysts. The precipitating agent used during catalyst preparation was Na_2CO_3. Standard samples that were used as references for GC analysis include methanol (99.8%) from EMD chemicals, ethanol (USP grade) from Pharmco, acetone (HPLC grade) from EMD chemicals, isopropyl alcohol (99.99%) from EMD chemicals, n-propanol (99.7%) from Sigma-Aldrich, n-butanol (99.8%) from Sigma-Aldrich, ethylene glycol (100%) from J.T. Baker, hydroxyacetone (90%) from Sigma-Aldrich, and 1,2 propanediol (99.5%) from Alfa Aesar.

3.2.2 Catalyst Preparation

The supported nickel (Ni) catalysts were prepared via precipitation or impregnation method. The precipitation method was used for the preparation of Ni catalysts supported on Al_2O_3, MgO, CaO, ZnO, MgO-Al_2O_3, CaO-Al_2O_3, and ZnO-Al_2O_3. As an example, with a target amount of 40 g, 25 wt% Ni supported on alumina (Ni/Al_2O_3) prepared by precipation was carried out by adding 50.54 g $Ni(NO_3)_2 \cdot 6H_2O$ and 221.98 g $Al(NO_3)_3 \cdot 9H_2O$ to 400 mL of deioinized (D.I.) water in a 2L glass container and stirred for at least an hour. Precipitation was achieved through drop-wise addition of 1.5 M Na_2CO_3 (1 L). The mixture was allowed to age for at least 24 hours prior to filtration. The solid precipitate was filtered using a 202-Whatman® filter paper of 15-19μm porosity. After filtration, the solids were washed in place with D.I. water (at least 4L). The washed precipitate was then dried in a 60˚C oven for at least 48 hours prior to calcination. Calcination of the precipitate was achieved by loading the dried precipitated into a muffle furnace heated at 550˚C for 4 hours. The calcined precipitate was then crushed to a powder (approx. 100-200 mesh) using a mortar and pestle before being loaded to the reactor for pre-reduction/activation. Reduction of the catalyst was carried out at 200˚C for 4 hours under 5.2 MPa of H_2 gas. Catalyst preparation via the impregnation method was used for preparation of Ni catalysts supported on SiO_2, CeO_2, and SiO_2-Al_2O_3. As an example, 40 g of 25 wt% Ni supported on silica (Ni/SiO_2) prepared by impregnation was carried out by adding 50.54 g $Ni(NO_3)_2 \cdot 6H_2O$ and 30 g SiO_2 to 250 mL of D.I. water in a 400-mL beaker and stirred for at least 24 hours. The mixture was heated to evaporate the water until it is visibly dry. The precipitate was dried further in a 60˚C oven for at least 48 hours prior to calcination. Calcination and pre-reduction/activation were done in the same manner for catalysts prepared via precipitation method.

3.2.3 Catalytic Activity Testing

Glycerol hydrogenolysis reactions were carried out in a 300-mL batch pressure reactor (4561-Parr Instrument Company, Moline, IL). Appropriate amounts of glycerol, water, and catalyst were added to the 300 mL vessel. The headspace was flushed with hydrogen for at least 3 times, and the reactor was pressurized with hydrogen before being heated to the desired temperature. Agitation was supplied a few degrees (30-40˚C) before reaching the desired temperature, which was noted as the time of reaction initiation. After the designated reaction time, the reactor was quenched to lower the temperature to at least 15˚C prior to gas venting and liquid sampling. Liquid products were analyzed using a gas chromatograph (Agilent 6890N) equipped with a flame ionization detector (FID) and DB wax (30 m long, 0.32 mm inside diameter, and 0.5 μm film thickness) [22]. Samples were prepared by adding 100 μL of sample with 100 μL of standard solution (5 wt % n-butanol, internal standard) and 800 μL of HPLC grade acetone.

The results are reported as percent glycerol conversion, percent selectivity towards a specific product, and yield of a specific product.

Percent glycerol conversion was computed as:

$$\text{Conversion (\%)} = \frac{G_c}{G_i} \times 100 = \frac{G_i - G_f}{G_i} \times 100$$

where: G_c - moles of glycerol converted, G_i – moles of glycerol before reaction, G_f- moles of glycerol after reaction

Selectivity towards a specific product was computed as:

$$\text{Selectivity (\%)}=S_i=\frac{P_i}{G_c}\times 100$$

where: S_i- selectivity towards a specific product, P_i – moles of specific product produced after reaction

Yield of a specific product was computed as:

$$\text{Yield (\%)}=\frac{S_i\times \text{Conversion}}{100}$$

3.2.4 Catalyst Characterization

3.2.4.1 XRD

XRD scans were collected on a Siemens D5000 theta-theta diffractometer using Cu κ-α radiation [1.54 angstrom] from 2 to 80˚ 2ϴ at 0.02˚/step and 1s/step scan rate.

3.2.4.2 H_2 Temperature Programmed Reduction (H_2-TPR)

H_2 temperature programmed reduction (H_2-TPR) was conducted on a Micromeritics AutoChem II 2920 Chemisorption Analyzer equipped with a thermal conductivity detector (TCD). Approximately 50 mg of sample was loaded in a U-shaped quartz reactor. The sample was pretreated with flowing He (50 sccm) at 200˚C (473 K) for 1 hour with the temperature brought down to 50˚C (323 K). It was purged until a stable base line was reached. The temperature was raised to 600 ˚C (873 K) at a rate of 10˚C/min under flowing H_2-Ar (10% H_2) gas mixture at 50 sccm.

3.2.4.3 Basic Sites

Bromothymol blue of 0.002 N in benzene, an indicator for total basic sites determination, was prepared by adding 0.128 g of bromothyhmol blue in 100 mL of benzene. Benzoic acid of 0.1 N, used as the titrating agent, was prepared by adding 2.4424 g in 200 mL of benzene. A catalyst sample of approximately 0.1 g was placed in a 100-mL Erlenmeyer flask containing 5 mL of bezene with 0.2 mL of indicator solution. The 0.1 N benzoic acid in benzene was added dropwise using a titration burrette. The end-point was taken as the point at which all the green color disappeared. The total amount of basic sites is expressed in the units of mmoles/g of catalyst [23].

3.3 Results and Discussions

The experiments were done in duplicates except for the screening of various supports (1 trial) due to the number of preliminary experiments carried out (120 runs= 6 months of work). A set of experiments were done in triplicates using a commercial and a developed catalyst to determine an average coefficient of variation (Appendix B). The average coefficient of variation for the commercial catalyst and developed catalyst is at 3.72% and 5.96%, respectively. The differences between the measured values from the average value obtained in this study are well within this variation, which means the average values are representative and reliable enough for comparisons.

3.3.1 Screening of Catalyst with Ni on Various Supports

In earlier studies, Ni catalysts showed some potential to produce ethanol from glycerol hydrogenolysis which could be due to its ability to achieve C-O cleavage for dehydration, C-C cleavage to produce lower carbon chained molecules, and hydrogenation [17-19]. In this work, Ni catalysts on various metal oxides or combinations as support were screened for its ability to produce ethanol and 1,2 PDO from glycerol hydrogenolysis (Table 3.1). Among them, the Ni catalyst on ZnO gave the highest 1,2 PDO selectivity at 74.44% for 80.47% glycerol conversion at the tested conditions. However, its selectivity towards ethanol is just 1.02%. This could signify its poor ability to cleave C-C bond for ethanol production. The Ni catalysts on MgO, CeO_2, and SiO_2-Al_2O_3 achieved a selectivity towards ethanol of at least 3%, which are better than the Ni catalysts on SiO_2 and Al_2O_3 that were reported to give high selectivity towards ethanol and 1,2 PDO [18-19]. Among the three combinations, the Ni catalyst on CeO_2 gave the highest ethanol selectivity. It also gave better 1,2 PDO and EG selectivities, which are thought to be precursors for ethanol production [18, 20]. Although the Ni catalyst on ZnO may have a higher potential for ethanol production due to high selectivity for 1,2 PDO, the mechanism for 1,2 PDO production from glycerol is pretty well established [24] as compared to ethanol production. It may be more difficult to improve selectivity towards ethanol when starting with a catalyst that has a high selectivity for 1, 2 PDO than increasing the 1, 2 PDO selectivity starting with a catalyst that has a better ethanol selectivity. In that regard, the catalyst of 25 wt% Ni/CeO_2 was further investigated for ethanol and 1,2 PDO production from glycerol hydrogenolysis.

Table 3.1 Nickel catalyst screening; Reaction conditions: feed-100 g (60 wt% glycerol in H_2O), 5 g catalyst, pH_2 = 4.1 MPa, T= 215˚C, t= 24 h

Catalyst	Conversion (mol%)	Ethanol		Ethylene glycol		n-Propanol		1,2 PDO		Others
		S	Y	S	Y	S	Y	S	Y	S
25% Ni/Al_2O_3	7.74	ND	ND	2.90	0.22	ND	ND	16.17	1.25	80.93
25% Ni/SiO_2	52.42	1.19	0.62	0.83	0.52	ND	ND	12.34	6.47	85.64
25% Ni/MgO	87.44	3.24	2.83	1.95	1.71	9.82	8.58	0.73	0.64	84.26
25% Ni/CaO	48.65	1.31	0.63	2.1	1.02	ND	ND	18.02	8.77	78.57
25% Ni/ZnO	80.47	1.02	0.82	2.06	1.65	0.24	0.19	74.44	59.90	22.24
25% Ni/CeO_2	69.97	3.69	2.58	6.08	4.25	1.06	0.74	39.50	27.64	49.67
25% Ni/ MgO-Al_2O_3	35.31	ND	ND	0.66	0.23	ND	ND	1.94	0.60	97.40
25% Ni/ CaO-Al_2O_3	29.85	ND	ND	10.07	3.00	ND	ND	4.59	1.37	85.34
25% Ni/ ZnO-Al_2O_3	31.53	ND	ND	ND	ND	ND	ND	3.28	1.03	96.72
25% Ni/ SiO_2-Al_2O_3	33.99	3.50	1.19	2.99	1.01	1.67	0.57	32.23	10.95	59.61

S-selectivity of product (mol%), Y-yield of product (mol%), ND- none detected

3.3.2 Effect of Temperature on the Catalysts of 25% Ni on CeO_2

The effect of reaction temperature on the activity of the catalyst of 25 wt% Ni/CeO2 for glycerol hydrogenolysis was investigated at 215-245˚C (Fig. 3.2). Glycerol conversion improved with increase in reaction temperature from 81.64% at 215˚C to 91.81% and 96.87% at 230˚C and 245˚C, respectively. The 1,2 PDO selectivity greatly declined with the increase in reaction temperature from 47.29% at 215˚C to 23.56% and 4.72% at 230˚C and 245˚C, respectively. On the contrary, n-propanol selectivity improved with the increase in reaction temperature temperature from 2.57% at 215˚C to 7.56% and 8.28% at 230˚C and 245˚C, respectively. As for ethanol, the highest selectivity observed was at 230˚C with an ethanol selectivity of 9.47% as compared to 6.74% and 4.84% at 215˚C and 245˚C, respectively.

The results for the effect of reaction temperature on glycerol conversion, 1,2 PDO selectivity and n-propanol are in agreement with previous reports [17-18] were an improvement in glycerol conversion, decline in selectivity for 1,2 PDO selectivity, and increase in selectivity for n-propanol were observed which used the catalyst of Raney® Ni, Ni/SiO_2, or Ni/Al_2O_3. However, the selectivity towards ethanol started to decline after 230˚C as compared to a previous study using the Ni catalyst on SiO_2 or Al_2O_3 [18] where an increase selectivity for ethanol from 230˚C to 320˚C was still observed. This difference may be attributed to the catalysts working temperatures for glycerol hydrogenolysis, the huge decline in the selectivity towards 1, 2 PDO, increase in selectivity towards n-propanol and other unknown by-products, or a combination of each of these factors. Although a higher selectivity was observed at 230˚C, glycerol conversion at 215˚C has the potential to increase selectivity and yield for ethanol due to higher 1,2 PDO production. Ethanol selectivity has also been observed to improve with the increase in reaction time along with the decline in 1,2 PDO selectivity [17].

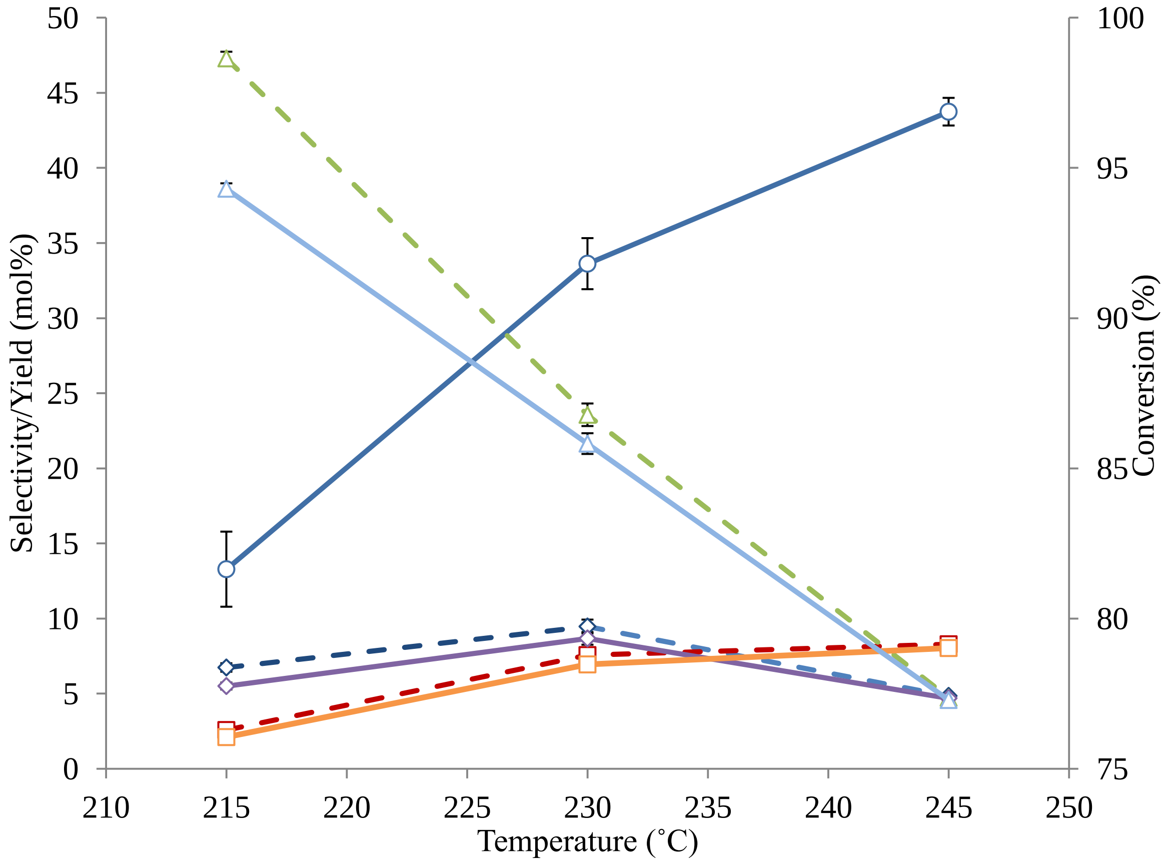

Figure 3.2 Effect of temperature with 25% Ni on CeO_2; Reaction conditions: feed-100 g (60 wt% glycerol in H_2O), 10 g catalyst, pH_2 = 6.9 MPa, t= 24 h; Legend: solid lines for glycerol conversion and product yields, dashed lines for product selectivity, (○) glycerol conversion, (◇) ethanol, (□) n-propanol, (△) 1,2 PDO; Error bars are based on absolute error from average value of duplicate.

3.3.3 Effect of Varying Nickel Content for the Catalyst Ni supported on CeO_2

The Ni content of the catalyst was varied in the range between 15-50 wt% (Fig. 3.3) to investigate its effect on glycerol hydrogenolysis for ethanol production, since around 45-55% Ni catalyst on SiO_2 or Al_2O_3 was used in an earlier work [18] concerning glycerol hydrogenolysis to produce lower alcohols.

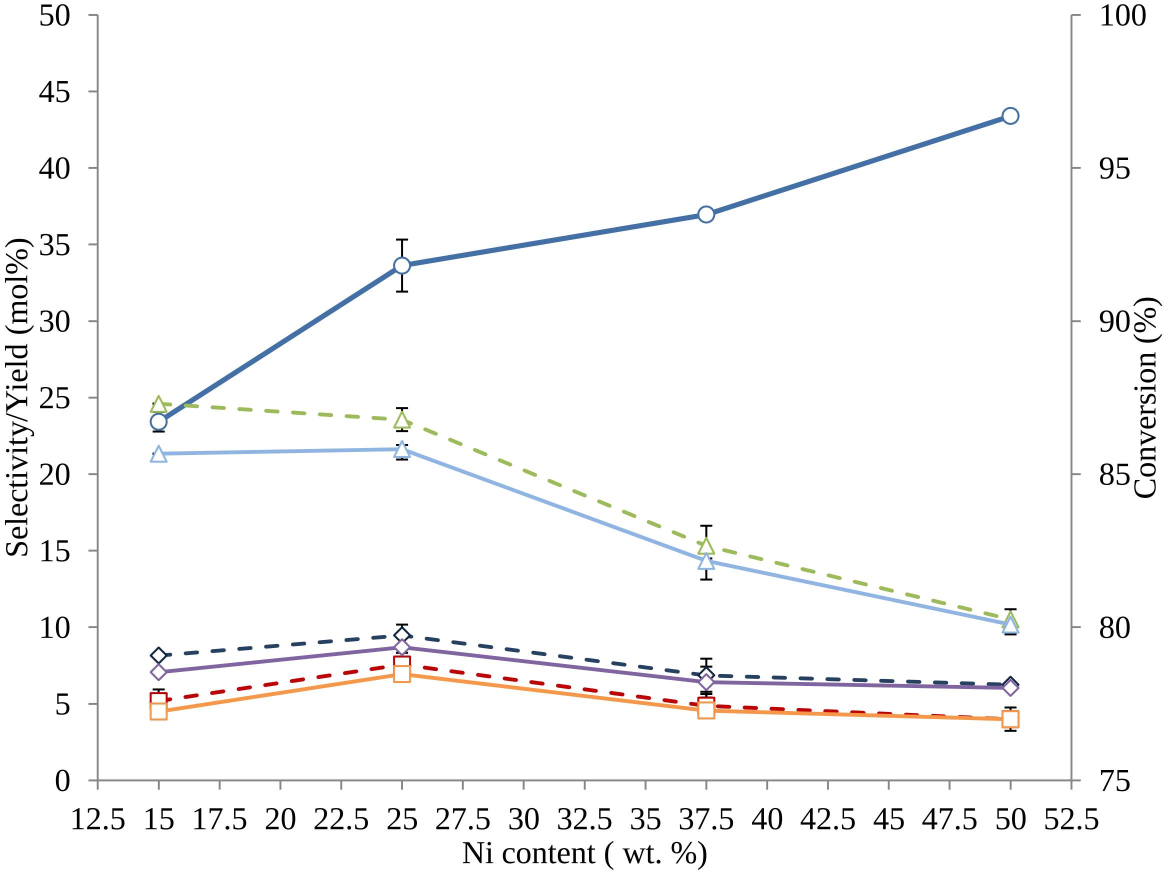

Figure 3.3 Effect of nickel content for Ni on CeO_2; Reaction conditions: feed-100 g (60 wt% glycerol in H_2O), 10 g catalyst, pH_2 = 6.9 MPa, t= 24 h; Legend: solid lines for glycerol conversion and product yields, dashed lines for product selectivity, (○) glycerol conversion, (◇) ethanol, (□) n-propanol, (△) 1,2 PDO; Error bars are based on absolute error from average value of duplicate.

Glycerol conversion improved from 86.71% at 15 wt% Ni to 96.7% at 50 wt% Ni with an increase in Ni content, which may be caused by the additional active Ni metal available for glycerol conversion. The 1,2 PDO selectivity was maintained with the increase of Ni content of the catalyst from 15 wt% to 25 wt%, while further increase to 37.5 wt% caused its decline from 23.56% to 15.32%. Both ethanol and propanol were observed to be highest with 25 wt%

Ni at 9.47% and 6.86%, respectively. Although glycerol conversion increased with Ni content, its further increase from 25 wt% may have favored further hydrogenolysis or production of other by-products. Based on this information acquired, Ni content was maintained at 25 wt% for further studies.

3.3.4 Effect of promoters with the catalyst of 25 wt% Ni on CeO_2

To improve the product selectivity towards 1,2 PDO and ethanol, the effect of adding the promoters Al, Si, Zn, and Mg to Ni on CeO_2 on catalyst activity was investigated (Table 3.2). A decline in glycerol conversion was observed in all cases. Their addition also altered product distribution, while it improved the 1,2 PDO selectivity. The 1,2 PDO selectivity was improved from 47.29% to 55.1%, 59.41%, 68.10%, and 75.41 upon the addition of Al, Si, Mg, or Zn, respectively. The support CeO_2 is known to be amphoteric in nature [25] with a slight surface basicity [26], while Al_2O_3 and SiO_2 contain surface acid sites [18, 26-27]and ZnO and MgO having surface basic sites [28-29, 26]. The addition of these promoters may have provided additional and necessary acid or basic sites to aid the hydrogenolysis of glycerol and selectively produce 1,2 PDO. The highest selectivity for EG was observed with the addition of Si at 13.97%, which is about twice the selectivity in the absence of Si. A lower selectivity for n-propanol was observed in all cases and none was detected with the addition of Mg, which may have been due to lower conversion as higher selectivity for n-propanol has been observed with the increase in glycerol conversion or reaction time [30]. The addition of both Si and Mg improved selectivity towards ethanol from 6.72% to 10.12% and 9.0%, respectively. Although addition of Si gave a slightly higher selectivity for ethanol as compared to Mg, the Ni catalyst on Ce:Mg combination may have a better potential for ethanol production. This combination has approximately 14.5% higher selectivity towards 1,2 PDO, while only approximately 1% lower selectivity towards ethanol, and almost twice lesser selectivity towards EG, with no detectable n-propanol produced.

Table 3.2 Effect of addition of promoters to the catalyst of 25 wt% Ni on CeO_2; Reaction conditions: reactant 100 g (60 wt % glycerol in H_2O), 10 g catalyst, pH_2 = 6.9 MPa, t= 24 h

Catalyst	Conversion (mol%)		Ethanol		Ethylene glycol		n-Propanol		1,2 PDO		Others
	AE	RE	S	Y	S	Y	S	Y	S	Y	S
			AE	RE	AE	RE	AE	RE	AE	RE	
25% Ni/CeO_2	81.64		6.72	5.49	5.76	5.77	2.57	2.10	47.29	38.61	37.66
	1.25	1.53	0.44	6.56	0.04	0.64	0.06	2.38	0.44	0.93	
25% Ni/Ce:Zn	51.27		ND	ND	6.56	3.37	0.75	0.39	75.41	38.67	17.28
(80:20 mol:mol)	0.57	1.11	-	-	0.99	15.1	0.12	15.38	2.50	3.31	
25% Ni/Ce:Mg	31.16		9.0	2.81	6.10	1.90	ND	ND	68.1	21.22	16.8
(80:20 mol:mol)	1.95	6.26	0.27	3.00	0.19	3.11	-	-	1.62	2.38	
25% Ni/Ce:Al	56.76		6.77	3.84	7.86	4.46	2.01	1.14	55.51	31.51	27.85
(80:20 mol:mol)	1.78	3.14	0.11	1.56	0.35	4.48	0.02	1.00	2.38	4.28	
25% Ni/Ce:Si	42.92		10.12	4.35	13.97	6.00	1.56	0.67	59.49	25.54	14.82
(80:20 mol:mol)	0.56		0.54	5.29	0.49	3.5	0.05	2.99	0.07	0.12	

S=selectivity of product (mol%), Y=yield of product (mol%), ND-none detected, AE = Absolute Error(%)= measured value - average value, RE =Relative Error(%)= (AE/average value) x100

3.3.5 Effect of Varying Mg Content

The effect of Mg content on the catalyst activity was studied by varying the Ce:Mg ratio from 100:0 to 80:20 mol% (Fig. 3.4). Glycerol conversion declined from 81.64% to 37.74%, 28.63%, and 31.16% upon the increase in Mg content from 0% to 5%, 10%, and 20%, respectively. Among the tested ratios, 20% Mg gave the highest 1,2 PDO selectivity at 68.10%. The 1,2 PDO selectivity was maintained at 62.14% and 65.24% at an Mg content of 10% and 5%, respectively, before declining to 47.29% at 0% Mg. The ethanol selectivity was also affected by Mg content. The highest ethanol selectivity was obtained with 10% Mg at 15.28%. Lower ethanol selectivities were achieved at 6.72%, 13.09%, and 9.0% for 0%, 5%, and 20% Mg, respectively. The n-propanol selectivity declined with Mg content from 2.57% to 1.38%, 0%, and 0% for 0% to 5%, 10%, and 20% Mg, respectively. This may be due to increased specificity towards ethanol, basic property of the catalyst, other hydrogenolysis products, or lesser glycerol conversion at higher Mg content or a combination these possibilities. Although having 20% Mg in the catalyst resulted in a higher 1,2 PDO sselectivity, it doesn’t seem to readily produce ethanol as compared with the catalyst containing 10% Mg. Also considering for both Mg content, the proximitiy in glycerol conversion, and the differences in there 1,2 PDO and ethanol selectivities. The Ni catalyst on Ce:Mg (90:10) may have a better potential for ethanol production from glycerol hydrogenolysis.

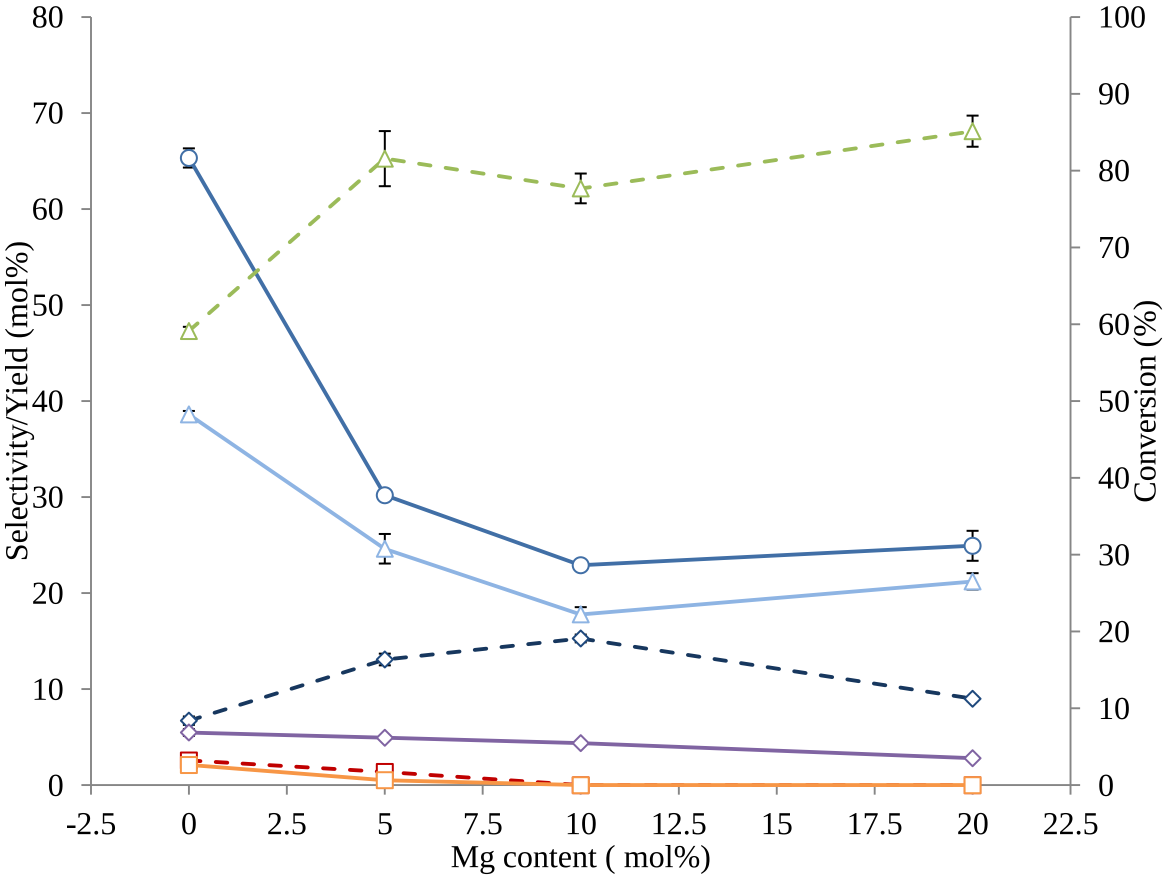

Figure 3.4 Effect of Mg Content for Ni on Ce:Mg; Reaction conditions: feed 100 g (60 wt% glycerol in H_2O), 10 g catalyst, pH_2 = 6.9 MPa, T= 215˚C, t= 24 hrs; Legend: solid lines for glycerol conversion and product yields, dashed lines for product selectivity, (○) glycerol conversion, (◇) ethanol, (□) n-propanol, (△) 1,2 PDO; Error bars are based on absolute error from average value of duplicate.

3.3.6 Catalyst Characterization

3.3.6.1XRD Patterns

The XRD patterns were taken for activated/reduced of the catalyst Ni/CeO_2 with or without promoters prepared via impregnation method calcined at 550˚C to check the effect of the promoters and Mg content on the structure of the catalyst (Fig. 3.5). The catalysts seem to preserve the crystalline the crystalline structure of the support CeO_2 [31-32]. Intensity of the peaks related to NiO is higher for catalysts with promoters as well as the catalysts with higher Mg content. This suggests that lesser dispersion of NiO results when promoters are added and lesser dispersion is attained with increase in promoter concentration. A slight shift in peak positions from the peaks associated with CeO_2 was also observed for each catalyst and increased with decreasing Mg content. This behavior could be due to the formation of a solid solution of NiO-CeO_2, promoter-CeO_2, or NiO-promoter-CeO_2 [33-34]. The lesser NiO dispersion upon addition of promoters may have contributed to the observed decrease in glycerol conversion for the catalysts with promoters (Table 3.2), while the formation of solid solution may have contributed to the observed difference in the catalysts selectivity.

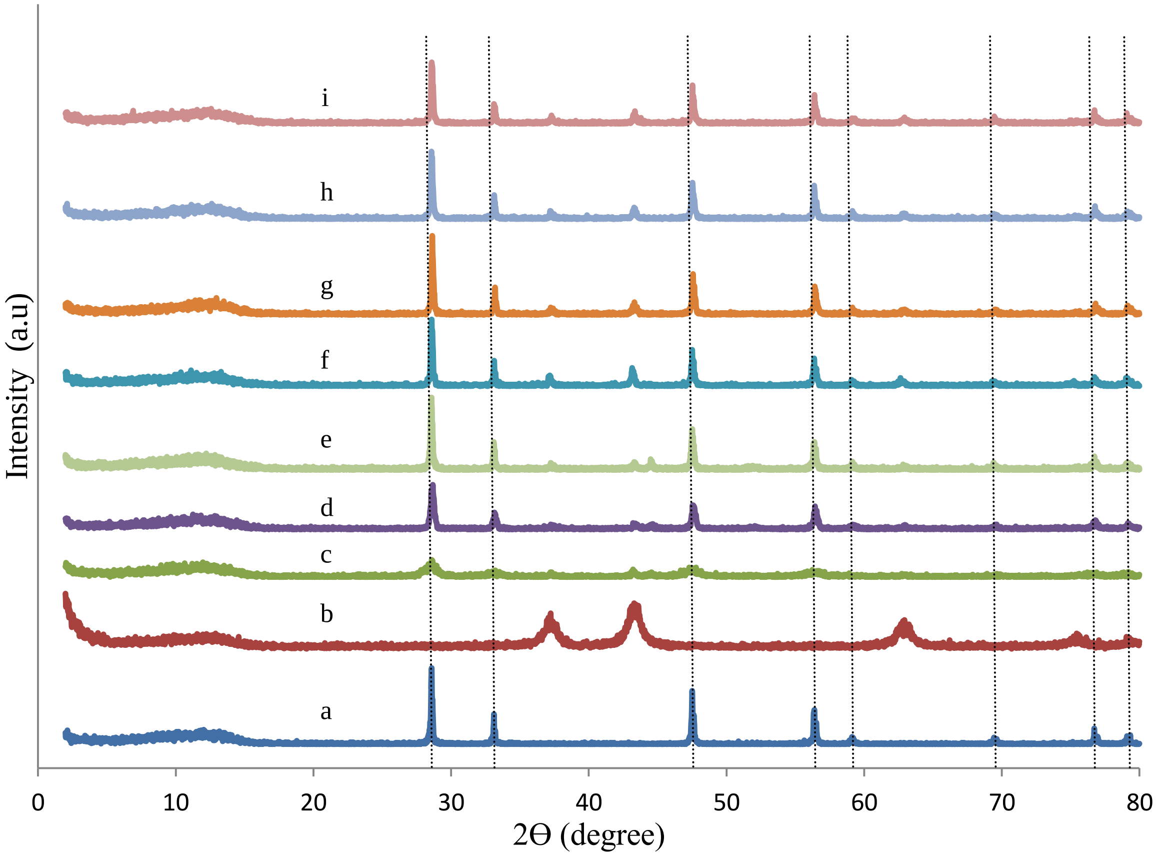

Figure 3.5 – XRD patterns of (a) CeO_2, (b) NiO, (c) 25 wt%Ni/CeO_2, (d) 25 wt%Ni/Ce:Al (80:20), (e) 25 wt%Ni/Ce:Si (80:20), (f) 25 wt%Ni/Ce:Zn (80:20), (g) 25 wt%Ni/Ce:Mg (80:20), (h) 25 wt%Ni/Ce:Mg (90:10), (i) 25 wt%Ni/Ce:Mg (85:15)

3.3.6.2 H_2-TPR Profiles of Ni on CeO_2 with or without Promoters

The reducibility of NiO species, metal support interaction, and effect of promoters on metal support interaction was studied using H_2-TPR experiments [35]. The peaks observed were at 369˚C, 398˚C, 369˚C, 456˚C, 406˚C, and 400˚C for the catalysts of Ni/CeO2, Ni/Ce:Al (80:20), Ni/Ce:Si (80:20), Ni/Ce:Zn (80:20), Ni/Ce:Mg (80:20), and Ni/Ce:Mg (90:10), respectively (Fig. 3.6). These peaks are likely from the reduction of surface bulk NiO species, while the different peak temperatures attributed to the extent of NiO and support interaction [35-37]. The addition of Al, Zn, and Mg resulted in a shift of the peaks of hydrogen consumption to higher temperatures, suggesting an alteration of the support properties and strengthening of Ni and support interaction [35-37].

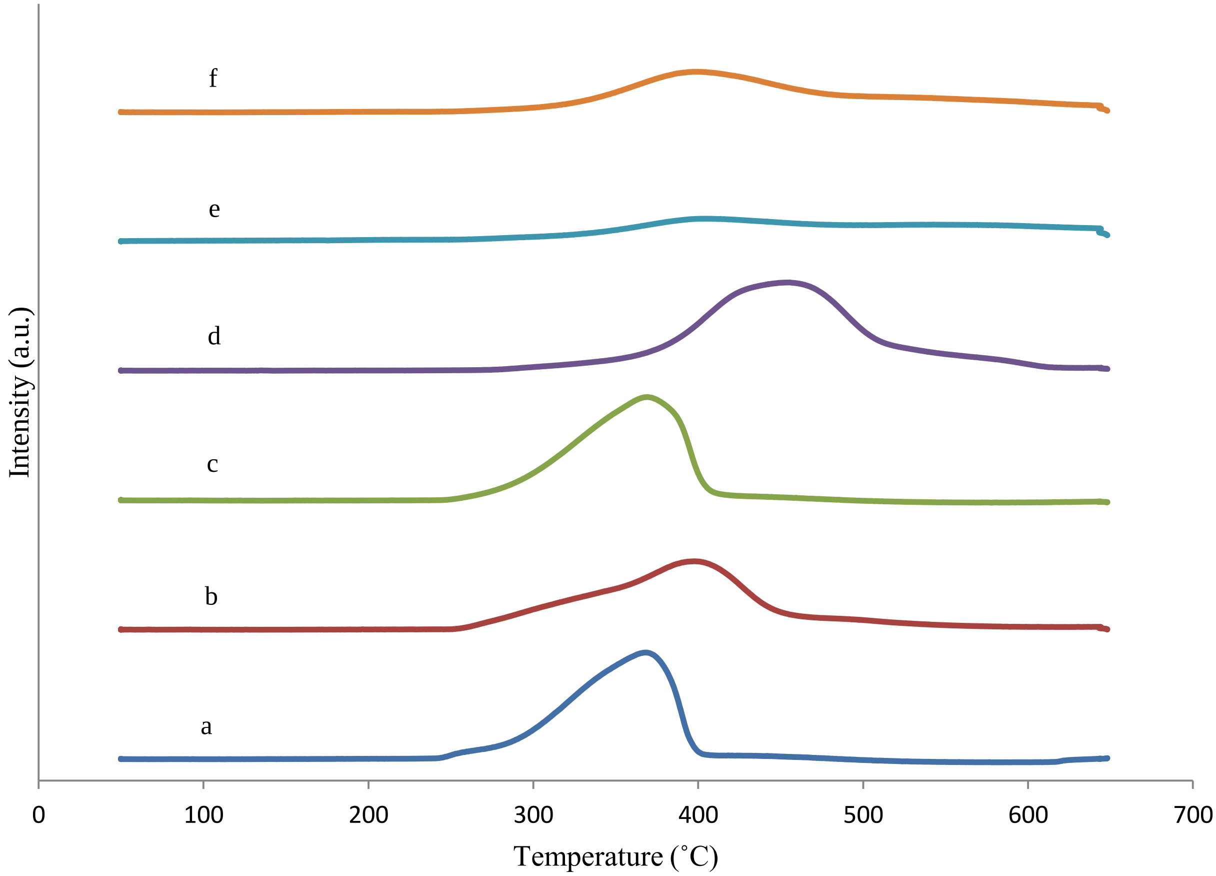

Figure 3.6 H_2-TPR profiles of the catalysts 25 wt% Ni/CeO_2 with or without promoters; (a) 25 wt%Ni /CeO_2, (b) 25 wt%Ni /Ce:Al (80:20), (c) 25 wt%Ni /Ce:Si (80:20), (d) 25 wt% Ni/Ce:Zn (80:20), (e) 25 wt% Ni/Ce:Mg (80:20), (f) 25 wt% Ni/Ce:Mg (90:10)

There was no shift in peak with the addition of SiO_2, which suggests that there was no change in the metal to support interaction. The precursor used for SiO_2 is silica gel (solid) as compared to Al, Zn, and Mg which were in the soluble nitrate form. It is likely that SiO_2 did not deposit on CeO_2. Rather, it may have served as another support for NiO which mixed physically or sintered with CeO_2 as the same TPR profile and peak temperature (370˚C) for the Ni catalyst on SiO_2 has been reported [36]. The altered active metal to support interactions may have contributed to the changes in product profiles and improvement in the 1,2 PDO and ethanol selectivities. The increase in Mg content from 10% to 20% slightly shifted the peak from 400˚C to 405˚C, which suggest a stronger Ni to supporter interaction at higher Mg content. This shift in peak temperature may also signify a difference in support properties [35-37], which may have contributed to the change in its activity and selectivity.

3.3.6.3 Basicity of the Catalyst Ni/CeO_2 with or without Promoters

The addition of MgO and ZnO to the catalyst of 25 wt% Ni/CeO_2 greatly enhanced the 1,2 PDO selectivity from glycerol hydrogenolysis, suggesting that catalyst basic sites provide a key role in this improvement. Due to this observation, the total amounts of basic sites on the surface of the catalysts with or without promoters were determined (Table 3.3). There were no detectable surface basic sites for the catalyst of 25 wt% Ni/CeO_2 without promoter as well as the catalyst with Al and Si as promoters. Surface basic sites were detected for the catalyst promoted with Zn and Mg, with the latter providing more surface basic sites than the former. The presence of surface basic sites in these catalysts supports the suggestion that basic sites may have provided a key role in the improved 1,2 PDO selectivity. As the Mg content of the catalysts was reduced, total amount of surface basic sites were also reduced. The change in total amount of surface basic sites may have also contributed to differences in the activity and selectivity of the catalyst containing varied amounts of basic sites.

Table 3.3 Total basic sites of the catalyst Ni/CeO_2 with or without promoters.

Catalyst	Total amount of basic sites (mmoles/g catalyst)
25 wt% Ni/CeO_2	ND
25 wt% Ni/Ce:Al (80:20)	ND
25 wt% Ni/Ce:Si (80:20)	ND
25 wt% Ni/Ce:Zn (80:20)	0.012
25 wt% Ni/Ce:Mg(80:20)	0.040
25 wt% Ni/Ce:Mg(90:10)	0.022
25 wt% Ni/Ce:Mg(95:05)	0.009

ND- none detected

3.4 Conclusions

Among various supports screened, the Ni catalyst on CeO_2 showed potential in the selective production of both ethanol and 1,2 PDO from glycerol hydrogenolysis. Raising reaction temperature from 215˚C to 245˚C improves glycerol conversion and propanol selectivity, but decreases 1,2 PDO. The hHighest selectivity for ethanol attained with 25 wt% Ni catalyst on CeO_2 reached 9.47% at 230˚C, but better overall selectivity for ethanol and 1,2 PDO is attained at 215˚C. Increasing Ni content in the range of 15-50 wt% improves glycerol conversion, but reduces ethanol and 1,2 PDO selectivities upon further increase from 25 wt% Ni. The addition of Al, Si, Zn, or Mg as promoters at 4:1 (Ce:promoter molar ratio) to the Ni catalyst on CeO_2 reduces the glycerol conversion, but improves the 1,2 PDO selectivity in the order Zn>Mg>Si>Al. The addition of Si or Mg to the Ni catalyst on CeO_2 also improves ethanol selectivity and reduces n-propanol selectivity. The catalyst of 25 wt% Ni/Ce:Mg provides better overall selectivity towards 1,2 PDO and ethanol at 68.10% and 9.0%, respectively. Increasing Mg content from 0 to 20% (Mg:Ce) improves 1,2 PDO selectivity, while 10% Mg produces the highest selectivity for ethanol at 15.28%.

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Chapter 4

Effect of Preparation Method and Operating Parameters on Activity of 25 wt% Ni/Ce:Mg (9:1) Catalyst for Selective Hydrogenolysis of Glycerol to Ethanol and 1,2 PDO

Abstract

The catalyst of 25 wt% Ni/Ce:Mg (9:1) developed for selective production of ethanol and 1,2 PDO from glycerol hydrogenolysis was further improved by changing the preparation method from impregnation to deposition precipitation (DP) and adjusting calcination temperatures. The effects of operating parameters including reaction temperature, initial water content, initial hydrogen pressure, and reaction time were also investigated using the new developed catalyst. The catalyst prepared via the DP method improved glycerol conversion, while maintaining the selectivities for ethanol and 1,2 PDO production. Lower calcination temperature gave better ethanol and 1,2 PDO selectivity. The catalyst attained selectivities of 15.61% for ethanol and 67.93% for 1,2 PDO when calcined at 350˚C. Increase in reaction temperature and time improved glycerol conversion and ethanol selectivity, but reduced 1,2 PDO selectivity. A reduction in initial water content improved glycerol conversion, but reduced the selectivities for ethanol and 1,2 PDO production. The increase in initial hydrogen pressure improved glycerol conversion. However, it caused a reduction in the 1,2 PDO and ethanol selectivities. A comparison between the commercial Raney® Ni and the catalyst developed showed that our catalyst has a better potential for the selective production of ethanol and 1,2 PDO from glycerol hydrogenolysis.

4.1 Introduction

The near depletion of fossil fuel reserves calls for the need to secure long term economic and energy security, and the emergence of climate change has drastically increased the interest in utilizing renewable resources for production of fuels and valuable chemicals [1]. Biodiesel, considered as the main renewable alternative of diesel fuel [2], is typically produced from vegetable oils or animal fats [3]. An oil or fat is combined with an alcohol, usually methanol, via the transesterification reaction with the aid of a suitable catalyst and process conditions producing a mixture of fatty acid methyl esters (FAME) and glycerol (Fig. 4.1) [2-4].

Biodiesel production rose from 8 million liters in 2000 to 1.2 billion liters in 2010 [5], while the global market is estimated to reach 37 billion gallons along with about 4 billion gallons of glycerol by-product produced in 2016 [6]. Glycerol's huge surplus in supply, due to the recent surge in biodiesel production and its projected increase in production, caused a significant drop in its selling price for both the crude and purified forms [7-8]. This development has been seen as an opportunity to utilize glycerol as a cheap alternative renewable feedstock for the production of valuable chemicals [9]. Various options are available for the conversion of glycerol into valuable chemicals, which can be achieved through the chemical, biochemical or thermochemical route [7-8, 10].

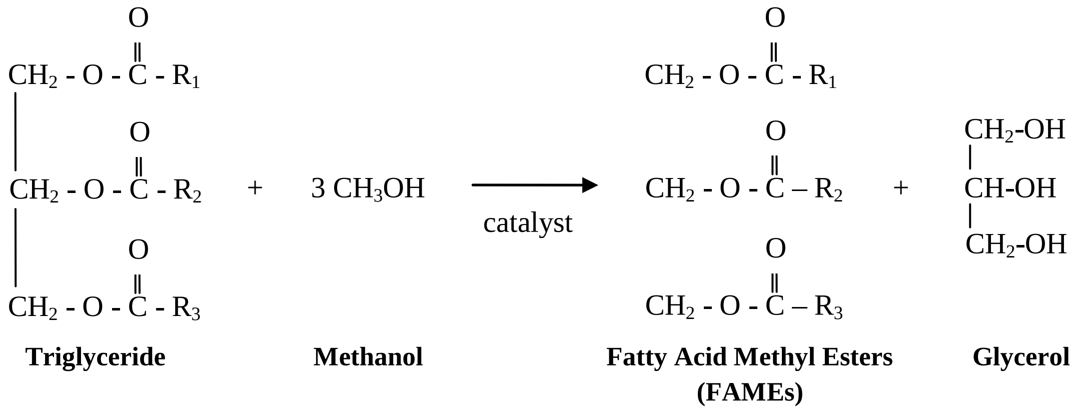

Figure 4.1 Biodiesel and glycerol production via transesterification

Depending on the process conditions and catalysts employed in the thermochemical route, glycerol may be converted through pyrolysis, gasification, oxidation, dehydration, or hydrogenolysis [10]. Ethanol, a widely used transportation biofuel [11] also used as a solvent, raw material in chemical synthesis, and beverage [12], can be produced from glycerol hydrogenolysis along with the other alcohols such as 1,3 propanediol (1,3 propylene glycol), 1,2 propanediol (1,2 propylene glycol), propanol, isopropanol, ethylene glycol, and methanol [13-17]. According to the proposed glycerol hydrogenolysis pathway, ethanol may be produced from glycerol with 1, 3 propanediol, ethylene glycol, or 1,2 propanediol as the intermediates [14].

Only a few studies reported satisfactory yields for ethanol from glycerol hydrogenolysis using Ni catalysts [14-17]. In the hydrogenolysis of glycerol using Raney® Ni catalyst, ethanol was produced in high quantities along with 1,2 PDO reaching a selectivity of up to 40% and 48%, respectively, for a 91% glycerol conversion at 210˚C under a hydrogen environment [15]. Increases in both the reaction temperature and time improved glycerol conversion and ethanol selectivity. The addition of Bu_4PBr and $(C_6H_{13})_3C_{14}H_{29}PCl$ reduced glycerol conversion and the ethanol selectivity was improved by the addition of the former, but declined upon addition of the latter. The use of Ni catalysts supported on SiO_2 [14, 16] and Al_2O_3 [14] allowed ethanol production from glycerol hydrogenolysis, which increased with temperature due to the increase in degradation products. Ethanol selectivities of 16.8% and 20.2% were observed at 320˚C using Ni catalysts on Al_2O_3 and SiO_2, respectively [14]. Under the same conditions, 1,2 PDO and n-propanol selectivities were at 1.8% and 35.3%, respectively, using the catalyst Ni on Al_2O_3. While, a 1,2 PDO selectivity of 4.6% and n-propanol selectivity of 42.8% were achieved using the Ni catalyst on SiO_2 [14]. In a separate study, we reported a novel catalyst for the selective production of ethanol and 1,2 PDO from glycerol hydrogenolysis using Ni catalyst on Ce-Mg (9:1). We were able to produce ethanol at a selectivity of 15.28% with a 1,2 PDO selectivity of 62.14% and no detectable amount of n-propanol [17].

Aside from the effect of catalyst composition, the catalyst activity for the hydrogenolysis of glycerol may be affected by the choice of preparation method and conditions as well as the reaction conditions [17]. In this work we aim to further improve the catalytic activity of the Ni catalyst on Ce-Mg with a (90:10 mol ratio) for ethanol and 1,2 PDO production from glycerol through hydrogenolysis. The effects of preparation method (impregnation vs. deposition precipitation method), calcination temperature, reaction temperature, water content (initial), hydrogen pressure (initial), and reaction time on the catalyst activity for the hydrogenolysis of glycerol to ethanol and 1,2 PDO are reported.

4.2 Materials and Methods

4.2.1 Materials

Glycerol (<99.5%) obtained from Macron chemicals and D.I. water were used as the mixed reactant for the aqueous phase reaction. The precursors $Ni(NO_3)_2 \cdot 6H_2O$ (98%) from Alfa Aesar, , $Mg(NO_3)_2 \cdot 6H_2O$ from Ward’s Science, and CeO_2 from Acros Organics were used for preparing the catalysts. The precipitating agent used during catalyst preparation was Na_2CO_3. The commercial catalyst Raney® Ni was obtained from Aldrich Chemistry. Standard samples that were used as references for GC analysis include methanol (99.8%) from EMD chemicals, ethanol (USP grade) from Pharmco, acetone (HPLC grade) from EMD chemicals, isopropyl alcohol (99.99%) from EMD chemicals, n-propanol (99.7%) from Sigma-Aldrich, n-butanol (99.8%) from Sigma-Aldrich, ethylene glycol (100%) from J.T. Baker, hydroxyacetone (90%) from Sigma-Aldrich, and 1,2 propanediol (99.5%) from Alfa Aesar.

4.2.2 Catalyst Preparation

Catalysts were prepared by either the impregnation method (IM) or the deposition precipitation (DP) method as used in the literature [19]. The impregnation method was carried out by adding prepared amounts of $Ni(NO_3)_2{\cdot}6H_2O$ (50.54 g) , $Mg(NO_3)_2{\cdot}6H_2O$ (4.84 g), and CeO_2 (29.24 g) to D.I. water (250 mL) in a beaker (400 mL) and stirring for at least 24 hours then evaporating the water until it is visibly dry [17]. The precipitate was further dried in an oven at 60˚C for at least 48 hours prior to calcination. Calcination of the precipitate was achieved by loading the dried precipitate into a muffle furnace heated at 550˚C for 4 hours. The calcined precipitate was then crushed to a powder (approx. 100-200 mesh) using a mortar and pestle before being loaded in the reactor for pre-reduction/activation. Reduction of the catalyst was carried out at 200˚C for 4 hours under 5.2 MPa of H_2 gas. The deposition precipitation method was carried out by adding prepared amounts of $Ni(NO_3)_2{\cdot}6H_2O$ (50.54 g) , $Mg(NO_3)_2{\cdot}6H_2O$ (4.84 g), and CeO_2(29.24 g) to D.I. water (400 mL) in a 2-L glass beaker and stirred for about an hour. Precipitation was achieved through drop-wise addition of 1.5 M Na_2CO_3 (1 L). The mixture was allowed to age for at least 24 hours prior to filtration. The solid precipitate was filtered using a 202-Whatman® filter paper with a pore size of 15-19 μm. After filtration, the solids were washed in place with D.I. water (at least 4 L). The washed precipitate was then dried in a 60˚C oven for at least 48 hours prior to calcination. Calcination of the precipitate was achieved by loading the dried precipitate into a muffle furnace heated at the desired temperature for 4 hours. The calcined precipitate was then crushed to a powder using a mortar and pestle before being loaded to the reactor for pre-reduction/activation. Reduction of the catalyst was carried out at 200˚C for 4 hours under 5.2 MPa of H_2 gas.

4.2.3 Catalytic Activity Testing

Glycerol hydrogenolysis was carried out in a 300-mL batch pressure reactor (model 4561-Parr Instrument Company, Moline, IL). Appropriate amounts of glycerol, water, and catalyst were charged into the reactor before it was ready for testing. The headspace was flushed with hydrogen at for least 3 times, then the reactor was pressurized with hydrogen until desired pressure before being heated up to the desired temperature. Agitation was supplied 30-40˚C before reaching the desired temperature, which was taken as the starting time. After the designated reaction time, the reactor was quenched using a water bath to lower the temperature to at least 15 ˚C prior to gas venting and liquid sampling. Liquid products were analyzed using a gas chromatograph (Agilent 6890N) equipped with a flame ionization detector (FID) and DB wax (30 m long, 0.32 mm inside diameter, and 0.5 μm film thickness) [17].

The results are reported as percent glycerol conversion, percent selectivity towards a specific product, and yield of a specific product.

Percent glycerol conversion was computed as:

$$\text{Conversion (mol \%)} = \frac{G_c}{G_i} \times 100 = \frac{G_i - G_f}{G_i} \times 100$$

where: G_c - moles of glycerol converted, G_i – moles of glycerol before reaction, G_f- moles of glycerol after reaction

Selectivity towards a specific product was computed as:

$$\text{Selectivity (mol \%)} = S_i = \frac{P_i}{G_c} \times 100$$

where: S_i- selectivity towards a specific product, P_i – moles of specific product produced after reaction

Yield of a specific product was computed as:

$$\text{Yield (mol \%)} = \frac{S_i \times \text{Conversion}}{100}$$

4.2.4 Catalyst Characterization

4.2.4.1 XRD

XRD scans were collected on a Siemens D5000 theta-theta diffractometer using Cu κ-α radiation [1.54 angstrom] from 2 to 80˚ 2ϴ at 0.02˚/step and 1s/step scan rate.

4.2.4.2 Textural Properties

Nitrogen adsorption-desorption experiments were recorded by a Micromeritics TriStar II 3020 Automatic Physisorption Analyzer. Before adsorption analysis, samples were degassed under vacuum at 573 K for 1 hour. BET surface area was obtained using the Brunauer-Emmett-Teller (BET) model

4.2.4.3 H_2 Temperature Programmed Reduction (H_2-TPR)

H_2 temperature programmed reduction (H_2-TPR) was conducted on a Micromeritics AutoChem II 2920 Chemisorption Analyzer equipped with a thermal conductivity detector (TCD). Approximately 50 mg of sample was loaded in a U-shaped quartz reactor. The sample was pretreated with flowing He (50 sccm) at 473 K for 1 hour with the temperature brought down to 323 K. It was purged until a stable base line was reached. The temperature was raised to 873 K at a rate of 10˚C/min under flowing H_2-Ar (10% H_2) gas mixture at 50 sccm.

4.3 Results and Discussions

4.3.1 Catalyst Characterization

4.3.1.1 Textural properties of the catalyst of 25 wt% Ni/Ce:Mg (9:1)

In order to determine the effects preparation method and calcination temperature have on the textural properties of Ni/Ce:Mg (9:1), BET-surface area and pore volume were determined using an N_2 adsorption-desorption experiment (Table 4.1). Higher specific surface area (BET-Surface) and pore volume, but lower pore diameters were achieved when the catalyst was prepared via DP as compared to the catalyst prepared by IM. Raising the calcination temperature from 350˚C to 550˚C resulted in the decline of both specific surface area and pore volume and an increase in the pore diameter, while it was maintained upon further increase to

650˚C. The decline in surface area and pore volume and the increase in pore diameter with temperature have also been observed with other supported Ni catalysts [20-21] and DP prepared zirconia supported Cu catalyst [19].

Table 4.1 Textural properties of the catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared via different methods.

Catalyst Preparation	BET surface area (m^2/g)	Pore volume[a] (cm^3/g)	Pore diameter[b] (nm)
Impregnation Calcined at 550˚C	8.08	0.0521	270.70
DP Calcined at 550˚C	27.33	0.0879	101.86
DP Calcined at 650˚C	27.78	0.0832	103.79
DP Calcined at 350˚C	70.78	0.0973	45.52

a-BJH Adsorption cumulative pore volume, b- BJH Adsorption average pore width

4.3.1.2 XRD Patterns of 25 wt% Ni/Ce:Mg (9:1)

The XRD patterns were obtained from the activated/reduced Ni catalysts on Ce:Mg (9:1) prepared via impregnation method calcined at 550˚ and the DP method calcined at 350˚C, 550˚C, and 650˚C (Fig. 4.2) to evaluate the effects of preparation method and calcinations temperature on the structure of the catalyst. The catalysts seem to preserve the crystalline structure of the support CeO_2 [22-23]. The intensity of the peaks for NiO decreased with the change in preparation method from impregnation to DP. This result suggests that a better dispersion of NiO is achieved with the catalysts prepared by the DP method as compared to those prepared by impregnation. A slight shift in peak positions relative to the peaks associated with pure CeO_2 was also observed for each catalyst, which increased with change in preparation method from impregnation method to DP method and decreased calcination temperature. This behavior could be due to the formation of a solid solution of NiO-CeO_2, MgO-CeO_2, or NiO-MgO-CeO_2 [24-25].

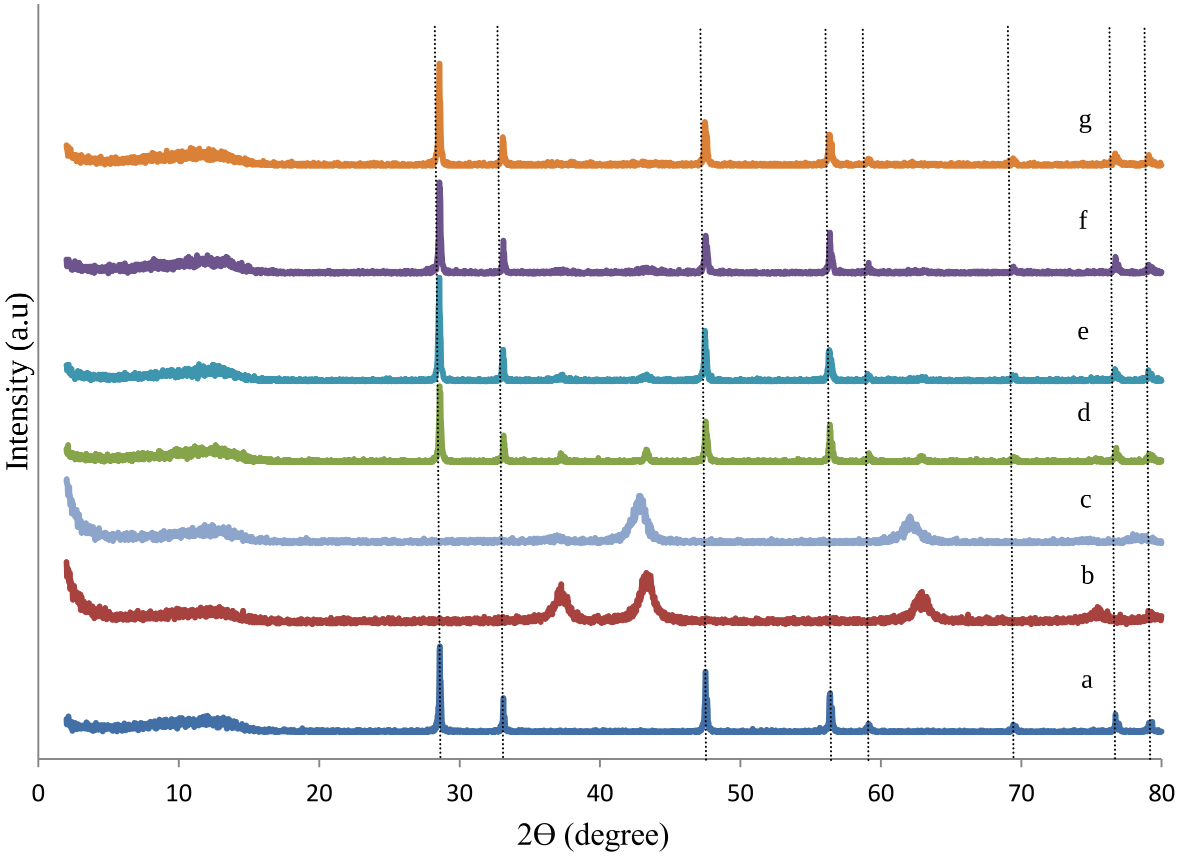

Figure 4.2 – XRD patterns of (a) CeO_2, (b) NiO, (c) MgO, (d) Ni/Ce:Mg (9:1) prepared by impregnation calcined at 550˚, (e) Ni/Ce:Mg (9:1) DP calcined at 650˚C, (f) Ni/Ce:Mg (9:1) DP calcined at 550˚C, and (g) Ni/Ce:Mg (9:1) DP calcined at 350˚C.

4.3.1.3 Temperature Programmed Reduction (H_2-TPR)

The reducibility of NiO species and metal support interaction of the catalysts of 25 wt% Ni/Ce:Mg (9:1) prepared via impregnation and DP methods calcined at 350˚C, 450˚C, and 550˚C were studied using H_2-TPR experiments (Fig. 4.3) [26]. The major peaks observed were at 400˚C, 400˚C, 357˚C, and 465˚C, for the catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared via impregnation and calcined at 550˚C, DP and calcined at 550˚C, 350˚C, and 650˚C, respectively. These peaks are likely from the reduction of surface bulk NiO species, while the different peak temperatures attributed to the extent of the interaction between NiO and support [26-28]. The change in preparation method didn’t alter the peak temperature, suggesting that there was no change in interaction between the active metal and the support. Raising the calcination temperature of the DP-prepared catalyst shifted the major peaks to higher temperatures, suggesting alteration of support properties and strengthening of Ni and support interaction [26-28]. The shift of major peaks to higher temperatures with the increase in calcination temperature has also been observed in Ni catalysts [20-21]. A distinct minor peak at around 213˚C was observed with the DP-prepared catalyst calcined at 350˚C, which could be from the reduction of NiO with no or minimal interaction with the support [20, 29].

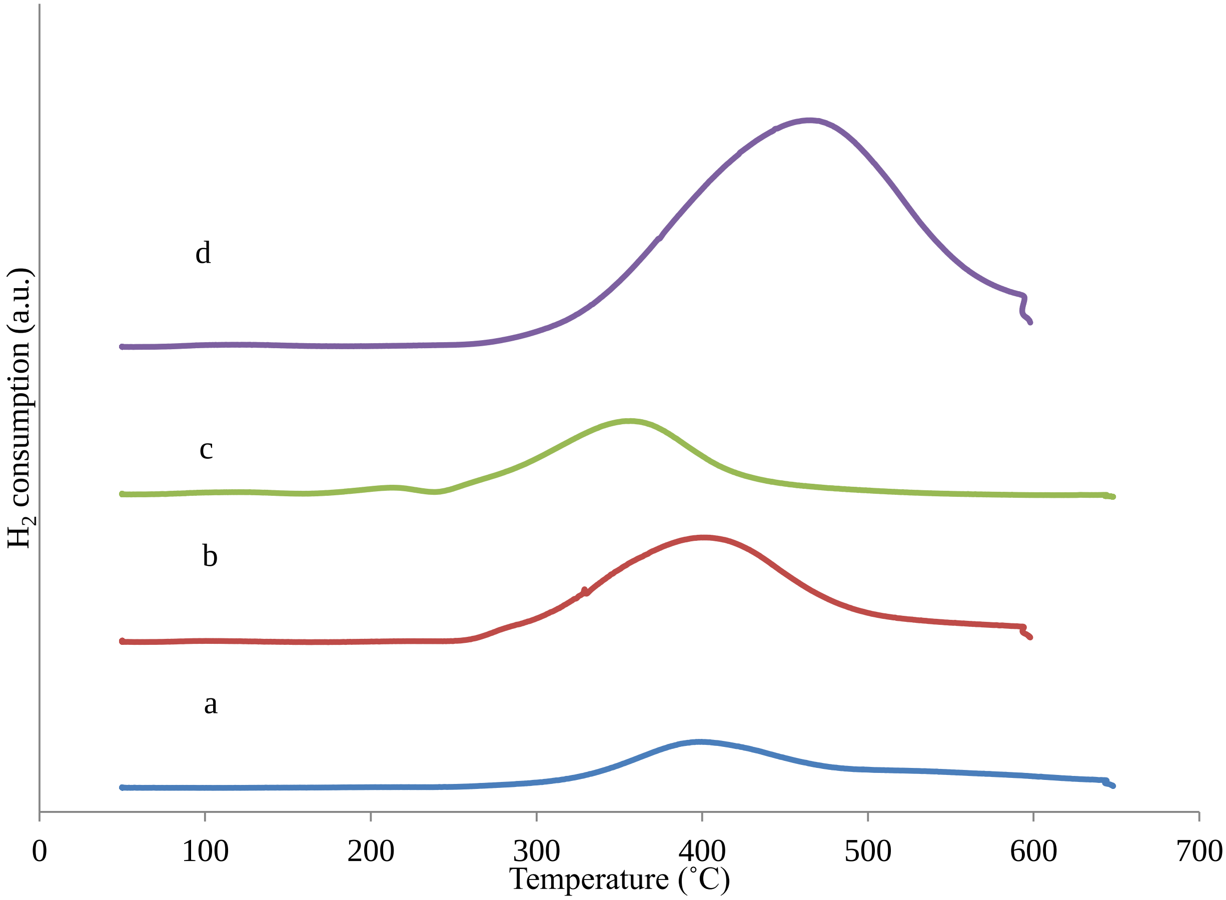

Figure 4.3 H_2-TPR profiles of the catalysts of 25 wt% Ni/Ce:Mg (9:1).
(a) 25 wt% Ni/Ce:Mg (9:1) prepared by impregnation calcined at 550˚, (b) 25 wt% Ni/Ce:Mg (9:1) DP calcined at 550˚C, (c) 25 wt% Ni/Ce:Mg (9:1) DP calcined at 350˚C, and (d) 25 wt% Ni/Ce:Mg (9:1) DP calcined at 650˚C.

4.3.2 Effect of Preparation Method

The catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared via DP method gave a higher glycerol conversion at 45.71% as compared to 28.63% of the catalyst prepared by impregnation (Table 4.2). The improvement in glycerol conversion may have been due to better dispersion of Ni and Mg onto CeO_2 as suggested by the XRD results. The observed increase in surface area and pore volume (Table 4.1) may also have contributed to the improved glycerol conversion. The increase in surface area and pore volume would allow better accesibility to reacting species, given the same amount of catalyst used, which could result in a higher conversion rate. The selectivities towards 1,2 PDO, ethanol, EG, and n-propanol were not altered by the preparation method. The peak temperatures in the H_2-TPR experiments (Fig. 4.3) were not altered by the choice of preparation method either. The H_2-TPR result suggests that there was no change in interaction between the active metal and support when the catalyst preparation method was changed from impregnation to DP. This might explain why there was no difference in product selectivity for the catalyst prepared via impregnation and deposition precipitation methods.

Table 4.2 Effect of preparation method on the activity of the catalysts of 25 wt% Ni/Ce:Mg (9:1); Reaction conditions: reactant 100 g (60 wt % glycerol in H_2O), 10 g catalyst, pH_2 = 6.9 MPa (initial), T= 215˚C, t= 24 h.

Catalyst Preparation (method)	Conversion (mol%)		Ethanol		Ethylene glycol		n-Propanol		1,2 PDO		Others
			S	Y	S	Y	S	Y	S	Y	S
	AE	RE	AE	RE	AE	RE	AE	RE	AE	RE	
Impregnation	28.63		15.28	4.38	5.34	1.53	ND	ND	62.14	17.79	17.25
	0.48	1.68	0.41	0.68	0.17	3.18	-	-	1.55	2.49	
Deposition Precipitation	45.71		15.26	6.98	5.76	2.63	ND	ND	63.64	29.09	15.34
	2.26	4.94	0.57	3.74	0.36	6.25	-	-	4.28	6.72	

S-selectivity of product (mol%), Y-yield of product (mol%), ND-none detected, AE = Absolute Error(%)= measured value - average value, RE =Relative Error(%)= (AE/average value) x100

4.3.3 Effect of Calcination Temperature on DP Prepared Ni/Ce:Mg (9:1)

The effect of calcination temperature on the catalytic activity on the catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared by DP was studied by varying calcination temperature at 350˚C, 550˚C, and 650˚C (Fig. 4.4). Comparable glycerol conversions of 43.29% and 45.71% were observed with the catalysts calcined at 350˚C and 550˚C, respectively. Further increase in calcination temperature to 650˚C, resulted in a noticeably higher glycerol conversion at 59.83%. The 1,2 PDO selectivity was observed to be highest at 67.93% with catalyst calcined at 350˚C. A similar 1,2 PDO selectivity was obtained with the catalysts calcined at 550˚C and 650˚C, which were 63.65% and 64.99%, respectively. The selectivity for ethanol was maintained upon the increase in calcination temperature from 350˚C to 550˚C at 15.61% and 15.26%, respectively, but declined to 11.22% upon further increment to 650˚C. No n-propanol formation was detected with the catalysts calcined at 350˚C and 550˚C, but was observed at a selectivity of 0.83% with the catalyst calcined at 650˚C. In terms of selectivity, the catalyst calcined at 350˚C gave the highest overall preference towards ethanol, 1,2 PDO, and EG and was further used to study the effect of process conditions.

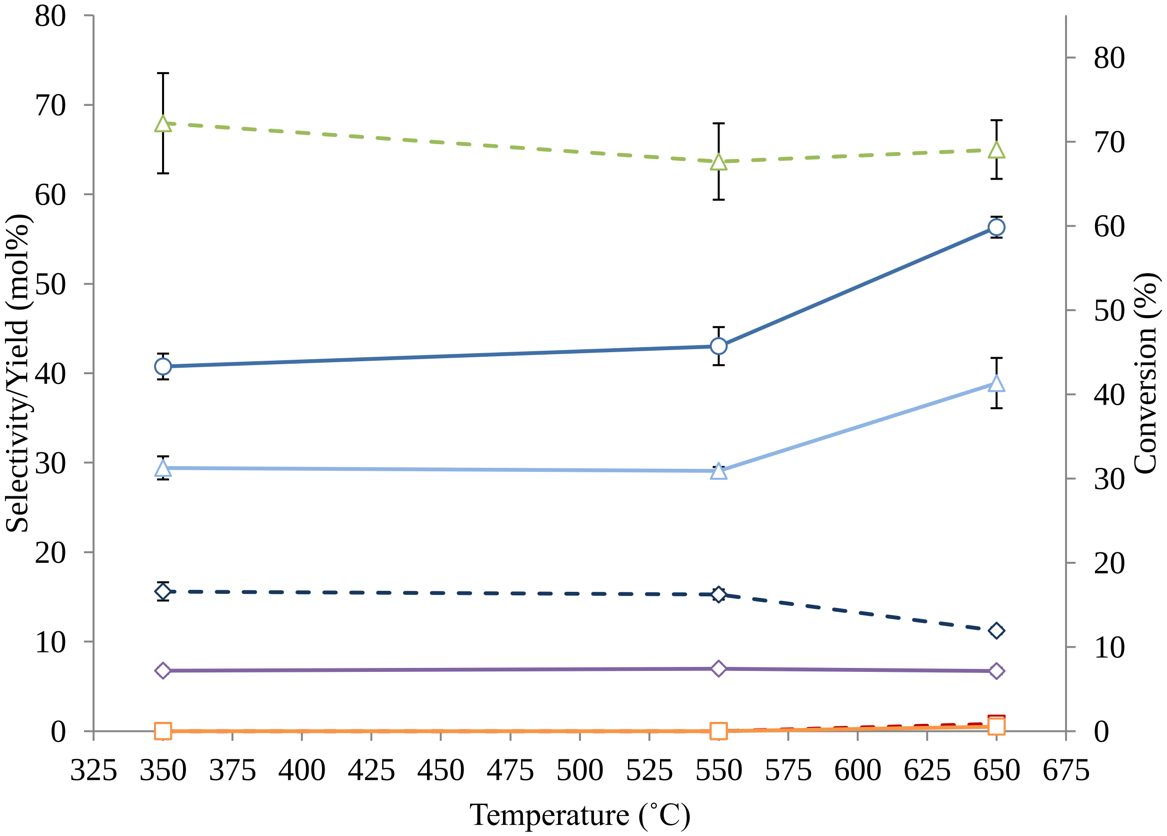

Figure 4.4 Effect of calcination temperature on the activity of the catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared by DP; Reaction conditions: reactant 100 g (60 wt% glycerol in H_2O), 10 g catalyst, pH_2 = 6.9 MPa (initial), T= 215˚C, t= 24 h; Legend: solid lines for glycerol conversion and product yields, dashed lines for product selectivity, (○) glycerol conversion, (◇) ethanol, (□) n-propanol, (△) 1,2 PDO; Error bars are based on absolute error from average value of duplicate.

The differences in activity and selectivity of the catalysts prepared by DP may have been due to the differences in their physical and structural characteristics [20]. Although the catalyst calcined at 350˚C has a higher surface area and high pore volume, Ni metal interaction with the support is much weaker than that of the catalysts calcined at 550˚C and 650˚C. This very combination may have also contributed or led to the improved overall selectivity towards the desired products and the catalyst activity similar to 550˚C calcined catalyst. Catalysts calcined at 550˚C and 650˚C have similar physical properties, but the interaction of Ni to support is greater for the latter. The stronger metal-support interaction has been shown to improve the dispersion and surface area of Ni in catalysts, while preventing agglomeration [20]. The improved dispersion and surface area of Ni in the catalysts may have contributed to the increase in glycerol conversion. The catalyst calcination at different temperatures may have altered support properties, as indicated by the shift of reduction peaks (Fig. 4.3) and slight shifts in XRD peaks (Fig. 4.2), which may have contributed to the slight differences in the product selectivity. Glycerol conversion increased from 27.57% to 43.29% and 68.87% when temperature was raised from 200˚C to 215˚C and 230˚C, respectively. The selectivity of 1,2 PDO improved from 60.87% to 67.93% upon the increment in temperature from 200˚C to 215˚C, but declined to 47.57% at 230˚C.

4.3.4 Effect of Reaction Temperature

The effect of reaction temperature on the catalytic activity of the catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared by DP was investigated at 200˚C, 215˚C, and 230˚C (Fig. 4.5). Glycerol conversion improved from 27.57% to 43.29% and 68.87% when temperature was raised from 200˚C to 215˚C and 230˚C, respectively. The 1,2 PDO selectivity was improved from 60.87% to 67.93% upon the increase in reaction temperature from 200˚C to 215˚C, but declined to 47.57% at 230˚C. The ethanol selectivity improved with the increase in the reaction temperature from 9.99% to 15.61% and 19.02% at 200˚C, 215˚C, and 230˚C, respectively. The n-propanol was only detected at 230˚C reaching a selectivity of 2.36%.

The increase of glycerol conversion with temperature may have been due to increase in energy intensity at higher temperatures for the reaction to occur, especially the dehydration process in the hydrogenolysis of glycerol. Better selectivity for 1,2 PDO at 215˚C may have been caused by favorable balance in dehydration and hydrogenation reactions, since dehydration is favored at higher temperatures and hydrogenation at lower temperatures [30]. The decline in the 1,2 PDO selectivity at 230˚C may have been caused by further hydrogenolysis, which is supported by higher ethanol and n-propanol production. Similar trends were observed when using the Ni catalysts on SiO_2 or Al_2O_3 for the hydrogenolysis of glycerol [14]. Although a higher selectivity for ethanol was observed at 230˚C, glycerol hydrogenolysis at 215˚C may have a better potential for ethanol production due to a much higher selectivity towards 1,2 PDO and much lower selectivity towards n-propanol.

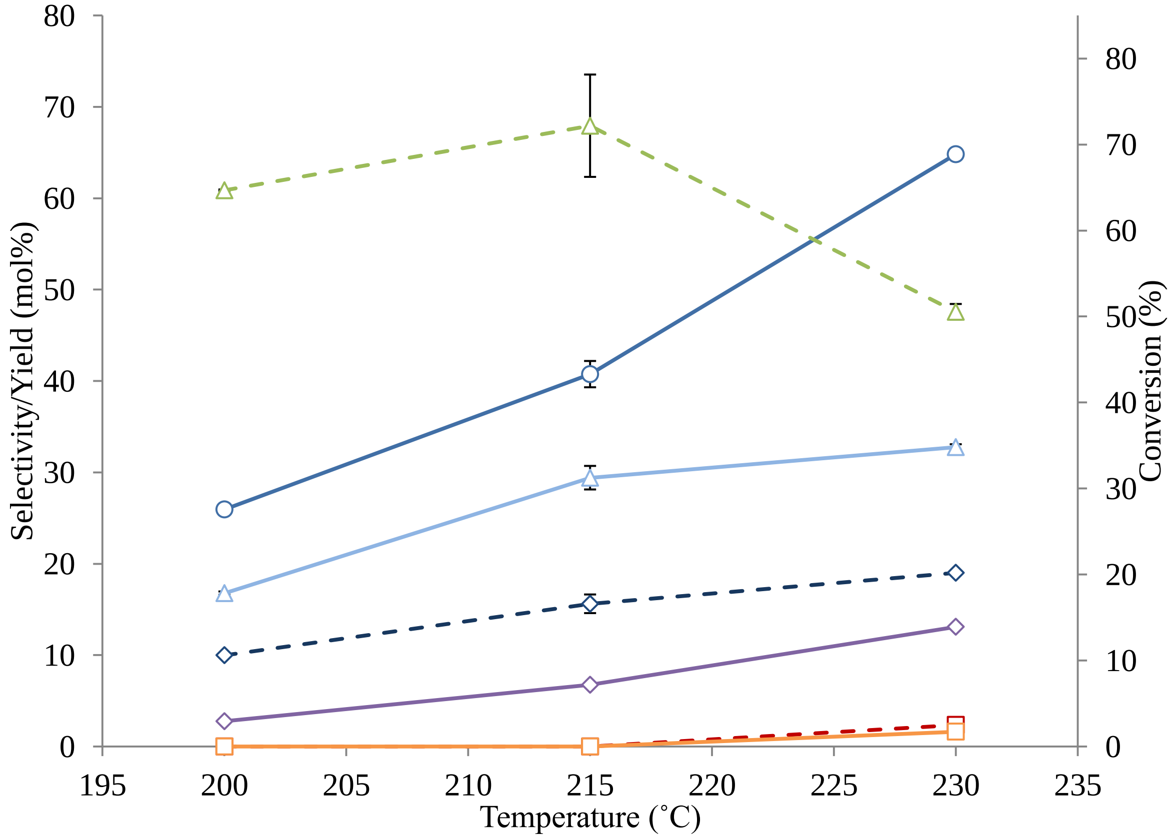

Figure 4.5 Effect of reaction temperature on the activity of the catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared by DP and calcined at 350˚C; Reaction conditions: reactant 100 g (60 wt% glycerol in H_2O), 10 g catalyst, pH_2 = 6.9 MPa (initial), t= 24 h; Legend: solid lines for glycerol conversion and product yields, dashed lines for product selectivity, (○) glycerol conversion, (◇) ethanol, (□) n-propanol, (△) 1,2 PDO; Error bars are based on absolute error from average value of duplicate.

4.3.5 Effect of Water Content

The effect of water content on the catalytic activity of the catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared by DP was investigated by varying the water content from 0 to 40 wt% (Fig. 4.6). Glycerol conversion declined from 80.14% to 64.18% and 43.29% upon the increase in water content from 0 to 20 wt% and 40 wt%, respectively. The 1,2 PDO selectivity was maintained at the levels of 56-58% with an increase in water content from 0 to 20 wt%, while it improved to 67.93% with the water content raised to 40 wt%. The selectivity for ethanol improved with the increase in water content from 11.76% to 13.61%, and 15.61% with 0 wt%, 20 wt%, and 40 wt% water in glycerol, respectively.

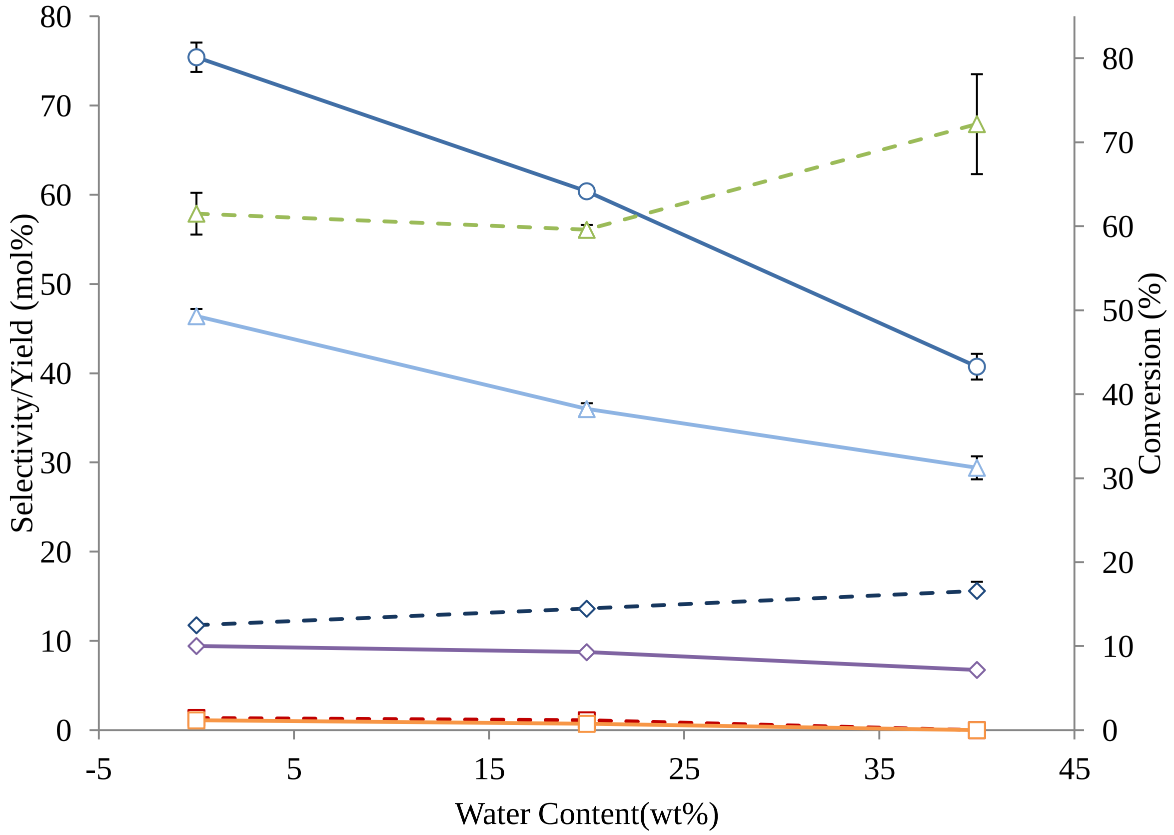

Figure 4.6 Effect of initial water content on the activity of the catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared by DP and calcined at 350˚C; Reaction conditions: reactant-60 g glycerol, 10 g 25 wt% Ni/Ce:Mg (9:1) DP calcined at 350˚C, pH2 = 6.9 MPa (initial), t= 24 h; Legend: solid lines for glycerol conversion and product yields, dashed lines for product selectivity, (○) glycerol conversion, (◇) ethanol, (□) n-propanol, (△) 1,2 PDO; Error bars are based on absolute error from average value of duplicate.

On the other hand, n-propanol selectivity declined with the increase in water content. The n-propanol selectivity was observed to be low at 1.37%, 1.10%, and 0% with 0 wt%, 20 wt%, and 40 wt% water in glycerol, respectively.

The decline in glycerol conversion with the increase in water content may have been due to the dilution effect of water as a solvent and its inhibition of the hydrogenolysis reaction. Since water is a by-product in the hydrogenolysis of glycerol, its presence favors the reverse reaction of dehydration thereby inhibiting the hydrogenolysis reaction [31-32]. At a lower water content, the 1,2 PDO and ethanol selectivities declined, which may have resulted from the degradation [33-34] or polymerization [35] of these products. Ethanol selectivity may also have decreased due to an increase n-propanol production at lower water content, thereby competing with and then reducing ethanol production. The production of n-propanol from glycerol requires the dehydration of two water molecules, and the presence of excess water did not favor its production as observed with its decreasing selectivity upon the increase in water content.

4.3.6 Effect of Hydrogen Pressure

The effect of initial hydrogen pressure on glycerol hydrogenolysis using the catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared by DP and calcined at 350˚C was investigated in the range of 6.9 MPa to 8.6 MPa (Table 4.3). Raising the initial hydrogen pressure slightly improved glycerol conversion and n-propanol selectivity. It also caused a reduction of 1,2 PDO and ethanol selectivities. Hydrogen is a reactant in the hydrogenolysis reaction and the increase in initial hydrogen pressure in the enclosed batch process also increases the initial amount of hydrogen present. The presence of excess water may have favored the forward reaction for hydrogenolysis with the preference to glycerol utilization and n-propanol production. The increase in glycerol utilization and n-propanol production may have inhibited/reduced ethanol production/selectivity. The decline in 1,2 PDO selectivity may have resulted from increase in n-propanol and EG production [14].

4.3.7 Effect of Reaction Time

The effect of reaction time on glycerol hydrogenolysis with the catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared by DP and calcined at 350˚C as catalyst was investigated by extending the reaction time to 48 hours (Table 4.3). Glycerol conversion and ethanol selectivity improved, but the 1,2 PDO selectivity declined. The 1,2 PDO selectivity may have declined due to further hydrogenolysis as observed with the increase in ethanol and n-propanol selectivities. These results are in agreement with previous studies, which 1,2 PDO is considered as a precursor for ethanol and propanol production [15,36].

Table 4.3 Effect of initial hydrogen pressure and time
Reaction conditions: reactant 100 g (60 wt % glycerol in H_2O), 25 wt% Ni/Ce:Mg (9:1) DP calcined at 350˚C, T=215˚C.

Conditions pH_2 (MPa); time (h)	Conversion (mol %)		Ethanol		Ethylene glycol		n-Propanol		1,2 PDO		Others
			S	Y	S	Y	S	Y	S	Y	S
	AE	RE	AE	RE	AE	RE	AE	RE	AE	RE	
6.9 ; 24	43.29		15.61	6.75	6.80	2.94	ND	ND	67.93	29.41	9.66
	1.53	3.53	1.02	6.53	0.54	7.94	-	-	5.6	8.24	
8.6 ; 24	51.40		12.40	6.38	7.38	3.80	0.73	0.38	64.12	33	15.37
	1.66	3.23	0.04	0.32	0.3	4.07	0.01	1.37	1.50	2.34	
8.6 ; 48	75.64		15.43	11.68	7.30	5.53	1.34	1.02	60.81	46.0	15.12
	1.93	2.55	0.65	4.21	0.08	1.10	0.07	5.22	0.36	0.59	

Notes: pH_2=initial Hydrogen pressure (at room temperature), WC=water content, ND= none detected, AE = Absolute Error(%)= measured value - average value, RE =Relative Error(%)= (AE/average value) x 100

4.3.8 Comparison of 25 wt% Ni/Ce:Mg (9:1) DP Calcined at 350˚C Activity with Raney® Ni Catalyst

The catalytic activity of the catalyst of 25 wt% Ni/Ce:Mg (9:1) prepared by DP and calcined at 350˚C was compared to the commercial Raney® Ni, which is known to produce selectively 1,2 PDO and ethanol from glycerol hydrogenolysis [15, 36] (Table 4.4). The Raney® Ni clearly showed higher activity as it gave similar glycerol conversion with 25 wt% Ni/Ce:Mg (9:1) at half amount of the catalyst used and one fourth the reaction of time as compared to the catalyst of 25 wt% Ni/Ce:Mg (9:1). Selectivity-wise though, it was observed at all temperatures tested that the 25 wt% Ni/Ce:Mg (9:1) catalyst developed in our study provides higher 1,2 PDO and ethanol selectivities. The results suggest that the catalyst of 25 wt%

Ni/Ce:Mg (9:1) DP has a good potential for the selective production of 1,2 PDO and ethanol from glycerol hydrogenolysis.

Table 4.4 Catalyst activity comparison of 25 wt% Ni/Ce:Mg (9:1) DP calcined at 350˚C with Raney® Ni; Reaction conditions: feed 100 g (60 wt% glycerol in H_2O), pH_2 = 6.9 MPa

Catalyst	T(˚C)	Conversion (mo%)		Ethanol		Ethylene glycol		n-Propanol		1,2 PDO		Others
				S	Y	S	Y	S	Y	S	Y	S
		SD	CV	SD	CV	SD	CV	SD	CV	SD	CV	
25 wt% Ni/Ce:Mg (9:1)	200	27.57		9.99	2.75	5.77	1.59	ND	ND	60.87	16.78	23.37
		0.46	1.66	1.06	9.95	0.17	2.84	-	-	3.49	5.54	
	215	43.29		15.61	6.75	6.80	2.94	ND	ND	67.93	29.41	9.66
		2.58	5.80	1.76	10.70	0.85	11.72	-	-	5.41	7.93	
	230	68.87		19.02	13.10	6.80	2.94	2.36	1.63	47.57	32.76	22.62
		0.62	0.91	1.31	7.18	0.15	2.55	0.16	6.34	1.76	3.63	
Raney® Ni	200	31.00		4.59	1.42	52.80	16.39	ND	ND	22.34	6.93	20.27
		1.09	3.50	0.41	8.93	1.89	3.57	-	-	0.36	1.59	
	215	49.40		9.07	4.48	34.73	17.16	0.76	0.38	26.15	12.92	29.9
		1.34	2.72	0.26	2.82	1.33	5.73	0.01	1.29	0.60	2.29	
	230	67.46		11.43	7.71	18.63	12.57	1.19	0.80	26.70	18.01	42.05
		2.62	3.88	0.33	2.85	1.73	9.28	0.04	3.66	0.34	1.29	

Notes: for Raney® Ni 5 g catalyst was used with t= 6 h, for 25 wt% Ni/Ce:Mg (9:1) 10 g catalyst was used with t= 24 h, S- selectivity of product (mol%), Y-yield of product (mol%); SD (%)=absolute value of the standard deviation (%), CV= Coefficient of Variation (%)=(SD/Average value) x100

4.4 Conclusions

A change in the preparation method for the catalyst of 25 wt% Ni/Ce:Mg (9:1) from impregnation to DP results in higher catalytic activity, while retaining similar levels of ethanol and 1,2 PDO selectivities. The increase in calcination temperature of the catalyst 25 wt% Ni/Ce:Mg (9:1) prepared by DP from 350˚C to 650 ˚C improves glycerol conversion, but reduces the overall selectivities of 1,2 PDO and ethanol. An increase in the reaction temperature from 200˚C to 230˚C improves glycerol conversion, ethanol selectivity, and propanol selectivity. Among the temperatures tested, the highest 1,2 PDO selectivity reached 67.93% at 215˚C. Overall selectivity of 1,2 PDO and ethanol is favored at 215˚C with a combined selectivity of 83.54%. The increase in initial water content reduces glycerol conversion, while improving the selectivities of 1,2 PDO and ethanol, but reduces the n-propanol selectivity. Hydrogen initial pressure increase from 6.9 MPa to 8.6 MPa improves glycerol conversion. It also reduces the selectivities of ethanol and 1,2 PDO. Extension of the reaction time from 24 to 48 hours increases glycerol conversion, the selectivities of ethanol and n-propanol, while it decreases 1,2 PDO selectivity. A comparison of the catalytic activity of Raney® Ni catalyst and the catalyst of 25 wt% Ni/Ce:Mg (9:1) in the temperature range of 200˚C-230˚C reveals that the latter has a better potential for the selective production of ethanol and 1,2 PDO from glycerol hydrogenolysis.

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Chapter 5

Summary and Recommendations for Future Research

5.1 Summary

A supported Ni catalyst was developed for the selective production of ethanol and 1,2 propanediol (1,2 PDO) from glycerol hydrogenolysis. Among various supports screened, the combination of Ni catalyst on CeO_2 showed the highest potential in producing both ethanol and 1,2 PDO from glycerol hydrogenolysis. Raising the reaction temperature from 215˚C to 245˚C increased glycerol conversion and propanol selectivity, but decreased the selectivity towards 1,2 PDO. Highest selectivity for ethanol attained with Ni catalyst on CeO_2 reached 9.47% at 230˚C, but higher overall combined selectivity for ethanol and 1,2 PDO is attained at 215˚C. Increasing Ni content in the range of 15-50 wt% improved glycerol conversion, while reducing ethanol and 1,2 PDO selectivity at 25 wt% Ni onwards. The addition of Al, Si, Zn, or Mg as promoters at 80:20 (Ce:promoter molar ratio) to Ni/CeO_2 combination reduced glycerol conversion, but improved selectivity for 1,2 PDO in the order of Zn>Mg>Si>Al. Addition of Si and Mg also improved the ethanol selectivity, while reducing selectivity for n-propanol. The Ni/Ce:Mg catalyst provided better overall selectivity towards 1,2 PDO and ethanol at 73.10% and 8.0%, respectively. Increasing Mg content from 0 to 20% (Mg:Ce) improved 1,2 PDO selectivity, and 10% Mg gave the highest selectivity for ethanol at 15.28%.

A change in the preparation method for the catalyst of 25 wt% Ni/Ce:Mg (9:1) from impregnation to DP results in a higher catalyst activity, while retaining similar levels of ethanol and 1,2 PDO selectivities. The increase in calcination temperature of the catalyst 25 wt% Ni/Ce:Mg (9:1) prepared by DP from 350˚C to 650 ˚C improved glycerol conversion, but reduced the overall selectivities of 1,2 PDO and ethanol. An increase in the reaction temperature from 200˚C to 230˚C improved glycerol conversion, ethanol selectivity, and propanol selectivity. Among the temperatures tested, the highest 1,2 PDO selectivity reached 67.93% at 215˚C. Production of 1,2 PDO and ethanol was favored at 215˚C with a combined selectivity of 83.54%. The increase in initial water content reduced the glycerol conversion and n-propanol selectivity, while it improved the selectivities of 1,2 PDO and ethanol. Hydrogen initial pressure increase from 6.9 MPa (1000 psi) to 8.6 MPa (1,250 psi) improved glycerol conversion, reduced ethanol and 1,2 PDO selectivities. Extension of the reaction time from 24 to 48 hours improved glycerol conversion, the selectivities of ethanol and n-propanol, but decreased 1,2 PDO selectivity.

After the comparison of the catalytic activity to that of Raney® Ni in the temperature range of 200˚C-230˚C, 25 wt% Ni/Ce:Mg (9:1) shows a lower rate of glycerol conversion. However, it has a higher selectivity towards ethanol and 1,2 PDO, thus has a higher potential for the selective production of ethanol and 1,2 PDO from glycerol hydrogenolysis.

5.2 Recommendations for Future Research

The catalyst of 25 wt% Ni/Ce:Mg (9:1) has a great potential for selective production of ethanol and 1,2 PDO from glycerol hydrogenolysis. However, there are some important aspects that need to be investigated in order to assess the catalyst further, especially for the production of ethanol. Therefore, I recommend the investigation of the following in future works:

1) The use of the catalyst in a continuous mode of reaction to assess the stability of the catalyst and its potential for actual practical use in large scale production of ethanol and 1,2 PDO from glycerol.

2) The use of the catalyst with 1,2 PDO as the starting feed stock to assess the potential of a two stage process. In this case, a catalyst with a very high 1,2 PDO selectivity from glycerol hydrogenolysis can be used then 1,2 PDO produced will be converted to ethanol by using the catalyst of 25 wt% Ni/Ce:Mg (9:1).

3) The use of crude glycerol as the feedstock to assess the effect of impurities on the activity of the catalyst for glycerol hydrogenolysis and to determine the minimal purification process to allow the direct use of crude glycerol for the selective production of ethanol and 1,2 PDO from glycerol hydrogenolysis.

Appendix A

Detailed Materials, Equipments, and Experimental Methods

A.1 Materials:

In this work, glycerol (<99.5%) obtained from Macron chemicals and D.I. water were used as the reactant for the aqueous phase reaction. The chemicals for use as precursors for preparing the catalysts include $Ni(NO_3)_2 \cdot 6H_2O$ (98%) from Alfa Aesar, $Al(NO_3)_3 \cdot 9H_2O$ from J.T. Baker, $Mg(NO_3)_2 \cdot 6H_2O$ from Ward's Science, $Ca(NO_3)_2 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ from Aqua Solutions, SiO_2 (silica mesh 230-400, Fisher) and CeO_2 from Acros Organics. The precipitating agent used during catalyst preparation was Na_2CO_3. The reference commercial catalyst Raney® Ni was obtained from Aldrich Chemistry.Standard samples that were used as references for the GC analysis include methanol (99.8%) from EMD chemicals, ethanol (USP grade) from Pharmco, Acetone (HPLC grade) from EMD chemicals, isopropyl alcohol (99.99%) from EMD chemicals, n-propanol (99.7%) from Sigma-Aldrich, n-butanol (99.8%) from Sigma-Aldrich, ethylene glycol (100%) from J.T. Baker, hydroxyacetone (90%) from Sigma-Aldrich, and 1,2 Propanediol (99.5%) from Alfa Aesar. Bromothymol blue from Aqua solutions, Benzoic acid (ACS grade) and benzene from EMD (ACS grade) were used for the determination of catalyst basic sites.

In this study batch experiments were conducted in a 300-mL reactor (model 4561-Parr Instrument Company, Moline, IL) that can be operated up to 350 ˚C and 20.6 MPa. It was equipped with a process controller to regulate and monitor the process temperature, pressure, and agitation speed,

A.2 Experimental Methods

A.2.1 Catalyst Preparation (screening)

The supported catalysts of nickel (Ni) were prepared via the precipitation or impregnation method. Precipitation was used for the preparation of Ni catalysts supported on Al_2O_3, MgO, CaO, ZnO, MgO-Al_2O_3, CaO-Al_2O_3, ZnO-Al_2O_3. As an example, 40 g of 25 wt% Ni supported on Alumina (Ni/Al_2O_3) prepared by precipitation was carried out by adding 50.54 g $Ni(NO_3)_2 \cdot 6H_2O$ and 221.98 g $Al(NO_3)_3 \cdot 9H_2O$ to 400 mL of Deioinized (DI) water in a 2 L glass container and stirred for at least an hour. Precipitation was achieved through drop-wise addition of 1.5 M Na_2CO_3 (1 L). The mixture was allowed to age for at least 24 hours prior to filtration. The solid precipitate was filtered using a 202-Whatman® filter paper of 15-19 μm porosity. After filtration, the solids were washed in place with DI water (at least 4 L). The washed precipitate was then dried in a 60˚C oven for at least 48 hours prior to calcination. Calcination of the precipitate was achieved by loading the dried precipitated into a muffler furnace heated at 550˚C for 4 hours. The calcined precipitate was crushed to a powder (100-200 mesh) using a mortar and pestle prior to being loaded to the reactor for pre-reduction/activation. Reduction of the catalysts was carried out at 200˚C for 4 hours under 5.2 MPa (750 psi) of H_2 gas.

Catalyst preparation via the impregnation method was used for preparation of supported Ni catalysts on SiO_2, CeO_2, and SiO_2-Al_2O_3. As an example, 40 g of 25 wt% Ni supported on Silica (Ni/SiO_2) prepared by impregnation was carried out by adding 50.54 g $Ni(NO_3)_2 \cdot 6H_2O$ and 30 g SiO_2 to 250 mL of DI water in a 400 mL beaker and stirring for at least 24 hours. The mixture was heated at 80-90˚C to evaporate the water until it is visibly dry. The precipitate was further dried in a 60˚C oven for at least 48 hours prior to calcination. Calcination and pre-reduction/activation were done in the same manner with catalysts prepared via the precipitation method.

A.2.2 Catalytic Activity Testing

Testing of the catalyst activity was carried out in batch experiments. In a typical batch reaction 60 g of glycerol, 40 g of DI, and 5 g of activated catalyst were weighed and placed into the batch reactor vessel. Initial reaction pressure was set at 4.1 MPa for hydrogen. Agitation was set at 500 rpm and started as soon as the vessel temperature reached the reaction temperature desired. Starting time was based on the time agitation of the vessel started.

A.2.3 Analytical Methods

Quantitative analyses of reaction products and residual glycerol were carried out using a gas chromatograph (Agilent 6890N) equipped with a flame ionization detector (FID) and DB wax column (30 m long, 0.32 mm inside diameter, and 0.5 μm film thickness). The initial oven temperature was set at 30 ˚C for 10min and ramped to 220 ˚C at 30˚C/min with a final hold time of 13 min. Samples of 1 µL were injected with a split ratio of 60:1 and inlet port temperature of 250 ˚C. Helium was used as the carrier gas with starting pressure of 48 kPa (7 psig) and a holding time of 10 minutes and then ramped up to 103 kPa (15 psig) at a rate of 34.5 kPa/min (5 psi/min). The FID was set at 300 ˚C with a nitrogen makeup gas of 30 mL/min [1]. Samples were prepared by adding 100 µL of sample with 100µL of standard solution (5 wt% n-butanol), and 800 µL of HPLC grade acetone.

The results are reported as molar glycerol conversion, selectivity towards a specific product, and yield of a specific product as defined below.

Glycerol conversion was computed as:

$$\text{Conversion (\%)}=\frac{G_c}{G_i}\times 100=\frac{G_i\text{-}G_f}{G_i}\times 100$$

where: G_c - moles of glycerol converted, G_i – moles of glycerol before reaction, G_f- moles of glycerol after reaction

Selectivity towards a specific product was computed as:

$$\text{Selectivity (\%)}=S_i=\frac{P_i}{G_c}\times 100$$

where: S_i- selectivity towards a specific product, P_i – moles of specific product produced after reaction

Yield of a specific product was computed as:

$$\text{Yield (\%)}=\frac{S_i\times \text{Conversion}}{100}$$

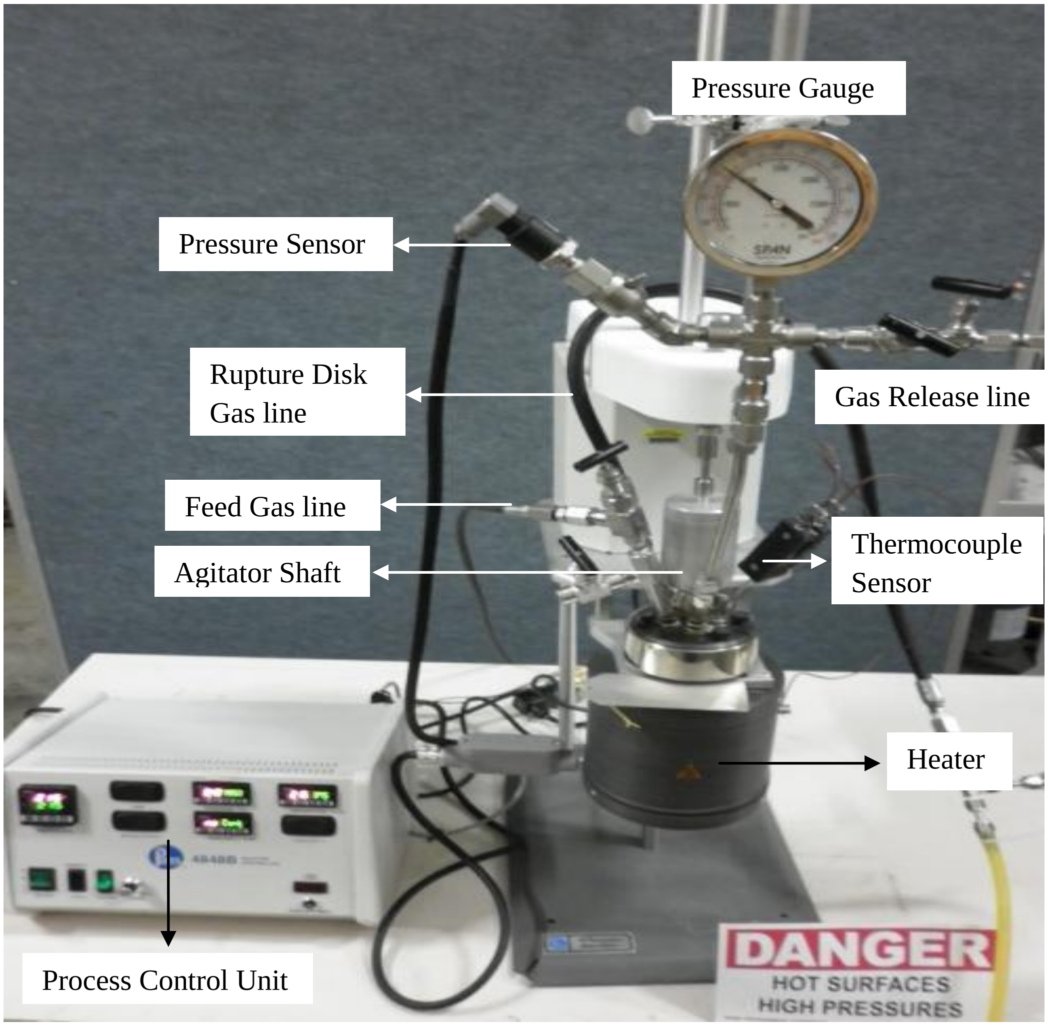

Figure A.1 Batch reactor set-up used in this study (model 4561-Parr Instrument Company, Moline, IL).

A.3 Catalyst Characterization

A.3.1 XRD

XRD scans were collected on a Siemens D5000 theta-theta diffractometer using Cu κ-α radiation [1.54 angstrom] from 2 to 80˚ 2Ө at 0.02˚/step and 1s /step scan rate.

A.3.2 Textural Properties

Nitrogen adsorption-desorption experiments were recorded on a Micromeritics TriStar II 3020 Automatic Physisorption Analyzer. Before adsorption analysis, samples were degassed under vacuum at 573 K for 1 hour. BET surface area was obtained using the Brunauer-Emmett-Teller (BET) model.

A.3.3 H_2 Temperature Programmed Reduction (H_2-TPR)

H_2 temperature programmed reduction (H_2-TPR) was conducted by a Micromeritics AutoChem II 2920 Chemisorption Analyzer equipped with a thermal conductivity detector (TCD). A sample of approximately 50 mg was loaded in a U-shaped quartz reactor. The sample was pretreated with flowing He (50 standard cubic centimeters per minute-sccm) at 473 K for 1 hour with the temperature brought down to 323 K. It was purged until a stable base line was reached. The temperature was raised to 873 K at a rate of 10˚C/min under flowing H_2-Ar (10% H_2) gas mixture at 50 sccm.

A.3.4 Determination of Total Basic Sites

Bromothymol blue of 0.002 N in benzene, an indicator for total basic sites determination, was prepared by adding 0.128 g of bromothyhmol blue in 100 mL of benzene. Benzoic acid of 0.1 N, used as the titrating agent, was prepared by adding 2.4424 g in 200 mL of benzene. A catalyst sample of approximately 0.1 g was placed in a 100-mL Erlenmeyer flask containing 5 mL of bezene with 0.2 mL of indicator solution. The 0.1 N benzoic acid in benzene was added dropwise using a titration burrette. The end-point was taken as the point at which the green color disappeared. The total amount of basic sites is expressed in the units of mmoles/g of catalyst. [2]

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Appendix B

Basis for standard deviation

Table B1 Computed values of standard deviation for Raney® Ni at 200˚C.

Temperature (˚C)	Conversion (mol%)	Selecivity (mol%)			
		Ethanol	n-Propanol	1,2 PDO	Ethylene glycol
200	31.99	4.61	0	22.39	51.14
	31.17	4.94	0	21.98	52.71
	29.84	4.13	0	22.69	54.9
Average (Ave)	31.00	4.56	0	22.35	52.92
Standard deviation (SD)	1.09	0.41	NI	0.36	1.89
Coefficient of Variation (CV)	0.035	0.089	NI	0.016	0.036

NI-not included in computations

Table B2 Computed values of standard deviation for Raney® Ni at 215˚C.

Temperature (˚C)	Conversion (mol%)	Selecivity (mol%)			
		Ethanol	n-Propanol	1,2 PDO	Ethylene glycol
215	50.85	8.79	0.77	25.48	21.7
	48.2	9.2	0.76	26.6	24.27
	49.14	9.26	0.78	26.41	23.57
Average (Ave)	49.40	9.08	0.77	26.16	23.18
Standard deviation (SD)	1.34	0.26	0.01	0.60	1.33
Coefficient of Variation (CV)	2.72	2.82	1.30	2.29	5.73

Table B3 Computed values of standard deviation for Raney® Ni at 230˚C.

Temperature (˚C)	Conversion (mol%)	Selectivity (mol%)			
		Ethanol	n-Propanol	1,2 PDO	Ethylene glycol
230	70.41	11.24	1.24	26.64	16.83
	65.41	11.27	1.16	27.06	20.27
	66.57	11.82	1.17	26.38	18.93
Average (Ave)	67.46	11.44	1.19	26.69	18.68
Standard deviation (SD)	2.62	0.33	0.044	0.34	1.73
Coefficient of Variation (CV)	3.88	2.85	3.66	1.29	9.28

$$\mathrm{AVE} = \frac{\mathrm{X1} + \mathrm{X2} + \mathrm{X3}}{3}$$

$$\mathrm{SD} = \pm\sqrt{\frac{(\mathrm{X1} - \mathrm{AVE})^2 + (\mathrm{X2} - \mathrm{AVE})^2 + (\mathrm{X3} - \mathrm{AVE})^2}{3 - 1}}$$

Sample Computations:

For glycerol conversion at 200˚C

$$\mathrm{AVE} = \frac{31.99 + 31.17 + 29.84}{3} = 31.00$$

$$\mathrm{SD} = \pm\sqrt{\frac{(31.99 - 31.00)^2 + (31.17 - 31.00)^2 + (29.84 - 31.00)^2}{3 - 1}} = 1.09$$

$$\mathrm{CV} = \frac{\mathrm{SD}}{\mathrm{AVE}}\mathrm{X}100 = \frac{1.09}{31.00} \times 100 = 3.50$$

Taking the average of all CV:

$$= \frac{3.50 + 8.93 + 1.59 + 3.57 + 2.72 + 2.82 + 1.30 + 2.29 + 5.73 + 3.88 + 2.85 + 3.66 + 1.29 + 9.28}{14}$$

$$= \pm 3.72\ \%\ \text{of average value}$$

Therefore:

The average SD based on the percentage from the average value is 3.72%

Table B4 Percentage of deviation based on average value (assuming normal distribution).

Confidence Interval (%)	Number of Standard Deviations	Expanded Uncertainty (relative to the average value)
65	1	3.72
95	2	7.44
99	3	11.16

Example:

Average value is a 31.00 at 95% Confidence Interval:

$$\text{Actual Expanded Uncertainty} = \frac{7.44}{100}\text{X}31.00 = 2.31$$

Therefore at 95% Confidence Interval the measurement could lie in the interval

31.00±2.31 or in the range of 28.69 to 33.31.

Table B5 Computed values of standard deviation of the catalyst of 25 wt% Ni/Ce:Mg(9:1) at 200˚C.

Temperature (˚C)	Conversion (mol%)	Selecivity (mol%)			
		Ethanol	n-Propanol	1,2 PDO	Ethylene glycol
200	27.82	9.84	0	60.98	5.73
	27.31	10.19	0	60.81	5.81
	28.23	11.82	0	66.93	6.05
Average (Ave)	27.79	10.62	0	62.91	5.86
Standard deviation (SD)	0.46	1.06	NI	3.49	0.17
Coefficient of Variation (CV)	1.66	9.95	0	5.54	2.84

NI-not included in computations

Table B6 Computed values of standard deviation of the catalyst of 25 wt% Ni/Ce:Mg(9:1) at 215˚C.

Temperature (˚C)	Conversion (mol%)	Selecivity (mol%)			
		Ethanol	n-Propanol	1,2 PDO	Ethylene glycol
215	44.82	14.66	0	62.72	6.32
	41.76	16.63	0	73.53	7.34
	46.89	18.18	0	68.5	8
Average (Ave)	44.49	16.49	0	68.25	7.22
Standard deviation (SD)	2.58	1.76	0	5.41	0.85
Coefficient of Variation (CV)	5.80	10.70	0	7.93	11.72

Table B7 Computed values of standard deviation of the catalyst of 25 wt% Ni/Ce:Mg(9:1) at 230˚C.

Temperature (˚C)	Conversion (mol%)	Selectivity (mol%)			
		Ethanol	n-Propanol	1,2 PDO	Ethylene glycol
230	68.29	18.99	2.38	48.42	5.9
	69.44	19.03	2.33	46.73	5.72
	68.45	16.74	2.62	50.25	5.61
Average (Ave)	68.73	18.25	2.44	48.47	5.74
Standard deviation (SD)	0.62	1.31	0.16	1.76	0.15
Coefficient of Variation (CV)	0.91	7.18	6.34	3.63	2.55

Table B8 Percentage of deviation based on average value (assuming normal distribution)

Confidence Interval (%)	Number of Standard Deviations	Expanded Uncertainty (relative to the average value)
65	1	5.96
95	2	11.93
99	3	17.88