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COMPARATIVE STUDY OF Co/MESOPOROUS SILICA AND Co-NH_2/MESOPOROUS SILICA CATALYSTS ACTIVITY IN WASTE COCONUT OIL HYDROCRACKING

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ABSTRACT

Production of Cobalt/Mesoporous silica (Co/MS) and Cobalt-NH_2/Mesoporous silica (Co-NH_2/MS) catalysts had been carried out where the Co metal content was 2 wt.% against mesoporous silica. The deposition of Co metal on mesoporous silica was executed using the wet impregnation method. The functionalization of $–NH_2$ from the 3-APTMS compound was done by the grafting method. Both catalysts were compared their catalytic activity and selectivity through the hydrocracking process of waste coconut oil into biofuel (gasoline and diesel fractions). The result showed that the Co/MS-2% catalyst had a larger surface area (23.2191 m^2/g) than the Co-NH_2/MS-2% catalyst (17.7923 m^2/g). The Co/MS-2% catalyst produced slightly more liquid product (77.008 wt.%) than Co-NH_2/MS-2% (76.767 wt.%). Meanwhile, the Co-NH_2/MS-2% catalyst produced more biofuel (74.54%) than the Co/MS-2% catalyst (70.86%). Furthermore, the selectivity of the catalyst against the gasoline fraction (40.2643 wt.%) was obtained by the Co-NH_2/MS-2%, while the selectivity of the catalyst against the diesel fraction (17.7118 wt.%) was produced by Co/MS-2%.

Keywords: Cobalt, NH_2, Mesoporous Silica, Hydrocracking, Waste Coconut Oil

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INTRODUCTION

The fossil energy crisis is one of the main problems that is faced by the world today. The increase of motor vehicles that use gasoline and diesel as fuel from year to year is the main cause. One alternative energy as a substitute for fossil fuels is fuel from renewable sources such as plants and animals. The product of this fuel is often mentioned as biofuel.

Indonesia is one of the biggest producers of coconut oil. Coconut oil that is used repeatedly will produce waste coconut oil. Therefore, waste coconut oil is one of the potential raw materials for the production of biofuel in Indonesia. The oil was developed to maintain food stability and to reduce it in the environment. The oil contains the main compound of free fatty acids.[1] The largest content of free fatty acids (FFA) includes lauric acid, myristic acid, palmitic acid, and oleic acid.[2] This FFA has a large molecular size so that, to convert it into biofuel, mesoporous material is needed in the process of adsorption and separation of molecules.[3]

Research on mesoporous materials has become a major topic in the field of catalyst[4] and adsorption.[5] The main material in the formation of mesoporous materials includes silica, carbon, alumina, and others. One of the most commonly used materials is silica inasmuch as it has characters such as thermally stable, chemically inert, safe, non-toxic, abundant, and inexpensive.[6] Silica-based mesoporous materials commonly utilized include MCM-41[7], SBA-15[8], and mesoporous silica (MS).[9] The formation of these materials is needed a template that usually comes from surfactants.[10] The most well-known template as a mesopore structural directing agent is CTAB.[11] CTAB is a quaternary ammonium compound that is not sensitive to pH or amine.[12] This surfactant family has been widely studied in the synthesis of MS.

Although MS has good adsorption ability, it still has low catalysis ability. This is because this material has a low acidity value which is only from the Bronsted acid site. The acidity value of the catalyst material is a very important property for its catalytic activity. Therefore, to increase the acidity value in

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MS, the transition metal is loaded on the carrier material because it has the empty p orbital as a Lewis acid site.[13] The cobalt metal has been widely used because it has Lewis acid sites and three unpaired orbitals which make it easier to capture hydrogen radicals from hydrogen gas homolysis during the hydrocracking process. Moreover, it is still active by carbon deposition after hydrocracking.[14] Modification of the -NH_2 group aims to avoid the metal leaching on MS.[15] This group includes an active site of amino-silane that is strongly bound to the carrier. Besides, this group can also be an adsorbent to capture FFA in waste coconut oil because of its base property.[16]

Based on this description, this study aims to synthesize Co/MS and Co-NH_2/MS and compare their catalytic activity in the conversion of waste coconut oil. Mesoporous silica was synthesized from Lapindo mud silica with CTAB as a mesoporous template.

EXPERIMENTAL

Materials and Methods

Mesoporous silica (material character include total volume 0.9326 cc/g, pore diameter 3.280 nm, surface area 291.444 m^2/g) was obtained by Trisunaryanti *et al.* research,[17] cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \bullet 6H_2O$) by Merck, 3-APTMS (3-amino-propyl trimethoxy silane) compound, hydrogen gas, nitrogen gas, methanol, toluene, and waste coconut oil.

Synthesis of Co/MS-2% Catalyst

This synthesis was carried out through the wet impregnation method. The precursor salt of Co $(NO_3)_2 \bullet 6H_2O$ (2 wt.% of Co metal content) was mixed with MS in the beaker. This solution was stirred overnight at room temperature. The solution was evaporated and dried in an oven at 100 °C overnight. The generated solid was calcined with nitrogen gas at a flow rate of 20 mL/min for 2 hours at 500 °C then reduced with hydrogen gas for 3 hours at same temperature to produce a Co/MS-2% catalyst. This catalyst was characterized using XRD and SAA.

Synthesis of Co-NH_2/MS-2%

This catalyst was prepared via the grafting method. Firstly, the 3-APTMS was refluxed in 20 mL toluene at 90 °C for 20 minutes. The 3-APTMS (5 wt.%) solution was then added with Co/MS-2% and refluxed at 90 °C for 5 hours. The reflux result was centrifuged at 200 rpm for 20 minutes. The produced solid was then rinsed using toluene once and methanol twice. The solid was dried in an oven at 50 °C overnight to produce Co-NH_2/MS-2%. This catalyst was examined by XRD and SAA.

Catalytic Activity Test

The weight ratio of waste coconut oil (feed) and catalyst used was 50:1 respectively. The Co/MS-2% and Co-NH_2/MS-2% catalysts were compared for the activity. The catalytic activity test was done in a stainless steel reactor from a semi-batch system at 450 °C for 3 hours under the flow of hydrogen gas. Hydrocracking products consist of liquid, gas, and coke. The liquid was then investigated by GC-MS to confirm the compounds contained in it. The catalyst selectivity to gasoline, diesel, and other fractions can be calculated from the %area GC-MS. The pore images of catalysts before and after hydrocracking catalysts were taken by TEM.

Detection Method

The crystallinity of catalysts was measured by X-ray Diffractometer (XRD, Philips X-pert Powder Diffractometer), Surface Area Analyzer (SAA, St 2 on NOVA touch 4LX) was used to evaluate the textural parameters (surface area, pore-volume, and pore diameter) of the sample. The liquid from the conversion of waste coconut oil was tested using Gas Chromatography-Mass Spectrophotometer (GC-MS, Shimadzu QP2010S). The pore structure was photographed by a Transmission Electron Microscope (TEM, JEM-1400).

RESULTS AND DISCUSSION

Analysis of X-Ray Diffraction

The XRD spectra of (a) Co/MS-2% and (b) Co-NH_2/MS-2% catalysts are shown in Fig.-1. As we know, the MS does not show sharp diffraction peaks. This is because the MS has an amorphous structure so that it only shows a broad peak in the XRD spectra. The broad peak of MS is in the 2θ range of 15-30°. This

peak was also observed for all catalysts related to the amorphous silica phase including Co/MS-2% and Co-NH_2/MS-2%. In the Co/MS-2% catalyst, the loading of Co metal in the MS did not result in a new peak from its crystal field. This is because the Co metal impregnated into the MS was very low of 2 wt.%. This is a similar case with previous studies that the intensity of the Co/MCM-41-10% catalyst is broader than other metal catalysts.[18-19] Meanwhile, the functionalization of the organic molecule of the amine group in Co-NH_2/MS-2% also did not produce a new peak. This is also agreed with cases from previous reports even in wide angle[20] and small angle[21-24] XRD spectra did not show new peaks in NH_2/MCM-41. It has been declared that the peak intensity of XRD depends on the contrast of electronic scattering between the inorganic amorphous silica wall and the organic phase located within the porosity.[25] Also, the absence of other peaks shows the loss of organization during the grafting process. However, in the XRD spectra, the peak intensity of Co-NH_2/MS-2% was higher than Co/MS-2%. Therefore, it can be concluded that both the development of Co and the functionalization of the -NH_2 group in MS, the amorphous structure of silica was still maintained.

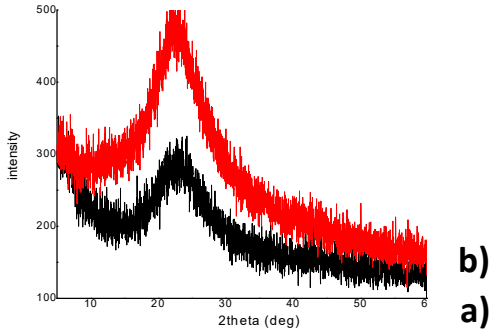

Fig.-1: XRD Spectra of (a) Co/MS-2% and (b) Co-NH_2/MS-2%

Analysis of Surface Area Analyzer

The adsorption-desorption isotherms of N_2 gas on Co/MS-2% and Co-NH_2/MS-2% catalysts are shown in Fig.-2. Both Co/MS-2% and Co-NH_2/MS-2% catalysts showed an IV isotherm pattern with H4 hysteresis type according to the IUPAC rule. A similar case was stated by Li *et al.*[26] in the synthesis of Co/MCM-48 and Jin *et al.*[27] in the synthesis of NH_2/MCM-41. However, the Co/MS-2% catalyst showed that the type IV isotherm pattern was not fit. This is possible because the analysis process is not good or the desorption running process is less than perfect. To, the existence of the same isotherm pattern on both catalysts indicates that mesoporous material has formed. The functionalization of the -NH_2 group in Co/MS-2% also did not have a significant change in the isotherm pattern of the Co-NH_2/MS-2%. The H4 hysteresis type also provides information that the resulting material pores are in the form of narrow parallel pores relatively uniform as wormholes-like pores.

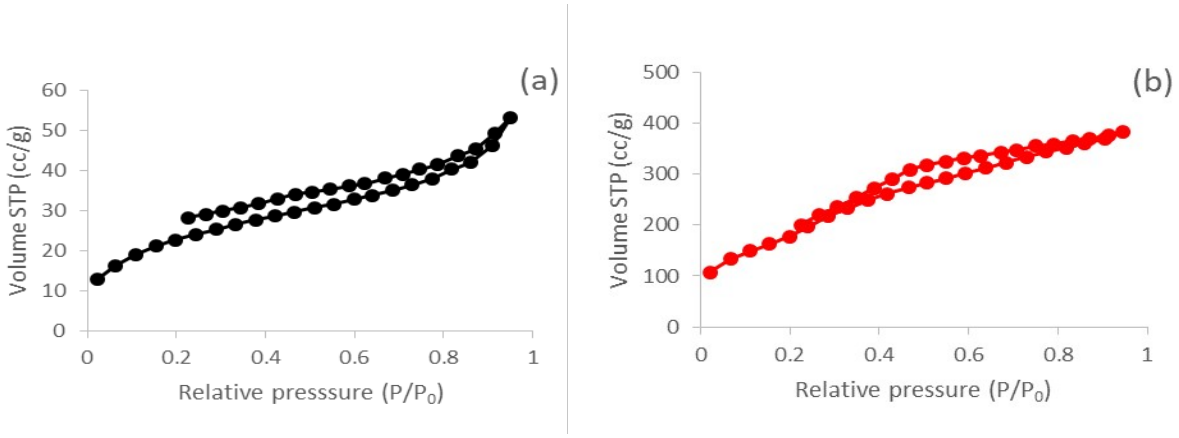

Fig.-2: Adsorption–desorption Isotherm N_2 on (a) Co/MS-2% and (b) Co-NH_2/MS-2%

The pore size distribution on the Co/MS-2% and Co-NH_2/MS-2% catalysts is shown in Fig.-3. In the graph, both catalysts exhibit a close range of pore size distribution between 3-9 nm. However, the average pore diameter of Co/MS-2% and Co-NH_2/MS-2% was around 3 nm, respectively 3.2703 and 3.5738 nm. This pore diameter was not different significantly, also was the total pore volume. This supports the previous analysis of XRD spectra and BET isotherms. Meanwhile, the surface area of the Co-NH_2/MS-2% was slightly smaller than the Co/MS-2% as listed in Table-1. The decrease in surface area is another proof of the success of NH_2 functionalization in the MS pore wall.

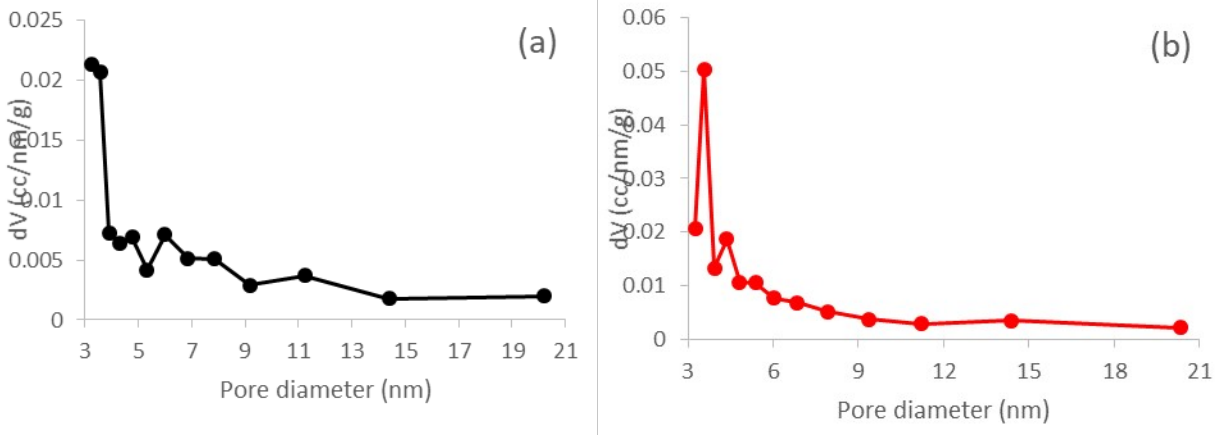

Fig.-3: Pore Size Distribution on (a) Co/MS-2% and (b) Co-NH_2/MS-2%

Table-1: Textural Character of Catalysts

Catalyst	Total Pore Volume (cc/g)	Pore Diameter (nm)[a)]	Surface Area (m^2/g)[b)]
Co/MS-2%	0.0826	3.2703	23.2191
Co-NH_2/MS-2%	0.0885	3.5738	17.7923

Notes: [(a)] Pore diameter calculated based on desorption BJH method
[(b)] Surface area calculated based on adsorption BJH method

Analysis of Gas Chromatography-Mass Spectrophotometry

The produced catalysts were used in the hydrocracking process of waste coconut oil to compare their catalytic activity. Based on Table-2, there were three fractions of hydrocracking products including liquid, gas, and solid (coke). The catalyst Co/MS-2% produced a slightly more liquid fraction than Co-NH_2/MS-2%. This is because the specific surface area of the Co/MS-2% catalyst was also slightly larger. Both of them also produced gas and coke fractions because they have relatively similar catalyst characteristics.

Table-2: Hydrocracking Product of Waste Coconut Oil

Catalyst	Product Conversion (wt.%)		
	Liquid[(a)]	Gas[(b)]	Coke[(c)]
Co/MS-2%	77.008	21.286	1.706
Co-NH_2/MS-2%	76.767	21.590	1.642

Notes: [(a)] Liquid calculated from (liquid weight/feed weight) x 100%
[(b)] Coke calculated from (coke weight/feed weight) x 100%
[(c)] Gas calculated from 100% – (liquid + coke)

The liquid product was evaluated using GC-MS to find out the compounds contained in it. Based on Table-3, waste coconut oil consisted of 3 groups of hydrocarbon compounds (C_5-C_{12}, C_{13}-C_{17}, and >C_{18}) and organic compounds include alcohol, ketones, carboxylic acids, and esters. Hydrocracking using Co-NH_2/MS-2% catalyst produced more hydrocarbon compounds (biofuel) than Co/MS-2% catalyst as shown in Table-4. This is because this catalyst had two active sites namely Co and -NH_2 which work simultaneously (bifunctional). The –NH_2 group is an adsorbent to capture FFA in waste coconut oil and convert them into long-chain hydrocarbons, while Co catalyzes to convert long-chain hydrocarbons to

shorter chain hydrocarbons.[28] Therefore, the content of organic compounds with the Co/MS-2% catalyst was slightly more because this catalyst was not supported by the presence of the NH_2 group.

Table-3: Compounds in the Liquid Product based on GC-MS Results

Catalyst	Compounds in the Liquid Product (%Area)				
	C_5-C_{12}	C_{13}-C_{17}	>C_{18}	Organic Compound	Total
Co/MS-2%	47.87	23.00	3.82	25.31	100.00
Co-NH2/MS-2%	52.45	22.09	4.65	20.82	100.01

To confirm the selectivity in biofuel, it can be seen in the amount of gasoline and diesel fractions. Gasoline is a hydrocarbon with a carbon number of C_5-C_{12}, while diesel is a hydrocarbon with a carbon number of C_{13}-C_{17}. Based on Table-4, the two catalysts produced more products of the gasoline fraction than the diesel fraction. However, if the two catalysts are compared to a deeper level, the Co-NH_2/MS-2% catalyst is more selective towards gasoline products, while the Co/MS-2% catalyst is more selective towards diesel products.

Table-4: Catalyst Selectivity in the Liquid Product

Catalyst	Selectivity in the liquid product (wt.%)			Percentage of Biofuel in Liquid Product[d)]
	Gasoline Fraction[a)]	Diesel Fraction[b)]	Total Biofuel[c)]	
Co/MS-2%	36.8637	17.7118	54.5755	70.87%
Co-NH_2/MS-2%	40.2643	16.9578	57.2221	74.54%

Notes: [a)] Gasoline fraction calculated from (%area GC C_5-C_{12} / %relative total) x liquid product
[b)] Diesel fraction calculated from (%area GC C_{13}-C_{17} / %relative total) x liquid product
[c)] Total biofuel calculated from (gasoline fraction + diesel fraction)
[d)] Percentage of biofuel in liquid product calculated from ((total biofuel/liquid product) x 100%)

Analysis of Transmission Electron Microscopy

TEM analysis was carried out to determine the pore shape of the catalyst produced. Based on Fig.-4, the Co/MS-2% catalyst before hydrocracking had a pore structure like a wormhole. This is consistent with the H4 hysteresis type described before. Meanwhile, after the catalyst has been used for the hydrocracking process of waste coconut oil, the pores in the material were almost completely lost. This is because the catalyst was blocked by coke trapped in the pore of the material after hydrocracking[29] as shown in Fig.-4.

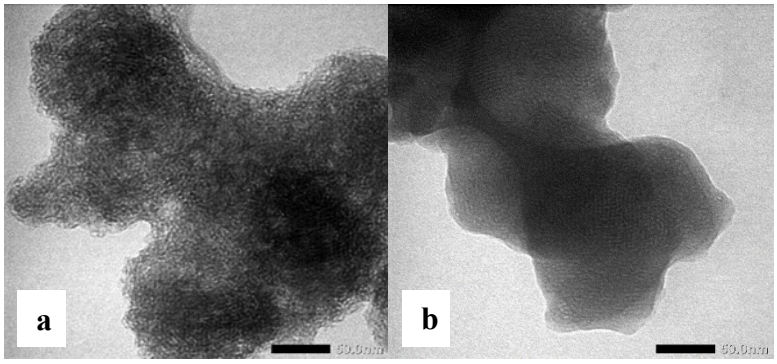

Fig.-4: TEM Images of Co/MS-2% (a) before and (b) after hydrocracking

CONCLUSION

The Co/MS-2% catalyst had a slightly larger surface area (23.2191 m^2/g) than the Co-NH_2/MS-2% catalyst (17.7923 m^2/g). This character caused the liquid product generated from the waste coconut oil hydrocracking process through the Co/MS-2% catalyst slightly more (77.008 wt.%) than the Co-NH_2/MS-2% catalyst (76.767 wt.%). However, the Co-NH_2/MS-2% catalyst produced more biofuel products (gasoline and diesel fractions) than Co/MS-2% because it had two active sites that work simultaneously. Based on the selectivity result of the catalyst, the Co-NH_2/MS-2% catalyst was more selective towards gasoline, while the Co/MS-2% catalyst was more selective towards diesel.

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