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by M Munasir

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Aging Time Effect on Porous Characteristics of Natural Mud-based Silica Prepared by Hydrothermal-Coprecipitation Route

A Ubaid¹, N Hidayat² and Munasir¹

¹Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Surabaya (UNESA) Jl. Ketintang, Surabaya 60231, Indonesia

²Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang (UM), Jl. Semarang 5, Malang 65145, Indonesia

Email: munasir_physics@unesa.ac.id

Abstract: In this present study, we report the influence of aging time on porous characteristics and chemical bonding within structurally related silicates of silica. The silica was well prepared by using a combination of hydrothermal and coprecipitation methods. Local natural mud from Sidoarjo, Indonesia was preferred as a starting material, rather than the expensive commercial ones. The aging time was set at 20, 24, 28, and 32 hours. The X-ray fluorescence (XRF) test revealed that the produced porous silica has a purity of 98.9%. The Fourier Transform of Infra-Red (FTIR) analysis showed that $\equiv\text{Si-OH}$ and $\equiv\text{Si-O-Si}\equiv$ functional groups were found in the samples. The pores of the silica, after Brunauer–Emmett–Teller (BET) measurement, found to be macropore and mesopore. The prepared silica with different porous characteristics were strongly influenced by the chemical activities during the synthesis, known as syneresis and Ostwald processes.

Keywords: porous silica, aging time, natural mud, hydrothermal-coprecipitation

1. Introduction

Porosity is a vital parameter for adsorbent materials. Higher porosity will lead to better adsorption performance of an adsorbent. Regarding porosity, silica is one of the well-known materials that possess a high level of porosity which turns to meet the criteria of adsorbent materials [1]. Many experts and scientists have widely searched the new synthetic approaches of silica, particularly porous silica, as well as its advanced applications. To address some of its applications, a porous silica can be applied as an adsorbent [1], catalyst and water filter [2], and drug delivery system [3]. Porous characteristics of materials can influence other important desired properties of the materials [4]. The porous characteristics can be controlled by specific treatments, e.g. heating [5] and aging [6]. During an aging process, there will be a reaction that leads to better characteristics of the material in terms of its rigidity and strength [7].

Aging is expected to cause the formation of pores with controlled characteristics regarding radius, volume, and surface area of the pores [6,8]. Pores are formed in several shapes such as a cylinder, funnel, and flask [4,9,10]. The pore has an influence on the physical and chemical properties of the material, such as density, conductivity and surface area [11,12]. Since there are many influences of porous silica and the need for the specifications, it is, therefore, a challenging task to explore the



effective route in synthesizing the porous silica. On top of that, we introduce the chance of using natural mud from Sidoarjo, which has been erupting for a decade, as the raw material to produce the porous silica.

2. Experimental Method

In this study, the natural mud from Sidoarjo, Indonesia, was extracted and immersed in 2 M HCl for 2 hours. The solution was then precipitated and washed with distilled water before obtaining the precipitates. Afterward, a hydrothermal process was carried out by stirring the precipitated solution in 7 M of NaOH for 2 hours at 80 °C. HCL was then wisely added to the stirred solution to reduce the pH to 4 before aging for 20, 24, 28, and 32 h. After aging, the silica was finally washed with distilled water and dried overnight. The produced silica was characterized by using Surface Area Analyzer (SAA), Brunauer–Emmett–Teller [13], Fourier Transform Infra-Red (FTIR), and X-ray fluorescence (XRF) Spectroscopy. Samples with aging time of 20, 24, 28, and 32 h were coded as SA20, SA24, SA28, and SA32, respectively.

3. Results and Discussion

The produced silica in this study had a purity of 98.9%. The result is closely to the purity of silica that was synthesized by using alkali fusion route was 98.9% [5,14], the continuous method was 98.8%, co-precipitation method was 97.6% , 96.1% [15], the drying process was 96.5% [14], and the extraction was 95.6% [16]. In this experiment, the mass of the obtained silica was approximately of 1.2 - 2.3 grams.

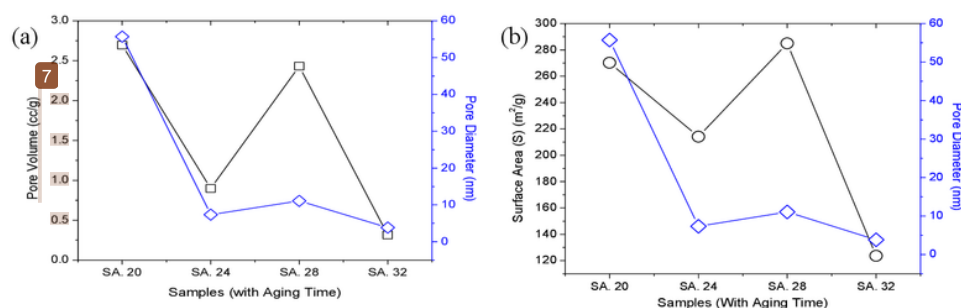


Figure 1. Absorption: (a) pore diameter and volume of samples, (b) surface area and pore diameter

The difference masses of the porous silica depend on the quantity of the sodium induced by NaOH solution. A previous study inferred that the greater the moles of NaOH, the greater the mass of the produced silica. Moreover, the reaction rate of the natural mud in the hydrothermal process and the final pH titration also affected different masses. It determined the quantity of the sodium induced by NaOH solution and the reaction rate of the natural mud in the hydrothermal process affecting the amount of the Na₂SiO₃ formation. The final pH affected the separation process of sodium from the Na₂SiO₃ and formed NaCl [14].

Figure 1 presents pore diameter and pore volume of the samples at adsorption phenomena [13]. The ratio of pore diameter and pore volume of SA20, SA24, SA28, and SA32 were 55.7 nm and 2.7 cc/g, 7.3 nm and 0.9 cc/g, 11.1 nm and 2.4 cc/g, 3.8 nm and 0.3 cc/g, respectively. Fig. 1 b represents the surface area and pore diameter at adsorption phenomena. The ratio of pore diameter and surface area of SA20, SA24, SA28, and SA32 were 55.7 nm and 270 m²/g, 7.3 nm and 214 m²/g, 11.1 nm and 285 m²/g, 3.8 nm and 124 m²/g, respectively. The obtained surface area was relatively smaller compared to previous studies in which the aging for 24, 48, 72 hours produced an area of 380 m²/g, 366 m²/g, 111 m²/g [8,11].

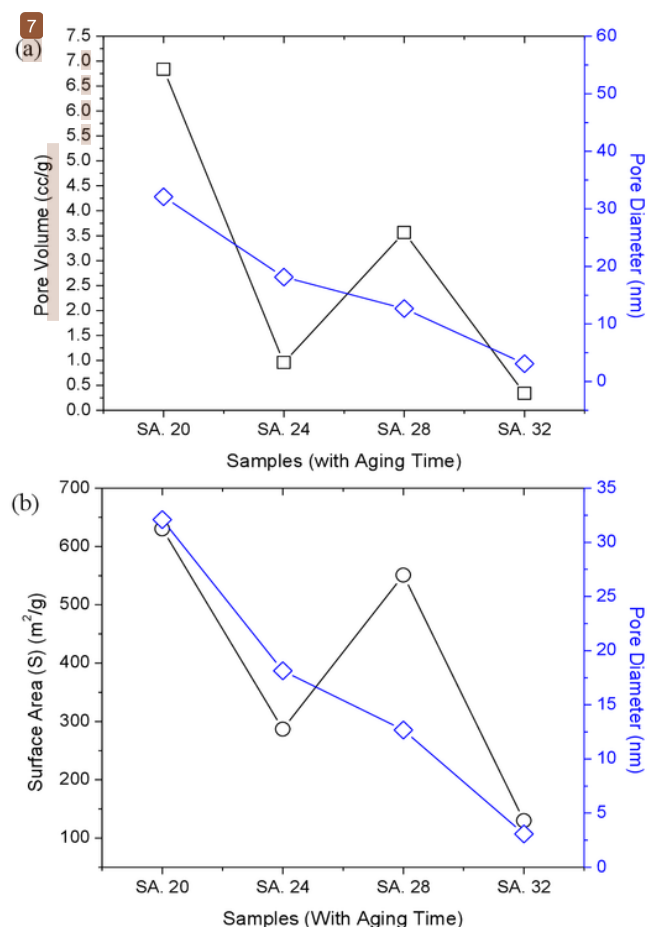


Figure 2. Desorption: (a) pores diameter and volume of samples, (b) surface area and pore diameter

There was a decrease in pore size on silica aging, but SA28 had a pore size that was larger than SA24 and SA32. Increased pore diameter, pore volume, and surface area on SA28 related to the formation of pores. The pore shapes are usually affected by the particle size when it is added wisely by HCl to obtain the final pH. If the size of silica particle was large, the phenomena of aging formed a large capacity of silica pore. The SA28 was known to have a small pore diameter but has a large pore volume and surface area. The inequality demonstrated different pore shapes of SA28 with SA20, SA24, and SA32. Thus it was possible to form pores in the forms of ink bottle pores or interconnected pores in SA28 [6].

Figure 2 represents pore diameter and pore volume of samples at desorption phenomena. The ratio of pore diameter and pore volume of SA20, SA24, SA28, and SA32 were respectively 32.1 nm and 6.8 cc/g, 18.6 nm and 1 cc/g, 12.7 nm and 3.6 cc/g, and 3.1 nm and 0.3 cc/g. Fig. 2 b represents surface area and pore diameter at desorption phenomena. The ratio of pore diameter and surface area of SA20, SA24, SA28, and SA32 were respectively 32.1 nm and 630 m²/g, 18.1 nm and 287 m²/g, 12.7 nm and 551 m²/g, 3.1 nm and 130 m²/g. The sizes of pore volume-pore diameter and surface area-pore diameter had the same pattern. Wherein the pore decreased at SA20, SA24, SA28, SA32 [10,17].

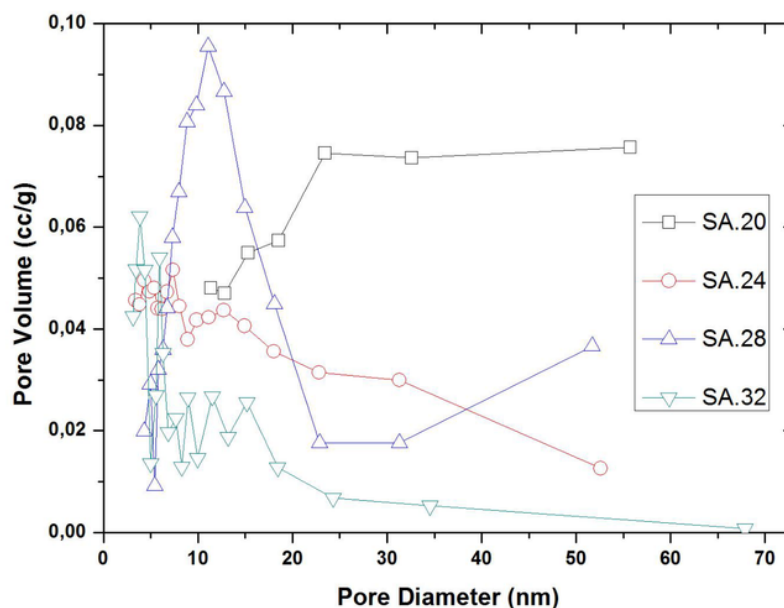


Figure 3. Pore size distribution of the produced silica

Figure 3 represents the distribution of as-prepared silica pore size taken from the results of surface area analyzer. It can be revealed that the silica pore size was macroporous and mesoporous. The smallest pore sizes of SA20, SA24, SA28, and SA32 are respectively 11.33 nm, 3.41 nm, 4.3348 nm, and 3.1113 nm; and the pore volume of each is of 0.04802 cc/g, 0.04563 cc/g, 0.01989 cc/g, and 0.04250 cc/g. On the SA20, the large pore volume was found by increasing the pore diameter, and the majority of the pore diameter is of >10 nm. At SA24, the majority of the pore diameter was <10 nm with the large pore volume that did not get much different and decreased by increasing the pore diameter. At SA28, the majority of the pore diameter was <10 nm, but it had the largest pore size in the pore diameter ± 11 nm and then it was decreased by increasing the pore volume of the pore diameter. At SA32, the majority of pores <10 nm but the different pore volume was more striking than the SA24 [17].

9 From Figure 1, Figure 2 and Figure 3, it is clearly seen that there was a decreasing pattern of the pore diameter, pore volume, and surface area. It was due to the particle size and aging process with the phenomena known as syneresis and Ostwald ripening [3]. An Ostwald ripening occurs when there is driving force to break the bond within the silicate. This phenomenon caused smaller silica particles that were able to fill pores formed from large silica particles that were firstly settled. Syneresis caused two groups $\equiv\text{Si-OH}$ adjacent the surface of silica that may be linked to each other and form $\equiv\text{Si-O-Si}\equiv$ [3]. The change of $\equiv\text{Si-OH}$ groups into $\equiv\text{Si-O-Si}\equiv$ may affect the morphology of the silica produced. There were some differences in pore size between the SA28 and SA24. This possibility occurred because of the effectiveness of the aging process and the effects of the circumstance such as the pH and the size of the current particle when it was synthesized to heat during the aging.

Figure 4 shows the Fourier transform Infrared spectrum. From Figure 4, identical groups of silica were found with the same results as other reports [3,18]. The assigned peaks for the Si-O vibrational mode, Si-O-Si vibrational group, Si-O-Si deformation, $\equiv\text{Si-O}$ vibrational bond, Si-O bonding, OH vibrational mode, and H_2O molecule absorption were 463.6 cm^{-1} , 799.9 cm^{-1} , 947.3 cm^{-1} , 1102 cm^{-1} , 1638.8 cm^{-1} , and 3425 cm^{-1} , respectively. In addition, a functional group had widening wave numbers that bond the silica, $\equiv\text{Si-O}$ vibration, and the vibration of water molecules adsorbed. It can be

identified that there was found the wave number that vibrated differently from one to others in a function group.

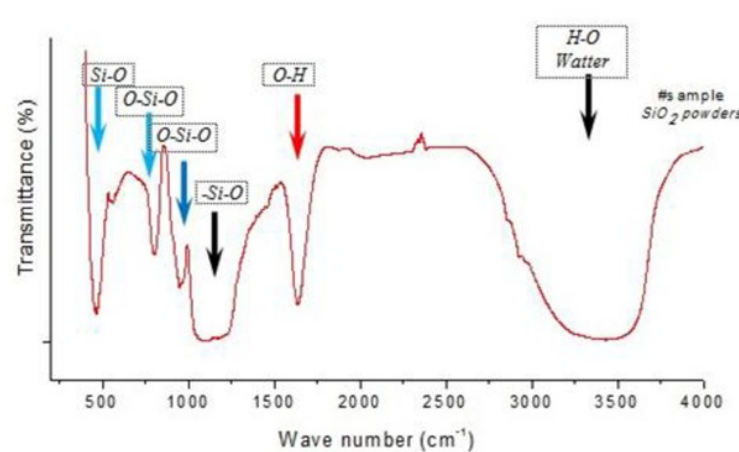


Figure 4. FTIR spectrum forming the porous silica produced by hydrothermal-coprecipitation process

There was an interesting effect of the aging on the wavenumbers that were detected by the FTIR, where the formation of bonds between the silica $\equiv\text{Si-O}$ on the surface of pores. It is also observed that the shift of peaks are due to the phenomenon of syneresis, i.e. the aging process that caused the energy between the atoms bind differently from one to others. The deformation of silica absorption's peak during the syneresis phenomenon is possible. However, the broadening of silica wavenumbers can be minimized by decreasing the pH and titration [6,19,20]. As a result, it will reduce the quantity of the produced silica as a result of the acid that degrades the sample with binding energy which shown by the deformation of the transmission peaks.

4. Conclusion

From our experiment, it can be concluded that the mass of the porous silica produced by a combination of hydrothermal-coprecipitation was found around 1.2 to 2.3 grams with the purity of 98.9%. The important functional groups of $\equiv\text{Si-OH}$ and $\equiv\text{Si-O-Si}\equiv$ groups were observed. The pore size was in the form of the macropores and mesopores. The aging process affected the pore size of the silica through syneresis and Ostwald ripening phenomena that caused the pore size reduction that decreased the pore radius, pore volume, and pore surface area. From the pore size distribution of silica, it can be seen a shift in the dominant pores from a greater to a smaller range.

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