Hydrodeoxygenation of furfural-acetone condensation adduct over alumina-zirconia and silica-zirconia supported nickel catalysts

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Abstract. Hydrodeoxygenation (HDO) reaction of furfural-acetone condensation adduct (FAA) using Ni-supported catalyst were investigated. The used of alumina-zirconia and silica-zirconia served as the support of Ni catalyst. The physicochemical properties of the catalysts were evaluated by X-Ray Diffraction (XRD) and N2-physisorption. The catalyst testing using 10% Ni/Al2O3-ZrO2 and 10% Ni/SiO2-ZrO2 for HDO reaction of FAA for 4 h in the presence of water using batch reactor at 200°C showed the network reaction containing partial and total hydrogenation, ring opening and hydrocracking into furanyl-alkane derivatives and hydrocarbon derivatives, such as, 4-(furan-2-yl)butan-2-one (4); 4-(4,5-dihydrofuran-2-yl)butan-2-one (5); 4- (tetrahydrofuran-2-yl)butan-2-one (6); (E)-1,5-di(furan-2-yl)pent-1-en-3-one (7); 1,5-di(furan-2-yl)pentan-3-one (8); 1-(furan-2-yl)-5-(tetrahydrofuran-2-yl)pentan-3-one (9); non-1-en-3-one (10); and decane (11), with the total yield in 55-81%. By increasing the Ni loading into 20%, the increasing conversion of HDO product is observed. The used of Al2O3-ZrO2 and SiO2-ZrO2 as support catalysts direct product selectivity. The Ni/SiO2-ZrO2 promote the formation of 1,5-di(furan-2-yl)pentan-3-one (8), whereas Ni/Al2O3-ZrO2 gave non-1-en-3-one (10) as major compound.

1. Introduction
The exploration of alternative energy sources has been a great concern due to the increasing energy demand and gradual depletion of fossil fuels. Many researchers give a big attention towards the production of clean liquid fuel to reduce CO and/or CO2 emission in an environment. The promising precursor for liquid fuels is biomass since it is contained with a carbohydrate such as, hemicellulose, cellulose, and lignin which can directly transform into hydrocarbon derivatives. The catalytic sequence for the production of liquid fuels from biomass is proposed by dehydration of biomass, condensation reaction and hydrogenation and/or deoxygenation reaction [1-4].

The dehydration of biomass gave furfural, the five-membered ring heterocyclic compounds with one carbon replaced by oxygen. The direct conversion of furfural is failed to gives long chain hydrocarbon derivatives except for the formation of gaseous [5]. In order to get the longer carbon chain, the condensation of furfural with ketone/aldehyde is subjected to give monomer/dimer of furanyl derivatives with carbon chain varied from C8 to C15 [6, 7]. The condensation products contain conjugated ketone C=O, aliphatic C=C, and cyclic C=C furan bond which can be converted into liquid hydrocarbons through catalytic hydrodeoxygenation reaction (HDO) reaction [8-10]. Based on this
background, a synthetic strategy to produce diesel-like hydrocarbon via catalytic HDO reaction has been intensively examined.

The catalyst screening showed that noble metal catalysts, such as Pd and Pt are the most promising selective metal catalyst for HDO reaction [11]. However, the economic calculation showed the inefficiency used of the noble metal-based catalyst. In addition, the absorption of low-boiling point compounds on the active site of Pd catalyst supposed to promote the deactivation of catalyst [10]. Meanwhile, nickel as a non-noble metal catalyst has the promising properties for hydrodeoxygenation by the selectivity over C=O bond and low-cost production [12].

The use of support is also important to increase the activity of the catalyst. Mixed oxides support catalyst seems to be a more promising alternative due to their wide surface area, a combination of their acidic and basic sites properties, and have moderate hydrothermal stability. The mixed oxides with different types of acidic sites and strengths are interesting matrices from a catalytic point of view [13]. Herein, we reported HDO reaction of the furfural-acetone adduct (FAA) using Ni/Al2O3-ZrO2 and Ni/SiO2-ZrO2 catalysts.

2. Experimental

2.1. Materials

Furfural was purchased from Sigma-Aldrich (Singapore) in >98% purity and used without redistillation. The chemicals Ni(NO3)2.6H2O, ZrOCl2.8H2O, Al2O3, SiO2, and dichloromethane were supplied by Merck Germany. Acetone was obtained from Smart Lab Indonesia. The gas, N2, and H2 are obtained from PT. Tira Austenite Indonesia.

2.2. Instrumentations

The crystallinity of catalysts was analysed by X-ray diffraction (XRD) Pan Analytical Expert MPD using Cu-Kα at λ=1.5406 Å at 40 kV and 30 mA in 2θ=20–80° (scan rate at 1°/min). The physical properties of catalysts were analysed by Quantachrome NOVA1200 using N2 at 77 K and degassed at 300°C to determine the surface area and pore volume. The hydrodeoxygenation product was determined using Gas Chromatography-Mass Spectrometer (GC-MS) Agilent 7890A using HP Innowax column (30 m with ID=0.25 mm) with injected column temperature at 300°C and increasing rate at 5°C.

2.3. Methods

2.3.1. Preparation of Ni/Al2O3-ZrO2 (NiAZ) and Ni/SiO2-ZrO2 (NiSZ) catalyst. Ni/Al2O3-ZrO2 and Ni/SiO2-ZrO2 were synthesized according to the published method by Zhang et al. [14] with some modification on the weight of precursor. The ZrO2 support was prepared by precipitation of ZrOCl2.8H2O using NH4OH to form Zr(OH)3, then calcination at 500°C gave ZrO2. The ratio of Al2O3/ZrO2 in the support was 50:50 (wt/wt). Amount of Al2O3 was added with deionized water then stirred with ZrO2. Continue the stirring until 12 h at 75°C, filtered and dried for a night at 120°C. The following calcination at 500°C for 5 h under N2 gas gave Al2O3-ZrO2 (AZ). The SiO2-ZrO2 was prepared by the same method by replacing Al2O3 with SiO2, then designated as SZ support oxide.

The impregnation of nickel (Ni) in the AZ and SZ support was theoretically calculated for 10% and 20% Ni loading by the method reported in previous [15]. The catalyst abbreviated as 10NiAZ, 20NiAZ, 10NiSZ and 20NiSZ. The precursor for nickel is Ni(NO3)2.6H2O, dissolved in deionized water, added with AZ or SZ support and stirred for 24 h at ambient. After finished, the solvent was removed under in vacuum and dried in the oven at 120°C for a night. The metal catalysts were obtained after calcination under N2 at 500°C for 5 h and reduction using H2 at 500°C for 5 h.

2.3.2. Catalytic test. Prior to HDO reaction, furfural-acetone adduct (FAA) for the catalytic test was prepared based on Claisen–Schmidt condensation reaction between furfural and acetone (1:1 mol ratio) according to Ulfa et al. [15]. The HDO reaction was carried out in a batch reactor which connected with a gaslever for N2 and H2 gas insertion during the reaction. Before the reaction, the catalyst was activated
in-situ at 200°C for 1 h under H₂ pressure. For each run, 0.02 g of catalyst, 1 g FAA, and 30 mL solvent (deionized water) were put into the reactor. The reactor was then filled with H₂ gas to 12 bar. The HDO reaction was performed at 200°C for 4 h under stirring condition. The liquid product was filtered and extracted using dichloromethane. The product was obtained after removing the excess solvent under vacuum.

3. Result and Discussion

3.1. Characterization of catalysts
The X-ray Diffraction profile of the NiAZ and NiSZ are depicted in figure 1. Diffraction of Ni metal is appeared at 2θ=44.44° (111), 51.80° (200), 76.28° (220) (JCPDS 96-210-2279). The peaks of NiO at 2θ=37°, 43°, and 64° were not observed, which mean that the reduction at 500°C completely reduced Ni²⁺ into Ni⁰. The different Ni loading has a correlated with the intensity of the diffraction. The Ni intensity increases with the increase in the amount of nickel added.

The physical properties of the catalysts are tabulated in table 1. Surface areas between 17.865 to 69.029 m²/g were observed for NiAZ and NiSZ. The isotherm of NiAZ and NiSZ are shown in figure 2 and presented type IV isotherm which is typical of capillary condensation taking place in mesoporous with hysteresis loop at P/Po=0.4-0.8. It exhibits a type H3 hysteresis loop, often formed by aggregation process (loose assemblages) of plate-like particles forming slit-like pores [16]. The NiAZ and NiSZ catalysts exhibit mesopores with pore diameter between 3.832 nm and 7.763 nm.

Table 1. N₂ physisorption of the catalysts.

| Catalyst | S_BET (m²/g) | Pore Volume (cc/g) | Pore Diameter (nm) |
|----------|--------------|--------------------|--------------------|
| 10NiAZ   | 48.616       | 0.199              | 7.763              |
| 20NiAZ   | 65.314       | 0.250              | 6.580              |
| 10NiSZ   | 69.029       | 0.385              | 6.583              |
| 20NiSZ   | 17.865       | 0.181              | 3.832              |
The $S_{\text{BET}}$ of 20NiAZ was found to be larger (65.314 m$^2$/g) compared with 10NiAZ (48.616 m$^2$/g), whereas $S_{\text{BET}}$ of 20NiSZ was smaller (17.865 m$^2$/g) than 10NiSZ (69.029 m$^2$/g). The increasing of nickel loading on SZ via impregnation induced a decreasing of $S_{\text{BET}}$ caused by sintering effect. On the other hand, 20NiAZ showed the higher $S_{\text{BET}}$ and pore volume compared with 10NiAZ. This might be due to unstable aggregation between nickel [13]. Pore size distribution of NiAZ and NiSZ catalysts displayed in figure 3. In accordance with the previous analysis, 10NiAZ, 20NiAZ and 10NiSZ have a large pore size 6-7 nm with convergent distribution from 3-15 nm. Meanwhile, the average pore size of 20NiSZ was smaller (3.832 nm) which might suggest shrinkage in pores during calcination and reduction process [17]. This also explained that 20NiSZ catalyst has a small pore diameter which direct to microporous properties.

![Figure 2. Isotherm adsorption of catalyst](image1.png)

![Figure 3. Pore sizes distribution of catalyst](image2.png)

### 3.2. Catalytic test for HDO reaction

The starting material FAA (2 and 3) was obtained from the Claisen–Schmidt condensation reaction between furfural and acetone (1:1 mol ratio) as shown in scheme 1. The ratio of 2 and 3 on FAA is observed in 18:7 mol ratio by batch reaction [13]. The FAA has a unique conjugation system between furan and an exocyclic alkene. Therefore, the reduction of double bond, ring opening and elimination of the oxygen atom are needed to form diesel-like hydrocarbon.
The mixture of 2 and 3 (FAA) was subjected for direct HDO reaction using autoclave batch reactor, stirred and heated for 4 h at 200°C. Analysis GCMS of the product showed the formation of furanyl-alkane derivatives (4-9), oxy-compound (10) and hydrocarbon (11), depicted in scheme 2. The product obtained is 4-(furan-2-yl)butan-2-one (4); 4-(4,5-dihydrofuran-2-yl)butan-2-one (5); 4-(tetrahydrofuran-2-yl)butan-2-one (6); (E)-1,5-di(furan-2-yl)pent-1-en-3-one (7); 1,5-di(furan-2-yl)pentan-3-one (8); 1-(furan-2-yl)-5-(tetrahydrofuran-2-yl)pentan-3-one (9); non-1-en-3-one (10); decane (11); and others. Parallel reaction suggested by the length of reaction time. The hydrocracking, hydrogenation, ring opening, and deoxygenation reaction was occurred giving the varied products.

According to the proposed reaction pathway for HDO reaction of FAA (scheme 3), the furanyl-alkane derivative products (4-9) produce from partial and total hydrogenation of FAA (2-3). It was proposed that compound 10 comes from partial hydrogenation followed by hydrocracking, ring opening and partial deoxygenation reaction of 3. In this reaction, the hydrocarbon derivative product i.e. decane (11) is observed. Decane may be obtained from HDO reaction followed by hydrocracking of 3. Hydrogenation products were observed in the consecutive process, suggesting that the ring-opening and the subsequent hydrodeoxygenation are the rates determining steps [18].

**Scheme 1.** Synthesis of FAA by Claisen–Schmidt condensation.

**Scheme 2.** HDO reaction of FAA.
Scheme 3. The proposed product formation from HDO reaction of FAA.

3.2.1. Effect of catalyst support (AZ and SZ). The yield and selectivity of the HDO product are summarized in Table 2. The data showed that the support catalyst Al$_2$O$_3$-ZrO$_2$ (AZ) and SiO$_2$-ZrO$_2$ (SZ) affect the product selectivity. The NiAZ promote the formation of non-1-en-3-one (10), whereas NiSZ gave 1,5-di(furan-2-yl) pentan-3-one (8) as a major compound. These results support our previous report that alumina-zirconia (AZ) support leads to the formation of alkene derivatives [15, 19]. On the other hand, silica-zirconia (SZ) seems more selective for hydrogenation reaction.

Based on the physical characterization of catalyst (Table 1), 20NiSZ catalyst showed unfavourable properties with small surface area and pore diameter. Interestingly, the formation of decane is detected only for the reaction using 20NiSZ. The following reaction such as hydrocracking and deoxygenation reaction might be occurred due to the higher pressure of H$_2$ gas (12 bar).

| Entry | Catalyst | Conversion (%) | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|-------|----------|---------------|---|---|---|---|---|---|----|----|
| 1     | 10NiAZ   | 78.16         | 5.17 | 0.55 | 2.89 | 20.06 | 20.52 | 3.82 | 7.12 | -   |
| 2     | 10NiSZ   | 98.85         | 7.96 | 3.00 | 6.17 | -   | 17.76 | 9.94 | 1.65 | -   |
| 3     | 20NiAZ   | 100           | 7.55 | 5.18 | 10.58 | - | - | - | 37.20 | - |
| 4     | 20NiSZ   | 98.65         | 26.90 | - | 3.69 | -   | 43.08 | 5.13 | - | 1.07 |

3.2.2. Effect of nickel loading. The HDO reaction using NiAZ and NiSZ gave various furanyl-alkane derivatives, oxy-compounds, and hydrocarbon as products with various selectivity as shown by Fig. 4. The used of 20% nickel loading lead higher yield of products compared with 10% nickel loading catalyst. It indicated that the higher Ni loading showed better performance and lead the product selectivity.
4. Conclusion
HDO reaction of FFA using NiAZ and NiSZ catalysts was successfully conducted in autoclave batch reactor at 200°C. Partial and total hydrogenation (HDG), ring opening and hydrocracking (HDC) into furanyl-alkane derivatives are observed. By increasing the Ni loading into 20%, the conversion of HDO product becomes higher. Then, the influence of Al₂O₃-ZrO₂ (AZ) and SiO₂-ZrO₂ (SZ) also derived the product selectivity. The NiAZ promote the formation of non-1-en-3-one (10), whereas NiSZ gave 1,5-di(furan-2-yl)pentan-3-one (8) as a major compound. Alumina-zirconia (AZ) support leads to the formation of alkene derivatives.

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