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Synthesizing and Characterizing Mesoporous Silica SBA-15: A Hands-On Laboratory Experiment for Undergraduates Using Various Instrumental Techniques

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ABSTRACT

In this laboratory experiment, students learn how to synthesize mesoporous silica of SBA-15 type, and explore how the different synthesis steps affect the final material. Mesoporous materials, especially SBA-15, are often used in the development of new methods for drug delivery, catalysis, and separation, due to the flexibility of tailoring these materials to optimize the performance in the different applications. However, the synthesis of mesoporous materials is rarely introduced to undergraduate students. The material synthesis is a simple sol-gel process, where small alterations in the synthesis steps can significantly change the material characteristics. The presented laboratory experiment aims at introducing undergraduate students to the synthesis of mesoporous silica of SBA-15 type, with different pore sizes due to alterations in the hydrothermal treatment time and/or temperature, as well as to expose and give students hands-on experience with important characterization tools using physisorption, XRD, FTIR spectroscopy, and TGA, to understand the effect of hydrothermal treatment and surfactant removal. Additional synthesis parameters to study, such as surfactant removal, silica precursor, and pore swelling agents, are also presented. The experiment has been used in teaching of both bachelor and master students, and can be adapted to various instrumental techniques, e.g. SEM for morphology studies, or TEM for pore structure characterization, etc.

ABSTRACT GRAPHIC **KEYWORDS**

Upper-Division Undergraduate, Laboratory Instruction, Hands-On Learning / Manipulatives, Materials Science, Nanotechnology.

Mesoporous silica is an excellent example of how one base material can be chemically modified and used in several applications of importance for our sustainable future e.g. drug delivery¹, solar cells², catalysis³, as a host for composite materials⁴, and batteries⁵. A mesoporous material is defined to have pores in the range of 2-50 nm⁶, and one of the characteristics of this material family is the large specific surface area, often 500 – 1000 m²/g. The large surface area enables the material to be used in applications where it is desired to have many active sites in a small volume, e.g. catalysis or gas storage. It is further possible to control the particle morphology to manufacture materials suitable for cellular uptake in drug delivery systems⁷. The most common chemical composition is silica, which is cheap to produce, and also simple to functionalize in different ways.

The synthesis of mesoporous silica is most often performed using the sol gel route. There are many different material families, e.g. the MCM (Mobil Crystalline Material)⁸, SBA (Santa Barbara Amorphous)⁹, or MSU (Michigan State University)¹⁰, which all comprise different types of surfactants, pH, etc, which gives them different pore characteristics and particle morphologies. However, the main synthesis route is to use surfactants, forming micelles in aqueous solution, followed by additions of a silica precursor, often an alkoxide, such as tetraethyl orthosilicate, or sodium metasilicate, and subsequent heat treatments. Finally,

the surfactants are removed by oxidation or calcination, leaving free mesopores. All these parameters may be added to the presented experiment.

By controlling the size and shape of the micelles, it is possible to control the pore size and structure of the material. This is often done by the addition of oils¹¹, by combining reduced temperatures with oils and salt¹², or by, as in this laboratory experiment, changes in the hydrothermal treatment time and/or temperature¹³. Notable, just small alterations in this sol gel system is sufficient to greatly impact the materials properties, and one can tailor make a material for a specific application. To put focus more on the silica chemistry, this laboratory experiment can be combined with the sol-gel preparation experiment from Buckley *et al.*¹⁴.

Mesoporous materials are sometimes used in laboratory experiments for students, e.g. for testing gas adsorption¹⁵ or dark field microscopy¹⁶. However, there is no laboratory experiment presently that gives the students practical understanding of the different synthesis steps in the standard synthesis of mesoporous silica, only a very specific microwave synthesis method for synthesis of ionic liquids is available¹⁷. The general synthesis route presented in this laboratory experiment can also be adopted to more application oriented tasks. This has not been performed by the students in the present experiment, but the task can easily be modified to perform the material functionalization either during the material synthesis, e.g. through doping with metals¹⁸ or by the addition of silanes attached to the desired functional group¹⁹, or by grafting functional groups on the material surface after the removal of surfactants³. It is also possible to multi-functionalize the material by first grafting one type of functional group on the external surfaces, remove the surfactants, and then functionalize the pore walls with another group²⁰. This is often done when the silica will be used as templates for nanoparticle growth or in drug delivery.

To summarize, the field of mesoporous materials is well established, and it is therefore of importance that students should be familiar with this family of materials. In addition it this, it is crucial for young chemists to be familiar with the common characterization techniques, and try these hands-on. The experiment described provides students insight into the sol-gel synthesis process, and how the different steps affect the material properties, as well as

giving them the opportunity to test fundamental characterization techniques. Furthermore, the students have been given the opportunity to present their findings to other students in written and oral forms. In this paper, a basic synthesis and characterization of mesoporous silica of SBA-15 type is described as a laboratory experiment for a higher level course of materials chemistry, solid state chemistry, or inorganic chemistry.

EXPERIMENTAL

Each student requires a hot plate with a magnetic stirrer, a round flask, an oil/water bath, a thermometer, a magnet, a condenser, a funnel, and filter paper. The required reagents are: HCl, Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) average $M_n \sim 5,800$ (Pluronic P123), and tetraethyl orthosilicate (TEOS). Prior to the experiment, each student should have prepared answers to the questions in the instructions, including calculating the correct amounts of all reagents. The answers are given in the Supporting Information Instructors' notes. The students work in groups of 2 – 4 persons and each student shall independently perform at least one synthesis. During a synthesis, the surfactant, P123, is dissolved in an HCl solution to act as a structure directing agent. The silica precursor, TEOS, is then added to the micellar solution, and the mixture is stirred for at least 2 h at a reaction temperature of 40 °C. During this process, the spherical micelles will elongate upon the addition of the silica precursor, and the ordered material will form²¹. After this step, a condenser is attached to the round flask, and the temperature is elevated to 100 °C for the hydrothermal treatment that lasts for 6-72 h, where the time should vary between students. Alternatively, the hydrothermal treatment temperature can be altered between 80-130 °C and be kept at a constant time, e.g. 24 h. During the hydrothermal treatment the hydrophilic parts of the P123 will become less soluble in water, and hence retract into the hydrophobic core of the micelle. Altering the hydrothermal treatment time or temperature are common pore size controllers for mesoporous materials. Finally, the material is recovered by filtration, washed with deionized water, dried, and calcined in a furnace at 550 °C for 5 h. Parts of the product should be collected prior to the calcination for characterization.

The calcined materials are characterized using nitrogen physisorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and Fourier transformed infrared spectroscopy

(FTIR), and the uncalcined materials using TGA and FTIR. Alternative parameters that can be added are: the removal of surfactants, addition of swelling agents, and alternative silica precursors. All parameters can be analyzed with the methods described in the experiment, and can be combined together. Detailed experimental procedures for these additional parameters, and suggestions for additional characterization, are found in the Supporting Information, Instructors' notes.

HAZARDS

Common lab safety rules, including gloves, lab coat and safety goggles, should be followed. Special care should be taken upon handling 37 % HCl due to its corrosiveness. Care should also be taken when handling TEOS, since it is skin and eye irritant, and flammable. P123 is not considered to be hazardous. The synthesis should be performed in a fume hood.

After the calcination, it is important to let the furnace cool down to avoid burn injuries when removing the material – keep in mind that the crucible can be very hot. The final material is a white, light powder and should be handled with care, preferably in a fume hood to avoid exposure to, and spreading of, the powder since it can be irritant upon skin and eye contact and if inhaled. During the preparation for physisorption, liquid nitrogen is used. Face protection, gloves, and long sleeves should be worn to reduce the risk of burns. Always handle liquid nitrogen in rooms with good ventilation.

RESULTS AND DISCUSSION

This laboratory experiment is suitable for three students, working individually with one synthesis parameter each, but can be performed by one to two students as well. The number of hydrothermal treatment times and/or temperatures can be altered according to the number of students or, if there are few students the batches can be split into several to increase the number of samples. The experiment is preferably performed during a project course rather than at fixed weekly sessions due to the long times required for dissolving the polymers, hydrothermal treatment time, etc. However, it is possible to narrow the initial time for the experiment by providing pre-dissolved micellar solutions and a reaction time of just 2 hours. It should though be noted that many of the steps during the synthesis only

require 30 min from the students, e.g. adding a condenser and increasing the temperature, or filtration and collection of the final material. The total time for characterization has been ~8 h, split into two sessions. Details regarding the time consumption in the project is given in the Supporting Information, Instructors' notes, but in total 16-20 h of laboratory time is required, including characterization. The laboratory experiment has been performed as a small project with undergraduate students (in total 9 students) within a nanotechnology course, as well as a laboratory project within a course entitled *Materials for a Sustainable Energy Production* for master students (in total 20 students). In both courses, the students have presented their findings to each other during a seminar. In the nanotechnology course, a literature study was added, and the students presented their findings also in a report written as a scientific manuscript. During the presentation, the students presented both the syntheses and the characterization results, which clearly showed if they had understood the experiment at hand. The project has been well received from the students who appreciated both the lab work and the hands-on training of analysis instruments. During the experiment, the students have gotten to know this material family, and many questions and discussions regarding applications and syntheses have occurred. In the end, the students have presented their findings either as a written report in manuscript style, and/or as an oral presentation which has trained their skills in communicating with students not familiar with the material family.

Among the pre-lab questions, the students have had the largest difficulty in calculating the amount of reagents. They often forget that the HCl solution also contain H₂O. The answers to all other questions are available in the instructions, but the questions force the students to think ahead about the material.

Figure 1. Data from (a) XRD, and (b) physisorption analysis of the synthesized materials show that the pore size and unit cell parameter with increasing hydrothermal treatment times.

The results from XRD and physisorption, presented in Figure 1, revealed a change in the pore size and unit cell parameter upon alterations in the hydrothermal treatment time, due to the retraction of the hydrophilic PEO chains from the silica template. This was due to the decreased hydrophilicity when the temperature is increased. The three peaks in the XRD diffractogram, seen in Figure 1(a)), indicate the hexagonal order of the mesopores. FTIR spectroscopy and TGA, Figure 2, show the effect of the calcination. Using TGA, the students observed that the majority of the surfactants were burned off at ~ 200 °C, where a large mass loss occurred. The FTIR spectra revealed whether any residues of the surfactants remained in the pores after the calcination through monitoring the carbon containing peaks at $\sim 1250 - 1500$ cm^{-1} and $\sim 2800 - 3100$ cm^{-1} . These are related to the surfactant and should disappear after the calcination, while the other peaks are associated with the silica network and should not change significantly. It was observed that all of the surfactants should be removed upon calcination at 550 °C as is illustrated in Figure 2. The results presented here are representative for the outcome of the experiment.

Figure 2. The effect of calcination shown with (a) FTIR and (b) TGA, which reveal that the surfactants are removed from the mesoporous silica upon calcination.

One of the most common problem the students have encountered is that the pore size does not follow the inverse of the specific surface area of the material. A longer hydrothermal treatment time should yield, especially during the first 48 h, a larger mesopore size and a decreased specific surface area, due to the retraction of PEO chains from the silica network, and after this time a plateau is reached and the effect of the hydrothermal treatment time is not as pronounced. However, since the students are synthesizing their own batch, a difference in synthesis temperature, during the initial reaction or the hydrothermal treatment, or the stirring rate during the reaction, can strongly affect the extension of PEO chains into the silica network. It is hence crucial that all the students have the same reaction temperature throughout the synthesis reaction, and also if the hydrothermal treatment time is the studied variable.

Depending on instrument availability, and the course curriculum, the instructor is of course free to pick and choose the suitable analysis techniques. Additional techniques of interest are e.g. scanning and/or transmission electron microscopy to study the particle morphology and pore structure.

ASSOCIATED CONTENT

Supporting Information

Student handout and notes for the instructor. This material is available via the Internet at <http://pubs.acs.org>

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Supporting information for

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Using Various Instrumental Techniques

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Synthesis and characterization of mesoporous silica templates

Instructors' notes

List of chemicals

Name	CAS number	Amount / student
Hydrochloric acid 37%	7647-01-0	4.3 mL
Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) $M_n \sim 5\,800$ (P123)	9003-11-6	1.2 g
Tetraethyl orthosilicate (TEOS)	78-10-4	2.7 mL

Answers to pre-lab exercises

- 4.27 mL HCl 37%
36.73 mL H₂O
1.16 g P123
2.67 mL TEOS
- In the beginning, the P123 form spherical micelles in the aqueous solution. When the TEOS is added, it hydrolyses and starts to bind to the PEO chains of the P123. These bonds lead to a change in the c_{pp} and therefore an elongation of the micelles, which becomes cylindrical and aggregates into the hexagonal structure. The silica continues to condense around the micelles and form the silica walls.
- When the time and/or temperature is increased, the pore size will increase while the specific surface area will decrease. This is due to that the PEO chains in the P123 becomes more hydrophobic at elevated temperatures, and will retract from the silica walls. This leads to an expansion of the hydrophobic core which pushes out the silica walls and makes them denser, i.e. the microporosity decreases. When the material then is calcinated, the mesopore size is determined by the size of the core of the micelles.
- Host for catalysts, drug delivery, templates for nanoparticles, molecular sieves, gas storage, and sensors.

Time required for the different steps of the exercise

Synthesis

The synthesis requires following steps:

- 4 h for discussion of pre-lab exercises, preparation of HCl solution (if not provided by the instructor), dissolution of P123 (~2 h) at 40 °C, and the addition of TEOS.
- Wait 2-20 h for the reaction to occur. This step does not require coverage by the students.
- 1 h for preparations for the hydrothermal treatment, i.e. add condensers and increase the temperature. If oil bath with analogue thermometers are used, add some extra time to make sure that the temperature is stable.
- Hydrothermal treatment for 6 – 72 h. This step does not require coverage by the students.
- ½ h for filtration of the materials.
- Let the materials dry.
- ½ h to divide the materials and put parts of them in the furnace for calcination.
- Calcination overnight (5 h + time for ramp up (1-10 °C/min) and cooling down).
- ½ h for collecting and labelling the final materials.

Characterization

The characterization takes ~8 h split into two sessions.

- Session 1:
One TGA measurement is started, using the same ramp and temperature as is used for calcination.
Physisorption samples should be prepared and set to degas.
Either the XRD or FTIR measurements should be performed.
- Session 2:
Start the physisorption analyses.
Run the second TGA measurement.
The XRD/FTIR analysis which was not performed during the first session.

If only one instrument is available for physisorption, individual appointments must be made with the students. Allocate ½ h/student including weighing the sample and addition of liquid nitrogen.

Additional parameters

The presented laboratory exercise focuses on pore size control by alterations in the hydrothermal treatment time and/or temperature. To further expand the experimental room some additional parameters that can be included are listed above. It is possible to combine them all if wanted.

- **Pore swelling agents**

It is possible to alter the mesopore size by using swelling agents, e.g.

1,3,5-Trimethylbenzene (TMB) (CAS: 108-67-8). This oil will go into the micellar core and expand it prior to the addition of the silica precursor.

With this parameter, add TMB (amount: 0-0.25 mL) to the micellar solution when the P123 has been dissolved, and stir it for 1 h prior to the addition of TEOS. Then follow the exercise as described. The pore swelling will be observed in physisorption and XRD data.

Details regarding the interpretation of the physisorption isotherm is found at: [dx.doi.org/ 10.1021/la000660h](https://dx.doi.org/10.1021/la000660h). However, the given amount of TMB should give cylindrical pores.

- **Alternative methods for removing the P123**

- *Extraction with ethanol*: mix the dry powder with ethanol (267 mL ethanol / 1 g mesoporous silica) and reflux under stirring at 60 °C for 24 h. Filter and dry the powder.
- *Extraction with methanol*: mix the dry powder with methanol (100 mL methanol / 1 g mesoporous silica) and sonicate in an ultrasonic bath for 5 min. Filter and dry the powder.
- *Extraction with H₂O₂* (CAS: 7722-84-1): mix the material with H₂O₂ (120 mL H₂O₂ / 1 g of mesoporous silica) and stir it under reflux at 100 °C for 24 h. Filter and dry the powder.

Compared to calcination, all the oxidations methods will yield larger mesopore sizes. With this parameter, the TGA and FTIR should be performed on all samples to compare the different removal methods. A drop in the TGA or extra peaks in the FTIR spectrum indicate that there are residues of P123 in the silica matrix. These residues can also be seen as a decreased surface area in the physisorption measurements. The oxidation methods will also lead to a higher silanol concentration, which can be observed as an increase in the peak around 960 cm⁻¹ in the FTIR spectrum.

Details regarding the synthesis procedure can be found here:

- ethanol and methanol: dx.doi.org/10.1039/C3GC40474A
- H₂O₂: dx.doi.org/10.1016/j.micromeso.2010.04.016

- **Alternative silica precursor**

The silica precursor, TEOS, can be exchanged with equimolar amounts (1.46 g) of sodium metasilicate (CAS: 6834-92-0) which is dissolved with ~5 mL of the 1.3 M HCl prior to the addition to the micellar solution.

Here it can be observed that the solution will turn white faster, since sodium metasilicate is already hydrolyzed when it is added to the micellar solution. Also, slightly thicker silica walls will be observed. If possible, it would be interesting to add SEM for characterization, to see if the particle morphology is affected by the change of silica precursor.

Sodium metasilicate is a cheaper alternative to TEOS, and also does not give ethanol as a waste product, which is preferable upon upscaling of the material.

Additional characterization techniques

If the course allows, other characterization techniques can be added to the laboratory task.

- SEM to study the particle morphology. It may also be possible to look at the pore arrangement, but that depends on the microscope resolution. The pores are in the range of 5-10 nm in diameter.
- TEM to look at the pore structure. Confirm that the pores are cylindrical and hexagonally arranged.

Contact

If you have any questions or comments, please contact me on e-mail: emma.bjork@liu.se

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Synthesis and characterization of mesoporous silica templates

Students' handout

Introduction

Mesoporous materials are materials with a pore diameter of 2-50~nm. These materials are of great interest due to their large surface area which makes them suitable as catalysts. They are also used as templates for making nanoparticles, chemical sensors and as molecular sieves. The synthesis of these materials are of great interest, since small changes in the procedure can result in large changes in morphology, pore structure and size of the mesopores.

In this lab, the hydrothermal treatment time will be varied during the synthesis to study if that will affect the pore size of mesoporous silica SBA-15. The synthesized materials will be characterized using thermogravimetric analysis, infrared spectroscopy, physisorption and X-ray diffraction.

SBA-15

In 1992 a new family of mesoporous materials, M41S, was discovered. The material possessed regular arrays of uniform channels which diameter could be tailored through the choice of surfactant and reaction conditions. This was the start of a new era in material science. The first mesoporous silica made with amphiphilic triblock copolymers were reported in 1998. These materials are called SBA-X where SBA stands for Santa Barbara Amorphous and X represents a number so that e.g. SBA-15 represents a 2-dimensional hexagonal structure, SBA-12 a 3-dimensional hexagonal structure and SBA-11 has a cubic structure.

SBA-15 is a very popular material since it is possible to make during various conditions and it is quite easy to control the pore size with the use of swelling agents such as 1,3,5-trimethylbenzene (TMB). In the first study of SBA-15 it was reported that it is possible to form pores in the range 46-300 Å. This is unfortunately not completely true since the material undergoes a phase transition when too much TMB is used, forming a mesocellular foam, MCF, when the pore size of SBA-15 exceeds 12 nm due to too much TMB.

Structure

In SBA-15, the mesopores are cylindrical and organised in a hexagonal lattice. Between the cylindrical pores, there are micropores which connect the cylinders to each other. The size of the mesopores in SBA-15 varies between 6-18 nm and the thickness of the pore walls range from 1 to 4 nm. These mesopores are connected by micropores through the silica walls. These smaller pores are disordered and non-uniform since they do not give any peaks in the XRD. From calculations of the nitrogen isotherms it is possible to estimate the microporosity of materials. In this case, the material showed a broad distribution of small pores with a maximum at around 2 nm. The microporosity can also be confirmed by

carbon replicas of the structure, see figure 1. The micropores around each mesopore are called the corona.

Figure 1: Structure of SBA-15 and its replica as rods and tubes.

Carbon replicas

One material often used for making replicas of SBA-15 is carbon. It is possible to fill the silica mesopores completely to make carbon rods or just partly, resulting in carbon tubes. Both the tubes and the rods are connected through the filling of interconnecting micropores in the silica walls. When the silica is etched away, these carbon structures can be used for e.g. templates for other materials or as mesoreactors since the carbon is more reactive than the silica. When tubular carbon is synthesized it will have a surface area of $\sim 2000 \text{ m}^2/\text{g}$ (1/4 of a football field) which makes it suitable for catalysis or storage of e.g. hydrogen.

The structure of the carbon replicas are completely dependent of the structure of the silica template. By varying the pore size and thickness of the silica walls it is possible to vary the pore size and wall thickness of the carbon replica, e.g. thin silica walls and large pores in the SBA-15 will give thick walls and small pores in the carbon replica.

Synthesis

Surfactant

The surfactant used for the formation of SBA-15 is P123 which is a triblock PEO-PPO-PEO copolymer with $M_n \sim 5\,800$ g/mol. The structure of this molecule is seen in figure 2. P123 is an amphiphilic molecule where the PEO parts are hydrophilic and PPO part is hydrophobic. The PEO parts are in this work referred to as EO chains and PPO as PO chain. The amphiphilic behaviour of P123 makes it form spherical micelles in water with the EO chains towards the water and the PO chains in the core of the micelles.

Figure 2: Structure of P123.

The concentration and EO/PO ratio of the polymers are very important in the formation of mesoporous materials. An EO/PO ratio above 1.5 tends to favour the formation of cubic mesoporous silica structure while a lower ratio at 0.07-1.5 will favour a hexagonal structure. If the ratio is less than 0.07 and the concentration is low, 0.5-1 wt%, a hexagonal SBA-15 structure will be formed but if it is higher it will form lamellar mesostructured silica

Silica precursor

In this study two Tetraethyl orthosilicate (TEOS) with $M = 208.33$ g/mol was used as silica precursor. This molecule is in the group of tetra-alkoxysilanes and its structure is seen in figure 3.

Figure 3: Structure of TEOS.

The rate of hydrolysis of the tetra-alkoxysilanes depends on the environment. Variables such as temperature, amount of ions and also the type of solvent are important for the rate of hydrolyzation of the precursors.

Synthesis and formation

There are four main steps in the preparation of SBA-15. The first step is the synthesis of the mesoporous structure using a block copolymer, in our case P123, and a silica precursor, in our study TEOS. The second step is the hydrothermal treatment at a higher temperature. Filtration and washing the samples are the third step and the fourth step is removing the polymer by calcination. A schematic of the formation process is seen in figure 4.

Figure 4: Start with a solution containing spherical micelles, add TEOS and the micelles will be elongated when the silica walls begin to be formed. The cylinders attach in a hexagonal structure and the walls become more dens. Finally the product is calcinated to remove the micelles.

In the synthesis the surfactants are added to a homogeneous, acidic solution containing distilled water and HCl. In some cases swelling agents are added to the solution before adding the surfactant. For SBA-15 the triblock copolymer P123 is used as the surfactant. The P123 forms spherical micelles in the solution. When the silica precursor is added it hydrolyses and bond to the micelle forming a silica network that will be the walls in the particles. At this step the micelles becomes elongated from spheres to cylinders which together form a hexagonal structure. With time, the silica walls become denser.

The shape of the micelles depends on the critical packing parameter

$$CPP = \frac{v}{a_0 l_c} \quad (2)$$

v is the volume of the hydrophobic tale.

a_0 is the area of the hydrophilic head

l_c is the length of the hydrophobic tale

Different micelle structures are seen in figure 5. When TEOS is added to the synthesis, it will form droplets in the solution and hydrolyse in the water/droplet interface. The hydrolysed spices starts to bond to the hydrophilic parts of the micelles and screen the ions in the solution decreasing the area of the hydrophilic head. This changes the cpp and give the phase transformation from spherical to cylindrical micelles.

Figure 5: Various morphologies and their c/p ratio: (a) spherical, $c/p < 1/3$, (b) cylindrical, $1/3 < c/p < 1/2$, (c) bilayer, $1/2 < c/p \leq 1$, and (d) inverted micelle, $c/p > 1$.

The hydrothermal treatment increases the pore diameter and reduces the silica wall in SBA-15. During this step the temperature is elevated which reduces the hydrophilicity of the EO chains. This leads to that the chains go into the core of the micelles and thereby expands them, pushing out the silica walls. The silica then becomes denser and closes the voids from the withdrawn EO chain, thereby decreasing the microporosity in the wall.

During the calcination the hydrothermally treated samples have a lower shrinkage than untreated samples and this together with the expanded core give a larger pore size, see figure 6.

Figure 6: The effect of hydrothermal treatment.

Analysis

The materials will be characterized using four different methods.

Thermogravimetric Analysis

Thermogravimetric Analysis, TGA, is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. In this the method is used to study the calcination of the silica. During the analysis, the temperature is raised at the same rate as during the calcination to the calcination temperature, 560°C and the change in weight of the sample is recorded. By adding a mass spectrometer it is possible to see the degradation components of the polymer.

Fourier Transformed Infrared Spectroscopy

Fourier transformed infrared spectroscopy, FTIR, is used to see the functional groups in the products and to see if there are residues of P123 or alkanes in the product. With FTIR it is possible to study the vibrations and rotations of atoms in molecules due to their discrete energy levels. This energy corresponds to a frequency which is determined by the masses of the atoms and the type of movement.

To make measurements with FTIR the powdered product must be formed into a pellet. This is done by mixing 120 mg KBr, which is invisible for the radiation, with 0.7-1.0 mg sample. The product and KBr are mixed and crushed together with a mortar. The powder is put in a holder and pressed together to form a pellet.

Physisorption

In physisorption a gas is adsorbed on the surface of the sample through Van der Waals interactions. Analysing the amount of adsorbed gas at different pressures, isotherms, gives information about the surface area and pore structure.

The sample is degassed to remove all moisture from it. Then the sample tube is immersed into liquid nitrogen and the pressure in the sample tube is lowered to $\sim 2 \mu\text{mHg}$. Nitrogen gas is then added to the sample in a series of controlled pressures. Nitrogen molecules will be adsorbed on the surface and the sample. First, the micropores are filled with gas molecules that condense on the surface and then the free surfaces are covered with condensed nitrogen. When enough amount of nitrogen is added also the large pores are filled. This process continues until the relative pressure in the sample tube is close to 1 (atmospheric pressure). At this pressure the total pore volume is measured. Then the pressure is reduced again in a series of controlled pressures. Now, the molecules adsorbed

to the surface will be released. The result of this measurement is a curve called sorption isotherm.

Most physisorption isotherms can be grouped into six categories which are seen in figure 7a. The fourth category is associated with mesoporous materials. The characteristics of this isotherm are the hysteresis loop and the limiting uptake at high pressures. The type IV isotherm can be divided into three parts. At first, the isotherm increases rapidly when a monolayer of gas covers the material. The second part is almost linear and is due to multilayer adsorption. The hysteresis loop is the third part, which is associated with capillary condensation in the mesopores. There are different shapes of the hysteresis curves, which can be seen in figure 7b, associated with specific pore structures. The distance between adsorption and desorption in this loop gives information about the pore size distribution and plugs in the pores.

Figure 7: Types of (a) physisorption isotherms and (b) hysteresis loops.

The BET specific surface area is calculated using adsorption isotherms in the relative pressure range 0.08 to 0.20 and the pore size distribution is calculated using the Kruk-Jaroniec-Sayari, KJS, method. This method has been successfully for MCM-41 materials which have a smaller pore size than SBA-15 and MCM-41 also lacks the interconnecting microporous network found in SBA-15. This method can be applied also for SBA-15 materials but gave an overestimation of the pore size for this material. The method was further developed and in 2006 one found an improved model that gives a distribution even for SBA-15 materials that fits results from SAXS and XRD measurements.

X-Ray Diffraction

Measurements with X-Ray Diffraction (XRD) show if there is an ordered structure of the pores in the mesoporous material. The basic principle of XRD is the Bragg condition and is illustrated in figure 8.

$$n\lambda = 2d_{hkl} \sin \theta \quad (1)$$

λ is the wave length of the X-rays

d_{hkl} is the distance between the planes with indexes h, k and l

θ is the angle at which constructive interference occurs

Figure 8: Schematic illustration of Bragg's law.

The sample is scanned in a range of θ and the intensity of the outgoing beam is detected. This gives a spectrum with peaks for constructive interference. In this case XRD is used to receive information about the d-spacing. Since SBA-15 has a hexagonal symmetry lattice the (100), (110) and (200) usually can be seen in the range of 0° - 3° . An increase of the d-spacing indicates an expansion of the hexagonal unit cell.

Laboratory assignments

Synthesis

Every synthesis has the molar ratio

$$\text{P123} / \text{HCl} / \text{H}_2\text{O} / \text{TEOS} = 1 / 261 / 10854 / 60$$

For every synthesis do following steps:

1. Make a micellar solution with HCl, water and P123 and wait until the P123 has dissolved completely ~2 h. Use a stirring rate of 300 rpm. The temperature of the solution should be 40 °C.
2. Add TEOS to the above solution. Increase the stirring rate to ~750 rpm. Leave the reactions stirring for 2 – 20 h.
3. Add condensers to the flasks and increase the temperature to 100 °C. Turn the stirring off. Hydrothermally treat the syntheses for 6, 24 and 72 h, or alternatively, use the temperatures 80 °C, 100 °C, and 130 °C for 24 h.
4. Filter and wash the products with deionised water.
5. Remove some of the products for TGA and IR measurements. Calcinate the rest at 550 °C for 5 h.

Analysis

TGA	run a program identical to the calcination program on one uncalcinated sample and one calcinated samples.
FTIR	make spectra for one uncalcinated sample and one or more calcinated samples.
Physisorption	do measurements on the three calcinated samples.
XRD	make diffractograms for the three calcinated samples.

Hazards

The synthesis should be performed in a fume hood due to the corrosiveness of the HCl. Common lab safety rules, including wearing gloves, lab coat, and safety goggles, should be followed, and special care should be taken upon handling 37 % HCl. TEOS is skin and eye irritant, and flammable. **P123 is not considered to be hazardous.**

Let the furnace cool down after the calcination to avoid burn injuries.

The final material is a light powder, and should be handled with care, preferably in a fume hood to avoid inhalation of the product since it can irritate the air ways. It is also irritant upon skin and eye contact.

When handling of liquid nitrogen during the preparation of physisorption measurements, face protection, gloves, and long sleeves should be worn to reduce the risk of cold burns. Liquid nitrogen should always be handled in rooms with good ventilation.

Pre-lab exercises

- Calculate the amounts of all reagents in the three syntheses when 40 ml 1.3 M HCl is used. Assume that you have access to HCl 37 w%.
- Describe the formation process of SBA-15.
- Explain what you think will happen to the material when the hydrothermal treatment time and/or temperature is increased?
- Suggest 5 applications for SBA-15.