Linköping Studies in Science and Technology
Dissertation No. 1542

Mesoporous Building Blocks – Synthesis and Characterization of Mesoporous Silica Particles and Films

Emma M. Björk

Linköping University

Nanostructured Materials
Department of Physics, Chemistry and Biology (IFM)
Linköping University

2013

On the cover, the structure of SBA-15 is illustrated. Inside the pores SEM micrographs have been inserted showing (clockwise from the top): rods, fibers, a film consisting of rods grown on a substrate, a film consisting of platelets grafted on a substrate, short rods, and platelets. In the center the sheet morphology is presented.

© Emma Björk, unless otherwise stated.

ISBN: 978-91-7519-516-2

ISSN: 0345-7524

Printed by LiU-tryck, Linköping, Sweden, 2013

Research is formalized curiosity. It is poking and prying with a purpose
Zora Neale Hurston (1903-1960)

ABSTRACT

Catalyst supports, drug delivery systems, hosts for nanoparticles, and solar cells are just some examples of the wide range of exciting applications for mesoporous silica. In order to optimize the performance of a specific application, controlling the material's morphology and pore size is crucial. For example, short and separated particles are beneficial for drug delivery systems, while for molecular sieves, the pore size is the key parameter.

In this thesis, mesoporous silica building blocks, crystallites, with hexagonally ordered cylindrical pores were synthesized, with the aim to understand how the synthesis parameters affect the particle morphology and pore size. The synthesis of the particles is performed using a sol-gel process, and in order to increase the pore size, a combination of low temperature, and additions of heptane and NH_4F was used. By variations in the amounts of reagents, as well as other synthesis conditions, the particle morphology and pore size could be altered. Separated particles were also grown on or attached to substrates to form films. Also, a material with spherical pore structure was synthesized, for the first time using this method.

It was found that a variation in the heptane concentration, in combination with a long stirring time, yields a transition between fiber and sheet morphologies. Both morphologies consist of crystallites, which for the fibers are joined end to end, while for the sheets they are attached side by side such that the pores are accessible from the sheet surface. The crystallites can be separated to a rod morphology by decreasing the stirring time and tuning the HCl concentration, and it was seen that these rods are formed within 5 min of static time, even though the pore size and unit cell parameters were evolving for another 30 min. Further studies of the effects of heptane showed that the shape and mesoscopic parameters of the rods are affected by the heptane concentration, up to a value where the micelles are fully saturated with heptane. It was also observed that the particle width increases with decreasing NH_4F concentration, independent of heptane amount, and a platelet morphology can be formed. The formation time of the particles decrease with decreasing NH_4F , and the growth mechanism for platelets was further studied. The pore sizes for various morphologies were altered by e.g. variations in the hydrothermal treatment conditions, or the method for removing the surfactants.

The separated particles can be attached to substrates, either during the particle synthesis or by post grafting prior to calcination. The film formation during the one-pot-synthesis was studied and a formation mechanism including nucleation of elongated micelles on the substrate was suggested. During the post grafting film synthesis, the medium in which the particles are dispersed, as well as functionalization of both particle and substrate are crucial for the post grafting process. The pores are easily accessible independent of the method, even though they are aligned parallel to the substrate when the one-pot-method is used, while post grafting gives a perpendicular pore orientation.

In summary, this work aims to give an understanding for the formation of the synthesized material, and how to tune the material properties by alterations in parameter space. Successful syntheses of four different particle morphologies and two new types of films were performed, and the pore size could easily be tuned by various methods.

POPULÄRVETENSKAPLIG SAMMANFATTNING

Vad har läkemedelstransport, katalys, gaslagring och nanopartiklar gemensamt förutom att de är högtintressanta forskningsområden med avsikt att förbättra och förenkla våra liv? Jo, de kan alla förbättras med hjälp av mesoporösa material. Ett mesoporöst material definieras av att det har porer i storleksordningen 2 till 50 nm, vilket är ca en tiotusendel av tjockleken på ett hårstrå. Den här typen av material kan tillverkas i flera olika kemiska sammansättningar men den vanligaste, som även används i det här arbetet, är kiseldioxid. En illustration av materialet finns i Figur 1 nedan.

Figur 1. Strukturen hos det mesoporösa materialet som studeras i avhandlingen.
Hexagonalt ordnade cylindriska porer sträcker sig genom en kristallit.

För att optimera materialet för varje tillämpning krävs det att man kan kontrollera såväl porernas som de porösa partiklarnas storlek och form. Detta är det övergripande målet för forskningen som presenteras i denna avhandling: att öka förståelsen för hur dessa partiklar bildas och vad som kontrollerar dess porstorlek och form.

I arbetet som utförts inom ramen för avhandlingen har material som ser ut som fibrer, ihåliga sfärer, korta stavar eller breda hexagoner tagits fram. Alla former består av små partiklar, *kristalliter*, som antingen sätts ihop på olika sätt eller som är fria och dess dimensioner kan regleras genom variationer i sammansättningen under tillverkningen. Kristalliterna kan också växa eller landa på en yta, ett substrat, och bilda en film med porerna antingen parallella eller vinkelräta mot substratet.

Det som skiljer det här arbetet från andra studier av samma typ av material är att syntesprocessen är förändrad på så sätt att reaktionstemperaturen är lägre och tillsatser av heptan och ammoniumfluorid har använts. Detta resulterar i ett material med ovanligt vida och korta porer jämfört med standardtillverkade

material, vilket kan vara till fördel för applikationer som läkemedelstransport och katalys. Nya metoder för att tillverka mesoporösa filmer med enkel tillgång till porerna har också utvecklats.

Kristalliternas form har studerats med svepelektronmikroskopi. Porstrukturen studerades med både transmissionselektronmikroskopi, röntgendiffraktion och kvävesorption. I ett transmissionselektronmikroskop skickar man elektroner genom ett tunt prov för att sedan landa på en fluorescerande skärm. Med denna teknik kan man se hur porerna är ordnade i materialet och vilken form de har. Röntgendiffraktion ger en bild av om porerna sitter i ett ordnat mönster genom att röntgenstrålning sprids olika beroende på om den stöter på hålrum (porerna) eller kiseldioxidväggarna. Kvävesorption är en metod som används för att studera materials tillgängliga yta och porstruktur. Genom att låta kväve kondensera vid olika tryck på ett nedkyllt prov kan man förutom ytans storlek få information om porstorlekar, porvolym och, genom att tolka isothermerna, även porernas form.

Resultaten visar att det är möjligt att få kristalliterna att fästa ihop i olika konstellationer såsom fibrer och flak. Parametern som styr detta är hur mycket heptan som tillsätts och som en ytterligare effekt ökar porstorleken med ökande oljemängd. Kristalliterna kan separeras genom att minska omrörningstiden samt att sänka pH. De separata partiklarna kan ändra längd och även bredd för att slutligen gå från avlånga stavar till platta hexagoner genom att ändra sammansättningen i den initiala lösningen i reaktionen. Genom att tillsätta ett substrat kan partiklarna växa direkt på detta och på så sätt bilda en film av separata kristalliter med öppna porer orienterade parallellt med substratet. Det har även observerats att kristalliterna formas via en väg som skiljer sig från den vanliga, samt att tillväxten beror starkt på mängden ammoniumflorid i lösningen.

PREFACE

The work presented in this thesis is a result of my doctoral studies in the Nanostructured Materials Division at Linköping University between 2008 and 2013. The work is a continuation of my Licentiate thesis, *Controlling the Pore Size and Morphology of Mesoporous Silica* (Licentiate Thesis No. 1451, Linköping Studies in Science and Technology (2010)), and the introductory chapters are to a large extent based on, and expanded from, this work. The results are presented in the appended papers.

In 2012 I changed my surname from Johansson to Björk and for all following publications I publish as E.M. Björk. The research was financially supported by the Swedish Research Council (VR).

INCLUDED PAPERS

PAPER I

Synthesis and characterization of large mesoporous silica SBA-15 sheets with ordered accessible 18 nm pores

E.M. Johansson, J.M. Córdoba, and M. Odén

Materials Letters **63** (2009) 2129-2131

PAPER II

Synthesis of hollow silica spheres SBA-16 with large-pore diameter

M.A. Ballem, E.M. Johansson, J.M. Córdoba, and M. Odén

Materials Letters **65** (2011) 1066-1068

PAPER III

Effect of heptane addition on pore size and particle morphology of mesoporous silica SBA-15

E.M. Johansson, J.M. Córdoba, and M. Odén

Microporous and Mesoporous Materials **133** (2010) 66-74

PAPER IV

Rapid synthesis of SBA-15 rods with variable lengths, widths and tuneable 11-17 nm sized pores

E.M. Johansson, M.A. Ballem, J. M. Córdoba, and M. Odén

Langmuir **27** (2011) 4994-4999

PAPER V

Tuning the shape of mesoporous silica particles by alterations in parameter space - from rods to platelets

E.M. Björk, F. Söderlind, and M. Odén

Accepted for publication in Langmuir (2013)

PAPER VI

Single-pot-synthesis of ordered mesoporous silica films with unique controllable morphology

E.M. Björk, F. Söderlind, and M. Odén

Journal of Colloid and Interface Science **413** (2014) 1-7

PAPER VII

Grafting mesoporous silica particles to substrates – a method for synthesizing mesoporous films with cylindrical pores perpendicular to the substrate

E.M. Björk, F. Söderlind, and M. Odén

In manuscript

MY CONTRIBUTION TO THE PAPERS

PAPER I

I planned the project and performed all material synthesis and characterization, except the TEM where I participated. I wrote the paper.

PAPER II

I took part in the planning of the project and discussed the results. I contributed to the writing of the paper.

PAPER III

I planned the project and performed all material synthesis and characterization, except the TEM where I participated. I wrote the paper.

PAPER IV

I planned the project and performed all material synthesis and characterization. I wrote the paper.

PAPER V

I planned the project and performed all material synthesis and characterization. I wrote the paper.

PAPER VI

I planned the project and performed all material synthesis and characterization, except for making the cross section TEM sample using FIB. I wrote the paper.

PAPER VII

I planned the project and performed all material synthesis and characterization except for the FT-IR measurements. I wrote the paper.

PAPERS NOT INCLUDED IN THE THESIS

PAPER VIII

Copper nanoparticles synthesized via electroless copper deposition in sheet-like mesoporous type SBA-15

H.-T. Tsai, J.M. Córdoba, E.M. Johansson, M.A. Ballem, and M. Odén

Journal of Nanoscience and Nanotechnology **11** (2010) 3493-3498

PAPER IX

Annealing of thermally sprayed Ti₂AlC coatings

J. Frodelius, E.M. Johansson, J.M. Córdoba, M. Odén, P. Eklund, and L. Hultman

International Journal of Applied Ceramic Technology **8** (2011) 74-84

PAPER X

Growth of single crystalline dendritic Li₂SiO₃ arrays from LiNO₃ and mesoporous SiO₂

J.M. Córdoba, M.A. Ballem, E.M. Johansson, and M. Odén

Journal of Solid State Chemistry **184** (2011) 1735-1739

PAPER XI

Low temperature Nanocasting of hematite nanoparticles using mesoporous silica molds

M.A. Ballem, X. Zhang, E.M. Johansson, J.M. Córdoba, and M. Odén

Powder Technology **217** (2012) 269-273

PAPER XII

Immobilization of lipase from *Mucor miehei* and *Rhizopus oryzae* into mesoporous silica – The effect of varied particle size and morphology

H. Gustafsson, E.M. Johansson, A. Barrabino, M. Odén, and K. Holmberg

Colloids and Surfaces B: Biointerfaces **100** (2012) 22-30

PAPER XIII

Shape engineering vs organic modification of inorganic nanoparticles as a tool for enhancing cellular internalization

D. Sen Karaman, D. Desai, R. Senthilkumar, E.M. Johansson, N. Råttts, M. Odén, J.E. Eriksson, C. Sahlgren, D.M. Toivola, and J.M. Rosenholm

Nanoscale Research Letters 7 (2012) 358

ACKNOWLEDGEMENTS

I would like to thank all people that have been involved in this work. Without the help and support from you, this thesis would never have been written.

- I am sincerely grateful to my supervisor *Professor Magnus Odén*. Thank you for giving me the opportunity to do this work and explore the nature of mesoporous materials. Your vast guidance, encourage, support, and patience have made me a better researcher. Thank you!
- I will also thank my co-suprvisors *Dr. Fredrik Söderlind* and *Dr. José Córdoba* for support and useful discussions. Thank you for teaching me the chemistry and guiding me in the lab.
- My collaborators all over the world, *Dr. Jessica Rosenholm*, Åbo Akademi, *Dr. Hanna Gustafsson*, Chalmers University of Technology, and *Dr. Duangamol Nuntasri*, Chulalongkorn University, and all co-authors from their departments are strongly acknowledged. Thank you for fruitful projects, and inspiring discussions. You have taught me many things, and I truly appreciate your experience and the broadened view of materials research that you have given me.
- Many thanks to my colleagues and co-workers in the lab, *Mohamed, Jeffery*, and *Aylin*. I have enjoyed working with you, and I wish to thank you for all your input, ideas, discussions, support, and extra hands when needed.
- I am most happy to have spent these years in the *Nanostructured Materials group*. You have been great colleagues and you make me look forward to go to work every day.
- Also, a big thank you to *Friends and co-workers at IFM*, both the ones that have left and those that are still here (you know who you are). I thank you for all help, both regarding work, and in life itself. Thank you for great times and coffee breaks, movie nights and barbeques.
- I thank my *Family* for all their love and support. For that you always take your time to listen, encourage, but also to question.
- Finally, *Jonas* and *Elsa*, I love you! Thank you for always being by my side and giving my life I deeper meaning.

ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CMC	Critical Micelle Concentration
CMT	Critical Micelle Temperature
CP	Cloud Point
CPP	Critical Packing Parameter
CTAB	Hexadecyltrimethylammonium bromide
EASA	Electro-Assisted Self-Assembly
EISA	Evaporation-Induced Self-Assembly
FFT	Fast Fourier Transforms
FIB	Focused Ion Beam
FT-IR	Fourier Transformed-Infrared Spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
MCF	Mesocellular Foam
MCM- <i>n</i>	Mobil Composition of Matter-number <i>n</i>
KJS	Kruk-Jaroniec-Sayari
OTS	Octadecyltrichlorosilane
<i>P</i>	Equilibrium pressure
<i>P/P</i> ₀	Relative pressure
<i>P</i> ₀	Saturation pressure
PEO	Poly(ethylene oxide)
PPO	Poly(propylene oxide)
SBA- <i>n</i>	Santa Barbara Amorphous-number <i>n</i>
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TEOS	Tetraethyl ortosilicate
TGA	Thermogravimetric analysis
TIPB	1,3,5-triisopropylbenzene
TMB	Trimethylbenzene
TMOS	Tetramethyl orthosilicate
XRD	X-Ray Diffraction

TABLE OF CONTENTS

1	INTRODUCTION	1
1.1	Objective	1
1.2	Outline.....	1
2	POROUS MATERIALS	3
2.1	Definitions and classifications	3
2.2	General synthesis methods for nanoporous materials.....	5
2.3	Mesoporous silica	5
2.4	SBA-15.....	6
2.5	SBA-16.....	7
2.6	Applications of SBA-15	7
3	COLLOID AND SOL-GEL CHEMISTRY	11
3.1	Surfactants	11
3.2	Non-ionic triblock copolymers, Pluronics	13
3.3	Micelle formation with Pluronics.....	13
3.4	Silica precursor	17
4	SBA-15 SYNTHESIS AND FORMATION	19
4.1	The synthesis process	19
4.2	Formation	19
4.3	Hydrothermal treatment	22
4.4	Removal of surfactants	23
5	TUNING THE PROPERTIES OF SBA-15	27
5.1	Morphology	27
5.2	Pore size	31
5.3	Wall thickness and microporosity	35
6	MESOPOROUS FILMS	39
6.1	Evaporation-Induced Self-Assembly.....	39
6.2	Electro-Assisted Self-Assembly	41
6.3	Grafting particles on substrates	42

6.4 Freestanding films at interfaces	42
7 ANALYSIS TECHNIQUES	43
7.1 Physisorption	43
7.2 X-ray diffractometry	50
7.3 Electron microscopy	52
7.4 Thermogravimetric analysis	54
7.5 Fourier transformed infrared spectroscopy	54
8 SUMMARY OF RESULTS	57
8.1 Paper I	57
8.2 Paper II	57
8.3 Paper III	58
8.4 Paper IV	59
8.5 Paper V	60
8.6 Paper VI	61
8.7 Paper VII	62
9 FUTURE WORK	65
9.1 Future particle syntheses	65
9.2 Mesoporous films	65
9.3 Applications	66
10 BIBLIOGRAPHY	67

PAPERS I-VII

I INTRODUCTION

An illustrative way to describe the essence of working with porous materials is to use the old Chinese proverb by Lao Tzu:

“Mold clay to form a bowl. It is the empty space which makes the bowl useful.”

Even though the proverb is old, the discovery of how to synthesize mesoporous materials was not made until the early 1990's. Due to the empty space, the pores, this type of materials possesses many attractive properties, such as large specific surface area and narrow pore size distribution. This makes the materials useful for many important applications, such as hosts for catalysts, drug delivery systems, solar cells, templates for nanoparticle growth, etc. In order to optimize the material for each area of usage, control of the material properties, e.g. pore size and morphology, is crucial.

1.1 Objective

The main objective with this thesis is to understand the parameters determining the morphology and pore size for mesoporous silica of SBA-15 type, with hexagonally ordered cylindrical pores, and to attach the material to a substrate in order to make a mesoporous film. The synthesis method used here differs from the standard manufacturing route, since it is a low temperature method using alkanes and salt additions. It yields a material with unusually short and wide pores compared to the standard route. The material can be synthesized in different morphologies, which all consist of nanosized crystallites. One of the aims with this work has been to control the attachment of these crystallites to each other, and also to separate them completely by alterations in the parameter space. Furthermore, the separated crystallites have been grown onto, or grafted, on various substrates in order to form mesoporous films with easy accessible cylindrical pores. The synthesis method has also been adapted to other systems, such as SBA-16 and SBA-15 synthesized with a different surfactant.

1.2 Outline

A brief historical overview to mesoporous materials in general, and mesoporous silica in particular, is given in Chapter 2, which also contains details of the structures of SBA-15 and SBA-16. The chemistry used to synthesize the materials is briefly explained in Chapter 3, and Chapter 4 presents the synthesis steps and

formation of the material. Methods to control the material properties are given in Chapter 5. Chapter 6 is devoted to mesoporous films, and how they commonly are synthesized. All characterization techniques used in this work are presented in Chapter 7. Finally, Chapter 8 contains a summary of the results in the appended papers, and Chapter 9 gives an outlook for coming studies.

2 POROUS MATERIALS

Here, the concept of porous materials, and the definition of the materials studied in this thesis, are presented.

2.1 Definitions and classifications

Pores can have many different shapes, which is illustrated in Figure 1. In a solid, the definition of a pore is simply cavities, channels or interstices, which are deeper than they are wide [1].

Figure 1. Definitions of pores in a solid material: closed pore (a), ink-bottle shape (b), cylindrical shape (c), funnel shape (d). (e) is defined as surface roughness. Modified from ref. [1].

Another important issue is whether the pores are open or closed. Examples of closed pores are shown in Figure 1 (a), while (b)-(d) are considered to be open, even though some of them are open only in one end. Closed porosity influences materials properties such as density, thermal conductivity, and mechanical strength [1], while materials with high open porosity have a large available surface area compared to materials with no or closed porosity, which is illustrated in Figure 2 .

Pores are also classified by their pore size, and it is common to use the IUPAC classification [2] of materials, stating that

micropores have a diameter < 2 nm,
mesopores have a diameter between 2 and 50 nm, and
macropores have a diameter > 50 nm.

Figure 2. Available surface in (a) non-porous solids and materials with (b) closed and (c) open porosity.

Another size classification is nanoporous materials in which the pores are 1-100 nm large [3]. Hence, all mesoporous materials can also be considered as nanoporous. The mesopores can have different shapes, such as spherical or cylindrical, and be arranged in varying structures, see Figure 3. Some structures have pores larger than 50 nm in one dimension, see e.g. the two first structures in Figure 3. In these cases, the width of the pore is in the meso-range, although the pore length can be several micrometers. Such materials are still considered to be mesoporous.

Figure 3. Different pore structures of mesoporous materials.

Mesoporous materials can have a wide range of compositions but consist mainly of oxides such as SiO_2 , TiO_2 , ZnO_2 , Fe_2O_3 or combinations of metal oxides, but also mesoporous carbons have been synthesized [4-8]. The most common approach is to use a micellar solution and grow oxide walls around the micelles. Both organic metal precursors such as alkoxides [9-11] as well as inorganic salts,

e.g. metal chloride salts [5] can be used. Alternatively, a mesoporous template is used to grow another type of mesoporous material inside it. This is often implemented for synthesizing mesoporous carbon [8,12,13].

2.2 General synthesis methods for nanoporous materials

For syntheses of materials at the nanoscale, it is common to use one of two possible paths: top-down or bottom-up. In the top-down approach one starts from a larger unit, and shape this unit into a nanostructure, for example by cutting or milling. The top-down approach is used for manufacturing e.g. microchips and micro-patterning. The bottom-up approach is based on properties of single molecules that self-assemble into desired structures. This approach is common for synthesizing mesoporous materials. These are synthesized by self-assembly of surfactants to form micelles and condensation of metal species onto these micelles. Variations in the final material such as different pore sizes and morphologies can be obtained by altering the properties of the original molecule.

2.3 Mesoporous silica

In 1992 a new family of ordered mesoporous materials was reported [4,9] which became the starting point of a new research field. These materials were named MCM-X (Mobil Crystalline of Materials) and were synthesized by Mobile Corporation laboratories. Mesoporous silica with different pore structures were synthesized, e.g. MCM-41 with hexagonally ordered cylindrical pores and MCM-48 with a cubic pore structure. These materials are synthesized with cationic surfactants under basic conditions.

This was though not the first attempt of synthesizing mesoporous silica. A patent from 1971 covers the synthesis of low-density silica using cationic surfactants [14]. In this patent there is no report concerning porosity, only the low bulk density was of importance. Later this material has been synthesized, characterized and compared to MCM-41 [15]. It is clear that this material is a predecessor to the mesoporous silica that is synthesized today, even though the importance of this type of material was not recognized at that time.

The MCM materials were followed by other families, such as MSU [16], KIT [17], FDU [18] and AMS [19], where the materials are synthesized with variations in e.g. synthesis conditions, silica precursors, and surfactants.

In 1998 came the first report by Zhao *et al.* [10,20] of a new type of mesoporous

silica with unusually large and ordered pores. These materials are named SBA- X (Santa Barbara Amorphous) where X is a number corresponding to a specific pore structure and surfactant. E.g. SBA-15 has hexagonally ordered cylindrical pores synthesized with P123 as surfactant, while SBA-16 has spherical pores arranged in a body centered cubic (bcc) structure and is synthesized with F127. The used surfactants are described in Section 3.2. SBA-15 is the most extensively studied mesoporous silica and also the main subject of attention in this thesis.

2.4 SBA-15

SBA-15 is a mesoporous silica with cylindrical pores arranged in a hexagonal structure, which is illustrated in Figure 4. For this material, the pore size refers to the width of the cylindrical pores which can be tuned between 5 and 26 nm [10,20-22] even though pore sizes above 12 nm are rare. The length of the pores varies from ~200 nm [23,24] to several microns [25,26].

Surrounding each mesopore is a microporous network called the corona [27,28]. This network interconnects the mesopores with each other and is responsible for the high surface area of SBA-15. The microporous network was first seen by the use of platinum replicas [28], where nanorods from filled mesopores were interconnected by the network. This keeps the nanorods in the hexagonal arrangement even after removal of the silica, see Figure 4.

Figure 4. The structure of mesoporous silica SBA-15 (to the left) and its replica in form of rods (top right) and straws (down right).

The corona is supposed to originate mainly from trapped hydrophilic chains of the surfactants [29-31]. An additional explanation for the corona is stress-induced defects, where the micropore fraction increases with the ratio between effective pore wall thickness and average pore diameter [32]. The micropores are present up to 1173 K, but above this temperature the network disappears and the

material has similar structure to MCM-41 [28].

The corona plays a crucial role when using SBA-15 as a template for other materials. Replicas can be synthesized in two variants, one rod-like and one straw-like, see Figure 4. Since also the micropores will be filled with the replica material, the mesopore replicas will be fixed in the hexagonal structure and the particle morphology will be retained. If instead MCM-41 is used as template, the end result is more similar to spillikins.

2.5 SBA-16

SBA-16 is another member of the SBA family [10] with spherical pores arranged in a bcc structure. A replica of SBA-16 is illustrated in Figure 5. The pores are interconnected by narrow necks, and the walls include micropores in the same manner as SBA-15.

Figure 5. Replica of the pore structure of SBA-16.

In this thesis SBA-16 only appears in **Paper II**. Its synthesis procedure is similar to the one of SBA-15, and the material properties can be tuned in similar ways. Hence, the rest of the introduction chapters will focus on the synthesis of SBA-15, which is the main topic of this work.

2.6 Applications of SBA-15

There are many applications of SBA-15. A search in the article data base Science DirectTM with the criteria “SBA-15 application” results in more than 10 000 hits. The material’s narrow pore size distribution makes it suitable for molecular sieves, as well as templates. Also, the specific surface area is commonly 500-1000 m²/g, which is approximately the area of a handball court in the volume of a Schnappsglass. This property makes the material an excellent substrate for catalysts and mesoreactors where chemical reactions take place in the pores. Some of the implemented applications are given below.

2.6.1 Templates

The narrow pore size distribution of mesoporous silica also makes it suitable as templates for other materials, and as a constrainer when growing nanoparticles inside the pores.

As mentioned earlier platinum replicas of SBA-15 have been synthesized, but the most common material for SBA-15 replicas is carbon. These replicas can be formed either as rod-like or straw-like [7,28,33,34], see Figure 4. The replicas can then be used as new templates for other mesoporous materials [35], as supports for e.g. platinum particles [12], as storage units for e.g. hydrogen or methane [36,37], or electrochemical sensing [38]. Replicas of SBA-15 can also be synthesized as metal oxides such as CeO_2 , Cr_3O_4 , MnO_2 or WO_3 , see e.g. ref. [35] and references therein.

2.6.2 Hosts for catalysts

The silica framework itself is not a functional catalyst, but by proper functionalization of the silica walls, catalytic reactions can be realized at the surface. The silica can be used in two ways: either as a template for catalysts with wires or nanoparticles [39-41], or by adding functional groups to the silica walls [41].

Examples of the usage of SBA-15 as a host for catalysts are: incorporation of Ti for hydrogen storage and photovoltaic applications [42-44], addition of FeW for hydrotreating heavy gas oil, and storage of methanol [45].

The presence of silanol groups in the silica walls makes it possible to tune and tailor the properties of the material. These functional groups can be exchanged with e.g. amino groups [46-50] for drug delivery, Co(II) cation, or polymerization of olefins, or sulfonic groups [51-53].

2.6.3 Drug delivery

Mesoporous silica has been shown to be an excellent carrier for drugs [54-64]. The large pore size makes it possible to put large drug molecules within the pores, and then the particle is externally functionalized with a responsive coating. The drugs can be delivered both orally [57], injected into the blood stream [65], or in bone tissue engineering [58].

Adding drugs to a carrier have many advantages; e.g. drugs with poor solubility can be put into the pores and hence be delivered [57], and by having the

responsive coating, the drugs are released e.g. within a cancer cell without damaging the surrounding healthy cells. Parameters such as pore size, surface area, surface chemistry, and particle morphology have been shown to impact the drug delivery, see for example [63,66,67]. Hence, the detailed design of the particles is crucial for their efficiency.

It should be noted that one concern about using mesoporous materials as a drug carrier is the safety of using these materials in the body [55-57], for which studies are in progress.

2.6.4 Energy applications

Green energy has become a hot topic in both research and the society, and mesoporous silica has found its place also here. SBA-15 can e.g. be used as a template for anode or cathode materials for batteries [68-70]. Furthermore, it can also be used in solar cell applications, both as a template for incorporation of titania or cobalt nanoparticles [42,44,71-73], and as a scattering layer for improving the cell efficiency [74].

3 COLLOID AND SOL-GEL CHEMISTRY

The synthesis method of SBA-15 and SBA-16 are so called sol-gel synthesis. The solution (sol) is a colloidal system where surfactants form dispersed micelles in an aqueous solution. When the silica precursor is added to the sol it hydrolyses and a silica network is formed in which the liquid is enclosed, i.e. a gel. The transition between sol and gel is gradual and the sol becomes a gel when it can support a stress elastically. Here, the basic chemistry used for the synthesis of SBA-15 and SBA-16 is presented.

3.1 Surfactants

Surfactants (surface active agents) are amphiphilic molecules, i.e. they are composed of a hydrophilic and a lipophilic part, see Figure 6. Surfactants are classified by their head group: anionic, cationic, zwitterionic and non-ionic depending on the group's charge, and the lipophilic part is often a hydrocarbon chain. Due to their amphiphilicity, the surfactants form micelles in oil or aqueous solutions to lower the free energy in the system. If the solvent has two immiscible phases the surfactants are located in the oil/water interface with the hydrophilic part towards the water and the lipophilic part in the oil.

Figure 6. Schematic picture of a surfactant.

3.1.1 Micelle formation and structures

When the concentration of surfactants in an aqueous solution is low, the surfactants are located as separate molecules in the air/water interface. This reduces the surface tension since it is larger for water than for the hydrocarbons. Increasing the surfactant concentration in the solution further reduces the surface energy until a critical value. At this point, the critical micelle concentration (CMC) is reached and aggregates of surfactants (micelles) are formed. The CMC is determined by two competing factors; bringing the nonpolar chains out of the water phase into the oil phase (hydrophobic effect)

and repulsion between the polar head groups which opposes the formation of micelles [75]. The CMC and shape of the micelles are determined by the nature of the surfactant and conditions in the solution such as temperature and salt additions.

Figure 7. Critical packing parameters of surfactant molecules and preferred aggregate structures for geometrical packing reasons [76]. Reprinted with permission from John Wiley & Sons Ltd.

The aggregate structure of the amphiphilic molecules is determined by the critical packing parameter (CPP)

$$CPP = \frac{v}{l \cdot a} \quad (1)$$

where v is the volume of the hydrophobic chain [nm^3], a is the area of the hydrophilic part [nm^2] and l [nm] the length of the hydrophobic chain. The volume v and length l can be expressed by

$$v = 0.027(n_C + n_{\text{Me}}), \quad (2)$$

$$l = 0.15 + 0.27n_C, \quad (3)$$

where n_C is the number of carbon atoms and n_{Me} the number of methyl groups. The relation between CPP and aggregate structure is illustrated in Figure 7. The cylindrical micelles necessary for growing SBA-15 has a $1/3 < CPP < 1/2$.

3.2 Non-ionic triblock copolymers, Pluronics

When mesoporous silica is synthesised, several types of surfactants can be used e.g. cationic CTAB [4,9], non-ionic PEO surfactants [16], or Pluronics [10]. In this work the non-ionic amphiphilic triblock copolymers, P123 (Paper I, III-VII) (Figure 8), and F127 (Paper II) have been used.

Figure 8. Chemical formula and properties of the surfactant P123.

There are several non-ionic triblock copolymers under the trademark Pluronics. These polymers were patented in 1973 and are also called Poloxamers [77]. They all consist of hydrophilic polyethylene oxide chains (PEO) and hydrophobic polypropylene oxide chains (PPO) with varying molecular weights and PEO/PPO ratios ($\text{EO}_x\text{PO}_y\text{EO}_x$).

3.3 Micelle formation with Pluronics

As mentioned earlier, the concentration of surfactants and temperature of the solvent are crucial for the formation of micelles. These two parameters vary for

the PEO-PPO-PEO surfactants with respect to the structure and weight of the polymers. For example, both the CMC and critical micelle temperature (CMT) decrease with increasing PPO size for Pluronics with PEO segments of the same size. The size effect of the PEO chain is less pronounced compared the PPO size and the micelle formation is driven by the PPO chain [78-80]. The micelles consist of a hydrophobic PPO core surrounded by hydrophilic PEO chains that form a corona around the core.

3.3.1 Sphere-to-rod transition

In order to form the cylindrical pores in SBA-15, the micelles must change their CPP in order to undergo a transition from spherical to cylindrical shape. During the synthesis, the temperature and surfactant concentrations are kept constant. Hence, other parameters during the synthesis are responsible for this change in CPP leading to the sphere-to-rod transition.

During the synthesis, the sphere-to-rod transition occurs upon addition of the silica precursor, TEOS, which will be thoroughly discussed in Section 4.2. The transition can also occur upon additions of salt [81], or increasing the temperature [82] since these decrease the hydrophilic area of the surfactants due to dehydration of the PEO chains.

3.3.2 Temperature dependence

The properties of the PEO and PPO blocks are highly temperature dependent since the hydration of methyl groups in both blocks depends on the temperature [80,83]. During the micelle formation process there are three temperature regions of importance: the unimer region (where the surfactants are not aggregated), the transition region, and the micelle region [84,85].

In the unimer region, the methyl groups of the PPO blocks become hydrated and can form hydrogen bonds with the water. When the temperature is increased the methyl groups rotate and the hydrogen bonds are broken [83,86]. At CMT and through out the transition region micelles and unimers coexist. In this region the interaction between PPO and water is reduced and the PPO chains instead interact with each other. Thereby the micelles with nonpolar, hydrophobic cores are formed. This is happening gradually for a small temperature interval of $-10\text{ }^{\circ}\text{C}$ [83,86]. Finally the micelle region is reached and all surfactants are aggregated into micelles. Above the CMT the spherical micelles increase in size with increasing temperature until the micellar core reaches the radius of a completely stretched PPO chain. At this point the structure of the micelles changes from

spheres to cylinders [85].

Figure 9. The relation between micelle concentration and solution temperature. Data from ref. [78].

When further increasing the temperature, water becomes a worse solvent for the PPO and PEO chains due to the increasing number of polar states. Above a critical temperature, the cloud point (CP), the surfactants can no longer be dissolved to form micelles and instead they precipitate from the solution [87,88].

Knowledge of how a specific surfactant behaves at different temperatures and concentration is crucial during the synthesis of mesoporous materials. As shown in Figure 9, the CMT depends on the surfactant concentration, but it can be changed for a given surfactant concentration by adding salts, which will be discussed further in Section 3.3.3. Figure 10 shows the phase diagram for P123, i.e. how the micelle structure can be tuned by varying the synthesis temperature or surfactant concentration.

Figure 10. Phase diagram of P123 in water. After ref. [80].

3.3.3 Salt additions

The addition of salt to the synthesis of SBA-15 makes it possible to decrease the synthesis temperature from 35-55 °C to as low as 10 °C [21,89-93], since the properties of Pluronics are strongly affected by salt additions. By adding salts, CMT, the sphere-to-rod transition, and CP can be shifted, and the shifts are proportional to the concentration of salt [94]. It has been shown that $CMT_{\text{salt}} - CMT_{\text{no salt}} = CP_{\text{no salt}} - CP_{\text{salt}}$ when salt are added to a solution except for I^- which instead increases CP and decreases CMT. This is very useful, since sometimes only one of these two parameters can be studied [95].

The Hofmeister series

Most, but not all, salts decrease the solubility of organic polymers (the salting out phenomena). Some salts act as structure makers for the water and increases the self-hydration of water through hydrogen-bonding. Other salts act as structure breakers and decrease the number of hydrogen-bonded OH groups [96]. Anions give a stronger effect on solubility of polymers [79,95], and their salting out strength at a given molar concentration follows the Hofmeister series: $SO_4^{2-} \approx HPO_4^{2-} > F^- > Cl^- > Br^- > I^- > SCN^-$. Ions preceding Cl^- in the series are polar water-structure makers and those after Cl^- water-structure breakers. Cl^- has little effect on water structure [97]. Hence, F^- , Cl^- , Br^- , Na^+ , K^+ and Li^+ decreases the CMT, sphere-to-rod transition and CP while SCN^- increases the solubility of PI23 that gives higher temperatures for the transitions.

The effect of cations on the other hand is less pronounced and does not follow the Hofmeister series. Instead the effect depends on the counter ion [81]. This could be due to that the size differences between cations are smaller compared to anions [98]. For Cl^- as anion, the effectiveness of cations follow $Cs^+ \approx K^+ > Li^+$ [81].

The salting-out effect

It is commonly said that salts increase the solvophobicity of PEO and PPO chains and therefore induce micelle formations [88], and it is known that PEO chains form aggregates in water solutions with salt additions. It has been suggested that this aggregation is driven by the structuring of water [99], in which the PEO chains are surrounded by a zone where water has an increased structure [100]. When an ion approaches a PEO segment the amount of water between these two decreases. PEO is far less polarizable than water and the removal of the polarized water induces a repulsive force between the ion and PEO chains. On the other hand, the removal of water leads to an attractive force between the PEO chains. The total force from these two contributions depends on the ion. The larger the ion, the more attractive the force will become, since for larger ions, a larger

amount of structured water will be expelled [95,98].

Adding salts with salting-out properties, e.g. KCl, affect the aggregation number of the micelles, i.e. a concomitant increase in the micellar radius [101]. It is also possible to control the ionic surrounding by altering the acidic source, due to the anion coming from the acid. The effect of this also follows the Hofmeister series [102,103].

3.4 Silica precursor

Several types of silica precursors can be used in the synthesis of mesoporous silica. The most common ones are alkoxides, especially tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS), see Figure 11, but other alkoxides with longer alkyl chains can be used [104,105]. An alternative, cheaper, silica precursor that can be used is sodium silicate [106,107], which also can be combined with alkoxides [108]. In this work, only TEOS has been used as the silica source, except for one of the control syntheses in **Paper V** where TMOS was used. Hence, only alkoxides will be discussed in the case of silica precursor in the following sections.

Figure 11. Chemical formula of the silica precursor TEOS.

3.4.1 Hydrolysis and condensation

In aqueous solutions the alkoxides hydrolyses (i) and polymerises to form a silica network (ii) and (iii). Both steps can be controlled by varying the pH and by adding salts to the aqueous solutions, see reviews [109-111] and references therein.

- (i) Hydrolysis $\equiv \text{Si} - \text{OR} + \text{H}_2\text{O} \leftrightarrow \equiv \text{Si} - \text{OH} + \text{ROH}$
- (ii) Alcohol condensation $\equiv \text{Si} - \text{OR} + \text{HO} - \text{Si} \equiv \leftrightarrow \equiv \text{Si} - \text{O} - \text{Si} \equiv + \text{ROH}$
- (iii) Water condensation $\equiv \text{Si} - \text{OH} + \text{HO} - \text{Si} \equiv \leftrightarrow \equiv \text{Si} - \text{O} - \text{Si} \equiv + \text{H}_2\text{O}$

In general, short alkyl chains hydrolyse faster than long chains, e.g. TMOS has a faster hydrolysis rate than TEOS [112]. The hydrolysis of TEOS needs an acidic or

basic catalyst to occur, and the hydrolysis rate is in general directly proportional to the concentration of acid or base, except for when only small amounts of acids are present [113,114]. Hydrolysis and gelatation occur simultaneously. H_3O^+ increases the rate of hydrolysis while OH^- increases the gelatation rate. Hence, at a pH suitable for synthesis of SBA-15 ($\text{pH} \leq 2$) the hydrolysis is fast but the polymerization is slow.

Figure 12. Schematic representation of the pH dependences of the hydrolysis, condensation, and depolymerisation rates of TEOS. After ref.[109].

By tuning the hydrolysis and condensation rates, the properties of the silica gel can be controlled. When a fast hydrolysis rate in combination with slow condensation is used, a larger and more dense gel is formed, in comparison to when the hydrolysis is slow and the condensation rapid [115].

3.4.2 The effect of fluoride ions

It is well known that fluoride ions act as a nucleophilic catalyst and accelerates the hydrolysis and condensation rates of TEOS [116-120]. The increased hydrolysis comes from a nucleophilic attack, where the fluoride ion assists with the removal of an alcohol chain. It has been observed that for $\text{pH} < 2$, the polymerization rate of TEOS is proportional to the concentration of H^+ and F^- [120]. This has been explained in several ways, such as: the increased co-ordination of silicon from four to five or six [120], localized attraction between silanol species due to that the F^- displaces OH^- , or that the F^- substitution of OH^- decreases the electron density and hence makes Si more susceptible to the nucleophilic attack [109].

4 SBA-15 SYNTHESIS AND FORMATION

In this chapter the synthesis and formation of SBA-15 is presented. A detailed understanding of the formation during the synthesis is crucial for the possibility of manipulating the material's shape and other properties.

4.1 The synthesis process

The synthesis of SBA-15 is often straight forward and uncomplicated. During a standard synthesis the surfactant, P123, is dissolved in hydrochloric acid and then the silica precursor, e.g. TEOS, is added. The solution is stirred for 20 h at 35-40 °C, and at this step the material's pore structure and morphology is determined. This is followed by the hydrothermal treatment where the material is heated to 80-130 °C for 24-72 h in order to finalize the condensation of TEOS and complete the pore formation. Finally, the product is collected by filtration and calcinated at 550 °C to remove the surfactants. There are several ways to control the pore size, microporosity and particle morphology to obtain the optimal product, e.g. addition of salt, swelling agents and/or temperature variations which will be discussed in Chapter 5.

4.2 Formation

Most of the material formation occurs during the reaction step. The formation mechanism has been discussed in several papers, and at the moment two main theories have been developed. Initially, the formation of SBA-15 was assumed to be similar to the formation of MCM-41, suggested by Beck et al. to be a liquid crystal mechanism [9]. This route is illustrated in Figure 13. The micelles start as spherical and when the silica precursor is added they become elongated and arrange themselves in a hexagonal pattern, while the silica condenses on them to form the silica walls. Finally, the surfactants are removed, in order to obtain the porous structure.

Several studies of the formation of SBA-15 have been performed with e.g. SAXS, SANS, NMR, and cryo-TEM [30,102,103,121-128], or by theoretical modelling [129]. The many different techniques used give results that can be difficult to interpret, and sometimes they even contradict each other. In the following section, I will give my interpretations of the combined results.

Figure 13. Illustration of the formation mechanism suggested by Beck et al. [7].

4.2.1 From spheres to hexagonal aggregates

The formation of SBA-15 can be divided into three parts: the initial solution with spherical micelles of P123 and hydrolysis of the alkoxide, the sphere-to-rod transition, and condensation in the hexagonal mesophase.

The reaction starts with the addition of the silica precursor to the micellar solution. At the common synthesis temperatures (20-65 °C), the micelles are always spherical, even at strongly acidic conditions, and SANS experiments have shown that during the hydrolysis of the alkoxide, the spherical micelles remain unchanged [102,124,125]. When the TEOS is added, an emulsion of hydrophobic TEOS droplets is formed. This emulsion is though only present until the TEOS is completely hydrolysed [124]. The hydrolysis of TEOS occurs at the water/TEOS interface, and the condensation process starts as soon as hydrolysed species are available [102]. However, an EPR study suggests that the silica precursor penetrates into the core of the micelles [121]. This seems though unlikely, considering that no expansion of the micelles was observed.

As soon as the hydrolysed silica oligomers start to interact with the corona, the micelles undergo a sphere-to-rod transition, forming short, cylindrical micelles. These micelles continue to elongate and form long threadlike micelles. During this step, spherical and cylindrical micelles are coexisting which is confirmed by cryo-TEM [123]. This coexistence indicates the presence of two phases: one more concentrated including TLMs, and one more dilute where the spherical micelles exist. Upon further condensation of the silicate oligomers, the TLMs become straighter and less flexible, and finally the hexagonal structure is formed [123]. Studies using SAXS and SANS further confirm the presence of cylindrical micelles prior to aggregation of flocs [122,124].

The elongation of micelles is due to the decrease of the curvature of the corona, and swelling of the hydrophobic core. The silicate oligomers interact with the

PEO chains in the core-corona interface, and decrease the effective volume of the PEO chains [103,123,127,128]. The main interaction between the silicate oligomers and the PEO is the formation of hydrogen bonds between them [128]. The reaction process travels from the core-corona region and outwards with time [121]. Also, ethanol is a decay product of TEOS, and within the relevant temperature range PPO is soluble in ethanol and not in water. When the ethanol goes into the hydrophobic core of the micelles, the core volume expands and the CPP increases according to Eq. (1) [130].

The diameter of the PPO core is equal to the pore size of SBA-15, but increasing the temperature to 80-100 °C or calcination leads to further condensation and densification of the structure, and hence a decrease in unit cell parameter and increase of pore size occur [125]. During the formation of cylindrical micelles, the radius of the PPO core decreases initially [127]. This is most probably due to the interaction of silica and PEO in the core/corona region where the silica can partly penetrate into the core and remove water, causing a contraction of the core.

During the formation of the hexagonal structure, the voids between the cylindrical micelles decrease, and the solvent in the voids is replaced with silicate species [122].

Theoretical modelling of the formation of mesoporous materials has shown that the silica preferably adsorbs onto low curvature sections of the micelles. During the elongation of the micelles the relative surface energy of the spherical caps at the micelle ends increases and therefore no silica attach there, leaving the pore ends open in the calcinated material [83].

4.2.2 Kinetics

The formation rate of the material depends on several parameters, such as the choice of silica precursor [105], ions from salts or acids [102,105,131], and temperature [132]. By altering these parameters, a deeper understanding of the formation mechanism for SBA-15 can be found.

The understanding of the kinetics is of importance, not only in the tailoring of the material, but also in order to have as efficient syntheses as possible. For example, in the original synthesis of SBA-15, 20 h of reaction time is used, but it has been shown that this time can be decreased to 2 h, [107], and even further down to 0.5 h [133]. This has been studied in **Paper III-V**.

4.3 Hydrothermal treatment

When the formation of SBA-15 is finished, the temperature is increased and the hydrothermal treatment begins. As mentioned in Section 3.3.2, the properties of P123 is temperature dependent, and therefore this is a good way of tuning the properties in term of pore size, micropore volume and specific surface area of the final product. Several studies of the effect of the hydrothermal treatment have been performed on standard syntheses [14,84-87], with varying silica precursors [73], and syntheses with swelling agents [88].

The effect of the hydrothermal treatment is twofold. First, following the formation of the hexagonal structure, the PEO chains are trapped into the silica network [26,86] and they are the source for the micropores in the final product. When the temperature is elevated, the hydrophilicity of the PEO chains change, making them more hydrophobic. The chains then retract from the silica wall and go into the more hydrophobic core of the micelles. This results in an increased pore size, and reduced microporosity and surface area. Secondly, the hydrothermal treatment decreases the shrinkage of the silica walls upon calcination. The effect of hydrothermal treatment is illustrated in Figure 14.

Figure 14. The effect of the hydrothermal treatment.

By increasing the hydrothermal treatment temperature from 35 to 130 °C it is possible to increase the mesopore size with several nanometers, with significant changes noticed above 60 °C [86]. Also, above 60 °C the microporosity and surface area are decreased and when the treatment is performed at 130 °C no micropores remains and all surface originates from the mesopores. The unit cell

parameter is nearly constant for calcinated samples with hydrothermal treatment temperature exceeding 60 °C, so during the increase of mesopore size the wall thickness decreases and the wall becomes denser and the microporosity is lost [23,86]. It should though be noticed that the micropores do not disappear, but rather increase their size. A SAXS study [134] has shown that increasing the hydrothermal treatment temperature from 60 to 180 °C actually increases the intrawall pore size from 1.5 to 5.2 nm, creating voids in the silica walls. These voids are most probably the reason for the large overestimation of mesopore sizes when a high hydrothermal treatment temperature and/or time is used.

A similar effect, but not as pronounced, is obtained by increasing the hydrothermal treatment time. Later studies have shown that for samples with plugged pores the increased hydrothermal treatment time removes primarily plugs, while the increased synthesis temperature affects both the plugs and the mesopores size [135]. During the hydrothermal treatment, free flocs of silicated micelles in the solution act as repairing units to decrease the number of defects in the hexagonal structure [136]. Hydrothermal treatment in pure water instead of the synthesis solution yields a defect rich material with many holes and plugs.

4.4 Removal of surfactants

The final step of the synthesis is the removal of the surfactants. This is most often done by calcination, but there are alternatives such as chemical removal of the template or decomposition by microwaves, see Figure 15. Regardless of which method used, the aim is always to completely remove the surfactants in a way that is as cheap and time effective as possible.

4.4.1 Calcination

Calcination is the most common way to remove the surfactants from SBA-15. During the calcination, which is performed in air, the material is heated to 550 °C and this temperature is held for 5 h before the material is cooled down to room temperature.

Figure 15. The surfactants can be removed using various techniques, e.g. calcination or oxidation using H_2O_2 .

Most of the surfactants decompose between 150-250 °C and at this stage the hexagonal structure retains its size. Above 300 °C water is released and the rest of the polymers are combusted and the hexagonal framework is decreased probably due to condensation in the framework and closing of micropores [89]. During the shrinkage of the hexagonal structure, the mesopore volume is decreased but the micropore volume is almost constant [90]. This indicates that the micropores are still being emptied from surfactant residues simultaneously to the framework shrinkage.

Calcination was used as the method for removing surfactants in Paper II, IV-VII.

4.4.2 Chemical removal

An alternative route to removal of the surfactants is to chemically oxidize the PI23. By using this alternative route there is no shrinkage in the hexagonal structure, which is the case for calcination, and it is possible to functionalize the material in multiple steps. For this purpose, chemicals such as ethanol, hydrogen peroxide, sulphuric acid or ammonium perchlorate can be used.

Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is an oxidation agent that can be used for removal of the surfactants. By treating the SBA-15 with H_2O_2 at 100 °C for 24 h, the polymer template can be completely removed [97]. This method gives a product with slightly larger mesopores, a higher micropore volume and thereby a larger specific surface area. Figure 15 shows that the H_2O_2 treatment is equivalent

compared to calcination with respect to surfactant removability. Another difference in the final product is the increased amount of silanol groups in the silica walls when this method is used compared to calcination. Silanol groups can be used as reaction and anchor sites when functionalizing the final product [98]. The H_2O_2 method has been used in Paper I and III.

Ethanol

Ethanol was used as an alternative to calcination for removing P123 in the first reports of SBA-15 [8,14]. By refluxing the silica in ethanol at 78 °C for 24 h the P123 can be removed. An advantage with this method is that the surfactants are not decomposed but can be recovered and reused for syntheses. Also, there is a larger amount of silanol groups in the silica walls which is preferable when functionalizing the surface. Drawbacks are that there can be residues of P123 in the micropores [91,92] and that large amounts of ethanol are needed during the treatment [93]. The method is suitable for materials where the surfaces have been functionalized during the synthesis process or to functionalize the surface during the ethanol extraction process [94-96].

Sulphuric acid

If instead sulphuric acid (H_2SO_4) is used to remove the surfactants it is possible to control the removal in different parts of the material. H_2SO_4 is selective in the oxidation of the polymer and decomposes only the PPO chains of the surfactant [99,100]. This makes it possible to functionalize the mesopores prior to removing the PEO chains. The PEO chains are removed by low temperature calcination at 200 °C. Similar to the H_2O_2 treatment, the mesopore size and micropore volume are larger for these samples compared to ordinary calcinated samples. The advantage of this method is that triple functionalized samples can be synthesized, with an outer functionalization prior to the first step of the template removal followed by a second and third functionalization in the meso- and micropores respectively.

Ammonium perchlorate

Ammonium perchlorate (AP) mixed with HNO_3 can also be used to selectively remove the surfactants [101]. In this case ethane groups are left on the silica framework. Compared to the H_2O_2 removal of the template, this method is faster with all surfactants completely removed after 12 h treatment in 80 °C.

4.4.3 Microwave digestion

The fastest method to remove the template from mesoporous silica is to use microwave digestion. When SBA-15 is mixed with HNO_3 and H_2O_2 [91] or

alternatively ethanol and hexane [102] and exposed to microwave radiation for 2 min the surfactants are completely removed. These samples also contain higher silanol concentration compared to calcinated samples. Moreover, there is no shrinkage of the framework using this method which yield higher surface area, larger pore size and pore volume compared to calcination [91].

5 TUNING THE PROPERTIES OF SBA-15

SBA-15 can be tuned in many ways. Different morphologies can be synthesized, the pore size can be altered from 5-26 nm, and the microporosity, surface area and wall thickness can be varied. Here, some methods for tuning the material properties, such as additions of swelling agents, salts, and reaction temperature are presented.

5.1 Morphology

The morphology of SBA-15 can be tuned in many ways, see Figure 16. The most common morphology is the fiber- or rodlike structure where the particles are attached end-to-end. Other structures such as doughnuts, gyroids, rods, platelets and hollow spheres can be synthesized by changing some of the synthesis parameters, e.g. [137,138]. For many applications such as adsorption of biomolecules, short, well separated particles are preferable [139].

Figure 16. SBA-15 in the form of (a) fibers, (b) sheets/ hollow spheres, (c) rods, and (d) platelets.

5.1.1 Fibers

Fibers are, by far, the most common morphology for SBA-15. They consist of smaller particles attached with the pore ends facing each other, as seen in Figure 16 (a). This end-to-end attachment between particles occurs in order to reduce the energy of the system. The basal plane, with the micellar caps, is more hydrophobic than the other planes due to its higher surface energy, related to the curvature of the micellar caps [140]. The end-to-end attachment is also favoured

by the active hydroxyl groups on the basal plane. During the silica precursor polymerization, the number of hydroxyl groups responsible for attaching particles to each other is diminished. This passivation is more severe for the mantle surface since the hydroxyl groups at the ends are relatively shielded from the acid by the micelles. A higher acid concentration gives a stronger passivation and thereby particles can be separated into rods [141].

Even though the morphology is the same, the crystallites building the fibers can have various dimensions. For example, the particle size achieved in the low temperature synthesis is affected by the alkane used. The shortest pores are ~150 nm when nonane is used, which should be compared with 800-1000 nm for dodecane or without alkanes [91]. This variation is due to the different solubility of the alkanes in the micelles. At a fixed temperature, larger amounts of short alkanes can be dissolved in the core of the micelles [142]. The quantity of alkane in the core affects the length of the rods in the sphere-to-rod transitions. Hence, a larger amount of alkane (shorter alkane chain) yields shorter pores.

5.1.2 Spherical particles

Spherical particles with ordered pores are commonly hollow, formed around droplets of gas or oils in aqueous solutions. Alternatively, solid spherical particles can be synthesized with additions of co-surfactants and co-solvents. This morphology is of interest for applications such as drug delivery systems or storage of gas.

The hollow spheres formed around droplets have ordered pores, perpendicular to the particle surface. By controlling the droplet size with e.g. CO₂ [143] or oil concentration, as shown in **Paper I-III**, hollow spheres with easy access both to the mesopores and the hollow core can be synthesized.

Additions of the co-surfactant CTAB and ethanol yield solid, spherical SBA-15 particles [144-146]. Ethanol both decreases the hydrolysis rate of TEOS and reduces the polarity of the aqueous solution which makes it possible to synthesize this morphology [147]. It should though be noted that despite the fact that the PSD is narrow, the pore order is lost in these materials.

5.1.3 Rods

A rod is a straight isolated particle in which the pores are running through the particle, most often through the long dimension. Most rods are synthesized by decreasing the stirring time from 20 hours to a few minutes and careful control of

the synthesis composition.

By decreasing the stirring time from 20 h to 5 min followed by 20 h static condensation of the silica monodispersed silica rods, 1-1.5 μm long and -0.5 μm in diameter, can be synthesized [148]. The formation of this morphology was explained by the absence of shear flow and a lower rate of precipitation during the static conditions. The same effect has been observed when sodium metasilicate has been used as the silica precursor. Stirring times as short as 30 s yield monodispersed rods, while stirring continuously during the synthesis results in fiber like morphologies in which the rods act as building blocks [149]. Furthermore, it was also shown that the composition in the synthesis is of great importance for the morphology of the final product. The sizes of the resulting rods are also similar in size and 1-2 μm monodispersed rods can be synthesized using both TEOS and sodium metasilicate as silica precursor. The pore sizes in these studies have been tuned by varying the hydrothermal treatment time and a range of sizes between 5.5 and 12.5 nm was obtained. Sodium metasilicate reacts faster than TEOS [150] which can be the reason for the short stirring time required.

Alternatively, addition of inorganic salts such as KCl in combination with stirring for 8 min followed by static condensation for 20 h yield 1-2 μm long straight rods [137]. In this case the HCl to P123 ratio is slightly lower (-316 compared to -348 in the above syntheses). These rods are although not completely separated which can be due to the slightly longer stirring time.

The length of monodispersed rods can be controlled by varying the amount of HCl [25,141,151]. This has been observed both without additives [25], or with additions of glycerol [141], and when TEOS and BTMSE are used as silica precursors [151]. In general, a higher HCl concentration yields shorter rods. The decreased length has been attributed to the catalytic effect of HCl on the silica precursor [141,152]. Additionally, the effect has also been assigned to the adsorption behaviour of H^+ on the PEO chains of micelles, which differs between the micellar caps and the micellar sides [25].

Alternatively, the rod length can be tuned by alterations in the composition of the silica precursor. When sodium silicate is used as the silica precursors, the rod length increases, and the particles become narrower for a decreased silica to sodium ratio [153]. This was explained by an increased number of silica seeds that increases when the amount of silica is increased, and the growth behaviour by attachment between them.

5.1.4 Platelets

A platelet is a particle in which the base is wider than the height of the particles. The particle shape is often hexagonal and the platelets have pores going through the short axis of the particle. This morphology is rare but can be found when PI04, with a PEO to PPO ratio that is higher compared to PI23, is used as surfactant [132,139,154,155].

When PI04 is used, it is possible to tune the morphology from fibers to platelets by decreasing the reaction temperature from 60-65 °C to 50-55 °C [132,154,155]. Both the fibers and platelets consist of primary particles that attach to each other in different orientations. It has also been observed that the attachment between primary particles can be tuned by salt additions [156]. Alternatively, it is possible to form 300 nm thick platelets by the addition of K_2SO_4 [139]. Increasing the K_2SO_4 concentration yields thinner walls, larger pores, and the thickness to width ratio decreases. Even though it is not mentioned in the paper [139], it seems like these platelets consist of separate particles attached side by side.

Additions of $ZrOCl_2$ in varying concentrations also yield 150-300 nm thick and 800-1000 nm wide platelets [157]. It was suggested that the Zr(IV) ions increase condensation rate of TEOS and rods are formed faster compared to syntheses without Zr ions present. Hence, the formation of platelets was preferred to the formation of fibers.

As shown in Paper V, platelets can be formed by decreasing the NH_4F concentration in the low temperature synthesis including heptane. Platelets have also been synthesized in a similar system by complete removal of the NH_4F [158]. It has also been shown that increasing the TEOS to PI23 molar ratio in a system including decane makes it possible to form the platelet morphology [91].

The suggested mechanism for the formation of platelets is that the particle shape is determined by the relative growth rate of the different planes of the particle [159]. The platelets are most often hexagonal with varying heights and each particle has two (001) and six (100) surfaces, see Figure 17. By varying the synthesis conditions as mentioned previously, the growth rate of the edges can be varied. The height to width ratio is determined by the surface tension of the particle in the relation

$$\frac{h}{w} = \sqrt{3} \frac{\gamma_{001}}{\gamma_{100}}. \quad (4)$$

Figure 17. Schematic illustration of a SBA-15 particle with its defined (001) and (100) surfaces.

Additionally, as discussed in **Paper V**, the formation of platelets depends on the availability of the PEO chains. For example, a lower reaction temperature increases the solubility of PEO chains, and also, PI04 has larger PEO blocks than PI23. Furthermore, by decreasing the amount of salting-out ions (F^-) the solubility of the PEO chains also increases, and the addition of larger amounts of TEOS increases the size of the silicated PEO chain. Hence, larger, or more accessible, PEO domains favour the formation of platelets, most probable due to easier entanglement between the micelles.

In opposite, if the concentration of TEOS is decreased and octane is used as swelling agent, small separate particles, 50-80 nm wide and 100-200 nm long can be synthesized [24]. This would then be due to the smaller silicate PEO chains, which are more difficult to grow together.

5.2 Pore size

As mentioned earlier, the hydrothermal treatment is one way to change the pore size of SBA-15. But with this method, the wall thickness and microporosity are also affected. Other ways to tune the mesopore size are additions of salt, co-surfactants, oils, or changing the reaction temperature. All these methods will be discussed in this section.

5.2.1 Swelling agents

A swelling agent is a non-polar reagent that goes into the hydrophobic core of the micelles and expands them, thereby increasing the pore size of the final product.

TMB

In the first report of SBA-15 1,3,5-trimethylbenzene (TMB) was used as a swelling agent, and it was believed that the pore size could be tuned between 5 and 30 nm [20]. But it was later shown that for oil/PI23 mass ratios exceeding 0.2

the micelles transform from cylinders to a mesocellular foam (MCF) where spherical pores are attached to each other by smaller windows [130,160]. This is illustrated in Figure 18.

Figure 18. Transition from hexagonal cylinders to MCF by increasing oil content.

When small amounts of oil is added to the synthesis it swells the PPO chains and increase the micelle size. But when the PPO chains are fully saturated the excess oil form pure oil cores in the micelles. The limited amount of P123 must completely cover the oil droplets and therefore the micelles become more spherical and the intermediate structure shown in Figure 18 is formed. By further increasing the amount of oil the nodes on the intermediate shape become sharper and finally the spheres are separated. The process is driven by the need to decrease the surface-to-volume ratio when the amount of oil to P123 ratio is increased. The maximum pore size for the cylindrical pores when just oil, such as TMB, is added to the synthesis is 12 nm [130]. TMB addition is still the most common way to increase the pore size of SBA-15, e.g. [59,161-163].

PPO

An alternative, but not as efficient, swelling agent is PPO, identical to the hydrophobic block in P123 [164,165]. Additions of this polymer increase the pore size from 4 nm to ~5-6 nm depending on the molecular weight of the polymer.

Alkanes and substituted benzene

Other hydrocarbons used as swelling agents are alkanes (8-20 carbons) and methyl- or isopropyl-substituted benzene. These can be used as swelling agents following a route similar to the original synthesis and adding the hydrocarbon to the micellar solution prior to the addition of silica precursor [166]. However, the temperature of the solution after the addition of swelling agent, but prior to the addition of TEOS, was altered in several steps from room temperature to 50 °C and back to 35 °C. By using the substituted benzene the pore size could be tuned between 7-43 nm, but only MCF were obtained. For alkanes, MCFs were obtained with octane and nonane but with alkanes with 10 or more carbons ordered hexagonal structures were obtained and the pore size could be increased

to 10 nm (for decane). The pore size was decreasing with increasing number of carbons in the alkanes.

Hydrocarbons at low temperature

Shorter alkanes with 6-16 carbons can also be used as swelling agent in a low temperature synthesis in combination with additions of NH_4F . By combining the effects of low temperature, salt additions and swelling agents, SBA-15 with pores larger than 12 nm can be synthesized in varying morphologies [23,24,91]. Variations within this synthesis route, including heptane as the swelling agent, are used in Paper I-VII.

The large pore size is a result of the combination of low temperature, oil additions, and salt. The amount of alkanes used to synthesize a hexagonally ordered material can widely exceed the amount of TMB that induces the phase transformation from ordered hexagonal structures to MCFs [90,91,130]. This is due to the effect of low temperature and additions of NH_4F . The alkanes can be varied from hexane to hexadecane and the pore size depends on the alkane used, varying from 12.0 nm (dodecane-hexadecane) to 15.7 nm (hexane) [91]. The decrease in pore size with increasing hydrocarbon length is due to the solubility of the hydrocarbons in the micellar core [90]. By varying the hydrothermal treatment time and temperature it has been possible to tune the pore size between 9 and 18 nm when hexane was used as swelling agent [167].

As an alternative to alkanes, 1,3,5-triisopropylbenzene (TIPB) can be used in a similar synthesis, but the temperature needs to be decreased further [21,22,93,158]. Again, the solubility of the swelling agent in the micellar core is the key for forming the large pores. In this case an ordered porosity is only possible using reaction temperatures lower than 14 °C [21,93]. This resulted in 26 nm large pores, according to the KJS-method, and a unit cell parameter of 25.8 nm [21], which is the largest pore size for SBA-15 until now.

5.2.2 Temperature

The pore size is approximately equal to the core radius of the micelles. Therefore, the pore size can easily be tuned by varying the synthesis temperature since it tunes the properties of the surfactants, see Section 3.3.2. Within the “normal” synthesis temperature range (30 – 60 °C) the pore size is proportional to the expression

$$R_p \sim (T - T_C)^{0.2} \quad (5)$$

where T is the temperature of the aqueous solution and T_c the CMT [168]. The expansion is due to the increasing micellar core, and hence a larger aggregation number [103].

Lowering the temperature decreases the solubility of PI23 in water since the hydrophobic PPO chain becomes more hydrated at lower temperatures. This increases CMC and finally only separate surfactants are present in the solution and no micelles are formed. The effect of temperature is seen in the synthesis of SBA-15, for which the pore size can be increased with more than 1 nm when the synthesis temperature is raised with 10 °C [149,169,170].

5.2.3 Salt additions and acidic source

Addition of inorganic salts, such as NaCl, KCl, and K_2SO_4 , increases the pore size [131,139,170,171]. As discussed in Section 3.3.3, addition of salts cause dehydration of ethylene oxide units from hydrated PEO from the side of the PPO core. This leads to an increase in the core radius [101,172], and the increase of the hydrophobic part of the micelles induces the formation of micelles and the sphere-to-rod transition which enhances the order of the material and a slight increase in the pore size. If instead a salt with salting-in properties is used, e.g. NaBr or NaI, the pore size will be decreased [131].

Salts affect the pore size, pore ordering and micropore volume of SBA-15. As mentioned earlier, additions of CTAB as a co-surfactant can be used to tune the pore size but the pore ordering is lost. However, additions of NH_4F and KCl made it possible to synthesize highly ordered structures with CTAB as the co-surfactant [173]. It is also possible to perform syntheses at lower temperatures when salts are added [89].

As mentioned in Section 3.3.3, the anion gives the largest effect on the micelle structure. Hence, alterations in the acidic source can give similar effects as salt additions. For example, exchanging HCl for HNO_3 , HBr, H_2SO_4 , or H_3PO_4 gives alterations in pore size; with the smallest size for HNO_3 since the NO_3^- is a salting in ion, and the largest size is synthesized with H_3PO_4 , which gives the strong salting-out ion [103].

5.2.4 Co-surfactants

Additions of other surfactants can help tuning the pore size. By adding the cationic surfactant CTAB, the pore size can be decreased from 8.5 to 4.8 nm [173]. Although the pore order is lost, it can be regained by additions of NH_4F

and KCl. It was further suggested that CTAB causes hydration of the PPO chain in P123 and thereby decreases the hydrophobic volume of the micellar core.

If instead CTAB is added to the synthesis together with TMB, the pore size can be increased up to 12.7 nm [168].

5.2.5 Silica precursor

Substituting TEOS with sodium metasilicate, a small decrease in pore size can be noticed [107,174]. The reason for this is not discussed, but one explanation can be that there is no ethanol rest product from sodium metasilicate that can expand the hydrophobic core of the micelles. The effect of hydrothermal treatment is though the same regardless of silica source used.

By mixing TEOS with sodium metasilicate in a pH 4.4 buffer solution the pore size could be tuned from 10 to 16 nm with increasing TEOS/sodium metasilicate molar ratio [175]. Also here there is a transition from ordered hexagonal structures to MCF for larger pores; the maximum d-spacing for the ordered material is 12 nm.

5.3 Wall thickness and microporosity

The thick walls of SBA-15 are one of the advantages that make this material superior to other mesoporous silicas with the same pore structure. The control of these walls and the microporosity within them are essential for optimizing the material, e.g. walls with low microporosity have higher thermal stability than high porosity walls [176] and adsorption selectivity of hydrocarbons is affected by the microporosity [171,172].

As mentioned earlier, the microporosity is caused by entrapments of PEO chains in the silica walls prior to calcination of the material. Hence, by varying the entrapment of the chains, the microporosity can be tuned.

5.3.1 Hydrothermal treatment

As described in Section 4.3, the wall thickness and microporosity is affected by the hydrothermal treatment. At elevated temperatures, the PEO chains retract into the hydrophobic core of the micelles due to reduced hydration of the chains. This leads to less PEO chains trapped in the silica walls which yield thinner walls with decreased microporosity.

5.3.2 Surfactant removal

The microporosity and wall thickness is also affected by the surfactant removal technique used, see Section 4.4.

At calcination temperatures as high as 950 °C, the pores can be completely closed, leaving separated mesopores in the silica matrix [177-179]. The material with high closed porosity can be of interest for applications where materials with low dielectric constant are desired. This is mostly used for materials with spherical pores connected by small necks, where the necks close due to sintering at higher temperatures [178], but the technique can also be used for SBA-15 types of materials with plugs inside the mesopores [177].

5.3.3 Salt additions

Addition of salts with salting-out properties decreases the wall thickness and micropore volume of SBA-15 [137,139]. This effect is similar to increasing the temperature, as mentioned in Section 3.3.3. When sufficient amounts of salts are used in combination with high hydrothermal treatment temperatures, the microporosity is almost completely lost [137].

Lately, it has also been shown that adding a salt with salting-in properties, e.g. NaI, at the right time during the synthesis removes almost all microporosity. For this to work, the salt should be added when the structure has formed, but while the system is still responsive [180].

5.3.4 The SiO₂ to P123 molar ratio

By changing the molar ratio of silica precursor to P123 it is also possible to control the wall thickness, pore size, and microporosity. In syntheses performed at a lower HCl concentration (0.1 M) the unit cell parameter increases with the amount of TEOS. At the same time the pore size and total porosity decrease, and at TEOS/P123 molar ratio of 75 the replica of the SBA-15 structure is similar to the ones from MCM-41. The increase of wall thickness is pronounced and is more than doubled when the molar ratio increases from 45 to 75. The lower reaction rate due to the low acidity in the synthesis gives the silica species time to condense on the PEO chains, which if the amount of silica is increased, leads to a decreased PEO-PEO interaction between different micelles [138].

There can though be problems using this technique since plugs of silica can be left inside the mesopores and form constrictions [135,151,181]. At HCl concentrations common in the synthesis of SBA-15 (~1.4-2 M), only parts of the

silica species can react with the PEO chains. The excess silica will penetrate the micellar structure and condense there, forming plugs and constrictions [135]. It should be noted that the amount of TEOS used in these studies sometimes exceeds the ones performed at lower HCl concentration.

5.3.5 Reaction temperature

The microporosity of SBA-15 can be controlled by varying the temperature in the first 10 minutes of the synthesis. Both the hydrophilicity of the PEO chain and the rate of polymerization of TEOS are temperature dependent (see Section 3.3.2 and 3.4). When the initial temperature of the synthesis is varied between 28 °C and 55 °C followed by further reaction at 35 °C and hydrothermal treatment at 100 °C, the microporosity in the material decreases with increasing initial temperature [182]. For a fixed hydrothermal treatment time and temperature, variations in microporosity depend on the amount of PEO chains trapped in the silica network.

6 MESOPOROUS FILMS

Mesoporous films are of great interest for applications such as catalysts, solar cells and batteries. There are several ways to synthesize these films, e.g. Evaporation-Induced Self-Assembly (EISA) by dip- or spin-coating, or self-formed films in the solvent/air or solvent/oil interfaces.

One of the biggest challenges regarding SBA-15 film synthesis is controlling the pore orientation. The cylindrical pores of SBA-15 are most often aligned parallel to the film surface [183] which makes it difficult to access the pores from the film surface [184]. The access is much easier for films with spherical or wormlike pore structures, but for some applications, such as fuel cells [185], or templating, cylindrical pores are preferable. Hence, it is of large interest to synthesize films with cylindrical pores with easily accessible cylindrical pores, and this has been realized in **Paper VI** and **Paper VII**.

6.1 Evaporation-Induced Self-Assembly

EISA is the most common method for synthesizing mesoporous silica films, and it is used for e.g. spin- or dip-coating [186-188]. In EISA, the starting solvent consists of a silica precursor and surfactants dissolved in a water/ethanol solution. The surfactant concentration is here below CMC. By varying the initial composition of the surfactant containing solution, it is possible to vary the structure of the final film. A substrate is alternatively dipped and withdrawn from the solution or the solution is spin coated onto the substrate, commonly silicon wafers or glass substrates. After deposition of the solution onto the substrate, the ethanol evaporates and the concentration of water and surfactants increase. Hence, the surfactant concentration increases above CMC and micelles start to form on the substrate [188-190]. The process is illustrated in Figure 19.

6.1.1 Deposition techniques and film thickness

As previously mentioned, EISA is most commonly used for dip- or spin-coating, but also techniques such as laser printing can be used for depositing the sol. The thickness of the films can be controlled by varying the deposition rate of the films and the amount of solvent in the solution [191-193].

Figure 19. The formation of ordered structures in mesoporous films using EISA.

6.1.2 Pore orientation

For thin films (thickness < 200 nm) it is possible to control the horizontal orientation of the cylinders by controlling the flow direction of the solution [194]. Alternatively, the pores can be oriented into doughnut shapes by laser induced patterns on the substrate [195]. But it is still not possible to create a film with cylindrical pores perpendicular to the substrate using these methods. It is however possible to form films with perpendicular pores to the substrate with EISA: by substrate manipulation.

By using alumina substrates with conical holes the orientation of the mesopores can be changed from parallel to perpendicular to the substrate by changing the depth and width of the conical holes [195]. Holes with small aspect ratio are filled with sponge-like mesostructures which yields films with perpendicular and tilted cylinders. These cylinders start to grow from the mesostructures in the holes. When the aspect ratio is increased, the conical holes are filled with cylindrical mesopores in a doughnut like stacking which acts as the start for mesoporous films with pores running parallel to the substrate.

It has also been shown that surface modifications can tune the pore orientation of mesoporous films [196]. By using octadecyltrichlorosilane (OTS) to make the surface of silicon wafers more hydrophobic it has been possible to synthesize thin mesoporous films in which the pores are like craters -40 nm wide but only -1 nm deep. The width of these craters corresponds well with the length of the extended P123 molecule.

6.1.3 Drawbacks

Even though EISA gives a rapid way to synthesize mesoporous films, there are some drawbacks with the method. As already mentioned, the orientation of cylindrical pores are in general parallel to the substrate, and this prevents easy access to the pores and transport throughout the film [197].

Another drawback with the EISA synthesized films is that the pore size is difficult to control, and pores larger than 9 nm are very rare [198]. Also, the structure is unstable and often collapses in the presence of water [194,199,200].

Finally, EISA is used by spin- or dip-coating, and hence it is only possible deposit homogenous films on flat substrates.

6.2 Electro-Assisted Self-Assembly

One method to synthesize mesoporous films with pores oriented perpendicular to the substrate is Electro-Assisted Self-Assembly (EASA). With this method, an electrode is immersed in a sol containing surfactants and hydrolysed TEOS. A cathodic potential is applied to the electrode in order to generate hydroxyl ions that catalyses the polycondensation of the silica precursor. A self-assembled film consisting of hexagonally packed cylindrical channels grow perpendicularly to the electrode surface [201].

The film thickness can be increased by increasing the deposition time [202,203], or an increased cathode potential [201,203]. Alternatively, by addition of methyltriethoxysilane, the film growth rate can be decreased resulting in thinner films, down to -100 nm [204]. The lattice parameter is tuned by altering the length of the surfactant alkyl chain [203].

An advantage with this type of deposition technique is that the film can take any shape, instead of just covering a flat surface. It can e.g. be used to grow mesopores on a macroporous substrate, creating a material with hierarchic pore structure [202]. It can also be functionalized during the synthesis process with

aminopropyl groups, making the films suitable for sensing applications [205]. A drawback is the small pore size, which can be tuned by altering the surfactant length. But, since CTAB surfactants are used, the pores will always be smaller than those in SBA-15.

6.3 Grafting particles on substrates

By preparing mesoporous particles and depositing them on a substrate, it is possible to synthesize films with a completely controlled pore structure. But an optimum grafting procedure that yields one monolayer with particles that completely cover the substrate has still not been obtained.

40 nm small silica particles with unordered pore structure can be bound to a substrate using aminopropyltrimethoxysilane (APTMS) [206]. The film was used for enzyme immobilization. However, the particles can form clusters and does not completely cover the substrate.

In the work presented in this thesis, a new approach was investigated. This study is presented in **Paper VII**.

6.4 Freestanding films at interfaces

When an SBA-15 film is formed at an oil/water or water/air interface it is possible to align the pores perpendicular to the film surface.

Exchanging HCl for H_3PO_4 gives the possibility to form films in the air/water interface under static conditions. In the solution, cakelike structures consisting of agglomerated particles are formed. If instead stirring is used, the common fiberlike structure is formed [207,208].

Also, by creating a bilayer of C_{16}MTAB and sodium dodecylsulfate (SDS), micrometer large platelets < 200 nm thick with pores perpendicular to the surface can be synthesized. By drying some of the synthesis solution on a silicon wafer, a mesoporous film with preferable pore orientation was synthesized [209].

7 ANALYSIS TECHNIQUES

There is not one universal analysis technique that provides all information necessary to characterize a porous material. The surface area, pore size, pore volume, and, to some extent, pore shape of the materials are measured using physisorption with N_2 gas but this technique does not reveal the pore order. This information is instead given by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The particle morphology, and in some cases also the pore structure, is imaged using scanning electron microscopy (SEM), and also TEM for the mesoporous films. In that case a focused ion beam (FIB) technique was used to prepare the TEM sample. The functional groups attached to the material walls have been studied with Fourier transformed infrared spectroscopy (FT-IR), and the removal of polymers and functional groups was followed by thermogravimetric analysis (TGA).

7.1 Physisorption

Gas sorption is a technique used for characterizing porous materials. With this method a material's specific surface area, pore volume and pore size distribution can be determined.

7.1.1 Physisorption isotherms

The physisorption data is presented in sorption isotherms with the amount of gas adsorbed on the solid plotted versus the relative pressure. The isotherms can be grouped into six types [2] which are shown in Figure 20.

Type I isotherms: This type is characteristic for microporous materials. In micropores there is an increased adsorbent-adsorbate interaction. The nearly horizontal plateau is reached at low relative pressures, which indicates a small external surface area.

Type II isotherms: These isotherms are typical for non-porous, microporous and macroporous materials. Here there is a monolayer-multilayer adsorption on an open and stable surface. The knee-point at B indicates where the monolayer adsorption is complete and multilayer adsorption begins. B indicates the material's monolayer capacity as it is measured how much adsorbate is required to cover the unit mass of solid surface with a monolayer of adsorbate molecules.

Figure 20. The six main types of adsorption isotherms according to the IUPAC classification [2].

Type III isotherms: These isotherms are very uncommon and are characteristic for materials with very weak adsorbate-adsorbent interactions.

Type IV isotherms: This type of isotherm is typical for porous materials. At the beginning the isotherm is similar to the type II isotherms. The knee-point at B indicates here, as well as for type II isotherms, the monolayer capacity of the material. At higher pressures, there is a hysteresis loop, for different types of hysteresis loops see Figure 21, which is characteristic for type IV isotherms.

Type V isotherms: The type V isotherms are characteristic for porous materials with weak adsorbate-adsorbent interactions. Initially they are similar to the type III isotherms but at higher pressures there is a hysteresis loop.

Type VI isotherms: These isotherms are due to layer-by-layer adsorption on a highly uniform surface. The steps are formed by separate layers adsorbing onto each other.

Figure 21. The four main types of hysteresis loops according to IUPAC classification [2].

The four types of hysteresis loops, seen in Figure 21, indicate how the pores are shaped and if there are any inclusions or plugs in them.

H_1 : This type of hysteresis loop has steep parallel adsorption and desorption isotherms. At these steps all pores are filled (adsorption) and emptied (desorption). It is typical for mesoporous materials with uniform pores.

H_2 : The H_2 hysteresis loop has a smoother adsorption step and a sharp desorption step. It is typical for materials with non-uniform pore shapes and/or sizes, e.g. silica gel or other metal oxides.

H_3 : This type of hysteresis loop is associated with slit-shaped pores. These often arise from agglomerates of plate-like particles.

H_4 : The H_4 hysteresis loop is similar to H_3 but has a more horizontal plateau which indicates microporosity in the material.

7.1.2 Specific surface area determination, the BET method

The most frequently used procedure to determine the surface area of a porous material is the Brunauer-Emmet-Teller (BET) method [210]. The method has evolved from the Langmuir theory [211] with multilayer corrections. It is assumed that

1. the adsorbent surface is uniform and all adsorption sites are equivalent
2. adsorbed molecules do not interact
3. all adsorption occurs through the same mechanism
4. at the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other adsorbed molecules of adsorbate, only on the free surface of the adsorbent.

To calculate the BET surface area the monolayer capacity, n_m , of the material is determined from the BET-plot. This is the best linear fit of the adsorption isotherm that includes the B point, see Figure 20, and is derived by the linear BET equation

$$\frac{P/P_0}{n(1 - P/P_0)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} \cdot \frac{P}{P_0} \quad (6)$$

where P/P_0 is the relative pressure, n the amount adsorbed, n_m the maximum amount adsorbed i.e. the monolayer capacity, and C a system dependent constant. A sharp point B is indicative of a high value of C and thereby of a high adsorbent-adsorbate interaction.

The BET specific surface area is then calculated by

$$a_s = \frac{A_s}{m} = \frac{n_m N_A \sigma}{m} \quad (7)$$

where a_s is the specific surface area, A_s the total surface area, m the mass of the sample, N_A Avogadro's number, and σ the molecular cross-sectional area occupied by the adsorbate molecule in the complete monolayer [2,212].

7.1.3 Micropore volume and external surface area

Each adsorbate-adsorbent system yields a unique isotherm due to variations in the interaction between the species. Therefore each system needs a standard isotherm to estimate the micropore volume, internal and external surface area. The standard isotherm can also be used as a reference for adsorbed layer thickness. This isotherm is measured for a nonporous sample of the same

material as the specimen analyzed. For silica, standard nitrogen adsorption data for LiChrospher Si-4000 silica is available for the P/P_0 $5.55 \cdot 10^{-7}$ -0.988 [213] as a standard isotherm.

In this work, the micropore volume was estimated by using a t -plot [214], see Figure 22. The thickness of the adsorbed layer is determined by

$$t = t_m \frac{n}{n_m} \quad (8)$$

where t_m is the thickness of a monolayer, for nitrogen $t_m = 3.54 \text{ \AA}$. In order to relate the layer thickness to the relative pressure, several methods can be used, e.g. the Halsey [215], Harkins and Jura [216] or Broekhoff-de Boer methods, or the reference isotherm.

When using the KJS method, described in Section 7.1.4, the Harkins-Jura equation

$$t \left(\frac{P}{P_0} \right) = 0.1 \left[\frac{60.65}{0.03071 - \log \frac{P}{P_0}} \right]^{0.3968} \quad (9)$$

is used to determine the thickness.

To determine the micropore volume and external surface area, the volume adsorbed is plotted against t . The micropore volume is found as the intercept of the extrapolated first linear region of the t -plot and the y -axis and the external surface area (the surface area from meso- and macropores and the true external surface) is determined as the slope of the second linear region, see Figure 22.

Figure 22. t-plot for SBA-15.

7.1.4 Mesopore size analysis

There are several methods, such as the BJH [217], BdB [218-220] or KJS [221,222] methods, alternatively NLDFT [223-225], used to determine the pore size distribution (PSD) from nitrogen sorption isotherms. Different methods are suitable for different pore shapes and sizes. In this work, only the KJS-method has been used.

The main principles for calculating pore sizes are based on the concept of capillary condensation and the Kelvin equation

$$\ln \frac{P}{P_0} = -\frac{2\gamma V_L}{RT} \left(\frac{\cos \theta}{r_K} \right) \quad (10)$$

where γ is the surface tension of the adsorptive liquid, V_L the molar volume of the liquid, R the molar gas constant, T the temperature, θ the contact angle between the solid and the condensed phase, and r_K the mean radius of the liquid meniscus. When a critical pressure is reached, the adsorptive will condensate in the pores. Hence, the pore radius will determine if condensation can occur at a given pressure as illustrated in Figure 23. This is seen as the hysteresis loop from the physisorption data.

Figure 23. Capillary condensation at a given pressure is determined by the pore radius. The pore size is given by $2 \cdot (r_K + t)$.

The BJH method

Most calculation methods are based on the Barrett-Joyner-Halenda (BJH) method. Here, it is assumed that all pores have a cylindrical shape, that the simple Kelvin equation (Eq. (10)) is applicable, the meniscus is hemispherical with $\theta=0$ and that the correction for multilayers is valid.

For capillary condensation in cylindrical pores, the Kelvin radius as a function of relative pressure can be written as

$$r_K \left(\frac{P}{P_0} \right) = \frac{2\gamma V_L}{RT \ln \frac{P}{P_0}} \quad (11)$$

The pore size, r_p , is then obtained by adding adsorbed layer thickness, t , to r_K [212], so the pore width is

$$r_p = 2 \cdot (r_K + t). \quad (12)$$

For each step in the isotherm, the difference in amount of adsorptive represents the core volume filled or emptied in that step. The thickness of the adsorbed layer remaining on the pore walls is calculated with some method, this will be discussed in following paragraph. Using Eq. (11) and (12) the pore size can now be calculated.

To decide the amount of pores with this size, the shape of the pores is assumed to be homogenous for all pores, e.g. cylindrical. Using the difference in core

volume and the volume of a cylinder with the radius r_p , the total length of pores with this radius can be calculated. From this, the area of these pores can be calculated. By performing these calculations for all steps in the isotherms, the total PSD can be obtained.

The KJS method

This method was developed in the late 90's to improve the PSD from the BJH method. It is based on the BJH method and uses the Kelvin equation and Harkins-Jura thickness equation. Furthermore, the sum in Eq. (12) underestimates the pore size with -0.3 nm. Hence, the final expression for the pore size [nm] is according to the KJS-method

$$r_p \left(\frac{P}{P_0} \right) = \frac{2\gamma_L}{RT \ln \frac{P}{P_0}} + 0.1 \left[\frac{60.65}{0.03071 - \log \frac{P}{P_0}} \right]^{0.3968} + 0.3. \quad (13)$$

The method was first developed and calibrated for MCM-41 with maximum 6.5 nm pores. This led to an overestimation of 1-2 nm in pore size when measuring on SBA-15 [226] and therefore a correction for larger pore sizes was made to the method [222]. The pore size is now calculated as

$$r_p \left(\frac{P}{P_0} \right) = -\frac{1.15}{\log \left(0.875 \frac{P}{P_0} \right)} + 0.2 \left[\frac{60.65}{0.03 - \log \frac{P}{P_0}} \right]^{0.397} + 0.27. \quad (14)$$

7.1.5 Porosity

The porosity of a material is determined by the total pore volume divided with the volume of the material. The total pore volume, v_p , is taken as the liquid volume adsorbed at a given pressure e.g. $P/P_0 = 0.99$. Since the amount adsorbed by the material when $P/P_0 \rightarrow 1$ depends on the magnitude of the external area and the upper limit of the pore size distribution this method is not always satisfying. [212]. In the case of a type IV isotherm there is often a horizontal plateau after the filling of the mesopores. It is generally assumed that the amount adsorbed at this plateau is a measure of the adsorption capacity.

7.2 X-ray diffractometry

XRD is a technique used to study periodically ordered structures at atomic and nano scales. The wavelengths of X-rays are in the same order of magnitude as the

distance between lattice planes in crystalline materials. When the X-rays enter the material they will be scattered by the electron clouds around the atoms. The periodicity of the lattice planes gives rise to constructive interference of the X-rays, see Figure 24, and the intensity of the scattered X-rays is plotted against the scattering angle 2θ . From the plotted peaks the lattice distance can be calculated using Bragg's law

$$n\lambda = 2d_{hkl} \sin \theta \quad (15)$$

where n is the order of diffraction, λ the wavelength, d_{hkl} the distance between lattice planes and θ half the scattering angle.

Figure 24. Schematic illustration of diffraction according to Bragg's law.

For crystalline materials the lattice planes are often in the order of a couple of Å which gives a scattering angle of $\sim 20^\circ$ if $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) is used and scans between $20\text{--}80^\circ$ are common for characterization of the atomic structure of the material. For amorphous materials, such as mesoporous silica, there are no periodic atomic planes but the technique is still useful for characterization of the ordered pore structure. SBA-15 has a hexagonally ordered pore structure. As illustrated in Figure 25, the unit cell size, a , can be calculated from the first Bragg peak position

$$a = \frac{2}{\sqrt{3}} d_{100}. \quad (16)$$

Figure 25. Schematic illustration of a hexagonal structure with the d_{100} spacing and unit cell parameter a .

Mesoporous materials with periodically ordered pores give reflections for low angles, $2\theta < 3^\circ$, see Figure 26. These low angles makes detection by reflection difficult since some of the direct X-ray beam can go straight into the detector and cause high background radiation which makes it difficult to see and identify the peaks. Therefore a transmission detector is preferable when measuring on mesoporous materials.

Figure 26. X-ray diffractogram from SBA-15.

7.3 Electron microscopy

For studies of the pore structure and particle morphology of the materials electron microscopy is used to visualize the structures. Optical microscopes do not have sufficient resolution to picture the particle morphology. Furthermore, physisorption and XRD is not enough to characterize the pore structure since there can be mixtures of pore orderings or regions with unordered pores.

The smallest distance between two objects that can be resolved is described by the Rayleigh criterion

$$d = 0.62 \frac{\lambda}{n \sin \theta} \quad (17)$$

where d is the resolution, λ the wavelength, n the refractive index of the medium and θ the angle of the collected light. Using an acceleration voltage of 200 keV gives the electrons a wavelength of -1 pm which gives a much higher resolution compared to optical microscopes where the wavelength is -100 nm. Both scanning and transmission electron microscopes can be used for structural and

elemental analysis, but only the techniques used in this work will be mentioned here.

Figure 27. Micrographs and Fourier transform of SBA-15 sheets imaged using (a) SEM and (b) TEM.

7.3.1 Scanning electron microscopy

SEM is used to study the topography of materials, see Figure 27 (a), and has a resolution of ~2 nm. An electron probe is scanning over the surface of the material and these electrons interact with the material. Secondary electrons are emitted from the surface of the specimen and recorded. The height differences in the sample give contrast in the image. In this work, SEM has been used to study morphology of the particles and the pore direction in the mesoporous films.

7.3.2 Transmission electron microscopy

With TEM it is possible to resolve features in the range of 1 Å. In TEM a beam of electrons is transmitted through a thin sample and the electrons are scattered in the specimen. The transmitted electrons are directed to a fluorescent screen or CCD camera by electromagnetic coils and the image is formed. The image contrast originates from mass-thickness differences where thicker regions of the specimen (in this case the silica walls) absorb or scatter more of the electrons compared to thinner regions. Furthermore, it is possible to increase the contrast by blocking out some of the diffracted beams which will result in an image where areas that strongly diffract the electrons (here again, the silica walls) will appear darker in the micrograph.

Fast Fourier transforms (FFT) of the TEM micrographs gives the diffraction pattern of the specimen. This is similar to the information given by XRD but it is calculated from the micrograph and not measured from the whole sample. It can be used to study e.g. grain orientations in polycrystalline materials or pore

structures in the mesoporous silica. In this work TEM and FFT has been used to study the pore structure of the materials, an example is shown in Figure 27 (b).

7.3.3 Focused ion beam

A FIB combines an SEM with an additional source with gallium ions. The ion beam can be used for milling holes in the samples, making it possible to choose an area of interest and cut out cross sections of a material.

This technique was used for making the cross section TEM sample in Paper VI. There, the sample was first coated with a protective layer of platinum in order not to damage the film. Then the ion beam was used to mill the long sides of the sample. The sample is then attached to a needle, lifted out from the large film, and attached to a Cu grid used as a sample holder for TEM. Then, further thinning and cleaning of the sample was made by the ion beam [227].

7.4 Thermogravimetric analysis

TGA is used to study mass changes in a material due to changes in temperature. It is used to study e.g. oxidation of materials or, as in this case, decomposition of polymers.

The sample is placed on a high-precision balance and subsequently heated following a given temperature program. Varying atmospheres such as air, argon or helium can be used depending on the purpose of the measurement. During the heating, the sample weight is recorded as a function of temperature.

An example of TGA results is shown in Figure 15 where different techniques for removal of surfactants in SBA-15 are studied. In this study TGA and FT-IR were used to study if the surfactants were completely removed by H_2O_2 and the results were compared to results from calcinated and uncalcinated samples. The heating program was similar to the calcination program with a temperature ramp of $10\text{ }^\circ\text{C}/\text{min}$ up to $550\text{ }^\circ\text{C}$ and then held there for 1 h.

7.5 Fourier transformed infrared spectroscopy

FT-IR is used to study functional groups on the surface of materials using the discrete energy levels for vibrations of atoms in these groups. In this work FT-IR has been used to compare different techniques to remove P123.

When light with a specific energy is transmitted through the sample it can be absorbed by groups of atoms in the material. This occurs when the frequency of

the incoming light corresponds to the vibrational frequency of bonds between atoms. The vibrational energy depends on the masses and chemical environment of the atoms, the type of vibration.

By scanning over a range of wavelengths (in this case $400\text{--}4\,000\text{ cm}^{-1}$) and recording the amount of transmitted light for each wavelength it is possible to determine which functional groups that are present on the surface of the material.

8 SUMMARY OF RESULTS

8.1 Paper I

In this letter the synthesis of SBA-15 with 18 nm large pores in a sheet morphology is reported. The combination of low temperature, heptane and NH_4F yields the unusually large pore size. The oil also acts as a structure directing agent for the SBA-15 crystallites which attach to each other mantle surface to mantle surface, forming the sheet morphology shown in Figure 28. The pores size was estimated to -18 nm using the KJS-method, and the pores are directed perpendicular to the sheet surface.

Figure 28. (a) SEM and (b) TEM micrographs of SBA-15 sheets with pores running perpendicular to the sheet surface. Modified from Paper I.

8.2 Paper II

This letter is an extension of Paper I. Here, SBA-16 was synthesized with the same method, i.e. at low temperature and additions of heptane and NH_4F . The material consists of hollow SBA-16 spheres with cubically ordered spherical pores. Again, heptane is acting as a structure directing agent during the formation of the morphology, and a formation mechanism is presented. The spheres are 10-13 μm in diameter, have a pore size of 9 nm, and a wall thickness of 700 nm.

8.3 Paper III

In this study, the effect of heptane additions on pore size and morphology of SBA-15 synthesized in a low temperature synthesis was monitored. It was shown that heptane is acting as a pore swelling agent, resulting in 13-18 nm large pores ordered in a hexagonal structure. Furthermore, it was observed that the material consists of crystallites with ordered pores running through them, and that heptane is acting as a structure directing agent for these crystallites, as is illustrated in Figure 29. This results in two morphologies: fibers and sheets.

Figure 29. Schematic illustration of the role of heptane during the formation of different morphologies of SBA-15, from Paper III.

For both morphologies the pore size increases with increasing heptane to P123 molar ratio. At the morphological transition there is a drop in pore size, due to that the crystallites rearrange around and stabilize heptane droplets, in addition to swelling the micelles. Additionally, we confirmed that H_2O_2 can be used to completely remove P123 and thereby avoid shrinkage of the framework upon calcination, resulting in an even larger pore size.

Finally, it was shown that the pore order can be controlled by tuning the water to P123 molar ratio. Small changes (± 2.5 v.%) of the water amount drastically alter the pore structure from disorder to hexagonal order and back to disorder.

8.4 Paper IV

This paper shows that it is possible to synthesize large pore, well dispersed SBA-15 rods in a rapid synthesis. Also in this paper, a low temperature synthesis and additions of heptane and NH_4F were used to enable the particle formation and increase the pore size. The rods are presented in Figure 30.

The separation of particles is performed by decreasing the stirring from the normal 20 h to 4 min. This stirring is followed by keeping the synthesis solution at 20 °C under static conditions prior to the hydrothermal treatment. The static time was varied between 0 and 180 min. It was shown that the morphology was completely formed within 5 min of static time, but additional 30 min was needed to reach the final pore size and wall thickness. Hence, this method makes it possible to synthesize well dispersed, ordered rods in less than 1 h, which should be compared to the 20 h previously reported.

Figure 30. SEM and TEM micrographs of the rod morphology. The micrographs are from Paper IV.

Furthermore, it was shown that the length and width of the rods can be controlled by variations in the HCl concentration. A higher HCl concentration, i.e. lower pH, increases the hydrolysis rate of TEOS which leads both to an increased formation rate of the particles and an earlier passivation of the hydroxyl groups on the mantle surface of the particles. Due to this early passivation, less micelles can attach to each other and the final particle shape is thinner. Simultaneously, the rapid hydrolysis rate increases the formation rate of cylindrical micelles, such that they are more elongated, narrow and more homogenous in length compared to those synthesized with lower HCl concentrations.

Finally, the pore size was controlled by changes in the hydrothermal treatment time and/or temperature. As previous reports have shown, the pore size increases with increasing hydrothermal treatment time and/or temperature. Thus, for a

given HCl concentration, the pore size could be varied between 11 and 17 nm according to the KJS-method.

8.5 Paper V

This work further explores the effect of several synthesis parameters of SBA-15. Parameters such as heptane concentration, pH, salt additions, and silica precursor were altered. This resulted in the tools to tune the particle width from rods to platelets by a smooth transition, and also to tune the rod length from 300 nm to 600 nm.

Figure 31. The morphology shifts depending on the synthesis composition.

It was observed that heptane affects both the rod length and width, especially when low heptane concentrations are used. When the heptane amount increases the particles elongate and become narrower. Also the pore size and unit cell increases, until a plateau value is reached at the heptane to P123 molar ratio > 50 . Further increase of the heptane concentration does not yield any alterations in the particles aspect ratio or mesoscopic properties. This was attributed to the solubility of TEOS in heptane.

NH_4F tunes the particle width, independent of the heptane amount. Decreasing the amount of NH_4F broadens the particles. The particle height, and hence pore length, is constant, but a decrease from a NH_4F to P123 molar ratio of 1.83 to 0.45 broadens the particles from 200 nm to $> 3 \mu\text{m}$. It is possible to synthesize platelets without NH_4F , but then a longer static time is needed. Also, the pore size is decreasing with reduced additions of NH_4F due to the salting-out effect of F^- , which expand the hydrophobic parts of P123. This effect is also the reason for the particle broadening since the hydrophilic PEO chains become larger and more available when the concentration of salting-out ions is reduced. This leads to an easier entanglement between silicate species, encouraging side by side attachment of cylindrical micelles and hexagonally aggregated silicate species.

In general, F^- is acting as a catalyst for the hydrolysis and condensation of TEOS, and hence, the formation time for platelets is longer compared to the formation time of rods. This gave the opportunity to study the formation process for this system in detail. It was observed that it differs from the conventional formation route described in Section 4.2. Instead the material is formed during a process that includes foam, MLVs and hexagonally ordered aggregates.

8.6 Paper VI

In this paper the short mesoporous rods described in Paper V were used to synthesize films. The films consist of a monolayer of SBA-15 rods grown on OTS-treated silicon wafers, as shown in both the top view and cross section in Figure 32. As seen in the micrographs, the particles are not attached end-to-end which facilitates access to the pores. The film thickness depends on the particle height, and is in this case ~90 nm.

The film synthesis was performed by adding the OTS-treated silicon wafer to the synthesis solution shortly into the static time. Parameters such as addition time of the substrate, formation time of the films, and the effect of hydrothermal treatment were studied separately.

Figure 32. Top view and cross section of a film consisting of a monolayer of short SBA-15 on an OTS-treated silicon wafer. The micrographs are from Paper VI.

The growth behaviour of the films was studied and correlated to the formation process of the rods, and the optimum time for adding the substrates was 15–45 s into the static time. At this time the synthesis solution consists of a mixture of spherical and cylindrical micelles. As shown in the TEM micrograph in Figure 32, the particles are grown from the substrate, and already formed particles are not attached to the surface. This was also confirmed during the study of the formation time, which showed that after 5 min in the solution, the films consisted of elongated micelles coated with spherical micelles. After 10 min in the solution, the final film morphology was apparent.

Altering of the hydrothermal treatment temperature was used to tune the pore size. The temperature was varied between 80-130 °C which yielded pore sizes from 10.7 nm to 13.9 nm. It was also seen that the amount of MCF was reduced when the higher temperatures were used. This indicates a low hydrothermal stability of the MCF.

Finally, this synthesis does not only give mesoporous films easily access to the unusually large cylindrical pores, which is rare; it also gives free SBA-15 rods as the rest product. As reported in other studies, these are most useful for other applications such as drug delivery or enzyme immobilization [67,228].

8.7 Paper VII

Here, a method for grafting SBA-15 platelets on substrates in order to create mesoporous films with pores perpendicularly oriented to the substrate was developed. The platelets used were developed in Paper V, and their properties were altered by tuning the hydrothermal treatment temperature.

Figure 33. A film consisting of platelets grafted on a glass substrate.

The packing of the uncalcinated particles was studied by alterations in pH, substrate functionalization, salt additions, and TEOS's prehydrolysis time. By combining a low pH with an OTS-treated substrate, the highest particle packing was obtained. The effect of pH was twofold: (i) increasing the hydrophobicity of the silica sides of the platelets, and (ii) increasing the hydrophilicity of the OTS-treated substrate since H_3O^+ is located in the OTS/water interface. It was observed that the packing of particles is closely related to the hydrophobicity of the substrate, and that a hydrophilic substrate is preferred.

Furthermore, it was found that the prehydrolysis time of TEOS is a key

parameter for binding the particles to the surface, and that particle functionalization strongly affect the ability for TEOS to bind platelets to the surface. It was observed that when TMCS was used for functionalization, the platelets became embedded in a silica film, while OTS functionalized particles did not attach to the substrate.

9 FUTURE WORK

The work presented in this thesis is aimed to be the foundation for future research. Here, some of the possible pathways for upcoming research are presented.

9.1 Future particle syntheses

The synthesis pathway including low temperature, salt, and swelling agents was developed for SBA-15 synthesis using P123. In Paper II, we showed that the route also can be used for SBA-16 and F127. It would be interesting to continue this exploration by using other surfactants, e.g. P104 which would yield large pore SBA-15 with thicker walls. Furthermore, P104 often form the platelet morphology which is useful for the film synthesis.

As shown in Paper V, the formation process for the rods and platelets in this work differs from the ordinary formation path, since it includes foams and MLVs. A detailed study of this formation including e.g. *in-situ* SAXS and cryo-TEM would further increase the understanding of the formation of this material, and hence give more opportunities for further manipulation of its structure.

9.2 Mesoporous films

Regarding the films presented in Paper VII, there are still many things to be done. Firstly, the packing of platelets on the surface should be improved. This can most probably be done by adjustments of the solvent, the prehydrolysis time of TEOS and altering the functional groups on the platelets.

After improving the packing of the particles, other type of platelet materials will be synthesized, e.g. with TIPB as a swelling agent to reach the >20 nm large pores, and the above discussed P104 particles, post grafted on the substrate. If this is successful, it will be possible to synthesize films with perpendicular pores in the size range of 5-21 nm and wall thicknesses of 2-5 nm.

Finally, studies of other possible substrates should be performed in order to increase the applicability of the films.

9.3 Applications

The separated particles presented in Paper IV and Paper V are already in use for drug delivery studies [67], and for enzyme immobilization [228], and this work should be ongoing. Furthermore, the catalytic performance of fibers and rods are tested, and doping experiments of the rods in combination with nanoparticle growth in the pores are currently performed for their use in methanol conversion.

The films with parallel pores are potential candidates for catalyst hosts and also nanoparticle templates, while the films with perpendicular pores are interesting in applications such as solar cells, templates, and nanobatteries, where rods or tubes of different materials can be grown.

10 BIBLIOGRAPHY

- [1] J. Rouquerol, D. Avnir, C.W. Fairbridge, D.H. Everett, J.M. Haynes, N. Pernicone, J.D. Ramsay, K.S.W. Sing, K.K. Unger, *Pure and Applied Chemistry*. 66 (1994) 1739-1758.
- [2] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquérol, T. Siemieniewska, *Pure and Applied Chemistry*. 57 (1985) 603-619.
- [3] K. Ishizaki, S. Komarneni, M. Nanko, *Porous Materials : Process Technology and Applications*, Kluwer Academic Publishers, Dordrecht ;Boston, 1998.
- [4] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature*. 359 (1992) 710-712.
- [5] P. Yang, D. Zhao, D.I. Margolese, B.F. Chmelka, G.D. Stucky, *Nature*. 396 (1998) 152-155.
- [6] F. Jiao, P.G. Bruce, *Angewandte Chemie International Edition*. 43 (2004) 5958-5961.
- [7] S. Jun, S.H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, *Journal of the American Chemical Society*. 122 (2000) 10712-10713.
- [8] R. Ryoo, S.H. Joo, M. Kruk, M. Jaroniec, *Advanced Materials*. 13 (2001) 677-681.
- [9] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T. Chu, D.H. Olson, E.W. Sheppard, C.T. McCullen, J.B. Higgins, J.L. Schlenker, *Journal of the American Chemical Society*. 114 (1992) 10834-10843.
- [10] D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, G.D. Stucky, *Journal of the American Chemical Society*. 120 (1998) 6024-6036.
- [11] I. Kartini, P. Meredith, J.C. Diniz da Costa, J.D. Riches, G.Q.M. Lu, *Current Applied Physics*. 4 (2004) 160-162.

- [12] S.H. Joo, S.J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, *Nature*. 412 (2001) 169-172.
- [13] M. Kruk, M. Jaroniec, T. Kim, R. Ryoo, *Chemistry of Materials*. 15 (2003) 2815-2823.
- [14] V. Chiola, J.E. Ritsko, C.D. Vanderpool, 3556725 (1971).
- [15] F. Di Renzo, H. Cambon, R. Dutartre, *Microporous Materials*. 10 (1997) 283-286.
- [16] S.A. Bagshaw, E. Prouzet, T.J. Pinnavaia, *Science*. 269 (1995) 1242-1244.
- [17] R. Ryoo, J.M. Kim, C.H. Ko, C.H. Shin, *The Journal of Physical Chemistry*. 100 (1996) 17718-17721.
- [18] C. Yu, Y. Yu, D. Zhao, *Chemical Communications*. (2000) 575-576.
- [19] S. Che, A.E. Garcia-Bennett, T. Yokoi, K. Sakamoto, H. Kunieda, O. Terasaki, T. Tatsumi, *Nature Materials*. 2 (2003) 801-805.
- [20] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science*. 279 (1998) 548-552.
- [21] L. Cao, T. Man, M. Kruk, *Chemistry of Materials*. 21 (2009) 1144-1153.
- [22] L. Cao, M. Kruk, *Colloids and Surfaces A*. 357 (2010) 91-96.
- [23] H. Zhang, J. Sun, D. Ma, X. Bao, A. Klein-Hoffman, G. Weinberg, D. Su, R. Schlogl, *Journal of the American Chemical Society*. 126 (2004) 7440-7441.
- [24] J. Sun, H. Zhang, R. Tian, M. Ding, X. Bao, D.S. Su, H. Zou, *Chemical Communications* (2006) 1322-1324.
- [25] Y. Ding, G. Yin, X. Liao, Z. Huang, X. Chen, Y. Yao, J. Li, *Microporous and Mesoporous Materials*. 170 (2013) 45-51.
- [26] G. Prieto, A. Martínez, R. Murciano, M.A. Arribas, *Applied Catalysis A*. 367 (2009) 146-156.
- [27] M. Impérator-Clerc, P. Davidson, A. Davidson, *Journal of the American Chemical Society*. 122 (2000) 11925-11933.

- [28] R. Ryoo, C.H. Ko, M. Kruk, V. Antochshuk, M. Jaroniec, *The Journal of Physical Chemistry B*. 104 (2000) 11465-11471.
- [29] M. Kruk, M. Jaroniec, C.H. Ko, R. Ryoo, *Chemistry of Materials*. 12 (2000) 1961-1968.
- [30] S. Ruthstein, V. Frydman, S. Kababya, M. Landau, D. Goldfarb, *The Journal of Physical Chemistry B*. 107 (2003) 1739-1748.
- [31] C. Göltner-Spickermann, *Current Opinion in Colloid and Interface Science*. 7 (2002) 173-178.
- [32] L. Vradman, L. Titelman, M. Herskowitz, *Microporous and Mesoporous Materials*. 93 (2006) 313-317.
- [33] A.-H. Lu, W.-C. Li, W. Schmidt, W. Kiefer, F. Schüth, *Carbon*. 42 (2004) 2939-2948.
- [34] A.B. Fuertes, D.M. Nevskaya, *Journal of Materials Chemistry*. 13 (2003) 1843-1846.
- [35] M. Tiemann, *Chemistry of Materials*. 20 (2008) 961-971.
- [36] M. Armandi, B. Bonelli, E.I. Karaindrou, C.O. Areán, E. Garrone, *Catalysis Today*. 138 (2008) 244-248.
- [37] H. Zhou, S. Zhu, I. Honma, K. Seki, *Chemical Physics Letters*. 396 (2004) 252-255.
- [38] J.C. Ndamaniha, L. Guo, *Analytica Chimica Acta*. 747 (2012) 19-28.
- [39] G. Satishkumar, L. Titelman, M.V. Landau, *Journal of Solid State Chemistry*. 182 (2009) 2822-2828.
- [40] W. Yue, W. Zhou, *Progress in Natural Science*. 18 (2008) 1329-1338.
- [41] A. Taguchi, F. Schüth, *Microporous and Mesoporous Materials*. 77 (2005) 1-45.
- [42] S.K. Das, M.K. Bhunia, A. Bhaumik, *Journal of Solid State Chemistry*. 183 (2010) 1326-1333.

- [43] W.A. Adams, M.G. Bakker, T. MacÍas, I.A. Jefcoat, *Journal of Hazardous Materials*. 112 (2004) 253-259.
- [44] L. Chen, B. Yao, Y. Cao, K. Fan, *The Journal of Physical Chemistry C*. 111 (2007) 11849-11853.
- [45] P.E. Boahene, K.K. Soni, A.K. Dalai, J. Adjaye, *Applied Catalysis A*. 402 (2011) 31-40.
- [46] A. Szegedi, M. Popova, I. Goshev, J. Mihály, *Journal of Solid State Chemistry*. 184 (2011) 1201-1207.
- [47] C. McManamon, A.M. Burke, J.D. Holmes, M.A. Morris, *Journal of Colloid and Interface Science*. 369 (2012) 330-337.
- [48] S. Chen, C. Huang, T. Yokoi, C. Tang, S. Huang, J. Lee, J.C.C. Chan, T. Tatsumi, S. Cheng, *Journal of Materials Chemistry*. 22 (2012) 2233-2243.
- [49] J.S. Lee, J. Yim, J. Jeon, Y.S. Ko, *Catalysis Today*. 185 (2012) 175-182.
- [50] H. Wang, X. Gao, Y. Wang, J. Wang, X. Niu, X. Deng, *Ceramics International*. 38 (2012) 6931-6935.
- [51] D. Margolese, J.A. Melero, S.C. Christiansen, B.F. Chmelka, G.D. Stucky, *Chemistry of Materials*. 12 (2000) 2448-2459.
- [52] R. van Grieken, J.A. Melero, G. Morales, in: G.G.a.F.T. R. Aiello (Ed.), *Studies in Surface Science and Catalysis*, Elsevier, 2002, pp. 1181-1188.
- [53] L.M. Yang, Y.J. Wang, G.S. Luo, Y.Y. Dai, *Microporous and Mesoporous Materials*. 84 (2005) 275-282.
- [54] I.I.I. Slowing, *Advanced Drug Delivery Reviews*. 60 (2008) 1278-1288.
- [55] J.M. Rosenholm, C. Sahlgren, M. Lindén, *Nanoscale*. 2 (2010) 1870-1883.
- [56] V. Mamaeva, C. Sahlgren, M. Lindén, *Advanced Drug Delivery Reviews*. Rev. 65 (2013) 689-702.
- [57] W. Xu, J. Riikonen, V. Lehto, *International Journal of Pharmaceutics*. 453 (2013) 181-197.

- [58] D. Arcos, M. Vallet-Regí, *Acta Materialia*. 61 (2013) 890-911.
- [59] A.L. Doadrio, E.M.B. Sousa, J.C. Doadrio, J. Pérez Pariente, I. Izquierdo-Barba, M. Vallet-Regí, *Journal of Controlled Release*. 97 (2004) 125-132.
- [60] L.B. Fagundes, T.G.F. Sousa, A. Sousa, V.V. Silva, E.M.B. Sousa, *Journal of Non-Crystalline Solids*. 352 (2006) 3496-3501.
- [61] D. Molina-Manso, M. Manzano, J.C. Doadrio, G. Del Prado, A. Ortiz-Pérez, M. Vallet-Regí, E. Gómez-Barrena, J. Esteban, *International Journal of Antimicrobial Agents*. 40 (2012) 252-256.
- [62] M. Moritz, M. Łaniecki, *Powder Technology*. 230 (2012) 106-111.
- [63] F. Qu, G. Zhu, S. Huang, S. Li, J. Sun, D. Zhang, S. Qiu, *Microporous and Mesoporous Materials*. 92 (2006) 1-9.
- [64] S. Zhu, Z. Zhou, D. Zhang, C. Jin, Z. Li, *Microporous and Mesoporous Materials*. 106 (2007) 56-61.
- [65] J.M. Rosenholm, V. Mamaeva, C. Sahlgren, M. LindÅn, *Nanomedicine*. 7 (2012) 111-120.
- [66] V. Cauda, L. Mühlstein, B. Onida, T. Bein, *Microporous and Mesoporous Materials*. 118 (2009) 435-442.
- [67] D. Sen Karaman, D. Desai, R. Senthilkumar, E. Johansson, N. Ratts, M. Oden, J. Eriksson, C. Sahlgren, D. Toivola, J. Rosenholm, *Nanoscale Research Letters*. 7 (2012) 358.
- [68] Y.-X. Jiang, Z.-F. Chen, Q.-C. Zhuang, J.-M. Xu, Q.-F. Dong, L. Huang, S.-G. Sun, *Journal of Power Sources*. 160 (2006) 1320-1328.
- [69] J. Procházka, L. Kavan, M. Zukalova, O. Frank, M. Kalbác, A. Zukal, M. Klementova, D. Carbone, M. Graetzel, *Chemistry of Materials*. 21 (2009) 1457-1464.
- [70] J. Xi, X. Qiu, X. Ma, M. Cui, J. Yang, X. Tang, W. Zhu, L. Chen, *Solid State Ionics*. 176 (2005) 1249-1260.

- [71] H. Ding, H. Sun, Y. Shan, *Journal of Photochemistry and Photobiology A*. 169 (2005) 101-107.
- [72] F. Xia, E. Ou, L. Wang, J. Wang, *Dyes and Pigments*. 76 (2008) 76-81.
- [73] H. Lachheb, O. Ahmed, A. Houas, J.P. Nogier, *Journal of Photochemistry and Photobiology A*. 226 (2011) 1-8.
- [74] C. Yang, Y.R. Zheng, *J. Power Sources*. 201 (2012) 387-394.
- [75] D.F. Evans, H. Wennerström, *The Colloidal Domain: Where Physics, Chemistry, Biology and Technology Meet*, 2nd ed., Wiley-VCH, New York, 1999.
- [76] B. Jönsson, B. Lindman, K. Holmberg, B. Kronberg, *Surfactants and Polymers in Aqueous Solution*, 2: nd ed., John Wiley & Sons, West Sussex, England, 1998.
- [77] I.R. Schmolka, (1973).
- [78] P. Alexandridis, J.F. Holzwarth, T.A. Hatton, *Macromolecules*. 27 (1994) 2414-2425.
- [79] E.B. Jorgensen, S. Hvidt, W. Brown, K. Schillen, *Macromolecules*. 30 (1997) 2355-2364.
- [80] G. Wanka, H. Hoffmann, W. Ulbricht, *Macromolecules*. 27 (1994) 4145-4159.
- [81] A.G. Denkova, E. Mendes, M.-O. Coppens, *The Journal of Physical Chemistry B*. 112 (2008) 793-801.
- [82] H. Heerklotz, A. Tsamaloukas, K. Kita-Tokarczyk, P. Strunz, T. Gutberlet, *Journal of the American Chemical Society*. 126 (2004) 16544-16552.
- [83] C. Guo, H.-Z. Liu, J.-Y. Chen, *Colloid & Polymer Science*. 277 (1999) 376-381.
- [84] Z. Zhou, B. Chu, *Journal of Colloid and Interface Science*. 126 (1988) 171-180.
- [85] K. Mortensen, W. Brown, *Macromolecules*. 26 (1993) 4128-4135.
- [86] Y. Su, J. Wang, H. Liu, *The Journal of Physical Chemistry B*. 106 (2002) 11823-11828.

- [87] R.M. Pashley, M.E. Karaman, *Applied Colloid and Surface Chemistry*, Wiley, West Sussex, 2004.
- [88] N.P. Shusharina, S. Balijepalli, H.J.M. Gruenbauer, P. Alexandridis, *Langmuir*. 19 (2003) 4483.
- [89] C. Yu, B. Tian, J. Fan, G.D. Stucky, D. Zhao, *Chemical Communications*. (2001) 2726-2727.
- [90] J. Sun, H. Zhang, M. Ding, Y. Chen, X. Bao, A. Klein-Hoffman, N. Pfänder, D.S. Su, *Chemical Communications*. (2005) 5343-5345.
- [91] H. Zhang, J. Sun, D. Ma, G. Weinberg, D.S. Su, X. Bao, *The Journal of Physical Chemistry B*. 110 (2006) 25908-25915.
- [92] J. Sun, M. Ding, H. Zhang, C. Wang, X. Bao, D.S. Su, A. Klein-Hoffman, G. Weinberg, S. Mann, *Journal of Materials Chemistry*. 16 (2006) 1507-1510.
- [93] M. Kruk, *Accounts of Chemical Research*. 45 (2012) 1678-1687.
- [94] E. Hecht, H. Hoffmann, *Colloids and Surfaces A*. 96 (1995) 181-197.
- [95] P. Alexandridis, J.F. Holzwarth, *Langmuir*. 13 (1997) 6074-6082.
- [96] W.A. Luck, *Topics in Current Chemistry*. 64 (1976) 113-180.
- [97] K.D. Collins, M.W. Washabaugh, *Quarterly Reviews of Biophysics*. 18 (1985) 323.
- [98] E. Florin, R. Kjellander, J.C. Eriksson, *Journal of the Chemical Society, Faraday Transactions*. 1. 80 (1984) 2889.
- [99] P. Thiyagarajan, D.J. Chaiko, R.P. Hjelm, *Macromolecules*. 28 (1995) 7730-7736.
- [100] R. Kjellander, E. Florin, *Journal of the Chemical Society, Faraday Transactions*. 1. 77 (1981) 2053.
- [101] N.J. Jain, V.K. Aswal, P.S. Goyal, P. Bahadur, *Colloids and Surfaces A* 173 (2000) 85-94.

- [102] S. Manet, J. Schmitt, M. Imprator-Clerc, V. Zholobenko, D. Durand, C.L.P. Oliveira, J.S. Pedersen, C. Gervais, N. Baccile, F. Babonneau, I. Grillo, F. Meneau, C. Rochas, *The Journal of Physical Chemistry B*. 115 (2011) 11330-11344.
- [103] S. Manet, A. Lecchi, M. Imprator-Clerc, V. Zholobenko, D. Durand, C.L.P. Oliveira, J.S. Pedersen, I. Grillo, F. Meneau, C. Rochas *The Journal of Physical Chemistry B*. 115 (2011) 11318-11329.
- [104] K. Kang, H. Rhee, *Microporous and Mesoporous Materials*. 84 (2005) 34-40.
- [105] P. Linton, A.R. Rennie, V. Alfredsson, *Solid State Sciences*. 13 (2011) 793-799.
- [106] J.M. Kim, G.D. Stucky, *Chemical Communications*. (2000) 1159-1160.
- [107] P.F. Fulvio, S. Pikus, M. Jaroniec, *Journal of Colloid and Interface Science*. 287 (2005) 717-720.
- [108] J. Liu, Q. Yang, X.S. Zhao, L. Zhang, *Microporous and Mesoporous Materials*. 106 (2007) 62-67.
- [109] C.J. Brinker, *Journal of Non-Crystalline Solids*. 100 (1988) 31-50.
- [110] L.L. Hench, J.K. West, *Chemical Reviews*. 90 (1990) 33-72.
- [111] R. Aelion, A. Loebel, F. Eirich, *Journal of the American Chemical Society*. 72 (1950) 5705-5712.
- [112] T.N.M. Bernards, M.J. van Bommel, A.H. Boonstra, *Journal of Non-Crystalline Solids*. 134 (1991) 1-13.
- [113] A.H. Boonstra, T.N.M. Bernards, *Journal of Non-Crystalline Solids*. 105 (1988) 207-213.
- [114] A.H. Boonstra, J.M.E. Baken, *Journal of Non-Crystalline Solids*. 122 (1990) 171-182.
- [115] C.J. Brinker, K.D. Keefer, D.W. Schaefer, C.S. Ashley, *Journal of Non-Crystalline Solids*. 48 (1982) 47-64.

- [116] C. Boissiere, d.L. van, A. El Mansouri, A. Larbot, E. Prouzet, *Chemical Communications*. (1999) 2047-2048.
- [117] C. Boissière, M.A.U. Martines, M. Tokumoto, A. Larbot, E. Prouzet, *Chemistry of Materials*. 15 (2003) 509-515.
- [118] D.Y. Nadargi, R.R. Kalesh, A.V. Rao, *Journal of Alloys and Compounds*. 480 (2009) 689-695.
- [119] E.M. Rabinovich, K. Nassau, A.E. Miller, P.K. Gallagher, *Journal of Non-Crystalline Solids*. 104 (1988) 107-111.
- [120] R.K. Iler, *The Chemistry of Silica*, Wiley, New York, 1979.
- [121] S. Ruthstein, V. Frydman, D. Goldfarb, *The Journal of Physical Chemistry B*. 108 (2004) 9016-9022.
- [122] A.Y. Khodakov, V.L. Zholobenko, M. Impéror-Clerc, D. Durand, *The Journal of Physical Chemistry B*. 109 (2005) 22780-22790.
- [123] S. Ruthstein, J. Schmidt, E. Kesselman, Y. Telmon, D. Goldfarb, *Journal of the American Chemical Society*. 128 (2006) 3366-3374.
- [124] M. Imperor-Clerc, I. Grillo, A.Y. Khodakov, D. Durand, V.L. Zholobenko, *Chemical Communications*. 0 (2007) 834-836.
- [125] V.L. Zholobenko, A.Y. Khodakov, M. Impéror-Clerc, D. Durand, I. Grillo, *Advances in Colloid and Interface Science*. 142 (2008) 67-74.
- [126] J.L. Blin, M. Imperor-Clerc, *Chemical Society Reviews*. 42 (2013) 4071-4082.
- [127] A. Sundblom, C.L.P. Oliveira, A.E.C. Palmqvist, J.S. Pedersen, *The Journal of Physical Chemistry C*. 113 (2009) 7706-7713.
- [128] A. Sundblom, C.L.P. Oliveira, J.S. Pedersen, A.E.C. Palmqvist, *The Journal of Physical Chemistry C*. 114 (2010) 3483-3492.
- [129] N. Gov, I. Borukhov, D. Goldfarb, *Langmuir*. 22 (2006) 605-614.

- [130] J.S. Lettow, Y.J. Han, P. Schmidt-Winkel, P. Yang, D. Zhao, G.D. Stucky, J.Y. Ying, *Langmuir*. 16 (2000) 8291-8295.
- [131] C.V. Teixeira, H. Amenitsch, P. Linton, M. Linden, V. Alfredsson, *Langmuir*. 27 (2011) 7121-7131.
- [132] P. Linton, A.R. Rennie, M. Zackrisson, V. Alfredsson, *Langmuir*. 25 (2009) 4685-4691.
- [133] T. Benamor, L. Vidal, B. Lebeau, C. Marichal, *Microporous and Mesoporous Materials*. 153 (2012) 100-114.
- [134] S. Pikus, E.B. Celer, M. Jaroniec, L.A. Solovyov, M. Kozak, *Applied Surface Science*. 256 (2010) 5311-5315.
- [135] M. Kruk, M. Jaroniec, S.H. Joo, R. Ryoo, *The Journal of Physical Chemistry B*. 107 (2003) 2205-2213.
- [136] R. Che, D. Gu, L. Shi, D. Zhao, *Journal of Materials Chemistry*. 21 (2011) 17371-17381.
- [137] C. Yu, J. Fan, B. Tian, D. Zhao, G.D. Stucky, *Advanced Materials*. 14 (2002) 1742.
- [138] M. Choi, W. Heo, F. Kleitz, R. Ryoo, *Chemical Communications*. (2003) 1340-1341.
- [139] X. Cui, S. Moon, W. Zin, *Materials Letters*. 60 (2006) 3857-3860.
- [140] Y. Fahn, A. Su, P. Shen, *Langmuir*. 21 (2005) 431-436.
- [141] Y. Wang, F. Zhang, Y. Wang, J. Ren, C. Li, X. Liu, Y. Guo, Y. Guo, G. Lu, *Materials Chemistry and Physics*. 115 (2009) 649-655.
- [142] R. Nagarajan, *Polymers for Advanced Technologies*. 12 (2001) 23-43.
- [143] Y. Zhao, J. Zhang, W. Li, C. Zhang, B. Han, *Chemical Communications*. (2009) 2365-2367.
- [144] A. Katiyar, S. Yadav, P.G. Smirniotis, N.G. Pinto, *Journal of Chromatography A*. 1122 (2006) 13-20.

- [145] Y. Ma, L. Qi, J. Ma, Y. Wu, O. Liu, H. Cheng, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 229 (2003) 1-8.
- [146] W.J.J. Stevens, K. Lebeau, M. Mertens, G. VanTendeloo, P. Cool, E.F. Vansant, *The Journal of Physical Chemistry B*. 110 (2006) 9183-9187.
- [147] K. Kosuge, P.S. Singh, *Chemistry of Materials*. 13 (2001) 2476-2482.
- [148] A. Sayari, B. Han, Y. Yang, *Journal of the American Chemical Society*. 126 (2004) 14348-14349.
- [149] K. Kosuge, T. Sato, N. Kikukawa, M. Takemori, *Chemistry of Materials*. 16 (2004) 899-905.
- [150] N. Yu, Y. Gong, D. Wu, Y. Sun, Q. Luo, W. Liu, F. Deng, *Microporous and Mesoporous Materials*. 72 (2004) 25-32.
- [151] X. Bao, X.S. Zhao, X. Li, J. Li, *Applied Surface Science*. 237 (2004) 380-386.
- [152] X.Y. Bao, X.S. Zhao, X. Li, P.A. Chia, J. Li, *The Journal of Physical Chemistry B*. 108 (2004) 4684-4689.
- [153] Y. Ding, G. Yin, X. Liao, Z. Huang, X. Chen, Y. Yao, *Materials Letters*. 75 (2012) 45-47.
- [154] P. Linton, V. Alfredsson, *Chemistry of Materials*. 20 (2008) 2878-2880.
- [155] P. Linton, J.-C. Hernandez-Garrido, P.A. Midgley, H. Wennerström, V. Alfredsson, *Physical Chemistry Chemical Physics*. 11 (2009) 10973.
- [156] P. Linton, H. Wennerstrom, V. Alfredsson, *Physical Chemistry Chemical Physics*. 12 (2010) 3852-3858.
- [157] S. Chen, C. Tang, W. Chuang, J. Lee, Y. Tsai, J.C.C. Chan, C. Lin, Y. Liu, S. Cheng, *Chemistry of Materials*. 20 (2008) 3906-3916.
- [158] L. Cao, M. Kruk, *Journal of Colloid and Interface Science*. 361 (2011) 472-476.
- [159] M. Chao, D. Wang, H. Lin, C. Mou, *Journal of Materials Chemistry*. 13 (2003) 2853-2854.

- [160] P. Schmidt-Winkel, J. Lukens W.W., D. Zhao, P. Yang, B.F. Chmelka, G.D. Stucky, *Journal of the American Chemical Society*. 121 (1999) 254-255.
- [161] N. Calin, A. Galarneau, T. Cacciaguerra, R. Denoyel, F. Fajula, *Comptes Rendus Chimie*. 13 (2010) 199-206.
- [162] H. Jaladi, A. Katiyar, S.W. Thiel, V.V. Guliants, N.G. Pinto, *Chemical Engineering Science*. 64 (2009) 1474-1479.
- [163] Y. Wang, M. Noguchi, Y. Takahashi, Y. Ohtsuka, *Catalysis Today*. 68 (2001) 3-9.
- [164] J.C. Park, J.H. Lee, P. Kim, J. Yi, in: Sang-Eon Park, Ryong Ryoo, Wha-Seung Ahn, Chul Wee Lee and Jong-San Chang (Ed.), *Studies in Surface Science and Catalysis*, Elsevier, 2003, pp. 109-112.
- [165] X. Cui, J. Ahn, W. Zin, W. Cho, C. Ha, in: Sang-Eon Park, Ryong Ryoo, Wha-Seung Ahn, Chul Wee Lee and Jong-San Chang (Ed.), *Studies in Surface Science and Catalysis*, Elsevier, 2003, pp. 117-120.
- [166] S.K. Jana, R. Nishida, K. Shindo, T. Kugita, S. Namba, *Microporous and Mesoporous Materials*. 68 (2004) 133-142.
- [167] M. Kruk, L. Cao, *Langmuir*. 23 (2007) 7247-7254.
- [168] T. Yamada, H. Zhou, K. Asai, I. Honma, *Materials Letters*. 56 (2002) 93-96.
- [169] T. Klimova, A. Esquivel, J. Reyes, M. Rubio, X. Bokhimi, J. Aracil, *Microporous and Mesoporous Materials*. 93 (2006) 331-343.
- [170] Z. Jin, X. Wand, X. Cui, *Colloids and Surfaces A*. 316 (2008) 27-36.
- [171] S. Kubo, K. Kosuge, *Langmuir*. 23 (2007) 11761-11768.
- [172] B.L. Newalkar, N.V. Choudary, U.T. Turaga, R.P. Vijayalakshmi, P. Kumar, S. Komarneni, T.S.G. Bhat, *Chemistry of Materials*. 15 (2003) 1474-1479.
- [173] W. Zhang, L. Zhang, J. Xiu, Z. Shen, Y. Li, P. Ying, C. Li, *Microporous and Mesoporous Materials*. 89 (2006) 179-185.

- [174] P.F. Fulvio, S. Pikus, M. Jaroniec, *Journal of Materials Chemistry*. 15 (2005) 5049-5053.
- [175] J. Liu, C. Li, Q. Yang, J. Yang, C. Li, *Langmuir*. 23 (2007) 7255-7262.
- [176] F. Zhang, Y. Yan, H. Yang, Y. Meng, C. Yu, B. Tu, D. Zhao, *Journal of Physical Chemistry B*. 109 (2005) 8723-8732.
- [177] M. Mandal, M. Kruk, *Chemistry of Materials*. 24 (2012) 149-154.
- [178] M. Kruk, C.M. Hui, *Journal of the American Chemical Society*. 130 (2008) 1528-1529.
- [179] K. Yu, B. Smarsly, C.J. Brinker, *Advanced Functional Materials*. 13 (2003) 47-52.
- [180] N. Reichhardt, T. Kjellman, M. Sakey, F. Paulsen, J. Smatt, M. Linden, V. Alfredsson, *Chemistry of Materials*. 23 (2011) 3400-3403.
- [181] P. Van Der Voort, P.I. Ravikovitch, K.P. De Jong, M. Benjelloun, E. Van Bavel, A.H. Janssen, A.V. Neimark, B.M. Weckhuysen, E.F. Vansant, *The Journal of Physical Chemistry B*. 106 (2002) 5873-5877.
- [182] N. Brodie-Linder, G. Dosseh, C. Alba-Simonesco, F. Audonnet, M. Impéror-Clerc, *Materials Chemistry and Physics*. 108 (2008) 73-81.
- [183] P.C.A. Alberius, K.L. Frindell, R.C. Hayward, E.J. Kramer, G.D. Stucky, B.F. Chmelka, *Chemistry of Materials*. 14 (2002) 3284-3294.
- [184] K.C.-W. Wu, X. Jiang, Y. Yamauchi, *Journal of Materials Chemistry*. 21 (2011) 8934-8939.
- [185] S. Song, Y. Liang, Z. Li, Y. Wang, R. Fu, D. Wu, P. Tsiakaras, *Applied Catalysis B*. 98 (2010) 132-137.
- [186] D. Grosso, A.R. Balkenende, P.A. Albouy, A. Ayral, H. Amenitsch, F. Babonneau, *Chemistry of Materials*. 13 (2001) 1848-1856.
- [187] D. Grosso, F. Babonneau, P. Albouy, H. Amenitsch, A.R. Balkenende, A. Brunet-Bruneau, J. Rivory, *Chemistry of Materials*. 14 (2002) 931-939.

- [188] D. Grosso, F. Cagnol, G. . . . Soler-Illia, E. . Crepaldi, H. Amenitsch, A. Brunet-Bruneau, A. Bourgeois, C. Sanchez, *Advanced Functional Materials*. 14 (2004) 309-322.
- [189] C.J. Brinker, Y. Lu, A. Sellinger, H. Fan, *Advanced Materials*. 11 (1999) 579-585.
- [190] K. Chao, P. Liu, K. Huang, *Comptes Rendus Chimie*. 8 (2005) 727-739.
- [191] L.C. Huang, E.K. Richman, B.L. Kirsch, S.H. Tolbert, *Microporous and Mesoporous Materials*. 96 (2006) 341-349.
- [192] D.C. Arnold, J.M. O'Callaghan, A. Sexton, J.M. Tobin, H. Amenitsch, J.D. Holmes, M.A. Morris, *Applied Surface Science*. 255 (2009) 9333-9342.
- [193] X. Collard, B.V.d. Schueren, J.C. Rooke, C. Aprile, B. Su, *Journal of Colloid and Interface Science*. 401 (2013) 23-33.
- [194] W. Cho, T. Kim, K. Char, C.L. Soles, *Microporous and Mesoporous Materials*. 131 (2010) 136-140.
- [195] Y. Yamauchi, T. Nagaura, A. Ishikawa, T. Chikyow, S. Inoue, *Journal of the American Chemical Society*. 130 (2008) 10165-10170.
- [196] M. Dutreilh-Colas, M. Yan, P. Labrot, N. Delorme, A. Gibaud, J. Bardeau, *Surface Science*. 602 (2008) 829-833.
- [197] C. Song, G. Villemure, *Microporous and Mesoporous Materials*. 44-45 (2001) 679-689.
- [198] D. Zhao, P. Yang, N. Melosh, J. Feng, B.F. Chmelka, G.D. Stucky, *Advanced Materials*. 10 (1998) 1380-1385.
- [199] M. Etienne, A. Quach, D. Grosso, L. Nicole, C. Sanchez, A. Walcarius, *Chemistry of Materials*. 19 (2007) 844-856.
- [200] C. Sanchez, C. Boissiere, D. Grosso, C. Laberty, L. Nicole, *Chemistry of Materials*. 20 (2008) 682-737.
- [201] A. Walcarius, E. Sibottier, M. Etienne, J. Ghanbaja, *Nature Materials*. 6 (2007) 602-608.

- [202] M. Etienne, S. Sallard, M. Schröder, Y. Guillemin, S. Mascotto, B.M. Smarsly, A. Walcarius, *Chemistry of Materials*. 22 (2010) 3426-3432.
- [203] A. Goux, M. Etienne, E. Aubert, C. Lecomte, J. Ghanbaja, A. Walcarius, *Chemistry of Materials*. 21 (2009) 731-741.
- [204] Y. Guillemin, M. Etienne, E. Aubert, A. Walcarius, *Journal of Materials Chemistry*. 20 (2010) 6799-6807.
- [205] M. Etienne, A. Goux, E. Sibottier, A. Walcarius, *Journal of Nanoscience and Nanotechnology*. 9 (2009) 2398-2406.
- [206] C. Thörn, H. Gustafsson, L. Olsson, *Microporous and Mesoporous Materials*. 176 (2013) 71-77.
- [207] R. Pitchumani, W. Li, M. Coppens, in: Abdelhamid Sayari and Mietek Jaroniec (Ed.), *Studies in Surface Science and Catalysis*, Elsevier, 2005, pp. 83-88.
- [208] R. Pitchumani, W. Li, M. Coppens, *Catalysis Today*. 105 (2005) 618-622.
- [209] B. Chen, H. Lin, M. Chao, C. Mou, C. Tang, *Advanced Materials*. 16 (2004) 1657-1661.
- [210] S. Brunauer, P.H. Emmett, T. Teller, *Journal of the American Chemical Society*. 60 (1938) 309-319.
- [211] I. Langmuir, *Journal of the American Chemical Society*. 38 (1916) 2221-2295.
- [212] J. Rouquerol, F. Rouquerol, K.S.W. Sing, *Adsorption by Powders and Porous Solids - Principles, Methodology and Applications*, Academic Press, San Diego, 1999.
- [213] M. Jaroniec, M. Kruk, J.P. Olivier, *Langmuir*. 15 (1999) 5410-5413.
- [214] B.C. Lippens, B.G. Linsen, J.H.d. Boer, *Journal of Catalysis*. 3 (1964) 32-37.
- [215] G. Halsey, *Journal of Chemical Physics*. 16 (1948) 931-937.
- [216] W.D. Harkins, G. Jura, *Journal of the American Chemical Society*. 66 (1944) 1366-1373.

- [217] E.P. Barrett, L.G. Joyner, P.P. Halenda, *Journal of the American Chemical Society*. 73 (1951) 373-380.
- [218] J.C.P. Broekhoff, J.H. De Boer, *Journal of Catalysis*. 9 (1967) 15-27.
- [219] J.C.P. Broekhoff, J.H. de Boer, *Journal of Catalysis*. 9 (1967) 8-14.
- [220] J.C.P. Broekhoff, J.H. De Boer, *Journal of Catalysis*. 10 (1968) 153-165.
- [221] M. Kruk, M. Jaroniec, A. Sayari, *Langmuir*. 13 (1997) 6267-6273.
- [222] M. Jaroniec, L.A. Solocycoc, *Langmuir*. 22 (2006) 6757-6760.
- [223] P.I. Ravikovitch, A.V. Neimark, *Colloids and Surfaces A*. 187-188 (2001) 11-21.
- [224] A.V. Neimark, P.I. Ravikovitch, *Microporous and Mesoporous Materials*. 44-45 (2001) 697-707.
- [225] P.I. Ravikovitch, A.V. Neimark, *Langmuir*. 18 (2002) 1550-1560.
- [226] S.S. Kim, A. Karkamkar, T.J. Pinnavaia, M. Kruk, M. Jaroniec, *The Journal of Physical Chemistry B*. 105 (2001) 7663-7670.
- [227] R.M. Langford, A.K. Petford-Long, *Journal of Vacuum Science & Technology A*. 19 (2001) 2186-2193.
- [228] H. Gustafsson, E.M. Johansson, A. Barrabino, M. Odén, K. Holmberg, *Colloids and Surfaces B*. 100 (2012) 22-30.

Included Papers

The articles associated with this thesis have been removed for copyright reasons. For more details about these see:

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-99858>