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Synthesis of Ni Catalyst Supported on SiO₂-ZrO₂ Binary Oxide for Hydrodeoxygenation of Phenol

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Abstract. Hydrodeoxygenation is a one-step reaction that involve the hydrogenation of unsaturated carbon followed with the deoxygenation of the carbon-oxygen bond. This reaction is effective for converting biomass-derived chemicals from bio-oils, fats, woods, and lignocellulosic materials into biofuels using metal-based oxide catalysts. A Ni based-metal oxide catalyst is reported for hydrodeoxygenation reaction of phenol. The catalyst was prepared by a wet-impregnation method using Ni(NO₃)₂·6H₂O dissolved in deionized water and mixed with the previously prepared SiO₂-ZrO₂ binary oxide as support. After calcination and reduction at 500 °C, Ni/SiO₂-ZrO₂ catalyst was obtained. The XRD results showed 2θ peaks for metallic Ni at 30°, 44° and 76°. Additional peaks were detected at 2θ = 35°, 50°, 51°, and 60° for ZrO₂ tetragonal phase. However, peaks were not detected for SiO₂ suggesting amorphous SiO₂-ZrO₂ composite formation. The XRF analysis of Ni loading was detected at 16.45%. The catalyst activity test for hydrodeoxygenation of phenol was performed using a batch reactor at 200 °C for 2 h and 8 h. The GC-MS analysis gave product conversion for 2 h at 16.84% with the selectivity formation of cyclohexanol and cyclohexanone at 48.10% and 45.78% yield, respectively. After a prolonged reaction time of 8 h, 100% selectivity for cyclohexanol was achieved. Product distribution showed that the catalyst is active for hydrogenation of benzene better than -OH or C=O deoxygenation. The results suggest Ni/SiO₂-ZrO₂ could be a potential catalyst for biofuel production via hydrogenation reaction.

Keywords: hydrogenation, deoxygenation, biofuel, Ni/SiO₂-ZrO₂

1. Introduction

Fossil fuels are indispensable in today's world, but their source is projected to deplete rapidly in years to come [1-2]. Fossil fuels increase greenhouse gas emissions such as CO₂ in the atmosphere [3-4]. The impacts of greenhouse gas emissions are warmer atmospheric temperature and climate change. As a result, there is a need for an alternative energy source that is cheap, green and sustainable of which biofuels presence a potential option [5-6]. Biofuels have several advantages compared to conventional fossil fuels such as low carbon emissions and biodegradability. Numerous sources of biofuels including carbohydrates for bioethanol, microalgae, lipids, fats, and oils for biodiesel have been investigated [7-8]. For example, EU targets to replace 20% of conventional fuels with renewable fuel in the transport sector by 2020 [9].

Lignin biomass can be depolymerized into phenol and phenol derivatives such as guaiacol, catechol, and cresol [10]. These bio-based compounds are potential feedstocks for hydrodeoxygenation into biofuel. Cyclohexanone, cyclohexanol, methylcyclohexane, and cyclohexane have been reported as major products obtained from hydrodeoxygenation of lignin-based biomass compounds [11]. The



advantages of biofuels obtained from lignin-based feedstock hydrodeoxygenation are saturated benzene ring formation and complete removal of oxygen content.

Pd and Pt metals supported on SiO₂, ZrO₂, Al₂O₃, carbides, and zeolites are promising catalysts for hydrodeoxygenation of bio-based chemicals to biofuels [12]. Pt/Al₂O₃ catalyst has been used to deoxygenate model compound methyl-octanoate and methyl-stearate into hydrocarbons suitable for biofuels [13]. Pd/zeolite prepared by microwave polyol method has also been reported to show good catalytic activity for hydrodeoxygenation of oleic acid into biofuel [14]. However, the drawbacks of Pt and Pd catalysts are the high cost of catalyst production. Thus, there is a need for the synthesis of a cheap catalyst suitable for bio-based chemical hydrodeoxygenation to biofuel. In this, Ni-based catalysts supported on binary oxides present a viable option. Ni has high catalytic activity that makes it a suitable metal choice for hydrodeoxygenation reaction [15]. Ni metal can be obtained from inexpensive and widely available chemicals such as Ni(NO₃)₂·6H₂O or Ni(NO₃)₂ and impregnated via wet-impregnation method on Al₂O₃-ZrO₂, SiO₂-ZrO₂, and SiO₂-Al₂O₃ support. Binary oxides of Al₂O₃-ZrO₂, SiO₂-ZrO₂ and SiO₂-Al₂O₃ have been used with Ni, Co, Mo active metals and tested for biomass-derived feedstock hydrodeoxygenation to biofuels [16]. These oxides have shown good catalytic activity for support material due to moderate acidic property suitable for hydrodeoxygenation.

In this study, we report on the synthesis of a low-cost Ni catalyst from Ni(NO₃)₂·6H₂O prepared by a wet-impregnation method. Ni was impregnated on a previously prepared SiO₂-ZrO₂ binary oxide support and tested for phenol hydrodeoxygenation reaction. Catalyst activity test was conducted using phenol as a model compound and heated in autoclave batch reactor suspended in oil-bath for 2 h and 8 h respectively at 200 °C, pressurized under 0.3 MPa H₂ gas [17-18]

2. Experimental

2.1. Materials

The materials used in this research are ZrOCl₂·8H₂O, Ni(NO₃)₂·6H₂O, anhydrous Na₂SO₄, phenol, and silica gel as a precursor for SiO₂ all of which purchased from Merck KGaA and used as obtained. Deionized water (DI), dichloromethane (CH₂Cl₂), ammonium solution (NH₄OH) were purchased from a vendor in Malang City, Indonesia. Silver nitrate (AgNO₃) solution was obtained from the analytical chemistry laboratory, University of Brawijaya. Hydrogen (H₂ > 99.95% purity) and Nitrogen (N₂) gas was supplied by TIRAGAS, Malang City, Indonesia.

2.2. Methods

2.2.1. Catalyst preparation. The catalyst preparation followed a previous method reported by Adam, JPACR (2016); Ulfa, IOP (2017) with some modifications. SiO₂-ZrO₂ support was prepared by mixing 13 g of ZrOCl₂·8H₂O with 25 ml deionized water. Ammonium solution was added dropwise in the mixture and constantly stirred until pH 8 with the formation of Zr(OH)₄ precipitate. The precipitate was filtered and washed twice with 20 ml of deionized water. The precipitate was then dried at a constant weight and uniformly mixed with 5 g of silica gel. The mixture was aged for 10 h at a constant temperature of 75 °C with continuous magnetic stirring. After aging, the solid mixture was filtered and then washed with deionized water. The washed filtrate was tested for Cl⁻ ions with few drops of 0.05 M AgNO₃. The obtained solid mixture was dried at a constant weight and then calcined at 500 °C for 5 h under a continuous flow of nitrogen gas (N₂) to form SiO₂-ZrO₂ binary oxide.

A 7.4 g Ni(NO₃)₂·6H₂O was mixed with 10 g of the prepared SiO₂-ZrO₂ in deionized water following a wet-impregnation method. The solution was agitated overnight and then evaporated to dryness. The obtained solid was calcined at 500 °C for 5 h with the continuous flow of N₂ gas to form NiO/SiO₂-ZrO₂. The NiO/SiO₂-ZrO₂ powder was reduced under H₂ gas flow for 5 h at 500 °C to obtain 15%Ni/SiO₂-ZrO₂ catalyst.

2.2.2. Catalyst characterization. The catalyst crystal structure was studied with an X-Ray Diffractometer (XRD) XPER-PRO instrument operated at 40 kV, 35 mA and Cu-K α radiation of $\lambda=1.54060$. The diffraction range was between 10° to 90°. Ni loading on the SiO₂-ZrO₂ binary oxide support was determined by an X-Ray Fluorescence (XRF) Pan Analytical Type Minipal 4 instrument.

2.2.3. Catalytic hydrodeoxygenation of phenol. Hydrodeoxygenation reaction was carried out in a stainless autoclave batch reactor following methods previously reported by Ulfa, AIP (2018). Before each reaction, 0.1 g of the catalyst was loaded in the reactor and activated for 1 h at 200 °C and 0.3 MPa pure H₂ gas pressure. The reactor was completely cooled down and hydrodeoxygenation followed by inserting 1.0 g phenol and 20 ml deionized water (solvent) in the reactor with the activated catalyst. Hydrodeoxygenation reaction was conducted at 200 °C for 2 h and 8 h under 0.3 MPa H₂ gas. The obtained liquid product was filtered to separate from the catalyst and then extracted with 25 ml of dichloromethane. After standing and layering in a separating funnel, the bottom layer was collected and mixed with small amounts of anhydrous Na₂SO₄. The mixture was filtered to remove the Na₂SO₄. Finally, the obtained liquid was evaporated to separate the product from the dichloromethane solvent.

2.2.4. Product analysis. The qualitative and quantitative composition of the HDO phenol liquid products were obtained from a GC-MS instrument injected on a Shimadzu (GCMS QP2010 Ultra) operated under a column oven temperature between 40 °C – 250 °C with a splitless injection mode, total flow rate of 30 mL/min and an FID detector (FID) between 50 – 600 m/z.

3. Results and discussion

3.1. Characterization of 15%Ni/SiO₂-ZrO₂ catalyst

The XRD peaks 2 θ at 30°, 44° and 76° in Figure 1. show nickel metal in the face-centered cubic form with the lattice parameter of $a=3.5231\text{Å}$. The peaks at 2 $\theta=35^\circ, 50^\circ, 51^\circ,$ and 60° show the tetragonal crystallite phase of ZrO₂ which is in line with a report by Zhang et al. 2013. Furthermore, peaks for SiO₂ were not detected suggesting SiO₂ composite formation with ZrO₂ [19]. Catalyst calcination at 500 °C for 5 h under continuous H₂ gas flow successfully reduced NiO to Ni in the catalyst since NiO peaks are not observed. Table 1. shows X-Ray Fluorescence result for actual Ni metal loading on SiO₂-ZrO₂ support. Ni loading was detected at 16.45% slightly higher than the expected 15%. It means that all the Ni deposited well in the support surface. It can be confirmed by SEM analysis shown in Figure 2, that the catalyst surface consists of tiny particles with irregular forms subjected to Ni metal deposition.

Table 1. Physical properties of 15%Ni/SiO₂-ZrO₂ catalyst

Catalyst	%Ni loading ^a	Catalyst crystallite size (nm) ^b	
15%Ni/SiO ₂ -ZrO ₂	16.45	Ni	34.54
		ZrO ₂	22.04
		SiO ₂	-----

^a According to X-Ray Fluorescence result

^b According to Scherrer's Equation from XRD data

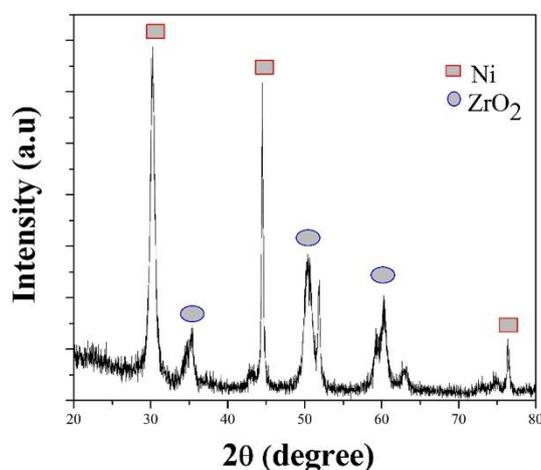


Figure 1. XRD spectra of 15%Ni/SiO₂-ZrO₂ catalyst

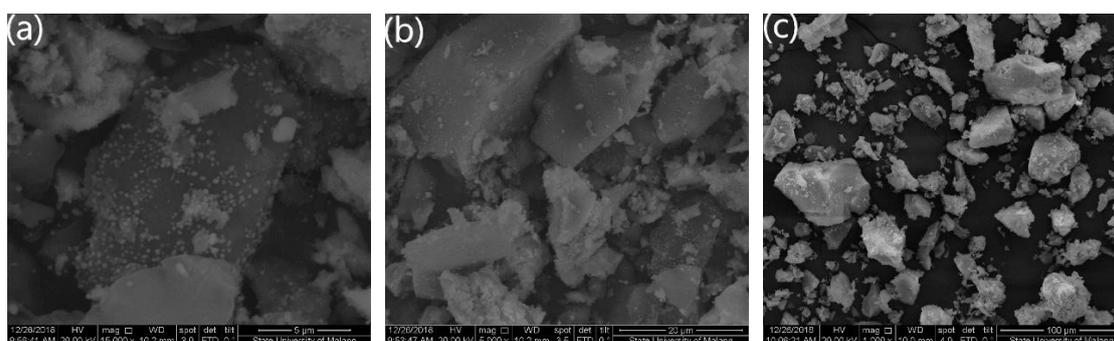


Figure 2. SEM image of 15%Ni/SiO₂-ZrO₂ catalyst

3.2. Hydrodeoxygenation reaction of phenol

Figure 4a. shows phenol conversion achieved for 2 h and 8 h respectively at 200 °C. A total saturated compound yield of 94% is achieved within 2 h with 45.78% and 48.10% selectivity for cyclohexanone (**2**) and cyclohexanol (**3**), respectively. Furthermore, after a prolonged reaction time of 8 h, the sole form of cyclohexanol (**3**) was achieved but a decrease in phenol conversion is observed (Figure 4b). At a reaction time of 8 h, it is suggested that cyclohexanone served as an intermediate and was converted to cyclohexanol with 100% selectivity. As reported by [20], product distribution in Figure 3. shows Ni/SiO₂-ZrO₂ better catalytic performance for hydrogenation compared to deoxygenation. This can be understood since hydrogenation occurs at a temperature below 260 °C and deoxygenation above 300 °C [6]. Phenol conversion of 16.85% at 2 h and 2.25% at 8 h shows decrease Ni/SiO₂-ZrO₂ catalytic performance after a prolonged reaction time. This can be attributed to catalyst deactivation over time [21]. The results show reaction time significantly influenced the phenol conversion rate and selectivity for cyclohexanone and cyclohexanol respectively, which is in accordance with a report by Zhang et al. [21].

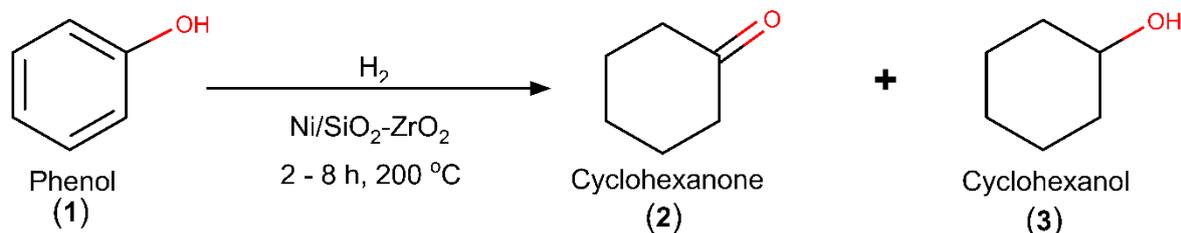


Figure 3. Schematic for phenol HDO

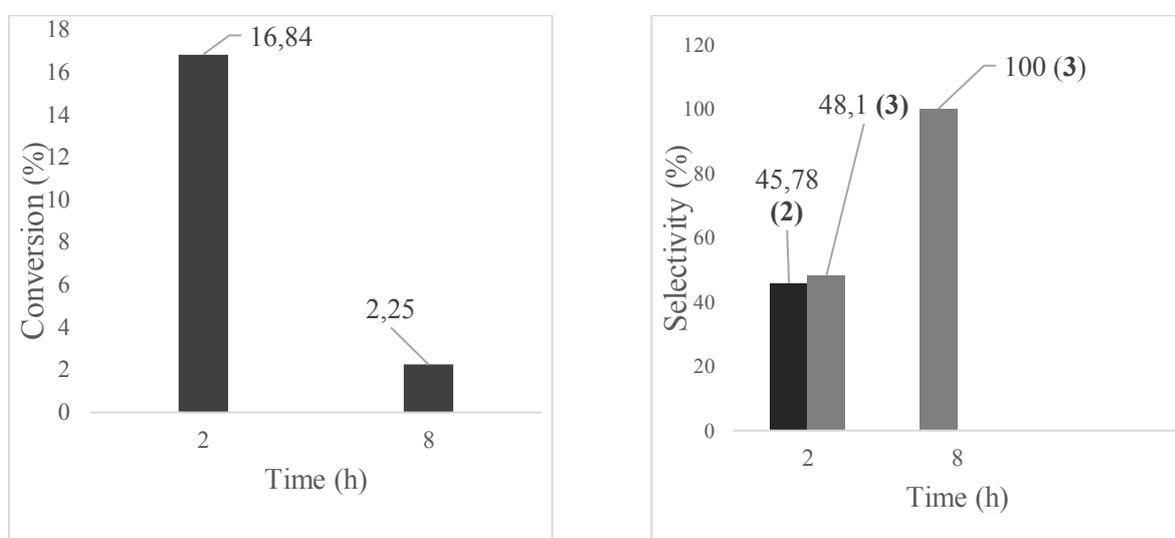


Figure 4. (a) Product conversion and (b) product selectivity of HDO phenol

4. Conclusion

Binary oxide support was synthesized and impregnated with Ni obtained from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to give $\text{Ni}/\text{SiO}_2\text{-ZrO}_2$ catalyst. The catalyst activity test for hydrodeoxygenation of phenol was conducted at $200 \text{ }^\circ\text{C}$ for 2 h and 8 h respectively. The catalyst showed better activity at 2 h with 16.45% phenol conversion but the selectivity increased with prolonged reaction time to 8 h leading to the sole formation of cyclohexanol. The catalyst showed better activity for hydrogenation of aromatic compound compared to -OH or C=O deoxygenation which could be attributed to catalyst deactivation with time.

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