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PREPARATION, CHARACTERIZATION AND ACTIVITY ASSAY OF NiO-CoO-MoO/ZEOLITE-Y CATALYST ON HYDROCRACKING OF CASHEW NUT SHELL LIQUID IN FIXED-BED REACTOR

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ABSTRACT

Preparation and characterization of NiO-CoO-MoO/zeolite-Y (ZY) catalyst for hydrocracking of Cashew Nut Shell Liquid (CNSL) to gasoline and diesel fractions have been investigated. Impregnation of Ni, Co, and Mo was carried out using $Ni(NO_3)_2$, $Co(NO_3)_2$, and $(NH_4)_6Mo_7O_{24}$ (90 $^\circ$C, 5 h). The solvent was then evaporated at 120 $^\circ$C for 2 h. The samples were activated by microwave (450 watt, 10 min), then oxidized by O_2 at 500 $^\circ$C for 2 h. The characterization of catalyst including determination specific surface was done by gas sorption analyzer, total acid site were determined by ammonia and pyridine gas adsorption, and crystallinity by X-ray Diffraction. The thermal and catalytic hydrocracking of CNSL was carried out in a flow system fixed-bed stainless steel reactor (400 $^\circ$C, 450 $^\circ$C) with catalyst : feed ratio of 0,17, 0,25, and 0,50 (w/w). The liquid products were analyzed by GC. The result of characterization showed that the ZY and NiO-CoO-MoO/ZY have specific surface area of 342,651 m^2/g and 499,246 m^2/g. The highest liquid product was 74,90 % achieved by NiO-CoO-MoO/ZY catalyst (400 $^\circ$C), catalyst:feed ratio of 0,5 (w/w), with selectivity for gasoline, diesel and heavy oil fractions was 49.77, 23.35, and 27.88 wt.%, respectively.

Keyword: *Zeolite-Y (ZY), impregnation, hydrocracking, Cashew Nut Shell Liquid (CNSL)*

INTRODUCTION

Many researches have been done in attempt to search for alternative renewable energy resources such as using hydrocracking process on plastic waste [1], waste lubricant oils [2,3] and vegetable oils in to fuel [4,5,6]. Another potential candidate for this type of process is hydrocracking of cashew nut shell [7]. Cashew nut is widely used as food but the shell has not been used. Hydrocracking of Cashew Nut Shell Liquid (CNSL) as an alternative energy resource is expected to produce hydrocarbon compound at gasoline and diesel quality.

Hydrocracking can proceed either by thermal or by using catalyst. Thermal cracking is less efficient than catalytic cracking due to the high energy required [8]. Metals such as Fe, Co, Ni, Rd, Ru, Pd, Os, Ir and Pt have been used as catalysts [9]. The use of pure metal(s) as catalyst leads to sintering process which caused the loss of active surface on the metal(s). One alternative option to overcome this problem is impregnating the metal(s) on to a supporting

material such as zeolite. Impregnated Ni-Mo and Ni-Pd on zeolite Y are widely used on natural fuel processes [10]. Zeolite Y is a thermally stable synthetic zeolite with homogenous pore structure and relatively abundant acid sites [11, 12]. Acid sites on the zeolite Y can also serve as active site on the impregnated metal-zeolite sample.

In this research, we impregnated NiO-CoO-MoO on zeolite Y and characterize it. We also asses the activity and selectivity of this particular catalyst sample on hydrocracking reaction of CNSL.

METHODOLOGY

Materials. All chemicals ($Ni(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$, $(NH_4)_6Mo_7O_{24}.4H_2O$, hydrochloric acid) were purchased from Merck. Zeolite-Y was purchased from TOSOH-Japan. Cashew Nut Shell Liquid was purchased from Wonosari. Oxygen and hydrogen gas were purchased from PT. Samator Gas.

Catalyst preparation. Metals impregnation $(NH_4)_6Mo_7O_{24}.4H_2O$ (0.607 g) was dissolved in aqueous media. Zeolite-Y was then added in to the solution. Upon addition of zeolite-Y, the mixture was then refluxed at 80 °C for 5 hours. After reflux, the mixture was dried to produce Mo-ZY catalyst. Similar procedure was applied on $Co(NO_3)_2.6H_2O$ (1.670 g) and $Ni(NO_3)_2.6H_2O$ (1.627 g) to produce NiCoMo-ZY catalyst. The solid mixture of NiCoMo-ZY catalyst sample was then calcinated using microwave method (450 watt) for 10 minutes and followed by oxygenation (15 mL/min) at 500 °C for 2 hours.

Catalyst characterization. The acidity of the catalyst sample was determined using gravimetric method with ammonia gas adsorption for total acidity and pyridine gas for surface acidity determination. Crystalinity assay of the catalyst sample was determined using XRD. Surface area, total pore volume and average pore size were determined using BET based on monolayer gas adsorption phenomenon at constant temperature.

Catalytic activity assay. Hydrocracking of CNSL was carried out with hydrogen gas flow (20 mL/min) in reactor system (Sriningsih, 2014). The process used catalyst : feed ratio of 0.17, 0.25 and 0.50 w/w. Both catalyst and feed were weighed and catalyst was then put in each chamber. Both chambers were then put in a fixed bed reactor system which made from stainless steel. The reactor was then put in a furnace and heated at 400 °C. The products were collected through a silicon pipe that passed through a condenser. Liquid product was analyzed using gas chromatography (GC). Products were divided in to liquid, gas and coke. The amount of each product was calculated with the following equation.

Wt % of coke = $\frac{Ws1-Ws2}{Wf}$ x 100%   (1)

Wt % of liquid yield = $\frac{Wl}{Wf}$ x 100% (2)

Wt % of residue = $\frac{Wr}{Wf}$ x 100% (3)

Where :

Ws1 = the weight of catalyst before hydrocracking process
Ws2 = the weight of catalyst after hydrocracking process
Wf = the weight of feed
Wl = the weight of liquid
Wr = the weight of residue.

The amount of gas product was calculated using the following equation.

Wt % of gas product = 100%- (% of liquid yield+ % of coke + % of residue) (5)

The ratio of the products was calculated as follow.

C % of G/D/HO = $\frac{CAGC_{G/D/HO}}{CAGC}$ x 100% (6)

Where C is chromatogram, G is gasoline, D is diesel, HO is heavy oil, CAGC is chromatogram area of gas chromatography.

Similar procedure was applied on zeolite-Y without any metal and also on thermal cracking as control.

RESULT AND DISCUSSION

Characterization. Acidity is a property of all catalyst. Acidity of a catalyst is the millimole acid over the surface area of the catalyst. Determination of acid site using pyridine as adsorbate will give the surface acidity with an assumption that the relatively large size of pyridine molecule can only be adsorbed on the surface. The determination of acid sites using ammonia gave the total acid site with the assumption that the relatively small size of ammonia can penetrate in to the catalyst pores. Table 1 below presents the acid site of the catalyst sample.

Table 1.Total and surface Acid site

Catalyst	Acid site	
	Pyridine (mmol/gram)	Ammonia (mmol/gram)
ZY	2,13	6,82
NiO-CoO-MoO/ZY	2,85	13,43

As can be seen on Table 1, the acidity of NiO-CoO-MoO/ZY is higher than ZY catalyst. This result is due to the uniformly impregnated Ni, Co and Mo metals in the supporting ZY. Metals such as Ni, Co and Mo can serve as Lewis site because they have degenerated empty d orbital and thus can accept electron effectively from base such as pyridine and ammonia.

Catalyst sample surface area was determined in order to assess the influence of metals impregnation on specific surface area, total volume and average pore radius of the ZY. Specific surface area can determine the absorbing ability of a catalyst in hydrocracking process.

Table 2. Specific surface area, total pore volume and average pore radius

Catalyst	Surface area (m2/g)	Pore Volume (cc/g)	Average pore radius(Å)
ZY	342,651	$2,362 \times 10^{-1}$	13,783
NiO-CoO-MoO/ZY	499,246	$3,191 \times 10^{-1}$	12,781

As shown in Table 2, the impregnation of Ni, Co and Mo on ZY altered the characteristics of ZY. Surface area and pore volume were increasing, while the average pore radius was decreasing. These results imply that the impregnation of all three metals did not cause any sintering. The impregnation process is considered to form new pores on the ZY.

X-ray diffraction was utilized to identify christalinity of the catalyst sample. XRD result on both ZY and NiO-CoO-MoO/ZY can be seen on Fig 1.

As shown in Fig 1, the impregnation of all three metals Ni, Co and Mo did not change the crystalinity of ZY, although the intensity on 2θ (degree) 15.95 was decreasing from 983 to 678 on 2θ (degree) 16.08, and on 2θ (degree) 23.99 was also decreasing from 996 to 706 on 2θ (degree) 24.15. The decreasing peak intensity of NiO-CoO-MoO/Zeolit Y compare to ZY indicated the decreasing of its crystalinity. This lower crystalinity did not indicate the loss of crystalinity. The peaks of NiO-CoO-MoO/Zeolit Y are at the same area with the ZY catalyst but have lower intensity. The latest result suggested that impregnation of the three metals did not alter the crystal structure.
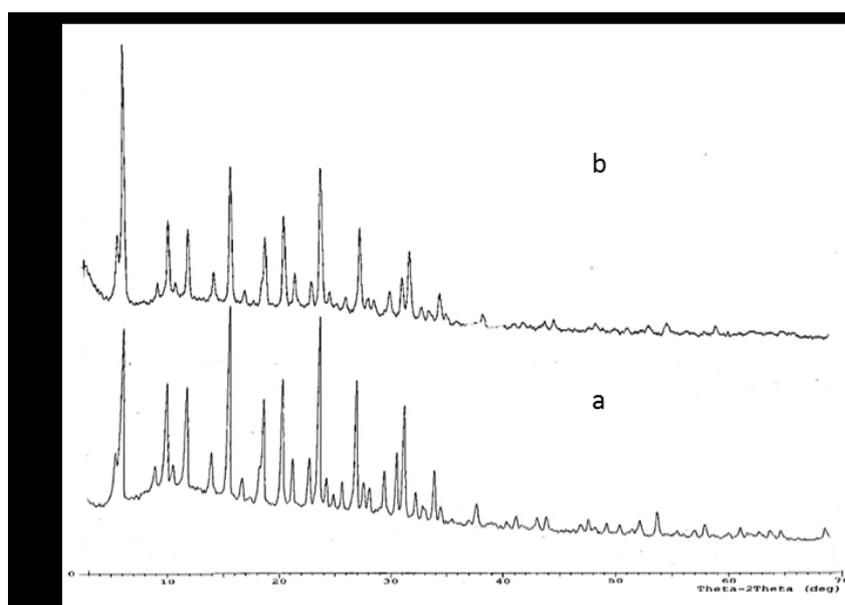

Figure 1. XRD results of (a) Zeolite Y and (b) NiO-CoO-MoO/Zeolite Y

Catalytic activity assay. In this hydrocracking process, catalyst with different character resulted in different activity based on the products (Fig.2). Catalytic activity is described from the percentage of liquid product. Fig 2 showed the highest percentage of liquid product, 74.90 %, was obtained when NiO-CoO-MoO/ZY is used as catalyst at 400 °C with catalyst : feed ratio of 0.5 w/w. This result is due to the high acidity and larger specific surface area of NiO-CoO-MoO/ZY compare to ZY catalyst. High acidity means more H^+ is released from hydrocarbon chain to form carbonium ion and thus trigger the hydrocracking process. Besides liquid and gas products, this reaction also produced coke. According to Alenazey, the formation of coke is initialized by the chemosorption of hydrocarbon and then followed by dehydrogenation to form non saturated alifatic compound on the surface and thus trigger the depolimerization to produced coke deposit [13]. This latest argument was olso mentioned in Hughes. Hughes mentioned that any catalyst that has been used in a catalytic reaction of organic compound can form carbon residue (carbonaceous deposit or coke) on its surface[14]. In Fig 2, we can also see the coke production of ZY catalyst is proportional with its liquid production while in NiO-CoO-MoO/ZY catalyst, the increasing of liquid production was not accompanied by the coke production. This implied that the impregnation of Ni, Co and Mo metals that served as promoter and co promoter in the catalyst sample can prevent the production of the coke. This fact is in line with Beurden et al statement which stated that the addition of promoter can increase the surface area, prevent side reaction to proceed (coke formation) and thus increase the overall catalytic surface area [15].
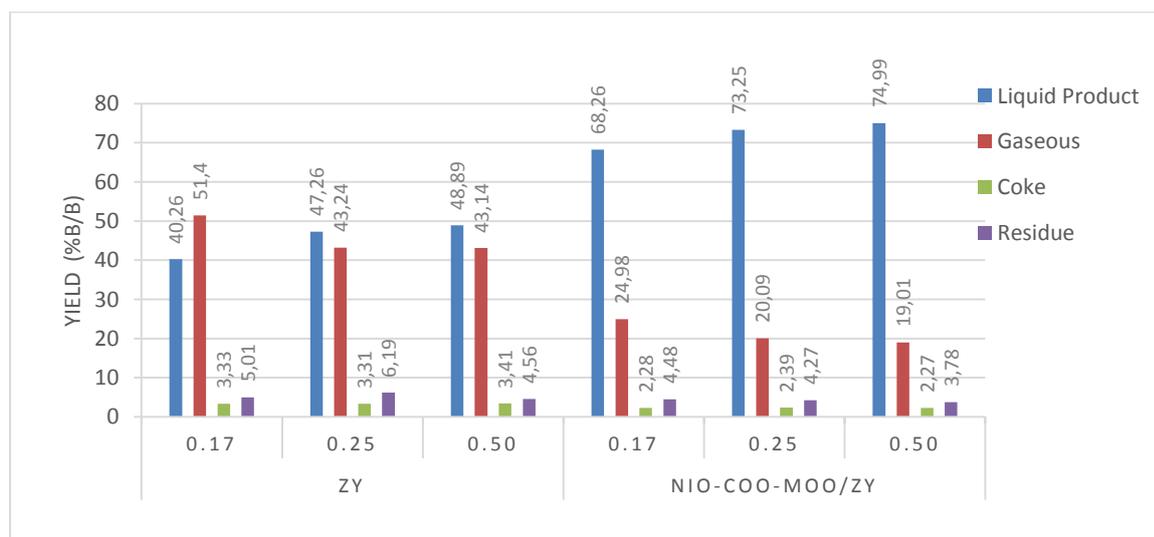

Figure 2.The distribution of CNSL Catalytic Hydrocracking products at 400 °C.

The high ratio of catalyst : feed gave higher chance for reactant to interact with the catalyst. Both ZY and NiO-CoO-MoO/ZY catalysts at higher catalyst : feed ration gave higher liquid yield.

Catalyst Selectivity. Selectivity describes the tendency of a catalyst to produce a certain product. The catalyst selectivity for gasoline, diesel and heavy oil is shown in Fig 3. In Fig 3, the selectivity of NiO-CoO-MoO/ZY for gasoline production is higher than ZY catalyst while ZY is more selective to produce heavy oil than NiO-CoO-MoO/ZY. This was due to the higher acid sites on the NiO-CoO-MoO/ZY catalyst surface that enable it to produce short chain hydrocarbon and made it more selective for gasoline production.   The   impregnation   of Ni,Co, Mo metals on supporting ZY increased the activity and selectivity of the catalyst. It increased the acidity, specific surface area, average pore radius and total pore volume of the catalyst. Highest liquid yield, 74.90 %, and highest selectivity for gasoline, 49.77 %, production were given by NiO-CoO-MoO/ZY with catalyst : feed ratio of 0.5 at 400 °C
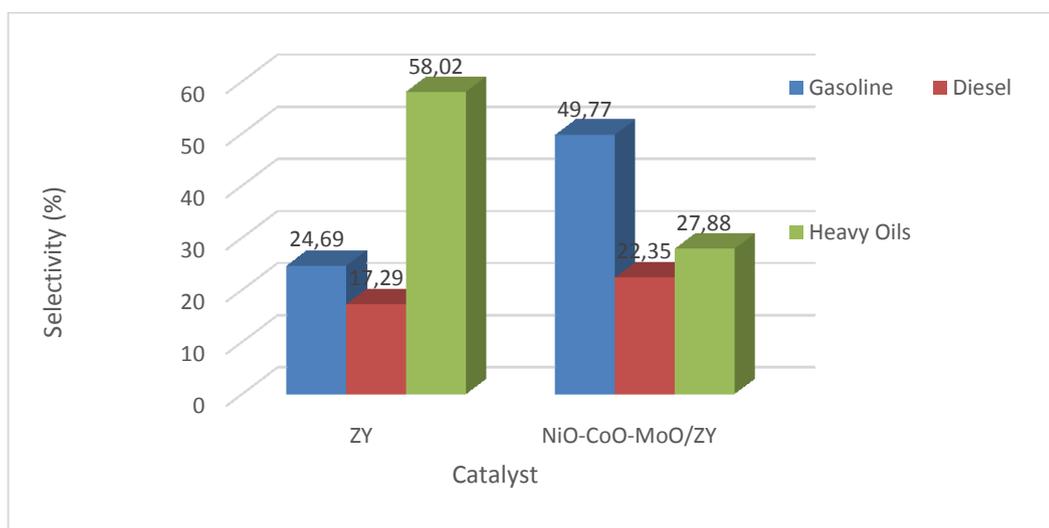

Figure 3. The selectivity of the catalyst for liquid yield

CONCLUSION AND PROSPECT

The following are several conclusion that can be driven from this research.

1. The impregnation of NiO, CoO and MoO metals on supporting ZY increased the acidity, specific surface area, average pore radius and total volume of the catalyst.

2. The activity of NiO-CoO-MoO/ZY catalyst is higher than ZY catalyst as can be seen on the liquid yield of both catalyst at 400 °C with catalyst : feed ratio of 0.5.

3. The selectivity of NiO-CoO-MoO/ZY catalyst for gasoline is higher compare to ZY catalyst. The selectivity of NiO-CoO-MoO/ZY catalyst for gasoline, diesel and heavy oil were 49.77 %, 22.35 % and 27.88 %, respectively.

This research describes the possibility of gasoline and diesel production from plant and food waste as the alternative fuel source. In future, we are planning to conduct more research on different catalysts, plants and waste to find the best formula in producing gasoline and diesel.

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