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Synthesis of Amorphous Silica from Rice Husk Ash: Comparing HCl and CH_3COOH Acidification Methods and Various Alkaline Concentrations

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Abstract. High purity silica has been successfully synthesized from rice husk ash (RHA) by alkaline extraction using the reflux process followed by acidification. For this study, rice husk was burned in an electric furnace at 700°C for 5 hours to produce RHA. The RHA was refluxed using sodium hydroxide with concentrations of 1.25×10^{-3} M (equal to 5% NaOH) and 2.5×10^{-3} M (equal to 10% NaOH). The acidification process was performed using hydrochloric acid (HCl) 1 M and acetic acid (CH_3COOH) 1M to produce silica gel. Then, the silica gel was heated to 120°C for 12 hours to produced silica. The characterization of silica was determined using energy-dispersive X-ray analysis, Fourier-transform infrared spectrometry, the Brunauer–Emmet–Teller method, and X-ray diffraction. The results show HCl acidification produced silica of a higher purity than that produced by CH_3COOH acidification. The higher concentration of sodium hydroxide led to higher purity of silica. Based on X-ray diffraction, the silica extracted from RHA was found to be amorphous, and Fourier-transform infrared spectrometry revealed bending and stretching vibrations of Si-O and Si-O-Si. The silica extracted by HCl acidification had a surface area of 236 m^2/g, a total pore volume of 0.54 cc/g, and an average pore diameter of 9 nm. The silica extracted by CH_3COOH acidification had a surface area of 204 m^2/g, a total pore volume of 0.43 cc/g, and an average pore diameter of 8.4 nm.

Keywords: Acidification; Reflux; Rice husk ash; Silica gel; Xerogel

1. Introduction

Rice husk accounts for a significant amount of agricultural waste in many rice-producing countries. In 2015, Indonesia produced about 75 million tons of paddy, and rice husk accounts for 20–22% of the weight of paddy (Saleem et al., 2014). The accumulation of rice husk waste can pose a threat to the environment if it is not properly controlled. Rice husk is separated from rice grains during the milling process because it is low in nutrients (Lee et al., 2017). Due to its poor nutrient composition, rice husk is usually used as an animal food ingredient and as a low-cost burning fuel, which is ineffective and can lead to air pollution. Nevertheless, compared to other biomass fuels, rice husk contains unusually high levels of cellulose, lignin, and ash, which are its major constituents. The actual composition varies, but the typical composition is as follows: 38% cellulose, 22% lignin, 20% ash, 18% pentosanes, and 2% other organics (Chandrasekhar et al., 2003). Rice husk ash (RHA)

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contains amorphous silica in the range of 20–25 wt.%.

In recent times, rice husk has been utilized in various applications such as in the manufacture of fertilizer (due to its high lignin content), in the preparation of activated carbon, and as an industrial fuel for gasification or combustion boilers (Namdeo, 2018). Scientists are particularly attracted to the potential of rice husk as a raw material for silica-based materials, as well as pure silicon, silica nitride, silicon tetrachloride zeolite, and amorphous silica (Sun and Gong, 2001).

Controlled combustion of rice husk produces ash that contains high purity amorphous silica. Amorphous silica can be obtained from RHA when the rice husks are burned at a temperature of 700°C, and this is transformed into crystalline silica when it is burned at a temperature of over 850°C (Fernandes et al., 2016). This silica has many applications as a filler, adsorbent, catalyst support, a component of star gels, and a source for producing superior quality silicon and its compounds.

Silica is a basic raw material that is widely used in semiconductors, ceramics, polymers, and several industries, such as the rubber industry and pharmaceuticals (Fernandes et al., 2016). In particular, silica can be used for gas adsorption (Dhaneswara et al., 2019, Fatriansyah et al., 2019) and heavy metal remediation in water (Dhaneswara et al., 2018). In mesoporous form, silica can be used too in gas adsorption application (Dhaneswara and Nofrijon, 2016, Wilson and Mahmud, 2015).

Since silica can be produced from RHA, several reports have addressed the extraction of silica from rice husk. This process not only produces valuable silica but also reduces pollution problems caused by the uncontrolled combustion of rice husk.

Many researchers have developed methods for extracting silica from rice husks. Riveros and Garza (1986) reported that silica can be recovered from rice husk by acid leaching. Later, Kalapathy et al. (2000) discovered the alkaline extraction sol-gel method for recovering silica from rice husk, which is based on the fact that silica can be dissolved in alkaline solution. Because silica has high solubility in a solution with a pH above 10, it can dissolve in alkaline solution to form sodium silicate (Qomariyah et al., 2019). Acidification is also a necessary part of the process to produce silica gel. This process has numerous advantages; it is not as costly or as damaging to the environment as the quartz fusing method (Todkar et al., 2016). It has been reported that the character and purity of silica are more affected by chemical treatment than by thermal treatment (Daifullah et al., 2004).

This study aims to synthesize amorphous silica using rice husk waste as a raw material of SiO_2. A simple reflux process using an alkaline solution (sodium hydroxide) was followed by acidification to form silica gel. Then, the effects of various alkaline concentrations and the two acidification methods were investigated by examining the physical, structural, and mechanical properties of the amorphous silica obtained from rice husk waste.

2. Methods

2.1. Materials

Wet rice husk was obtained from Paddy Mill Industry, Leuwiliang, Bogor and dried for 8 hours under sunlight. Distilled water, sodium hydroxide, hydrochloric acid, and acetic acid were obtained from C.V. Mitra Bersama and used as they were without any further purification. Rice husk ash was obtained from the controlled combustion of the rice husk at 700°C for 5 hours. Alkaline solutions were made by dissolving 5 g of sodium hydroxide in 100 ml of distilled water to produce 1.25×10^{-3} M natrium hydroxide, equal to 5% NaOH, and by dissolving 10 g of sodium hydroxide in 100 ml distilled water to produce 2.5×10^{-3} M natrium hydroxide, equal to 10% NaOH. HCl 1 M was obtained by diluting 20.72 ml of 37%

hydrochloric acid in 229.28 ml of distilled water, and acetic acid solution 1 M was obtained by diluting 14.28 ml of glacial acetic acid in 235.72 ml of distilled water.

2.2. Experimental Procedures

Silica was extracted from RHA using alkaline methods according to the method described by Kalapathy et al. and Anuar et al. to dissolve silica in RHA and obtained sodium silicate (Kalapathy et al., 2000; Okoronkwo et al., 2013; Anuar et al., 2018). First, 5 g of RHA was placed in a three-neck round-bottom flask, and an alkaline solution was added. Then, this was refluxed and stirred for an hour at 80°C. The process produced a sodium silicate solution with a white and clear appearance. The reaction between RHA and sodium hydroxide solution is given in Equation 1 below.

$$SiO_2\,(ash) + 2NaOH \rightarrow Na_2SiO_3 + H_2O \tag{1}$$

The sodium silicate solutions were cooled at room temperature until its temperature dropped to 30°C. Then, the solutions were filtered through Whatman Grade No. 41 ashless filter paper, after which they were titrated slowly to HCl 1M or CH_3COOH 1M with constant stirring to achieve a pH of 7. The solution had to be stirred at a constant rate to avoid local changes in pH during gel formation. Silica wet gels began to form when the pH decreased below 10. The titration process was continued carefully until the pH of the solution was exactly 7. The reaction of the acidification of sodium silicate using hydrochloric acid is given in Equation 2, and the acidification of sodium silicate using acetic acid is expressed in Equation 3.

$$Na_2SiO_3 + HCl \rightarrow SiO_2 + NaCl + H_2O \tag{2}$$

$$Na_2SiO_3 + CH_3COOH \rightarrow SiO_2 + CH_3COONa + H_2O \tag{3}$$

The silica wet gels were then filtered and heated at 120°C for 12 hours. The silica wet gels became xerogel when they were dried (Aripin et al., 2017). Then, the xerogel was washed using 100 ml of distilled water at 80°C for 15 minutes with constant stirring to dissolve any salts that might have formed. Finally, the precipitate was filtered and heated at 120°C for 4 hours. This process was repeated at least three times for one hour to ensure the salt content in the xerogel was completely dissolved in distilled water.

2.3. Analysis Techniques

Silica extracted from RHA with various concentrations of sodium hydroxide and different acidification methods was characterized using the Brunauer–Emmett–Teller method (BET), Fourier-transform infrared spectrometry (FTIR), energy-dispersive X-ray analysis (EDX), and X-ray diffraction (XRD). The specific surface area of the silica produced from RHA was evaluated using the nitrogen BET adsorption technique. Samples were degassed under vacuum at 300°C for 3 hours.

The chemical composition was analyzed using EDX, and the organic bonds were characterized using FTIR. The amorphous nature of silica was determined by XRD in an X-ray diffractometer (LynxEye) using CuKα under the following experimental conditions: 40 kV, 35 mA, 2θ scanning range from 2º to 50º. Finally, the physical morphology of the synthesized silica was identified using a scanning electron microscope (SEM).

3. Results and Discussion

3.1. Composition Analysis of Silica Produced from Rice Husk Ash

Fourier-transform infrared spectroscopy characterization was carried out to examine the functional group characteristics of the silica synthesized from RHA. The spectra were obtained at wavenumber 4000–400 cm^{-1}, and the results are shown in Figure 1. As Figure

1 shows, the silica produced from HCl acidification had a lower FTIR transmission intensity. Therefore, it can be concluded that this method produced a stronger Si-O-Si bond than CH3COOH acidification. Thus, silica synthesized from RHA by HCl acidification has more Si-O-Si bonding than silica produced from RHA by CH_3COOH acidification. The appearance of the synthesized silica titrated by hydrochloric acid indicates asymmetric stretching vibration of the siloxane bonds (Si–O) at 1071.89 cm^{-1} and 789.33 cm^{-1}. The peaks appearing at 453.13 cm^{-1} and 413.94 cm^{-1} can be attributed to Si-O-Si bending vibration. Acidification using acetic acid showed some peaks which indicate not only the occurrence of a Si-O-Si bond but also that of a -OH bond. The notable absorption peaks, such as that at 3406.61 cm^{-1}, show the occurrence of hydrogen-bonded -OH stretching bands of silanol groups (Si-OH) (Okoronkwo et al., 2013). The peak at 1630.38 cm^{-1} indicates -OH bending vibration of silanol groups (Si-OH). Furthermore, the peaks at 1071.33 cm^{-1} and 959.66 cm^{1} are identified as asymmetric stretching vibration of the siloxane bonds (Si-O). The broadband at 455.24 cm^{-1} corresponds with Si-O-Si stretching and bending vibrations (Daifullah et al., 2004; Okoronkwo et al., 2013).

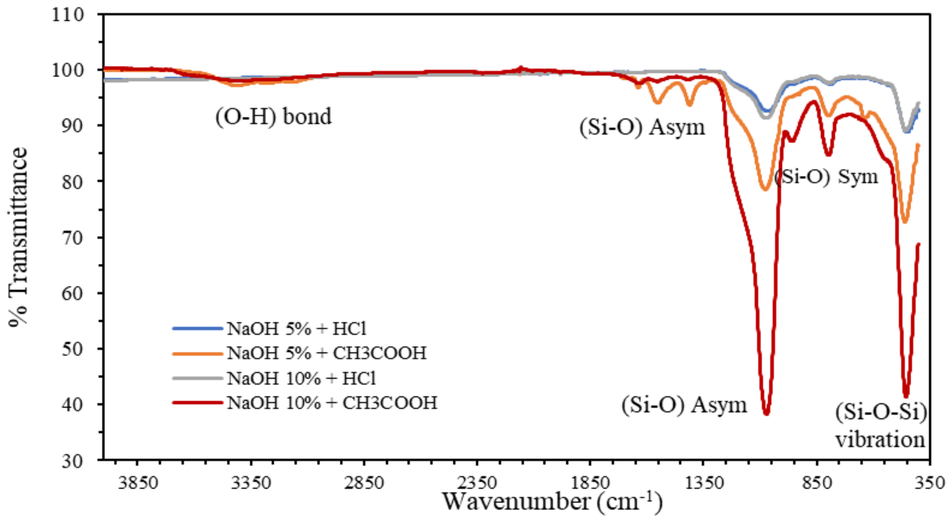

Figure 1 Fourier-transform infrared spectra of silica synthesized from rice husk

3.2. Energy-Dispersive X-Ray Analysis

The original contents of rice husks, such as hemicellulose, lignin, pentosanes, and other organics, were removed during thermal decomposition by burning the rice husk in the electric furnace. However, burning rice husk directly in the electric furnace produced metallic impurities in the RHA. The major elemental impurities in the RHA were potassium, magnesium, and calcium. These metallic impurities were removed by reflux and sol-gel process due to the reaction of acid and alkali solution. The impurities from the ash were separated and removed using filter paper, while the SiO_2 was dissolved in a strong alkali solution (NaOH) to form a colorless sodium silicate solution. The reaction is given in Equation 1. Then, silica was obtained by adding hydrochloric acid and acetic acid slowly until a pH of 7 was reached. The reaction is presented in Equations 2 and 3. The addition of acid promotes the formation of high purity silica due to Na+ exchange from the sodium silicate structure to the hydrochloric acid solution.

The elements contained in the silica extracted from RHA were determined using EDX. Table 1 shows the elemental compositions in the silica synthesized from rice husk waste. In this study, the purity of the silica obtained was around 98–99 wt.% As shown in Table 1, the silica with the highest purity was obtained using acetic acid 1M and 10% of sodium hydroxide solution, 99.99 wt.% Table 1 shows that potassium (K) was the only impurity detected in the synthesized silica. Different types of acids did not produce significantly different purities of silica. The role of the sodium hydroxide solution was to dissolve the silica from the RHA. Sodium hydroxide is used in research because it has strong base properties compared to other types of bases. This is in line with the results of this study, which show that the higher the concentration of sodium hydroxide, the more effective it is for dissolving silica.

Table 1 Elements in silica extracted from RHA with various of concentrations of NaOH and acidification methods

Elements %	NaOH 1.25×10^{-3} M + CH_3COOH 1 M	NaOH 2.5×10^{-3} M + CH_3COOH 1 M	NaOH 1.25×10^{-3} M + HCl 1 M	NaOH 2.5×10^{-3} M + HCl 1 M
Si	35.07	48.30	46.69	46.72
O	64.10	51.69	53.03	53.18
K	0.83	-	0.28	0.10
Yield (%. wt)	99.17	99.99	99.72	98.92

3.3. X-Ray Diffraction Analysis of Silica

The XRD patterns of the silica synthesized from rice husk waste with various concentrations of sodium hydroxide and different acidification methods are shown in Figure 2. Broad diffused peaks with maximum intensity at $2\theta = 22°$ can be observed, indicating the typical nature of silica. None of the XRD patterns of any of the samples shows specific peaks or sharp peaks. Silica obtained by alkaline extraction is completely amorphous. This is because sodium hydroxide only solubilizes amorphous silica, which is subsequently precipitated (Fernandes et al., 2016). The XRD patterns of silica produced from RHA by acetic acid acidification are similar to those of silica produced from RHA with hydrochloric acid acidification, which indicates that both forms of silica are amorphous. The structure of silica synthesized from rice husk waste depends on the temperature at which the rice husk is burned to produce RHA. According to the International Agency for Research on Cancer, which is part of the World Health Organization, crystal SiO_2 poses a carcinogenic risk to humans (Mukherjee and Roy, 1991). Heating rice husk at temperatures of over 900°C produces RHA with a highly ordered structure. In this study, all the samples were burned using controlled combustion at 700°C for 5 hours in an electric furnace.

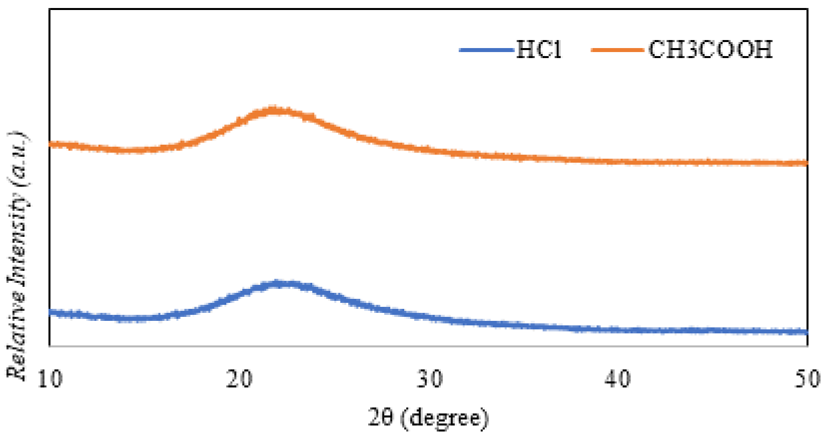

Figure 2 X-ray diffraction patterns of silica obtained by: (a) acetic acid (CH_3COOH) acidification; and (b) hydrochloric acid (HCl) acidification

3.4. Brunauer–Emmett–Teller Analysis of Silica

The surface area, pore volume, and pore diameter of the silica synthesized from rice husk were measured using BET. Table 2 summarizes the results for total pore volume, specific surface area, and average diameter of silica. The RHA refluxed with 2.5×10^{-3} M sodium hydroxide (10% NaOH) followed by acidification using hydrochloric acid produced a silica sample with a high surface area and pore volume of 236.2 m^2/g and 0.54 cm^3/g, respectively. The surface area of the silica was reduced when acetic acid was used for the acidification process and the concentration of sodium hydroxide was lower (5% NaOH). These samples had a surface area and total pore volume of up to 76.75 m^2/g and 0.28 nm, respectively. The large surface area of the silica produced from rice husk is due to the removal of organic matter and impurities during the reflux process using sodium hydroxide.

Furthermore, the silica extracted from RHA using a higher concentration of sodium hydroxide and a similar acid concentration has a higher surface area. This indicates that both the acidification method and the concentration of the alkaline solution both have a significant effect on the surface area of silica. Moreover, the silica synthesized using hydrochloric acid had a higher total pore volume (0.54–0.64 nm) than the samples synthesized using acetic acid (0.28–0.43 nm). The average pore diameter of the silica produced using a higher concentration of sodium hydroxide was 8.4–9 nm, which is smaller than that of the silica obtained with a lower concentration of sodium hydroxide, which was 12.6–15 nm.

Table 2 BET surface area of silica produced from RHA

Sample	BET surface area, m^2/g	Total pore volume, cm^3/g	Average pore diameter, nm
Silica produced from RHA using NaOH 5% + CH_3COOH 1 M	76.75	0.28	15
Silica produced from RHA using 10% NaOH + CH_3COOH 1 M	204.8	0.43	8.4
Silica produced from RHA using 5% NaOH $\times10^{-3}$ M + HCl 1 M	203.6	0.64	12.6
Silica produced from RHA using 10% NaOH + HCl 1 M	236.2	0.54	9

As Table 2 shows, the pore diameter of the silica obtained from the extraction process is about 8.4–12.6 nm. This indicates that the silica is a mesoporous material. According to International Union of Pure and Applied Chemistry, a mesoporous material is a material whose pores measure less than 50 nm in diameter. Thus, it can be concluded that silica extracted from RHA using an alkaline extraction process produces silica of an amorphous and mesoporous nature. Moreover, the adsorption behaviors of silica produced from rice husk are shown in Figure 3. The upper portion of a loop is recognized as desorption and the lower portion is adsorption. According to Figure 4, the adsorption behaviors possess a type IV isotherm and a type H3 hysteresis loop. The type IV isotherm indicates a mesoporous material, and the type H3 hysteresis loop shows the physical appearance of silica, that is non-rigid aggregates of plate-like particles (slit-shaped pores).

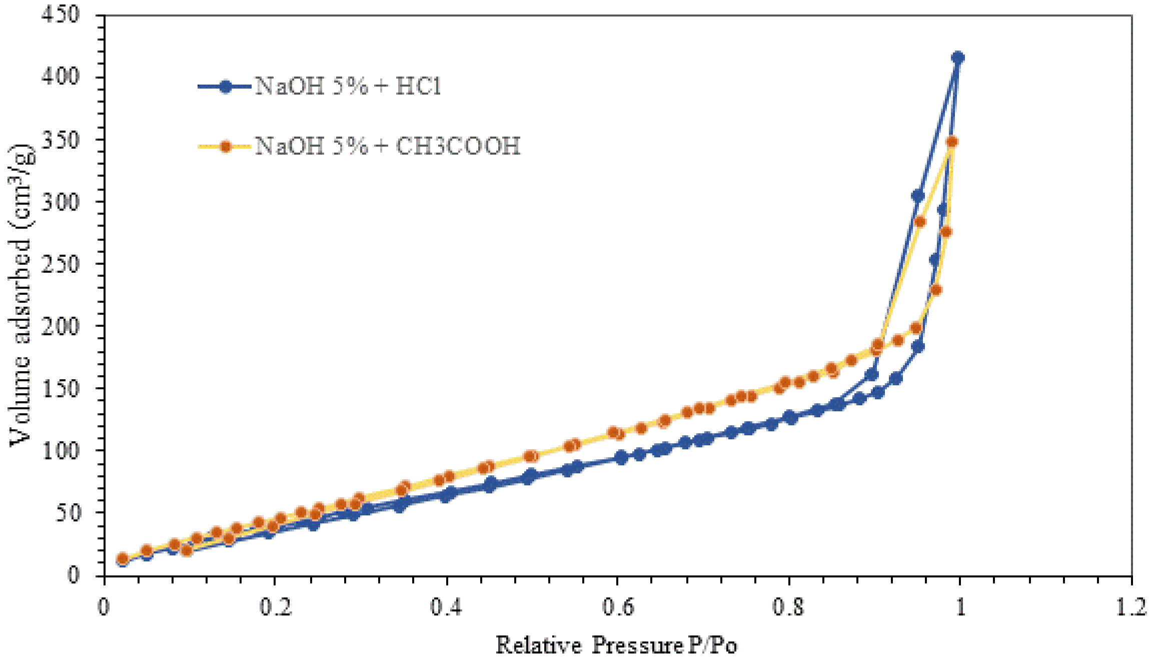

Figure 3 Adsorption-desorption isotherms of nitrogen for samples extracted using sodium hydroxide and acidification using acetic acid and hydrochloric

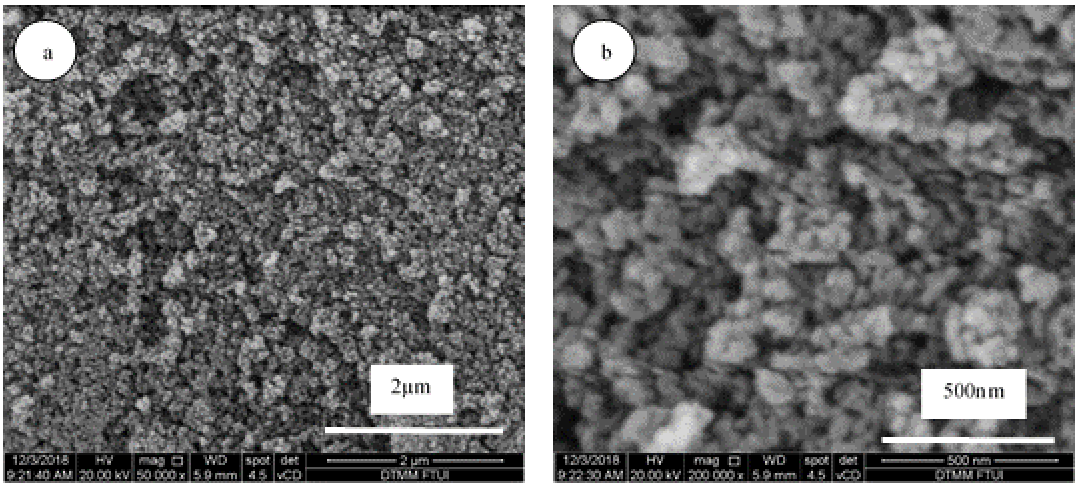

Figure 4 SEM micrograph of silica from rice husk using magnification: (a) 50.000× and (b) 200.000×

3.4. Scanning Electron Microscope Analysis of Silica

Amorphous silica was successfully synthesized by alkaline extraction using a reflux process followed by an acidification process using either acetic acid or hydrochloric acid. Scanning electron microscope images of the amorphous silica were used to analyze the surface morphology. The images were taken at magnifications of 50,000× and 200,000×. Figure 4 shows that the grain of the synthesized silica from rice husk has an irregular shape and a size of 9–12 nm. Figure 4b, which presents a higher SEM magnification, clearly shows that grain sizes and of varying sizes can be clearly seen, which indicates that the synthesized silica can be identified as heterogeneous mesopore silica. The brightly colored surfaces indicate amorphous silica, whereas the dark-colored surfaces indicate pore cavities. This is supported by the data in Figure 3, which shows that the synthesized silica is a type IV silica with a mesoporous structure. However, the structure of the synthesized silica shows a tendency to agglomerate.

4. Conclusions

This study demonstrates that high purity silica can be obtained from rice husk using a simple alkaline-acidification process. Amorphous silica with a purity of 98–99% was obtained from rice husk by alkaline extraction using a reflux process followed by acidification. In this study, the silica extracted from rice husk by acidification using HCl had the highest purity and the largest surface area (236.2 m^2/g). Moreover, dissolving the silica in a higher concentration of alkaline solution also had a significant effect, resulting in a higher surface area but a smaller total volume and average diameter. Fourier-transform infrared spectra characterization shows that the synthesized silica has both Si-O-Si and Si-O bonds, and the XRD pattern shows that it has an amorphous structure. Silica with a large surface area can be used for various applications, such as catalysts and adsorbents.

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