



CHARACTERIZATION AND CATALYTIC ACTIVITY OF Os/BENTONITE CATALYST FOR HYDROGENOLYSIS OF GLYCEROL

(Pencirian dan Aktiviti Pemangkin Os/Bentonit untuk Tindak Balas Hidrogenolisis Gliserol)

Noraini Hamzah^{1*}, Wan Zurina Samad², Nazrizawati Ahmad Tajuddin³, Mohd Ambar Yarmo⁴

¹*School of Chemistry and Environment, Faculty of Applied Sciences,
Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia*

²*Department of Chemistry, Kulliyah of Sciences,
International Islamic University Malaysia, 25200 Kuantan, Pahang, Malaysia*

³*Department of Chemistry,
Universiti Teknologi MARA, Perak Branch, Tapah Campus, 35400 Tapah, Perak, Malaysia*

⁴*School of Chemical Science and Food Technology, Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia*

*Corresponding author: pnoraini@salam.uitm.edu.my

Received: 13 September 2018; Accepted: 29 July 2019

Abstract

In this study, osmium catalysts (Os/Bentonite, Os/TiO₂) and ruthenium catalysts (Ru/Bentonite, Ru/TiO₂) with 5% wt/wt metal loading were prepared using impregnation method and applied to convert glycerol, a renewable feedstock, to value-added chemical, 1,2-propanediol. Among these catalysts, the bentonite supported Os catalyst showed high performance with conversion and selectivity to 1,2-propanediol which were 63.3% and 82.7%, respectively. Catalytic performances of these catalysts were evaluated in glycerol hydrogenolysis using stainless steel autoclave reactor equipped with a magnetic stirrer at 150 °C, hydrogen pressure 20 - 40 bar for 7 hours reaction. The effect of glycerol concentration and reaction temperature were investigated to obtain optimum conditions due to glycerol conversion and products selectivity greatly depend on these factors. Experimental results show that hydrogenolysis of glycerol at 160 °C reaction temperature and 5% glycerol concentration gives a conversion of glycerol up to 100.0% with 82.9% selectivity of 1,2-propanediol. This study showed that bentonite which is cheap and abundant clay is potentially a good catalyst support material. The Os/bentonite catalyst was characterized by Temperature Programmed Reduction (TPR), nitrogen adsorption-desorption analysis (BET), Temperature Programmed Desorption-Ammonia (TPD-NH₃) for obtaining some physicochemical properties of the catalysts.

Keywords: osmium, bentonite, glycerol hydrogenolysis, 1,2-propanediol

Abstrak

Dalam kajian ini, pemangkin osmium (Os/bentonit, Os/TiO₂) dan pemangkin ruthenium (Ru/bentonite, Ru/TiO₂) dengan muatan logam 5% wt/wt disediakan dengan menggunakan kaedah impregnasi dan diaplikasikan kepada penukaran gliserol yang merupakan bahan mentah yang boleh diperbaharui kepada bahan kimia yang bernilai tinggi iaitu 1,2-propanadiol. Antara pemangkin yang dikaji, Os berpenyokong bentonit menunjukkan sifat pemangkin yang baik dengan nilai peratus penukaran dan pemilihan masing-masing adalah 63.3% dan 82.7%. Aktiviti pemangkin diuji dalam tindak balas hidrogenolisis gliserol menggunakan reaktor autoklaf tahan karat yang dilengkapi dengan pengacau magnetik pada suhu 150 °C, tekanan hidrogen 20-40 bar selama 7 jam. Kesan kepekatan gliserol dan suhu tindak balas didapati memberi kesan signifikansi terhadap peratus penukaran gliserol dan pemilihan produk. Keputusan kajian menunjukkan bahawa keadaan optimum pada suhu 160 °C dan kepekatan gliserol 5% (wt/wt) memberikan penukaran gliserol sehingga 90.0% dengan peratus pemilihan terhadap 1,2-propanadiol 82.9%. Kajian ini menunjukkan bahawa bentonit yang merupakan tanah liat murah dan mudah didapati adalah berpotensi digunakan sebagai penyokong mangkin. Pemangkin Os/bentonit dicirikan menggunakan suhu pemrograman

penurunan (TPR), analisis jerapan-nyahjerapan nitrogen (BET), suhu pemrograman nyahjerapan ammonia (TPD-NH₃) bagi mendapatkan maklumat mengenai sifat fizikal dan kimia pemangkin.

Kata kunci: osmium, bentonit, hidrogenolisis gliserol, 1,2-propanadiol

Introduction

Catalytic conversion of renewable biomass resources, as feedstocks for the chemical industry, becomes more and more important because of the worldwide and serious energy and environment problems [1]. Transesterification of triglycerides with methanol in the presence of basic or acidic catalysts produced biodiesel that consists of fatty acid methyl esters. Production of every 9 kg biodiesel, about 1 kg of the crude glycerol by-product is also formed [2].

Nowadays, biodiesel derived from vegetable oils and animal fats has received considerable attention. The recent rapid development of biodiesel processes has caused some concern over the oversupply of glycerol. The glycerol market will likely to be saturated because of limited utilization of glycerol at the present time [3]. It is known that glycerol can be catalytically converted into functionalized and value-added chemical *via* a variety of reaction routes such as oxidation, hydrogenolysis, dehydration, pyrolysis, steam reforming, etherification, esterification, oligomerization and polymerization [4]. The hydrogenolysis of glycerol produces 1,2-propanediol (1,2-PDO) and ethylene glycol (EG) as a major product with a 4% annual market growth [5]. Typical uses of 1,2-propanediol are in unsaturated polyester resins, functional fluids, pharmaceuticals, cosmetics, paints, etc [6]. Therefore, the new usages of glycerol are being requested widely.

Several review papers [7-15] have reported on different catalyst systems, including supported transition metal catalyst such as Rh, Ni, Ru, Pt, Pt-Ru and Cu catalyst, for the hydrogenolysis of glycerol. Tomishige and co-workers developed Ru-solid acid bifunctional catalyst system for the hydrogenolysis of glycerol. However, the highest selectivity to 1,2-PDO achieved was 82% with 40% conversion of glycerol [16-19]. Besides that, Lahr et al. [20] have also investigated the effect of sulphur addition to Ru/C catalyst, in which the selectivity to 1,2-PDO increased linearly with sulphur loading. It is clear that from the literature Pt and Ru catalyst exhibited higher activity among the noble catalysts for the hydrogenolysis of glycerol, but Ru leads to C-C bond cleavage forming undesirable byproducts such as ethylene glycol and propanol while Pt catalyst gives higher selectivity to lactate [20].

1,2-PDO formation *via* glycerol hydrogenolysis involves selective cleavage of a C-O bond without breaking the C-C bond. Furthermore, bentonite is potentially a good and cheap catalyst support material. For the example, previous study prepared novel solid acid catalyst, bentonite supported polytrifluoromethanesulfonilaxane and used in the Friedel-Crafts acylation of ferrocene and gave 70% yield of aliphatic acyl ferrocene [11]. Natural clay minerals known as bentonite are a type of environmentally benign material. Bentonite (BEN) is a clay consisting predominantly of montmorillonite with a layered structure, large surface areas and cation exchange capacity. The special properties of bentonite make it a valuable material for a wide range of applications such as catalysis, pharmaceuticals, cosmetics, environment and agriculture [12].

Effective catalysts which work under mild conditions are required in the hydrogenolysis of glycerol to produce propanediols. Therefore, we aimed to develop new supported metal catalyst which is osmium supported on bentonite that will exhibit good catalytic performance and do not require any promoter for the glycerol hydrogenolysis. Until today, no documented paper reported on the performance of Os/bentonite catalyst for glycerol hydrogenolysis. In our preliminary study, Os/bentonite exhibited good activity, which is glycerol conversion was achieved at 63.3% with 82.7% selectivity to 1,2-PDO under a mild condition at 150 °C, 2MPa initial hydrogen pressure for 7 hours reaction time. The catalyst was characterized for its physiochemical properties based on which the observed activity results have been discussed. Effect of various reaction parameters on conversion of glycerol and selectivity to 1,2-PDO has also been reported for the Os/bentonite catalyst.

Materials and Methods

Materials

Glycerol (99.9%) and ruthenium trichloride, RuCl₃ precursor and TiO₂ used as support were purchased from Sigma-Aldrich. The clay mineral used in this work is a calcium-rich bentonite (CaB) was obtained as a powder from PT Superintending Company of Indonesia also used as support. The bulk chemical analysis of bentonite (mass%) is SiO₂, 64.15; TiO₂, 0.47; CrO₃, 0.003; Al₂O₃, 0.70; Fe₂O₃, 0.10; MgO, 0.70; CaO, 0.03; Na₂O, 0.20; K₂O, 0.50 and loss on ignition (LOI), 22.61.

Catalyst preparation

All supported catalysts with 5% metal loading were prepared by impregnation method. Titania, TiO₂ (anatase >99%, Aldrich) and bentonite (Aldrich) were used as the support material. Both of supports were calcined in air at 300 °C for 24 hours before used to remove moisture and impurities. The precursor used for Os and Ru were OsCl₃ and RuCl₃, respectively. For preparation with a nominal metal loading of 5 wt%, 100 mg of precursor catalyst was dissolved in acetone and stirred at room temperature for 15 minutes. This resulting solution was poured into the support (1800 mg) and sonicated for 60 minutes. The catalysts were then dried in an oven at 60 °C during 12 hours. In the next step, the catalyst was calcined in N₂ flow at 200 °C for 2 hours and further reduced with a hydrogen stream at 200 °C for 2 hours. Then the catalyst was used directly for hydrogenolysis without any further treatment.

Catalyst characterization

The surface area of the supported metal catalyst was measured using the BET method (N₂ adsorption) with a Gemini apparatus (Micromeritics Instrument Corporation). The reduction characterizations of the catalyst were studied by a temperature programmed reduction (TPR) using the same apparatus and pretreatment method for the CO pulse chemisorption-TPD measurements. After pretreatment, the temperature was raised from 30 °C to 600 °C at a rate of 10 °C/min in a 10% H₂/He flows (30 cm³/min). The acidity properties of the catalyst were measured by a temperature-programmed desorption ammonia (TPD-NH₃). The sample was heated in a helium flow at 150 °C for 30 minutes. After a cooling temperature of 70 °C, the sample was exposed to ammonia and flushed with a 50 mL/min helium for 60 minutes. The TPD measurement was carried out with a heating rate 10 °C/min up to 750 °C under a flowing helium (50 mL/min). The desorption of ammonia was monitored by a thermal conductivity detector (TCD).

Hydrogenolysis of glycerol

The catalytic hydrogenolysis reactions were carried out in a 50 mL stainless-steel autoclave, PARR reactor equipped with an electronic temperature controller and a mechanical stirrer. The reaction was normally conducted under the following standard conditions: 150 °C temperature, 20 bar initial hydrogen pressure, 1.0 g catalyst weight, 23 ml of 20 wt.% aqueous solution of glycerol, 7 hours reaction time and at constant stirring speed.

The hydrogenolysis reaction sequence was as follows: loading of the reactor with an aqueous solution of glycerol and the appropriate amount of catalyst. Then the reactor was flushed three times with N₂ in order to remove oxygen gas and pressurized with H₂ to 20 bar. The mixture of glycerol and the catalyst was heated up to 150 °C at constant stirring speed and maintained for 7 hours.

Product characterization

After the reaction, the reactor was cooled at room temperature and the liquid phase products were separated from the catalyst by centrifuge at 4000 rpm for 15 minutes then filtered. These products were analysed using a gas chromatograph (GC-Hewlett Packard Model 6890N) equipped with a flame ionization detector (FID). The GC column used was a DB-WAX capillary column (30 m x 0.32 mm x 0.5 mm) manufactured by Agilent Technologies. Solutions of n-butanol and 1,4- butanediol with known amounts of internal standards were used for quantification of various glycerol-derived compounds in the product. The conversion of glycerol, the selectivity of propanediol, ethylene glycerol and other products (propanol (1,2), ethanol and methanol) were the factors used to evaluate the catalyst performance. The conversion and selectivity of glycerol are calculated as the following equations:

$$\text{Conversion(\%)} = \frac{\text{amount of glycerol (g)}}{\text{total amounts of glycerol in the feed (g)}} \times 100\% \quad (1)$$

$$\text{Selectivity (\%)} = \frac{\text{amount of product produced (g)}}{\text{amount of glycerol converted (g)}} \times 100\% \quad (2)$$

Only selectivities to 1,2-propanediol (1,2-PDO) and ethylene glycol (EG) were discussed in this study in view of their commercial important and relatively large amounts detected in the products.

Results and Discussion

Effect of support

Figure 1 shows the performances of Ru and Os metal catalyst prepared with different supports. The amounts of Ru and Os metal catalysts were kept the same. All the catalysts were evaluated at a reaction condition of 150 °C, 20 bar initial hydrogen pressure and 7 hours reaction time. In this study, we only focused on 1,2-propanediol and ethylene glycol since these products produced as a major in hydrogenolysis glycerol. In term of conversion, these results revealed that bentonite supported catalysts were most active than TiO₂ supported catalysts. Such results indicate that the nature of support has a strong effect on the performance of the tested catalyst. When we make a comparison between the catalytic activity and BET result, it seems that bentonite support with the highest surface area is more suitable for hydrogenolysis glycerol. Between two bentonite supported catalysts, the result clearly shows that Ru/bentonite exhibited the highest activity with glycerol conversion reached to 79.6%. In contrast, Os/bentonite catalyst only gave 63.3% conversion. This result was not significant with EDX analysis because Os metal dispersed more (3.49%) than Ru metal (2.81%). Therefore we make the conclusion that metal dispersion seems to be unrelated with the activity of the catalysts.

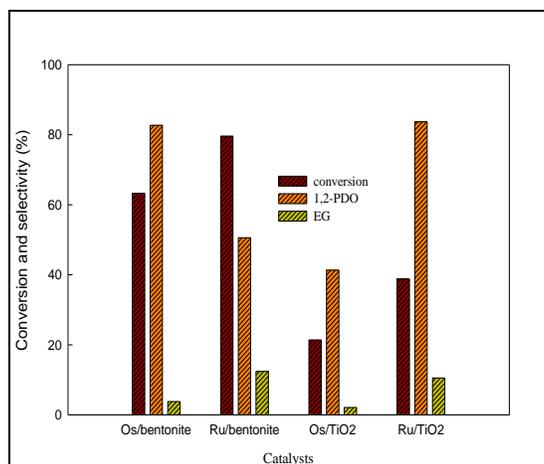


Figure 1. Performance of Ru and Os catalysts on different supports

On the other hand, selectivity to 1,2-propanediol is most predominant over Os/bentonite and Ru/TiO₂ with 82.7% and 83.7% selectivity, respectively. However, as we mentioned earlier activity of Os/bentonite catalyst was double compared to Ru/TiO₂. Therefore, from these screening, we conclude that Os/bentonite catalyst was the best catalyst in glycerol hydrogenolysis due to highest selectivity (82.7%) with the conversion of glycerol 63.3% at mild reaction condition of 150 °C, 20-40 bar hydrogen pressure for 7 hours. Normally, hydrogenolysis of glycerol was conducted at higher temperature and pressure [21, 22]. For further study, Os/bentonite catalyst was selected to optimize two parameters namely are glycerol concentration and reaction time.

Effect of glycerol concentration

In order to achieve maximum productivity of 1,2-PDO, the effect of aqueous glycerol concentration on the conversion was also studied. Figure 2 shows that the conversion of glycerol decreased from 100% to 58.1% with an increase in glycerol concentration up to 20 wt.%. This is because the limiting number of catalytic active sites was

available since the catalyst concentration was constant. A similar observation was reported by another researcher [23]. For further study, we choose concentration 5 wt(%) glycerol rather than 1 wt(%) glycerol due to practically practice. There was not the much different effect of glycerol concentration on the selectivity pattern of 1,2-PDO and EG.

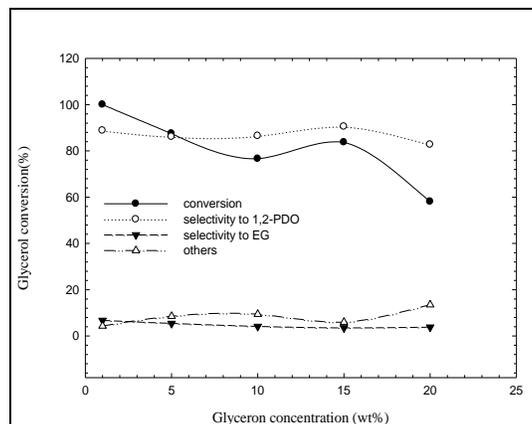


Figure 2. Effect of glycerol concentration. Reaction conditions : 20-30 bar H₂ pressure, 1.0g catalyst, 150 °C (423 K), 7 hours

Effect of reaction temperature

Figure 3 shows the influence of reaction temperature on conversion and selectivity pattern in 5 wt(%) glycerol hydrogenolysis over Os/bentonite catalyst. Glycerol conversion increased from 45.6% to 100% with an increase in temperature from 120 °C to 160 °C. Maximum conversion of 100% was obtained at 160 °C however, selectivity to 1,2-PDO decreased slightly from 100% to 83.7%, correspondingly increasing the selectivity to others from 0% to 11.7%. This result indicates that at higher temperature favoured degradation products due to excessive hydrogenation of 1,2-PDO to propanol. Interestingly, there was insignificant effect of reaction temperature on selectivity to EG. It seems that Os/bentonite catalyst was highly selective to 1,2-PDO. Os/bentonite was a new catalyst which is favoured to C-O cleavage without the addition of any promoter. Furthermore, Os/bentonite catalyst gave 100% conversion with 83.7% selectivity to 1,2-PDO at a shorter time (7 hours). Until today, none catalyst was reported can perform 100% conversion at 160°C, 20 bar initial H₂ pressure for 7 hours reaction time.

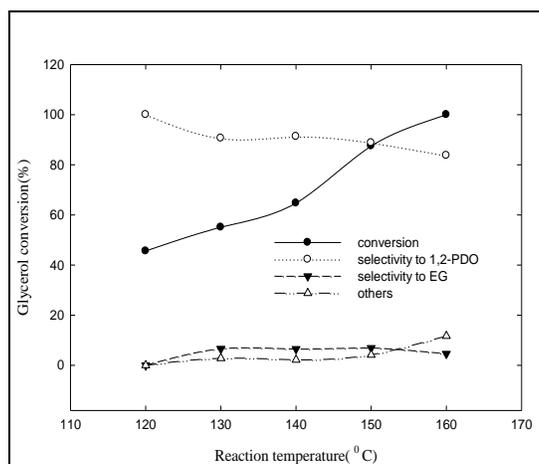


Figure 3. Effect of reaction temperature. Reaction conditons : 5 wt(%) glycerol aqueous solution (20 g) 20-30 bar H₂ pressure, 1.0g catalyst, 7 hours

Catalyst characterization: BET surface area

The BET surface area, pore volume and pore diameter of osmium supported catalysts are summarized in Table 1. Os/Al₂O₃ and Os/SiO₂ have the highest surface area followed by Os/bentonite and Os/TiO₂. The result shows that Os supported on bentonite and TiO₂ have a low BET surface area which are not contributed to the good performance of the catalyst in hydrogenolysis of glycerol. Similar result was reported that surface is not the main factor for the performance of the catalyst [20]. The good catalytic of Os/bentonite might be due to the amount of acidity in the catalyst and TPD-NH₃ analysis was done to confirm this property.

Table 1. Physical parameter of support and supported catalysts

Catalyst	S _{BET} (m ² /g)	d _{pore} (m ² /g)	V _{pore} (cm ³ /g)
Os/TiO ₂	8.0	0.038	26
Os/Al ₂ O ₃	142	0.239	7
Os/SiO ₂	130	0.834	26
Os/bentonite	8.2	1.800	0.0009

TPR analysis

Redox properties of Os/bentonite catalyst at different loading was measured using H₂-TPR analysis and the profiles are shown in Figure 4. A small peak observed at temperature of 230 °C for bentonite support, might be due to reduction of oxide species on the surface of the bentonite support [24]. This TPR profile shows that reduction of oxide osmium occurred at a temperature around 140 °C. It was found that the intensity of the peak becomes obvious with increasing metal loading of Os metal from 0.01 wt(%) to 5.0 wt(%). This result indicated that Os/bentonite catalyst could be easily reduced at a reaction temperature of 150 °C and provided good active site for the hydrogenolysis of glycerol. Percentage of glycerol conversion was increased with increasing of metal loading of Os/bentonite in hydrogenolysis of glycerol. It was found that best conversion was obtained at metal loading of 5 wt(%) with 70%. This might be due to more active site are available to convert glycerol into 1,2-propanediol.

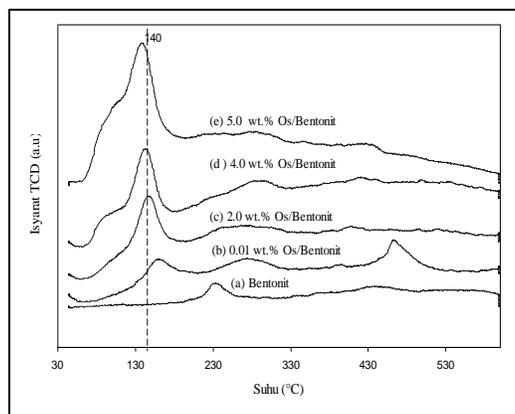


Figure 4. TPR analysis of Os/bentonite at different metal loading

TPD-NH₃ analysis

The acidity of the catalysts was quantified by the integration of the desorption curves for TPD-NH₃. The areas under the curves were considered as proportional to the number of moles of gas desorbed from the surface. The maximum temperature on the curves was designated as T_{max}. The TPD profiles of the osmium supported on the different

support were shown in Figure 5. The TPD-NH₃ analysis result indicated that Os/bentonite catalyst has strong acid site because desorption of ammonia occurred at temperature above 400°C with total acidity of 117.45 mmol NH₃ per gram catalyst.

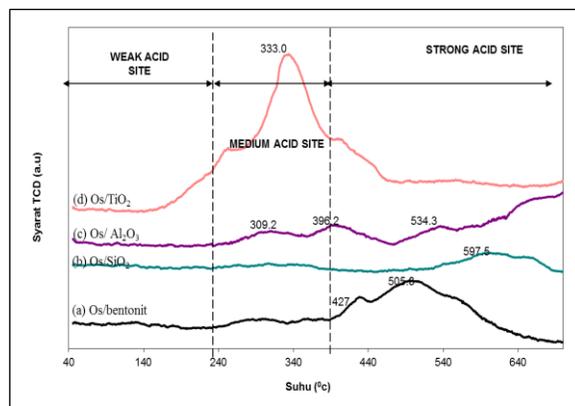


Figure 5. TPD-NH₃ analysis of Os/bentonite at different support

The total acidity of supported Os catalyst was listed in Table 2. The acidity strength was characterized by the temperature of the desorption peak, meanwhile, the number of acidic sites was measured by the amount of ammonia desorbed [9]. Os/ TiO₂ catalyst has high total acidity (254.87 mmol of NH₃/ g catalyst), however, this catalyst did not perform well in glycerol hydrogenolysis due to acid site medium. This result shows that hydrogenolysis of glycerol need the optimum strong acid site to convert glycerol into 1,2-propanediol.

Table 2. TPD-NH₃ analysis of Os supported at the different support

Catalyst	Total Acidity (mmol of NH ₃ /g Catalyst)
Os/TiO ₂	254.87
Os/Al ₂ O ₃	53.93
Os/SiO ₂	102.55
Os/bentonite	117.45

Conclusion

Os/bentonite catalyst exhibits good performance for catalyzing the hydrogenolysis of aqueous glycerol to produce 1,2-PDO at mild reaction condition. 100% conversion of glycerol and 82.9% selectivity of 1,2-PDO could be achieved when using 5 wt.% aqueous glycerol at 160 °C, 20-40 bar hydrogen pressure, 7 hours. The characterization results suggested that the high surface area is not the main factor that contributed good catalytic of the catalyst.

Acknowledgement

The authors would like to acknowledge the Research Management Centre (RMC), Ministry of Education (MOE) and Universiti Teknologi MARA (UiTM) to finance the project under BESTARI fund (600-IRMI/DANA 5/3 BESTARI (050/2017))

References

1. Huang, Z., Cui, F., Kang, H., Chen, J. and Xia, C. (2009). Characterization and catalytic properties of the CuO/SiO₂ catalysts prepared by precipitation-gel method in the hydrogenolysis of glycerol to 1,2-propanediol: effect of residual sodium. *Applied Catalysis A: General*, 366(2): 288-298.
2. Vasiliadou, E. S., Heracleous, E., Vasalos, I. A. and Lemonidou, A. A. (2009). Ru-based catalysts for glycerol hydrogenolysis-effect of support and metal precursor. *Applied Catalysis B: Environmental*, 92 (1-2): 90-99.
3. Feng, J., Fu, H., Wang, J., Li, R., Chen, H. and Li, X. (2008). Hydrogenolysis of glycerol to glycols over ruthenium catalysts: Effect of support and catalyst reduction temperature. *Journal of Catalysis Communications*, 9(6): 1458-1464.
4. Jiang, T., Zhou, Y., Liang, S., Liu, H. and Han, B. (2009). Hydrogenolysis of glycerol catalyzed by Ru-Cu bimetallic catalysts supported on clay with the aid of ionic liquids. *Green Chemistry*, 11(7): 1000-1006.
5. Chaminand, J., Djakovitch, L., Gallezot, P., Marion, P., Pinel, C. and Rosierb, C. (2004). Glycerol hydrogenolysis on heterogeneous catalysts. *Green Chemistry*, 6: 359-361.
6. Maris, E. P., Ketchie, W. C., Murayama, M. and Davis, R. J. (2007). Glycerol hydrogenolysis on carbon-supported Pt-Ru and Au-Ru bimetallic catalysts. *Journal of Catalysis*, 251(2): 281-294.
7. Shinmi, Y., Koso, S., Kubota, T., Nakagawa, Y. and Tomishige, K. (2010). Modification of Rh/SiO₂ catalyst for the hydrogenolysis of glycerol in water. *Applied Catalysis B: Environmental*, 94(3-4): 318-326.
8. Wang, S. and Liu, H. (2007). Selective hydrogenolysis of glycerol to propylene glycol on Cu-ZnO catalysts. *Catalysis Letters*, 117(1-2): 62-67.
9. Yu, W., Zhao, J., Ma, H., Miao, H., Song, Q. and Xu, J. (2010). Aqueous hydrogenolysis of glycerol over Ni-Ce/Ac catalyst: Promoting effect of Ce on catalytic performance. *Applied Catalysis A: General*, 383(1-2): 73-78.
10. Zheng, J., Zhu, W. C., Ma, C. X., Jia, M. J., Wang, Z. L., Hou, Y. H. and Zhang, W. X. (2009). Hydrogenolysis of glycerol to 1,2-propanediol over Cu/SiO₂ catalysts prepared by ion-exchange method. *Polish Journal of Chemistry*, 83(7): 1379-1387.
11. Zhou, J., Zhang, J., Guo, X., Mao, J. and Zhang, S. (2012). Ag/Al₂O₃ for glycerol hydrogenolysis to 1,2-propanediol: activity, selectivity and deactivation. *Green Chemistry*, 14(1): 156-163.
12. Basit, A., Suzana, Y., Armando T. Q., Ruzaimah, N. M. K., Yoshifumi S., Muhammad A., Tetsuya K. (2016). Pretreatment and bentonite-based catalyzed conversion of palm-rubber seed oil blends to biodiesel. *Procedia Engineering*, (148): 501-507.
13. Banu, M., Sivasanker, S., Sankaranarayanan, T. M. and Venuvanalingam, P. (2011). Hydrogenolysis of sorbitol over Ni and Pt loaded on nay. *Catalysis Communications*, 12(7): 673-677.
14. Kwak, B. K., Park, D. S., Yun, Y. S. and Yi, J. (2012). Preparation and characterization of nanocrystalline CuAl₂O₄ spinel catalysts by sol-gel method for the hydrogenolysis of glycerol. *Catalyst Communications*, 24: 90-95.
15. Montassier, C., Ménézo, J. C., Hoang, L. C., Renaud, C. and Barbier, J. (1991). Aqueous polyol conversions on ruthenium and on sulfur-modified ruthenium. *Journal of Molecular Catalysis*, 70(1): 99-110.
16. Shinmi, Y., Koso, S., Kubota, T., Nakagawa, Y. and Tomishige, K. (2010). Modification of Rh/SiO₂ catalyst for the hydrogenolysis of glycerol in water. *Applied Catalysis B: Environmental*, 94(3-4): 318-326.
17. Miyazawa, T., Koso, S., Kunimori, K. and Tomishige, K. (2007). Development of a Ru/C catalyst for glycerol hydrogenolysis in combination with an ion-exchange resin. *Journal of Applied Catalysis A: General*, 318: 244-251.
18. Miyazawa, T., Kunimori, K. and Tomishige, K. (2006). Glycerol hydrogenolysis in the aqueous solution under hydrogen over Ru/C⁺ an ion-exchange resin and its reaction mechanism. *Journal of Catalysis*, 240(240): 213-221.
19. Maris, E. P. and Davis, R. J. (2007). Hydrogenolysis of glycerol over carbon-supported Ru and Pt catalysts. *Journal of Catalysis*, 249(2): 328-337.
20. Lahr, D. G. and Shanks, B. H. (2003). Kinetic analysis of the hydrogenolysis of lower polyhydric alcohols: Glycerol to glycols. *Industrial and Engineering Chemistry Research*, 42(22): 5467-5472.
21. Zheng, J., Zhu, W., Ma, C., Hou, Y., Zhang, W. and Wang, Z. (2010). Hydrogenolysis of glycerol to 1,2-propanediol on the high dispersed Sba-15 supported copper catalyst prepared by the ion-exchange method. *Reaction Kinetics, Mechanisms and Catalysis*, 99(2): 455-462.

22. Zhou, Z., Li, X., Zeng, T., Hong, W., Cheng, Z. and Yuan, W. (2010). Kinetics of hydrogenolysis of glycerol to propylene glycol over Cu-ZnO-Al₂O₃ catalysts. *Chinese Journal of Chemical Engineering*, 18(3): 384-390.
23. Ma, L., He, D. and Li, Z. (2008). Promoting effect of rhenium on catalytic performance of Ru catalysts in hydrogenolysis of glycerol to propanediol. *Catalysis Communications*, 9(15): 2489-2495.
24. Jiménez-Morales, I., Vila, F., Mariscal, R. and Jiménez-López, A. (2012). Hydrogenolysis of glycerol to obtain 1,2-propanediol on Ce-promoted Ni/Sba-15 catalysts. *Applied Catalysis B: Environmental*, 117-118(1): 253-259.