

Effect of electrolyte additives on sol-precipitated nano silica particles

Sung-Soo Kim^a, Hyun-Seok Kim^a, Sun Geon Kim^b, Woo-Sik Kim^{a,*}

^aDepartment of Chemical Engineering, KRRC, Kyunghee University, Yongin Kiheung Seochun 1, Kyungki-Do, 449-701, South Korea

^bDepartment of Chemical Engineering, Joongang University, Dongjak-ku Heuksuk-dong 221, Seoul, 156-756, South Korea

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Abstract

The effect of mono-valent electrolyte additives on nanosized silica particles, synthesized via the sol-precipitation method, was investigated. Without additives, the particle size varied from about 35 nm to hundreds of nm depending on the TEOS, water, and ammonia concentrations. The addition of a small amount of electrolytes (below the optimal concentration) reduced the particle size up to 17.5 nm, due to an enhanced particle surface electric charge, thereby inhibiting particle growth. Meanwhile, a further increase in the additive concentration (above the optimal concentration) significantly increased the particle size, due to neutralization of the particle charge, thereby promoting particle growth. Among the present additives, sodium iodine had the most effect on reducing the particle size, while cesium chloride had the least.

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1. Introduction

Controlling the particle size and distribution in sol-precipitation continues to be a major concern in the production of advanced ceramics. According to the Bogush and Zukoski's model, which describes the particle growth of silica in sol-precipitation, stable silica particles are formed and grown via the aggregation of primary particles that are nucleated in a supersaturated solution [1–3]. Therefore, the particle size and distribution change significantly according to the solvent, solution pH, and reactant and catalyst concentrations, all of which affect the nucleation and aggregation of the primary particles. For example, with uniform seed particles of silica in the sol-precipitation [4], a multi-modal particle size distribution can be obtained by modifying the particle nucleation and growth processes via varying the TEOS concentration, amount of seed particles, and admixture concentration.

Surfactants that form micell in the solution are often applied to the sol-precipitation process to control the size and uniformity of silica particles [5–7]. A uniform particle size originates from the molecular interaction with the surfactant, which provides the driving force for particle aggregation [5,6]. The use of an anionic surfactant enables us to produce nano-sized particles of silica and its mechanism is also suggested based on primary particle aggregation [7].

The potential of electrolyte additives, which are highly effective in controlling particle growth, has not yet received significant attention in the synthesis of nano-sized particles via sol-precipitation. Accordingly, the current study investigates the potential application of mono-valent electrolyte additives for nano-particle synthesis in sol-precipitation at a high concentration of TEOS in relation to the practical application of the sol-precipitation method.

2. Experimental

Initially, a 350 ml mixture of de-ionized water, methanol (Junsei, ACS grade), and ammonia (Showa,

* Corresponding author. Tel.: +82-31-201-2576; fax: +82-31-202-1946.

E-mail address: wskim@khu.ac.kr (W.S. Kim).

ACS grade) was loaded in a semi-batch reactor, then 100 ml of a TEOS (Fluka, ACS grade) reactant solution was fed into the reactor at a constant flow rate of 3.33 ml/min. The concentrations of TEOS, H₂O, and NH₃ in the reactor were changed from 0.02 to 1.0 mol/l, 1.12 to 22.5 mol/l, and 0.224 to 1.8 mol/l, respectively. To modify the sol-precipitation process, mono-valent electrolytes of NaOH, NaCl, NaI, KCl, CsCl, and CsI were added to the mixture initially loaded in the reactor. The electrolyte concentration in the reactor was varied between 10⁻⁶ and 10⁻³ mol/l. In the present experiment, the above concentrations indicate values based on the final mixture volume in the reactor.

After feeding, the product suspension was continuously agitated for 48 h to complete the reaction in the reactor. Thereafter, the product suspension was analyzed using a particle size analyzer (Zetasizer, Malvern, UK), transmission electron microscopy (H-600, Hitachi, Japan), and zeta potentiometry.

3. Results and discussion

3.1. Effect of reaction conditions

Based on the particle formation mechanism in the sol-precipitation process [2,3], a huge number of primary particles is first nucleated in the initial high supersaturated solution. Then, the primary particles are rapidly aggregated to form stable particles, which grow with the further aggregation of primary particles. After this particle induction period, any further primary particles generated under supersaturation are consumed for the growth of stable particles. As such, the resulting particles in the product suspension were highly mono-

dispersed in size and spherical in shape, as shown in Fig. 1.

However, if the generation of primary particles by supersaturation exceeds the consumption of primary particles for the growth of stable particles during sol-precipitation, new stable particles are spontaneously formed by the self-aggregation of the extra primary particles, resulting in a multi-modal distribution of particle sizes in the product suspension [8]. Yet, in the present study, the mono-dispersity of the particle size was maintained even over a wide range of TEOS, H₂O, and NH₃ concentrations, implying that the population of stable particles formed during the induction period was sufficient to consume the primary particles nucleated after the induction period. Furthermore, the initial supersaturation level (supersaturation level during induction period) was critical in determining the particle size of the product suspension in the sol-precipitation, as the higher particle formation with a higher initial supersaturation resulted in a smaller particle size in the product suspension. Therefore, as shown in Fig. 2, the increased particle size with increased water, TEOS and NH₃ concentrations may have been due to the initial nucleation at a lower supersaturation level resulting from the promotion of the hydrolysis and condensation reactions, as demonstrated in a previous study [9–11]. It is interesting to note that the particle size was almost independent of the H₂O concentration over a wide range of values, due to the extreme excess of H₂O in the hydrolysis reaction. Meanwhile, the TEOS and NH₃ concentrations had a linear effect on improving the particle size because the hydrolysis and condensation reactions were proportionally facilitated.

3.2. Effect of admixtures

Under fixed reaction conditions for TEOS, NH₃, and H₂O, as shown in Fig. 3, the particle size was clearly reduced by the addition of a small amount of electrolytes. However, a further increase in the electrolyte addition caused a significant increase in the particle size. For the mono-valent electrolytes NaOH, NaCl, NaI, KCl, CsCl, and CsI, the optimal electrolyte concentration for minimizing the particle size occurred around 1.0 × 10⁻⁵ to 1.0 × 10⁻⁴ mol/l, and the minimum particle size at this optimal concentration varied between 30.0 and 17.5 nm. Furthermore, the particle size trend relative to the electrolyte concentration was similar for all the electrolytes.

The addition of electrolytes above the optimal concentration reduced the repulsive interaction between the particles by neutralizing the particle charge, thereby promoting particle aggregation and particle growth. Conversely, the addition of electrolytes below the optimal concentration increased the particle charge due to effects of the surface conductivity and double layer

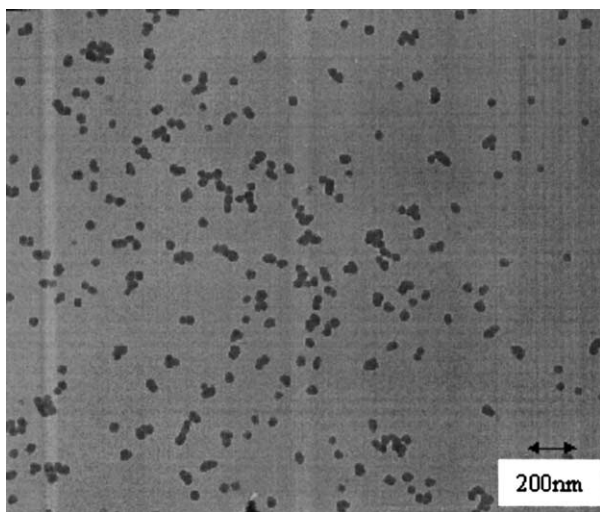


Fig. 1. Typical TEM image of nano-particles of silicon oxide synthesized by sol-precipitation at 0.224 mol/l of TEOS, 4.48 mol/l of water, and 0.448 mol/l of ammonia.

relaxation, thereby reducing the particle size [12–14]. Among the electrolytes used in the current study, ions with a higher electronegativity had a stronger effect on the particle size. As such, Na^+ had more effect on reducing the particle size than K^+ and Cs^+ , while Cl^- and I^- had more effect on reducing the particle size than OH^- . Therefore, the maximum particle size reduction (from 34.3 to 17.5 nm) was achieved with NaI at 2.0×10^{-5} mol/l, while the minimum (from 34.3 to 29.5 nm) was achieved with CsCl at 9.0×10^{-5} mol/l. It is also interesting to note that the optimal electrolyte concentrations for the maximum particle size reduction were consistent with the maximum electric charge of the particles observed in previous studies in a dilute electrolyte solution [12–14].

To confirm the additive effect on particle size, the zeta potential of the particles relative to the electrolyte concentration was investigated based on 34.3 nm silica particles prepared under fixed reaction conditions for TEOS, NH_3 , and H_2O without an additive. As shown in Fig. 4, the negative zeta potential of the particles increased with the electrolyte concentration until the optimal concentration, then reduced with a further increase in the electrolyte concentration above the optimal concentration. Among the electrolytes tested, NaI had the most effect on the particle zeta potential, while CsCl had the least, as also observed in the additive effect on the particle size. Accordingly, this result suggests that the effect of electrolytes on reducing the particle size of silica in sol-precipitation originates from the

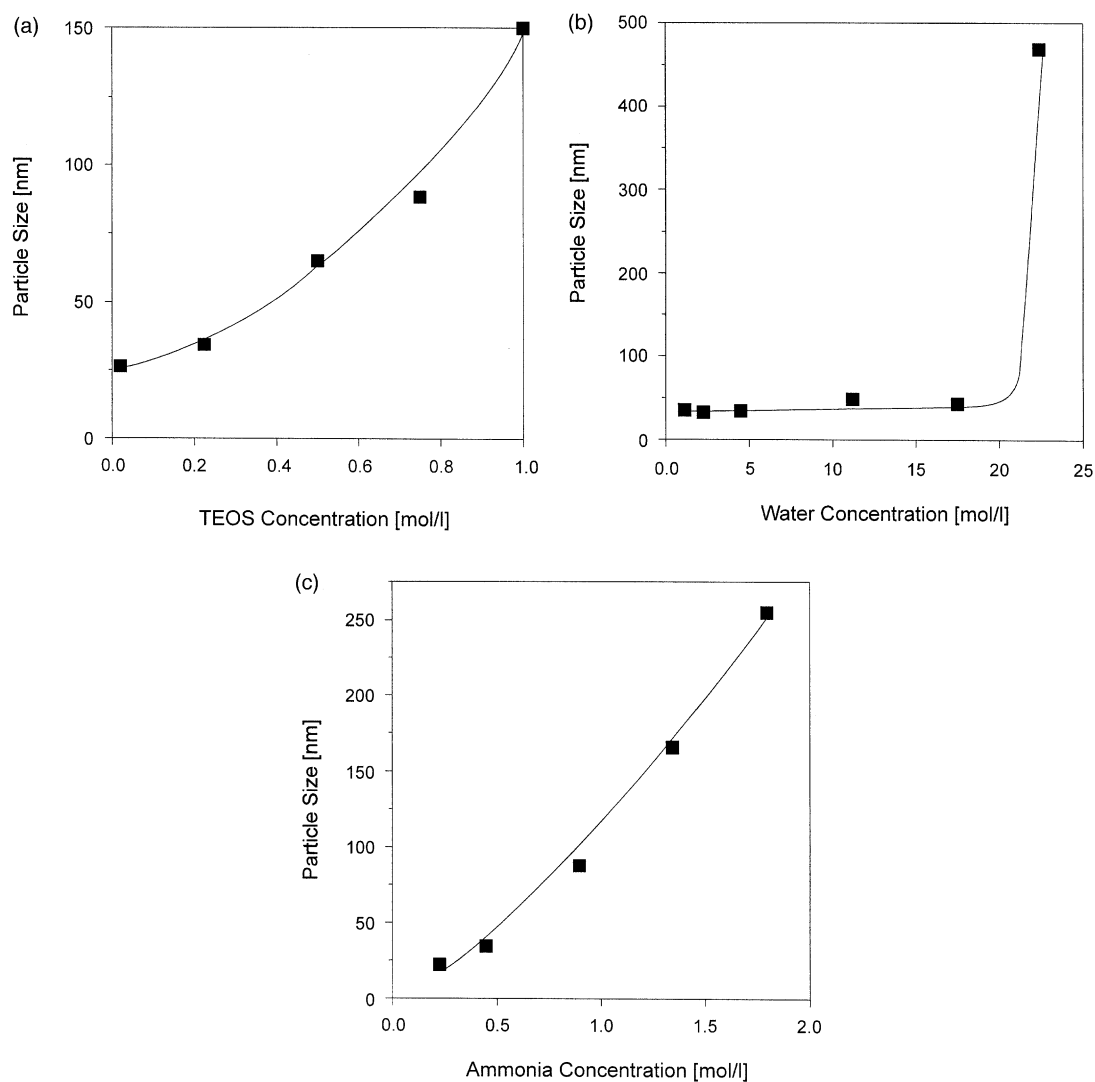


Fig. 2. Effect of reaction conditions on particle size of sol-precipitation. (a) variation of TEOS concentration with 4.48 mol/l of water and 0.448 mol/l of ammonia, (b) variation of water concentration with 0.224 mol/l of TEOS and 0.448 mol/l of ammonia, and (c) variation of ammonia with 0.224 mol/l of TEOS and 4.48 mol/l of water.

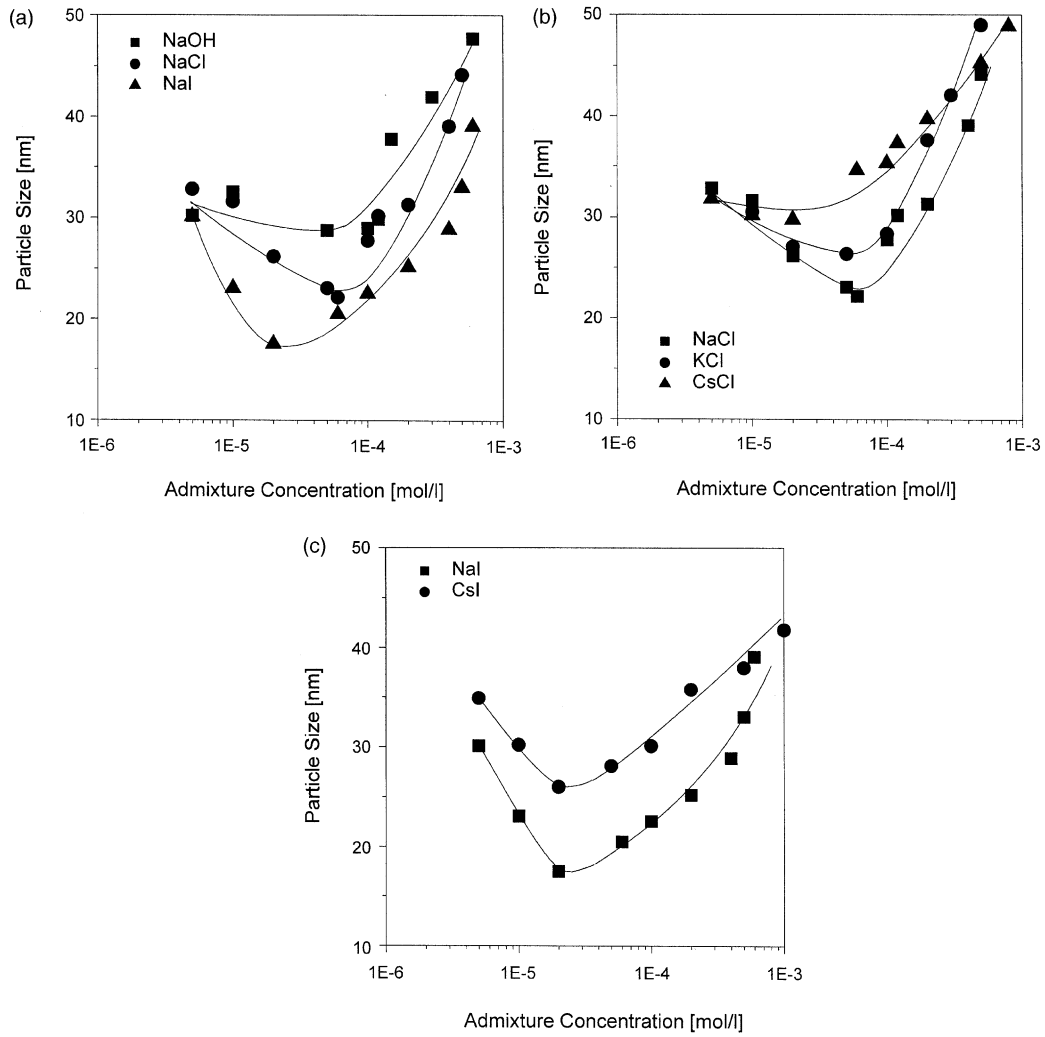


Fig. 3. Effect of electrolyte additives on particle size of silicon oxide in sol-precipitation under fixed reaction conditions of 0.224 mol/l of TEOS, 4.48 mol/l of water, and 0.448 mol/l of ammonia. (a) variation of hydroxide, chloride, and iodine anions with common cation of sodium, (b) variation of sodium, potassium, and cesium cations with common anion of chloride, and (c) variation of sodium and cesium cations with common anion of iodine.

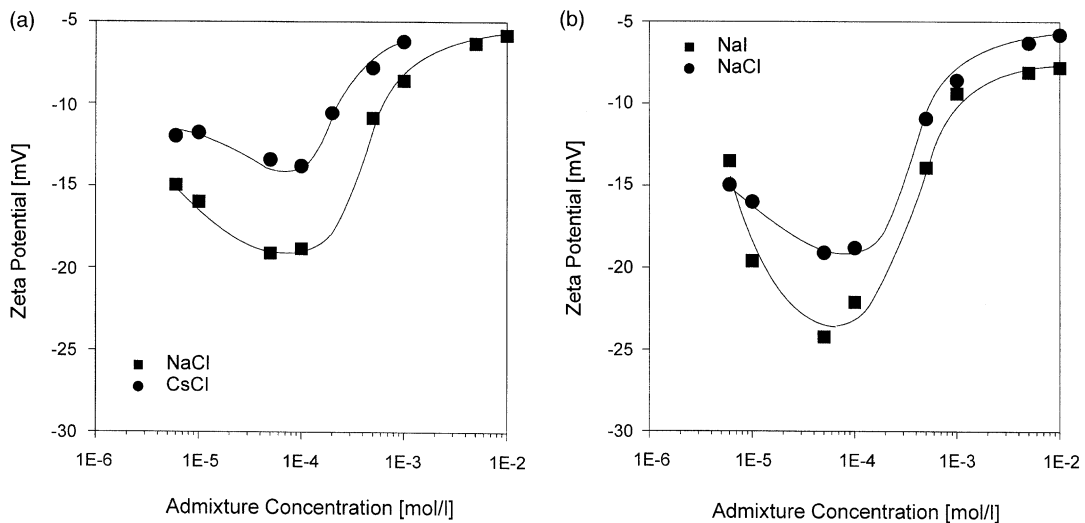


Fig. 4. Effect of electrolyte additives on zeta potential of particles prepared under fixed reaction conditions of 0.224 mol/l of TEOS, 4.48 mol/l of water, and 0.448 mol/l of ammonia without additive. (a) variation of sodium and cesium cations with common anion of chloride and (b) variation of chloride and iodine anions with common cation of sodium.

modification of the particle charge, thereby preventing aggregation for particle growth.

4. Conclusion

In the sol-precipitation method, the particle size of silicon oxide was found to vary significantly with changes in the reaction conditions and the addition of electrolytes. As the particle size is predominantly determined by the particle nucleation in the initial induction period, the particle size was enhanced when increasing the TEOS and NH_3 concentrations, which promoted the TEOS hydrolysis and condensation reactions.

The effect of electrolytic additives on the particle size was found to originate from the modification of the particle charge, as particle growth is achieved via aggregation of the primary particles. Below the optimal electrolyte concentration, which maximized the particle zeta potential and minimized the particle size, the particle charge was improved by the addition of the electrolyte, resulting in a reduced particle size. However, above the optimal concentration, the particle size was enhanced with an increase in the electrolyte concentration, as particle aggregation was promoted via depression of the particle charge due to the adsorption of the electrolyte onto the particles.

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