

Preparation and Characterization of NiMo/Al₂O₃ Catalyst for Hydrocracking Processing

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Abstract. Hydrocracking is a chemical process used in petroleum refineries for converting high boiling hydrocarbons in petroleum crude oils to more valuable lower boiling products such as gasoline, kerosene, and diesel oil that operate at high temperature and pressure. Catalyst was used in hydrocracking to reduce temperature and pressure. Hydrocracking catalyst are composed of active components and support. Alumina is widely used in hydrocracking process as catalyst support due to its high surface area, high thermal stability, and low prices. The objective of this research was prepared NiMo/Al₂O₃ catalyst that used as hydrocracking catalyst. Catalyst was synthesized by wetness impregnation method and simple heating method with various kind of Al₂O₃. The physicochemical properties of catalyst were investigated by X-ray diffraction (XRD) to determine type of crystal and scanning electron microscopy (SEM) to determine morphology of the catalyst. The NiMo/Al₂O₃ catalyst prepared by aluminium potassium sulfate dodecahydrate exhibited the highest crystallinity of 90.23% and it is clear that MoO₃ and NiO crystallites are highly dispersed on the NiMo/Al₂O₃ catalyst which indicates as the best catalyst. The catalytic activity in hydrocracking process was successfully examined to convert fatty acid into hydrocarbon.

1 Introduction

Energy needs in Indonesia keeps increase from year to year. This occurred in all sectors which include industrial, transportation, commercial, and household sector. The transportation sector is one of the largest sector in consuming energy compared to other sector that were still reliant on fossil fuel [1] Gasoline, diesel, and kerosene was the most widely used in this sector. The growing demand of gasoline, diesel, and kerosene continues to increase progressively in the recent years. Many efforts have been conducted to overcome the crisis energy in the transportation sector. Biofuels as a predominant source of energy from biomass may offer a solution to this problem [2]. Biofuel as alternative energy source have many benefits with respect to environmental concerns [3].

Plant oils cannot be used directly as fuel due to several drawbacks. This problem can be resolve by using some processes such as pyrolysis and hydrotreatment. Although both processes produce hydrocarbon as main product, there exits significant differences between both process. Pyrolysis is less complicated process. However, pyrolysis produces organic acids short chain cracking and aromatic products rather than pure hydrocarbon.

Hydroprocessing is much different process from pyrolysis, it can remove all oxygen content from the plant oils and produce pure low boiling point hydrocarbon [4]. Hydroprocessing consist hydrotreating and hydrocracking processes that needs hydrogen gas to convert fatty acid directly to hydrocarbons and water. Hydrotreatment offers a simpler and better option because it can be used in the existing refinery and produce hydrocarbons that similar to hydrocarbons produced from petroleum [5].

Catalyst is needed to reduce the temperature and pressure of this process. Many studies have been conducted on catalyst used in hydroprocessing of vegetable oil. Catalyst support like alumina, zeolite, and activated carbon were used for hydrocracking reactions. All this support were impregnated with active metals like Pd, Pt, NiMo, and CoMo for hydrogenation/dehydrogenation [6-9]. Catalyst which has highly porous and thermostable is not only able to disperse the metal but also can increase its thermal stability. The use of support can enhance the activity of catalyst due to its higher surface area and thermal stability [10].

Simple heating method can increase the surface area of the catalyst. In simple heating method, high molecular weight polymer is needed as a continous media [11]. Mixed solution of metal and continous

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media were stirred and heated to evaporate water in the mixed solution. This continuous media must be remained until the end of process because it can avoid agglomeration of catalyst particle. Finally, the continuous media will be vaporized get nano particle catalyst by heating the solution above the polymer decomposition temperature [12]. Support like alumina is widely used in hydro processing due to its high surface area, high thermal stability, and low prices [13]. However, the pore size distributions are not efficient for catalytic reaction.

In this study, NiMo/Al₂O₃ catalyst was prepared with various kind of alumina by simple heating and wetness impregnation methods. In order to know the physicochemical properties of the catalyst with various kinds of alumina, the NiMo/Al₂O₃ catalyst were characterized by several techniques including scanning electron microscopy (SEM) to determine morphology and composition of catalyst and x-ray diffraction (XRD) to determine crystal size and type of crystal.

2 Experimental

2.1 Materials

Aluminium potassium sulfate dodecahydrate (KAl(SO₄)₂.12H₂O), aluminium nitrate nonahydrate (Al(NO₃)₃.9H₂O, Merck), aluminium hydroxide (Al(OH)₃.xH₂O, Merck), alumina (Al₂O₃, PT. Inalum), commercial gamma-alumina (γ-Al₂O₃), nickel(II) nitrate hexahydrate (Ni(NO₃)₂.6H₂O, Merck), ammonium heptamolybdatetetrahydrate ((NH₄)₆Mo₇O₂₄.4H₂O, Merck), and poly ethylene glycol (PEG-4000).

2.2 Catalyst Preparation

The Al₂O₃ support for NiMo/Al₂O₃ catalyst were prepared by various kind of Al₂O₃ (A-E) using (A) aluminium potassium sulfate dodecahydrate (KAl(SO₄)₂.12H₂O), (B) aluminium nitrate nonahydrate (Al(NO₃)₃.9H₂O), (C) aluminium hydroxide (Al(OH)₃.xH₂O), (D) alumina (Al₂O₃), and (E) gamma-alumina (γ-Al₂O₃). The NiMo/Al₂O₃ catalyst (A, B, C) were prepared by simple heating methods and (D,E) were prepared by wetness impregnation method. These are summarized in Table.1. The metal loading of nickel and molybdenum were assigned as 5% wt of NiMo/Al₂O₃ for all catalyst. For simple heating method, ammonium heptamolybdatetetrahydrate ((NH₄)₆Mo₇O₂₄.4H₂O) and nickel(II) nitrate hexahydrate (Ni(NO₃)₂.6H₂O) were dissolved in aquadest. Then, various kind of Al₂O₃ (A-C) and required amounts of polyethylene glycol was added to the solution with constant stirring and heating at 100°C for 1 hours to evaporate the water in the solution. The solution was dried at 110°C for 1 hours and calcined at 600°C for 30 minutes. For wetness impregnation method, ammonium heptamolybdatetetrahydrate ((NH₄)₆Mo₇O₂₄.4H₂O) and nickel(II) nitrate hexahydrate (Ni(NO₃)₂.6H₂O) were

dissolved in aquadest. Then, various kind of Al₂O₃ (D,E) was added to the solution with constant stirring for 12 hours. The solution were dried at 110°C for 24 hours and calcined at 600°C for 5 hours.

Table 1. NiMo/Al₂O₃ catalyst prepared from various kind of aluminium compounds

Catalyst	Methods	Al Compound
A	Simple Heating	KAl(SO ₄) ₂ .12H ₂ O
B	Simple Heating	Al(NO ₃) ₃ .9H ₂ O
C	Simple Heating	Al(OH) ₃ .xH ₂ O
D	Wetness Impregnation	Al ₂ O ₃
E	Wetness Impregnation	γ-Al ₂ O ₃

2.3 Catalyst Characterization

The physicochemical properties of NiMo/Al₂O₃ catalyst were characterized by X-ray diffraction (XRD) to determine type of crystal and crystallinity of the catalyst and scanning electron microscopy (SEM) to determine morphology and composition of the catalyst.

Table 2. NiMo/Al₂O₃ catalyst crystallinity

Catalyst	Crystallinity (%)
A	90.23
B	62.99
C	61.84
D	59.69
E	53.19

2.4 Hydrocracking of Dirty Palm Oil

The hydrocracking process was carried out to check the activity of NiMo/Al₂O₃ catalyst. Dirty palm oil was used as feed for hydrocracking process. Hydrocracking of dirty palm oil was carried out in custom made batch autoclave reactor with an internal diameter of 90 mm and length of 160 mm. 100 gr of dirty palm oil and 1 gr of NiMo/Al₂O₃ catalyst was loaded into the reactor and the H₂ was injected with initial pressure of 3 atm. The reactor was heated to 550°C and the reaction was performed for 1.5 hours. The reactor was cooled and the liquid product was collected for GCMS analysis.

3 Results and Discussion

3.1 XRD Characterization

Fig.1 shows the XRD patterns of NiMo/Al₂O₃ catalyst with various kind of alumina. The characteristic peak position were observed at 2θ. Three strongest peak of NiMo/Al₂O₃ catalyst A (2θ = 22.40°, 31.4°, 33.33°), B (2θ = 23.53°, 26.40°, 27.50°), C (2θ = 23.37°, 25.47°, 28.85°), D (2θ = 23.33°, 26.74°, 66.85°), E (2θ = 22.09°, 23.31°, 26.20°) were obtained.

It can be seen from XRD diffractogram that there is no nickel and molybdenum diffraction peaks found in XRD patterns of catalyst (B,C,D,E) which indicate that nickel and molybdenum species are well dispersed on the support. The peak of catalyst (A) were comparatively weaker than the supports because the

material was covered by the active metal component after impregnation and diffraction peaks of NiO and MoO₃ can be clearly seen which indicate the growth of MoO₃ and NiO crystals over the catalyst.

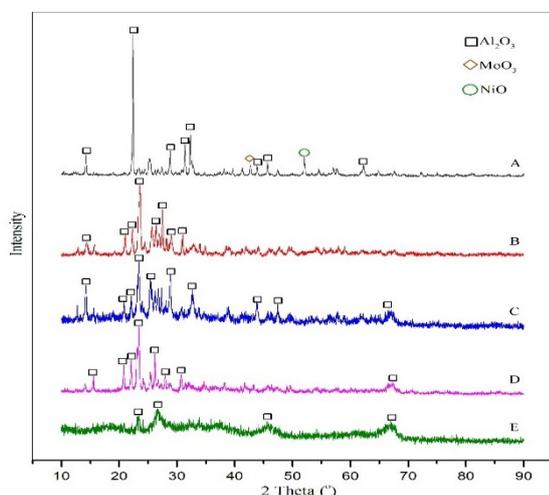


Fig. 1. XRD diffractogram of the NiMo/Al₂O₃ catalyst prepared from various kind of aluminium compounds

The intensity of the peak represents the crystallinity of the catalyst [10]. Sharper peak means particles tend to get higher crystallinity. High crystallinity will affect catalytic activity and stability at higher temperature [12]. Crystallinity of NiMo/Al₂O₃ catalyst with various kind of alumina were summarized at Table. 2. It can be observed that simple heating methods has higher crystallinity than wetness impregnation methods due to the addition of PEG as continuous media avoid the agglomeration of impurities in solution that make the impregnation in simple heating methods free from impurities. Catalyst (A) have the highest crystallinity than the other catalyst because it have the highest acidity in alumina support so the impregnation of catalyst (A) produced the best crystal of NiMo/Al₂O₃.

3.2 SEM Characterization

The morphological properties of the catalyst were determined using scanning electron microscopy (SEM). Catalyst NiMo/Al₂O₃ (A) have the highest crystallinity

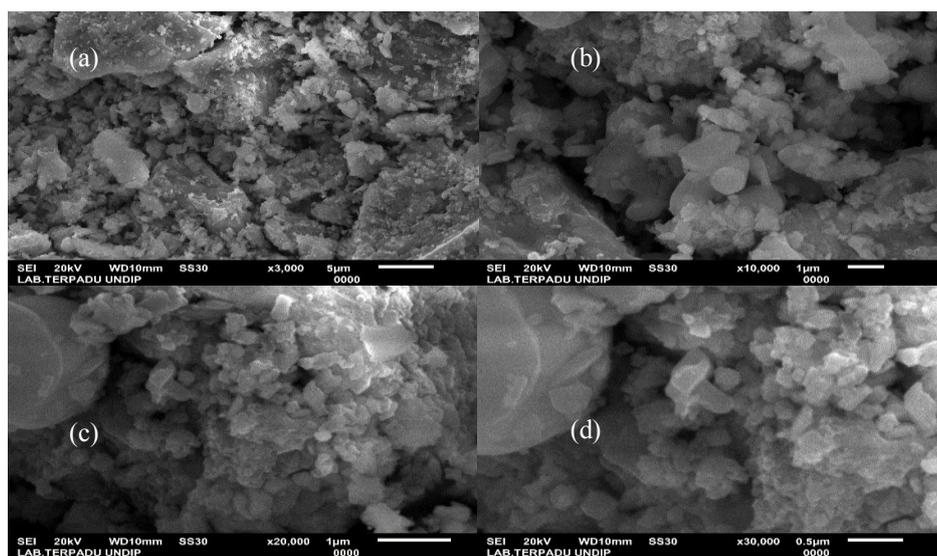


Fig. 2. SEM photographs of the NiMo/Al₂O₃ catalyst (A) at (a)3000x, (b)10000x, (c)20000x, and (d)30000x magnification

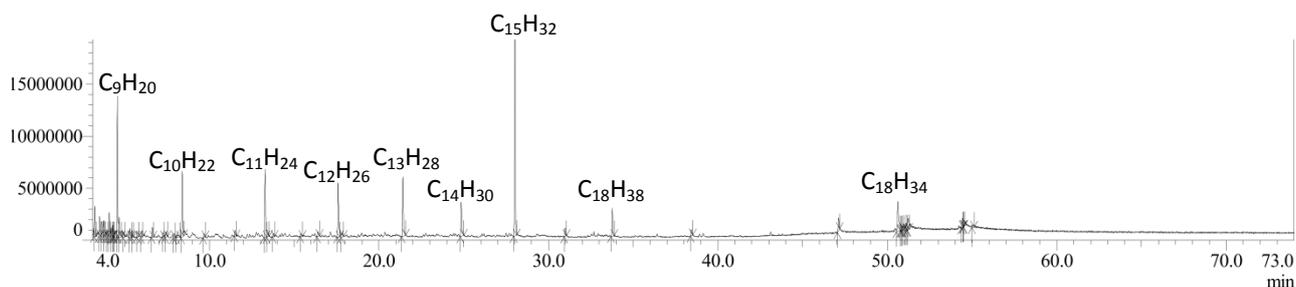


Fig. 3. Gas Chromatograms of hydrocracking product

Table 3. Hydrocracking product

Fraction	Percentage(%)
<C ₅	7.67
C ₆ -C ₈	8.28
C ₉ -C ₁₅	70.79
C ₁₆ -C ₁₉	8.28
>C ₁₉	4.97

than the other catalyst (B-E). The SEM micrographs of catalyst NiMo/Al₂O₃ (A) from 3000x, 10000x, 20000x, and 30000x magnification are displayed in Fig. 2 respectively. Morphology plays an important role in activity and selectivity of the catalyst [10]. The presence porous agglomerates was revealed that this agglomerates are composed of small spherical particles show irregular shapes of alumina which were coated by MoO₃ and NiO fine particle. Coating tended to occur on cracked alumina [14]. In other words, small size alumina particles coated with MoO₃ and NiO have a higher thermal stability and it is clear that MoO₃ and NiO crystallites are highly dispersed on the NiMo/Al₂O₃ catalyst.

3.3 Hydrocracking Process

The GCMS analysis of the hydrocracking product shows that the NiMo/Al₂O₃ catalyst successfully convert fatty acid in dirty palm oil into hydrocarbon. The hydrocarbon yield was ranged from light hydrocarbon (<C₅), naphtha (C₆-C₈), kerosene (C₉-C₁₅), diesel (C₁₆-C₁₉), and heavy hydrocarbon (>C₁₉).

The dirty palm oil used in this study was composed of mainly C₁₆-C₁₈ fatty acids. The hydrocarbon product consists 7.67% light hydrocarbon, 8.28% naphtha, 70.79% kerosene, 8.28% diesel, and 4.97% heavy hydrocarbon.

4 Conclusion

In this study, NiMo/Al₂O₃ catalyst with five kinds alumina supports were prepared by simple heating method using KAl(SO₄)₂.12H₂O, Al(NO₃)₃.9H₂O, Al(OH)₃.xH₂O and wetness impregnation methods using Al₂O₃ and γ -Al₂O₃ to be alumina resources. The XRD characterization of catalyst have shown the nickel and molybdenum species are well dispersed on the support. Simple heating methods has higher crystallinity than wetness impregnation methods due to the addition of PEG as continuous media avoid the agglomeration of impurities in solution that make the impregnation in simple heating methods free from impurities. NiMo/Al₂O₃ catalyst (A) have the highest crystallinity than the other catalyst because it have the

highest acidity in alumina support so its produced the best crystal of NiMo/Al₂O₃.

The SEM characterization of catalyst (A) shows that alumina particles were coated with MoO₃ and NiO and it is clear that MoO₃ and NiO crystallites are highly dispersed on the NiMo/Al₂O₃ catalyst. This two characterizations of catalyst indicates the simple heating method with KAl(SO₄)₂.12H₂O as alumina resources was the best catalyst due to its highest crystallinity and high metal loading dispersion in the catalyst. The catalytic activity of the NiMo/Al₂O₃ catalyst in hydrocracking process was successfully examined to convert fatty acid in dirty palm oil into hydrocarbon.

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