FORMATION AND REACTION TEMPERATURE DEPENDENCE OF MONODISPERSED SILICA PARTICLES

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abstract

Particle size - reaction condition relationship of the monodispersed silica formation reaction by hydrolysis of tetraethoxysilane(TEOS) in ammonia water was studied.

Particle size increased from 0.1 to 0.8 μm as temperature decreased in the range from 10°C to 50°C. Below 10°C, irregular shaped particles were formed in the solution conditions while small monodispersed particles were obtained at low TEOS concentration.

This temperature dependence may be explained by the nucleation and growth mechanism in conjunction with the further temperature dependence of the reaction rates.

1 Introduction

Monodispersed Silica particles are synthesized by hydrolysis of silicon alkoxides in an ammonia water and alcohol mixture[1].

These particles are capable of a wide range of applications, including use as raw materials for high purity silica glass, fillers for IC packaging, columns of a chromatography and spacers for a liquid crystal display.

In order to fulfill those applications, it is necessary to produce the wide-sized particles.

Stöber et al[1] synthesized 0.05 to 2μm particles using several silicon alkoxides and solvents. On tetraethoxysilane(TEOS) - ethanol system, the relationship of the final particle sizes to reagent concentrations was shown by Van Helden et al[2]. Bogush et al[3] studied the effects of the reaction temperature, and showed that the particle size increased as the temperature decreased in the range from 9 to 55°C.

In this paper, we report (1) the particle size - solution condition relationship which shows the best conditions for producing each size, (2) the results of low temperature synthesis.

2 Experimental Procedure

Tetraethoxysilane(TEOS) - ethanol - water system was selected for use in our study.

All of Kanto Chemical Co.'s Ammonia water, ethanol and TEOS was used as received.

At the first stage of the synthesis process, ammonia water, deionized water and ethanol were mixed in a reaction vessel placed in a water bath and stirred by magnetic stirrer. After the temperature of the solution had become constant, TEOS that had been diluted by ethanol was slowly added at a rate of about 1 liter par hour while stirring. Stirring was continued for about 1 hour after the addition of the TEOS solution in order to complete the hydrolysis and polymerization.

The particle sizes and shapes were evaluated by a transmission electron microscope JEOL JEM400FX and a scanning electron microscope JEOL JSM 5200.

3 Results and Discussion

3-1 Reagent concentration dependence

Reagent concentration dependence of the particle size at 25°C was investigated. Fig.1 shows the particle size change in relation to the amount of 15% ammonia water in a solution condition of TEOS 100g, ethanol 400g. Maximum particle size was observed in about 105g ammonia water additives.

Fig.2 shows particle size change corresponding with TEOS amount in a solution condition of ammonia water 140g, ethanol 400g. In order to obtain monodispersed silica particles, TEOS concentration should be kept within a limit determined by the ammonia and ethanol concentration. The higher the TEOS concentration is above the limit, the wider the particle size distribution becomes.

Fig.3 shows a typical configuration of monodispersed silica particles.

These results qualitatively agree with those of previous report[1][2][3].

3-2 Reaction temperature dependence

Reaction temperature dependence of the particle size at TEOS100g, ammonia water 105 g and ethanol 400g is shown in fig.4. Monodispersed silica particles were obtained in the temperature range from 12°C to 50°C, and particle size increased with decreasing temperature.

Below this temperature range, irregular shaped particles were formed under similar reagent conditions. Fig.5 shows a SEM photograph of the silica particles obtained. However, the monodispersed silica was able to be synthesized at such lower temperatures when the TEOS concentration was decreased. However only small particles of up to 0.4μm were obtained. Fig.6 shows the TEOS concentration range at which spherical particles were obtained.

Bogush et al[4] reported a silica particle formation model where nucleation and growth of the particle took place by secondary coagulation of the precipitated silica. However, it is difficult to apply their model as an explanation for our results at low temperature. The usual nucleation and growth model from homogeneous solution reported by Lamer[5] seems to be preferable.

The particle formation reaction proceeds from 1) hydrolysis of TEOS to form silisic acid, and 2) polymerization condensation of Si-OH groups to make silica cluster.

At high temperature, both reaction rates are so fast that the precursor concentration increases rapidly far from the nucleation line. Then a large number of nuclei are formed, and the precursor concentration decreases rapidly through the particle growth region and reaches a solubility limit.

In the moderate temperature range, hydrolysis reaction rate is not so fast as to cause a rapid increase in the precursor concentration. A gradual increase in the precursor concentration above the nucleation line allows the formation of a small number of nuclei compared to the number formed at high temperature. The precursor concentration decreases slowly while crossing to the particle growth region until the solubility limit is reached. Therefore large size particles were obtained.

At low temperature, both reaction rates, especially for polymerization reaction, are slow. The precursor concentration increases slowly but steadily, and reaches the unstable concentration region. Then spontaneous precipitation like the spinodal decomposition[6] proceeds to form irregular shaped particles.

However in the low TEOS concentration at low temperature, nucleation and growth proceeds, because the precursor concentration maximum remains beneath to the limit.

Fig.7 shows these reaction mechanism schematically by using

Lamer, s model.

4 Conclusion

0.1～0.8μm monodispersed silica particles were synthesized by hydrolysis of TEOS in ammonia - water - ethanol solutions.

Particle size increased with decrease in temperature in the range from 10 to 50℃.

below 10℃, small monodispersed particles were synthesized only at low TEOS concentrations. Irregular shaped particles were obtained at high TEOS concentrations.

This temperature dependence may be explained by the nucleation and growth mechanism in conjunction with the further temperature dependence of the reaction rates.

5 References

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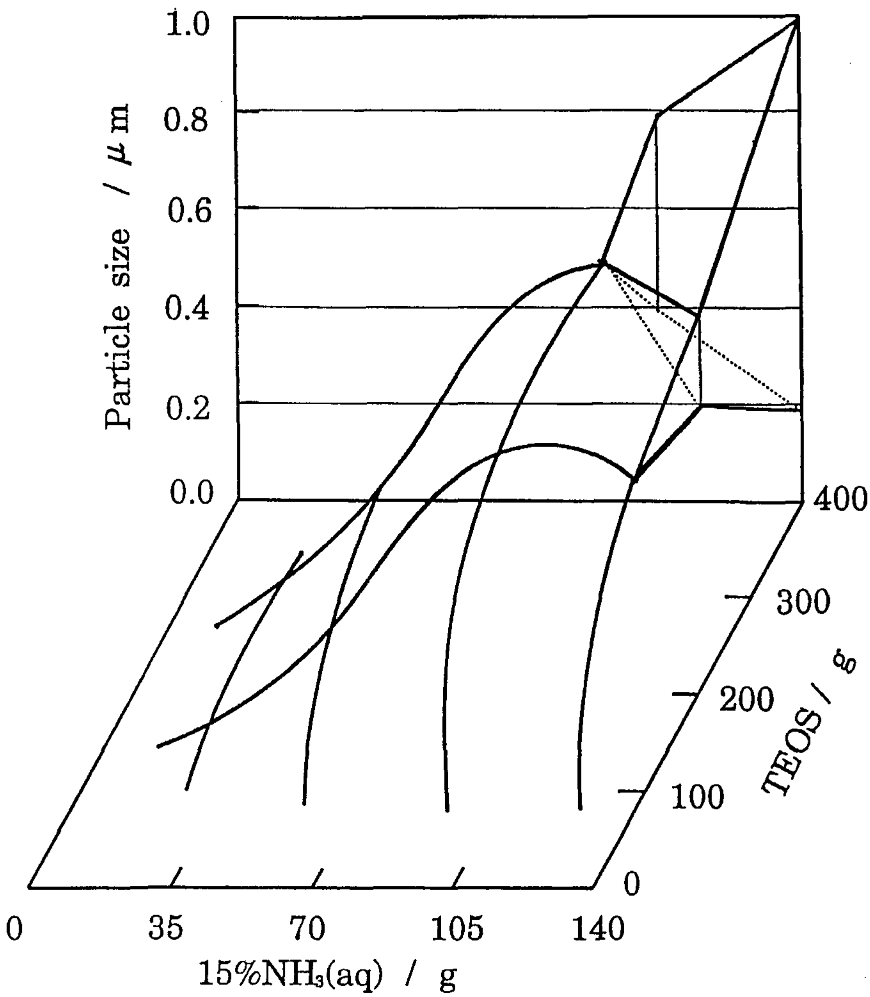

Fig.1 Particle size as a function of TEOS and ammonia water concentration at ethanol 400g at 25°C

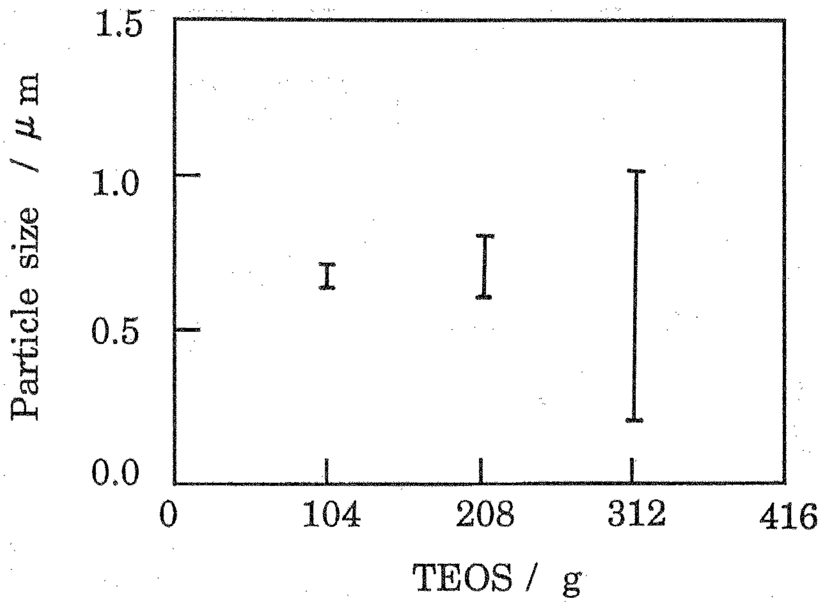

Fig. 2 Particle size distributions as a function of TEOS amount at 15% ammonia water 140g, ethanol 400g at 25°C

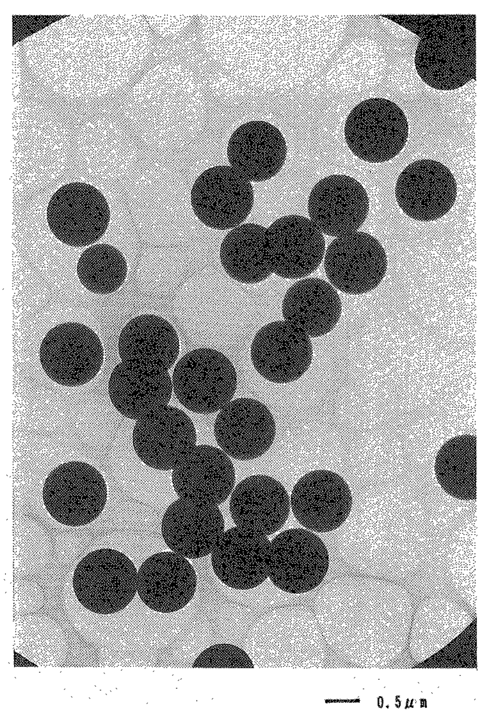

Fig. 3 Electron micrograph of typical monodispersed silica particles

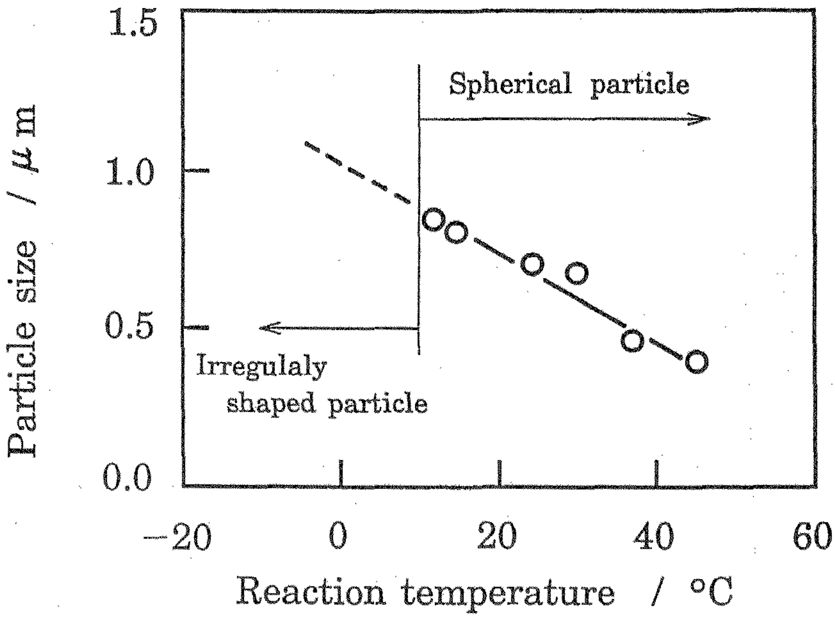

Fig. 4 Particle size vs reaction temperature relationship at TEOS 100g, 15% ammonia water 140g, ethanol 400g

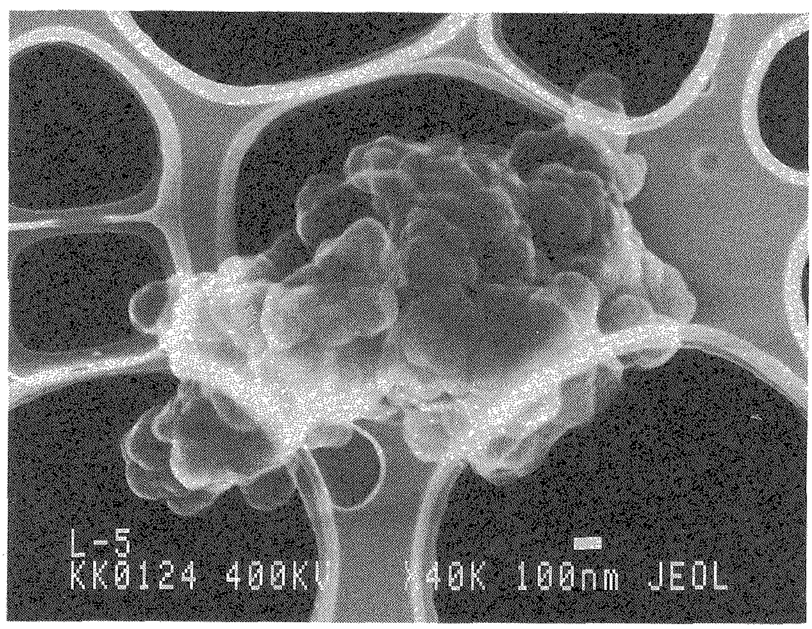

Fig. 5 Electron micrograph of irregular shaped particles synthesized at −4°C

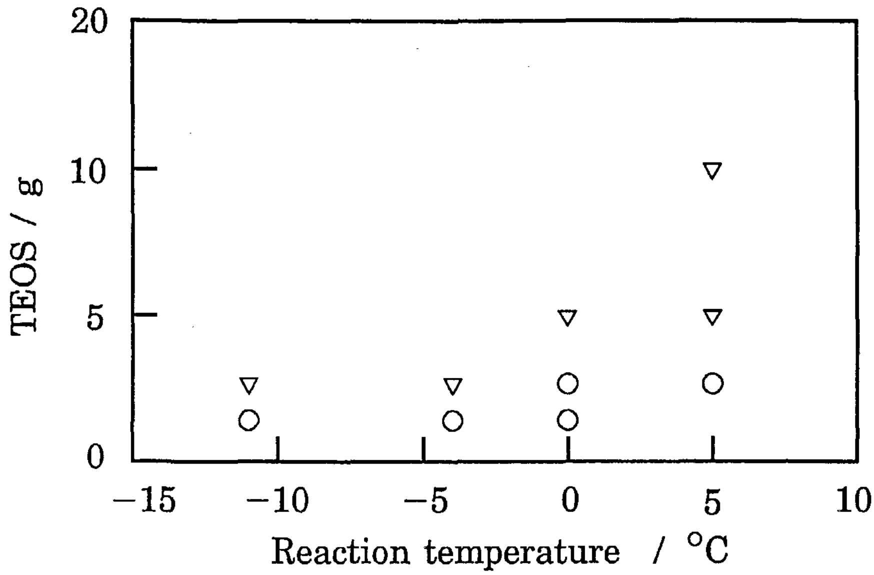

Fig. 6 Spherical particle formation range as a function of reaction temperature and TEOS amount.

○ Spherical particle

▽ Irregular shaped particle

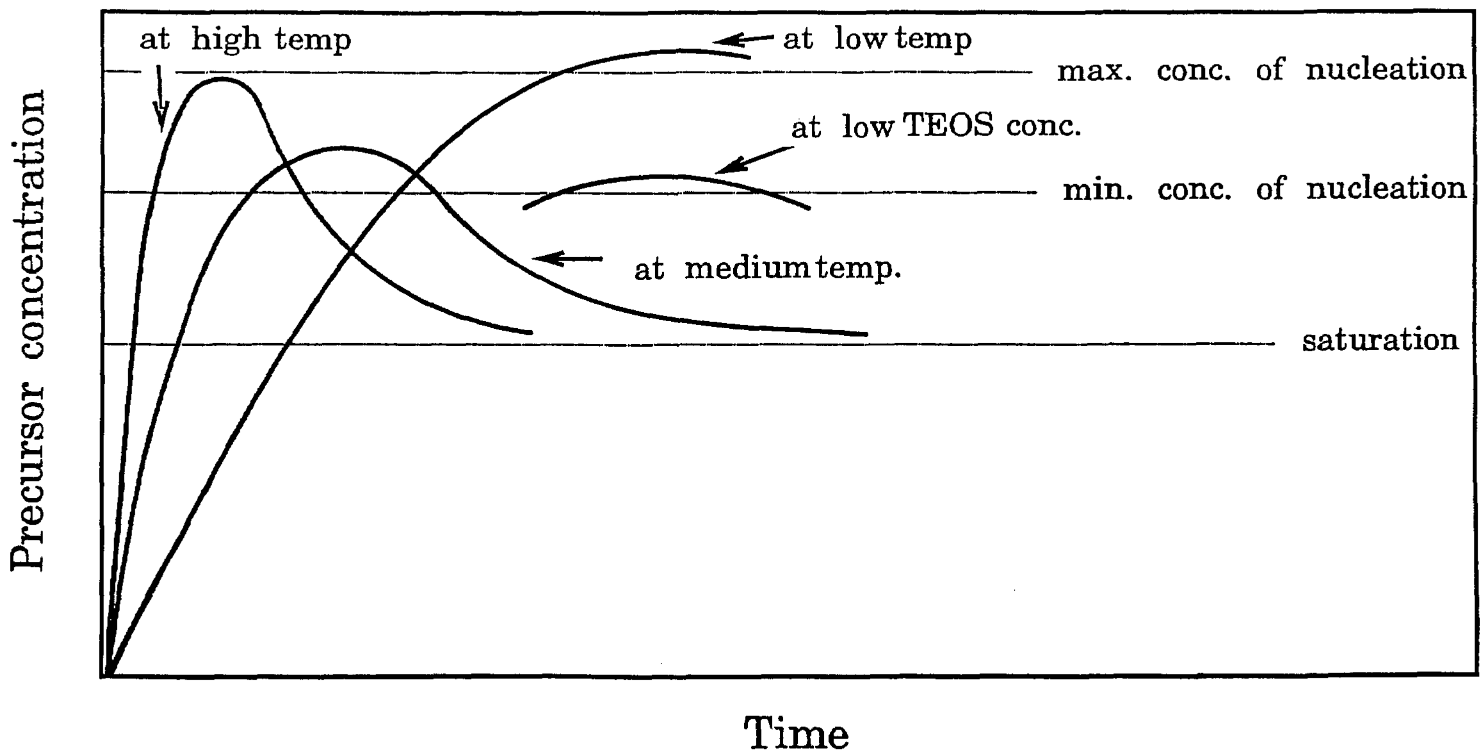

Fig. 7 A schematic model to explain the particle formation reaction