



Synthesis of Co, Ni, and Pd Metals Supported on Mesoporous Carbon as Catalysts for Hydrocracking of Waste Lubricant

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Abstract : Synthesis of Co, Ni, and Pd metals supported on mesoporous carbon as catalysts for hydrocracking of waste lubricant has been conducted. The mesoporous carbon (MC) was synthesized using SBA-15 as a hard template and gelatin from bovine bone as carbon precursor. The carbon was treated at temperature of 900 °C. The MC was characterized by Gas Sorption Analyzer (GSA), and Transmission Electron Microscope (TEM). The Co, Ni and Pd were loaded onto the MC by impregnation method produced the Co/MC, Ni/MC and Pd/MC catalyst, respectively. The catalysts were characterized by Gas Sorption Analyzer. The activity of catalysts were tested in hydrocracking of waste lubricant. The result showed that the MC had a bimodal pore diameter distribution majority at around 3.85 and 6.58 nm with high surface area, and pore volume of 743.22 m²/g, and 1.17 cm³/g, respectively. The Co/MC, Ni/MC and Pd/MC catalyst had surface area of 702.68 m²/g, 636.19 m²/g, and 644.98 m²/g, respectively. The Pd/MC catalyst showed the highest catalytic activity in producing liquid fraction of 61.20 wt.% which consists of gasoline and diesel fractions of 52.33 and 8.87 wt.%, respectively.

Keywords : Carbon, Cobalt, Nickel, Palladium, Catalyst, Hydrocracking.

Introduction

Fossil fuels is one of non-renewable sources that consumed by people as a main source of energy for cooking activity, transportation, and industry. In order to find an alternative energy source for replacing fossil fuels, a variety ways had been taken such as by converting waste such as plastic¹, palm oil², and lubricants³ into fuel fraction.

In recent decades, researchers have emphasized the development of refining techniques based on cheaply available feedstocks, such as coal, low grade petroleum oil or wax⁴, heavy oil⁵, waste material⁶. These feedstocks are used for the synthesis of many petroleum products including transport fuels and other low boiling point liquid products, plastics, synthetic fibers, solvents, fertilizers, pesticides, detergents, lubricants, fine chemicals, pharmaceuticals, waxes, and coke^{7,8}.

The waste lubricants could be converted into either a fuel fraction of gasoline (C₅-C₁₂) or diesel fractions (> C₁₂) by hydrocracking process. Catalysts which are widely used for hydrocracking process are transition metals. Cobalt⁹, Ni¹⁰, Pd¹¹ and Pt¹²⁻¹⁵ are the most common transition metals that have high activity and selectivity for the hydrocracking. However, if the metals are used as a pure metal catalyst, sintering and agglomeration of the metals will be occurred. Therefore, metal transition catalyst was usually supported in a solid, such as zeolite, clay and other porous materials. Mesoporous carbon was one of the material that was generally

used as a catalyst¹² or the catalyst supported^{13,14}. Caused by its unique properties i.e. high surface areas, large pore diameter and volumes, as well as good chemical and thermal stability^{15,16}.

The synthesis of MC had been successfully carried out using bovine bone gelatin as a carbon precursor^{17,18}. To investigate the characters of transition metal catalyst supported on mesoporous material, the authors undertaken impregnation of Co⁹, Ni¹⁰, Pd¹¹ and Pt¹²⁻¹⁵ metals onto MC. The catalyst were used for hydrocracking of waste lubricant to produce fuel fractions (gasoline and diesel fraction).

Experimental

Materials

Bovine bone from Pakem market in Sleman, glacial acetic acid, sodium hydroxide, hydrofluoric acid, ethanol, sulfuric acid, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, PdCl₂, potassium iodide, sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O), and ammonia analytical grade were obtained from E-Merck (Germany). All materials used were analytical grade and used without further purification.

Instrumentation

Nitrogen adsorption-desorption technique was used to determine pore volume, pore size distribution and specific surface area of catalysts using a Quantachrome NOVA WIN2 version 11.0 instrument. Fourier transform infrared (FTIR) measurements were recorded on KBr pellets with Shimadzu IR Prestige-21. Fourier transform infrared (FTIR) spectrometer equipped with mercury-cadmium-telluride (MCT) detector. Microscopy images were acquired using a JEOL-1400 transmission electron microscope (TEM) with a tungsten cathode operated at 120 kV. The total acid sites amount (acidisty) was calculated by gravimetric method based on the amount of NH₃ base vapor adsorbed by acid sites in a solid material.

Extraction of gelatin

The extraction of gelatin was carried out according to Trisunaryanti *et al.*¹⁶⁻¹⁸ with slight modification. The gelatin was obtained from Javanese bovine bone. The bovine bone was pretreated with 4% glacial acid (1:2 w/v) for 9 days that replaced every 3 days. The sample was pretreated with 0.1 M sodium hydroxide (1:6 w/v) for 24 h followed by treating with 1.0 M hydrochloric acid (1:3 w/v). The extracted gelatin was dissolved in distilled water at 100 °C for 5 h (1:6 w/v). The filtered using a Whatman 42 filter paper followed by evaporated at 70 °C.

Synthesis of mesoporous carbon (MC)

The synthesis of mesoporous carbon was done according to Ulfa^{17,18} with slight modification. Mesoporous carbon was synthesized using SBA-15 silica material as a template and gelatin as the carbon precursor. The silica was subjected for impregnation with gelatin solution. Ten grams of SBA-15 was added into a solution prepared by dissolving 10 g of gelatin and 2 g of H₂SO₄ in 1000 mL of distilled water. The mixture was heated in oven for 6 h at 100 °C, then heated at 160 °C for 6 h. The silica-carbon composite containing partially polymerised and carbonised gelatin, was subjected to subsequent impregnation with a solution containing 8 g of gelatin and 2 g of H₂SO₄ in 1000 mL of distilled water. The material was heated for 6 h at 100 °C, and then heated at 160 °C for 6 h. Subsequently, the material was subjected for carbonization for 4 h at 900 °C in argon flow (flow rate of 40 cm³/min). The mesoporous carbon (MC) was recovered after dissolution of the silica template in 10 wt.% of hydrofluoric acid at room temperature followed by filtration, washing with ethanol, and drying at 100 °C over night.

Synthesis of metal/MC catalysts

The Co, Ni and Pd catalyst were loaded on to the MC in 1 wt.% of metal towards the MC by wetness impregnation method using aqueous solution of Co(NO₃)₂·6H₂O, Ni(NO₃)₂ or PdCl₂, respectively. The mixture of MC and metal precursor solution was refluxed for 5 h at 90 °C. The solvent was removed by evaporator and drying at 90 °C in oven overnight. Finally, all catalysts were calcined at 420 °C for 3 h and then reduced using hydrogen at 400 °C for 3 h (heating rate 5 °C/min, H₂ flow rate 20 cc/min).

Hydrocracking of waste lubricant

The activity of catalysts for hydrocracking of waste lubricant was studied in a semi flow reactor system. The hydrocracking process was carried out at 450 °C for 150 min. under H₂ gas flow of 20 mL/min. under catalysts/feed weight ratio of 1:50. The products were collected then analyzed by SHIMADZU QP 2010S gas chromatography-mass spectroscopy (GC-MS). Condensate mixture was carried using He gas and separated on Agilent HP 1MS capillary column then analyzed on flame ionization detector (FID). The total conversion of hydrocracking of waste lubricant was calculated as (100-residues) wt.%. The product selectivity was determined by percentage area of the chromatogram of gasoline fraction (C₅-C₁₂) or diesel fractions (C₁₃-C₂₀) towards the total conversion of liquid product.

Results and Discussion

Synthesis and characterization of mesoporous Carbon (MC)

The adsorption-desorption isotherm and braunauer-jenkins-teller (BJH) pore size distribution of the MC was shown in Fig. 1. The MC had isotherms of type IV according to the classification of IUPAC¹⁴. The isotherm of type IV was the adsorption occurred on the surface of mesoporous material which the adsorption occurred from monolayer to multilayer accompanied by difference N₂ gas volume at the time of adsorption and desorption that caused of capillary condensation.

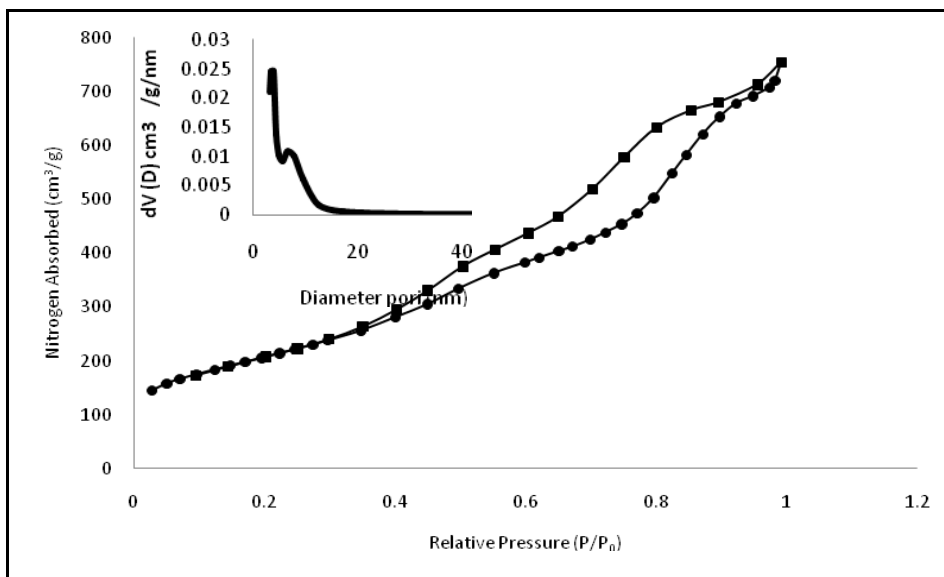


Fig. 1 N₂ adsorption-desorption isotherms of the MC. The *Inset* showed the BJH desorption of pore size distribution.

The pore size distribution of the MC showed that the MC had a pore size distribution in the range of mesopore¹⁹⁻²¹. The inset showed the appearance of two main peaks of pore diameter distribution in around 3.85 and 6.58 nm. This result indicated that the MC has a bimodal pore diameter distribution.

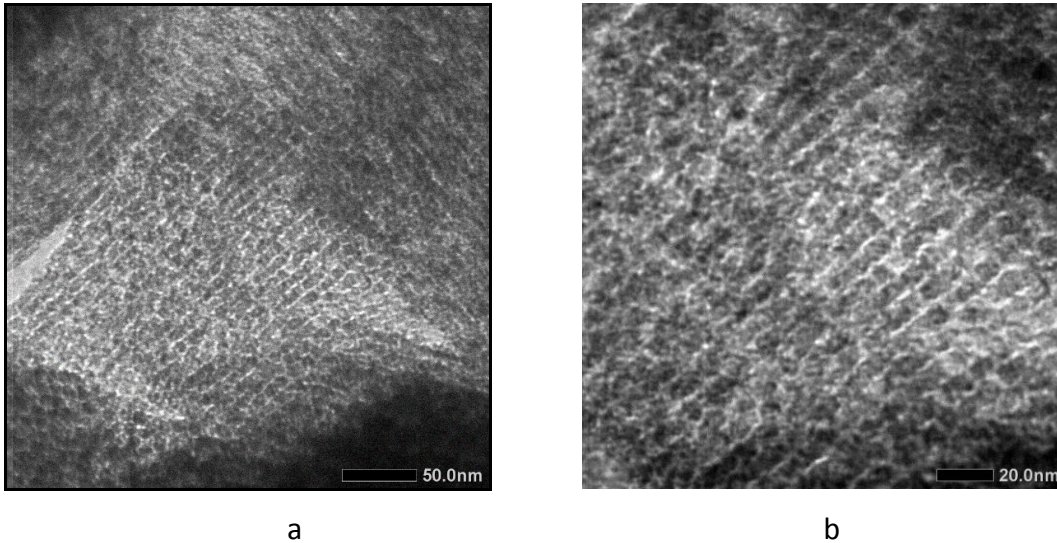


Fig.2 TEM images of the MC : (a) 0.0 nm and (b) 20 nm scale.

The morphology of the MC could be observed in Fig. 2. The MC showed the high porosity material as a honey come-like material viewed from the front cross-section, or at the pore mouth, which consisted of a cylindrical rod of carbon (black line) and mesoporous channel (white line).

Synthesis and characterization of Co/MC, Ni/MC and Pd/MC

The N_2 adsorption–desorption isotherms for Co/MC, Ni/MC and Pd/MC depicted in Fig.3. All isotherms resembled the Type IV isotherm, a typical characteristic for mesoporous materials. The hysteresis loop associated with isotherms is attributed to the capillary condensation which also confirms the presence of mesoporous structure. While the M/MC catalysts isotherm showed a H2 type hysteresis loop corresponding to the ink bottle shaped pores. The shape of the hysteresis loops were relatively similiar upon incorporation of metal particles, indicating no significant change in the textural properties^{19,20}. A sharp rise in N_2 uptake at relative pressure above 1 is due to the N_2 condensation in inter-particle pores.

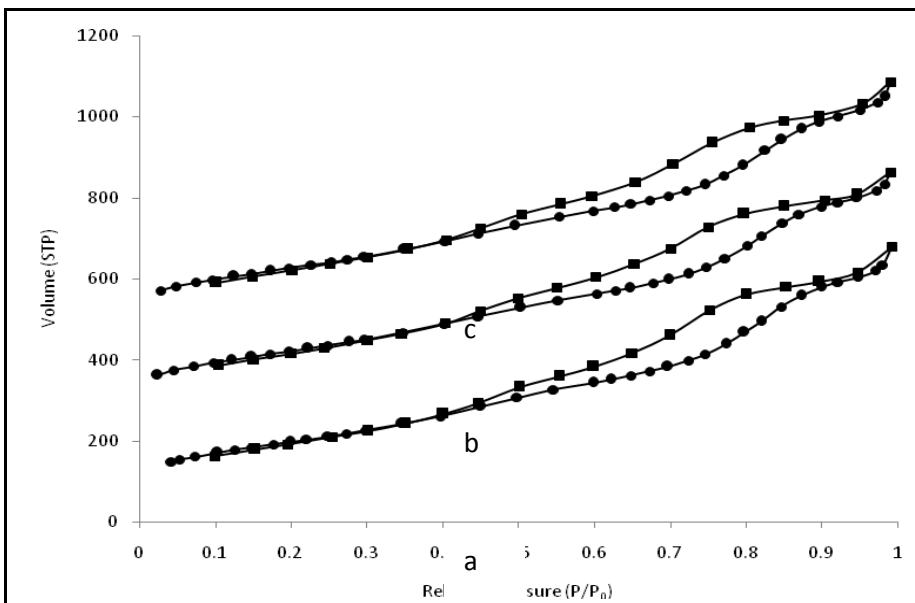


Fig.3 N_2 adsorption–desorption isotherms of: a. Co/MC, b. Ni/MC, and c. Pd/MC.

Fig. 4 depicted the BJH pore size distribution of Co/MC, Ni/MC and Pd/MC catalysts indicating the available of narrow bimodal pore diameter distribution majority at around 3.40 and 6.8 nm. Table 1

summarized the BET surface areas, pore diameter and volumes and acidity of the Co/MC, Ni/MC and Pd/MC catalyst. The MC showed a high surface area of 743.22 m²/g, main pore diameter of 3.85 nm and pore volume of 1.17 cm³/g. Depending on the type of metal incorporated on to the MC, the surface area, pore diameter, and pore volume varied between 636.19–702.68 m²/g, 3.42–3.82 nm, and 0.95–1.05 cm³/g, respectively, indicating a strong influence of the metal towards the MC textural properties. The incorporation of Ni, Pd and Co on to the MC significantly decreased the surface area of the MC.

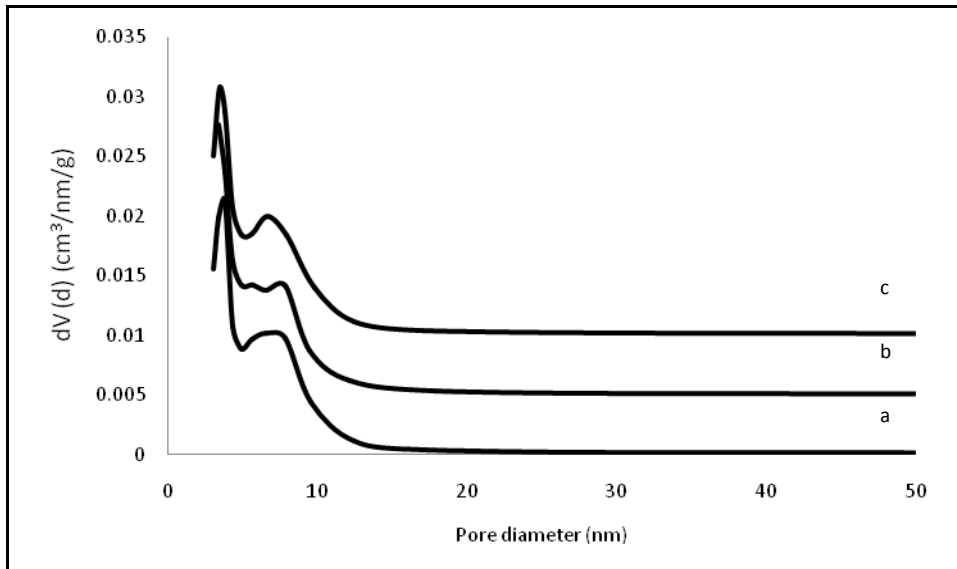


Fig.4BJH pore size distribution of: a. Co/MC, b. Ni/MC, and c. Pd/MC

Table. 1 The results of SSA and acidity test of MC and catalysts.

Sample	S_{BET} (m ² /g)	Vt (cm ³ /g)	Bimodal Pore Diameter (nm)		Acidity (mmol/g)
			D ₁	D ₂	
MC	743.22	1.17	3.85	6.58	4.56
Co/MC	702.68	1.05	3.82	7.82	4.78
Ni/MC	636.19	0.95	3.42	7.81	12.41
Pd/MC	644.98	0.98	3.42	6.65	14.09

Note : S_{BET} : BET specific surface area, Vt:total pore volume, D₁: low main pore diameter, D₂: high main pore diameter

Catalytic activity

The activity of thermal and catalytic hydrocracking of waste lubricant was showed in Table 2. The total conversions of all runs were not significantly different, but the liquid product conversion showed a significant difference. The different liquid products amount are significantly influenced by the presence and the character of the catalyst²². The character of catalyst would determine the reaction mechanism in the formation of the product. The liquid product was produced through the mechanism of carbonium ion in the catalytic hydrocracking. During the hydrocracking process, the mechanism of carbonium ion competed with radical mechanism caused by the influence of temperature. If the carbonium mechanism was dominant more liquid would be produced. On the other hand, if the radical mechanism was predominant hydrocarbon compounds with small amount of carbon would be produced thus allowing more gas fraction^{23,24}. The hydrocracking requires both hydrogenation activity (metal sites) and cracking activity (acid sites)²³. The acid sites strength of the current catalysts are found in the following order: Pd/MC > Ni/MC > Co/MC.

Table 2 shown that gaseous product was dominant without catalyst (thermal cracking). It was caused by the mechanism of thermal cracking occurred through the mechanism of radical triggered by high temperature. While the utilization of catalysts increased the rate of the hydrocracking reaction to produce liquid fraction. The

highest conversion of liquid fraction was 61.20 (wt.%) produced by Pd/MC catalyst which also produce the lowest content of coke. The doped metals was also influent the adsorption capacity of reactant in the hydrocracking. The transition metals have unpaired electrons in *d* orbitals that can homolytically dissociated the H₂ molecules into the H radicals that completed the unpaired electron in *d* orbital.

Table 2. Product distribution of hydrocracking of waste lubricant

Catalyst	Product distribution (wt%)					Total Conversion* (wt%)
	Liquid	Gas	Coke	H ₂ S (Sulfur)	Residue	
Thermal	25.94	71.53	-	0.35 (0.32)	2.20	97.80
MC	30.25	66.17	1.21	0.37 (0.34)	2.03	97.97
Co/MC	36.44	59.24	1.90	0.31 (0.29)	2.17	97.83
Ni/MC	50.10	46.62	1.26	0.18 (0.18)	1.84	98.16
Pd/MC	61.20	37.62	0.24	0.05 (0.04)	1.18	98.81

Note : *) total conversion = (100 – residue) wt.%

Selectivity of liquid product

Selectivity described the tendency of the hydrocracking to produce certain components. In this study, the expected components were gasoline and diesel fractions. The amount of gasoline fraction and diesel fraction could be determined by calculating the percentage of the area of each fraction from the GC-MS.

Table 3. The selectivity product in liquid fraction

Sample	Liquid Product Selectivity (%)	
	Gasoline Fraction	Diesel Fraction
Thermal	10.45	15.49
MC	7.18	23.07
Co/MC	15.93	20.51
Ni/MC	34.04	12.06
Pd/MC	52.33	8.87

Table 3 showed an increase amount of gasoline fraction in the liquid product using metal/MC catalysts. It was affected by the increase of the catalyst's acidity. The higher acidity of the metal/MC catalyst enabled to protonate cyclopropane in the feed and produced gasoline fraction larger than that of the thermal and MC catalyst hydrocracking. The catalyst selectivity for producing gasoline fraction followed the order of Pd/MC > Ni/MC > Co/MC.

Conclusion

The MC has successfully synthesized from bovine bone gelatin as a carbon precursor and SBA-15 as a template. The MC had a bimodal pore diameter distribution majority at around 3.85 and 6.58 nm with high surface area, and pore volume of 743.22 m²/g, and 1.17 cm³/g, respectively. Synthesis of Co, Ni and Pd metals supported on MC as catalyst for hydrocracking of waste lubricant into gasoline and diesel fraction had been successfully carried out. Synthesized Co/MC, Ni/MC, and Pd/MC catalysts showed high surface areas in the range of 702.68 m²/g, 636.19 m²/g, and 644.98 m²/g, respectively. The average pore size after added these metals are in the range of 3.42-3.82 nm (low main pore diameter) and 6.65-7.82 nm (low main pore diameter). The Pd/MC catalyst produced the lowest coke (0.24 wt.%) and the highest liquid fraction (61.20 wt.%) which consisted of gasoline fraction (52.33 wt.%) and diesel fraction (8.87 wt.%).

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