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Influence of the Precursor Concentration on the Characteristics of Silica Powder Obtained from Na_2SiO_3 by a Facile Low Temperature Synthesis Process

Chieko Yamagata, Daniel Ricco Elias, Mayara Rafaela Soares Paiva, Agatha Matos Misso and Sonia Regina Homem Mello Castanho

Nuclear and Energy Research Institute, Department of Science and Materials Technology, CCTM, São Paulo, Brazil

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Abstract: A convenient synthesis, as well as distinctive structure and physical-chemical properties provide silica materials suitable for a wide range of potential applications, such as catalysts, functional coatings, chemical and biological sensors and drug delivery. In this work a facile route has been successfully developed, at ambient pressure and temperature; to synthesize uniform silica particles, from Na_2SiO_3 waste solution. Non-aggregated silica was prepared by surfactant template sol-gel techniques, via acid-catalyzed hydrolysis by HCl. The influence of the precursor's concentration on the characteristics of the silica powders was investigated. Powders have spherical morphology, and diameter between 0.1 and 5 μm with a narrow size distribution. Results of BET specific surface area analysis were in range 276.26 to 961.54 $m^2 \cdot g^{-1}$. This proposed route possesses advantage over known method for synthesis of silica from silicon alkoxides, because of its low cost and environment friendly, since it employs a waste matter as precursor of silica.

Key words: Silica, sol-gel, non-aggregate powder, sodium silicate.

1. Introduction

In last decade has seen an enormous interest in silica nanoparticles based materials [1-3], because of their wide uses in various applications [4-12], such as catalysis, electronic and film substrates, electronic and thermal insulators, humidity sensors, in pigments, pharmacy and environmental chemistry. The quality of these products is highly dependent on size and size distribution of the silica nanoparticles. Stober et al. [13] reported a pioneering method for synthesis of spherical and monodisperse silica nanoparticles from aqueous alcohol solutions of silica alkoxides in presence of ammonia as catalyst. Different sizes of silica nanoparticles were prepared ranging from 50 to 1 μm with a narrow size distribution. At present, silica nanoparticles materials are prepared by several methods [14, 15], such as sol-gel, vapor-phase reaction and thermal decomposition technique. Among these methods, the sol-gel is largely applied, due to low cost and simplicity of preparation and easily controlling the size, morphology and distribution of the particles [16, 17]. The important advantage is also the fact that is an effective means of producing high-quality materials. Silica nanostructured aerogels are usually synthesized by sol-gel process. This nanostructured material consists of interconnected nanoparticles building blocks which form highly porous three-dimensional silica network that confers many exceptional properties such as high surface area (500-1000 m^2/g), low bulk density (10-200 $Kg \cdot m^{-3}$), low thermal conductivity (~0.01 W/m·K), high porosity (~99%), high optical transmission (99%), low dielectric constant (~1.0-2.0), low refractive index (~1.05) and low sound velocity (100 m/s) [18-21]. Due to rapid development of

Corresponding author: Chieko Yamagata, Dr., research field: materials science. E-mail: yamagata@ipen.br.

sol-gel techniques during the past two decades it has observed fast progress in the deliberate synthesis of porous materials. These techniques complement conventional procedures used for preparation of amorphous solids or glasses, such as precipitation or impregnation methods followed by high temperature treatment [22]. The sol-gel processing can usually be divided into the following steps: forming a solution, gelation, aging, drying and densification. Alkoxides are the most common sol-gel precursor [23]. It is very difficult to predict the kind of precursor to be used for a given purpose, because of its reactivity not depend only on its chemical nature but also on the applied reaction conditions [24]. Tetramethoxysilane (TMOS) undergoes a more rapid hydrolysis than tetraethoxysilane (TEOS) and extensive use to produce monolithic silica aerogels [25]. Comparing the aerogels obtained from three different precursors: TEOS [26], TMOS [27] and PEDS [28] (Polyethoxydisilane), the TMOS yields narrow and uniform pores and higher surface area than TEOS. Alkoxides are expensive and hazardous materials, which prohibit commercialization. Alkoxides precursors can be substituted by cheaper and water soluble precursor such as Na_2SiO_3 (sodium silicate or waterglass) for sol-gel processing. It has been and probably will always be the cheapest source of silicic acid from which silica gel can be made. Sodium silicate reacts with water to give silicic acid and then this acid polymerizes and forms silica gel according to the following reactions:

$$Na_2SiO_3 + H_2O + HCl \rightarrow Si(OH)_4 + 2NaCl \quad (1)$$

The silicic acid condenses to form small silica particles and chains consequently form a network resulting in a silica gel as showing below:

$$n\ Si(OH)_4 + (OH)_4Si \rightarrow$$

$$n\mathrm{OH}-\underset{\mathrm{OH}}{\overset{\mathrm{OH}}{\mathrm{Si}}}-\mathrm{O}-\underset{\mathrm{OH}}{\overset{\mathrm{OH}}{\mathrm{Si}}}-\mathrm{OH} + 2nH_2O \quad (2)$$

From reactions (1) and (2) the structure of sol-gel glasses involves sequentially as the product of successive hydrolysis and condensation reactions. The hydrolysis is catalyzed by addition of an acid or a base [29]. The final form of hydrolyzed silica depends on the pH of the solution. At low pH high acidic, the silica particles tend to form a linear chain with low crosslink density. The mole ratio of Na_2O:SiO_2, Na_2SiO_3:H_2O and silica contents of waterglass solution are important parameters for synthesis of silica aerogel. Na_2SiO_3/H_2O molar ratio $> 8 \times 10^{-3}$, results in aerogels having optimum hydrophobicity and physical properties [30]. The best value of Na_2O/SiO_2 is 1:3.3 and the best silica contents of solution are 4%-8% [31]. With respect to silica particle growth in wet gel, the excess water molecules interact with the free hydroxyl on the surface of the silica gel particles through hydrogen bonds. When particles get close, these molecules can join adjacent particles mutually to form big particles. The formed particles can easily connect into large particles. To avoid this connection, a surfactant can be used to cover then. In 1992, a synthesis of ordered mesoporous metal oxide using surfactant template was reported [32]. Silica spheres have been obtained by using a biphasic system of a quaternary ammonium surfactant [33, 34], nonionic polyethylene-oxide-based surfactant [35] and dual templates [36]. In recent years, silica spheres of hollow morphologies have attracted increasingly more attention due to their potential applications in variety technological areas [37, 38], such as in drug release control, adsorption, and catalysis. Several chemical and physicochemical methods have been used to synthesize hollow spheres, including emulsion phase separation techniques, emulsion interfacial polymerization, and templating colloidal particle techniques [39, 40]. Present study reports a simple, cost effective and environment friendly process to obtain nanostructured silica spheres by using sodium silicate, a waste matter derived from alkali fusion of zircon sand, as silica

source and a tertiary amine ethoxylate as surfactant template agent. Silica sol was obtained via acid-catalyzed hydrolysis by reacting sodium silicate with hydrochloric acid. The effect of each reagent, (hydrochloric acid, ethanol and water) on final spherical particle characteristics was investigated. The particle size was examined under scanning electron microscopy and the specific surface was determined by nitrogen absorption measure (BET method).

2. Experiments

Na_2SiO_3 solution (an effluent derived from alkali fusion of zircon sand) [41] were used as the starting material. The step involved in the obtaining Na_2SiO_3 is showed in below reaction:

$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O \quad (3)$$

This transparent Na_2SiO_3 solution contains approximately 2 wt.% of SiO_2 and 10 wt.% NaOH. Silica powders were synthesized by using a modified sol-gel process, i.e., a water-based sol-gel process. Using Na_2SiO_3 solution as silica source, spherical silica aerogels particles were prepared in HCl medium in presence of a tertiary amine ethoxylate (from Akzo Nobel Surface Chemistry) as surfactant template agent for modification of the wet gel. In a typical synthesis, 3 g of surfactant was dissolved in 10 ml of ethanol and then 52 ml of HCl solution was added to the surfactant dissolved solution, resulting in a clear homogeneous mixture. Solution of silica source (40 ml of Na_2SiO_3 solution) was added at drop wise to the above mixture with constant magnetic stirring at room temperature. After complete addition, the mixture was kept, without stirring at room temperature. After 90 minutes a white turbid suspension was obtained. The resulting product was recovered by filtration followed by exhaustive washing with distilled water and to finish by ethanol wash. The washed particles of silica gel were dried in the oven at 70 °C for 12 h, and further calcined at 600 °C for 1 h to get the spherical silica powders. Specific surface areas of the samples were determined by BET method. For SEM examination, specimens were prepared by placing the particles on the carbon tape. Same samples were observed using field emission scanning electron microscopy (FE-SEM, JEOL, F 6500, Japan). Experiments were conducted with variation of the concentration of SiO_2; hydrochloric acid; ethanol and water, to investigate the effect of each reagent on final spherical particle size.

3. Results and Discussion

Various parameters play an important role in size and size distribution of silica particles: concentrations of SiO_2, HCl, ethanol, water and surfactant. A systematic study was carried out using different concentration of those reagents. Table 1 shows the BET specific surface area under different reaction condition. From the BET specific surface area analysis observed in Table 1, it is clear that in all cases relatively high surface was obtained in range 276.26 to 961.54 $m^2 \cdot g^{-1}$. In sample A16, no white turbid suspension was resulted after 90 minutes keeping on, so the reaction conditions in this sample was not favorable to precipitate gel of silica. Only after 24 h a slight precipitate was observed.

From Table 1, there is no rational conclusion about the effect of the parameters on the specific surface area, because no significant variation of area was observed, but it is clear that in almost all cases aero gel silica [21] was obtained due to the characteristic high surface area. Spherical particles were obtained for all samples. Fig. 1 exhibits FE-SEM image of silica particles prepared with conditions of sample H8, as showed in Table 1.

It can be seen that the silica nanoparticles have shared to form a submicron spherical particle, i.e., the spherical particle is composed of smaller material. This nanostructure is similar to nanostructured silica powders derived from the method of sol spraying colloidal suspension [22]. Fig. 2 shows FE-SEM image particle surface of silica obtained from the same experimental conditions of sample A2, as showed in

Table 1 BET specific surface area under different reaction condition.

Sample	surfactant ($g \cdot L^{-1}$)	HCl (M)	Ethanol ($g \cdot L^{-1}$)	H_2O ($g \cdot L^{-1}$)	Si O_2 ($g \cdot L^{-1}$)	BET ($m^2 \cdot g^{-1}$)
A2	26.78	2.14	59.5	71.4	5.83	533.14
A4	13.39	1.07	29.8	71.4	2.92	660.95
A8	6.69	0.54	14.9	71.4	1.46	513.48
A16	3.34	0.26	7.4	71.4	0.73	-
H2	26.78	4.28	59.5	71.4	5.83	654.25
H4	13.39	4.28	29.8	71.4	2.92	685.24
H8	6.69	4.28	14.9	71.4	1.46	656.51
H16	3.34	4.28	7.4	71.4	0.73	516.84
H10	53.57	1.2	119.0	71.4	11.66	961.54
H20	26.78	2.4	59.5	63.5	5.83	720.77
H40	13.39	4.8	29.8	47.6	2.92	276.26
H60	6.69	7.2	14.9	31.7	1.46	314.69
H70	3.34	8.4	7.4	23.8	0.73	753.01

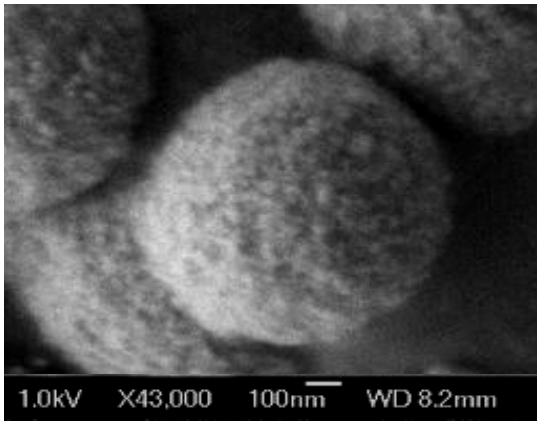

Fig. 1 FE-SEM micrographs of silica nanoparticles obtained from experimental conditions: 4.28 M HCl, 14.88 $g \cdot L^{-1}$ Ethanol, 1.46 $g \cdot L^{-1}$ SiO_2, 71.4 $g \cdot L^{-1}$ H_2O and 6.69 $g \cdot L^{-1}$ surfactant.

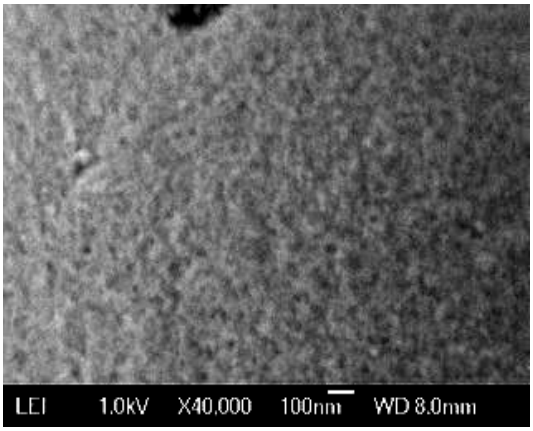

Fig. 2 FE-SEM image particle surface of silica aerogel obtained from experimental conditions: 2.14 M HCl, 59.5 $g \cdot L^{-1}$ Ethanol, 5.83 $g \cdot L^{-1}$ SiO_2, 71.4 $g \cdot L^{-1}$ H_2O and 26.78 $g \cdot L^{-1}$ surfactant.

Table 1. It can be observed the surface is consisted of nanoparticles and high porosity is present.

SEM images of the samples A2, A4, and A8, prepared by sequential dilution of all reagents, except H_2O, are showed in Fig. 3. It can be seen that decreasing the concentration of the reagents, the size of the particles practically is not affected. In samples A2 and A8, homogeneous particles are observed. In sample A4, the particles are connected constituting hard agglomerates, as can see from the two images of A4. It is important to notice that the hard agglomerates only were observed in the sample A4.

Fig. 4 shows SEM images of the samples H2, H4, H8 and H16, prepared by sequential dilution of SiO_2, ethanol and surfactant. By decreasing the concentrations of SiO_2, ethanol and surfactant, the size of silica particles decreases. It also can affirm that uniform sized silica particles, i.e., a narrow distribution is observed in samples H4, H8 and H16.

Samples H10, H20, H40 H60 and H70 were prepared by sequential increasing of HCl concentration. In Fig. 5 it can see SEM images of those samples. Increasing HCl concentration or increasing H_2O concentration, a decreasing in the particle size is observed. According to a previous work [42] the increase in water concentration yields smaller particles, while in another study [43], larger particles were obtained at higher water concentrations.

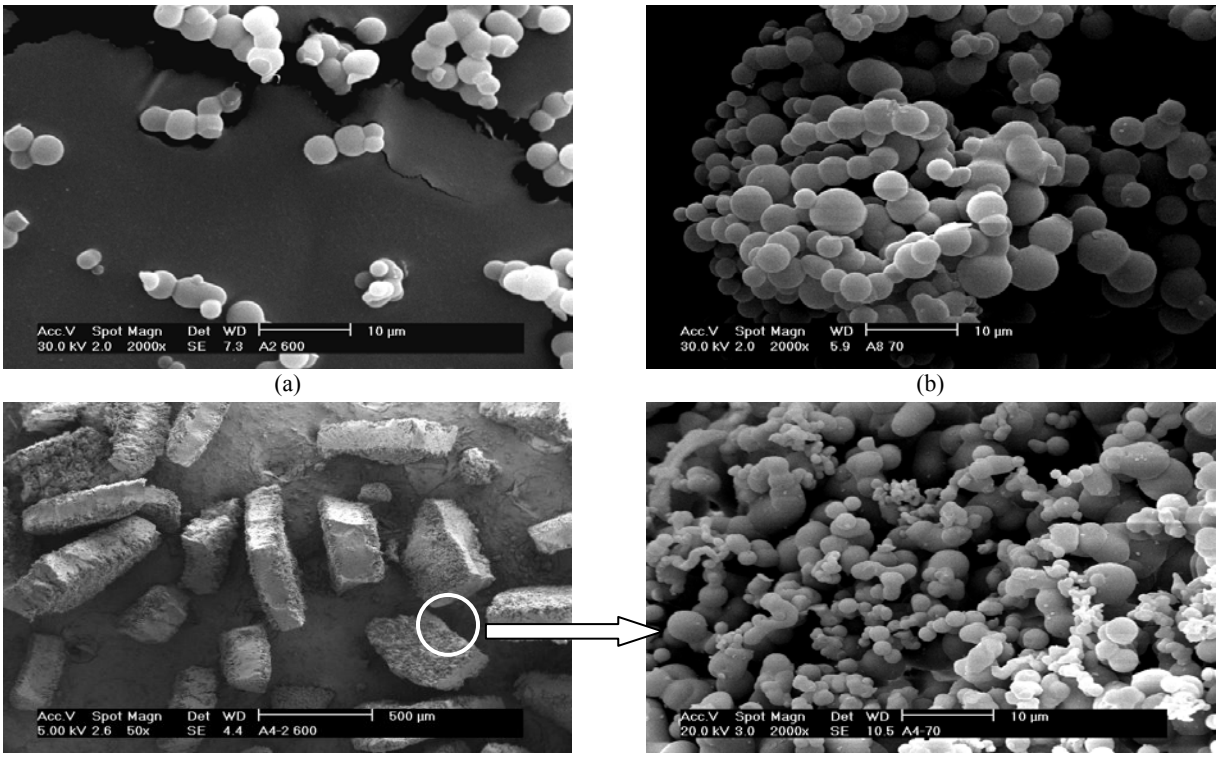

Fig. 3 SEM images of SiO_2 particles prepared by sequential dilution (specified in Table 1) of all reagents except H_2O, samples A2, A4 and A8. (a) A2, (b) A8, (c) A4 and (d) A4 (high magnification).

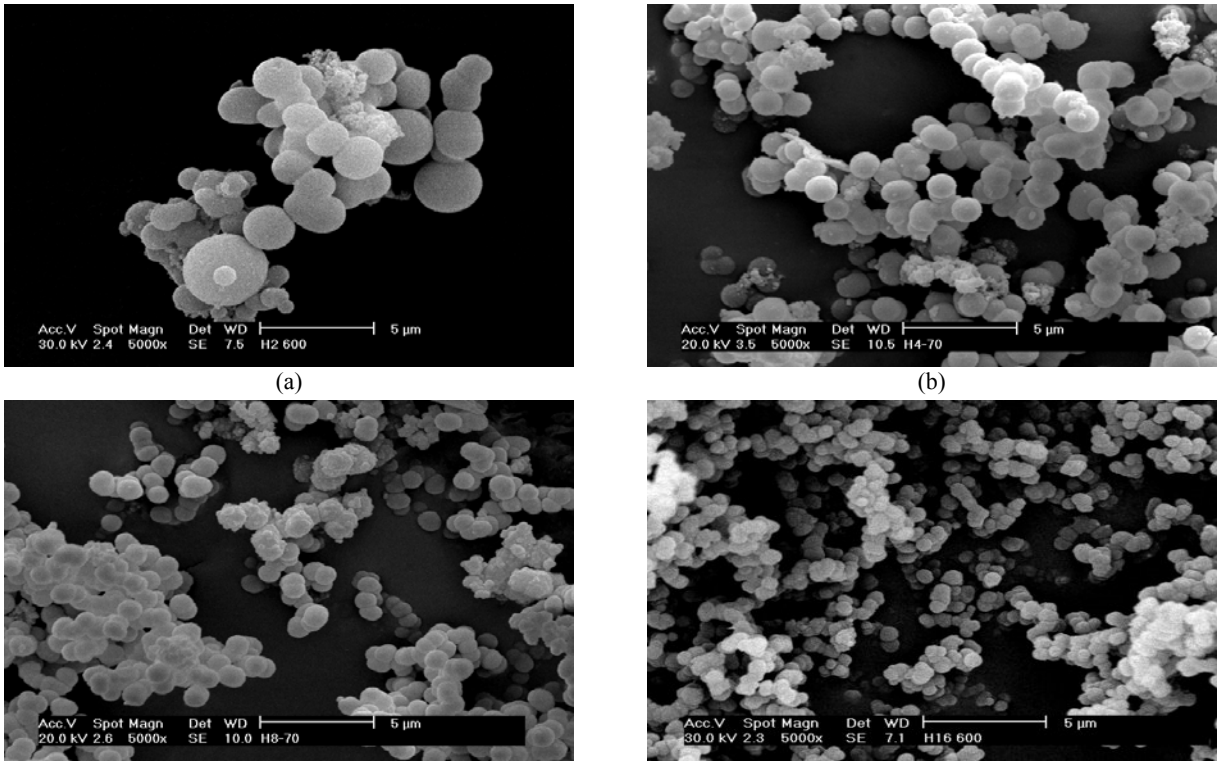

Fig. 4 SEM images of SiO_2 particles, samples (a) H2, (b) H4, (c) H8 and (d) H16, prepared by sequential dilution of SiO_2, ethanol and surfactant concentration, as specified in Table 1.

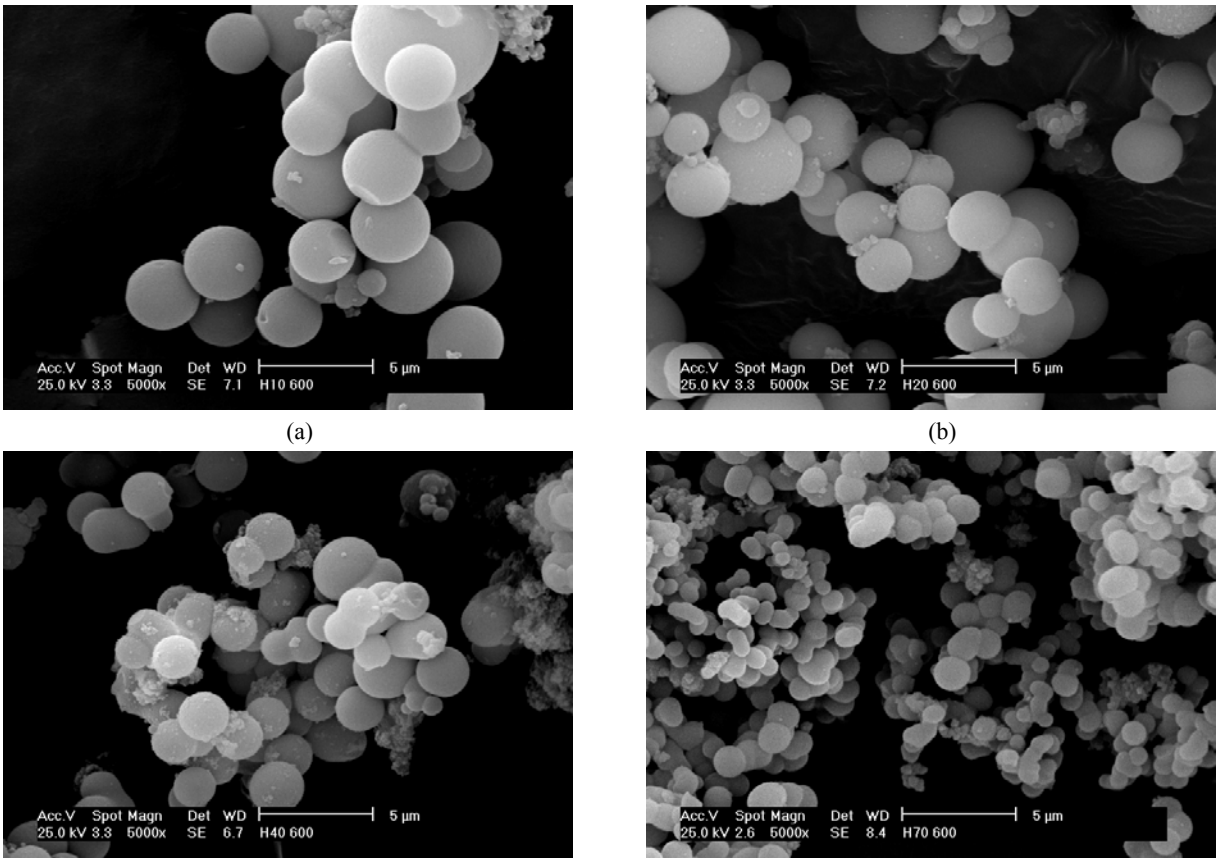

Fig. 5 SEM images of SiO_2 particles, samples (a) H10, (b) H20, (c) H40 and (d) H70, prepared by increasing HCl concentration, as showed in Table 1.

Therefore the effect of each parameter depends on the others applied reaction conditions, therefore the final conclusion is difficult to be achieve.

4. Conclusions

Compared to other used techniques, a simple, convenient and one-step method to synthesize nanostructured silica powders was reported. Spherical particles were obtained for all samples. From results of BET specific surface analysis, obtained in range 276.26 to 961.54 $m^2 \cdot g^{-1}$, aerogel silica was attained. The effect of the reagent concentrations of hydrochloric acid; ethanol; water; surfactant and SiO_2 on the final spherical particle size was studied. The size of silica particles decreases with decreasing the concentration of SiO_2, ethanol and surfactant. Increasing H_2O concentration, a decreasing in the particle size is observed. The use of the low-cost and environmentally friendly sodium silicate, a waste solution derived from alkali fusion of zircon sand, is by far the main advance of the present work.

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