

EFFECT OF CALCINATION TEMPERATURE ON THE PROPERTIES OF SILICA-SUPPORTED Ni-Cu CATALYST FOR THE HYDROCRACKING REACTION OF USED COOKING OIL TO BIOFUEL

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ABSTRACT:

The hydrocracking reaction is a reaction that breaks hydrocarbon bonds from vegetable oil into shorter hydrocarbons so that they can be used as biofuel. Ni and Cu metals are quite commonly used in this reaction, where Ni metal functions as an active catalyst in the reaction, and Cu metal plays a role in increasing the stability of Ni metal from coke formation during the hydrocracking reaction. Mesoporous silica is used as a carrier for Ni and Cu metals because it has high stability and porosity. Calcination is one of the processes in the synthesis of mesoporous silica which aims to remove the template from the silica and plays a role in the formation of silica crystallinity and porosity. Changes in calcination temperature will affect the porosity and crystallinity of silica which causes differences in the distribution of Ni and Cu metals. The difference in the distribution of Ni and Cu metals affects the surface area of the active site which can influence the activity and selectivity of the catalyst in the hydrocracking reaction. This research aims to synthesize a Ni-Cu/Silica catalyst for the hydrocracking reaction of used cooking oil into biofuel. Mesoporous silica is synthesized by the hydrothermal method. Then, the Ni-Cu/Silica catalyst was synthesized by impregnating and reducing Ni and Cu metal into mesoporous silica. The Ni-Cu/Silica catalyst was then applied to the used cooking oil hydrocracking reaction to test its activity and selectivity. The results of characterization using FTIR show that the Ni-Cu/Silica catalyst has a vibration peak which indicates the presence of silanol (Si-O-Si) and siloxane (Si-OH) groups. Based on the acidity test, the SM-400, SM-500, and SM-600 catalysts have Lewis acid sites and Brønsted acid sites detected on the FTIR absorption peak with SM-500 having the highest acidity level. The XRD results show that the Ni-Cu/Silica catalyst has amorphous crystallinity and has Ni and Cu metal sites detected in the XRD diffractogram. The GSA results show that the SM-400, SM-500, and SM-600 catalysts have dominant pore sizes in the mesoporous region. The GC-MS results show that hydrocracking using a catalyst produces more product compared to hydrocracking without a catalyst and the SM-500 catalyst has the highest activity and selectivity compared to other variations of catalyst.

Keywords: Ni-Cu/Silica catalyst, mesoporous silica, hydrocracking reaction, calcination temperature

1. INTRODUCTION

Continuously rapid economic growth means the need for energy to support all sectors will increase. Despite this, Indonesia still relies heavily on petroleum to meet its energy needs. Petroleum derived from fossils is a non-renewable natural resource, so if it is used continuously, its availability will decrease until there is nothing left at all. Therefore, the

use of energy resources other than petroleum is increasingly being intensified, one of which is by using biofuels.

The cracking reaction is one method that is often used to process vegetable oil into biofuel. Cracking reaction methods are divided into two, namely thermal cracking and catalytic cracking. Catalytic cracking is more commonly used because the use of a catalyst can reduce the temperature required and also help the reaction run so that it is more energy efficient and increases the amount of product produced.

The catalyst used in the cracking reaction requires a carrier that functions as a catalyst site and increases the reaction surface area. Silica has a large surface area and porosity and has good stability. Therefore, silica is often used as a catalyst carrier [1]. One of the processes in the synthesis of mesoporous silica is the calcination stage. The template that forms the silica framework will evaporate and silica crystallinity will form at this stage so that the right calcination temperature can increase crystallinity and increase silica porosity [2].

Ni metal can be synthesized by dissolving its precursor metal $\text{Ni}(\text{NO})_3 \cdot 6\text{H}_2\text{O}$ using the impregnation method. The presence of Ni metal will increase the active site thereby increasing acidity and catalytic activity to obtain the desired product [3]. However, according to Liew & Hill [4], Ni metal has disadvantages, namely that it is easily deactivated by coke because its surface can be covered by coke as a by-product of the hydrocracking reaction. Therefore, it is necessary to add other metals that can increase the stability of the catalyst. The use of copper metal (Cu) can increase the stability and activity of the catalyst. This is because the addition of Cu metal will prevent the formation of coke on the catalyst surface and increase the distribution of Ni metal on the mesoporous silica surface [5].

Suseno [6; 7] have synthesized mesoporous silica using Tetraethylorthosilicate (TEOS) as a source of silica and *Cetyltrimethylammonium bromide* (CTAB) as a surfactant and water as a solvent in the hydrocracking reaction of palm oil to become biogasoline. Basso [2] has researched the effect of variations in calcination temperature on the characteristics of KIT-16 and SBA-15 mesoporous silica materials and found that variations in calcination temperature can affect the silica surface area and pore volume.

Based on the background that has been described, this research will use calcination temperature as an independent variation in the synthesis of the Ni-Cu/silica catalyst with TEOS precursor as the silica source and NaHCO_3 as the surfactant. The synthesized catalyst was then characterized using FTIR, XRD, and GSA. Then its catalytic activity was tested in hydrocracking using cooking oil into biofuel. The product obtained will then be characterized using GC-MS to determine the content of the product.

2. RESEARCH METHODS

Material

The materials used in this research are Tetraethyl orthosilicate (TEOS) (Merck), Sodium Bicarbonate (NaHCO_3) (Merck), Aquabides, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck), Oil cooking waste from frying.

Tool

The tools used in this research are a set of laboratory glassware (herma), Whatman 42 filter paper, magnetic bar, Teflon container, hydrothermal equipment, oven (Fischer scientific), 200 mesh sieve, spatula spoon, porcelain cup, hydrocracking reactor, analytical

balance (Ohaus), funnel (Herma), dropper pipette, measuring pipette (iwaki), mortar, hot plate (thunder), parafilm, pH paper (merck), pot, stative, desiccator, injection, thermometer, watch glass, condenser (pyrex), Gas Chromatography-Mass Spectrometry (GC-MS) instrument, X-Ray Diffraction (XRD) instrument (Quantachrome Instrument), FTIR Spectroscope (Perkin Elmer).

Silica Synthesis

Silica synthesis begins by dissolving 0.1848 g of sodium bicarbonate into 10 mL of aquabides, the solution is then stirred using a magnetic stirrer on a hot plate. The solution was then added with TEOS 2 mL drop by drop and heated until the solution temperature reached 80⁰C while continuing to stir using a magnetic stirrer. 1 mL of 2 M NaOH was then added to the solution drop by drop. The solution continues to be heated for approximately 2 hours until a white precipitate forms. Then the solution and precipitate were put into a Teflon container which was then put into a hydrothermal apparatus at a temperature of 100 ⁰C for 24 hours. The tool was then cooled overnight until it reached room temperature, then the sediment was filtered and rinsed using distilled water and the pH of the sediment was checked up to 7 using pH paper. The precipitate was then heated in an oven overnight at 80⁰C. Finally, the precipitate was calcined at varying temperatures of 400 ⁰C, 500 ⁰C, and 600 ⁰C for 4 hours with N₂ gas flowing through it.

Synthesis of Ni-Cu/Silica Catalyst

Catalyst synthesis begins by dissolving Ni(NO₃)₂.6H₂O and Cu(NO₃)₂.3H₂O in a 3:1 ratio of 5 using aquabides, then 2 g of silica was slowly dissolved into the Ni-Cu solution and stirred using a magnetic stirrer for 15 minutes. Then the mixture was shaken for 24 hours using a shaker. The mixture is evaporated on a hotplate until the water content disappears. The precipitate was then heated in an oven overnight at 80oC. The catalyst obtained 1 was then calcined at 500 ⁰C for 4 hours under N₂ gas. The catalyst was then allowed to stand until it reached room temperature, which was then reduced to 350 ⁰C for 3 hours using H₂ gas. The three catalysts were then named sequentially SM-400, SM-500, and SM-600 according to the variation in calcination temperature in silica synthesis.

Gravimetric Catalyst Acidity Test

The purpose of determining acidity using gravimetry is a method to determine the total acid sites that a catalyst has by using ammonia as the adsorbate base. The acidity of the catalyst itself is defined as the number of moles of NH₃ that are adsorbed in each gram of catalyst weight. The acidity test is carried out by weighing an empty porcelain cup as W₁. Then the catalyst is put into a cup and weighed as W₂. The cup is then placed in a desiccator, vacuumed, and supplied with ammonia gas for 24 hours. After that, the catalyst and cup samples were weighed again as W₃. The formula for the total acidity of the catalyst is described as follows:

$$\text{Total Acidity (mmol/g)} = \frac{W_3 - W_2}{(W_2 - W_1) \times Mr} \times 1000$$

Information:

- W_1 = weight of empty porcelain cup (g)
- W_2 = weight of cup + sample before adsorption(g)
- W_3 = weight of cup + sample after adsorption(g)
- Mr = molecular weight of ammonia (g/mol)

Characterization of Ni-Cu/Silica Catalyst

The Ni-Cu/Silica catalyst was characterized using several methods and instruments, such as a gravimetric acidity test to determine the number of acid sites contained in the catalyst. FTIR spectroscopy testing at wave numbers 500 - 4000 cm^{-1} to determine the functional groups of the catalyst. GSA Quantachrome Nova testing with a degradation temperature of 300 $^{\circ}\text{C}$ to determine surface area, pore diameter, and adsorption-desorption isotherms. Lastly is testing with XRD with an angle calculation of $2\theta = 20^{\circ} - 80^{\circ}$ with operating conditions of CuK α radiation of 0.1540 nm to determine the crystallinity structure of the catalyst.

Application of Catalysts in Used Cooking Oil Hydrocracking to Biofuels

Cracking begins by weighing the catalyst and used cooking oil in a ratio of 1:100. Then the catalyst is put into the catalyst reactor column, while the used cooking oil is put into the evaporator column in the reactor. The reactor was then supplied with H $_2$ gas at a flow rate of 20 mL/minute. The reactor containing the catalyst is heated first at a temperature of 350 $^{\circ}\text{C}$. Then the reactor containing used cooking oil was heated at 400 $^{\circ}\text{C}$ for 1 hour. The product obtained is in the form of a liquid which is then weighed and characterized using GC-MS to determine the components of the biofuel produced.

3. RESULTS AND DISCUSSION

Characterization of Ni-Cu/Silica Catalysts using FTIR Spectroscopy

The aim of characterization using FTIR is to identify the functional groups present in the catalyst. Apart from that, FTIR functions as an acidity analysis, namely, to determine the presence of Bronsted-Lowry acid and Lewis acid absorption peaks on the SM-400, SM-500, and SM-600 catalysts after gravimetric method treatment.

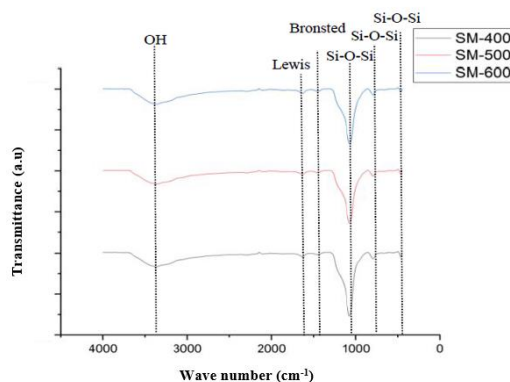


Figure 1. FTIR spectra of SM-400, SM-500, and SM-600 catalysts

In Figure 1, it is seen the presence of siloxane groups on the SM-400, SM-500, and SM-600 catalysts, namely in the wave number range of 1073 cm^{-1} , 1073 cm^{-1} , and 1071 cm^{-1} . The vibration band in the wave range of 1635 cm^{-1} is the absorption band of water molecules, while the wide band that appears at wave numbers $3450 - 3470\text{ cm}^{-1}$ is the OH stretch of water molecules (H-O-H) and the overlapping Si-OH band of the silanol surface with water molecules (SiOH...H₂O) [8].

Deconvolution of FTIR spectra peaks made using *ftvik* in the wave number range $1390 - 1690\text{ cm}^{-1}$ peaks in the range $1450 - 1500\text{ cm}^{-1}$ which aim to determine the presence of Brönsted acid sites and Lewis acid sites are in the wave number range $1600 - 1650\text{ cm}^{-1}$ on the Ni-Cu/silica catalyst [9]. The Brönsted peak areas on the SM-400, SM-500, and SM-600 catalysts were detected at wave numbers 1478 , 1458 , and 1452 cm^{-1} , respectively. The Brönsted acid site peak indicates that there is absorption of NH bonding found in ammonia. The peak is caused by ammonia being protonized by the silanol groups on the catalyst.

The main peaks of the Lewis acid sites at SM-400, SM-500, and SM-600 are respectively at wave numbers 1642 cm^{-1} , 1643 cm^{-1} , and 1645 cm^{-1} . The presence of a peak indicates that there is NH bonding absorption in ammonia. The peak is caused by transition metals which have empty orbitals in the d subshell which can be electron acceptors such as ammonia which has two lone pairs of electrons.

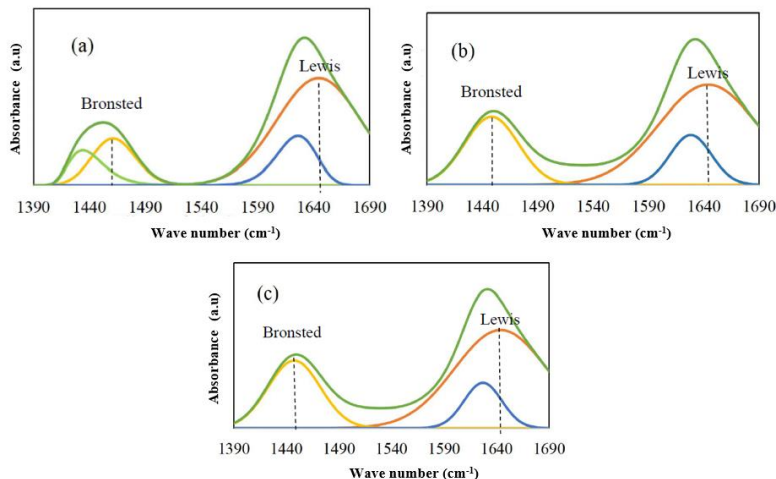


Figure 2. Ammonia adsorption on Brönsted acid and Lewis acid sites in (a) SM-400, (b) SM-500, and (c) SM-600

Total Acidity of Ni-Cu/Silica Catalyst

Catalyst acidity is the ability of each gram of catalyst to adsorb several moles of acid. One way to determine the acidity of a catalyst is by the gravimetric method, which is a measurement based on the difference in weight of the catalyst before and after adsorbing the Lewis base. The acidity level indicates the number of active sites contained in a catalyst, so if the catalyst's acidity level is high, the catalytic activity will also be greater [6].

Table 1: Ni-Cu/Silica Catalyst Acidity

Catalyst	Acidity (mmol/g)
SM-400	2,187
SM-500	3,090
SM-600	2,200

Table 1 shows that SM-500 has the highest acidity level. This is because SM-400 was only given a calcination treatment at 400⁰C, so the structure was not fully formed, whereas SM-600 was given a calcination treatment at 600⁰C, so due to the temperature being too high, the silica structure collapsed so that the active site became reduce.

Characterization of Ni-Cu/Silica Catalysts using XRD

The aim of catalyst analysis using X-Ray Diffraction is to determine the level of crystallinity and determine the presence of Ni and Cu metals because of the reduction of NiO and CuO.

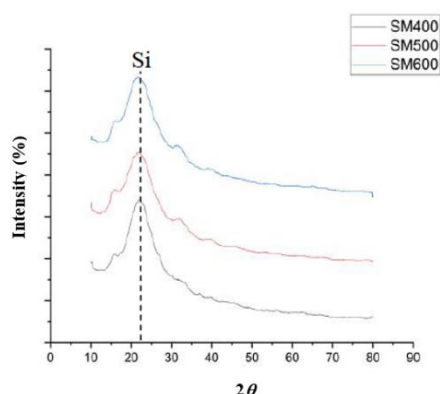


Figure 3. Image of diffractogram of SM-400, SM-500, and SM-600 catalysts

Figure 3 shows that the three graphs have peaks that widen at angle $2\theta = 23^{\circ}$ which indicates that the three samples have amorphous properties [10]. The XRD diffractogram can also detect the presence of Ni, Cu, as well as NiO and CuO metals but the intensity, is very small compared to the silica diffractogram, and the metal peaks are close to each other making the Ni, Cu, NiO, and CuO peaks difficult to see, so it is necessary to carry out XRD deconvolution with the aim of to detect the presence of Ni and Cu metals as well as NiO and CuO on the XRD diffractogram.

Figure 4 shows the peak at $2\theta = 44.50^{\circ}; 51.87^{\circ}; 76.37^{\circ}$ (COD No. 9008509) and $2\theta = 43.47^{\circ}$ (COD No. 5000216). The presence of NiO and CuO was also detected in Figure IV.5 which was characterized by the peak at $2\theta = 37.28^{\circ}; 43.29^{\circ}; 62.91^{\circ}$ (COD No. 1010093) and $2\theta = 35.41^{\circ}; 35.54^{\circ}$ (COD No. 7212242). The presence of NiO and CuO indicates that the reduction process of NiO and CuO has not been completely reduced to Ni and Cu.

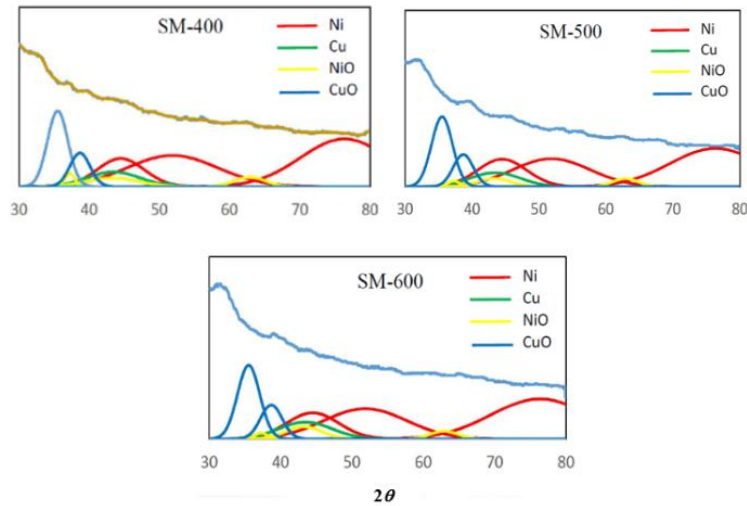


Figure 4. XRD deconvolution of SM-400, SM-500, and SM-600 catalyst

Characterization of Ni-Cu/Silica Catalysts with GSA

Table 2: Size distribution of particles

Catalyst	Surface area (m ² /g)	Pore Volume (cc/g)	Radius size Average Pore (nm)
SM-400	185,285	0.4163	4.49332
SM-500	142,830	0.3591	5.02768
SM-600	129,014	0.3170	4.91342

Table 2 shows that SM-400 has the largest total surface area, this is due to the lack of distribution of Ni and Cu metals in the impregnation and reduction processes so that there are still many pores that are not blocked by metal, which causes the surface area to not decrease significantly.

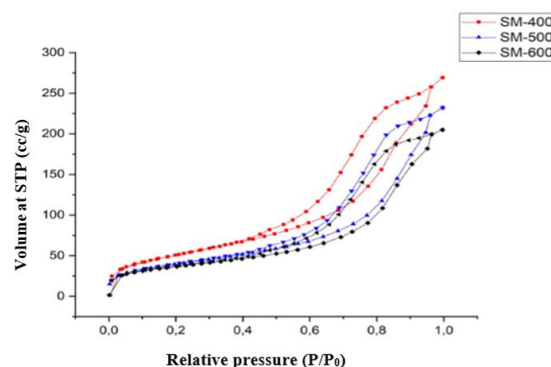


Figure 5. Catalytic Nitrogen Gas Adsorption- Desorption Isotherm Curve SM-400, SM-500, and SM-600

The isotherm graph is a graph that shows the relationship between adsorbed and desorbed nitrogen gas at STP and the relative pressure of the gas at constant temperature (P/P_0). Figure 5 shows that all catalysts follow the IV curve model, where this model is characterized by a sharp slope at relatively high pressure.

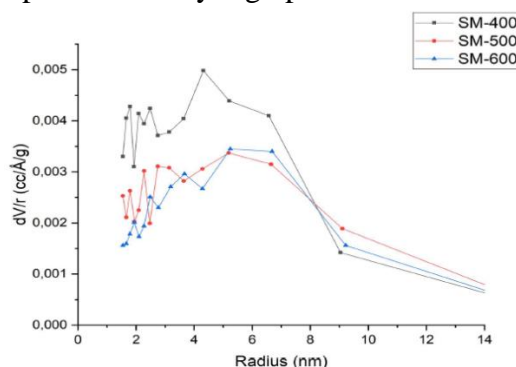


Figure 6. Pore Size Distribution Curves of SM-400, SM-500, and SM-600 Catalysts

Figure 6 shows that the pore distribution of the SM-400, SM-500, and SM-600 catalysts is in the range of 1.53 - 168.62 nm. The SM-400 catalyst is dominant at 4.31nm, SM-500 is dominant at 5.19 nm, and SM-600 is dominant at 5.25 nm. This shows that the silica-bearing catalyst has dominant pores of mesopore size. This is reinforced by the percentage distribution of pores shown in Table 3.

Table 3: Pore Size Distribution Percentage

Catalyst	Intensity(%)		
	Micropores	Mesoporous	Macropores
SM-400	-	99.96	0.04
SM-500	-	99.95	0.05
SM-600	-	99.94	0.06

In Table 3, the SM-400, SM-500, and SM-600 catalysts have high mesopore size pore percentages, namely 99.96; 99.95; and 99.94, while the three catalysts do not have pores with a micropore size and a macropore size with a percentage of 0.04; 0.05; 0.06. Based on this, it shows that the silica carrier in the catalyst is mesoporous silica. This statement is also by the interpretation of the adsorption-desorption isotherm curve in Figure 5.

Characterization of Hydrocracking Products using GC-MS

Catalytic activity is the amount of conversion or the amount of product produced compared to the amount of reactant used during a certain reaction time. SM-400, SM-500, and SM-600 catalysts were used in the hydrocracking reaction of used cooking oil to test their activity. Tests were carried out using 10 g of used cooking oil as initial feed, and 0.1 g of catalyst. Then the catalyst is heated at a temperature of 350 °C and the oil at a temperature of 400 °C for 1 hour with N₂ gas flowing through it. The function of the N₂ gas flow is to carry feed steam to the condenser and to prevent the presence of oxygen which causes the formation of other products such as H₂O, CO, and CO₂ [11].

The activity of a catalyst can be determined by calculating the conversion and selectivity of the biofuel produced. Catalyst selectivity is the ability of a catalyst to determine the formation of a certain type of product. Catalyst selectivity in biofuels is grouped into three based on the number of carbon chains, namely gasoline (C5 - C12), kerosene (C13 - C15), and diesel (C16 - C18).

Based on the results of the GC-MS analysis shown in Table 4, the SM-500 catalyst has the highest conversion rate and total biofuel, namely 98.94, and 69.93. This is because SM-500 has a large pore volume, and the highest acidity level so most used cooking oil is converted into biofuel.

Apart from that, hydrocracking without using a catalyst (thermal) even though it has a high total biofuel, has the lowest gasoline fraction, namely 29.54, and the lowest total conversion, namely 48.83. This is due to the absence of a catalyst which makes the hydrocracking reaction only depend on thermal. So the product obtained is lower than using a catalyst.

Table 4: Distribution of Used Cooking Oil Hydrocracking Products

Treatment	Biofuel Selectivity (%)			Total Biofuels	Conversion Total
	Gasoline (C5-C12)	Kerosene (C13-C15)	Diesel (C16-C18)		
Thermal	29.54	27.8	37.11	94.45	48.83
SM-400	37.86	24.31	20.72	82.86	64.09
SM-500	38.68	24.35	35.91	98.94	69.93
SM-600	49.53	40.39	1.97	91.89	50.24

Table 5: Compound Composition of Biofuel Products (in %)

	SM-400	SM-500	SM-600
Paraffin	52.34	40.04	58.88
Olefins	41.60	48.82	28.50
Cyclical	4.57	4.21	10.69
Aromatic	0.90	-	1.87

Table 5 shows that SM-400 and SM-600 have more paraffin compounds than SM-500 so the amount of paraffin products increases as the silica pore size decreases. The SM-500 catalyst has the most olefin products, so the amount of olefin products will increase as the pore size increases.

Relationship of Acidity Level to Selectivity and Catalyst Activity

Based on Figure 7, SM-500 has the highest level of selectivity and activity, namely 98.94 % and 69.93 %, which is directly proportional to the highest acidity level of SM-500, namely 3.09 mmol/g. This shows that the catalyst activity will increase as the acidity of the catalyst increases.

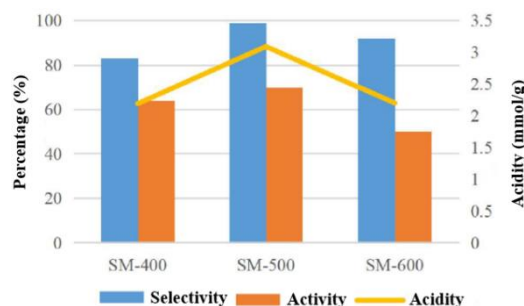


Figure 7. The relationship between acidity level and selectivity and activity

High acidity levels indicate active catalyst sites on many catalyst surfaces. High catalyst active sites will increase the total reaction taking place thereby increasing the amount of product formed and catalyst activity in the hydrocracking reaction.

Relationship of Pore Size to Hydrocracking Products

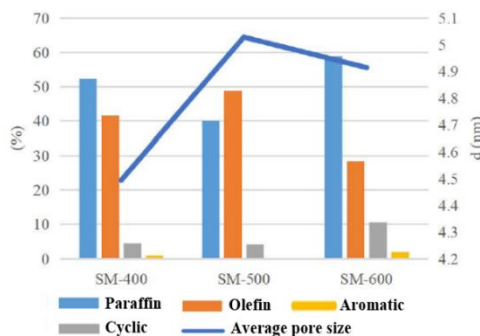


Figure 8. The relationship between average pore size and type of hydrocracking product

Based on Figure 8, the SM-500 catalyst has the largest average pore size compared to other catalysts. The SM-500 catalyst also has the largest olefin-type products and the fewest paraffin-type products among the other catalysts. This is because SM-500's pores are large so that olefin products can escape before the hydrolysis reaction occurs to become paraffin products.

4. CONCLUSION

The Ni-Cu/Silica catalyst has been successfully synthesized with varying calcination temperatures of 400, 500, and 600 °C. Variations in calcination temperature can affect the crystallinity and porosity of silica, thus affecting the distribution of Ni and Cu metals which leads to differences in the level of activity and selectivity of the catalyst in the hydrocracking reaction of used cooking oil into biofuel and the highest conversion was produced by the SM-500 catalyst, namely 69.93 %, and product selectivity of 98.94% with product components consisting of 38.68 % gasoline, 24.35 % kerosene, and 35.91% diesel.

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