

Dehydroxylation of Glycerol to Propylene Glycol over Cu-ZnO/Al₂O₃ Catalyst: Effect of Feed Purity

Thitipong Auttanat, Siriporn Jongpatiwut, and Thirasak Rirksomboon

Abstract—The catalytic dehydroxylation of glycerol to propylene glycol was investigated over Cu-ZnO/Al₂O₃ prepared by incipient wetness impregnation (IWI) method with different purity feedstocks - refined glycerol and technical grade glycerol. The main purpose is to investigate the effects of feed impurities that cause the catalyst deactivation. The prepared catalyst were tested for its catalytic activity and selectivity in a continuous flow fixed bed reactor at 523 K, 500 psig, H₂/feed molar ratio of 4 and WHSV of 3 h⁻¹. The results showed that conversion of refined glycerol and technical grade glycerol at time on stream 6 hour are 99% and 71% and selectivity to propylene glycol are 87% and 56% respectively. The ICP-EOS and TPO results indicated that the cause of catalyst deactivation was the amount of impurities in the feedstock. The higher amount of impurities (especially Na and K) the lower catalytic activity.

Keywords—Cu-ZnO/Al₂O₃, dehydroxylation, glycerol, propylene glycol.

I. INTRODUCTION

THE development and commercial use of biodiesel has been encouraging and rapidly expanding. The prominent superiority of biodiesel over petroleum diesel towards health and environment (free sulfur content, low content of harmful emission) as well as engine performance. Despite the rapid pace of biodiesel development and commercialization, there are several key challenges emerging and these must be addressed efficiently.

One key problem that is being focused is the inevitable low value production of glycerol as co-product of biodiesel transesterification. Stoichiometrically, 10 wt.% glycerol is produced in the biodiesel production. As the biodiesel production is increasing, the crude glycerol is also produced in a large quantity [1-3].

Despite of the wide applications of pure glycerol in food, pharmaceutical, cosmetics, and many other industries, it is too costly to refine the crude glycerol to a high purity, especially for medium and small biodiesel producers. The utilization of glycerol to produce other valuable chemical becomes an interesting topic. One of the promising routes is the conversion of glycerol to propylene glycol by glycerol dehydroxylation. In the reaction pathway, glycerol is first dehydrated to 1-hydroxypropan-2-one (acetol) or 3-hydroxypropanal (3-HPA), which are subsequently hydrogenated to propylene glycol, respectively [4].

Glycerol naturally occurs during the biodiesel production process and is specifically produced in the transesterification process. The glycerol produced at this stage is crude glycerol and is about 50 to 60 % pure still containing contaminants like soap, methanol and water. In order to turn this crude glycerol into a usable state for existing or emerging uses, a purification process must take place. During this refinement process residual organic matter, water, salt, methanol, and odors are removed [5]. There are many different types of glycerol grades ranging from crude glycerol, technical glycerol, yellow glycerol and refined glycerol. The specification of glycerol using in this research is shown in Table 1.

The catalytic dehydroxylation of glycerol to propanediol can be carried out in the presence of metallic catalysts and hydrogen [3,6-8]. A previous study [9] has demonstrated the effectiveness of Cu/Al₂O₃ catalyst. The results showed that 100% glycerol conversion and 90% propylene glycol selectivity were obtained. However, the conversion decreased drastically after 6 h. Swangkotchakorn [10] introduced ZnO into Cu/Al₂O₃ catalyst and found that the addition of ZnO could prolong the stability of the catalyst. Chirddilok [11] found that the Cu-ZnO/Al₂O₃ catalyst showed the best catalytic activity compared with Cu/Al₂O₃ and Cu/ZnO catalysts. The maximum activity was obtained from the catalyst prepared by co-precipitation as compared with incipient wetness impregnation. Suchart [12] concluded that the Cu-ZnO/Al₂O₃ catalyst prepared by the incipient wetness impregnation method exhibited the highest catalytic activity and stability as compared to the ones prepared by the Sol-Gel and co-precipitation methods.

In the present work, the catalytic dehydroxylation of glycerol to propylene glycol will be conducted over the Cu-ZnO/Al₂O₃ catalyst prepared by incipient wetness impregnation method focus on using different types of glycerol. The main purpose is to investigate the effects of feed impurities that cause the catalyst deactivation.

T.A. is with The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phyathai Road, Pathumwan, Bangkok 10330, Thailand (e-mail: thitipong.au@hotmail.com).

S.J. is with Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn

University, Soi Chula 12, Phyathai Road, Pathumwan, Bangkok 10330, Thailand (e-mail: siriporn.j@chula.ac.th).

T.R. is with Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Soi Chula 12, Phyathai Road, Pathumwan, Bangkok 10330, Thailand (e-mail: t.rirksomboon@unb.ca).

TABLE I
SPECIFICATION OF EACH FEED GLYCEROL

Feed	Glycerol (wt%)	Methanol (wt%)	MONG (wt%)	Water (wt%)	Ash (wt%)
Refined glycerol	99.5	< 0.5	< 1	< 0.5	< 0.5
Technical grade glycerol	80	< 1	< 20	< 1	< 0.1

II. EXPERIMENTAL

A. Materials and Gases

Refined glycerol ($\text{C}_3\text{H}_5(\text{OH})_3$, 99.9% glycerol) technical grade glycerol ($\text{C}_3\text{H}_5(\text{OH})_3$, 80-85% purity) was obtained from PTT Chemical Public Company Limited, Thailand. Aluminum oxide ($\gamma\text{-Al}_2\text{O}_3$, extrudate with 99% purity) was provided by Saint-Gobain NorPro Corporation. Copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, lab grade $\geq 99\%$ purity), zinc (II) nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, reagent grade, 98% purity), Hydrogen (H_2 , HP grade, 99.99% purity), Helium (He, HP grade, 99.99% purity), Nitrogen (N_2 , HP grade, 99.99% purity), and Air Zero (HP grade, 99.99% purity) were supplied from Thai Industrial Gas Public Company Limited.

B. Catalyst Preparation Procedures

The Cu–ZnO/ Al_2O_3 catalyst was prepared by incipient impregnation method using gamma alumina as the catalyst support. The extrudate alumina was first ground and sieved to the size between 20 and 40 meshes (425–850 nm). Copper and zinc were impregnated into the alumina support with a mixed aqueous solution of copper nitrate and zinc nitrate. After the impregnation, the catalysts were dried at 383 K overnight and subsequently calcined at 773 K for 6 h.

C. Catalyst Characterization

Temperature programmed reduction (TPR) was employed for evaluating the number and quantity of the reducible species present in the prepared catalyst and the temperature, at which the reduction itself takes place as a function of temperature. A 50 mg of catalyst was placed in a quartz reactor, and heated (10 K/min) under a He flow up to 823 K, and held at the temperature for 1 h in order to remove moisture from the catalyst surface. The sample was then cooled down to 303 K. Then, the sample was exposed to a stream of 5% H_2/Ar with a flow rate of 20 ml/min. After that, the sample was heated to 873 K with a ramping rate of 10 K/min. The consumption of hydrogen consumed was monitored on-line by an SRI model 110 FID detector as a function of temperature. Temperature-programmed oxidation (TPO) was employed to analyze the amount and characteristics of coke deposited on the catalyst surface after the course of reaction. The oxidation of coke was performed in a 4 mm I.D. quartz tube reactor. A 30 mg of spent catalyst was placed in the reactor between two layers of quartz wool. The sample was purged at room temperature by flowing 2% O_2 in He for 30 min to stabilize the signal before ramping the temperature linearly to 1073 K (10 K/min). The CO_2/CO produced by the oxidation of the coke species was converted to methane using a methanator filled

with 15% $\text{Ni}/\text{Al}_2\text{O}_3$ and operated at 673 K in the presence of H_2 . The evolution of methane was analyzed by an FID detector. A nitrogen sorption system (Autosorb-1, Quanta chrome) was employed to quantify the specific surface area and mean pore size distribution of the prepared catalysts. The Brunauer–Emmett–Teller (BET) method was used to determine the specific surface area. All the samples were outgassed under vacuum at 523 K for 6 h prior to the analysis to remove moisture and volatile substances on the catalyst surface.

D. Catalytic Activity Measurements

The catalytic activity was examined using a 16mm O.D. continuous flow stainless steel packed bed reactor. In each test, a 2 gram of catalyst was placed at the center of reactor between two layers of glass bead and glass wool. A thermocouple was placed concentrically in the reactor to control the temperature in the catalyst bed. The reactor was pressurized by hydrogen to a reduction pressure. All catalysts were reduced at 573 K for 1 h in a hydrogen flow prior to the activity evaluation. After that, the reactor was cooled to the working temperature at 523 K, and the hydrogen pressure was adjusted to 3.2 MPa. An aqueous solution of 80 wt. % glycerol will be continuously supplied to the reactor via a pump together with a flow of hydrogen controlled by a mass flow controller (Brooks 5850E). The WHSV (WHSV is given as the ratio between the hourly flow of liquid and the weight of the catalyst) will be 3 h^{-1} . After the reaction, the products were collected in a stainless steel cylinder trap immersed in an ice bath.

E. Feed Characterization

All feedstocks were analyzed by an Agilent model 6890N gas chromatograph equipped with a flame ionization detector. A Stibilwax® capillary column (diameter, 0.53 mm; length, 30 m) will be used for feed separation.

All feedstocks were analyzed for trace amount of impurities (i.e. P, K, Ca, Na, and Mg) by ICP-OES (inductively coupled plasma optical emission spectrometry). The residual substance from burning feedstock at 823 K for 150 min was dissolved in HNO_3 at 343 K for 20 min and then mix with nitric acid aqueous solution before filtered and diluted to 100 ml. Then the sample solution was fed by peristaltic pump into a nebulizer where it is changed into mist and introduced directly inside the high temperature plasma flame of about 7000 K. The intensity of the emission is indicative of the concentration of the element within the sample.

F. Product Analysis

The products obtained from the reaction were analyzed by an Agilent model 6890N gas chromatograph equipped with a flame ionization detector. A Stibilwax® capillary column (diameter, 0.53 mm; length, 30 m) will be used for product separation.

The GC operating conditions are summarized as follows:

Injection temperature: 493 K
Oven temperature: 353 to 473 K held 10 min (Heating rate 10 K/min)

Carrier gas: High purity helium
 Carrier gas flow rate: 7 mL/min
 Carrier gas velocity: 52 cm/s
 Column type: Stabilwax Capillary column
 Detector temperature: 523 K

III. RESULTS AND DISCUSSION

A. Catalytic Activity Testing

Prior to catalyst testing, blank test with pure Al_2O_3 was investigated under the identical catalyst testing conditions. No glycerol conversion was observed over the pure substrates. Therefore, conversion of glycerol observed over the catalysts is due to the $\text{Cu-ZnO/Al}_2\text{O}_3$ catalyst. The major products observed in this study were propylene glycol and acetol with minor amounts of primary alcohols (methanol, ethanol, and propanol). The plots of glycerol conversion, propylene glycol selectivity, and acetol selectivity as a function of time on stream over the different glycerol feedstock (refined glycerol and technical grade glycerol) are illustrated in Fig. 1a-c, respectively.

The results show refined glycerol exhibited the higher conversion and selectivity as compared to technical grade glycerol. Moreover, the conversion and selectivity of refined glycerol exhibited high and almost constant during the test but conversion and selectivity of technical grade glycerol is high at the beginning, and then dropped considerably. As the conversion decreased, the propylene glycol selectivity decreased with increasing acetol selectivity. These results agree well with the mechanism proposed by Dasari [2] that propylene glycol is produced via two steps; (1) glycerol dehydration to acetol and (2) acetol hydrogenation to propylene glycol. The results also indicated the deactivation of hydrogenation sites simultaneously. These results also agree well with inductively coupled plasma optical emission spectrometry result that will discuss in the next part.

B. Feed Characterization

The amount of glycerol in each feedstock was analyzed by gas chromatograph equipped with a flame ionization detector. The result showed that the amount of refined glycerol and technical grade glycerol are 99% and 80%, respectively. This result indicated that the higher glycerol concentration in feedstock, the higher conversion and selectivity of propylene glycol.

The inductively coupled plasma optical emission spectrometry (ICP-EOS) was used to detect the amount of trace impurities in feedstocks. The impurities investigated in this work are Mg, Na, P, Ca and K. The amount of impurities in each feedstocks are shown Table III. The result showed the amount of metal impurities in technical grade glycerol is higher than in refined glycerol. Especially, the amount of Na and K in technical grade glycerol is much higher than in refined glycerol, this result may come from the catalyst using in transesterification reaction in biodiesel production. The result also indicated that the conversion and selectivity may be affected by impurities. The higher concentration of impurities

(Na and K) tended to give the lower conversion and selectivity which may result from their deposited on catalyst.

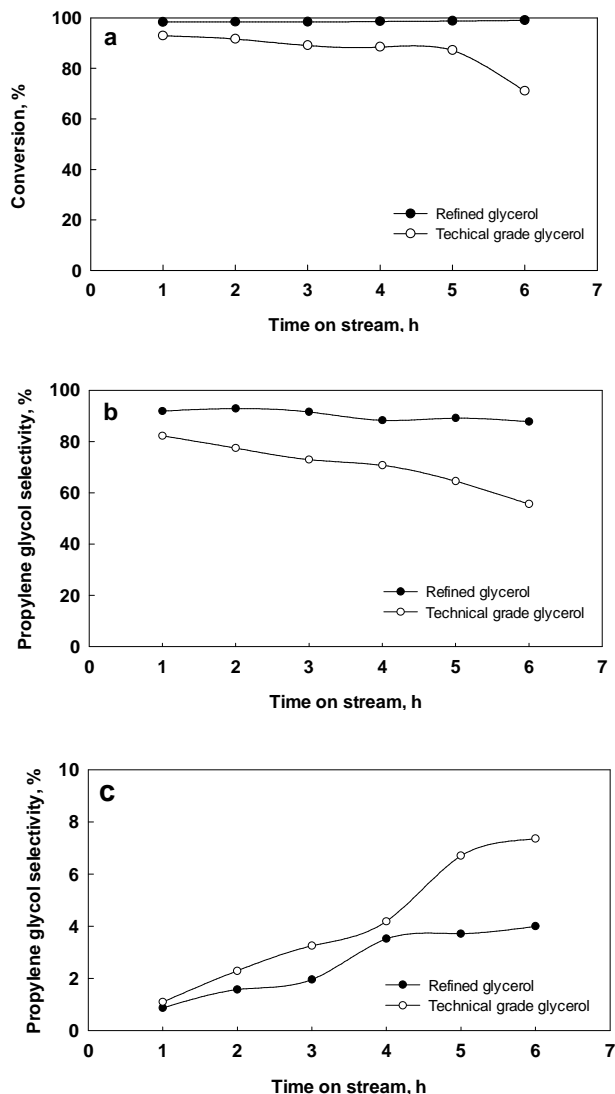


Fig. 1 Plots of (a) glycerol conversion, (b) propylene glycol selectivity, and (c) acetol selectivity as a function of time on stream over $\text{Cu-ZnO/Al}_2\text{O}_3$ catalysts over different glycerol feedstock (reaction conditions: 523 K, 3.2 MPa, H_2 :glycerol = 4:1, and $\text{WHSV} = 3 \text{ h}^{-1}$)

C. Catalyst Characterization

The TPR profile of the fresh catalyst is shown in Fig 2. The fresh catalyst showed the reduction peaks at temperature below 623 K, indicating the reduction of highly dispersed copper oxide clusters on the catalyst, while the reduction of pure CuO used as a reference appeared at 667 K [13]. This result is in good agreement with the $\text{Cu-ZnO/Al}_2\text{O}_3$ prepared by co-precipitation investigated earlier in literatures [14, 15]. The catalyst exhibited a main reduction peak at 523 K represents the small uniform of CuO grains. While the shoulder peak at 543 K represents the larger grains of CuO ,

which correspond to the reaction of bulk CuO. From TPR result, the suitable reduction temperature is 623 K.

The BET results of Al₂O₃ support and Cu-ZnO/Al₂O₃ catalyst are shown in Table II. The BET surface area and pore volume of Cu-ZnO/Al₂O₃ catalyst were lower than those of alumina support, this loss of pore volume could be due to the high amount of metal loading. However, the pore diameter remained invariant indicating that the loaded metal particles did not block the pores. The BET surface area, pore volume, and pore diameter of the fresh Cu-ZnO/Al₂O₃ catalyst were 130 m²/g, 0.394 cm³/g, and 8.92 nm, respectively.

The carbon deposit on the spent Cu-ZnO/Al₂O₃ catalysts after 8 h reaction analyzed by TPO of refined glycerol and technical grade glycerol are 18% and 12%, respectively. The results indicated that metal impurities, especially Na and K, in glycerol may cause the deactivation on active site of catalyst, resulting in lower coke formation.

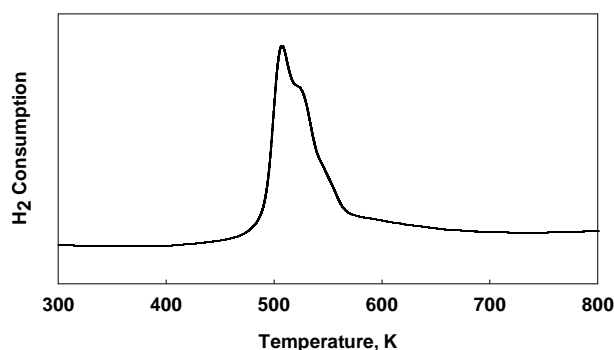


Fig. 2 TPR profile of Cu-ZnO/Al₂O₃ catalysts

TABLE II
TEXTURAL PROPERTIES OF THE CATALYSTS

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
Al ₂ O ₃	256	0.834	8.94
Cu-ZnO/Al ₂ O ₃	130	0.394	8.92

TABLE III
CONCENTRATION OF MAIN IMPURITIES IN EACH FEEDSTOCK

Feed	Mg (ppm)	Na (ppm)	K (ppm)	Ca (ppm)	P (ppm)
Refine glycerol	< 1	4	< 1	16	< 1
Technical glycerol	2	1034	4853	24	24

IV. CONCLUSIONS

For the catalytic dehydroxylation of glycerol to propylene glycol using Cu-ZnO/Al₂O₃ catalyst using refined glycerol as feedstock gave the higher catalytic activity than technical grade glycerol. The ICP-EOS results indicated that the cause of catalyst deactivation is the concentration of impurities in the feedstocks. The higher amount of impurity (especially Na and K) the lower catalytic activity.

ACKNOWLEDGEMENTS

The authors would like to gracefully acknowledge the PTT Public Company Limited, Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, and The Petroleum and Petrochemical College, Chulalongkorn University, for the support.

REFERENCES

- [1] M. Pagliaro, M. Rossi, The future of glycerol: new usages for a versatile raw material, RSC Publishing, Cambridge, 2008.
- [2] Dasari, M.A., Kiatsimkul, P., Sutterlin, W.R., and Suppes, G.J. (2005). Low-pressure hydrogenolysis of glycerol to propylene glycol. *Applied Catalysis A: General*, 281(1-2), 225–231.
- [3] Z. Chi, D. Pyle, Z. Wen, C. Frear, S. Chen, A laboratory study of producing docosahexaenoic acid from biodiesel-waste glycerol by microalgal fermentation, *Process Biochem.* 42 (2007) 1537–1545.
- [4] T. Miyazawa, Y. Kusunoki, K. Kunimori, K. Tomishige, *J. Catal.* 240 (2006) 213.
- [5] M. Hájek, F. Skopal, Treatment of glycerol phase formed by biodiesel production, *Bioresour Technol* 101 (2010) 3242–3245.
- [6] I. Gandarias, P.L. Arias, J. Requies, M. El Doukkali, M.B. Güemez, (2011). Liquid-phase glycerol hydrogenolysis to 1,2-propanediol under nitrogen pressure using 2-propanol as hydrogen source, *J.Cat.* 282. 237–247.
- [7] E.P. Maris, W.C. Ketchie, M. Murayama, R.J. Davis, *J. Catal.* 251 (2007) 281. [9] L. Ma, D. He, Z. Li, *Catal. Commun.* 9 (2008) 2489.
- [8] D.G. Lahr, B.H. Shanks, *J. Catal.* 232 (2005) 386.
- [9] Sitthisa, S. (2007). Dehydroxylation of glycerol for propanediols production. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University.
- [10] Swangkotchakorn, C. (2008). Dehydroxylation of glycerol for propanediols production: Catalytic activity and stability Testing. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University.
- [11] Chirddilok, I. (2009). Dehydroxylation of glycerol to propylene glycol over copper/zinc oxide-based catalysts: Effect of catalyst preparation. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University.
- [12] S. Panyad, S. Jongpatiwut, T. Sreethawong, T. Rirksomboon, S. Osuwan, (2011). Catalytic dehydroxylation of glycerol to propylene glycol over Cu-ZnO/Al₂O₃ catalysts: Effects of catalyst preparation and deactivation, *Catalysis Today*, 174. 59–64.
- [13] L. Zhang, X. Wang, B. Tan, U.S. Ozkan, *J.Mol. Catal. A: Chem.* 297 (2009) 26–34.
- [14] P. Kurr, I. Kasatkin, F. Girgsdies, A. Trunschke, R. Schlögl, T. Ressler, *Appl. Catal. A: Gen.* 348 (2008) 153–164.
- [15] J.-P. Shen, C. Song, *Catal. Today* 77 (2002) 89–98.