

Effect of NiMo Catalysts Preparation on the Deoxygenation of Palm Oil to Green Diesel

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Abstract. Deoxygenation of triglyceride content in palm oil was performed in a fixed-bed reactor over commercial and prepared Nickel-Molybdenum catalysts (NiMo) at reaction temperature between the interval of 573 K to 613 K, pressure of 500 psi, palm oil flow rate of 0.02 mL/min and under the presence of H₂ flow rate of 200 mL/min. The prepared NiMo catalysts were characterized by N₂ sorption, X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy. An increase in calcination temperature used after impregnation of Ni metal was found to reduce the surface area of the catalyst, which caused the production of total desired hydrocarbons (C₁₅- C₁₈) to decrease. SEM and EDX analysis of the catalyst surface showed an improvement of the dispersion of Mo metals after the amount of Ni metals used was increased in relation to Mo metals from 2:8 to 3:7. Better metal dispersion has also been shown to increase the performance of the catalyst regarding the production of total desired hydrocarbons. X-ray diffraction patterns revealed if the calcination temperature is as high as 1023 K, then Nickel metal in any form will not be detected on the surface of the catalyst.

Keywords: Deoxygenation, Palm oil, Nickel-Molybdenum, Decarboxylation, Decarbonylation

1. Introduction

Due to shortage in petroleum supply, research into synthesis of alternative transportation fuel has grown rapidly over recent years within both the academic and industrial community. It was reported by the International Energy Agency (IEA) that our economy had not received enough supply of petroleum oil since 2012 [1]. As a result, more consumers are now turning to biodiesel fuel instead of petroleum-based diesel for transportation [2]. Unfortunately, biodiesel gave low oxidative stability, and undesirable cold flow properties [3].

Deoxygenation is a series of reactions that convert the molecular structure of triglyceride in vegetable oil to linear hydrocarbons, known as green diesel. The process deoxygenation consisted of decarboxylation, decarbonylation and hydrogenation reaction. By eliminating the carboxylic functional group, decarboxylation reaction converts the fatty acids to saturated hydrocarbons and carbon dioxide. Similarly, decarbonylation transforms fatty acids to unsaturated hydrocarbons, carbon monoxide and water. Since palm oil consisted of mostly stearic acid (C₁₆:0) and linoleic acid (C₁₈:1), the products after either decarboxylation or decarbonylation, will contained on less carbon atoms [4,5]. Under H₂ gas, hydrogenation can also take place, which convert fatty acids directly to hydrocarbons and water with losing any carbon atom [6,7].

Various researches have been devoted to finding the most efficient catalyst to optimize the production of hydrocarbons or green diesel from triglyceride. Most deoxygenation catalysts were prepared by impregnating metal, such as Pd, Pt, Ni or Mo onto the surface of a support. One report stated that Pd metals performed better than Pt metals, because surface analysis indicates that the affinity of Pd metals toward the Al₂O₃

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surface is stronger compared to the Pt metals [8]. In contrary, it was reported in another work that Ni/Al₂O₃ catalyst was observed to be less active because it has larger particle size compared to Pd and Pt [9,10,11].

The aim of this experiment is to investigate the effect of reaction temperature, ratio of Ni to Mo metal and calcination temperature during the catalyst preparation step on the conversion of triglyceride content in vegetable oil to linear diesel-like hydrocarbons. Additionally, these catalysts will be characterized to find surface area, metal dispersion and an image of the catalyst surface.

2. Experimental

2.1. Catalysts Preparation

Initially, alumina support was treated by drying for 12 h in an oven at 383 K and then impregnated with Ni(NO₃)₂ · 6H₂O (Ajax Fine Ltd). Following this, the catalysts were kept overnight for 8 hrs and dried at 383 K for 12 h. The calcination of Ni-impregnated support was then performed at 723 K, 873 K or 1023 K. Mo-precursor was then loaded onto the Ni-alumina by using (NH₄)₆Mo₇O₂₄ (Ajax Fine Ltd) to give either 2:8 or 3:7 ratio of Ni to Mo metal. Then the binary metals alumina was calcined again for the second time at 873 K for all samples and kept in the humidifier storage. The final sample of catalysts were denoted as NiMo-x-y, where x is the temperature of the first calcination step for Ni-alumina and y is the ratio of Ni to Mo. The commercial catalyst, COM-NiMo, was also dried at 383 K for 3 hours.

2.2. Characterization

N₂ adsorption can be used to measure specific surface areas of the catalysts using the Quantachrome Autosorb®-1-C analyser. Before adsorption, the samples were degassed at 413K for 10h to 13h. X-ray diffraction scattering of the catalysts were carried out using the Bruker AXS (Diffraktometer D8, Kalsruhe, Germany) instrument with Cu K α radiation (40 kV, 40 mA) at a scanning speed of 2°/min and between 2 θ range of 10 to 80°. Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX) images were obtained on a JSM-4600 and operated at 15kV having an x5000 magnification.

2.3. Catalytic Testing

Deoxygenation reaction was performed in a fixed-bed reactor (shown in Fig. 1). The reaction temperatures were varied between 573 K and 613 K and pressure was kept at 500 psi (3.5MPa). The catalysts were reduced in H₂ gas, at 450°C for 5 hours prior to catalytic testing. The flow rate of palm oil into the system was 0.02 mL/min and the amount of catalyst was 5g. Hydrogen gas was fed into the reactor at 200 ml/min. Gas chromatogram was obtained using HP 8690 equipped with DB-1 capillary column and was used to calculate eq.1 and eq.2. In equation 2, i represent the hydrocarbon having 15 to 18 carbon atoms.

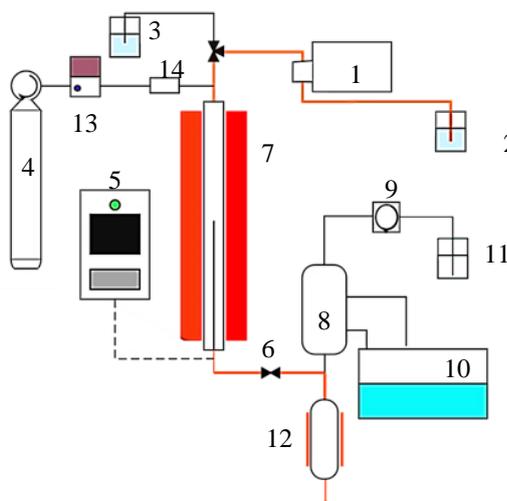


Fig. 1: Catalyst testing set-up using fixed-bed with high-pressure apparatus for deoxygenation reaction; 1.High pressure pump, 2. Feedstock, 3.Sample Vent, 4.H₂ gas cylinder, 5.Temperature controller, 6.Split-furnace, 7.Fixed-bed reactor, 8.Separator, 9.Back pressure, 10.Gas vent, 11.Water circulator, 12.Sampling vessel, 13. Flow-meter and 14.Check valve.

$$\text{Total desired products(\% wt)} = \frac{C_{15} + C_{16} + C_{17} + C_{18}}{\text{Total weight of samplae(g)}} \times 100\% \quad \text{Equation.1}$$

$$\text{Selectivity for component i(\%)} = \frac{C_i}{\text{Total desired products(g)}} \times 100\% \quad \text{Equation.2}$$

3. Results and Discussion

3.1. Catalyst Characterization

An increase in calcination temperature from 723 K to 1023 K was found to cause a decrease in the surface area of the catalyst from 285 m²/g to 121 m²/g. This reduction in the surface area is due to the collapse of walls inside catalyst pore at high calcination temperature. In Fig. 2a crystals on the surface of the NiMo-723-2:8 catalysts are obviously different in size and contain large cluster, which indicate metal agglomeration during the catalyst preparation stage. In contrast, the crystals on the surface of the NiMo-723-3:7 catalysts (Fig. 3a) appear to be smaller and more uniform. Lumps of vacant space are clearly observed, especially in the mapping of Mo metals on NiMo-723-2:8 catalyst (Fig. 2c). On the other hand, when the metal content of Ni was increased, Mo metal was found to be more dispersed as shown in Fig. 3c.

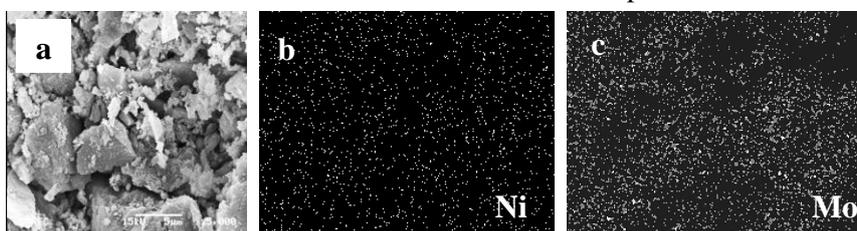


Fig. 2: SEM image (a) and EDX mapping of NiMo-723-2:8 for (b) Ni metals and (c) Mo metals.

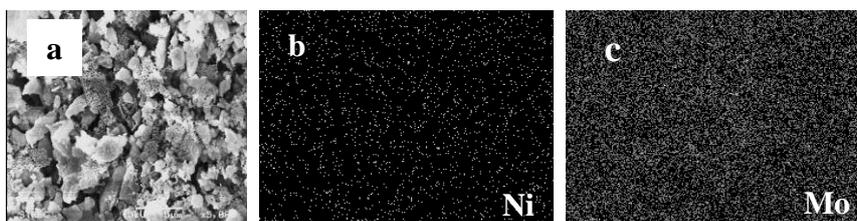


Fig. 3: SEM image (a) and EDX mapping of NiMo-723-3:7 for (b) Ni metals and (c) Mo metals.

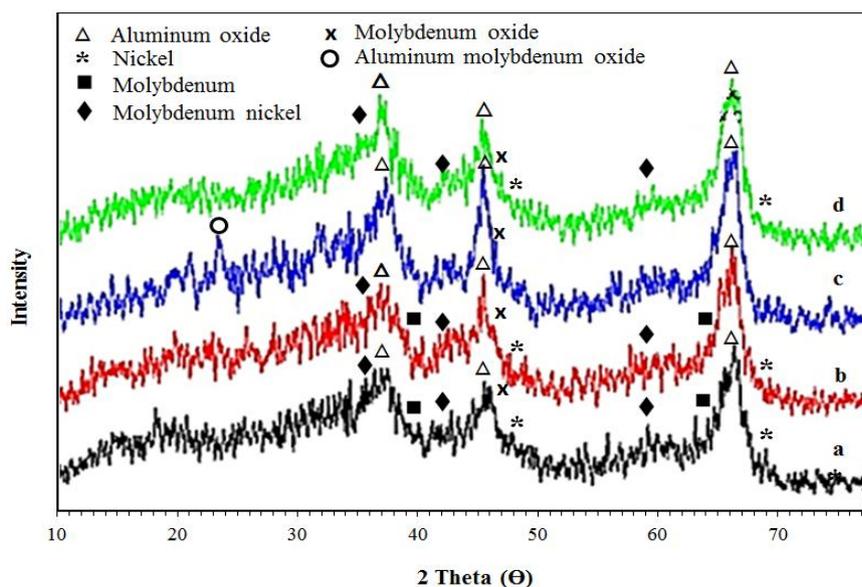


Fig. 4: XRD patterns of (a) NiMo-723-2:8, (b) NiMo-873-2:8, (c) NiMo-1073-2:8, and (d) NiMo-723-3:7.

As illustrated in Fig. 4, the presence of aluminum oxide represented by reflections at 2 Θ equaled to 38°, 45°, and 67° are present on all of the XRD patterns. Mo metals were found to be transformed to either

molybdenum oxide or aluminum molybdenum oxide when the calcination temperature was increased to 1023 K. On the other hand, nickel metal was detected only on catalysts that were calcined at 723 K and 873 K. When the ratio of Ni to Mo metals increased from 2:8 to 3:7, it is observed that the Mo metals were not detected. This indicated that all of the Mo metals on the NiMo-723-3:7 catalyst were already transformed to molybdenum oxide after calcination at 723 K

3.2. Effect of Ratio between Ni and Mo Metal

According to Fig. 5, more total desired products can be produced by using commercial catalyst compared to the prepared catalysts. Additionally, an increase in the calcination temperature from 723 K to 873 K during the preparation step cause total desired product to decrease significantly from 63.7% to 31.7%. This may be related to a reduction in the surface area of the catalyst as a consequence of the increase in calcination temperature after the impregnation step. An increase in the Ni metals content from 2:8 to 3:7 caused the total desired products to increase from 31.7% to 58.6%. This is because, according to Fig. 2c. and Fig. 3c, better dispersion of Mo metals were observed when the amount of Ni metals were increased from 2:8 to 3:7.

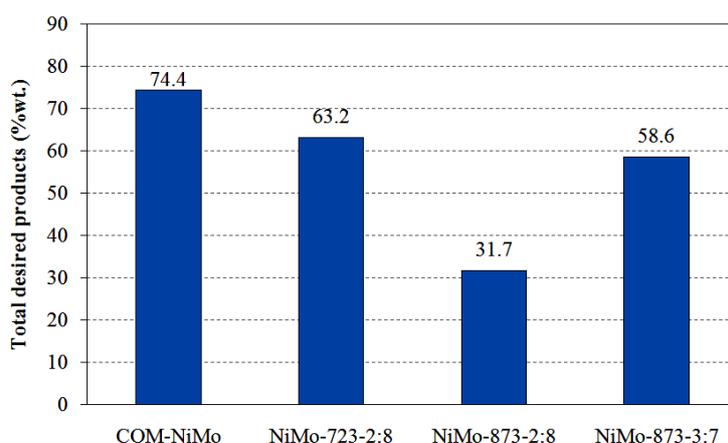


Fig. 5: Amount of desired products from commercial and prepared NiMo catalysts. Temperature = 593 K, pressure = 500 psi and H₂ flow rate = 200 mL/min

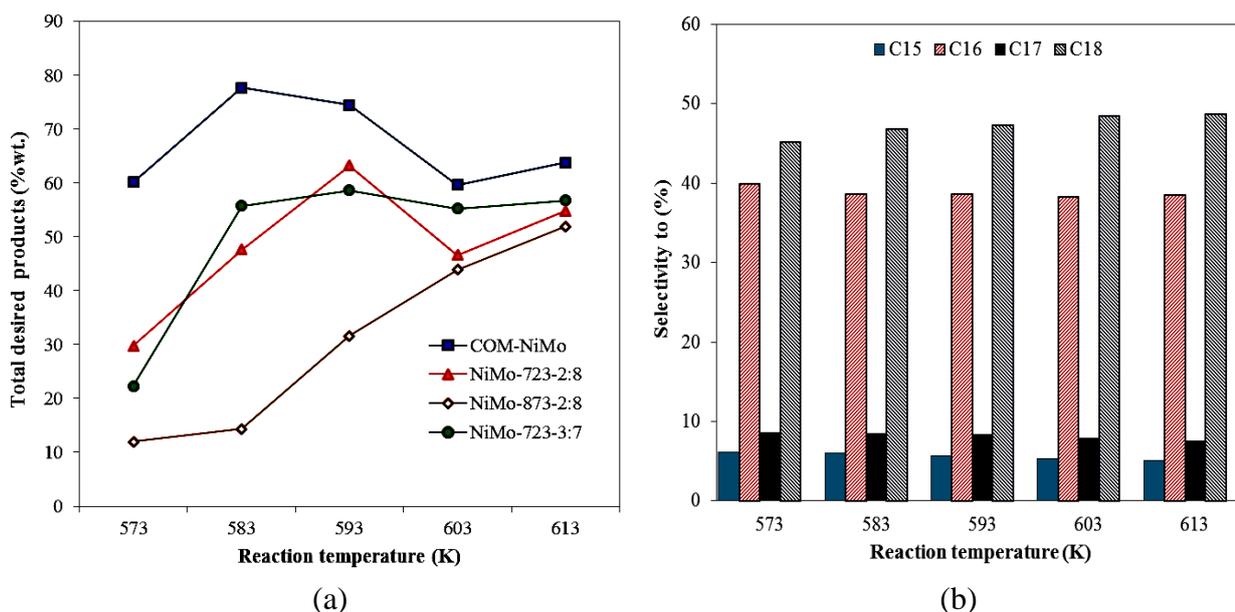


Fig. 6: Effect of reaction temperature on (a) total desired products from different NiMo catalysts and on (b) selectivity to hydrocarbons over NiMo-873-2:8. Pressure = 500 psi and H₂ flow rate = 200mL/min

3.3. Effect of Reaction Temperature

According to Fig. 6a, commercial catalyst was found to give the most desired hydrocarbons at all temperature compared to the prepared catalysts. The optimized reaction temperature for deoxygenation over commercial catalyst was 583 K. For NiMo-723-2:8 catalysts, the optimized reaction temperature that gave total desired products of roughly 60% was at 593 K. NiMo-873-2:8 was found to give lower amount of desired products at all temperature compared to the NiMo-723-2:8 catalysts. For NiMo-873-2:8 catalyst the reaction temperature needed to be increased to as high as 613 K in order for it to be almost as effective as the NiMo-723-2:8 catalyst.

The selectivity to each hydrocarbon product does not depend on the reaction temperature. As shown in Fig. 6b, the C₁₈ selectivity was from 45% to 49%, the C₁₇ selectivity was from 6% to 8%, for C₁₆ the selectivity was 38% to 40%, and for C₁₅ the selectivity was 5% to 7%.

4. Conclusion

In conclusion, NiMo catalysts were successfully prepared for conversion of triglyceride to linear hydrocarbons in the range of C₁₅ to C₁₈, which can be used instead of petroleum-based diesel fuel. Calcination temperature after the first stage of preparation was found to reduce the surface area of the catalyst, which results in a decrease in conversion of triglyceride to linear hydrocarbons. The impact of Ni to Mo metals ratio on crystal size and metal dispersion was observed using SEM-EDX. It was observed that an increase in the amount of Ni metal was responsible for the improvement of the dispersion of Mo metals on the support. Consequently, catalytic testing demonstrated an increase in the production of linear hydrocarbons as the ratio of Ni to Mo metal changed from 2:8 to 3:7. XRD patterns revealed clearly the crystalline phases that exist on each catalyst. It suggested that nickel metals were not present when the calcination temperature was above 1023 K. The optimum reaction temperature depends strongly on the characteristic of the catalyst.

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6. References

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