Effect of reaction time on formation of silica core/shell particles

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Abstract

The silica core/shell nanostructures were prepared by a wet-chemical process. Silica core particles were prepared by hydrolysis and condensation of tetraethylorthosilicate. The obtained particles (average size ~0.4 µm) were used as templates for assembling of silica nanoparticles generated from highly basic sodium silicate solution. The silica core particles were functionalized with 3-aminopropyltriethoxysilane (APTES) to allow electrostatic assembling of silica nanoparticles on the surface of silica core particles. In order to find the optimal conditions for synthesis of silica core/shell particles with mesoporous shells, the effect of reaction time on formation of silica nanoparticles was investigated. The effect of process parameters on generation and aggregation of silica nanoparticles prepared from highly basic sodium silicate solution was also investigated. It was shown that the size of silica nanoparticles and tendency towards aggregation increase with increasing the reaction time and temperature. These behaviours were reflected on the formation of mesoporous silica shell around silica core particles. Thin and uniform mesoporous silica layers were obtained if reaction times were kept short. When the reaction time was prolonged, the thicker and non-uniform shells were obtained.

Keywords: core/shell particles, silica, assembling, mesoporous, reaction time

I. Introduction

Mesoporous silica particles are the most suitable matrices for enzyme immobilization in industrial manufacturing of enzyme-processed products [1], as well as for research purposes [2,3]. The main advantages of the mesoporous silica materials are high surface area and high total pore volume with narrow pore size distribution [4]. Additionally, these materials are chemically stable, biocompatibile and non-toxic which make them suitable for enzyme immobilization [1,4]. In recent years, great efforts have been made to synthesize composite silica nanoparticles with core/shell structure which makes the mesoporous materials more applicable to practical, academic and industrial demands [5–8]. These particles may be composed of dense silica core and mesoporous silica shell. The formation of mesoporous silica layers around dense cores is mainly based on the use of surfactants that are aggregated on the surface of the cores and then condensation of TEOS is carried out on the surface of modified cores [5–7]. In these cases calcination or extraction had to be performed to remove template from the structure. However, mesoporous silica shell can be synthesized without templates by simply procedure where silica nanoparticles, prepared from highly basic sodium silicate solution, were electrostaticaly deposited on the surface of functionalized cores [8]. It may be noted that these multifunctional core-shell particles composed of mesoporous silica shell around dense cores have also found application in enzyme immobilization [9,10].

Herein, we report some discoveries during formation of silica nanoparticles by acidic neutralization of a highly basic sodium silicate solution. The influence of temperature and reaction time on the structure of silica nanoparticles was analysed. The investigation is important as it might help in finding optimal conditions for the synthesis of core/shell particles with desirable structure of mesoporous silica shells.

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II. Experimental

2.1. Synthesis of silica core particles

The silica core particles were synthesized in two steps, first by hydrolysis and condensation of tetraethylorthosilicate, TEOS ($Si(OC_4H_9)_4$, Fluka) [11] and then by their functionalized with 3-aminopropyltriethoxysilane (APTES) [9]. In the first step, TEOS was dissolved in anhydrous ethanol and hydrolyzed with distilled water under basic conditions (25% NH_3, Merck). The sample was prepared using a molar ratio $TEOS:H_2O:NH_4OH = 1:40:2$ and TEOS concentration of 0.25 mol/l [8]. The prepared suspension was continuously stirred at room temperature for 1 hour. The white precipitated powder was centrifuged and washed with distilled water until the effluent was free of $NH_4$1 groups, and finally dried at 120 °C for 1 day.

In the second step, the prepared core particles were functionalized with APTES by dispersing the previously prepared silica particles (1.2 g) in anhydrous acetone (70 ml) and adding of 1 ml APTES. The obtained suspension was continuingly stirred for 24 hours. After that the functionalized silica core particles were centrifuged, extensively washed with anhydrous acetone and finally dried by the removal of excess solvent at 80 °C.

2.2. Synthesis of silica nanoparticles

The silica nanoparticles, used for formation of the silica shell, were prepared from highly basic sodium silicate solution (Water glass, Alumina Factory-Birač, Zvornik) having SiO_2/Na_2O molar ratio $M = 2.5$ mol/mol and concentration of SiO_2 $C = 55$ g/l. Sulphuric acid was slowly added into well stirred sodium silicate solutions at different temperatures to precipitate fine silica particles. During the reaction colour of the aqueous sodium silicate solution changed from colourless to milky while the viscosity of the sol increased. The small amount of silica sols was separated from the prepare samples at different time intervals and used for the investigation of growing process.

2.3. Synthesis of core/shell particles

The silica core/shell particles were prepared by assembling of the synthesized silica nanoparticles on the surface of the functionalized silica core particles. The functionalized SiO_2 core particles were dispersed in highly basic sodium silicate solution (Water glass, Alumina Factory-Birač, Zvornik) having SiO_2/Na_2O molar ratio 2.5 mol/mol and concentration of SiO_2 55 g/l. Sulphuric acid ($H_2SO_4 = 1$ mol/l) was slowly added into a well stirred sodium silicate solution containing the dispersed APTES-functionalized SiO_2 core particles at 70 °C to decrease pH value and enable the silica shell formation. Different reaction times, after which the particles were separated from the liquid phase by centrifugation, were used. The obtained particles were washed with distilled water and finally dried at 100 °C for one day.

2.4. Characterization

The particle size was measured by dynamic light scattering (Zetasizer Nano ZS, Malvern Instruments, United Kingdom). The size and morphology of the particles were examined using a scanning electron microscope (JEOL JSM 6460 LV, Tokyo, Japan) operating at 20 kV and transmission electron microscopy (Philips CM 20, Eindhoven, The Netherlands) operating at 200 kV. Prior to SEM imaging, the samples were sputtered with gold while TEM samples were prepared by drying one drop of ultrasonically dispersed particles on a carbon film supported by a Cu-grid.

III. Results and discussion

The silica core/shell particles were obtained in two steps – the first by the formation of silica nanoparticles after neutralization of sodium silicate solution with sulphuric acid, and then by electrostatic assembling of the formed silica nanoparticles on the surface of the functionalized silica core particles. Structure of the silica shell formed around the functionalized core particles depends on the condition for nucleation and growth from the sodium silicate solution, but the reaction time seems the most important. Thus, we have investigated the influence of the reaction time on the formation of silica nanoparticles and silica core/shell particles.

Prior to evaluate the influence of reaction time on the formation of silica shell around the functionalized silica core partices, we investigated the effect of process parameters, such as reaction time and temperature, on formation and aggregation of silica nanoparticles generated by neutralization of the sodium silicate solution without the presence of the functionalized silica core particles. This investigation has demonstrated that the formation of silica nanoparticles by neutralization of sodium silicate solution is very complex process.
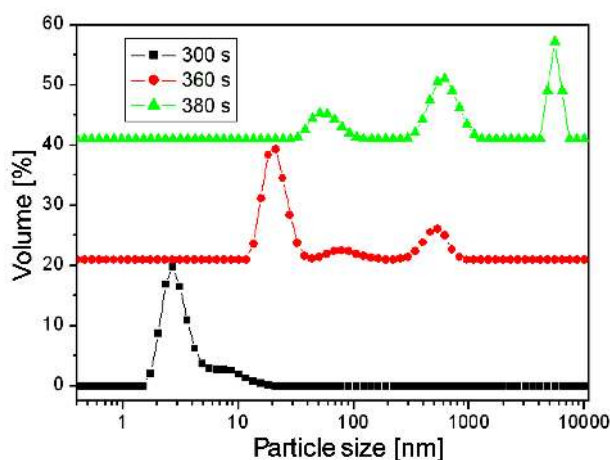

Figure 1. Effect of reaction time on size of silica particles obtained by acidic neutralization of highly basic sodium silicate solution ($C = 55$ g/l, $M = 2.5$) at 70 °C
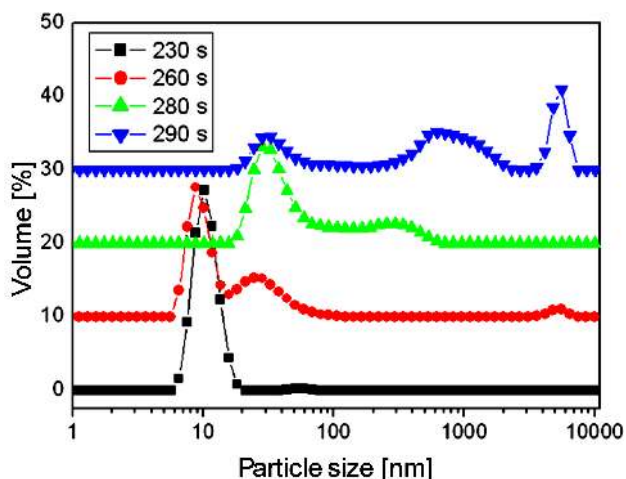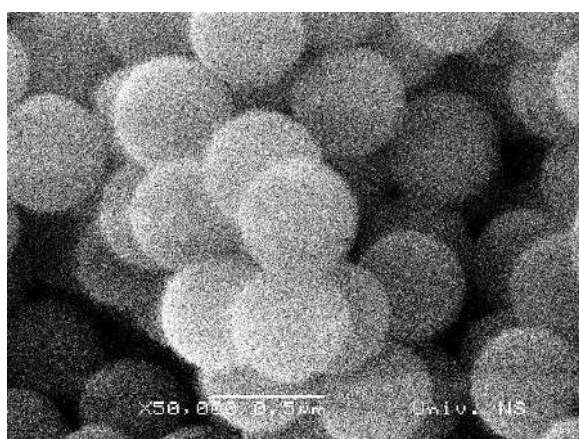
Figure 2. Effect of reaction time on size of silica particles obtained by acidic neutralization of highly basic sodium silicate solution (C = 55 g/l, M = 2.5) at 90 °C

Figure 1 shows particle size distributions of the samples obtained by neutralization of sodium silicate solution having SiO_2 concentration of 55 g/l and SiO_2/Na_2O molar ratio of 2.5 mol/mol and taken from vessel during the reaction at three different time intervals. Sulphuric acid was slowly added into the well stirred sodium silicate solution at 70 °C so that the speed of neutralization was constant in whole reaction time. Slow increase of the average particle size with time from 3 nm at 300 s, 25 nm at 360 s to 65 nm at 380 s can be seen (Fig. 1). However, a bimodal size distribution is obvious already after 360 s due to appearance of big aggregates having size of about 0.6 μm. Further prolongation of reaction time results in appearance of the third pick in size distribution formed by very large aggregates with average size ~6 μm (Fig. 1).

Particle size distributions of the samples taken from reaction vessel at somewhat higher temperature (90 °C) are shown in Fig. 2. As it can be seen the reaction is much faster. Thus, already after 230 s silica nanoparticles were formed by neutralization of sodium silicate solution. The particle size distribution is unimodal and shows peak at 10 nm (Fig. 2). A bimodal particle size distribution with the high-intensity peak at 10 nm and the smaller one at 30 nm was observed after 260 s of reaction. It can be suggested that at this stage the Ostwald ripening process is carried out [12]. During this process, the smaller silica nanoparticles with average particle size of 10 nm dissolve and are redeposited onto
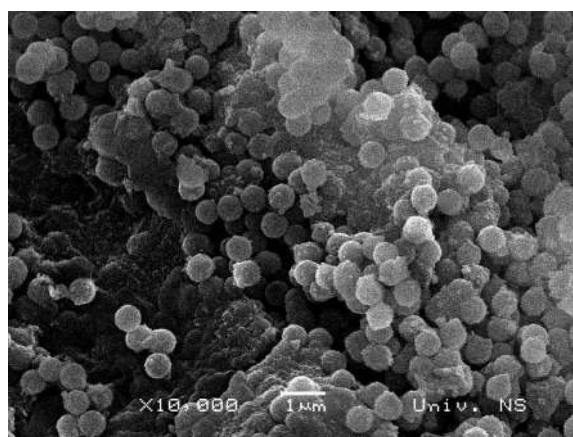

(a)
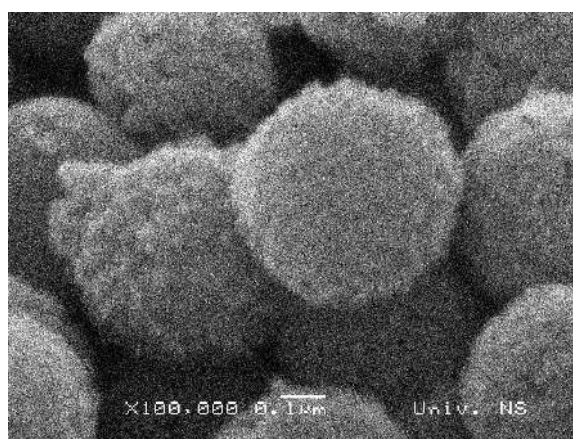
(b)
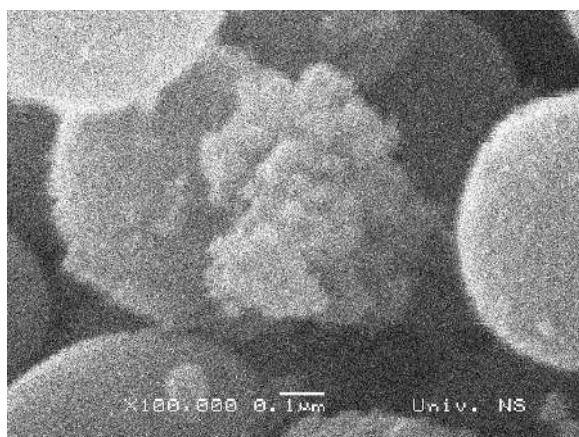
(c)

(d)

Figure 3. SEM images of: (a) core SiO_2 particles synthesized from TEOS, (b) core/shell particles formed after 420 s, (c) core/shell particles formed after 450 s and (d) gel sample formed after 600 s
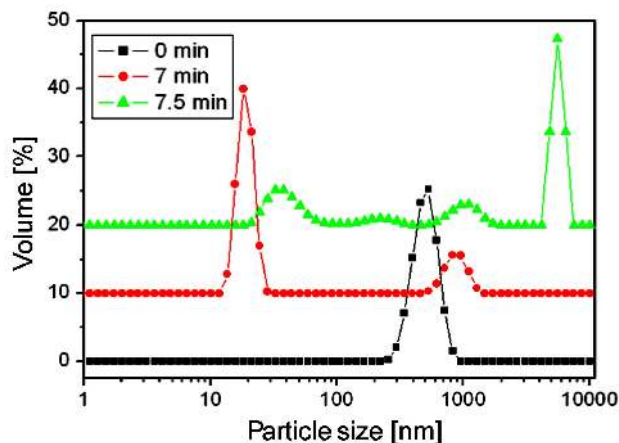
Figure 4. Effect of reaction time on size of core/shell particles synthesized at 70 °C (C = 55 g/l, M = 2.5)

the larger ones until the difference in solubility between the smallest and the largest particles becomes negligible [12]. After 280 s, the bimodal particle size distribution is more pronounced (Fig. 2) and shows the peak at 45 nm which represents larger silica nanoparticles obtained by the Ostwald ripening process and the smaller peak at ~290 nm which represents large particles formed by aggregation of small silica nanoparticles. As the reaction continued the aggregation became dominant and very large particles of about 5 μm were formed already after 290 s.

As it was already mentioned, it is obvious that during the formation of silica core/shell particles it is very important to control reaction time. We investigated the influence of reaction time on the formation of core/shell particles at 70 °C using the sodium silicate solution having SiO_2 concentration of 55 g/l and SiO_2/Na_2O molar ratio of 2.5 mol/mol. In this case the smooth surfaces of the silica core particles (Fig. 3a) were roughened due to deposition of the primary silica nanoparticles within a short reaction time of sodium silicate solution with sulphuric acid. This resulted in formation of uniform and continuous shell around the silica core particles (Fig. 3b). Separate silica aggregates were not observed indicating that precipitation of primary silica nanoparticles was performed only on the surface of the functionalized core particles (Fig. 3b). With further reaction separate silica aggregates can be seen (Fig. 3c) and finally gelation occurs (Fig. 3d).

The obtained results were confirmed by DLS measurements (Fig. 4) showing particle size distributions of the samples obtained before and after the addition of sulphuric acid into the reaction vessel containing functionalized silica core particles dispersed in sodium silicate solution having SiO_2/Na_2O molar ratio of 2.5 mol/mol, SiO_2 concentration of 55 g/l and temperature of 70 °C. Schematic illustration, shown in Fig. 5, might help in visualization of the whole process. Thus, before addition of sulphuric acid, there is unimodal particle size distribution with average particle size of ~500 nm which refers to the silica core particles dispersed in sodium silicate solution (Fig. 4). After 420 s of reaction, a bimodal distribution with two peaks at ~18 nm and ~0.75 μm was obtained (Fig. 4). The first peak represents non-aggregated silica nanoparticles generated by neutralization of the sodium silicate solution while the second peak represents the core-shell particles formed by deposition of silica nanoparticles on the surface of the APTES-functionalized silica core particles (Fig. 5). It can be noted that silica shell obtained after 420 s (Fig. 6b) is thicker than that obtained after 360 s (Fig. 6a). After 450 s of reaction, there is a multimodal particle size distribution. The first peak at 35 nm represents small silica nanoparticle while the peak at 200 nm represents silica particles formed by aggregation of the smaller nanoparticles (Fig. 4). The third peak at 1 μm probably represents larger core-shell particles while the peak at 7 μm refers to huge aggregates composed of the core-shell particles and mesoporous silica particles (Fig. 4).

The results describing the formation of the silica nanoparticles (Fig. 1) and silica core/shell particles (Figs. 3 and 4) are well complied. However, somewhat longer time characterizes the later system, and this can be explained by presence of the silica core particles behaving as heterogeneous nucleating centres.

In our previous work [8], we have shown that the silica shell obtained from the sodium silicate solution had mesoporous structure while the silica core particles prepared from TEOS had microporous structure. It was also found that the total pore volume of obtained silica core/shell particles was increased by increasing the thickness of silica shell. Thus, the obtained silica core/shell particles might be used in bioengineering for the immobilization of enzymes inside mesoporous silica shell.
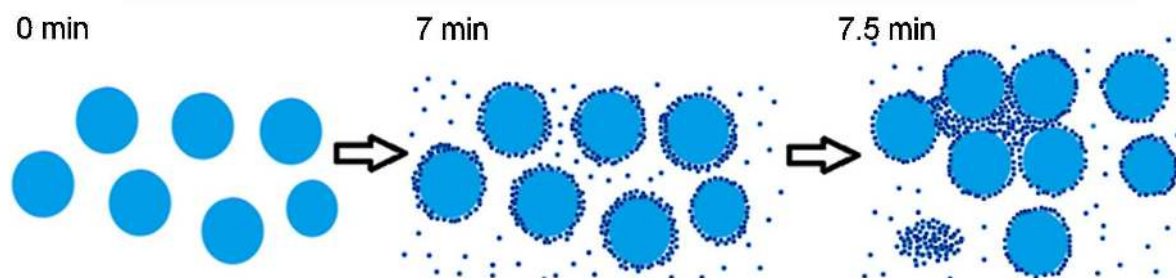

Figure 5. Schematic representation of core/shell particle formation depending on reaction time
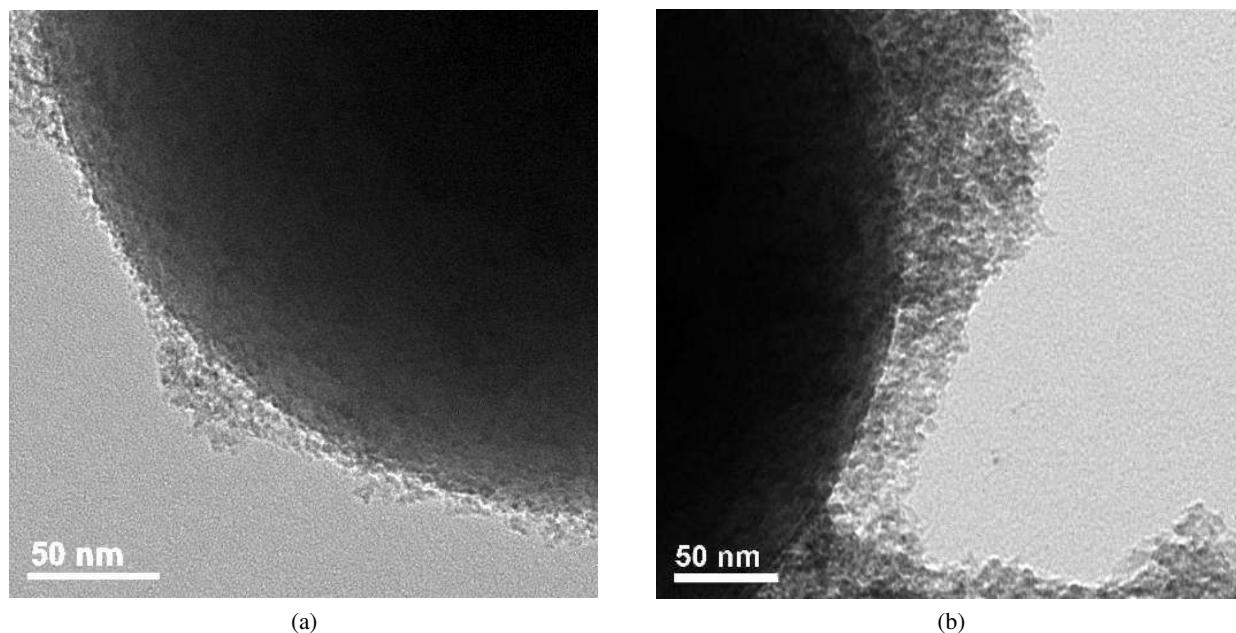
(a)

(b)

Figure 6. TEM micrographs of core-shell particles synthesized at 70 °C ($C = 55$ g/l, $M = 2.5$) after: a) 6 and b) 7 minutes

IV. Conclusions

The formation of silica nanoparticles by neutralization of highly basic sodium silicate solution and their deposition on the surface of functionalized silica core particles were strongly influenced by various experimental conditions such as reaction time. It was shown that size and degree of aggregation of the obtained silica nanoparticles increase with an increase of the temperature and reaction time. In the early stage of the reaction when there is no strong tendency towards aggregation, uniform and continuous silica layers were formed around functionalized silica core particles. However, as the reaction progresses, separate aggregates of silica nanoparticles were formed and obtained silica layers were thicker but non-uniform. At the final stage of reaction, gel point was reached which resulted in linking all the particles inside gel matrix.

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