Novel Syntheses, Structures and Functions of Mesoporous Silica Materials

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Abstract

The field of mesoporous silica has been studied for about 20 years but it is still an area attracting a lot of attention. The use of novel templating molecules and several issues related to the synthesis and fine structural details are still poorly understood. These aspects are of special relevance to the theme of this thesis, which includes novel work on three fronts; the synthesis, characterization and applications of mesoporous materials.

The work described in this thesis aims to contribute to the mesoporous field by developing novel methods of mesoporous silica synthesis without relying on surfactant micelles as the templating agent but focusing instead on the stacking arrangement of aromatic molecules such as folic acid. The novel route presented here leads to 2D hexagonal structures with $p6mm$ symmetry possessing high mesoporosity and large surface areas. The versatility of this route at various synthesis temperatures and using hydrothermal treatments has also been investigated.

A novel strategy is also proposed for the synthesis of mesocaged materials with $Pm3n$ symmetry structures. The mechanism relies on the penetration of the neutral propylaminomoiety of a co-structure directing agent into the hydrophobic core of the surfactant micelles. Beside these novel pathways, the effect of hydrothermal treatment (HT) at 100 °C on the 3D cubic $Ia3d$ structure (AMS-6) over a long period of time was also examined, and the results show a phase transformation from a 3D cubic $Ia3d$ to a 2D hexagonal $p6mm$ structure and a return to the 3D cubic $Ia3d$ structure at a later stage in the synthesis. This unexpected result is discussed.

In this work, the detailed structural characterization of mesoporous materials using electron microscopy techniques is an important task. In particular, to extend previous knowledge, the fine structural details of mesocaged materials possessing $Pm3n$ symmetry prepared with various amphiphilic surfactants under acidic and alkaline conditions has been investigated using electron crystallography and sorption studies. The results show subtle fine structural differences with materials prepared under alkaline conditions exhibiting the largest mesocage sizes. The cage and window sizes are primarily determined by the charge density of the surfactant and the thickness of the hydration layer surrounding the surfactant micelles.

The relationship between the mesoporous structure and its function has been investigated by evaluating the rate of release of amphiphilic molecules, used as model molecules, from the internal pore structures of mesoporous materials with different pore geometries. In a similar study, the rate of proton diffusion from a liquid surrounding the mesoporous nanoparticles into the pore system of AMS-$n$ was also assessed. The results show that the diffusion coefficients for the proton absorption process are higher than those for the release of the surfactant template molecules, with more complex 3D mesocaged particles showing the highest diffusion coefficients in both cases.

Finally, the quantity of CO$_2$ adsorption was measured by modifying the internal surfaces of mesocaged material with $n$-propylaminogroups. Results show that the cage-connecting window sizes limit the surface coverage of $n$-propylaminogroups by pore blocking and affect the volume of CO$_2$ adsorption. In addition, at the molecular level, CO$_2$ adsorption shows physisorption or chemisorption depending on the localized distribution of $n$-propylaminogroups, as studied by in-situ infrared spectroscopy.

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Nothing else is necessary but these - *love, sincerity, and patience*.

-Swami Vivekananda

To My Family
List of Papers

This thesis is based on the following Papers, which are referred to in the text by their Roman numerals. Reprints were made with the permission of the respective publishers.

I  Non-Surfactant Supramolecular Templating Synthesis of Ordered Mesoporous Silica  
Rambabu Atluri, Niklas Hedin and Alfonso E. Garcia-Bennett, *Journal of the American Chemical Society*, 2009, 131 (9), 3189-3191.

II  Co-Structure Directing Agent Induced Phase Transformation of Mesoporous Materials  

III  Hydrothermal Phase Transformation of Bicontinuous Cubic Mesoporous Material AMS-6  

IV  Structural Variations in Mesocaged Materials with Cubic $Pm\bar{3}n$ Symmetry  
Rambabu Atluri, Zoltan Bacsik, Niklas Hedin and Alfonso E. Garcia-Bennett, *Microporous and Mesoporous Materials* (Accepted, March 2010)

V  Sustained Release from Mesoporous Nanoparticles: Evaluation of structural properties associated with controlled release rate  

VI  Proton Absorption in as-synthesised Mesoporous Silica Nanoparticles as a Structure-Function Relationship Probing Mechanism  

VII  Temperature-Induced Uptake of CO₂ and Formation of Carbamates in Mesocaged Silica Modified with n-propylamines  
My Contribution to the non-first-author Papers

In all the publications, the materials synthesis and material characterization was performed by me, except for the NMR data presented in all the papers.

**Paper V:**
Synthesis of the materials, XRD, SEM, N2-Isotherms, TGA experiments and partly involved in the writing process.

**Paper VI:**
Synthesis of the materials, XRD, SEM, N2-Isotherms, TGA experiments and partly involved in the writing process.

**Paper VII:**
Synthesis and n-propylamino grafting of the materials, XRD, SEM, N2-Isotherms and TGA experiments and partly involved in the writing process.

Other Relevant publications not included in this thesis:

I. Formation mechanism of Folic Acid-templated Mesoporous Silica Materials  
   Rambabu Atluri, Luis Angel Villaescusa and Alfonso E. Garcia-Bennett *(In Preparation)*

II. Mesoporous silica-based nanomaterials for drug delivery: evaluation of structural properties associated with release rate  
   Maria Strømme, Ulrika Brohede, Rambabu Atluri, and Alfonso E. Garcia-Bennett *Wiley Interdisciplinary Review: Nanomedicine and Nanobiotechnology*. 1, (2009), 140-148.

III. Properties of covalently bonded fluorescent mesoporous AMS-6 nanoparticles  
   Natalia Kupferschmidt, Rambabu Atluri and Alfonso. E. Garcia-Bennett *(In preparation)*
Contents

1. General Introduction........................................................................................................11

2. Aims of the thesis ............................................................................................................12

   3.1 Chemistry of Templating Molecules .....................................................................13
   3.2 Co-Structure Directing Agent (CSDA)...............................................................17
   3.3 Chemistry of Silicates in Acidic and Alkaline Solutions ......................................17
   3.4 Synthesis Mechanisms .........................................................................................18
   3.5 Structural variations ..............................................................................................20
   3.6 Applications of Ordered Mesoporous Materials ....................................................24

4. Experimental...................................................................................................................27
   4.1 Synthesis ...............................................................................................................27
       4.1.1 Synthesis of Nanoporous Folic Acid Materials ............................................27
       4.1.2 Synthesis of AMS-n materials ....................................................................28
       4.1.3 Synthesis of $Pm\bar{3}n$ structures ............................................................29
   4.2 Characterization Techniques ..................................................................................30
       4.2.1 Powder X-Ray Diffraction Analysis (XRD) .................................................30
       4.2.2 Small Angle X-Ray Scattering (SAXS) .......................................................31
       4.2.3 Nitrogen Adsorption/Desorption isotherms .................................................32
       4.2.4 Scanning Electron Microscopy (SEM) .........................................................34
       4.2.5 Transmission Electron Microscopy (TEM) .................................................34
       4.2.6 Thermogravimetric Analysis (TGA) .............................................................36

5. Novel synthesis, Structure and Function of Mesoporous silica Materials .........................37
   5.1 Novel Synthesis Routes and the Effect of Synthesis Parameters .........................37
       5.1.1 Novel Synthesis of Ordered Mesoporous Silica ..........................................37
       5.1.2 Penetration-Induced Synthesis of $Pm\bar{3}n$ Structure ...............................45
       5.1.3 Effect of Hydrothermal Treatment in AMS-6 Synthesis .............................49
   5.2 Structural Variations in $Pm\bar{3}n$ Symmetry Structures .........................................55
   5.3 Structure-Function Relation of Mesoporous Silica Materials ................................62
       5.3.1 Structure-Function Relationship through Diffusion Process ....................62
       5.3.2 CO$_2$ Adsorption in Cage-type Mesoporous Silica Materials ..................65

6. Conclusions ....................................................................................................................69
Abbreviations

2D  2-dimensional
3D  3-dimensional
\( \alpha \)  Unit cell parameter
AMS  Anionic Surfactant-templated Mesoporous Silica
APES  3-Aminopropyltriethoxysilane
BET  Brunauer-Emmett-Teller
BJH  Barrett-Joyner-Halenda
CMC  Critical micelle concentration
\( C_{m-s-1} \)  Divalent quaternary ammonium surfactant of \( m \) carbons within the tail and \( s \) carbon atoms between the ammonium groups (e.g. gemini surfactants)
C\(_{12}\)Ala  N-lauroyl-L-alanine
C\(_{12}\)GluA  N-lauroyl-L-glutamic Acid
C\(_{16}\)TMABr  Cetyltrimethylammonium bromide
C\(_{16}\)TEABr  Cetyltriethylammonium bromide
CSDA  Co-structure Directing Agent
FSM  Folded sheet mesoporous materials
FDU  Fudan University (Shanghai, China)
FA  Folic Acid
FTIR  Fourier Transform Infrared Spectroscopy
\( g \)  Surfactant packing parameter
SEM  Scanning Electron Microscopy
HRTEM  High Resolution Transmission Electron Microscopy
LCT  Liquid crystal template
MAS  Magic angle spinning
MCM  Mobil Composition of Matter
NFM-1  Nanoporous Folic Acid Material-1
NLDFT  Non-local Density Functional Theory
NMR  Nuclear magnetic resonance spectroscopy
P123  Poly (ethylene oxide)-poly (propylene oxide)-poly(ethylene oxide)
SBA  Santa Barbara Amorphous
TEOS  Tetraethyl orthosilicate
TGA  Thermogravimetric Analysis
XRD  X-Ray diffraction
A good cup of coffee cannot be prepared without the use of a filter paper, and hence the filter paper which possesses a specific pore size is an important aspect of brewing good coffee. The pores in the filter paper are on a micrometer (μm) scale. The science of making porous materials of molecular size is industrially important, as these are essential for gas separation, drug delivery, catalysis and other applications of great value to modern society. The development of porous materials with a large internal surface area and controlled pore size has always been a challenge in the field of materials science. A variety of porous materials including zeolites, carbons and amorphous glasses exhibit extremely narrow pore size distributions in the range of 0.5-2 nm and are referred to as microporous solids.\(^1\) These materials possess properties such as high thermal stability and catalytic activity useful in applications such as catalytic cracking processes, as ion exchange media, drying agents and gas separation materials. One of the fast growing classes of microporous solids is metal organic frameworks (MOFs) which involve metal ions and organic bridging ligands.\(^2\) In spite of the large amount of work dedicated to zeolites and related crystalline molecular sieves, the dimensions and accessibility of pores are limited to the sub-nanometer scale due to use of pore templates which are on this length scale. Zeolitic materials are prepared largely through synthesis mechanisms that are not compatible with large pore templates required to form pores on the mesoscale (i.e. 2-50 nm).

Early in the 1990s, the seminal works of Yanagisawa \textit{et al}\(^3\) and Kresge \textit{et al}\(^4,5\) describing respectively so called FSM-\textit{n} and M41S families of mesoporous silicas were published. The former group designed mesoporous silica known as FSM-16 involving the intercalation of long chain cetyltrimethylammonium cations (C\(_n\)TMA) into the layered silicate kanemite (NaHSi\(_2\)O\(_5\). 3H\(_2\)O). The latter group, with the Mobil Corporation, employed a new concept in the synthesis of porous composite materials involving the use of self-assembled surfactant micelles such as cetyltrimethylammonium bromide (C\(_{16}\)TMABr) as the structure-directing agent or pore template. The success of these research groups has generated an intense interest among chemists, biologists, engineers and materials scientists. At first, it was the catalysis community that exploited the industrial applications of these new materials, but today the focus is spreading to areas such as sensors and electronic devices as well as the life sciences.
2. Aims of the thesis

Since the discovery of mesoporous silica, the literature has been overloaded with materials prepared with surfactants as templating agents. The majority of surfactants are however toxic as for example cationic surfactants. Hence, it is important to replace these templates and to find new strategies for the synthesis. An understanding of the fine structural details and structure-function relation of mesoporous silica structures is also essential for the greater selectivity of these materials towards commercial applications. Work described in thesis aims at developing novel synthesis methods and elucidating the fine structural details of a cage type of mesoporous structures.

Specific aims of the work were:

- To study the factors affecting the synthesis of anionic-surfactant-templated mesoporous silica materials, AMS-\(n\) (Paper III).
- To develop a novel synthesis route for a mesoporous material by controlling the synthesis parameters of surfactant-templated materials and to find novel templates other than surfactants (Papers I).
- To investigate the factors which influence the size of the cage and cage-connecting windows with respect to the synthesis conditions and surfactant types and to identify possible synthetic design tools that will allow the control of such fine structural details with a view to using these solids as efficient and selective gas-separation and gas-sequestration materials (Paper II and IV).
- To investigate the potential of mesoporous silica materials as drug carrying vehicles and as adsorbents in relation to their structural complexity (Papers V, VI, and VII).
3. Mesoporous Materials

3.1 Chemistry of Templating Molecules

Amphiphilic surface active agents, surfactants, consist of at least two parts; a hydrophilic (head group) and hydrophobic (tail), and they have been widely used as templates for the preparation of mesoporous structures. The tendency to accumulate at an interface (e.g. water-air, water-oil) is a fundamental property of a surfactant. The driving force is the lowering of the interfacial free energy/interfacial tension of the interphase boundary. Another fundamental characteristic of surfactants is that the surfactant monomers in a solution tend to form aggregates called micelles. The formation of micelles reduces the free energy of the system since the monomers absorb at the interface by rearranging hydrophobic groups in contact with the water. The formation of micelles depends on the concentration of the surfactant in the solution, and the limit at which the micelles start to form is called the critical micellar concentration (CMC). Surfactants in a lyotropic system can form different liquid crystal (LC) phases including isotropic micellar, micellar cubic, hexagonal columnar, bicontinuous cubic, lamellar, and reversed micelle phases depending on the concentration and temperature of the system. A dimensionless packing parameter $g$ was first introduced to explain the aggregation behaviour of amphiphilic molecules in aqueous solutions, $g = \frac{v}{a*l}$, where $a$ is the head group area, $l$ is the hydrophobic chain length and $v$ is the volume of the hydrophobic part of a surfactant molecule. The packing parameter is useful for predicting and explaining the final mesostructure. The expected shape of the LC phase depends on $g$; spherical micelles ($0 \leq g \leq 1/3$), rod-like micelles ($1/3 \leq g \leq 1/2$) and spherical bilayer vesicles ($1/2 \leq g \leq 1$).

Depending on the polarity of the head group, surfactants are classified as anionic, cationic, non-ionic (neutral) and zwitterionic. In addition, a subclass of cationic amphiphilic surfactants called gemini surfactants has attracted much attention with various industrial and academic research groups. These surfactants are more rigid and show special properties such as a low CMC and a high viscosity. A conventional surfactant consists of a linear hydrophobic chain and a polar head group. but, a gemini surfactant possesses two hydrophobic and two polar groups which are separated by a spacer $s$ ($C_{m-s-m}$, where $m$ and $s$ are the hydrophobic chain and spacer length respectively). Another type of gemini surfactant is the family of bolaform surfactants which consist of two polar groups and a single hydrophobic chain.
linked by a spacer ($C_{m-s-1}$). The types of surfactant employed in this thesis and their geometries are shown in Scheme 1. Anionic and cationic surfactants with various degrees of head group area and hydrophobic tails of length 12 and 16 respectively were used. The CMCs of anionic surfactants are 9.7 mM and 6.3 mM for N-lauroyl-L-alanine ($C_{12}\text{Ala}$) and N-lauroyl-L-glutamic acid ($C_{12}\text{GluA}$) respectively at 40 °C. The CMCs of cationic surfactants are 0.91 mM and 0.73 mM for cetyltrimethylammonium bromide ($C_{16}\text{TMABr}$) and cetyltriethylammonium bromide ($C_{16}\text{TEABr}$) at 25 °C respectively. A double head group cationic surfactant ($C_{16-3-1}$) was also employed for the synthesis of cage type structures. In the case of the gemini surfactant (CMC for $C_{12-3-1}$ is 0.03 mM), at least 20 wt% of surfactant concentration is required to form the cubic liquid crystalline phase in aqueous solutions.

In addition to the surfactant liquid crystalline phases, aromatic molecules often form a variety of LC phases. Guanosine, folic acid and their derivates are examples of self-aggregating supramolecular structures. The folic acid molecule consists of a pterin group, a p-aminobenzoyl group and a glutamic acid moiety (Scheme 2(a)). They are analogous to the well-known G-quartet structures formed by guanosine molecules. Folic acid forms liquid crystalline phases of both cholesteric and hexagonal types in water. Surprisingly, folic acid derivatives that have several lipophilic alkyl groups (e.g. 2-(3,4-dialklyoxyphenyl) ethyl groups) also have the ability to self-aggregate and form other phases including cubic $Pm\bar{3}m$. The basic building block for these phases is the pterin tetramer which consists of four pterin groups held together by Hoogsteen-type hydrogen bonds. The carbon at the centre of the glutamic acid possesses (L-isomeric form) chirality and leaves the two carboxylate groups ($\alpha$-COOH and $\gamma$-COOH) on the exterior of the pterin tetramers. The disc shaped (Scheme 2(b)) pterin tetramers (which act as a core) self-aggregate through aromatic interactions, spaced at a distance of 3.2-3.4 Å and form helical columns. There have been speculative discussions in the literature about the arrangement and interaction of these stacks.

![Scheme 1. The molecular structures of various surfactants used in this work.](image-url)
Scheme 2. (a) chemical structure of the folic acid, (b) Hoogsteen-type interactions between pterin groups and they tend to form disc like tetramers which acts as a core of the folic acid stack, (c) π-σ attraction between the pterin and phenyl rings leads to an edge-to-face interaction; where one π-system is offset laterally to the other, (d) the π-electron density obtained by the pterin tetramer and the contribution from the σ framework around the pterin tetramer lead to an extended-core density (sum of π-σ density) and (e) the repeated units (i.e. interaction of π-σ and σ–π between alternating stacks) of the extended cores result in a columnar stacks of finite length.

The pterin group in the folic acid molecule forms a negatively charged π-electron density known as the face and the p-aminobenzoyl group forms a positively charged σ-framework known as the edge. The probability of these
two subunits folding onto each other is negligible, since the folic acid is a linear molecule so that there must be an alternating interaction between the folic acid molecules. Therefore, the interaction between these two subunits of the folic acid is either face-to-face or edge-to-face (so-called T-shaped geometry). It has been shown on the basis of NMR studies that the stacking interactions between the folate tetramers are due to alternating π and σ interactions (edge-to-face) where the π-electron density of the molecule is in orientation with respect to the σ portion of the next alternating molecule. As shown in Scheme 2(c), the π-σ attraction is the dominant interaction, where one π-system is offset laterally to the other, whilst in the face-to-face geometry; π-π electronic repulsion dominates. The overall electron density of a stack comes from the π-electron density obtained from the pterin tetramer while the contribution of the σ framework surrounding the pterin tetramer leads to an extended-core (Scheme 2(d)) of the stack. The glutamic moiety of the folic acid falls outside the extended core and the repeated units of the extended cores result in columnar stacks of finite length (Scheme 2(e)). The length of the columnar stacks can be tailored by introducing cationic species into the folic acid solution, where the cations sandwich between stacks and improve their stability.

Utilizing the LC phases of aromatic molecules as a template for mesoporous material synthesis is interesting, as this may simplify the synthetic pathway and may increase the choice of templates for mesoporous materials. However, careful tailoring of the synthetic chemistry compatible for forming mesoporous silica at various pHs is essential if folic acid is used as a templating agent. As described above, the CMC is the barrier for the surfactants self-assembly, which is a prerequisite for some of the mesoporous synthesis. However, self-aggregation of folic acid occurs even at a low concentration of >0.6 mM by circular dichroism and hence the concentration of folic acid is not really the critical parameter for forming pterin tetramers. The neutral state (above pKa of 8) of the amino group (NH2) on the pterin group is however a prerequisite for forming a hydrogen-bonded (Hoogsteen-type) pterin tetramer, and thereby forming folate stacks. The deprotonation of the carboxylate groups α-COOH (pKa = 3.5) and γ-COOH (pKa = 4.9) is easily achieved above a pH of 5 Therefore, for the synthesis of folic acid - templated mesoporous silica, the pH must be above 8, which can be achieved by using an organoalkoxy silane-based catalyst.

In this work, folic acid has been used as a templating molecule for the first time by taking advantage of the self-aggregation of pterin groups and a cationic amino group of an organoalkoxysilanes as a co-structure directing agent (CSDA). The function of the CSDA is to achieve charge matching between negatively charged carboxylate groups and to facilitate the condensation of the silica species.
3.2 Co-Structure Directing Agent (CSDA)

Previous syntheses using anionic surfactant mesoporous materials have resulted in an amorphous phase,\textsuperscript{26, 27} due to the repulsive interaction under basic conditions and only an attractive interaction under acidic conditions between silicate and anionic species. However, by introducing organoalkoxy silanes with quaternary ammonium groups, an \textit{electrostatic interaction} can be achieved with the anionic surfactant, leading to the formation of the silica framework through co-condensation with the TEOS. Tastsumi \textit{et al}\textsuperscript{28} first employed this concept, using 3-aminopropyltriethoxysilane (APES) as the CSDA and sodium dodecyl sulfate (SDS) as the surfactant. A strong electrostatic interaction between the positively charged propylamino group (-NH\textsubscript{3}\textsuperscript{+}) in APES and the negatively charged surfactant SDS head group (-OSO\textsubscript{3}\textsuperscript{-}) leads to anionic-surfactant-templated mesoporous silica (AMS). However, the structural order of the AMS mesoporous silica was very poor. Che \textit{et al}\textsuperscript{29} extended the synthesis of AMS using a variety of anionic surfactants e.g. N-acyl-L-alanine and an organoalkoxysilane e.g. APES as the CSDA. Their synthetic effort has led to a range of well ordered structures (AMS-\textit{n}) including 2D hexagonal and 3D cubic structures. In addition, the CSDA approach gives a wide distribution of functional organic groups within the silica wall.\textsuperscript{29, 30} In the present work (Section 5.1.3), the effect of synthesis conditions such as hydrothermal treatment on the cubic AMS-6 structure with \textit{Ia}3\textit{d} symmetry was studied. The pKa value of amino groups in APES is close to 10.6 and this property was best utilized, where the neutral state of the propylamino groups at the synthesis pH of 11.2 enables them to penetrate into the hydrophobic core of the micelles and form a \textit{Pm}3\textit{n} structure (Section 5.1.2). Similarly, APES was also used for the synthesis of a folic acid-templated mesoporous silica material (Section 5.1.1).

3.3 Chemistry of Silicates in Acidic and Alkaline Solutions

Since silica precursors polymerize to form an amorphous framework (\textequiv\text{Si-O-Si\textequiv}) around the templating molecules, it is important to understand the characteristics of silica precursors under different conditions and at different pHs. Common silica precursors used for mesoporous silica synthesis are sodium silicate (Na\textsubscript{2}SiO\textsubscript{3}) and alkoxy silanes e.g. tetramethyl orthosilicate TMOS, tetraethyl orthosilicate TEOS, and tetrapropyl orthosilicate TPOS. The rate of hydrolysis decreases with increasing size of the alkoxy group of the silane.\textsuperscript{31} An intermediate ethoxy-substituted silane, TEOS, was employed for the synthesis of all the samples mentioned in this thesis. Polymerization of silica precursors occurs via hydrolysis and condensation reactions; the hydrolysis reaction replaces the alkoxy groups (OR)
with hydroxyl groups (OH) to produce silanol groups (≡Si-OH) and subsequent condensation reactions involving the silanol groups lead to siloxane bonds (≡Si-O-Si≡). The detailed reaction mechanisms under (a) acidic, and (b) basic, conditions are as follows.  

\[(a) \text{ Hydrolysis} \quad \begin{align*} &\text{Fast} \quad \xrightarrow{\text{Fast}} \quad \text{Condensation} \\ &\begin{array}{ll} &\begin{array}{l} \text{Si} - \text{OR} + H^+ \rightarrow \text{Si} - \text{OH} + \text{ROH} + H^+ \\
\end{array} \\
&\begin{array}{l} \text{Si} - \text{OH} + \text{Si} - \text{OR}' + H^- \rightarrow \text{Si} - \text{O} - \text{Si}' + \text{ROH} \\
\end{array} \\
&\end{array} \end{align*} \]

\[(b) \text{ Hydrolysis} \quad \begin{align*} &\text{Slow} \quad \xrightarrow{\text{Slow}} \quad \text{Condensation} \\ &\begin{array}{ll} &\begin{array}{l} \text{Si} - \text{OR} + \text{OH}^- \rightarrow \text{Si} - \text{OH} + \text{OR}^- \\
\end{array} \\
&\begin{array}{l} \text{Si} - \text{OH} \rightarrow \text{Si} - \text{O} + \text{H}_2\text{O} \rightarrow \text{Si} - \text{O} - \text{Si}^- + \text{RO}^- \\
\end{array} \\
&\end{array} \end{align*} \]

The rate of polymerization of alkoxysilanes depends mainly on the pH of the solution. An acid enhances the hydrolysis more than condensation due to the electron-withdrawing capacity of the proton from the silicon making it more electrophilic. However, a basic catalyst increases the condensation rate more than the hydrolysis rate because the hydroxyl ions make the silicon more nucleophilic, and further deprotonate (≡Si-O⁻) the silanol groups. In addition to the strength of the catalyst, the temperature and solvent also affect the polymerization. The extent of the silica hydrolysis and condensation can be evaluated by using ²⁹Si NMR where distinct resonances are observed for the siloxane (Qⁿ) and organo siloxane (Tᵐ) units, where Qⁿ = Si(OSi)ₙ(OH)₄₋ₙ, n=2-4 and Tᵐ =RSi(OSi)ₘ(OH)₃₋ₘ, m =1-3.

### 3.4 Synthesis Mechanisms

The synthesis of a mesoporous material involves the replication of a surfactant liquid crystal structure and the polymerization of a metal oxide precursor. Removal of the organic surfactant through calcination leads to a porous structure supported by a hard silica framework (Scheme 3).

A large number of studies have been carried out to investigate the mechanism of formation of surfactant-templated mesoporous materials. Firstly, scientists in Mobil Corporation proposed two models, namely: ⁵ (i) the liquid crystal templating (LCT) mechanism and (ii) the co-operative mechanism. In the LCT model, surfactants initially form pre-defined lyotropic liquid crystalline phases followed by the migration and polymerization of the inorganic silicate species (Scheme 3). In the co-operative mechanism, surfactants and
silicate species co-assemble to form an organic-inorganic mesostructure. The LCT mechanism is limited by the surfactant concentration, i.e. ordered mesoporous materials should be formed only above the CMC of the particular surfactant. Davis et al.\textsuperscript{35} proposed a new mechanism where the formation of an ordered liquid crystal phase is not a prerequisite for the formation of an ordered mesostructure and different structures can be accessible by various synthesis precursors and conditions, even when the surfactant concentration is below its corresponding CMC.

![Scheme 3. A generalized synthesis route of mesoporous materials, which rely on surfactant LC phases.](image)

Davis et al.\textsuperscript{35} suggested that randomly ordered rod-like organic micelles interact with silicate species to yield two or three monolayers of silica encapsulated around the external surfaces of the micelles. Subsequent polymerization of silicates leads to a hexagonal structure analogous to MCM-41. The co-operative mechanism was further developed by Stucky et al., who proposed a silicatropic liquid crystal (SLC) mechanism.\textsuperscript{36} The SLC mechanism was explained on the basis of (1) ion-exchange between surfactant halide counterions and silicate anions, (2) a true cooperative self-assembly of the silicates and surfactants leading to a liquid-crystal-like mesophase, followed by (3) condensation of the silicate species giving the desired mesoporous structure. In the co-operative templating mechanism,\textsuperscript{36-38} the degree of ionization of the silicate species and its hydrolysis and condensation rates influence the ordering of the surfactant micelles in the solution, directing them towards the desired liquid crystal phase. The key aspect is the interaction between silicate species and surfactants i.e. the matching of charge density. Hence, charge matching is an important parameter for achieving the desired mesostructure.

The formation of phase pure mesoporous structures strongly depends on the synthesis conditions such as temperature, reaction time, pH, solvents, silica/surfactant ratio, hydrothermal treatment (HT) and drying/calcination routes.\textsuperscript{39-42} Variations in the synthesis conditions often lead to a rearrangement of the surfactant/silica composite i.e. to a phase transformation. Synthesis pH and hydrothermal treatment are the common parameters that in-
duce phase transformation. Changing the synthesis pH leads to a change in the degree of ionization of a surfactant, as exemplified by the phase transformation from higher curvature structures (tetragonal $P4_2/mnm$; cubic $Pm\bar{3}n$ and $Fd\bar{3}m$) to cylindrical (hexagonal $p6mm$; cubic $Ia\bar{3}d$, and $Pn\bar{3}m$) and to a lower curvature structure (lamellar). After the synthesis, aging the gel between room temperature and $150 \degree C$ is a common process to obtain a stable structure. Treatment of the synthesis gel at higher temperature (above $80 \degree C$) leads to an increase in the degree of condensation of the silica wall, and this causes the charge density of the silica network to decrease. In order to maintain the charge matching at the interface (silica/surfactant), surfactants may change their packing arrangement, and this may lead to a phase transformation from a low curvature structure to a high curvature structure. The phase transformation due to high temperature treatment of the synthesis gel has also been explained as being due to dissolution-reprecipitation and also solid state transitions.

Many synthesis mechanisms have been postulated, concentrating on the head group charge of the templating molecule (S), the mediating ions (anions X, cations M), the organic amines (N) and the charge on inorganic silica species (I). These mechanisms are very versatile and different interactions exist between the inorganic components and the head group of the surfactants in acidic, basic and neutral media, including electrostatic: $S^+I^-$, $S^+X^+I^-$, $S^+M^+I^-$, $S^-I^+$; $S^0X^+I^+$ and hydrogen bonding: $S^0I^0$, $S^0N^0$. This has resulted in a series of mesoporous families such as the M41S, FSM-$n$, HMS-$n$, SBA-$n$, FDU-$n$, and MSU-$n$. In contrast to the cationic ($S^+$), neutral ($S^0$) surfactants, the interaction between anionic ($S^-$) surfactants and silicate species leads to disordered structures. However, by inducing charge matching through the use of CSDA, a family of ordered mesoporous silica structures (AMS-$n$) has been synthesized. This mechanism has been described as $S^-N^+\sim I^-$, where $N^+$ are cationic amino groups of organoalkoxy silanes.

In addition to the synthesis methods mentioned above, a non-aqueous synthesis route was proposed, termed Evaporation-Induced Self-Assembly (EISA). This method involves the prehydrolysis of silica precursors catalyzed by acids such as HCl and the subsequent evaporation of the solvent (e.g. ethanol, acetonitrile). This method is particularly convenient for the preparation of thin mesoporous films, membranes and monoliths. This method has not been used in this thesis.

### 3.5 Structural variations

A standard definition of a mesoporous material is usually a material with a pore width between 2 and 50 nm, but a crystallographic definition of a mesoporous material is based on the arrangement of pores, ordered or disordered.
dered, in an amorphous framework. This arrangement of pores is complex, ranging from short interconnected 1D pores, through 2D cylindrical pores to 3D interconnected pores. X-ray diffraction patterns of the ordered mesoporous materials give reflections centering at two regions; sharp peaks between \( -0.5^\circ \) and \( 6^\circ \) related to a periodicity of the pores and a broad peak between \( 20^\circ \) and \( 24^\circ \) represents the amorphous silica framework. Ordered mesostructures can be defined by crystallographic space group symmetries, whereas disordered mesostructures have no such notation. However, the characteristic properties such as porosity and stability of disordered materials are comparable to those of ordered structures. A fundamental question which arises when considering the mesoporous materials for potential applications is thus which mesostructure is most beneficial, ordered or disordered? This is difficult to resolve but one may prioritize the selection with respect to the pore characteristics. Ordered porous materials possess narrow pore size distribution and have advantages in aspects such as their tunable porosity, high surface areas, and broad range of molecular size for adsorption and for active compound release properties. The characteristics of disordered porous materials, on the other hand, are governed by the randomness, connectivity and tortuosity of the pore space.

Ordered mesoporous structures can be classified according to their structural dimensions and pore geometry, e.g. either (2D- or 3D-) cylindrical pores or (3D-) interconnected cage type pores. Structures with cylindrical pores such as MCM-48, \(^5\) AMS-6, \(^5^8\) FDU-5, \(^5^9\) (Ia \(_3\) d), AMS-10 \((Pn \_3 m)\) \(^6^0\) and MCM-41, \(^5\) SBA-15 \((p6mm)\) \(^6^1\) possess uniform pore diameters (Figure 1(a), (b), (c)). On the other hand, structures with interconnected cage type pores such as FDU-1, \(^5^0\) FDU-12, \(^5^4\) SBA-16, \(^5^0,\) \(^5^4,\) \(^6^2\) \((Im \_3 m)\), SBA-1, SBA-6 \((Pm \_3 n)\), \(^3^8,\) \(^6^3\) SBA-2, SBA-12 \((P6 \_3/mmc)\) \(^5^2,\) \(^6^4,\) \(^6^5\) and AMS-8 \((Fd \_3 m)\) \(^6^6\) consist of spherical or ellipsoidal cages that are 3D connected by smaller cage-connecting pores called windows. These mesocaged materials possess features of both the microporous domain in the form of narrow windows and mesoporous voids in the form of cages (Figure 1(d, e)).

The most common method for determining the porosity of a mesoporous material is by nitrogen adsorption-desorption measurements (see Section 4.2.3). The structure can be determined by a combination of X-Ray diffraction (XRD) and electron microscopy. Characterization of 2D cylindrical pores is simple and straightforward, as one can obtain data from XRD, sorption isotherms and HRTEM analysis. MCM-41 and SBA-15 with a space group symmetry of p6mm are the most extensively characterized mesoporous materials synthesized using \( C_8 \) TMABr and triblock copolymer P123 (poly(EO\(_{20}\)-PO\(_{70}\)-EO\(_{20}\))) under basic and acidic conditions, respectively. \(^6^7\) A typical pore size of MCM-41 is about \( \sim4 \) nm\(^5\) whereas SBA-15 materials can be obtained a pore width of up to 30 nm. \(^6^1,\) \(^6^1,\) \(^6^8\) The pore width of MCM-41 materials can be increased by using surfactants with a long alkyl chain length, \(^6^9\) by hydrothermal treatment \(^7^0\) or by the swelling agents. \(^7^1\) Interest-
ingly, SBA-15 mesoporous materials also possess micropores within the pore walls. These are caused by the spreading of poly(ethylene oxide) chains of triblock copolymer into the silica walls depending on synthesis conditions.\textsuperscript{72}

![Figure 1](image)

Figure 1. Various pore geometries of mesoporous structures, (a) 2D hexagonal \( p6mm \), (b) bicontinuous cubic \( Ia\bar{3}d \), (c) bicontinuous cubic \( Pn\bar{3}m \), (d) cage type \( Pm\bar{3}n \) and (e) cage type \( Im\bar{3}m \) structures. Reprinted from ref\textsuperscript{60, 63, 73, 74}

In contrast to 2D cylindrical porous structures, the characterization of 3D mesoporous structures is rather difficult due to their complex pore geometry. Bicontinuous cubic and cage type structures fall under this category. The bicontinuous cubic structures are characterized by two interwoven independent channels which are separated by a silica wall. The most studied bicontinuous cubic structures such as MCM-48, FDU-5 and AMS-6 are defined by the gyroid (G-surface) minimal surface with a space group \( Ia\bar{3}d \), templated by \( C_n\)TMABr, P123 and \( C_{12}\)Ala under basic, acidic and basic conditions respectively. Che \textit{et al.} reported a new bicontinuous cubic structure AMS-10 with a space group of \( Pn\bar{3}m \) (Figure 1(c)), which exhibits a diamond (D-surface) minimal surface, templated by \( C_{14}\)GluA and N-trimethoxysilylpropyl-N, N, N-trimethylammonium chloride (TMAPS) as the CSDA.\textsuperscript{60} Besides these bicontinuous cubic structures, Zou \textit{et al.} recently reported a tri-continuous hexagonal structure IBN-9 with a space group symmetry \( P6_3/mcm \). The structure is characterized by three independent and interpenetrating channels which are separated by a silica wall with a hexagonal (H-surface) minimal surface.\textsuperscript{75}

Cage-type porous structures are attractive for a variety of applications (Section 3.6) due to their pore characteristics such as cages and cage-connecting windows. Cage-connecting windows limit the accessibility to the mesocage and offer an additional design parameter in comparison with cylindrical mesoporous structures.\textsuperscript{76} Cage-type structures are further classified
by their space group symmetries $Im\bar{3}m$, $Pm\bar{3}n$, $Fd\bar{3}m$, $Fm\bar{3}m$ or $P6_3/mmc$ and may be templated by F127 (poly (EO$_{106}$-PO$_{70}$-EO$_{106}$)), C$_{16}$TEABr, C$_{12}$GluA, F127 (poly (EO$_{106}$-PO$_{70}$-EO$_{106}$)) and gemini (C$_{m-3.1}$ and C$_{m-6.1}$) under various synthesis conditions, respectively. The pore characteristics of each structure differ with respect to their symmetry. In a typical $Pm\bar{3}n$ structure, each lattice consists of two types of cages (spherical cages A and ellipsoidal cages B) with open cage-connecting windows to their neighboring cages (Figure 1(d)). $Fd\bar{3}m$ mesostructures are characterized by 16 small cages and 8 large cages per unit cell while in $Im\bar{3}m$ structures (Figure 1(e)) all the cages are of the same size and each cage is connected by 8 neighboring cages with a small window.

For the characterization of cage-type structures, sorption isotherms are widely used. Adsorption measurements, and in particular the analysis of adsorption data based on Non-local Density Functional Theory (NLDFT) is useful, as one can apply model pore geometries (spherical or cylindrical model) to fit the experimental data. The NLDFT developed by Ravikovitch and Neimark extended the adsorption theories to a variety of cage-type structures enabling the sizes of cages and cage-connecting windows to be determined in combination with X-ray diffraction measurements. The Ink-Bottle method (Pores consisting of wide bodies with a narrow neck) developed by Broekhoff is also applicable to spherical cages with a pore diameter larger than 10 nm. However, detailed pore characteristics such as the arrangement of cages in a unit cell and their shapes are not detectable by sorption measurements; particularly for window sizes below 4 nm where desorption occurs via spontaneous cavitation of the condensed fluid.

It is interesting to know that, irrespective of the surfactant size, the cage-connecting window sizes are less than half the surfactant size. So, a question arises: how are the cage-connecting windows formed in 3D cage-type materials? Few studies of this topic have explored the reasons in terms of synthesis conditions and surfactant type. Terasaki et al. first used High Resolution Electron Microscopy (HRTEM) to solve the pore characteristics of a mesoporous material MCM-48. Later, the same group extended the approach to cage-type structures SBA-1 (space group $Pm\bar{3}n$) and SBA-6 (space group $Im\bar{3}m$) and concluded that they possess a bimodal cage structure. This approach has been shown to be a very efficient way of obtaining detailed structural information about mesoporous structures, and it has successfully been applied to characterize various other mesostructures with respect to their symmetry such as $p6mm$, $Ia\bar{3}d$, $Pn\bar{3}m$, $Im\bar{3}m$, $Fd\bar{3}m$, $P6_3/mmc$, $P6_3/mcm$, and $P4_2/mmm$. This method provides a direct representation of a 3D mesostructure including cage/window sizes, shapes and their arrangement within a lattice. This method is based on electron crystallography and image processing. Fourier Transformation (FTs) diffractograms derived from HRTEM images recorded along different directions have been used to refine amplitudes and phases in 3D reciprocal
space. A set of structure factors can be determined through amplitudes and phases. After the correction of contrast transfer function (CTF), a 3D-electrostatic potential density map can be obtained by an inverse FT. A large number of software packages are available for extracting amplitudes and phases directly from the TEM images, including CRISP developed by Hovmöller and Zou. Although crystallographic image processing is attractive for resolving 3D mesostructures, it still relies on the pore volumes obtained from sorption measurements to determine the threshold (which defines a boundary between pore and silica wall) for the electron density maps. Anderson et al. and Kleitz and Mika et al. have recently proposed alternative methods for solving 3D mesostructures involving structural models derived from known X-Ray diffraction data, without relying on sorption data.

Previous publications on the synthesis of mesoporous cage materials suggest that the same symmetry structure can be prepared with various templates and synthesis conditions, so that the main difference in structures with the same symmetry is their cage/window sizes and connectivities. This thesis presents a detailed investigation of the relation between the surfactant type and the pore connectivity of the mesoporous structure. The formation of cage-connecting windows for both acid- and base-catalyzed syntheses (Section 5.2) was also investigated. Mesocaged materials with $Pm\bar{3}n$ symmetry have been selected as the model system to reveal the structural differences using a variety of surfactants having slightly different geometries. The structural variations were revealed through electron crystallographic image processing and sorption data.

3.6 Applications of Ordered Mesoporous Materials

Since the discovery of the first mesoporous material in the early 1990s, tremendous progress has been made in their synthesis, controlling the pore characteristics and solving the fine structural details, and this has led to more than 14000 publications. At the same, potential applications of mesoporous materials have also been studied, and the focus has been in the fields of catalysis, bio-applications (incl. bio-catalysts, bio-sensors, drug carriers, etc.), energy storage, adsorption and gas separation. These research efforts towards the commercialization of the mesoporous materials have already led to the publication of more than 4000 patents. Although these statistics are inspiring, there is as yet no breakthrough industrial application of mesoporous materials. This may be due to the toxicity of surfactants, the high expense for large-scale production, biocompatibility and other envi-

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i Obtained from a search engine Scopus with a key word “Mesoporous Material”

ii The number of patents registered in US patent office, obtained by searching in Scopus
ronmental issues, which still need to be investigated.\textsuperscript{100} These problems may be overcome in the near feature. The present thesis is directed towards a study of the properties of mesoporous materials for drug delivery and gas adsorption.

One fundamental property of a mesoporous silica material is its ability to provide space for functional organics (amine, thiol, etc.) on the silica wall. Mesoporous silica posses a high density of silanol groups after the removal of a template by calcination. The reaction of the silanol groups with organoalkoxysilanes (post-synthetic method) leads to a random distribution (heterogeneous) of functional groups on the silica framework. However, by the simultaneous condensation of silica and organosilicas precursors in a single step (co-condensation method) a homogeneous distribution of functional groups on the silica wall may be achieved.\textsuperscript{30} These processes provide numerous possibilities for selecting these materials as drug carriers, adsorbents and catalytic supports.\textsuperscript{101-105} If mesoporous materials are to be used as drug carriers, adsorptive properties such as pore width, surface area and pore volume are also the essential parameters to consider.\textsuperscript{98} Regi \textit{et al.} showed that the amount of drug released is dependent on the pore width, as exemplified by the release of Ibuprofen from MCM-41 materials with different pore widths where 45 \% and 65 \% of the loaded Ibuprofen was released from materials with pore widths of 2.5 nm and 3.6 nm respectively within the same time.\textsuperscript{106} The same researchers have also shown that release of the Ibuprofen drug is dependent on surface area and pore volume.\textsuperscript{102} However, a few other reports show that the uptake and release of molecules also depends on additional factors such as pore connectivity, the geometry of the pores and the external morphology of the mesoporous particles.\textsuperscript{103, 104,107-109}

To date, the research on the use of mesoporous materials for drug delivery systems is still in its early stages and need to overcome the following difficulties: (1) the complex mechanism of interactions between drug molecules and silica surfaces where drug-drug interactions may be possible instead of drug-silica surface interactions,\textsuperscript{110} (2) post-functionalization of silica surfaces often leads to pore blocking where as in the direct functionalization of surfaces, complete removal of the organic template is difficult,\textsuperscript{111} (3) the geometry of the substrate (e.g. 3D cage-type structures) with respect to specific function of the guest molecules is independent (i.e. the structure-function relationship is complex to investigate), (4) Lin \textit{et al} successfully demonstrated the biocompatibility and stability of the mesoporous silica-based nanospheres with neuroglial cells.\textsuperscript{112} The biocompatibility of these materials still needs to be explored, however, especially when large quantities of inorganic particles are used.\textsuperscript{113} In this thesis, a simple study was carried out to clarify the relationship between structure and function (Section 5.3.1) by following the release of the surfactant molecules present in the uncalcined materials and the diffusion of protons into the pores of AMS-\textit{n} materials.
Adsorption and separation of gases are another interesting area of attracting lot of attention. Surface functionalization of mesoporous materials with several types of functional groups for these applications has been recently reported. The studies reported indicate that the co-condensation method leads to better results in terms of adsorption of gases or metal ions than post-synthesis functionalization.\textsuperscript{111, 114} This property is important particularly for achieving a high capacity for CO\textsubscript{2} adsorption because 2 moles of amino groups react with one mole of CO\textsubscript{2} to give one mole of ammonium carbamate (RNCO\textsubscript{2} \textsuperscript{-} NH\textsubscript{3}\textsuperscript{+}) as the by-product, and hence a high amine content is needed in the mesoporous material. In addition to the quantity of surface functional groups, structural variations such as 2D cylindrical pores or 3D cage-type pores are also important. The 3D cage-type structures offers more advantageous pore characteristics than cylindrical pore structures such as the presence of cages (meso scale) and cage-connecting windows (micro scale). As discussed in Section 3.5, there are already many varieties of cage-type structures and their characteristic properties such as pore size and connectivity differ considerably depending on the synthesis conditions and template. To understand better the impact of structural variations and mode of functionalization, it is best to study the adsorption on the same symmetry structures. In this thesis, mesocaged materials with a \textit{Pm\bar{3}n} symmetry were therefore employed to investigate the CO\textsubscript{2} adsorption capacities (Section 5.3.2).
4. Experimental

4.1 Synthesis

For the synthesis of various mesoporous materials, anionic surfactants such as N-lauroyl-L-lysine (C_{12}Ala) and N-lauroyl-L-glutamic acid (C_{12}GluA), the cationic surfactant cetyltrimethylammonium bromide (C_{16}TMABr, 99.5%), folic acid (FA, 99%), 3-aminopropyltriethoxysilane (APES, 99%), and tetraethyl orthosilicate (TEOS, 98%) were used. C_{16}TEABr and gemini surfactants were made in the laboratory using 1-bromohexadecane, triethylamine and (3-bromopropyl) trimethylammonium bromide (BPTMA, 99.5%), 1-(dimethylamino) hexadecane N, N-dimethyl palmitylamine (DMHDA, 98%). Most of the chemicals were purchased from Sigma-Aldrich except for the anionic surfactants which were purchased from Nanologica AB, Sweden.

4.1.1 Synthesis of Nanoporous Folic Acid Materials

A series of Nanoporous Folic Acid (NFM-1) samples were synthesized by varying the temperature, composition and amount of CSDA in order to optimize the synthesis conditions by trial and error method and synthesis details are shown in Table 1.

The typical synthesis of NFM-1 was as follows: the folic acid solution in distilled water was stirred at room temperature overnight in a closed bottle, and after adjustment to the desired temperature, APES was added under stirring, until the solution became clear owing to the change in solubility of the FA molecules. The pH changed upon addition of the APES from a value of 4.1 to a value of 8.5. Finally, approximately one minute after the addition of APES, the silica source, TEOS was added under stirring. The gel was allowed to stand (ageing) unstirred for different periods after which a hydrothermal treatment was conducted at 100 °C for a period of 0-24 hr. The samples designated NFM-1_R, NFM-1_S and NFM-1_G were aged for 12 hr at 5 °C, 60 °C and 60 °C respectively, followed by HT for 6 hr. The precipitated samples of NFM-1_X were aged at various temperatures (X) for 36 hr and the NFM-1_X_HT samples were kept static for 12 hr at various temperatures (X), followed by HT at 100 °C for 24 hr; where X = room temperature(RT), 40 °C, 50 °C and 60 °C. The solid yellow product was recovered by filtration and washed with 50 ml of distilled water, and dried at room temperature under atmospheric conditions overnight.
Table 1. Synthesis of NFM-1 samples under various conditions and various compositions.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Molar composition</th>
<th>Synthesis temperature</th>
<th>Ageing</th>
<th>HT at 100 °C (Time)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Temperature</td>
<td>Time</td>
</tr>
<tr>
<td>NFM-1_R</td>
<td>0.13FA: 230.5H₂O: 0.45APES: 1TEOS</td>
<td>5 °C</td>
<td>5 °C</td>
<td>12 hr</td>
</tr>
<tr>
<td>NFM-1_S</td>
<td>0.16FA: 270H₂O: 0.45APES: 1TEOS</td>
<td>60 °C</td>
<td>60 °C</td>
<td>12 hr</td>
</tr>
<tr>
<td>NFM-1_G</td>
<td>0.13FA: 230.5H₂O: 0.33APES: 1TEOS</td>
<td>60 °C</td>
<td>60 °C</td>
<td>12 hr</td>
</tr>
<tr>
<td>NFM-1_X</td>
<td>0.13FA: 230H₂O: 0.33APES: 1TEOS</td>
<td>X</td>
<td>X</td>
<td>36 hr</td>
</tr>
<tr>
<td>NFM-1_X_HT</td>
<td>0.13FA: 230H₂O: 0.33APES: 1TEOS</td>
<td>X</td>
<td>X</td>
<td>12 hr</td>
</tr>
</tbody>
</table>

Organics in the NFM-1 samples were removed either by solvent extraction followed by calcination (extraction-calcination) or by direct calcination at 550 °C. A 20/80 volume % of 37% HCl and 99.5% ethanol was employed for solvent extraction for each gram of sample and the solution was stirred for 12 hr at 60 °C. Filtered and air-dried samples were calcined at 550 °C.

4.1.2 Synthesis of AMS-n materials

Anionic surfactant-templated mesoporous silica materials (AMS-n) were synthesized as follows. The AMS-6 (Ia₃d) and AMS-3 (p6mm) samples were templated by C₁₂Ala, the AMS-2 (C₁₂GluA-Pm₃n), AMS-8 (Fd₃m) and AMS-9(P4₂/mnm) samples by the C₁₂GluA surfactant.

After complete dissolution of the surfactant (C₁₂GluA or C₁₂Ala), the APES was added under stirring at the temperature (60 °C or 80 °C) followed by the addition of the silica source TEOS after a delay of t min. The gels of AMS-3, AMS-6(x) were aged at 60 °C while the AMS-2, AMS-8 and AMS-9 samples were aged at room temperature, 24 hr, before they were transferred to an oven at 100 °C. The final white solid was filtered and air dried at room temperature. The full list of synthesis details is presented in Table 2. For AMS-6(x) samples, the final synthesis mixture was kept sealed in a stainless steel Teflon-lined autoclave (150 mL, Parr) without stirring at 100 °C for periods of between 0 and 60 days. The solids are denoted AMS-6(x), where x is the length of hydrothermal treatment (HT) in days. The AMS-3 is an intermediate sample of the AMS-6(x) series obtained after a period of 9 days of HT. The AMS-8 and AMS-9 samples were treated at 100 °C for 2 days.
Table 2. Synthesis details of Anionic Surfactant-templated Mesoporous Silica materials (AMS-n)

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Molar composition</th>
<th>APES-TEOS (min.)</th>
<th>Synthesis temperature</th>
<th>Ageing Temperature</th>
<th>Time (day)</th>
<th>HT at 100 °C (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS-2 (C12GluA-Pm3n)</td>
<td>0.08C12GluA: 154.3H2O: 0.23APES: 1TEOS</td>
<td>3.5</td>
<td>60 °C</td>
<td>60 °C</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>AMS-3</td>
<td>0.15C12Ala: 447.6H2O: 0.2APES: 1TEOS</td>
<td>2</td>
<td>80 °C</td>
<td>RT</td>
<td>1</td>
<td>9</td>
</tr>
<tr>
<td>AMS-6(x)</td>
<td>0.15C12Ala: 447.6H2O: 0.2APES: 1TEOS</td>
<td>2</td>
<td>80 °C</td>
<td>RT</td>
<td>1</td>
<td>x=0 to 60</td>
</tr>
<tr>
<td>AMS-8</td>
<td>0.08C12GluA: 154.3H2O: 0.23APES: 1TEOS</td>
<td>4</td>
<td>60 °C</td>
<td>60 °C</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>AMS-9</td>
<td>0.08C12GluA: 154.3H2O: 0.23APES: 1TEOS</td>
<td>5</td>
<td>60 °C</td>
<td>60 °C</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

4.1.3 Synthesis of $Pm\bar{3}n$ structures

A novel synthesis route was proposed (Paper II) for the synthesis of the $Pm\bar{3}n$ symmetry structure using the cationic surfactant C16TMABr. Different molar ratios of surfactant to APES at different temperatures led to a novel route for the synthesis of the $Pm\bar{3}n$ structure. The synthesis was performed as follows: to a homogeneous mixture of aqueous surfactant solution consisting of C16TMABr and NaOH (2 M), a mixture of APES and TEOS was added and kept stirring (at 500rpm) for 3hr. The molar composition of the gel obtained was 0.06C16TMABr: 4.35NaOH: 267.6H2O: (x)APES: (1-x)TEOS, where x is the molar ratio of C16TMABr/APES and varied from “0.1 to 10” and with “No APES”. At a molar ratio of C16TMABr/APES = 0.6, the $Pm\bar{3}n$ structure was observed. After the synthesis, the precipitated white solid was treated hydrothermally at 100 °C for 24 hr in the same synthesis vessel. After filtration, the solids were calcined in a flow of oxygen at 550 °C for a period of 6 hr. Alternatively the as-synthesized sample of $Pm\bar{3}n$ structure was solvent-extracted in copious amounts of ethanol in a reflux condenser at 90 °C.

The other $Pm\bar{3}n$ symmetry structures were prepared using C12GluA, C16TEABr and gemini ([CH3(CH2)15 N (CH3)2(CH2)3N(CH3)3]Br2, C16-3-1) surfactants, and the synthesis details are shown in Table 3. The synthesis of anionic templated mesocaged material C12GluA-$Pm\bar{3}n$ was similar to that of AMS-2 described in Section 4.1.2. The surfactants C16TEABr and gemini C16-3-1 were laboratory made and materials were synthesized as follows: to a homogeneous solution of surfactant at room temperature, the desired amount of TEOS was added. The synthesis gel of C16-3-1-$Pm\bar{3}n$ was aged at +4 °C for 72 hr while the synthesis gel of C16TEABr-$Pm\bar{3}n$ sample maintained at
+4 °C for 24 hr, before hydrothermal treatment at 100 °C for 24 hr. The final
samples were filtered and air dried for 12 hr.

Table 3. Synthesis of $Pm\bar{3}n$ structures.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Molar composition</th>
<th>pH</th>
<th>Synthesis temperature</th>
<th>Ageing</th>
<th>HT at 100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{16}$TMABr-$Pm\bar{3}n$</td>
<td>0.06C$_{16}$TMABr: 4.35NaOH: 267.6H$_2$O: 0.6APES: 1TEOS:</td>
<td>11.2</td>
<td>RT</td>
<td>RT</td>
<td>3 hr</td>
</tr>
<tr>
<td>C$_{12}$GluA-$Pm\bar{3}n$</td>
<td>0.08C$_{12}$GluA: 154.3H$_2$O: 0.22APES: 1TEOS:</td>
<td>9.6</td>
<td>60 °C</td>
<td>60 °C</td>
<td>24 hr</td>
</tr>
<tr>
<td>C$_{16}$TEABr-$Pm\bar{3}n$</td>
<td>0.2C$_{16}$TEABr: 56HCl : 600 H$_2$O: 1TEOS:</td>
<td>1.7</td>
<td>RT</td>
<td>+ 4 °C</td>
<td>24 hr</td>
</tr>
<tr>
<td>C$_{16,3,1}$-$Pm\bar{3}n$</td>
<td>1.25C$_{16,3,1}$: 20HCl: 147H$_2$O: 1TEOS:</td>
<td>2</td>
<td>RT</td>
<td>+ 4 °C</td>
<td>72 hr</td>
</tr>
</tbody>
</table>

Prior to the CO$_2$ adsorption studies on the $Pm\bar{3}n$ structures (Paper VII),
the internal pore structure of the samples was modified with n-propylamino
groups either by extraction or by a post-synthesis process. The co-condensed
samples of C$_{16}$TMABr-$Pm\bar{3}n$ and C$_{12}$GluA-$Pm\bar{3}n$ were solvent-extracted in
80/20 volume % of ethanol/HCl under reflux conditions at 80 °C for 12 hr.
The extraction was performed with repeated washing (with ethanol) and
filtration. The samples are designated as extracted-1 and extracted-2 respecti-
vally. The calcined C$_{16}$TMABr-$Pm\bar{3}n$ and the other two acid-catalyzed
$Pm\bar{3}n$ samples, such as C$_{16}$TEABr-$Pm\bar{3}n$ and C$_{16,3,1}$-$Pm\bar{3}n$, were post-
synthetically modified using APES under reflux conditions. The samples are
designated as post-synthesis-1, post-synthesis-2 and post-synthesis-3 respecti-
vally. Before this procedure, the calcined silica samples were refluxed with
water at a temperature of 60 °C for 6 hr, allowing internal surfaces of the
silica to be hydrated. After repeated washing of the hydrated silica powder
with toluene, the filtered powder was suspended in a flask containing toluene
and an appropriate amount of APES. The mixture was refluxed at 60 °C for
24 hr followed by a series of washings with toluene and air dried for 24 hr.

4.2 Characterization Techniques

4.2.1 Powder X-Ray Diffraction Analysis (XRD)

The powder X-ray diffraction technique is a fundamental technique for the
identification of mesophases. When an incident beam of X-rays (a form of
electromagnetic radiation with a wavelength of 1 Å) interacts with a target
sample, the waves are scattered from lattice planes separated by an
interplanar distance $d$. The scattered waves interfere constructively and the
path difference between two waves undergoing constructive interference is
given by $2d\sin\theta$, where $\theta$ is the scattering angle. The intensity of the scattering wave as a function of scattering angle gives a diffraction pattern. Both the positions and the relative intensities of the diffraction peaks are indicative of a particular structure, such as cubic, hexagonal etc. The structural identification of mesoporous materials is rather difficult because most of the peaks appear at low angles and in some materials the peaks overlap due to multiple structures. Due to the presence of organic/inorganic material in the as-synthesized samples of mesoporous materials, the phase contrast and hence the peak intensities are rather weak, whereas the calcined samples (after the removal of organics) typically show clear peaks of high intensity. However, for a detailed analysis of the structures, HRTEM studies are also necessary.

Low angle X-ray powder diffraction (XRD) patterns of all the samples presented in this thesis were performed on a XPert Pro diffractometer using Cu Kα radiation ($\lambda=1.5418$ Å) at 45 kV and 35 mA. The diffraction patterns were recorded between $1^\circ$ and $6^\circ$ (low angle) and $6^\circ$ - $30^\circ$ (high angle) 2θ using an increment of 0.02° 2θ and a 200s step time. The XRD results presented in Paper II were however obtained on a Siemens D500 diffractometer using Cu Kα radiation ($\lambda=1.5418$ Å) at 45 kV and 40 mA with the same scanning parameters.

4.2.2 Small Angle X-Ray Scattering (SAXS)

Compared to laboratory X-Rays, the synchrotron radiation sources give more intense and higher energy radiation with very shorter angles of scattering $\theta < 0.10$. Another difference is that, an in-situ SAXS pattern can be recorded in a short time while the XRD pattern needs at least a couple of minutes for acceptable data. The structural growth information from the nucleation stage during the synthesis can thus be accessible with the SAXS technique. SAXS is also an X-ray diffraction-based technique, where synchrotron radiation is used as a source, which occurs when charged particles are accelerated in a curved path or orbit. Any charged particle which moves in a curved path or is accelerated along a linear path will emit electromagnetic radiation. When the wavelength of the electromagnetic radiation is of the same order as the length of a sample particle, the particle will scatter the radiation. Detection and analysis of this scattering pattern can yield valuable information about the size, shape, and internal structure of the particle.

In this thesis, time resolved in-situ SAXS measurements were performed on the NFM-1 samples and on the $Pm\bar{3}n$ symmetry sample (Paper II) to give a better understanding of the self-aggregation of liquid crystals and to follow-up the formation of the novel mesostructures. In-situ synchrotron SAXS was performed using beam line I711 at MAX lab, Sweden (see below photograph). The beam is focused vertically by a bendable mirror and horizontally
by an asymmetrically cut Si (111) monochromator. The wavelength range is 0.8±1.5 Å with a measured flux at 1 Å. A sample-to-detector distance of 1.5 m was employed. A capillary tube 25×2 mm in size was used as a sample holder and both ends of the tube were connected to a flow meter through silicon tubes. The flow meter was used to circulate the synthesis solution in and out through the capillary tube. The silica sources were added in the synthesis bottle from outside the hutch through a syringe connected to a long silicon tube by pushing with high pressure, called the “pop” method.

A photograph from the inside of the hutch showing (a) sample holder for mounting capillary tube, (b) experimental table, (c) flow meter and (d) an image plate detector.

4.2.3 Nitrogen Adsorption/Desorption isotherms

Gas adsorption is a prominent method for the comprehensive characterization of porous materials. The adsorption of gases (adsorbate) at various relative pressures on a porous solid (adsorbent) gives information about textural properties including surface area, pore volume, and pore size. Depending on the strength of the interaction, the adsorption can be described as being either physical or chemisorption. Chemisorption is characterized mainly by a strong interaction between adsorbate-adsorbent, while physical adsorption is due to mainly dispersion forces, i.e. weak intermolecular forces between non-polar molecules. The latter is more favored for porosity measurements because of its non-destructive nature and the ease of quantification of the adsorbate. However, the adsorbate must exhibit no localized adsorption i.e. the adsorption must be not restricted to a specific site. Nitrogen, as an adsorbate, exhibits the unusual property of preventing localized adsorption as it possesses a sufficiently small heat of adsorption in the first adsorbed layer.
The measurement is performed volumetrically; Calibrated volumes of gas are added to a sample tube that is immersed in liquid nitrogen with a known amount of sample. The amount of gas adsorbed can be calculated from the measured pressure difference in the sample tube after the addition of a known volume. If the amount of adsorbed gas is plotted against the pressure, an isotherm is obtained. From this plot, the internal pore surface area, pore volume, and pore size can be derived. As shown in Figure 2, the resulted isotherms can be grouped into six types. For microporous materials, the pore filling occurs in a continuous way (Type I) and the majority of micropore filling occurs at relative pressures below 0.1. The Type II isotherm is typical for macro porous and non-porous solids where monolayer coverage is followed by multilayers at high relative pressures. Type III and Type V isotherms are characteristic of weak adsorbate-adsorbent interactions and are most commonly associated respectively with non-porous and microporous adsorbents and microporous or mesoporous solids. Type IV isotherms are typical for mesopores where pore-filling occurs by pore condensation. In some cases, adsorption occurs at a higher pressure than desorption, a phenomenon called hysteresis. The reasons for hysteresis are still under debate. One explanation is that hysteresis is caused by a difference in contact angle between adsorption and desorption.

![Typical sorption isotherms of different porous materials.](image)

Figure 2. Typical sorption isotherms of different porous materials.

In this work, nitrogen sorption isotherms of all the samples were obtained at a liquid nitrogen temperature (77K) using a Micromeritics ASAP2020 volumetric adsorption instrument. Before measurement, the calcined silica samples were degassed under vacuum for 10 hr at 120 °C. The BET (Brunauer-Emmett-Teller) equation was used to calculate the surface area ($S_{BET}$) from the adsorption data obtained in the relative pressure ($p/p_o$) range from 0.05 to 0.3. The total pore volume ($V_{tot}$) was calculated from the amount of gas adsorbed at $p/p_o \approx 0.94$. The pore size distributions (PSD) of the samples were calculated from the adsorption branch of the isotherm by fitting a variety of models. Most widely accepted PSD models used in this thesis where
the Barrett-Joyner-Halenda (BJH), Horvath-Kawazoe (HK), Derjaguin-Broekhoff-de Boer (DBdB) and nonlocal density functional theory (NLDFT) models. The BJH model is based on a modified Kelvin equation and predicts that the condensation occurs in pores that already have some adsorbed nitrogen multilayers on the walls. This model underestimates the small and medium sized mesopores. However, the NLDFT model provides a microscopic treatment of sorption phenomena (i.e. based on statistical mechanics) in micro and mesopores on a molecular level. Based on the thermodynamic properties of the pore fluid, the equilibration density profile for all locations in the pore is calculated by minimizing the free energy for a pore system with a bulk gas phase. The HK method was originally developed for calculating microporous slit type pores in carbon materials. Later this method was extended to cylindrical and spherical pore geometries. On the other hand, DBdB is most the widely accepted method for macroscopic models based on ink-bottle type pores, and it is most suitable with spherical cavities larger than 10 nm in diameter.

4.2.4 Scanning Electron Microscopy (SEM)

For morphology observations, SEM was employed. A beam of electrons emitted by a filament is allowed to focus on the sample. The electrons interact with atoms that make up the sample producing signals that contain information about the sample’s surface topography, composition etc.. The types of signal produced at the sample surface include secondary electrons (SE), back-scattered electrons, characteristic X-rays, etc. The detectors collect the required signals and convert them to a signal that is sent to a viewing screen. In this thesis, all the SEM images were recorded using a LEO 1550 SEM, equipped with a Schottky field emission gun, operated at an accelerating voltage of 1-3 kV and at magnifications of between 20 000 and 50 000x, on samples with no sputtered coating. An in-lens detector was used to collect the SE signals, the detector being located beside the pole piece of the microscope column.

4.2.5 Transmission Electron Microscopy (TEM)

Structural information about mesoporous materials described by XRD gives limited information, which is not sufficient to refine the structure of a mesoporous material. Direct imaging by TEM images gives not only the amplitude but also the phase information of the structure factors of the crystal. The indexed Fast Fourier Transform (FFTs) of the TEM images can be further used to refine the lattice parameters and thereby the crystal symmetry. TEM information is obtained from a single crystal (~10^8 times smaller than the size of specimen for XRD) whereas XRD data is from the bulk material. Compared to SEM, TEM gives local structural information while the
SEM gives surface information about bulk materials. TEM image information is therefore crucial for a full understanding of mesoporous structures.

The electron beam emitted by a filament is accelerated through a large potential difference in an electron gun. This high-energy electron beam interacts with and is transmitted through the sample, focused into an image and projected onto the fluorescent screen. The electron beam is focused through a series of electromagnetic lenses such as a condenser lens, an objective lens, an intermediate lens and a projector lens. The focus of each lens is controlled by the current in the lens coils. In addition, the objective aperture and the selected area aperture are important parts of the TEM, which make it possible to select specific diffracted beams and specific areas, respectively. Although, both TEM and SEM use the electron beam (but vary the wavelength of electrons) as the source for structural characterization, SEM gives surface topography information while the TEM provides images of the crystallographic structure of the sample on the atomic scale (because of the high-energy electrons).

The resolution of TEM is primarily limited by the imperfections or aberrations of the electromagnetic lenses. The most important types of aberration are spherical, chromatic and astigmatism. Spherical aberration arises as a result of a phase-shift of the diffracted beams that are brought into focus at the Gaussian image plane. This results in a lot of focal points and limits the image resolution. The spherical aberration constant, Cs, indicates the extent of phase-shift and determines the resolution of the microscope. Chromatic aberration originates from a range of wavelengths present in the electron beam, and leads to a blurred image in the final image plane. Depending on the energy spread of the electron beam, the chromatic aberration constant, Cc, can be easily corrected and minimized (hence the cost of the microscope is mostly depends on the Cs corrector). When the electrons spiral around the optical axis, a non-uniform magnetic field caused by the lens leads to astigmatism. Astigmatism can be easily corrected by using a stigmator, a special type of lens that introduces a compensating field to balance the non-uniform field. An overall correction of lens aberrations results in TEM images with high structural information on an atomic scale. The brighter areas of the image represent areas where more electrons have passed through the sample. The darker areas represent areas where fewer electrons have passed through as a result of a higher material density. Therefore, a calcined mesoporous silica sample can show a higher contrast difference in the TEM image than an as-synthesized sample containing organic templates. The contrast in the final image is determined by a mathematical function called the contrast transfer function (CTF), which is a function of the limiting apertures and aberrations in the imaging lens of the microscope. CTF correction is a necessary step for obtaining 3D electron density maps of a sample through image processing.
In this thesis, transmission electron microscopy (TEM) was conducted with a JEOL-3010 microscope, operating at 300 kV (Cs 0.6 mm, resolution 1.7 Å). Images were recorded using a CCD camera (Multi scan model 794, Gatan, size 1024 x 1024, pixel size 24 x 24 μm) at 30 000-100 000x magnification using low-dose conditions on calcined samples. To obtain structural information (presented in Papers II and IV), images taken along the [100], [110] and [111] directions were chosen for further analysis and an electron crystallography 3D-reconstruction process. For each HRTEM image, a thin area of the image was selected to generate a FFT diffractogram. Crystallographic image processing (see Paper IV for details) was carried out using the commercial software package CRISP and the 3D potential density maps were created using commercially available Mathematica 6.0 software. Detailed information about the image processing and the electron crystallographic procedure utilized here have already been published elsewhere. Briefly, the plane group symmetry of each zone axis such as [100], [110] and [111] is determined in order to define the origin of the unit cell. By imposing the plane group over each zone axis, phases and amplitudes are obtained. The amplitudes are further refined by normalizing with values from different zone axes. The final structure factor amplitudes \( F_{hkl} \) are calculated after correction of the contrast transfer function (CTF). From these final structure factors, a 3D potential map can be evaluated by performing an inverse Fourier transformation. However, the reconstructed model is not valid without specifying a correct boundary between a pore space and silica wall and a so-called threshold value is needed. Using the pore volume \( v \) obtained from the N\(_2\) isotherms and by assuming a silica wall density \( d_w \) of 2.2 cm\(^3\)/g, the pore volume fraction is obtained using the formula: \( 1/(1+1/(v \times d_w)) \). By assuming a volume fraction for a given threshold density, a threshold in the potential density is obtained in order to differentiate the silica wall and the pore.

4.2.6 Thermogravimetric Analysis (TGA)

TGA is a simple analytical technique that determines the weight loss of a material as a function of temperature. To study the thermal degradation of the surfactants and the amount of functional amino groups in the mesoporous silica materials, the thermogravimetric analysis was performed on a Mettler TGA instrument by heating the samples from 25 to 900 °C at a rate of 5 °C/min on an alumina holder under a flow of air of 20 ml/min.
5. Novel synthesis, Structure and Function of Mesoporous silica Materials

5.1 Novel Synthesis Routes and the Effect of Synthesis Parameters

5.1.1 Novel Synthesis of Ordered Mesoporous Silica

As discussed in Section 3.4, the synthesis of mesoporous material was usually begun with the formation of surfactant micelles and their LC phases in a solution. In this work, a novel route to synthesize 2D hexagonal mesostructure without reliance on the formation of the surfactant micelles has been presented. In the preparation, folic acid (FA), a biologically important substance promoting cell growth and a member of the vitamin B family, was used. The self-organization of pterin groups was stabilized through Hoogsteen-type hydrogen bonding. This exposes the glutamate moieties of FA to the exterior in an array of stacks. A co-structure-directing agent, APES was used, to achieve a charge matching between the negatively charged glutamate groups of the folic acid (pKa ≈8) and the hydrolyzing and condensing silica oligomers derived using the common silica precursor TEOS. A variety of temperatures and reaction conditions were investigated to determine the most favorable synthetic approach. Three methods (Section 4.1.1) designated by their morphology (Nanoporous Folic Acid Material-1_Gyroid) NFM-1_G, NFM-1_R (Rods) and NFM-1_S (Spherical) were found to be the most reproducible materials.

Figure 3 shows structural data derived from powder X-ray diffraction (XRD) on solid as-synthesized, extracted, and calcined samples of NFM-1_G. Low angle diffraction peaks 10, 11 and 20 can be indexed by a 2D-hexagonal unit cell, analogous to MCM- 41 (p6mm symmetry), with a unit cell parameter 43.0 Å for the as-synthesized sample and 42.3 and 40.9 Å for the extracted and calcined samples, respectively. Surprisingly, three peaks were observed at higher angles (which is not typical for mesoporous silica materials) for the as-synthesized NFM-1_G sample; the broadest centered at 22°(2θ) is consistent with the amorphous nature of the silica wall, while the diffraction peak observed at 26.66°(2θ) can be associated with the stacking of pterin (d =3.36 Å). The sharp peak at 44.30° 2θ (d =2.04Å), in contrast to X-ray data obtained from folate solutions, indicates a lack of translational motion of the pterin stacks perpendicular to the c-axis of the hexagonal unit
cell. A solvent extraction treatment before calcination (extraction-calcination) reduced the unit cell shrinkage and gave functional amino groups in the silica wall. The NFM-1_R and NFM-1_S samples show little or no difference in the XRD patterns, but are similar in profile to the NFM-1_G sample.

![Figure 3. X-ray diffraction patterns of as-synthesized, extracted and calcined mesoporous material NFM-1_G, templated by FA. Inset shows the XRD pattern of an as-synthesized sample recorded between 10-70° 2θ.](image)

To derive textural data of NFM-1_G, nitrogen adsorption-desorption isotherms were obtained for extracted and calcined samples. The isotherms are characterized by the absence of the hysteresis loop typical of a Type IV isotherm. Pore size distributions reveal a small pore diameter for both extracted and calcined (extracted-calcined) samples, possessing sharp pore size distributions centered on 25 and 30 Å, respectively. The calcined sample of NFM-1_G shows the highest surface area of 1155 m²/g. Small variations in reactant molar composition and synthesis temperature have led to various morphologies as shown in Figure 4. The SEM images of sample NFM-1_G (Figure 4(a)) synthesized at 60 °C shows gyroid particles 4 μm in size. Changing the temperature to +5 °C and the addition of a higher amount of APES led to the formation of faceted hexagonal rod-type particles (NFM-1_R) with diameters between 0.5 and 3 μm and lengths between 5 and 20 μm (Figure 4(b)). Chiral motifs are clearly observed for short spacings of a few micrometers in length along the c-axis of these particles. Although the chiral pitch is not homogeneous throughout the sample, only right-handed chiral twists could be observed on the basis of SEM investigations.

A simple study of the morphological variations with respect to the APES/FA ratio was performed. The molar composition of the synthesis mixture was 0.14 FA: 233 H₂O: xAPES: 1TEOS where x is the molar ratio of APES to FA. The interaction of different proportions of the APES with the carboxylate groups (α-COOH and γ-COOH) of the glutamate moiety of the
folic acid lead to various morphologies. As shown in Figure 5, a transformation from rod-shaped particles with a diameter of 200 nm to spherical particles with a diameter of 1-3 \(\mu\)m has been observed. Surprisingly, the sample with the highest APES/FA ratio shows very poor structural order, as confirmed by XRD (not shown). However, by varying the amount of the silica source, TEOS, a highly ordered structure with spheres 2-4 \(\mu\)m in diameter were obtained (the sample denoted NFM-1_S).

Figure 4. SEM images of mesoporous samples templated with folic acid. (a) NFM-1_G showing gyroid type particles and (b) NFM-1_R showing chiral elongated particles.

Figure 5. SEM images of folic-acid-templated mesoporous structures at various APES/FA molar ratios: (a) 0.5, (b) 1.4, (c) 2.8 and (d) 4.3.
Figure 6. TEM images of the sample NFM-1_R, showing the chiral arrangement of pores, insets show pores parallel to the hexagonal unit cell.

TEM images of calcined samples confirm the hexagonal structure with p6mm symmetry. Surprisingly, the TEM image (Figure 6) of the hexagonal rod-type particle NFM-1_R shows the chiral nature of the pores; fringes corresponding to the 10 planes of the hexagonal structure are clearly shown in the inset figures.

Although, a well-defined 2D-hexagonal structure was formed, the driving force for the formation of the hexagonal phase is still unclear. For a better understanding of the aggregation of the folic acid and the growth towards the 2D-hexagonal structure, in-situ SAXS measurements were closely followed. Analogous to NFM-1_G, numerous syntheses were performed at various temperatures, with and without hydrothermal treatment (HT).

Figure 7 shows the SAXS patterns of NFM-1 samples synthesized at various temperatures. The data recorded at reaction times shorter than 10 min are from the folic acid solution i.e. without silica precursors and they show no prominent signal. This indicates that the folic acid is an isotropic phase and confirms that the stacks are not formed at the concentration of 1.4 wt % of folic acid. After the addition of mixture of APES and TEOS to the folic acid solution, all the samples show two reflections, and the intensities of the reflections increase with increasing the synthesis temperature. These low-angle peaks are consistent with the 2D-hexagonal phase and the peaks are indexed as 10 and 11. At a low temperature, the scattering intensity of the 11 peak increases after the 10 peak tends to disappear, and it grows con-
continuously with increasing reaction time. At higher temperatures, the samples show both the reflections 10 and 11 simultaneously. However, in all the samples, the 10 peak disappears in the middle of the hexagonal phase formation, while the 11 reflection continues to grow.

Figure 7. Time-resolved *in-situ* SAXS patterns recoded on NFM-1_X synthesis; (a) X= room temperature, (b) X= 40 °C, (c) X= 50 °C and (d) X= 60 °C. The 10 peak disappears in the middle of the synthesis while the 11 peak intensity increases with increasing synthesis temperature.

The SAXS data in Figure 7 show only a few minutes of the reacted synthesis of NFM-1 samples. Further evidence of the formation of the final structures was obtained by X-Ray diffraction measurements on filtered and air-dried as-synthesized samples. Figure 8 and Figure 9 show lower and higher angle diffraction patterns of the as-synthesized NFM-1_X and NFM-1_X_HT samples, respectively. Note that the NFM-1_X samples were without HT while the NFM-1_X_HT samples were HT treated at 100 °C for 24 hr. The low angle XRD of NFM-1_X samples shows the 11 peak as a higher intensity than the 10 peak, while the opposite was observed for the NFM-1_X_HT samples, for shows the 10 peak was the higher intensity, analogous to the XRD pattern of the MCM-41 structure. This evidence indicates that the growth of structure is affected by the synthesis temperature and HT. This
has previously been observed during the formation of MCM-41 type silica where the ratio of the 11 to the 20 reflection intensity increases with synthesis time, due to the higher degree of silica condensation which contributes to a greater electron density contrast in the XRD pattern.\textsuperscript{125, 126} Therefore, the variation in the intensity distribution of the NFM-1 samples is also expected to be the effect of the different silica condensation rates at different synthesis temperatures and HT. The $d_{10}$-spacing of the 2D hexagonal structures (Table 4) was approximately 50 Å during the initial stages of synthesis, as derived from SAXS. However, XRD data shows a decrease in the $d_{10}$-spacing to ca.33 Å for the NFM-1_X and ~36 Å for the NFM-1_X_HT samples. At higher angles, the as-synthesized NFM-1_X samples show a very clear peak at a $d_{10}$-spacing of ~3.26 Å associated with the stacking distance (Figure 8(right)). However, the NFM-1_X_HT samples show a very poor intensity of stacking distance at a $d$-spacing of 3.34 Å (Figure 9(right)). XRD patterns of extracted-calcined samples of NFM-1_X and NFM-1_X_HT also show three well resolved reflections consistent with the 2D hexagonal phase. The XRD patterns of direct-calcined samples of NFM-1_X show two peaks at low angles and are not indexable with any of the crystal lattices, due to a structural disorder indicative of a higher lattice shrinkage. However, by employing solvent extraction before the calcination, a high stability structural order is achieved. Compared to extracted-calcined NFM-1_X samples, the extracted-calcined samples of NFM-1_X_HT show very little lattice shrinkage after calcination, and hence the high stability of the NFM-1_X_HT samples is evident (Table 4).

![Figure 8. XRD patterns of nanoporous folic acid materials (NFM-1_X); lower angles (left) and higher angles (right) synthesized at temperatures of (a) room temperature, (b) 40 °C, (c) 50 °C and (d) 60 °C.](image-url)
The morphology (not shown) of NFM-1_X samples shows transformation from rod-shaped particles at low temperature to spherical particles at high synthesis temperature. It was also found that the NFM-1_X_HT samples also exhibit the same trend in the particle morphology but with more spherical particles in all the samples. Based on TEM images, it is confirmed that all the calcined samples possess a 2D-hexagonal structure with $p6mm$ symmetry.

Figure 9. XRD patterns of nanoporous folic acid materials (NFM-1_X_HT); lower angles (left) and higher angles (right) synthesized at (a) room temperature, (b) 40 °C, (c) 50 °C and (d) 60 °C.

Table 4. Structural and textural properties of NFM-1_X and NFM-1_X_HT derived from SAXS, XRD and sorption isotherms.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SAXS $d_{10}$ (Å)</th>
<th>XRD$^a$ $d_{10}$ (Å)</th>
<th>XRD$^b$ $d_{10}$ (Å)</th>
<th>BET $m^2$/g</th>
<th>Pore width (Å)</th>
<th>Pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NFM-1_RT</td>
<td>50.2</td>
<td>33.5</td>
<td>27.0</td>
<td>295</td>
<td>18.8</td>
<td>0.180</td>
</tr>
<tr>
<td>NFM-1_40</td>
<td>49.7</td>
<td>33.3</td>
<td>27.9</td>
<td>306</td>
<td>19.0</td>
<td>0.161</td>
</tr>
<tr>
<td>NFM-1_50</td>
<td>49.5</td>
<td>32.5</td>
<td>30.2</td>
<td>354</td>
<td>20.6</td>
<td>0.190</td>
</tr>
<tr>
<td>NFM-1_60</td>
<td>50.0</td>
<td>34.1</td>
<td>33.9</td>
<td>467</td>
<td>23.1</td>
<td>0.269</td>
</tr>
<tr>
<td>NFM-1_RT_HT</td>
<td>50.2</td>
<td>36.8</td>
<td>36.0</td>
<td>794</td>
<td>30.3</td>
<td>0.400</td>
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<tr>
<td>NFM-1_60_HT</td>
<td>50.0</td>
<td>38.0</td>
<td>36.5</td>
<td>882</td>
<td>30.2</td>
<td>0.437</td>
</tr>
</tbody>
</table>

$^a$Data collected from the as-synthesized NFM-1 samples $^b$Data derived from extracted-calcined samples of NFM-1
Nitrogen sorption measurements of the extracted-calcined NFM-1_X and NFM-1_X_HT samples show type IV isotherms similar to that of NFM-1_G. The properties derived from the isotherms are listed in Table 4. The samples show considerable differences in the pore size distribution with ca.20 Å and ca.30 Å for NFM-1_X and NFM-1_X_HT, respectively. In addition, the NFM-1_X_HT samples have almost twice the BET surface area of the NFM-1_X samples. The porosity variations compensate for the synthesis conditions, where a greater structural shrinkage for samples NFM-1_X leads to a decrease in the pore size.

Over all, it appears that the formation of mesoporous materials templated by folic acid is a controllable process, which involves three stages;

(1) Addition of APES increases the solution pH, and the pterin groups therefore tend to form tetramers. The pH maintained in the synthesis is an important parameter for forming the tetramers and subsequent stack alignment. The amino groups (-NH₂) in the pterin group of the folic acid are protonated at a pH below 8 whereas, at a pH above 10.6, the amino groups of the APES are in a neutral state (pKa = 10.6). The synthesis pH must therefore between 8 and 10.6 to form the pterin tetramers, which eventually lead to columnar stacks of a certain length (see Section 3.1). The length of each stack is not clear at this stage, but the stacking forces (i.e extended π-σ core interactions) play a dominant role in stabilizing the stacks during the initial stages of the synthesis.

(2) The charge matching between the glutamic moiety of the folic acid and the propylamino groups of the APES leads to the formation of a thin layer of silica around the columnar stacks, analogous to the silica-rod assembly proposed by Davis et al. This is the reason why a high electron density along the columnar axis leads to a strong 11 reflection in the SAXS pattern, with an intensity which increases with increasing synthesis temperature (Figure 7). As is evident in the XRD patterns of the NFM-1_X samples, a very clear high angle peak at a d-spacing of ~3.3 Å confirms the high stability of the stacks at a low synthesis temperature.

(3) Finally, the interaction of APES with the glutamic moiety of the folic acid enables the TEOS to hydrolyze along the columnar axis, which stabilizes the hexagonal mesostructure. At higher hydrolysis and condensation rates of silica, the bulk silica (TEOS) polymerization drives the folic acid columnar assembly to re-aggregate more rapidly towards the [10] axis of the hexagonal lattice. Hence the differences in the 10 and 11 peak intensities for the NFM-1_X_HT samples compared to those of the NFM-1_X samples. The pore width data also supports the speculation that a higher condensation rate leads to a low structural shrinkage after calcination and hence a greater pore width.
5.1.2 Penetration-Induced Synthesis of $Pm\bar{3}n$ Structure

With respect to the structural properties, the cylindrical pore structures possess a uniform pore diameter and thus may limit their applications compared to those of 3D-mesocaged materials which possess features of both the microporous domains in the form of narrow cage-connecting windows and mesoporous voids in the form of cages (Section 3.5). Mesoporous materials with $Pm\bar{3}n$ symmetry are unique among the range of cage-type materials so far prepared, as a result of their wide presence in surfactant phase diagrams, and their close proximity in micellar curvature to well-known 2D hexagonal $p6mm$ mesophases.\textsuperscript{63, 85, 127} The use of $Pm\bar{3}n$ mesoporous structures in applications such as catalysis or gas separation appears to be hindered by the difficulty of using conventional functionalization routes to prepare active surfaces. Silylation routes and the use of functional organoalkoxysilanes are most favored as a starting step towards surface functionalization, since these methods are compatible with the mesoporous silica surface. Several routes have been developed including post-synthesis and direct co-condensation (one-pot synthesis) with organoalkoxysilanes.\textsuperscript{128, 129} The use of various combinations of organoalkoxysilane e.g. APES and TEOS precursors\textsuperscript{130, 131} has led to the synthesis of cylindrical 2D hexagonal mesostructures with space group $p6mm$ and adequate levels of functional groups on the mesoporous surface. Increasing the amount of these silane precursors results in disordered structures.\textsuperscript{114, 132}

In this work, the common silane precursors, APES and TEOS, were used for the preparation of 3D cubic mesocaged material with $Pm\bar{3}n$ symmetry with the surfactant C$_{16}$TMABr, simply by adjusting the molar ratio of the surfactant to the organic functional groups (C$_{16}$TMABr/APES). This simple route for the synthesis of $Pm\bar{3}n$ under basic conditions using C$_{16}$TMABr, has surprisingly not previously been reported in the synthesis involving this common surfactant and co-condensation method. This is the first synthesis of $Pm\bar{3}n$ symmetry with organically functionalized amino groups through a one-pot method under alkaline conditions at room temperature. This synthesis was unexpected and happened during the synthesis of MCM-41 type structures.

Figure 10(a) shows powder XRD patterns of calcined mesoporous silica prepared at room temperature with various C$_{16}$TMABr/APES molar ratios (between 0.1-10 and without APES). As expected, in the absence of APES, this led to the formation of a 2D hexagonal phase with three diffraction peaks which may be indexed as 10, 11, 20 reflections of the well-known MCM-41 phase. Only at a higher APES content (C$_{16}$TMABr/APES= 0.6) were three well-resolved peaks, consistent with the 200, 210 and 211 reflections of the cubic structure observed. Increasing the APES content even further resulted in disordered structures showing broad diffraction peaks. X-ray diffraction patterns of as-synthesized, extracted and calcined cubic mesopor-
ous solids (C\textsubscript{16}TMABr/ APES=0.6) are shown in Figure 10(b). All the samples show a range of well resolved peaks consistent with a cubic unit cell, where a\textsubscript{0}= 110 Å, 107.3 Å and 101.4 Å for the as-synthesized, extracted and calcined solids respectively. The N\textsubscript{2} adsorption-desorption isotherm (Figure 2 of Paper II) of calcined and extracted cubic mesoporous solids shows a Type IV profile with capillary condensation steps at P/P\textsubscript{0} of 0.3-0.4. A small hysteresis is observed owing to the small cage size; 36.7 Å and 41 Å for calcined and extracted samples respectively. The structural and textural properties of the calcined sample of the C\textsubscript{16}TMABr templated \textit{Pm\textbar{3}n} structure are shown in Table 6. Further structural details of the cubic sample synthesized at a molar ratio of C\textsubscript{16}TMABr/ APES=0.6 were observed through HRTEM images recorded along the [100], [110] and [111] directions (Figure 3 of Paper II) and their Fourier Transform diffractograms (FTs). By careful observation of the FT-diffractograms, the extinction conditions were derived, and these confirmed the space group symmetry as \textit{Pm\textbar{3}n}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10}
\caption{(a) Powder X-ray diffraction patterns of mesoporous samples synthesized with different molar ratios of C\textsubscript{16}TMABr/APES. (b) X-ray diffraction patterns of as-synthesized, extracted and calcined mesoporous solids prepared at RT with molar ratio of C\textsubscript{16}TMABr/APES=0.6 showing well resolved peaks consistent with a cubic structure (b).}
\end{figure}

\textit{In-situ} SAXS measurements were performed to follow the mechanism of formation of \textit{Pm\textbar{3}n} structure and to determine whether a phase transformation does indeed occur from the hexagonal phase to the cubic structure. In
Figure 11, the first spectrum was recorded prior to the addition of the silica sources (i.e. mixture of APES and TEOS) and shows a single broad peak (Figure 11a). This peak corresponds to a $d$-spacing of 54 Å, consistent with the presence of spherical micelles at 0.4 wt% surfactant concentration. However, after the addition of the silica sources, the mesophase immediately changes and shows three well-resolved peaks (Figure 11b). A series of spectra were recorded at 3-minute intervals during the reaction. The intensity of the peaks increased with time indicating a high degree of crystal order. These peaks can also be indexed as 200, 210, and 211 based on a cubic structure and are consistent with the immediate formation of the $Pm\bar{3}n$ phase after the addition of APES and TEOS. This structural change demonstrates that the silica species, i.e. the APES, plays a co-structure-directing role during the first few seconds of the structure formation. Under the synthesis conditions presented here, at pH 11.2, the silica species are expected to hydrolyze rapidly.

Figure 11. A series of in-situ SAXS patterns recorded in order to follow the mechanism of formation of a $Pm\bar{3}n$ structure with the molar ratio $C_{16}TMABr/\text{APES} = 0.6$, where (a) shows the SAXS pattern of the surfactant in solution prior to addition of TEOS and APES, and (b) are a series of SAXS patterns recorded at 3 minutes after the addition of the silica sources.
Scheme 4. Proposed mechanism based on the penetration of a propylamino moiety into the micellar core, leading to the formation of cubic material with \(Pm_3n\) symmetry at a molar ratio of \(C_{16}TMABr/\text{APES} = 0.6\). Such a mechanism is denoted as \(S^+\text{NoI}^-\), where the uncharged amine at complete micellar coverage is responsible for maintaining the spherical geometry of micelles. With less micellar coverage and less penetration of the APES (i.e. at a molar ratio of \(C_{16}TMABr/\text{APES} < 0.6\)) a transformation to the \(p6mm\) cylindrical structure occurs.

As illustrated in Scheme 4, the surfactant initially forms spherical micelles. In the absence of APES (only TEOS), the curvature of the micelle varies from spherical to cylindrical leading to the 2D-hexagonal MCM-41 type phase. This can also be defined as an increase in the surfactant packing parameter, \(g\). The pKa of amino groups is 10.6, so that on addition of APES a large number of amino groups are expected to be in their neutral state (-NH\(_2\)). The hydrophobic part of the APES must penetrate slightly into the hydrophobic core of the micelles. Only on addition of a defined amount of APES, is the curvature of the spherical micelles maintained, despite penetration of the hydrophobic tail of the propylamino moiety (-C\(_3\)H\(_7\)NH\(_2\)) of APES. The mechanism proposed here is considerably different from those described above. There is indeed a co-structure-directing effect of the APES, but this is governed by penetration of the neutral propylamine moiety and not by interaction, as in the AMS-\(n\) systems. The mechanism can be denoted, following the nomenclature described above, as \(S^+\text{NoI}^-\). The degree of functionalization in extracted materials has been determined through TGA/DTG studies. Extracted samples of the cubic mesostructure with \(Pm_3n\) symmetry possess a surface coverage of propylamino groups of 2.15 mmol/g. The cal-
cined and functionalized cubic $Pm\bar{3}n$ samples have been further used to study the structural variations (Section 5.2) and adsorption capacities (Section 5.3.2).

Under the synthesis conditions presented here, the concept of penetration by a co-structure-directing agent has also been applied by employing other CSDAs such as 3-cyanopropyltriethoxysilane (CPTS), mercaptopropyl trimethoxy silane (MPTS) and N-trimethoxysilylpropyl-N, N, N-trimethylammonium chloride (TMAPS). Preliminary characterization was done by powder X-Ray diffraction. None of the samples showed any prominent peaks on the meso scale, but a broad peak between 1.5 and 3°20 degrees. The reasons for obtaining a broad peak are not clear at this stage, but they might indicate a disordered structure. However, further characterization through HRTEM may give some indications of the structural order. It can be speculated that the CSDAs used have different ionic groups and attaining a neutral state strictly depends on the synthesis pH. For example, the pKa of thiol functional groups is much closer to the synthesis pH (~11) used in this work, it many not be possible to get the same effect of penetration. A further increase in the pH leads to silica which must be dissolved. Hence it is expected to form only a disordered phase.

5.1.3 Effect of Hydrothermal Treatment in AMS-6 Synthesis

As a result hydrothermal treatment (HT), the folic acid-templated mesoporous samples (NFM-1) showed drastic variations in their structural and textural properties and this affected the growth direction by accelerating the polymerization rate of silica. Surprisingly, the classical mesoporous silica materials have undergone various phase transitions at various synthesis temperatures and HT. Phase transformations from lower interfacial curvature to stable higher curvature structures, as exemplified by the transition from cubic 3D cylindrical MCM-48 to hexagonal 2D cylindrical pore MCM-41, are common in the mesoporous synthesis literature. On the other hand, new mesostructures can be obtained through changes in the micellar conformation by inducing surfactant mesophases to undergo controlled phase transitions. Varying the silica source (e.g. TEOS, TMOS, TPOS), the addition of cosolvents, and the introduction of ionic species to the synthesis medium, are usual methods to induce phase transformations. As discussed in Section 3.4, the synthesis pH and hydrothermal treatment are the key parameters that induce the phase transformation. In this part of the thesis, the HT-induced transformations in a certain anionic-surfactant-templated mesoporous silica (AMS-$n$) materials is presented. This structure has previously been termed as AMS-6 (space group $Ia\bar{3}d$) and the effect of HT over long time periods (up to 60 days) was studied.
Figure 12. X-Ray powder diffractions of calcined samples of (a) AMS-6\(x\), \(x = 0, 2, 8, 9\) and 11 days of HT and (b) AMS-6\(x\) prepared with 15, 19, 22, 30 and 60 days of HT.

XRD patterns of calcined mesostructures prepared with hydrothermal treatment (HT) for 0-12 days are shown in Figure 12(a). The samples are denoted AMS- 6\(x\), where \(x\) is the duration of the HT treatment in days. Sample AMS-6(0) shows a range of well-resolved peaks with peak positions consistent with the cubic structure with unit-cell parameter \(a_0 = 105.8\ \text{Å}\). Reflections from samples AMS-6(2), AMS-6(3), and AMS-6(5) typically show more intense diffractograms, which can also be indexed by a cubic unit cell, showing an increase in the degree of order with increasing HT. Table 5 summarizes the structural data derived from XRD for these and similar samples. Samples AMS-6(8), AMS-6(9), AMS-6(10) and AMS-6(11) exhibit three XRD reflections corresponding to a 2D hexagonal mesostructure \((p6mm)\) with an average unit cell of 51.1 Å. Sample AMS-6(12) showed broad peak positions and it was not possible to obtain structural information from XRD alone. Experiments were continued to check possible further structural alterations with extended HT. The XRD pattern of the calcined sample AMS-6(15) shows 4 peaks between 2\(\theta\) values of 2-4° (Figure 12(b)) consistent with a 2D hexagonal structure \((p6mm)\) but with broader peaks than the samples treated for 8-11 days. An increase in the XRD peak intensi-
ties was observed in sample AMS-6(19) between 2θ angles of 2 and 2.3°. It is not possible to index these peaks based on either cubic or hexagonal structures. Prolonging the HT for more than 19 days, as shown in Figure 12(b), results in five or more well-defined diffraction peaks, with reciprocal spacing (1/dhkl) ratios of √6, √8, √14, √16, √22 and √26, confirming the presence of a cubic AMS-6 (Ia3d) structure.

Table 5. Textural and structural properties of mesoporous silica AMS-6(x) hydrothermally treated from 0-60 days.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter, a (Å)a</th>
<th>% Shrinkageb</th>
<th>Mesophase</th>
<th>DFT pore width (Å)</th>
<th>Pore volume (cm³/g)</th>
<th>Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS-6(0)</td>
<td>105.8</td>
<td>10.4</td>
<td>Ia3d</td>
<td>36.6</td>
<td>0.93</td>
<td>881.3</td>
</tr>
<tr>
<td>AMS-6(2)</td>
<td>110.8</td>
<td>7.8</td>
<td>Ia3d</td>
<td>39.5</td>
<td>0.75</td>
<td>781.3</td>
</tr>
<tr>
<td>AMS-6(3)</td>
<td>109.7</td>
<td>8.3</td>
<td>Ia3d</td>
<td>49.0</td>
<td>0.63</td>
<td>661.7</td>
</tr>
<tr>
<td>AMS-6(5)</td>
<td>109.6</td>
<td>4.4</td>
<td>Ia3d</td>
<td>43.1</td>
<td>0.76</td>
<td>712.7</td>
</tr>
<tr>
<td>AMS-6(8)</td>
<td>49.7</td>
<td>1.7</td>
<td>p6mm</td>
<td>45.2</td>
<td>0.77</td>
<td>702.7</td>
</tr>
<tr>
<td>AMS-6(9)</td>
<td>51.4</td>
<td>0.5</td>
<td>p6mm</td>
<td>45.2</td>
<td>0.99</td>
<td>902.9</td>
</tr>
<tr>
<td>AMS-6(10)</td>
<td>51.3</td>
<td>1.1</td>
<td>p6mm</td>
<td>45.2</td>
<td>0.77</td>
<td>676.2</td>
</tr>
<tr>
<td>AMS-6(11)</td>
<td>52.3</td>
<td>1.8</td>
<td>p6mm</td>
<td>45.2</td>
<td>0.73</td>
<td>675.6</td>
</tr>
<tr>
<td>AMS-6(12)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>42.4</td>
<td>0.57</td>
<td>479.0</td>
</tr>
<tr>
<td>AMS-6(15)</td>
<td>51.0</td>
<td>1.7</td>
<td>p6mm</td>
<td>45.2</td>
<td>0.81</td>
<td>719.4</td>
</tr>
<tr>
<td>AMS-6(19)</td>
<td>109.1</td>
<td>0.8</td>
<td>Ia3d</td>
<td>45.2</td>
<td>0.64</td>
<td>587.9</td>
</tr>
<tr>
<td>AMS-6(22)</td>
<td>106.7</td>
<td>4.2</td>
<td>Ia3d</td>
<td>42.4</td>
<td>0.61</td>
<td>583.9</td>
</tr>
<tr>
<td>AMS-6(30)</td>
<td>104</td>
<td>3.3</td>
<td>Ia3d</td>
<td>45.2</td>
<td>0.62</td>
<td>531.5</td>
</tr>
<tr>
<td>AMS-6(60)</td>
<td>114.4</td>
<td>0.9</td>
<td>Ia3d</td>
<td>45.2</td>
<td>0.57</td>
<td>536.4</td>
</tr>
</tbody>
</table>

aCalculated from calcined samples. bCalculated based on the XRD patterns of as-made and calcined samples.

The degree of silica condensation/polymerization can be followed by ex-situ 29Si NMR spectra (Figure 6 of Paper III) of as-synthesized AMS-6(x) samples. The 29Si NMR spectra indicate that the AMS-6 samples prepared with short HT times have a less well-formed silica network. The initial sample AMS-6(0) has a less condensed framework as indicated by the higher Q3/(Q4 + Q5) ratios. In addition, this sample has a large T3/(Q4 + Q5) ratio. Both these ratios decrease with increasing HT (T3 indicates the presence of the organoalkoxysilane APES). The AMS-6(9) sample in particular, showed a large reduction in the relative amount of organo-silica moieties after 9 days of HT, and the Q3/(Q4+Q5) ratio decreases, indicating a large condensation of silica on prolonged HT. It can be speculated that this exclusion (or decomposition) of organo-silica moieties and condensation of the silica network are the molecular reasons for the two phase transitions found.
Figure 13. HRTEM of cubic samples treated for prolonged periods of HT: (a) and (b) 22 days, and (c) and (d) 60 days. All images are recorded along the [111] incidence and there is a clear evidence of an external porous layer outward towards the particle surface.

TEM evidence confirms the formation of well-ordered bicontinuous 3D cubic structures of AMS-6 in samples treated for up to 5 days and between 19 and 60 days, as well as the presence of a 2D hexagonal (p6mm) mesostructure after 8 days of HT (Figure 3 of Paper III). Further TEM analysis on the 3D cubic samples based on tilting experiments and FFT diffractograms recorded over thin specimen regions reveals that the mesostructures are consistent with the $Ia\overline{3}d$ space group symmetry, satisfying extinction conditions such as the absence of the 110 reflections along the [111] incidence. TEM observations also revealed an external porous layer surrounding the mesoporous nanoparticles. This layer varied in thickness from one sample to another, ranging from 5 to 20 nm, and it is surprisingly absent in AMS-6(12), which in turn showed a disordered mesostructure. The formation of an external porosity was also observed (Figure 13) in samples AMS-
6(22) and AMS-6(60), but surprisingly no external porosity was observed at HT times of 19 and 30 days.

A detailed analysis of the structural data suggests that the transformation from cubic to hexagonal is kinetically faster between 3 and 5 days of the HT than the hexagonal to cubic transformation, which clearly shows intermediate mesophases over a longer time period between 15 and 22 days of HT. In the AMS system reported here, where an anionic head group in combination with a CSDA was used, the electrostatic environment around the surfactant head group (including entropic contributions) has been found to play a leading role in the effective surfactant curvature. Several mesophase transitions have been reported as a result of the addition of NaOH and HCl to the synthesis mixture, which influences the surfactant packing arrangement.\textsuperscript{138} In addition, mesophase transitions from the cubic $Ia\bar{3}d$ to the 2D hexagonal $p6mm$ through high temperature treatment involve an increase in the surfactant packing parameter, $g$, which has previously been used to quantify changes in micellar curvatures.\textsuperscript{39, 41} It is thought that when a surfactant is heated, thermally excited hydrocarbon chains increase the overall molecular micellar volume, leading to an increase in $g$. However, such curvature changes alone do not explain the slow time scale of phase transformations observed here. A transition from a bicontinuous cubic structure to a hexagonal structure cannot be simply rationalized for packing reasons without an increased level of hydration or head group repulsion. Such repulsion or hydration can definitely be associated with the exclusion of the organo-silica (a large reduction in the organo-silica groups after 9 days of HT was confirmed by $^{29}$Si NMR) and the associated changes in the properties of the inorganic wall. During prolonged hydrothermal treatment, silanol groups and deprotonated silanol groups condense, liberating hydroxide anions which increase head group repulsion. This leads to a change in micellar conformation as the packing of surfactant molecules seeks to maintain van der Waals interactions between the hydrocarbon tails while the distance between head group charges increases, consistent with the previous findings.\textsuperscript{40, 135}

Further evidence of the structural differences between materials prepared here was obtained by nitrogen sorption isotherms (Figure 7 of Paper III). All the samples showed a Type IV nitrogen sorption isotherm. The comparative structural and textural properties of AMS-6(x) samples are summarized in Table 5, where it is clear that the pore width is influenced by the HT and that the pore width increases with increasing HT. TGA/DTG curves of the as-synthesized AMS-6(x) samples treated for 0 to 60 days of HT were also analyzed (Figure 8 of Paper III). All the AMS-6(x) samples show three distinct stages of weight loss and the amount of decomposition associated with the anionic surfactant and APES between 200 and 400 $^\circ$C clearly decreased with HT. The values suggest a migration of the surfactant out of the polymerizing structure with HT, perhaps due to decomposition of the surfactant via thermal degradation.\textsuperscript{139} Combined with the pore width and TGA, the data support
the speculation that the initial phase transformation (bicontinuous cubic \(Ia\bar{3}d\) to hexagonal \(p6mm\)) is driven by the exclusion of organo-silica, leaving the final material with a slightly thinner wall. Hence, the greater pore widths in the final cubic material compared with the initial AMS-6(0) solid can be explained by “etching” of the wall and a more condensed silica network. The level of condensation is also accessed though TGA, where a smaller weight loss at the higher temperature (third stage 400 - 900 °C) is accompanied by the condensation of silanol groups. A decrease in % weight loss due to condensation of approximately 45% was observed when the AMS-6 samples were hydrothermally treated for two days (AMS-6(2)), highlighting the large differences in degree of polymerization and silica wall density obtained through this short thermal treatment.

Overall, the results indicate that the phase transformation described here from cubic \(Ia\bar{3}d\) to hexagonal \(p6mm\) is accompanied with a greater degree of silanol group rearrangement than the reverse transformation from lower curvature to higher curvature (Figure 9 of Paper III). Data from TGA and \(^{29}\)Si NMR seem to confirm that the initial mesophase transformation is governed by changes in silica rearrangement through etching and increased head group repulsion, or hydration level, in the surfactant head group region of the CSDA with HT, whereas the secondary mesophase transformation is driven primarily by changes in charge matching at the silica/organic interface, because of increased polymerization of the silica wall and an increase in wall density. The observation of external porosity or surface features in certain samples but not others during HT must suggest an ongoing growth of the silica particles and changes in the concentration of growth “nutrients” at the growing surfaces. A synthesis pH of 9 attained during the synthesis gradually changed to 6.9 after days of HT and finally 7.5 after 22 days of HT. It is therefore expected that a certain amount of dissolution and reprecipitation must occur in the AMS-6 system described here.

In addition to the study of the effect of hydrothermal treatment on the AMS-6 structure, a simple study with a view to enlarging the pore size of the AMS-6 was also investigated by employing 1,3,5-trimethyl benzene (TMB) as a swelling agent. The results showed a considerable increase in the pore width of up to 5 nm. The addition of TMB also led to a phase transformation from an AMS-6 (\(Ia\bar{3}d\)) to an AMS-10 (\(Pn\bar{3}m\)) structure. Interestingly, a new structure was also discovered as an intermediate phase between these two structures. The preliminary characterization of this material showed that it has a cubic structure but the symmetry of this structure is not yet solved due to lack of the purity of the sample. It is found to be difficult to isolate the new structure, and this may require good control of the synthesis conditions.
5.2 Structural Variations in $Pm\bar{3}n$ Symmetry Structures

This part of the thesis presents a detailed investigation onto the structural variations in a meso-cage material is presented (Paper IV). The meso-cage material with $Pm\bar{3}n$ symmetry has been chosen as a model structure in which to study the structural variations. The first preparation of such a cubic structure, known as SBA-1, was reported by Huo et al.\textsuperscript{38} under highly acidic conditions. Later work has made use of non-ionic polymeric surfactants, bolaform surfactants, dicationic gemini surfactants and anionic surfactants for the synthesis of similar materials with the same space group symmetry.\textsuperscript{13, 63, 71, 93} Most of the published work on $Pm\bar{3}n$ has focused on controlling the particle morphology and improvements in the synthesis methods.\textsuperscript{44, 127, 140-145} Recently, Anderson \textit{et al} and Sakamoto \textit{et al}. have initiated an understanding of the connectivity of the cage of the $Pm\bar{3}n$ structure through XRD structural analysis and electron crystallography, respectively.\textsuperscript{63, 85} The main aim of the present study is; (1) to understand what factors influence the size of the cage-connecting windows with respect to the synthesis conditions and surfactant types, (2) to identify possible synthetic design tools that will allow the control of such fine structural details, and (3) to understand better the formation of cavities and their connecting windows with respect to the synthesis conditions. As discussed in Section 3.5, electron crystallography combined with N$_2$ sorption data is one of the few methods available to reveal such fine details of a porous material on a mesoscale.

![Figure 14](image)

Figure 14. SEM images of mesoporous materials show rhombic dodecahedral and multi-facetted particle morphologies, templated by (a) C$_{16}$-3-1 and (b) C$_{16}$TEABr surfactants respectively.

$Pm\bar{3}n$ symmetry mesostructures were synthesized using the C$_{12}$GluA, C$_{16}$TMABr surfactants under alkaline conditions and APES as CSDA; and C$_{16}$TEABr and C$_{16}$-3-1 under acidic conditions without the use of CSDA. Samples are denoted with respect to the surfactant used as C$_{12}$GluA-$Pm\bar{3}n$, C$_{16}$TMABr-$Pm\bar{3}n$, C$_{16}$TEABr-$Pm\bar{3}n$ and C$_{16}$-3-1-$Pm\bar{3}n$. The sample C$_{12}$GluA-$Pm\bar{3}n$ was synthesized at 60 °C. Samples C$_{16}$-3-1-$Pm\bar{3}n$ and C$_{16}$TEABr-$Pm\bar{3}n$ samples were prepared at +4 °C, while C$_{16}$TMABr-$Pm\bar{3}n$
sample (the same sample as that described in Section 5.1.2) was prepared at room temperature.

All the samples have been well characterized through X-ray powder diffraction and the reflections are consistent with the cubic structure (Figure 1 of Paper IV). The structural properties of these materials were further determined primarily through TEM analysis, as discussed below. Table 6 summarizes the structural parameters derived from XRD data. Variations in the particle morphology were also observed by SEM for the samples prepared here (Figure 14). All the samples possessed well-defined morphologies with relatively homogeneous shapes. The samples prepared under alkaline conditions, C_{16}TMABr-Pm\text{3}n\text{m} and C_{12}GluA-Pm\text{3}n, show rough surface textures with little or no faceting. In contrast, the samples synthesized under acidic conditions and at low temperatures possess clear facetted particle morphologies. Figure 15(a) shows typical nitrogen adsorption-desorption isotherms for the calcined solids prepared in this study. For comparison purposes, BJH, HK and DFT models (see Paper IV) were used to calculate the pore size distributions (PSD). Even though all the models showed the same porosity trend, the pore widths obtained by BJH and HK models has values 10-50% lower than those derived from the DFT model. The pore size distribution plots drawn according to the DFT method (Figure 15(b)) shows two steps which may be associated with the filling of the void in the materials. The region labeled (I) 18 and 25 Å may be associated with the presence of the complementary pores while the broader 26-45 Å region (II) may be related to the filling of the cavities of the Pm\text{3}n symmetry mesostructures. The textural characteristics of the mesoporous materials prepared are summarized in Table 6.

Figure 15. (a) N\text{2} isotherm curves of calcined structures with Pm\text{3}n\text{m} symmetry. (b) NLDFT pore size distribution derived assuming a spherical pore geometry.
Table 6. Detailed structural and textural properties of calcined mesoporous materials with Pm\textit{3n} symmetry.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>(a_0) XRD (Å)\textsuperscript{a}</th>
<th>(a_0) XRD (Å)\textsuperscript{b}</th>
<th>(a_0) TEM (Å)</th>
<th>BET Area (m\textsuperscript{2}g\textsuperscript{-1})</th>
<th>Pore volume (cm\textsuperscript{3}g\textsuperscript{-1})</th>
<th>Pore size DFT (Å)</th>
<th>Pore volume fraction (%)</th>
<th>Cage/Window Size (Å)\textsuperscript{c}</th>
<th>Ratio of Average Window to cage size (Å)\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{16}TMABr - Pm\textit{3n}</td>
<td>110</td>
<td>101.4</td>
<td>98.8</td>
<td>579.7</td>
<td>0.43</td>
<td>24.6</td>
<td>37.5</td>
<td>46</td>
<td>49</td>
</tr>
<tr>
<td>C\textsubscript{12}GluA - Pm\textit{3n}</td>
<td>98.2</td>
<td>93.5</td>
<td>91.3</td>
<td>853.6</td>
<td>0.58</td>
<td>25.8</td>
<td>37.8</td>
<td>54</td>
<td>50</td>
</tr>
<tr>
<td>C\textsubscript{16}TEABr - Pm\textit{3n}</td>
<td>89.9</td>
<td>81.4</td>
<td>80.5</td>
<td>959.6</td>
<td>0.55</td>
<td>21.4</td>
<td>34.0</td>
<td>52</td>
<td>39</td>
</tr>
<tr>
<td>C\textsubscript{16,3,1} - Pm\textit{3n}</td>
<td>90.1</td>
<td>76.9</td>
<td>75.5</td>
<td>1243.6</td>
<td>0.62</td>
<td>21.2</td>
<td>29.2</td>
<td>55</td>
<td>39</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculated from the as-synthesized samples of mesocaged \(Pm3n\) structures, \textsuperscript{b} Calculated from the calcined samples of mesocaged \(Pm3n\) structures, \textsuperscript{c} Obtained from the 2D electrostatic potential maps of \(Pm3n\) structures which were the result of 3D reconstructed models, \textsuperscript{d} The average value of the cages and the cage-connecting windows are calculated by considering; 6 B-cages and 4 A-cages; 6 B-B cage windows and 24 A-B cage windows per unit cell.
To further elucidate the connectivity of cage and overall structural characteristics of the mesocage materials prepared in this work, HRTEM and structural reconstructions based on electron crystallography were performed. Typical HRTEM images recorded along [111] direction and corresponding FFT diffractograms of all the samples are shown in Figure 16 (other HRTEM images along the [100] and [110] which have been used in this study are shown in Figure 5 of Paper IV & supporting Information SI). The unit cell parameters derived from TEM are consistent with the XRD data (Table 6). The reflection conditions are derived from the TEM images and their corresponding FFTs, and are consistent with $h00$: $h=2n$, $0k0$: $k=2n$, $00l$: $l=2n$, $hhl$: $l=2n$, $hkk$: $h=2n$, and $hhk$: $k=2n$, which confirms the space group symmetry as being either $Pm\bar{3}n$ or $P43n$. However, by considering the highest symmetry, the final space group symmetry for all the samples can be unambiguously assigned as $Pm\bar{3}n$.

Figure 16. TEM images of calcined materials (a) $C_{16}$TMABr-$Pm\bar{3}n$, (b) $C_{12}$GluA-$Pm\bar{3}n$, (c) $C_{16}$TEABr-$Pm\bar{3}n$ and (d) $C_{16-3-1}$-$Pm\bar{3}n$ along the [111] direction. Inset shows indexed FT diffractograms of the images.
The pore structures of calcined samples can be visualized from the 3D-electrostatic potential maps reconstructed from the structure factors obtained from electron crystallography (See Paper IV-SI for a complete list of structure factors). The 3D-electrostatic potential maps for all the samples are shown in Figure 17. The color scheme represents areas of high silica density (yellow) and areas at the centre of the pore space (black). According to Figure 17, each lattice consists of two types of cavities with open cage-connecting windows to the neighboring cavities. The face cavities are noted type B, while the corner cavities type A. All the samples show distinct variations in the cage-connecting window sizes between the cavities B and A, marked by arrows in Figure 17. The 2D-electrostatic potential density maps of the structures at various slice thicknesses along the [100] orientation (Figure 7 of Paper IV) are also constructed in order to obtain the structural data which are listed in the Table 6.

The type A cages are spherical in shape and the type B cavities are ellipsoidal, as was confirmed by slicing the unit cells at different positions along the [100] orientation. The samples prepared under alkaline conditions, C_{16}TMABr-Pm\text{3}n and C_{12}GluA-Pm\text{3}n, show larger cage sizes than those prepared under acidic conditions and are in the same range as the values derived from sorption data using the DFT model, but considerably larger than those obtained with the BJH and HK models. The average cage-connecting window sizes were in the following order: C_{16}TMABr-Pm\text{3}n < C_{16}TEABr-Pm\text{3}n < C_{16-3-1}-Pm\text{3}n < C_{12}GluA-Pm\text{3}n. Overall, the data obtained from electron microscopy suggest that the size of the surfactant head group or the head group charge density may play an important role in determining the size of the cage-connecting windows, and the use of CSDAs in the synthesis mechanism.

It has previously been suggested that the size of the cage-connecting windows and of the cages depends largely on the ionic environment at the silica/surfactant interface and the surfactant properties. Sakamoto et al. reported a Pm\text{3}n symmetry structure (SBA-1) with cage size 33x41 Å and a connecting window size of 8 Å measured by electron crystallography reconstruction. Considering the unit cell shrinkage, and the expected size of the micelles, it appears safe to assume that the cage-connecting windows are not formed as a result of the presence of a smaller micelles between the cage connections. As illustrated by Anderson et al. under acidic conditions, the formation of cage-connecting windows in the Pm\text{3}n structure is associated with the thickness of an adsorbed water layer and the contact angle between the adjacent micelles. Although a thicker hydration layer surrounding the micelles is expected at low pHs, as represented in Scheme 5(a), clearly the lower degree of silica condensation plays a final role in the cage sizes in calcined materials. In the TGA analysis, a large weight loss was observed at temperatures above 550 °C for acid-catalyzed materials, which can be interpreted as a silanol condensation within the mesoporous silica wall. The per-
centage silica shrinkage due to calcination was also higher for $C_{16-3-1}^{\text{Pm}\bar{3}n}$ (14.6%) and $C_{16}\text{TEABr}^{\text{Pm}\bar{3}n}$ (9.5%). Hence, the acid-catalyzed mesocaged materials possess lower cage sizes than those prepared under alkaline conditions. The acid-catalyzed samples showed only subtle structural differences (B-A and B-B window sizes) with respect to their cage-connectivity. The *gemini* surfactant $C_{16-3-1}$ possessed a doubly charged head group and twice as many counterions, whilst the charged ammonium cation of $C_{16}\text{TEA}^+$ was more shielded by the bulky ethyl groups in the head group. Hence, the small variations in B-A cage size between these two structures can be due to the differences in charge density at the surfactant head group.

![Figure 17. 3D-electrostatic potential density models of calcined mesocaged materials prepared with (a) C$_{16}\text{TMABr}$, (b) C$_{16}\text{TEABr}$, (c) gemini C$_{16-3-1}$ and (d) C$_{12}\text{GluA}$ surfactants shown with respect to increasing cage-connecting window size.](image)

Under alkaline conditions, it has already been shown that the surfactant C$_{16}\text{TMABr}$ possesses spherical micelles at low surfactant concentration and under aqueous conditions. In both systems studied here, the use of CSDAs was necessary in order to increase the electrostatic interactions between the surfactant head group and the silicate wall. In the case of the highly alkaline (pH=11.2) C$_{16}\text{TMABr}^{\text{Pm}\bar{3}n}$ synthesis, the mechanism is thought to be governed by penetration of the neutral amine group in APES within the micelle, driving the formation of the $\text{Pm}\bar{3}n$ phase (Section 5.1.2). In the case of the di-anionic surfactant C$_{12}\text{GluA}$ synthesis, the ammonium cation electrostatically interacts with the surfactant head group. The use of CSDAs may also explain why the cage sizes observed in these solids are considerably larger than those in mesocaged materials prepared under acidic conditions. Firstly, the propyl groups of the CSDA will render a degree of hydrophobicity to the
micellar interphase and hence the concept of a hydration layer is not strictly applicable. Further, under alkaline conditions, the silica condensation is relatively fast and leads to the rapid formation of a silica network at the micellar interface. This is corroborated by a smaller unit cell shrinkage upon calcination in samples prepared under alkaline conditions owing to more condensed silica walls. It can be postulated that the silica network joins all the micelles with open windows filled with a water layer between adjacent micelles as represented in Scheme 5(b). Samples C\textsubscript{16}TMABr-Pm\textbar n and C\textsubscript{12}GluA-Pm\textbar n also showed variations in cage-connecting windows where the B-B opening was approximately twice as large as B-A window. Since very different mechanisms are involved, i.e. CSDA penetration within the micelle and charge matching electrostatic interactions, it is likely that the differences in cage-connecting windows are inherent in the micellar formation of Pm\textbar n symmetry structures.

Scheme 5. Illustration of the formation of the cages and cage-connecting windows in Pm\textbar n structure under a) acidic conditions, where the gemini surfactant with double charge groups interacts with the positively charged protonated silanol (=Si (OH\textsubscript{2})\textsuperscript{+}) groups mediated by chloride anions, and b) basic conditions, where the cationic surfactant with a single charge group and CSDA (i.e. APES) penetrates at the micellar surface; blue=silica wall, black=adsorbed water layer and white=micelles. In the acidic synthesis, the micellar surface is covered with the water layer and connects the neighboring micelles, whereas in the basic synthesis the water layer separates the neighboring micelles and creates a large cage-connecting window size.

Overall the structural and textural information indicate two important parameters that determine the size of the cage-connecting windows: (i) the charge density at the surfactant head group, and (ii) the presence of organoalkoxysilane CSDA. Although our results clearly demonstrate that the packing parameter of a surfactant systems is clearly governed by the surfactant geometry (chain length, head group size, etc), they suggest that the fine structural details of mesocaged materials with Pm\textbar n symmetry may be controlled by a careful tailoring of the charge density and of the hydration layer adsorbed between the surfactant and silica interface.
5.3 Structure-Function Relation of Mesoporous Silica Materials

In the above sections, it has been shown that there is a non-surfactant synthesis route, a penetration-induced route and even phase transformation pathways for the synthesis of several of 2D and 3D mesoporous structures. The physical and textural properties of these materials have been well characterized through XRD, N$_2$ isotherm and electron microscopy. An important finding is that, although the symmetry of the structure is the same for cage-type mesoporous structures, the cage and cage-connecting window sizes are very different and are largely dependent on the geometry of the surfactant and on the synthetic environment. This is important when considering these materials for different applications. Mesoporous materials have already shown a potential for use in catalysis, adsorption and the life sciences (Section 3.6). Before these materials can be employed for applications where entities such as drugs, peptides, proteins, are to be protected and released in a predetermined manner, methods are needed to evaluate how the geometry of the internal pore system in the particles affects diffusive transport. It is therefore important to study and understand the relationship between the structural properties and function in mesoporous materials. Ways to study the relationship are (1) by evaluating the diffusion of guest molecules in and out of the porous structures with different structural complexity and (2) by in-situ analysis of the adsorption of gases with respect to their structural properties and mode of functionalization.

5.3.1 Structure-Function Relationship through Diffusion Process

AMS-$n$ derived structures were employed to study the controlled release of amino acid-derived molecules (i.e. anionic surfactants as the model drugs) from the internal pore structure of mesoporous nanoparticles as drug delivery systems with different structural properties, viz.: cylindrical (AMS-3, p6mm) and AMS-6, Ia3d) and cage type structures (AMS-8, Fd3m and AMS-9, P4$_2$/mnm) with various degrees of complexity. The synthesized materials (Section 4.1.2) were well characterized using XRD, N$_2$-isotherms, SEM, TEM and TGA which confirmed that all the AMS-$n$ structures possessed a well-defined structural order. The AMS-8 structure is known to be composed of two networks of cages of different sizes, whilst the AMS-9 structure is thought to be composed of three networks of cages with different sizes and to have a lower symmetry than AMS-8.$^{66,93}$

Release measurements were performed at 60 °C in a measuring cell by using the Alternating Ionic Current (AIC) technique.$^{147}$ For each 100 mg of solid sample, 20 ml of distilled water was used as the dissolution medium.
An effective diffusion coefficient for the surfactant release processes was extracted according to the Higuchi square-root-of-time law. Release of amphiphiles obtained by AIC measurements have been interpreted in terms of specific structural and textural parameters of the porous nanoparticles such as pore geometry and connectivity. Results indicate that diffusion coefficients are lower by as much as four orders of magnitude in 2D structures than in 3D mesoporous solids (Table 2 of Paper V). The AMS-8 and AMS-9 cage types released $\approx 50\%$ of the total amphiphile content during the first 8 hr of the release experiment. For the cylindrical type AMS-3 and AMS-6 structures, the corresponding amounts released were $\approx 6\%$ and $\approx 39\%$ after about 57 hr and 18 hr, respectively. The 2D-hexagonal structure showed the slowest diffusion coefficient of all the AMS-$n$ materials, while all the 3D cubic structures showed higher diffusion coefficients and larger amounts of amphiphile released per unit time.

From these models it is possible to appreciate how a larger amount may be released from a cage structure. There are numerous connections between cages and more connections to the external surface which although the tortuosity of the cage structure is increases, may nevertheless contribute largely to the faster diffusion coefficients calculated for these structures. In the case of the cylindrical pore systems, there is no connection between cylindrical channels, and the diffusion is limited by the number of openings to the external surface. It is clear from this work, that the connectivity (2D or 3D) of the pores is the key to controlling the release rate, with an increase in diffusion coefficient of several orders of magnitude from 3D porous networks with similar textural properties. From this study it can also be concluded that the pore geometry can play an important role in controlling the release rate and for speeding up the release of molecules from the internal cavities, as exemplified by the faster diffusion coefficients in the AMS-8 and AMS-9 cage structures.

Irrespective of the release of surfactants from the pore structure as described above, a new method to investigate the effect of pore geometry on the diffusion has also been presented. This method is based on the study of proton diffusion from a liquid surrounding the mesoporous particles into the particle pore system. The driving force behind the proton diffusion into the mesoporous silica particles is the concentration gradient introduced at the interface between the high proton concentration solution outside the particles and the aqueous monolayer present in the uncalcined particle pores. The same series of AMS-$n$ (AMS-3, AMS-6, AMS-8 and AMS-9 particles with 2D and 3D connectivity) was employed for the proton absorption analysis. In each measurement, a similar concentration of protons was maintained by dissolving 100 mg of the mesoporous solids in 20 ml of nitric acid with an initial pH of around 2. The experimental set-up used was identical to that used for the surfactant release experiments such as the AIC technique. Figure 18 shows how the conductance in an aqueous solution of hydrogen...
nitrate (nitric acid) changes as a function of time when four different types of uncalcined mesoporous silica particles are introduced. The initial conductance decrease is associated with an increase of the solution pH and can be related to protons diffusing into the particles, thus leaving fewer charge carriers in the solution contributing to conductance. Matching the conductance to the measured pH, the initial contribution to the conductance from ionic species other than protons can be subtracted and the proton concentration as a function of time for the initial decay can be extracted (Figure 18 (b)). In order to extract the proton diffusion coefficient in the mesoporous structures (see Paper VI for equations), proton concentration versus the square root of time was plotted and a linear fit to the data was made.

Figure 18. (a) Conductance changes in nitric acid solution as a function of time when four different types of uncalcined mesoporous AMS-\textit{n} silica particles are introduced. The figure (b) displays the solution proton concentrations as a function of time for the initial conductance decay period.

The results show that the diffusion coefficients were higher for proton absorption than for surfactant release, and that they overall followed the same trend, with the more complex 3D mesocaged materials showing the highest diffusion coefficients (Table 1 of Paper VI). Unexpectedly, the same ranking of the three-dimensional (3D) AMS-6, 8, and 9 structures in terms of diffusion speed was obtained using both surfactant release and proton absorption to monitor the structures. The proton diffusion coefficient in these three structures was $\sim2$ orders of magnitude larger than that for the surfactant release. This is the same relationship between surfactant and proton diffusion coefficients as in free water. The sizes of the pore space left by the surfactants and entered by the protons are very different; the surfactants leave a
pore structure corresponding to that of a calcined material, albeit with a layer of functional groups on the pore wall surface, while the protons enter an environment in which the mesopores are almost entirely filled by surfactants. This strongly indicates that it is the geometry, in terms of pore connectivity and tortuosity, rather than the pore size and pore wall interaction that determine the diffusion speed both for the surfactant release process and for the proton absorption process in AMS-6, 8, and 9. For the two dimensional (2D) AMS-3 nanoparticles, as found above, it is very difficult for the surfactants to escape the structure in spite of the very low tortuosity of the hexagonal cylindrical 2D pores. It was argued that the low diffusion coefficient found for the surfactant release process from this structure could be linked to the lack of connectivity between the 2D cylinders and also to the relatively few openings to the external surface. In the case of the proton absorption process, these factors do not appear to pose hindrance for the proton movement, as the diffusion coefficient was found to be almost 4 orders of magnitude higher than that for the surfactants, and of the same order of magnitude as that in the 3D cylindrical cubic AMS-6 structure. The fact that the proton movement occurs at a similar speed in these two structures with a similar pore shape (cylindrical channels) indicates that proton diffusion is a better probe of the structure than the diffusion coefficient for the much larger surfactants. It was also found that the 3D material (AMS-6) with cylindrical and uniform pores provided lower diffusion coefficient then the 3D material with cage like pores. Since their level of connectivity is different, it is expected that the diffusion rates to differ. Although cage windows may offer a diffusion barrier, it appears that for smaller probe molecules (ions, protons) the connectivity of the probe structure itself may play a more important role in determining the speed of diffusion. Overall, it appears that proton diffusion is a better tool to obtain information about pore geometry in porous nanoparticles than assessment of movement of larger ionic species.

5.3.2 CO₂ Adsorption in Cage-type Mesoporous Silica Materials

As discussed in Section 5.2, all the \( Pm\bar{3}n \) structures showed considerable variations in their cage and cage-connecting window sizes, and the details are presented in Table 6. These fine structural details are essential for studying the sorption behaviour of various gases. To study the importance of the structural details and their function towards high adsorption capacities, the temperature-induced uptake of CO₂ was studied on the same \( Pm\bar{3}n \) structures. In addition to the structural properties, the quantity of functional groups in the silica wall also affects the adsorption rate. It has been shown that mesoporous silica modified with amines adsorbs a large amount of CO₂, due to its high basicity. The functional amino groups on the silica wall can
be modified either a post-synthetic method or by a co-condensation method (Section 4.1.3). The samples designated extracted-1 and extracted-2 were synthesized by co-condensation of APES and solvent extraction of the C_{16}TMABr and C_{12}GluA surfactants from non-calcined materials led to a homogeneous distribution of amino groups in the silica wall. The surface coverage of amino groups was estimated from TGA, and the estimated amine content of the extracted-1 and extracted-2 samples were 2.16 mmol/g (2.81/nm²) and 3.07 mmol/g (3.10/nm²), respectively. For the post-synthesis modification, three calcined samples designated post-synthesis-1, post-synthesis-2 and post-synthesis-3 were used, and the samples were templated by C_{16}TMABr, C_{16}TEABr and gemini surfactants, respectively. The post-synthesis modification of the calcined mesoporous silica materials with n-propylamino groups was performed by tethering APES to the internal surfaces under autocatalytic reaction conditions. The estimated amine content of the samples fell in the range of 1.38 to 2.59 mmol/g (1-1.62 /nm²). When compared with their respective calcined materials, the overall pore characteristics after the functionalization were considerably reduced for all the samples. Particularly, the post-synthesis samples show very low BET-surface area and pore volume. It has been discussed in Section 5.2 that the mesocaged materials possessed bimodal porosity in the form of cages and cage-connecting windows (Table 6). Hence, it is expected that the tethered APES moieties might blocked the cage entrances of the post-synthesis samples. The volumetric uptake of CO₂ gas under equilibrium conditions were measured at different temperature and pressure using a Micrometritics Gemini 2375 device. To study the molecular details of the adsorption of CO₂ in propylamine-coated mesocaged silica materials, in-situ FTIR spectroscopy was used. This novel technique relies on various vibration frequencies for physisorbed CO₂, which are close to the gaseous CO₂, and for chemisorbed CO₂ resulting from propylamine groups reacting with the CO₂ gas (which results in ammonium-carbamate salts).

From the volumetric adsorption analysis, the temperature-dependent (-20 °C, 25 °C and 70 °C) uptake of CO₂ showed subtle variations with respect to the structural properties and the localized distribution of n-propylamino groups in the silica wall (Figure 5 of Paper VII). The post-synthesis-1 sample showed a very low adsorption, 0.71 mmol/g of CO₂ at 70 °C compared to the post-synthesis-2 (0.99 mmol/g) and post-synthesis-3 (0.90 mmol/g) samples, consistent with its small cage-connecting window size. Due to the small window size (6 Å), the post-modification of post-synthesis-1 sample may suffer pore blocking and hence a low distribution of amino groups (1.38 mmol/g) within the silica wall. However, the post-synthesis-2 and 3 samples possess an average window sizes of 10 Å and 13.5 Å, respectively, and the accessibility for the n-propylamino groups is higher, 2.59 mmol/g and 2.07 mmol/g, respectively. These differences in the quantity of amino groups on the silica wall are central for the adsorption of different amounts of CO₂.
which depends on the cage-connecting window size. Hence, understanding the fine structural details of the mesocaged structures often provides greater selectivity for potential applications. With respect to the mode of functionalization, the extracted-1 sample shows a higher rate of CO$_2$ adsorption at low temperatures while the post-synthesis-1 sample shows a completely different trend with a higher rate of adsorption at higher temperature (Figure 19). In fact, all the extracted and post-synthesis samples follow the same trend of higher CO$_2$ adsorption at a low temperature and high temperature, respectively. Since adsorption is an exothermic process, the trend of CO$_2$ adsorption on extracted samples is consistent with the temperature, but for the post-synthesis samples, this trend is not typical.

Molecular aspects of the temperature-dependent uptake of CO$_2$ were further studied using an in-situ transmission IR cell equipped with a heat controller and pressure transducers (Figure 3 of Paper VII). FTIR spectra of extracted-1 and post-synthesis-2 samples measured at three pressures are shown in Figure 20. Two prominent signals are observed at 2341 cm$^{-1}$ which correspond to an asymmetric stretching band of physically adsorbed CO$_2$ and another at a broad signal range of 1750-1200 cm$^{-1}$ which correspond to various forms of chemisorbed CO$_2$ (ammonium-carbamates). The post-synthesis sorbents showed significantly smaller fractions of physisorbed CO$_2$ than did extracted samples, as deduced from the relative intensities of the bands at 2341 cm$^{-1}$ and from the relative intensities of the bands of chemisorbed species.

From in-situ FTIR measurements, the extracted samples show (Figure 8 of Paper VII) mostly physisorbed CO$_2$ while the post-synthesis samples show (Figure 9 of Paper VII) a higher degree of chemisorption of CO$_2$ in the form of carbamates-propylammonium ion pairs (Scheme 1 of Paper VII). These differences can be explained by the degree of heterogeneity in the n-propylamine coating, as the homogeneity of the propylamine modification in the extracted samples is too high and the primary amine groups appear to be
to far from each other to form carbamate-ammonium ion pairs, so that the adsorption is primarily governed by physisorption. Surprisingly, post modification of n-propylamino groups on the post-synthesis samples leads to a random distribution of the n-propylamine coating, and this promotes the formation of carbamate-ammonium ion pairs at elevated temperatures.

Figure 20. In-situ transmission FTIR spectra for mesocaged \((Pm\bar{3}n)\) silica materials with propylamine moieties. Spectra are recorded for (a) extracted-1 at 2, 40 and 100 torr, and for (b) post-synthesis-2 at 1, 40, and 100 torr (from bottom to top).

Overall, the mesocaged samples show different trends of CO\(_2\) adsorption depending on their structural variations and the localized distribution of n-propylamino groups. The size of the cage-connecting window may have a considerable effect in controlling the spread of functional groups without pore blocking, while the method of surface modification promotes either physisorption or chemisorption.
6. Conclusions

With respect to the classical surfactant-templating methods for the synthesis of mesoporous structures, a novel templating approach for ordered mesoporous materials through the use of folic acid as the only pore forming agent has been presented. The glutamic moieties of the stacked array of pterin tetramers interact electrostatically with the amino groups of CSDA followed by silica polymerization, and this leads to a novel 2D hexagonal Nanoporous Folic acid Material (NFM-1). The mechanism of formation of this material has also been investigated and results show that the CSDA primarily encapsulates the folic acid stack and facilitates the polymerization of TEOS along the column.

In addition, a novel synthesis strategy was proposed for the synthesis of amino-functionalized $Pm\bar{3}n$ mesocaged solids based on the micellar penetration of a CSDA (i.e. APES). In-situ SAXS studies confirmed the formation of the mesophase directly after the addition of a silica source to the surfactant C$_{16}$TMABr solution. The addition of APES under strongly alkaline conditions at a molar ratio of C$_{16}$TMABr/APES=0.6 results in the penetration of the hydrocarbon chain of APES within the micelle, leading to a $Pm\bar{3}n$ structure. The addition of a small amount of APES results in the formation of a 2D-hexagonal $p6mm$ structure, while increasing the amount of APES results in disordered material. The mechanism of penetration can be summarized with the notation $S^+\sim N\theta T$.

The effect of hydrothermal treatment (HT) over long periods has also been studied on a selected AMS-$n$ structure, the AMS-6 a bicontinuous cubic structure with $Ia\bar{3}d$ symmetry. Longer periods of HT lead to a phase transformation from cubic $Ia\bar{3}d$ to hexagonal $p6mm$ after 8 days. Surprisingly, the hexagonal structure was not stable for a long period and a return to the cubic phase $Ia\bar{3}d$ was observed after 22 days. $^{29}$Si NMR and TGA showed that the AMS-6 solid was initially depleted of organo-silica moieties. This depletion happens concurrently with a transition from cubic to hexagonal structure. At longer HT treatment times the silica network condenses and the material transform from a hexagonal to a cubic structure. In order to study structural variations, the mesocaged material with $Pm\bar{3}n$ symmetry has been used as a model structure and the materials have been prepared with various surfactants C$_{16}$TMABr, C$_{12}$GluA, C$_{16}$TEABr and C$_{16-3-}$ under alkaline and acidic conditions. The sizes of the mesocages and their cage-connecting windows have been determined through crystallographic
reconstruction models and compared with those derived from sorption models. All the samples showed subtle fine structural differences and the variations in the cage-connecting windows and mesocage sizes were governed primarily by the charge density of the surfactant and the thickness of the hydration layer surrounding the spherical micelles.

The relationship between structure and function was investigated by evaluating the diffusion coefficients of amphiphiles released from the internal pore and the absorption of protons into the pore structure. The results show that the diffusion coefficients are higher for proton absorption than for surfactant release, and overall they follow the same trend, with 3D mesocaged materials showing the highest diffusion coefficients. The pore connectivity (cylindrical versus cage type) and tortuosity rather than the pore size and pore wall interaction determine the diffusion rate for both the surfactant release process and the proton adsorption process. Volumetric uptake and FTIR spectroscopy experiments were used to study CO$_2$ adsorption on the aforementioned $Pm\bar{3}n$ mesocaged structures and the degree of heterogeneity was varied by modifying the internal surfaces of sorbents with n-propylamino groups by a post-synthesis or a co-condensation route. The size of the cage-connecting window has a major effect on the accessibility of amino groups, and blocked the pore entrances lead to a low quantity of n-propylamino groups on the silica surface. The sorbents produced with post-synthesis modification take up more CO$_2$ at a high than at a low temperature. A clear correlation was found between the degree of heterogeneity in the propylamine coating and the formation of chemisorbed CO$_2$, in the form of carbamate–propylammonium ion pairs. The sorbents with a co-condensation route showed mostly physisorption, while the post-synthetic modified samples showed chemisorption, as confirmed by in-situ FTIR.
7. Future Work

The folic acid-templated mesoporous silica material (NFM-1) is quite new to the mesoporous field, and there are still many interesting properties to be investigated, e.g. the chirality of the NFM-1 samples and their separation, ways to increase the pore size, silica framework modification by employing a variety of silica sources, anchoring a variety of functional groups within the silica walls, CO2 gas adsorption studies on extracted NFM-1 samples and their potential use as a host for drug delivery systems.

Success was achieved in using aromatic molecule as a template for mesoporous materials, and it is also interesting to extend the synthetic pathways to other complex molecules including 5-guanine monophosphate (GMP) and its derivatives.

As shown, the hydrothermal treatment of the AMS-6 material leads a phase transformation from cubic $Ia\bar{3}d$ to hexagonal $p6mm$ and a return to cubic $Ia\bar{3}d$ occurred after 60 days of HT. The intermediate samples of cubic $Ia\bar{3}d$ showed an external porous layer, the reasons for which are not yet clear. It would be interesting to study these surface features and their growth mechanism, which may give information about their structural growth. In addition, the intermediate structure found between AMS-6 ($Ia\bar{3}d$) and AMS-10 ($Ia\bar{3}d$) by the addition TMB also needs to be investigated by HRTEM and image processing.

Since the 3D cage-type structures are very important for catalysis and as drug vehicles, it is important to know the fine structural details such as cage size, cage-connecting window sizes. As already shown in this work, $Pm\tilde{3}n$ structures prepared with variety of surfactants have already revealed the importance of fine structural details. So as future work, I would prefer to study other cage type structures including $Fd\tilde{3}m$, $Im\tilde{3}m$ through electron crystallography and image processing.
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Denna avhandling handlar om tillverkning och analys av mesoporösa kiselbaserade nanopartiklar. Med mesoporös menas att partiklarnas porer är 2-50 nanometer i diameter, och de partiklar som tillverkats har haft storleken 100-1000 nm. Enkelt beskrivet, inleds syntesen med att man blandar de två huvudkomponenterna; ett ämne som bildar porerna samt ett kiselinnehållande ämne. De porbildande molekylerna arrangerar sig därefter spontant i en ordnad struktur (Bild 1), före de kiselinnehållande molekylerna reagerar med varandra för att bilda hårdna nanopartiklar. Efter att partiklarna bildats kan de porbildande molekylerna brännas bort genom uppvarmnning till 550 ºC, vilket gör att de porbildande molekylerna ersätts av tomma porer.

Bild 1: Bilden visar en transmissionelektronmikroskopi (TEM) bild av mesoporösa kiselbaserade partiklar. Porerna är de vita prickarna i partikeln.

De porbildande ämnen som använts i detta arbete har mestadels varit s.k. surfaktanter, d.v.s. molekyler som består av en vattenlöslig och en fettlöslig del. Surfaktanter av olika typ och laddning har använts för att skapa partiklar med olika porstruktur. Avhandlingsarbetet är på många sätt banbrytande, bl.a. genom att folsyra för första gången använts som porbildande ämne. Folsyra är ett vitamin och ett viktigt näringsämne för människan, och det kunde användas som porbildare eftersom det bildar ordnade strukturer i när-
varo av vissa hjälpämnen. I en typ av experiment har den porbildande folsyran inte bränts bort; istället har folsyran diffusion ut ur partiklarna studerats, och systemet har liknats vid läkemedelsbärande partiklar som frisätter läkemedel.

Avhandlingen presenterar ny kunskap om hur man kan styra vilken porstruktur partiklarna ska få, genom sitt val av utgångsmaterial och syntesbetingelser. Avhandlingen presenterar också nya rön angående hur man kan styra moleylers diffusionshastighet in i och ut ur partiklarna, genom att kontrollera porernas storlek och struktur. Mesoporösa nanopartiklar förväntas användas inom många olika områden i framtiden, och används redan idag som läkemedelsbärare för kontrollerad frisättning av läkemedel i människokroppen. Denna avhandling kommer att vara till nytta för alla som i framtiden vill skapa mesoporösa partiklar med specifika egenskaper, t.ex. partiklar som avger läkemedel med en bestämd hastighet.
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