Research Article

Graphitization of Coconut Shell Charcoal for Sulfonated Mesoporous Carbon Catalyst Preparation and Its Catalytic Behavior in Esterification Reaction

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Abstract

Here, we reported the utilization of coconut shell charcoal used for solid acid catalysts and its performance in the esterification reaction of acetic acid and methanol. The graphitization of coconut shell charcoal was carried out by the calcination and KOH activation at the temperature of 400 °C for an hour and continued at the temperature of 800 °C for an hour under nitrogen flow resulted in graphitic carbon. The effect of the addition of KOH activation was observed by varied the weight ratio of coconut shell charcoal as raw material (RM) and KOH. The selected weight ratio of RM:KOH was 1:1, 1:2, and 1:4. The resulted graphitic carbon was sulfonated by heating with the sulfuric acid to obtain a solid acid catalyst. The sulfonic time was evaluated for 5 and 10 hours. The generated particles were characterized to examine the morphology, the crystallinity, the specific surface area, the chemical bonding, and the ionic capacity using Scanning Electron Microscopy (SEM), X-Ray diffraction (XRD), nitrogen gas absorption-desorption, Fourier Transform Infrared Spectroscopy (FTIR), and titration method, respectively. The best condition for graphitization of raw material is the use of RM:KOH = 1:4, resulting in the highest surface area reaching 1259.67 m^2/g and the most dominant of the sulfonic group of $-SO_3$ bond. Furthermore, increasing the sulfonating time from 5 to 10 hours led to the increase of the yield of esterification reaction from 85% to 96.57% for graphite synthesized using RM:KOH = 1:4. Copyright © 2020 BCREC Group. All rights reserved

1. Introduction

Esterification of acetic acid with methanol producing methyl acetate is widely used as a solvent in many commodities such as glues, perfumes, resins, plasticizers, and paint polish removers. Methyl acetate is also used as a solvent for extractions and production of coating materials, nitro-cellulose, cellulose acetate, and cellulose ethers [1,2]. The acid catalyst is used to accelerate the esterification reaction that can be homogenous or heterogeneous catalysts. The use of homogenous catalysts is usually low cost and high catalytic activity because of the same

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phase between catalyst, reactant, and product [3]. However, the limitation of homogenous catalysts is reactor corrosion generation, environmental pollution, and the difficulties in catalyst recycle. In addition, the recovery of the homogeneous catalyst from the reaction medium is high cost and not an easy process. The advantages of heterogeneous catalysts are easily separated from the reaction media, recycle ability, improved selectivity, and reducing process stages and wastes [4,5]. Nevertheless, the preparation of heterogeneous catalysts is also not easy because the catalytic activity is enhanced by the number of active sites as a result of a combination of the higher surface area and higher porosity [6,7].

The performance of various heterogeneous catalysts for the esterification reaction has been reported. The use of various commercial ion exchange resins as the catalyst and commercial solid acid catalysts for the esterification reaction has been evaluated [1,8–10]. It is also reported that the catalytic activity of carbon-based solid acid catalysts is five times higher than that of a kind of ion exchange resin catalyst for oleic acid esterification [11].

Graphene oxide processed through the oxidation of natural graphite powder was used as a catalyst for the esterification reaction of acetic acid with methanol, biodiesel production from microalgae, and diindolyl-oxindole derivatives synthesis [12–15]. The activity of the catalyst was enhanced by grafting the active sulfate groups on its surface. The sulfonated ordered mesoporous carbon-based solid acid using sucrose as carbon source exhibited yield at around 90% for esterification reaction of free fatty acids [16,17] and transesterification of fatty acid methyl esters [18] in waste frying oil. Carbonization of glucose and starch mixture and ß-cyclodextrin to generate solid acid catalyst was also reported having the highest esterification activity at certain condition process [19,20]. The sulfonated carbon base catalysts from glucose revealed a stable condition even at the temperature of 400 °C [21]. The waste utilization of rice husk and glycerol as sulfonated carbons used for solid acid catalysts were also reported for the esterification reaction [22,23]. The sulfonated coal-based heterogeneous acid catalyst claimed that it can reach 97% acid reduction efficiency by optimizing the carbonization and sulfonating temperatures [24]. Besides, the sulfonated carbons from the palm kernel shell also showed higher activity than the commercial acid resins for cellobiose hydrolysis reactions [25].

Here, we reported the utilization of coconut shell charcoal that activated using potassium hydroxide, calcined under nitrogen flow, and then sulfonated with sulfuric acid that resulted in sulfonated mesoporous graphitization carbon catalyst. The effects of potassium hydroxide addition and the duration of the sulfonating process on the characteristics of the particles were studied. Furthermore, the ion capacity and the catalyst activity in the acetic acid esterification with ethanol were examined.

2. Materials and Methods

2.1 Materials and Chemicals

Coconut shell charcoal was obtained from CV. Atma Multidaya Makmur, Indonesia. The potassium hydroxide (purity 85%, Merck) and the sulfuric acid (purity 98%) were used as the activated agent and as the sulfonating agent, respectively. The 20% of sulfuric acid was used to eliminate the contaminant in the generated graphite. Chloride acid and sodium hydroxide were used for ionic capacity determination. Nitrogen gas (99.99%, PT. Aneka Gas) was used as an inert carrier gas in the graphitization process. Demineralized water was used as a washing agent and dilution process.

2.2 Catalyst Preparation

Firstly, the graphite particles were prepared. Coconut shell charcoal was crushed and sifted through a 75 mesh sieve. Then, the raw material of coconut shell charcoal powder (RM) was mixed into the crushed potassium hydroxide (KOH) with RM:KOH weight ratio of 1:1, 1:2, and 1:4. The samples laid on the combustion boat were calcined in a tubular furnace (Thermo Scientific Lindberg, Germany, inside diameter of tube 2.54 cm and length 30 cm) at the temperature of 400 °C for an hour and continued at the temperature of 800 °C for an hour under nitrogen flow. After the temperature of samples was the same as the room temperature, each sample was soaked with 20% sulfuric acid for 45 minutes. In the next step, each sample was filtered and dried in an oven at a temperature of 80 °C for 18 hours.

Hereafter, the sulfonated graphite was prepared by soaking the graphite in concentrated sulfuric acid (98%) in which a gram of graphite required 25 mL sulfuric acid at a temperature of 150 °C. The sulfonating duration was 5 and 10 hours. Next, the sulfonated graphite particles were allowed to decrease the temperature up to the room temperature at around 30 °C and then washed with demineralized water. Fi-

nally, the samples were dried in an oven at a temperature of 80 °C for 18 hours. The sulfonated graphite samples were named GxSy (x = KOH weight per weight RM, y = sulfonating duration).

2.3 Particles Characterization

The crystallinity of catalysts was analyzed using X-Ray diffraction (XRD, PanAnalytical X'Pert MPD System). Scanning Electron Microscopy (SEM, FEI Inspect S50) was used to analyze the surface morphology of the catalyst. The chemical bonding of the catalysts was studied using Fourier Transform Infrared Spectroscopy (FTIR, Nicolet iS10). The specific surface area, pore size, and pore volume were measured using nitrogen gas absorption-desorption (Nova 1200e, Quantachrome).

2.4 Catalyst Performance Examination

The ion capacity was determined by acid-base titration. The sulfonated sample was soaked in 0.1 M NaOH solution for 48 hours with the ratio of 25 mL NaOH solution for 0.2 gram sample. Then the sample was titrated with 0.1 M HCl. The ion capacity, K_i was determined from the number of Na^+ which reacted with $-SO_3H$ grafted in the graphite surface using the following equation:

$$K_i\left(\frac{mmole\ equivalene}{gram\ sample}\right) = \frac{\left(V_{NaOH} \times N_{NaOH}\right)_{initial} - \left(V_{HCl} \times N_{HCl}\right)_{titration}}{gram\ sulfonated\ graphite} \quad (1)$$

The sulfonated sample was used as a catalyst for the esterification of methyl acetate from acetic acid and methanol. The 96% methanol was reacted with glacial acetic acid in the three-neck bottle equipped with a reflux con-
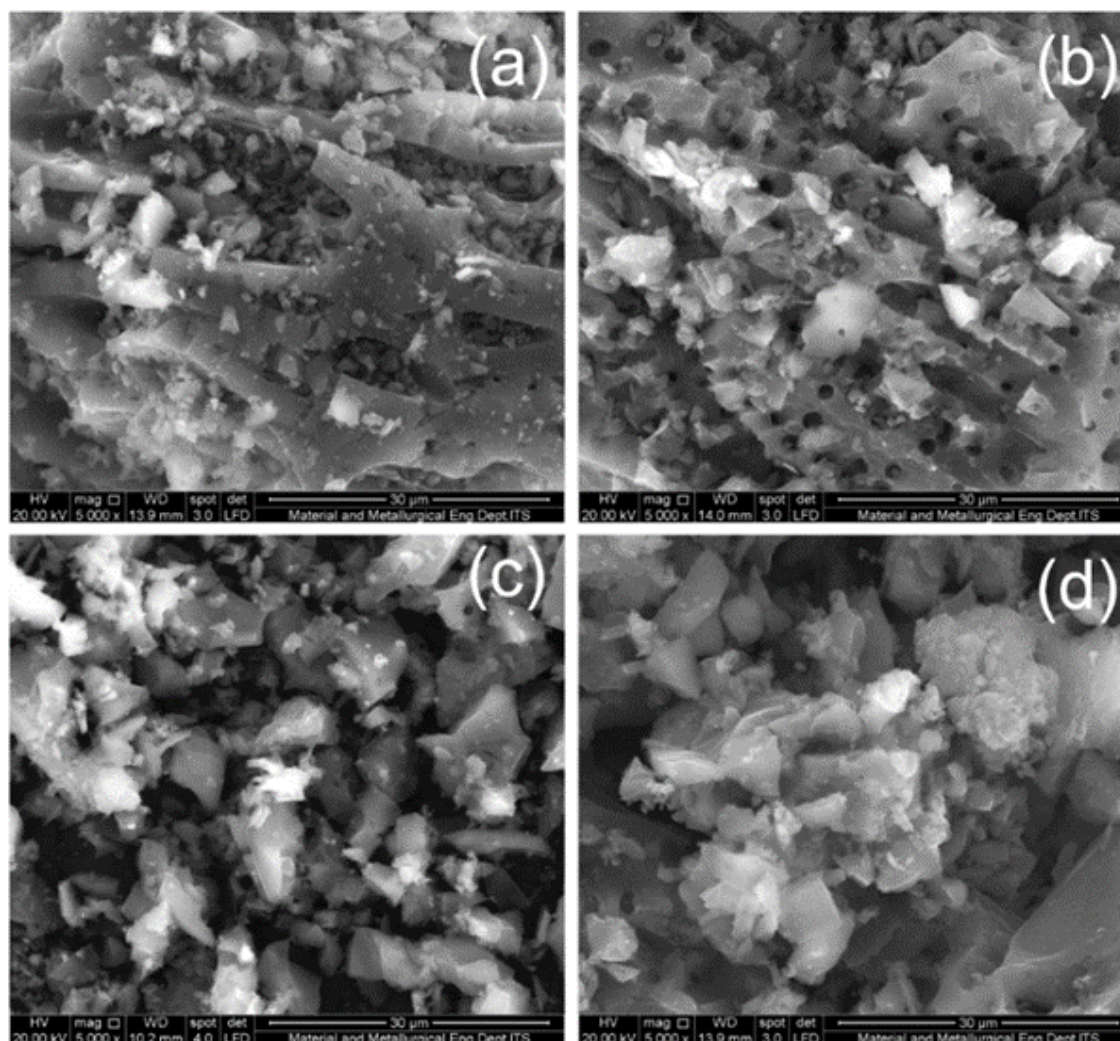

Figure 1. SEM images of (a) raw material (RM), graphite synthesized using RM:KOH weight ratio of (b) 1:1, (c) 1:2, and (d) 1:4.

denser for three hours. The produced methyl acetate was purified with simple distillation. The distillate product was analyzed using GC to calculate the amount of methyl acetate. The yield of the produced methyl acetate was then calculated.

3. Results and Discussions

3.1 Effect of KOH Activation on the Generated Graphite Particles

Figure 1(a-d) shows the surface morphology of the samples by scanning electron microscopy (SEM) of raw material (RM), carbonized raw material KOH activated with RM:KOH ratio of 1:1, 1:2, and 1:4, respectively. It can be seen that the surface morphology of raw material is a solid and irregular shape. Carbonization and activation made the raw material smaller in size with increasing the weight of KOH as an activated agent, as shown in Figures 1(b-d). Further examination on the surface area, pore size, and total volume are indicated by particle surface area analysis by BET and BJH methods.

Table 1 shows the surface area, average pore diameter, and pore volume total of raw material, carbonized and activated samples of RM:KOH weight ratio of 1:1, 1:2, and 1:4. Following the SEM images, increasing the KOH weight as an activated agent led to an increase in the particle surface area. Using the Brunauer-Emmett-Teller (BET) method, the specific surface area increases significantly. The pore diameters determined by the Barrett-Joyder-Halenda (BJH) desorption algorithm also indicated that the pore diameters increased with the increase of the weight of KOH. RM:KOH weight ratio of 1:2 and 1:4 have pore diameters of 2.07 and 2.30 nm that were categorized to mesopores particles. Also, the total pore volume also increased with the increase of the weight of KOH. Particles carbonized with RM:KOH ratio of 1:4 resulted in the highest surface area and total pore volume, which characterized graphitic carbons. XRD analysis is needed for further examination in the graphitic R-ray diffraction patterns.

Figure 2 shows the X-Ray diffraction patterns of the raw material of coconut shell char-
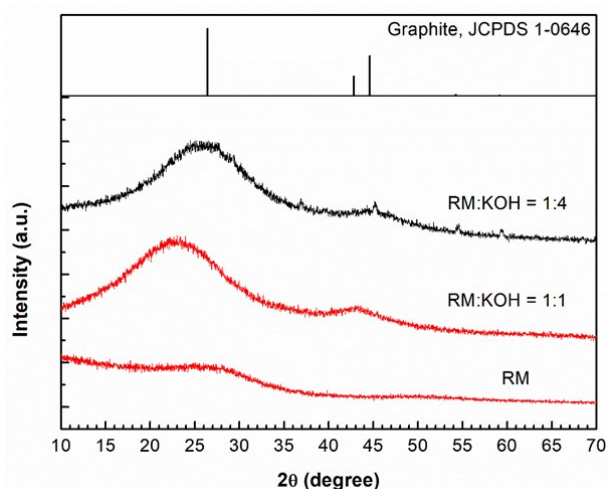

Figure 2. XRD pattern of raw material (RM), graphite synthesized using RM:KOH of 1:1 and 1:4.
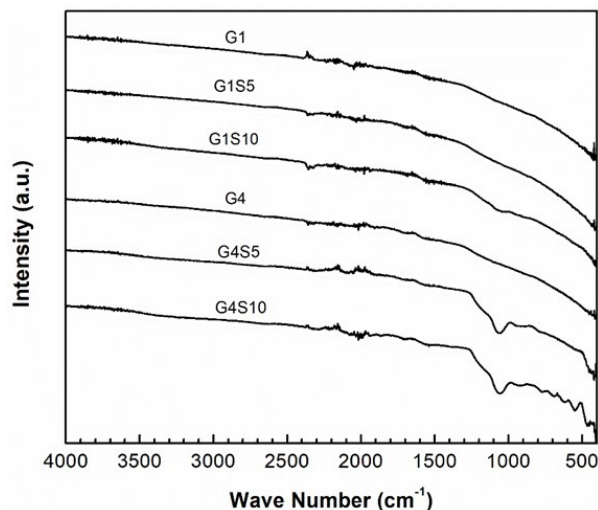

Figure 3. FTIR spectra of graphite and sulfonated graphite with duration 5 and 10 hours.

Table 1. BET surface areas, average pore diameter, and pore volume total of samples.

	Surface area (m²/g)	Pore diameter (nm)	Total pore volume (cm³/g)
Raw material (RM)	75.71	2.23	0.026
RM:KOH = 1:1 (G1)	554.84	0.57	0.079
RM:KOH = 1:2 (G2)	621.25	2.07	0.321
RM:KOH = 1:4 (G4)	1259.67	2.30	0.723

coal (RM), graphite synthesized using RM:KOH of 1:1 and 1:4. They indicated the low crystallinity that increased with the carbonization treatment under nitrogen and the addition of KOH as an activated agent. The carbonization treatment and KOH activation led to the graphitization process of the raw material. It can be seen in the figure that the XRD pattern of the RM sample is a sloping peak. The carbonization treatment and the use of KOH as an activation agent with ratio 1:1 shows the significant peak intensity at 2θ centered at around 23.8° that left-shifted for the highest peak of the graphite reference. The peak of the XRD pattern of RM:KOH = 1:4 at 26.5° was the same as the graphite reference of JCPDS 1-0646. The most intensive diffraction intensity of 2θ at 26.5°, can be indexed to (002) diffraction, which is the typical graphite carbons.

3.2 Effect of the Sulfonating Time on the Esterification Reaction

Before investigating the performance of the esterification reaction of acetic acid and methanol, the analysis of FTIR and ion capacity were carried out to investigate the bonds of the sulfonic group and the number of sulfonic ions, respectively, after sulfonating the graphite particles. Sulfonating time for 5 and 10 hours were compared. Figure 3 shows the FTIR spectra of graphite synthesized using RM:KOH ratio of 1:1 (G1) and 1:4 (G4). For G1, the sulfonic group of $-SO_3$ bond was slightly observed after the G1 was sulfonated for 5 hours (G1S5) and increases slightly after increasing the sulfonation time for 10 hours (G1S10) at wave number around 1050 cm^{-1}. On the other hand, the sul-

fonic group of $-SO_3$ bond clearly appeared after the G4 sample was sulfonated for 5 hours (G4S5), and the intensity was higher than that of G1S10. The intensity of the sulfonic group of $-SO_3$ bond increased by increasing the sulfonating time to 10 hours (G4G10). The noticeable intensity of the sulfonic group of $-SO_3$ bond correlated to the specific surface area of the samples. Increasing the specific surface area gives rise to the surface for bonding the sulfonic group. The ionic capacity calculated using Equation 1 also supported the FTIR results. As shown in Figure 4, increasing the sulfonating time and the weight of KOH led to an increase in the ionic capacity.

Figure 5 shows the effect of the RM:KOH ratio and the sulfonating time on the yield of methyl acetate. The yield of the reaction was affected by the number of KOH added to the raw material that increases with the increase of RM:KOH ratio for both sulfonating times of 5 and 10 hours. For 5 hours of sulfonating time, the yield increase from 32.62 to 85.00% by increasing the RM:KOH ratio from 1:1 to 1:4. Sulfonating time from 5 to 10 hours was also contributed to the increase of the yield from 85.00 to 96.57% for the case of graphite synthesized with RM:KOH = 1:4.

4. Conclusions

The graphitization of coconut shell charcoal was successfully synthesized for solid acid catalyst applications. The catalyst was examined for the esterification reaction of acetic acid and methanol. Carbonization of coconut shell charcoal was carried out by calcination under nitrogen flow and KOH activation. Graphite parti-
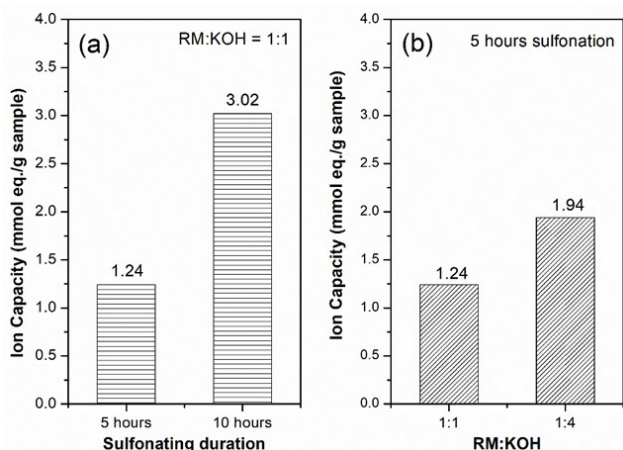

Figure 4. Ion capacities for (a) constant ratio of RM:KOH and (b) constant sulfonating duration.
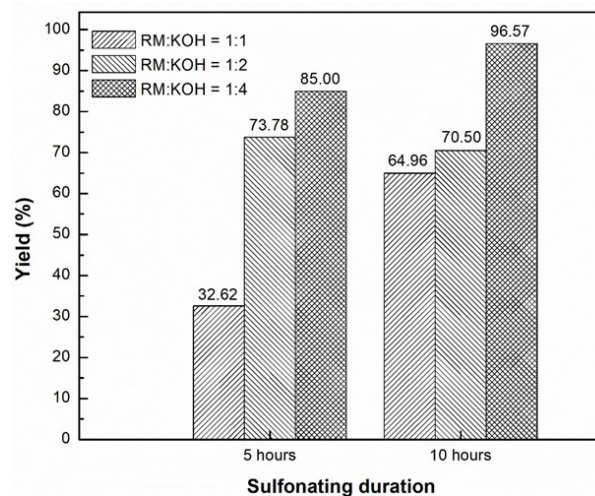

Figure 5. Yield of esterification reaction using synthesized catalysts at various RM:KOH ratio and sulfonating duration.

cles as a result of the carbonization process were sulfonated by heating with the sulfuric acid. The highest yield was obtained by particles carbonized using RM:KOH ratio of 1:4 and 10 hours sulfonating time, reaching 96.57%. This condition resulted in the highest specific surface area of 1259.67 m^2/g with an average pore diameter of 2.30 nm and a total pore volume of 0.723 cm^3/g. The high surface area contributed to the high surface acid content. The surface acid was assigned as a sulfonic group $-SO_3$ bond that the most intensity observed for particles carbonized using RM:KOH ratio of 1:4 and 10 hours sulfonating time.

Acknowledgments

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