Synthesis of Mesoporous SiO$_2$ Xerogel from Geothermal Sludge using Sulfuric Acid as Gelation Agent

H. Widiyandari*, P. Pardoyo, J. Sartika, O. A. Putra, A. Purwanto, L. Ernawati

* Department of Physics, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Indonesia
\^ Department of Chemistry, Faculty of Science and Mathematics, Diponegoro University, Indonesia
\^ Department of Chemical Engineering, Faculty of Engineering, Sebelas Maret University, Indonesia
\^ Department of Chemical Engineering, Institut Teknologi Kalimantan, Balikpapan, Indonesia

1. INTRODUCTION

Finding new generations of energy sources highly recommended due to an increase in energy demand worldwide. The one alternative solution to overcome potential problems of worldwide energy deficiency is using new and renewable energy (NRE). One of the promising NRE technology for developing countries such as Indonesia is geothermal energy. Geothermal energy harnesses the energy generated below the surface of the earth via steam generation. Such energy source is available abundantly and does not depend on the availability of fossils-based fuel [1]. One of the problems faced while producing electric power plants in Indonesia could exceed 165 tons per month while its utilization is minimal.

SiO$_2$ has good chemical stability, is not soluble in water, and resistant to high temperatures. In general, SiO$_2$ can be obtained from inorganic materials and organic materials. The most widely known silica is silica TEOS (Tetraethyl orthosilicate) and TMOS (Tetramethyl orthosilicate), which have the advantage of being able to bind aggregate rock into monolithic material. However, this silica has a weakness, both of which have prices that are relatively expensive, difficult to obtain, and not environmentally friendly [4]. Based on the disadvantages

A large amount of sludge is produced by the geothermal brine at the Dieng Geothermal power plant, exceeding 165 tons per month. This sludge is generally not utilized, except for use in landfills. The precipitate (sludge) is primarily composed of silica. The aim of this research is to synthesize mesoporous silica (SiO$_2$) xerogel from geothermal sludge (GS) and to investigate the effects of pH as an effort to elevate the economic value of sludge through alkaline extraction followed by acidification. SiO$_2$ xerogel was prepared by extracting the GS to become sodium silicate ($Na_2SiO_3$) assisted by a base NaOH and precipitated using H$_2$SO$_4$ as a gelation agent. The FTIR analysis of the SiO$_2$ xerogel showed a group of silanol (Si-OH) and siloxane (Si-O-Si). The XRD analysis indicated that SiO$_2$ xerogel was amorphous. Furthermore, it was observed from nitrogen absorption-desorption using BET (Brunauer-Emmett-Teller) method test that decreased pH tends to the specific surface area increase, and the pore size becomes decrease. The largest specific surface area observed at SiO$_2$ xerogel prepared at pH of 5.5 reached 400.10 m$^2$/g with a pore size of 4.5 nm. The pore sized for all cases was in the range of 4 –12 nm, indicating that the SiO$_2$ xerogels were mesoporous. Pore size of the as-prepared silica affected the thermal stability property of the sample.

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of silica source, TEOS and TMOS, the previous researchers conducted a lot of research to obtain alternative silica by utilizing natural ingredients that were not too useful before. SiO$_2$ can be produced in several forms including fused quartz, crystals, irritated silica (or pyrogenic silica, colloidal SiO$_2$), SiO$_2$ gel and aerogels [5-7]. SiO$_2$ aerogel is a substance made from silicon and is the low density solid. It is formed from 99.8% air and rigid foam with a density of 3 mg cm$^{-3}$, low density, high surface area and low thermal conductivity [8]. With the advancing technology, SiO$_2$ from the waste could also be utilized as precursors of nanosilica [9,10] or mesoporous SiO$_2$ xerogel which could be applied as catalysts [11,12], adsorbents [13-15], ultrafiltration [16,17], drug delivery [18,19] and other applications [20-22].

Previous researchers have done a lot of research to synthesis SiO$_2$ using various plants such as rice husk waste [7,8]. However, there are still few researchers conducted research by utilizing geothermal sludge (GS) as an alternative raw material for SiO$_2$. SiO$_2$ from wastes or natural resources could be obtained through facile alkaline extraction and acidic precipitation method [23-25]. This process and its product characteristics are strongly affected by pH level during the synthesis. Muljani et al. [26] have successfully produced mesoporous SiO$_2$ gels from geothermal sludge HCl and tartaric acid as gelling agents. In the sol-gel preparation, others hydrolysis catalysts were used such as HNO$_3$ and H$_2$SO$_4$ as gelling agent. It has also been reported that sulfated SiO$_2$ as solid acid catalyst is one of the modified silica gel products by reacting silica gel with sulfuric acid. The utilization of SO$_4^{2-}$ anion display an increase in acidic properties of silica as well as physical properties [27, 28].

Different from the previous research, herein, we improved a modification of synthetic route to prepare mesoporous SiO$_2$ xerogel with geothermal sludge (GS) from Dieng Mountain as raw material. The modification is done to maximize the work of SiO$_2$ gel, especially for catalysts in the acidification process using H$_2$SO$_4$. We further investigate the effects of pH during the formation of mesoporous SiO$_2$ xerogel. This work is done as our contribution and effort to elevate the economic value of geothermal sludge (GS).

2. MATERIALS AND METHODS

2.1. Material and Synthesis

The materials used in this study were Mount Dieng Geothermal Sludge (GS), Indonesia. Solvents and reagent used were analytical grade of ethanol (Merck, 96%), distilled water, sodium hydroxide (NaOH, Merck), and sulfuric acid (H$_2$SO$_4$, Merck 96%).

The GS was dried in an oven at 80°C for 60 minutes, ground and screened using 80 and 200 meshes filters. 10 g of the prepared solid waste was extracted in reflux using 1.25 M NaOH (Merck) solution for an hour at 80°C and stirred continuously at 300 rpm. Extraction solution was cooled to room temperature and filtered using Whatman number 42 filter paper. The filtrate was sodium silicate. The sodium silicate solution was dissolved 5 times in demineralized water. 1 N solution of H$_2$SO$_4$ were added into the dissolved solution until the pH reached 10. The as-prepared solution was aged for 2 hours and reintroduced with 1N H$_2$SO$_4$ until the solution reaches various pH level (9, 8, 7, 6 and 5.5). After the desired pH level achieved, each solution was aged for 18 hours. The formed gel was dissolved using 300 mL of demineralized water and filtered by vacuum. The residue was dried in a oven at 80°C for 12 hours and washed three times using demineralized water. The washed residue was dried furtherly at 100°C for 24 hours. The SiO$_2$ xerogel was obtained. Figure 1 shows the schematic diagram of the material preparation.

2.2. Material Characterization

The functional groups of starting material and samples were analyzed using Shimadzu IR Prestige 21 FTIR (Fourier Transform Infra-Red). X-ray diffraction pattern of starting material and SiO$_2$ xerogel sample were studied using Shimadzu XRD-7000 Maxima X-Ray Diffractometer (XRD) with CuK$_\alpha$ ($\lambda$ = 0.154 nm), scanning speed of 0.02°, 20 angle range of 10° - 90°, and applied power of 3 kW. The surface area were analyzed using BET (Brenner Emmet Teller) method using ASAP 2020 V4.20E Surface Area Analyzer (SSA). The morphology was characterized by Scanning Electron Microscopy (JEOL, JCM-7000 NeoScope™ Benehtop SEM) with voltage of 10 kV. TG/DSC (Hitachi STA200R) was used to characterize the thermal stability, adjusted to a temperature range from 25 to 1000 °C in an air atmosphere at a heating rate of 10 °C/min.

3. RESULTS

The formation of SiO$_2$ xerogel from PLTP (Geothermal Power Plant) Dieng by alkaline extraction are expressed...
in Equations (1), (2) and (3) [4, 29].

\[ \text{SiO}_2(s) + 2\text{NaOH}(aq) \rightarrow \text{Na}_2\text{SiO}_3(aq) + \text{H}_2\text{O}(l) \quad (1) \]

During the extraction of silica, the silica reacts and dissolves into this alkaline NaOH solution to form sodium silicate (\(\text{Na}_2\text{SiO}_3\)) solution. To reduce the particle sizes of \(\text{SiO}_2\) xerogel, demineralized water is added to the sodium silicate solution to increase its concentration. Thus, when precipitation occurs, small precipitate is formed due to slow nucleation process.

\[ \text{Na}_2\text{SiO}_3(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{H}_2\text{SiO}_3(aq) + \text{Na}_2\text{SO}_4(aq) \quad (2) \]

The next process is a metasilicate acid formation by adding aqueous sulfuric acid \(\text{H}_2\text{SO}_4\) into the sodium silicate solution. With the increasing amount of \(\text{H}_2\text{SO}_4\), a polymerization reaction of silicate acid occurs.

\[ \text{H}_2\text{SiO}_3(aq) + \text{H}_2\text{O}(aq) \rightarrow \text{Si}(\text{OH})_4(aq) \quad (3) \]

Gel formation occurs due to hydrolysis reaction of polymeric silicate acid with demineralized water while the xerogel were formed due to the drying of gel at 100°C for 24 hours. The porous xerogel is formed. Infra-red adsorption from difference group functions in geothermal sludge and prepared samples are shown in Figure 2. FTIR characterisation of each samples are based on the study performed by Brinker and Scherer. The adsorption on wave number 3400 cm\(^{-1}\), 1630 cm\(^{-1}\), 1430 cm\(^{-1}\), 1099 cm\(^{-1}\) and 950 cm\(^{-1}\) show stretch vibration of –OH from Silicanol (Si-OH) or \(\text{H}_2\text{O}\), -OH from Si-OH, C-H, Si-O from Siloxane (Si-O-Si), Si-O from Si-OH respectively. Wavenumber of 790 cm\(^{-1}\) shows symmetrical Si-O from Si-O-Si stretch vibration, wavenumber of 450 cm\(^{-1}\) and 2300 cm\(^{-1}\) show bending vibration of Si-O=Si [30–32].

The increasing of adsorption Intensity at wavenumber 1630 cm\(^{-1}\) from sample S0 (waste), S1 (pH 9), S2 (pH 7) and S3 (pH 5.5) happened due to the proton content in the solution during the synthesis forming Si-OH. High level of pH causes the reaction tendency to form Si-O-Si (siloxane) proved by the increasing intensity at 1060 cm\(^{-1}\). The hydrocarbon impurities (1430 cm\(^{-1}\)) are detected in geothermal sludge sample and the peak is shifted after the end of the process or when the xerogel is formed.

X-ray diffraction patterns of the samples are presented in Figure 3. The XRD pattern showed the amorphous nature of the SiO\(_2\) xerogels. The broad XRD pattern was typical for an amorphous structure [33]. This is indicated by the appearance of a widening peak centered at an area of 20 around 25° where silica with an amorphous structure gives a diffraction that widens at 20 around 21-25°. Impurities peaks (19° and 31°) of sodium sulfate (Na\(_2\)SO\(_4\)) is detected in sample 2 (pH 9) and sample 3 (pH 7). The presence of impurities could be caused by an unfinished cleaning process or salt entrapment in SiO\(_2\) matrices [29]. Aside from the impurity peak, all peaks from all samples are well indexed to JCPDS 7757-82-628.

Surface analysis of each sample is performed by BET method and the result is presented in Table 1. Based on the result, the highest surface area, 400.10 m\(^2\)/g, is exhibited by sample synthesized at pH level of 5.5. With the increasing pH, the surface area of the sample is

![Figure 2. FTIR spectra of geothermal sludge and SiO\(_2\) xerogel synthesized at various pH level](image)

![Figure 3. XRD Pattern of geothermal sludge and silica xerogel synthesized at various pH level](image)

| Samples | Specific Surface Area [m\(^2\)/g] | Specific Pore Volume [cm\(^3\)/g] | Pore Diameter [nm] |
|---------|----------------------------------|----------------------------------|-------------------|
| GS      | 100.50                           | 0.11                             | 4.3               |
| pH 9    | 159.55                           | 0.47                             | 11.8              |
| pH 8    | 151.74                           | 0.34                             | 8.9               |
| pH 7    | 223.44                           | 0.48                             | 8.7               |
| pH 6    | 321.25                           | 0.40                             | 4.9               |
| pH 5.5  | 400.10                           | 0.45                             | 4.5               |
decreased. This phenomenon is mainly caused by the slow formation of gel and slow nucleation of SiO\textsubscript{2} occurred at low pH level [29].

The amount of Nitrogen (N\textsubscript{2}) adsorbed into the SiO\textsubscript{2} xerogel at various pH level synthesized shown in Figure 4. The isothermal adsorption of N\textsubscript{2} shows the pore volume capacity of SiO\textsubscript{2} xerogel. The highest pore volume is exhibited by the sample synthesized at pH 7 with the value of 0.48 cm\textsuperscript{3}/g. Based on the pore volume data stated in Table 1, there is no significant effect of pH toward the pore volume of SiO\textsubscript{2} xerogel. In the other hand, the pore diameter is significantly impacted by the pH level of synthesis. Figure 5 shows that the pore diameter is decreased with the decreasing pH level while the specific surface area is increasing. The specific surface area in samples aged at pH level 5.5 increased by 2.5 times compared to samples aged at pH 9 and 4 times compared to raw material (GS). The pore diameter of samples is within the range of 4-12 nm which could be concluded that the porous material has mesoporous size (2-50 nm).

A side from the pore diameter, the mesoporous SiO\textsubscript{2} xerogel is classified based on its adsorption-desorption profile. Figure 6 shows type-IV-like adsorption-desorption curve which could be applied for porous material hence the samples exhibits mesoporous size (2-50 nm). Type-IV curve initiated with slow adsorption due to the stronger intermolecular interaction between adsorbate than with the adsorbents. Then the curve is slightly bent due to the pore filling by the adsorbate [34–36].

Structure and properties of xerogels are influenced by gelation pH. Because condensation reactions are favored and hydrolysis reactions are restricted under alkali conditions formed particles are fewer in number but larger and denser than particles formed under acidic conditions. Since pH affects the coagulation process, experiments were run at different initial pH 1N H\textsubscript{2}SO\textsubscript{4} until the solution reaches various pH level (9, 8, 7, 6 and 5.5). SEM results showed that SiO\textsubscript{2} particles are agglomerated at different pH values. The morphology of materials has distributed with diverse morphological structure. Figure 7f shows the chemical composition of the produced silica xerogel. The sample consist of Si (silicon) and O (oxygen).

TG/DSC was performed to characterize the thermal stability of SiO\textsubscript{2}. Figure 8 shows the TG/DSC of SiO\textsubscript{2} prepared at different pH level at temperature from 25 to 1000°C in air atmosphere at heating rate of 10°C/min. The weight loss and endothermic peak below 150°C are primarily caused by the desorption of physically adsorbed water [37]. The weight loss and broad
Figure 7. SEM images of SiO$_2$ particle at different pH values. (a) pH=5.5; (b) pH=6; (c) pH=7; (d) pH=8; (e) pH=9, and (f) EDX-spectra of sample.

Figure 8. TGA/DSC thermograms of synthesized SiO$_2$ under different pH values. (a) pH=5.5; (b) pH=6; (c) pH=7; (d) pH=8; (e) pH=9, and (f) DSC curve of SiO$_2$ at different pH level.

4. CONCLUSIONS

SiO$_2$ xerogel was successfully synthesized from geothermal sludge by alkaline extraction and acidic precipitation using sulfuric acid. The characteristics of prepared material are strongly affected by the pH level of synthesis. From the FTIR analysis, silanol group and siloxane group is detected in every sample. XRD pattern shows amorphous structure of xerogel. Based on the BET analysis, at a lower pH level of synthesis (pH=5.5), larger surface area was produced (400.10 m$^2$/g). The pore diameter of each SiO$_2$ xerogel was categorized as mesoporous (2-50 nm). Pore diameter and specific surface area of the as-prepared silica affected the thermal stability property of the sample. SEM results showed that SiO$_2$ particles are agglomerated at different pH values.

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