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Synthesis parameters for control of mesoporous silica nanoparticles (MSNs)

Juliana Jorge [1], Marc Verelst [2], Gustavo Rocha de Castro [3], Marco Antonio Utrera Martines [1,*]
[1]Institute of Chemistry, Federal University of Mato Grosso do Sul, UFMS, CEP 79074-460, Campo Grande, MS, Brazil
[2]Centre d'Élaboration de Matériaux et d'Etudes Structurales, CEMES-CNRS, BP 94347, 31055 Toulouse, France
[3]Institute of Biosciences of Botucatu Sao Paulo State University, UNESP, P.O.Box 510, CEP 18618-000, Botucatu, SP, Brazil
*corresponding author e-mail address: ***marcomartines@gmail.com***

ABSTRACT
MSNs are excellent host matrices for molecules and biomolecules, making this material very promising for several nanotechnological applications in industry scale, chemical engineering, environmental, medicine and biology; for instance, as catalysts; adsorbents of heavy metals for depollution; drug delivery systems; and biomarkers, respectively. Here, we report our efforts to obtain MSNs type MCM-41, with controlled particle size (100 to 150 nm), spherical shape, no agglomeration, high surface area, a high pore volume and hexagonal arrangement by full optimization of procedure, studying the influence of parameters as reactants concentrations, temperature and reaction time. Herein, we discussed all performed experiments, the nanoparticles formation, as well as the results are presented and argued according literature data.
Keywords: *silica nanoparticles, mesoporous nanomaterials, MCM-41, TEM, SEM.*

1. INTRODUCTION

Mesoporous silica nanoparticles (MSNs) are excellent matrices for molecules and biomolecules anchorage, making these materials very promising for several nanotechnological applications in industry scale, chemical and environmental engineering, medicine and biology; for instance, as catalysts [1]; adsorbents of heavy metals for depollution [2]; drug delivery systems [3]; and biomarkers [4], respectively.

From first synthesis of mesoporous silica, especially MCM-41 type of M41S family, thousands of studies were reported about its properties and formation, due strong interest for applications in many fields as adsorption, separation, catalysis and advanced materials. Especially as regards the control of the particle size, morphology and porosity, advancements in the synthesis of mesoporous silica materials along with their chemical stability, have made silica matrices highly attractive as the structural basis for a wide variety of nanotechnological applications [1].

Therefore, from points of view scientific and industrial, it is very important attend to preparation condition of MSNs, as well their precursors [5-7]. MSNs are widely different of silica nanoparticles non-porous related to amphiphilic molecules used as templates for porous formation. Also it is important to note that when nanoparticles have not complete mesostructure, the expression MSN is used, for instance, when molar ratio of precursor solution is less than 0.13 [8].

MSNs have some interesting properties, as facile functionalization and also, several unique characteristics like as high specific surface area, high pores volume, adjustable pores structure, and excellent physical-chemical stability. Then, studies about it applications in biomedical field have been attracted great attention. MSNs have been intensively suggested for bone regeneration [9,10], drug delivery systems [11]; bio-signals sensing, gene expression and transport, biomarkers [4], and many other important applications. Hence, as a good kind of bio-carrier, its potential bio-effects related cytotoxicity, bio-distribution, bio-retention, biodegradation, biocompatibility and hemolysis, have been attracted great attention [11], and many studies about this have been developed.

However, actual size used on nanoparticles bioengineering is similar to many biological molecules (for instance, proteins) and structures (as virus), moreover nanoparticles may be not cross free or indiscriminately all biological barriers, but may be governed by physical-chemical specific properties of nanoparticles, as well functional molecules adhered in its surface [12]. Therefore, due its interesting and desirable properties for use in biological area remains a great challenge in developing methodologies for synthesis of small MSNs with ordered pores, controlled size and monodisperse particles.

Lechevallier *et al*. (2013), obtained monodisperse nanoparticles with average size diameter of 100 nm, hexagonal arrangement mesopores highly-ordered of MCM-41 type, by typical sol-gel synthesis, using cetyltrimethylammonium bromide (CTAB) as cationic surfactant [5]. Nooney and co-authors (2002) used different synthesis with two surfactants, one cationic as a structure template and another nonionic as controlling or suppressing particles grown, and concluded that the insertion of a second surfactant not deforms the hexagonal mesostructure, and may be obtained nanoparticles with small size diameter with hexagonal mesostructure highly ordered [13]. He and co-authors (2010) achieved MCM-41 type NPs of 150 nm in average size diameter, varying of 130 to 170 nm, with well-ordered hexagonal arrangement mesopores, using also typical sol-gel synthesis, using CTAB as cationic surfactant [11]. Suzuki, Ikari and Imai (2004) reported MSNs PEGylated synthesized by homogeny and heterogenic synthesis, varying molar ratios reagents, using anionic and neutral surfactants, water and ethanol as solvent which

provided irregular and smooth spheres shape, highly ordered pores with obtained by heterogenic and homogeny with anionic surfactant synthesis, in homogeny synthesis with anionic surfactant, a starburst shape of porous was obtained, and regular monodisperse spheres with disordered pores arrangement were obtained from homogeny synthesis with nonionic surfactant [12]. Already Monnier *et al*. (1993) reported an one-pot synthesis procedure, using triethanolamine (TEA) base for controlling size particles to give also MSNs PEGylated with uniform shape and narrow distribution size, controllable size particles from varying the concentration of TEA base used in this synthesis [14]. Ikari, Suzuki and Imai (2004) also published another study involving a typical sol-gel synthesis, using cetyltrimethylammonium chloride (CTAC) as cationic surfactant and ammonium as base, and achieved particles and pores with controllable size (10-100 nm and 2-3 nm, respectively), adjusting the concentration of CTAC and ammonium used in this synthesis [15]. Zhang and co-authors (2014), carried out sol-gel synthesis varying cationic surfactant/Si precursor molar ratios, and observed that in low molar ratios mesostructure wormhole-like type are formed, and the mesopores not pass through the outer surface of the particles completely. In higher molar ratios the mesostructure is extended to outer surface completely. Moreover, in low molar ratios the particle size founded was 100 nm or more, and as the molar ratio increases the average particle size decreases, due an increase of dispersity of alkoxysilanes in water, which becomes faster the hydrolysis rate of alkoxysilanes leading to an increase of nucleation, as compared to nanoparticles growth. Also, in low molar ratios, particles primary aggregated are not involved into mesostructured formation process, but are adsorbed onto nanoparticles, differently in higher molar ratios that surfactant micelles are adsorbed in the particles primary surface, resulting on dispersion of particles due the electrostatic repulsion. Molar ratios of 0.13 or higher are ideals for preparation of MSNs highly disperses [16]. Also, Liu and co-authors (2014) reported MSNs obtained by typical sol-gel synthesis, using CTAB as cationic surfactant and demonstrated a safe and effectively drug delivery system of MSNs of average size diameter of 100 nm, with pores average size 2.64 nm, hexagonal arrangement mesopores highly-ordered [17].

Therefore, in this work, we report our efforts to obtain MSNs with controlled particle size (100 to 150 nm), spherical shape, no agglomeration, high surface area, a high pore volume and hexagonal arrangement by full optimization of procedure, studying the influence of parameters as reagents concentration, temperature and reaction time.

2. EXPERIMENTAL SECTION

2.1. Synthesis of mesoporous silica nanoparticles.

All reagents and products were purchased from Sigma-Aldrich, PRS Panreac, Ega Chimie, Merck, J.T. Baker, and used as received, purified water used was obtained using a Millipore Milli-Q system. The different procedures of synthesis used in this work were based on He *et al*. (2010) [11], Suzuki *et al*. (2004) [12], and Nooney *et al*. (2002) [13], and below summarized in Table 1 where, in addition, are showed the results of diameter average size of particles estimated by *ImageJ* [1-8], small angle X-ray scattering (SAXS) and porosity measurements results. Furthermore, after reproduction of these synthesis procedures, several parameters were change like as silica precursor and surfactant concentrations, as well as temperature and reaction time used. Table 1 shows all procedures synthesis performed.

The synthesis procedure in the most cases of this study, followed the typical procedure, an alkaline mean was produced by mix of sodium hydroxide (NaOH) and distilled water and after cationic surfactant was added. After this, the mix was keep still at constant stirring and the temperature was increase until desired temperature, and tetraethyl orthosilicate (TEOS) was add as the silica precursor, dropwise slowly. In some synthesis procedure here, a non-ionic surfactant was added to control the size of MSNs, and chloride acid in addition to base. Then, the mix remained under vigorous or slow stirring for each desired time of synthesis. Elapsed the time, the obtained precipitate was centrifuged and washed. The sediment of centrifugation was rapid dried between 70 ºC, after the material passed through for thermal treatment for 1º C min^{-1} until 500 ºC for 5 h, in order to complete removal of surfactant.

2.2. Characterization techniques used.

The obtained material passed through the following characterization techniques: porosity measurements with N_2 adsorption-desorption isotherms by BET and BJH methods acquired by a Micromeritics ASAP2000. Small-angle X-ray scattering (SAXS), analyses performed on an INEL XRG3D device, SAXS signal from mesoporous silica was obtained with X-ray produced by a Cu anode, the X-ray beam was filtered and focused onto the specimen using Kirkpatrick-Baez mirrors, delimiting a small and no divergent beam. Scattered intensity was record on an imaging plate, located 38 cm behind the specimen. Scanning Electron Microscopy (SEM) was carried out in electronic a microscope JEOL SEM-FEG JSM 6330F, and in a microscope JEOL 6490. Transmission Electron Microscopy (TEM), images were obtain using a CM20 Phillips microscope of high tension operating up to 200 kV, and having as electrons source LaB_6.

3. RESULTS SECTION

An overview of SEM and TEM images showed from Figure 1 and Figure 2, respectively, reveals particles with heterogeneous morphology, going to nanometric to micrometric size, and spherical to no defined shape. Cause, as early mentioned, the final structure and morphology are highly dependent on the parameter of the reaction mean, such as a local interaction created by the lipophilic/hydrophilic equilibrium, the Brownian motion that destroys the network, the hydrolysis kinetic and

polymerization of silica [19]. Smaller size of particles was found in those synthesis using vigorous stirring and temperature larger than 80 ºC as well hexagonal pores arrangement verified by SAXS measures. Some samples showed no definite shape with any diffraction peaks when analyzed by SAXS. Other samples exhibited two or three groups of size, in a same sample, varying to nanometric to micrometric scale of particles. These data are seen for those methodologies, which used few amount of silica precursors, temperatures smaller than 80 ºC, slow stirring, and ammonium hydroxide to pH control and catalysis of silica condensation.

Because the microstructure spontaneously formed in complex fluids, such as surfactant micellar solutions or polymer gel, can be manipulated by the composition or condition of the fluid [20-28]. Such fluids attract attention as media for the formation of monodispersed microparticles [20-28]. In this case, two effects due to the fluid structure on the particle formation are expected: size of the final particles will be reflecting the size of the mediating fluid structure, which can be manipulated by varying the fluid composition or preparation conditions [20-28]. And CTAB is known to form rod-shaped micelle concentration to and assemble into hexagonal liquid crystals [13]. That's explains very agglomerate particles, no definite shape and bigger size, seen in SEM images of samples from synthesis 17 (Figure 2E) and 21 (Figure 2F). An example of how the fluid microstructure influences on the final size of particles is the use of reverse microemulsion as structural media for the generation of monodispersed microparticles. In this method, particles are formed in dispersed water micropools inside the spherical reverse micelles and consequently the obtained particle size will be reflecting the size of the reverse micelles [21,28-33]. A second effect is the growth rate of particles, which is influenced by the translational motion of the particles in the presence of the fluid microstructure. In the formation of particles in liquid phase, small precursory clusters are first formed and they aggregate into particles, these grow by coalescence with each other or with residual clusters by collision. Thus, the dynamic behavior of particles is an important factor affecting their growth. In micro or mesoscopically structured media, the movement of particles is likely to deviate from that in uniform media. Polymer or surfactant gels are expected to work as those distinctive media. Gels have a complicated network structure formed by the overlap of long constituents. However, particles in a gel may have diffuse motions distinct from the usual Brownian motion in uniform solvent due of the difficulty of motion by the gel structure [21,28-33]. MCM-41 is a silica-based material with a regular hexagonal array of cylindrical pores. The pore walls are amorphous but the regular array of cylindrical mesopores generates diffraction peaks at low scattering angles. Accurate information about the pore structure must be known before its influence on hydrogen adsorption can be determined [34]. Therefore, SAXS is an important measure for determine as pores of MSNs type MCM-41 arrays. From SAXS spectra of MSNs, was possible to verify three distinct and well-defined diffraction peaks indexed to (100), (110) and (200) planes, respectively, reveals two basic information, a relatively good quality of samples, and MSNs have the highly ordered MCM-41-type 2D hexagonal (*P6mm*) symmetry. The samples obtained from synthesis 02, 03, 16, 17, 19, 20, 21, 22 and 23 not exhibited diffraction peaks, which is related to early discussion about reactional means of particles formation. Moreover, for those samples analyzed by TEM (Figure 2A and 2B), the SAXS measurements indicated that MSNs have almost identical mesostructure and morphology. A well summary of structure information of the samples is detailed in the Table 1, previously showed.

The porosity measurements, showed a classical type-IV N_2 adsorption–desorption isotherm at 77K with well-defined steps at relative pressures (P/P_0) [13,35]. Absence of hysteresis and shape of the curves reveals mesoporous material characteristics [13,35]. It suggests that MSNs have uniform mesoporous channels and narrow pore size distribution, which are also according with the results obtained from TEM images and SAXS, for these samples and which is suggested for all samples with hexagonal arrangement and not agglomerated. In addition, MSNs have high specific surface area and large cumulative pore volume, which are calculated and are summarized in the Table 1, previously showed.

Based on its founded and taking in account the methods of synthesis displayed in this work, a simple scheme of MSNs formed is showed in the Figure 3, and which regards 3 basic steps: micelle formation, which is depend of pH mean and CMC of surfactant used; micelle organization, that characterize the type of structure of mesoporous material obtained; and finally, hydrolysis and polycondensation reactions after addiction of silica precursor.

The synthesis 10, following the procedure of He *et al*., 2010 [11]; obtained NPs with average size of 67-740 nm, irregular and smooth spheres shape, highly ordered pores with obtained by heterogenic and homogeny with anionic surfactant synthesis, in homogeny synthesis with anionic surfactant, a starburst shape of porous was obtained, and regular monodisperse spheres with disordered pores arrangement were obtained from homogeny synthesis with nonionic surfactant. In our procedure following part of this study, was possible to achieve NPs with average size between 200 and 500 nm which is in according to reference. In addition, non-defined shape of particles and disordered pores arrangement were obtained for all synthesis protocols. For synthesis from 20 to 23, of Suzuki and co-authors, 2004 [12]; the average size of NPs obtained was 20 nm, and the insertion of a second surfactant not deforms the hexagonal mesostructure, and may be obtained nanoparticles with small size diameter with hexagonal mesostructure highly ordered. Following this procedure, we found that NPs average size was 150-300 nm, the diameter estimated was not according to reference, and the obtained particles are much larger than nanoparticles of reference. Non-defined shape of particles and disordered pores arrangement were obtained for one synthesis protocol. And finally, synthesis 18 and 19 from Nooney et al., 2002 [13]; the NPs average size founded was 150 nm, varying of 130 to 170 nm, with hexagonal arrangement mesopores well-ordered. In our assay following this procedure, we achieved NPs with 137 nm average size which is in according to reference. The nanoparticles exhibited hexagonal arrangement mesopores, well-ordered pores and well disperse nanoparticles.

For the other synthesis carried out, some considerations may be done, the synthesis from 01 to 03 provided NPs with average size between 125 to 1200 nm, herein a large variation of average size diameter was noted. Non-defined shape of particles

and disordered pores arrangement were obtained for synthesis 03, and then the average size could not be estimated. For synthesis from 04 to 09, the average size estimated was 117-600 nm, in these NPs the average size diameter is too varied. All synthesis rendered nanoparticles which exhibits hexagonal arrangement of mesopores, well-ordered pores and well disperse nanoparticles. For 11 to 15 synthesis, best synthesis procedures performed, the average size obtained was 110 – 200 nm, here the size diameter is most controlled only changing the reaction time. Decreasing reaction time decreases consequently size diameter of nanoparticles. All synthesis rendered nanoparticles which exhibits hexagonal arrangement of mesopores, well-ordered pores and well disperse nanoparticles. And finally, synthesis 16 and 17 obtained average size of NPs between 50 to 2500 nm, and pores arrangement are disordered for both syntheses. For synthesis 16, the NPs were well size controlled in 50 nm, and for synthesis size estimated had large variation, size founded until 2500 nm.

Table 1. All procedures synthesis performed.

Synthesis	Ref.	Average size (nm)	Pores Arrangement	Porosity measures (BET/BJH)
01	-	125	Hexagonal	-
04	-	117	Hexagonal	a_{surf}= 1018 m^2 g^{-1}; v_p= 1.39 cm^3 g^{-1}; p_d= 5.5 nm
07	-	120	Hexagonal	-
09	-	125	Hexagonal	-
10	He, 2010[11]	137	Hexagonal	a_{surf}= 875 m^2 g^{-1}; v_p= 1.07 cm^3 g^{-1}; p_d= 4.9 nm
11	-	125	Hexagonal	-
12	-	>200	Hexagonal	-
13	-	110	Hexagonal	-
14	-	110	Hexagonal	-
15	-	>200	Hexagonal	-
16	-	50	-	-
18	Nooney, 2002[13]	150	Hexagonal	-

Footnote: The (-) indicates not results obtained.

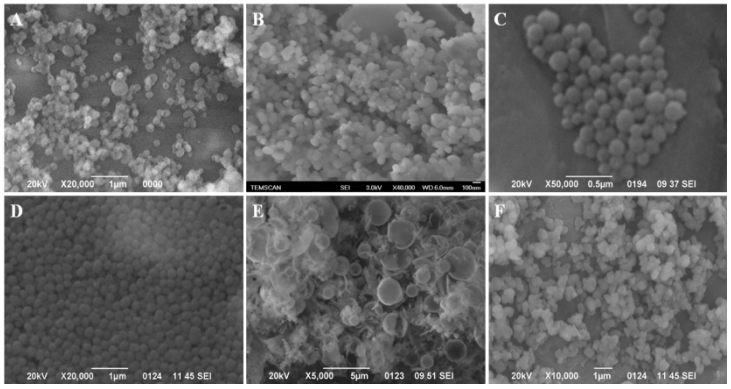


Figure 1. SEM images of samples from synthesis (a) 01; (b) 09; (c) 11; (d) 14; (e) 17; and, (f) 21.

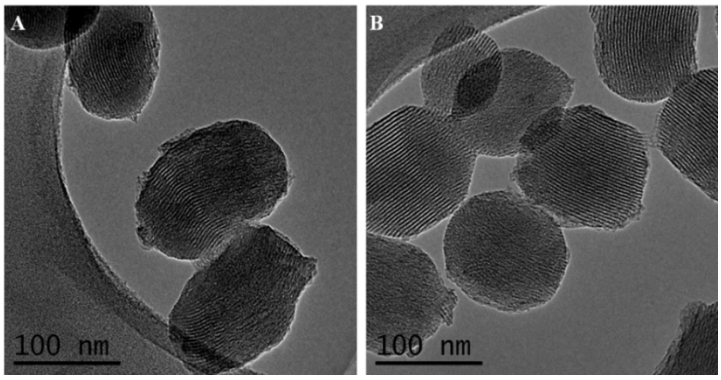
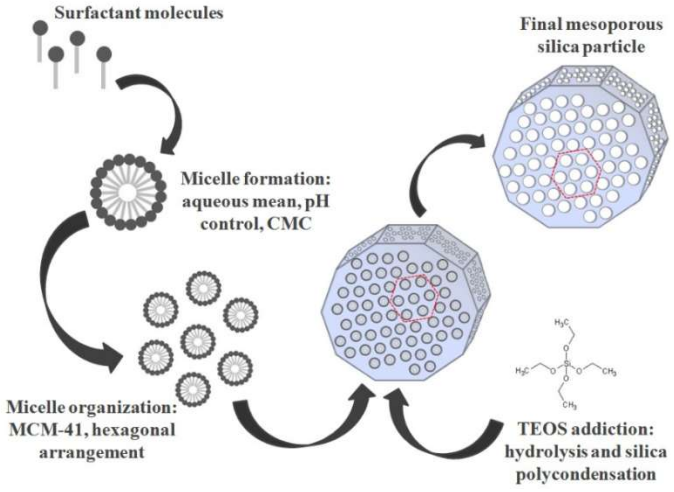


Figure 2. TEM images of samples from synthesis (a) 04 and (b) 10.



Scheme 1. Scheme of typical synthesis of mesoporous silica MCM-41.

4. CONCLUSIONS

This way a close control of synthesis parameters should be required for obtainment of MSNs type MCM-41, with structural organization and highly ordered pores. And after analysis of the obtained results, it is possible to confirm that this work achieved the proposed aims, i.e., obtainment of monodispersed NPs with a maximum length between 100 to 150 nm (herein we obtained 137 nm), spherical shape, with no agglomeration or aggregation, high surface area, high pore volume and hexagonal arrangement, mainly by the synthesis 11 to 15, whose the reaction time was varied and smaller sizes were, consequently, obtained. Then, the main factor for reduction of the particle size is decreasing reaction times.

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