Influence of Solvent on Liquid Phase Hydrodeoxygenation of Furfural-Acetone Condensation Adduct using Ni/Al₂O₃-ZrO₂ Catalysts

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Abstract. Influence of water and acidic protic solvent on hydrodeoxygenation (HDO) of the furfural-acetone adduct (FAA) over Ni/Al₂O₃-ZrO₂ (NiAZ) catalysts were investigated. The HDO of FAA was carried out in a batch reactor at 150°C for 8 hours. The NiAZ catalysts were home-made catalysts which were prepared by wet impregnation method with 10 and 20% nickel loading. The HDO reaction of FAA using 10NiAZ in water at 150°C gave alkane and oxygenated hydrocarbons at 31.41% with selectivity over tridecane (C13) in 6.67%. On the other hand, a reaction using acetic acid:water (1:19 v/v) in similar reaction condition gave only oxygenated compounds and hydrocracking product (C8-C10). The formation of tridecane (C13) was proposed by hydrogenation of C=O and C=C followed by decarboxylation without hydrocracking process. The presence of water facilitated decarboxylation mechanism by stabilized dehydrogenated derivatives of FAA.

1. Introduction
The limitation used in fossil fuels have led to the research of renewable material for supplying the energy demand. Different with other energy sources such as, solar, wind and geothermal; biomass is the most promising alternative resources since it can provide the liquid fuels directly by a sequence of chemical reactions [1, 2]. Upgrading of lignocellulosic biomass into diesel fraction have been intensively studied by catalytic hydrogenation-deoxygenation of furfural-acetone condensation adduct as chemical precursor [3].

Furfural is the bio-based-chemical which can be obtained from acid hydrolysis and dehydration of pentose. The condensation of furfural with ketone/aldehyde gives monomer/dimer of furanyl derivatives with carbon chain varied from C8-C15. From this reaction, the complex molecules with ketonic C=O, aliphatic C=O, and furanic C=C bond should be converted into valuable liquid hydrocarbons. Thus, the catalytic hydrogenation followed by deoxygenation is proposed in one-step reaction using Ni/Al₂O₃-ZrO₂ catalysts with the variation of solvent and nickel loading.

The selection of catalyst plays an important role. Among different metal loading, the noble metal such as platinum (Pt) and palladium (Pd) have been revealed as suitable metals for hydrogenation reaction [4, 5]. However, the high prices of these noble metal failed to impress the industrial scope. As a consequence, the development of non-noble metal catalyst seems more rational. The used of support also important to increase the activity of catalyst. The α-Al₂O₃ was previously used as a hydrogenating agent of oxygenated compounds, but severe coke formation was observed [6]. Moreover, it is not
suitable for the reaction in the presence of water because of partially transform into boehmite [7]. To overcome these problems, the addition of ZrO$_2$ was reported increasing the activity of the catalyst by activated oxy-compounds and decreasing carbon deposition on the surface [8]. The crystal structure of ZrO$_2$ is relatively stable in water and organic solvent. Therefore, the reaction under liquid phase is favorable.

Herein, we reported liquid phase hydrodeoxygenation (HDO) of furfural-acetone adduct (FAA) using Ni/Al$_2$O$_3$-ZrO$_2$ in the presence of water and acidic solvent in one-pot reaction. The linear alkane as n-tridecane was identified as the selective product under water solvent.

2. Experimental

2.1. Materials

Furfural as starting material for condensation reaction was obtained from Sigma-Aldrich with >98% purity and used as received. Analytical grade of Ni(NO$_3$)$_2$.6H$_2$O, ZrOCl$_2$.8H$_2$O, γ-Al$_2$O$_3$, methanol, and dichloromethane were bought from Merck Germany. Acetone was purchased from Smart Lab Tbk. Technical grade of MgO and CaO was obtained from the local vendor and calcined at 650°C for 2 hours under N$_2$ flowing before used. N$_2$ gas in >99.99% purity for calcination and condensation reaction, Ultra-High-Purity (UHP) H$_2$ gas for hydrodeoxygenation (HDO) reaction was supplied by PT. Samator, Tangerang, Indonesia.

2.2. Methods

2.2.1. Preparation of Ni/Al$_2$O$_3$-ZrO$_2$ (10NiAZ and 20NiAZ)

Ni/Al$_2$O$_3$-ZrO$_2$ was prepared according to Zhang et al methods [9] with modification on the synthesis of the Al$_2$O$_3$-ZrO$_2$ support. The ratio of Al$_2$O$_3$/ZrO$_2$ in the support was 50:50 (wt/wt). Based on the stochiometric calculation, to prepared 7 g of Al$_2$O$_3$-ZrO$_2$, 3.5 g of γ-Al$_2$O$_3$ was mixed with Zr(OH)$_4$ slurry which obtained from precipitation of 9.15 g ZrOCl.18H$_2$O dissolved in deionized water with the dropwise addition of ammonium solution until pH equal to 8. Additional stirring the slurry for 12 h at 75°C, then filtered, dried for a night and calcined at 550°C for 5 h under N$_2$, by which the complex oxide of Al$_2$O$_3$-ZrO$_2$ was prepared. The sample was then designated as AZ support oxide.

Impregnation of nickel in the AZ was calculated for 10 and 20%, then each catalyst abbreviated as, 10NiAZ and 20NiAZ. The 10NiAZ was prepared by dissolved 2.96 g of Ni(NO$_3$)$_2$.6H$_2$O in water and added with 5.96 g of AZ composite. On the other hand, the 20NiAZ was made from 7.14 g of nickel nitrate stirred with 7.20 g of AZ for 24 h at room temperature. After filtration dried the precipitate at 120°C for a night then calcined and reduced at 500°C for each 5 h under N$_2$ and H$_2$ gas.

2.2.2. Characterization

The catalysts obtained from previous methods were analyzed by X-ray diffraction (XRD) Pan Analytical Expert MPD. The measurements using Cu-Kα radiation at λ=1.5406 Å with the voltage and current held at 40 kV and 30 mA (2θ = 20–80°) at a scan rate of 1°/min. SEM data was collected from portable Hitachi TM3000 connected with EDX Swift ED3000 analyzer. The actual nickel content was analyzed using XRF PANalytical Type Minipal 4. FTIR spectrum was recorded by Shimadzu 8400S using KBr pellet in the range of 400–4000 cm$^{-1}$. The surface area and pore volume of the 10NiAZ and 20NiAZ are determined from BET adsorption isotherms using nitrogen at 77 K were measured by Quantachrome NOVA1200 analyzer after degassed at 300°C. Conversion and selectivity of hydrodeoxygenation (HDO) products were analyzed using Gas Chromatography Mass Spectrometer (GCMS) injected on GCMS QP5050A Shimadzu with FID detector and ZB-1MS column (30 m with ID = 0.25 mm).
2.2.3. Condensation reaction
Furfural-acetone adduct (FAA) as starting material for HDO reaction was synthesized based on Claisen–Schmidt condensation reaction according to previous methods [10]. Activated MgO and CaO were used as base-catalyst and deionized water as a solvent. The used of water is the most effective solvent according to Faba et al [11]. The reaction performed in sealed tube connected with a gas lever to removed oxygen and purged with an inert gas (N₂) to prevent oxidation. The reaction using reflux under N₂ atmosphere were also performed for comparison.

2.2.4. Hydrodeoxygenation (HDO) reaction
The HDO reaction was carried out in liquid phase reaction using sealed tube connected with a gas lever for inserting H₂ gas prior to reaction. The procedure of HDO reaction followed the previous report of our group [12]. For each run, 0.02 g of catalyst, 0.5 g FAA, and 20 mL of deionized water were put into the reactor, closed the lid and purged the air. Before the reaction, the reactor was filled with H₂ to 40 psi, then heated at an ambient temperature (150–200°C) for 8 h. The effect solvent is evaluated by modifying the acidity of solvent. An acidic protic solvent, that is, AcOH:H₂O (1:19 v/v) were used for HDO using 10NiAZ and 20NiAZ catalysts in a similar method. Conversion and selectivity of the products were calculated based on GCMS analysis using the equation below.

3. Results and discussion
3.1. Characterization of 10NiAZ and 20NiAZ
Figure 1 showed the morphology of the catalysts measured by Scanning Electron Microscopic (SEM). The particle size of AZ is larger than 10NiAZ or 20NiAZ. It means that impregnation of nickel broke the support and resulted in an irregular shape with smaller particle size. Agglomeration with irregular shapes is easily formed when impregnation method is used for the preparation of catalysts [13].

![SEM micrograph of (a) AZ; (b) 10NiAZ; (c) 20NiAZ](image)

**Figure 1.** SEM micrograph of (a) AZ; (b) 10NiAZ; (c) 20NiAZ

The crystallinity of 10NiAZ and 20NiAZ were recorded by X-Ray Diffraction (XRD) Pan Analytical Expert MPD using Cu-Kα radiation at λ=1.5406 Å. The XRD profile of the catalyst showed in Figure 2. Compared with AZ, all catalysts gave the diffraction of metallic nickel appeared at 2θ = 44.44, 51.80, 76.28 (JCPDS 96-210-2279); no diffraction peaks of NiO at 2θ = 37°, 43°, and 64° were observed. We believed that NiO was completely reduced to Ni during the reduction at 500°C for 5 h. Furthermore, the diffraction of Al₂O₃ cannot be detected, except the sharp peak of ZrO₂ in cubic phase (JCPDS 96-900-9052). It can be inferred that nickel species strongly interact with AZ and increasing the crystallinity of the support as reported by Han, et al (2013) [14]. Different intensity of Ni diffraction correlated with nickel loading in both catalysts.
According to N2 isotherm (Figure 3), all the catalysts showed the type IV with hysteresis loop at P/Po = 0.6-1.0, typical of mesoporous catalyst. The BET surface \( (S_{\text{BET}}) \), pore volume and pore diameter of the catalysts showed in Table 1. The \( S_{\text{BET}} \) of AZ was found to be the larger (122.9 m\(^2\)/g) compared with 10NiAZ (48.6 m\(^2\)/g) and 20NiAZ (65.3 m\(^2\)/g). The introduction of nickel on AZ via impregnation induced a decreasing of \( S_{\text{BET}} \) caused by the sintering effect. On the other hand, 20NiAZ showed the higher \( S_{\text{BET}} \) and pore volume compared with 10NiAZ. This might be explained by unstable aggregation between nickel [13]. A higher surface area facilitated the reactant to access the active sites, decrease coke formation and improve catalytic activity [14].

**Table 1. Surface area of the catalysts**

| Catalyst | \( S_{\text{BET}} \) (m\(^2\)/g) | Pore Volume (cc/g) | Pore Diameter (nm) | Metal Loading (%)\(^a\) |
|----------|-------------------------------|-------------------|-------------------|------------------|
| AZ       | 122.945                       | 0.330             | 5.639             | -                |
| 10NiAZ   | 48.616                        | 0.199             | 7.763             | 10.2             |
| 20NiAZ   | 65.314                        | 0.250             | 6.580             | 17.58            |

\(^a\)According to X-Ray Fluorescence analysis
Figure 3. Isotherm adsorption of (a) AZ; (b) 10NiAZ; (c) 20NiAZ

3.2. Condensation reaction

The condensation reaction of furfural (1) and acetone was carried out using MgO and CaO solid bases catalyst. The yield of condensation products FAA after reaction for 6 h is depicted in Table 2. From the analysis of the products by GCMS, 2-(4-furyl)-3-buten-2-on (2, C8) and 1,5-bis-(furan-2-yl)-pentan-3-one (3, C13) was identified as main product with the most stable conformation, trans-C8 and trans-trans-C13 (Figure 4). The formation of cis-cis-C13 (3a) was observed as a minor product, similar to the finding of Faba et al (2012), the longer the condensation reaction, the most stable isomer were formed [11].

Among both methods, condensation with reflux using CaO exhibit a high yield product (33.98%) with a ratio of C8 and C13 is almost 1:1. In contrast, the reaction in a batch reactor gave 26.8% with selective formation of C8. This phenomenon was previously reported in our group and explained that vapor-phase condensation suppressed the formation of C13 by steric hindrance [15].

![Figure 4. Isomer identification of condensation products](image)

Table 2. The yield of FAA prepared by batch and reflux method

| Method        | Furfural (1) (mol) | Acetone (mol) | Catalyst | Yield of FAA (mol %)* |
|---------------|-------------------|---------------|----------|-----------------------|
| Batch reactor | 1                 | 2             | MgO      | 17.39                 |
| Re flux       | 1                 | 2             | CaO      | 18.06                 |

*quantitative analysis by GCMS
3.3. Catalytic Performance for Hydrodeoxygenation (HDO) reaction

The mixture of 2 and 3 (FAA) was subjected for direct aqueous HDO using the batch reactor, stirred and heated for 8 h at 150 and 200°C. Compound 2 and 3 have conjugated system, a furan ring, and carbonyl, then activity and selectivity of 10NiAZ and 20NiAZ can be evaluated for parallel reaction. The solvent for HDO was varied from neutral and acid to explore the effect of acidic solvent on the selectivity of the product.

Analysis of the product by GCMS showed the formation of alkane derivatives (4, 5, and 6) and oxygenated hydrocarbons (7, 8, and 9), depicted in Scheme 1. Parallel reaction suggested by the length of reaction time. The hydrocracking followed by hydrogenation, ring opening, and deoxygenation reaction was occurred giving the varied hydrocarbon derivatives [12].

![Scheme 1. HDO reaction of FAA](image)

3.3.1. Effect of solvent

Total carbon yield and selectivity of HDO product are summarized in Table 3. Entry 1 showed that reaction in neutral water at 150°C using 10NiAZ gave the total carbon in moderate yield with selectivity over oxygenated hydrocarbons (7–9). Interestingly, the formation of n-tridecane (6) as linear alkane is detected only in this reaction. The similar reaction condition (entry 2) using AcOH:H₂O as a solvent didn't give compound 6. The detected products were partial HDO compounds, that is linear alkene 4–5. The formation of 6 proposed by hydrogenation of C=C, followed by ring opening of furan and deoxygenation of C=O bond of trans-trans-C13 (2) (Scheme 2) [16]. Increasing reaction temperature until 200°C (entry 4) only gave hydrocracking product 8–9. Based on this result, HDO reaction is influenced by the kind of solvent rather than the reaction temperature. The higher the temperature promote the cracking of C–C bond afforded a molecule with lower weight or gas phase. Whereas, the used of neutral solvent endorsed decarbonylation/decarboxylation lead to higher molecular weight products or liquid phase [17]. However, the hydrogenation of simple molecules, such as phenol only gave hydrogenation product when using neutral solvent [18].

| Entry | Catalyst | T (°C) | Solvent          | Total carbon yield (mol %) | Selectivity (mol %) |
|-------|----------|--------|------------------|---------------------------|---------------------|
|       |          |        |                  |                           | 4      | 5    | 6    | 7     | 8    | 9    |
| 1     | 10NiAZ   | 150    | H₂O              | 37.49                     | -     | 2.67 | 6.67 | 2.59  | 17.98| 7.22 |
| 2     | 10NiAZ   | 150    | AcOH:H₂O         | 56.94                     | 22.4  | 10.06| -    | 2.68  | 8.08 | 13.72|
| 3     | 20NiAZ   | 150    | AcOH:H₂O         | 37.46                     | -     | 6.33 | -    | 2.84  | 12.14| 16.15|
| 4     | 10NiAZ   | 200    | AcOH:H₂O         | 22.14                     | -     | -    | -    | -     | 9.96 | 12.18|

*Reaction condition: FAA (0.5 g), H₂O (20 mL), catalyst (0.02 g), AcOH:H₂O (1:19 mL), 8 h reaction time, 40 psi H₂.*
Scheme 2. Proposed reaction pathways for one-step HDO reaction of FAA

3.3.2. Effect of nickel loading

The HDO reaction using 10NiAZ and 20NiAZ in an acidic solvent (entry 3–4, Table 3) gave with various alkane and oxy-compounds as products with various selectivity. The used of 10NiAZ lead higher yield of products compared with 20NiAZ. This is out of hypothesis that the higher Ni loading should be given the better performance. Based on the physical characterization of 10NiAZ and 20NiAZ, it is showed that the latter catalyst has smaller pore diameter (6.580 nm) compared with previous (7.763 nm) (Table 1). By the used of bulky FAA-C13 (3) as a precursor, the reaction limited only on the surface of catalyst and reaction in the pore of catalyst didn't occur [19].

4. Conclusion

One pot hydrodeoxygenation reaction of furfural-acetone adduct using Ni/Al₂O₃-ZrO₂ to liquid alkane was investigated in a liquid phase. The solvent has influenced the formation of alkane by suppressing decarbonylation/decarboxylation and hydrocracking process. The reaction in the presence of water using 10% nickel loading at 150°C gave n-tridecane (6.67%) selectively. Addition of acidic solvent promote the hydrocracking process, thus the oxygenated compound and alkene derivatives were observed.

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**Acknowledgments**

This work was supported financially by the PUPT research grant from Directorate General of Research, Technology and Higher Education number: 007/Add/SP2H/PL/DIT/LITABMAS/V/2015. We thanks to Prof. Didik Prasetyoko of ITS Surabaya for his guidance using SEM, XRD, and isotherms analysis and Ms. Indah Nur Pramesti for GCMS analysis.