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New approach for the control of size and surface characteristics of mesoporous silica particles by using mixed surfactants in W/O emulsion

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Abstract

Mesoporous silica micro-spheres have been prepared using an emulsion-gel method in W/O emulsion consisting of aqueous solution of SDS or Tween 20 and *n*-octanol of hydroxypropyl cellulose (HPC) and Span 80. The morphology of water droplets in W/O emulsion was controlled by the concentration of the water-soluble surfactants of SDS and Tween 20 and the oil-soluble surfactant of Span 80. Since water droplets serve as a supporting structure for particle growth and aggregation, their morphology influences the shape, size, and size distribution of particles. When 3 wt.% and 5 wt.% of Span 80 were employed in our system, the effect of surfactant on the particle size distribution was more prominent than when 7 wt.% was used. Anionic surfactants were hardly used in aqueous phase to make mesoporous silica particles and one or more water-soluble surfactants were only used in aqueous phase to control the shape of particles. Interestingly, the particles of mesophase structure were synthesized when the anionic surfactant, SDS, was added to the water phase and the nonionic surfactant, Span 80, was employed in the oil phase. As the concentration of SDS and Tween 20 increases, the pore size of samples is altered from 7.2 nm up to 44.4 nm. This change of surface morphology occurred due to the solubilization ability of water-soluble surfactants. Moreover, depending on whether the anionic surfactant or nonionic surfactant is used, the degree of the change in pore size distribution of silica particles is relatively different. When SDS is used, the maximum peaks of the pore size distribution are located on the right rather than those in silica particles prepared using Tween 20. The structure of these materials was characterized by optical microscope, field-emission scanning electron microscopy, and nitrogen adsorption and desorption (BET isotherms and BJH pore size distribution measurements).
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Keywords: Silica; Mesoporous; Mixed surfactant; W/O emulsion; Solubilization

1. Introduction

Over 10 years after the discovery of micelle-templated mesoporous materials [1], great efforts have been made to modify a control of mesoporous structures within the range of 2–50 nm such as SBA-15 [2], MSU-n [3], and other mesoporous materials. These materials have been approached on their versatile application in catalysis [4], separation [5], and drug delivery [6]. Generally, sol–gel synthesis [7] in surfactant micelles template usually involves a subtle balance of cooperative thermodynamic and kinetic mechanisms. Mesoporous materials are based on the interactions between micelles that are influenced by the concentration of surfactant and the synthesis condition. In this phenomenon, different shapes of framework such as hexagonal [2], cubic [8], or 3D wormhole [9] are obtained and they are important factors in the formation of mesoporous materials.

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Recently, one of the interesting subjects in mesoporous materials is the synthesis of mesophase structures with controllable morphologies for the purpose of industrial applications. Since the first study in which the formation of M41S-type mesoporous silica spheres was reported through a modification of Stöber's procedure [10], many kinds of mesoporous silica spheres have been introduced. The preparation of spherical mesoporous particles in the micrometer-size range has received much attention because of packing easily into reactors, columns, or diverse systems. Therefore, mesoporous spheres with micrometer size would be more preferred in broad applications than mesoporous materials with uncontrolled structures. Moreover, various hollow mesoporous silica spheres have been obtained by nonionic emulsion [11] or at the air/water interface [12].

Many electrostatic charge-matching pathways have been introduced to synthesize the mesostructed silica. The $[S^+I^-]$ and $[S^+X^-I^+]$ pathways have found a wide application in the synthesis of silica-cationic surfactant mesophases. The formation of silica-nonionic surfactant mesophases has been reported to follow a $[S^0I^0]$ pathway [13]. A similar pathway, defined as $[S^0H^+][X^-I^+]$ using poly-(ethylene oxide) (PEO) nonionic surfactant templating, has been proposed for the fabrication of silica-nonionic surfactant mesophases at low pH [14]. The $[S^-I^+]$ and $[S^-X^+I^-]$ pathways involving anionic surfactants have been developed essentially for the preparation of alumina or transition metal oxide phases [15].

In particular, using two or more different types of surfactants as soft-templates were more advanced methods and the exploitation of this knowledge in the preparation of materials has provided a variety of reliable and flexible methods to control pore size and other properties. Kushalani et al. [16] used a mixed system of two cationic surfactants as a template. Ryoo et al. [17] tested cationic surfactants with different length of nonionic surfactants, and Chen et al. [18] used the mixture system of cationic and anionic surfactants with a low surfactant-to-silica molar ratio and surfactant concentration. Also, Antonietti et al. [19] showed that the size of mesopores and the microporosity depends on a fraction of the PEO block lengths or volumes. Dai et al. [20] reported the synthesis of mesoporous silica using mixtures of cationic surfactant and nonionic surfactant. In above-mentioned synthetic methods, the pore sizes were controlled by changing the molar ratio of surfactant mixtures or by increasing the chain length of nonionic surfactant, and those silica particles were synthesized in the aqueous phase using only water-soluble surfactants.

It is important in the synthesis of porous materials that the products have a controllable pore size and particle size. Although using surfactants or their mixtures in the aqueous solution is very effective in controlling the size of mesopores and microporosity, it hardly influence the control of the size of mesoporous silica particles with controllable morphology like silica sphere, simultaneously. However, in this paper, we describe the synthesis of silica particles that involve mixed surfactants, oil-soluble surfactant and water-soluble surfactant, in two phases of W/O emulsion, instead of the aqueous phase in pre-mentioned papers. Through utilizing the emulsion technology, it is possible to increase the particle size to some micrometers and control the surface morphology of silica particles. The porous silica micro-spheres were formed by means of using an inorganic silica precursor with surfactants in two different phases under basic condition. It was observed that the concentration of anionic surfactant or nonionic surfactant could lead to changes in pore sizes and surface morphology.

2. Experimental section

2.1. Materials and synthesis

Tetraethyl orthosilicate (Si–(OC$_2$H$_5$)$_4$, TEOS) as a silica source, hydroxypropyl cellulose (HPC, average M_w ca. 370,000, Scheme 1a) as a stabilizer of emulsion, and SDS and Tween 20 (Scheme 1b) as a high HLB surfactant were purchased from Aldrich Chemical Company. The 1-octanol as an oil phase was obtained from Junsei Chemical Company. Sorbitan monooleate (Span 80, Scheme 1c) as a low HLB surfactant was purchased from Sigma Chemical Company. Ammonium hydroxide (NH$_4$OH, 25%+) as a catalyst was purchased from Wako pure chemical industry. All commercial chemicals were used without further purification. Water was purified using a Milli-Q reagent water system.

Mesoporous silica spheres were synthesized according to the two-step reaction process. The precursor solution was used; one was based on a hydrophobic TEOS solution and the other was based on a basic aqueous solution. Hydroxypropyl cellulose (HPC) was dissolved in 1-octanol at 80 °C. This solution was cooled to 40 °C and then 3 wt.% of sorbitan monooleate (Span 80) was mixed. SDS or Tween 20 was dissolved in deionized water containing NH$_4$OH. After complete dissolution, the emulsion was prepared by addition of the basic aqueous solution to the oil phase under moderate magnetic stirring. The weight ratio of water phase to oil phase in emulsion was kept as 1:9. After the W/O emulsion was formed, TEOS of $R_w = 10$ (R_w = the molar ratio of water to TEOS) was added to a previously prepared W/O emulsion to initiate the sol–gel reaction for the synthesis of silica micro-spheres. Added TEOS molecules were reacted with water droplets for 6 h. The reaction temperature was maintained at 40 °C. The final products were washed repeatedly with ethanol and kept at room temperature for 24 h, and then calcined at 600 °C for 3 h in air.
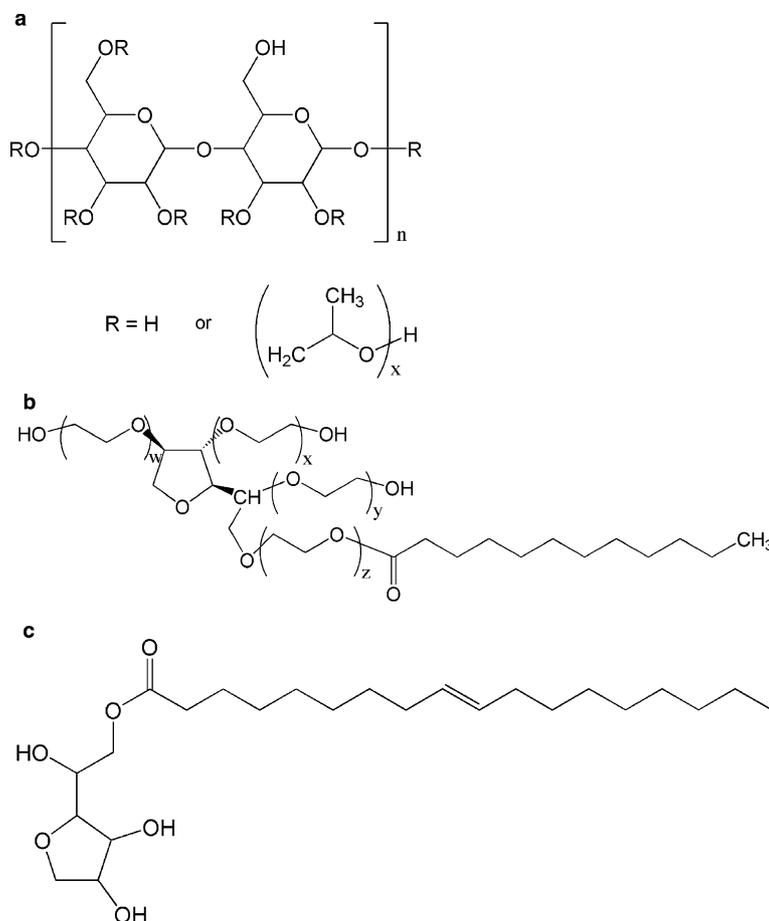
Scheme 1. Molecular structures of HPC (a), Tween 20 (b), and Span 80 (c).

2.2. Characterization

To estimate the size of the water droplet in W/O emulsion, we used an optical microscope (OM) with a camera (Optiphot-2, Nikon) just after the W/O emulsion formation. Field emission scanning electron microscopy (FE-SEM) images were obtained with a JEOL JSM-6700F. Nitrogen adsorption–desorption measurements at 77 K were performed on ASAP 2000 (Micrometric, Norcross, GA) BET surface analyzer system. Before the measurements, the samples were outgassed at 100 °C for 3 h. The pore diameter and the pore size distribution (PSD) were determined by the BJH (Barret, Joyner, Halenda) method [21]. Although it is well-known that this method gives an underestimated pore size and that some new methods like NLDFT have been developed [22,23], we use it here for the sake of simplicity. Moreover, mathematical algorithm will not affect significantly the systematic comparison of PSDs depending on the kind and the concentration of surfactants. Also, PSD curves were obtained from the analysis of desorption branch of the isotherm because PSDs estimated from desorption branch more exactly showed their change tendency, though a little difference between

pore sizes measured from adsorption branch and desorption branch exists.

3. Results

3.1. Control of particle size

The effects of concentration of SDS and Tween 20 in water phase and the weight ratio of Span 80 in oil phase on particle size were investigated. As shown in Figs. 1 and 2, it is obvious that the particle size of the silica micro-spheres strongly depends on the size of water droplets in emulsion. The concentration of Span 80 dissolved in each sample was fixed, while the weight ratio of water-soluble surfactants (SDS and Tween 20) was altered. To estimate the size of water droplets in W/O emulsion, we observed the water droplets directly by an optical microscope. Fig. 1 shows the images of W/O emulsions recorded by an optical microscope under several respective conditions. The water droplets from a W/O emulsion in Fig. 1b are clearly larger than those of other emulsions shown in Fig. 1c–f. It is found that the size of water droplets in the W/O emulsion (Fig. 1)
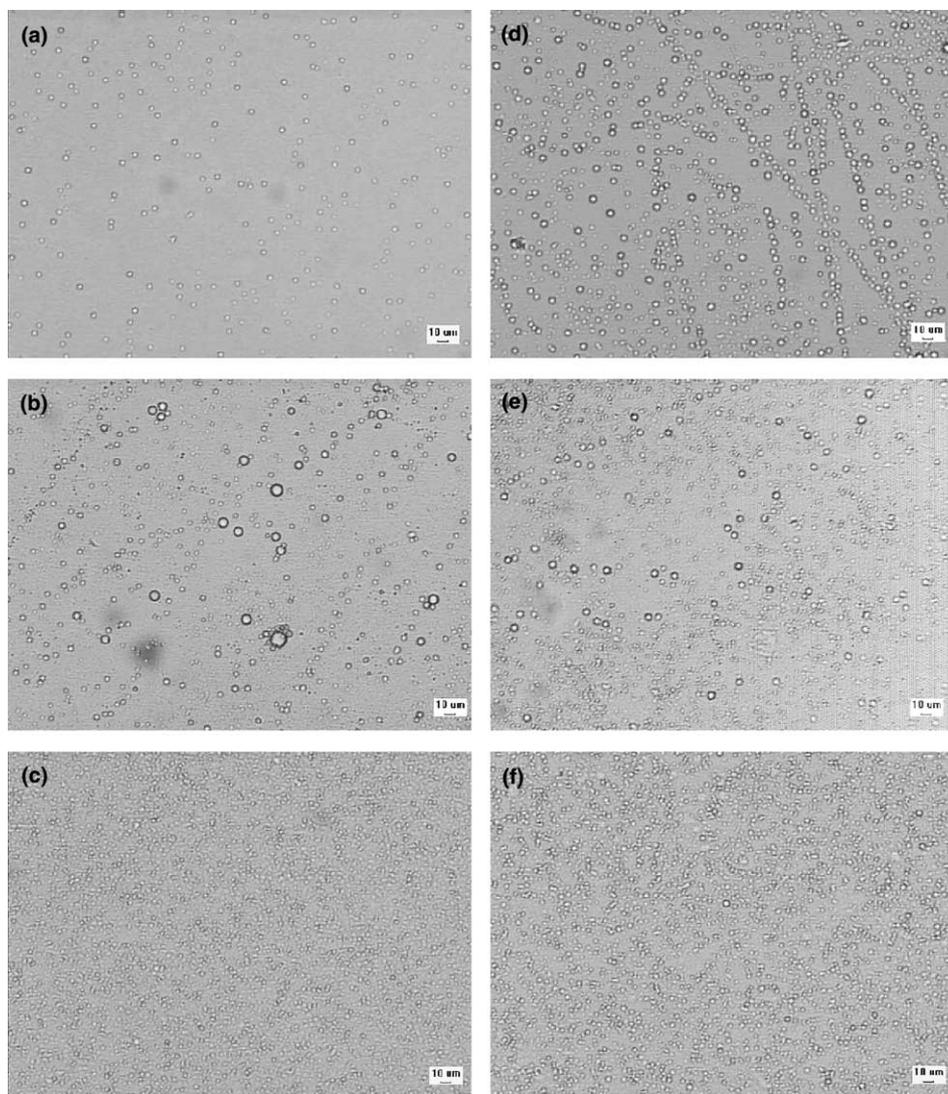
Fig. 1. Optical microscope images of water droplets in W/O emulsions formed under various conditions. The scale bars are 10 μm. (a) SDS 3% Span 3%, (b) SDS 5% Span 3%, (c) SDS 10% Span 3%, (d) Tween 3% Span 3%, (e) Tween 5% Span 3% and (f) Tween 10% Span 3%.

were influenced by the concentration of SDS or Tween 20.

The silica micro-spheres prepared by these emulsions are summarized in Fig. 2, indicating that the particle sizes of the micro-spheres are changed with the weight ratio of surfactants. When 3 wt.% and 5 wt.% of Span 80 were employed in our system, the effect on the particle size distribution was more prominent than when 7 wt.% was used. These results conclude that 7 wt.% of Span 80 is not successful for the control of the particle size of the silica micro-sphere in the emulsion. Also, in the case of 3 wt.% of Span 80, the particle size increased as the following order of the concentration of the water-soluble surfactant; 5 wt.% > 10 wt.% > 3 wt.%. However, in 5 wt.% of Span 80, the order is changed as follow: 3 wt.% > 10 wt.% > 5 wt.%. The range of particle size was less than about 6 μm.

3.2. The characterization of surface morphology of mesoporous silica micro-spheres

Some SEM pictures of typical samples prepared at different conditions are shown in Fig. 3 and others are shown in Fig. S-1 in the Supporting Information. All samples are calcined at 600 °C for 3 h. When 3 wt.% of SDS or Tween 20 is used, the pore size of silica particles is the smallest of all samples and the maximum peak of the pore size distribution is located at the most left-side. On the other hand, as the concentration of water-soluble surfactants increases, the larger pores were observed at the surface and inside silica particles. All samples clearly exhibit completely different surface morphology depending on the surfactant concentration. The nitrogen adsorption–desorption isotherms of the samples in Fig. 3 are reported in Fig. 4
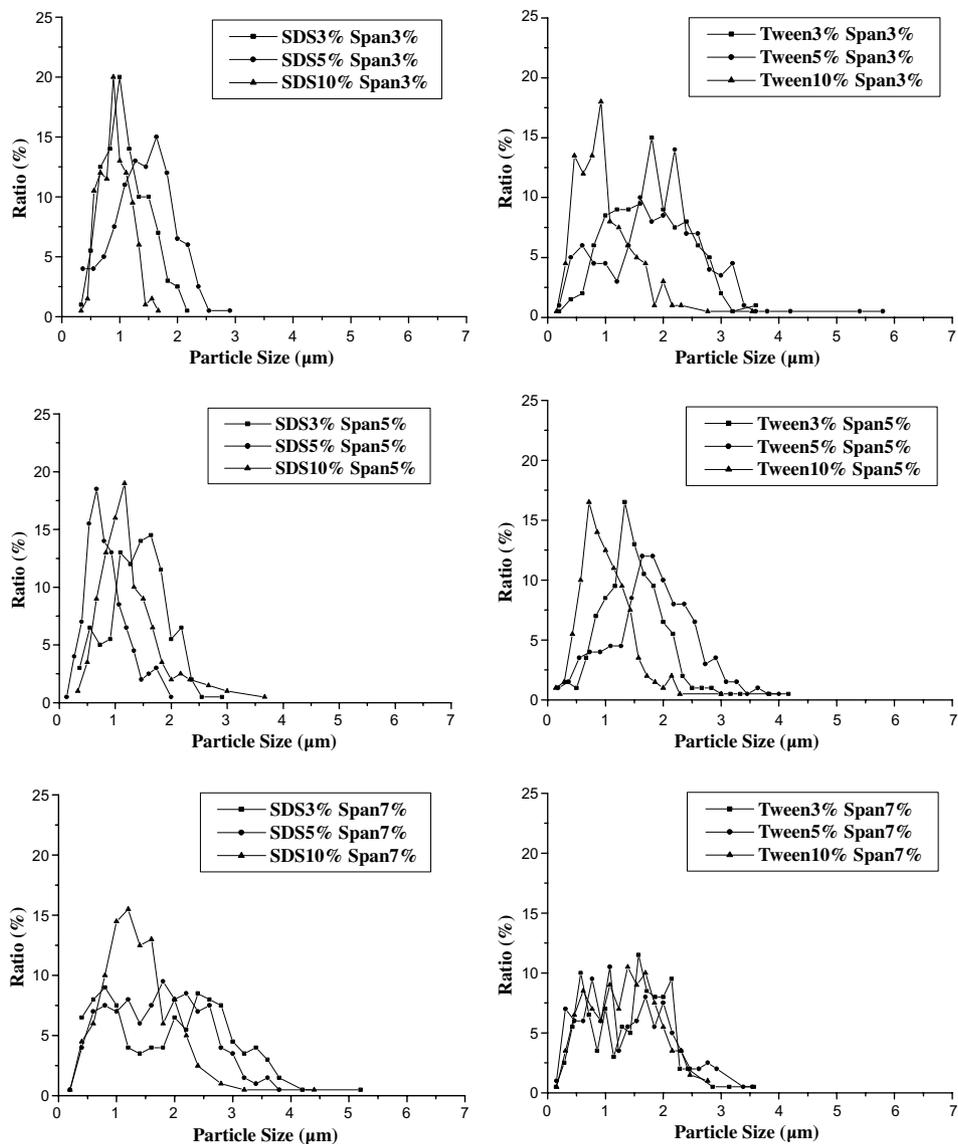
Fig. 2. Particle size distribution of silica samples in W/O emulsions formed under various conditions.

and other isotherms are shown in Fig. S-2 in the Supporting Information. As the concentration of surfactants increases, the adsorption step shifts toward high pressure, characteristic of an increasing pore size. All of the isotherms present a Type IV shape, characteristic of mesopores, with a desorption loop due to the nitrogen condensation within mesopores. As recommended in the IUPAC manual, a classification of hysteresis loops is characterized as H1 type [24]. Under various concentrations of surfactants, the surface area varies from 39 to 331 m^2/g and the pore volume from 0.46 to 1.05 cm^3/g (Tables 1 and 2). Fig. 5 shows the pore size distribution of the mesoporous products. The pore size was expanded with an increase of the concentration of the surfactant under the same reaction condition, as summarized in Tables 1 and 2. The

enlargement is also meaningful, since it can vary from 7.2 nm to 44.4 nm regularly, only by varying the surfactant between 3 wt.% and 10 wt.%.

Fig. 6 shows the effect of the concentration of Span 80 on the pore size of silica particles. When 3 wt.% and 5 wt.% of Span 80 are used in the emulsion medium, the increase of the concentration of water-soluble surfactants strongly influences the increase of the pore size and pore size distribution of silica micro-spheres. However, in the case of using 7 wt.% of Span 80, this relationship is reduced and the pore sizes are similar and increase smoothly.

The XRD patterns for well-ordered mesoporous silicas such as SBA-15 and MCM-41 exhibit several pronounced peaks indicating high structural ordering [25,26]. However, the XRD patterns for mesoporous
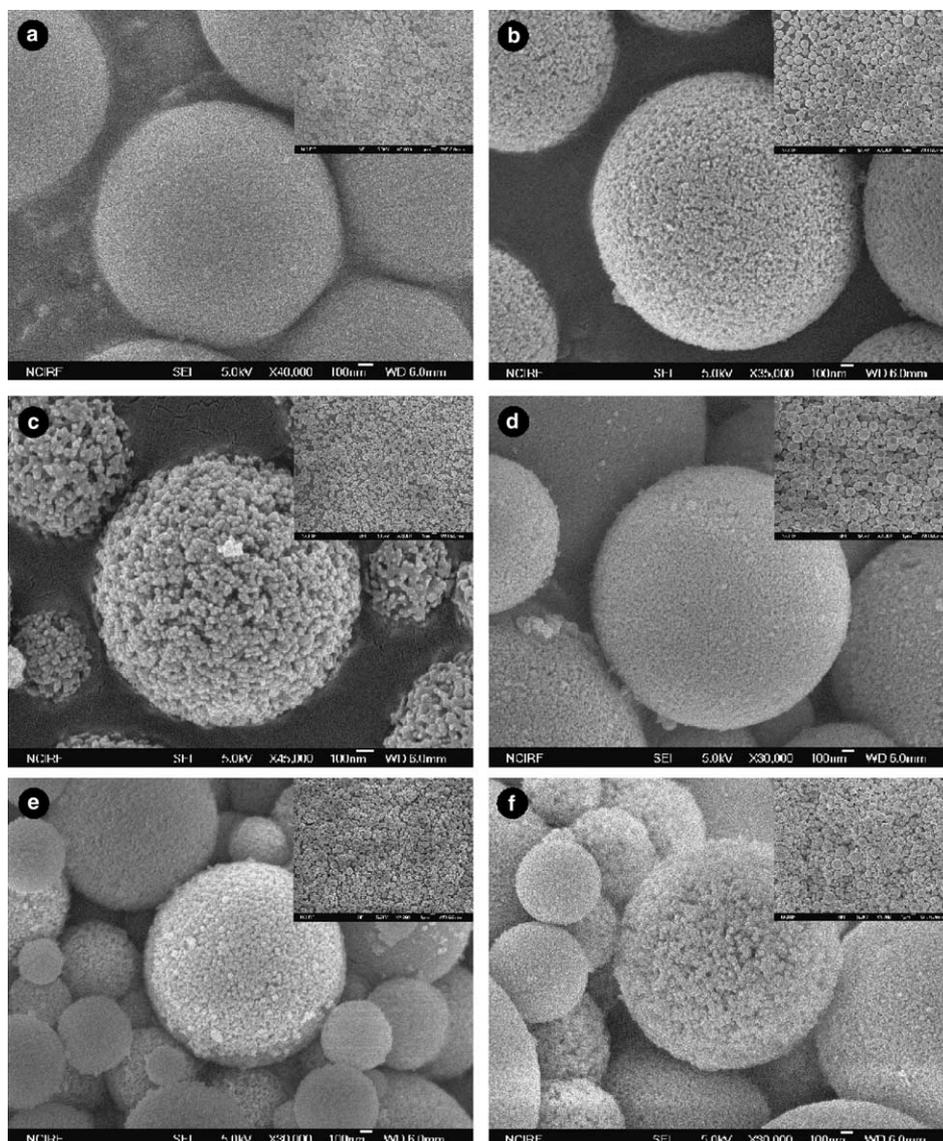
Fig. 3. FE-SEM micrographs of typical samples of which the names are denoted in Tables 1 and 2. Each scale bar is equal to 100 nm and 1 μm (inset).
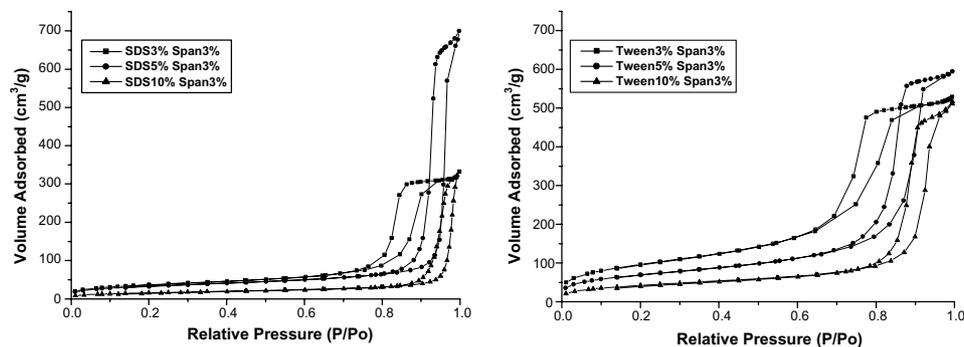

Fig. 4. Nitrogen adsorption–desorption isotherm of typical silica samples prepared using various concentrations of surfactants in W/O emulsion.

silica micro-spheres prepared in our system exhibited no peaks of ordered structure, even in the low angle. These results show that all samples are amorphous even in nano-level.

Table 1

Physicochemical properties of mesoporous silica micro-spheres synthesized with SDS and Span 80

Sample name	Species[a]	Surface area (m^2/g)	Pore diameter[b] (nm)	Pore volume[c] (cm^3/g)
a	SDS 3% Span 3%	155	12.9	0.69
b	SDS 5% Span 3%	115	25.7	1.05
c	SDS 10% Span 3%	55	31.8	0.48
d	SDS 3% Span 5%	141	19.4	0.96
e	SDS 5% Span 5%	104	30.0	0.92
f	SDS 10% Span 5%	39	44.4	0.46
g	SDS 3% Span 7%	219	13.3	0.92
h	SDS 5% Span 7%	202	14.2	0.91
i	SDS 10% Span 7%	198	14.4	0.88

[a] In water/in oil weight ratio.
[b] The pore size distribution was determined by Barret–Joyner–Hallenda method when indicated.
[c] The total porous volume was determined as the total adsorbed volume for $P/P_0 \approx 0.99$.

Table 2

Physicochemical properties of mesoporous silica micro-spheres synthesized with Tween 20 and Span 80

Sample name	Species[a]	Surface area (m^2/g)	Pore diameter[b] (nm)	Pore volume[c] (cm^3/g)
j	Tween 3% Span 3%	331	7.2	0.81
k	Tween 5% Span 3%	240	12.2	0.91
l	Tween 10% Span 3%	146	16.4	0.77
m	Tween 3% Span 5%	257	10.1	0.84
n	Tween 5% Span 5%	250	11.0	0.87
o	Tween 10% Span 5%	218	13.6	0.87
p	Tween 3% Span 7%	246	13.2	0.99
q	Tween 5% Span 7%	231	12.4	0.83
r	Tween 10% Span 7%	196	14.3	0.76

[a] In water/in oil weight ratio.
[b] The pore size distribution was determined by the Barret–Joyner–Hallenda method when indicated.
[c] The total porous volume was determined as the total adsorbed volume for $P/P_0 \approx 0.99$.

4. Discussion

4.1. Preparation of silica particles in W/O emulsion

In 1968, Stober et al. [27] reported that the hydrolysis reaction of tetraethyl orthosilicate (TEOS) in alcoholic solutions could be controlled under basic condition to produce monodisperse sub-microsized spherical particles of amorphous silica. Since then, this technique generally available for the synthesis of many inorganic particles has been broadly introduced.

In contrast to the homogeneous system, emulsion medium of heterogeneous system has been utilized to obtain microsized silica particles. An emulsion is the stable suspension of particles of liquid of a certain size within a second, immiscible liquid. It is well known that an emulsion is generally formed and stabilized by adsorbing surfactants, polymers, proteins, solid particles, or their mixtures onto immiscible liquid–liquid interfaces. Emulsions such as macroemulsion, microemulsion, and multiple-emulsion have been extensively studied in the various fields like medicine, pharmaceutics, food products, and cosmetics. Recently, they serve as the medium to synthesize inorganic particles for the

purpose of drug delivery [11]. In our previous studies, W/O emulsion was used to synthesize the spherical silica particles with dimple [28] or hollow structure [29]. Under our reaction conditions, the TEOS molecules are dissolved in oil phase (1-decanol or 1-octanol), but the hydrolysis and condensation reaction takes place not in the oil phase but in the W/O interface and within the aqueous droplets which act as model micro-reactors.

Hydroxypropyl cellulose (HPC) plays an important role in preparing spherical silica particles. First, HPC polymer prevents phase separation and increases the stability of W/O emulsion during the reaction process. As the concentration of HPC increased, the stability of W/O emulsion increased. However, HPC polymer below 1.4 wt% of the oil phase was used in our system because, above this concentration, the solution was so viscous that it was difficult to handle. Second, TEOS molecules are very oil-soluble but the flux of mineral precursors into water droplets is limited by HPC polymer. Since HPC polymer chain swells in the oil phase and increases the viscosity, they limit the excessively fast penetration of TEOS molecules throughout the interface of water droplets. The $Si(OH)_x(OCH_2CH_3)_y$ molecules
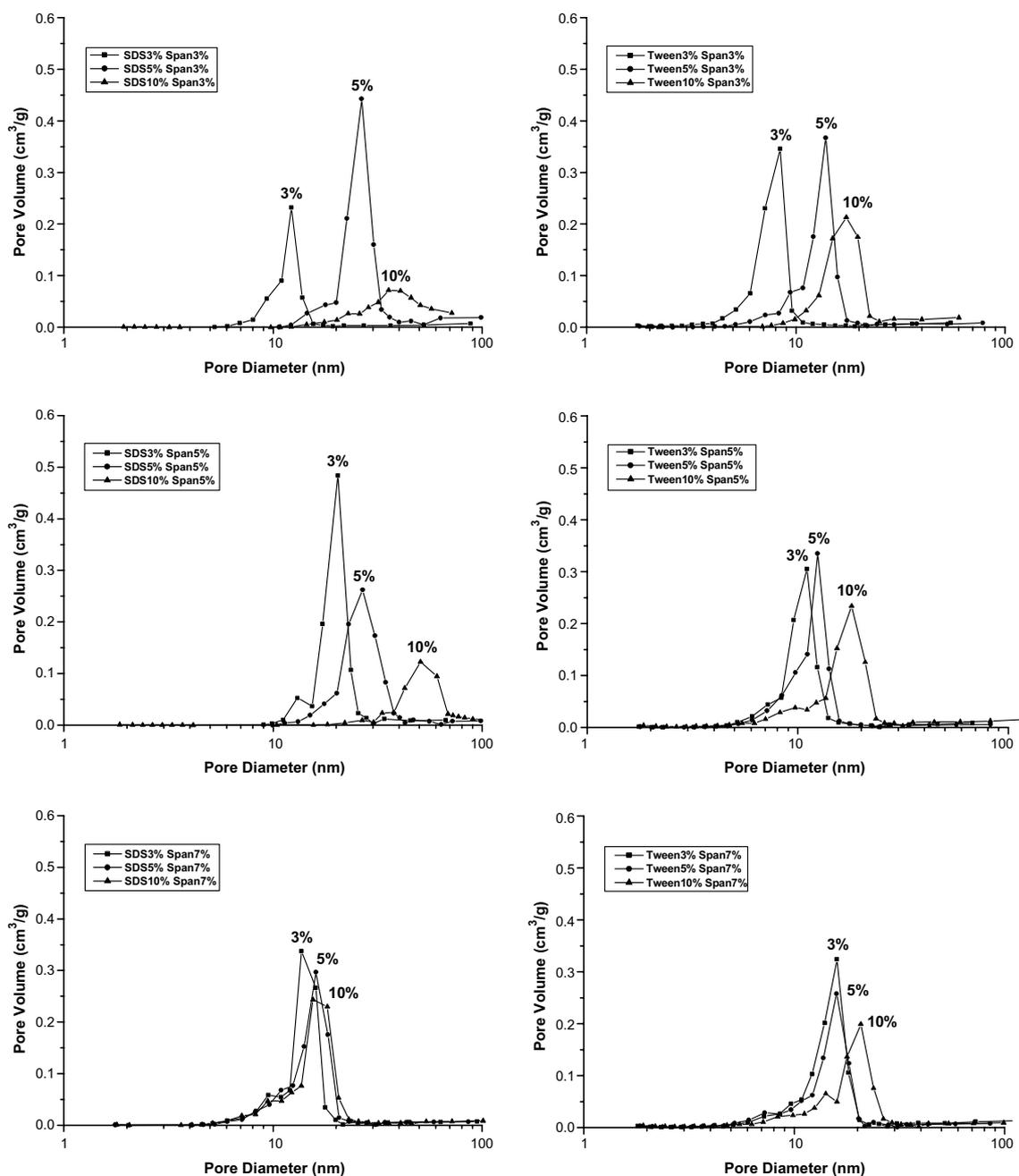
Fig. 5. Pore size distribution of silica samples prepared using various concentrations of surfactants in W/O emulsion.

hydrolyzed by the contact with water molecules at the W/O interface are polar and hence have a natural tendency to accumulate at the W/O emulsion interface. Since more and more hydrolyzed TEOS molecules are accumulated at the W/O interface, our system can be viewed as micro-reactors where the concentration of one reactant is progressively increasing as time elapses. As the hydrolysis proceeds, the SiOH-based molecules become more and more water-soluble because of the presence of polar silanol groups in the molecule. Hence the condensation takes place inside the water droplets and at the W/O interface. In the case of base catalyzed

reactions, successive hydrolysis steps occur increasingly rapidly, and the fully hydrolyzed species undergo the fastest condensation reactions. Thus, under the high pH condition, the condensation might result in mono-disperse spherical particles consisting of smaller primary particles. Moreover, water droplets serve as a supporting structure for particle growth, thus reflecting the shape, size, and size distribution of particles. As shown in Figs. 1 and 2, the fact that the size of water droplets is similar to that of spherical silica particles and secondary spherical silica particles are composed of smaller primary particles supports this explanation.
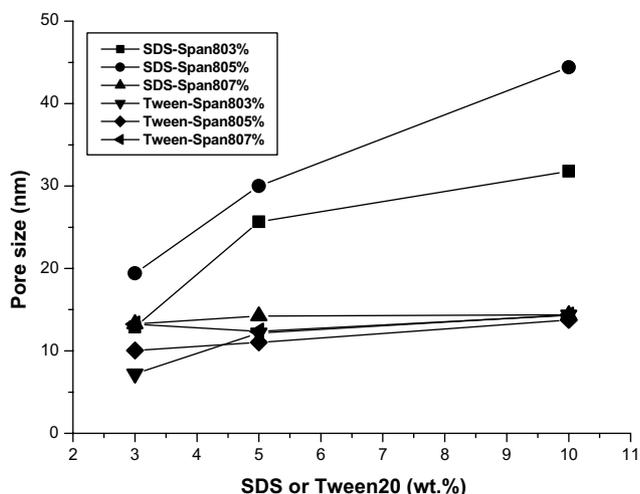
Fig. 6. Comparison of the pore size of the silica micro-spheres as a function of the weight ratio of SDS or Tween 20.

## 4.2. Effect of surfactants on the surface morphology of silica particles

The increase of the concentration of water-soluble surfactants such as SDS and Tween 20 leads to the enlargement of pore diameters and the change of pore size distribution. On the other hand, it results in the decrease of the surface area and adsorbed pore volume except the unusual results in 3 wt.% of Span 80. It is thought that this regular change of surface morphology is correlated with the self-assembly behavior of water-soluble surfactants inside water droplets. In general, the micelles of water-soluble surfactants like SDS and Tween 20 [30] serve as the soft templates for the ordered mesoporous silica particles. In this method, since the pore size of mesoporous silica is determined by the size of surfactant aggregates as a soft template, the pore size of synthesized silica is in the range from 2 nm to 5 nm. However, the average pore size of silica particles synthesized in our study reaches about from 7 nm to 45 nm. As a result, the self-assembly behavior of water-soluble surfactants is insufficient for accounting for this pore size distribution.

To understand why the increase of the concentration of water-soluble surfactants leads to the change of pore diameters and pore size distribution, it is suggested that the different morphology of silica particles is governed by solubilization ability of surfactants during the synthesis process in emulsion system. One of the important properties of surfactants that are directly related to micelle formation is solubilization. It may be defined as the spontaneous dissolving of a substance (solid, liquid, or gas) by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. McClements et al. [31] and Hilbers et al. [32] proposed that oil molecules

were transferred from the oil phase to the surfactant micelles by three solubilization mechanisms: (1) direct dissolution of oil molecules in water, and then capture by micelles in the aqueous phase, (2) solubilization of oil molecules to micelles through a soft collision between oil droplets and micelles, (3) collective desorption of a number of surfactants and the oil molecules from the oil droplet surface. In our previous study, W/O emulsion simply converted into O/W/O multiple-emulsion by means of the solubilizing capability of a surfactant, Tween 20 [33]. Described above by McClements et al. and Hilbers et al., a small amount of n-octanol is diffused into water droplets containing surfactant micelles, and then n-octanol molecules are solubilized inside them. Moreover, the solubilization capacity increases approximately with the increase of the concentration of the surfactant [34]. As a result, the size of the swollen micelles by the solubilization of oil molecules can become larger and they be used as templates for larger mesopores (Scheme 2). According to this similar mechanism: Su et al. [35], Jaroniec et al. [36], and Yang et al. [37] studied the enlargement of the pore size of MCM-41 using surfactants and swelling agents such as decane or amines.

The pore size distribution of silica particles shows the difference depending on whether anionic surfactant or nonionic surfactant is used. As shown in Fig. 5, when the anionic surfactant, SDS, is used, the maximum peaks of the pore size distribution are located in the right side rather than when the nonionic surfactant, Tween 20, is used. In general, solubilization capacity is greater for polar solubilizates than for nonpolar because of the larger volume available at the surface of the micelle than in the interior [38]. As a result, since SDS micelles contain n-octanol molecules more than Tween 20 micelles, the greater pores based on the solubilized micelle templates were formed in the case of using the SDS surfactant and the right-side shift of the pore size distribution took place. Moreover, it is possible that electrostatic charge-matching pathways are responsible for this result. Very recently, Tatsumi et al. [39] reported a synthesis method of anionic-surfactant-templated ordered mesoporous silica using SDS with 3-aminopropyl triethoxysilane (APTES) in place of silicon alkoxides as a silica source under the basic condition. Also, they firstly introduced the $S^-M^+I^-$ (S^-: anionic surfactant, M^+: counter-cation, I^-: anionic silicates) electrostatic charge-matching pathway. In our research, ammonium ions in ammonium hydroxide as a catalyst and counter-cation of SDS exist [40] in the water droplets (Scheme 2a). In contrast to Tween 20 associated with water molecules and silicates by hydrogen bonding (Scheme 2b) [41], the combination of these positive ions with SDS micelles and silicates can influence the pore size distribution.

It is shown that the oil-soluble surfactant, Span 80, plays a role that is different from water-soluble
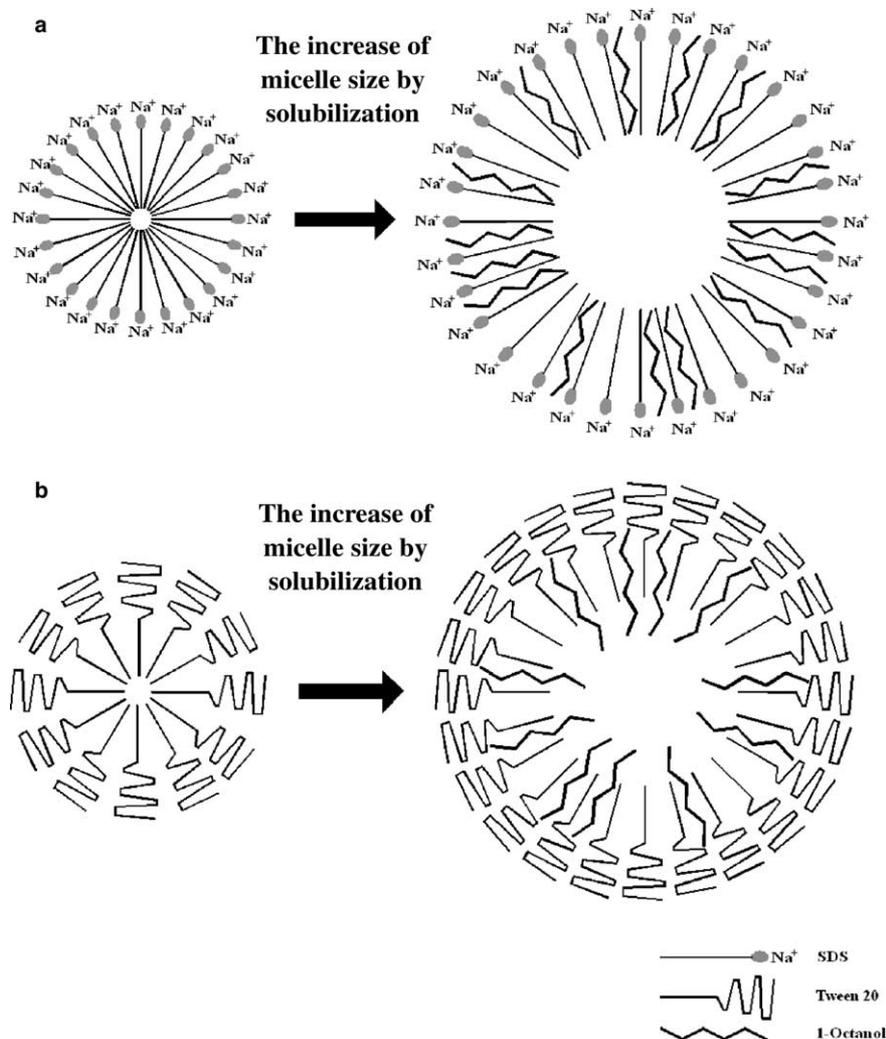
Scheme 2. Proposed schemes of the increase of micelle size by solubilization; Formation of micelle using SDS (a) or Tween 20 (b).

surfactants. As the concentration of Span 80 increases, the degree of change in the pore size distributions decreases though the concentration of water-soluble surfactants increases identically. Moreover, in case of using 7 wt.% of Span 80, the shift of pore size distribution occurred little in all the cases of SDS and Tween 20. It is perhaps for the reason that the W/O interface is more stabilized and strongly packed by many surfactant molecules and so the diffusion of oil molecules into the water phase through W/O interface is difficult. As a result, when the concentration of oil-soluble surfactant increases, the effect of the concentration of water-soluble surfactants on the pore size decreases.

5. Conclusions

Mesoporous silica micro-spheres can be prepared by a simple reaction using W/O emulsion system. The emulsion consists of aqueous solution of SDS or Tween 20 and 1-octanol solution of hydroxypropyl cellulose (HPC) and Span 80. HPC polymer and Span 80 play an important role in preparing spherical silica particles. It is shown that Span 80 surrounding water droplets and HPC polymer swollen in the oil phase prevent the disruption of emulsion structure and limit the behavior of primary silica particles. Since water droplets serve as a supporting structure for particle growth and aggregation, their morphology influences the shape, size, and size distribution of particles. When 3 wt.% and 5 wt.% of Span 80 was employed in our system, the effect on the particle size distribution was more prominent than when 7 wt.% was used.

The pore properties of silica micro-spheres can be dominated by the weight ratio of SDS, Tween 20, and Span 80. The successful controls of pore size of the mesoporous silica micro-spheres were achieved by changing the concentration of surfactants. The increase of water-soluble surfactants (SDS or Tween 20) resulted in the enlargement of pore size. To understand why the

increase of the concentration of water-soluble surfactants leads to the change of surface morphology, it is suggested that the solubilization ability of surfactants influences the different morphology during the synthetic process in emulsion system. When SDS is used in the water phase, the pore size of silica particles is larger than when Tween 20 is used. However, as the concentration of Span 80 increases, the degree of the change in the pore size distribution decreases though the amount of water-soluble surfactants increases. It is found that oil-soluble surfactant and water-soluble surfactant have a different role in the synthesis of silica particles. In contrast to the oil-soluble surfactant which mainly influences the size of particle size, the water-soluble surfactant primarily influences the pore size in particle.

These unique features of reaction using the W/O emulsion system will create novel methodologies in inorganic materials. The details of the unique features of the reaction and further application are under investigation in our laboratory.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.micro-meso.2005.07.012.

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