

소듐실리케이트로부터 실리카 솔 製造 및 成長[†]

[‡]尹虎成 · 金哲主 · 金聖敦 · 張喜棟

韓國地質資源研究院 資源活用素材研究部

Preparation and Growth of Silica Sol from Sodium Silicate[†]

[‡]Ho-Sung Yoon, Chul-Joo Kim, Sung-Don Kim and Hee-Dong Jang

Korea Institute of Geoscience and Mineral Resources, 92 Gwahang-no, Yuseonggu, Daejeon, 305-350 KOREA

요 약

본 연구에서는 소듐실리케이트로부터 실리카 솔의 형성과 성장에 관한 연구를 고찰하였다. 황산으로 소듐실리케이트 수용액을 산화시킬 때 실리카 함량은 2%가 적절하였으며, 수용액 내 나트륨 이온 제거 후 안정한 실리케이트 수용액을 얻기 위해서는 수용액 pH를 9 이상 유지하여야 한다. 소듐실리케이트와 실리케이트 수용액을 혼합하여 pH 10으로 유지하여 80°C로 가열하여 10 nm 크기의 실리카 솔을 제조할 수 있었다. 또한 실리케이트 용액을 실리카 솔 용액에 첨가하여 실리카 솔을 50 nm로 성장시킬 수 있었다.

주제어 : 실리카 솔, 소듐실리케이트, 축합중합반응, 실리케이트 수용액

Abstract

The formation of silica sol from sodium silicate solution and the growth of silica sols were investigated in this study. The SiO₂ content of 2% in sodium silicate solution was proper to oxidize sodium silicate with sulfuric acid. After the removal of sodium ions in sodium silicate solution, the pH of silicate solution had to be controlled above 9 for a stable silicate solution. The silica sol, which size is about 10 nm, could be prepared by heating the mixed solution of sodium silicate and silicate solution removed sodium ions at pH 10 and 80. And the silica sol grew into about 50 nm as silicate solution was added to silica sol solution.

Key words : silica sol, sodium silicate, condensation, silicate solution

1. Introduction

The formation process of colloidal silica was an old nanotechnology since 19th century¹⁾. Recently, it has been applied in the modern industries, such as binder in inorganic paint, stiffener in hard coating reagent and especially as an abrasive particle of chemical mechanical polishing slurry.

Stöber and Rang used Si(C₂H₅OH)₄[TEOS, Tetra Ethyl Ortho-Silicate] and NH₄OH as the raw materials, which reacted in alcohol solution to form the mono

disperse silica²⁾. Coenen and De Kruij used Stöber process, but used commercial Ludox as the seeds to synthesis and grow the colloidal silica particles³⁾. Coenen indicated that the particle size of composite silica can be estimated if assume the process under controlling in the surface control range. Chen et al. studied the new particle formation in the monosize silica seeds who used Si(OH)₄ from TEOS hydrolysis as the raw material⁴⁾. Chen et al. indicated that the new particles are formed in the certain conditions, such as the early stage of growth of silica particles are controlled by diffusion of condense species, and have electric charge against an electrostatic repulsion onto the surface of silica seeds. Tsai et al. found that the

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[‡] E-mail: hsyoon@kigam.re.kr

titrating rate, the formation temperature and especially the concentration of KOH are very important to the surface growth of colloidal silica⁵.

Precipitated silica is commonly used in various consumer products. One industrial production of precipitated silica from sodium silicate and sulfuric acid is used to economically produce a large amount of silica. Despite its wide range of application this production process has not been thoroughly investigated yet. Although extensive literature exists on the individual physical and chemical phenomena, an integrated overall account of this process from a scientific viewpoint is not available in literature to date.

One industrial silica precipitation process among others is characterized by the continuous addition of sulfuric acid and sodium silicate to a mixture of water and an initial amount of sodium silicate. Since the condensation reaction of silicic acid is strongly pH dependent, an initial amount of sodium silicate in the reactor serves to buffer any initial pH variation due to incomplete mixing after the addition of sulfuric acid has started.

Therefore the effects of the experimental conditions such as the content of silica in aqueous solution, pH of solution and reaction temperature on the formation of silica sol was surveyed for the preparation process of colloidal silica sol from sodium silicate in this study.

2. Experimental

2.1. Materials

Sodium silicate[water glass] obtained from siliceous mudstone in Korea was used as starting material and its composition was displayed in Table 1.

Sulfuric acid(95%, Dongyang Chemical Co.), ammonium hydroxide(28%, Dongyang Chemical Co.), hydrochloric acid(35%, Dongyang Chemical Co.) and hexa-ammonium hepta-molybdate tetrahydrate(99%, Junsei chemical co.) was used. Reagent-grade water was produced by a Milli-Q filtration system.

The pH of the aqueous sodium silicate solution was

Table 1. The composition of sodium silicate

Composition	Na ₂ O	SiO ₂
Content(%)	7	27

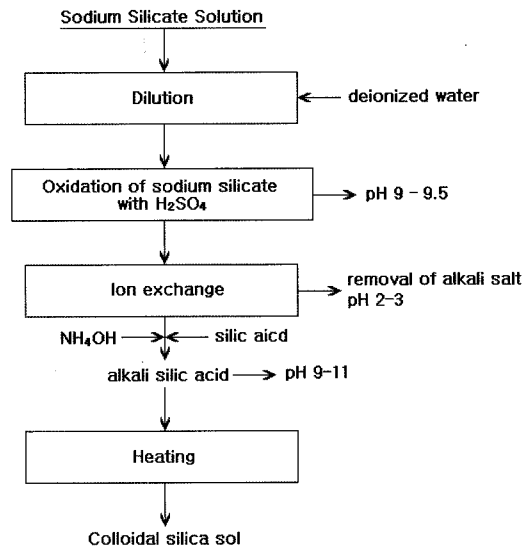


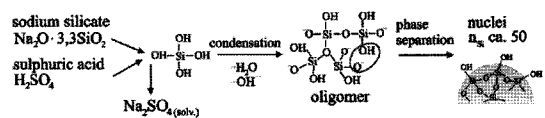
Fig. 1. Preparation process of silica sol.

measured by pH meter(Model 920A, Orion Research Inc.), and the behavior of the silicic acid and polysilicic acid solution was detected by UV-Vis spectrophotometer(Specord S 100, Analytik Jena AG). The shape and size of silica sol was characterized by TEM(Model CM 12, Philips).

2.2. Preparation Process of Silica Sol from Sodium silicate

The preparation process of the silica sol was described in Fig. 1.

Diluted sodium silicate solution is oxidized by sulfuric acid as follows⁶:



The silicic acid condenses to form larger oligomers during the first stage. Generally, it is assumed that these polymeric clusters are initially stabilized by solvation. However, as they grow in size and become more compact, they collapse and a phase separation results with the formation of silica nuclei. This initial stage can be referred to as a growth process. At high pH values a significant amount of silanol[Si-OH] group on silicon dioxide particles and on monomers

are charged negative. This charge catalyzes the further growth process of the particles by monomer addition.

An ion-exchange process was applied in order to achieve a substitution of sodium ions by protons. The ion-exchange was carried out at a pH of 2 using the batch method, i.e., the diluted sodium silicate solution and ion exchange resins(H⁺ type) were mixed, stirrer for 10 min and filtered.

3. Results and Discussion

3.1. Content of SiO₂ in Sodium silicate for Oxidation

The sodium silicate solution was diluted to a certain silica concentration with distilled water, then oxidized by addition of sulfuric acid. Sulfuric acid was added to the solution until the solution pH reached at pH 9.5.

Fig. 2. shows the oxidized sodium silicate solution with silica content.

When the content of SiO₂ in the diluted sodium silicate solution is above 3%, the solution became silica gel during oxidization. Therefore the sodium silicate had to be diluted with distilled water until the content of SiO₂ in the solution was below 2% in this study.

3.2. Investigation of Sodium silicate solution

From the above results, it seems that the diluted sodium silicate solution has many kinds of silicic acid species such as monomer, oligomer and polymeric silicic acid due to the gelation in oxidization stage.

The reaction of molybdic acid with monomeric Si(OH)₄ to give the yellow silicomolybdic acid is indispensable in investigating the behavior of soluble and colloidal silica. It is obvious that only Si(OH)₄, but not polymers thereof, can react directly with acidified

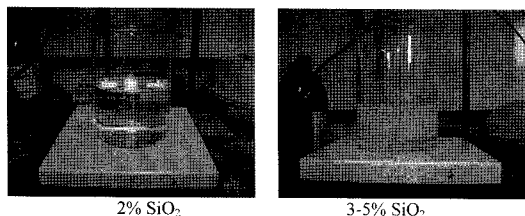
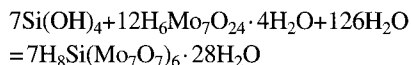


Fig. 2. The oxidized sodium silicate solution with SiO₂ content.

ammonium heptamolybdate to form the yellow silicomolybdic acid, since latter molecule contains only one silicon atom:



Iler found that with a H⁺:MoO₄²⁻ ratio of 5.3, the pH was 1.2 and silicic acid monomer reacted fully in 2 min, and the color was stable for 2 hr¹⁾.

Therefore the recommended procedure proposed by Iler was used to determine the species of silicic acid in the silicate solution.

Fig. 3 shows the absorption spectrum of the silicate solution removed sodium ions by UV-Vis spectrophotometer.

The intensity at 410 nm increased with increasing reaction time with molybdic acid solution. If silicic acid monomers exist only in silicate solution, the intensity at 410 nm would be constant with reaction time. Fig. 4 shows the intensity at 410 nm of silicate

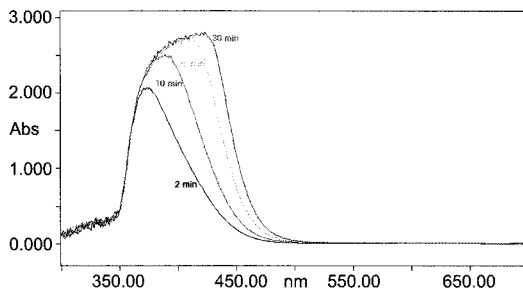


Fig. 3. The absorption spectrum of the silicate solution.

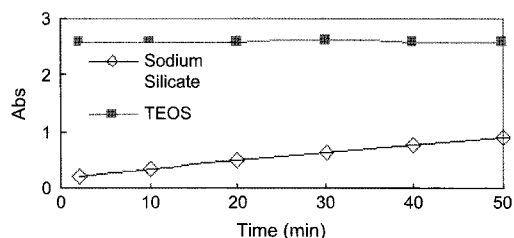


Fig. 4. The absorbance at 410 nm of silicate solution and TEOS with molybdic acid reaction time.

Table 2. Gelation time of silicate solution with pH

pH of solution	2.0	3.0	5.0	6.5	7.0	7.5	9.0	10.0
Gelation time(hr)	240	140	5	10	14	20	-	-

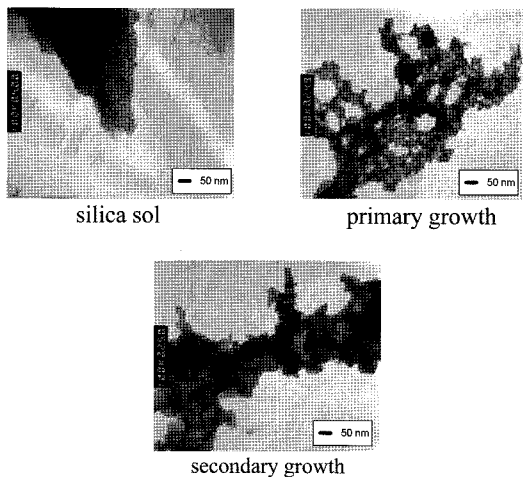


Fig. 5. TEM images of silica sol.

solution and TEOS. TEOS is only composed of $\text{Si}(\text{OC}_2\text{H}_5\text{OH})_4$ monomers, so that the intensity at 410 nm did not change with reaction time with molybdic acid. But the intensity of silicate solution changed with reaction time. Thus it could be known that the silicate solution was composed of monomeric and polymeric silicic acid.

Generally, the polymerization of silicic acid monomer to large particles and gels or powders has been represented schematically by Iler as in Fig. 5¹⁾. This applies to aqueous systems, in which silica somewhat soluble. Monosilicic acid is soluble and stable in water at 25°C for long periods of time if the concentration is less than about 100 ppm as SiO_2 .

When a solution of monomer, $\text{Si}(\text{OH})_4$, is formed at a concentration greater than about 100-200 ppm as SiO_2 , that is, greater than the solubility of the solid phase of amorphous silica, and in the absence of solid phase on which the soluble silica might be deposited, then the monomer polymerizes by condensation to form dimer and higher molecular weight species of silicic acid. The condensation polymerization involves an ionic mechanism.

Above pH 2 the rate is proportional to the concentration of OH^- ion and below 2 to H^+ ion⁷⁾.

Therefore the effect of solution pH on the gelation of silicate solution was surveyed and displayed in Table 2.

The content of SiO_2 in silicate solution was about 5% in order that the effect of pH on the gelation of

silicate solution was investigated accurately. Similarly above mentioned, the gelation time of silicate solution decreased with increasing pH of solution until 5 due to the increase of OH^- ions. But above pH 6.5 the gelation time increased with increasing pH of solution. The increase of the gelation time for pH values larger than 6 can be explained by the increase of the surface charge and the corresponding increase of Coulomb repulsion^{1, 8)}. And the gelation did not occur at the pH of solution above 9. From these results, it could be known that the pH of the silicate solution has to be controlled above 9 for obtaining a stable silicate solution.

3.3. Preparation of Silica Sol & Growth

The silica sol was prepared by using the mixed solution of oxidized sodium silicate solution and silicate solution removed sodium ions. In this case, the content of SiO_2 was 4% in the mixed solution.

Silica nuclei formed by oxidation of sodium silicate with sulfuric acid did not grow at room temperature in the range of pH 9-11. Generally, silica nuclei is grown by condensation of nuclei and silicic acid monomer, and OH^- ion catalyze the condensation in alkali region. In the alkali region, silica begins to dissolve as silicate, the silica particles are negatively charged and repel each other¹⁾. Therefore it could be known that silica nuclei did not grow in this condition.

Silicic acid has a strong tendency to polymerize in a such way that in the polymer there is a maximum of siloxane (Si-O-Si) bonds and a minimum of uncondensed SiOH groups. Thus at the earliest stage of polymerization, condensation quickly leads to ring structures, for example, the cyclic tetramer, followed by addition of monomer to these and linking together of the cyclic polymers to larger three dimensional molecules. These condense internally to the most compact state with SiOH groups remaining on the outside. The resulting spherical units are, in effect, the nuclei that develop into larger particles. The solubility of these very small particles depends on the particle size, that is, the radius of curvature of the surface. It also depends on the completeness of the dehydration of the internal solid phase. If the latter is formed at ordinary temperature it may contain uncondensed OH groups but if formed above 80°C, and especially above

pH 7, it is almost anhydrous. Because small particles are more soluble than larger ones and since not all the small three-dimensional particles are the same size, the particles grow in average size and diminish in numbers as the smaller ones dissolve and the silica is deposited upon the larger ones(Ostwald ripening)¹⁾.

Accordingly, heating process was introduced for the preparation of silica sol.

When the preparation process was carried out at pH 10 of the mixed solution, the mixed solution was gelled during heating. When the pH of mixed solution was 10, then the mixed solution did not gelled during heating until 80°C.

Fig. 5. shows the shape and size of silica sol analyzed by TEM.

The silica sol, which size is about 10 nm, could be prepared by heating the mixed solution of sodium silicate and silicate solution removed sodium ions at pH 10 and 80. And the silica sol grew into about 50 nm as silicate solution was added to silica sol solution.

4. Conclusions

The preparation of silica sol and growth processes were investigated by using sodium silicate solution obtained from siliceous mudstone in Korea. The SiO₂ content of 2% in sodium silicate solution was proper to oxidize sodium silicate with sulfuric acid. After the removal of sodium ions in sodium silicate solution, the pH of silicate solution had to be controlled above 9 for a stable silicate solution. The silica sol, which size is about 10 nm, could be prepared by heating the mixed solution of sodium silicate and silicate solution

removed sodium ions at pH 10 and 80°C. And the silica sol grew into about 50 nm as silicate solution was added to silica sol solution.

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尹 虎 成

- 현재 한국지질자원연구원 책임연구원
 - 당 학회지 제 11권 2호 참조
-

金 哲 主

- 현재 한국지질자원연구원 선임연구원
 - 당 학회지 제 11권 2호 참조
-

金 聖 敦

- 현재 한국지질자원연구원 책임연구원
 - 당 학회지 제 12권 5호 참조
-

張 喜 棟

- 현재 한국지질자원연구원 책임연구원
 - 당 학회지 제 12권 5호 참조
-