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Synthesis of mesoporous silica particles with controlled pore structure

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Abstract

Silica particles, with controllable porosity, were synthesized using two different precursors, tetraethylortosilicate (TEOS) and sodium silicate, but without the addition of template. Characteristics of silica particles (aggregates) prepared by these two methods were compared. The pore structure was tuned only by changing the processing parameters, such as precursor concentration, base concentration, temperature and reaction time. The pore structure of prepared silica particles (aggregates) is strongly influenced by processing conditions and easy controllable in broad range of the specific surface area, pore size, size distribution and pore volume. However, the silica particles synthesized from TEOS have very low total pore volume (ranging from 0.06 to 0.2 cm^3/g) and a large portion of pores smaller than 4 nm. On the other side, the silica particles prepared from sodium silicate can be defined as a mesoporous silica with the average pore size up to ~20 nm and much higher total pore volume (ranging from 0.8 to 1.5 cm^3/g), which are important advantages for their application in encapsulation of enzymes.

Keywords: A. Powder: chemical preparation; B. Porosity; D. SiO_2

1. Introduction

Mesoporous silica particles, material with high surface area and pore sizes in the range of 2–50 nm, possess high surface free energy and have attracted much attention for numerous applications in adsorption, separation, catalysis and drug delivery. Different mechanisms for the formation of silica particles were suggested. According to the model proposed by LaMer and Dineger [1] particles are initially nucleated within a short period of time in a highly supersaturated solution of silicon oxide as a result of hydrolysis and condensation. The nucleation process decreases considerably the concentration of silicon oxide species in the solution and only the growth process proceeds by integration of the silicon oxide on the particle surface, forming dense monodisperse particles. According to Chen et al. [2] if the production of silicon oxide by hydrolysis and condensation is faster than the consumption for particle growth by diffusion, secondary particles are generated, thereby producing the multi-modal distribution of the particle size. On the other side, Boukari et al. [3,4] proposed that the first particles to form in the solution are mass fractals with polymeric open structure and could be considered as the primary silica particles. The possibility of porous particle formation was also described by the aggregation growth model [5,6]. This model states that particle growth occurs due to an aggregation of primary particles which are nucleated in a supersaturated solution, producing a porous structure. However, pores could be closed during aging in the solution due to the dissolution/reprecipitation process. Thus, depending on the synthesis parameters, the structure of prepared silica particles may vary from isolated dense particles to porous agglomerates with different pore size and shape, pore size distribution and pore volume.

Several preparation methods were used for preparation of mesoporous silica particles. The most popular one is the sol–gel synthesis proposed by Stöber et al. [7] that is based on hydrolysis and condensation of highly reactive silicon-alkoxide precursor at low temperature. Thus, silica particles with various characteristics were prepared by ammonia-catalyzed reactions of tetraethylortosilicate (TEOS) with water in low molecular

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weight alcohol [7–12]. Recently, a modified sol–gel route employing the templates, such as ionic/neutral surfactants [13–15] or nonsurfactant organic molecules [16,17], has been used for preparation of well controlled pore structure and ordered mesoporous materials. Due to a high cost of these processes, applicability of other precursors has also been investigated. Thus, different types of mesoporous silica particles were prepared from sodium silicate [18,19] or even an environmentally safe and renewable resource, such as a rice husk ash [20].

The aim of this work is to synthesize mesoporous silica particles which can be used for encapsulation of enzymes, the field that has recently attracted considerable attention [17,21–23]. For this purpose silica particles with controllable porosity were synthesized using two different precursors, tetraethylortosilicate and sodium silicate, but without the addition of any template. Characteristics of silica particles prepared by these two methods were compared. The pore structure (specific surface area, average pore size, size distribution and pore volume) was tuned only by changing the processing parameters, such as precursor concentration, base concentration, temperature and reaction time.

2. Experimental

Mesoporous silica particles were synthesized by the hydrolysis and condensation of tetraethylortosilicate, TEOS ($Si(OC_4H_9)_4$, Fluka). TEOS was dissolved in anhydrous ethanol and hydrolyzed with distilled water under basic conditions (25% NH_3, Merck). The H_2O:TEOS molar ratio was kept constant at 40, but the TEOS concentration and NH_4OH:TEOS molar ratio were changed from 0.25 to 0.50 mol/l and from 1 to 4, respectively (Table 1). After feeding, the product suspension was continuously stirred at room temperature for 1 or 10 h. The white precipitated powders were centrifuged and washed with distilled water until the effluent was free of NH_4 groups, and finally dried at 120 °C for 1 day.

Mesoporous silica particles were prepared from highly basic sodium silicate solutions (Water glass, Alumina Factory-Birač, Zvornik), having two Na_2O/SiO_2 molar ratios (1.1 and 1.6 mol/mol) and three different concentrations of SiO_2 (0.6, 0.9 and 1.3 mol/l). Sulfuric acid (H_2SO_4 = 3.7 mol/l) was slowly added into a well stirred sodium silicate solutions at 50 and 90 °C to precipitate silica particles (Table 2). Finally, pH was adjusted at value of ~4 to prevent dissolution process. The white precipitated powders were washed with distilled water, separated from liquid phase by filtration and finally dried at 120 °C for 1 day.

The specific surface area (according to the BET method), pore size distribution (according to the BJH method) and pore volume of as-synthesized powders were measured by low temperature nitrogen adsorption using a Quantachrom Autosorb-3B instrument. Fourier-transformed infrared spectra were taken by Nicolet-Nexsus 670 FT-IR instrument from 650 to 4000 cm^{-1} using KBr as reference. Size and morphology of particles were examined using a scanning electron microscope (SEM JEOL, 6460LV, operating at 20 kV).

3. Results and discussion

3.1. Silica particles prepared from TEOS

It is well known that spherical silica particles with narrow size distribution could be synthesized from TEOS, which is also confirmed with our results presented in Fig. 1a. In addition, it has been shown [7–12] that size and distribution of the synthesized silica particles are very sensitive to the TEOS:NH_4OH:H_2O molar ration and TEOS concentration. However, it is still not completely clear how someone can control the porosity inside those as-synthesized particles (aggregates) simply by changing the processing parameters (without the addition of pore-forming agents, i.e. templates). Thus, four silica powders were synthesized from TEOS under different

Table 1
Sample notation and synthesis conditions for silica powders prepared from TEOS.

Sample notation	Precursor	TEOS [mol/l]	NH_4OH/TEOS [mol/mol]	H_2O/TEOS [mol/mol]	*T* [°C]	Reaction time [h]
T_h4-1	TEOS	0.5	4	40	25	1
T_l4-1	TEOS	0.25	4	40	25	1
T_l1-1	TEOS	0.25	1	40	25	1
T_l1-10	TEOS	0.25	1	40	25	10

Table 2
Sample notation and synthesis conditions for silica powders prepared from sodium silicate.

Sample notation	Precursor	SiO_2 [mol/l]	NaOH/SiO_2 [mol/mol]	*T* [°C]	Reaction time [h]
S_h1-50	Sodium silicate	1.3	0.56	50	1
S_m1-50	Sodium silicate	0.9	0.56	50	1
S_h1-90	Sodium silicate	1.3	0.56	90	1
S_m1-90	Sodium silicate	0.9	0.56	90	1
S_l1-90	Sodium silicate	0.6	0.56	90	1
S_h2-50	Sodium silicate	1.3	0.8	50	1
S_m2-50	Sodium silicate	0.9	0.8	50	1

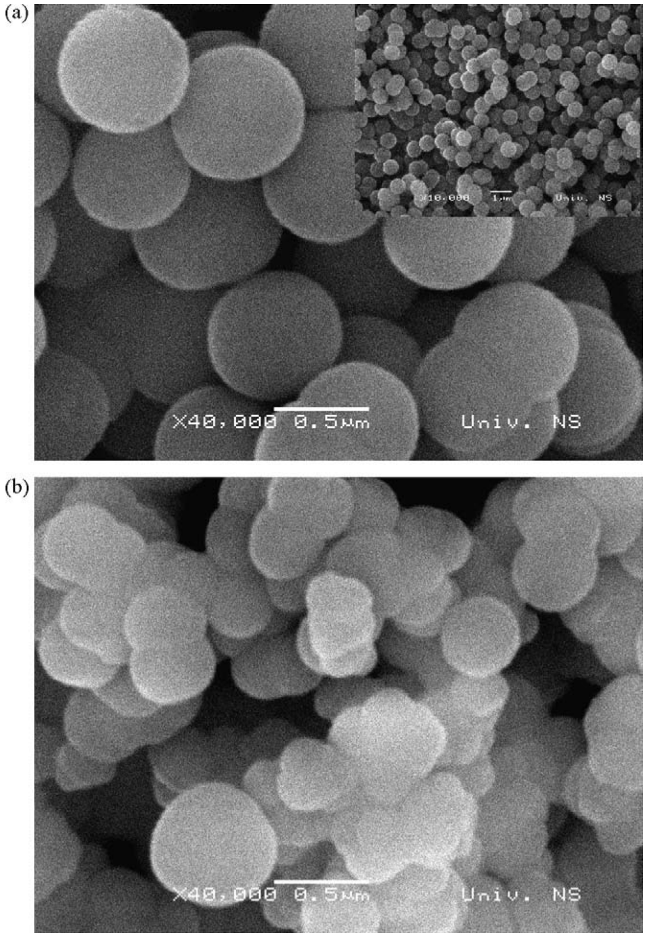

Fig. 1. SEM micrographs of silica particles prepared with the molar ration TEOS:NH_4OH:H_2O = 1:40:4 and TEOS concentration of (a) 0.25 mol/l (the sample T_l4-1) and (b) 0.5 mol/l (the sample T_h4-1).

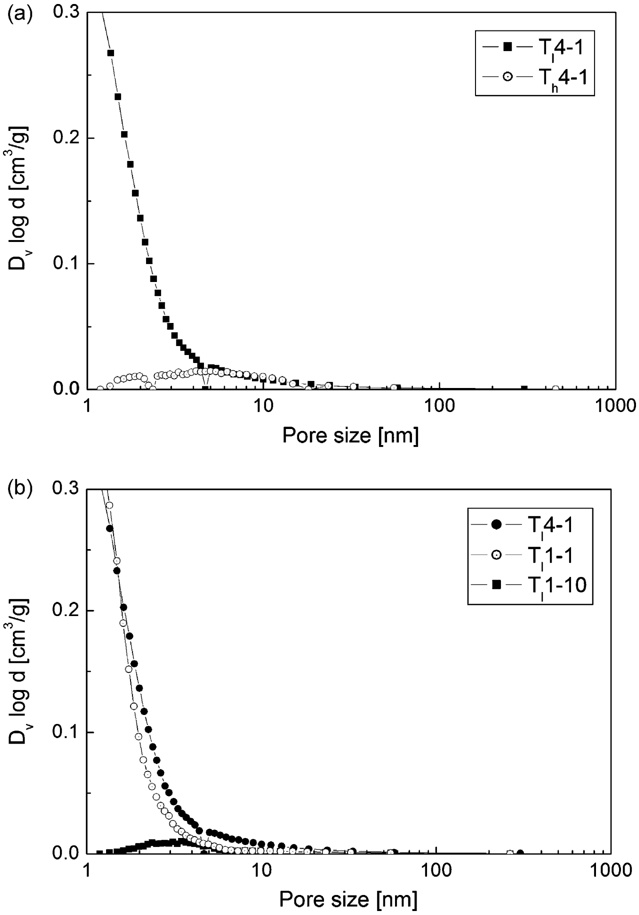

Fig. 2. Pore size distribution in silica particles prepared using: (a) different TEOS concentration and (b) different NH_4OH concentration and reaction time.

conditions (Table 1) with the main goal to clarify it and to define the type of the obtained pore structures.

The specific surface area of the samples synthesized using a common molar ratio TEOS:H_2O:NH_4OH = 1:40:4 and reaction time of 1 h decreases from 324 to 9.4 m^2/g when the TEOS concentration is increased from 0.25 to 0.5 mol/l (Table 3), confirming that porosity of the prepared silica particles is very sensitive to the TEOS concentration. Pore size distribution of the sample T_l4-1 (having the TEOS concentration of 0.25 mol/l) is presented in Fig. 2a, and reveals the existence of a very high portion of pores smaller than 4 nm. Small size of primary particles and their fractal structure are the reasons for the formation of very fine porosity. In concentrated solution (the sample T_h4-1, prepared with the TEOS concentration of 0.5 mol/l) aggregates having very small pore volume and the average pore size of 4.5 nm are formed (Table 3). Higher TEOS concentration speeds up the hydrolysis/condensation reactions and causes formation of larger primary particles and almost complete closing of small pores (Fig. 2a). Higher reaction rate does not have influence only on structure of primary particles, but also on the size and distribution of secondary particles (aggregates). Thus, aggregates with a smaller size and broader size distribution are formed if the TEOS concentration is higher (Fig. 1).

Table 3
Characteristics of pore structure of particles synthesized from TEOS.

Sample notation	Specific surface area [m^2/g]	Average pore size [nm]	Total pore volume [cm^3/g]
T_h4-1	9.4	4.5	0.066
T_l4-1	324	2.2	0.181
T_l1-1	385	2.0	0.216
T_l1-10	104	3.4	0.088

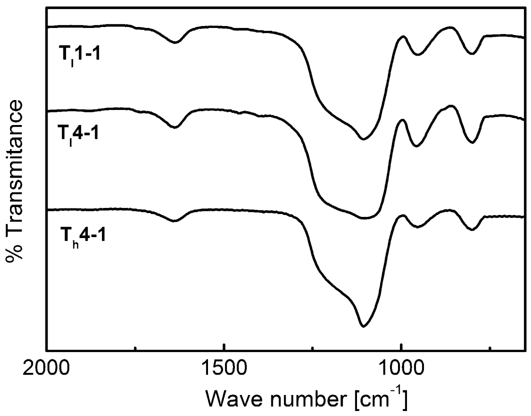

Fig. 3. FTIR spectra of silica samples prepared from TEOS.

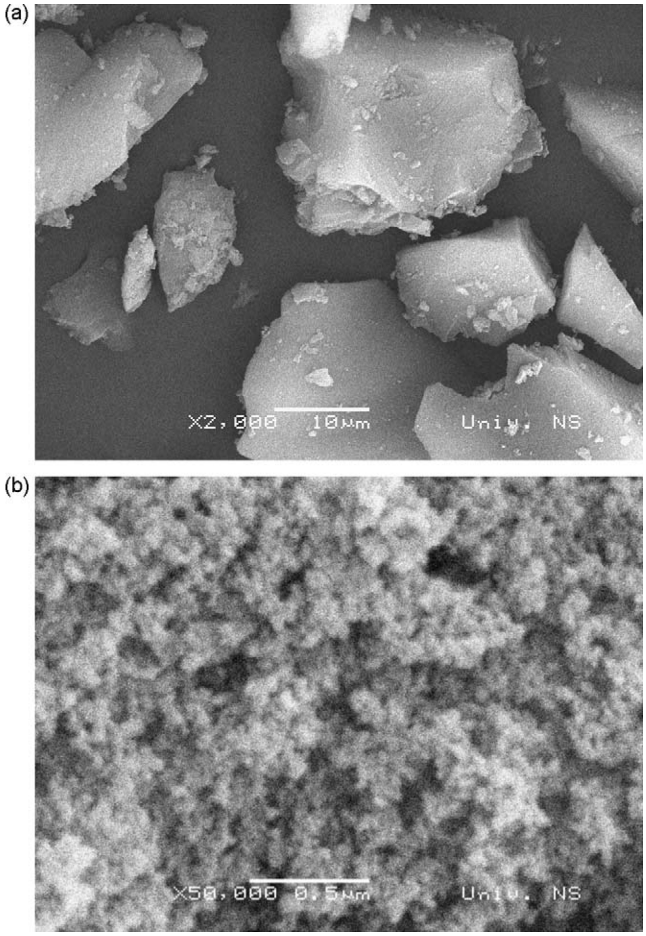

Fig. 4. SEM micrographs of silica particles prepared from sodium silicate at: (a) low magnification (S_h1-50) and (b) high magnification (S_h1-90).

Resolution of scanning electron microscopy was not high enough to detect very fine porosity inside the silica aggregates (Fig. 1). However, the difference in pore structure could be observed with FTIR, presented in Fig. 3. In all spectra (Fig. 3), in the low wave number range, two typical bands of silica are clearly visible corresponding to the transverse optical modes at 795 and 1080 cm^{-1} [24]. The band at 966 cm^{-1}, due to the stretching of non-bridging oxygen atoms, e.g. Si–O–(H···H_2O) [24,25], is very pronounced in the sample T_l4-1. This could be explained with higher portion of surface O–(H···H_2O) groups bounded to Si, due to higher specific surface area and finer pore structure of this powder. The large absorption band between 1250 and 1000 cm^{-1} has been described as an overlap of various SiO_2 peaks and peaks due to residual organic groups [24]. Shoulder around 1250–1130 cm^{-1}, which is more pronounced in the sample T_l4-1, indicates higher portion of unreacted organic groups and could be connected with slower reactions in this sample.

Table 4
Characteristics of pore structure of particles synthesized from sodium silicate.

Sample notation	Specific surface area [m^2/g]	Average pore size [nm]	Total pore volume [cm^3/g]
S_h1-50	539	6.6	0.894
S_m1-50	512	5.6	0.719
S_h1-90	280	19.0	1.121
S_m1-90	337	16.5	1.392
S_l1-90	359	15.8	1.415
S_h2-50	394	15.0	1.480
S_m2-50	562	6.7	0.951

Decreasing of the NH_4OH concentration, i.e. the NH_4OH/TEOS molar ratio from 4 to 1 (the samples T_l4-1 and T_l1-1, respectively), causes small increase of the specific surface area, but small decrease of the average pore size (Table 3). Pore size

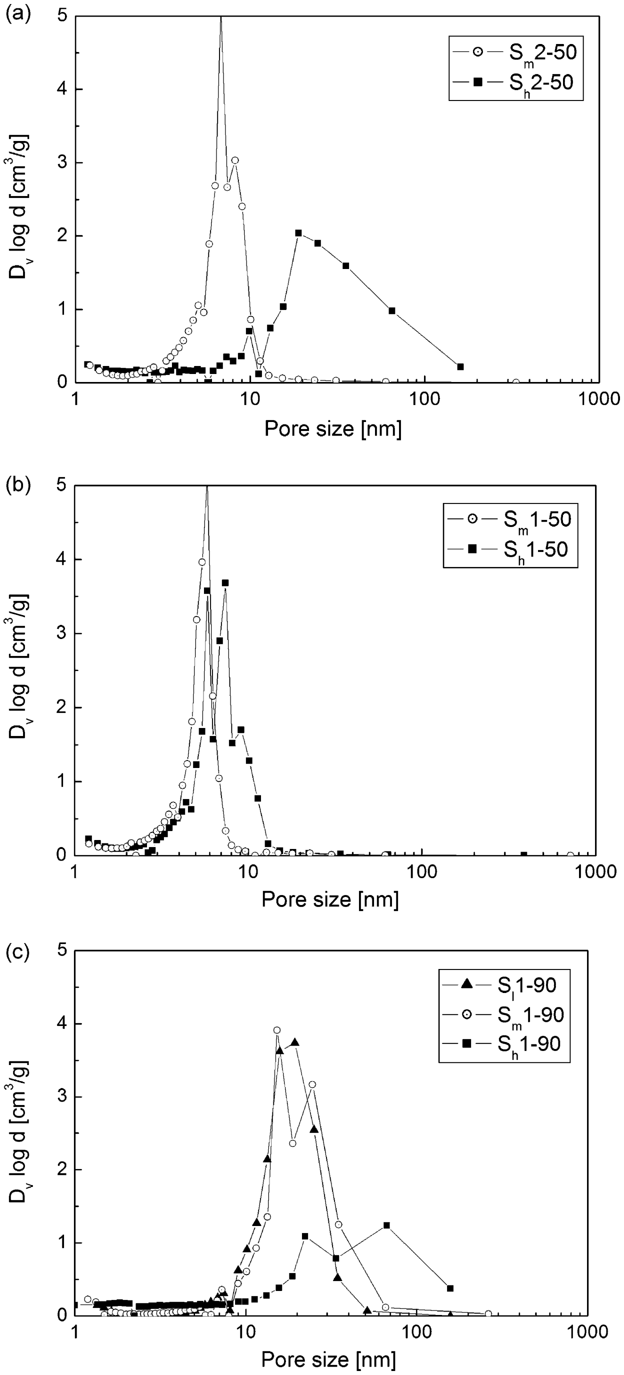

Fig. 5. Pore size distribution in silica particles prepared from sodium silicate, using: (a) $NaOH/SiO_2 = 0.8$ and $T = 50\,^{\circ}C$, (b) $NaOH/SiO_2 = 0.56$ and $T = 50\,^{\circ}C$ and (c) $NaOH/SiO_2 = 0.56$ and $T = 90\,^{\circ}C$.

distribution curves of the samples with different NH_4OH/TEOS molar ratio (the samples T_l4-1 and T_l1-1) are presented in Fig. 2b. Both curves have similar shape, but the sample T_l1-1 has higher portion of small pores. Thus, it can be concluded that if lower concentration of NH_4OH is used hydrolysis/ condensation reactions are slower and somewhat smaller primary silica particles are formed. However, pore structure inside aggregates is not changed considerably.

Using the molar ratio TEOS:H_2O:NH_4OH = 1:40:1 and TEOS concentration of 0.25 mol/l it could be seen (Table 3) that porosity of the prepared silica aggregates is also very sensitive to the reaction time. Thus, the specific surface areas of 385 and 104 m^2/g were obtained when synthesis times were increased from 1 to 10 h, respectively (Table 3). Pore size distribution is also changed considerably (Fig. 2b). It seems that aging enable efficient closing of pores, i.e. fine porosity (pores smaller than 4 nm), observed in the sample T_l1-1 (synthesized for 1 h) completely disappear with prolongation of the reactions (the sample T_l1-10) most probably due to the dissolution/ reprecipitation process.

It can be concluded that the TEOS concentration and aging have strong influence on the porosity in as-synthesized silica particles (aggregates), whereas the influence of the NH_4OH:TEOS molar ration (in the range 1–4) is not so pronounced. However, the total pore volume of samples synthesized from TEOS is very low (Table 3), which is important disadvantage for the application of those powders for encapsulation of enzymes.

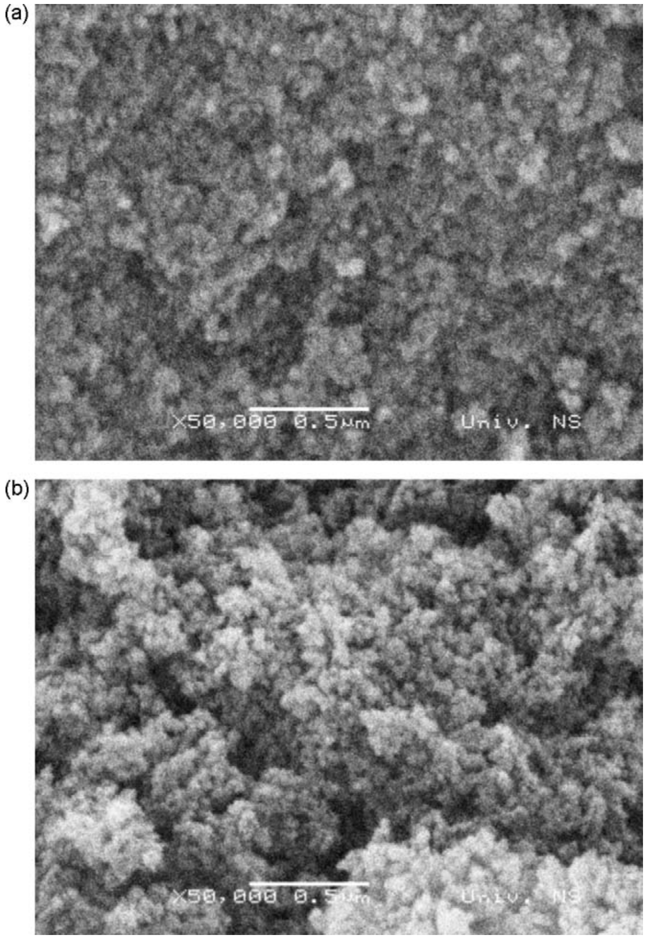

Fig. 6. SEM micrographs of silica powders prepared at $NaOH/SiO_2 = 0.56$, $T = 90$ °C and different SiO_2 concentration: (a) S_m1-90 (0.9 mol/l) and (b) S_h1-90 (1.3 mol/l).

3.2. Silica particles prepared from sodium silicate solution

As the total pore volume of samples synthesized from TEOS (without the addition of template) was very low, another synthesis technique, with a sodium silicate solution as precursor, was adopted for preparation of porous silica particles. Again, different synthesis conditions (without the addition of pore-forming agents, i.e. templates) were used to evaluate their influence on the characteristics of as-synthesized powders. In contrast to the silica synthesized from TEOS (Fig. 1), aggregated silica particles prepared from sodium silicate solution do not have spherical shape and unimodal size distribution (Fig. 4a). In addition, primary particles synthesized from sodium silicate solution could be clearly distinguished on SEM micrographs (Fig. 4b) and are considerably larger than that prepared from TEOS. This is the reason why all the as-prepared powders can be defined as mesoporous silica (Fig. 5) with much higher total pore volume (up to 1.5 cm^3/g) and average pore size (up to ~20 nm) than the samples synthesized from TEOS (Table 4).

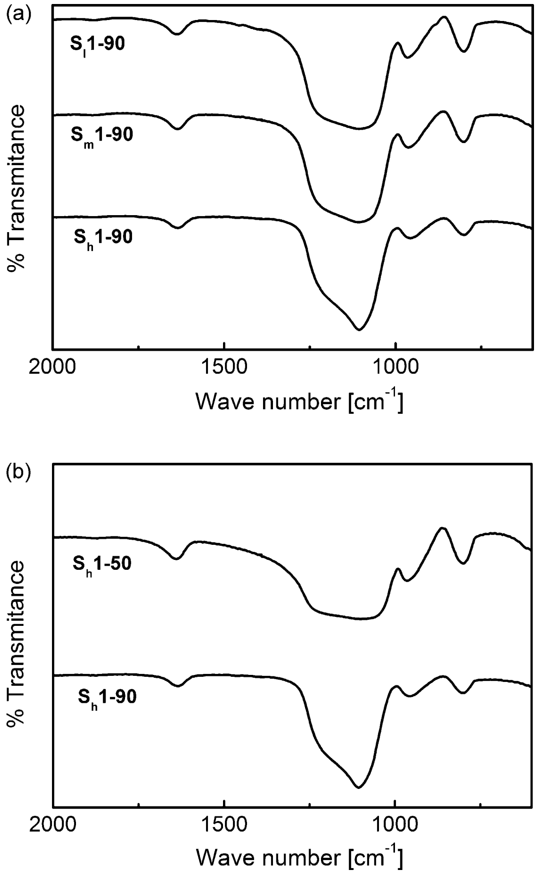

Fig. 7. FTIR spectra of silica samples prepared from sodium silicate using: (a) different SiO_2 concentration at $NaOH/SiO_2 = 0.56$ and $T = 90$ °C and (b) different temperature at $NaOH/SiO_2 = 0.56$ and SiO_2 concentration of 1.3 mol/l.

The decrease of the SiO_2 concentration from 1.3 mol/l (the samples S_h2-50, S_h1-50 and S_h1-90) to 0.9 mol/l (the samples S_m2-50, S_m1-50 and S_m1-90) causes increasing of the specific surface area, decreasing the average pore size and narrowing of the pore size distribution (Table 4 and Fig. 5). The reason is formation of smaller silica particles (Fig. 6) and slower reaction at low SiO_2 concentration. The difference in pore structure could be also recognized in FTIR results, presented in Fig. 7a. In all spectra (Fig. 7a), two typical bands of silica are clearly visible corresponding to the transverse optical modes at 795 and 1080 cm^{-1}. The band at 966 cm^{-1} and shoulder around 1250–1130 cm^{-1} become more pronounced with the decrease of the SiO_2 concentration. This could be explained with higher portion of residual organic and surface O–(H···H_2O) groups bounded to Si in the sample S_l1-90, due to its higher specific surface area and finer pore structure than for the S_h1-90 and S_m1-90 powders.

Increase of temperature from 50 °C (the samples S_h1-50 and S_m1-50) to 90 °C (the samples S_h1-90 and S_m1-90) decreases the specific surface area, increases the average pore size and total pore volume (Table 4) and broadens the pore size distribution (Fig. 5b and c). In addition, the FTIR spectra of the sample S_h1-50 and S_h1-90, synthesized at 50 and 90 °C, presented in Fig. 7b, confirmed that the band at 966 cm^{-1} (due to surface O–(H···H_2O) groups bounded to Si) and shoulder around 1250–1130 cm^{-1} (due to higher portion of residual organic) are very pronounced in the powder S_h1-50 synthesized at lower temperature. The main reason for the observed differences is the fact that at low temperature reactions are slow and, thus, the formed primary particles are small (Fig. 8).

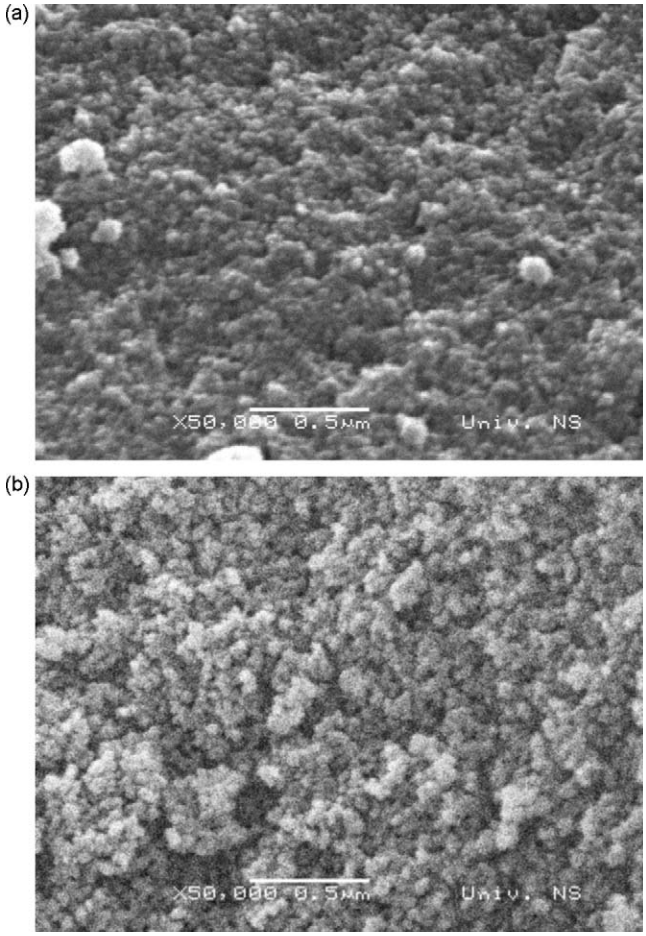

Fig. 8. SEM micrographs of silica powders prepared at $NaOH/SiO_2 = 0.56$, SiO_2 concentration of 1.3 mol/l and different temperatures: (a) 50 °C (S_h1-50) and (b) 90 °C (S_h1-90).

The decrease of the base concentration from the molar ratio $NaOH/SiO_2 = 0.8$ (the samples S_h2-50 and S_m2-50) to $NaOH/SiO_2 = 0.56$ (the samples S_h1-50 and S_m1-50) causes increasing of the specific surface area, decreasing the average pore size and total pore volume (Table 4) and narrowing of the pore size distribution (Fig. 5a and b). The reasons are formation of smaller silica particles and slower reaction at low base (NaOH) concentration.

The investigated reaction time (aging) has small influence on the structure of the synthesized mesoporous silica particles.

4. Conclusions

Silica particles with controllable porosity were synthesized using two different precursors, tetraethylortosilicate and sodium silicate, but without addition of template. The pore structure of prepared silica particles (aggregates) is strongly influenced by processing conditions and easy controllable in broad range of the specific surface area, pore size, size distribution and pore volume. However, the silica particles synthesized from TEOS have very low total pore volume (ranging from 0.06 to 0.2 cm^3/g) and a large portion of pores smaller than 4 nm. On the other side, the silica particles prepared from sodium silicate can be defined as a mesoporous silica with much higher total pore volume (ranging from 0.8 to 1.5 cm^3/g), which are important advantages for their application for encapsulation of enzyme.

The same processing parameters have the similar influence on the structure of the synthesized silica particles in both synthesis methods. Thus, decrease of silica concentration decreases the size of primary particles and causes increasing of the specific surface area and decreasing of the average pore size. The decrease of the base concentration causes increasing of the specific surface area, decreasing of the average pore size and total pore volume and narrowing of the pore size distribution. The reaction time (aging) has strong influence on the structure of the silica particles synthesized from TEOS, but small influence on the structure of the mesoporous silica particles prepared from sodium silicate solution.

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