

## Previous aging as a parameter for a liquid phase synthesis of ceramic nanoparticles

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Particular attention has been paid to the “age” of the starting solution for a liquid phase synthesis of ceramic nanoparticles. That is, starting solutions were prepared and kept in a container for several days and then were used to make a precipitation. Metal oxalates (hydrate) were precipitated from ethanolic solutions of oxalic acid and metal nitrate (hydrate). Aging of the starting solutions resulted in a marked delay of the precipitation. Silica spheres were prepared from ethanolic solutions of tetraethylorthosilicate (TEOS) and ammonia water. Aging of the starting solutions enhanced the size and monodispersibility of the spheres. We infer that the delay in precipitation is due to microscopic homogenization in the solution structure among ethanol, water, and solute species. That is, even when the prepared starting solutions look clear, transparent, and homogeneous, they may involve less-dispersed aggregates of solute/solvent, which would enhance heterogeneous nucleation to reduce the delay.

**Key words:** aging, oxalate precipitation in ethanolic solution, oxalic acid, silica sphere, Stober method.

### Introduction

Ceramic particles can be prepared either by milling a solid or by controlling nucleation and growth in a liquid or a gaseous phase. When we wish to produce nanosized particles with controlled shapes at cheaper cost, liquid phase synthesis is the best way. Needless to say, those who synthesize particles in a liquid phase must prepare a starting solution. There are three parameters in general to describe a starting solution; i.e., species of solute, species of solvent, and the ratio of them (concentration). In this study, we pay our attention to a fourth factor, the “age” of the starting solution, which means the time after dissolving a solute in a solvent.

It has been reported that the number of nuclei [1] and the particle size [2] of BaSO<sub>4</sub>, which is followed by the reaction, BaCl<sub>2</sub> + SO<sub>4</sub><sup>2-</sup> → BaSO<sub>4</sub> + 2Cl<sup>-</sup>, changes with the aging time of an aqueous starting solution of BaCl<sub>2</sub>. They explained that the incompletely-dissolved BaCl<sub>2</sub> aggregates which serve as nuclei for BaSO<sub>4</sub> decrease with aging time and consequently the particle size increases with aging time. Although their consideration was not quantitative, it is worth while noting that a transparent solution may not be homogeneous at microscopic levels as far as the precipitation units are concerned. In this sense, we need to notice that the visible transparency of a solution only means that the

dissolved and/or dispersed particles are so small that they do not scatter visible light, whose wavelength of 390-760 nm are much larger than the size of ions, molecules, nuclei, or clusters.

In this paper, we introduce two cases indicating the aging effect on the precipitation behavior of ceramic particles. One is an oxalate precipitation induced by the reaction between ethanolic solutions of metal salt and oxalic acid. The other is a synthesis of spherical silica from ethanolic solutions of alkoxide and ammonia water.

### Experimental

#### Oxalate Precipitation in Ethanol Solution

Commercial chemical reagents of MgNO<sub>3</sub>·6H<sub>2</sub>O (purity 99.0%, Wako Chemicals, Tokyo, Japan) and anhydrous H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (purity 98%, *ibid.*) were chosen as starting materials because they are easily soluble in both ethanol and water [3, 4] and also because the product oxalate, MgC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O is insoluble and has an identifiable crystal structure. Dehydration of the nitrate was not done. Concentration of each starting solution was fixed at Mg<sup>2+</sup> = 0.1 mol/dm<sup>3</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> = 0.2 mol/dm<sup>3</sup>. Dehydrated ethanol with a controlled amount of water was used as a solvent. After both starting solutions were aged without agitation at constant temperature, 50 cm<sup>3</sup> of the oxalic acid solution was poured into the same amount of the nitrate solution with mechanical stirring.

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### Synthesis of Silica Spheres

Commercial reagents of tetraethylorthosilicate (TEOS), ammonia, and absolute ethanol and distilled water were used without further purification. The concentration was fixed at  $\text{TEOS} = 0.1 \text{ mol/dm}^3$ ,  $\text{NH}_3 = 1.8 \text{ mol/dm}^3$ ,  $\text{H}_2\text{O} = 7.6 \text{ mol/dm}^3$  in ethanol solvent as a whole. Half of the total ethanol was used to prepare an ethanolic solution of TEOS. The other the half of the ethanol was used to prepare an ethanolic solution of ammonia water.

Starting solutions were tightly sealed in a brown glass container and aged at room temperature in the shade. Synthesis of spheres was executed by mixing the two solutions in a transparent beaker at a constant temperature of  $10^\circ\text{C}$  using a magnetic stirrer. A reaction time of 120 minutes was found to be sufficient to complete the reaction. Finally the product was centrifuged, washed several times by ethanol, and dried at  $60^\circ\text{C}$  in an oven.

### Characterization

The initial effect of aging on the oxalate precipitation can be confirmed by the naked eye; i.e., when the starting solutions were mixed soon after each of them was prepared, in other words, when the starting solutions were fresh, the mixed solution became cloudy at the moment of mixing. After they were aged for a long time, on the contrary, the mixed solution remained strangely transparent. After a sufficient time, the transparent solution turned cloudy. The incubation period (IP) for the precipitation, i.e., the time from the mixing of the two solutions to the appearance of the cloudiness, was measured by the naked eye in a white light. This primitive measurement was found to be sufficiently reproducible if something black is placed at the back of a glass beaker containing the precipitating solution and if it is compared with a beaker of pure water. After the precipitation was executed with mechanical stirring for a certain time, the products were centrifugally separated, washed with pure ethanol, and then dried in air. The products were subjected to X-ray diffractometry (XRD) and scanning electron microscopy (SEM) etc.

## Results and Discussion

### Aging Effect on the Oxalate Precipitation

Figure 1 shows the incubation period as a function of aging time. Clear and obvious results were that aging of the starting solutions caused an abrupt delay of precipitation. Temperature was also found to be effective to enhance the aging process. XRD analyses indicated that no phases other than  $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  were involved in the product either from fresh or from aged starting solutions. The product yields after 24 hours' reaction are shown in Fig. 2. They also decreased with increasing aging time and increasing aging temperature.

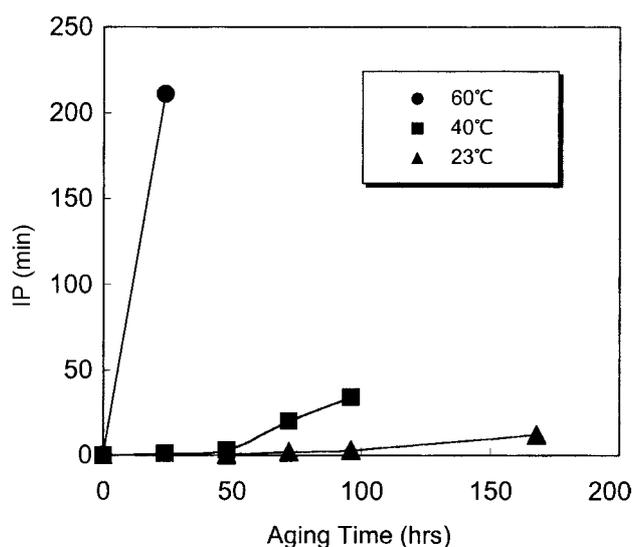


Fig. 1. Delay in the precipitation of magnesium oxalate from aged solutions.

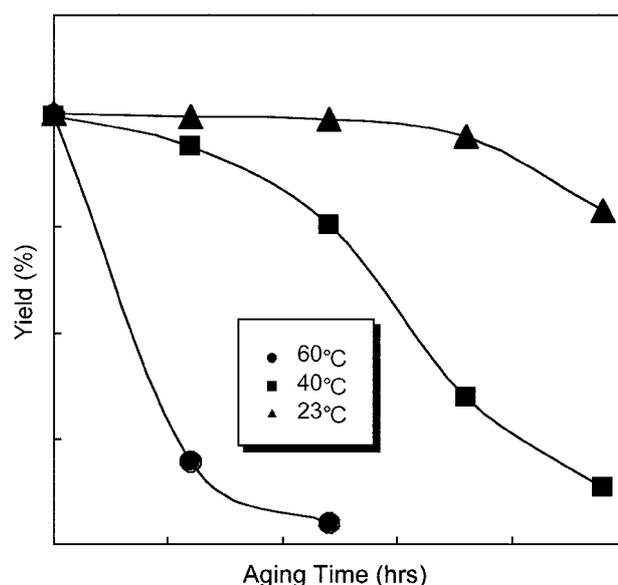
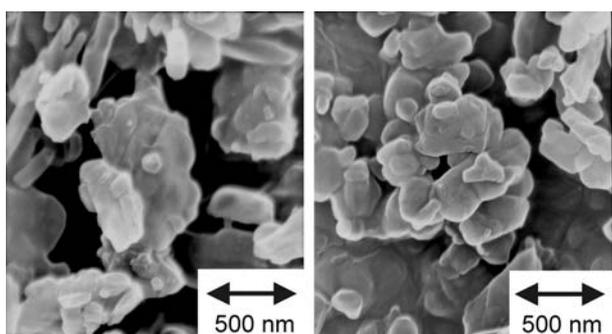


Fig. 2. Aging time dependence of the precipitation yield (reaction time=24h) of magnesium oxalate from starting solutions aged at various temperatures.

Figure 3 shows SEM pictures of the oxalate products after 24 hours' reaction from fresh and aged ( $40^\circ\text{C}$ , 96h) solutions. It can be recognized that the particles from aged solutions appear to have a definite and homogeneous morphology.

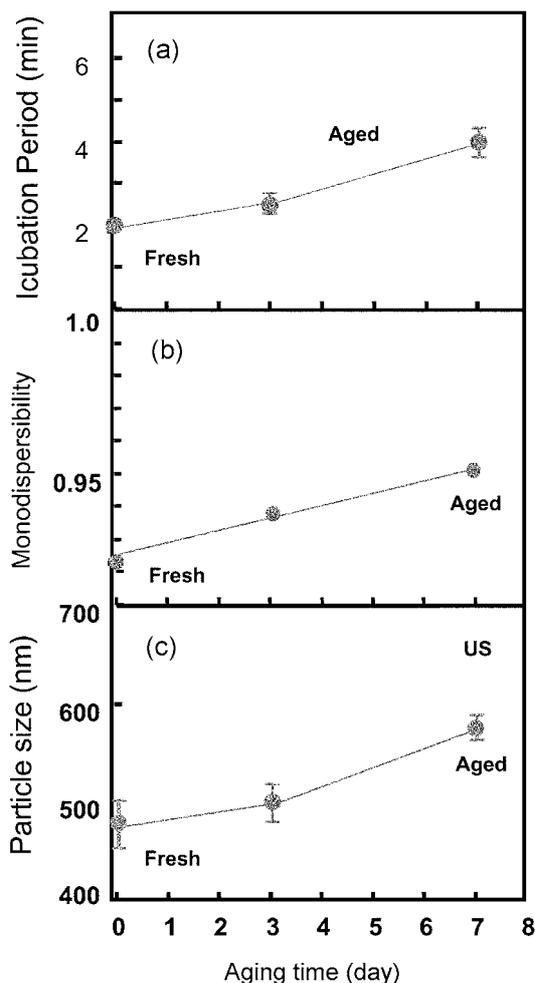
### Aging Effect on the Nucleation of Silica Spheres

Figure 4(a) shows that IP for silica synthesis became longer with aging. Comparing to the case of oxalate precipitation (Fig. 1), the IP values in Fig. 4 are much smaller but show a similar tendency. After a sufficient reaction time of 120 minutes, the size of the spheres was measured from SEM pictures. Several hundred spheres were counted and ranked in order of size.



**Fig. 3.** Magnesium oxalate particles from fresh (left) and aged (right) solutions. (Aging time=96h, Reaction time=24h)

Sphere sizes at the top 10% (D10) and at the bottom 10% (D90) were used to evaluate the monodispersibility (D90/D10) of each sample. The closer the value of D90/D10 reaches to 1, the higher the monodispersibility is. The monodispersibility and median size of the spheres after 120 minutes' synthesis are shown in Figs. 4(b) and (c), respectively. It is obvious that the aging



**Fig. 4.** Effect of aging on (a) incubation period, (b) monodispersibility, and (c) particle size of silica spheres. Reaction time was 120 minutes for (b) and (c).

process enhanced both of them.

Here we would like to calculate the number of nuclei based on a simple assumption. Firstly, how many moles of SiO<sub>2</sub> (M.W.=60 g/mol) were involved in a single sphere (density;  $\rho \approx 1.8 \text{ Mg/m}^3$ ) with a diameter of D [m] ? This may represent the degree of polymerization (SiO<sub>2</sub>)<sub>n</sub>;

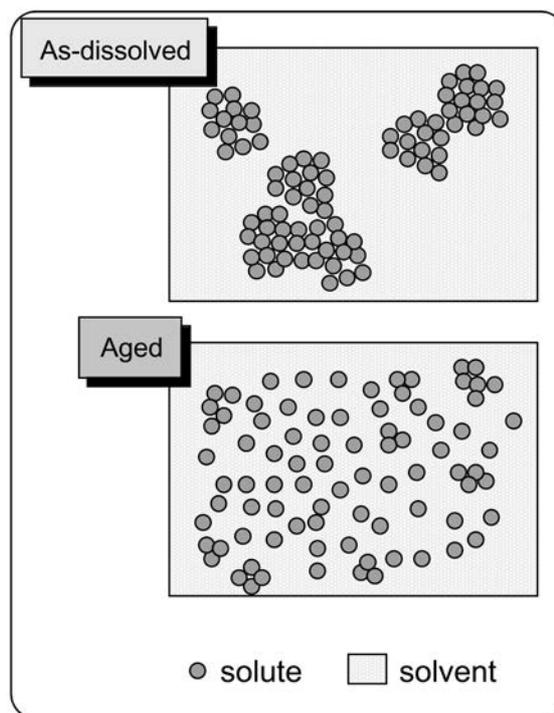
$$n \text{ [mol/particle]} = \frac{\frac{4}{3}\pi\left(\frac{D}{2}\right)^3 \cdot \rho}{M.W.}$$

Assuming that the C (=0.1 mol/dm<sup>3</sup>) TEOS was fully hydrolyzed to form monodispersed spheres of D [m], the solution should have contained the following number of particles per unit volume.

$$\frac{C}{n} \text{ [particles/dm}^3\text{]} = \frac{6C \cdot M.W. \cdot D^{-3}}{\pi\rho}$$

This value can represent the number of nuclei (N). By comparing the size of spheres prepared from a fresh solution (D<sub>fresh</sub>=470 nm) and that from a 7 days-aged solution (D<sub>7d</sub>=580 nm), the number ratio of nuclei (N<sub>7d</sub>/N<sub>fresh</sub>) equal to (D<sub>fresh</sub>/D<sub>7d</sub>)<sup>3</sup>, which is calculated to be about 0.53. In conclusion, the number of nuclei decreased to half when the starting solutions were aged for 1 week. This should be related to the fact that we could determine a clear difference in IP's for fresh and aged runs in Fig. 4(a).

Needless to say, it is quite easy to prepare a "homogeneous" starting solution because either TEOS



**Fig. 5.** Assumed schematic for the change of solution structure during aging. Large clusters in the as-dissolved solution may induce heterogeneous nucleation.

or water is very soluble in ethanol. However, we must note here that a "transparent" solution means only that it does not scatter visible light. Considering wavelengths of visible light, "transparent homogeneity" does not at all guarantee the homogeneity at a molecular level. One hypothesis to explain the results in Fig. 4 is shown in Fig. 5. Just after a solute is dissolved in a solvent, it may not be well dispersed at a microscopic level. Large clusters in the as-dissolved (fresh) solution act as a heterogeneous nucleation site to degrade monodispersibility. After these clusters break up during aging, nucleation would be more homogeneous and the particle size becomes larger.

Our hypothesis is also based on the premise that water and ethanol may not be so miscible at a microscopic level where a unit of precipitation phenomenon, ions or solvent molecules, are concerned. Considering that an alcohol with a larger alkyl group is like an oil which is immiscible with water, ethanol is at least less miscible than methanol. This is not our own idea. Many physical scientist [5-11] have discussed the solution structure of water-alcohol mixtures. It will be an interesting approach for us to combine the precipitation phenomena, as presented in this paper, with direct evidence of the structural analysis of a starting solution.

### Conclusions

In the wet-chemical synthesis of particles and powders using precipitation phenomena, we might not pay much attention to starting solutions if they are visibly transparent and clear. Sometimes we use a stock solution for a series of experiments, which could take more than 1 week. It was found in this study that the aging of starting solutions can influence the incubation period, particle size, and morphology.

We are presuming that this is due to the microscopic

homogenization in solution structure. This sort of behavior is likely to occur with an organic solvent but is unlikely to occur in an aqueous system since water strongly hydrates the solute ions to disperse them effectively due to the high value of its dielectric constant ( $\epsilon=78.5$ ). Although organic solvents (e.g.,  $\epsilon=25$  for ethanol) are becoming to be avoided owing to environmental issues, they are definitely necessary for the synthesis of many specific materials. The fourth factor, the age of the starting solution, could be a useful parameter to control the nucleation and growth in these cases.

### References

1. J.D. O'Rourke and R.A. Johnson, *Anal. Chem.* 27[11] (1955) 1699-1704 .
2. E.J. Bogan and H.V. Moyer, *Anal. Chem.* 28[4] (1956) 473-476.
3. H. Yamamura, M. Tanada, H. Haneda, S. Shirasaki, and Y. Moriyoshi, *Ceram. Intl.* 11[1] (1985) 23-26.
4. B.M. Song, D.Y. Kim, H. Yamamura, S. Shirasaki, and M. Tanada, *Jpn. J. Appl. Phys.* 24 Suppl. 24-2, pp. 439-441 (1985).
5. S. Dixit, J. Crain, W.C.K. Poon, J.L. Finney, and A.K. Soper, *Nature* 416[25] (2002) 829.
6. A.K. Soper and J.L. Finney, *Phys. Rev. Lett.* 71[26] (1993) 4346.
7. K. Egashira and N. Nishi, *J. Phys. Chem. B* 102 (1998) 4054.
8. Y. Amo and Y. Tominaga, *Chem. Phys. Lett.* 320 (2000) 703.
9. A. Wakisaka, S. Komatsu, and Y. Usui, *J. Mole. Liq.* 90 (2001) 175.
10. K. Matsushita, M. Nishina, T. Asakura, S. Kamei, M. Suzuki, and K. Yabe, *Physiol. Chem. Phys. & Med. NMR* 32 (2000) 13-19.
11. T. Haseba, K. Matsushita, T. Asakura, K. Kameyama, T. Tamaki, S. Okouchi, and T. Watanabe, *Alcoholism: Clinical and Experimental Res.* 17[5] 963-967 (1993).