

Experiment NC11: Synthesis of rope/rod-like, nanostructured periodic mesoporous silica particles with hexagonal symmetry

Aims

1. Know the basic structure of triblock copolymers (hydrophobic and hydrophilic part)
2. Learn how to use triblock copolymers as templates for the preparation of periodic mesoporous silica with hexagonal symmetry under acidic conditions
3. Try to understand interactions between triblock copolymer and inorganic silica frameworks, and the corresponding reaction mechanism
4. Know that the use of different surfactants influences the final structure and pore size of obtained mesoporous silicas such as MCM-41 and SBA-15

1. Basic principle

In **Experiment NC10**, we got to know the classification of surfactants according to the charge of their head group(s). Herein, we will introduce nonionic surfactants in detail, and their application in the synthesis of periodic mesoporous silica materials.

Nonionic surfactants include oligomeric alkyl-ethylene oxides, long carbon chain alcohols and block copolymers.

Prominent among these are the fatty alcohols $[\text{CH}_3(\text{CH}_2)_n\text{CH}_2\text{OH}]$, when $n = 14$, it is cetyl alcohol or hexadecyl alcohol, stearyl alcohol or octadecyl alcohol ($n = 16$), and oleyl alcohol $[\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_2\text{OH}]$. Some routine nonionic surfactants are shown below:

Polyoxyethylene glycol alkyl ethers series (Brij): Typical formula is $\text{CH}_3(\text{CH}_2)_m(\text{OCH}_2\text{CH}_2)_n\text{OH}$,

Where $m = 11$, $n = 5$, pentaethylene glycol monododecyl ether $[\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_5\text{OH}]$, or C_{12}EO_5 ;

$m = 11$, $n = 4$, tetraethylene glycol monododecyl ether (C_{12}EO_4 , Brij30);

$m = 11$, $n = 8$, octaethylene glycol monododecyl ether (C_{12}EO_8);

$m = 11$, $n = 23$, $\text{C}_{12}\text{EO}_{23}$ or Brij 35;

$m = 15$, $n = 2$, diethylene glycol hexadecyl ether (C_{16}EO_2 , Brij 52);

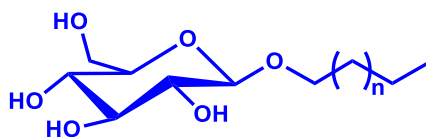
$m = 15$, $n = 10$, $\text{C}_{16}\text{EO}_{10}$ or Brij 56;

$m = 15$, $n = 20$, $\text{C}_{16}\text{EO}_{20}$ or Brij 58;

$m = 17$, $n = 10$, $\text{C}_{18}\text{EO}_{10}$ or Brij 76;

$m = 17$, $n = 20$, $\text{C}_{18}\text{EO}_{20}$ or Brij 78.

Glucoside alkyl ethers: $\text{CH}_3(\text{CH}_2)_n(\text{O-Glucoside})_{1-3}\text{OH}$, its basic structure is as follows.



Where $n = 5$, octyl glucoside; $n = 7$, decyl glucoside; $n = 9$, lauryl glucoside.

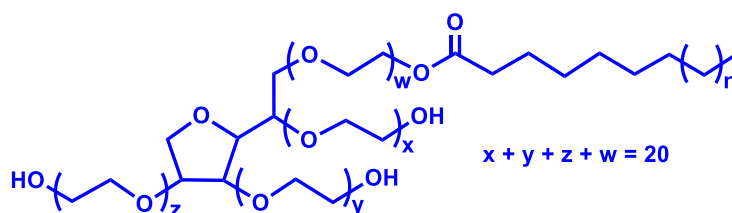
Polyoxyethylene glycol octylphenol ethers:

$\text{CH}_3\text{CMe}_2\text{CH}_2\text{CMe}_2(\text{C}_6\text{H}_4)(\text{OC}_2\text{H}_4)_n\text{OH}$, where $n = 10$, Triton X-100; $n = 5$, Triton X-114.

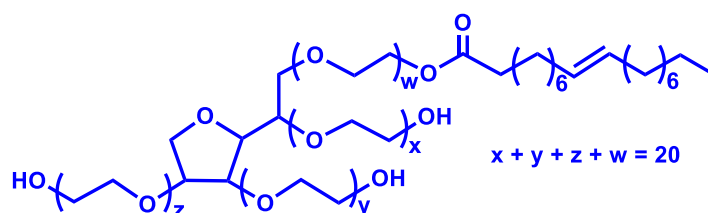
Polyoxyethylene glycol alkylphenol ethers: $\text{CH}_3(\text{CH}_2)_8(\text{C}_6\text{H}_4)(\text{OC}_2\text{H}_4)_n\text{OH}$, where $n = 5$, Nonoxynol-5; $n = 9$, Nonoxynol-9.

Glycerol alkyl esters: $\text{CH}_3(\text{CH}_2)_n\text{COOCH}(\text{CH}_2\text{OH})_2$, where $n = 10$, glyceryl laurate or 1,3-dihydroxy-2-propanyl laurate.

Polyoxyethylene glycol sorbitan alkyl esters (Tween series): Polysorbate



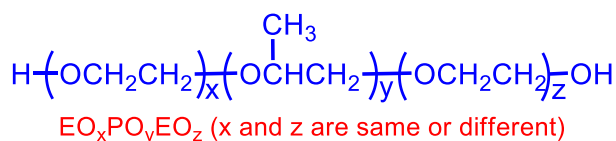
Where $n = 4$, poly(ethylene oxide)(20) sorbitan monolaurate (Tween 20); $n = 8$, poly(ethylene oxide)(20) sorbitan monopalmitate (Tween 40); $n = 10$, poly(ethylene oxide)(20) sorbitan monostearate (Tween 60). In addition, poly(ethylene oxide)(20) sorbitan monooleate (Tween 80) is shown as follows:



Dodecyldimethylamine oxide: $[\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{N}^+\text{Me}_2\text{O}^-]$ — zwitterionic surfactant.

Polyethoxylated tallow amine (POEA) — $\text{H}(\text{OCH}_2\text{CH}_2)_m\text{N}(\text{R})(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, where R is alkyl group.

Block copolymers of polyethylene glycol and polypropylene glycol: Poloxamers, such as Pluronics. Basic structure is shown in [Scheme 11-1](#).



Scheme 11-1. A representative structure of nonionic triblock copolymer.

Routinely used Pluronics include Pluronic L121 (x = z = 5, y = 70), Pluronic L64 (x = z = 13, y = 30), Pluronic P65 (x = z = 20, y = 30), Pluronic P85 (x = z = 26, y = 39), Pluronic P103 (x = z = 17, y = 56), Pluronic P123 (x = z = 20, y = 70), Pluronic F68 (x = z = 80, y = 30), Pluronic F127 (x = z = 106, y = 70), and Pluronic F88 (x = z = 100, y = 39) etc.

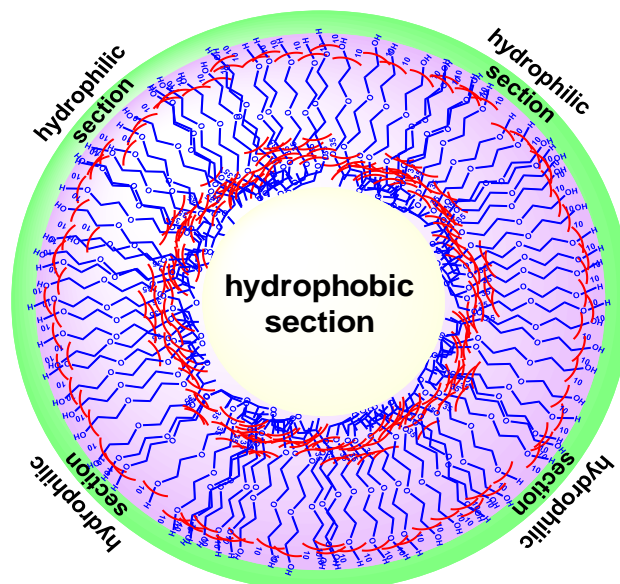
All the above-mentioned nonionic surfactants can be used as a structure-directing agent (SDA) or a template for the preparation of periodic mesoporous silica materials under suitable conditions.

In 1995, *Pinnavaia and co-workers* used a nonionic surfactant to synthesize wormlike disordered mesoporous silicas (MSU series: Michigan State University) under neutral aqueous conditions. After removal of the surfactant by calcinations, uniform sizes of 2 - 6 nm were obtained. In 1998, *Zhao and co-workers* extended this method and used nonionic amphiphilic triblock copolymer of larger molecular weight as a template under acidic conditions to prepare large pore periodic mesoporous silica materials (Santa Barbara Amorphous (SBA) materials at the University of California, Santa Barbara) SBA-15, SBA-16 etc.

As routine the surfactant structure of nonionic triblock copolymers is composed of a hydrophobic and a hydrophilic unit, such as poly(alkylene oxide) block copolymer, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol), EO_xPO_yEO_z (Scheme 11-1). As can be seen in Scheme 11-1, the three basic units are poly(ethylene glycol), poly(propylene oxide) and poly(ethylene glycol). In general, the middle part of triblock copolymer is hydrophobic such as poly(propylene oxide) — (OCHMeCH₂O)_y. The hydrophilic group/part is poly(ethylene glycol). Owing to the difference of the degree of polymerization (x, y and z), the same typical nonionic surfactant often shows different molecular weights that can be expressed by using an average molecular weight, such as Pluronic P123 (average molecular weight is 5800) and Pluronic F127 (*M*_{av} = 12600).

We know that, under basic conditions, the formation of periodic mesoporous silica nanospheres with hexagonal symmetry stems from silica-surfactant self-assembly, occurring simultaneously with the condensation of inorganic silica species. However, how do nonionic triblock copolymers as structure-directing agents drive the formation of periodic mesoporous silica under acidic conditions?

Under acidic conditions, the poly(ethylene glycol) parts are protonated, enhancing the hydrophilicity of the whole triblock copolymer PEO-PPO-PEO and the corresponding poly(propylene oxide) part shows more hydrophobicity than the poly(ethylene glycol), especially, the reaction temperature ranges from 35 °C up to 80 °C. This greatly increases the tendency of the occurrence of mesoscopic ordering, and the formation of self-assembled micelles of triblock copolymers (Scheme 11-2).



Scheme 11-2. Illustration of self-assembly of nonionic triblock copolymer surfactants under acidic conditions.

Hence, under strongly acidic conditions (pH is close to 1), the positively charged protonated silicate species ($\equiv\text{Si-OH}_2^+$) preferentially interact with the more hydrophilic poly(ethylene glycol) blocks to promote cooperative self-assembly of a silica-triblock-polymer-rich mesophase from a dilute aqueous solution by a pathway that involves combination of electrostatic and hydrogen-bonding interactions. Concurrent and consecutive condensation of silicate species results in the formation of mesoporous silica in the presence of triblock copolymer surfactant. Based on this, a $\text{S}^0(\text{X}^-\text{I}^+)$ mechanism for the formation of periodic mesoporous silica was suggested in the presence of triblock copolymer under acidic conditions (see Scheme 10-2 in **Experiment NC10**). In addition, previous reports revealed that pH range of 2 to 7 could not drive the formation of ordered mesoporous silicas. In this case, amorphous or disordered silicas were often obtained. Therefore, strongly acidic conditions are necessary to ensure the formation of long-range ordering of pore arrays in the mesoporous silicas.

In the present experiment, we will use tetraethyl orthosilicate [$\text{Si}(\text{OEt})_4$, TEOS] as a silica precursor and triblock copolymer surfactant Pluronic P123 as a template or a structure-directing agent under a strongly acidic condition to prepare hexagonal

periodic mesoporous silica SBA-15 with rod-like morphology (space group is $p6mm$). It is note that the use of triblock copolymer under acidic conditions often induces the formation of microporous structures in the obtained mesoporous silica materials, too.

However, how to confirm that the as-made and calcined materials are of the SBA-15 type with hexagonal symmetry ($p6mm$)? For this purpose we need to measure powder X-ray diffraction patterns on a Bruker Advance D8 diffractometer in the range of $0.5\text{-}10^\circ$ of 2θ . The obtained diffraction peaks can be used to determine the pore structure of the material. According to Bragg's law: $d_{hkl} = \lambda / (2 \sin\theta)$, we can calculate lattice spacing (d-spacing) of every resolved diffraction peak, herein, λ is the wavelength of x-rays ($\lambda = 1.5406 \text{ \AA}$), θ is the diffraction angle and hkl is the diffraction plane, at which we observe peaks in the diffraction pattern.

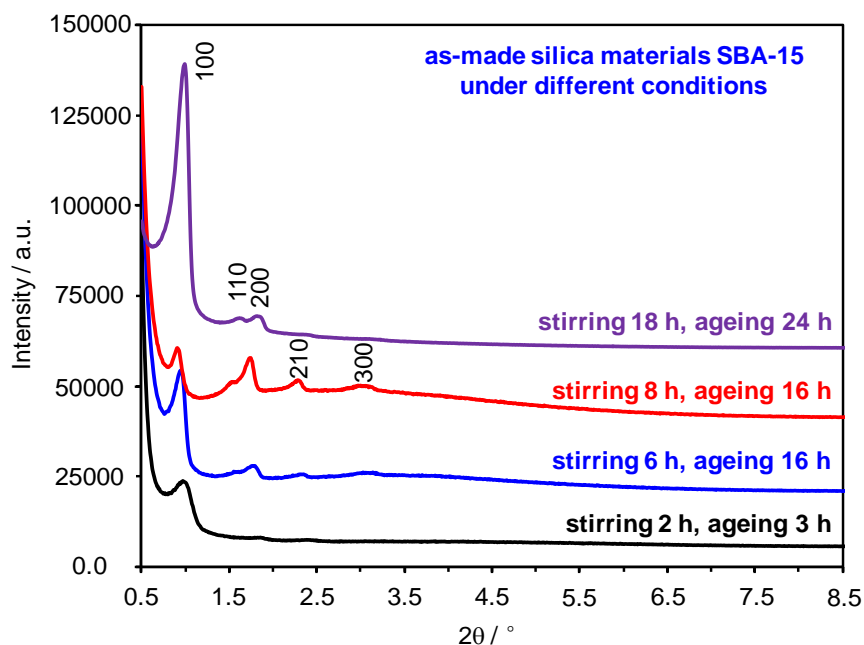


Figure 11-1. Powder X-ray diffraction patterns of as-made silica materials SBA-15 synthesized by using different stirring and ageing times.

For a successful experiment, the as-made material will show three well-resolved diffraction peaks which are indexed as the (100), (110), and (200) planes, indicating a typical hexagonal $p6mm$ pore structure (Figure 11-1). After addition of TEOS, it is note that the suspension has to be stirred at 35°C for at least 18 h in order to fabricate a stable mesoporous material, otherwise the obtained as-made silica material will show a metastable structure (after removal of surfactant templating, the ordered mesoporous structure collapses, Figure 11-2). In general, for a stable as-made mesoporous silica material, after removal of the surfactant by calcinations, the calcined silica will show four or five well-resolved peaks (100), (110), (200), (210) and (300) with increasing intensities — a typical silica material SBA-15 (Figure 11-2)

compared to that of the as-synthesized material, revealing an increasing scattering contrast between pore and pore wall. If as-made silica materials are unstable, its structures will be destroyed after high-temperature calcinations.

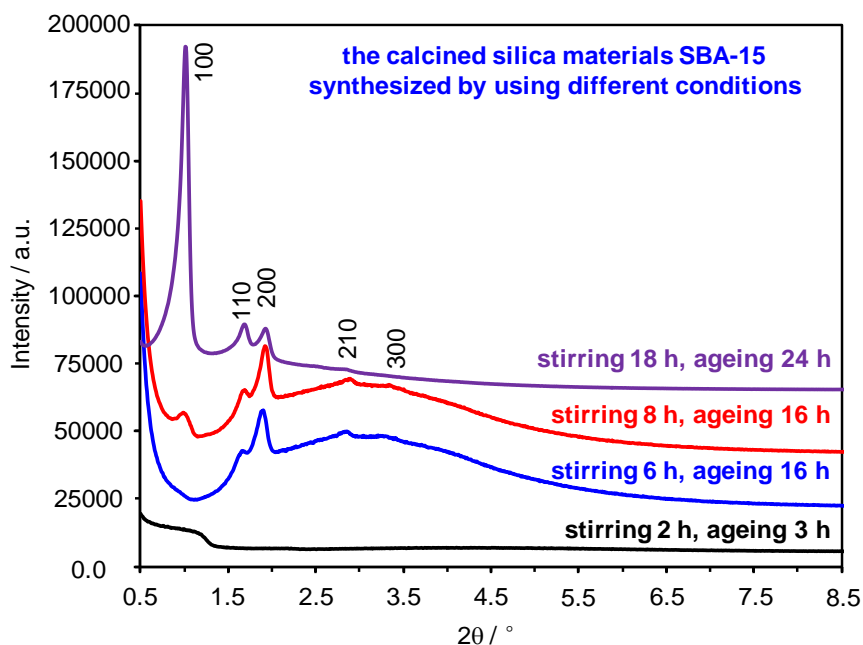


Figure 11-2. Powder X-ray diffraction patterns of the calcined silica materials SBA-15 synthesized by using different stirring and ageing times.

Moreover, the specific Brunauer-Emmett-Teller (BET) surface area and the pore size distribution by Barrett-Joyner-Halenda (BJH) method as well as pore volume can be determined by N₂ adsorption-desorption analysis. It is noteworthy that pore parameters of periodic mesoporous silica materials obtained under different synthetic conditions, are different, such as specific BET surface area, pore diameter and pore volume (Table 11-1, Figure 11-3 and Figure 11-4).

Table 11-1. Pore parameters of SBA-15 synthesized under different conditions.

sample	$a_s / \text{m}^2 \text{g}^{-1}$	$d_{p, \text{adsorption}} / \text{nm}$	$d_{p, \text{desorption}} / \text{nm}$	$V_p / \text{cm}^3 \text{g}^{-1}$
SBA-15 (1)	773	7.0	5.6	0.89
SBA-15 (2)	788	7.5	6.1	1.02

In Table 11-1, SBA-15 (1) was synthesized under the following condition: Stirring at 35 °C for 8 h and then ageing at 90 °C for 16 h ageing time, followed by calcination. SBA-15 (2) was synthesized at 35 °C for 18 h stirring and then at 90 °C for 24 h ageing, followed by calcination. It is obvious that longer stirring and ageing time led to the formation of stable mesopore structure with larger pore size and pore volume.

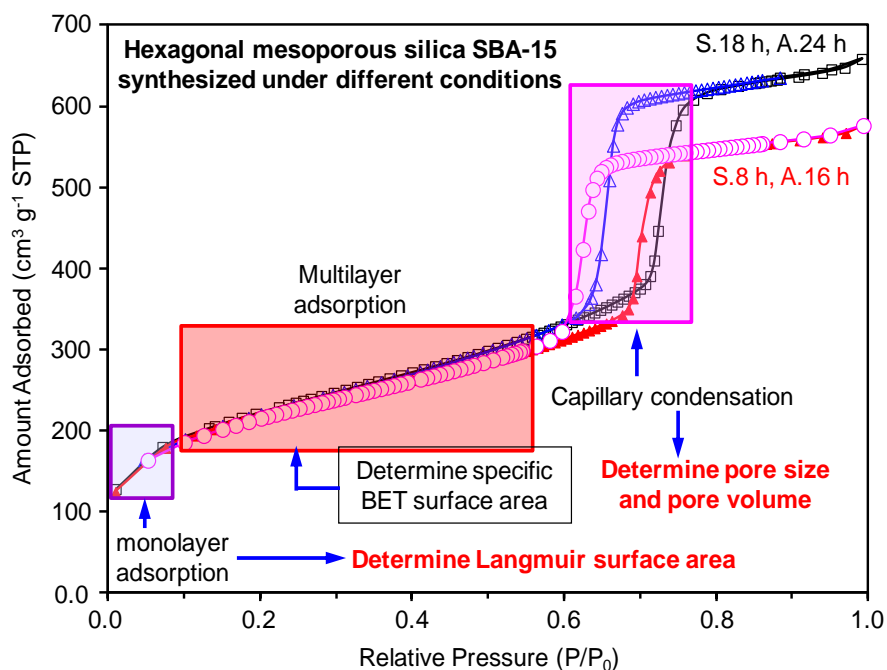


Figure 11-3. N₂ adsorption-desorption isotherm of SBA-15 synthesized under different conditions but with an identical molar composition.

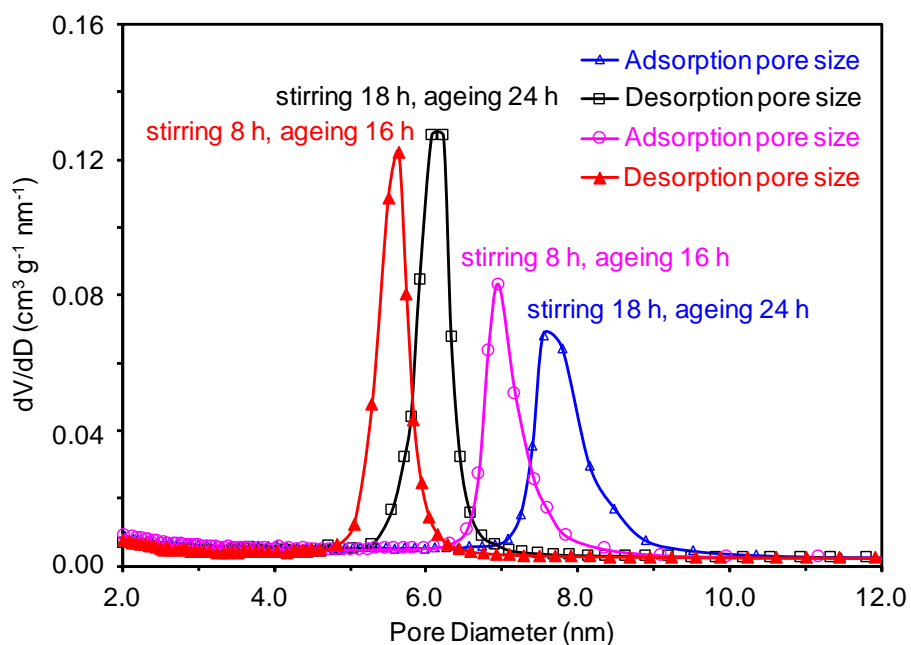


Figure 11-4. The BJH pore size distribution of SBA-15 synthesized under different conditions but with an identical molar composition.

2. Experimental section

2.1. Chemicals used

Surfactant: Pluronic P123 triblock copolymer [H-(OCH₂CH₂)₂₀(OCHMeCH₂)₇₀(OCH₂-CH₂)₂₀OH], poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol), EO₂₀PO₇₀EO₂₀, average M_{av} ~5,800

Silica precursor: tetraethyl orthosilicate (TEOS)

2M HCl solution

deionized water

2.2. Equipment/Materials

250 mL polyethylene bottle with cap, magnetic stirrer with stirring bar, graduated cylinder (100 mL), pipette (10 mL), water bath, thermometer (~ 150 °C), glass pipette, bulbs, X-ray diffractometer, N₂ physisorption instrument.

2.3. Experimental procedure

i) In a 250 mL polyethylene bottle, 1.00 g of Pluronic P123 triblock copolymer (Aldrich, M_n = 5800) is weighed, and a mixture of 7.5 g of H₂O and 30.0 g of 2 M HCl solution is added to this bottle. A magnetic stir bar is then added. The mixture is heated to 35 °C under stirring until Pluronic P123 is completely dissolved.

ii) 2.10 g of TEOS (>98%) is added slowly (drop by drop) to the above-prepared solution under stirring. The reactant composition is 0.017 P123 : 1 TEOS : 5.71 HCl : 193 H₂O. After being stirred for 5 min, the mixture is statically kept in an oven at 35 °C for 24 h.

iii) Then the suspension is hydrothermally treated: Heating to 90 °C in an oven and holding this temperature under static conditions for another 24 h.

iv) After the mixture is naturally cooled to room temperature, the solid product is collected by suction filtration, washed with deionized water, and dried in an oven at 60 °C overnight to get as-prepared SBA-15.

v) Characterization of the as-synthesized SBA-15: Measure powder X-ray diffraction pattern of the as-synthesized SBA-15.

vi) The as-synthesized SBA-15 is calcined in air at 540 °C for 4 h by using temperature-controlled program to remove surfactant and yield the calcined SBA-15.

vii) PXRD measurement and nitrogen adsorption-desorption analysis of the calcined SBA-15 material. Choose three samples with a nice XPD patterns to measure Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

3. References





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4. Questions

1. What are possible silicon species after hydrolysis under acidic conditions? Are they the same as under basic conditions?
2. Elucidate the roles of all the chemicals in the reaction system!
3. Describe the interaction between the nonionic triblock copolymer and silica under acidic conditions by drawing an illustration!
4. According to 2θ values that stem from powder X-ray diffraction patterns of your as-made and the calcined materials, you can calculate lattice spacings (d_{hkl}) of diffraction planes (100), (110), (200), (210) and (300).

5. Operating instructions (according to § 14 Gefahrstoffverordnung of 26.11.2010 and Material Safety Data Sheet from Sigma-Aldrich)

5.1. Used chemicals

Description	Hazard statements	Precautionary statements	Carcinogen	Hazard symbol
Tetraethyl orthosilicate	226, 319, 332, 335	261 305+351+338	-	 
P123	-	-	-	-
Hydrochloric acid	314, 335	261, 280, 305+351+338, 310	-	 

5.2. Dangers for human and environment

Substances used	Hazard statements
Tetraethyl orthosilicate	Flammable liquid and vapour. Causes serious eye irritation. Harmful if inhaled. May cause respiratory irritation.
P123	-
Hydrochloric acid	Causes severe skin burns and eye damage. May cause respiratory irritation.

5.3. Protection measures and behavior rules

Substances used	Precautionary statement(s)
Tetraethyl orthosilicate	Avoid breathing dust/ fume/ gas/ mist/ vapours/spray. IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Avoid contact with skin and eyes. Avoid inhalation of vapour or mist. Keep away from sources of ignition - No smoking. Take measures to prevent the build up of electrostatic charge. Store under nitrogen. Store in cool place. Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage. Moisture sensitive.
P123	Provide appropriate exhaust ventilation at places where dust is formed. Store in cool place. Keep container tightly closed in a dry and well-ventilated place.
Hydrochloric acid	Avoid breathing dust/ fume/ gas/ mist/ vapours/ spray. Wear protective gloves/ protective clothing/ eye protection/ face protection. IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Immediately call a POISON CENTER or doctor/ physician. Avoid contact with skin and eyes. Avoid inhalation of vapour or mist. Store in cool place. Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage.

5.4. Measures in case of danger

Substances used	Treatment
Tetraethyl orthosilicate	Use personal protective equipment. Avoid breathing vapours, mist or gas. Ensure adequate ventilation. Remove all sources of ignition. Evacuate personnel to safe areas. Beware of vapours accumulating to form explosive concentrations. Vapours can accumulate in low areas. Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Contain spillage, and then collect with an electrically protected vacuum cleaner or by wet-brushing and place in container for disposal according to local regulations. In case of fire, use water spray, alcohol-resistant foam, dry chemical or carbon dioxide to extinguish.
P123	Use personal protective equipment. Avoid dust formation. Avoid breathing vapors, mist or gas. Ensure adequate ventilation. Avoid breathing dust. Do not let product enter drains. Pick up and arrange disposal without creating dust. Sweep up and shovel. Keep in suitable, closed containers for disposal. In case of fire, use water spray, alcohol-resistant foam, dry chemical or carbon dioxide to extinguish.
Hydrochloric acid	Wear respiratory protection. Avoid breathing vapours, mist or gas. Ensure adequate ventilation. Evacuate personnel to safe areas. Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Soak up with inert absorbent material and dispose of as hazardous waste. Keep in suitable, closed containers for disposal. In case of fire, use extinguishing measures that are appropriate to local circumstances and the surrounding environment.

5.5. First aid measures

Substances used	Description
Tetraethyl orthosilicate	<p>If inhaled: If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.</p> <p>In case of skin contact: Wash off with soap and plenty of water. Consult a physician.</p> <p>In case of eye contact: Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.</p> <p>If swallowed: Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.</p>
P123	<p>If inhaled: If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.</p> <p>In case of skin contact: Wash off with soap and plenty of water. Consult a physician.</p> <p>In case of eye contact: Flush eyes with water as a precaution.</p> <p>If swallowed: Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.</p>
Hydrochloric acid	<p>If inhaled: If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.</p> <p>In case of skin contact: Take off contaminated clothing and shoes immediately. Wash off with soap and plenty of water. Take victim immediately to hospital. Consult a physician.</p> <p>In case of eye contact: Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.</p> <p>If swallowed: Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.</p>