Journal of Ceramic Processing Research. Vol. 6, No. 4, pp. 286~289 (2005)

J O U R N A L O F
Ceramic Processing Research

Effect of soft sonication on starting solution for spherical silica synthesis

Naoya Enomoto*, Akihiro Kumagai[a] and Junichi Hojo

Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Japan

[a]Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi, Fukuoka 812-8581, Japan

Monodispersed spheres of silica were prepared with particular attention to the age of starting solutions, and a subtle irradiation (~mW power) of ultrasonic vibration, which we termed soft sonication, was applied to enhance the aging process. Aging effects on the precipitation behavior are as follows, (1) increase of the incubation period for precipitation, (2) increase of the final particle size, (3) improvement of the monodispersibility. The increment of the final particle size as a function of aging time is twice larger in the case of soft sonication than in the case of normal aging. We assume from these results that a starting solution, especially that including an organic solvent with a low dielectric constant, may be inhomogeneous at the microscopic level just after the preparation. In other words, the as-prepared solution may involve some clusters, which may cause unfavorable nucleation to degrade the monodispersibility. It is inferred that these "clusters" can be broken or dispersed by aging for days or weeks. Reduction of the aging period by soft sonication would be due to high frequency (~tens of kHz) and small amplitude (~nm) of the vibration.

Key words: ultrasound, sol-gel process, solution structure, water-ethanol mixture.

Introduction

Monodispersed spheres of silica [1] have been prepared by controlled hydrolysis of a metal alkoxide such as tetraethylorthosilicate (TEOS). Although the process is controlled by adjusting temperature, concentration, and pH, there may be an unexpected change of the particle size or an undesirable degradation of monodispersibility for an unknown reason. Commercially available monodispersed spheres are supposed to be prepared and then classified to guarantee the monodispersibility.

It has been suggested by our group [2] that an "age" of starting solutions, which means a standing time after preparation, is influential to the size and the monodispersibility of silica spheres, which are synthesized from an ethanolic solution of TEOS and an ethanolic solution of ammonia water. Our assumption is that the microscopic mixing state of the starting solutions is inhomogeneous which induces an extra nucleation, while the aging process enhances the homogeneity of them.

Another important assumption in this paper is that the solution structure could be effectively changed or homogenized at the microscopic level using soft sonication (weak irradiation by ultrasonic vibration). The late Mr. Asakura and co-workers introduced soft sonication to the aging of an ethanol-water mixture [3] or real liquor (wine [4]) and studied its amazing effects on metabolism in mice [3] and humans [4]. The present work is a very first trial to apply the soft sonication technique to aging of the starting solutions for chemical synthesis. It must be emphasized in the beginning that soft sonication does not involve the formation of cavitation because the intensity is very low (~mW in power). There is a specific research field called sonochemistry in which a strong ultrasound (several tens of Watt in power) is expected to induce chemical changes [5]. By contrast, we do not expect any chemical effects of ultrasound in using soft sonication but we expect physical enhancement of aging in the starting solutions.

*Corresponding author:
Tel : +81-92-642-3544
Fax: +81-92-642-3544
E-mail: enomoto@cstf.kyushu-u.ac.jp

Experimental

Two starting solutions, an ethanol solution of TEOS (denoted Solution A) and an ethanol solution of ammonia and distilled water (denoted Solution B), were easily prepared by stirring very soluble materials for several minutes. The concentration was fixed at TEOS = 0.1 mol/dm^3, NH_3 = 1.8 mol/dm^3, H_2O = 7.6 mol/dm^3 in the ethanol solvent as a whole. The starting solutions were tightly sealed in brown glass containers to be aged at room temperature with or without soft sonication. As shown in Fig. 1, both sonicated and non-sonicated (control) solutions were aged under the same temperature history. The soft sonication plate (~40 kHz) was provided by Kyowa Jukusei Kagaku Co., Ltd., Japan.

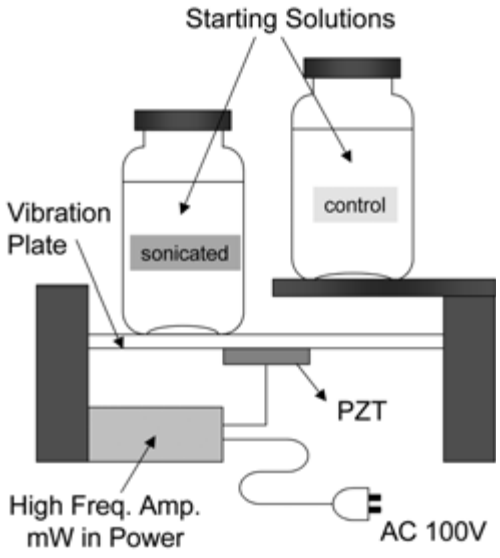

Fig. 1. Schematic of the soft sonication apparatus.

Synthesis of spheres was executed by mixing the two solutions in a transparent beaker at a constant temperature of 10°C. The incubation period (IP) of the precipitation was estimated by carefully watching the formation of turbidity in the reacting solution by naked eye. This rough method gave sufficiently reproducible and meaningful results. The reaction time was 120 minutes at maximum. In order to investigate the growth of spheres, small amounts of the reacting solution were occasionally sampled and diluted in ethanol to stop the reaction and were subjected to scanning electron microscopy (SEM). The sizes of spheres were measured from SEM pictures. Several hundreds of spheres were counted and ranked in order of size. The sphere size at the top 10% (D_{10}) and that at the bottom 10% (D_{90}) were used to evaluate the monodispersibility (D_{90}/D_{10}) of each sample.

Results and Discussion

Effect of Aging on Formation and Size of Spheres

Figure 2 shows the growth curves of silica particles prepared from differently aged solutions. It is confirmed that the growth behavior is quite similar and that a reaction time of 120 minutes is enough. The finally obtained particles are quite spherical and monodispersed as shown in Fig. 3. Minute examinations of the final particle size suggest an obvious effect of aging treatment.

Figure 4(a) shows that the incubation period (IP) for the appearance of turbidity becomes longer as aged [6]. Monodispersibility and the median size of the spheres after 120 minutes' synthesis are shown in Figs. 4(b) and (c), respectively. It is obvious that the aging process has enhanced every parameter in Fig. 4 and also almost doubly enhanced in the presence of soft sonication process.

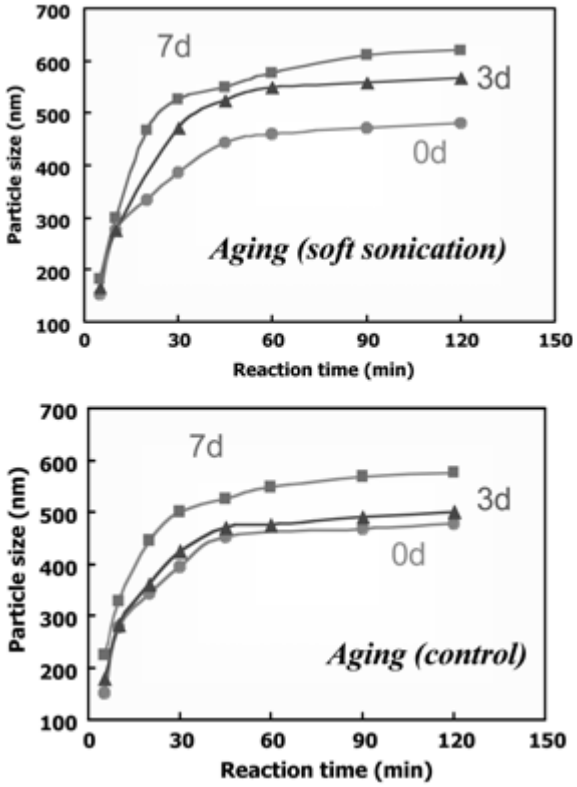

Fig. 2. Growth curves for silica spheres prepared from variously aged starting solutions.

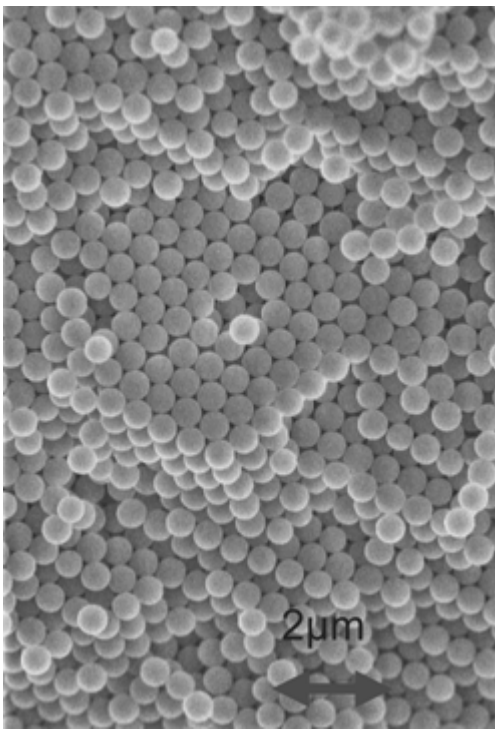

Fig. 3. Scanning electron micrograph of silica spheres.

As reported in the previous paper [2], the delay of the precipitation and the increase of particle size and monodispersibility are supposed to be due to micro-

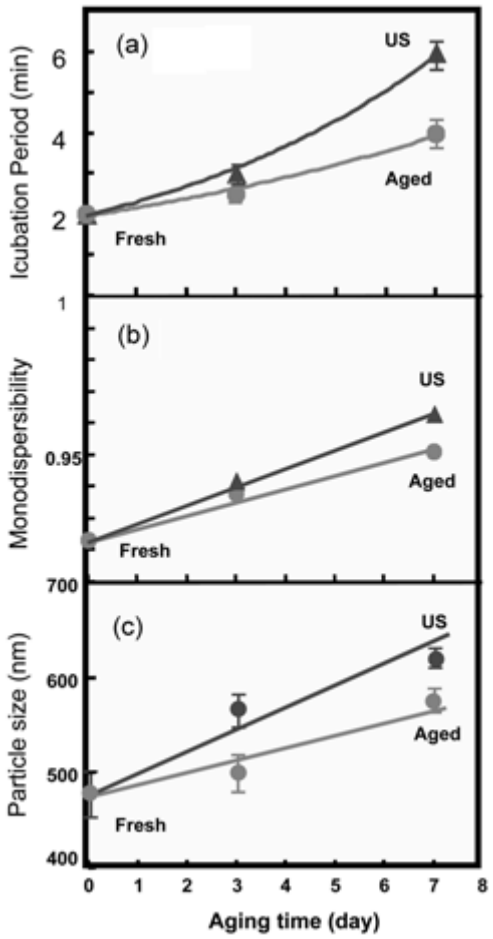

Fig. 4. Aging effect of starting solutions on precipitation behavior (top), monodispersibility (middle), and final sphere size (bottom).

scopic homogenization of the starting solutions, which may involve comparatively large clusters to enhance heterogeneous nucleation just after the preparation. Figure 5 is a schematic showing an ultrasonic wave of condensation and rarefaction in a liquid. The wavelength in water is as large as several centimetre according to a simple equation of $\lambda = c/f$. While, the inset equation indicates the vibration amplitude (ξ) is dependent upon the intensity of the ultrasound. Fluid particles in the medium move back and forth on this scale in principle. When the intensity reaches the milliwatt level, the amplitude becomes to the nanometre scale. Although the size of fluid particles or clusters are not definite, the nanoscaled vibration at a frequency of several tens of kHz could be effective in breaking or dispersing the clusters of hydrogen-bonded molecules of ethanol and water.

Crossover Experiment

In the above experiments, two solutions A and B were equally aged and then reacted. In order to better understand the aging effect, a fresh solution of A and an aged solution of B, and *vice versa*, were reacted to synthesize spheres. Notation "F/A" means the reaction between Fresh Solution A and the Aged Solution B. The aging time was 7 days. Figure 6 shows the final sphere size and the IP's for four different combinations. The IP values are found to be almost the same when either solution was aged. Comparing the sphere size of A/F and F/A, the latter is found to be larger. This means that the aging of Solution B is a little more efficient than that of Solution A. According to the

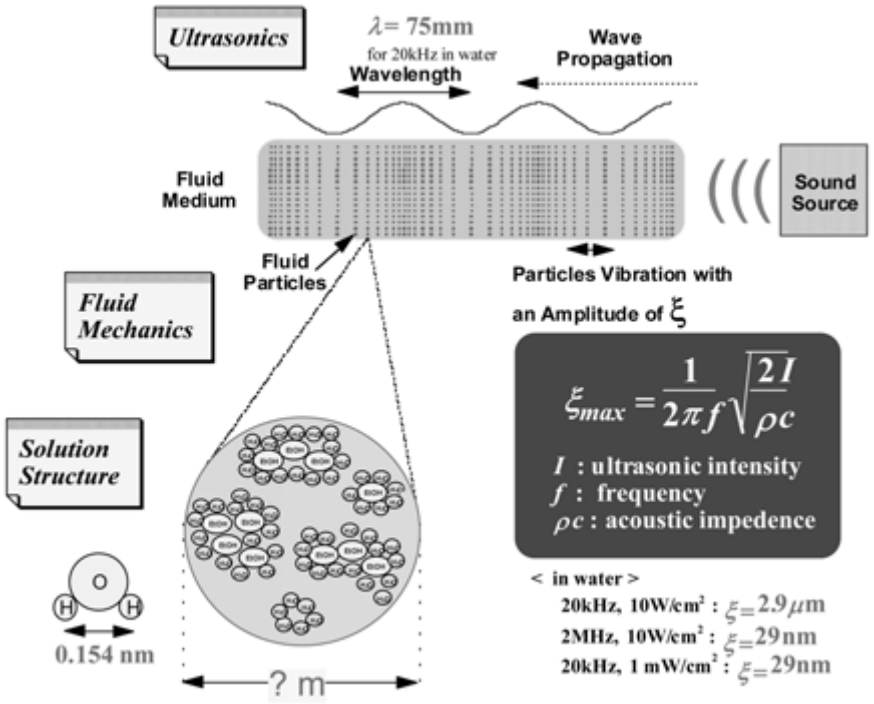

Fig. 5. Comparison of size parameters in an ultrasonic-stimulated solution of water-ethanol mixture.

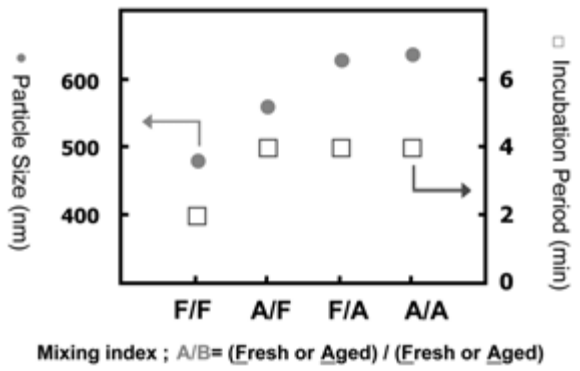

Fig. 6. Results of crossover experiment. Notation "F/A" means that Fresh Solution A and Aged Solution B were mixed to react. Reaction time was 120 min.

hypothesis that a well-mixed solution yields larger spheres, as described in the former section, it is inferred that the "microscopic" miscibility of the water-ethanol mixture is less than that of the TEOS-ethanol mixture.

It is well known that water and ethanol are miscible through the whole composition range. Here we would like to propose a simple question --- Is it truly easy to mix ethanol and water? It should be noticed here that an alcohol ($C_nH_{2n+1}OH$) with a larger alkyl group (n > ~5) is immiscible with water like oil. Then, we may reasonably say that ethanol (n = 2) is less miscible with water than methanol (n = 1). It is reported from a medical point-of-view that the intoxication of a water-ethanol mixture or liquor is decreased by aging [3, 4]. In short, experimental mice dosed with a well-aged mixture recover from a hangover earlier than those dosed with a less-aged one. Also, curious and obvious changes were detected due to aging. Thermal analysis [7] indicated that the freezing point tends to be lower for the well-aged mixture. ^{2}H-NMR spectroscopy [4] showed that relaxation time (T_1) of the well-aged mixture is slightly but essentially longer than that of the less-aged one. According to their interpretation, aging makes the solution structure more compact and homogeneous. This may also be applicable to explain our results in Fig. 4.

Effect of Intentional Addition of a Little Water

It should be additionally mentioned that we briefly examined the effect of moisture in ethanol because it may be involved intrinsically or absorbed from the atmosphere during the process. Although we employed absolute ethanol and always used a new bottle of it to start a series of experiment, a trace of water in ethanol may be inevitable in practice. In order to look at the effect of water, 1 mass% of water was deliberately added to some samples of Solution A prior to aging. As a result, the difference of the sphere size for the runs with and without water additions was not apparent. It is inferred that the hydrolysis of TEOS in the absence of (ammonia) catalyst at low (room) temperature is so slow that a trace of water in Solution A is negligible in the present aging condition.

Conclusions

In the synthesis of spherical silica with starting solutions of different ages, we demonstrate the following effects of aging on the precipitation behavior; (1) an increase of the incubation period for precipitation, (2) an increase of the final particle size, and (3) an improvement of the monodispersibility. The increment of the final particle size as a function of aging time is twice larger in the case of soft sonication than in the case of normal aging.

Ultrasonic technology has been widely used in various fields of science and technology. The concept of soft sonication is newly developed and begins to be applied to aging liquors. It may be challenging to consider an artificial modification of solution structure since it is in general considered to be a non-kinetic matter. We would like to emphasize that our experimental results are quite reproducible and we do not have any other interpretation of them apart from considering the solution structure. It is the plan of our future study to catch direct evidence upon the change of solution structure by use of spectroscopic methods such as NMR, Raman, or mass cluster analysis [8, 9].

References

1. W. Stöber, A. Fink, and E. Bohn, J. Colloid Interface Sci. 26 (1968) 62-69.
2. N. Enomoto, A. Kumagai, and J. Hojo, J. Ceram. Processing Res. 5[4] (2004) 391-394.
3. T. Haseba, K. Matsushita, T. Asakura, K. Kameyama, T. Tamaki, S. Okouchi, T. Watanabe, and H. Uedaira, Alcoholism: Clinical and Experimental Res. 17[5] (1993) 963-967.
4. K. Matsushita, M. Nishina, T. Asakura, S. Kamei, M. Suzuki, and K. Yabe, Physiol. Chem. Phys. & Med. NMR, 32 (2000) 13-19.
5. S.V. Ley and C.M.R. Low, Ultrasound in Synthesis, Springer-Verlag, Berlin, Heidelberg (1989).
6. N. Enomoto, J. Shiihara, T. Hongo, and Z. Nakagawa, J. Ceram. Soc. Jpn. 107[3] (1999) 285-288.
7. T. Haseba, K. Mikami, Y. Ohno, K. Kameyama, T. Tsujii, C. Saeki, T. Asakura, and H. Uedaira, Proc. 14th Mtg. Int'l Assoc. Forensic Sci., volume 2, pp 322-324, Shunderson Comm., Canada (1997).
8. A. Wakisaka, S. Komatsu, and Y. Usui, J. Mole. Liq. 90 (2001) 175-184.
9. K. Yamaguchi, J. Mass Spectrom. 38 (2003) 473-490.