SCREENING OF PROMOTED CeO$_2$/Al$_2$O$_3$ CATALYSTS IN AQUEOUS PHASE GLYCEROL REFORMING AND HYDROGENOLYSIS INTO 1,2-PROPANEDIOL

(Penyaringan Mangkin Penggalak CeO$_2$/Al$_2$O$_3$ dalam Fasa Akueus Pembaharuan dan Hidrogenolisis Gliserol Kepada 1,2-Propanadiol)

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Abstract

A series of promoted CeO$_2$/Al$_2$O$_3$ catalysts (10Cu-90CeO$_2$/Al$_2$O$_3$, 10Ni-90CeO$_2$/Al$_2$O$_3$, 10Co-90CeO$_2$/Al$_2$O$_3$) were synthesized via method of impregnation and later calcined at 600 ℃. Those catalysts were formerly tested for their physico-chemical properties by X-ray diffraction (XRD), H$_2$-temperature programmed reduction (H$_2$-TPR), and NH$_3$-temperature programmed desorption (NH$_3$–TPD). After characterized, it was then evaluated in the performance of catalytic glycerol conversion into 1,2-propanediol; propylene glycol (1,2-PDO; PG) via aqueous phase glycerol reforming and hydrogenolysis route under inert N$_2$ flow. Among the examined catalysts, CeO$_2$/Al$_2$O$_3$ with 10wt% Cu loading (10Cu-90CeO$_2$/Al$_2$O$_3$) showed optimum catalytic activity with 88.5% glycerol conversion (GC) and 35.5% PG selectivity at 300 ℃ reaction temperature, 2 h duration test, 30 cc/min of N$_2$ initial pressure, 0.1 g catalyst dosage and 10wt% glycerol concentration. The high catalytic performance of 10Cu-90CeO$_2$/Al$_2$O$_3$ was owing to the good copper-cerium-alumina interaction via its good metal reducibility at low temperature along with good acid capacity for the reaction.

Keywords: copper, cerium, alumina, acid capacity, glycerol conversion

Abstrak

Satu siri mangkin penggalak CeO$_2$/Al$_2$O$_3$ (10Cu-90CeO$_2$/Al$_2$O$_3$, 10Ni-90CeO$_2$/Al$_2$O$_3$, 10Co-90CeO$_2$/Al$_2$O$_3$) telah disintesis menggunakan kaedah pegisitepuan lalu dikalsinkan pada 600 ℃. Kesemua mangkin telah dikaji sifat fiziko-kimia dengan menggunakan pembelauan sinar-X (XRD), penuruan suhu terprogram H$_2$ (H$_2$-TPR), dan nyahjerapan suhu terprogram NH$_3$ (NH$_3$-

TPD). Ia kemudian dinilai dalam penukaran pemangkinan gliserol kepada 1,2-propanadiol; propilena glikol (1,2-PDO; PG) melalui pendekatan pembaharuan dan hidrogenolisis fasa akueus dibawah aliran N$_2$. Diantara mangkin yang diuji, CeO$_2$/Al$_2$O$_3$ dengan 10wt% muatan Cu (10Cu-90CeO$_2$/Al$_2$O$_3$) telah menunjukkan aktiviti pemangkinan yang optimum dengan 88.5% penukaran gliserol (GC) dan 35.5% keterpilihan PG pada suhu tindak balas 300 °C, tempoh masa 2 jam, 30 cc/min tekanan awal N$_2$ dan 0.1 g dos mangkin dan 10wt% kepekatan gliserol. Prestasi pemangkinan yang tinggi oleh 10Cu-90CeO$_2$/Al$_2$O$_3$ didorong oleh interaksi baik antara kuprum-ceria-alumina melalui penurunan logam yang baik pada suhu rendah dan kapasiti asid yang sesuai untuk tindak balas.

Kata kunci: kuprum, serium, alumina, kapasiti asid, penukaran gliserol

Introduction

The amount of glycerol produced as primary by-product of biodiesel worldwide is far exceeds the current market demand thus resulted in a surplus of crude glycerol, which then impacted the refined glycerol market. It was expected that the global crude glycerol market to provide approximately 680,000 tonnes by 2024 [1-2]. Therefore, one of the opportunities for valorising crude glycerol is by recycling and producing a demanded value-added product from it which is propylene glycol (PG) or 1,2-propanediol (1,2-PDO). This product is essentially used as an industrial solvent, intermediate chemical or multipurpose solvent, additive in food products, unsaturated polyester resins, pharmaceuticals, and cosmetics [3-4]. At present, PG is industrially produced by hydrating propylene oxide to 1,2-PDO from the oxidised propylene via petrochemical route [5-6]. With diminishing returns from petroleum and concerns over detrimental environmental effects on the rise, methods of synthesising PG from renewable sources would significantly desired. Therefore, to cope with uprising production and recycling glycerol from industry, catalytic aqueous phase hydrogenolysis (APH) intertwined with aqueous phase reforming (APR) of glycerol are among the routes that was opted as they can be operated at the same reaction conditions. By coupling both reactions, no external supply of hydrogen is required since in situ generated hydrogen obtained from glycerol reforming process is being utilised in same the reactor. This made the aqueous glycerol hydrogenolysis via reforming route as an alternative to the conventional hydrogenolysis since it can be run even at mild pressure with an inert gas environment without being equipped with external source of hydrogen to the reaction system [7]. However, it could not be denied that conventional hydrogenolysis could offer better product selectivity than the APR approach since the molecular hydrogen supplied could effectively react with the glycerol to give the desired product within low hydrogen pressure [4,6,10].

During aqueous hydrogenolysis process, glycerol is dehydrated and the primary C-OH bonds is cleaved over acid sites to form unstable intermediates such as acetol and it was further hydrogenated by which hydrogen atom was added to acetol over metal sites catalyst to give desired APH product which is propylene glycol [8]. However, formation of lower alcohol such as methanol as side reaction products could happen in the reaction due to the excess C-C cracking of the intermediate acetol [9]. Cerium oxide catalysts have been given more attention due to their effectiveness in various catalytic and hydrogenation reaction used as support, co-catalyst or promoter attributable to its good acid capacity as well as metal reducibility [7,10-11]. As well, a modification of cerium oxide as based-catalyst with promoter/co-catalyst such as Cu and Ni have been reported to improve and strengthen the metal-metal interactions and improved the catalytic performance via their chemical strength, acidity, metallic phase dispersion and reducibility (oxygen ion mobility) [12]. Therefore, the good features of a promoted CeO$_2$ catalyst would possibly enhance and promote efficiency towards primary C-OH bond cleavage of glycerol which eventually rearranged to activate/break the C=O bond of acetol before it undergoes hydrogenation in a second step to give PG product [13]. Furthermore, Al$_2$O$_3$ with high availability, unique acid properties and strong metal-support interaction has been selected as catalyst support to facilitate adequate surface area to allow active phase deposition, prevent sintering and therefore offering hydrogen spill medium for it to moves towards metal surface during reaction. Hence both metal and acid sites surface are the active sites for the reaction. The

performance of a series of promoted CeO_2/Al_2O_3 catalysts were tested in the glycerol conversion to produce PG under 300 °C reaction temperature, 2 h reaction time, 30 cc/min of N_2 pressure, 10wt% glycerol concentration, and 0.1 g catalyst dosage to relate the role of catalyst's metal reducibility and acid capacity in the reaction performance.

Materials and Methods

Chemicals

Aluminium oxide beads, Al_2O_3 (3mm) and cerium(II) nitrate hexahydrate ($Ce(NO_3)_2.6H_2O$) with 99% purity was supplied by Sigma-Aldrich. Copper(II) nitrate trihydrate, $Cu(NO_3)_2.3H_2O$ (≥99%) (MW: 241.60 g/mol), nickel(II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) (≥99%) (MW: 290.79 g/mol), and cobalt(II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) (≥99%) (MW: 291.03 g/mol) were obtained from R&M Chemicals. Glycerol (≥99.5%) and N-methyl-N (trimethylsilyl)trifluoroacetamide (MSTFA) (≥98.5%) used as derivatizing agent GC derivatization was from Sigma Aldrich while pyridine (C_5H_5N) as binder solvent in derivitization process was from Merck. All chemicals used in this study were of either analytical or of reagent grade.

Preparation of catalyst

The catalysts were prepared by impregnation method. Prior to preparation, monometallic cerium was prepared first using 5g of precursor $Ce(NO_3)_2.6H_2O$ which was discretely dissolved and stirred homogeneously in 5 mL of distilled water. The solution was then added in 5g alumina beads (Al_2O_3) (referred as solution 1). The mixture was then stirred, left dried in drying oven for 24 hours at 90 °C, and calcined at 600 °C for 3 hours in a tube furnace with static air and a ramping rate of 10 ºC/min. The synthesised catalyst was denoted as CeO_2/Al_2O_3 catalyst. For preparing promoted CeO_2/Al_2O_3 catalyst, solution 1 was added with a proper amount of $Cu(NO_3)_2.3H_2O$ at 10wt% copper loading. After which, the similar method as indicated in preparation of Ce/Al_2O_3 was followed. The promoted catalyst was named as $10Cu-90CeO_2/Al_2O_3$ catalyst. Other promoted catalysts were prepared using similar method indicated by $10Cu-90CeO_2/Al_2O_3$.

Characterisation of catalyst

The phase composition structure and crystallite size of the catalysts were measured using X-ray diffraction (XRD) using Shimadzu diffractometer model XRD-6000. Hydrogen-temperature programmed reduction (H_2-TPR) was used to evaluate metal reducibility using a Thermo-Finnigan TPD/R/O 1100 SERIES equipped with a TCD (thermal conductivity detector). Typically, catalyst sample of 0.05g was placed in a U-shaped quartz reactor and pre-treated in flowing N_2 (30cm^3/min) for 0.5 h at 150 ºC to remove any moisture content followed by cooling it until room temperature. After pretreatment, H_2 chemisorption analysis was performed from temperature 50 ºC to 1000 ºC at a rate 10 ºC/min under 5%H_2/He flow (30cm^3/min). For determination acid sites of the catalyst, NH_3-temperature programmed desorption NH_3-TPD was used. The experiments were conducted on the same apparatus as the TPR experiments described above. The analysis that was conducted in this present study has already been explained in great detail in our previous study [14].

Set up for experiment

The catalytic reaction was carried out in a mechanically stirred 100 mL two-necked round bottom flask connected to N_2 gas flow (30 cc per min) of semi-batch reactor. In a typical run, 10 wt.% glycerol and 0.1g of catalyst was added into the reactor. Prior to reaction experiment, the reactor contained aqueous mixture was vacuumed and purged with N_2 for 10 min to remove the air inside. The reaction was then performed at 300 ºC and 2 h reaction time. Liquid product from the reaction was collected from the released of vapour species which then undergo condensation using external water-cooling circulator. Once reaction duration was completed, the reactor was cooled down to room temperature before the liquid product was collected and filtered from present catalyst upon analysis.

Product analysis

The liquid product of the experiment was analysed using a gas chromatography–mass spectrometry (GC-MS) coupled with an HP-5 capillary column after it had been extracted thrice using ethyl acetate. Prior for the sample preparation, the liquid product was derivatized with silyl

agent of N-Methyl-N-(trimethylsilyl)trifluroacetamide (MSTFA) and was then dissolved in pyridine (C_5H_5N) as binding solvent at 1:1:1 ratio followed by 30 min heating in oven at 70 ºC to allow complete bonding of silylation reaction. Next, 1 µL sample was injected into the GC inlet at 250 ºC and helium gas was served as the carrier gas. The initial temperature of the oven was set at 40 ºC and held for 6 min, then ramped up to 270 ºC with heating rate of 7ºC min^{-1}. The glycerol conversion and selectivity were determined by comparing the retention time of standard with experimental-based products.

Results and Discussion

Figure 1 shows the XRD analysis of CeO_2/Al_2O_3 and promoted CeO_2/Al_2O_3 catalysts (10Cu-90CeO$_2$/Al$_2$O$_3$,

10Ni-90CeO$_2$/Al$_2$O$_3$, 10Co-90CeO$_2$/Al$_2$O$_3$). As seen in Figure 1, for all catalysts, the intensity of each peak is hardly distinguished could possibly be due to the amorphous character of alumina present in the catalyst. Broad diffraction peaks of CeO_2 ($2\theta = 29.2º$, $32.5º$, $48.2º$ and $57.3º$) and Al_2O_3 ($2\theta = 32º$, $38.1º$, $47º$, $57º$ and $67.2º$) phases were observed with low crystallinity in all catalysts. For promoted catalysts, formation of CuO, NiO and CoO peaks at was detected with the similar peak of CeO_2 and/or Al_2O_3 peak respectively as the oxides could be getting embedded inside the bulk of CeO_2/Al_2O_3 and hard to be distinguished. From Table 1, it was observed that the addition of metal species on CeO_2/Al_2O_3 increased the bulk metal's crystallite of CeO_2 at $2\theta = 29.2º$ due to the metal species filled the interstitial spaces of bulk CeO_2.
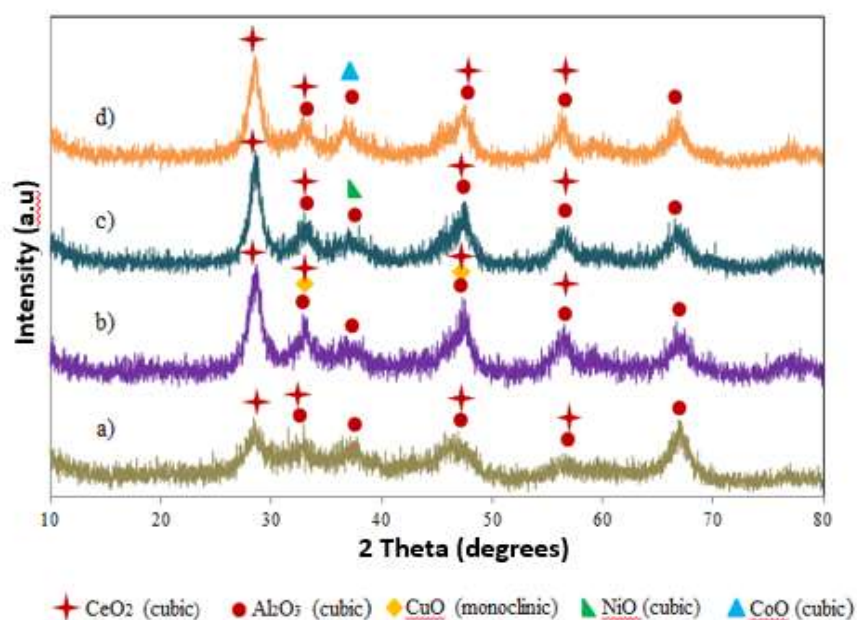

Figure 1. XRD diffractograms of calcined (a) CeO_2/Al_2O_3, (b) 10Cu-90CeO$_2$/Al$_2$O$_3$, (c) 10Ni-90CeO$_2$/Al$_2$O$_3$ and (d) 10Co-90CeO$_2$/Al$_2$O$_3$ catalysts

Figure 2 shows H_2-TPR profile of CeO_2/Al_2O_3 and promoted CeO_2/Al_2O_3 catalysts. From Figure 2, all catalysts gave reduction peak at higher temperature of ~800 ºC. The reduction peak at 800 ºC for all catalysts was indicated by the reduction of bulk ceria from CeO_2 to Ce_2O_3 since the reduction profile for CeO_2/Al_2O_3 was reduced at that temperature [15]. However, when copper was incorporated into CeO_2/Al_2O_3 matrix, a new

reduction with high peak appeared at a much lower temperature ~180-330 ºC indicating reduction of the non-associated oxide of dispersed CuO species and the bulk reduction of CuO species, respectively since > 260 ºC was for reduction of CuO species interacted with support of either CeO_2 or Al_2O_3 [16-17]. The peaks could be attributed to the two steps reduction of CuO to Cu^+ and to metallic Cu^0 species [18]. Meanwhile, the

broader reduction peak of 10Ni-90CeO$_2$/Al$_2$O$_3$ than unpromoted CeO$_2$/Al$_2$O$_3$ was noticed at ~900 ºC. This could be due to the reduction of sintered oxide species or bulk nickel oxide interacted strongly with support. Accordingly, the broader reduction profile was caused by the slow diffusion or H$_2$ adsorption by the interphase due to the presence of clusters of well sintered metal species or alloy cluster [18]. For 10Co-90CeO$_2$/Al$_2$O$_3$, a reduction peak at ~1000 ºC was shifted to higher reduction temperature of CeO$_2$/Al$_2$O$_3$ attributing to the

reduction of the metal oxide in complex species, where the interactions with the support were strong [19-20]. The findings in this study indicates that the addition of CuO with 10wt% Cu loading to the CeO$_2$/Al$_2$O$_3$ exhibited a significant promoting effect towards lower reduction temperature. Therefore, embedding Cu species into CeO$_2$/Al$_2$O$_3$ matrix resulted in good interactions between the Cu-Ce-alumina species that enhanced the reduction properties and thus metal reducibility of the catalysts.

Table 1. Physicochemical properties of the catalysts

Catalyst	XRD	H$_2$-TPR		H$_2$-TPR	NH$_3$-TPD
	Crystallite Size[a] (nm)	H$_2$ Consumed at Different Temp (µmol/g)		Total Amount H$_2$ Consumed (µmol/g)	Total Amount NH$_3$ Adsorbed (µmol/g)
		150-550 ºC	> 550 ºC		> 550 ºC
CeO$_2$/Al$_2$O$_3$	25.6	19	148	167	345
10Cu-90CeO$_2$/Al$_2$O$_3$	43.9	340	84	424	1009
10Co-90CeO$_2$/Al$_2$O$_3$	34.4	-	221	221	1007
10Ni-90CeO$_2$/Al$_2$O$_3$	32.1	-	978	978	1442

[a]The data were estimated according to the Debye Scherrer equation using the FWHM of the CeO$_2$ peak at $2\theta = 29.2º$.

As seen from Table 1, amount of H$_2$ uptake for promoted CeO$_2$/Al$_2$O$_3$ catalysts was increased than the unpromoted catalyst indicating more H$_2$ was consumed since more oxides species was reducible at larger

exposure area which increased H$_2$ adsorption. This was corroborated with the high and broader reduction peaks profile of the 10Cu-90CeO$_2$/Al$_2$O$_3$ and 10Ni-90CeO$_2$/Al$_2$O$_3$, respectively.
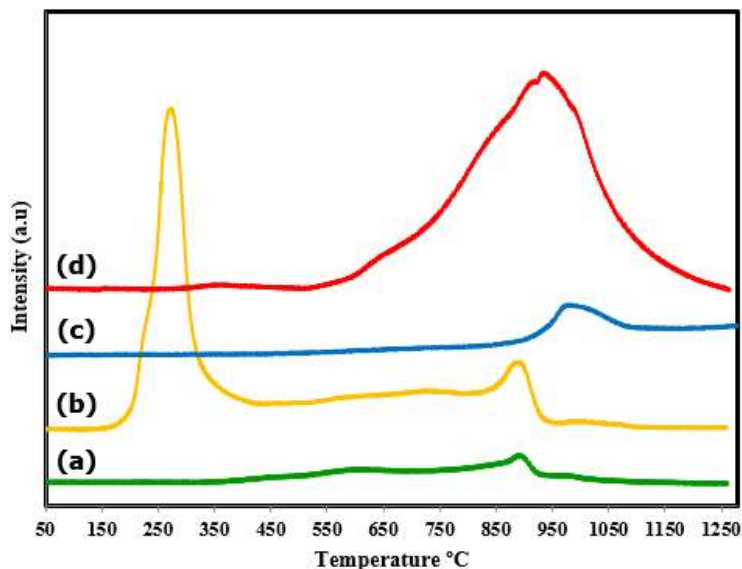

Figure 2. H$_2$-TPR reduction profile of calcined (a) CeO$_2$/Al$_2$O$_3$, (b) 10Cu-90CeO$_2$/Al$_2$O$_3$, (c) 10Co-90CeO$_2$/Al$_2$O$_3$ and (d) 10Ni-90CeO$_2$/Al$_2$O$_3$ catalysts

According to Zhu et al. [21], the acid sites of catalysts facilitated the activation of the C-OH bonds during dehydration step of glycerol to form unstable intermediate product before formation of PG. Figure 3 depicts the NH_3-TPD profiles of all catalysts while Table 1 lists their corresponding amount NH_3 desorption. The finding showed that the acidity was increased for promoted CeO_2/Al_2O_3 catalysts than the

unpromoted CeO_2/Al_2O_3 with the order of CeO_2/Al_2O_3 < 10Co-90CeO_2/Al_2O_3 ≈ 10Cu-90CeO_2/Al_2O_3 < 10Ni-90CeO_2/Al_2O_3. This result demonstrated that the incorporation of copper, cobalt, and nickel oxide species into CeO_2/Al_2O_3 matrix promoted higher acid sites capacity since the presence more oxides species provide larger exposure area for NH_3 adsorption [8].
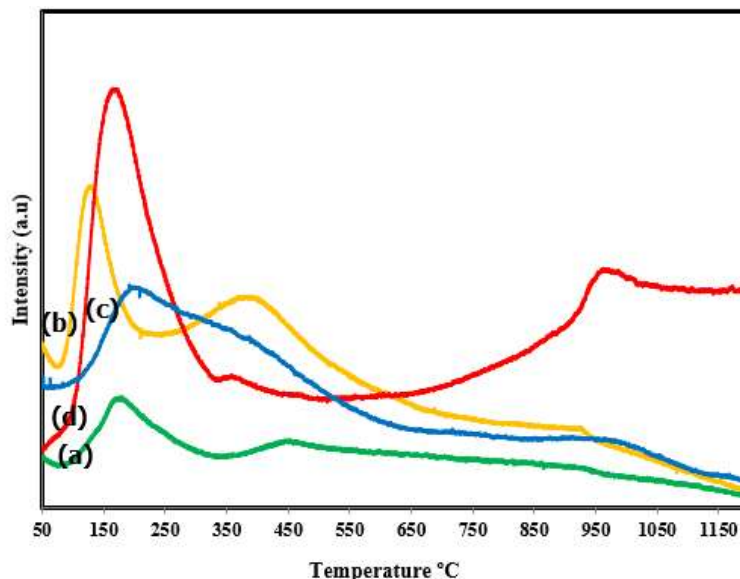

Figure 3. NH_3-TPD profile of calcined (a) CeO_2/Al_2O_3, (b) 10Cu-90CeO_2/Al_2O_3, (c) 10Co-90CeO_2/Al_2O_3 and (d) 10Ni-90CeO_2/Al_2O_3 catalysts

Table 2 shows the catalytic activity of CeO_2/Al_2O_3, and all promoted CeO_2/Al_2O_3 catalysts. All catalysts were evaluated based on their ability to convert glycerol and product selectivity to PG and methanol. From Table 2, the conversion of glycerol and PG selectivity were low with CeO_2/Al_2O_3 catalyst, however the activity was increased with the presence of promoted CeO_2/Al_2O_3 catalysts in the reaction. Among all tested catalysts, 10Cu-90CeO_2/Al_2O_3 contributed the highest glycerol conversion of 88% and 35.5% PG selectivity with the trend of CeO_2/Al_2O_3 < 10Ni-90CeO_2/Al_2O_3 < 10Co-90CeO_2/Al_2O_3 < 10Cu-90CeO_2/Al_2O_3. The high catalytic performance of 10Cu-90CeO_2/Al_2O_3 was attributed to its adequate acid sites (1009 µmol/g) that facilitated the dehydration of glycerol to form unstable intermediates which later converts into PG. The reduction profile of 10Cu-90CeO_2/Al_2O at significantly lower temperature with peak maxima of 260 ºC also

contributed to the high activity performance as agreed with other studies suggesting that the reduction of copper oxide species was active at 200-300 ºC [16-17]. At that temperature, copper oxide species was reduced into metallic copper since that temperature was active for CuO reduction. In other words, reduction of copper oxide was occurred in situ by which the presence of metallic species would in turn hydrogenate the unstable intermediate on its surface into desired PG. Formation of of methanol in the reaction was due to the breaking of C-C bond [22]. In addition, when the activity of catalysts in this study was compared with the reported catalyst from literature [23] as shown in Table 2, the catalyst in this study exhibited good glycerol conversion and 1,2-PDO selectivity. This could be due to the catalyst's metal-metal interaction and acidity which contributed to the desired results during catalytic reaction.

Table 2. Performance by catalytic reaction of all catalysts

Sample	GC Conversion (%)	Product Selectivity (%)		Ref
		PG	Methanol	
CeO_2/Al_2O_3	14.8	6.13	93.9	This work
10Cu-90Ce/Al_2O_3	88.0	35.5	64.5	This work
10Co-90Ce/Al_2O_3	84.5	12.3	87.7	This work
10Ni-90Ce/Al_2O_3	63.7	12.9	87.1	This work
Ni/SiO_2–Al_2O_3	40.0	7.9	1.21	[23]

Reaction conditions: 300ºC temperature, 2 h of reaction time, 30cc/min of N_2 initial pressure, 10wt% aqueous glycerol solution and 0.1 g of catalyst dosage

Conclusion
Among all the promoted CeO_2/Al_2O_3 catalysts tested, 10Cu-90CeO_2/Al_2O_3 catalyst gave the highest conversion of glycerol (88%) and PG selectivity (35.5%) over reaction temperature of 300 °C, 2 hours reaction duration, 30 cc/min of N_2 initial pressure, 0.1g of catalyst dosage and 10wt% aqueous glycerol solution. This was attributed to the good Cu-Ce-Al_2O_3 interactions via its adequate acid capacity and the ability to be reduced at lower reduction temperature in the range that close to the experimental reaction temperature of 300 °C.

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