Synthesis of Silica Nanopowder Produced from Indonesian Natural Sand via Alkalifussion Route

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Abstract. An extraction of silica from natural sand has been conducted by means of alkalifusion route using NaOH. The silica sand was mined from Slopeng, Indonesia. This study was designed to obtain amorphous silica. Preliminary study from XRF characterization revealed that the silica sand contains 65.9 wt% SiO_2 and and some other compounds in smaller percentages. The alkaliffusion perfomed an optimal result when the sand was immersed in 2M HCl for 10 hours with a composition (in wt%) of 12.5 sand and 87.5 NaOH and sintered at 500 °C for 2 hours. The purity of the silica was 98.9 wt%. XRD patterns indicated that the silica formed amorphous phase. Micro structural profile of the silica by TEM clearly revealed that the particle size was in the order of nano meter (< 100 nm). The geometrical shapes were circular and oval with agglomerated behavior. Furthermore, the XRD analysis was consistently confirmed by the TEM image, i.e. the silica was found in the amorphous phase.

Keywords: amorphous silica, natural sand, alkalifusion
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INTRODUCTION

The natural sand has been successfully purified and synthesized into silica nanoparticle. It has so far been produced a very high purity of silica up to more than 99% from baggase ash (organic material) [1]. A 98% purity of nano-silica has also been fabricated from rice husk ash by means of coprecipitation [2] and a 95.7% of nano-silica from Sidoarjo mud by also means of coprecipitation as well [3]. Trabelsi, et al., have completely synthesized an amorphous silica from inorganic material, i.e., natural sand from Deuriet, by reacting sodium carbonate (Na_2CO_3) with heating temperature of 1030 °C [4]. Meanwhile, Mori has proposed another synthesis approach to obtain 99.9% of silica in a way of breaking the chemical bonding using alkali solution, e.g., KOH and NaOH, followed by bonding the silica (SiO_2) from waste colored glasses, this method is known by alkalifussion method [5-6].

There are three main steps of the silica extraction in this study.The first step is to prepare sodium silicate (Na_2SiO_3) from silica sand using NaOH. The silica powder is mixed with NaOH to form sodium silicate. The second step is to prepare silicic acid ($Si(OH)_4$). At this point, the solution of sodium silicate is reacted with HCl to form a precipated silica gel which is still in mixing with NaCl. Since the $Si(OH)_4$ cannot be dissolved in any strong acid like HCl, HNO_3, and H_2SO_4, the precipated of $Si(OH)_4$ can then be separated from its solution of (NaCl). The third step is to preparae SiO_2 by drying the silica gel $Si(OH)_4$. At this final step, water was evaporated in furnace. The reaction processes that may occur are as the following [1-4,6]:

$$SiO_{2\ (\text{sand powders})} + NaOH \rightarrow Na_2SiO_{3\ (l)} + H_2O_{(l)} \quad (1)$$

$$Na_2SiO_{3(l)} + 2HCl_{(l)} + H_2O_{(l)} \rightarrow 2NaCl_{(s)} + Si(OH)_{4(aq)} \quad (2)$$

$$Si(OH)_{4(aq)} \rightarrow SiO_{2(s)} + 2H_2O \quad (3)$$

Silica sand is, however, an oxide that the occurrence in nature is mixing with other minerals. It is then needed to separate other minerals from the silica sand to obtain high purity silica. Besides, it also challenges to synthesize amorphous silica having the size of nano meter from silica sand. The use of alkalifussion also becomes another challenge. This study aims to: (1) fabricate a high purity silica nanopowder and (2) examine the alkalifussion method in forming the silica nanopowder.

MATERIAL AND METHOD

The raw material that is used in this study were silica sand from Slopeng (Indonesia) with a concentration of 65.9 wt% SiO_2 (characterized by XRF), 37% HCl, 99% NaOH, and aquades. The equipments were baker glass with the size of 100, 250, 400, and 800 ml; measuring glass, pipette, glass and metal spatula, funel, ceramic cup, mortar, aluminum

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foil, thermometer, filter paper, lamp for drying, balance, furnace and magnetic stirrer.

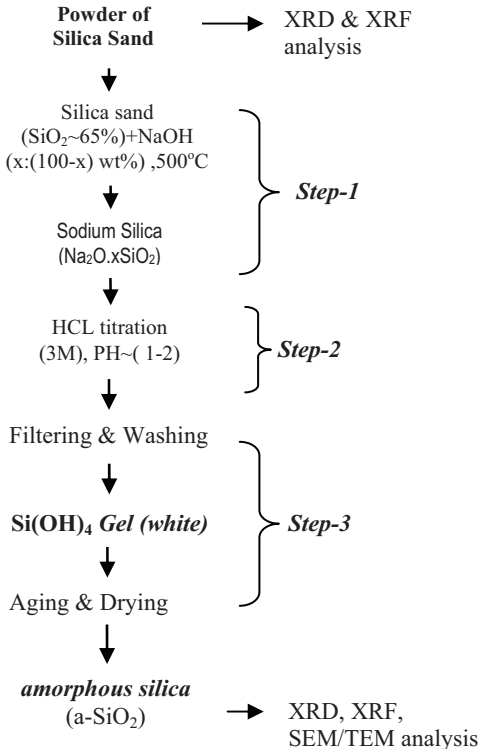

FIGURE 1. The Alkalifusion Route to Synthesize Amorphous Silica.

The synthesis method of silica gel in this study can be elaborated into some steps, i.e. (1) bonding and separating silica (SiO_2) from the impurities using alkali attack media at heating temperature of 500-1200°C [5] to form sodium silicate ($Na_2O.xSiO_2$). This step is so called purification step; (2) forming the silica gel (SiO_2) in the sodium silicate solution that was wisely added by HCl to reach a desired PH arround 1-2; (3) cleaning out the NaCl in the solution using aquades to obtain high purity silica gel (> 95%).

The separation the silica from the impurities was executed by immersing the sands in 2M HCl for 10 hours. HCl, as a strong acid, can dissolve some chemical compounds in material, so that the alkalifussion process can be performed optimally. The sand powder was then mixed with NaOH, having a composition (in wt%) of 12.5 sand and 87.5 NaOH and heated at 500°C for 2 hours. After heating, a dry sodium silicate was obtained (Na_2SiO_3). Furthermore, a dilution with aquades was conducted and stirred with hotplate stirrer to obtain a yellowish transparent solution, followed by titrating the solution with 3M HCl to reach pH about 1-2 to form clean white silicic acid ($Si(OH)_4$) gel which was mixed with NaCl. Cleaning the white gel and washing using aquades for 1-10 times were conducted to separate SiO_2 from other compounds (NaCl and acid). The final white gel was dried at 100°C. The dry white silica gel was then ground and characterized by means of XRF, XRD and SEM.

RESULT AND DISCUSION

The XRF characterization of the silica sand is represented in Table 1. As shown from the result, we can clearly see that the silica sand is dominated by Si, Ca and Fe, or in term of the oxides, SiO_2, CaO and Fe_2O_3. After all, the SiO_2 is 65.90%. The elemental content of the sample was characterized by means of XRF using energy of 20 keV without any filter. The content of silica increased to 98.9 % but another compounds like CaO, Fe_2O_3, and TiO_2 decreased. Even the other oxides like Cr_2O_3, MnO, K_2O, CuO, SrO, ZrO_2 and In_2O_3 had been reduced completely. A surprising result is the existance of aluminum oxide Al_2O_3 in the sample, it can be caused by the impurity during grinding process by mortar or during the heat treatment process in the furnace (the residu of another samples).

The XRD characterization of the silica sand revealed that the crystal planes (peaks) are dominated by ***quartz*** and ***calcite***. A search-match analysis of the XRD data for the sample that was immersed in HCl (Fig. 2(a)) showed the presence of quartz dan calcite as well (*x*), with Bragg angle range (2θ) of 5-90°. Another search-match analysis of the XRD data for the sample, in which after immersing in HCl (Fig. 2(b)) showed the presence of quartz only. Those results implied that the initial immersion of the silica sand in HCl can reduce the precence of calcite in the sample. Physically, the effect of the immersion in HCl can be known by the mass decreasing of the silica sand before and after the immersion.

TABLE 1. XRF Characterization of Silica Sand and Amorphous Silica (Synthesis)

Sample	***Element* (wt%)**					***Oxide* (wt%)**				
	Si	Ca	Fe	Ti	Others	SiO_2	CaO	Fe_2O_3	TiO_2	Others
Sand Powder	58.20	34.10	5.46	1,34	< 0,10	65.90	28.60	3.19	0,86	< 0,10
a-Silica (*product*)	89,50	4,12	1,45	0,22	<0,01	98,9	0,42	0,23	0,32	<0,01

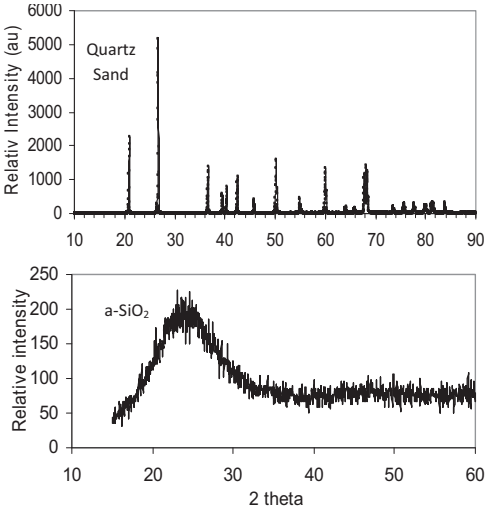

FIGURE 2. XRD Pattern of silica sand and amorphoussilica (a-SiO_2) produced by alkalifussion method.

From the Fig. 2, the XRD pattern of the quartz sand performs high peaks with the highest intensity of 11911.48 counts indicating that the sample has crystallized well. From this XRD pattern, the phase constituents can be identified by applying search match technique. This XRD pattern used radiations of K-Alpha 1 = 1.54056 Å and K-Alpha 2 = 1.54439 Å. From Fig. 2, we find 20 peaks that turn up very well. The highest intensity was found at $2\theta = 26.64002^{o}$ of 11911.48 counts/s. This peak was identified as quartz. After defining the peaks from the XRD pattern, a search match analysis was then conducted to know the phases content. From the data analysis, there exists 3 phases, i.e. quartz SiO_2 (PDF No. 48-1045), calcite $CaCO_3$ (PDF No. 24-0027), and Ca-Mg-Al-Si-O (PDF No. 03-0418). The crystal planes of Ca-Mg-Al-Si-O do not appear in the XRD pattern explicitly

The xrd pattern of nano silica produced by alkalifussion method is shown in fig. 3. The xrd pattern exhibits a wide peak and low intensity (~ 150-200 counts) revealing that the silica powder is an amorphous phase with the particle size of the order nanometer (< 100 nm), it is in accordance with the result obtained by nittaya [2] and van hoek [7] which was also confirmed by tem characterization. Based on the xrd data, again, the presence of peaks at 2θ arround 20^{o} to 35^{o} has the same pattern with the data reported by nittaya [8] and the previous studies, it is the unique xrd profile of an amorphous silica.

The DTA/TG characterization of the silica powder from the natural sand is represented in Fig. 3. The test sample was silica powder with a mass of 3.3039 mg, the setting temperature of DTA/TG was set up to 1500 ^{o}C having a rate of 15^{o}/min, the reference material was platinum (Pt) 70 ml and synchronization enable measurment condition. The DTA/TG profile informed us that at temperature of 145.8 ^{o}C (105 ^{o}C for onset and 168.8 ^{o}C for endtset) existed an endothermic process. A mass difference appeared up to temperature of 1000 ^{o}C. A mass loss up to 0.5295 mg (8.091%) was found at temperature between 271 ^{o}C and 800 ^{o}C. The final residual mass of silica was 86.6490% or 2.868 mg. While above temperature of 1000 ^{o}C, we almost cannot see any mass changes, but at temperature between 1230 ^{o}C and 1368 ^{o}C the formation of crystalline phase [10].

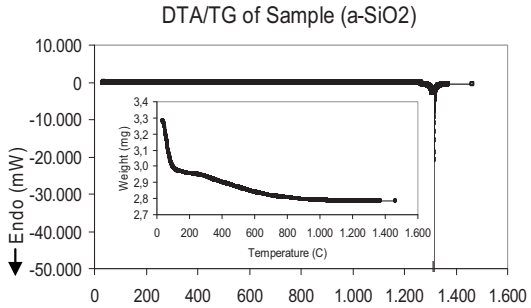

FIGURE 3. DTA/TG of amorphous silica (a-SiO_2) produced by alkalifussion method.

The characterization of micro structure of the sample was conducted by means of TEM (*Tunneling Electron Microscopy*), Tecnai-20, Digital-TEM (Eo:200kV,Ro:0,23nm). From this characterization, we can obtain many informations regarding its grain marphology grain, grain size and distribution, as well as its crystalline state (i.e. crystal or amorphous) and any phases that may be formed.

Fig. 4(a) showed the morphological profile of silica powder (sample) with oval and circle agglomerated grains having particle size of nanometer (< 200nm). Further analysis using ring pattern (Fig. 4(b)) revealed that, again, the amorphous phase is in a greater quantity than the crystal. A crystalline phase exists within the amorphous phase. This result is mutually strengthen with the XRD pattern.

The alkalifussion method has been generally used for extracting silica from inorganic materials like sand and reusing of waste glass. Mori has successfully produced a 99% high purity of silica by means of alkali compounds of NaOH [6]. In this study, NaOH was also used as Na ion source during the alkalifussion process. It was done under the consideration not only the effortless in obtaining the material, but also the requisite of quite low energy. In other words, it only needed a temperature of 500 °C to complete the synthesis, instead of choosing Na_2CO_3 as the alkali compound which requires higher energy consuming with temperature of 1400-1500 °C. A composition (in wt%) of 12.5 sand and 87.5 NaOH was chosen by taking consideration of the availably of sodium silicate formation at the initial silica purification.

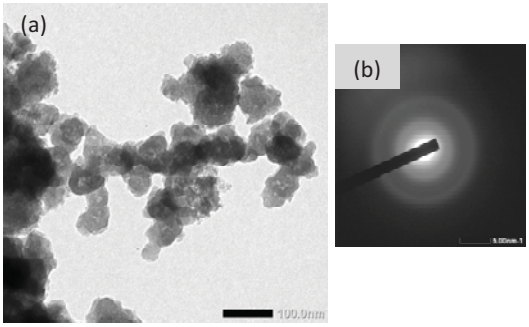

FIGURE 4. TEM images of produced silica (extraction with 87,5 wt% NaOH), (a) agglomerated grains with particle size of < 100 nm and (b) ring pattern indicating the presence of amorphous phases.

According to Mori, the optimum outcome of the alkalifussion process based NaOH-SiO_2 can be reached with concentrations of $SiO_2 \leq 20$ wt% and NaOH ≥ 80 wt% and melting temperature ≥ 2 hours [6]. The physical parameter of the formation of sodium silicate and dissolving in H_2O is the change in solution color from white to transparent.

The step during this synthesis approach was started by immersing the sample in 2M HCl for 10 hours. The aim of this step, particularly immersion in HCl, is to dissolve another materials instead of SiO_2. The characteristic of HCl as a strong acid is its ability to dissolve some compounds contained in a material, so that Na can optimally bind SiO_2 to form sodium silicate (Na_2SiO_3) during the alkalifussion process for which undicated by the decreasing of impurity within the sample. The mass of the sand changed from 7 g to 6.2 g. The titration of HCl was set in a very strong acid condition (i.e. pH $\approx 1 - 2$), in order Na, Al, Ca, and Cu can dissolve in the solution but the other unexpected elements can be reduced as well [6]. After all, we obtained a very high purity of SiO_2 with a concentration of 98.9% and very small amount of CaO (0.42 %), Fe_2O_3 (0.23 %), and TiO_2 (0.32 %).

CONCLUSION

The conclusions of this study are: (1) an amorphous silica can be well synthesized from silica sand by means of alkalifussion method using NaOH at heating temperature of 500 ^oC.; (2) the amorphous silica produced by alkalifussion method is 98.9 wt%; (3) comprehensive characterizations by XRD, SEM and TEM revealed to the same results, i.e., the silica exhibits a nanomaterial behavior with the particle size of ~60 nm.

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