The Urushibara Catalyst for Glycerol Hydrogenolysis

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This work aimed to study the catalytic activity of catalysts containing various metal elements on glycerol hydrogenolysis. The catalyst was prepared using copper, nickel, and copper-nickel in a metal mass ratio of 1. The metal chloride solution was precipitated with zinc powder to form metal alloy, which was then digested using acetic acid to create a type of porous particles. All catalysts were characterized using X-ray fluorescence, N_2-physisorption, and temperature-programmed reduction. Glycerol hydrogenolysis was conducted with an initial pressure of 40 bar, a temperature of 220 °C, and a stirrer speed of 500 rpm for 6 h, using a 2 % catalyst loading. The results showed that Urushibara copper can be used for glycerol hydrogenolysis, as it achieved glycerol conversion, Urushibara nickel and Urushibara copper-nickel did not exhibit catalytic activity. Catalyst characterization revealed a difference in the textural properties, which were found insignificant to glycerol conversion. The XRF results showed that the U-Cu catalyst has a higher zinc content than the other catalysts. The difference in composition affects the catalytic ability, with the zinc content contributing to glycerol dehydration to acetol.

1. Introduction

Over the past decade, there has been a growing interest in alternative energy sources as a replacement for fossil fuels. One particularly popular alternative is biodiesel. During biodiesel production, a transesterification reaction typically yields 3 mol of biodiesel and 1 mol of glycerol (Nakagawa and Tomishige, 2011) and glycerol. The increasing supply of biodiesel has led to a significant increase in the production of glycerol. Consequently, there is a need to find value-added products from glycerol (Okolie et al., 2022).

There is a strong emphasis on utilizing renewable sources to replace petrochemicals, and glycerol hydrogenolysis serves as an excellent example in this context (Frolich et al., 2022). Glycerol hydrogenolysis offers the potential for the production of various valuable chemicals including propylene glycol, 1,2-propanediol, ethylene glycol, acrolein, and others (Sharma et al., 2014). Propylene glycol, for instance, can be derived from both petrochemical and renewable sources but the renewable source as glycerol is lower price and less toxicity (Kumpradit and Jitkarnka, 2019). It is a high-value compound with versatile applications as a humectant, solvent, and antifreeze agent in the pharmaceutical, food, and cosmetic industries (Jacob et al., 2018).

Typically, glycerol hydrogenolysis is carried out in the liquid phase using a heterogeneous catalyst. Both noble metals and transition metals have shown promising catalytic performance in this process. Transition metals such as copper, nickel, and cobalt are particularly attractive due to their lower cost compared to noble metals. They exhibit good hydrogenation activity. The primary requirements for effective propylene glycol production through glycerol hydrogenolysis are the cleavage of C-O bonds and efficient hydrogenation, as depicted in Figure 1. C-O bond cleavage leads to the formation of 1,2-propanediol (propylene glycol) and 1,3-propanediol, while C-C bond cleavage results in ethylene glycol. Studies have highlighted the selectivity of copper for propylene glycol, whereas nickel and cobalt are known for their strong hydrogenation capabilities. Various methods exist for catalyst synthesis, including co-precipitation, impregnation, and sol-gel techniques. Typically, catalyst preparation involves dispersing the metal onto a high-surface-area support to maximize the active

surface. Higher metal dispersion leads to increased exposure of metal active sites, enabling better reactant transfer and catalytic activity (Okolie et al., 2022). The Urushibara catalyst method employs a unique approach that focuses on achieving a high active surface area through the formation of porous metal particles. The Urushibara catalyst method involves the synthesis of porous metals, such as nickel. The process consists of two steps: firstly, precipitating a metal chloride solution with zinc powder to form an alloy, and secondly, digesting the alloy with acid to remove the zinc and create porous particles. Normally, Urushibara catalyst always focuses on monometallic compounds such as Ni, Cu, or Co but the synthesis of bimetallic is one way to enhance the catalyst, resulting in two functional catalysts. The synthesis of Urushibara catalyst in a bimetallic form and the use of Urushibara catalyst in glycerol hydrogenolysis are of particular interest.

In this study, the focus is on the synthesis of copper and nickel catalysts using the Urushibara method and observe possibility to synthesize bimetal catalyst as copper-nickel cause of Ni is beneficial for hydrogenation and Cu is effective for C-O bond cleavage, which contributes to a high selectivity for propylene glycol, as well as investigating their catalytic potential in glycerol hydrogenolysis. Detailed analysis of the catalyst's composition, textural properties, and hydrogen consumption is carried out to determine the key factors influencing the reaction.
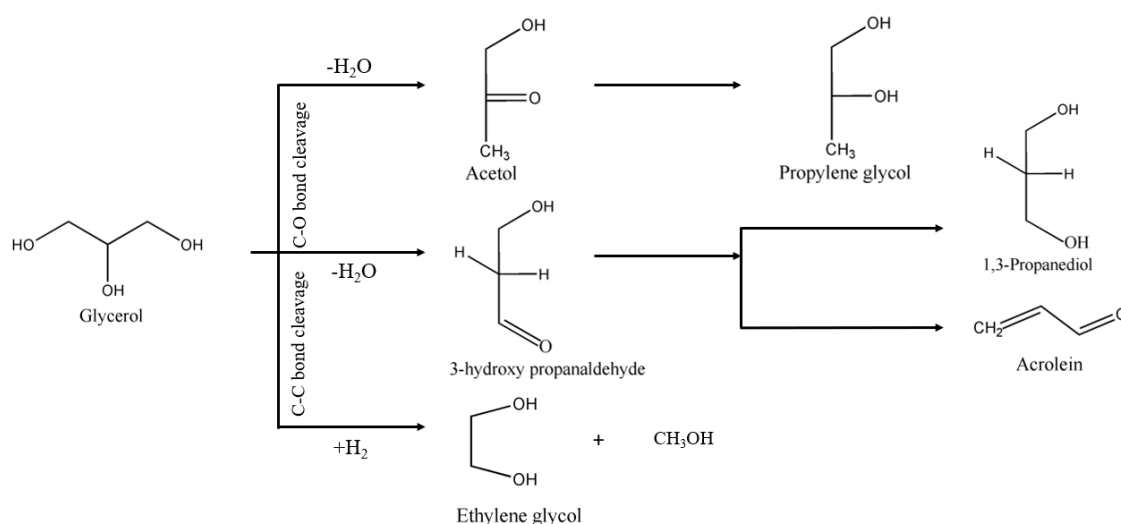

Figure 1: Major products of glycerol hydrogenolysis

2. Experimental

2.1 Materials

$CuCl_2 \cdot 2H_2O$ (99 %) was purchased from Loba Chemie, $NiCl_2 \cdot 6H_2O$ (99 %), zinc powder (99.9 %), and glycerol (99.5 %) were purchased from Kemaus.

2.2 Catalyst synthesis

The Urushibara catalyst preparation involved two steps: precipitation and leaching. For the precipitation step, 10 g of zinc powder was combined with 1 g of the metal. To achieve a mud-like consistency, 3 mL of boiling water were added to the zinc powder, and the mixture was stirred until well-mixed. The metal solution was prepared separately by dissolving 1 g of the metal (specifically, 2.68 g of copper II chloride dihydrate, 4.04 g of nickel II chloride hexahydrate, or 1.34 g of copper II chloride dihydrate with 2.02 g of nickel II chloride hexahydrate) in 10 mL of boiling water. The metal solution was then poured into the zinc mixture. To remove chloride ions and gas, the resulting mixture was washed 4-5 times with distilled water, followed by draining of the water. Subsequently, the solid residue was subjected to leaching with 160 mL of 13 % acetic acid to eliminate the zinc. After leaching, the catalyst was washed with distilled water until the pH reached 7. The water was then drained, and ethanol was added for storage purposes. To characterize all catalysts, physisorption and chemisorption techniques were employed, including BET (Brunauer-Emmett-Teller), T-Flex, and XRF (X-ray fluorescence). BET techniques were used to analyze the catalysts' properties in terms of surface area and pore size distribution, T-Flex were used for temperature programmed reduction to find temperature reduction and hydrogen consumption of catalyst. XRF was used for determination of element composition of catalyst.

2.3 Catalyst activity

Before using the catalyst, the Urushibara catalyst was dried at 60 °C to remove ethanol. The dried catalyst was then reduced by flowing 10 % H_2-N_2 (0.3 mL/min) at 200 °C for 2 h, based on the TPR results. After the catalyst reduction, all the reduced catalyst was added to 250 mL of a 60 % w/v glycerol solution in water (this concentration was used for catalyst comparison), and then transferred to the reactor chamber. The reactor chamber, controlled by an electronic controller, was equipped with a Parr reactor. To purge the air in the reactor, nitrogen gas was flushed, and then the reactor was pressurized with hydrogen gas to the desired pressure (40 bar). The reactor was heated to the desired temperature (220 °C), stirred at 500 rpm, and all experiments were conducted for 6 h. After the reaction, the reactor was cooled to ambient temperature, and the reaction mixture was filtered using vacuum pump and filter paper (No. 1, Whatman) to separate the catalyst from the mixture. The product mixture was then analyzed for composition using gas chromatography (GC-2010, Shimadzu) with a ZB-Wax column. The glycerol conversion ($X_{glycerol}$) and the propylene glycol selectivity ($S_{propylene\ glycol}$) were calculated following to Eq(1) and (2).

$$X_{glycerol} = \frac{n_{glycerol}^0 - n_{glycerol}}{n_{glycerol}^0} \qquad (1)$$

$$S_{propylene\ glycol} = \frac{n_{propylene\ glycol}}{n_{glycerol}^0 - n_{glycerol}} \qquad (2)$$

where $n_{glycerol}^0$ is the mole glycerol added, $n_{glycerol}$ and $n_{propylene\ glycol}$ are the mole glycerol and propylene glycol at the end of reaction.

2.4 Catalyst characterization

XRF: X-ray fluorescence of samples (U-Cu, U-Ni, and U-CuNi (the mass ratio of metal preparation = 50:50)) was performed with a S2 PUMA, Bruker AXS device. The element composition of catalyst was determined by this device.

N_2-physisorption: the textural properties of the catalyst, including specific surface area, pore volume, and mean pore diameter, were determined using the nitrogen physisorption technique. Prior to the analysis, the sample was pretreated with a flow of 50 mL/min of helium at 180 °C for 3 h. Subsequently, the sample was cooled to - 196 °C using liquid nitrogen. The nitrogen physisorption measurement was conducted by introducing nitrogen gas and measuring the volume of nitrogen adsorbed at different pressures to determine the textural properties. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method, while the pore volume and pore size were determined using the Barrett-Joyner-Halenda (BJH) method, considering the desorption of nitrogen from the sample.

TPR (Temperature-programmed reduction): the method was conducted using a 3Flex adsorption analyzer. A 0.1 g catalyst sample was subjected to reduction using a mixture of 10 vol.% H_2 in Ar at a flow rate of 50 mL/min. The temperature increased gradually at a ramp rate of 10 °C/min, with a final temperature of 800 °C. The reduction process and the corresponding temperature changes were monitored using this technique. The consumption of hydrogen during the reduction was determined by analyzing the thermal conductivity signal.

3. Results and Discussion

3.1 X-ray fluorescence

The elemental composition of the samples (U-Cu, U-Ni, and U-CuNi) was determined using XRF analysis, as presented in Table 1. The U-Cu sample contains 41.45 % wt of copper (Cu) and 57.89 % wt of zinc (Zn), while the U-Ni and U-CuNi samples contain approximately 18 % wt of zinc and 81 % wt of metal (copper or nickel). All of the samples obtained zinc from the precipitation process. These results suggest that the digestion process was unable to completely remove all of the zinc, and the U-Cu exhibited a higher zinc content. This indicates that the Cu-Zn alloy particles are more resistant to zinc leaching compared to the particles containing nickel. Maybe the precipitated Cu can form in strong structure and have more acid resistance than the precipitated particles contain with Ni.

Table 1: Composition of Urushibara catalysts by XRF

Composition (% wt)	U-Cu	U-Ni	U-CuNi
Cu	41.73	-	50.03
Ni	-	81.20	31.68
Zn	58.27	18.80	18.29

3.2 N$_2$-physisorption

The adsorption isotherm of Urushibara catalysts were shown in Figure 2. From the IUPAC physisorption isotherm, U-Cu, U-Ni, and U-CuNi are type 4 and the hysteresis loop are type H4 (Thommes et al., 2015). This adsorption isotherm indicates that these particles are mesoporous material and type H4 is the loops always found with the aggregated of crystals, some mesoporous particles as zeolites and micro-mesoporous of carbons (Mel'gunov, 2023). The textural properties, such as surface area, pore volume, and pore size, are presented in Table 2. It is observed that the surface area of U-Cu is lower than that of the other catalysts, which corresponds to a lower pore volume. This difference in surface area can be attributed to the difficulty in digesting the Cu-Zn alloy with acetic acid compared to the Ni-Zn alloy. As a result, the formation of porous particles in U-Cu is less than in U-Ni. When comparing Cu-Ni with Ni alone, the presence of copper in the Cu-Ni catalyst leads to a decrease in surface area and pore volume. From the BJH plot, it shows that the pores of all particles are mesoporous, the pore size distribution almost found in range of 3-5 and 20-25 nm.
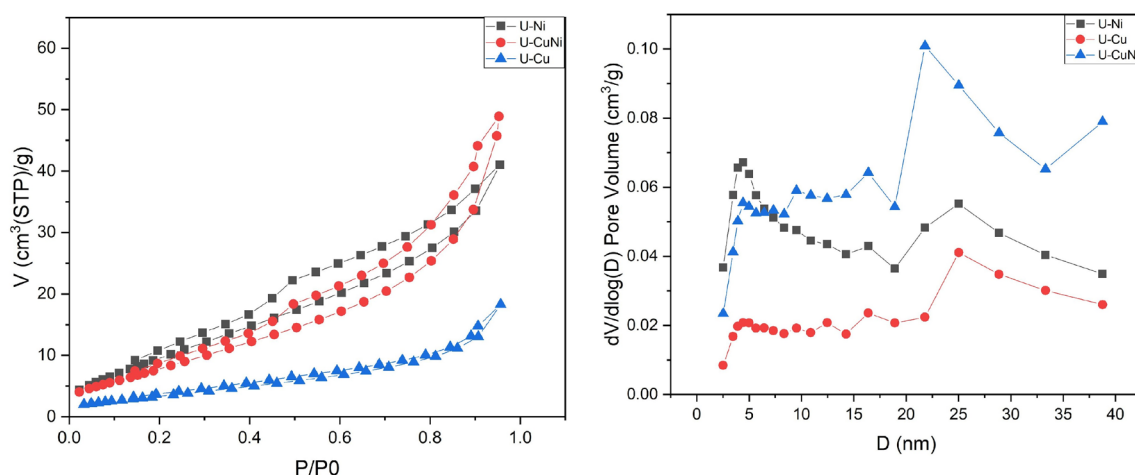

Figure 2: The adsorption isotherm and BJH plot of U-Cu, U-Ni, and U-CuNi

Table 2: The textural properties of catalysts

Catalyst	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
U-Cu	13.6	0.028	8.33
U-Ni	41.9	0.064	6.06
U-CuNi	34.6	0.076	8.75

3.3 Temperature programmed reduction

The H$_2$-TPR results are shown in Figure 3. The procedure took place in the temperature range of 50–800 °C. The reduction peak of copper oxide appeared in range of 100–200 °C while the reduction peak of nickel oxide appeared in range of 220–600 °C, the reduction peak of nickel oxide was observed in U-Ni and U-CuNi while U-Cu appear only peak of copper oxide, all of temperature reduction were used for catalyst reduction to form in metal that ready to catalysis.
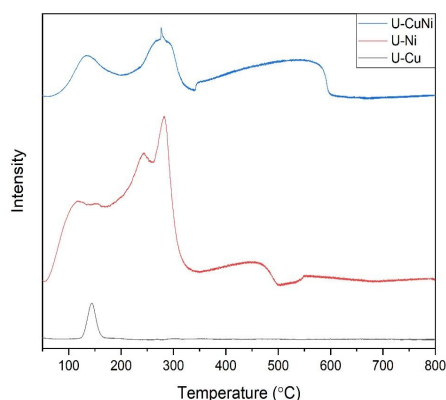

Figure 3: H$_2$-TPR of Urushibara catalyst

The area of TPR corresponds with amount of hydrogen consumption and shows that U-Ni has highest hydrogen consumption while the presence of Cu leads the decrease of hydrogen consumption. Hydrogen consumption is one of the catalyst properties which is required for glycerol hydrogenolysis.

3.4 Catalyst activity

The Urushibara catalyst's performance was evaluated in the glycerol hydrogenolysis reaction. When using U-Cu as the catalyst, glycerol conversion of 19.27 % was achieved, with a selectivity of 75.35 % towards propylene glycol. When U-Ni and U-CuNi were used as catalysts, no conversion of glycerol to other products was observed (Figure 4).
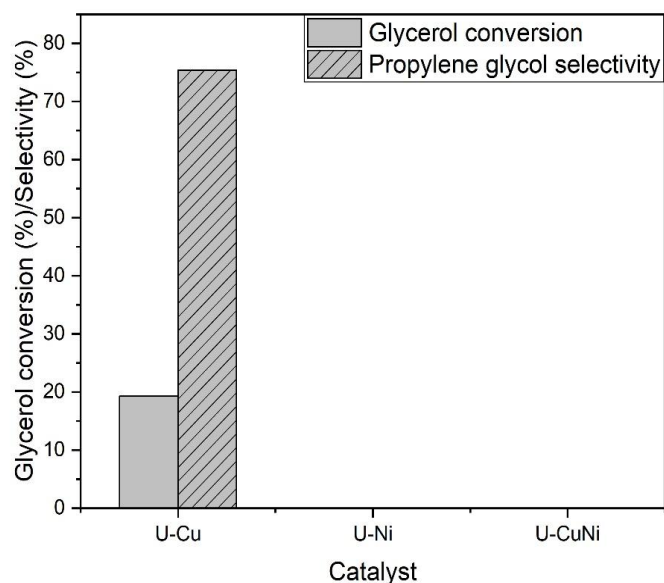

Figure 4: The glycerol conversion and propylene glycol selectivity by Urushibara catalyst

It is worth noting that despite U-Ni and U-CuNi exhibiting favorable properties such as higher surface area and hydrogen consumption compared to U-Cu, they were not effective catalysts in this study. Interestingly, previous research by other scientists has reported that ZnO exhibits activity in glycerol dehydration due to its acid site properties (Wang and Liu, 2007), while Cu is known for its hydrogenation capabilities (Singh et al., 2022) and the step of glycerol dehydration is hardly to occur. These findings align with the XRF results, which indicate a higher zinc content in U-Cu compared to U-Ni and U-CuNi, at 40 wt%. The proposed reaction pathway for glycerol hydrogenolysis is depicted in Figure 5, where glycerol undergoes dehydration to form acetol, which is then hydrogenated to produce propylene glycol.
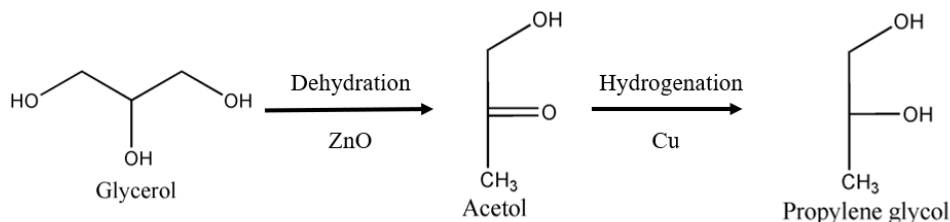

Figure 5: Reaction pathway associated with glycerol hydrogenolysis over Cu/ZnO (Omar et al., 2021)

A study conducted by Zhou et al. on the kinetic aspects of glycerol hydrogenolysis using a Cu-Zn-Al$_2$O$_3$ catalyst supports the validity of the dehydration-hydrogenation pathway via acetol (Zhiming et al., 2010). An excessive zinc content can result in a high acid concentration, which may lead to lower propylene glycol selectivity (Frolich et al., 2022). A high number of acid sites can facilitate the cleavage of C-C bonds, leading to the conversion of glycerol to alternative pathways such as the production of ethylene glycol and methanol.

4. Conclusion

The Urushibara catalysts, including Cu, Ni, and CuNi variants, are synthesized for the catalytic of glycerol hydrogenolysis, which is performed in the liquid phase. The variation in the type of metal results in differing zinc content after digestion process, with U-Cu having a higher zinc content than U-Ni and U-CuNi. The catalyst's ability to catalyze the hydrogenolysis of glycerol is influenced by its zinc content. When using U-Cu as a catalyst, which has a high zinc content (57.89 %), a significant glycerol conversion was observed. This high zinc content contributes to a larger surface area, facilitating the dehydration of glycerol, which is the initial step in glycerol hydrogenolysis, leading to the formation of acetol. Subsequently, the Cu surface promotes the hydrogenation of acetol, converting it to propylene glycol. Interestingly, despite U-Ni exhibiting the highest hydrogen consumption and surface area among the characterized catalysts, it did not demonstrate catalytic activity. On the other hand, U-Cu, with lower hydrogen consumption and surface area, exhibited catalytic activity. These results suggest that the metal surface's role in hydrogenation is not the primary driving factor for this reaction. It appears that glycerol dehydration is more challenging than hydrogenation in this context. This might explain why U-Cu, which exhibits lower hydrogen consumption, can catalyze the reaction more effectively than the others.

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