RESEARCH ARTICLE

Advanced Science Letters
Vol. 23, 12002–12006, 2017

Synthesis of Nano SiO_2 Powders from Lusi with Continuous Method

Munasir[1,2,*], A. J. Hairin Pribadi[1], Z. A. Imam Supardi[1], Moch. Zainuri[3], Triwikantoro[3], and Darminto[3]

[1]*Physics Department, Universitas Negeri Surabaya (UNESA), Ketintang-Surabaya 60231, Indonesia*
[2]*Natural Material Laboratory, UNESA, Ketintang-Surabaya 60231, Indonesia*
[3]*Physics Department, Institut Teknologi Sepuluh Nopember (ITS), Sukolilo-Surabaya 60111, Indonesia*

Lusi (Sidoarjo mud) is a type of volcanic mud in Sidoarjo East Java Indonesia area, a source of silica and alumina minerals which promises potential applications. The Lusi contains SiO_2 (54–55%), Al_2O_3 (19–25%), and a small amount of Fe_2O_3, MgO, CaO, K_2O, Na_2O and some other minerals that are less than 1%. Separation of silica (SiO_2) from other elements has been conducted, as well as minimizing the particle size to the nanoscale. The purification and size reduction of SiO_2 nanoparticles were developed by continued methods using the alkali compound of solvent medium (sodium hydroxide) with varying molarities (i.e., 5 M, 6 M, and 7 M), respectively as samples L-NS1, L-NS2 and L-NS3 by hydrothermal processes, obtained sodium silicate solution. The next stage addition of a strong acid HCl in a solution of sodium silicate slowly, obtained silicic acid $Si(OH)_4$ (stage process of co-precipitation), the final pH is PH 7. The final product was in the form of white powder with a silica purity of 98.40%, which was then characterized by XRF, XRD and SEM. Between this extracted and commercial silica, the profile and size of grain also revealed a different characteristic. SEM results showed that the silica powder from Sidoarjo mud extraction has a smaller size of the order of 100 nm than the commercial one.

Keywords: Mud Volcano, Nano Silica, Hydrothermal, Coprecipitation.

1. INTRODUCTION

Silica is a compound of the largest constituent of the earth's crust. A nano-silica can be obtained from silica sand, which is very abundant in Indonesia, or from the destruction of waste glass. Besides that, other sources of silica are organic materials of rice husk ask[1] and baggage ash.[2] The synthesis methods of producing nano silica from natural materials, like sand, clay, and waste glass, typically used in high-temperature combustion process inside the furnace with alkali compounds media (KOH, NaOH and Na_2CO_3).[3–6] While the effective synthesis approach of nano silica from organic materials, like rice husk ash and bagasse ash, has been done by means of co-precipitation method already.[1,2,7]

The Lusi is Sidoarjo vulcanic mud, a type of volcanic mud that covers an area of over 6.5 square kilometers, it has been dislocating more than 30.000 people since the first flow. On 30th of October 2008, the flow reached 100.000 m^3 per day, and it is predicted to continue for the next 30 years.[8]

The Lusi, however, can be well proposed to be an abundant source of silica and has a great chance to be used for the development of science and technology. It is based on many studies that has tried to take the advantages of the mud, such as a mixture of bricks, zeolite, etc., concluding that the silica content in the Lusi was significant enough to be separated. Another study was conducted by Jalil et al.,[8] indicating that the minerals content in the Lusi or Lapindo vulcanic mud were SiO_2 (53.40%), Al_2O_3 (23.80%), Na_2O (5.59%), Fe_2O_3 (5.47%), MgO (2.62%), Cl (2.89%), CaO (2.40%), K_2O (1.64%), SiO_3 (1.24%), and TiO_2 (0.64%), and it lead to the summary that silica and alumina were the most predominant constituents of the Sidoarjo mud.[8] The results of chemical analysis of LuSi in locations Siring-Sidoarjo conducted by Deputy TPSA-BPPT indicated mineral content Silica: Si (61.46 atomic percent or 25.67 mass percent) and the compound SiO_2 (54.92%).[9] While other research results reported by Totok Noerwarsito (2006), there are mineral (mass percent): Clay (71.43%), Silt (10.71%), and Sand (17.86%).[9]

Various new solutions as alternative and effort to use the Sidoarjo mud into other forms of material which has high economic added value have been carrying out, such as the manufacture of ceramics, mixed concrete (geopolymer), multi-purpose sand, paving blocks, bricks, concrete, tile, and paving, etc.[10,11] Silica nanopowders have been widely used in applications for the tire industry, rubber, paint, cosmetics, film, toothpaste, electronics, and ceramics. The worth application is the addition nano silica on tires that will make the tires perform a better adhesion even more on the snow road, reducing the noise generation, and

*Author to whom correspondence should be addressed.

 1936-6612/2017/23/12002/005 doi:10.1166/asl.2017.10561

the age of the tires over a display of the product without the addition nano silica tires.

This study, then, introduces a new alternative solution as the positive impact of Sidoarjo mud flow by utilizing the mud as a source of silica which has a promising application. By means of the extraction for purifying/separating the silica (SiO_2) from other oxides, and hydrothermal-co-precipitation assisted synthesis route of silica nanopowder, which ultimately could provide enormous added value to the prospects for its application. The limitation of this study is to find answers to questions:

(1) how to purify and synthesize the silica of Lusi from the other chemical elements or mixed oxides,

(2) how to produce nano-sized powder of silica powder from Lusi by means of continue method.

2. MATERIAL AND SYNTHESIS METHOD

The raw materials in this study were as follows: (1) Lusi (Sidoarjo vulcanic mud); (2) HCl 37%; (3) NaOH 99%; and (4) aquades. While the equipment for characterizations:

(1) XRF to identify the percentage of SiO_2;

(2) a quantitative phase characterization was done by means of X-ray diffraction,

(3) shape and size particles by SEM and TEM.

The synthesis steps of silica were as follows (Fig. 1):

(1) Hydrothermal:

(i) Sample preparation: the mud was firstly dried, and then ground to gain smaller size and finer powder and to obtain a good solubility in the solvent material, followed by filtrating the dried sample; the filtrated powder was then used for characterization, but the un-filtrated one was reground. For the characterization, the sample was investigated by means of XRD to identify the phase content and XRF to know the element and compound content of the Lusi;

(ii) Silica purification: the ground mud was weighed using digital balance and read to be 8 g; then washed with 2 M HCl; and then dissolved into 60 ml NaOH with varying molarities (i.e., 5 M, 6 M, and 7 M) while wisely stirred by magnetic stirrer at temperature of 70 °C for 10 hours to form sodium silicate.

(2) Co-precipitation: followed by filtrating process; the solution was then titrated by using 3 M HCl and stirred by magnetic stirrer to reach pH close to 7 and form a white precipitated, and filtrated and washed by aquades to lose the acid, base, or any salt within the sample.

The white gel which was in turn dried (100 °C furnace temperature) was conducted to lose any water content. The XRD characterization to know the diffraction pattern and XRF characterization to investigate the percentages of its elemental content was also performed.

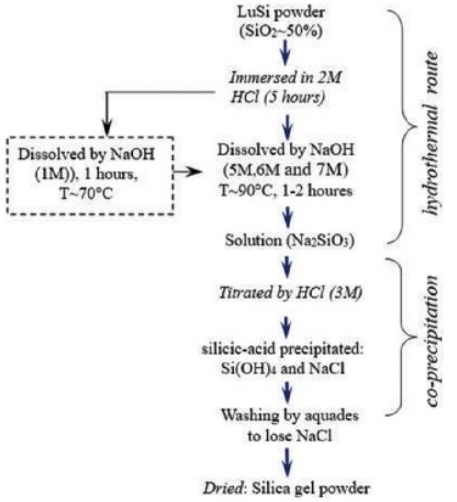

Fig. 1. The step-synthesis of silica gels from Lusi.

3. EXPERIMENTAL RESULT

3.1. Preliminary Characterization of Lusi

There were three spots (certain locations) in taking the Sidoarjo mud, i.e.,

(1) spot area A (SA-A), a location where the mud is dry and the color is gray like cement,

(2) spot area B (SA-B), a flooded location where the mud is wet and the color is white gray,

(3) spot area C (SA-C), a location sludge discharge pipeline which is directed towards the river Porong, near the source of mud flow.

The XRF analysis revealed that the most predominant content of silica was the Lusi in the spot A, i.e., 55.0% (Table I).

3.2. XRD Patterns of Synthesized Silica Gel

Subsequent to synthesis, at the purification stage, we obtained a sodium silicate (Na_2SiO_3) that was wisely titrated using HCl to form SiO_2 following the chemical reaction bellow:

$$\text{Lusi powder } (x\text{SiO}_2) + 2\text{NaOH} \rightarrow \text{Na}_2\text{O}\cdot x\text{SiO}_{2\,(l)} + \text{H}_2\text{O}_{(l)} \quad (1)$$

$$\text{Na}_2\text{O}\cdot x\text{SiO}_{2\,(l)} + 2\text{HCl}_{(l)} + \text{H}_2\text{O}_{(l)} \rightarrow 2\text{NaCl}_{(l)} + \text{Si(OH)}_{4\,(aq)} \quad (2)$$

$$\text{Si(OH)}_{4\,(aq)} \rightarrow \text{SiO}_{2\,(s)} + 2\text{H}_2\text{O} \quad (3)$$

The samples were washed to reduce NaCl within the silica gel and then dried to form fine powders to be characterized by XRD. It was done not only to know the phase content of the sample but also to verify the presence of NaCl compound. The sample which was synthesized with varying molarities of NaOH: 5 M (L-NS1); 6 M (L-NS2) and 7 M (L-NS3) have the XRD patterns like shown in Figure 2. It's clearly showed that for NaOH of 5, 6, and 7 Molar, the XRD pattern has the highest intensity of only 200 counts, a broad peak centered at 2θ angle of (26°–29°) tends to shift to the higher 2θ. While for the commercial silica, a broad peak centered at 2θ angle of 23°. The peak started to

Table I. XRF characterization results of the Sidoarjo mud: Oxides.

	Oxide content (wt%)						
Samples	SiO_2	Al_2O_3	Fe_3O_4	CaO	K_2O	TiO_2	Others
SA-A	55.0	19.1	15.3	4.4	2.2	1.3	<1%
SA-B	55.1	19.1	15.1	4.3	2.2	1.3	
SA-C	54.2	19.0	15.0	4.3	2.2	1.4	

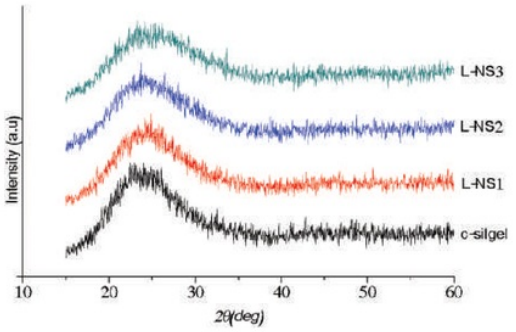

Fig. 2. XRD patterns of SiO_2: A comparison of XRD patterns between *c*-silgel (*commercial silica*) and synthesized silica powder from Lusi: With varying molarities of NaOH: L-NS1, L-NS2 and L-NS3.

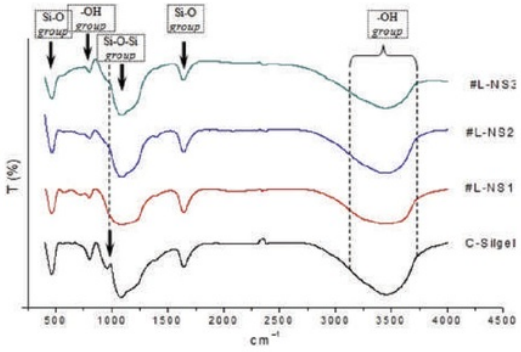

Fig. 3. I-R spectroscopy of groupe-vibration SiO_2 particles.

increase at $2\theta \sim 18°$ but decrease at $2\theta = 36°$. A greater molarity of NaOH may increase the amount of SiO_2 that could be reacted with NaOH to form more Na_2SiO_3 and SiO_2 after titrating with HCl. To gain a maximal mass of SiO_2, it require a heat treatment to break the chemical bonding.

3.3. XRF of Synthesized Silica Gel

The XRF characterization result is represented in Table II. According to Table II, there is a significant difference content of SiO_2, there exists a significant increase from 55% to 98.50% (L-NS3) and 95.7% which revealed that the purification of Lusi was successfully performed. By continue method, NaOH (i.e., 5 M; 6 M and 7 M) dissolution and HCl (3 M) titration can effectively form a fine silica powder with a high purity greater than 95%.

In Table II can be seen the results of XRF testing both compounds and building blocks of all samples. It appears that sample purity silica based compound constituent (SiO_2) was 96.9 wt%, 97.6 wt% and 98.5 wt% respectively for sample L-NS1, L-NS2 and L-NS3. In addition to the compounds SiO_2, CaO and Fe_2O_3, the building blocks of other samples are: compound TiO_2, Cr_2O_3, NiO, CuO, and K_2O. Meanwhile, based on the purity of the constituent elements (Si) amounted to 92.3 wt%, 94.3 wt% and 96.4 wt% respectively for sample L-NS1, L-NS2 and L-NS3. Building blocks of synthesized samples in addition to elements of Si, Ca, and Fe, there are also other elements that number is very small that is the element K, Ti, V, Cr, Ni, Cu, Zn, Ga, Yb, and Re. Purity silica synthesized in the study was higher than the results of previous studies in the amount of 88.4 to 95.7 wt%.[5]

3.4. FTIR of Synthesized Silica Gel

Figure 3 is a FTIR testing results. FTIR testing was conducted to determine the functional groups of materials. After the FTIR results obtained, further uptake patterns formed matched to the pattern of uptake previous studies. The FTIR results matching needs to be done to discern the functional groups that have been formed from samples that have been tested. Table III is an absorption matching results that form the absorption patterns of functional groups on the previous SiO_2.[6,9–11] From these results, for all the samples, can be seen in Figure 2, the absorption at wave numbers 465–475 cm^{-1}, 800–870 cm^{-1} and 3000–4000 cm^{-1} shows the pattern of absorption of Si–O functional groups, OH group of Si–O, and the OH group. Uptake of the match-absorption characteristics of silica uptake pattern obtained from the reference. The pattern of uptake groups Si–O–Si (*siloxane*) which has a frequency range between 1050–1115 cm^{-1}.[6,7]

Table II. XRF characterization results of synthesis.

	Oxide content (%wt)			Atomic element (%Wt)			
Samples	SiO_2	CaO	Fe_3O_4	Si	Ca	Fe	Others
SA-A	55.00	4.38	15.30	92.30	1.30	2.73	3.67
L-NS1	96.90	0.55	1.12	92.30	1.30	2.73	3.67
L-NS2	97.60	0.47	1.28	94.30	1.10	3.14	1.46
L-NS3	98.50	0.41	0.67	96.40	1.00	1.67	0.93
C-silgel	99.20	0.43	0.13	98.00	1.10	0.33	0.57

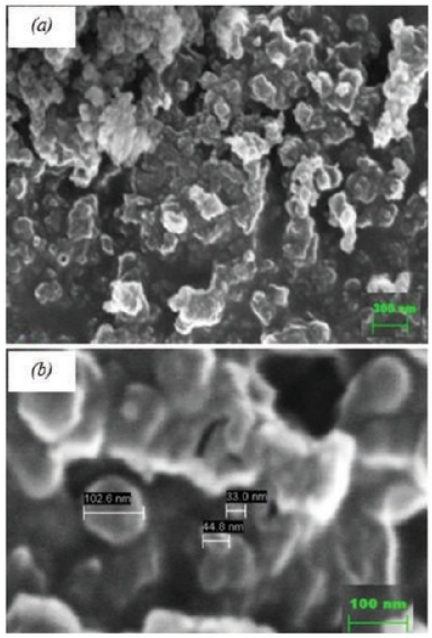

Fig. 4. SEM images of (L-SN3) produced by continued method (a–b).

The results of the test Infra-red spectroscopy, showed a shift to the absorption wave numbers lower than *c*-silgel wavenumber (1114 cm^{-1}), namely: L-NS1 (1103 cm^{-1}), L-NS2 (1108 cm^{-1}), and silica L-NS3 (1109 cm^{-1}). This allegedly caused by the change of environment groups Si–O–Si (siloxane) which is the result of the condensation between the silicate anion with silanol (Si–OH) (Mujiyanti et al., 2010). Besides the pattern of functional groups OH (water molecules) which has an absorption at wave number 1639 cm^{-1} also experienced a shift to the absorption wave numbers lower i.e., the *c*-silgel (1624 cm^{-1}), L-NS1 (1619 cm^{-1}), L-NS2 (1623 cm^{-1}), and L-NS3 (1621 cm^{-1}) samples, it is suspected due to the bound water molecules in the void of silica molecules.[12]

3.5. SEM Patterns of Synthesized Silica Gel

The silica gel synthesized by continued method of Lusi and the commercial base material (white silica gel) were characterized microstructurally using Scanning Electron Microscopy of Zeiss having the type of EVO MA 10, 20 kV energy activation. A different profile of microstructure between the synthesized and commercial samples can be well seen in Figure 4. It showed that the particle size of the synthesized silica (Figs. 4(a and b)) is smaller than the commercial one (Figs. 5(a and b)).

Generally, the grain geometry of silica was observed to be in a sphere shaped with radius ~100 nm for the synthesized sample, and radius ≥ 100 nm for the commercial sample (see also Fig. 4(b)). In Figure 4, the microstructure image analysis can be estimated the size of the silica particles, namely the identification of the particle diameter of the SiO_2 particle shape. Analysis techniques such as by software Image-J, which is considered in this way has an 80% accuracy.[15,16] The results of SEM image processing using Image-J indicated earned an average diameter of L-NS1, L-NS2 and NS3 respectively amounted nm 26.824, 26.898 and 27.289 nm. Based on the results of this analysis can be shown that nanometer-sized silica particles already is ~nanometer size (Fig. 6(b)).

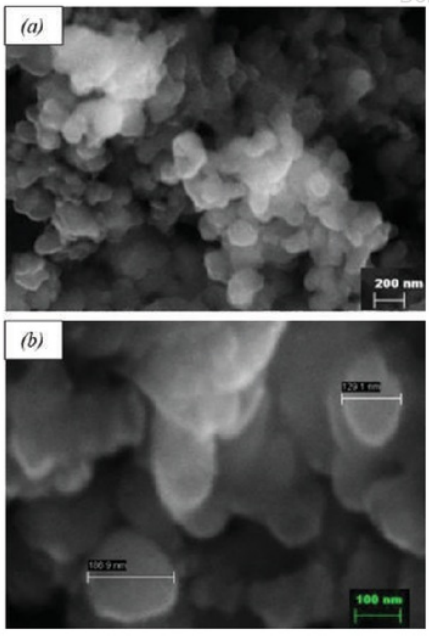

Fig. 5. SEM images of (SiO_2) produced by continue method from commercial *c*-silgel (a, b).

4. DISCUSSION

In general, the hydrothermal-coprecipitation route can be used as a reference method to sieze silica out of the mud, but still have a small mass levels, that is to say from 8 g of mud could only be taken only less than 1 g of silica. It is because it is hard to break the bonding of SiO_2 that exists in the mud and so it can not form sodium silicate for being further titrated with HCl to form SiO_2. When producing sodium silicate, there were lots of mud that still remained unreacted requiring a new breakthrough to increase the percentage of SiO_2 that can be extracted from the Sidoarjo mud. It has been successfully synthesized silica with a purity of 98.50 (Wt%) or Si (96.40%) by continue method.

Silica powder as product synthesis, showed Lusi of 8 g powder using various molarity of NaOH (method continue) produced range: 0.12 to 0.553 g SiO_2 powder. There is quite a striking decrease, namely from 8 g powder dry Lusi, only gained about 6.9% silica powder nano-meter size (dry). There are several reasons to cause it to happen, SiO_2 content in Lusi is only 50%, SiO_2 compounds in Lusi did not really react with alkaline NaOH because of strong ties (in the process of hydrothermal), in addition to technical matters during the synthesis process.

5. CONCLUSIONS

According to the experimental results, it can be concluded that a continue method: i.e., hydrothermal and co-precipitation route, can be performed to synthesize amorphous silica from Lusi. A separation of SiO_2 from its impurities like Al_2O_3, Fe_2O_3, CaO, K_2O and Na_2O can be done by using NaOH solvent (i.e., hydrothermal process) and HCl solvent (i.e., co-precipitation process). Variation of NaOH molarities and the final pH of $Si(OH)_4$ obtained a various final mass product of silica gel (dry) ~0.12 g–0.553 g. As well as the peak shift tendency was also observed from the XRD patterns of silica produced by continue method in comparison with the commercial silica. Finally, the continued method can be used to precede silica purification from Lusi with a high purity of 98.50% of agglomerated spherical silica. It, however, needs to chase a further study to produce a higher purity of silica that can be extracted from the Lusi and to obtain the maximal mass product of silica. A temperature treatment in term of applying heat is also desired to break the chemical bonding in SiO_2 to be able to form sodium silicate (Na_2SiO_3) and hence obtain more SiO_2.

Acknowledgments: This research was supported by research grant of DRPM Higher Education, The authors would like to thank the Universitas Negeri Surabaya (UNESA) and DRPM-Ministry of Higher Education and Research and Technology, Indonesia.

References and Notes

1. A. N. Nittaya Thuadaij, *Chiang Mai J. Sci.* 35, 206 **(2008)**.
2. S. Affandi, H. Setyawan, S. Winardi, A. Purwanto, and R. Balgis, *Adv. Powder Technol.* 20, 468 **(2009)**.

3. H. Mori, *J. Mater. Sci.* 38, 3461 **(2003)**.
4. W. Trabelsi, M. Benzina, and S. Bouaziz, *Phys. Procedia* 2, 1461 **(2009)**.
5. Munasir, A. Sulton, Triwikantoro, M. Zainuri, and Darminto, Synthesis of silica nanopowder produced from Indonesian natural sand via alkalifussion route, *AIP Conf. Proc.*, AIP Publishing **(2013)**, pp. 28–31.
6. Munasir, Triwikantoro, M. Zainuri, and Darminto, *Mater. Sci.-Pol.* 33, 47 **(2015)**.
7. U. Kalapathy, A. Proctor, and J. Shultz, *Bioresour. Technol.* 73, 257 **(2000)**.
8. A. A. Jalil, S. Triwahyono, S. H. Adam, N. D. Rahim, M. A. A. Aziz, N. H. H. Hairom, N. A. M. Razali, M. A. Z. Abidin, and M. K. A. Mohamadiah, *J. Hazard. Mater.* 181, 755 **(2010)**.
9. E. W. Setyowati, *J. Rekayasa Sipil.* 3, 29 **(2009)**.
10. D. Wiyono, Antoni, and D. Hardjito, *Procedia Eng.* 125, 747 **(2015)**.
11. D. Hardjito, Antoni, G. M. Wibowo, and D. Christianto, *Materials* 5, 1654 **(2012)**.
12. P. K. Jal, M. Sudarshan, A. Saha, S. Patel, and B. K. Mishra, *Colloids Surf. Physicochem. Eng. Asp.* 240, 173 **(2004)**.
13. S. Tabatabaei, A. Shukohfar, R. Aghababazadeh, and A. Mirhabibi, *J. Phys. Conf. Ser.* 26, 371 **(2006)**.
14. H. D. Jang, H. K. Chang, H. S. Yoon, K. Cho, J. H. Park, and S. Y. Oh, *Colloids Surf. Physicochem. Eng. Asp.* 313–314, 121 **(2008)**.
15. P. K. Jal, M. Sudarshan, A. Saha, S. Patel, and B. K. Mishra, *Colloids Surf. Physicochem. Eng. Asp.* 240, 173 **(2004)**.
16. A. Podlasov, Morphological reconstruction of semantic layers in map images **(2003)**, ftp://cs.uef.fi/pub/Theses/2004_MSc_Podlasov_Alexey.pdf, accessed January 2016.
17. G. H. Woehrle, J. E. Hutchison, S. Özkar, and R. G. Finke, *Image* 30, 1 **(2006)**.

Received: 15 August 2016. Accepted: 6 May 2017.