Preparation of Stable Colloidal Silica with Controlled Size Nano Spheres from Sodium Silicate Solution

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Abstract. The formation process of stable colloidal silica solution was discussed in this article. The affecting parameter including pH, zeta potential, and colloidal concentration was investigated to elucidate the stability of colloid. Sodium silicate was used as the silica source. The colloidal silica prepared via sol-gel method at the base condition. Sodium ion of sodium silicate was removed by ion-exchanging to obtain the active silicic acid which was titrated with potassium hydroxide (KOH) solution to form the colloidal silica. Size distribution and solution zeta potential were measured by Particle Size Distribution (PSA). In this experiment, the results showed that the higher solution pH (affect the decreasing of zeta potential value) and higher colloidal concentration (affect the increasing of zeta potential value) play important role in the stability of colloidal silica and controlling the particle growth to form the larger particle size. The colloidal silica formed at this condition was agglomeration free for a long period that indicated the colloids were stable.

Keywords: Colloidal silica, Sodium silicate, Stable colloid

1. Introduction
The formation process of colloidal silica via sol-gel method is of interest due to the fact that colloidal silica can be used in various fields. The colloidal silica has a series of good physicochemical properties, e.g. strong adsorb ability, large surface area and good binding properties [1]. The colloidal silica has potential application in casting, stiffener in hard coating reagent, and textile [2][3][4]. Recently, it has been applied to make paper using micro particles [5]. In making paper, a stable dispersion is very important to inhibit particle’s coalescing into larger agglomerates. Many commercial products already made using colloidal silica but used tetra esters as the raw materials [6][7][8]. However, this material was very expensive and toxic. It is necessary to use an abundant resource of silica such as sodium silicate solution or well known as water glass.

Colloidal silica has been synthesized by various method including sol-gel method [9][10][11], hydrothermal reaction [12][13], and chemical vapor deposition (CVD) [14]. The sol-gel method widely used to produce pure silica particles due to its ability to control the particle size and morphology through systematic monitoring of reaction parameters in ambient temperature [15].

The process used for making colloidal silica from sodium silicate using sol-gel method included ion-exchanging method [16]. This method can easily control the particle size and distribution in colloidal silica. Control of silica size in colloidal precursor was important due to it would influenced the bulk particle produced and the colloid stability. It enhanced by provide an electric charge on the surface of
dispersed particles. In colloidal system, high zeta potential value will provide the stability of the solution to repulsive the aggregation [17]. The like charge on the particles will prevent the agglomeration between particles. Many experiments conducted using sodium silicate as raw material, but only few kinds of literatures had discussed the controlling silica size in the colloidal solution by giving an electric charge on surface of dispersed particles. Tsai [3] has been studied the process parameters of the formation of colloidal silica via sodium silicate. The formation temperature, titration rate and alkali concentration affected the surface growth of silica particle. However, the colloidal silica particle formed in this method was unstable at high formation temperature and titration rate of silica seed. 

In present study, we report the synthesized of colloidal silica via sodium silicate at ambient temperature. This method has low heating consumption and formed stable colloidal silica. The colloidal silica was unstable at high formation temperature. So, it is important to study the colloidal silica formation at ambient temperature. Otherwise, colloidal silica pH value will give different surface particle charge as the present of different amount of potassium hydroxide concentration. Therefore, we investigated the effect of solution pH and solution concentration on the colloid stability and particle growth as the present of surface charge on the silica particles.

2. Experimental
Sodium silicate (Na$_2$O.nSiO$_2$.mH$_2$O, 8% Na$_2$O, 27% SiO$_2$, Merck) and potassium hydroxide (KOH, 85%, Merck) were used as received without further purification. Colloidal silica particles in the case of basic silica sol were prepared based on a method established by Liu [1]. Water glass diluted in distilled water to obtain 0.1, 0.2, and 0.3 N colloidal silica solution at ambient temperature. Subsequently, the diluted water glass was passed through a cation exchange resin (Amberlite™ IR120, Dow Chemical) to form active silicic acid solution. The sodium ion of the dilute sodium silicate solution was substituted by hydrogen ion on the exchange sites of cation resin.

Potassium hydroxide solution (0.1 M) was added drop-by-drop while the solution was stirred to adjust the solution pH from 8-11. At this condition, the polymerization of silicic acid leads to the formation of silica particles dispersed in water to give hydrosols. The precursors were used to study the effect of solution pH and concentration on the morphology of silica particles during the drying process. The experimental flowchart of formation colloidal silica had shown in figure 1. The stability of colloidal precursor very important in its application. The formed colloidal silica solutions were characterized by particle size analyzer and zeta potential (Malvern Zetasizer) to measure the particle size distribution and particle size.

![Figure 1. The experimental flowchart of formation colloidal silica.](image-url)
3. Result and Discussion

Figure 2 shows the silica particle size distribution in colloidal solution in different solution concentration at pH 8. It can be observed that the size of silica particle in colloidal precursor increased as the solution increased. The increasing of particle caused by the aggregation of seeds when the solution pH suddenly increased during the addition of KOH. The amount of silica particle in solution increased as a result of the increasing solution concentration from 0.1 N to 0.3 N. The homogeneous nucleation of active silicic acid in precursor solution, have been occurred first before the addition of KOH solution. The active silicic acid going through nucleation and polymerization process. Silicic acid undergoes the polymerization from monomer become dimer and finally silica particle. The particle growth from nanometer size to micrometer size [18]. The schematic of silica formation from sodium silicate with salt absent present in figure 3. The effect of solution pH on the particle size also described. The solution pH arranged at basic condition from 8 to 11. The particle size tends to increase from 3.146, 3.448 and 4.066 nm when the solution pH increased from 8 to 11 respectively. However, the particle size decreased become 3.55 nm at pH 11. At pH 11, all solid phases of silica dissolve in water, this resulted slow precipitation which causes the particles formed in droplets become small. This happens because of the hydroxyl ions that catalyze the dilution process of small particles that limit the formation of larger particles [19]. The particle formation of colloidal silica particle affected by the addition of potassium hydroxide solution.

![Figure 2](image2.png)

**Figure 2.** (a) The effect of solution concentration (a) 0.1 M; (b) 0.2 M; (c) 0.3 M to the particle size at pH 8.

![Figure 3](image3.png)

**Figure 3.** Silica particle formation at pH 7-10 with salt absent.
To investigate the effect of solution concentration to the stability of colloidal silica solution, zeta potential (ζ) measurement was conducted by Malvern Zetasizer instrument. Figure 4 (a) shows the effect of solution pH to the zeta potential value. Zeta potential value related to the particle surface charge, a property that all materials possesses, or acquire, when suspended in fluid. A high zeta potential value will provide the stability of the solution to repulsive the aggregation. The like charge on the particles will prevent the agglomeration between particles and thus maintaining the Brownian motion [20]. Colloidal stability achieves when the absolute value of ζ>+10 (positive charge) and ζ>-10 (negative charge). Based on Fig. 4 (a), the absolute zeta potential value higher than -10 indicated that the colloidal silica was stable. The value decreased as the solution pH increased. At the higher pH value, the extra electrolyte in the solution compressed the thickness of electrical double layer on the colloidal silica which made the zeta potential value decreased. This condition made the particle growth more easily. From this result, it is indicated that the solution pH can control the stability of colloidal silica and the particle size.

**Figure 4.** (a) The effect of solution pH to zeta potential; (b) The effect of solution concentration to zeta potential.

Figure 4 (b) shows the effect of solution concentration to the zeta potential value. The thickness of electrical double layer depends upon the concentration of electrolyte on the surface charge. As the concentration increased the amount of active silicic acid also increased, but the amount of electrolyte remains constant. This result indicated that the absolute zeta potential increase as the electrolyte concentration that compress the electrical double layer decrease. The absolute zeta potential value higher than -10 indicated that the colloidal silica was stable. Different with the effect of solution pH, the particles growth in concentration effect due to the diffusion mechanism between particles has a strong effect. From this result, it is indicated that the solution concentration can control the stability of colloidal silica and the particle size.

Figure 5 (left) shows the photographs of colloidal silica after being storage for several times. The colloidal silica solutions have transparent appearance. The colloidal solution remains transparent for more than ten days. The increasing of solution concentration from 0.1 N to 0.3 N did not affecting the stability of solution. The stability of colloidal silica solution affected by zeta potential value. Higher zeta potential of silica particle value maintains the particle interaction to repulsive each other. This result indicated that the colloidal silica was stable, and no agglomeration occurs for a long times storage. The longer storage time for 30 days, the same colloidal solution remains transparent. It can be seen in Fig. 5 (right). This condition also happens in another pH condition (9, 10 and 11) in the same solution concentration range (not shown here). The appearance of colloidal solutions is transparent after the long storage time more than 30 days.
4. Conclusion
The process parameter of the formation of colloidal silica using sodium silicate via sol-gel method had been investigated. The results showed that the process parameters such as solution pH and solution concentration affected the colloidal stability and particle size distribution. The mean particle size increased with increasing solution pH and increasing solution concentration. The value of zeta potential particle above ±10. The colloidal silica produced at this condition was agglomeration free for a long period, indicated that the colloidal silica was stable.

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