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ECO-FRIENDLY METHOD FOR SYNTHESIS OF MESOPOROUS SILICA

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Mesoporous silica is an important class of materials, with remarkable structures and features, and applications in catalysis, drug carrier, pollutant removal, or nanocomposite filler. The synthesis of mesoporous silica is carried out by Stöber method, modified by adding a surfactant acting as pore-forming agent. A new, eco-friendly method using microwave-assisted extraction for surfactant removal was proposed. The obtained silica powder was characterized by infrared spectroscopy (FTIR), electron microscopy (SEM), Dynamic Light Scattering (DLS), and X-ray diffraction (XRD). The results show many similarities with hexagonally ordered mesoporous silica, obtained through the classical method consisting of reflux extraction of surfactant in acidified dioxane solution.

Keywords: eco-friendly synthesis**,** mesoporous silica, microwave, Dynamic Light Scattering, X-Ray Diffraction.

1. Introduction

Mesoporous silica nanomaterials (MSNs) comprise a wide range of highly ordered porous structures composed on silicate species (SiO_2), with pore width between 2 to 50 nm. [1] The porous nanostructure provides a high surface area, up to 1000 cm^2/g and a large pores volume. Moreover, the MSNs possess many hydroxyl functionalities on the surface, that enrich the surface chemistry. [2, 3]

Since the beginning of the 1990, the advancement of mesoporous silica materials started with the synthesis of MCM 41 (Mobil Crystalline Materials-41) and continued with SBA-15 (Santa Barbara Amorphous-15) synthesis, in 1998. These nano-structured silica materials have both a hexagonally symmetry of pores and differ by pores size and wall thickness. Subsequently, new ordered

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mesoporous silica structures were developed, for example: MCM-48, SBA-16 or KIT-5 (with cubic pore symmetry), and other. [1, 3] The high surface area and specific porosity made those materials suitable for various applications like catalysis, controlled drug delivery, aqueous and gaseous pollutants removal, or filler for advanced polymer composite materials. [3, 4, 5]

Several synthesis methods for obtaining silica materials with controlled shape, dimension, and morphology are known. All these take place in solution (water or alcohol), in acid or alkaline catalysis, use alkoxisilanes or silicates as precursors, and involve repeated hydrolysis (eq. 1) and condensation reactions (eq. 2) as in the "sol-gel" process. Such examples are Stöber method, core shell type or mesoporous silica syntheses. [5, 6]

$$Si(OR)_4 + 4H_2O \leftrightarrow HO - Si(OR)_3 + R - OH \qquad (1)$$

$$(RO)_3Si - OH + HO - Si(OR)_3 \leftrightarrow (RO)_3Si - O - Si(OR)_3 + H_2O \qquad (2)$$

Synthesis of mesoporous silica particles uses a modified Stöber method, where reactions occur in aqueous alkaline solution. The silica network is formed around a soft template, which could be ionic surfactant (cetyltriethylammonium bromide, CTAB; sodiumdodecyl benzenesulfonate, SDBS) or neutral macromolecules (P123, Pluronic) that self-assembles in solution. [6, 7, 9] In order to obtain a porous structure, the soft template must be removed after silica particles formation. The template removal could be made by chemical reaction (refluxing in acidic solution of dioxane or other solvent), by calcinations, at above 300 °C, by ultrasonication in solvent or by supercritical CO_2 extraction. [7] The shape and size of porous morphologies could be influenced by the surfactant used as template, and the number of silanol (Si-OH) superficial groups varies depending on the surfactant removal method. [7, 8]

The chemical removal of the template requires the reflux boiling of silica nanoparticles in solvent for a long while, at high temperature (e.g. min. 12 h, at 110 °C, in acidified water-dioxan solution). [9] Because it involves a long time and high energy consumption the present study proposed a method for shortening this period by microwaves heating of silica nanoparticles in solution.

It is known that microwaves assisted syntheses have some advantages over the conventional heating techniques because they increase yields and decrease reaction times. There are studies about microwaves synthesis of silica, for example, Lovingood et al. studied the mechanism of microwave-assisted growth of silica nanoparticles and obtained nanoparticles ranging from 30-250 nm. [10] The authors concluded that in microwaves controlled reaction, the nanoparticles were formed through equilibrium between polymerization and depolymerisation. They noted that acetone stabilized the silicic acid monomer in reaction solution and, along with high ratio $[H_2O]/[TMOS]$ and the acid catalysis contributed to depolymerisation reactions. Silicic acid concentrations and the irradiation time controlled the particle size. Another study described the synthesis of silica nanoparticles, in alcoholic solution, using TEOS as silica source and ammonium catalyst. After 2-18 minutes of microwaves irradiation, low molecular weight silica nanoparticles, with non-reacted functional groups, Si-OH and Si-OEt, was obtained. It was noticed that water and ammonia concentrations governed the conversion and the particle size. [11]

The present work emphasized the possibility to reduce time and energy consumption during mesoporous silica synthesis, through a microwave-assisted process. The template removal from mesopores was modified by heating the reaction mixture through microwave irradiation, in a laboratory oven. The composition and structure of products were analyzed and compared with those obtained for the conventional synthesized materials. The influence of two solvent, dioxane and ethanol, on the synthesis has been studied.

2. Experimental

2.1. Materials and methods

Tetraethyl orthosilicate (TEOS, 98 %), from Merck, Darmstadt, Germany), Cetyl-trimethylammonium bromide (CTAB, 98 %) and Dioxan (99.8%) from Merck, Darmstadt, Germany; Natrium hidroxide (NaOH, 99 %) and hydrochloric acid (HCl, 35-38%) from Silal Trading, Bucuresti, Romania; Ethyl alcohol (96 %), Methanol (99.9 %) and Acetone (p.a.) from Chimreactiv, Bucuresti, Romania; distilled water.

2.2. Mesoporous silica synthesis

Synthesis of mesoporous silica occurred in two stages. In the first stage, the surfactant, CTAB, self-arranged in micelles formed a hexagonal template. The silica network was built around it. This synthesis was done following a previously developed method. [9] The second stage consisted of the template removal. In this method, the CTAB template was removed by boiling the first-stage silica in an acidified solution of dioxan, at reflux: 110 °C, for 12 hours. In the present work, a different approach assisted by microwaves was used for removing the CTAB. Thereby, hydrolysis and condensation reactions took place in an aqueous solution, with alkaline catalysis. In the alkaline solution, prepared from 3.5 mL of 2M NaOH solution and 480 mL distilled water, 0.9 mg CTAB was added. The solution was magnetically stirred for 5 minutes and then heated up to 70 °C. When the temperature reached this value, 5.6 mL TEOS was added to the hot solution, drop by drop, under stirring. The reaction mixture was then kept for three hours at this temperature, with continuous stirring. In the meantime, the solution became cloudy, meaning that the sol of silica was formed. During the three hours of reaction, the sol turns into a gel of silica. After cooling, the product was separated by vacuum-forced filtration on the sintered glass disk (G_3) glass funnel. Further, the precipitate was successively rinsed on the filter, with distilled water, methanol, and acetone. Then, the reaction product was dried at 60 °C, in a vacuum oven, for two days. A powder of silica particles, with CTAB inside the pores, resulted. It was denoted (MS_I). Further, the product was divided in three parts, each being treated through a different approach for the template removal.

In this study, the CTAB template was digested in a microwave oven, in an acidified solution of dioxane at 110 °C, for 2 hours. Moreover, to study the influence of solvent, another sample was treated by microwaves in an acidified ethanol solution, for two hours, at 110 °C. A laboratory microwave oven Mars 6 iWave, from CEM Corporation, and EasyPrep Vessels, of 100 mL capacity each were used. This trial aimed to reduce the boiling times and the energy consumption. Practically, each vessel was loaded with: 0.5 g MS I, 20 mL H_2O, 25 mL Dioxane, and 2 mL concentrated HCl. After the microwaves treatment, the silica was separated by filtration on the G3 sintered disk glass funnel and then rinsed with methanol, distilled water, and acetone. The obtained precipitate was then dried in the vacuum oven, at 60 °C, for three days and the dried silica powder was denoted MS_II_Diox. The other sample obtained at microwaves, from acidified ethanol solution (0.5 g MS I, 20 mL H_2O, and 25 mL ethanol), was denoted MS_II_Et.

For comparison, a part of the silica MS_I was treated for removing the CTAB at reflux in an acidified solution of dioxane (110 °C, 12 hours). [9] Thereby, the reaction mixture was heated in the synthesis flask, on the oil bath, using a heated plate with magnetic stirrer. After this time the mesoporous silica powder was separated by filtration on G3 glass filter, and dried for three days at 60 °C in the vacuum oven. The resulted sample was denoted MS_II.

2.3. Characterization methods and devices

Elemental analysis was realized with a Flash 2000 device (Thermo Scientific, UK) with Poropack Q separation column and TCD detector. Infrared spectra were recorded with a Cary 630 ATR-FTIR spectrometer (Agilent Technologies, Inc., Santa Clara, CA, U.S.). Microstructural characterization was realized with the electronic microscope Sigma VP FEG Carl Zeiss, Germany (the samples were placed on adhesive carbonic support). The mean hydrodynamic diameter (d, nm), polydispersity (PdI), and zeta potential (ZP, mV) of silica particles were measured by Dynamic Light Scattering (DLS) technique (Zetasizer Nano ZS, Malvern Instrument, UK) and the Small-angle X-ray diffraction analyses were performed using a 9 kW Rigaku SmartLab diffractometer (Rigaku Corp., Tokyo, Japan, operated at 45 kV and 200 mA, CuKα radiation—1.54059 Å), in scanning mode $2\theta/\theta$, between 1° and 7° (2θ).

3. Results and discussion

Four samples of silica were selected and analysed by elemental analysis and Fourier Transform Infrared Spectroscopy (FTIR), to determine the composition and to confirm the removal of CTAB template by microwaves treatment. The four samples were: MS_I, the sample obtained in the first stage of synthesis, having CTAB inside the pores; MS_II, resulted after removing the CTAB template by refluxing in the acidified solution of dioxane (110 °C for 12 hours); MS_II_Diox and MS_II_Et, were the samples obtained after removing the CTAB by boiling the MS I by microwaves, for two hours, in the acidified solution of dioxane, respectively ethanol.

The elemental composition presented in Table 1 shows the amount of organic elements, carbon, hydrogen, and nitrogen in the silica samples expressed as atomic percent. It can be noticed a decrease in these values for all samples treated for CTAB removal.

Table 1.

Atomic percent of the elements in silica samples, determined by elemental analysis

Nr. crt.	Sample	***N (%)**	***C (%)**	***H (%)**
1	MS_I	2.02	27.37	5.79
2	MS_II	0.15	10.24	2.67
3	MS_II_Diox	0.4	3.99	1.36
4	MS_II_ Et.	1.34	5.75	1.7

***N**itrogen, **C**arbon, **H**ydrogen

Considering that the organic molecule of CTAB (Fig. 1) contains all three elements (C, H, N) detected by elemental analysis, the decreasing of their values reflects the removal of CTAB from silica samples.

$$[CH_3\text{-}(CH_2)_{15}\text{-}N^+(CH_3)_3]Br^-$$

Fig. 1 Chemical structure of CTAB

In this respect, the microwave-assisted methods lead to lower values for C and H than the refluxing method. Although the nitrogen values are higher for the microwave treated samples than for the refluxed ones, all these values are much lower than the nitrogen in MS_I. It means that the microwave-assisted methods are efficient for CTAB removal.

The Fourier Transform Infrared (FTIR) spectra of silica samples were recorded in the Attenuated Total Reflection (ATR) mode. Fig. 2 shows the overlapped spectra of silica with CTAB inside the pores (MS I) and mesoporous silica after the removal of the CTAB template assisted by microwaves (MS_II_Diox and MS_II_Et). In the inset is the infrared spectrum of mesoporous silica, obtained through reflux removal of CTAB (MS_II).

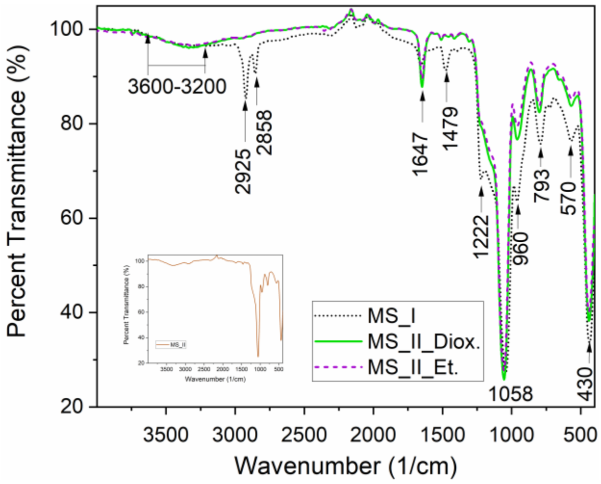
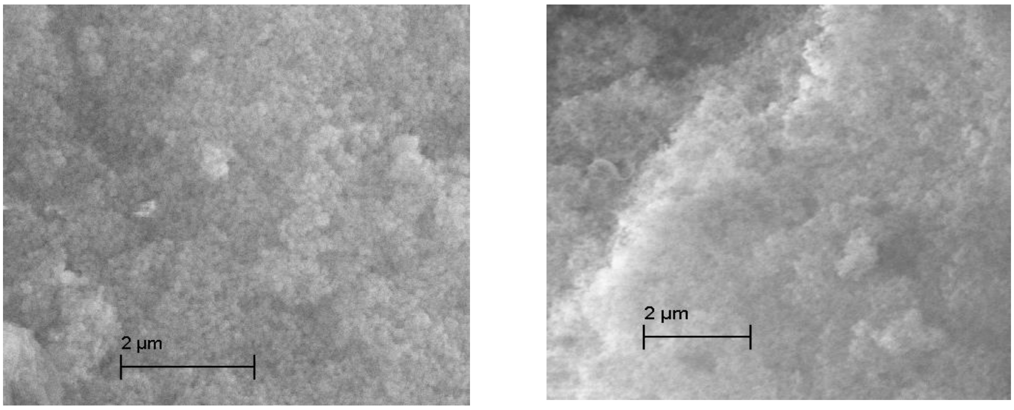


Fig. 2. FTIR spectra of the silica samples: MS I, with CTAB inside the pore, MS_II_Diox and MS_II_Et, silica samples, after removing the CTAB template, in Dioxan solution, respectively in ethanol solution. In inset – FTIR spectra of MS_II sample

There is a large band of absorption, present in all spectra between 3200-3600 cm^{-1}, corresponding to hydrogen bonds formed between the silanol groups or between water molecules absorbed on silica. Two sharp peaks specific for methylene (-CH$_2$-) groups are present in the MS_I spectrum, but not in the other spectra, at 2925, 2858 cm^{-1}. Also, the peak from 1479 cm^{-1} corresponds to the characteristic absorption of C-H bonds. The absence of these three peaks from MS_II, MS_II_Diox, and MS_II_Et spectra reflects the removing of hydrocarbon chains, ethyl, and cetyl from silica samples. The peak from 1647 cm^{-1}, present in the spectra of silica with CTAB template, MS I, and mesoporous silica after microwaves treatment MS_II_Diox and MS_II_Et is specific for –NH absorption. This peak does not appear in the FTIR spectra of silica sample treated at reflux for removing the CTAB (MS_II). This could be due to incomplete degradation of CTAB, respectively due to the three methyl amine residue present in microwave treated samples. The strong and sharp peak from 1058 cm^{-1} is due to the asymmetric stretching vibration and the weak and broad peak from 570 cm^{-1} is given by symmetric stretching of Si-O-Si bonds Also, the peak from 793 cm^{-1} could be attributed to Si-O-Si symmetric stretching vibration. The peaks from 960 cm^{-1} and 430 cm^{-1} are due to Si-O-C bonds asymmetric stretching, and respective, bending vibrations. All peaks characteristic for Si-O-Si and Si-O-C bonds are present in all four silica spectra. [12, 13, 14]

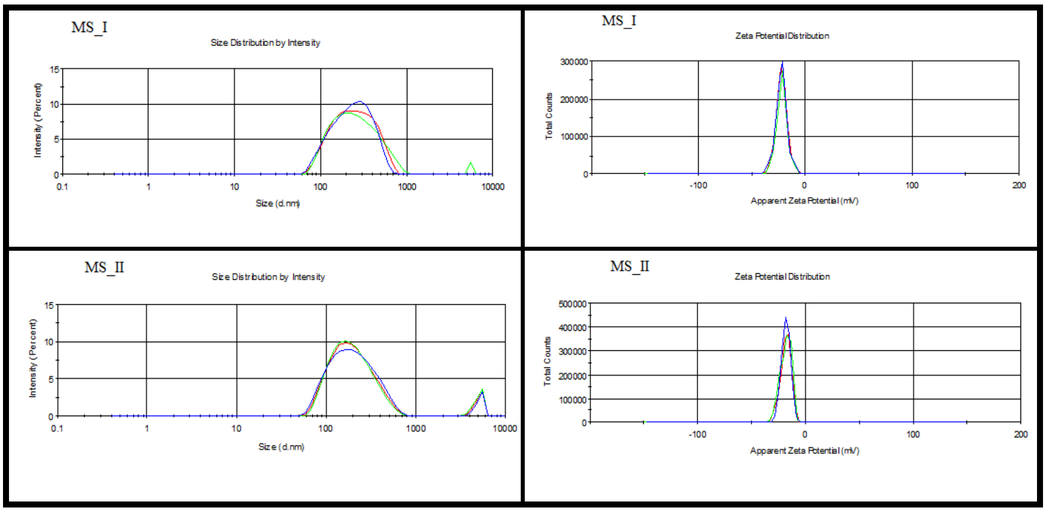
The microstructural images of mesoporous silica particles, recorded through Scanning Electronic Microscopy (SEM) for the sample obtained by refluxing (MS_II) and that obtained by microwaves (MS_II_Diox), are presented in Fig. 3 (a and b). We notice a well-defined nanoparticles structure for MS_II than for MS_II_Diox sample.



a) b)

Fig. 3 SEM images of mesoporous silica samples: a) MS_II; b) MS_II_Diox

To determine the hydrodynamic characteristics (d, PdI) through the Dynamic Light Scattering (DLS) method, the samples were diluted in ultrapure water, in the concentration of c = 0.5 mg/mL, and 15 successive cycles were run at 25 °C. Three measurements were done for each sample and the data were presented in mean ±SD (square deviation) (Table 2). The zeta potential (ZP) investigations were performed using the principle of laser Doppler velocimetry with the same equipment. The samples were diluted in 1mM NaCl, to ensure the optimal conductivity of the colloidal systems, and the measurements were performed at 25 °C. The reported ZP values (Table 2) are the averaged results of three measurements with 15 successive cycles. The graphic representation of particle size distribution and Zeta Potential distribution for all four samples are presented in Fig. 4.



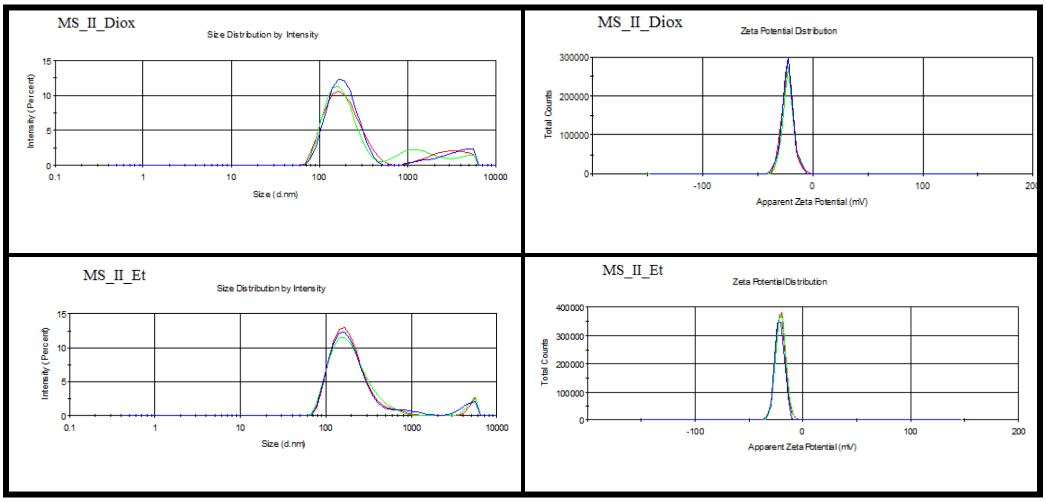


Fig. 4 The particle size distribution (left) and the Zeta Potential distribution (right) for the analyzed silica samples: MSI, MS_II, MS_II_Diox and MS_II_Et

The average diameter of the silica particles varies between 194.5 – 423.6 nm. The smaller dimensions have the particles of the samples obtained by microwave treatment: MS_II_Diox and MS_II_Et. The PdI values show a broad polydispersity for all silica particles, except MS_II_Diox, and MS_II_Et, the microwave–obtained sample, which have a moderate polydispersity. The negative values of zeta potential for all mesoporous silica (MS_II, MS_II_Diox, and MS_II_Et) show a negative charge of particles dispersed in solution, which is due to silanol superficial groups, -Si-OH.

Table 2

The hydrodynamic parameters of silica particles, determined by (DLS) method

No	Sample	c = 0.5 mg/mL		
		d (nm)	PdI	ZP (mV)
1	MS_I	420.4± 32.12	0.666± 0.193	29.4± 0.208
2	MS_II	423.6± 23.20	0.569± 0.145	-18.5± 0.28
3	MS_II_Diox	208.3± 2.84	0.362± 0.012	-22.5± 0.306
4	MS_II_Et	194.5± 4.82	0.325± 0.011	-21.5± 0.62

Generally, X-ray diffraction patterns reflect the crystalline structure of materials. Despite the silica is an amorphous material; the ordered pores structure of mesoporous silica gives specific reflection peaks in the small angle diffraction range, such as (100), (110), and (200), reflections characteristic for hexagonal pore structure, extended on a long-range, in one direction. [9, 16]. All XRD patterns of the four silica samples (Fig. 5) show the characteristic reflection peak (100) at 2θ = 2°. The other specific peaks of (110) and (200) reflections appear in the MS_II_Diox and MS_II_Et patterns, at 2θ = 3.5° respectively 2θ = 4°. The

MS_II pattern shows a broad reflection between 3°-4.5°, but not two distinct peaks. In the pattern of the MS_I silica sample, the (110) and (200) reflections are absent, the only peak is that of (100), at 2θ = 2°. One can conclude that ordered hexagonal long-range structure is characteristic just for mesoporous silica with CTAB removed by microwave treatment (MS_II_Diox and MS_II_Et).

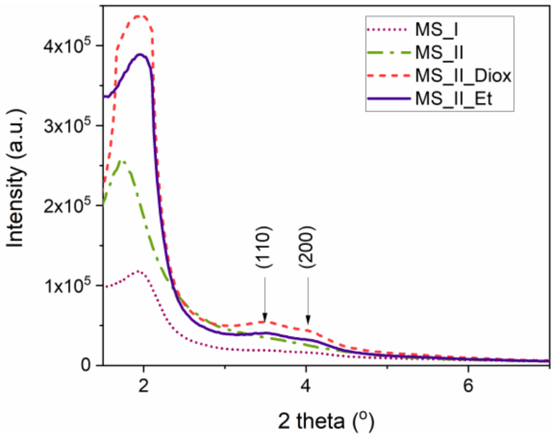


Fig. 5 Small-angle XRD patterns for mesoporous silica samples

4. Conclusions

Several mesoporous silica samples were synthesized through different approaches starting from a classic method described in the literature. This method was modified to decrease the synthesis time and energy consumption by changing the classic refluxing degradation of the template with microwave-assisted degradation. The synthesized samples were characterized by elemental analysis, Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy, Dynamic Light Scattering, and X-ray diffraction. The composition of samples was determined by elemental analysis and FTIR and the results highlight the removal of soft organic template. Thereby, the decrease of carbon, hydrogen, and nitrogen atomic percents (elemental analysis) confirms the CTAB degradation. Moreover, the disappearance of some peaks, 2925, 2858, and 1479 cm^{-1}, characteristic of the hydrocarbon chain supports the template degradation, too. The SEM images of mesoporous material show a homogeneous aspect of microstructure, with clearly outlined spherical particles for the sample obtained by reflux and less defined particles for the samples treated by microwave. However, the average particle diameter, determined by DLS, is lower for the microwave-synthesized materials. The XRD patterns of microwave-synthesized samples present the three reflection peaks at (100) (110), and (200), characteristic of log range hexagonal ordered porous materials. It can be concluded that template CTAB can be removed from mesopores of silica materials by microwave-assisted digestion and mesoporous silica with hexagonal ordered porous microstructure could be obtained. The microwave-assisted synthesis strongly decreases the time and energy consumption for obtaining the mesoporous silica particles.

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