International Journal of Engineering Research and Technology. ISSN 0974-3154, Volume 12, Number 12 (2019), pp. 2341-2345


# The Effect of Alcohol Solvents on Morphology of Silica Particles Synthesized from Silica Sand and Their Application as Hydrophobic Surfaces

**A. Ismail[1], D. Asrianti[2], A. A. Dwiatmoko[3], B. H. Susanto[1] and M. Nasikin[1, *]**

*[1]Department of Chemical Engineering, Universitas Indonesia, Depok 16424, Indonesia*
*[2]Department of Chemistry, Universitas Indonesia, Depok 16424, Indonesia*
*[3]Research Center of Chemistry, Indonesian Institute of Sciences, Serpong 15314, Indonesia*

**Abstract**

This article report on a study of silica particles prepared from silica sand under alkaline conditions using a sol gel method. Sodium silicate solution prepared from silica sand was diluted with water and dropped-wise in the mixture of ammonia/propanol, ammonia/ethanol, ammonia/methanol and ammonia/ethanol/methanol to form a sol. It was further dried prior to aging treatment for 7 days to obtain silica particles. The effect of alcohol solvent on the morphology and the particle size of silica particles was investigated using various characterization techniques such as scanning electron microscope, X-ray diffraction and particle size analyzer. It was found that the formation of non-agglomerated silica particle with homogenous spherical morphology greatly depended on the solubility of sodium silicate in organic solvent during sol gel synthesis. Furthermore, the produced particles possible for fabrication of hydrophobic surface was discussed in detail.

**Keywords:** Silica Sand, Sodium Silicate Solution, Organic Solvent, Alkaline Medium, Sol Gel

## I. INTRODUCTION

Non-agglomerated silica particles with spherical morphology are commonly synthesized using tetraethyl orthosilicate (TEOS) as a precursor in alkaline medium [1, 2]. Their particle size is easily tailored by varying the concentration of ammonia [3]. Furthermore, the presence of an organic solvent in an alkaline medium can increase the stability of the particles to prevent agglomeration [4]. However, compared to TEOS, sodium silicate solution is better due to its cost-effective, non-toxic and easily scalable characteristics. Therefore, the synthesis of silica particles using sodium silicate precursor has attracted the interests of researchers.

Previous studies reported the synthesis of silica particles using bentonite, rice husk, etc. which consisted of three step processes [5-7]. Firstly, sodium silicate solution was prepared by reacting silica sand and sodium hydroxide. Subsequently, silica gel $Si(OH)_4$ was evaporated to obtain silica particles prior to reacting the sodium silicate solution with strong acid like HCl, $HNO_3$ or $H_2SO_4$ through sol gel process. However, due to agglomeration issue, sodium silicate solution was used to produce silica particle in alkaline medium instead of in acid [8, 9].

Studies of sodium silicate solution as a precursor to produce non-agglomerated form in alkaline medium and organic solvent are still limited. The topic has not attracted the interest of researchers. Previous research found that as the size of the silica particles is reduced, when the ratio between the organic solvent and the alkaline medium increased [10]. It was also reported that the aging condition affected the morphology of silica particles on sol-gel process [11].

Silica sand with high purity silica content is highly abundant materials in Indonesia and accounted as a potential source to prepare sodium silicate solution as a precursor in silica particles fabrication. In the previous report, we have successfully shown the preparation of sodium silicate solution from local silica sand [12]. In this study, our work to prepare silica particles from sodium silicate solution is extended and the effect of morphology of silica particles on the mixture of ammonia and various alcohol solvents is investigated. Possible fabrication of hydrophobic surface of silica particles is also studied.

## II. METHOD

### 2.1. Reagents

Sodium silicate solution was prepared from silica sand as reported in the previous study [12]. The solution contains 8.5% $Na_2O$ and 28% $SiO_2$. Ammonia solution, methanol, ethanol and n-propanol with pure analysis grade were purchased from Merck.

### 2.2. Synthesis of silica particles

A mixture was prepared with ammonia and various alcohol solvents in equal ratios according to the previous report with slight modification [9]. As a precursor of silica, 5 mL of sodium silicate solution was added to 7 mL of distilled water and dropped with slow-rate of alcohol under alkaline medium. After aging period for about 7 days, the result of synthesis was dried to obtain silica particles prior to adding the water to control the pH until the neutral condition was reached. Some

procedures were repeated with three other alcohols in alkaline medium, as given in Table 1.

2.3. Surface modification of silica particles

0.1 g of the silica particle was added to 50 ml ethanol. The mixture was sonicated using ultrasonicator for 20 min. After that, different quantities of stearic acid, i.e. 0.1 and 0.5 g, were added in the mixture form followed by heating at 60°C for 2 hr.

2.4. Fabrication of hydrophobic surfaces

The glass substrates were cleaned by rinsing with ethanol and water, respectively. After that, the glass substrates were dipped into the modified silica particles solution from various alcohol solvent. Subsequently, the samples were dried by heating at 100°C for 10 min prior to measuring the contact angle.

2.5. Characterizations

The dry white silica was characterized using X-Ray diffraction (D8 Advance) to evaluate the amorphous nature of silica particles. Scanning electron microscopy (SEM) analysis was performed by using FEI Quanta 650 to investigate the morphology. The particle size distribution was analyzed using SALD 2300 particle size analyzer. For contact angle measurement an appropriate volume of water was dropped on the surfaces and captured using contact angle meter at BATAN (The National Nuclear Energy Agency)

**Table 1** Quantities of the material used for the synthesis of silica particles

| Sodium silicate solution (ml) | Water (ml) | Ammonia/ alcohol ratio (ml) | Ammonia (ml) | Type of alcohol |
|---|---|---|---|---|
| 5 | 7 | 1:1 | 30 | Ethanol |
| 5 | 7 | 1:1 | 30 | Methanol |
| 5 | 7 | 1:1 | 30 | Propanol |
| 5 | 7 | 1:1 | 30 | Ethanol+ methanol |

## IV. RESULT AND DISCUSSION

In order to synthesize silica nanoparticles, a precursor of sodium silicate solution was prepared. Silica sand was milled for 60 minutes by using high energy milling to obtain the silica powder with particle size of approximately 325 mesh. Afterwards, the obtained silica powder was reacted with sodium hydroxide to obtain sodium silicate solution. In the previous study [12], a smaller size of silica particles was obtained with milling process instead of without milling. The result indicated that milling process affected the silicon content at sodium silicate solution, leading to production of more nuclei due to enhanced solubility of particles. However, the result showed agglomerated silica particles due to the reaction condition in acid medium. Therefore, in this study, alkaline medium was used to prevent the agglomeration.

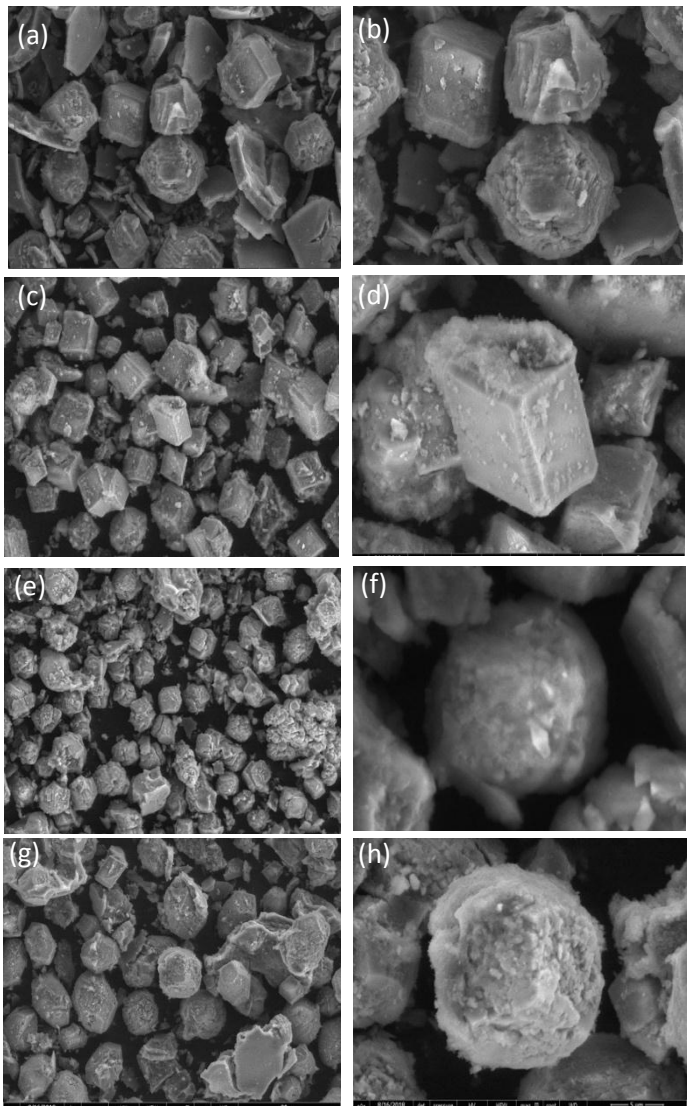


**Fig. 1** SEM images of silica particles produced by mixing sodium silicate solution in different alcohol solvent in alkaline medium. a and b, c and d, e and f, g and h represent the silica particle prepared in propanol, ethanol, methanol, methanol+ethanol, respectively

Figure 1 shows SEM images of silica particles in alkaline medium with various solvents produced from sodium silicate solution in equal ratio of ammonia/alcohol. Figure 1a, b shows the silica particles produced by the addition of sodium silicate solution in ammonia/propanol with various form of silica particles. However, some spherical shapes which appeared indicate the formation of silica particles. In contrast, the silica particles with homogenous shapes were formed in ammonia/ethanol as shown in Figure 1c, d. Even though the shape looked like a cube, the structure was amorphous, as

confirmed on the XRD (Figure 2). In addition, significant morphology changes occurred in the ammonia/methanol solution showing the formation of homogenous spherical shapes of silica particles (Figure 1e, f). The result confirmed that the solubility of sodium silicate in organic solvent during sol gel process affected the morphology of silica particles. Methanol as the shortest chain of alcohol was soluble which might give more silica nuclei to grow independently. To further investigate silica particles formation, solvent mixture consisting of ethanol and methanol was mixed in ammonia medium as shown in Figure 1g, h. It was found that the morphology of silica particles in solvent mixture also consisted of spherical and cubic-like shapes due to effect of ethanol in the system.

The XRD patterns of silica particles produced from various alcohol solvent in alkaline medium are presented in figure 2. The results indicate the amorphous characteristic of silica particles.

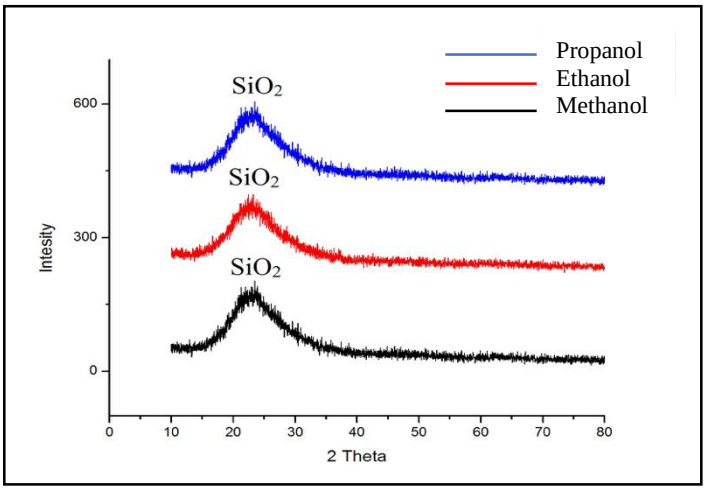


**Fig. 2** XRD patterns of silica particles

In order to evaluate the size distribution of silica particles with variation of alcohol solvent with ammonia mixtures, particle size analysis was performed and the results are shown in Figure 3. It can be observed that particle size distribution of silica decreased continuously with the decrease of alcohol chain. However, compared to methanol as solvent, propanol and ethanol exhibit a wide range of article size distributions. The results indicate that the particle size had various size and morphology as also confirmed by SEM study (figure 1). In contrast, silica particles that were formed in methanol had a narrow range that might imply homogenous form of silica particles.

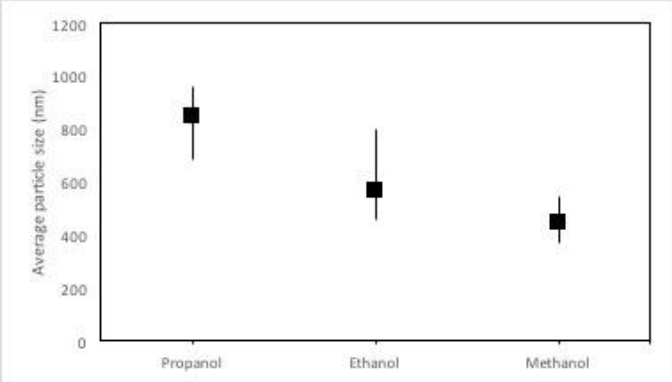


**Fig. 3** Particle size distribution of silica particles

It can be seen from this study that diluted sodium silicate solution in alkaline medium may lead to the formation of intermediate silicate followed by condensation of silica colloidal [13]. At high pH, the aggregation of particles could be prevented due to the increase of electrostatic repulsion of silica particles, while on the contrary, at low pH, the electrostatic repulsions are reduced [14]. In addition, the formation mechanism of silica particles also depends on the solubility of silica in the solvent. In propanol, the silica solubility was lowered which increased the supersaturation [4]. Apparently, sodium silicate solution was not able to reach a homogeneous form in the propanol. In contrast, the solubility of sodium silicate solution in ethanol and methanol is higher than propanol, resulting in the rapid nucleation and growth of silica particles. However, sodium silicate might be unable to reach a homogeneous segregation in the ethanol which followed in concentration gradients during particle nucleation and growth. To control the size of silica particles in the present system requires further investigation.

Figure 4 shows FTIR spectra of modified silica particles with different quantities of stearic acid observed. The peaks appearing at 1052 $cm^{-1}$ and 334.56 $cm^{-1}$ confirm the presence of Si–O–Si bonds. The functional moieties of Si–OH and O–H were detected by peaks at 945 and 3037-3550 $cm^{-1}$, respectively. The peaks corresponding to C–H stretching and C–H bending were identified at 2900 and 1392 $cm^{-1}$, respectively. The presence of C–H bonds confirms the grafting of methyl groups to silica particles, as also confirmed by previous studies [15 – 17]. In addition, the presence of C=O at 1720 $cm^{-1}$ corresponding to stearic acid was attached to silica particles. Therefore, FTIR result indicates the replacement of –OH moieties with $–Si–(CH_3)_3$ at the surface of silica particles. Different results between 0.1 gram (blue color) and 0.5 gram (red color) show the absorption of blue color shaper down compared to red color. It indicates that –OH bond at silanol (Si–OH) of blue color bigger than red color. The wave number shows the silanol group in red color smaller energy was absorption so it might indicate that the process of ester

synthesis in solution is closer to finish the reaction. The next study on the hydrophobic effect of modified silica particles, with 0.5 gram of stearic acid was conducted.

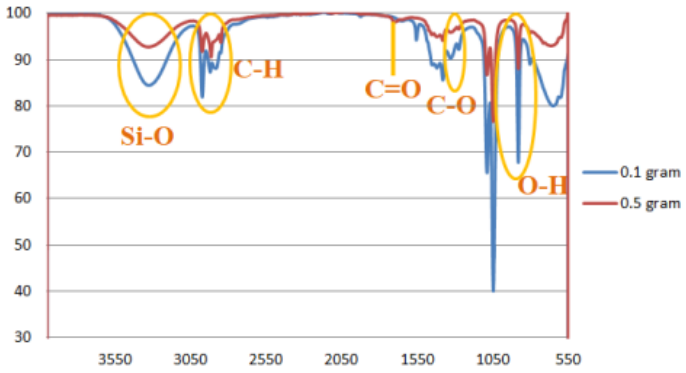


Figure 4 IR spectra of modified silica particles prepared by varying amounts of stearic acid

To further study the hydrophobic effect of silica particles in the material surface, the glass substrate was prepared to clean with ethanol and water, respectively. Afterward, dip coating process was conducted to coat modified silica particles in the glass substrate [18]. The hydrophobic effect was observed in hydrophobic silica nanoparticles synthesized in the present investigation, in which contact angle was increased by decreasing the chain of alcohol due to the homogeneous nature of the silica particles, as shown in Figure 5. The water contact angles were 91◦, 95◦ and 98◦ for the silica particle prepared in propanol (Figure 5a), ethanol (Figure 5b), methanol (Figure 5c), respectively. When silica particles size was decreased, surface tension between water and air increased. It has been observed that the roughness of the surface caused the water to be trapped in the valley of the surface, so that the water tended to be spherical in shape, making the contact angle increase. Hydrophobic effect occured when contact angle is more than 90◦ [19].

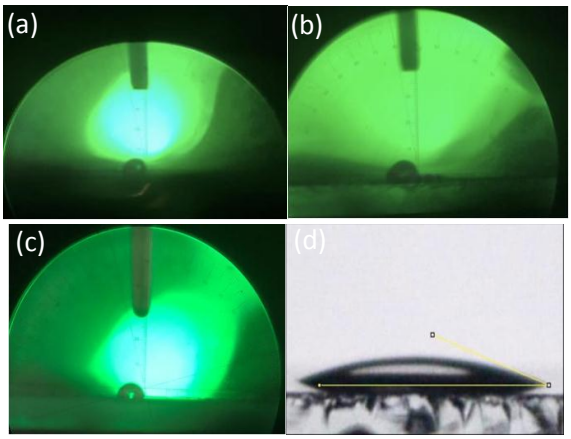


**Fig. 5** Contact angle water at glass substrate with modified silica particles in (a) propanol; (b) ethanol; (c) methanol and without (d) modified silica particles (source: Putri et. al, 2018)

In general, the glass coated with silica particles or hydrophobic material will increase the contact angle of the glass. The glass that has not been coated with silica particles hydrophobic material will produce a small contact angle at 20º shown in Figure 5d. This result indicates that due to the high level of roughness, so that the material structure coated by nano/micro-sized particles could be form to hydrophobic property. There was obvious because nano/micro-sized particles have a larger surface area. The surface area of particles that interacts with water will be increased the contact angle.

## VI. CONCLUSION

The morphology of silica particles in various alcohol solvents under alkaline condition was investigated. We found that the addition of sodium silicate solution into ammonia/propanol results in various forms of silica particles. In contrast, the silica particles with homogenous shapes were formed in ammonia/ethanol and ammonia/methanol. However, in ammonia/ethanol the shape is like a cube. The result confirms that the solubility of sodium silicate in organic solvent during sol gel process affected the morphology of silica particles, resulting in the nucleation and particle growth. As a result, silica particles formed in methanol had a narrow range that might imply homogenous form of silica particles. Furthermore, the modified silica particles can also be applied on the material surface because of their hydrophobic characteristic. This study is significant as it increases the value of silica sand for industry applications.

## Acknowledgement

This research was funded by Directorate of Research and Community Engagement Universitas Indonesia (DRPM UI) through International Indexed Publication Grant (PIT 9) with contract No: NKB-0045/UN2.R3.1/HKP.05.00/2019

## REFERENCES

[1] Isobe H, Utsumi S, Yamamoto K, Kanoh H, Kaneko K. Micropore to macropore structure-designed silicas with regulated condensation of silicic acid nanoparticles. Langmuir. 2005;21(17):8042–8047.

[2] Stober W, Fink A, Bohn E. Controlled growth of monodisperse silica spheres in the micron size range. J Colloid Interface Sci. 1968;26(1):62–69.

[3] Rahman IA, Vejayakumaran P, Sipaut CS, Ismail J, Bakar MA, Adnan R, Chee CK. An optimized sol–gel synthesis of stable primary equivalent silica particles. Colloids Surf A. 2007;294(1–3):102–110.

[4] Buining PA, Liz-Marzan LM, Philipse AP. A Simple Preparation of Small, Smooth Silica Spheres in a Seed

Alcohol for Stober Synthesis. J Colloid Interface Sci. 1996;179:318-321.

[5] Affandi S, Setyawan H, Winardi S, Purwanto A, Balgis R. A facile method for production of high-purity silica xerogels from bagasse ash. Advanced Powder Technology. 2009;20:468-472.

[6] Thuadaij N, Nuntiya A. Preparation and Characterization of Faujasite using Fly Ash and Amorphous Silica from Rice Husk Ash. Procedia Eng. 2008;35(1):206-211.

[7] Munasir A, Hidayatullah M, Triwikantoro, Zainuri M, Darminto. Sintesis Silika Amorf dari Bahan Alam Lumpur Sidoarjo dengan metode Kopresipitasi. SNF Procceding, Unnes. 2010;FM101:1-6.

[8] Howard AG, Khdary NH. Spray synthesis of monodisperse sub-micron spherical silica particles. Mater Lett. 2007;61(8–9):1951–1954.

[9] Zulfiqar U, Subhani T, Husain SW. Towards tunable size of silica particles from rice husk. J Non-Cryst Solids. 2015:429;61–69.

[10] Zulfiqar U, Subhani T, Husain SW. Synthesis of silica nanoparticles from sodium silicate under alkaline conditions. J Sol-Gel Sci Technology. 2016:77;753-758.

[11] Andreas A, Kristianto H, Kurniawan DF, Sintesis nanosilika dari sekam padi menggunakan metode sol gel dengan pelarut etanol. Proceeding of Seminar Nasional Teknik Kimia "Kejuangan", Yogyakarta. 2016, 17 March:L3 1-6.

[12] Ismail A, Alamsyah IA, Kholil M, Susanto BH, Nasikin M. The effect of milling time on the size of silica particles from silica sand. Material Science Forum. 2017:917;162-166.

[13] Godoi RHM, Fernandes L, Jafelicci M. Jr, Marques RC, Varanda LC, Davolos. Investigation of the systems silica and silica containing chromium in alcohol medium. J Non-Crystal Solids. 1999: 247;141–145.

[14] Wang J, Sugawara-Narutaki A, Fukao M, Yokoi T, Shimojima A, Okubo T. Two-phase synthesis of monodisperse silica nanospheres with amines or ammonia catalyst and their controlled self-assembly. ACS Appl Mater Interfaces. 2011:3(5);1538–1544.

[15] Sarawade PB, Kim J-K, Hilonga A, Quang DV, Kim HT. Effect of drying technique on the physicochemical properties of sodium silicate-based mesoporous precipitated silica. Appl. Surf. Sci. 2011:258(2);955-961.

[16] Parale VG, Mahadik DB, Mahadik SA, Kavale MS, Rao AV, Wagh PB. Wettability study of surface modified silica aerogels with different silylating agents. J. Sol-Gel Sci. Technol. 2012:63(3);573-579.

[17] He S, Li Z, Shi X, Yang H, Gong L, Cheng X. Rapid synthesis of sodium silicate based hydrophobic silica aerogel granules with large surface area. Adv. Powder Technol. 2015:26(2);537-541.

[18] Simpson JT, Hunter SR, Aytug T. Superhydrophobic materials and coatings: a review. Rep. Prog. Phys. 2015:78(8);086501.

[19] Yuan, Y, Lee, TR.: Contact angle and wetting properties. In Surface science techniques. Springer, 2013, 3-34.