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Preparation and Characterization of Ni/H-ZSM-5 Catalysts for Producing Green Diesel from Palmitic Acid

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Abstract

Biofuel is a promising alternative as a sustainable energy resource in the transportation sector in Indonesia. Green diesel is one of biofuels that can be produced from feedstock containing fatty acid. Fatty acid conversion to green diesel can be conducted via hydrodecarboxylation or hydrodeoxygenation process. Catalyst Ni/H-ZSM-5 is a potential catalyst to convert fatty acid to n-alkane which is the main component in green diesel. In this work, we prepared Ni/H-ZSM-5 catalyst with various Ni loading of 7%, 13%, 18%, and 25%, respectively. The catalysts were synthesized according to a simple incipient wetness impregnation method. Those catalysts were characterized with X-ray fluorescence, Field-Emission Scanning Electron Microscopy, and NH_3-TPD. The highest nickel-loading catalyst, Ni 25%/H-ZSM-5, gave the best dispersion. NH_3-TPD results showed the presence of two acid sites, namely Brønsted acid site and Lewis acid site. The presence of Brønsted acid sites is crucial to facilitate fatty acid conversion to n-alkane.

Keywords: *green diesel; nickel catalyst; H-ZSM-5; acid sites*

Introduction

Currently, Indonesia emerges as the largest palm oil producer in the world with a total production rate reaching 46 million tons of crude palm oil (CPO) per year (Gapki, 2022). In line with the huge production rate, oil palm plantations spread over 14.32 billion ha of area mainly located on Sumatera, Borneo, and Sulawesi Islands. CPO and its derivative products are exported as high as 27 million tons or equivalent to half of total CPO production in Indonesia (Direktorat Jendral Perkebunan, 2019).

Since the beginning of February 2023, Indonesia released a new policy to increase the use of B35 in diesel fuel (B35 means 65 % diesel fuel and 35% biodiesel). From technical aspects, there are no significant problems during the 50.000 km test drive which use various vehicles. In addition, B35 utilization can reduce carbon footprint to 27 – 29 billion CO_2 equivalent (Metro TV News, 2023).

Fatty acid is one of the feedstocks that can be used to produce green diesel and it can be produced from renewable feedstock. CPO contains 50% saturated fatty acid and 44% palmitic acid. Other fatty acids that are utilized to produce green diesel are stearic acid and oleic acid. There are many ways to produce green diesel, among them hydrodecarboxylation, hydrodeoxygenation, hydroisomerisation, and hydrocracking as shown in equation (1) – (4), respectively (Snare, 2006).

$$C_{15}H_{31}COOH + H_2 \rightarrow C_{15}H_{32} + H_2O + CO \quad (1)$$

$$C_{15}H_{31}COOH + 3H_2 \rightarrow C_{16}H_{34} + 2H_2O \quad (2)$$

$$C_{15}H_{32} \rightarrow iso - C_{15}H_{32} \quad (3)$$

$$C_{15}H_{32} \rightarrow iso - C_nH_{2n+2} + iso - C_{15-n}H_{2(15-n)+2} \text{ with } n<15 \quad (4)$$

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Basically, there are several catalysts that can be used for direct green diesel production via the above reaction pathways. Palladium catalysts supported on activated carbon show good performance in n-alkane production as the main component of green diesel, which can be synthesized by deoxygenation of stearic acid. The performance of the catalyst is shown by stearic acid conversion of up to 95% and n-alkane selectivity of more than 60% (Snåre et al. 2006).

Currently, there has been large interest to develop metal-based catalysts for fatty acid decarboxylation. Based on the active metal used, catalyst performance in decarboxylation can be classified as Pd>Pt>Ni>Rh>Ir>Ru>Os (Santillan-Jimenez and Crocker 2012). Although noble metal catalysts have good performance in decarboxylation and high selectivity, the price, ratio availability, and deactivation are unfavorable. Some of the metal-based catalysts with good performance are Cu, Ni, and Co. These catalysts have advantages in price and good performance in deoxygenation (Ferraz, 2021). As a catalyst support, zeolites are materials with a mesopore structure, so they have a large surface area (Hongloi, 2019). Zeolite ZSM-5 in H form has a good acidity level. Therefore, it had a better effect in the HDO process. In addition, metal dispersion in ZSM-5 showed better performance due to its surface area and it can reduce the cost of catalyst production because it is based on non-precious metal (Lee, 2021).

The objective of the present work was to evaluate palmitic acid conversion to green diesel by varying the Ni loadings. The prepared catalysts in this research were characterized by X-Ray Fluorescence (XRF), Temperature Programmed Desorption (TPD), and Field-Emission Scanning Electron (FE-SEM). We expect that the present catalyst could be an attractive alterntive to produce green diesel from CPO.

Materials and Method

2.1 Materials

The catalyst support was H-ZSM-5 powder (Si/Al ratio = 50 and surface area = 350 m^2/g) and was purchased from UD Cahaya Labsain, Boyolali, Central Java. Nickel nitrate (II) hexahydrate was purchased from Merck. Palmitic acid (pro analysis) and n – dodecane (pro analysis) was acquired from Merck. Hydrogen 99% v/v was acquired from local distributor WAP.

2.2 Preparation of Catalyst

All Catalysts in this study were prepared by incipient wetness impregnation. Those catalysts have nickel content starting from 7%, 13%, 18%, and 25%. Nickel nitrate (II) hexahydrate was dissolved in aquadest and dropped slowly into support (H-ZSM-5). The solution was then stirred to form a solid paste. The catalyst was dried in the oven (Thermo Fisher) at 100ºC for 5 h. Subsequently, all catalysts were calcined in air at 500ºC for 5 h. To activate the catalyst, all catalysts were placed in the quartz tube and reduced in a tubular furnace with a stable flow of H_2 99% at 550ºC for 5 h. The quartz tube was then cooled down to reach the ambient temperature. Subsequently, the catalysts were placed and stored in the vials to avoid air exposure. After reduction, catalysts were named as Ni 7%/H-ZSM-5, Ni 13%/H-ZSM-5, Ni 18%/H-ZSM-5, and Ni 25%/H-ZSM-5.

2.3 Characterization of Catalyst

The nickel content of each catalyst was determined by X-ray Flourosence (XRF) of S2 PUMA – Bruker. The measurement method was SMART-Oxides and Helium atmosphere. Besides that, Ni/H-ZSM-5 was also examined by a field emission scanning electron microscope (FE-SEM) to evaluate its surface morphology and topography. A scanning electron microscope (SEM) equipped with Schottky electron gun, Jeol JIB-4610F was used.

To measure the acidity of catalysts, temperature-programmed desorption (TPD) was used to measure it with Micromeritics ChemiSorb 2750. Prior to the test, 0.5-gram sample was preheated to 350ºC for 1 hour in helium flow to remove other gases and impurities. Adsorption of NH_3 (5% in Helium, v/v) was applied on catalysts at 100ºC for 30 minutes. To complete this process, the catalysts were purged with helium flow at the same temperature for 30 minutes. Then, the sample proceeded to the desorption process at 800ºC with a heating rate of 10ºC/minutes. All gas flow is 40 mL/minute. Finally, the amount of NH_3 was recorded by the temperature conductivity detector (TCD).

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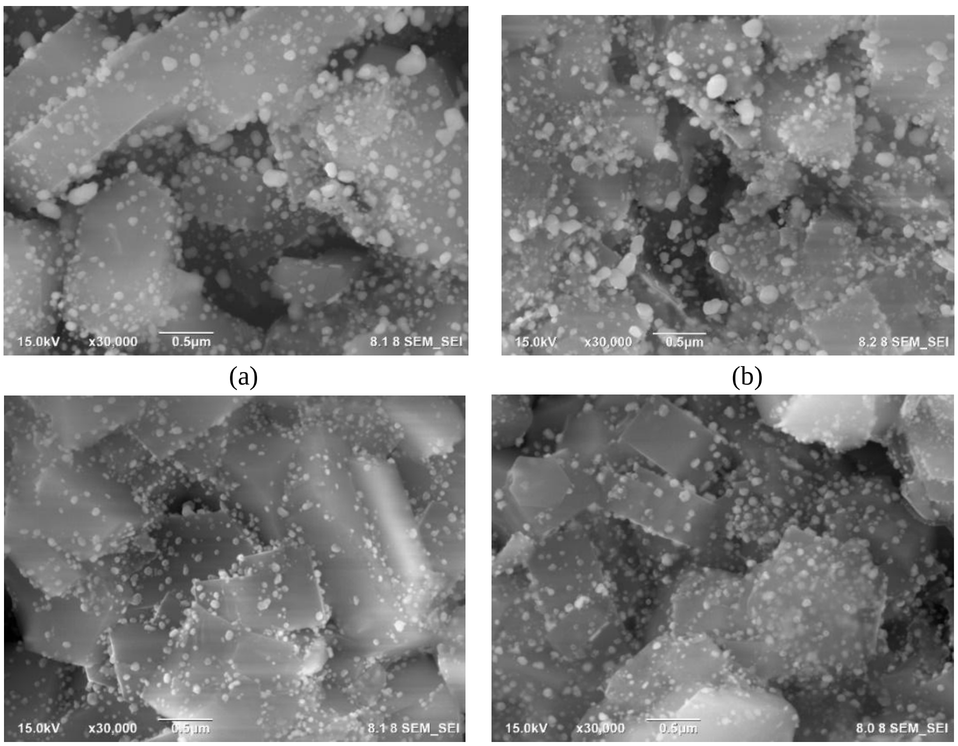
Result and Discussion

3.1 Characterization of Catalyst

The catalysts with nickel loading 5%, 10%, 15%, and 20% were analyzed by XRF successively and the results were 7%, 13%, 18%, and 25%, respectively. XRF results showed that nickel loading in Ni/H-ZSM-5 was not much different. The surface morphology and topography of all Ni/H-ZSM-5 catalyst was conducted with FE-SEM. FE-SEM images were depicted in Figure 1 for Ni 25%/H-ZSM-5 (a), Ni 18%/H-ZSM-5 (b), Ni 13%/H-ZSM-5 (c), and Ni 7%/H-ZSM-5 (d). The results showed that nickel with 20 – 50 µm size was still visible in FE-SEM. As we could see in the figures, we could show that nickel was dispersed well in H-ZSM-5. We could also show that the more nickel is loaded into the catalyst, the easier to see nickels on the catalyst's surface. It indicated that the more nickel loaded in H-ZSM-5, the more nickel dispersed in H-ZSM-5. This may occur because nickel particles partially enter the pore channel of H-ZSM-5 (Balasundram, 2018).



(a) (b) (c) (d)

Figure 1. SEM Result of all Ni/ZSM-5 Catalysts

The acidity of prepared catalysts can be measured by TPD-NH_3. Figure 2 shows NH_3-TPD Curves of Ni 7%/H-ZSM-5, Ni 13%/H-ZSM-5, Ni 18%/H-ZSM-5, and Ni 25%/H-ZSM-5. As seen here, there was significant desorption that occurred in the temperature range of 150ºC-600ºC. For comparison, NH_3-TPD over Cu-Fe/H-ZSM-5 catalyst, gave three distinct peaks at low (120-220ºC), medium (250-380ºC), and high (380-500ºC) temperatures (Doan, 2021). Physical adsorption of NH_3 at the Lewis acid site was represented with desorption at lower temperatures. Besides, desorption in high temperatures is related to physical adsorption on the Brønsted acid site (Long, 2001). The phenomenon was slightly different with the prepared catalyst (Ni/H-ZSM-5) when compared to the Cu-Fe/H-ZSM-5 catalyst. In the present work, Ni/H-ZSM-5 catalysts showed two peaks of desorption, peak at low temperature and peak at high temperature. When we compared all catalysts, we can infer that they have similar path in NH_3 desorption. They have lower temperature

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desorption at the range of 150-300ºC and higher temperature desorption at the range of 350-550ºC. It means that those catalysts have two kinds of acid sites.

Further assessment from Figure 2 showed that peaks at higher temperatures had a slightly wider area than that at lower temperature. In other words, apparently, there were more Brønsted acid sites than Lewis acid sites in all catalysts. The Brønsted acid sites promoted the transformation of methanol to alkenes, whereas the metal-Lewis acid sites played an important role in the dehydrogenation of alkenes to aromatics (Niu, 2017). We know that methanol has a —OH bond and it is like fatty acid which has a —OH bond in —COOH form. From this result, those catalysts have the potential for producing alkane from fatty acid with hydrodecarboxylation and hydrodeoxygenation paths.

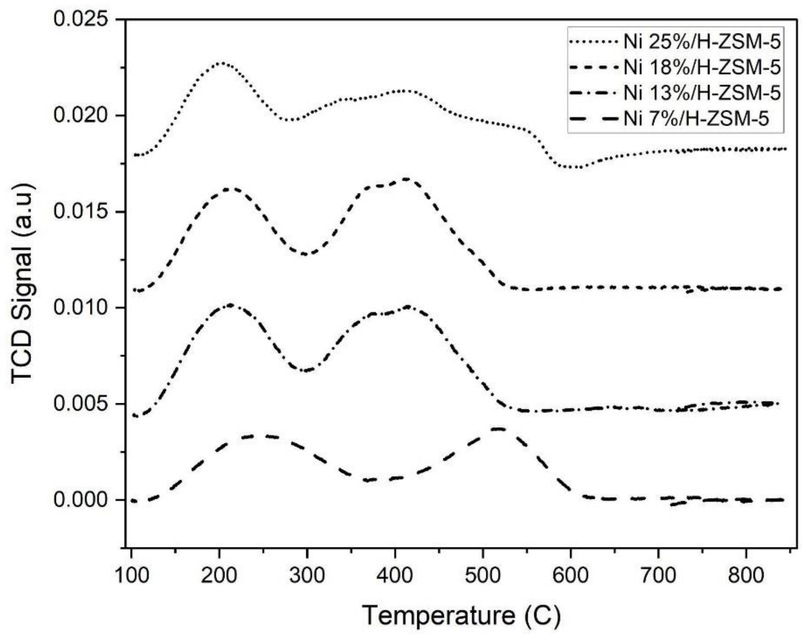

Figure 2. NH_3-TPD Curves of Ni 7%/ZSM-5, Ni 13%/ZSM-5, Ni 18%/ZSM-5, and Ni 25%/ZSM-5

Conclusion

In this research, nickel catalyst-supported zeolite (Ni/H-ZSM-5) was successfully synthesized with incipient wetness impregnation method. Here, the nickel loading was varied and characterized to evaluate their properties. It appears that catalysts with the highest nickel content (25%) have the best dispersion among the other catalysts (7%, 13%, and 18%). The prepared catalysts showed that they have two acid sites, the Brønsted acid site, and the Lewis acid site. The catalysts have more Brønsted acid sites based on their wider peak at high temperatures. Hence, the current catalysts can be used as a promising catalyst to produce alkane as green diesel components through hydrodecarboxylation and hydrodeoxygenation paths.

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