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Influence of reaction conditions on sol-precipitation process producing silicon oxide particles

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Abstract

The influence of TEOS, water, and ammonia concentrations on the sol-precipitation process for producing silicon oxide particles was investigated. When the hydrolysis and condensation were assumed as simple first-order reactions, the hydrolysis and condensation reaction coefficients were enhanced with an increase in the ammonia concentration due to its catalytic role in the reactions. Likewise, the increased hydrolysis coefficient with increased TEOS and water concentrations, as the reactant species, was due to the assumption of a simple first-order reaction for the hydrolysis. The dependency of the hydrolysis and condensation coefficients on the reaction conditions was estimated based on a function of the TEOS, water and ammonia concentrations, and was found to be in good agreement with the experimental data. The particle size of the silicon oxide increased with an increase in the TEOS, water and ammonia concentrations because of the promotion of hydrolysis and condensation reactions. By using correlations for the hydrolysis and condensation coefficients, the influence of the reaction conditions on the particle size was accurately predicted in line with the experimental data for the wide range of reaction conditions applied in the present study. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Sol-precipitation; Reaction conditions; Reaction coefficient; Particle size

1. Introduction

Since the sol-gel method for the synthesis of silicon oxide with silicon alkoxide was originally introduced by Stober et al. [1], many processes have been investigated to facilitate the engineering of ceramic powders in order to control their purity, composition, and size [2]. Among these processes, the sol-precipitation process is primarily focused on producing spherical ceramic particles.

In the sol-precipitation process for silicon oxide particles, hydrolysis, condensation, and particle growth are the most important elements for determining the particle size and distribution. Despite numerous investigations on the influence of reactants, solvents, pH, and additives etc. on particle size and morphology [3–8], the first model, called a 'monomer addition model', describing particle growth during the sol-precipitation process was suggested by LaMer and Dinegar [9]. According to this model, particles are initially nucleated within a short period in a high supersaturation solution of silicon oxide as a result of hydrolysis and condensation, after which they grow based on integration with the silicon oxide molecules on the particle surface. The particle size can thus be predicted using a simple molecular diffusion theory. Subsequently, the basic concept of the monomer addition model was adopted by Matsoukas and Gulari [10,11], and Chen et al. [12] who developed mathematical models to predict silicon particle growth in a sol-precipitation. In Matsoukas and Gulari's study, the particle size of silicon oxide is also determined by the molecular diffusion and integration rates as related to the particle growth in addition to the hydrolysis and condensation rates that initially produce the silicon oxide. During the seed particle growth of silicon oxide in a sol-precipitation, the multi-modal distribution of the particle size has been explained by Chen et al. using a diffusion theory. Accordingly, if the production of silicon oxide by hydrolysis and condensation is faster

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than the consumption for particle growth by diffusion, secondary particles are generated, thereby producing the multi-modal distribution of the particle size. Similarly, Nakanish and Takamiya [13] suggested a chronomal analysis to describe particle growth in the sol-precipitation process, which was originally derived to predict crystal growth in the crystallization process [14]. According to their model, the particle growth of silicon oxide is controlled by two-dimensional polynucleation on the particle surface, which is connected with molecular diffusion from the bulk solution to the particle [15].

Meanwhile, an aggregation growth model was suggested by Bogush and Zukoski [16–18] to describe silicon oxide particle growth in a sol-precipitation. This model states that particle growth occurs due to an aggregation of primary particles that is nucleated in a superaturation of silicon oxide. Therefore, according to this model the particle size would appear to be dominantly influenced by the reaction conditions of the sol-precipitation because the supersaturation is controlled by the hydrolysis and condensation relative to the reaction conditions.

In all the above models, the reaction kinetics of the hydrolysis and condensation must be determined prior to the prediction of the particle size in the sol-precipitation process. This is because the supersaturation, on which particle generation and growth depend, is produced by the hydrolysis and condensation reaction. However, until now there has been very little work on establishing a systematic relationship between the reaction conditions of sol-precipitation and hydrolysis and condensation. Accordingly, the present study investigated the influence of the reaction conditions on the hydrolysis and condensation in the sol-precipitation process in an attempt to determine the hydrolysis and condensation reaction kinetics. Thereafter, the dependency of the particle size produced in the sol-precipitation process on the reaction kinetics of hydrolysis and condensation was examined. As a result, it would appear that particle size can be predicted using reaction condition variables applied to the sol-precipitation process. The concentrations of TEOS, water, and ammonia were considered as the primary reaction condition variables in sol-precipitation. This investigation of the reaction kinetics of hydrolysis and condensation relative to various reaction conditions is also expected to provide valuable information for predicting and controlling particle size in other sol-precipitation processes.

1.1. Mathematical description

In the sol-precipitation process, silicon oxide is produced by consecutive reactions of hydrolysis and condensation. If a quasi-steady state is assumed for the intermediate species in the reaction, the hydrolysis and condensation can be simply described as [17,19],

$$\begin{tikzcd} \mathrm{Si(O\mathit{R})_4} \arrow[r, "k_1"] & \mathrm{SiO^-} \arrow[r, "k_2"] & \mathrm{SiO_2} \arrow[r] \arrow[dr] & \text{Particle nucleation} \\ & & & \text{Partilcle growth} \end{tikzcd} \qquad (1)$$

where SiO^- represents all kinds of silane formed during the hydrolysis, R indicates the ethyl group, and k_1 and k_2 are the reaction coefficients of the hydrolysis and condensation in the sol-precipitation process, respectively. If the hydrolysis and condensation are assumed to be first-order reactions, as suggested by Bogush and Zukoski [17,18], the material balances for each species in the semi batch reactor can be expressed as,

$$\frac{\mathrm{d}[\mathrm{Si(O}R)_4]}{\mathrm{dt}} = \frac{Q[\mathrm{Si(O}R)_4]_0}{V} - \left(k_1 + \frac{Q}{V}\right)[\mathrm{Si(O}R)_4] \qquad (2)$$

$$\frac{\mathrm{d}[\mathrm{SiO^-}]}{\mathrm{dt}} = k_1\,[\mathrm{Si(O}R)_4] - \left(k_2 + \frac{Q}{V}\right)[\mathrm{SiO^-}] \qquad (3)$$

$$\frac{\mathrm{d}[\mathrm{SiO_2}]}{\mathrm{dt}} = k_2[\mathrm{SiO^-}] - \frac{Q\,[\mathrm{SiO_2}]}{V} - f([\mathrm{SiO_2}]) \qquad (4)$$

where Q is the feed flow rate of the TEOS reactant solution and V is the solution volume in the reactor, which is related as $V_0 + Q_t$, in which V_0 is the initial solution volume in the reactor. In Eq. (4), $f([SiO_2])$ indicates the consumption rate of silicon oxide in the solution due to particle nucleation and growth. Since the kinetics of the particle nucleation and growth of silicon oxide in the supersaturation have not yet been established, it is basically impossible to describe the consumption rate as an analytical function of the silicon oxide concentration.

When a mixture solution of water, alcohol, and ammonia is initially loaded into the reactor without any seed particle, the sol-precipitation begins when the reactant TEOS solution is feed into the reactor, such that Eqs. (2)–(4) can be solved as,

$$[\mathrm{Si(O}R)_4] = \frac{Q[\mathrm{Si(O}R)_4]_0}{k_1(V_0 + Q\mathrm{t})}(1 - \exp(-k_1\mathrm{t})) \qquad (5)$$

$$[\mathrm{SiO^-}] = \frac{Q[\mathrm{Si(O}R)_4]_0}{(V_0 + Q\mathrm{t})} \left(\frac{1 - \exp(-k_2\mathrm{t})}{k_2} + \frac{\exp(-k_2) - \exp(-k_1)}{k_2 - k_1}\right) \qquad (6)$$

$$[\mathrm{SiO_2}] = \frac{Q[\mathrm{Si(O}R)_4]_0}{(V_0 + Q\mathrm{t})}\left\{\mathrm{t} - \frac{1 - \exp(-k_2\mathrm{t})}{k_2} - \frac{1}{k_1}\left(1 - \frac{k_1\exp(-k_1\mathrm{t}) - k_1\exp(-k_2\mathrm{t})}{k_2 - k_1}\right)\right\} \qquad (7)$$

It should be noted that the hydrolysis and condensation are not affected by the existence of a particles [17]. Therefore, the TEOS and silane concentrations [Eqs. (5)

and (6)] are independent of the particle generation. However, the silicon oxide concentration [Eq. (7)] is only valid until the particles are first nucleated in the reactor, which is called the induction period, because silicon oxide is consumed by the particle nucleation and growth. Based on a comparison of the species concentration profile with the model equation, the reaction kinetics of the hydrolysis and condensation, k_1 and k_2, can be estimated.

2. Experiment

Silicon oxide particles were synthesized by sol-precipitation in a semi batch reactor. Using a syringe pump, 100 ml of a TEOS (ACS grade, Fluka, Switzerland) reactant solution was fed into the reactor, in which a 350 ml mixture of de-ionized water, methanol (ACS grade, Junsei, Japan), and ammonia (ACS grade, Showa, Japan) was initially loaded. To change the reaction conditions for the sol-precipitation process, the reactant TEOS and water concentrations were changed from 0.11 to 1.0 mol/l and 2.5 to 22.5 mol/l, respectively. The ammonia concentration in the reactor was adjusted from 0.44 to 1.8 mol/l. In the present experiment, the above concentrations of TEOS, water, and ammonia were based on the final mixture volume in the reactor after feeding the TEOS reactant solution, for which the rate was fixed at 3.33 ml/min.

A standard Rushton reactor, designed with a working volume of 0.45 l [20], was used for the sol-precipitation to produce the particles. To agitate the solution, a six-paddle turbine impeller was used and the agitation speed was fixed at 900 rpm. While feeding the TEOS reactant solution into the reactor, samples of the product suspension in the reactor were intermittently taken to analyze the saline concentration using ammonium molybdate titration [21,22]. For the titration, a sample of the suspension was quickly diluted with a methanol solution to quench the reaction and then filtered using a 0.1 μm microfilter to remove all the particles in the suspension. After feeding the TEOS reactant solution, the product suspension was allowed to agitate for 24 h to complete the reaction and particle synthesis in the reactor. Thereafter, a sample of the product suspension was taken to analyze the particle size and morphology of the silicon oxide using a particle size analyzer (Zetasizer, Malvern, UK) and scanning electron microscope (Leica, Stereoscan 440, Germany), respectively.

3. Results and discussion

3.1. *Influence on hydrolysis and condensation*

During the sol-precipitation, the intermediate species concentration of silane (SiO^-) was frequently monitored to estimate the hydrolysis and condensation reaction rates [16,19]. The silane concentration profiles relative to time with various reaction conditions of TEOS, water, and ammonia concentrations are presented in Fig. 1. Since silane is generated by the hydrolysis of TEOS and then consumed by the condensation in the sol-precipitation, the increase in the silane concentration relative to time in the early stage indicated that during this stage the TEOS hydrolysis was dominant over the silane condensation. However, as the silane concentration increased, the condensation rate was enhanced. Thereafter, changes in the silane concentration became insensitive relative to time due to the close equivalence between the hydrolysis and the condensation. Similar time-relative profiles of the silane concentration were observed with all the reaction conditions of TEOS, water, and ammonia concentrations, although the silane concentration approach level varied.

By comparing the silane concentration profile with Eq. (6), the reaction coefficients of the hydrolysis and condensation, k_1 and k_2, respectively, were estimated for each reaction condition. As displayed in Fig. 2, the hydrolysis and condensation coefficients increased significantly with an increased ammonia concentration. Since the hydrolysis and condensation reactions occur based on attacks by hydroxyl anions and nucleophilic deprotonated silane on neutral silicate, respectively, as suggested by Iler [21], the ammonia would appear to act

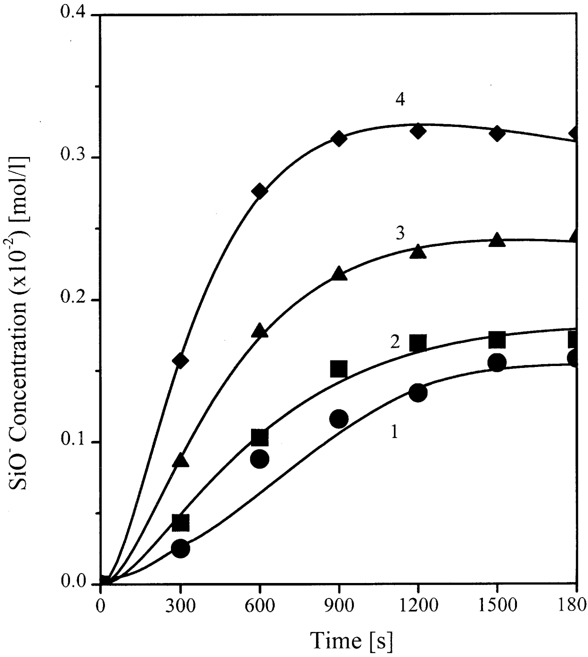

Fig. 1. Typical silane concentration profiles while feeding the reactant solution into semi-batch reactor with various reaction conditions: 1, 0.12 mol/l of TEOS, 4.48 mol/l of water and 0.89 mol/l of ammonia; 2, 0.224 mol/l of TEOS, 4.48 mol/l of water and 0.89 mol/l of ammonia; 3, 0.224 mol/l of TEOS, 11.2 mol/l of water and 0.89 mol/l of ammonia; 4, 0.224 mol/l of TEOS, 4.48 mol/l of water and 1.79 mol/l of ammonia.

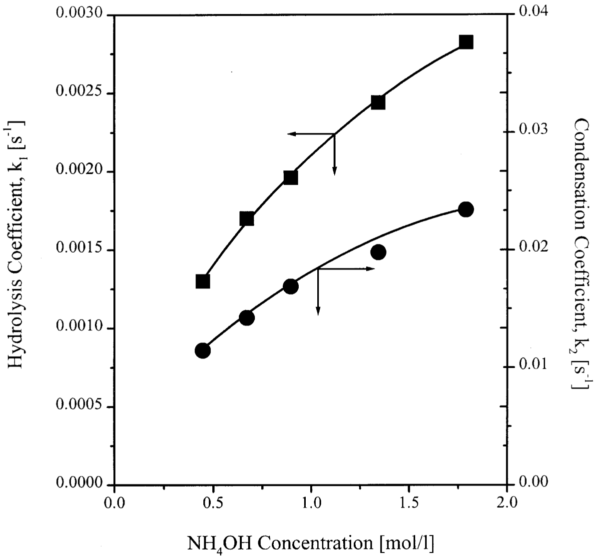

Fig. 2. Influence of ammonia concentration on hydrolysis and condensation coefficients in sol-precipitation. The other reaction conditions were fixed at 0.224 mol/l of TEOS and 4.48 mol/l of water.

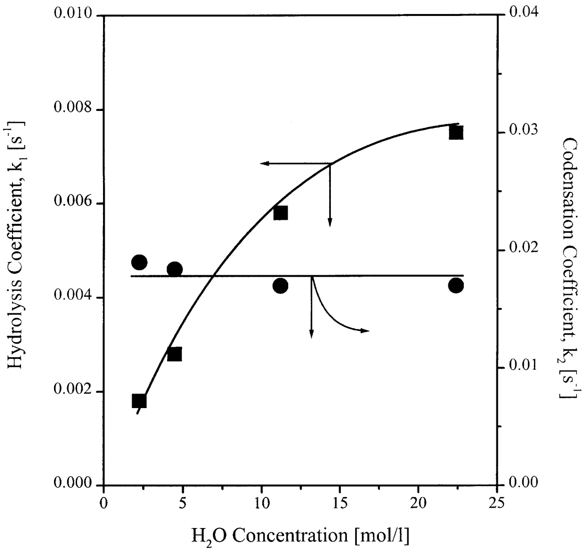

Fig. 4. Influence of water concentration on hydrolysis and condensation coefficients in sol-precipitation. The other reaction conditions were fixed at 0.224 mol/l of TEOS and 1.13 mol/l of ammonia.

as a basic catalyst by promoting the attacks and thereby increasing the reaction coefficients.

The influence of the TEOS and water concentrations on the hydrolysis and condensation was investigated, as displayed in Figs. 3 and 4. The hydrolysis coefficient was clearly enhanced with an increase in the TEOS and water concentrations, which participate in the hydrolysis reaction as reactants. However, in the general expression for hydrolysis, it is normal that the hydrolysis coefficient can be independent of the reactant TEOS and water concentrations. These results are possibly due to a first-order expression, which was adopted to simply describe the actual hydrolysis reaction. That is, when the hydrolysis of TEOS is carried out under conditions of excess water, a first-order reaction with the TEOS concentration is frequently assumed. However, since the actual hydrolysis reaction of the ethyl group of TEOS with water is performed through multiple elementary steps, a simple approximation of hydrolysis as the first-order reaction with a TEOS concentration may result in a reaction coefficient dependent on the reactant concentration. In this study, the dependency of the hydrolysis coefficient on the TEOS and water concentrations was not observed to be so complicated, therefore, a first-order expression was found to be appropriate to depict the silane concentration profile with various reaction conditions, as displayed above. It should also be mentioned that the hydrolysis coefficients estimated in the current study were similar in order of magnitude to those reported by Bogush and Zukoski [17] even though they did not consider a systematic variation of the reaction conditions.

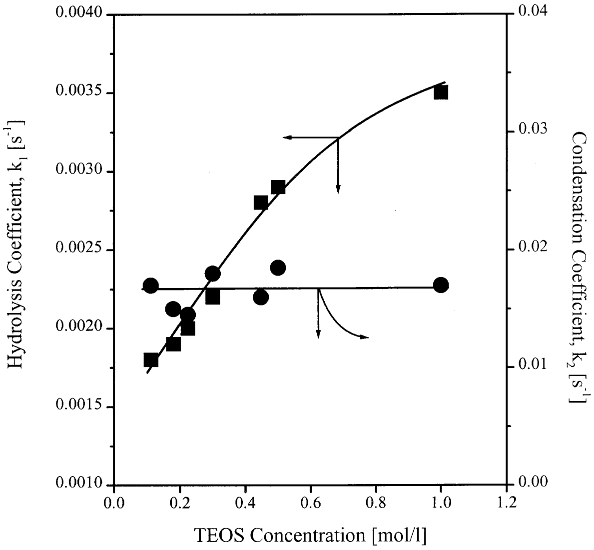

Fig. 3. Influence of TEOS concentration on hydrolysis and condensation coefficients in sol-precipitation. The other reaction conditions were fixed at 4.48 mol/l of water and 1.13 mol/l of ammonia.

Meanwhile, there was only a minimal change in the condensation coefficient relative to the reaction conditions of the TEOS and water concentrations. This result is consistent with the general expression for the condensation reaction and implies a first-order approximation for the actual condensation reaction. In sol-precipitation, it should be recognized that there are two kinds of condensation reaction; one is a reaction between hydroxide groups that generates water as the by-product (so called water condensation) and the other is a reaction between ethyl and hydroxide groups that generates ethanol (so called alcohol condensation). Whereas the ethyl group of TEOS participates in alcohol condensation, the hydroxide group of silane is involved in water condensation. Accordingly, from the experimental results, it would appear that the silicon oxide was predominantly produced by water condensation rather than alcohol condensation and be confirmed by the Yoon et al. study [23] that under basic conditions for hydrolysis and condensation of TEOS the reaction coefficient of water condensation is thousands times higher than one of alcohol condensation.

The dependencies of the hydrolysis and condensation coefficients on the reaction conditions of the ammonia, TEOS, and water concentrations were depicted as,

$$k_1 = \mathrm{A}_1\ [\mathrm{H_2O}]_0\ \left[\mathrm{Si}(\mathrm{O}R)_4\right]_0^{\mathrm{m}_1} \exp\left(-\mathrm{B}_1/[\mathrm{NH_4OH}]_0^{\mathrm{n}_1}\right) \quad (8)$$

$$k_2 = \ \mathrm{A}_2 \exp\left(-\mathrm{B}_2/[\mathrm{NH_4OH}]_0^{\mathrm{n}_2}\right) \quad (9)$$

where A_1, A_2, B_1, and B_2 are the proportional constants and m1, n_1 and n_2 are the exponent constants. Subscription 0 indicates the initial condition. In Eqs. (8) and (9), a power law expression was used to describe the influence of the TEOS and water on the hydrolysis coefficient because they participated as reactants. In contrast, since the effect of the ammonia on the hydrolysis and condensation coefficients was as a catalyst, it was depicted using Arrhenius' law. Th constants of the equations were fixed by the least square error method, as summarized in Table 1. Figs. 5 and 6 show a good correlation between the hydrolysis and condensation coefficients and the experimental data. Based on these correlations, it would appear that the condensation reaction coefficient was greater than the hydrolysis one, thereby implying that the silicon oxide production in the sol-precipitation was dominantly rate-controlled by the hydrolysis.

3.2. *Influence on particle size*

During sol-precipitation, silicon oxide particles are nucleated and grown under silicon oxide supersaturation, which is produced by hydrolysis and condensation. Therefore, the particle size of silicon oxide is closely related to those reaction conditions that influence the hydrolysis and condensation. According to Kim and Kim [19], the particle size is primarily determined by the silicon oxide supersaturation at the induction point, which is when the particles first appear. Before this induction point, the silicon oxide supersaturation in the solution increases monotonically relative to time because it is not being consumed. However, after the induction point, the silicon oxide supersaturation decreases rapidly due to its consumption by the nucleation and growth of the silicon oxide particles. Thereafter, any further nucleation of particles is significantly reduced and narrow mono-dispersed particles are obtained in the final product suspension. Kim and Kim also reported that as the hydrolysis and condensation is facilitated, the induction time is reduced so that the first nucleation of particles is induced at a lower supersaturation of silicon oxide, which results in fewer and larger particles in the final product suspension.

Table 1
Summary of correlation constants for hydrolysis and condensation reaction coefficients and particle diameter [Eqs. (8)–(10)]

Correlation constants for hydrolysis coefficient:
$\mathrm{A}_1 = 0.007$, $\mathrm{B}_1 = 2.3$, $\mathrm{m}_1 = 0.375$ and $\mathrm{n}_1 = 0.25$

Correlation constants for condensation coefficient:
$\mathrm{A}_2 = 2.73\times10^5$, $\mathrm{B}_2 = 16.57$ and $\mathrm{n}_2 = 0.031$

Correlation constants for particle diameter:
$\mathrm{A}_3 = 8.67\times10^4$ and $\mathrm{n}_3 = 0.861$

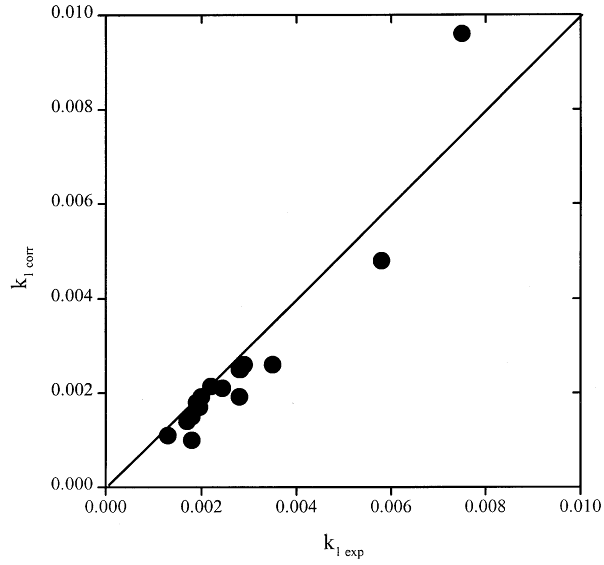

Fig. 5. Comparison of prediction of hydrolysis coefficient with experimental data.

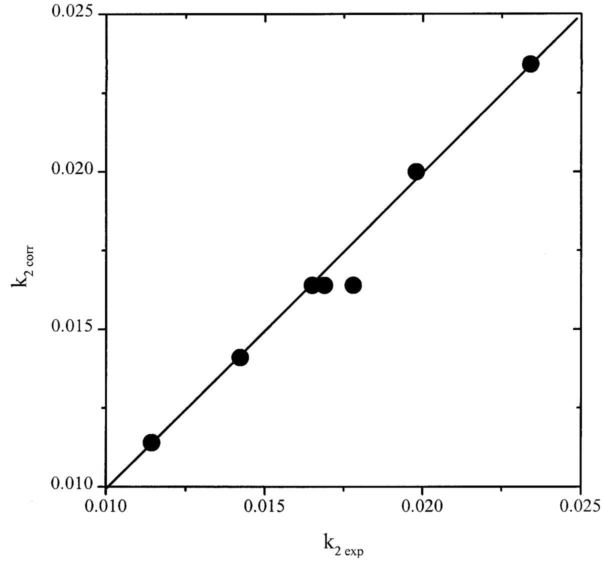

Fig. 6. Comparison of prediction of condensation coefficients with experimental data.

Similarly, in the current study, as the ammonia, water, and TEOS concentrations were increased, larger particle sizes were obtained in the product suspension, as shown in Figs. 7–9, due to the promotion of the hydrolysis and condensation. In addition, a significant decrease in the induction time was also observed with an increase in the ammonia, water, and TEOS reactant concentrations.

During sol-precipitation, since the particle size is predominantly controlled by the induction time, which in turn depends on the hydrolysis and condensation, the influence of the reaction conditions on the particle size in the product suspension can be described as a function of the reaction coefficients of hydrolysis and condensation, as follows:

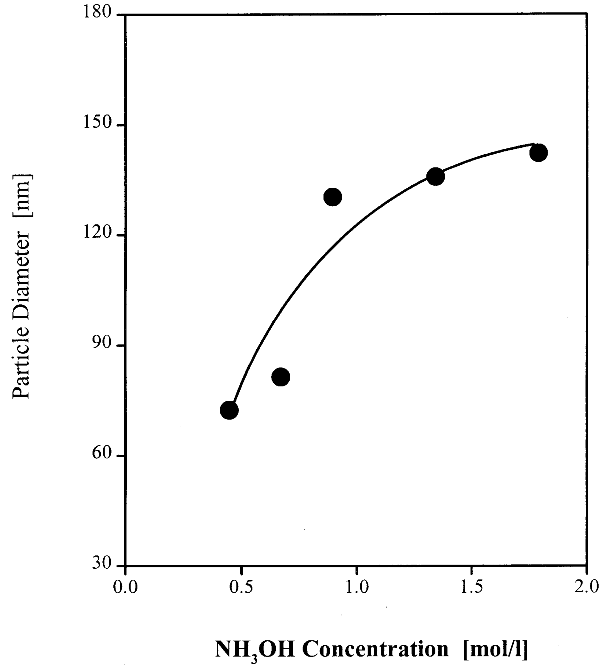

Fig. 7. Influence of ammonia concentration on particle diameter of silicon oxide produced in sol-precipitation. The other reaction conditions were fixed at 0.224 mol/l of TEOS and 4.48 mol/l of water.

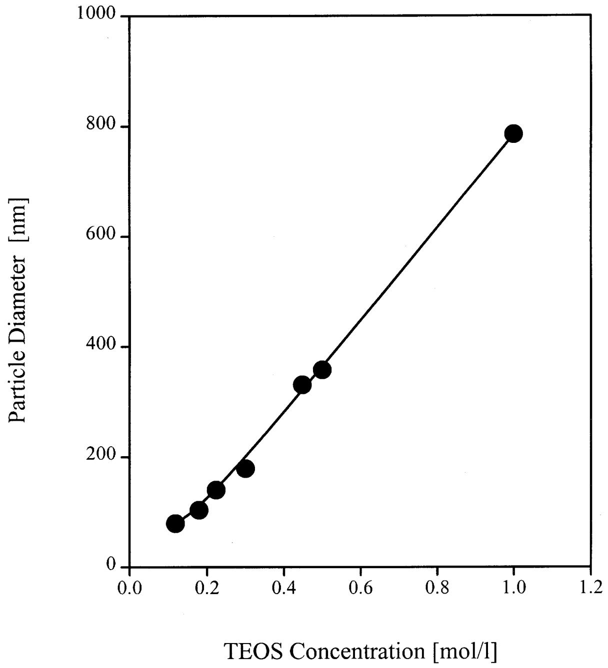

Fig. 8. Influence of TEOS concentration on particle diameter of silicon oxide produced in sol-precipitation. The other reaction conditions were fixed at 4.48 mol/l of water and 1.13 mol/l of ammonia.

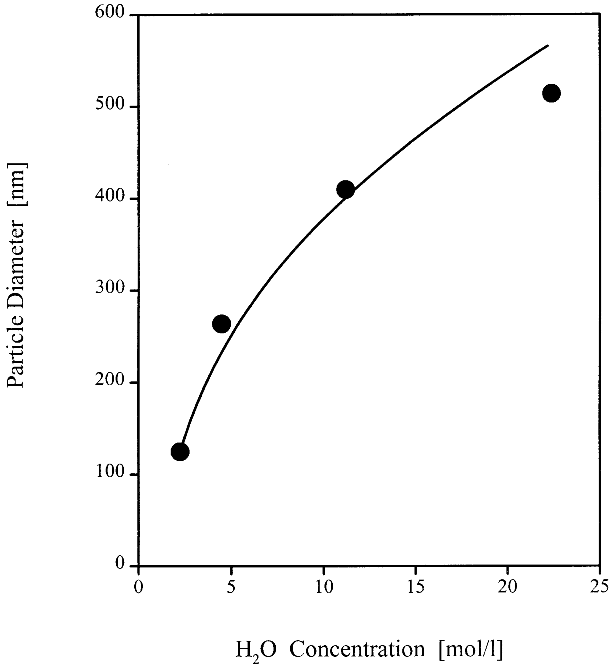

Fig. 9. Influence of water concentration on particle diameter of silicon oxide produced in sol-precipitation. The other reaction conditions were fixed at 0.224 mol/l of TEOS and 1.13 mol/l of ammonia.

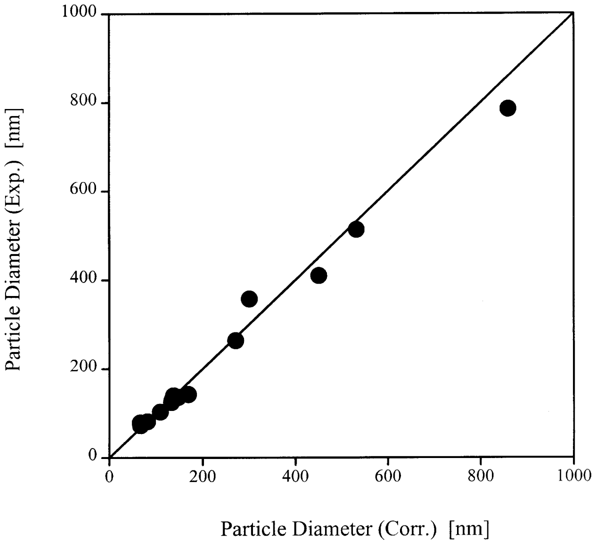

Fig. 10. Comparison of prediction of particle diameter of silicon oxide with experimental data in sol-precipitation.

$$D_F = A_3 \left(\frac{k_1 \, k_2}{k_2 - k_1} \left[\mathrm{Si(O}R\mathrm{)_4} \right]_0 \right)^{n_3} \tag{10}$$

where D_F is the particle diameter in the product suspension and A_3 and n_3 are the proportional and exponential constants, estimated as 8.67×10^4 and 0.861, respectively. As shown in Fig. 10, the prediction of the particle size was found to be in good agreement with the experimental data. Accordingly, based on Eq. (10), it is possible to determine the particle size using only the reaction conditions of the sol-precipitation because variables k_1 and k_2 are correlated with the ammonia, TEOS, and water concentrations, as suggested in Eqs. (8) and (9). It is interesting to note that Eq. (10) is similar to the model equation developed by Matsoukas and Gulari [11], which was analytically developed on the basis of a monomer addition growth mechanism to predict particle size in sol-precipitation.

4. Conclusion

During sol-precipitation, the hydrolysis, condensation, and particle size were all strongly influenced by the reaction conditions of TEOS and water as the reactant species, and ammonia as the catalyst. When the hydrolysis was depicted by a first-order reaction, the reaction coefficient of the hydrolysis was significantly enhanced with increasing TEOS, water, and ammonia concentrations. However, the enhancement of the hydrolysis coefficient by the ammonia was due to its catalytic effect in the hydrolysis, plus the dependency of the hydrolysis coefficient on the TEOS and water concentrations would appear to be attributable to a simple first-order expression for the hydrolysis reaction. Meanwhile, the condensation coefficient increased with an increase in the ammonia concentration due to its catalytic activity, and yet was hardly influenced by changes in the TEOS and water concentrations because they were not involved in the condensation reaction.

The dependencies of the hydrolysis and condensation reaction coefficients on the reaction conditions, depicted as a power law function for the TEOS and water as reactant species and as Arrhenius' law expression for the ammonia as a catalyst, were in good agreement with the experimental data. These experimental results imply that a simple first-order expression is appropriate to describe the hydrolysis and condensation reaction.

The particle size in the product suspension was also significantly influenced by the reaction conditions of the TEOS, water, and ammonia concentrations because the particle synthesis depended primarily on the silicon oxide supersaturation generated by the hydrolysis and condensation reactions. As the TEOS, water, and ammonia concentrations increased, the particle nucleation was initiated at a lower supersaturation due to the promotion of the hydrolysis and condensation reactions, thereby resulting in fewer and larger particles in the product suspension. Accordingly, the influence of the reaction conditions on the particle size was described as a function of the hydrolysis and condensation reaction coefficients. Consequently, the use of such correlations for the hydrolysis and condensation reaction coefficients, enables an accurate particle size prediction based on a reaction condition set of TEOS, water, and ammonia concentrations in sol-precipitation. The predicted particle sizes were consistent with the experimental data for the wide range of reaction conditions of TEOS, water and ammonia concentrations applied in the present study.

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