

VOLUME FRACTION DEPENDENT MORPHOLOGICAL TRANSITION OF SILICA PARTICLES DERIVED FROM SODIUM SILICATE

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ABSTRACT

The volume fraction dependent morphological transition of droplets during the evaporation of colloidal silica solution was investigated using the spray-drying method. The colloidal solution was prepared from sodium silicate using the sol-gel method. Spray drying with a tubular reactor was used in the experiment, with the volume fraction of the colloidal silica varying from 15 to 2%. It was demonstrated that a morphological transition from a sphere shape to a donut-like shape takes place at a colloidal volume fraction of between 4% and 2%, even when the drying rate remains moderate and is not extremely fast. A spherical silica particle shape was found at a colloidal volume fraction of between 15% and 8%. The morphological transition depends strongly on the volume fraction of the colloids in the droplets. Further, the ζ -potential of the particles in the droplet also affects the transition by applying an interparticle electrostatic force. The same high surface charge of sol silica provides a repulsive interaction between the sol particles inside the droplet. The transition is hindered when the colloid volume fraction is increased because of the inherent spatial constraint. The Fourier-transform infrared (FT-IR) spectra of both the spherical and donut-like particles confirm the chemical bonding of the powder silica product. Moreover, X-ray diffractometry (XRD) analysis revealed an amorphous phase of the silica particles produced from spray drying. These preliminary results open up a new path for controlling the formation of a wide variety of silica particles using the spray-drying method. In addition, the different silica particle morphologies enable a variety of particle applications.

Keywords: Colloidal silica; Particle morphology; Sodium silicate; Spray drying; Volume fraction

1. INTRODUCTION

The spray-drying method is an established technology for synthesizing a material with controllable morphology. The method enables continuous production of nanostructure powders with high surface area and high purity, and it can be scaled up to ton-order quantities (Xiong et al., 2017). In addition, the particles produced from this method are agglomeration-free and have a monodisperse size, which is highly useful for material processing (Nandiyanto & Okuyama, 2011). The industrial-scale spray-drying method has been long established because it is a simple, cost-effective system (Isobe et al., 2005).

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The production of silica particles by spray drying has attracted much interest in recent decades because of the ability of the method to produce several kinds of particles with different morphologies (Tsapis et al., 2005; Vehring et al., 2007). The morphology of silica particles determines their practical applications (Qomariyah et al., 2018a). Spray drying of colloidal precursors containing silica particles has been reported by several researchers (Waldron et al., 2014; Dixit et al., 2016). The reported applications of silica particles from spray drying include their use as catalysts and absorbents, as well as in chromatography and drug delivery systems (Bahadur et al., 2011; Wang & Friess, 2017).

Iskandar et al. (2003) used an aerosol-assisted spray method to produce silica particles, using a commercial colloidal silica suspension as the precursor. However, application on a large scale has been limited because of the high cost of the silica source (Ui et al., 2009). This drawback is an interesting topic for further study of the production of silica particles with controllable morphology using the spray-drying method with a low-cost silica source. In general, silica particles are synthesized using tetraethyl orthosilicate (TEOS) (Cho et al., 2009; Wang et al., 2010) or trimethoxy vinyl silane (TMVS) as the silica source to obtain monodisperse and spherical-shaped particles (Zainal et al., 2013; Wilson & Mahmud, 2015). Particle size can be altered by adding higher concentrations of TEOS and TMOS. Unfortunately, reliable preparation of larger amounts of silica particles and effective control of the reaction mechanism is difficult because of the high cost and rapid hydrolysis and condensation reaction rate of this silica source. Industry would prefer to use an alternative low-cost source of silica such as sodium silicate, which is also known as water glass.

In the drying process of the small droplets containing nanoparticles, evaporation drives the shrinkage of the droplets, and the constituent particles are assembled through particle interaction (Lyonnard et al., 2002). Furthermore, the oscillation of the droplet shape is a basic mechanism for the buckling process of the droplet. It has been observed that the drying process strongly affects the shrinkage of the droplet. When the rate of drying is slow enough, the droplet shrinks in an isotropic manner and the final particle shape remains spherical because of the high internal surface energy. However, if the rate of drying is sufficiently fast, droplet deformation occurs because of its instability. This leads to the formation of non-spherical shapes, such as donut-like particles. The formation of this kind of morphology can be affected by various factors, such as the volume fraction of the precursor. The parameter that determines the formation of particles inside the spray-drying reactor is called the Peclet number (Pe), which is defined as the ratio of the mixing time of the nanoparticles on the droplet to the droplet drying time. A Pe value much greater than 1 is regarded as a fast-drying process, which can produce hollow or donut-like morphologies. However, if $Pe \ll 1$, the drying process is slow enough for the particle to produce a spherical morphology because of isotropical shrinking of the droplet. Therefore, in addition to the volume fraction of the colloidal solution, the drying process plays a role in determining particle morphology.

In addition, the morphology of the synthesized particle through spray drying can be tuned by the physical properties of the drying medium. This tuning of the particle-particle interaction inside the droplets affects the final particle morphology (Qomariyah et al., 2018b). Other parameters, such as the particle concentration inside the initial droplet, droplet size, surface tension and hydrodynamic properties, can affect the sphericity of the final particle morphology (Iskandar et al., 2003; Widiyastuti et al., 2016). Several researchers (Iskandar et al., 2003; Pitchumani et al., 2009) have attempted to control the morphology of silica particles produced by the spray-drying method using sodium silicate solution as the silica source. However, to the best of the present authors' knowledge, none of the studies has considered the morphology change based on the drying process (slow or fast) in the spray-drying reactor. The morphology of particles is an important issue in the application of silica particles. Hollow particles are preferred for inorganic

catalyst, adsorption and gas separation applications. On the other hand, spherical and donut-like particles are desirable for pigments and as carrier particles in drug delivery.

This study was conducted to investigate the morphological transition of droplets consisting of sol silica particles with different volume fractions. It was observed that the morphology transition from spherical to donut-like shapes takes place solely by varying the volume fraction of sol silica particles in the initial droplet. Furthermore, the presence of particle interactions inside the droplets also strengthens the buckling process, even at a slow drying rate. A possible mechanism of the morphological transition is also discussed in this paper. An understanding of the morphological transition of silica particle formation will enable wider application of silica. The use of the spray-drying method is also feasible for large-scale production in industry.

2. METHODS

The schematic apparatus of the tubular heated spray-drying reactor for producing silica particles from a sodium silicate precursor is shown in Figure 1. The main equipment used in the experiment consisted of: (a) an ultrasonic nebulizer (Omron, NE-U17 1.7 MHz) to convert the colloidal solution into droplets; (b) a heated tubular furnace reactor; (c) a compressor to supply the carrier gas; (d) an electrostatic precipitator to collect the particles using a lab-built high-voltage generator; and (e) a water trap to catch the condensed water after the drying process.

The precursor solution was prepared from sodium silicate solution as the silica source. Colloidal silica in alkaline condition was prepared at ambient temperature. Sodium silicate (8 wt% Na₂O, 27 wt% SiO₂, Merck) was diluted in distilled water to obtain the 2%–15% volume fraction colloidal silica solutions, designated as S-2, S-4, S-8, S-10, S-12, and S-15. Subsequently, the diluted sodium silicate was passed through a cation exchange resin (Amberlite™ IR120, Dow Chemical) to remove the sodium ions and form the silicic acid solution. Complete removal of sodium ions was indicated by the absence of gel formation after the cation exchange process. Potassium hydroxide solution (KOH, 0.1 M, 85 wt%, Merck) was added drop by drop to the resulting silicic acid solution. The KOH acted as a base catalyst for the silica particles in the colloidal solution. Meanwhile, the solution was continually stirred at ambient temperature. The gelling structure of the silica was hindered in this case prior to the atomization process leading to the spray-drying reactor.

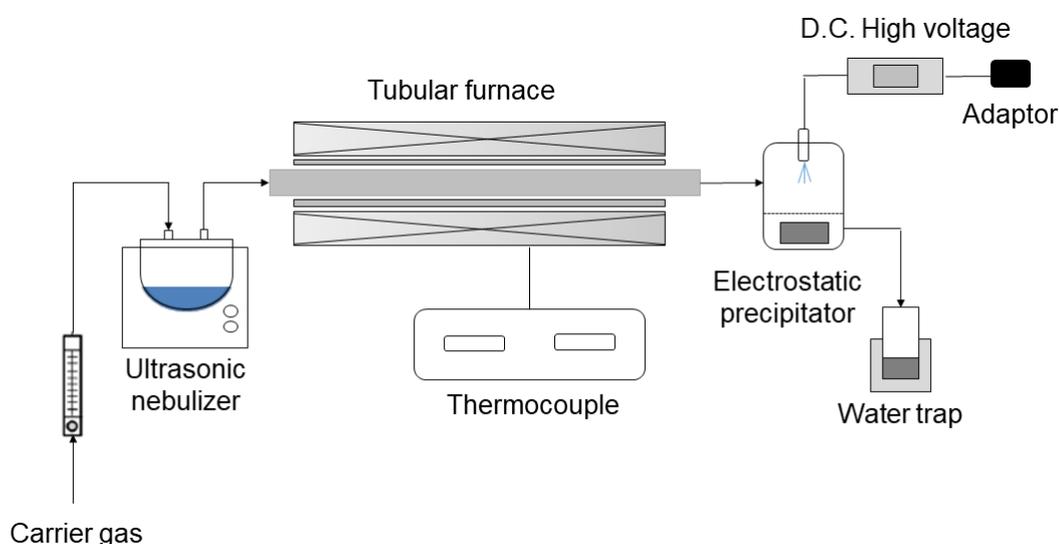


Figure 1 Experimental spray-drying apparatus

The precursor solution was pumped using a peristaltic pump leading to the ultrasonic nebulizer as the droplet generator. Air with a flow rate of 3 mL/min was used as the carrier gas to carry the droplets from the ultrasonic nebulizer to the heated tubular reactor. The heated tubular reactor had two heating zones, but both temperatures were set at 300°C. This temperature was chosen to complete the evaporation of the solvent inside the droplets. Moreover, we considered the melting point of the silica to be under 300°C; the sintering process was thus hindered during the spray-drying process. The reactor was an alumina tube with an inside diameter of 17 mm and length of approximately 800 mm. The evaporation process and the formation of silica particles took place in this reactor. Particles that passed through the furnace were collected in the electrostatic precipitator, which was maintained at 120°C to hinder water condensation.

The morphologies of the silica particles were examined using field-emission scanning electron microscopy (SEM). Dynamic light scattering (DLS) was used to measure the colloidal particle size and ζ -potential of the silica surface charge (Zetasizer Nano ZSP, Malvern Instruments Ltd., Malvern, UK). Fourier-transform infrared (FT-IR) spectra were recorded to investigate the chemical bonding in the silica particles (IRAffinity-1S; Shimadzu Corp. Japan), while X-ray diffractometry (XRD) was used to analyze the crystal structure of the particles.

3. RESULTS AND DISCUSSION

3.1. Morphological Characterization

Figure 2 shows typical SEM photographs of silica particles prepared from the colloidal precursor with volume fractions of 15, 10, 8, 4 and 2%. It is evident that the morphology of the particles comprises a definite spherical shape for S-15 to S-8 (where the concentration of colloidal silica is 15%, 10% and 8%) and is donut-like for S-4 and S-2 (where the concentration of colloidal silica is 4% and 2%, respectively). Furthermore, careful comparison shows that the silica particle morphologies are almost spherical in the case of the S-15 to S-8 samples, even in the larger particle sizes, whereas the S-4 and S-2 samples exhibit donut-like shapes for the larger particles and spherical shapes for smaller ones. This is caused by the increase in volume fraction, resulting in increasing sol silica concentration on the droplet, which causes an increase in droplet stiffness due to the increase in internal surface energy inside it. Therefore, when the volume fraction increases, the two droplet phases (solvent and solute) become stiffer and more stable with the spherical shape.

These observations clearly indicate that the concentration of the initial liquid droplet plays an important role in the transition from the spherical to donut-like morphology of the silica particles during the drying process. In addition, the size of the initial droplets may also play an important role in determining the morphological transition of silica particles. This is proven in the SEM images of S-4 and S-2. A higher droplet size implies droplet instability, which is favorable for the droplet deformation or buckling process. However, the droplet size is too small to deform their spherical shape because of the high internal surface energy, which stabilizes the spherical shape of the droplets.

Deformation of the droplets during spray drying has been conjectured by several researchers. It may occur because of various factors, such as hydrodynamic instability, thermodynamic instability, or particle-particle interactions during droplet drying. In this paper, we discuss the hydrodynamic effect, which is correlated with the drying rate. The Peclet number (Pe) is used to measure the drying strength, which is defined as the ratio of R^2 to $D\tau$, where R represents the droplet radius, D is the diffusion coefficient of the colloidal particles in the droplet, and τ is the droplet drying time. The drying process is regarded as slow if $Pe \ll 1$, and the droplets shrink isotropically throughout the process (Sen et al., 2007). However, for $Pe \gg 1$, the possibility of droplet deformation during the drying process is high because the process is sufficiently fast. The

value of D can be calculated from the Einstein-Stokes relation, $D = k_B T / 6\pi\eta r$, where k_B is the Boltzmann constant, η is the viscosity, and r represents the radius of the sol silica in the precursor solution. The D value was calculated to be 3.4×10^{-10} m²/s. This value was obtained by substituting the parameters $T = 30^\circ\text{C}$ (303 K) and $r = 10$ nm, obtained from DLS analysis of the colloidal silica, as shown in Fig. 3(a), and $\eta = 6.49 \times 10^{-4}$ Pa s (this value assumes the viscosity of pure water to be 303 K).

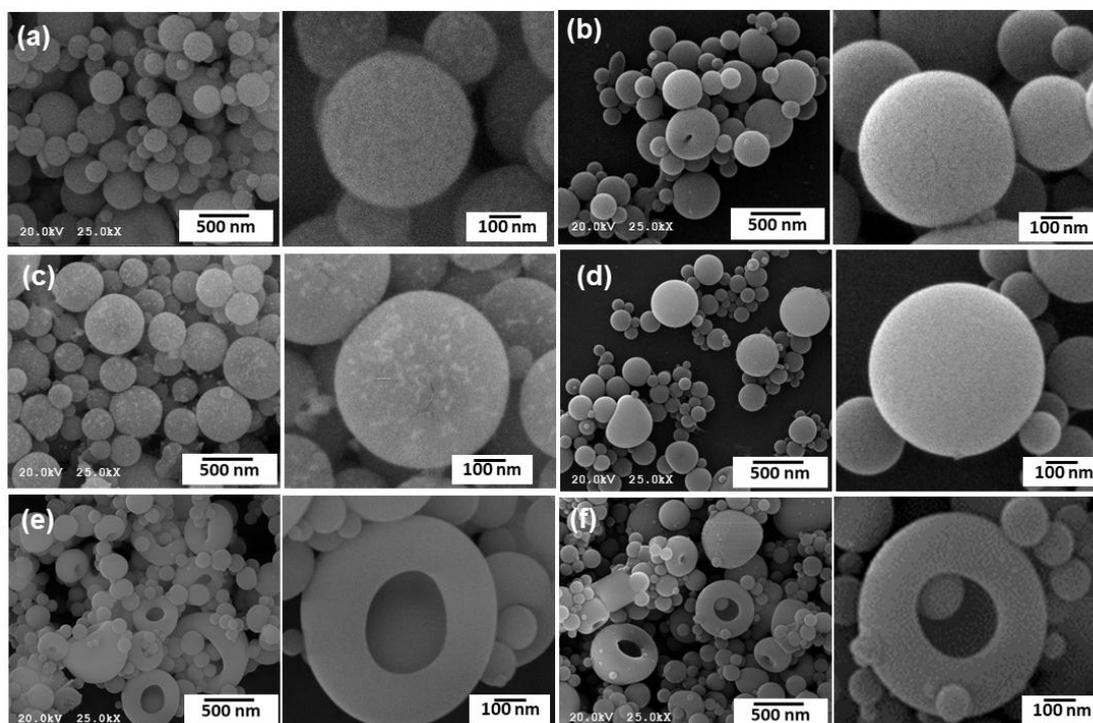


Figure 2 SEM images of silica particles prepared using colloidal precursors containing different volume-fraction silica: (a) 15%; (b) 12%; (c) 10%; (d) 8%; (e) 4%; and (f) 2%

The drying time (τ) can be calculated from the tube geometry, which was 800 mm in length and 17 mm in diameter, with a gas flow rate of 2 L/min. In this apparatus, the velocity of the carrier gas was calculated to be 0.147 m/s. Hence, the droplet drying time was 5.4 s. From this value, we can calculate the Pe number as 5.4×10^{-4} . This value, of course, is less than unity. It is notable that for a very fast drying process, Pe may be as large as 2000. However, the product morphology of silica in this case indicates that even at this intermediate drying rate, the morphological transition process takes place. This calculation was also made by Sen et al. (2009) in a spray-drying system using a different precursor.

3.2. Colloidal Solution Characterization

Photographs of the colloidal silica precursors used in the spray drying are shown in Figure 3. The volume fraction was varied from 15% to 2% by adding a different amount of sodium silicate solution. The transition of the color of the colloidal silica from milky to transparent indicates that the volume fraction has changed from high to low; the different colors indicate different sol silica concentrations in the solution. However, a higher volume fraction of sol silica was prevented prior to the atomization process (Eslamian & Ashgriz., 2006; Chang et al., 2008). If the gelling structure forms, it is difficult to atomize the precursor solution using an ultrasonic nebulizer. Higher volume fractions, such as 20%, tended to form a gelling structure on the colloidal solution in this study. Therefore, the maximum volume fraction used in this spray-drying method was 15%.

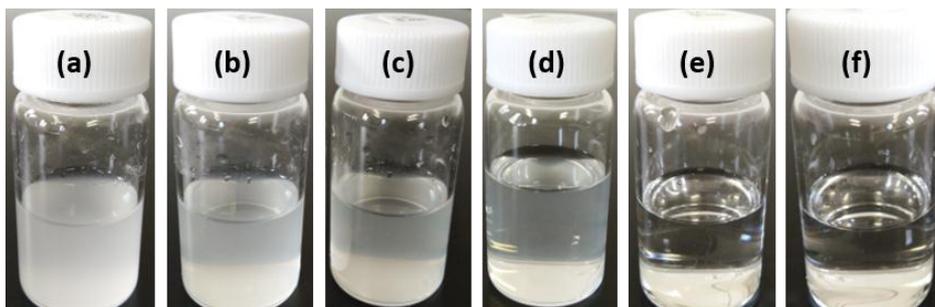


Figure 3 Photographs of colloidal silica precursors prepared at different volume fractions: (a) 15%, (b) 12%, (c) 10%, (d) 8%, (e) 4%, and (f) 2%

Further attempts to investigate the donut-like particle formation were made by measuring the sol silica size in the colloidal solution. The volume fraction of sol silica inside the colloidal solution also affected the sol silica size, as shown in Figure 4a. Higher volume fractions correspond to increasing sol silica size. The sol silica particle sizes increased from 6 to 12 nm as the volume fraction increased from 2 to 8%. This phenomenon can be explained by the silica formation in the colloidal preparation. The formation of sol silica in a colloidal solution is initiated by the polymerization of mono silicic acid. At an ambient temperature, mono silicic acid is soluble in water for long periods of time under unsaturated concentration. As saturated (or greater) concentration is achieved, the mono silicic acid is formed as SiO_2 , and in the absence of a solid phase on which the soluble silica might be deposited. Potassium hydroxide also acts as a catalyst to support the formation of sol silica. Subsequently, the monomer polymerizes by condensation to form a dimer and higher molecular species of silicic acid. In addition, the presence of a negative charge from the hydroxyl ions between the sol particles causes a repulsive interaction between the particles; hence, the sol particles grow continuously without collision. The increasing volume fraction is followed by an increasing quantity of solid-phase silica particles in the colloidal solution, which leads to the increasing size of the sol silica.

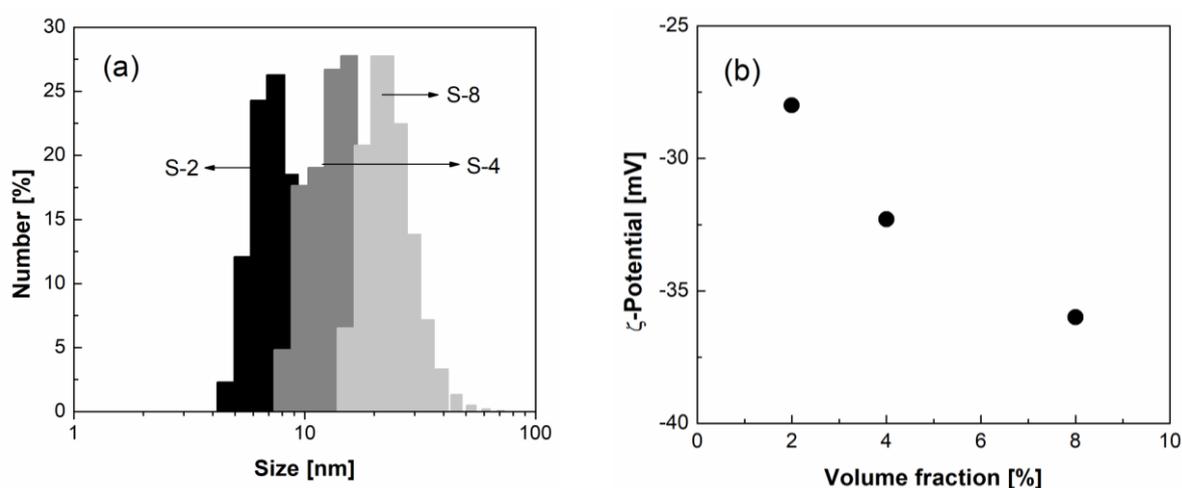


Figure 4 (a) Dynamic light scattering (DLS) data; (b) ζ -potential values for the colloidal silica samples with different volume fractions

Another factor that affects the buckling process of the droplet is particle-particle interaction. A surface charge approach was used to explain the morphological transition of the silica particles. Dynamic light scattering (DLS) was performed in order to measure the ζ -potential of the silica particles in the colloidal solution. As shown in Figure 4b, the different concentrations of silica particles exhibit different ζ -potential values. The zeta-potential value ranged from approximately

–28 mV to –35 mV. The same charge of the sol particles inside the droplets causes the repulsive interaction between them. This causes the formation of the donut-like particles with a central hole when the low volume fraction is applied. The repulsive interaction between particles does exist at higher volume fractions, but the inherent spatial constraint at higher volume fractions forms the spherical morphology. Further, the increase in the volume fraction (ϕ) of the solid particles inside the droplet causes an increase in droplet stiffness due to the increase in internal surface energy inside the droplet.

3.3. Particle Formation Mechanism

From these two observations, it is evident that the buckling process is strongly affected by hydrodynamic instabilities and particle-to-particle interaction. The initial spherical shape of the droplet shrinks isotropically, although densely packed particles are formed at its surface. Droplet shrinkage occurs because of the thermophoretic forces which are generated by the local temperature gradients created on the droplet surfaces. This is followed by the displacement of the sol towards the peripheral region on the surface of the droplet. In addition, the repulsive interaction force also supports sol displacement. The inertial effect is enhanced, which causes stronger deformation of the droplet towards the donut-like shape with a central hole (Iskandar et al., 2003). Because this process significantly depends on the volume fraction, a lower density of particles on the droplet is favorable for the donut-like formation. In the case of spherical shape formation, the higher density hinders the buckling process because of the inherent constraints of availability of space. A schematic representation of the particle formation is shown in Figure 5.

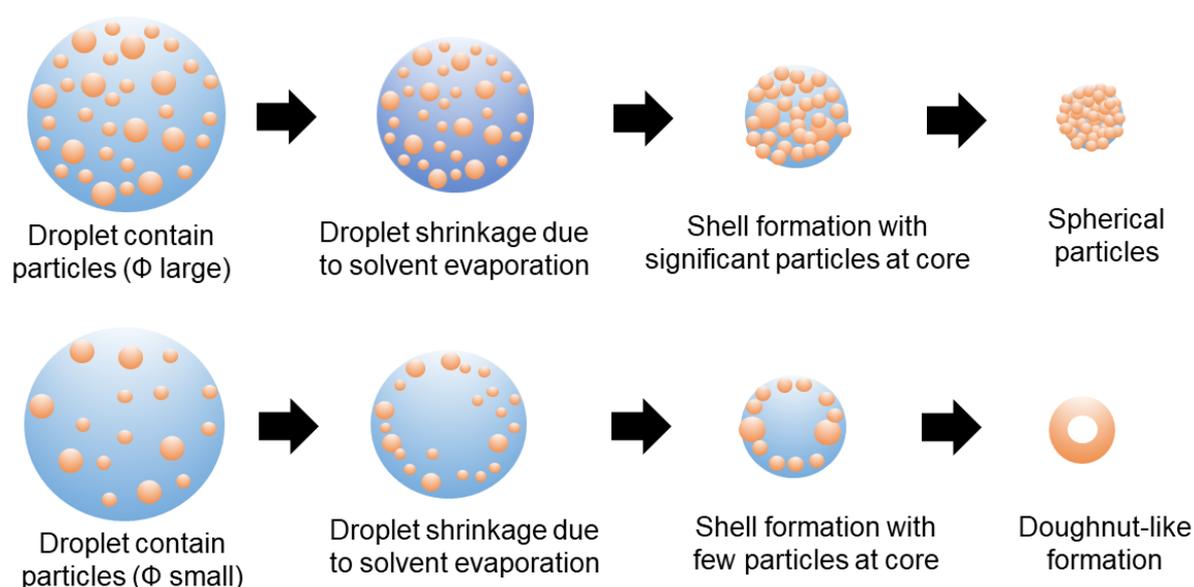


Figure 5 Particle formation mechanism during the drying process for small and large volume fractions

The formation of the donut-like particles can be explained from the viewpoint of the kinetics of silica formation while travelling along the tubular reactor. The droplet contains some sol silica particles with nanometer size. The mechanism potentially contributing to the donut-like particle formation is an electrostatic interaction between the sol particles inside the droplet. The repulsive interaction between sol particles causes the sol silica to move towards the peripheral region of the droplet. Therefore, the central region of the droplet is free from sol particles and donut-like particles are formed.

The movement of sol particles inside the droplet also depends on the size of the primary ones. The sol particle size measurements are shown in the DLS measurement results in Figure 4a. Smaller particles tend to move to the outer part of the droplet, while the larger ones remain in the

inner part (Iskandar et al., 2003). This is caused by the stronger thermophoretic displacement of the smaller particles compared to that of the larger ones. As a result, donut-like particles are produced at a low volume fraction, which has a smaller sol particle size.

3.4. Chemical Bonding and Structural Characterization

The chemical bond of the synthesized particles was also investigated, as shown in the FTIR analysis results of the selected silica particles for different volume fractions in Figure 6a. The FTIR spectrograms of powder silica particles were in transmittance mode, in the wave number range of 700 to 3800 cm^{-1} . We choose the S-8 sample, which has a spherical morphology, and S-4 and S-2 for the donut-like particle morphology. There was a strong absorption peak near 1071 cm^{-1} in all the samples, which indicates asymmetric vibration of Si-O-Si from the silica shells. The band near 790 cm^{-1} indicates the bending vibration of Si-O. These results show that a dense silica network was formed. The bending of O-H caused by the absorbed water is represented by the peak near 1510 cm^{-1} , and the peak representing the stretching of O-H can be seen near 3600 cm^{-1} . The FTIR result clearly confirms the presence of a silica network in the production of silica particles by the spray-drying method. The values in the FTIR spectra agree closely with those of previous studies (Widiyastuti et al., 2014). All the silica particles with spherical and donut-like morphologies exhibit the same peaks in the FTIR spectra.

The crystallinity of the produced particles was also examined using XRD analysis, which was conducted in the range of 10° to 60°. Figure 6b shows the XRD pattern of the selected silica particles, which were prepared at volume fractions S-8, S-4 and S-2 in different solution concentrations. All the selected silica particle results show that the particles obtained in this experiment had an amorphous phase. The XRD patterns did not have a sharper or significant peak, which would indicate the crystalline phase of the silica particles. Other parameters to control particle size and morphology, such as the hydrodynamic effect and other physical properties of the colloidal silica solution, need to be further investigated. However, our preliminary results suggest that the colloidal precursor condition greatly affects particle size and morphology.

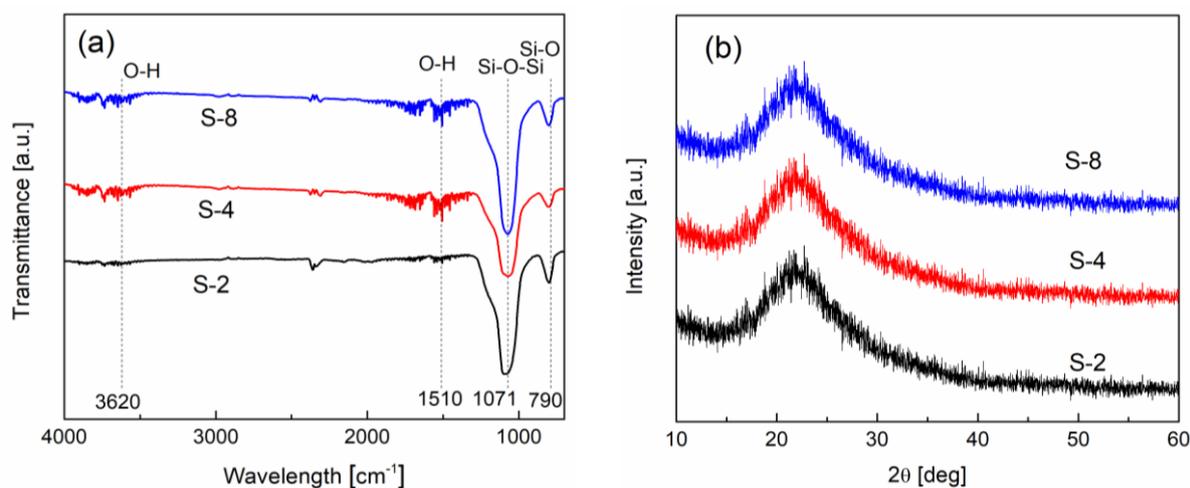


Figure 6 (a) FTIR and (b) XRD analysis of selected powder silica particles S-8, S-4 and S-2

4. CONCLUSION

The morphological transition of silica particles from spherical to donut-like particles was investigated regarding the dependence on volume fraction, which varied from 15% to 2%. Sodium silicate solution was used as the silica source. Even at a slow drying rate, the buckling process took place by hydrodynamic and particle-particle interactions, which eventually caused

the morphological transition when the colloid volume fraction was small. The spherical particles formed at colloidal volume fractions of between 15% and 8%, whereas the donut-like particles formed at lower volume fractions (4% to 2%). However, the higher colloid volume fractions of between 8% and 15% are favorable for spherical-shaped particle formation, because of the inherent constraints on space availability; the morphological transition to the donut-like shape is hindered. Particle interaction in the droplets containing sol silica particles also plays an important role in the formation of donut-like morphology. FTIR analysis revealed that the silica particles were formed by the presence of siloxane bonding in all the samples. XRD analysis also proved the formation of silica particles with an amorphous phase. This preparation method offers an economical approach that exploits an abundant and cheap material, sodium silicate, and the well-understood spray-drying technique. Furthermore, the method is suitable for economical and large-scale production of silica powder.

5. ACKNOWLEDGEMENT

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