SYNTHESIS OF Pd/SILICA-ALUMINA MESOPOROUS CATALYST BY USING CATFISH GELATIN AS TEMPLATE FOR HYDROTREATMENT OF PYROLYZED α -CELLULOSE

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ABSTRACT

Synthesis of Pd catalyst supported by mesoporous silica-alumina (MSA) from Sidoarjo mud with gelatin template from catfish bone for hydrotreatment of pyrolyzed α -cellulose had been carried out. The MSA was synthesized using hydrothermal method. The MSA was characterized by FTIR, SAA, XRD, AAS, TEM, and acidity test. The MSA synthesized in this work was impregnated with Pd metal using a wet impregnation method to produce Pd(A)/MSA (0.004 g Pd on 0.5 g MSA) and Pd(B)/MSA (0.008 g Pd on 0.5 g MSA) catalysts. The catalytic activity of Pd(A)/MSA and Pd(B)/MSA catalysts were evaluated in hydrotreatment of pyrolyzed α -cellulose. The MSA presented Si/Al ratio, acidity value, BET specific surface area, pore-volume, and BJH desorption pore diameter of 76.55; 6.52 mmol/g; 602.61 m²/g; 0.81 cm³/g and 3.60 nm, respectively. Pd(B)/MSA catalyst has Pd metal content of 0.83 wt.% and acidity value of 15.66 mmol/g shows the highest catalytic activity in producing a liquid product of 89.01 wt.% with the main product in the form of acetic acid compounds.

Keywords: Hydrotreatment, Silica, Alumina, Pd/MSA, Pyrolysis, Catalysts

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INTRODUCTION

Lignocellulose biomass is a complex matrix with three main components, namely cellulose (40-60%), hemicellulose (15-30%) and lignin (10-25%).¹ Cellulose is a carbon source that has a high abundance in nature and has great potential to be used as an alternative raw material for the production of bio-based valuable platform molecules.² Lignocellulose biomass is a renewable energy source that can reduce greenhouse gas emissions and environmental pollution.³

Pyrolysis is an integrated process for the production of liquid fuels that can be used directly and as a pretreatment step to convert biomass into liquids that have a higher energy content for further processing such as heat, power, biofuel, and chemistry.⁴ Pyrolysis is the heating of organic matter, such as lignocellulose biomass, at high temperatures without oxygen.⁵ The product of biomass pyrolysis consists of liquid products (bio-oil, tar, and water), solid or carbon products and gas mixtures. Bio-oil mostly contains 50–65 wt.% organic substances, include aldehydes, acids, furans, ketones, guaiacols, phenolics, sugars and syringols; 15–30 wt.% steam; and 20 wt.% colloidal compounds.^{4,6}

The oxygen content contained in bio-oil can cause undesirable characteristics such as low instability, energy density, corrosion and high viscosity.⁶ Therefore, dismissing excessive oxygen atoms is necessary for increasing bio-oil. To increase the bio-oil product from pyrolysis to diesel fuel, bio-oil requires additional hydrotreatment. Hydrotreatment is an effective way to improve the quality of bio-oil to remove oxygen at 400-773 K and high H₂ partial pressure.⁶ Bio-oil can be one of the renewable alternative energy sources that can provide valuable chemicals and liquid fuels in the future.

The choice of catalyst is one of the important parameters in the process of bio-oil hydrotreatment. Palladium (Pd) precious metals can be used as catalysts in the hydrocracking process.⁷ However, the use

of pure metal immediately as a catalyst is easy to undergo agglomeration and sintering. Therefore, the catalyst needs a support material that has a large amount of surface area to make the contact area between the active site of the catalyst and the feed becomes larger.⁸

Mesoporous silica-alumina (MSA), has been usually used as a catalyst support material, which is synthesized from silica and alumina extracted from Sidoarjo mud using gelatin bone catfish as a template.⁹⁻¹² Gelatin is a promising polymer utilized as a template for synthesis of mesoporous silica because it has a functional group N-H which interacts strongly with xylanol (Si-OH) groups in silicate species through multiple hydrogen bonds. MSA is widely studied because of the presence of acidic sites in Al at its structure, has optimal pore size, and large surface area.^{9,10,13,14} Silica-alumina is known to be very effective for hydrocracking reactions because it has significant acidity¹⁵. Pd/silica-alumina catalysts are reported to have high catalytic hydrogenation stability.¹⁶ Pd/silica-alumina catalysts are known to be useful in many hydrotreatment processes such as hydrogenation, dehydrogenation and hydrocracking process.¹⁶

EXPERIMENTAL

Materials

Catfish bone obtained from the Tegalrejo Village, Boyolali Regency, Central Java, Indonesia. Sidoarjo mud taken from Sidoarjo Regency, East Java, Indonesia. α -cellulose was purchased from Sigma-Aldrich. Palladium chloride, sodium hydroxide, acetic acid and pyridine were purchased from Merck. Hydrochloric acid was purchased from Mallinckrodt.

Synthesis of MSA

Catfish bone soaked in a base solvent (0.1 M NaOH) for a day (24 hours) then soaked with acid solvent (1 M HCl) for 1 hour. Gelatin was taken out from the bone of the catfish using aquabidest at 70 °C for 5 hours. Silica (SiO₂) and alumina (Al₂O₃) were taken out from Sidoarjo mud using 6 M NaOH and 6 M HCl solutions at 90 °C for 5 hours. Gelatin was liquified in aquabidest at 40°C and stirred for 30 minutes. The gelatin solution was added with Al₂O₃ and the mixture was stirred for 30 minutes. In another glass container, the silica was dissolved in aquabidest and stirred for 30 minutes. The silica solution was added with CH₃COOH 1 M solution to reach pH 4. The silica solution was introduced into the gelatin-alumina mixture and the gelatin-alumina-silica mixture was then stirred for 24 hours at room temperature. The formed gel was moved into the autoclave and heated to 100 °C for 24 hours. The solid obtained from autoclave was filtered and rinsed with aquabidest. The solid was then heated at 50 °C for 24 hours. The solid was calcined at 550 °C for 4 hours to remove the gelatin and the produced solid was the MSA. The obtained MSA was characterized by FTIR, XRD, AAS, SAA, TEM and acidity test.

Pd Metal Impregnation on MSA

Pd metal is 0.004 g Pd(A) and 0.008 g Pd(B) is applied to 0.5 g MSA with a wet impregnation method using PdCl₂ solution. The mixture of the MSA and PdCl₂ solution was stirred at room temperature for 24 hours and heated at 70 °C for 2 hours. The formed catalyst was calcined at 500 °C under N₂ gas stream. The produced catalysts were reduced using H₂ gas stream at 450 °C for 3 hours. The resulting catalyst named Pd(A)/MSA and Pd(B)/MSA were then analyzed by ICP to determine the metal content of the catalysts and acidity test.

Acidity Test

The MSA and catalysts were acidities tested using the gravimetric method of pyridine adsorption into the sample at room temperature for 24 hours under vacuum condition. The acidity value is calculated based on the weight of the sample before absorption (m_1) and the weight of the sample after pyridine absorption (m_2) using the following equation:

$$\text{Acidity Value} = \frac{m_2 - m_1}{m_1 \times Mr \text{ Pyridine}}$$

Hydrotreatment of Pyrolyzed α -Cellulose

α -cellulose pyrolysis was carried out at 600 °C for 3 hours with N₂ gas stream to generate the pyrolyzed α -cellulose. **z** was processed hydrotreatment at 450°C for 2 hours in a semi-batch stainless steel reactor

(id: 4.5 cm, od: 4.8 cm, length: 30 cm) using the synthesized catalyst. The catalyst to feed ratio is 1:30. Liquid products from hydrotreatment α -cellulose were analyzed with GC-MS.

Sample Characterization

The analysis instruments of gelatin characterization used in this research were the Fourier Transform Infrared/FTIR spectrometer (Shimadzu Prestige-21) fitted with data station in the range from 400 to 4000 cm^{-1} with a KBr disc technique. Silica and alumina extracts were characterized using an X-Ray Fluorescence XRF, PANalytical Type Minipal4) with mining mode analysis. The pore images of the MSA was taken using Transmission Electron Microscope/TEM (JEOL JEM-1400) at 120 kV accelerating voltage. The Atomic Absorption Spectrometer/AAS (PERKIN ELMER 5100) was used to determine Si and Al content of the MSA. X-Ray Diffraction/XRD (Rigaku MiniFlex 600) was used to inspect the crystallinity of the MSA and Surface Area Analyzer/SAA (NOVA 1200e) was used to determine the surface parameters (surface area, pore diameter and pore volume) of the MSA. Analysis of metal content in the catalyst was analyzed using Inductively Coupled Plasma (ICP, Shimadzu ICPE-9820). Liquid products obtained from pyrolysis and hydrotreatment processes α -cellulose were analyzed using gas chromatography-mass spectrometer/GC-MS (Shimadzu QP2010S) with helium gas as a carrier gas and an acceleration voltage of 70 Ev with a column diameter of 0.25 mm, the length of 30 m, the thickness of 0.25 μm at a temperature of 60-310 $^{\circ}\text{C}$.

RESULTS AND DISCUSSION

Characterization of Gelatin

Catfish bone as the source of gelatin was given base immersion treatment using 0.1 M NaOH solution for 24 h and continued immersion of acid with 1.0 M HCl solution for 1 h. Immersion with NaOH aims to dissolve non-collagen proteins while immersion with HCl aims to demineralize catfish bones. Generally, gelatin has five typical amide-adsorbing regions in the FTIR spectra called as amide I, amide II, amide III, amide A, and amide B. The FTIR spectra in Fig.-1 shows extracted gelatin containing five types of typical amide uptake of the gelatin molecule.

Fig.-1: FTIR Spectra of Gelatin

The amide A uptake occurs at 3425 cm^{-1} wavenumbers indicating the stretching vibration of the N-H and O-H groups^{17,18}. Amide B occurs at a wavenumber 2924 cm^{-1} indicating the presence of vibration asymmetry chain CH_2 ^{11,19-21}. Amide I appear on the wavenumber 1604 cm^{-1} which is the vibration of the C=O group¹⁷. Amide II appears at 1512 cm^{-1} wavenumbers indicating the bending vibration of the NH group and the stretching vibration of the CN group²². The observed absorption at 1211 cm^{-1} wave number

is called an amide III showing the combination peaks between NH deformation from amide linkages, CN stretching vibrations and CH₂ wagging vibrations¹⁸. The emergence of the amide III uptake shows the loss of the triple structure of the molecular helices due to the denaturation of collagen into gelatin²³. The yield of gelatin obtained was 6.58%. This gelatin is used as a mold in the synthesis of MSA.

Characterization of Alumina and Silica Extract From Sidoarjo Mud

The content of alumina and silica from Sidoarjo mud based on XRF analysis (Table-1) is quite high at 11% and 34%, respectively. It means that the Sidoarjo mud has the potential to be the source of alumina and silica in MSA synthesis. The results showed that the purity of alumina and silica produced from Sidoarjo mud was about 96.10% and 85.90%, respectively.

Table-1: Composition of Sidoarjo Mud

Metal Oxide	Content in the Sample (%)		
	Sidoarjo mud	Silika Extract	Alumina Extract
SiO ₂	34.00	96.10	-
Al ₂ O ₃	11.00	-	85.90
Others	55.16 ^a	3.84 ^b	14.18 ^c

^a P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Sr, Eu, Yb, and Re

^b K, Ca, Ti, V, Fe, and Cu

^c P, K, Ca, Sc, Cr, Fe, Ni, Cu, Zn, Ga, In, Nd, Yb, Re, and Ir

Characterization of MSA

The MSA characterization using FTIR aims to provide information about the functional groups on the MSA which is presented in Table-2. Table-2 shows the typical absorption produced by the silica-alumina material observed in FTIR spectra. Based on the FTIR spectrum of the MSA, it shows that there is absorption in the area of 3433 cm⁻¹ which shows the presence of OH stretching vibration bound to Si or Al. The absorption band at 1635 cm⁻¹ is indicated by water molecules adsorbed in the material. The absorption band at 1095, 802, and 470 cm⁻¹ correspond to the asymmetry and symmetry stretching vibration of T-O and bending vibration of T-O-T, respectively.²⁴

Table-2: Interpretation of FTIR SAM Spectra

Wave Number (cm ⁻¹)	Type of Vibration
3433	OH stretching vibration bound to Si or Al
1635	Bending vibration of the O-H groups
1095	Asymmetry stretching vibration of T-O
802	Symmetry stretching vibration of T-O
470	Bending vibration of T-O-T

Fig.-2: Adsorption-desorption Isotherm of MSA

The N_2 gas adsorption isotherm graph and N_2 gas desorption from the MSA are shown in Fig.-2. The isotherm adsorption and desorption patterns of N_2 of MSA gases are included in type IV isotherms based on the IUPAC classification indicating the formation of mesoporous material.^{11,19-21,25-27} The AAS analysis result shows that the Si/Al mole ratio in the synthesized MSA is about 76.55. The acidity value (the amount of pyridine absorbed by the acid site) from MSA is about 6.52 mmol/g. Based on N_2 adsorption-desorption analysis result, the MSA has a high surface area (S_{BET}) of 602.61 m^2/g , desorption BJH pore diameter 3.60 nm, and the total pore volume of 0.81 cm^3/g .

Fig.-3: TEM Images of MSA (a) 100 nm (b) 20 nm

The morphology of the MSA catalyst was characterized using TEM. TEM image of the MSA (Fig.-3) shows that the MSA has a pore with a structure similar to a wormhole. Wormhole-like structures produced from MSA material synthesized using gelatin molds have also been reported by previous studies. The structure of MSA was analyzed using XRD. Diffractogram of the MSA (Fig.-4) shows that the MSA has an amorphous structure which is characterized by the appearance of a peak that is wide enough at 2θ around 21° .^{18,20}

Fig.-4. Diffractogram of the MSA

Characterization of the Catalyst

The catalysts Pd(A)/MSA and Pd(B)/MSA obtained were investigated using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and acidity test. The analysis results using those two characterizations indicate that the catalyst Pd(A)/MSA and Pd(B)/MSA have Pd metal content of 0.44 wt.% and 0.83 wt.% as well as acidity value of 14.26 mmol/g and 15.66 mmol/g, respectively. Based on the data in Table-3, the acidity value of the MSA increases with increasing of Pd levels in the catalyst. Pd(B)/MSA catalyst has a higher acidity value than Pd(A)/MSA catalyst. Pd metal provides empty electron orbitals which can be used as Lewis acid sites to absorb pyridine vapour.¹¹ This makes the

amount of pyridine absorbed by catalyst Pd(B)/MSA more than catalyst Pd(A)/MSA. The high acidity of the catalyst is expected to increase its catalytic activity in the hydrotreatment process of pyrolyzed α -cellulose.

Table-3: Acidity Test and ICP Results

Catalyst	Pd Metal Content (wt.%)	Acidity Value (mmol/g)
MSA	0,00	6,52
Pd(A)/MSA	0,44	14,26
Pd(B)/MSA	0,83	15,66

The Activity of the Catalyst

Pyrolysis of α -cellulose at 600 °C produced a yellowish, thick, pungent liquid product, and it contains a lot of oxygenate compounds²⁸. Pyrolysis carried out in this study managed to convert α -cellulose into liquid products by 47.80 wt.%. The five main components of pyrolyzed α -cellulose in this study were acetone (11.07 wt.%), 9-octadecanoic acid (8.21 wt.%), hexadecanoic acid (5.86 wt.%), acetic acid (5.45 wt.%) and 1-hydroxy-2-propanone (3.92 wt.%). The synthesis catalyst was used for hydrotreatment of bio-oil from the pyrolysis of α -cellulose at 450 °C for 2 hours under H₂ gas stream (flow rate of 20 mL/minute). The catalyst to feed ratio is 1:30. For comparison, hydrotreatment process of bio-oil from the pyrolysis of α -cellulose was also carried out without using a catalyst (thermal).

Thermal hydrotreatment was carried out to evaluate the activity of the catalysts synthesized in this work in hydrotreatment process of the pyrolyzed α -cellulose. The hydrotreatment process of pyrolyzed α -cellulose produces three kinds of products which are a liquid fraction, coke, and gas fraction as presented in Fig.-5. Hydrotreatment of pyrolyzed α -cellulose using catalysts produced a larger amount of liquid product than the hydrotreatment process without using a catalyst. Hydrotreatment of pyrolyzed α -cellulose generated the highest amount of liquid product using Pd(B)/MSA catalyst (about 89.01 wt.%). This phenomenon indicates that hydrogenation activity increases with increasing metal content of the catalyst.⁷

Fig.-5: Distribution of Hydrotreatment Products of Pyrolyzed α -cellulose

The composition of liquid products obtained from the hydrotreatment process was analyzed using GC-MS. Table-4 presents the results. The liquid products from the hydrotreatment process of pyrolyzed α -cellulose with catalysts and without using a catalyst (thermal) contain compounds in the form of acids, aldehydes, and ketones. Hydrotreatment of pyrolyzed α -cellulose without using a catalyst produced 9-octadecanoic acid compound as the main product. Different results obtained in the hydrotreatment process using catalysts. The hydrotreatment of pyrolyzed α -cellulose using Pd(A)/MSA and Pd(B)/MSA catalyst

produce acetic acid compounds as the main product. The complete catalyst activity test results are presented in Table-4.

Table-4: Selectivity of Liquid Product of Hydrotreatment of Pyrolyzed α -cellulose

Group	Product	Composition (wt. %)			
		Thermal	MSA	Pd(A)/MSA	Pd(B)/MSA
Acid	Acetic acid	-	21.60	16.79	21.89
	Propanoic acid	-	-	6.58	8.11
	Hexadecenoic acid	12.29	-	-	-
	9,12-hexadecenoic acid	5.60	-	-	-
	9-octadecanoic	13.45	-	-	-
Ketones	1-hydroxy-2-propanone	5.89	17.19	14.78	13.70
	acetone	-	5.40	-	-
Aldehyde	2-furancarboxyldehyde	-	9.54	15.26	12.81
	Formaldehyde	6.74	-	8.77	10.61
	Acetaldehyde	-	7.95	-	-

CONCLUSION

MSA synthesized in this study had a specific BET surface area of 602.61 m²/g, the total pore volume of 0.81 cm³/g and a pore diameter of 3.60 nm based on the BJH desorption method. The MSA acidity value increases after the impregnation of Pd metal. Hydrotreatment of pyrolyzed α -cellulose produced the highest amount of liquid product using Pd(B)/MSA catalyst of 89.01 wt.% with the main product in the form of acetic acid compounds.

ACKNOWLEDGMENT

The authors thank the Ministry of Research Technology and Higher Education of Indonesia for financial support for this research under the PTUPT 2019 research fund at Universitas Gadjah Mada (Contract Number: 2744/UN1.DITLIT/DIT-LIT/LT/2019).

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[RJC-5630/2019]