ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 18, No. 1. 2012

Effect of Synthesis Time on Morphology of Hollow Porous Silica Microspheres

Qian CHEN [1] *, Juha LARISMAA [1], Anu KESKI-HONKOLA [1], Kati VILONEN [2], Outi SÖDERBERG [1], Simo-Pekka HANNULA [1]

[1] *Department of Materials Science and Engineering, Aalto University School of Chemical Technology, P.O. Box 16200, FI-00076, Aalto, Finland*
[2] *Department of Biotechnology and Chemical Technology, Aalto University, School of Chemical Technology, P.O.Box 16100, FI-00076 Aalto, Finland*

http://dx.doi.org/10.5755/j01.ms.18.1.1344

Received 01 June 2011; accepted 19 July 2011

Hollow porous silica microspheres may be applicable as containers for the controlled release in drug delivery systems (DDS), foods, cosmetics, agrochemical, textile industry, and in other technological encapsulation use. In order to control the surface morphological properties of the silica microspheres, the effect of synthesis time on their formation was studied by a method of water-in-oil (W/O) emulsion mediated sol-gel techniques. An aqueous phase of water, ammonium hydroxide and a surfactant Tween 20 was emulsified in an oil phase of 1-octanol with a stabilizer, hydroxypropyl cellulose (HPC), and a surfactant, sorbitan monooleate (Span 80) with low hydrophile-lipophile balance (HLB) value. Tetraethyl orthosilicate (TEOS) as a silica precursor was added to the emulsion. The resulting silica particles at different synthesis time 24, 48, and 72 hours were air-dried at room temperature and calcinated at 773 K for 3 hours. The morphology of the particles was characterized by scanning electron microscopy and the particle size distribution was measured by laser diffraction. The specific surface areas were studied by 1-point BET method, and pore sizes were measured by Image Tool Software. Both dense and porous silica microspheres were observed after all three syntheses. Hollow porous silica microspheres were formed at 24 and 48 hours synthesis time. Under base catalyzed sol-gel solution, the size of silica particles was in the range of 5.4 μm to 8.2 μm, and the particles had surface area of 111 m^2/g – 380 m^2/g. The longer synthesis time produced denser silica spheres with decreased pore sizes.

Keywords: silica, hollow porous microspheres, synthesis time, sol-gel, water-in-oil emulsion.

INTRODUCTION

In recent years, hollow porous micron or nanosized silica spheres have attracted great attention from both industry and academies due to the increasing applications of controlled release in pharmaceutics, cosmetic, food and coating industry [1 – 5]. Controlled release is a key function in drug delivery systems (DDS), in which a core-shell structure of the particles is formed by the encapsulation technique. The core materials may include drugs, enzymes, inks, dyes, vitamins and proteins [1, 2, 6 – 7]. Typically the encapsulating carriers/shells have been organic compounds, such as polymers [8, 9]. However, many polymers may decompose under acidic conditions so that the core materials lose their protection and will be exposed to the environment [10]. Hence, the inorganic oxides like amorphous silica are developed as encapsulating carriers in order to overcome the limitations of polymers [11]. Hollow silica microspheres with mesoporous structure (pore size 2 nm – 50 nm) are particular interesting due to their distinguished properties including: light weight, low density, large specific surface area, mechanical and thermal stability, surface permeability, optical transparency, chemical and biological compatibility [2, 6, 7, 12 – 14]. The hollow silica spheres have a high storage capacity as their core is acting as a “molecular reservoir”. The direct encapsulation and storage of water soluble molecules into silica microcapsules can be achieved using the water phase in a W/O emulsion as a container, forming an emulsion prior to addition of TEOS [14]. Furthermore, with the controlled pore size they also have desired release properties.

There has been a variety of approaches developed to fabricate hollow spheres of various compositions. These include nozzle reactor processes (spray drying or pyrolysis) [2, 15, 16], sol-gel/emulsion method [1, 2, 14, 17 – 18], sacrificial core techniques [7, 19], and layer-by-layer deposition [20]. Among these methods, hollow porous silica spheres prepared by sol-gel/emulsion method presents the most effective and economical solution [14]. By it the characteristic features of particles, e. g. particle shape and size, pore size, density, and micro or nanostructure, can be tailored by controlling the kinetics of reaction, especially the process of hydrolysis and condensation. Furthermore, the sol-gel/emulsion method takes place with simple facilities at ambient condition, thus offering a cost-saving process [1, 6, 10, 14].

The sol-gel technique is defined as a wet-chemical process to produce inorganic and hybrid materials at low temperatures [21 – 23]. Typically the process starts from metal precursors, such as Si alkoxides, and undergoes a series of hydrolysis and condensation under acid or base catalysts [23 – 25]. The hydrolysis reaction involves the replacement of alkoxy groups (OR) by hydroxo ligands (OH) (Eq. 1), and the subsequent condensation creates either water or alcohol to produce silicon dioxide (Eqs. 2 and 3) [24].

$$\equiv\text{Si–OR} + H_2O \leftrightarrow \equiv\text{Si–OH} + \text{ROH}\,, \qquad (1)$$

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*Corresponding author. Tel.: +358-9-47022671; fax.: +358-9-47022677.
E-mail address: *qian.chen@aalto.fi* (Q. Chen)

where R is an alkyl group, C_nH_{2n+1} .

$$\equiv Si–OR + HO– Si\equiv \leftrightarrow \equiv Si–O–Si\equiv + ROH . \quad (2)$$

$$\equiv Si–OH + HO– Si\equiv \leftrightarrow \equiv Si–O– Si\equiv + H_2O . \quad (3)$$

The sol-gel synthesis undergoes either at base or acid catalyst. The rate of hydrolysis exhibits a minimum at pH 7, and increases when the pH is smaller or higher than 7 [24]. In contrast, the rate of condensation exhibits a minimum around pH 2, obtains a maximum at pH 7 and starts to decline at pH > 7. Thus, acidic catalyzed sol-gel solution exhibits high rate of hydrolysis, and it tends to form homogeneous particles with loose and open structure that collapses upon drying. At base catalyzed solution, hydrolysis is hindered to some extent but high rate of condensation is promoted. This produces the middle products oxopolymers, hence, leading to inhomogeneous, cross-linking and dense structure [14, 24, 25]. The partially hydrolyzed middle product $Si(OR)_{4–n}(OH)_n$ can link together in a condensation reaction (Eqs. 4 and 5), and produce larger silicon containing molecules as the polymerization proceeds [24]:

$$(OR)_3Si–OH + HO–Si(OR)_3 \rightarrow$$
$$\rightarrow (OR)_3Si–O–Si(OR)_3 + H_2O \quad (4)$$

or

$$(OR)_3Si–OR + HO–Si(OR)_3 \rightarrow$$
$$\rightarrow (OR)_3Si–O–Si(OR)_3 + ROH . \quad (5)$$

Emulsion is a heterogeneous systems consisting of at least two liquids, in which one liquid phase in the form of droplets is dispersed into another in the presence of surfactants or polymers [2, 6, 26]. The emulsion system is stabilized by adsorbing surfactants or polymers onto the interfaces between immiscible phases [18]. There is a variety of emulsion systems, such as oil-in-water (O/W), water-in-oil (W/O), water-oil-water (W/O/W), and oil-water-oil (O/W/O) [10, 26]. The most common emulsion systems in synthesizing solid or hollow silica particles are oil-in-water (O/W) and water-in-oil emulsions (W/O) [26]. In sol-gel/emulsion method, silica particles are prepared via the emulsion droplets acting as microreactors for the hydrolysis and condensation reactions of Si alkoxides [10, 14, 27]. The balance of thermodynamic and kinetic mechanism is influenced by a number of processing factors, including: water-to-alkoxide ratio, type and amount of the catalysts, type and amount of the surfactants, type of the solvents, calcination temperature and time. Consequently these factors contribute to the resulting properties and surface morphology of silica particles.

The size of silica particles greatly depends on the emulsion parameters, such as type and concentration of surfactants and solvents. Typically nonionic surfactants (e. g. HPC, Span 80, Tween 20) and a non-polar solvent (e. g. 1-octanol) are selected in controlling the interfacial tension of W/O interface when mixing with sol-gel solutions. During mixing, polar sol-gel droplets are dispersed in the non-polar solvents and forms W/O interface acting as a microreactor in which the hydrolysis and condensation of silicon alkoxide takes place. Thus, the size of silica particles is dependent on the size of water droplet in the emulsion [1, 14, 18].

HLB (hydrophile-lipophile balance) value is denoted as the affinity of surfactants to water (hydrophilic) and to oil (lipophilic), and it is expressed as a ratio of hydrophilic and lipophilic groups of amphiphilic surfactants. HLB value < 10 indicates hydrophilicity, and HLB value > 10 lipophilicity. For synthesizing the microspheres with W/O technique HLB value of the surfactant should be less than 10, for example, as HLB = 4.3 for Span 80 [14]. The surfactant Span 80 surrounds water droplets thus limiting the size of primary silica particles [18]. If several surfactants are applied, their influence on the size of the microspheres depends on the concentration of surfactants, for example as in [18] that of the mixture of Tween 20, SDS (sodium lauryl sulfate) and Span 80.

HPC acts as a stabilizer in an emulsion that prevents the phase separation and influences to the solubility of TEOS. Its polymer chain swells in the oil phase, thus increasing the viscosity of the emulsion and enhancing the stability of emulsion system. The increased viscosity of emulsion system limits the penetration speed of TEOS as well as the mobility of water droplets, hence, preventing the aggregation between the primary silica particles [2, 14, 18]. In [2] where 3 wt.% of Span 80 was used in oil phase together with HCP concentrations of (0.8 – 1.4) wt.%, it was shown that with these HCP amounts the silica particle size distribution was 1 μm – 10 μm. Furthermore, it was observed that 1.4 wt.% of HPC results in more spherical particles.

The factors that affect the hydrolysis and condensation in the sol-gel process along with surfactants from the emulsion system influences the porosity properties of silica spheres [18, 26, 28].

As shown many researchers have studied the effect of the processing parameters on the physical properties and surface morphology of silica spheres [2, 6, 14, 18]. However, there are no reports published on the relation between properties of silica spheres and synthesis time. In this paper, we study the effect of synthesis time on morphology of hollow silica spheres synthesized by water-in-oil (W/O) emulsion mediated sol-gel technique.

MATERIALS AND METHODOLOGY

The materials used in the synthesis were tetraethyl orthosilicate ($Si–(OC_2H_5)_4$, TEOS, 98 %, Acros Organics) as a precursor, 1-Octanol ($C_8H_{18}O$, 99 %, Sigma-Aldrich) as an oil phase, hydroxypropyl cellulose (HPC, average Mw ca. 100,000, Acros Organics) as a stabilizer of emulsion, and Sorbitan monooleate ($C_{24}H_{44}O_6$, Span®80, Fluka) as a low-HLB surfactant to disperse the oil phase. Also Tween 20 (Acros Organics) as a high-HLB (hydrophilic-lipophilic balance) surfactant, deionized water, ammonium hydroxide (NH_4OH, 25 %, J. T. Baker) as a catalyst and ethanol (C_2H_5OH, 96.1 vol.%, Altia) as a washing reagent were used.

The hollow porous silica microspheres were synthesized by W/O emulsion combined with sol-gel technique (Fig. 1). First, the oil phase was prepared by dissolving 1.6 g HPC in 250 ml 1-octanol, the mixture was heated at 353 K and mixed by a magnetic stirrer with heating (RCT basic IKAMAG® safety control, IKA®-Werke, GmbH & Co.KG) for 0.5 h. Then 6.2 ml Span 80 was added to the oil phase, and was kept at 313 K for 0.5 h. Second, the water phase was prepared by mixing 2.2 ml ammonium hydroxide in 21 ml deionized water by a magnetic stirrer (KMO 2 basic IKAMAG®, IKA®-Werke, GmbH & Co.KG) for 0.5 h. Then 1.7 ml Tween 20 was added, and the mixture was stirred for another 0.5 h. Then the oil phase and water phase were mixed together at 313 K for 0.5 h, and 64.5 ml of TEOS was added drop wise to the emulsion. The molar ratio of TEOS: water: ammonium hydroxide was kept at 1 : 4 : 0.2. After this the silica synthesis stage was followed during the long stirring period. Three syntheses were carried out at a stirring rate of 550 rpm at 313 K for 24, 48, and 72 h, respectively. After the synthesis, the samples were aged at room temperature for 48 h, then washed with ethanol repeatedly and centrifuged for 3 min. The resulting white particles were dried in air for 24 h, and finally calcinated in air at 773 K for 3 h. Yield of powder from the 72 h synthesis was considerable more than that from the 24 h and 48 h processes.

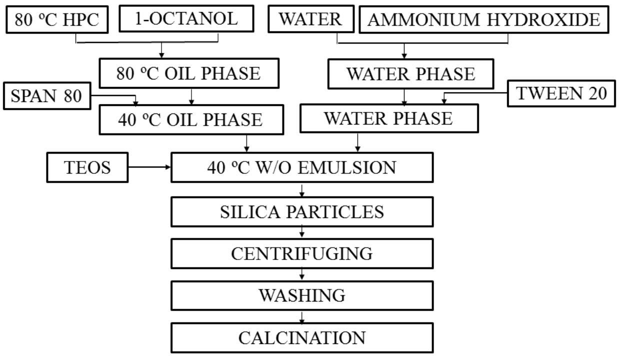

Fig. 1. The process of W/O emulsion combined with sol-gel method

Surface morphology of silica particles was observed by scanning electron microscopy (SEM, Hitachi-S4700 FEG-SEM). A small amount of silica particles was first diluted with ethanol, then mixed in an ultrasonic mixer (Ultrasonic M03, FinnSonic) and dropped onto a silicon wafer. After the evaporation of the ethanol, the dried sample was placed onto a carbon tape. The samples were sputtered with a gold-palladium layer by precision etching coating system (Gatan model 682).

Particle size distributions of the silica powders were determined by the laser diffraction (Malvern Mastersizer 2000, Malvern Instruments). The particle size distribution was calculated with Mie theory, using the refractive index 1.45 and absorption 0.1 for silica. For each powder type three measurements were made. Water was used as a dispersant to avoid agglomeration. The measurements were carried out at both with and without the ultrasonic mixing.

Specific surface areas of the silica particles were measured with the 1-point BET method by Micromeritics Flowsorp 2300 II instrument, using nitrogen-helium gas mixture, containing 30 vol.% nitrogen. Surface area calculations were based on the amount of adsorbed nitrogen at liquid nitrogen temperature (77 K), where it forms monomolecular layer on the surface of the particles.

RESULTS AND DISCUSSIONS

Fig. 2 shows the particle size distributions of the microspheres three samples with different synthesis times, 1# (24 h), 2# (48 h), and 3# (72 h), with (Fig. 2, a) and without (Fig. 2, b) the ultrasonic mixing. The mean size of the silica samples with different synthesis time, under ultrasonic mixing is in the range of 5.4 μm – 8.2 μm (Table 1, Fig. 2, a). With the ultrasonic mixing powders 1# and 2# exhibit nearly similar high peaks at about 5 μm – 6 μm, and 4 μm – 5 μm, respectively. In the sample 1# there is also a secondary peak at larger particle size (200 μm – 250 μm).

Table 1. Properties of silica porous spheres prepared at different synthesis time

Synthesis time (h)	Mean sphere size no ultrasonic mixing (μm)	Mean sphere size with ultrasonic mixing (μm)	Surface area (m^2/g)	Main structure
24	17.4	6.5	380	Hollow, porous
48	14.3	5.4	366	Hollow, porous
72	8.3	8.2	111	Porous

Also, in powder 2# there seems to be a tail in the pattern from the larger particles (sizes up to 200 μm). It is noteworthy that the sample 3# shows a mixed two-peak distribution, the lower peak being at smaller particle size (2 μm – 3 μm) than the higher one (9 μm – 10 μm). Furthermore, there seems not to be so large particles as in the powders 1# and 2#. The particle sizes of the sample 1# (24 h) vary from 1.4 μm to 316 μm, while they are in the sample 2# (48 h) 1.4 μm – 200 μm, and in the sample 3# (72 h) 0.6 μm – 60 μm. When the measurements were carried out without the ultrasonic mixing (Fig. 2, b) the results differ to some extent from the above mentioned. The sample 3# seems to behave similarly in both tests, but there is major difference in the other two. The sample 1# takes the mixed-two peak and separate third peak form. The first smaller peak is at the same size (~5 μm) as the high peak in the measurement with the ultrasonic mixing, while the highest peak is located at 20 μm – 25 μm, and the separate third peak still at 200 μm. The clearest change occurred in the sample 2# where the single peak turned to the mixed-three peak format and even the first highest peak was at larger size (4 μm – 5 μm) than in the measurement with the ultrasonic mixing. The second peak took place at 10 μm – 30 μm, and then the smallest elbow-like part was at 200 μm – 350 μm. Thus, it can be concluded that without the ultrasonic mixing, the samples 1# and 2# contain aggregated smaller particles, while in the sample 3# the size distribution is showing sizes of the actual particles formed in the long synthesis process.

The morphology of the synthesized particles was studied with SEM. Figs. 3, a – c, shows SEM images of silica spheres from different synthesis time. In all three processes, the majority of the silica spheres seem to be porous, but in all of them also some dense particles are

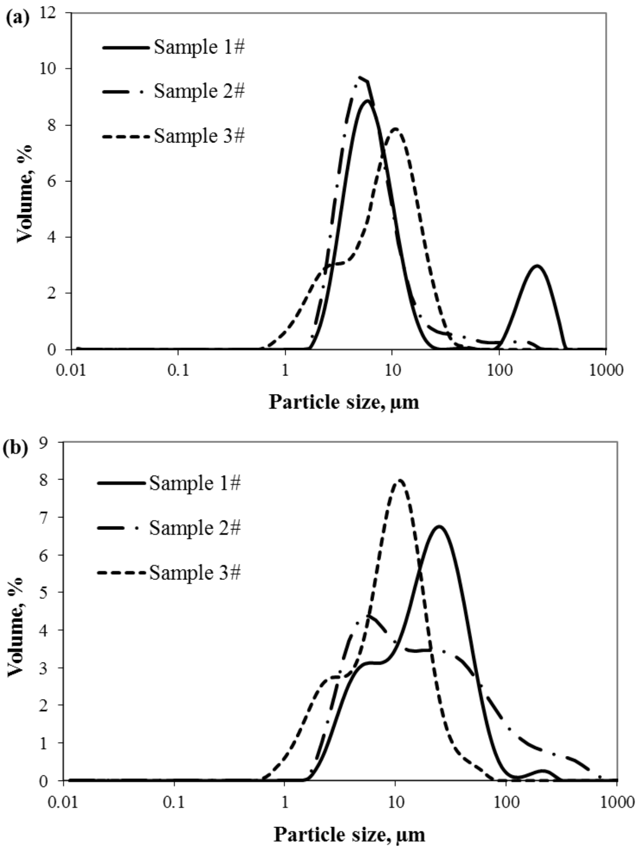

Fig. 2. Particle size distributions (a) with and (b) without ultrasonic mixing

present. In Fig. 3, a, the size distribution of 1# particles is also correlating to some extent with the particle size distribution measurements carried out with this powder as majority of the spheres are of size 4 µm – 6 µm, though there are smaller ones and one large one, too. The same applies to the Fig. 3, b, presenting the morphology of the powder 2# after 48 h synthesis. Here one can note that in addition to the spherical particles, also some with the unformed shape are present. The powder sample 3# in Fig. 3, c, has not as many particles as the previous ones. The particles have spherical form, and their size (about 4 µm – 5 µm) corresponds to the first lower size distribution peak (Fig. 2, a). The morphology of the hollow porous silica spheres is shown more in details for the samples from the different syntheses (Figs. 4, a – c). Hollow porous particle synthesized for 24 h seems to exhibit relatively thin shell structure that has cracked. Furthermore, the surface seems crater-like and the pore density is not as high as in the particles with longer processing times. The measurement of pore size by Image tool reveals that average pore size of silica spheres from 24 h syntheses time is greater than that of 48 h and 72 h. At 48 h synthesis, the shell structure seems to be thicker. After 74 h synthesis the particle surface resembles to some extent the previous one, but there appears kind of second surface shell layer. The particle seems to be more sponge-like than a hollow sphere. Maybe this assumption is supported by the surface area measurements which gave 111 m^2/g for the sample 3#, and 380 m^2/g and 366 m^2/g for the samples 1# and 2#, respectively.

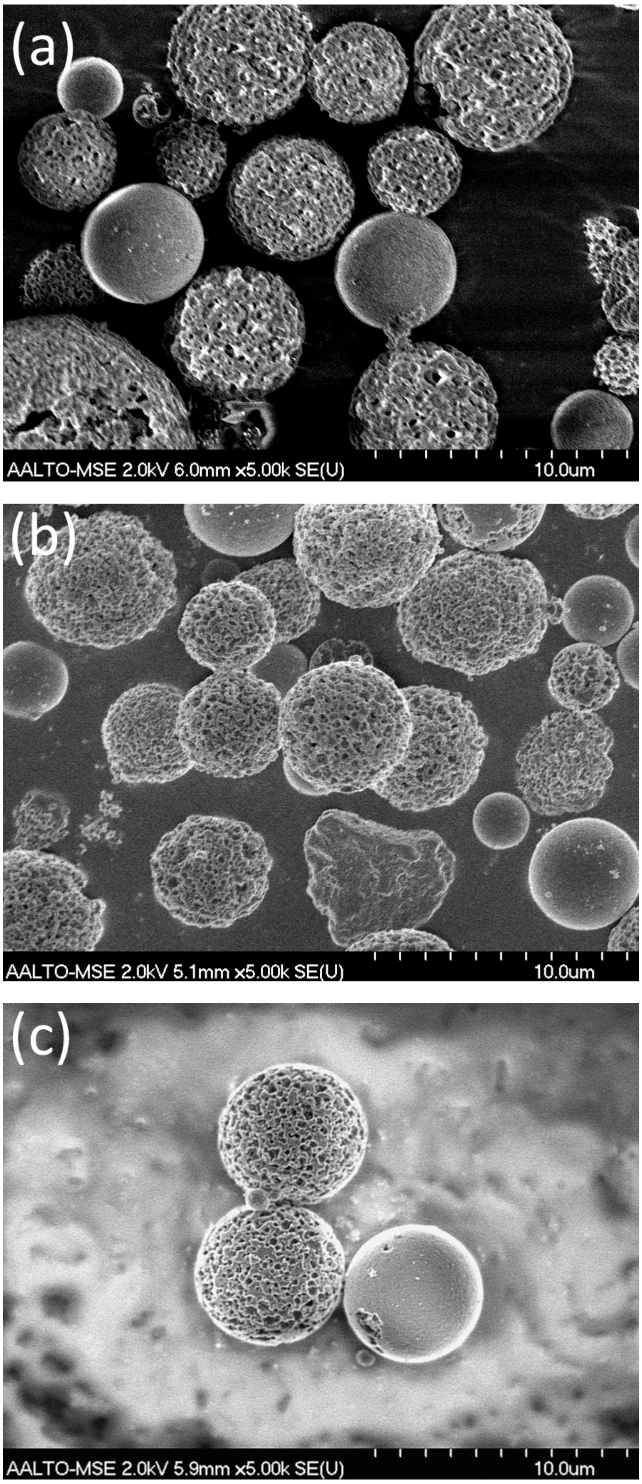

Fig. 3. Silica powders obtained with the different synthesis times a – 24 h (1#); b – 48 h (2#); and c – 72 h (3#)

The formation of hollow structure relates to the emulsion process. The nonpolar alkyl chains of TEOS molecules slowly diffuse through surfactants, and the sol forms at water/oil interface. The hydrolyzed TEOS molecules orient towards the nonpolar 1-octanol oil. As the proceeding of hydrolysis and condensation, the growth of silica shells performs. This stage is influenced by the synthesis time. In the present study 8 wt.% ammonium hydroxide in aqueous phase was added to reach approximately pH = 10 in the emulsion system. With the 24 h synthesis the particles were clearly hollow with relatively

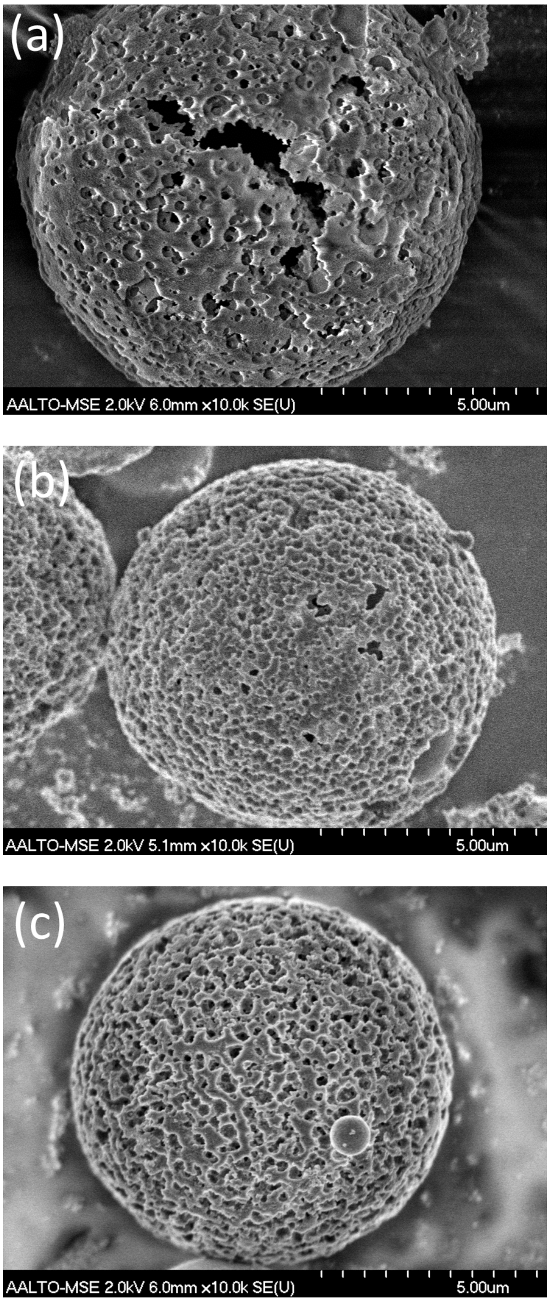

Fig. 4. Silica powders obtained with the different synthesis times: a – 24 h (1#); b – 48 h (2#); c – 72 h (3#)

thin shell wall, while with the longer processing time tended to favor more thick-walled, even particles which were not actually hollow, but sponge-like.

Typically for sol-gel/emulsion method, ionic and nonionic surfactants are used as structuring agents for pore formation because of their solubilization properties. This is related to the micelles interactions of surfactants to form thermodynamically stable isotropic solution with reduced thermodynamic activity of the solubilized material. The pore size is affected by the concentration of surfactants and synthesis conditions. For example, nonionic surfactants Tween 20 is associated with water and silicates by hydrogen bonding, and gives materials with larger pores and thicker shell walls. Increasing oil-soluble surfactant, e. g. Span 80, will decrease the pore size distribution. During air-drying, shrinkage and consolidation of silica network takes place, this affects the densification of the matrix and consequently the pore sizes [1, 18]. Furthermore, at base catalyzed sol-gel/emulsion reaction, increasing synthesis time favors smaller pore size of silica microspheres. This is in accordance with the pore size measurements carried out from the SEM pictures as the average pore size after 24 h is greater than that of 48 h and 72 h.

CONCLUSIONS

Hollow porous silica microspheres were synthesized at base solution by W/O emulsion combined with sol-gel method. The emulsion system consists of multiple surfactants, HPS, Tween 20 and Span 80, 1-octanol as external oil phase and TEOS as silica precursor. Three experiments with different synthesis time 24, 48, and 72 h were performed. Both dense and porous silica microspheres were observed with SEM after all syntheses. The SEM investigation and measurement of surface area reveals that the hollow porous silica microspheres were formed in the samples at 24 h and 48 h synthesis time, and porous silica microspheres were formed at 72 h. The impact of synthesis time on the mean value of particle size measured with ultrasonic mixing is insignificant, and the pore size of silica microspheres decreases with increasing synthesis time. Based on this study, we would later focus on the improvement of current process, such as, shortening the synthesis time by pre-hydrolyzing TEOS before the formation of emulsion.

Acknowledgments

The RESCOAT project funded by Tekes (the Finnish Funding Agency for Technology and Innovation), and consortium of Finnish companies is acknowledged for support.

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Presented at the 20th International Baltic Conference
"Materials Engineering 2011"
(*Kaunas, Lithuania, October 27–28, 2011*)