Studies on Nickel-based Bimetallic Catalysts for the Hydrodeoxygenation of Stearic Acid

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Abstract. Fatty acids, which are contained in vegetable oils, can be converted into alkanes through the hydrodeoxygenation (HDO) reaction, as an alternative fuel. In this study, the HDO of stearic acid was carried out in the presence of nickel-based bimetallic catalysts supported on Silica-Alumina (SiAl) in an autoclave batch reactor using decane as a solvent. Various metals, including Fe, Cu, and Co, were added into Ni catalysts using conventional wet impregnation method. Among others, additional Cu on Ni/SiAl increased the performance of the catalyst for the reaction.

1. Introduction

Fatty acids, one of renewable raw materials for biomass-derived fuels, are attractive to be upgraded into transport fuels [1, 2]. Commonly, biomass-derived fuels needs to be upgraded due to their high oxygen content[3]. Oxygen has a significant effect on physical and chemical properties of the derived fuel, such as miscibility with fossil fuels or stability during storage[4, 5]. Compared to bio-oils produced from lignocellulose[6], these fatty acids have low oxygen contents. Fatty acids can be converted into high-yield hydrocarbon fuels using the hydrodeoxygenation (HDO) process[7-9]. HDO is a series of reactions, which convert molecular structure of carboxylic acids into straight chain hydrocarbons, by removing oxygen as water in the presence of catalysts and hydrogen[10, 11].

Several studies reported HDO of various types of fatty acids, such as dodecanoic acid[12], linoleic acid[13, 14], stearic acid[15-17], oleic acid[18-20]. Yoosuk et al. reported that NiMoS2 catalyst showed high catalytic HDO activities for oleic acid (100% conversion with 78.8% n-C18 selectivity) and palmitic acid (95.2% conversion with 78.5% n-C16 selectivity). The results also found that the high pressure favored HDO pathway, while high temperature strongly affected the decarboxylation and decarbonylation pathways[21]. Recently, nitrogen-doped carbon–alumina hybrid supported iron (Fe-N-C@Al2O3) was used as a catalyst for HDO of stearic acid producing n-octadecane and n-heptadecane with yields of 91.9% and 6.0%, respectively[11].

Nickel-based catalysts has been employed for many types of reactions, including HDO[22-24]. Kumar et al. reported that complete conversion of stearic acid during HDO was accomplished with more than 80% selectivity to n-heptadecane at reasonable reaction temperature of 290 °C after 4 h of reaction using 15 wt.% Ni/γ-Al2O3 catalyst[25]. On the other hand, nickel-based bimetallic catalysts have attracted interest many researchers for a long time. For example, non-noble and non-expensive metals,
such as iron (Fe)[26, 27], copper (Cu)[28, 29], and cobalt (Co)[30] are extensively used as second metal in nickel (Ni) catalysts due to their enhanced performances and stabilities. These second metals decrease reduction temperatures of Ni catalysts, and subsequently increase the performance of the catalysts for HDO reaction[31]. Guo et al. reported high catalytic performance of Ni-Cu/ZrO$_2$ on the HDO of algae bio-oils with HDO efficiency were equal to 82–90%[32].

In this work, we studied the effects of non-noble metals (including Fe, Cu, and Co) addition as second metals on on the catalytic activity of Silica-Alumina (SiAl)-supported Ni-based catalyst in the HDO of fatty acids. SiAl is generally applied as a catalyst support since it has good mechanical stability and thermal stability. Stearic acid were employed for the catalytic test reaction.

2. Experimental

2.1. Materials

All chemicals were used without further purification unless indicated otherwise. Silica-Alumina catalyst support, Grade 135, decane (99%), eugenol (99%) were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). Nickel (II) nitrate hexahydrate (≤100%), iron (II) nitrate nonahydrate (99%), copper (II) nitrate trihydrate (99.5%), cobalt (II) nitrate hexahydrate (99%), stearic acid (97%), N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA, 98%), and dichloromethane (99.9%) were obtained from Merck (Kenilworth, New Jersey, USA).

2.2. Catalyst Preparations

Supported Ni on Silica-Alumina (Ni/SiAl) and Cu on Silica-Alumina (Cu/SiAl) catalysts were prepared by wet impregnation. SiAl powder was impregnated with Ni(NO$_3$)$_2$.6H$_2$O as a precursor for Ni (Ni loading = 20 wt%), calcined in a flow of air at 500 °C for 2 h, and then reduced in a flow of H$_2$ at 500 °C for 4 h. Finally, the prepared catalysts were stored under ambient conditions[33]. Similarly, supported Ni-based bimetallic catalysts (Ni-M/SiAl) catalysts were prepared by the same method. SiAl powder was simultaneously impregnated with Ni(NO$_3$)$_2$.6H$_2$O as a precursor for Ni (Ni loading = 10 wt%) and Cu(NO$_3$)$_2$.3H$_2$O as a precursor for Cu (Cu loading = 10 wt%) or Co(NO$_3$)$_2$.6H$_2$O as a precursor for Co (Co loading = 10 wt%) or Fe(NO$_3$)$_2$.9H$_2$O as a precursor for Fe (Fe loading = 10 wt%), then calcined in a flow of air at 500 °C for 2 h, and then reduced in a flow of H$_2$ at 500 °C for 4 h. Finally, the prepared catalysts were stored under ambient conditions[33].

2.3. Catalyst Characterizations

Transmission electron microscopy (TEM; Tecnai G2 20S-Twin, FEI, Hillsboro, Oregon, USA) images of as-prepared catalysts were obtained at an acceleration voltage of 200 kV at Research Center for Physics, Indonesian Institute of Sciences (LIPI). Powder X-ray diffraction (XRD; X-ray diffractometer, Rigaku, Tokyo, Japan) results were recorded using a CuKα (λ = 0.15406 nm) radiation source operated at 40 kV and 30 mA at Research Center for Physics, LIPI. Pore structures were calculated from N$_2$-physisorption isotherms recorded using a Micromeritics Tristar II instrument. Prior to these measurements, samples were evacuated at 200 °C for 3 h. Thermogravimetry analysis (TGA) of pre-calcined catalysts was done on a Linseis instrument (STA PT 1600, Germany) from 25 to 600 °C at a heating rate of 10 °C/min in air atmosphere by taking ca. 15 mg of sample. Catalyst acidity was studied by ammonia temperature-programmed desorption (NH$_3$ -TPD) using Micromeritics instrument (Chemisorb 2750, USA) equipped with TCD. Prior to adsorption, synthesized catalysts were pretreated in a flow of He (15 mL/min) at 400 °C for 30 min. NH$_3$ adsorption, a sample was subjected to a flow of diluted NH$_3$ (15 mL/min) at 100 °C for 30 min. The physisorbed NH$_3$ was removed in a flow of He at the same temperature for 30 min. Finally, TPD experiments were done in the temperature range of 100–600 °C with heating rate of 10 °C/min. Hydrogen temperature-programmed desorption (H$_2$-TPR) experiments were carried out in a flow of 5% H$_2$ in Ar mixtures (40 mL/min) in the temperature range 100–600 °C. Prior to analysis, the catalysts were pretreated in a flow of He (15 mL/min) at 200 °C for 1 h.
2.4. Catalytic Conversion of Fatty Acids
Catalytic hydrodeoxygenation of fatty acids over Ni-based catalysts was carried out using a 160 mL stainless steel autoclave batch reactor equipped with a magnetic stirrer. Typically, a mixture of fatty acid (0.4 g), n-decane (10 mL) and pre-reduced catalyst (0.05 g) was put into the reactor. After sealing, the reactor was flushed three times with He from a high pressure gas cylinder and charged with H$_2$ (40 bar) at room temperature. Then, the reactor was heated under stirring (200 rpm) at 300 °C for 3 h. After the reaction, the catalyst was separated from the mixture, and the liquid products were analyzed by gas chromatography–mass spectrometry (GC/MS; Agilent 7890A instrument featuring a 5975C inert MS XLD and equipped with an HP-5MS capillary column (60 m × 0.25 mm × 250 μm))[34]. Prior to analysis, the obtained product (100 μL) was derivatized using 50 μL of BSTFA which was heated at 70 °C for 30 min. After cooling, the mixture was then diluted with 350 μL of dichloromethane.

3. Results and Discussion
TGA measures weight loss of materials at a certain temperature to know their thermal stability. The weight loss was due to decomposition of the material at high temperatures. Based on the observed TGA results of pre-calcined catalysts in Fig. 1, there was no further decomposition of materials at the calcination temperature of 500 °C, indicating that all nitrate precursors has been converted into their corresponding oxides.

![Fig. 1. TGA results of pre-calcined SiAl-supported Ni-based catalysts](image)

N$_2$-physisorption analysis was carried out to determine the pore structure of the catalysts, and the results were shown in Table 1. According to the results, all the synthesized catalysts showed mesoporous property, which the pore size was in the range of 2-50 nm[35]. SiAl support showed high surface area (415.6 m$^2$/g). After impregnation, all the catalysts obtained a lower surface area, which was in the range of 74–268 m$^2$/g, depending on the type of metals. The decrease of surface area after impregnation indicates that there was partially blocking of the pore of the support by transition metals. The results of the measurement of the area of the bimetal catalyst have increased compared to the area of the monometal catalyst Ni / SiAl. NiFe / SiAl catalysts and NiCo / SiAl catalysts are bimetal catalysts which have the highest increase in surface area compared to other bimetal catalysts. NiFe/SiAl and NiCo/SiAl catalysts also have the highest micropore area compared to other bimetal catalysts, this indicates that NiFe/SiAl catalysts and NiCo/SiAl catalysts have more micro (<2 nm) pores.
Table 1. Pore properties of SiAl-supported Ni-based catalysts

| Catalyst     | BET Surface Area (m²/g) | Micropore Surface Area (m²/g) | Pore Volume (cm³/g) | Pore size (nm) |
|--------------|-------------------------|-------------------------------|---------------------|----------------|
| SiAl         | 415.6                   | 4.4                           | 0.70                | 2-22           |
| Ni/SiAl      | 74.3                    | 4.9                           | 0.10                | 2-12           |
| NiFe/SiAl    | 268.7                   | 20.0                          | 0.32                | 2-12           |
| NiCo/SiAl    | 244.4                   | 12.3                          | 0.32                | 2-13           |
| NiCu/SiAl    | 231.8                   | 10.0                          | 0.36                | 2-13           |

The surface morphologies of the supported Ni-based catalysts were determined by transmission electron microscopy (TEM) and shown in Fig. 2. Metal nanoparticles, imaged as small black spots, were observed on the surface of SiO₂-Al₂O₃. Average size of metal particles was calculated by measuring diameter of black spots (at least 50 spots) on the TEM images as nickel particles or a combination of nickel and second metals (Fe, Cu, Co) dispersed on the SiAl. All catalysts showed wide distribution of metal particle size, in which most of the size was in the diameter range of 11–20 nm. Average metal particle size were 31.2, 23.7, 46.4, and 36.4 for Ni/SiAl, NiFe/SiAl, NiCu/SiAl, NiCo/SiAl, respectively. Average metal particle size was less affected when Co was introduced on Ni catalyst. In the presence of Cu, the average size increased significantly, indicating that the metal exhibited lower dispersion. On the other hand, Fe improved the dispersion of metal nanoparticles, indicated from the smaller size of average metal particles.

Fig. 2. TEM images of (a) Ni/SiAl, (b) NiFe/SiAl, (c) NiCu, and (d) NiCo/SiAl catalysts

Analysis using NH₃-TPD aims to determine the effect of acidity of a catalyst if added to the metal, based on NH₃ gas adsorption. Acid site will adsorb NH₃, and then during desorption, this desorbed NH₃ gas was then detected by the detector. The acidity results can be seen in the following Table 2. The results show that the addition of metals has an influence on the acidity of the Ni/SiAl catalyst. Highest catalyst acidity was exhibited by Ni/SiAl with a total acidity of 0.23 mmol/g. The catalysts impregnated with Fe, Cu, and Co metals showed decreased acidity, indicating that impregnated metals cover the acidic side of the Ni/SiAl catalyst.
Table 2. Acidity of SiAl-supported Ni-based catalysts

| Catalyst    | Acidity (mmol/g) | Acidity (mmol/g) | Acidity (mmol/g) |
|-------------|-----------------|-----------------|-----------------|
|             | Weak Acid       | Strong Acid     | Total           |
| Ni/SiAl     | 0.06            | 0.17            | 0.23            |
| NiFe/SiAl   | 0.04            | 0.04            | 0.08            |
| NiCo/SiAl   | 0.03            | 0.007           | 0.037           |
| NiCu/SiAl   | 0.05            | 0.02            | 0.07            |

HDO reaction was carried out to determine the effect of the addition of Fe, Cu, and Co metals on nickel metal activity. HDO stearic acid reaction using catalysts Ni/SiAl, NiFe/SiAl, NiCu/SiAl, and NiCo/SiAl with a decane solvent. GC-MS analysis of liquid products showed that stearic acid was still detected after the reaction (Fig. 3), indicating that the full conversion of the acid was not achieved under our reaction conditions. Note that, the conversion value was difficult to calculate, since stearic acid was not fully soluble in n-decane at room temperature. In the presence of Fe and Ni, the conversion of stearic acid increased, with the minimum peak area of stearic acid after the reaction was obtained from the NiCu/SiAl catalyst. This indicating that the highest conversion of stearic acid was achieved.

Fig. 3. Normalized peak area of stearic acid in the liquid product after reaction. The area was normalized with internal standard peak.

Ni/SiAl catalyst is a catalyst that can form the largest heptadecane product compared to bimetal catalysts. This was proven by the research of Foraita et al., (2016) regarding HDO stearic acid using a Ni / ZrO2 catalyst, which produced a heptadecane product that was dominant compared to octadecane products. The addition of Fe, Cu, and Co metals to the Ni / SiAl catalyst can encourage the formation of octadecane products, as evidenced by the increase in the percentage of the octadecane product area on the bimetal catalyst. Ni / SiAl catalysts and Ni-M / SiAl bimetal catalysts (M: Fe, Cu, Co) used in the HDO reaction of stearic acids produce heptadecane and octadecane products with different area values. The product areas of heptadecane and octadecane resulting from HDO reaction of stearic acid can be seen in the following Fig. 4.
Fig. 4 shows that the four catalysts have different product areas. NiFe/SiAl catalyst is the catalyst with the smallest product area compared to other catalysts. The small value of the product area on the NiFe/SiAl catalyst indicates that the Fe metal is not an active metal as a second metal for Ni metals, so the NiFe/SiAl catalyst is not active for the reaction of HDO stearic acid.

The catalyst with the highest product area of alkane compounds was the NiCu/SiAl catalyst. Cu is an active metal as a second metal for Ni/SiAl catalysts. Li et al reported that the addition of Cu metal to Ni-based catalysts produced high selectivity, compared to the addition of Co and Sn metals[27]. The product area from GC-MS analysis is directly proportional to the product concentration, so the NiCu/SiAl catalyst that has the highest product area of alkane compounds indicates that the catalyst has a large product concentration value.

Heptadecane formed from the HDO reaction of stearic acid can be converted directly by stearic acid through the decarboxylation pathway or decarbonation pathway. Stearic acid undergoes decarboxylation by eliminating one CO\textsubscript{2} molecule, so heptadecane is formed. Stearic acid can also be decarbonated by eliminating one CO molecule and water, so that 1-heptadecene is formed, then 1-heptadecene is hydrogenated to form heptadecane[25].

The HDO reaction of stearic acid forms an intermediate compound in the form of octadecanol, in which the octadecanol compound undergoes transformation from two different pathways. Octadecanol is formed from stearic acid which is reduced by releasing H\textsubscript{2}O groups, where in the first path the octadecanol undergoes dehydrogenation to form an aldehyde group, namely 1-octadecanal. The 1-octadecanal group undergoes decarbonilation by eliminating one CO molecule to form heptadecane. The transformation of octadecanol in the second pathway is dehydrated to form 1-octadecene alkene groups, which then 1-octadecene undergoes hydrogenation to form octadecane. The results of data from the GC-MS analysis resulted that the NiCu/SiAl catalyst was the most active catalyst for the HDO reaction of stearic acid.

4. Conclusions
Metals, Fe, Cu, and Co influence Ni / SiAl catalysts. Fe, Cu, and Co metals are able to increase the area of the Ni / SiAl catalyst, and are able to influence the particle size of the Ni / SiAl catalyst. Fe, Cu, and Co metals are also able to influence the acidity of the Ni/SiAl catalyst. Based on the results of the reaction, the NiCu/SiAl catalyst gives the best effect on the performance of the reaction. NiCu / SiAl bimetal catalyst is the best catalyst for the HDO reaction of stearic acid.
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