NiO Supported on Porous Carbon From Merbau Wood: Synthesis and Characterization

D Santi, Triyono, W Trisunaryanti and I I Falah

1 Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Papua, Manokwari, Indonesia.
2 Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Yogyakarta, Indonesia.

d.santi@unipa.ac.id, triyn102@ugm.ac.id, wegats@ugm.ac.id

Abstract. Nickel oxide catalyst supported on porous carbon (NiO/C), the materials support were synthesized from Merbau wood. The metals were loaded onto the carbon by the wet impregnation method. After drying and calcination, NiO/C was obtained. The prepared catalyst was evaluated for the hydrocracking of pyrolyzed α-cellulose. The catalyst was characterized by XRD, SEM-EDX, FT IR, SAA, and acidity test by NH3 base vapor adsorption determined gravimetrically and by FT IR. The XRD results showed that the carbonaceous of materials support were amorphous materials that characteristic for mesopore carbon. The impregnation of nickel into carbon results in diffraction peaks that correspond to the presence of NiO, which was confirmed by EDX. The SEM image showed that the morphology of the catalyst samples was a honeycomb-like structure. The acidity test showed that the total acid amount of NiO/C samples was 3.05 mol/g, and the FT IR spectra indicated that there were Brönsted and Lewis acid sites on NiO/C catalyst. The SAA results showed that the specific surface area, total pore volume, and average pore diameter of the NiO/C catalyst were 520.41 m²/g, 0.27 cm³/g, and 2.083 nm, respectively.

Keywords: nickel oxide, Merbau wood, carbon, hydrocracking, α-cellulose

1. Introduction

Activated carbon has been developed as one of the most popular uses, as a material in environmental management technology, used as an electrode material, or as a catalyst support or as a catalyst in catalytic processes over the last decades. It has possessed good surface morphology such as high surface area and high pore volume, pore distribution, and surface functionality for its utilize as catalysts and adsorbents [1–3]. A variety of precursors can prepare to produce activated carbon. Generally, these precursors have volatile and high carbon content but low inorganic contents [4]. It is well known that various carbonaceous precursors can be found in agricultural residues, such as sugarcane bagasse [5], oil-palm fruit waste [6], palm shell and coconut shell [7], cotton stalks [8], pine chips [9], and rice husks [10]. As a renewable, inexpensive, sustainable, and environment-friendly feedstock, biomass has received considerable attention as the potential precursor [11,12].

Furthermore, the high concentration of volatiles is ideal for preparing the activated carbon matrix within a highly porous structure. The significant constitutive fractions, in the term of weight of these lignocellulose materials as the use as activated carbon precursor, are the hemicellulose, cellulose, and lignin. Merbau wood as lignocellulose materials has been known to have potential as a carbon
precursor [13]. Because of the difference in reactivity between these components during the pyrolysis step, the study of their carbonization is rather complicated. The nature of the precursor, conditions, and activation method determined the characteristics of activated carbon porosity properties, including porous domains (microporosity, mesoporosity, and macroporosity), pore size distribution, shapes of the pores, and surface chemistry was determined by Byrne and Marsh [14].

The methods for preparing an activated carbon involves two steps- pyrolysis and activation. In the pyrolysis step, the temperature of carbonization between 400 and 850 °C, sometimes reaches 1000 °C. In the activation process, these chars as a result of the pyrolysis step activated in oxidizing gas such as air, carbon dioxide, or steam at a temperature of about 800-1000 °C to produce the final activated carbon. The use of high temperature [15] and these types of selected gas result activated carbon with high micropore. Furthermore, the active catalyst support required the large surface area that provides sufficient active sites for loading catalytic metal nanoparticles.

Moreover, mesopore is required for adsorption purposes, diffusion, and accelerated transport [16,17]. The previous study revealed that the lower temperature, 350 °C with oxidized in the air, produced the mesoporous activated carbon [18]. However, there is no systematic study related to the preparation of carbon active derived from Merbau wood (Intsia, spp) and the use of oxygen as oxidizing gas at the temperature of 350 °C via the single-step process.

Cellulose was a representative biomass compound [16], one of the most abundant [17] and an inexpensive feedstock for energy production [18] and conversion into more valuable chemicals [19]. Cellulose conversion into fuels is inspiring and involving effective catalytic systems [18]. It has been reported that transition metals-modified dispersed to porous materials are used as a catalyst in hydrocracking reaction [18–20]. The benefits of this type of catalyst include the inclusion of metal acid sites and the avoidance of metal agglomeration due to the dispersal of transition metals into the porous system such as mesoporous silica [19], MCM-41 [21], and mesoporous carbon [13,18]. In this work, the main study was to investigate the catalytic performance of nickel oxide/carbon catalysts on the hydrocracking of pyrolyzed α-cellulose as a model of biomass.

2. Experimental

2.1. Materials

Merbau wood was obtained from Manokwari, Indonesia. KOH, NaOH, NaHCO₃, Na₂CO₃, Ni(NO₃)₂•6H₂O, acetone, HCl were analytical grade and obtained from Merck, α-cellulose was obtained from Sigma-Aldrich.

2.2. Carbonization and Oxidation of Merbau woods

The Merbau woods were heated up to carbonization temperature of 700 °C at the heating rate 10 °C/min, and were held for 2 h, under N₂ gas at a flow rate of 20 mL/min. The samples were cooled to room temperature under N₂ flow. Activation is carried out by streaming oxygen gas with a flow rate of 15 mL/min for 3 h, 350 °C at a heating rate of 10 °C/min. The results of this process were noted as C.

2.3. Catalysts Preparation

The C samples were soaked for 2 h and then filtered, by acetone and HCl, respectively. This step followed by thorough washing with deionized water and drying at 105 °C for 12 h. The impregnation of nickel (1.0 wt.%) on the C samples was done by the wetness impregnation technique. The solid was then calcined at 500 °C under nitrogen gas stream with a flow rate of 20 mL/min for 4 h. The final products were denoted as NiO/C catalysts. The catalyst was measured acidity value by acidity test using ammonia adsorption method. Characterization of the crystallinity sample was carried out by X-ray diffraction (XRD) using a Rigaku MiniFlex600, λ = 1,54 Å, 40 kV, 15 mA. The functional groups as analysis surface chemistry of the samples were recorded between 4000 and 400 cm⁻¹ using Fourier Transform Infrared Spectrometer (FTIR, Shimadzu Prestige-21) with KBr disc technique. The
morphology of the sample was characterized by scanning electron microscopy (SEM, Jeoul JSM-6510).

2.4. Catalyst Acidity Test
The acidity value of the catalysts was measured by the absorption of the ammonia vapor onto the NiO/C sample. The acidity value (g/mol) of the catalysts was calculated using the following equation [13] with any modification the type of gas adsorbate using the ammonia vapor:

$$\text{Acidity value} = \frac{(G - G_0)}{(G_0 \times M_{\text{ammonia}})}$$

Where G is the weight of samples after adsorption (g), G₀ is the weight of samples before adsorption (g), and M_{ammonia} is the molecular weight (g/mol).

3. Results and Discussion

3.1. Crystallographic Characterization

The XRD pattern of NiO/C (figure 1) showed the success of the nickel impregnation process on carbon as supporting material. The peak at 2θ = 37.07° and 43.05° was characteristic to the presence of NiO correspond to rhombohedral structure (JCPD: 44-1159), d_{200} [2 0 0] and d_{111} [1 1 1], respectively. The three broads peaks at these patterns similar to the precursor carbons material from coconut shells of Malaysian variety [22]. Typically, these peaks are amorphous carbon.

![Figure 1. XRD pattern of NiO/C catalyst](image)

3.2. Infrared Analysis

Figure 2 showed the presence of oxygen-containing functional groups of the NiO/C, after and before ammonia absorption. The existence of O-H stretching vibration was observed at the broadband of 3448 cm⁻¹ wavenumber. The presence of asymmetric and symmetric C-H stretching were shown at a weak peak at 29924 cm⁻¹ and 2862 cm⁻¹. The band at 1635 cm⁻¹ was associated with aromatic C=C stretching present in olefinic vibrations in the aromatic region. The existence of the band in 1442 cm⁻¹ assigns the presence of aromatic C, indicative of lignin C=C [23]. The band at 1118 cm⁻¹ was corresponding to C-O-C stretching. Aromatic C—H bending can be found at 871 cm⁻¹ [24].
IR spectra can be used quantitively to find out the existence of Lewis and Brönsted acid sites. Figure 2 showed the changes occurring in the absorption bands, a widening at 1604 cm\(^{-1}\) region a weak peak after the absorption of ammonia gas. It is indicated ammonia coordinately bonded to Lewis acid site [25]. The band at 1404 cm\(^{-1}\) corresponded to Brönsted acid sites, which is the characteristic peak of an ammonium ion and N-H bending vibration region[26].

3.3. Acidity Characterization
The determination of the acidity of NiO/C sample was done quantitatively by the absorption of ammonia gas method. The acidity value of NiO/C samples was 3.05 mmol/g, as presented in table 2. The presence of metals in supporting materials has been shown to contribute to the acidity value of the material [13]. The oxide form of nickel (as Lewis acid site) provides the orbitals to accept an electron from the NH\(_3\) molecule as the basic adsorbate.

3.4. Morphology and Metals Content Analysis
The morphology features of NiO/C analysis was carried out by SEM analysis. Figure 3 showed the image of NiO/C with magnification 1000x and distribution of carbon, oxygen, and nickel contained in NiO/C sample. This image presented a large number of different sizes of pores on the surface NiO/C. The pores showed the pattern of the overlapping honeycomb-shaped tunnel, with cross-connected orientation. The capture of the content of carbon, oxygen, and nickel showed distribution uniformly on the NiO/C surface.

**Figure 2.** FTIR spectra of NiO/C: a) NiO/C after ammonia absorption and b) NiO/C before ammonia absorption
Figure 3. SEM Image of a) NiO/C, b) mapping of carbon, c) mapping of Oxygen, d) mapping of nickel

The elemental analysis of samples was determined by EDX, as shown in figure 4 and table 1. The result was confirmed by small amounts of nickel, almost of the nickel was in oxide form in the NiO/C structure.

Figure 4. EDX spectra of NiO/C

| Sample  | Element (wt.%) | Oxide |
|---------|----------------|-------|
|         | C              | O     | Ni    | NiO   |
| NiO/C   | 99.4           | 0.13  | 0.47  | 0.6   |

3.5. Pore Structures Analysis
The pore size distribution and average pore diameter analyzed using the N₂ adsorption data with the Barrett-Joyner-Halenda (BJH) method. Table 2 showed that the average pore diameter of NiO/C was 2.083 nm and figure 5a presented that most of the mesopores were in the pore size range of 3-4 nm. Figure 5b showed the adsorption-desorption isotherm of the NiO/C, indicated that was of type II according to IUPAC classification, characteristic for nonporous and macroporous materials. Based on these data, the NiO/C has the characteristic pore size predominantly non-porous and macroporous-mesoporous. The synthesized NiO/C exhibited a high surface area of 520.407 (m²/g), which has the potential in catalyst applications, as well as an adsorbent.
Figure 5. (a) The pore size distribution of NiO/C. (b) N₂ adsorption-desorption isotherm of NiO/C. Filled and empty symbols represent the adsorption and desorption branches.

| Sample | Surface area (m²/g) | Pore diameter (nm) | Pore volume (cm³/g) | Acidity (mmol/g) |
|--------|---------------------|--------------------|---------------------|-----------------|
| NiO/C  | 520.407             | 2.083              | 0.271               | 3.05            |

4. Conclusion

In this study, the synthesis of support material of first-row transition metal derived from saw waste of Merbau wood is provided. The synthesized material has potential acid sites and surface characteristics for the application of catalyst materials. The synthesized NiO/C has pore distribution in the meso-sized range, with several mixtures of non-porous and macropore characters. All impregnated Ni metals in the material were characteristic to the presence of oxides correspond to the rhombohedral structure.

References

[1] Qian K, Kumar A, Zhang H, Bellmer D, Huhnke R 2015 Renew. Sustain. Energy Rev. 42 1055–64
[2] Ahmed S, Ramli A, Yusup S, Farooq M 2017 Chem. Eng. Res. Des. 122 33–42
[3] Maia D A S, de Oliveira J C A, Nazzarro M S, Sapag K M, López R H, de Lucena S M P, de Azevedo D C S 2018 Chem. Eng. Res. Des. 136 753–60
[4] Lua A C, Lau F Y, Guo J 2006 J. Anal. Appl. Pyrolysis. 76 96–102
[5] Cronje K J, Chetty K, Carsky M, Sahu J N, Meikap B C 2011 DES. 275 276–84
[6] Guo J and Lua A C 2002 Mater. Lett. 55 334–9
[7] Mohd W, Wan A, Shabuddin W, Ali W 2004 Bioresour. Technol. 93 63–9
[8] Girgis B S, Ishak M F 1999 Mater. Lett. 39 107–14
[9] Gaskin J W, Steiner C, Harris K, Das K C, Bibens B 2008 Trans. ASABE. 51 2061–69
[10] Zhang S, Dong Q, Zhang L, Xiong Y 2015 Bioresour. Technol. 191 17–23
[11] Ahmad F, Daud W M A W, Ahmad M A, Radzi R 2012 Chem. Eng. Res. Des. 90 1480–90
[12] Zhu M, Cai W, Verpoort F, Zhou J 2019 Chem. Eng. Res. Des. 146 130–40
[13] Prasiwi A D, Trisunaryanti W, Triyono T, Falah I I, Santi D, Marsuki M F 2019 Indones. J. Chem. 19 575–82
[14] Byrne J F and Marsh H 1995 Porosity in Carbons, ed J W Patrick (New York: Halsted Press) p 2-48
[15] Daud W M A W, Ali W S W, Sulaiman M Z. 2000 Carbon N. Y. 38 1925–32
[16] Grams J, Niewiadomski M, Ruppert A M, Kwapiński W 2015 J. Anal. Appl. Pyrolysis. 113 557–63
[17] Bartoli M, Rosi L, Giovannelli A, Frediani P, Frediani M 2016 J. Anal. Appl. Pyrolysis. 120 284–96
[18] Trisunaryanti W, Suarsih E, Triyono, Falah I I 2019 RSC Adv. 9 1230–37
Acknowledgments

The authors are grateful to Ministry of Education and Culture of the Republic of Indonesia-BUDI DN and Ministry of Finance-LPDP (grant number: PRJ-1475/LPDP.4/2019) for the Research Scholarship and PDUPT (2563/UN1.DITLIT/DIT-LIT/LT/2019).