Effect of Support on the Hydrodeoxygenation of Phenol using Ni-based Metal Catalysts: Ni/SiO$_2$, Ni/ZrO$_2$, and Ni/Al$_2$O$_3$

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Abstract: Hydrodeoxygenation (HDO) reaction is a fundamental step for producing bio-oil from lignocellulosic biomass. One of the major components from biomass is lignin which can be hydrolysed into phenolic derivatives. Here, we reported the preparation of Ni-based metal catalysts with the variation of a metal oxide for HDO of phenol. The Ni loading for each metal oxides is 15% (w/w), supported on SiO$_2$, ZrO$_2$, and Al$_2$O$_3$. The XRD analysis showed that Ni metal was detected in the SiO$_2$ support at $2\theta = 44.26^\circ$, $51.72^\circ$, $76.5^\circ$; Ni in ZrO$_2$ at $2\theta = 44.55^\circ$, $51.9^\circ$, $76.4^\circ$; and Ni in Al$_2$O$_3$ at $2\theta = 44.12^\circ$, $51.72^\circ$, and $76.78^\circ$. The catalytic test for HDO reaction was carried out in the autoclave oil batch reactor, heated for 2 hours at 200$^\circ$C with H$_2$ gas atmosphere. Based on GC-MS analysis, the reaction at 200$^\circ$C using Ni-SiO$_2$ gave the highest product conversion, that is 52.2% with the selective formation of 2-methyl-1-butanol (52.2%). On the other hand, the reaction using Ni/ZrO$_2$ only produce 17.64% of the products with selective formation of cyclohexanone (35.35%). The result showed that products distribution is significantly affected by the type of the support.

1. Introduction

The availability of fossil fuels is limited. Furthermore, the burning emissions can potentially pollute the environment and contribute the greenhouse effect [1]. This encourages scientists to look for alternative fuel resources that are easy to renew and environmentally friendly. Biomass is a biological material derived from organisms or living things formed from metabolic waste. It is reported as a potential material for alternative energy because the degradation of lignocellulosic polymer in biomass gave phenolic derivatives, such as phenol, guaiacol, and anisole which is rich in carbon sources [2], [3]. Unfortunately, the presence of hydroxyl groups possibly promote polymerization with aldehyde or ketone which affect the stability, viscosity, and corrosive of bio-oil. Therefore, catalytic hydrogenation and deoxygenation is needed to reduce the double bond and eliminate the oxygen to produce saturated hydrocarbons [2], [3].

The hydrodeoxygenation reaction (HDO) is a fundamental step for producing bio-oil from lignocellulosic biomass by reducing double bonds (hydrogenation) and/or eliminating oxygen atoms (deoxygenation) using a metal-based catalyst [4]. Generally, the metals used are Pt, Pd, and Ru which is less efficient because it has an expensive price [5]. Currently, the use of non-noble metals, such as Ni and Cu, is being developed. Ni metal has high hydrogenation activity for organic compounds because it has vacant d orbitals, so it is easy to promote the electron binding. In addition, Ni metal can be obtained from Ni-salt which is relatively cheap [1].
Besides the use of metals, support material as an oxide, such as, SiO$_2$, ZrO$_2$, and Al$_2$O$_3$ is important to consider. The SiO$_2$ is inert oxide which allows the increasing of BET surface, pore structure of the catalyst, and provide an active Bronsted-Lowry acid site [4]. Meanwhile, ZrO$_2$ is amphoteric which can prevent coke formation. ZrO$_2$ also has p-type semiconductor properties and strongly interacts with active species [1]. ZrO$_2$ can increase the activity of oxy compounds since the weak acidity of the surface [6]. Furthermore, alumina (Al$_2$O$_3$) has a high surface area of catalyst and have a Lewis acid site which is active when interact with H$_2$ gas [7]. However, Al$_2$O$_3$ is unstable under hydrothermal conditions [8].

Catalytic activity test was reported by Wang, *et al.* (2017). The 10Ni/Al$_2$O$_3$ and 10Ni/ZrO$_2$ catalysts were able to convert phenols up to 14%. The main conversion products gave cyclohexanone and cyclohexanol [9]. Another study, comparing 10Ni/Al$_2$O$_3$ and 10Ni/SiO$_2$ catalysts showed that the conversion and selectivity of 10Ni-SiO$_2$ catalyst products was better than 10Ni/Al$_2$O$_3$. This is due to the formation of coke when using a catalyst of 10Ni/Al$_2$O$_3$ [10]. The effect of temperature on the HDO reaction of phenol was reported by Ulfa *et al.* (2018). The higher the reaction temperature, the higher the conversion of the product [11]. By modifying temperature to 200°C, the reaction of phenol using Cu/Al$_2$O$_3$-ZrO$_2$ produce 4.3% of the product consist of the mixture of n-hexane, 3-methylpentane.

Here, in this study the HDO reaction of phenol was carried out using 15% Ni based metal catalyst deposited in SiO$_2$, ZrO$_2$, and Al$_2$O$_3$ to determine the activity of the metal oxide support. The catalyst activity test carried out in the presence of water solvent in autoclave oil batch reactor with temperature variations applied is 150°C, 180°C, and 200°C [12].

2. *Experimental*

2.1. *Materials*

Phenol from MERCK Singapore were used as a starting material for HDO reaction. The 15Ni-SiO$_2$ and 15Ni-Al$_2$O$_3$ catalyst were prepared previously. ZrOCl$_2$:8H$_2$O, ammonia, AgNO$_3$ 0.1 M, and Ni(NO$_3$)$_2$:6H$_2$O from MERCK Singapore used for preparation of 15Ni/ZrO$_2$ catalyst. The distilled water (HYDROBAT) from Indonesia. Ultra-High-Purity (UHP) N$_2$ and H$_2$ gas for calcination and reduction were supplied from Tira Austinate, Malang, Indonesia.

2.2. *Catalyst preparation*

The synthesis of catalyst is according to Zhang *et al.* (2013) method [2] and modified by Ulfa *et al.* 2016 [13], [14]. The SiO$_2$ and Al$_2$O$_3$ were used as received. ZrO$_2$ was obtained from precipitation of ZrOCl$_2$:8H$_2$O using NH$_4$OH until pH 8.00. The precipitate was filtered and washed with distilled water to remove chloride ions completely and tested by adding AgNO$_3$ 0.1 M to the filtrate. The solid obtained was dried overnight at 120°C and then calcined at 500°C for 5 h using N$_2$ gas to give ZrO$_2$.

The catalysts Ni/SiO$_2$, Ni/ZrO$_2$, and Ni/Al$_2$O$_3$ with Ni loading in 15% (w/w) were prepared by wet impregnation using Ni(NO$_3$)$_2$:6H$_2$O as nickel precursor. An appropriate amount of nickel nitrate was dissolved in a distilled water, followed by agitating for 24 h and evaporating to dryness. The composite was dried overnight at 120°C and calcined at 500°C for 5 h using N$_2$ gas followed by reduction using H$_2$ gas at 500°C for 5 h [15], [16].

2.3. *Catalyst characterization*

Catalysts were characterized by X-ray Diffraction (XRD) (PAN Analytical E’xpert Pro) with Cu Kα (λ=1.5406 Å) radiation. Samples were analyzed at angle 20 = 10° – 80°. XRF (X-ray Fluorescence) analysis was carried out on an equipment (PAN Analytical Minipal 4). SEM-EDX analysis was carried out on an equipment (Phenom). Fourier transform infrared spectroscopy (FT-IR) of the catalysts were acquired on a Shimadzu 8400. This characterization is carried out on the catalyst before and after used in the HDO reaction.
2.4. **Catalytic activity test**

The HDO reactions of phenols were carried out in a 200 mL stainless autoclave oil batch reactor with \( \text{H}_2 \) gas pressurized in 50 psi. For each run, activated catalyst (0.1 g), phenols (1 g), and water as a solvent (20 mL) were loaded into the autoclave equipped with magnetic stirrer. The reaction was carried out for 2 hours at 150°C, 180°C and 200°C. The HDO product is separated from the catalyst by filtration and then extracted using dichloromethane. The product is obtained after vacuum evaporation.

2.5. **Product analysis**

Liquid products obtained from the HDO of phenols were analyzed by FT-IR Shimadzu 8400S and GC-MS (Shimadzu QP2010 Ultra, Agilent column). The carrier gas was He and the oven temperature program increased from 40°C to 260°C at the rate 20 mL/min.

3. **Result and Discussion**

3.1. **Characterization of catalysts**

The crystal structure of Ni/SiO\(_2\), Ni/ZrO\(_2\), and Ni/Al\(_2\)O\(_3\) were analyzed by X-ray Diffraction (XRD). The XRD spectra of these catalysts shown in Figure 1. Ni metal was successfully deposited in the oxide surface identified by \( \theta = 44^\circ, 51^\circ, \) and 76° [17], [18]. The crystallinity of ZrO\(_2\) should be stronger than Al\(_2\)O\(_3\) and SiO\(_2\) because the sharp peak at \( \theta = 24.51^\circ, 28.30^\circ, 31.55^\circ, 34.25^\circ \) (\( m \)-ZrO\(_2\)); 41.69°, 50.22°, 59.99° (\( t \)-ZrO\(_2\)) is detected [6], [19]. Large hump between \( \theta = 20–30^\circ \) identified as amorphous silica [12].

![Figure 1. XRD pattern of catalysts](image)

The morphology and distribution of active metals on catalyst surface was carried out using SEM-EDX Phenom. All the catalysts have irregular shape with the order of particle size from the smaller to larger is Ni/ZrO\(_2\) < Ni/Al\(_2\)O\(_3\) < Ni/SiO\(_2\). From the EDX analysis, the metal is distributed evenly in the oxide surface (Figure 2).

3.2. **Product analysis**

3.2.1. **Effects of the support for HDO reaction.** The conversion of the product analyzed by GC-MS analysis is depicted in Figure 3a. The result showed that the conversion of phenol using Ni/SiO\(_2\) catalyst (52.2%) is higher compared with Ni/ZrO\(_2\) (17.64%) at 200°C. It is explained that SiO\(_2\) which have larger surface area and pore size influence the interaction of phenol with the catalyst. The higher surface area
the better chemisorption occurred between reactant and catalyst and it is increasing the product conversion [6].

![Figure 2. SEM analysis (magnification 15.000X): (a) Ni/SiO₂, (b) Ni/ZrO₂, dan (c) Ni/Al₂O₃](image1)

The selective product from HDO of phenol using Ni/SiO₂ is 2-methyl-1-butanol (52%) (Figure 3b). It is speculated that product was initiated from hydrogenation of phenol into cyclohexanone and cyclohexanol then followed by ring-opening and rearrangement reaction (Scheme 1). This phenomenon is explained by Bronsted-Lowry acid site of SiO₂ which play a role as proton donor and has the ability to crack the double bonds in hydrogenation reaction [4]. By that reason, the hydrogenation reaction is promoted by the Ni metal and SiO₂ support. In similar reaction using Ni/ZrO₂, the selective formation of cyclohexanone (35.35%) is observed (Figure 3b). The weak acidity of ZrO₂ increase the activity of oxy- compounds to attach on the support surface. The acidity of the support is related to hydrogenation, isomerization, dehydration, and cracking of bonds [20].

![Figure 3. (a) Product conversion of HDO phenol, (b) selectivity of the product](image2)

![Scheme 1. Plausible reaction mechanism](image3)
3.2.2. Effect of temperature on the HDO reaction. Apart from effect of the support, HDO reaction were also carried out by modifying the temperatures at 180° and 200°C using Ni/SiO₂. In Figure 4a, the product conversion at 180°C is 32.63%, whereas at 200°C is increasing into 52.20%. The higher reaction temperature, the collision between molecules is increased. Reaction at 180°C gave cyclohexanone (19.91%), but it didn't observed at 200°C. Reaction at higher temperature mainly gave alcoholic product (Figure 4b). Zhang, et al. (2013) reported that reaction temperature has an effect on the product conversion and distribution. Polymerization between molecules occurs at higher temperature. The selectivity of the products increased by the temperature. Thus, the temperature influence the product distribution [11].

![Figure 4a](image1.png) ![Figure 4b](image2.png)

**Figure 4.** (a) Conversion of HDO phenol by temperature, (b) selectivity of the product

3.2.3. Catalyst characterization using FT-IR. Based on the interpretation of functional groups on the two catalysts before and after use, it can be seen that there were no significant changes (Figure 5). The stretching of Ni-O on Ni/SiO₂ and Ni/ZrO₂ catalysts detected. It is shown that the Ni metal is bonded tightly and not leached after first reaction.

![Figure 5a](image3.png) ![Figure 5b](image4.png)

**Figure 5.** FT-IR spectra of (a) Ni/SiO₂ and (b) Ni/ZrO₂
4. Conclusion
The catalyst activity test for the HDO reaction of phenols resulted the highest product conversion using Ni/SiO\textsubscript{2} catalyst (52.2\%) compared with Ni/ZrO\textsubscript{2} (17.64\%) and Ni/Al\textsubscript{2}O\textsubscript{3} (13.18\%). The higher the reaction temperature influence the product selectivity and promote the hydrogenation products gave 2-methyl-1-butanol (53\%).

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