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SYNTHESIS AND CHARACTERIZATION OF SODIUM SILICATE-BASED MESOPOROUS SILICA FROM SILICA SAND IN WEST SUMATRA

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ABSTRACT

A study has been made on the production and analysis of mesoporous silica using sodium silicate derived from silica sand found in West Sumatra. Sodium silicate from silica sand was used as raw material to synthesize mesoprous silica together with non-ionic surfactant P104. The raw materials were based on their high abundance as a natural resource in West Sumatra and the use of non-ionic surfactants is cheap and does not produce harmful by-products. Sodium silicate is a white solid with a SiO_2/N_2O mole ratio of 0.58, which is in the range of commercial sodium, and aging time on the morphology and pore size of silica was studied using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM), adsorption-desorption isothermal analysis (BET) and Transmission Electron Microscopy (TEM). The hexagon spherical regular mesoporous silica with a pore diameter of 5.2 nm was obtained at mixed pH 5 and aging time for 6 hours.

Keywords: West Sumatra Silica-Sand, Mesoporous-Silica.

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INTRODUCTION

West Sumatra Province is abundant in both inorganic and organic natural resources, including silica sand, iron sand, tin, limestone, oil palm, coconut, and spices. West Sumatra is home to 82.5% of Indonesia's silica sand reserves.[1,2] The Department of Chemistry at Padang State University (UNP), which is part of the Faculty of Mathematics and Natural Sciences, has undertaken numerous research and community service projects focused on the utilization of local resources. These projects involve the synthesis and practical application of diverse materials[3], that have produced sodium silicate and mesoporous silica by using silica sand obtained from local natural resources. The sodium silicate produced falls within the range of a commercial sodium silicate mole ratio of 0.58 (Rm SiO_2/Na_2O 0.5-4).[4] Sodium silicate serves as a fundamental substance in the industry for the production of numerous compounds with greater market value, such as zeolites, mesoporous silica, fire-resistant paints, and others.[5,6] Mesoporous silica is a solid material formed through the polycondensation of silica Si-O-Si, which results in the creation of pores with sizes ranging from 2 to 50 nanometers.[7] Research on mesoporous silica is currently the center of attention of many researchers because it is a material with high thermal and chemical stability. Mesoporous silica has promising potential to be used in various fields, such as stationary phases for chromatography, polymer reinforcement materials, enzyme support in biomedicine, immobilization of metal/metal oxide nanoparticles in heterogeneous catalyst synthesis, and others.[8,9] Mesoporous silica can be synthesized from sodium silicate or silica alkoxide tetra methyl ortho silicate, and tetra ethyl ortho silicate (TMOS, TEOS).[10,11] The synthesis of mesoporous silica using TEOS and TMOS has been carried out by several researchers. However, the utilization of TEOS and TMOS as raw materials is costly and will result in the production of alcohol as a secondary product.[12] The utilization of sodium silicate as a precursor for the production of mesoporous silica offers several benefits. Firstly, sodium silicate is an economical source of silica. Additionally, the synthesis of mesoporous silica using sodium silicate can be conducted at low temperatures and within a short timeframe. Moreover, the synthesis process generates salts that facilitate the condensation process and are environmentally benign.[13-16] Mesoporous silica synthesis using Na_2SiO_3 can be carried out under acidic or basic conditions. The synthesis of silica using sodium silicate and non-ionic surfactants under acidic conditions is more favorable, namely short aging

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time, low temperature, more uniform particle size, and heat resistance. The study involved the synthesis of mesoporous silica by the sol-gel method, employing sodium silicate derived from silica sand and a non-ionic surfactant called P104. The synthesis was conducted under acidic circumstances. The sodium silicate utilized for the synthesis of mesoporous silica has a Na_2O/SiO_2 ratio that differs from the one employed by Kosuge, K., 2004.[17,18] This study examined the impact of pH and aging time on the crystallinity and shape of mesoporous silica generated throughout the synthesis process using sodium silicate precursors.

EXPERIMENTAL

Material and Methods

The materials used in this study were sodium silicate, NaOH, Na_2CO_3, water, pluronic P104, HNO_3, distilled water, and concentrated NH_4OH. The instruments used in this research the SEM, XRD, FTIR, BET, and TEM.

General Procedure

Synthesis of Sodium Silicate

Sodium silicate was synthesized by melting method as found by Aini, S. 2018; Silica sand with a percentage of SiO_2 98.38% (after being separated by a magnet and dissolved with 1M HNO_3) mixed with NaOH, Na_2CO_3, and water with a mol ratio is 1; 4; 0.75; 0.18, then heated at 300 °C for 1 hour.

Synthesis of Mesoporous Silica

The synthesis of mesoporous silica was carried out by utilizing sodium silicate derived from silica sand and Pluronic P104 as a surfactant, following the process outlined by K. Kosuge (2004).[17] 4 g of Pluronic P104 was dissolved in 150 ml of 2 M HNO_3, and 10 g of sodium silicate was dissolved in 50 ml of distilled water. The sodium silicate solution was added to the P104 solution by dropwise addition and while stirring vigorously. The pH of the mixture was immediately adjusted to pH variations of 3, 5, or 6 respectively with concentrated NH_4OH (mesoporous silica products such as SMpH-3, SMpH-5, SMpH-6). The resulting solution was stirred at 600 rpm for 2 hours and continued at 400 rpm at 85 C for 2 hours. The total stirring time (aging time) varied between 4 and 6 hours (the resulting products were SMA-4 and SMA-6). The solid products were washed with warm deionized water, dried at 110 ▫C for 2 hours, and then calcined at 600 C for 1 hour.

Characterization

The presence of meso-sized pores and morphology in the silica produced with varying pH (SMpH-3, SMpH-5, and SMpH-6) were characterized using X-ray at small angles (2Θ 0 - 10) and Scanning Electron Microscope (SEM). The presence of vibrational Si-O-Si groups, meso-sized pores, crystallinity and morphology, pore size, surface area and sorption-desorption isotherm type of silica produced with aging time of 4 and 6 hours (SMA-4, SMA-6) were characterized using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning electron microscopy (SEM), N2 adsorption and desorption isotherm analysis by Brunauer-Emmett-Teller (BET) method and Transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

The study of pH variation and aging time in the synthesis of mesoporous silica from sodium silicate silica sand aimed to obtain mesoporous silica with larger pore sizes in the meso range and more regular morphology. Mesoporous silica synthesized with pH variation was characterized by the presence of meso-sized pores and morphological regularity using x-ray diffraction at low 2θ angles and SEM. The optimum pH condition (the start of the formation of mesoporous silica with regular morphology) was used to synthesize mesoporous silica with varying aging times. The synthesized mesoporous silica with varying aging times was characterized using FTIR, small angle, and large angle X-ray diffractometer, SEM. TEM and BET.

Mesoporous Silica Synthesized at pH Variation

The presence of pores in the meso cellular-scale silica solids synthesized with pH variations of 3, 5, and 6 was evaluated by X-ray diffraction measurements at a small angle range of 2θ 1-10. Figure-1 shows the diffraction patterns of the SMpH-3, SMpH-5, and SMpH-6 products. The small angle diffractograms of

silica synthesized at various pH (SMpH-3, SMpH-5 and SMpH-6) show the diffraction pattern of mesoporous silica. Mesoporous silica is characterized by the presence of high-intensity diffractogram peaks at 2θ angles 1-3 followed by low-intensity diffractograms at 2θ angles between 3 and 10. The similar diffractogram patterns for the three silica solids produced indicated that all three reaction pH conditions could produce mesoporous silica. However, the highest diffractogram peak intensity was found in the silica produced at synthesis pH 5. Analysis of the optimum pH conditions for mesoporous silica synthesis was studied from the morphology of the silica produced using SEM. Figure-2 shows scanning electron microscope (SEM) pictures of silica generated through pH changes, namely SMpH-3, SMpH-5, and SMpH-6. Figure-2 demonstrates that mesoporous silica with variations in pH is generally lumpy or agglomerated. Regular silica morphology began to form on silica SMpH-5 with synthesis pH conditions of 5. From the result, the preparation of pH is too acidic and neutral and is not suitable for the formation of mesoporous silica with hexagonal spherical morphology. It is because the micelles of the surfactant P104 will be stable in an acidic atmosphere only at a certain pH, namely pH.[18,19] Hence, in this study, we conducted additional research to investigate the effect of the aging period and employed the optimal pH condition of 5.

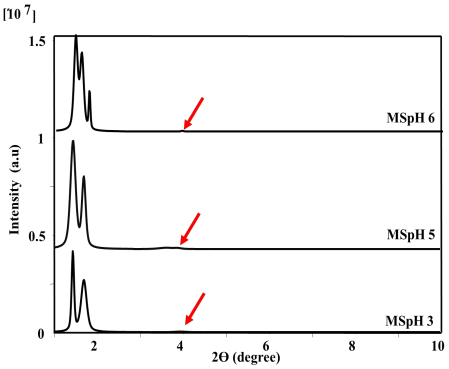


Fig.-1: X-ray Diffractogram Patterns of Mesoporous Silica Particles Synthesized at Various Preparation pHs

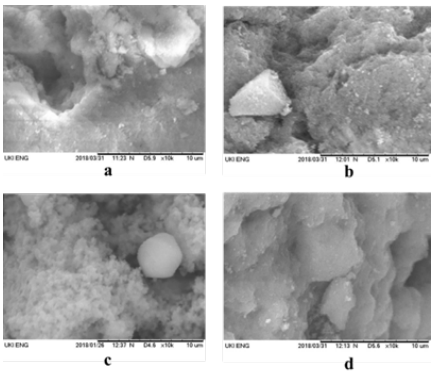


Fig.-2: Surface Morphology of Mesoporous Silica Synthesized at Formation pH vary a. 3, b.3 c.5 and d.6

Mesoporous Silica Synthesized at Varying Aging Times

Figure-3 shows the FTIR spectra characteristics of silanol (Si-OH) and siloxane (Si-O-Si) group vibrations found in porous silica with aging time variations of 4 and 6 hours (SMA-4 and SMA-6). The FTIR spectra for SMA-4 contained Si-OH bending vibrations at wave number 1636 cm-1, and Si-OH stretching vibrations at wave number 3449 cm-^{1}; siloxane vibrations are indicated by a band at 1103.40 cm^{-1} from Si-O-Si v(as), vibration bands at 802.30 cm^{-1} and 470.85 cm^{-1} which are Si-O-Si stretching and bending vibrations, respectively. The same pattern of vibrational bands of silanol and siloxane with higher intensity is shown by the infrared spectra of mesoporous silica with an aging time of 6 hours (SMA-6).

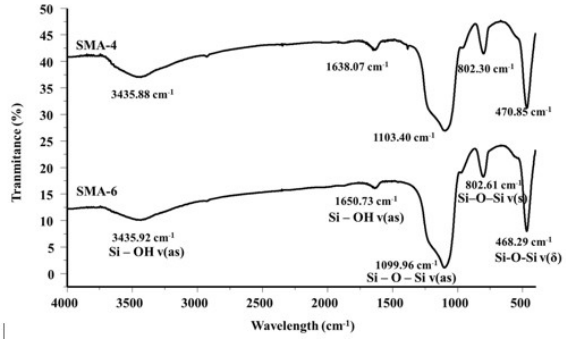


Fig.-3: FTIR Spectra of Mesoporous Silica at Varying Aging Times SMA-4 and SMA-6

The FTIR spectra of SMA-6 showed absorption bands for Si-O-Si bending vibrations at wave number 468.29 cm^{-1}, Si-O-Si stretching vibrations at wave number 802.61 cm^{-1}, asymmetric stretching vibrations

at wave number 1099.96 cm^{-1}, Si-OH bending vibrations at wave number 165.73 cm^{-1}, and Si-OH stretching vibrations at wave number 3435.92 cm-1. In general, it can be concluded that the mesoporous silica synthesized by aging time variations of 4 and 6 hours has the same FTIR spectrum as the original mesoporous silica and mesoporous silica was successfully synthesized from sodium silicate from silica sand.[20] The presence of silica nanoparticles and pores in the meso range of the products produced with variations in gelation time can be further characterized using an X-ray diffractometer. The diffractograms of silica produced with variations in aging time of 4 and 6 hours (SMA-4 and SMA-6) can be seen in Fig.-4 and 5. Figure-4 shows the high-angle diffractograms of silica produced with aging times of 4 and 6 hours, both showing broad peaks at 2θ between 19 and 30 with the highest peaks both at an angle of 2θ 22. This wide X-ray diffractogram peak pattern illustrates that the silica produced (SMA-4 and SMA-6) are both small/amorphous [Purnawira, B, 2019]. However, the intensity of the broad peak at 2θ 19-30 is higher in the diffractogram of the SMA-6 sample than the SMA-4 sample, this indicates that the crystallinity of SMA-6 is higher than SMA-4. Figure-5 shows the low-angle diffractogram of SMA-4; there are two main peaks at 2θ 1.4649 and 1.6938 and a small peak at 2θ 3.9314. While the low-angle X-ray diffractogram for SMA-6; there are 3 main peaks at 2θ 1.2999, 1.4834, 1.6947, and a small peak at 2θ 4.0900. The major peaks at 2θ between 0-3 and minor peaks at 2θ between 3-10 indicate that the resulting silicas (SMA-4 and SMA-6) have pores in the meso size range and are not uniform. The low-angle diffractogram pattern for MSA-6 has a higher intensity compared to the SMA-4 sample.[21] The results of low-angle and high-angle X-ray diffractogram analysis can be concluded that the SMA-6 sample is amorphous silica which has pores in the meso range with higher crystallinity compared to the SMA-4 sample.

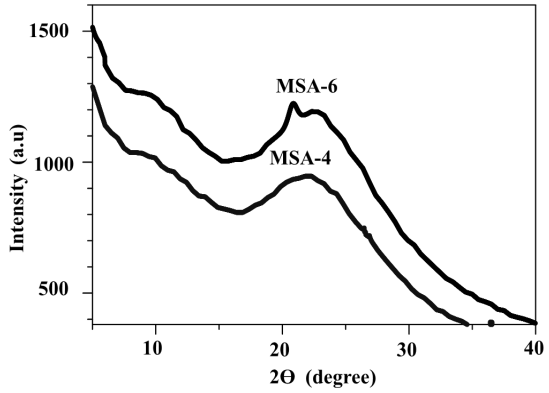


Fig.-4: High-angle X-ray Diffraction Patterns of Silica Synthesized at Various Aging Times of 4 and 6 Hours (MSA-4, MSA-6)

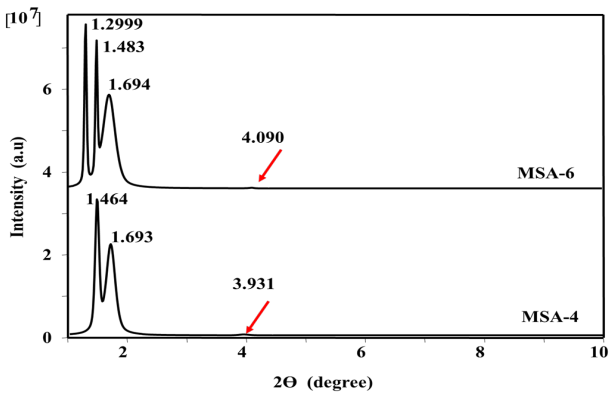


Fig.-5: Low-angle X-ray Diffraction Patterns of Silica Synthesized at Various Aging Ties of 4 and 6 Hours (MSA-4, MSA-6)

The nitrogen gas adsorption-desorption isotherm data can provide a more detailed analysis of the pore size of the resultant silica. Figure-6 illustrates the nitrogen adsorption/desorption isotherms of the silica generated with varying age times of 4 and 6 hours. Samples SMA-4 and SMA-6 show type IV isotherms, which are indicative of materials possessing mesoporous structures.

Table-1: Surface Area, Pore Volume, Pore Size of SMA- 4, and SMA-6

	Surface Area (m^2/g)	Pore Vol. (mL/g)	Pore size (A˚)
MSA-4	256.005	0.299	35.330
MSA-6	268.711	0.306	52.036

SMA-6 is silica with higher crystallinity, larger surface area, and diameter. Furthermore, the morphology and pore size of SMA-6 were analyzed using TEM and SEM, as shown in Fig.-7 below. Figure-7 a) shows the pore images of SMA-6 silica from a). vertical direction and b). horizontal direction. Referring to The N_2 hysteresis characteristic of materials with a regular size and shape distribution is in agreement with the IUPAC classification.[22] Table-1 presents the surface area, pore volume, and pore size diameter

data of the SMA-6 sample, which is greater in size compared to the SMA-4 sample. Both materials exhibited mesoporous pore size widths, measuring 3.533 nm and 5.2036 nm, respectively. Previous studies have reported that aging time will affect surfactant micellization, silica polymerization, and mesoporous silica morphology. This hypothesis is proven by the results of nitrogen sorption-desorption isotherms (Fig.-6) and SEM images of SMA-4 and SMA-6 samples (Fig.-7c), that the longer aging time will result in larger silica pore size and more regular silica morphology. SMA-6 is silica with higher crystallinity, larger surface area, and diameter.

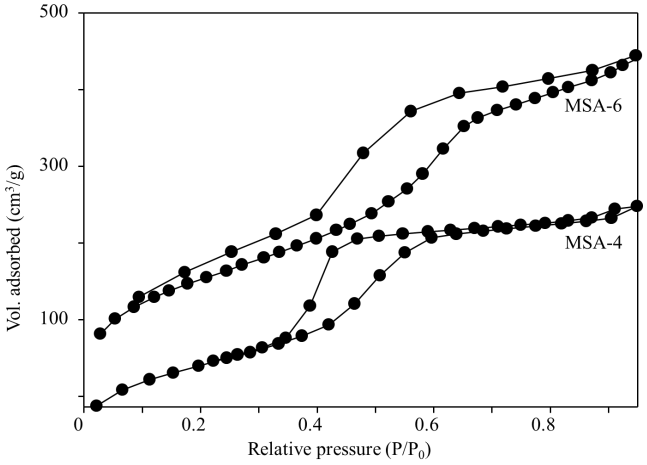
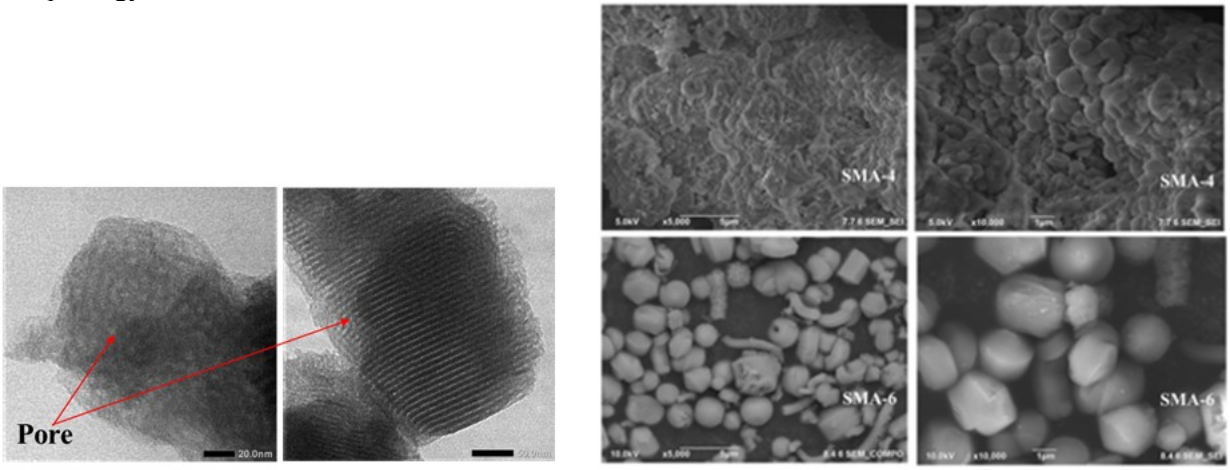


Fig.-6: Nitrogen Gas Adsorption-Desorption Isotherms of Mesoporous Silica Synthesized at Aging Times of 4 and 6 Hours (MSA-4, SMA-6)

Furthermore, the morphology and pore size of SMA-6 were analyzed using TEM and SEM, as shown in Fig.-7 below. Figure-7 a) shows the pore images of SMA-6 silica from a). vertical direction and b). horizontal direction. Referring to the scale bar in the figure (20 nm), the silica solid produced with an aging time of 6 hours (SMA-6) has pores with a pore diameter of less than 10 nm (5.2 nm) in the mesoporous range. In addition to the larger pore diameter in SMA-6, its morphology can be observed from the SEM image in Fig.-7 b). Mesoporous silica produced at an aging time of 6 hours (SMA-6) has a more regular morphology (hexagonal spherical shape). Meanwhile, SMA-4 still has a clumpy morphology.



(a) (b) (c)

Fig.-7: (a) and (b) TEM Image of Mesoporous Silica Obtained at 6 Hours Aging Time (SMA-6), (c) SEM Image of Mesoporous Silica Obtained at 4 and 6 Hours Aging Time (SMA-4, SMA-6)

CONCLUSION

Mesoporous silica was successfully synthesized using sodium silicate from silica sand as a silica source, and non-ionic surfactant Pluronic P104. The synthesis parameters of concern are the preparation pH, and

aging time (gelation and condensation time). From the results of the study, the preparation pH was too acidic, and neutral was not suitable for the formation of mesoporous silica with hexagonal spherical morphology. This is because the micelles of the surfactant P104 could only be stable in an acidic environment at a specific pH level, which is pH 5. The silica gel formed after a short gelation and condensation time of 4 hours resulted in the production of mesoporous silica with irregular or clumpy forms when it is dried and calcined. When the gelation time and condensation time were set to 6 hours, the resulting mesoporous silica precipitates would have a consistent hexagonal spherical form, a pore size of 5.2 nm within the meso range, and a surface area of 268.71 m^2/g.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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