

Effect of Reaction Condition and Solvent on The Size and Morphology of Silica Powder Prepared by An Emulsion Technique

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The spherical silica powder was synthesized by varying the kinds of solvent and mixing energy in emulsion method. The stirring speed varied from 500 to 1000 r.p.m. at 50°C for 2 h. Toluene in benzyl groups and a series of alkanes were used as dispersant. The average size of spherical silica particles decreased with increasing the stirring speed and the chain length of solvents used in this work. The average size was controlled in the range of 134~28 μm by selecting a proper solvent and stirring speed. The optimum processing parameters were described in details.

Key words: Spherical silica powder, Sol-gel process, Emulsion

I. Introduction

The spherical silica powder is being used as filler material in epoxy molding compounds (EMC) for the semiconductor encapsulation and the high performance liquid chromatography. Other applications such as optical materials for solid-state lasers, optical amplification, frequency doubling, and lasing by adding organic dye or inorganic materials including rare earth elements are also positively considered.¹⁾ A number of studies were performed to synthesize the silica powder in a spherical form using the sol-gel process.²⁻⁴⁾ The mono-size silica particles in a submicron were synthesized using the base catalyst for hydrolysis of TEOS,²⁾ which led to the size distribution in the range of 0.05 to 2 μm in diameter and high purity. However, such a size distribution caused a poor flowability while molding into EMC and limited the application to the semiconductor components. On the other hand, the seeded growth technique showed an advantage of synthesizing larger particle.⁴⁾ The size of silica powder prepared by this method, however, could not fulfill the required size of 20 μm for EMC and liquid chromatography.

The spherical silica particles larger than 10 μm could be readily made by either the emulsion technique⁵⁻¹⁰⁾ or neutralizing water-glass using acid, although the silica powder obtained from water-glass was hardly used as a EMC filler due to the low purity.¹¹⁾ Thus, the emulsion technique has advantages in the lights of particle size and purity. In fact, the spherical silica powder in the range of 5 to 50 μm and 10 to 40 μm was obtained in TEOS-CH₃COOH-H₂O and TEOS-H₂O-Decane systems, respectively.^{5,7)} The particle size obtained in TMOS-H₂O-CH₃OH-DMF system was in the range of 5 to 40 μm depending on the HLB values of surfactants, reaction

temperature and stirring speed.¹⁰⁾ These indicate the relationship between the particle size and reaction conditions including the stirring speed and kinds of solvent, although little work has been performed to elucidate the relation.

The objective of this work is systematically to relate the size and morphology of silica powder with the solvent and processing factors. For this, the effects of the solvents with different chemical structure and various stirring speeds on the size and morphology of silica powder prepared by an emulsion technique were studied in details.

II. Experimental Procedure

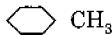
Various compositions of reactants used in this work are given in Table 1. TMOS (tetramethylorthosilicate) and acetic acid were used as silica source and catalyst for hydrolysis of TMOS, respectively. The surfactant was sorbitan mono-oleate (Span-80). The solvents for dispersing the droplets formed in emulsion are listed in the Table 2. The toluene of benzyl groups was mainly used in this work. In addition, the iso-octane, normal octane and other alkane series were used for comparison.

The organic solvent, water and surfactants (Span-80) were first mixed for 10 min and then acetic acid was added, prior to mixing for 5 min. Then, TMOS was added

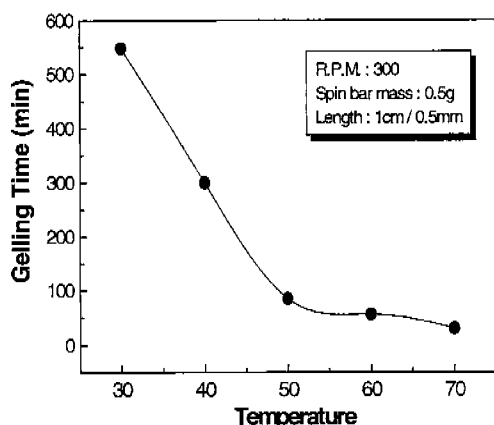
Table 1. Mole Ratios for Synthesis of Silica Powder

Composition No	TMOS	H ₂ O	CH ₃ COOH	Solvent
E-1	0.75 mol	8.26 mol	0.02 mol	36 ml
E-2	1 mol	12.4 mol	0.03 mol	36 ml
E-3	1.5 mol	16.5 mol	0.04 mol	36 ml

Table 2. Solvent Used in This Experiment

	Solvent	Chemical Formula	Structure	Estimated Chain Length
Benzyl Group	Toluene	$C_6H_5CH_3$		5.77 Å
	Iso-Octane	C_8H_{18}	<pre> CH₃ H H H H H C C C C C H H H H CH₃ CH₃ </pre>	8.44 Å
Alkane Group	Hexane	C_6H_{14}	<pre> H H H H H H H C C C C C C H H H H H H H </pre>	9.98 Å
	Heptane	C_7H_{16}	<pre> H H H H H H H H C C C C C C C H H H H H H H H </pre>	11.52 Å
	Octane	C_8H_{18}	<pre> H H H H H H H H H C C C C C C C C H H H H H H H H H </pre>	13.06 Å
	Nonane	C_9H_{20}	<pre> H H H H H H H H H H C C C C C C C C C H H H H H H H H H H </pre>	14.6 Å
	Decane	$C_{10}H_{22}$	<pre> H H H H H H H H H H H C C C C C C C C C C H H H H H H H H H H H </pre>	16.14 Å

to the mixture and mixed for 100 min at 50°C. The gelling time was measured in TMOS/H₂O/CH₃COOH=1/12.4/0.03 mole ratio (E-2 composition in Table 1) at various temperatures to determine the reaction temperature. The gelling time decreased with increasing the reaction temperature, as shown in Fig. 1. The lower the reaction temperature below 50°C, the broader the size of spherical silica gel powder. When the reaction temperature was higher than 50°C, the silica powder was aggregated to the gellatine powder. Thus, the optimum temperature was determined as 50°C for the spherical and individual silica gel particle. The wet powder was filtered and washed with methanol, and subsequently dried at 120°C for 24 h. The calcination temperature for amorphous silica powder was determined from TG-DTA data (Mac Science Co. Ltd. Thermal Ana-

**Fig. 1.** Gelling point of composition E-2.

lyzer System 001, Japan). The heating rate was 10°C per minute during the TG-DTA measurement. The average particle size and morphology of dried and calcined silica powders were estimated by measuring the particle size on the cross-sectional line of optical microscopic photographs.

III. Results and Discussion.

1. Effect of TMOS Concentration and Stirring Speed

The effect of the concentration of TMOS on the morphology and the size distribution of silica gel powder synthesized at 50°C by mixing for 100 min in toluene is shown in Fig. 2. The size of particles tends to be decreased with decreasing the concentration of TMOS and the distribution shows bi-modal pattern at the lowest concentration (E-1 composition). In contrast, the gel particle is getting larger by agglomeration with increasing the TMOS concentration increases (E-3 composition). The secondary growth of particles could occur at lower concentration of TMOS, whereas the excess TMOS at higher concentration caused the coalescence of gel particles. Thus a proper composition such as E-2 might exist in obtaining non-aggregated spherical gel powder at the same reaction condition. Therefore, the composition of E-2 was selected to study the effect of various solvents on the particle size and morphology of spherical silica powder.

Another important processing parameter in an emulsion process is the stirring speed. The average size of silica gel particles decreased significantly from 587 to 134 μm with increasing stirring speed from 500 to 1000 r.p.m. as demonstrated in Fig. 3. This tendency was also confirmed in

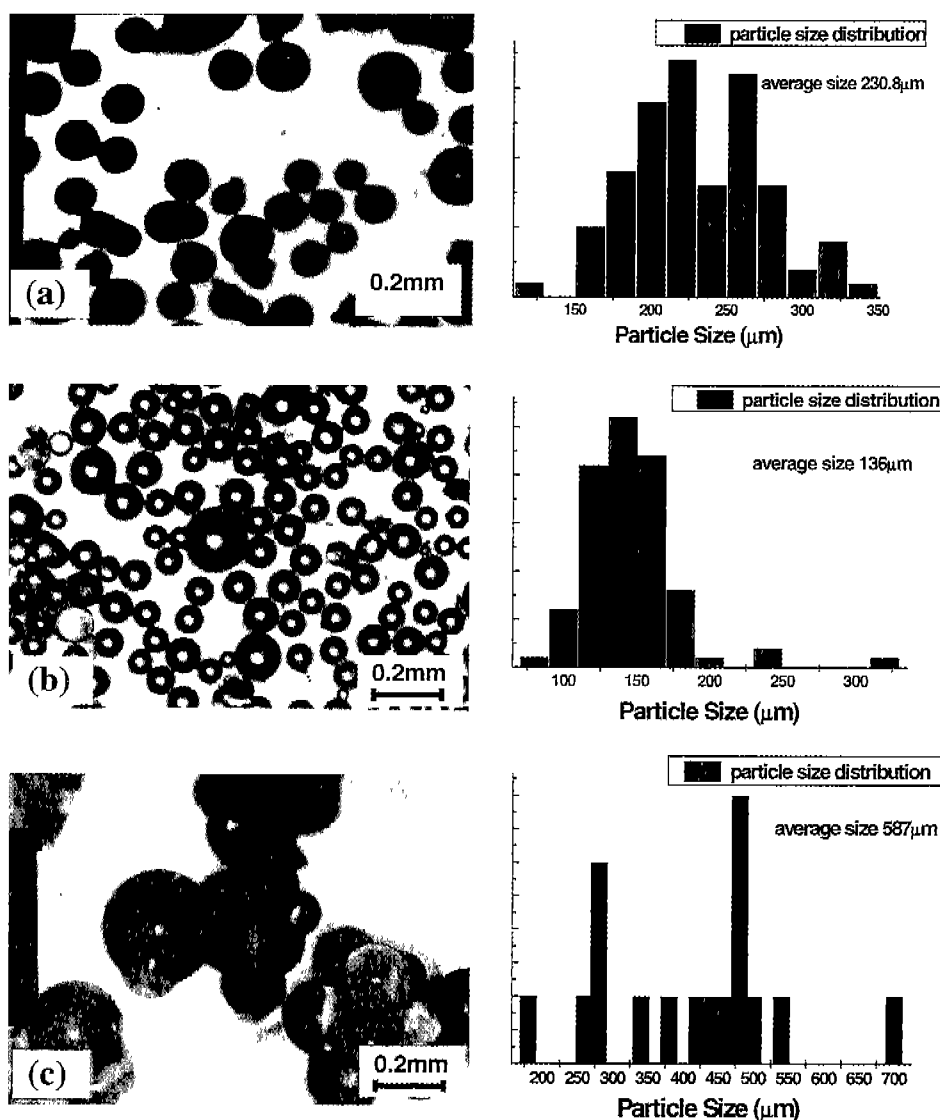


Fig 2. Optical microscopic photographs of silica gel powder prepared at different TMOS concentration in Toluene. Bar is 0.2 mm. (a) E-1, (b) E-2 and (c) E-3 composition.

TMOS- H_2O - CH_3OH -DMF system by Yamashita *et al.*¹⁰ since the more the mechanical energy input, the larger the surface area formed between two immiscible liquids, and the smaller the size of droplet in emulsion.

2. Effect of Solvents on the Size and Morphology

The average size of silica powder depended on the kinds of solvent, i.e., toluene in a benzyl group and iso-octane in an alkane group, as shown in Fig. 4. Other experimental conditions remained constant if they were not mentioned. The composition was TMOS/ H_2O / CH_3COOH = 1/12.4/0.02 in mole ratio (E-2) and reaction conditions was 50°C, 100 min and 1000 r.p.m. While using iso-octane solvent, the average particle size was smaller (62 μm) compared to that (134 μm) in toluene.

The droplet size in emulsion could be significantly influenced by the steric effect of solvents. The molecular struc-

ture of toluene is a ring type, whereas iso-octane has a long chain structure as shown in table 2. Though the surfactants could contribute to the stabilization of the water droplet size in emulsion, as stirring speed increases, i.e., mechanical energy increases, the droplet size decreases and each droplet tends to coalescence. The final size of water droplet approaches to constant value depending on the solvents used as dispersant. The toluene could be less efficient in hindering the coalescence and resulting in larger silica gel powder. In order to confirm this steric effect of organic solvents as dispersant in emulsion on silica gel powder size, the octane isomers of various structures while showing same chemical formula and a series of C_nH_{2n+2} alkane group series were used as shown in Figs. 6 and 7, respectively. The average size of particles in the octane isomers and alkane group series decreased with increasing chain length, as it might be expected. The average size obtained from iso-octane was 64 μm and that

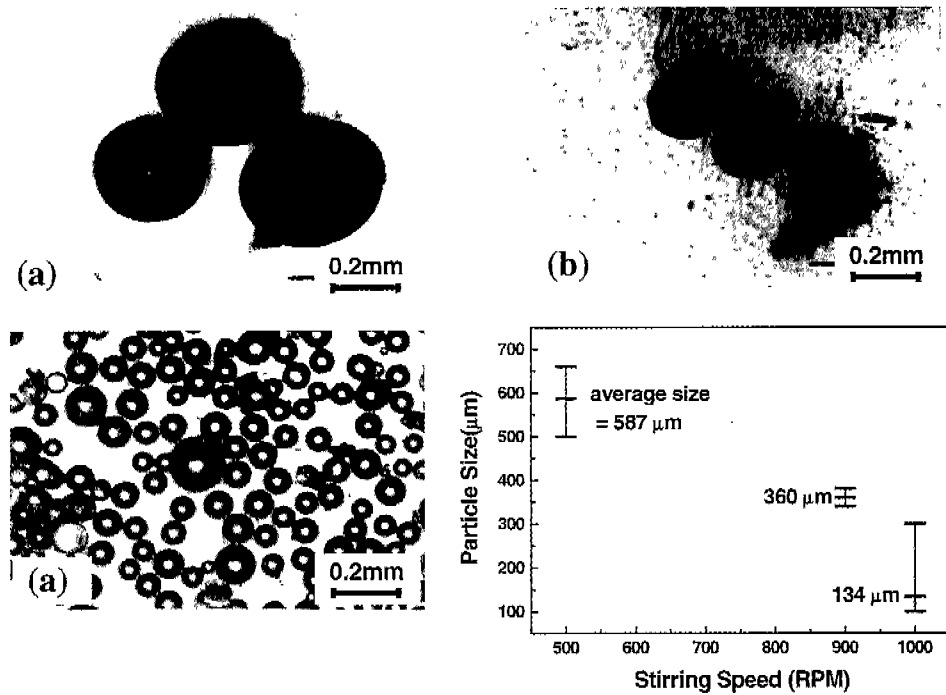


Fig 3. Optical microscopic photographs and particle size distributions of silica gel powder prepared at different stirring speed ($\times 50$). Bar is 0.2 mm. Stirring speed is (a) 500 r.p.m, (b) 900 r.p.m and (c) 1000 r.p.m.

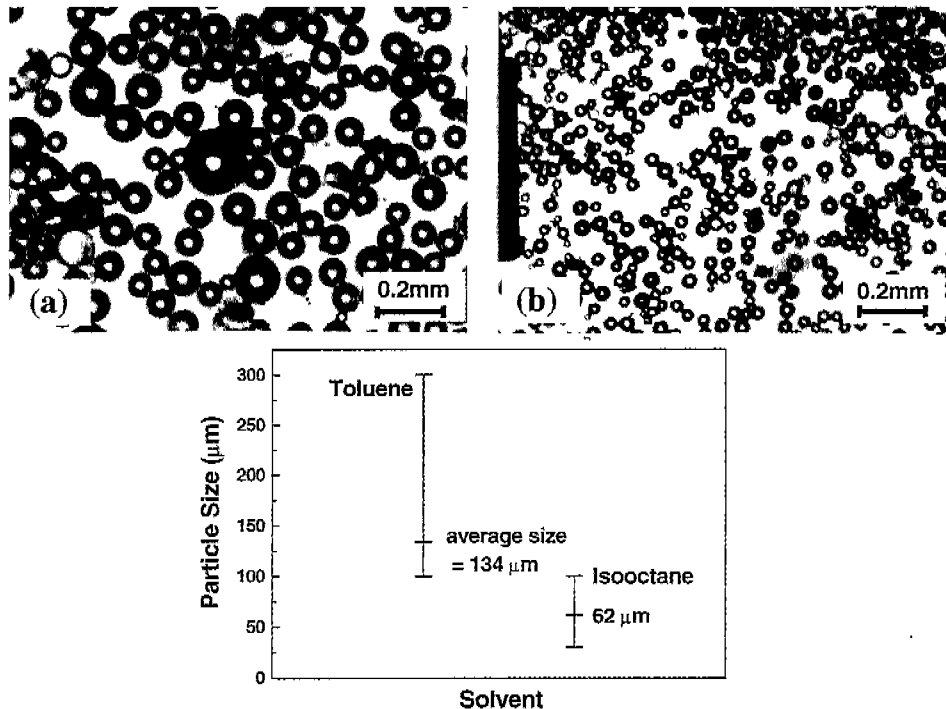


Fig 4. Optical microscopic photographs and particle size distributions of silica gel powder in different solvents ($\times 50$). Bar is 0.2 mm. (a) Toluene solvent and (b) Iso-octane solvent.

of octane was 46 μm . The average size of silica gel powder decreased gradually from 75 to 28 μm with increasing the chain length in an alkane group listed in Table 2, i.e., the value of n . The particle sizes obtained from n -Hexane (C_6H_{14}), n -Heptane (C_7H_{16}), n -Octane (C_8H_{18}), Nonane

(C_9H_{20}), n -Decane ($\text{C}_{10}\text{H}_{22}$) were 75, 51, 46, 44, 28 μm , respectively.

3. Effect of Heat-treatment

The results of TG-DTA curves of silica gel powders

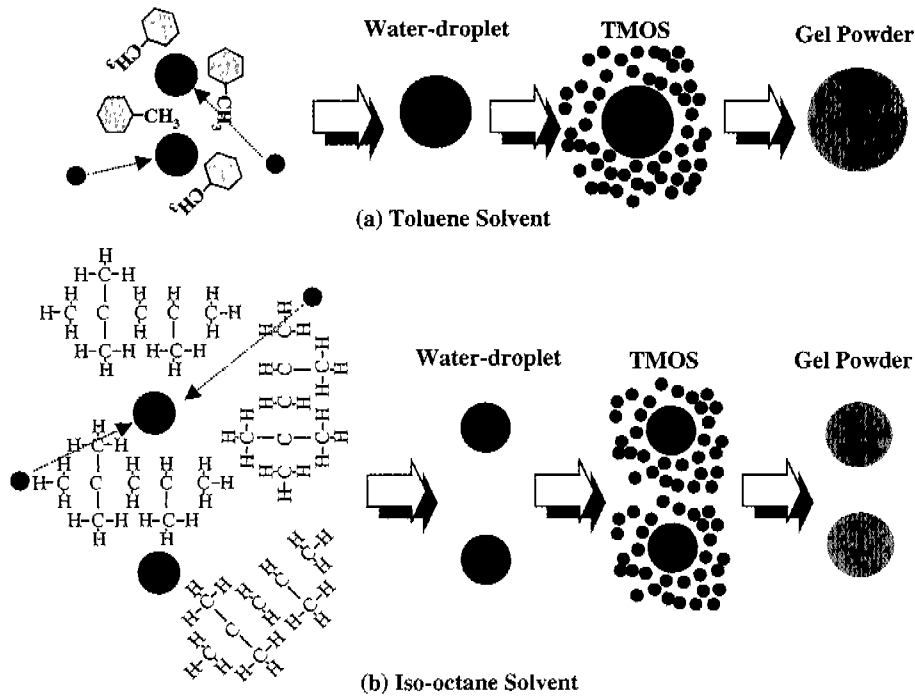


Fig 5. Steric effects scheme of solvents on water droplet size and final gel powder in emulsion. (a) Toluene solvent and (b) Iso-octane solvent.

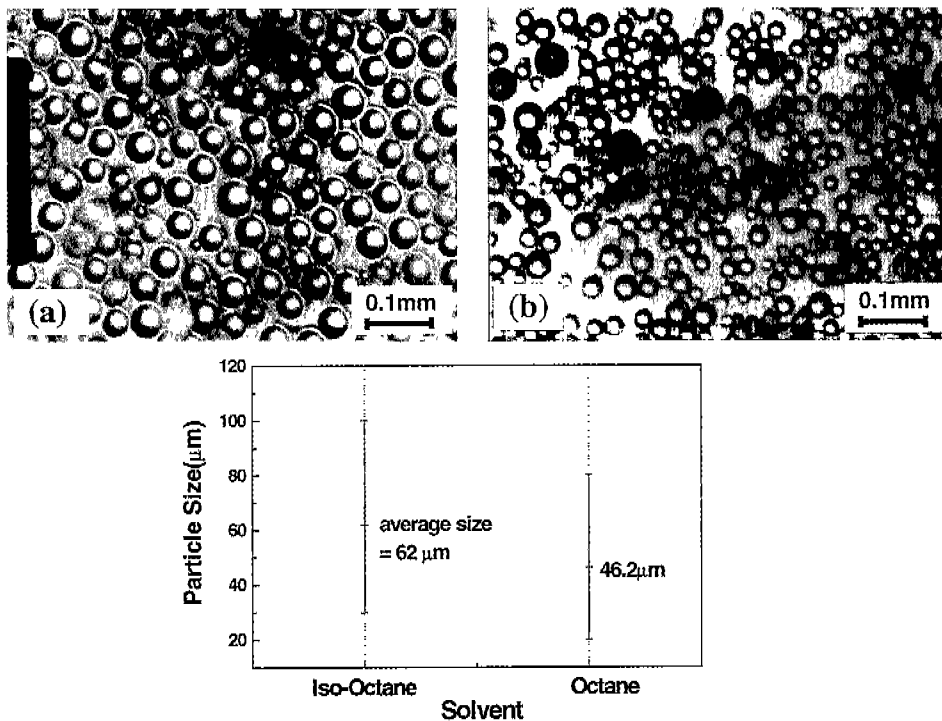


Fig. 6. Optical microscopic photographs and particle size distributions of silica gel powder in different solvents ($\times 100$). Bar is 0.1 mm. (a) Iso-octane solvent and (b) Octane solvent.

obtained using toluene and iso-octane solvents are presented in Fig. 8. In the case of the toluene solvent, exothermic peak supposed to be originated from the crystallization of silica did not appear up to 1200°C, while the weak shoulder assumed to be the crystallization of cristobalite

appeared at 1014°C in iso-octane solvent as indicated by an arrow in the figure. These results indicate that heat-treatment at 1000°C for 2 h could cause amorphous silica glass powder. The shrinkage of silica gel powders derived from toluene and iso-octane solvents were 8% and 6% with the

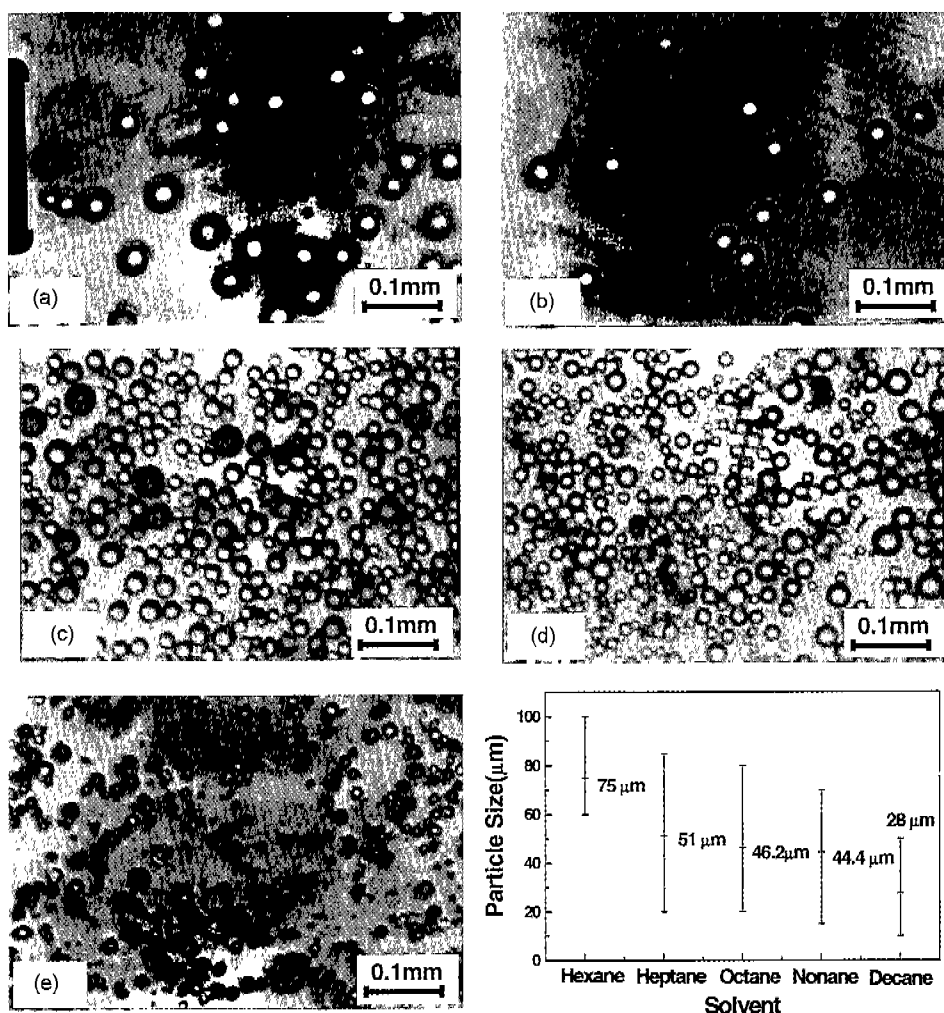


Fig. 7. Optical microscopic photographs of silica gel powder particle size distribution in alkane group($\times 100$). Bar is 0.1 mm. (a) Hexane(C_6H_{14}) (b) Heptane(C_7H_{16}) (c) Octane(C_8H_{18}) (d) Nonane(C_9H_{20}) and (e) Decane($C_{10}H_{22}$).

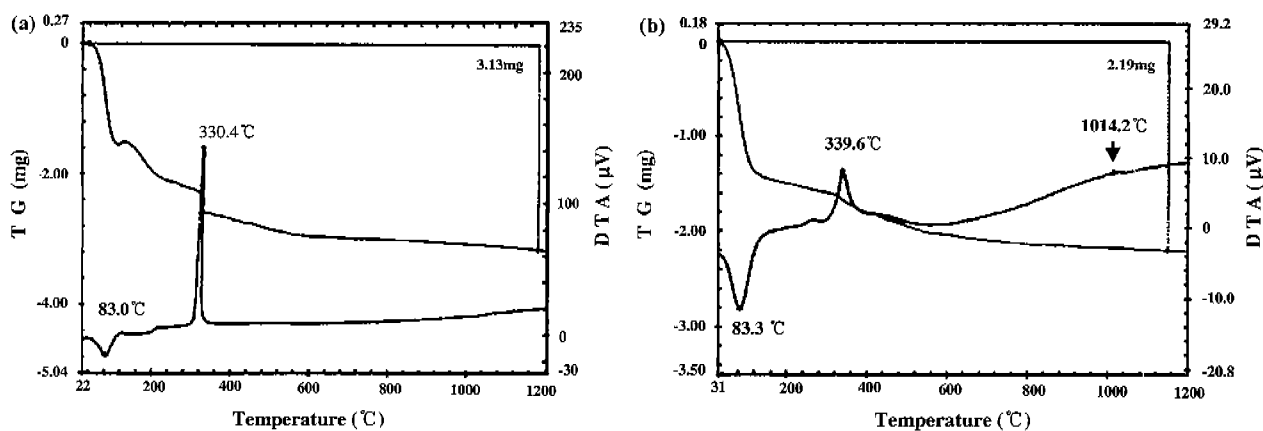


Fig. 8. TG-DTA diagram for calcined spherical silica powder. (a) Toluene solvent and (b) Iso-octane solvent.

average size of 123 and 58 μm , respectively, as shown in Fig. 9.

V. Conclusions

The silica gel powders with the average size of particle

in the range of 138 to 28 μm were synthesized by varying solvent and reaction condition in the emulsion method. Under the same reaction condition, the first major factor controlling the average size of silica gel powder is the stirring speed and the second factor is the steric hindrance of solvent that prevents the dispersed water droplets from

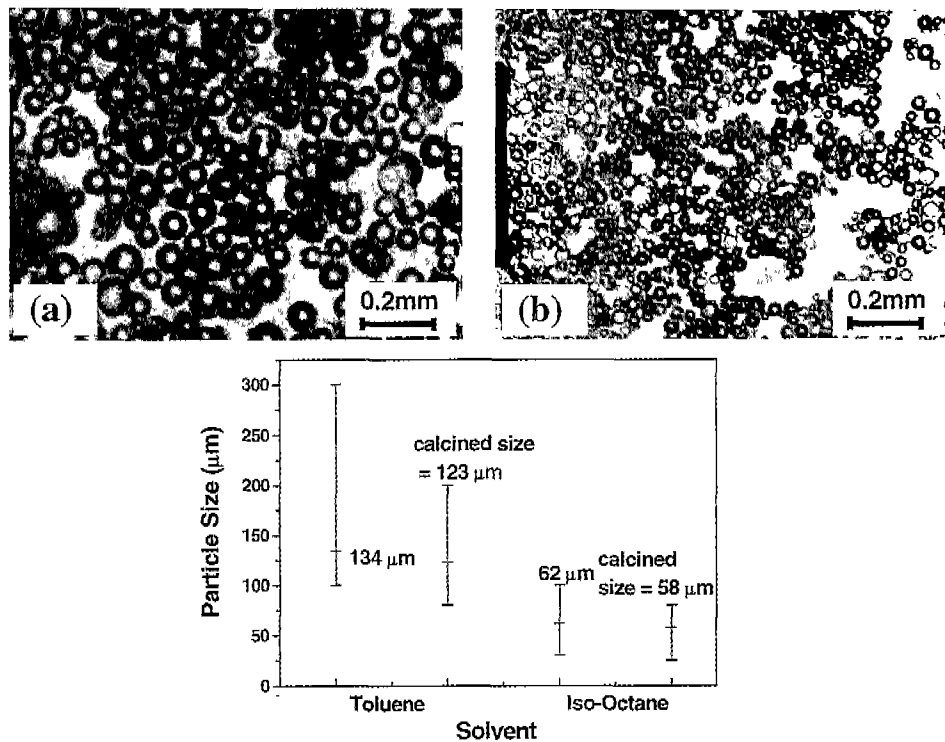


Fig. 9. Optical microscopic photographs and particle size distributions of calcined silica powder($\times 50$). Bar is 0.2 mm. (a) Toluene solvent and (b) Iso-Octane solvent.

coalescence. The shrinkage of silica gel powder by heat-treatment at 1000°C for 2 hours was 6~8% and the average sizes of silica glass powder obtained using toluene and iso-octane solvents were 123 and 58 μm , respectively.

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