



UNIVERSITI PUTRA MALAYSIA

**DEVELOPMENT OF DOLOMITE-SUPPORTED COPPER CATALYSTS
FOR GLYCEROL HYDROGENOLYSIS TO 1,2-PROPANEDIOL**

NORSAHIDA BINTI AZRI

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By

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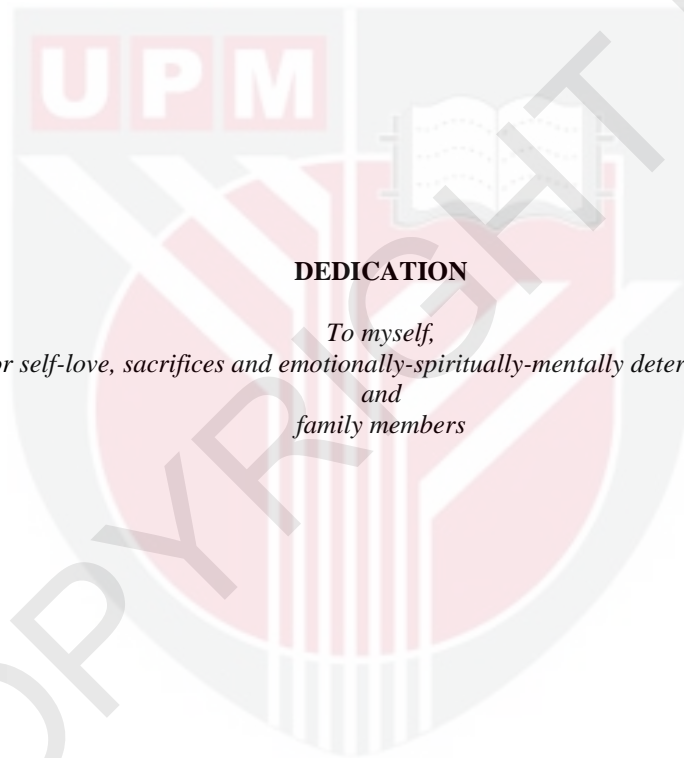
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July 2021

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DEDICATION

*To myself,
for self-love, sacrifices and emotionally-spiritually-mentally determination
and
family members*

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

DEVELOPMENT OF DOLOMITE-SUPPORTED COPPER CATALYSTS FOR GLYCEROL HYDROGENOLYSIS TO 1,2-PROPANEDIOL

By

NORSAHIDA BINTI AZRI

July 2021

Chairman: Associate Professor Irmawati binti Ramli, PhD
Faculty : Science

The strong growth of biodiesel production has led to a significant increase in glycerol, the by-product of the process. Therefore, this study focused into converting glycerol to high-value chemical which is 1,2-propanediol over heterogeneous catalyst. Metal supported catalyst was synthesized using wet impregnation method, later calcined, and subsequently reduced under 5% H₂ environment. The metals investigated were copper (Cu), nickel (Ni), cobalt (Co), zinc (Zn) and iron (Fe) while the supports used were dolomite (Dol), alumina (Al₂O₃), bentonite (Bent), montmorillonite (Mont), and talcum (Talc). Results showed that copper supported on dolomite (Cu/Dol) gave the best catalytic activity in glycerol hydrogenolysis. Henceforth, different loadings of copper on dolomite were synthesized. Cu/Dol catalyst calcined at 500 °C and reduced at 600 °C exhibited the highest glycerol conversion of 78.5% and 1,2-PDO selectivity of 79% at 200 °C reaction temperature, 4 MPa H₂, 10 h reaction time, 20wt% glycerol concentration, and 1 g catalyst dosage. After optimization study, it was demonstrated that the glycerol conversion and 1,2-PDO selectivity was increased with the increasing reaction temperature, hydrogen pressure, reaction time, catalyst dosage, glycerol concentration and copper metal loading up to their optimum value. The results were optimized at copper loading of 20wt%, 180 °C reaction temperature, 2 MPa hydrogen pressure, 6 h reaction time, 20wt% glycerol concentration, and 1 g catalyst dosage with maximum glycerol conversion of 100% and 1,2-PDO selectivity of 92.2%. It can be concluded that the high performance of 20%Cu/Dol catalyst was attributed to its macroporous and crystalline features, composed of mixed crystalline phases with calcium, magnesium, oxygen as main components, good copper surface area, copper dispersion and thermal stability. Also, the good copper-dolomite interaction, including high metal reducibility (~291 °C) and very importantly the presence of its high acid capacity (19528 μmol/g) with Lewis sites on the catalyst surface as the active reaction sites. In addition, the incorporation of copper to dolomite presented a promising reaction performance rather metallic copper and dolomite alone attributed to its improved acidity and metal reducibility. On subjecting the 20%Cu/Dol to reusability study in five reaction cycles, it maintained good performance in glycerol conversion but inferior in 1,2-PDO selectivity after the first use. The evidence indicated that the

reduced 1,2-PDO selectivity was due to the coke formation and leaching of metal active sites (Cu, Ca dan Mg). The conversion of glycerol to 1,2-PDO followed the dehydration–hydrogenation pathway while reaction towards C–C cleavage with methanol as side product was minimal.



Abstrak tesis dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMBANGUNAN MANGKIN DOLOMIT-TERSOKONG KUPRUM UNTUK HIDROGENOLISIS GLISEROL KEPADA 1,2-PROPANADIOL

Oleh

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Pembangunan biodiesel yang mampan telah memacu peningkatan terhadap gliserol, iaitu produk sampingan proses tersebut. Oleh itu, kajian ini dilakukan bertujuan untuk menukar gliserol kepada bahan kimia yang lebih bernilai iaitu 1,2-propanadiol menggunakan mangkin heterogen. Mangkin logam berpenyokong telah disintesis menggunakan kaedah pengisitepuan langsung, dikalsinasi dan kemudian diturunkan di dalam persekitaran 5% hidrogen. Logam yang dikaji adalah kuprum (Cu), nikel (Ni), kobalt (Co), zink (Zn) dan besi (Fe) sementara bahan penyokong yang digunakan adalah dolomit (Dol), alumina (Al_2O_3), bentonit (Bent), montmorilonit (Mont) dan talkum (Talc). Hasil kajian menunjukkan bahawa mangkin kuprum tersokong dolomit (Cu/Dol) memberikan hasil yang terbaik dalam hidrogenolisis gliserol. Seterusnya, mangkin kuprum tersokong dolomit pada muatan kuprum yang berbeza telah disintesis. Mangkin Cu/Dol yang dikalsinasi pada suhu 500 °C dan diturunkan pada suhu 600 °C mempamerkan penukaran gliserol yang paling tinggi iaitu 78.5% dan pemilihan 1,2-PDO iaitu 79% pada suhu tindak balas 200 °C, tekanan hidrogen 4 MPa, masa tindak balas 10 j, kepekatan gliserol 20bt%, dan berat mangkin 1 g. Selepas tindak balas lanjutan pula, ia menunjukkan bahawa penukaran gliserol dan pemilihan terhadap 1,2-PDO menjadi semakin bertambah seiring dengan suhu tindak balas, tekanan hidrogen, masa tindak balas, berat mangkin, kepekatan gliserol serta muatan logam kuprum sehingga paras optimal. Hasil kajian adalah optimal pada muatan kuprum 20bt%, suhu tindak balas 180 °C, tekanan hidrogen 2 MPa, masa tindak balas 6 j, kepekatan gliserol 20bt%, dan berat mangkin 1 g dengan hasil yang maxima iaitu 100% penukaran gliserol dan 92% pemilihan 1,2-PDO. Kesimpulannya, kecemerlangan prestasi oleh mangkin 20%Cu/Dol adalah didorong oleh sifat makroporos dan kristalnya, terdiri daripada campuran kalsium, magnesium, dan oksigen sebagai komponen teras, mempunyai luas permukaan logam kuprum, serakan logam kuprum serta kestabilan terma yang baik. Juga, interaksi diantara kuprum-dolomit yang baik, ini termasuklah penurunan logam yang tinggi (~291 °C) dan yang paling utama adalah kehadiran kapasiti asid yang tinggi (19528 $\mu\text{mol/g}$) dengan tapak Lewis pada permukaan mangkin yang bertindak sebagai tapak aktif pemangkinan. Selain itu, kehadiran logam kuprum terhadap dolomit menunjukkan aktiviti pemangkinan lebih bagus berbanding

dengan logam kuprum dan dolomit sahaja kerana didorong oleh tapak asid dan penurunan metal yang lebih bagus. Mangkin 20%Cu/Dol kemudiannya digunakan dalam kajian kebolehteran untuk lima kitaran tindak balas dan didapati ia mampu mengekalkan prestasi yang baik dalam penukaran gliserol, walaupun bagaimanapun pemilihan 1,2-PDO adalah berkurang setelah penggunaan yang pertama. Berdasarkan analisis yang diperolehi, pengurangan 1,2-PDO adalah disebabkan berlakunya pembentukan karbon dan juga pelarutlesapan tapak aktif logam (Cu, Ca dan Mg). Penukaran gliserol kepada 1,2-PDO mengikuti laluan penyahidratan-penghidrogenan serta tindak balas terhadap pemecahan ikatan C-C dengan methanol sebagai produk sampingan adalah tidak ketara.



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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BJH	Barret-Joyner-Halenda
DTG	Derivative Thermogravimetric
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscopy
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee on Powder Diffraction Standards
TGA	Thermogravimetric Analysis
TPD	Temperature Programmed Desorption
TPO	Temperature Programmed Oxidation
TPR	Temperature Programmed Reduction
P_0	Saturated Vapor Pressure
P/P_0	Relative Pressure

CHAPTER 1

INTRODUCTION

1.1 Background of research

Biodiesel is a biofuel which chemically known as fatty acid methyl ester produced mainly by transesterification reaction of different triglycerides from vegetable oil or animal fat (He et al., 2017; Nanda et al., 2017). It is a renewable and sustainable biofuel with high quality, nontoxic, has high cetane number, in-built oxygen content with higher combustion and complete carbon cycle. It is highly researched by industrialists and governments worldwide due to its inherent advantages. In addition to complement the already-dwindling petroleum products, and the foregoing directive of European Union (EU) legislation that conventional fuels should have an addition of at least 5.75% biodiesel by 2010, and with the possibility of increasing it to 20% by 2020, member countries have already responded to the production and use of biodiesel and made ensure that energy from renewable sources forms at least 10% of the transportation fuels (Comelli, 2011; Decision, 2009).

The compliance of EU efforts can be seen from the available data from various sources reporting that biodiesel production in EU member countries was put at 1.93 million tons in 2004, and after ten years, in 2013, it was put at 10.37 million tons, moving up to 11.58 million tons in 2016 (European Biodiesel Board). Similarly, the United States biodiesel production grew from 0.5 million gallons in 1999 to 250 million gallons in 2006 (Stelmachowski et al., 2014), and later to 2.89 billion gallons in 2016, indicating the capacity and actual growth of biodiesel production (National Biodiesel Board, U.S). However, the global status report in 2019 indicates that in 2019, the world biodiesel production was more than 30 billion liters, with the United States, Brazil, Germany, France and Argentina being the top five producers by the report of Statista 2021 published by N. Sönnichsen, Jan 6, 2021.

The biodiesel global production of the top 16 countries in 2019 is shown in Figure 1.1. It has also been stated in several works that biodiesel production will soar in the coming years, and this is evident from the series of diversified global research activities in boosting biodiesel production both in the areas of feedstock and catalysis to improve energy efficiency and reduce greenhouse gas emission.

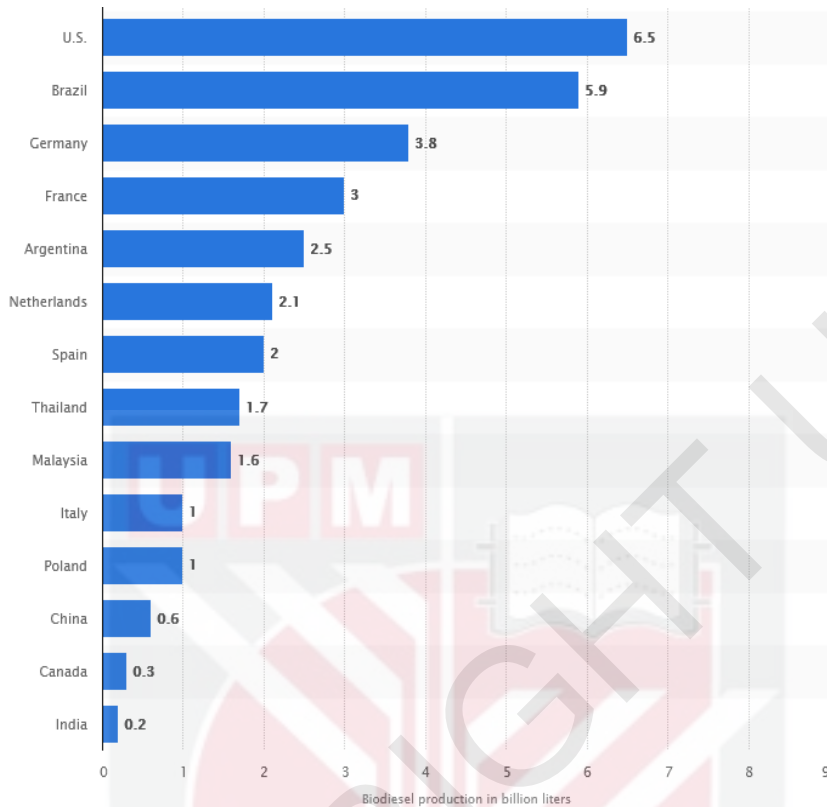


Figure 1.1: The biodiesel global production of the top countries in 2019 (Statista 2021)

In addition, it has been reported that 10-20% of the total volume of biodiesel produced is made up of glycerol. That is, with every 100 kg production of biodiesel, 10 kg of glycerol is generated as by-product, with purity of around 50%–55% (Bagnato et al., 2017; Quispe et al., 2013; Singhabhandhu & Tezuka, 2010). The balanced reaction from the triglycerides chemically reacts with alcohol (methanol) in the presence of catalyst is as shown in Figure 1.2. One mole of triglyceride reacts with three moles of alcohol to yield one mole of glycerol and three moles of fatty acid methyl esters (FAME).

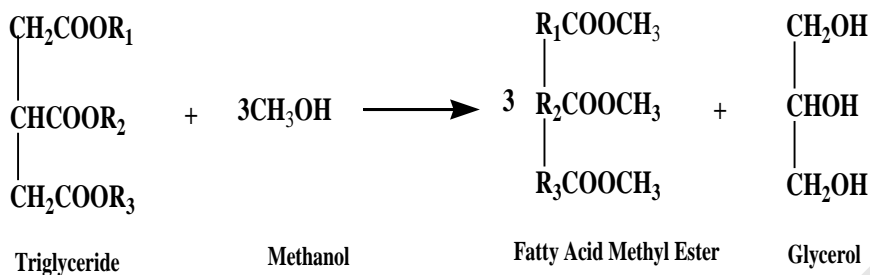


Figure 1.2: Production of biodiesel and glycerol via transesterification process

Apart from predominantly produced glycerol and already saturated market from biodiesel process, glycerol is also formed in large quantities as a by-product from soap manufacturing in the process of alkaline saponification as illustrated in Figure 1.3. In alkaline saponification (generally sodium hydroxide or potassium hydroxide), salts of the fatty acids (also called soap) and glycerol was produced. The soap production process as the essence of the commercial soap-making industry usually yields glycerol at about 10% of the value of the soap formed or 0.5 million tons per year (Nakagawa & Tomishige, 2011; Quispe et al., 2013; Tan et al., 2013).

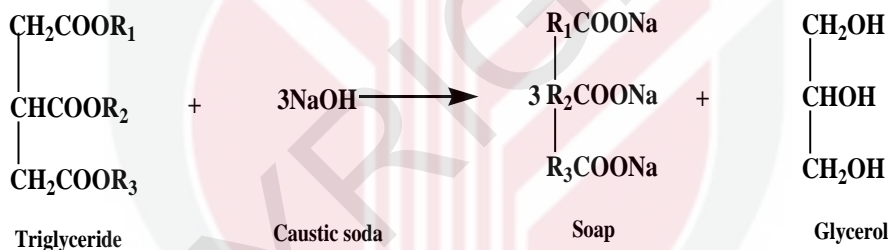


Figure 1.3: The saponification process from triglyceride to produce soap and glycerol as the by-product

In other reaction process, glycerol is also produced as by-product from hydrolysis of fatty acid for free fatty acid production. Hydrolysis is a reversible reaction whereby a molecule of steam breaks a fatty acid off the glycerol backbone of a triglyceride, resulting in a free fatty acid and glycerol. The reaction can be represented by the following equation as shown in Figure 1.4. Generally, hydrolysis reaction is similar to saponification reaction, but fat and oil reacts with water to yield a free fatty acid and glycerol in this case. During the hydrolysis reaction, each molecule of fat and oil will yield one mole of glycerol and three moles of fatty acid with approximately 100 g fat and oil with 6.1g of water produced 95.7g of free fatty acid and 10.4g of glycerol (Tan et al., 2013).

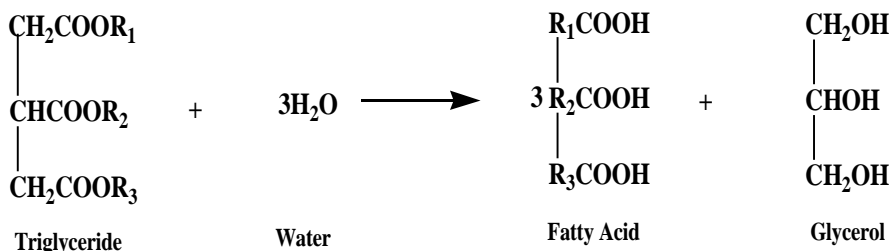


Figure 1.4: The hydrolysis process from triglyceride to produce fatty acid and glycerol as the by-product

The growing biodiesel industry as well as soap and hydrolysis production have resulted in a significant global glycerol supply and lead to the fall of glycerol market prices from 2000 to 2010 in particular for European Union (EU) from about 3200 \$/ton to 2000 \$/ton in EU and to under 500 \$/ton and 600 \$/ton in USA for refined glycerol price (Anitha et al., 2016; Yang et al., 2012; Yazdani & Gonzalez, 2007). Apart from becoming as a financial liability there are also social and environmental concerns for sustainability of glycerol waste disposal when discarded without adequate treatment. Hence, a lot of research is focused on the conversion of glycerol into high value and useful products with better reaction routes and reaction conditions through catalytic process is demanded (Anitha et al., 2016).

1.2 Potential applications of glycerol

The versatility of glycerol is well known in view of its applications in almost all the fields of human endeavors. However, for glycerol to be used as synthetic intermediates in the production of food, pharmaceutical, cosmetics and other personal care industries, it must be pure. Unfortunately, the purification process, which involves filtration, chemical treatment and vacuum distillation, is expensive, especially to the small and medium production plants, and therefore not commensurate with its current low market value (Comelli, 2011; Gupta & Kumar, 2012). Therefore much studies have sought the direct conversion route towards upgrading glycerol versatility of crude glycerol or partially-treated raw glycerol in the production of higher value added chemicals products for various industrial sectors via catalytic reaction process (Nanda et al., 2017).

Basically, glycerol can be transformed into many beneficial products which concept is known as biorefinery conversion technique through several chemical and biological processes, in the synthesis of hydrogen, as fuel additives, as a substrate for fermentation, as an animal feed, for methanol generation, in wastewater treatments and many others via process such as reforming, dehydration, direct hydrogenation, esterification, hydrogenolysis, oxidation, oligomerization and cyclization that led to various chemical products as shown in Figure 1.5.

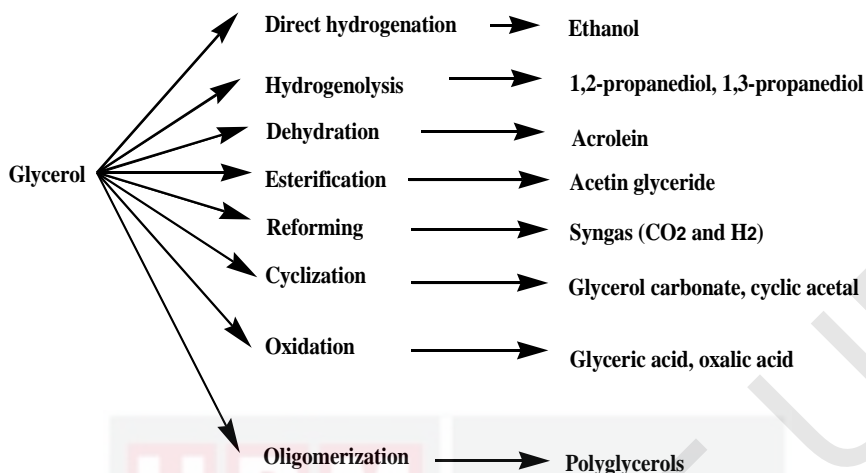


Figure 1.5: Summary for the glycerol conversion and their possible derivatives (Monteiro et al., 2018; Pradima et al., 2017)

Among the conversion routes, the case of 1,2-propanediol (1,2-PDO) production via catalytic glycerol hydrogenolysis offers great potential and highlighted as among the promising approach due to its various product applications. The 1,2-PDO is a high value added and important commodity chemical having major application as a coolant, airplane de-icing agent, in the production of pharmaceuticals, cosmetics, solvent and raw material for unsaturated polyester resins (Liu et al., 2019; Nanda et al., 2017; Soares et al., 2016). The global production of 1,2-PDO is constantly growing, having already reached approximately 1.4 million tons per year with the annual growth rate of 4% (Vasiliadou & Lemonidou, 2011) including annual production of about 1 million tons in the United States (Monteiro et al., 2018). This increase is due to its extensive use as an important chemical intermediary in the manufacture of products daily application such as in medicine, polymers, cosmetics, food, adhesives, antifreeze and deicing agents, pharmaceuticals, lubricants, liquid detergents, flavorings, and as solvent in unsaturated polyester resin (Monteiro et al., 2018). Without the use of glycerol, the synthesis of 1,2-propanediol involves environmental issues for which chemical process via petroleum feedstocks is preferred, especially in the hydration of ethylene oxide or propylene oxide. In this research, emphasise is given to the hydrogenolysis process of glycerol in the production of 1,2-PDO which is known as a bifunctional reaction since it required the use of acid and metal sites for its reaction.

1.3 Problem statement

Biodiesel production is going stronger each year as it seen as an alternative to fossil fuel that is facing existential threat. It is forecasted that the world dependence on biodiesel is continue to grow as it afford a much cleaner burning hence low environmental impact. However, the transesterification process for biodiesel production releases plenty of glycerol by products to the brink of oversupply. Therefore action has to be taken to utilize glycerol by converting it into high value chemicals

which will improve the commercial viability of biodiesel and at the same time promoting a circular economy.

In this study, glycerol is targeted to be converted into 1,2-propanediol via hydrogenolysis process over heterogeneous catalysts. Reports showed that the conversion of glycerol requires a dual catalyst sites which are metal site and acid site (Wu et al., 2013; Jiang et al., 2016). The acid site is required for the dehydration route while metal sites are for hydrogenation route during the catalytic process. Transition metal oxides such as copper, nickel, cobalt, iron and zinc have been used for hydrogenolysis of glycerol, unfortunately their low metallic dispersion, low ability for metal reduction and low acid capacity limited their potential and be the reason for their low hydrogenolysis performance. Even the noble metals of Pd, Pt and Ru have been reported to be effective in the hydrogenolysis reaction due to their good metallic dispersion and high metal reducibility, unfortunately their cost are expensive. Henceforth, transition metals were chosen to be investigated in this work. For that purpose, the oxides should be reduced to their metallic phase as site for hydrogenation of acetol intermediate to corresponding 1,2-PDO.

Henceforth, the transition metals must be supported to a support material to allow good metals distribution over the catalyst support. It is discovered that the presence of support could not only provide a surface for metal dispersion but at the same time an acid site as well. A range of supports materials have been widely reported for its application in glycerol hydrogenolysis such as commercial graphite, alumina (Al_2O_3), silica (SiO_2), titanium dioxide (TiO_2), zirconia (ZrO), zinc oxide (ZnO), magnesium oxide (MgO), sulfonated carbon based catalyst (H_3COH) and zeolite-based supports of MCM-41, HZSM-5, SBA-15 and SBA-16 (Montes et al., 2015; Pudi et al., 2016; Feng et al., 2016; Li et al., 2016). Nonetheless, quite many of them are rather limited in acid capacity and low regeneration activity. These weakness hence led to low selectivity towards 1,2-PDO (<40%) (Niu et al., 2013; Soares et al., 2016, Li et al., 2014; de Andrade et al., 2020) although the conversion of glycerol was appreciable (> 80%) (Montes et al., 2015; Pudi et al., 2016; Feng et al., 2016; Li et al., 2016). They are also less cost-effective due to the chemical production process. So, the low selectivity towards 1,2-PDO is a major problem that requires appropriate attention. For glycerol hydrogenolysis, the use of catalyst support with high acid capacity, rich in availability and high thermal stability is one of the concerns and must be the main feature in obtaining a high efficiency of catalytic reaction. Thereby, despite the attempts over different supported catalysts, the selectivity to 1,2-PDO, the most sought-after product of hydrogenolysis, should need improvement. Therefore, the interest now is to identify new catalyst material, which is inexpensive, environmentally friendly, high acid capacity, high metal reducibility and reusable to enhance the selectivity of 1,2-PDO and also glycerol conversion.

Dolomite as mineral catalyst has been identified as a potential good material for such catalytic synthesis. It comprised from a mixture of mainly calcium carbonate (CaCO_3) and magnesium carbonate (MgCO_3). Due to its high acid characteristic together with good thermal stability which has not been reported before in glycerol hydrogenolysis reaction, this study thus focuses on its development as catalyst support for the transition metals with purpose of catalyzing and improving the 1,2-PDO selectivity. In

addition to its acid characteristic, dolomite has gained attention due to its low-priced and high availability in Malaysia.

1.4 Objectives

This research aims to develop copper catalyst for glycerol hydrogenolysis to 1,2-PDO and the specific objectives are as follows:

1. To synthesize copper supported on different catalyst supports via impregnation method and characterize their physicochemical properties using several characterization techniques.
2. To synthesize different metal oxides supported on dolomite via impregnation method and characterize their physicochemical properties using several characterization techniques.
3. To synthesize different copper loadings supported on dolomite via impregnation method and characterize their physicochemical properties using several characterization techniques.
4. To test the catalytic activity over the prepared catalysts and hence to optimize the reaction condition at different parameters over the best catalyst.
5. To evaluate the reusability and regeneration study of copper supported on dolomite catalyst.

1.5 Scope of research

In the present work, all catalysts are prepared using impregnation method. For screening studies, copper catalyst supported on different supports (Cu/Dol, Cu/Al₂O₃, Cu/Talc, Cu/Bent, Cu/Mont) and a series of transition metals supported on dolomite (Cu/Dol, Ni/Dol, Co/Dol, Fe/Dol, Zn/Dol) has been conducted for comparison purpose. For the best catalyst, Cu/Dol, several characterization techniques to study the physicochemical properties such as TGA-DTG, N₂-physisorption, XRD, NH₃-TPD, H₂-TPR, FTIR-pyridine, FESEM-EDX and XPS has been carried out. Optimization and catalytic studies of Cu/Dol catalysts at different copper loadings (10wt%, 20wt%, and 30wt%), reaction parameters such as effect of reaction temperature, hydrogen pressure, reaction time, amount of catalyst dosage, amount of glycerol concentration and effect of different catalyst reduction temperatures are evaluated. Catalyst reusability and regeneration is conducted using the best catalyst at the best reaction condition. The deposition of carbon in spent catalyst is analysed using TGA, TPO, NH₃-TPD, H₂-TPR, XRD and FESEM-EDX.

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BIODATA OF STUDENT



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LIST OF PUBLICATIONS

Publication

- Azri, N., Ramli, I., Nda-Umar, U.I., Shamsuddin, M.R., Saiman, M.I., Taufiq-Yap, Y.H. (2020). Copper-Dolomite as Effective Catalyst for Glycerol Hydrogenolysis to 1,2-Propanediol. *Journal of the Taiwan Institute of Chemical Engineers*, 112, 34-51. **(Q1 in JCR)**
- Azri, N., Ramli, I., Nda-Umar, U.I., Saiman, M.I., Taufiq-Yap, Y.H. (2021). Promotional Effect of Transition Metals (Cu, Ni, Co, Fe, Zn)-Supported Dolomite on Hydrogenolysis of Glycerol into 1,2-propanediol. *Arabian Journal of Chemistry*, 14, 103047. **(Q2 in JCR)**
- Azri, N., Ramli, I., Nda-Umar, U.I., Saiman, M.I., Taufiq-Yap, Y.H. (2021). Effect of Different Supports for Copper as Catalysts for Glycerol Hydrogenolysis to 1,2-Propanediol. *Journal of King Saud University-Science*, 33, 101417. **(Q2 in JCR)**
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Conference

1. The 8th Asia-Pacific Congress on Catalysis (APCAT-8) (2019), 4th-7th August, Centara Grand & Bangkok Convention Centre at Central World, Bangkok, Thailand **(Oral Presenter)**. Abstract-Effect of Transition Metals for Production of 1,2-Propanediol via Catalytic Hydrogenolysis of Glycerol over Dolomite Supported Catalyst.
2. International Conference on Catalysis 2018 (Icat2018), 13th-15th November, Bangi-Putrajaya Hotel, Bangi, Selangor **(Oral Presenter)** Abstract-Utilization of tin-copper catalyst in transforming glycerol into 1,2-Propanediol via in situ generated hydrogen.



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