

Effect of fat chain length of sorbitan surfactant on the porosity of mesoporous silica

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ABSTRACT: The influence of the fat chain length of sorbitan surfactant was systematically explored, especially its influence on the material pore size. Then, mesoporous silica was synthesized according to a two-step process that provides intermediary stable hybrid micelles using ethoxylated derivative of fatty esters of sorbitan surfactants as the directing-structure agent and tetraethyl orthosilicate $\text{Si}(\text{OEt})_4$ as the silica source. Finally, the materials' porosity could be controlled by adjusting the preparation parameters during the two steps synthesis of mesoporous silica.

Keywords: mesoporous silica, non-ionic surfactant, ethoxylation degree

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Introduction

The intermediary region between the atomic and molecular physics and condensed matter physics can be defined as the region where mesometric-ordering materials can be obtained, this is located between the microscopic and macroscopic region. From a technologic point of view, understanding the problems related to catalysis, chemisorptions, aerosols, powder metallurgy, ferrofluid etc, is very important with regards to the study of matter system in this intermediate region. In addition, one expects that the next level of miniaturization of the photonic and microelectronic devices will depend on the systems of this intermediate region. From a basic point of view, the study of this state of matter, intermediary between molecule and solid, will be decisive and very important as it involves many chemical and physical principles that are usually dissimulated in infinitely sizable systems.

Since 1992, scientists working with zeolite syntheses and related materials such as catalyses and materials science [1], have been motivated with the discovery of mesoporous crystalline materials by the Mobil Research and Development Corporation research group [2, 3]. A large number of potential applications of these materials in the catalyses, separation [4] and advanced materials [5-8] areas have been developed in a short time. Microporous zeolites and molecular sieves have been expanded for the mesoporous region by mesoporous crystalline materials. Such findings created new opportunities, not only for catalysis, but also for areas involving applications of advanced materials. In the catalysis area, crystalline mesoporous materials are more efficient than conventional catalyser due to their high surface area and also because these materials present more accessible active sites [9]. The use of ordered silicates hosts for low dimensional quantum semiconductors was possible with the discovery of mesoporous materials [10]. The engineering of mesoporous materials with pore size between angstroms up to micrometer has been fruitful due to the use of organic molds to control inorganic solid structures [11]. The formation mechanism of mesoporous materials [12], from tetraethyl orthosilicate (TEOS), cethylmethylammonium bromide (CTAB) and water, involves a self assembly mechanism, where the electrostatic interactions between surfactants molecules and inorganic ions determine the mesophase obtained. In the presence of neutral surfactants, the hydrogen bonding in the place of electrostatic interactions becomes of crucial importance for the formation of organic-inorganic mesophase [13].

The pore size (or interlayer distance) of mesoporous materials is easily adjustable in the interval of 20 to 100 Å. In this context, the pore size can be adjusted by 3 different manners: (i) by changing the length of the chain alkyls group of surfactant

molecule; (ii) by adding the swelling agent (1,3,5-trimethylbenzene) that results in the expansion of micelle due to dissolution of the swelling agent into the hydrophobic region of micelle; or (iii) by aging the material prepared at low temperature (about 70 °C) into the mother liquid or high temperature (about 150 °C) for varying periods of time. Also, the pore size of silicates can be adjusted by silanization pos-synthesis. Materials with high surface area, frequently up to 1000 m²/g, can be obtained by calcination of stable phases of silicate and self-structured surfactant molecules. Moreover, these materials can easily be modified by the different incorporation of cations, becoming acid or redox properties [3].

In this work we describe the influence of the fat chain length of sorbitan surfactant in the mesoporosity of silica prepared by two-step synthesis route using non-ionic surfactant as template.

Material and Methods

Mesoporous silica was synthesized with PEO (polyoxyethylene) surfactants with different ethoxylation degree: Tween 20 (PEO sorbitan monolaurate) (Fluka Chemicals), Tween 40 (PEO sorbitan monopalmitate) (Sigma Chemicals), Tween 60 (PEO sorbitan monostearate) (Sigma Chemicals), and Tween 80 (PEO sorbitan monoolate) (Sigma Chemicals). The silica source was tetraethyl orthosilicate (TEOS, Si(OCH₂CH₃)₄) (Merck). We used sodium fluoride as a silica condensation catalyst (Merck). All reagents were used as received.

Mesoporous silica was prepared according to the two-step synthesis [14]. A 0.02 mol.L⁻¹ aqueous solution of surfactant was prepared and the pH was adjusted at 2 by adding 2 mL of a hydrochloric acid solution. TEOS was added under magnetic stirring to reach a final TEOS/surfactant molar ratio of 8. After aging for 12 h at room temperature without stirring, this solution was heated to 40 °C in a thermostated-shaking bath. The final condensation step was induced by the addition of 4% of sodium fluoride (0.25 M) to the solution that was kept in the thermostated bath at 40 °C for 3 days, with slow shaking (40 rpm). A white powder is obtained with a yield close to 100%. Afterward, it was filtered, dried, and calcined at 620 °C for 6 h after step at 6 h at 200 °C.

All measurements were performed on calcined powders. They were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry (XRD) and nitrogen adsorption/desorption. The TEM images were obtained with a Philips CM20 instrument operating at a 200 kV. The samples were ultrasonically dispersed in ethanol and dropped onto the carbon-coated copper grids prior to the measurements. The scanning electron microscopy work was performed with Jeol JSM-

5900 LV microscope of LME/LNLS, Campinas, operating at 20 kV. The samples were covered with Au to increase conductivity. XRD measurements were carried out with a Rigaku (Miniflex), with wavelength of the copper K-alpha line radiation ($\lambda = 1.5418 \text{ \AA}$). Most patterns exhibited a single diffraction peak that we assigned to pores length correlation [15]. This pore center to pore center correlation length will be named "d-spacing" to follow. Nitrogen absorption isotherms were measured at liquid-nitrogen temperature on a Micromeritics 2010 Sorptometer using standard continuous procedure. Surface areas were determined by the Brunnauer – Emmett – Teller (BET) method within a 0.05 – 0.02 relative pressure range. Pore size distributions were calculated only for sizes higher than 2.5 nm from the desorption branch by a polynomial correlation between relative pressure and pore diameter, deduced from the Broekhoff and Boer (BdB) model [16, 17]. To simplify comparison, we displayed the reduced adsorption curves (isotherms divided by the amount adsorbed at a relative pressure of 0.8) [18].

Results and Discussion

The synthesis of micelle-templated structures (MTS) is a multi-parameter process that includes structuralization of the surfactant at different pH values, pressure and temperature, as well as the nature and condensation of inorganic precursors. The interactions between organic templates and inorganic precursors remain a key factor that is applied at all times. The synthesis of mesoporous silica is based on the intermediate formation of hybrid micelles and is accomplished in two ways: the first one is the self-assembly of hybrid micelles and hydrolyzed inorganic precursor, this step is thermally controlled, and the second one is silica condensation into the hydrophilic region of micelles that is kinetically governed.

The TEM, Figure 1 image evidences that the particles contain domains of perfectly ordered structure. However, the TEM images show only microscopic part of the spherical particle, the overall view of the structure ordering of a macroscopic amount of the sample obtained by means of XRD, Figure 2 indicates structural uniformity of the material for silica with surfactant removed.

The chain length influence is illustrated by the synthesis of mesoporous silica with the Tween family (20, 40, 60 and 80) at synthesis temperatures adjusted in the shaking bath at 40 °C. The scanning electron microscopy images displayed in Figure 2 exhibit micrometric spherical particles characteristic of MSU-1 and 2 types of mesoporous silica [19-21]. The material was named Michigan State University type material, or MSU-X silica (X refers to the nature of the surfactant: 1 for alkyl-PEO, 2 for alkylaryl-PEO, 3 for polypropyleneoxyde-PEO block copolymer, and 4 for Tween-type nonionic ethoxylated

sorbitan esters) is prepared under neutral [13, 15] or mild acidic conditions [14].

The morphologies of mesoporous silica particles obtained in the Tween family are spherically shaped with micrometric and sub-micrometric particles size. The final nanostructure and the morphology of MSU-X type material are highly dependent on the parameter of the reactional 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 [22]. Synthesis of MSU-X type mesoporous silica based on hydrogen bonding illustrates perfectly the versatility of this approach, since the final material structure (pore diameter, particle size) can be readily modified by adjusting several synthesis parameters, with the same reaction medium.

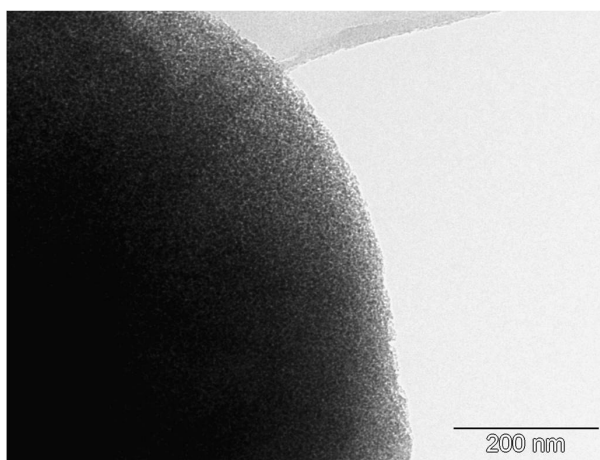


Figure 1. Transmission electron microscopy images of mesoporous silica prepared with Tween 60 as template.

MSU-4 type mesoporous silica samples have a highly ordered 3D wormhole mesostructure, as revealed by powder X-ray diffraction patterns, Figure 3. The overall quality of the structure can be estimated from the intensity of the diffraction line. The MSU-X silica X-ray pattern exhibits a single peak, characteristic of a single correlation length from pore center to pore center [15].

The mesoporous silica samples prepared in the presence of the Tween family exhibit a peaks on a specific degree, so, silica samples prepared with Tween 20, 40, 60 and 80 present a peaks at 46 Å, 48 Å, 50 Å and 52 Å, respectively. The samples' d-spacing increases with increasing chain length of the Tween family when we changed the ethoxylation degree during the mesoporous silica synthesis. The lengths of the hydrophobic chain of the Tween family are apparently marked by a parallel increase in the d-spacing, Figure 4. It is expected that the pore size changes the mesostructure with the length modification of the hydrophobic chain on the surfactant [2].

The nitrogen adsorption/dessorption isotherms, Figure 5, are characteristics of

mesoporous MTS-type materials. Therefore, all samples exhibit substantial framework-confined mesopores. The isotherm of the samples prepared with the Tween family does not exhibit any hysteresis, characteristic of pore necking, nor does the adsorption increase at high relative pressure, characteristic of a textural porosity. In addition, a parallel trend observed for the nitrogen adsorption/desorption isotherms with the adsorption jump shifted toward higher relative pressures is characteristic of an increasing pore size.

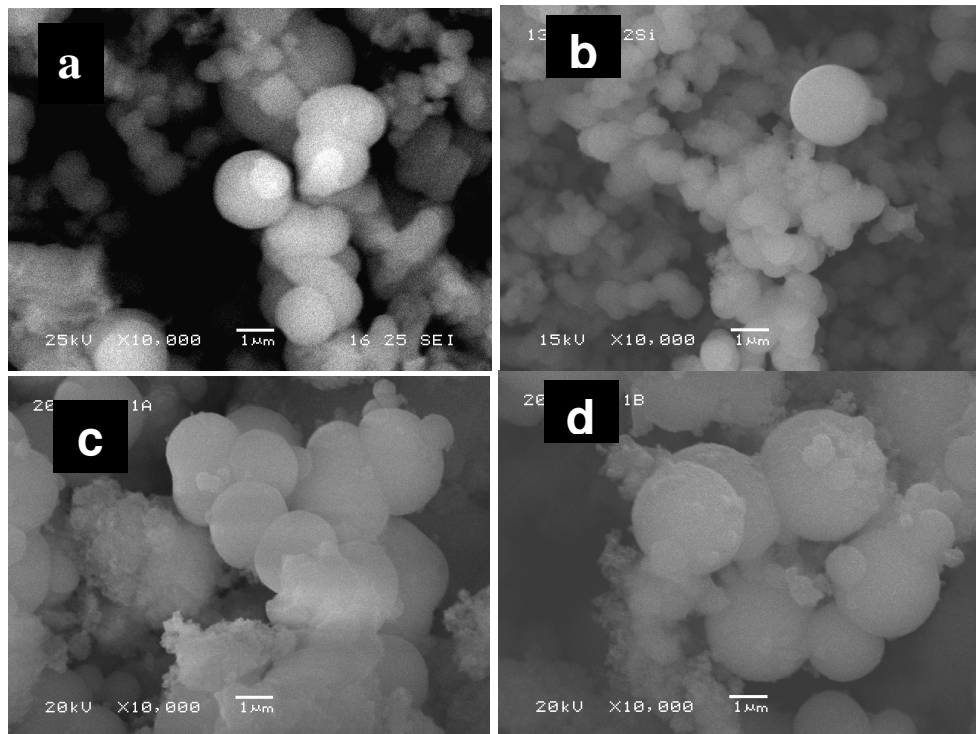


Figure 2. Scanning electron microscopy images of mesoporous silica prepared with Tween 20 (a), Tween 40 (b), Tween 60 (c) and Tween 80 as template.

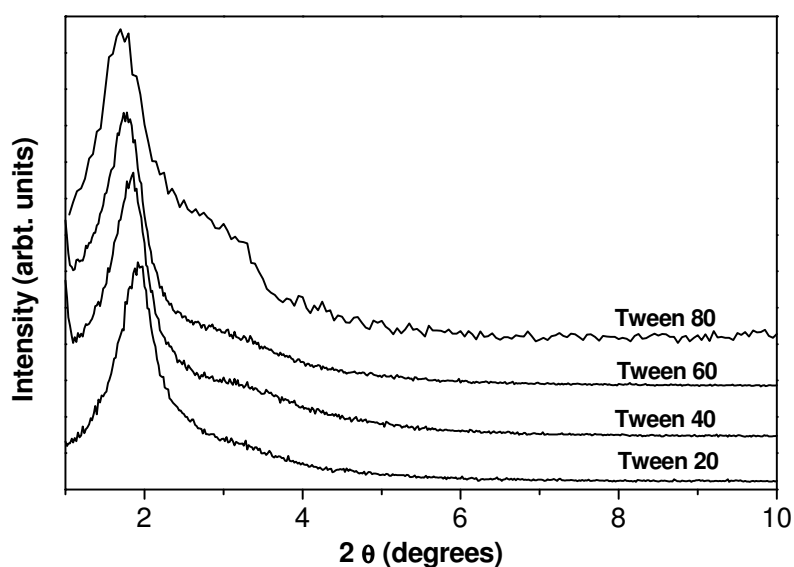


Figure 3. X-ray patterns of calcined mesoporous silica prepared at 40 °C as a function of Tween chain length: Tween 20 (a), Tween 40 (b), Tween 60 (c) and Tween 80 as template.

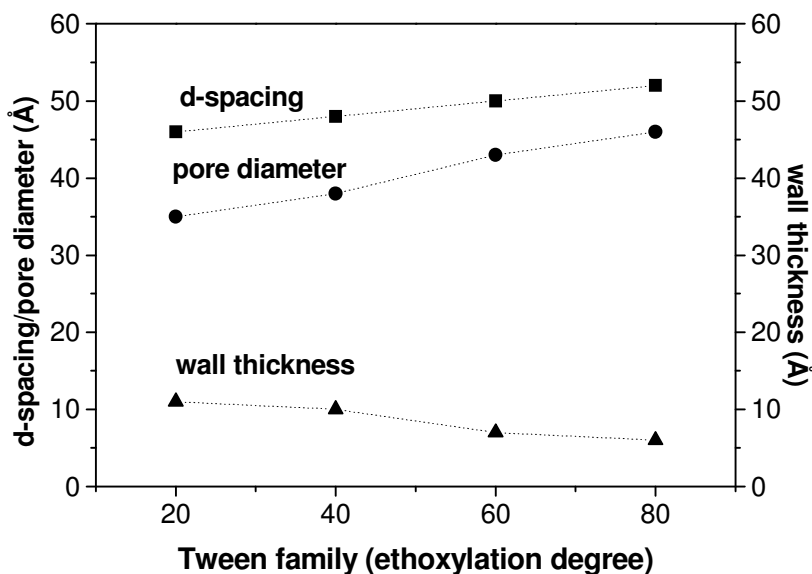


Figure 4. Evolution as a function of the chain length of Tween family of pore diameter of calcined mesoporous silica prepared at 40 °C with Tween X, when X (20, 40, 60 and 80) is the ethoxylation degree.

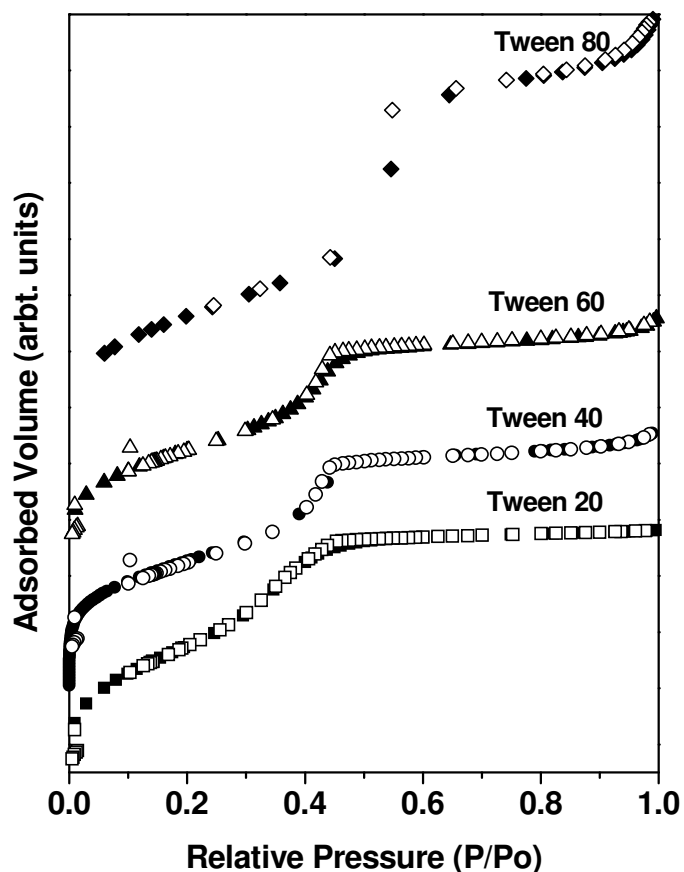


Figure 5. Reduced nitrogen adsorption (solid symbol)/desorption (open symbol) calcined mesoporous silica prepared at 40 °C as a function of Tween chain length: Tween 20 (a), Tween 40 (b), Tween 60 (c) and Tween 80 as template.

The pores size distributions for the samples are shown in Figure 6. The porosity of

mesoporous silica obtained in presence of the Tween family increases with increasing chain length of surfactant molecules used during the synthesis of mesoporous, thus, the pore size changed from 35 Å to 46 Å, when we changed the ethoxylation degree (Tween 20 to Tween 80) during the synthesis of mesoporous silica. Also, all samples presented pore size distributions, typical of mesoporous micelle-templated structures materials. The mesoporous silica, prepared in the presence of the Tween family as template, exhibit a high surface area. The surface area is 1016 m² g⁻¹, 780 m² g⁻¹, 868 m² g⁻¹ and 961 m² g⁻¹ for mesoporous silica prepared in the presence of Tween 20, 40, 60 and 80, respectively.

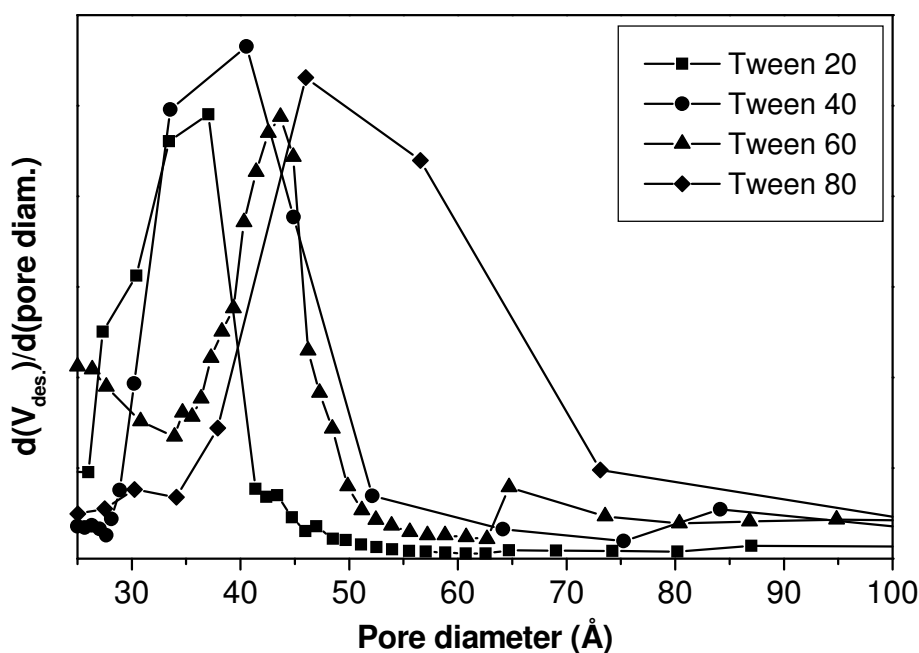


Figure 6. Evolution of pore diameter of calcined mesoporous silica prepared at 40 °C as a function of Tween chain length: Tween 20 (a), Tween 40 (b), Tween 60 (c) and Tween 80 as template.

In addition, the wall thickness (inorganic palisade) of mesoporous silica, calculated by the difference of the d-spacing and the pore size, decreased when it changed the ethoxylation degree (Tween 20 to Tween 80). This result is in agreement with XRD and pore size distribution, since the d-spacing and pore size increased with increasing chain length of surfactant molecules, Figure 4.

Conclusion

The mesoporosity of silica materials can be adjusted by the use of surfactants with different sizes of fat chains. The surface area is related with the average size of pores.

So, the use of surfactants with high ethoxylation degree produces materials with large pores that drive to a reduction of the specific area. Therefore, the mesoscopic characteristics of the silica material as its porosity, which can be controlled by adjusting its parameters.

Finally, the significant characteristic of these compounds is the considerable size of their pores, which makes them favorable candidates for posterior studies or applications; for example, mesoporous silica hierarchically organized is promising as materials standard for adsorption and catalyses studies for larges molecules.

Acknowledgments

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References and Notes

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