**Ordered Mesoporous Materials:
Template Removal, Frameworks and Morphology**

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1 Introduction and motivation

Porous solids are widely used as adsorbents, catalysts or hosts in numerous of technical processes, owing to their high surface areas and very well-defined physical and chemical properties. Generally, porous solids are distinguished by their pore size, their pore size distribution, and the structural arrangement and degree of ordering of the pores.

Ordered mesoporous inorganic solids form a specific class of very interesting molecular sieves. These periodic materials consist of extended inorganic or inorganic-organic hybrid arrays with exceptional long-range ordering, highly tunable textural and surface properties and controlled pore size and geometry. Typically, the structure of the pores is periodic and the pore size distributions are narrow with pore sizes ranging between 2 nm and 50 nm, which is known as the mesopore range. During the last decade, intensive scientific efforts have been devoted to synthesis, characterization and application of such ordered mesoporous materials, leading to more than 1500 publications. The growing demand for porous solids with specific framework and surface compositions which could exhibit structures controlled on several length scales has led to considerable developments, expanding the scope of research, bridging chemistry with physics or biology. Ordered mesoporous materials are now thought to find applications in fields as diverse as catalysis, delivery and release techniques, bio-medicals, sensors, electronic technologies and electro-optical devices. Increasing knowledge on mesoporous and mesostructured materials has led to an almost continuous development of new processes and techniques for synthesis and modification which overcome previous limitations. Nevertheless, many aspects of the processes involved in preparing and developing valuable porous materials still require greater insights.

The present work is concerned particularly with three important aspects of ordered mesoporous materials which are intimately related: 1) the removal of the liquid crystal template which is used to synthesize most of the ordered mesoporous solids, 2) the framework structure and composition of the materials, and 3) the morphology control of ordered mesoporous silica fibers.

Specifically, the aim of this work is to provide some answers to the following questions:

- 1) What are the physical and chemical processes involved in the calcination of well documented mesostructured silicas (M41S and SBA-type materials), and less investigated mesostructured solids based on transition metals? What are the specific effects observed on each of the different hexagonal and cubic phases?
- 2) Is it possible to develop and improve attractive porous non-siliceous mesoporous materials with highly ordered three-dimensional structures?
- 3) What is the role of co-surfactant species in the synthesis of mesoporous materials? Can the challenge of tailoring the structure be regarded as the challenge of relating the initial synthesis conditions to the porosity of the materials ultimately obtained?
- 4) How general is the internal architecture of spontaneously grown mesoporous silica fibers synthesized in a static acidic system? What could be learned about the growth kinetics, the formation mechanism, and the control of the structure on length scales ranging from nanometers to centimeters?

For this, the removal of the template by calcination will be studied by combining several analytical techniques, such as high temperature X-ray diffraction, Thermogravimetry-differential thermal analysis and mass spectrometry, allowing *in situ* investigations during thermal treatment. Furthermore, comparison will be made between materials with different mesoscopic structures, resulting from different synthesis routes and chemical treatment, with focus on solids based on silica, titania and zirconia. Transition metal based materials are especially interesting in this respect, since the thermal stability strongly depends on the pretreatment conditions. In addition, the synthesis and characterization of the first porous mesostructured zirconium oxo-phosphate with cubic (Ia3d) symmetry will be presented and discussed. Following this, the effects of specific alcohols and amines as co-surfactant on the mesoscopic ordering of mesoporous silica will be investigated. Finally, to investigate whether the circular structure revealed for some mesoporous silica fibers is a general feature of the

fiber synthesis, systematic synthesis variation will be applied to produce fibers and other morphologies with detailed characterization and kinetic studies.

Part of the work reported here has already been published in several publications. The corresponding references will be given in the respective chapters. A list of publications resulting from this work is given in chapter 8.5.

2 State of the art

2.1 General aspects on porous solids

Porous materials have attracted much scientific interests for applications in chemical separation and heterogeneous catalysis, which require overcoming the challenges of synthesis, processing, and characterization.^{1,2} Ideally, a porous material should have a narrow pore size distribution which is critical for size-specific applications and a readily tunable pore size allowing flexibility. In addition, it should show high chemical, thermal, hydrothermal and mechanical stability, with high surface area and large pore volumes. Furthermore, the material should have appropriate particle size and morphology.

Porous materials were originally defined in terms of their adsorption properties. From this, porous materials are distinguished by their pore size. According to the IUPAC definition,³ porous solids are divided in 3 classes: microporous (< 2 nm), mesoporous (2-50 nm) and macroporous (> 50 nm) materials (Figure 2.1). Well-known examples of microporous solids are zeolites and related compounds. Zeolites are crystalline aluminosilicates with periodic three-dimensional framework structures which contain voids.⁴⁻⁷ Other related compounds

usually possess similar structures with different framework compositions, such as aluminophosphates. Due to their crystalline network, zeolites and related materials exhibit an extremely narrow pore size distribution which allows their successful exploitation for size specific applications in adsorption, molecular sieving, host/guest chemistry and shape-selective catalysis.⁸⁻¹³ However, a major drawback for application is their limited pore size (< 1.42 nm) which excludes size-specific processes involving large molecules. Especially, larger pore size are required for heavy oil cracking and catalytic conversion of large molecules, separation media or host for bulky molecular species.

Figure 2.1: Pore size distribution for microporous, mesoporous and macroporous solids. Adapted from Behrens.¹

Sol-gel derived porous oxides are noncrystalline solids which, however, offer distinct advantages in terms of processability, that is tailoring on a macroscopic size scale to form membranes, monoliths, and fibers. In addition, they can be tailored on the molecular size scale.^{4,14} Such amorphous porous gels or aerogels and porous glasses can be made as mesoporous solids. In contrast to zeolites, they have disordered pore systems and exhibit therefore a rather broad pore size distribution. These materials are commonly used in separation processes and as catalyst support. The pore size can eventually reach the macroporous range for glasses (Figure 2.1).

At first, there have been numerous attempts to extend the hydrothermal synthesis procedures used to prepare microporous zeolites and related materials to the mesoporous range, but success was limited.¹³ Further attempts to achieve mesoporous materials with narrow pore size distribution were based on controlling the pore size of amorphous silica-aluminas by preparing them in the presence of alkyltrimethylammonium cations.¹⁵ Disordered silica-aluminas with pores in the mesopore region and a quite regular distribution were obtained, exhibiting high surface areas. Other ordered noncrystalline mesoporous oxide molecular sieves were synthesized by intercalation of layered materials (pillaring) such as double hydroxides, titanium and zirconium phosphates or clays. However, they exhibit broad mesopore-size distributions and additional microporosity.^{1,13}

2.2 Ordered mesoporous molecular sieves

The synthesis of an ordered mesoporous material was described in a patent filed in 1969.¹⁶ However, due to a lack of analysis these early scientists could not recognize the remarkable features of their product. In 1992, the same material was obtained by Mobil Corporation scientists.^{17,18} MCM-41 (*Mobil Composition of Matter* No 41) exhibits a highly ordered hexagonal array of unidimensional cylindrical pores with a narrow pore size distribution (Figure 2.2). The walls are, however, amorphous. Other related phases, such as cubic (MCM-48) and lamellar (MCM-50) were reported in the early publications as well.

The characteristic approach for the synthesis of ordered mesoporous materials is the use of liquid-crystals templates, that enable the specific formation of pores with predetermined size. However, in contrast to zeolite synthesis where single molecules serve as templates, aggregates of surfactant molecules are used to obtain the mesoporous materials. At

approximately the same time as the discovery of MCM-41, an alternative approach to mesoporous materials was described by Yanagisawa et al.,¹⁹ using kanemite, a layered silicate, serving as the silica source. The material is designated as FSM-n (Folded Sheet Mesoporous Materials-n), where n is the number of carbon atoms in the chain of the surfactant used. MCM-41 and FSM-16 are very similar, with however some slightly different adsorption and surface properties.²⁰

Figure 2.2: left) TEM image of MCM-41; right) representation of the hexagonal lattice.

The standard use of transmission electron microscopy (TEM), X-ray diffraction (XRD) and adsorption analysis allow independent reliable characterization of mesoporous materials. The hexagonal arrangement of uniform pores can be visualized by TEM, as shown in Figure 2.2. The pore sizes usually vary between 2 and 10 nm depending on the surfactant chain length, the presence of additional organic co-surfactants, or post-treatments. The pore wall thickness is usually evaluated to be between 0.7 and 1.1 nm. MCM-41 type mesoporous silicas are highly porous and commonly show BET surface areas exceeding 1000 m²/g and pore volumes up to 1 cm³/g. The N₂ sorption isotherm measured for MCM-41 is distinctive, being a Type IV isotherm which is generally observed for mesoporous materials³ (Figure 2.3), but with an unusually sharp capillary condensation step.

Mesoporous silicon oxide materials synthesized by surfactant templating are sometimes described in the literature as crystalline solids because of their long-range periodicity. This idea is, however, not quite correct since the pore walls of the materials always consist of amorphous silica, with neither short-range nor long-range order. Nevertheless, the regular arrangement of the pores can be considered as a kind of “*super-structure*” with long-range

ordering. MCM-41 exhibits long range periodicity in two directions. Along the c-axis, which is the axial direction of the pores, no periodicity is observed. The long-range ordering can be evidenced using X-ray diffraction where Bragg reflections can be detected at low 2 theta angles (Figure 2.4).

Figure 2.3: Nitrogen adsorption isotherm of MCM-41 at 77K.

Figure 2.4: X-ray diffraction pattern of a calcined MCM-41 sample.

The only reflections observed are due to the ordered hexagonal array of parallel pore walls and can be indexed as a hexagonal $p6m$ unit cell. No reflections at higher 2 theta are observed. Following works showed that mesoporous structures can also be formed in acidic medium, or by using neutral amine templating agents, non ionic surfactants, or block copolymers. In addition, heteroatoms could be incorporated into the mesostructured silicate frameworks, as is done with zeolitic frameworks. The concepts of mesoporous materials were also extended to fully non-siliceous frameworks. However, the removal of the template and the stability of the inorganic networks represent, in this latter case, major issues.

2.3 Inorganic polymerization and self-assembly

Formation of an inorganic surfactant composite mesophase is controlled by the chemistry of both the inorganic and organic parts of the system and the way the surfactant molecules interact with the inorganic species. MCM-41-type materials generally result from a process of

silica polymerization with which liquid-crystal supramolecular templating is simultaneously combined. The overall mesophase formation is driven by a cooperative assembly of the organic surfactant molecules and the inorganic solution species.

2.3.1 Silica polymerization

The methods employed to prepare mesoporous oxides molecular sieves are similar to the ones commonly used also for sol-gel-derived oxides.¹⁴ Both types of materials consist of noncrystalline oxidic frameworks. The main difference is the degree of order since porous sol-gel oxides are completely disordered. As mesoporous silicas were the first ones to be developed, the sol-gel process will be described in this section only for silicates. The silicon source usually plays an important role by determining the reaction conditions. For non-molecular silicon sources, silica is obtained as a gel formed from a nonhomogeneous solution. The gel is subsequently treated hydrothermally. In the case of molecular silicon sources, water, surfactant, and catalyst are first combined to form a homogenous micellar solution. To this solution, the silicon alkoxide is added and mesophase formation follows. In both cases the first step for inorganic polymerization is the formation of silanol group. This occurs either by a neutralization reaction or by hydrolysis of the alkoxysilane in water. In this latter case, hydrolysis of monomeric tetrafunctional silicon alkoxide precursors proceeds as in equation 2.1. Hydrolysis is generally catalyzed by a mineral acid (HCl) or a base (NaOH, NH₃).

The hydrolysis rate is furthermore affected by the nature of the silicon precursor. For example, the more hydrophobic or sterically hindered the precursor is, the slower the hydrolysis rate. Depending on the synthesis conditions, hydrolysis may be only partial or go to completion. In both cases, the silicic acid formed will undergo self-condensation or condensation with an alkoxysilane molecule producing siloxane bonds (Si-O-Si) and alcohol (equation 2.2) or water (equation 2.3). This type of condensation reactions leads to formation of oligomeric species which form chains, rings or branched structures and continues building larger polymeric silicates.

alcohol condensation (alcoxolation)

water condensation (oxolation)

The overall reaction proceeds as a poly-condensation to form soluble higher molecular weight polysilicates. This resulting colloidal dispersion is the *sol*. The polysilicates eventually link together to form a three-dimensional network which spans the container and is usually filled with solvent molecules, called the *gel*, or precipitate as precipitated silica. Sol-gel polymerization proceeds in several possibly overlapping steps which are polymerization to form primary particles, growth of the particles, and finally aggregation.¹⁴ Each step depends strongly on pH, temperature, concentration, and co-solvent effects. Hydrolysis and condensation depend most strongly on the nature and the concentration of the catalysts, resulting in a pH dependence. The pH dependence of the polymerization reactions which has been recognized for colloidal silica-water systems can be employed in the synthesis of silicate-surfactant mesophases. In this regard, the polymerization process can be divided in three pH domains, as described by Iler⁴: pH < 2, pH = 2-7, and pH > 7. pH = 2 corresponds approximately to the isoelectric point of silica, IEP (electrical mobility of silica particles equals zero) and the point of zero charge, PZC (surface charge is zero). Below pH = 2 the silicates species are positively charged. pH = 7 is a boundary since above this value solubility of the silicates increases strongly with the pH and the condensed species are likely to be ionized leading preferentially to the growth of large particles.

2.3.2 Template-assisted synthesis

A successful approach to generate tailored pores is based on the use of templates or “imprints” following biological models. The first success in templating was achieved in 1949 by the use of bioorganic molecules to create artificial antibodies.²¹ The principles of templating were, since then, adapted widely for the synthesis of many organic or inorganic materials. Templating comprises the use of synthesis solution and a template molecule or

assembly of molecules. The solutions from which the templated solid is produced contain precursors which allow some kind of solidification that can be precipitation from solution, sol-gel synthesis of inorganic materials, redox processes leading to metal deposition, or polymerization of organic monomers. During this, morphological construction occurs by direct imprinting of the shape and texture of template. A template is thus described as a central structure around which a network forms. The cavity created after the removal of the template retains morphological and stereochemical features of the central structure.^{22,23}

Figure 2.5: Representation of the ideal formation of microporous molecular sieves using a small single organic molecular template.

Zeolites and zeotype materials are synthesized in the presence of a single small organic template or structure directing agent, typically quaternary alkyl ammonium ions.²⁴ During the hydrothermal synthesis of zeolites, the inorganic phase precipitates around the organic structure directing agent creating a crystalline phase with pores filled with organic template molecules. The porosity is subsequently created by the removal of the template (Figure 2.5). However, examples of templating with exact geometrical correspondence are rare for zeolites, since the internal cavities usually do not conform rigorously to the molecule shape. Individual organic molecules do not act as true template but more typically direct structures by participating in the ordering of the reagents, and fill space in the porous product. Consequently, this results in a rather indirect correlation of the shape and size of the organic molecule to the structure and volume of the cavity created in the inorganic framework. Supramolecular assemblies²⁵ were also considered to be promising templates. Generally, these assemblies result from the association of a large number of small molecular building blocks into a specific phase with specific macroscopic characteristics and a well-defined microscopic organization *e.g.* amphiphilic or non-amphiphilic liquid crystalline phases. Supramolecular assemblies can be exploited as chemically and spatially specific interfaces for site directed growth and morphological patterning. Supramolecular engineering rapidly gave

access to the controlled generation of well-defined polymolecular architectures in layers, films, membranes, micelles, gels or mesophases.²⁶ The generation of ordered mesoporous materials is possible via templating by self-assembled liquid-crystalline phases. In this case, there is a geometrical correlation between the surfactants array size and shape and the final pore size and geometry in the mesophase. Surfactants consist of a hydrophilic part, *e.g.* ionic, non-ionic, zwitterionic or polymeric groups, often called the “head” and a hydrophobic part, the “tail”, *e.g.* alkyl or polymeric chains. This amphiphilic character enables surfactants molecules to associate in supramolecular micellar arrays.²⁷ Single amphiphile molecules tend to form aggregates in aqueous solution due to hydrophobic effects. Above a certain critical concentration of amphiphiles, formation of an assembly, such as a spherical micelle, is favored. In these aggregates,* the surfactant molecules are arranged such that the heads form the outer surface facing the water and the tails are clustered together pointing toward the center. The formation of micelles, the shape of the micelles, and the aggregation of the micelles into liquid crystals depend on the surfactant concentration. At very low concentration, the surfactant is present as free molecules dissolved in solution and adsorbed at interfaces. At slightly higher concentration, called the critical micelle concentration, CMC, the individual molecules form small spherical aggregates. At higher concentrations, CMC2, spherical micelles eventually coalesce to form elongated cylindrical rod-like micelles. CMC2 depends strongly on temperature, surfactant chain length and surfactant counter-anion binding strength. With increasing concentrations, liquid crystalline phases (LC) form. Initially, the rod-like micelles aggregate in hexagonal close-packed arrays. As the concentration increases further, cubic phases form followed by lamellar phases.^{23,27} Details of this sequence might vary, depending on the surfactant, but in general the sequences is valid for most systems.

Efficient template removal and faithful imprinting have been largely shown to depend on the nature of the interactions between the template and the embedding matrix, and the ability of the matrix to adapt to the template. The intimate template-matrix association required for supramolecular templating of inorganic mesophases is generally facilitated by the flexibility of amorphous inorganic networks with low structural constraints, small inorganic oligomers, and by the large radius of curvature of the organic template. Ideally, after removal of the core molecules from the surrounding matrix the shape of the voids that remain reflects the shape of the template.

* The term *aggregate* is used for the supramolecular array formed upon self-assembly of single surfactant molecule.

2.3.3 Mechanisms of mesostructure formation

Surfactant properties and concentrations, and additional ions determine which factors govern the synthesis most strongly. The original synthesis of mesoporous molecular sieves of the M41S family was performed in aqueous alkaline solution ($\text{pH} > 8$). At first, Beck and co-workers^{17,18} proposed a “liquid crystal templating” (LCT) mechanism (Figure 2.6), on the basis of the similarities between liquid crystalline surfactants phases and the mesostructured materials. In this hypothesis, the structure is defined by the organization of surfactant molecules into liquid crystalline phases which serve as templates for the building of M41S structures. The inorganic silicate species would occupy the space between a pre-formed hexagonal lyotropic crystal phase and are deposited on the micellar rods of the liquid crystal phase (pathway 1).

Figure 2.6: Liquid crystal templating mechanism (LCT) according to Beck et al.¹⁸ Pathway 1 is liquid-crystal initiated and pathway 2 is silicate-initiated.

However, since the liquid crystal structures, which are formed in surfactant solutions, are very sensitive to the characteristics of the solution, the same authors proposed that the addition of inorganics could mediate the ordering of the surfactants into specific mesophases (pathway 2). The reasons for several possible pathways lay in the large variation of the surfactant properties depending strongly on the concentration and the presence of electrolytes.²⁷ In both pathways, however, the inorganic species electrostatically interact with the charged surfactant head group and condense into a continuous framework which could be regarded as a hexagonal array of surfactant micellar rods embedded in an inorganic matrix. In agreement with pathway 2, Davis and co-workers²⁸ proposed in 1993 an alternative mechanism for the formation of MCM-41. Based on NMR spectroscopy of the quadrupolar ^{14}N nucleus, the

authors concluded that LC are not present in the synthesis medium during the formation of MCM-41. Therefore, they postulated that the process begins by deposition of two or three monolayers of silicate precursor onto isolated surfactant micellar rods which are present at the surfactant concentration studied. The silicate-surfactant rods which are initially randomly orientated eventually pack into a hexagonal mesostructure as condensation and self-organization proceed. Monnier et al.²⁹ investigated how MCM-41 forms at concentrations where only spherical micelles are present (1% g/g) and also proposed a silicate-initiated mechanism. They introduced a “charge density matching” model. The model is based on the cooperative organization of inorganic and organic molecular species into three-dimensional structures. In this model, 3 steps are involved in the formation of the silica-surfactant composite: 1) multidentate binding of the silicate polyions to the cationic head groups through electrostatic interactions leading to a surfactant-silica interface, 2) preferential silicate polymerization in the interface region, 3) subsequent charge density matching between the surfactant and the silicate. Before silicate addition, the surfactant molecules are in dynamic equilibrium between spherical or cylindrical micelles and single molecules. Upon addition of a silicon source, the multicharged silicate species displace the surfactant counteranions to form organic-inorganic ion pairs which reorganize first into the silicatropic mesophase followed by silica cross-linking. The nature of the resulting mesophase is controlled by the multidentate interaction via interface packing density.

A generalized cooperative mechanism of formation was proposed by Huo et al.^{30,31} based on the specific electrostatic interactions between an inorganic precursor I and a surfactant head group S. A number of different general strategies for obtaining a variety of ordered mesoporous materials have been identified. Along with S^+I^- , the cooperative interaction between inorganic and organic species based on charge interaction can be achieved by using the reverse charge matching SI^+ . Furthermore, synthesis routes involving interactions between surfactants and inorganic ions with similar charges are possible through the mediation of ions with the opposite charge (S^+XI^+ , X^- = halides or $S^-M^+I^-$, M^+ = alkali metal ion). Besides the syntheses based on ionic interactions, the LC approach has been extended to pathways using neutral (S^0)³² or non-ionic surfactants (N^0).³³ In the approaches denoted (S^0I^0) and (N^0I^0) hydrogen-bonding is considered to be the main driving force for the formation of the mesophase.

2.4 Synthesis pathways and concepts

2.4.1 Surfactant Packing

Predictions about the inorganic-surfactant phase behavior can be made based on models developed for dilute surfactant systems. The packing parameter concept is based on a model that relates the geometry of the individual surfactant molecule to the shape of the supramolecular aggregate structures most likely to form. According to Israelachvili et al.,³⁴ the preferred shape of the surfactant molecules aggregates above the CMC depends on the effective mean molecular parameters which establish the value of the packing parameter g . The dimensionless surfactant packing parameter g is defined by $g = V / a_0 l_c$, where V is the total volume of the hydrophobic chains plus any co-surfactant organic molecules between the chains, a_0 is the effective head group area, and l_c is the critical length* of the hydrophobic tail. The parameter g depends on the molecular geometry of the surfactant. The number of carbons in the hydrophobic chain, the degree of chain saturation and the size and charge of the polar head group influence the value of g . Additionally, pH, ionic strength of the solution, co-surfactant effects and temperature can be included in V , a_0 and l_c .³⁵ Spherical aggregates are preferentially formed by surfactants having large polar head groups. If on the other hand, the head groups can pack tightly, the aggregation number will increase, and rod-like or lamellar packing will be favored (Figure 2.7). Furthermore, for ionic surfactants the value of a_0 is strongly dependent on the degree of dissociation of the head groups and the ionic strength of the solution.

Figure 2.7: a) Surfactants with large head groups provoke large surface curvature.

Figure 2.7: b) Surfactants with large hydrophobic chain volume and relatively small head groups generate small surface curvature.

* l_c is also called kinetic length of the surfactant tail and represent normally 80-90 % of the fully extended hydrocarbon chain. The exact value of l depends on the extension of the chain.

With increasing g value, a phase transition reflects a decrease in surface curvature from the cubic (Pm3n) phase over the hexagonal to a cubic phase with (Ia $\bar{3}$ d) space group to finally a lamellar phase (Table 2.1). Therefore, the larger the value of g , the lower the curvature in the aggregate. The packing parameter g increases with increasing hydrophobic chain volume, smaller head group area and decreasing kinetic tail length. Moreover, the value of g between 1/2 and 2/3 for the cubic phase with Ia $\bar{3}$ d space group depends on the volume fraction of surfactant chains.³⁶ The model described above was expended to silica-surfactant mesophases by Stucky and co-workers, who included the inorganic components to predict the final mesostructures, including a 3-D hexagonal P6₃mmc phase.³⁷⁻³⁹

g	Expected structure	Space group	Name
$< 1/3$	hexagonal	P6 ₃ /mmc	SBA-2
1/3	cubic	Pm3n	SBA-1
1/2	hexagonal	p6m	MCM-41, FSM-16, SBA-3
1/2 - 2/3	cubic	Ia $\bar{3}$ d	MCM-48
1	lamellar	P2	MCM-50

Table 2.1: Surfactant packing parameter g and expected mesophase structures.³⁸

2.4.2 Silica polymorphs from the alkaline route (S⁺I⁻)

Mesoscopic polymorphs of silica synthesized under alkaline conditions have attracted the most scientific interest so far. Under these conditions anionic silicates I⁻, and cationic surfactant molecules S⁺, cooperatively associate and organize to form hexagonal, lamellar or cubic structures. This synthesis in alkaline medium can lead to three well defined structures MCM-41, MCM-48 and MCM-50.^{18,22}

Vartuli et al.²² showed that the surfactant-to-silica molar ratio is a critical variable in the formation of M41S materials. Using tetraethoxysilane (TEOS), they found that increasing the surfactant-to-silica ratio from 0.5 to 2.0 results in hexagonal (< 1), cubic Ia $\bar{3}$ d (1-1.5),

lamellar (1.2.-2) and uncondensed cubic octamer (> 2) composite structures. Moreover, structural phase transformations to lower energy configurations may be induced during hydrothermal treatment as changes in the charge density of the silicate occur upon condensation. In addition to the lamellar to hexagonal phase transition described by Monnier et al.,²⁹ transition from hexagonal to lamellar³⁸ and hexagonal to cubic⁴² geometries upon condensation, i.e. transition to lower curvature, can be observed. The phase transitions during hydrothermal treatment may generally be explained by further condensation of the silicate framework and subsequent restructuring which induces changes in the packing of the surfactant. In addition, structural transformations may also be coupled with temperature-dependent changes in hydration, silicate solubility, counter-ion binding and migration of organic co-solvent in the system.

The original synthesis of MCM-41 was carried out in aqueous alkaline solutions at elevated reaction temperatures (150°C) with nonmolecular silicon sources such as fumed silicas or water glasses. Grün et al.⁴⁰ proposed in 1997 a very efficient novel route in the synthesis of MCM-41 by fast hydrolysis of a molecular silicon source (TEOS) with ammonia as catalyst. This method provided a convenient route to high-quality product in a short period of time (1 hour) at room temperature, and yield Si-MCM-41 without sodium ion. The synthesis results in a highly reproducible product with respect to the specific surface area and the pore structural parameters. This procedure was subsequently modified to yield a Si-MCM-41 with increased structural order by aging the material at 90°C in the mother liquor for several days.⁴¹ MCM-48 can be prepared, via hydrothermal synthesis, either by adjusting the silica/CTAB ratio and variation of the synthesis conditions,^{22,42} or at room temperature by using gemini-type surfactants.³⁸ The structure of MCM-48 belongs to the $Ia\bar{3}d$ space group, which has also been found in the binary water/CTAB system.⁴³ The structure is considered to be bicontinuous with a simplified representation of two three-dimensional mutually intertwined, unconnected networks of rods. This structure contains a three dimensional channel network with channels running along the $[111]$ and $[100]$ axis directions.⁴⁴ The unit cell parameter measured for the cubic $Ia\bar{3}d$ MCM-48 is usually ranging between ca. 8 - 10 nm. MCM-50 contains a lamellar structure in the as-synthesized form. This phase can be represented by sheets or bilayers of surfactant molecules with the hydrophilic head group pointing towards the silicate at the interface. Removal of the template from between the silicate sheets results in the collapse of the lamellar structure, unless the material is stabilized.

2.4.3 Acidic route ($S^+X^-I^+$)

Huo et al.^{30,31} showed that mesoporous silicas are accessible at low pH. The formation of silica is possible by the cooperative assembly of cationic inorganic species with cationic surfactants. The syntheses are carried out under strong acidic conditions (1-7 M HCl or HBr) where silicate species are positively charged. 2-D hexagonal $p6m$, 3-D hexagonal $P6_3mmc$, cubic $Pm3n$ and lamellar structures could be obtained in the presence of HCl.^{31,38,39} In the pH range employed, silica polymerization proceeds through the condensation of cationic intermediates resulting in gel and glass morphologies very different from those obtained in basic medium.^{4,14} It is suggested that the main driving force for self-assembly at low pH is electrostatic interface energy, including hydrogen bonding. At high concentrations of HCl solutions, the cationic hydrophilic region of the surfactant is surrounded with a peripheral negative charge (S^+X^-). The positively charged species (I^+) resulting from the hydrolysis of the silicon sources (alkoxysilane or $SiCl_4$) at low pH are attracted electrostatically to the anionic portion of the surfactant ion pair forming a triple layer where the halide ions coordinate through Coulombic interactions to the protonated silanol groups. The formation of this triple layer ($S^+X^-I^+$) where the halide anions in the electrical double layer around the micellar aggregate serve as charge mediators is considered to account for the formation of the mesophase.³¹ During the cooperative assembly of the soluble molecular species in the silica synthesis under concentrated acidic conditions, precipitation and polymerization occur. In this process the protons associated with the silicates, along with associated excess halide ions, are excluded until a neutral inorganic framework remains. This quasi neutral polysilicic acid framework is hydrogen bonded to the S^+X^- complex. The mechanism for the $S^+X^-I^+$ synthesis is clearly not the same as that for the S^+I^- route. Generally, similar d -spacing are observed for mesostructured materials prepared at low and high pH. However, the physisorption results indicate that the materials prepared in acidic medium have smaller pores, thicker pore walls, and a very high adsorption capacity.³⁹ Moreover, the overall framework charge is different from the base-derived mesophase, due to the different precipitation conditions and charge balance requirements. The materials prepared according to the acidic route are often labeled SBA-3 (Santa Barbara N^o3)^{31,38} ($p6m$) or APM⁴⁵ (acid-prepared mesostructure). Although easily accessible, these materials are far less investigated than their base-derived counterparts. In particular, the origin of their texture and porosity remains under discussion.

2.4.4 Non ionic routes (hydrogen-bonding interactions S^0T^0 , N^0T^0)

Tanev and Pinnavaia developed the neutral templating route which is based on hydrogen-bonding and self-assembly between neutral amine surfactants and neutral inorganic precursors.³² According to the S^0T^0 approach, they used primary amines (C8-C18) to prepare a mesoporous product, named HMS, from precursor silica species at pH = 7. Neutral silicate species are suggested to interact with the micellar aggregates through hydrogen-bonding between the hydroxyl groups of hydrolyzed silicate species and the polar amine headgroups. Pinnavaia's group was then the first to use as template non-ionic poly(ethylene oxide) monoethers, as well as Pluronic-type surfactants in neutral aqueous media.³³ A non-ionic surfactant, neutral templating pathway to mesostructures is proposed with TEOS. It uses hydrogen bonding interactions between the hydrophilic surfaces of flexible rod or worm-like micelles and $Si(OC_2H_5)_{4-x}(OH)_x$ hydrolysis products to assemble an inorganic oxide framework. Worm-like disordered mesopores structures denoted MSU-X (Michigan State University) with uniform diameters ranging from 2.0 to 5.8 nm were obtained by varying the size and structure of the surfactant molecules. Important progress in the preparation of mesoporous silicas was made then by Zhao et al.⁴⁶ who used triblock polyoxoalkylene copolymer (Pluronic type) for the synthesis under acidic conditions of large-pore materials called SBA-15 (Santa Barbara N°15) and other related materials. However, here the mechanism of formation is proposed to be $S^+X^-T^+$ or $(S^0H^+)(X^-T^+)$ since the block-copolymer is positively charged under the reaction conditions. The use of such block-copolymers expanded considerably the accessible range of pore sizes. Hexagonally ordered SBA-15 can be prepared with pore sizes between 4.6 nm and 30 nm with wall thicknesses of 3.1 to 6.4 nm. SBA-15 exhibits large surface area and pore volumes up to 2.5 cm³/g. In addition, recent studies showed that the pore size distribution of the hexagonal SBA-15 is probably bimodal, in which the bigger, hexagonally ordered structural pores determined by the surfactant are connected by micropores through the silica walls.⁴⁷ These micropores do not seem to be well ordered and may likely result from the fact that the block copolymer penetrates the silica framework. Other related SBA-11 (cubic Pm3n), SBA-12 (3-D hexagonal P6₃mmc) and SBA-16 (cubic Im3n) were obtained with different non ionic block copolymers or non ionic oligomeric surfactants (Brij-type).⁴⁸

2.4.5 Pore size tailoring and structure engineering

Controlling the mesopore size is of importance because of the potential applications of these materials as catalysts, molecular sieves, and hosts for quantum size effect materials. A simple manner to tune the pore size of the inorganic-surfactant material is to change the length of the surfactant carbon chain.^{18,49} With C_n TAB, $n_c = 8, 10, 12, 14, 16$ and 18 , the pore size of the as-synthesized MCM-41 materials was shown to increase of about 0.45 nm by increasing n_c by two carbon atoms. The shortest chain surfactant from which mesophases could be made is usually $n_c = 8$. Long-chain surfactants ($n_c > 20$) are not commercially available and are virtually insoluble in water, and pore expansion is generally accompanied by a loss of order.¹⁸ Usually a linear relationship is observed between the pore sizes and the length of the carbon chain of the template. Changes in molecular geometry and chain length of non-ionic oligomeric surfactant and block-copolymers allow similar fine tuning of the pore size. The adjustment of the pore size here can be achieved continuously by varying the concentration of the templating agent and by changing the composition of the copolymers or block size.^{33,46,48} Another method to control the pore size of mesoporous solids is based on restructuring upon prolonged hydrothermal treatment. This can be done either directly in the mother liquor^{50,51} or at a different pH in water³⁸ or alcohol. For example, Khushalani et al.⁵⁰ showed that siliceous mesophases could be restructured at elevated temperatures in the alkaline mother liquor resulting in the expansion in pore size from ca. 3 to 7 nm. Generally, these post-synthesis treatments improve the thermal stability of samples obtained at room temperature and seem to afford materials with higher structural quality, upon promotion of the wall polymerization. However, the increased value of the unit cell is not always connected to an increase in pore size, but could also be due to increase of the wall thickness. The silicate framework consists of a large amount of silanols, which can further condensate and rearrange. Improved stability may arise from increased condensation within the framework, leading to less silanol groups and thicker walls. Further improvements of the long-range order of mesoporous silica molecular sieves or fine tuning of the pore size can be also achieved by adjusting the pH by adding the required amount of acid or base during the synthesis.⁵² This is likely based on the strong influence of the solution pH on the degree of condensation and polymerization of the inorganic oligomeric species, the charge density of the polyelectrolyte inorganic species involved, and the surfactant packing parameter g .

Solubilization of hydrophobic additives inside the core of the supramolecular assembly is another mean employed to increase the pore size of mesoporous silicas. Trimethylbenzene (TMB) has been the most widely used additive,^{18,38,53} although aliphatic hydrocarbons such as hexane have been used as well.⁵⁴ In the early work of the Mobil researchers, it was shown that the pore size of MCM-41 can be varied in a controlled manner between 1.5 nm and 10 nm by addition of TMB.¹⁸ A nearly linear increase in pore size was observed with increasing the oil concentration (TMB). Similarly, Stucky and co-workers used TMB to obtain ordered SBA-15 silicas with pore sizes up to 30 nm.⁴⁶

In general, hydrocarbons or hydrophobic aromatics (TMB, toluene⁵⁴) are considered to be swelling agents that are solubilized in the core of the surfactant aggregate. On the other hand, co-surfactant molecules, such as alcohol or amines, are accumulated in the palisade layer of the aggregates and can have therefore more complex effects. Both the phase behavior and the *d*-spacing of mesoscopically ordered silicates can be affected by adding either short-chain *n*-alcohols,⁵⁵ *n*-amines⁵⁶ or polar benzene derivatives⁵⁷ as co-surfactants. Differently, variation of the cohesive properties of the solvent by performing the synthesis in mixed solvents can be used to decrease the *d*-spacing of the resulting material, and allows a fine tuning of the pore size.⁵⁸ The type and the concentration of co-solvents used can affect the pore diameter, since co-solvents change the solution thermodynamics, which either alters the packing or the number of surfactant molecules in the micelles.

2.4.6 Framework and surface properties

Solid-state NMR was shown to be a powerful tool to characterize the framework local environments.¹⁸ Uncalcined MCM-41 shows three different signals in ²⁹Si NMR which can be assigned to Q², Q³ and Q⁴ silicon species. The ratio Q³/Q⁴ is commonly used to estimate the degree of condensation. After calcination, Q⁴ environments are formed at the expense of Q³ and/or Q² species. The degree of this transformation usually depends on the conditions employed for the removal of the template and the condensation of Si-OH groups.⁵⁹

The isomorphous substitution of heteroatoms,^{13,60,61} in siliceous amorphous frameworks is especially important with respect to catalytic applications, since substitution of silicon allows fine-tuning of the acidity or creation of redox properties, similar to zeolites. These mesoporous metallosilicates are usually synthesized by incorporating a tetrahedrally

coordinated tri- or tetravalent element, such as Al, B, Fe or Ga in the silica framework. Incorporation of aluminum for example in the framework of MCM-41 is expected to increase the acid site concentration, ion exchange capacity, and the hydrothermal stability of the material. In order to generate redox properties other metal ions were isomorphously substituted (Ti, Zr, V, Cr, Mn, Fe, Co, Mo) into silica frameworks. The resulting catalytic behavior is strongly influenced by the nature, the local environment and the stabilization of the metal introduced and by the hydrophobic properties of the surface.

The surface properties of the pore walls were studied by adsorption of molecules on the surface and by Fourier transform infrared (FTIR) spectroscopy. By carrying out the adsorption of polar and unpolar probe molecules, the relatively hydrophobic character of MCM-41 was clearly demonstrated.^{18,59,62} After removal of the template, MCM-41 adsorbs a much larger amount of organic species than water, which reveals that the internal surfaces are quite hydrophobic even though silanol groups are present. Small amounts of surface –OH sites were detected and at least three different types of silanol groups can be distinguished by using pyridine adsorption: single, hydrogen-bonded and geminal silanol groups.⁶³

2.5 Non-siliceous mesostructured and mesoporous materials

Shortly after the discovery of mesoporous M41S-type materials, the use of surfactant species to organize various non-siliceous mesostructured oxides was explored over a wide range of conditions.³⁰ Since then, a large number of mesoporous oxides, sulfide, phosphates and metals have been reported.^{64,65,66} However, compared to silica-based networks, non-siliceous ordered mesoporous materials have attracted considerably less attention, due to the relative difficulty to apply the principles employed to create mesoporous silicon oxides to non-silicates species. Moreover, other framework compositions are more susceptible to redox reactions, hydrolysis or phase transformations. Particularly, template removal needed to achieve porous materials has been shown to be a very critical point.⁶⁷ It was suggested in 1993 that it should be possible to synthesize non-siliceous materials by substituting the silicate by metal oxides that are able to form polyoxoanions.²⁹ Mesostructured surfactant composites of tungsten oxide, molybdenum oxide and antimony oxide were thus obtained. This approach was extended to the charge reverse system (S^{I+}) by using polyoxocations and to the mediated combinations S^+X^{I+} and S^-M^{I+} .^{30,67} Several authors reported afterwards⁶⁸ syntheses of mesostructured

vanadia with lamellar and hexagonal phase^{68b} and vanadium phosphorus oxide with hexagonal, cubic ($Ia\bar{3}d$), and lamellar phases.^{68a,c} However, due to a poor thermal stability, none of these structures could be obtained as template-free mesoporous solids. The poor thermal stability observed is most probably due to the different oxo chemistry of the metals compared to silicon. Several oxidation states of the metal centers are assumed to be responsible for oxidation and/or reduction during calcination.^{66,67} In addition, incomplete condensation of the framework is also possible.³⁰

The first porous transition metal oxide was reported by Antonelli et al. in 1995,⁶⁹ based on titania. The material was prepared by using an anionic surfactant with phosphate head groups and titaniumalkoxy precursors stabilized by bidentate ligands. After calcination at 350°C, hexagonally ordered porous TiO_2 with surface area of about 200 m²/g and narrow pore size distribution around 3.2 nm was obtained, with phosphate groups in the framework. However, the thermal stability of this material is not very high. Later, other materials based on titanium,⁷⁰⁻⁷² zirconium,^{73,74} niobium oxide,⁷⁵ and tantalum oxide⁷⁶ were synthesized. For the niobium and tantalum oxides, the redox stability problem was solved using a ligand-assisted templating pathway, with subsequent extraction of the template, avoiding calcination. The ligand-assisted pathway is based on covalent bonding between the inorganic species and the surfactant head groups (S-I). Materials with surface areas exceeding 400-500 m²/g were thus obtained. Other mesoporous titania molecular sieves were also obtained via ligand-assisted pathway with alkylphosphates⁷⁰ or amines as surfactants.⁷¹ Mesostructured zirconium-based composites with hexagonal phase could be readily produced with zirconium sulfate as the inorganic precursor and alkylammonium surfactants.⁷³ Zirconium sulfate proved to be an ideal precursor because the negatively charged solution species interact favorably with the cationic surfactant molecules. However, the presence of sulfate groups in the inorganic framework prevents full condensation, and leads to major framework destruction because of the removal of the sulfate upon calcination. By a post-synthesis treatment with phosphoric acid, materials with improved thermal stability were obtained.^{73,77} These

Figure 2.8: TEM of calcined zirconium oxo phosphate with hexagonal pore arrangement.⁷⁷

materials retain their mesoporosity upon thermal removal of the template. These porous solids are called zirconium oxo-phosphate and show structures analogous to MCM-41 as illustrated by the TEM image in Figure 2.8. Zirconium isopropoxide could also be used as the inorganic precursor and resulted in a material called zirconium oxide-sulfate. In this later case, sulfate ions were introduced to the synthesis mixture as $(\text{NH}_4)_2\text{SO}_4$. The thermal stability up to 500°C is due to crystallization delay caused by the sulfate or phosphate groups in the structure, so that the disordered wall structure favorable for mesoporous materials is retained. Both materials show relatively high surface areas and pore sizes in the range between micropores and mesopores. In addition, Ying and co-workers reported the preparation of a phosphated zirconium oxide, with moderate acidity through a one-pot synthesis with zirconium n-propoxide and alkylphosphates.⁷⁴ The phosphate groups that remain after calcination enhanced the thermal stability and contributed to an increased acidity. It was then demonstrated that it is possible to synthesize hexagonally ordered titanium oxo-phosphates⁷⁸ from titanium isopropoxide, sulphuric acid and simple cationic surfactants C16-TAB and C18-TAB, following the similar phosphatation procedure developed for zirconium based materials. The pore size of the materials lie in the super-micropore range and the materials are stable up to 350°C .

Stucky and co-workers⁷⁹ developed an interesting synthesis procedure for a very wide range of non-siliceous oxides (TiO_2 , ZrO_2 , Nb_2O_5 , Al_2O_3 , Ta_2O_5 , ...) using amphiphilic polyalkylene oxide block-polymers in non-aqueous solutions. The mesoporous solids obtained are thermally stable, ordered and show large pore size up to 14 nm. Whereas the pore walls of the materials described before are amorphous, these mesoporous materials contain nanocrystalline domains within relatively thick framework walls. The mesoporous oxides are believed to be formed through a mechanism that combines block-copolymers self-assembly with alkylene oxide complexation of the inorganic metal species.

Most of the mesoporous materials described so far are either hexagonally ordered or rather disordered. However, significantly less attention has been given to non-hexagonal structures, due mainly to the higher difficulty in achieving stable well-ordered porous solids. The cubic Im3n mesoporous TiO_2 described by Stucky and co-workers in 1998 remains until now the only template-free 3-D mesophase reported.⁷⁹

2.6 Removal of the template

When the material has reached a sufficient degree of condensation, the templating molecules are no longer needed and can be removed to open the porous structure. Since some composite mesophases can contain as much as 45-55% of organic material by weight, the removal procedure of the organics is of utmost importance in the preparation. Moreover, this step can considerably alter the final properties of the desired materials.

2.6.1 Calcination

The most common method used in laboratories to remove the template is calcination. In this method, the as-synthesized materials are alternatively heated in flowing nitrogen, oxygen or air, burning away the organics. Any necessary charge compensating counterions are supplied from the decomposition of organics. Usually, the heating rates required are slow with heating ramps such as 1°C/min up to 550°C for instance. It is followed by an extended period of heating at a temperature plateau (4 to 8h). In addition, calcination of as-synthesized mesophase containing large amounts of carbonaceous species can leave carbon deposits or coke as a contaminant in the porous materials, and pore blocking could occur. Generally, when the template is removed by calcination, characteristic features can be observed. The reflection intensities increase, the structure can shrink, and the mesoscopically ordered structure could be dramatically affected.^{53,78} However, few publications until now have focused on the removal of the template by calcination,^{80,81} and the processes involved during calcination are still not fully understood. Transition metal based materials are especially interesting in this respect, since the thermal stability strongly depends on the pretreatment conditions.

MCM-41 was originally calcined at 540°C in N₂ for 1h and then in O₂ for 6h.¹⁸ The reported framework condensation increases from Q³/Q⁴ of about 0.67 in the as-synthesized MCM-41 precursor (²⁹Si NMR data) to about 0.25 after calcination. Chen et al.⁵⁹ calcined MCM-41 samples at 540°C in air for 10 h with a slow heating rate (1°C/min). They observed up to 25% decrease of the unit cell constant depending on the synthesis conditions, a fact that is in strong contrast with crystalline silicates which change very little upon heating. In general, the reported conditions for calcination were found to vary widely. However, a standard general

procedure that can be used to calcine mesostructured materials (silica) is performed under air at 550°C during 5 h with a heating rate of 1°C/min.

Thermogravimetry was used by Chen et al.⁵⁹ to study the thermal behavior of surfactant containing MCM-41 mesophase. They recognized three distinct stages of weight loss: 1) 25-150°C, due to the desorption of water; 2) 150-400°C, caused by combustion and decomposition of the template, and 3) above 400°C attributed at that time only to water loss upon silanol condensation. The first investigations on calcination were however already described in the early report from the Mobil scientists on MCM-41.¹⁸ They studied the removal of the alkylammonium template by thermogravimetric analysis combined with temperature programmed amine desorption analysis (TPAD). The measurements were carried out on as-synthesized aluminum containing MCM-41 from room temperature to 900°C under a flow of He with titration of the evolving base. They observed two main weight loss maxima. The molecular weight of the decomposing species in the low-temperature weight loss was calculated to be 312 g/mol, which is close to the sum of the molecular weights (283 g/mol) expected for decomposition of $C_{16}H_{33}(CH_3)_3N^+$ to hexadecene (224) and trimethylamine (59). The amine desorption analysis suggested the association of $C_{16}H_{33}(CH_3)_3N^+$ with siloxy groups. The authors proposed that since the siloxy groups are stronger bases (silanols are weaker acids), they could promote the Hofmann elimination at lower temperatures. An important note is that the Hofmann elimination of the structuring molecules is commonly suggested in the cases of zeolites such as MFI-type ones (ZSM-5 or Silicalite-1).^{82,83} Parker et al.⁸⁴ proposed a general mechanism for the thermolysis of the tetrapropylammonium hydroxide that is occluded in the zeolites with MFI structure. The first step of this mechanism is the Hofmann elimination producing propylene, tripropylamine and water. It is followed by successive β -eliminations. In addition, depending on the framework structure and compositions several other types of chemical reactions may occur in porous solids (dehydroxylation, decomposition, cracking, oligomerization, rearrangements). Corma et al.⁸⁰ carried out *in situ* IR study of the template thermal desorption between 200°C and 500°C with a heating rate of 10°C/min. By increasing the temperature, they observed a decrease of the interaction of the silanol groups with the template molecules. Their analysis of the organic fragments detected above 400°C suggests that part of the carbon chain has been cracked and removed. In addition, the appearance of IR bands assigned to the $R-NH_3^+$ of the protonated amine supports the proposed mechanism of Hofmann degradation of the template. The removal of triblock copolymers species from as-synthesized SBA-15 was investigated by TG-DTA. Two main processes were observed: at low temperature (80°C), desorption of

physisorbed water takes place, followed at higher temperature (145°C) by the exothermic decomposition of the template.^{46,48} This relatively low temperature decomposition compared to that of cationic surfactants or the pure BCP may be catalyzed by the inorganic framework. In contrast to silicates, other compositions are usually more sensitive to thermal treatments and calcination can result in breakdown of the structural integrity. Hydrolysis, redox reactions or phase transformations account for this lower thermal stability. Therefore, the removal of the surfactant by thermal treatment happens to be more difficult in the case of non-siliceous mesostructured materials. Nevertheless, transition metal based mesostructured materials synthesized in the presence of block-copolymers may be calcined successfully at temperatures below 400°C,⁷⁹ these temperatures often being the upper thermal stability limit. In effect, many of the transition metal based mesostructured materials synthesized in the presence of cationic surfactants were shown to collapse during thermal treatments and the thermodynamically preferred denser crystalline phases are generally produced. The removal of the template through thermal treatment is the main method we will focus on in this work.

2.6.2 Solvent extraction

An alternative method for surfactant removal is based on the extraction of the organic template. This can be done either by liquid extraction,^{32,59,85} acid treatment,⁸⁶ oxygen plasma⁸⁶ treatment, or supercritical⁸⁷ fluid extraction. Dried as-synthesized MCM-41 samples are usually extracted in acid solutions, alcohols, neutral salt solutions, ammonium acetate, or mixtures of these. For example, Hitz et al.⁸⁵ showed that Al-MCM-41 sample could be extracted in acidic media for 1h at 78°C. Up to 73% of the template could be removed by extraction with solutions of an acid or salt in ethanol. These authors showed that when extracting with acidic ethanol, ion exchange of the counter cations for protons can be achieved simultaneously. Using strong acid or small cations was proved to be more efficient for the extraction of the template in ethanol, suggesting that the size and, thus, the mobility of the cations in the close packed micellar aggregates is one of the factors determining the extent of extraction. Acids with low acid dissociation constant such as CH₃COOH are less efficient. Moreover, it seems that more polar solvents are superior to dissolve the template ions. Accordingly, it is widely suggested that an ion-exchange mechanism occurs during solvent

extraction of M41S-type materials. The presence of cationic species in the extraction liquid for charge balance is therefore required for the ion-exchange. Various acidic media are used for surfactant extraction, ethanolic HCl solutions being the most commonly employed. The HMS or SBA-types frameworks are considered to be relatively neutral, and the resulting framework-surfactant interactions are weak. Such weak electrostatic interactions or hydrogen bonding are more favorable for surfactant extraction even in the absence of cationic species since counter cations are not needed. It is, for example, possible to remove large amounts of cationic surfactant from an SBA-3 mesophase by extraction in boiling ethanol for a short time.⁸⁸ The templates from mesophases obtained with long-chain amines,³² as well as transition metal based mesophases obtained from the ligand-assisted method^{75,76} are usually readily extracted. Also block copolymers could be extracted from SBA-15 using acidic ethanol solutions for short times and low temperatures.⁴⁷ Hence, extraction might provide an alternative to calcination especially in the case of low thermal stability non-siliceous mesophases. However, the possibility of extraction of the template molecules depends strongly on the nature of the interactions between template and inorganics, and the efficiency of this method relies on a balance between extraction time and temperature as well as on the composition and concentration of the extraction solution.

2.6.3 UV-Ozone treatment

A new method to remove the template from MCM-41 was pioneered recently by Keene et al.^{89, 90} Ozone was used to remove the organic surfactant species at room temperature from an as-synthesized mesophase to form mesoporous MCM-41. As-synthesized MCM-41 was treated by ozone using a UV lamp whose wavelength was known to produce ozone from atmospheric oxygen. The pore size of the resulting ozone-treated sample was apparently larger, the pore size distribution narrower and the hexagonal long range ordering of the pores seems to be improved compared to MCM-41 calcined in an ordinary box furnace. The unit cell parameter observed for the ozone treated sample was found to be the same as for the initial mesophase, which is in contrast with calcination or ion exchange of the template. The ozone treated samples seem to exhibit a higher Si-OH group density than the samples ordinarily calcined. UV-ozone treatment was subsequently applied to remove non-ionic surfactants from mesostructured silica thin films. Brinker and co-workers⁹¹ showed that room

temperature UV-ozone treatment provides an efficient mean for the removal of the template while simultaneously stabilizing the inorganic silica framework into a well-defined mesoscopic morphology. Their results established that ozone treatment leads to complete removal of the template, strengthens the inorganic framework by fostering silica condensation and renders the thin film surfaces highly hydrophilic. The main advantages of ozone treatment over conventional thermal treatments, are that elimination of organic molecules at room temperature might be applicable to thermally unstable mesoporous materials, and that no organic solvents are needed. However, it seems that the first ozone treatments performed on titania based mesophases led mainly to uncontrolled ozonation resulting in a highly exothermic reaction and the loss mesoscopic order.⁹²

2.7 Organized matter and morphology control

The mesoporous silicas obtained from the early syntheses were typically finely divided powders consisting of small particles ($< 10\ \mu\text{m}$) with no well defined morphology. However, the true liquid crystal templating mechanism introduced by Attard et al.⁹³ allowed the preparation of monoliths. Since 1996, a wide variety of other shapes, including thin films, spheres, fibers, tubes and many other more complex morphologies were reported.^{27,65,94-96} Some solids with defined macroscale morphology can be designed by the process conditions, such as dip-coating, spin-coating or emulsion templating. Others are formed spontaneously by a self-organization process. However, the origin of the different morphologies is not often established and the mechanisms of formation proposed are still highly hypothetical. Macrostructures can be considered as matter organized on different length scales. Control may be achieved on the molecular, supramolecular, macromolecular and colloidal scales. Such materials are often described as *hierarchical materials*, as they actually consist of primary *building blocks* associated with more complex secondary structures integrated in the next size level. Conceptually, these complex structures may arise from a shift from thermodynamic chemical regimes to kinetic regimes in which equilibrium phases are replaced by high-order organizational states of consolidated matter determined by local minimum rather than global energy minimum.⁹⁷ The motivations for the development of materials with defined morphology are very diverse: optics, electronics, photonics, separation, or biotechnology.⁹⁸⁻¹⁰¹

One very efficient way to create organized matter is through coupling the synthesis of silica-surfactant mesophases with high order patterning. Especially, the incorporation of organizational processes in sol-gel chemistry has been in the recent years a very promising and productive strategy.

By combining sol-gel technique and self assembly, Yang et al.¹⁰² showed that the synthesis of mesoporous silica following the acid route $S^+X^-T^+$ is particularly well suited for the preparation of large variety of different morphologies. This is likely based on the weaker interactions between surfactant and silicate surface and less charged framework walls, compared to the base-derived composites, allowing more flexibility for the mesophase.

Ordered thin films of thickness of 0.2-1.0 μm have been prepared under acidic conditions by heterogeneous nucleation at the air-water¹⁰³ and oil-water interfaces⁴⁵ as free-standing films, and at the solid-liquid interface on both mica¹⁰⁴ and graphite surfaces.¹⁰⁵ Furthermore, Ogawa prepared a self-supporting transparent hexagonal phase thin film, by slow evaporation of a sol mixture containing TMOS, water, CTAC and a mineral acid.¹⁰⁶ Brinker and co-workers¹⁰⁷ synthesized oriented mesostructured thin films with hexagonal, lamellar or cubic phases by dip-coating or spin-coating techniques. Slow evaporation of the solvent induced the surfactant concentration to cross the CMC and then provoke co-assembly of the silicate and the surfactant. The dip- and spin-coating techniques were applied, using non-ionic surfactant and block-copolymers under acidic conditions, to prepare oriented mesoporous thin films with 2-D hexagonal, 3-D hexagonal and cubic structures.¹⁰⁸

Through biphasic emulsion chemistry, the preparation of hollow spheres of mesoporous silica has been achieved under acidic conditions, with decisive control of the shearing rate.⁴⁵ Differently, Bruinsma et al.¹⁰⁹ reported the synthesis of hollow spheres by spray-drying techniques, based on very rapid solvent evaporation and retention of preformed shapes. Interestingly, particles with spherical morphology were also very successfully prepared under alkaline conditions. For instance, Huo et al.¹¹⁰ reported the preparation of hard transparent spheres from an emulsion at room temperature. Grün et al.^{40,111} modified the well-know Stöber¹¹² synthesis of monodisperse spheres and succeeded in the preparation of monodispersed mesoporous MCM-41 and MCM-48 spheres in the presence of ethanol and ammonium hydroxide (Figure 2.9).

Figure 2.9: SEM picture of MCM-48 spheres obtained by a modified Stöber synthesis.⁴¹

Figure 2.10: SEM pictures of MCM-41 tubes obtained under alkaline conditions.¹¹³

Lin et al.¹¹³ reported in 1996 a remarkable synthesis of hollow tubes with 0.3 to 3 mm in diameter and mesopores channels along the tubular axis. This *tubules-within-tubules* organization could be produced by careful control of the surfactant-water ratio and the rate of silica condensation at high pH (Figure 2.10). The mechanical method of preparation of porous silica gel fibers by spinning a high viscosity silica sol or by freezing a solution of silicic acid in water were applied under acidic conditions to produce mesoporous silica fibers (MSF). Bruinsma et al.¹⁰⁹ introduced a spinning process to synthesize mesoporous fibers with a cationic surfactant (CTAC). This dry spinning process is based on slow solvent evaporation, which drives mesophase formation, and an increased viscosity facilitated by the addition of a polymer (PEO). The fibers which are drawn from the mixture into continuous filaments, present pore channels oriented parallel to the fiber axis. Recently, MSF with large pore sizes were prepared similarly by drawing a gel strand from a highly viscous amphiphilic block-copolymer-silicate solution.¹¹⁴ The pores are also running parallel to the fiber axis.

The spontaneous formation of mesoporous silica fibers at the oil-water interface was demonstrated under strong acidic conditions by using low stirring rates.^{45,53} In a similar system, Huo et al.¹¹⁵ showed the exclusive formation of optically transparent mesoporous silica fibers using halide mediated, acidic conditions. Oil-in-water chemistry was used to grow silica fibers with a cross section ranging from 1 to 15 μm and lengths reaching 5 cm. The authors suggested at that time that a hydrophilic growth environment on the water side of the interface supports the silica fibers growth in contrast to the hydrophobic conditions in the oil region where other structures are formed. Among long homogeneous fibers with circular cross-section, different short fibers and helical fibers were observed. Well-defined fibers are

obtained preferentially when the oil-water interface is kept static. If the stirring speed is increased, the fiber morphology is no longer obtained, but rather spherical particles form.

Figure 2.11: SEM of mesoporous silica fibers synthesized with TBOS in a static acidic system.

Figure 2.12: TEM image of a fiber cross section showing the fiber center.¹¹⁷

The fibers are optically transparent in the visible region and the fiber can be doped with various dyes. Therefore, they could be used as high surface area optical waveguides,¹¹⁵ or as a new type of laser material.¹¹⁶ Marlow et al. succeeded in the synthesis of mesoporous silica fibers doped with rhodamine 6G as a laser dye.¹¹⁶ These fibers have a well defined pore environment and show order on different length scales. A perfect structure is observed on the nanoscale and the fibers are homogeneous on the micrometer scale. A single fiber is expected to have a relatively uniform thickness, absorption and birefringence along the fiber length that make them suitable for waveguiding. Upon laser irradiation the waveguide effect led to amplification of stimulated emission along the fiber axis. The beam-like light emitted from the end of the fibers was spectrally narrow and highly directional. Although one could foresee interesting optical applications, the internal structure of these fibers and the mechanism of mechanism remained under discussion. In 1997, it was stated that the fibers consist of hexagonally organized channels oriented parallel to the fiber axis,¹¹⁵ as it is suggested for other fibers.^{109,114} However, further optical and TEM investigations suggested that this hypothesis could be incorrect. Indeed, fibers synthesized with tetrabutoxysilane (TBOS) in the absence of additional oil were shown to have a circular inner architecture, consisting of hexagonally organized channels running circularly around the fibers axis (Figure 2.12).¹¹⁷ However, the question how general this structure is has not been addressed yet. Other silicon sources may indeed lead to different results. In addition, the growth kinetics has not been investigated yet and control of the synthetic parameters require additional studies.

2.8 Literature

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3 Characterization

In general, mesoporous materials are characterized by techniques including X-ray diffraction (XRD), electron diffraction (ED), small angle X-ray scattering (SAXS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), gas adsorption measurements, solid state nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared spectroscopy (FTIR) and thermogravimetry-differential thermal analysis. Techniques such as XRD, SAXS and high resolution TEM combined with ED have been proved to be useful for the elucidation of the structure and wall thickness. Gas adsorption measurements are used to determine surface area, pore size, and pore size distributions of template-free solids.

3.1 Powder X-ray diffraction (XRD)

3.1.1 Principle

When an X-ray beam with a wavelength λ strikes a crystalline solid or a material with periodic long range order, and the Bragg conditions are fulfilled, constructive interference occurs. It follows that selective reflections of intensity I for (hkl) planes will be observed in a diffractogram when the glancing angle satisfies the Bragg's law (Eq. 3.1):

$$n \lambda = 2 d \sin \theta \quad (\text{Eq. 3.1})$$

n : integer number of wavelengths (order of diffraction)

λ : wavelength

d : repeating distance between reflecting planes*

θ : glancing angle

* Separation of the lattice planes or d -spacing.

Since, the position of the reflections is defined by the symmetry and the unit cell parameter of the solid investigated, information about size and symmetry of the lattice can be obtained from the diffractogram. In addition, the intensity of the reflections is dependent on the scattering strength of each atom j which composes the periodic solid and their positions. The respective scattering strengths are measured by scattering factors, which are related to the electron density and the size of the atoms. The overall intensity of a wave diffracted by a plane (hkl) is given the structure factor, F_{hkl} . (Eq. 3.2):

$$F_{hkl} = \sum_j f_j e^{i\phi_j} \quad (\text{Eq. 3.2})$$

F : structure factor

hkl : Miller indices

f : scattering factor

ϕ : phase difference⁺

The main use of powder XRD is the rapid and reliable identification of substances. In general, comparison of the position and intensity of the reflections observed with databanks enables the qualitative identification. In addition, quantitative analysis can be performed with the use of internal standard. It is furthermore possible to evaluate the size of the particles, by using the Scherrer equation, which relates the size of the crystallites with the integral width of the reflections.

3.1.2 Indexing of the reflections for ordered mesoporous solids

In analogy with liquid crystal phases, mesostructured materials exhibit hexagonal, lamellar, or cubic phases. MCM-41 usually shows 4 or 5 reflections depending on the sample preparation. The reflections are indexed as (100), (110), (200), (210) and (300), corresponding to the

⁺ Phase difference between the (hkl) reflections of an atom located at the origin of the unit cell and an other atom.

hexagonal space group P6. The framework walls were shown to be amorphous, resulting in the absence of periodicity along the c-direction, and therefore, only $(hk0)$ reflections are detected. In a hexagonal lattice with a unit cell parameter a , the spacing d between the planes is given by equation 3.3:

$$1/d^2 = (4/3 a^2)(h^2 + k^2 + hk) + (l^2 / c^2) \quad (\text{Eq. 3.3})$$

and the unit cell parameter is obtained with $k = 0$ and $l = 0$ as equation 3.4:

$$a = 2d_{100} / \sqrt{3} \quad (\text{with } l = 0) \quad (\text{Eq. 3.4})$$

In contrast to the XRD pattern of hexagonal MCM-41, which shows only three to four reflections beside the (100) reflection, several reflections in the $3\text{--}7^\circ$ 2θ range can be observed for MCM-48. Assuming cubic symmetry for the unit cell, the diffraction pattern of MCM-48 is consistent with the body centered cubic Ia3d space group, in analogy to the respective liquid crystal phase (Figure 3.1). However, the determination of such a high symmetry only by powder XRD might be ambiguous, and needs additional methods such as simulation of diffractograms,¹ high resolution transmission electron microscopy, and electron diffraction experiments.²

Figure 3.1: X-ray diffraction pattern of a conventional MCM-48, showing reflections of the cubic Ia3d space group.

The unit cell parameter a of a cubic cell can be calculated with $d(211)$ from equation 3.5:

$$1/d^2 = (h^2 + k^2 + l^2) / a^2 \quad (\text{Eq. 3.5})$$

$$a = d_{211} \sqrt{6} \quad (\text{Eq. 3.6})$$

3.1.3 High temperature X-ray diffraction

The purpose of the present study is to investigate the removal of the template upon thermal treatment from mesostructured frameworks. For this, *in situ* high temperature powder X-ray diffraction methods have been used. The effect of temperature on the hexagonal, cubic or lamellar mesophase can be investigated appropriately by using a commercial high temperature XRD chamber (Figure 3.2) mounted on the goniometer of a diffractometer in Bragg-Brentano geometry (reflection system).

Figure 3.2: Water cooled high temperature X-ray diffraction chamber (Johanna Otto HDK S1), with a Pt/Rh heating element as a sample holder.

A Pt/Rh resistance heating band is used as the sample holder. The chamber is water cooled. Measurements can be performed stepwise from temperature of 20°C up to 1500°C, with adaptable temperature programs.

3.1.4 Measurements

The measurements were carried out on 3 different diffractometers:

1. Samples were analyzed with a STOE STADI P diffractometer equipped with a linear position sensitive detector in transmission geometry using Cu-K $_{\alpha 1}$ radiation allowing to measure 2 theta angles down to 1.0 °.
2. Samples were additionally analyzed on a GADDS diffractometer (Brucker AXS) using Cu-K $_{\alpha 1}$ radiation in transmission geometry. The setup (Göbel mirrors, HI-STAR Area Detector, collimator aperture 0.8 mm, measurement time 600 s) allowed measurements of 2 theta angles down to 0.5 °.
3. The *in situ* high temperature measurements were recorded on a STOE STADI P θ - θ powder X-ray diffractometer in reflection geometry (Bragg-Brentano) using Cu-K $_{\alpha 1+2}$ radiation with secondary monochromator and scintillation detector. A high temperature X-ray diffraction chamber (Johanna Otto HDK S1), with a Pt/Rh heating element as a sample holder, was mounted on the goniometer. The commercial setup was modified for these experiments. Since large amounts of template are evaporated during calcination and would coat the cold parts of the chamber including the windows, a makeshift vent was assembled by placing a funnel immediately above the sample to pump off all calcination products. XRD patterns were typically recorded with an automatic divergence slit configuration (ADS, receiving slit fixed at 0.8 mm), except SBA-15 samples which were measured in a fixed slit configuration (FS). Other samples were analyzed on the wide angles range with the fixed slit configuration. The difference between the diffraction patterns obtained in ADS and fixed slit configurations is illustrated Figure 3.3 for the example of MCM-41.

For *in situ* high temperature experiments, all the samples in the as-synthesized form containing the templating species were ground prior to analysis. A small amount of ethanol or hexane was used to disperse the materials homogeneously on the sample holder. The samples were heated stepwise with a heating rate of 1 or 5°C/min, depending on the materials, up to the final calcination temperature. This temperature was maintained for several hours, then the sample was cooled down.

Figure 3.3: X-ray diffraction patterns of a MCM-41 sample measured in fixed configuration and automatic divergence slit (absolute intensities are shown).

Calcination plateau steps at intermediate temperatures were eventually added. XRD measurements were performed every 50 °C during the heating process, every hour during the isothermal heating, and at various temperatures upon cooling. To adopt the usual oven calcination conditions, all the measurements were carried out in air. In addition, the thermal stability of the different materials was tested by measurements carried out up to 1000°C in air, with various heating protocols. The thickness of the sample preparation was about 0.5 mm, and the sample surface was homogeneous. The preparation has to be very thin to avoid any temperature gradient in the sample during thermal treatment. Therefore, the sample temperature is considered to be close to the temperature of the Pt/Rh band sample holder. Phenomena of “hot spots” and rapid overheating of the sample bed (glow effects)³ can be neglected and will not be considered. For a diffractometer, the instrumental error limits in the precision of the *d*-spacings measured at low angle for each mesostructured materials is of interest. Discrepancies may originate from differences in samples preparation, since

differences in scattering volume and packing density can lead to different diffraction pattern in terms of signal to noise ratio. Moreover, the accuracy, with regard to the positions of the reflections and their intensity, for measurements performed with material deposited on the Pt/Rh band is strongly influenced by the homogeneity and the thickness of the preparation. Therefore, materials treated *in situ* and under conventional conditions in a box furnace were compared to test the reproducibility and validity of the measurements.

Figure 3.4: Comparison between XRD patterns measured *ex situ* on the transmission diffractometer and *in situ* measurements. **Left)** SBA-3 p6m; **right)** cubic Ia3d zirconium oxo-phosphate.

Figure 3.4 show the X-ray diffraction patterns measured *ex situ* on the diffractometer in transmission geometry and *in situ* for mesostructured silica SBA-3 and zirconium oxo-phosphate, before and after calcination. In both cases, significant lattice shrinkage is observed upon the removal of the template, however, the matching positions of the low angle reflections indicate a good reproducibility and prove the *in situ* XRD measurements to be appropriate. A rough estimation of the measurement error during the different calcination protocols can be made giving average variations between *in situ* and conventional calcination procedures of about 0.1 nm for the repeat distances at low angle. Furthermore, it is recognized that an absolute error of about 0.1 nm due to the limits of the synthesis reproducibility can be observed for the d value measured for several syntheses of a same material. It is therefore reasonable to assume an absolute measurement error of 0.1-0.2 nm

3.2 Thermogravimetry and mass spectrometry (TG-DTA/MS)

In order to study the chemical and physical aspects of the surfactant degradation within the mesopores, thermogravimetry (TG) in combination with differential thermal analysis (DTA) experiments were carried out. TG enables to record the mass losses as a function of temperature, and the DTA enables the detection of enthalpic effects and the evaluation of heat exchanges. The conventional thermobalance has been coupled with a quadrupole mass spectrometer. This setup allows the characterization of the species evolved during thermal treatment.

The thermogravimetric analyses combined with differential thermal analyses were performed on a NETZSCH STA 449 C thermobalance coupled with a BALZERS ThermoStar 442 mass spectrometer (temperature of the gas phase is 160°C). The measurements were carried out under air with a heating rate of 5°C/min for as-synthesized samples prior to template removal. Solvent extracted and calcined samples were measured with heating rates of 10 or 20°C/min. All measurements were repeated 3 times to test the reproducibility and experiments were also performed on materials obtained from different synthesis batches. All TG-DTA and MS results are reproducible within an error estimated to be $\pm 10^\circ\text{C}$.

3.3 Nitrogen physisorption

3.3.1 Gas adsorption isotherms

Adsorption of probe molecules has been widely used to determine the surface area and to characterize the pore size distribution of solid catalysts. Basically, the process of adsorption that takes place on a solid surface, involves adsorption processes between a solid (adsorbent) and a gas (adsorbate). Adsorption of a gas by a porous solid is described quantitatively by an adsorption isotherm, representing the amount of gas adsorbed at a fixed temperature as a function of pressure. Porous materials are most frequently characterized in terms of pore sizes derived from the gas adsorption data, and IUPAC conventions have been proposed for classifying pore sizes and gas adsorption isotherms (Figure 3.5). The six types of isotherms are characteristic of adsorbents that are microporous (type I), nonporous or macroporous (type

II and III) or mesoporous (types IV and V). Type VI is the stepwise adsorption of layers. The shape of the isotherm gives direct information about the adsorbent-adsorbate interactions (weak or strong interactions), monolayer-multilayer adsorption, filling and emptying of the pores, pore structure (size and shape), and layer by layer adsorption. In particular, the adsorption process in mesopores is dominated by multilayer adsorption and capillary condensation, whereas filling of micropores is controlled by stronger interactions.

Figure 3.5: IUPAC classification of adsorption isotherms.⁴

3.3.2 The BET surface area

Originally, the concept of adsorption related to an exposed surface was developed by Langmuir. He suggested that adsorption corresponds to a dynamic equilibrium between a gas and a solid surface resulting in a surface layer that is only one molecule thick. Brunnauer, Emmett, and Teller⁵ (BET) extended this theory and introduced the concept of multi-molecular layer adsorption, if the first adsorbed layer acts as substrate for further adsorption.

From the BET equation (Eq. 3.7), it is possible to calculate the quantity of gas n_m necessary for a monolayer coverage of the surface.

$$\frac{n}{n_m} = \frac{C(p/p_o)}{(1 - p/p_o)(1 + C - p/p_o)} \quad (\text{Eq. 3.7})$$

- p : vapor pressure of the adsorbate
- p_o : saturation vapor pressure of the pure adsorbate
- n : total amount of adsorbate
- n_m : amount of adsorbate in the monolayer
- C : constant

The BET equation is conveniently expressed in the linear form ($y = ax+b$, with $x = p/p_o$), from which, if applicable, a BET-plot should be a straight line. From the slope of the plot and the intercept with the x axis, n_m and C can be obtained. The surface area S_{BET} is then calculated from n_m .⁶ Usually, linearity is observed in the range $p/p_o = 0.05\text{-}0.35$, which limits the validity of the BET equation. The values of the BET surface area have to be considered with care, since the linearity of the BET plot is not always observed. However, similar samples measured under the same conditions can be compared, since the error is systematic. Furthermore, in the case of micropores, multiplayer adsorption does not occur, which makes the BET model not valid for microporous materials. The analysis of the adsorption isotherm through the BET model is only valuable for nonporous, mesoporous and macroporous materials. Therefore, the use of the BET model can be criticized for the evaluation of data from materials with pore sizes in the intermediate range between micro- and mesopores.

3.3.3 Determination of the pore sizes

The pore systems of solids may vary substantially both in size and shape. Therefore, it may be difficult to determine the pore width, and more precisely, the pore size distribution of a solid. Usually the shape of the pores is assumed to be either cylindrical or slit shaped. To determine the pore size distribution of cylindrical pores, several methods are available, based on thermodynamics,⁷ geometrical considerations,⁸⁻¹⁰ or statistical thermodynamic approaches.¹¹

For cylindrical pores, the most commonly used method is probably the one described by Barret, Joyner and Hallenda (BJH)¹² taking into account the thickness of a multilayer of adsorbed nitrogen on the pore walls. However, compared to other more recent methods that rely on a localized description, such as density functional theory, the thermodynamically based BJH model has been shown to underestimate the pore diameter by about 1.0 nm.¹¹

Alternatively, Kruk et al.⁹ proposed a method which is based on a simple geometric relation between the specific pore volume and the pore size for an infinite area of cylindrical pores hexagonally arranged. The pore diameter denoted w can be obtained from the pore volume V_p and the d-spacing value d of the hexagonal phase measured by XRD:

$$w = cd \sqrt{\frac{\rho V_p}{1 + \rho V_p}} \quad (\text{Eq.3.8}), \quad \rho \text{ is the density of the pore walls. The pore volume is obtained}$$

from comparative plots methods. The most widely-used plot methods are t -plot and α_s -plot, which are rather similar. The t -plot method will be used, which is based on the transformation of the experimental isotherm in a plot which corresponds to the amount adsorbed n re-plotted against t , the standard multilayer thickness on a reference non-porous material at the corresponding p/p_0 . The finite intercept of the extrapolated t -plot to the n ordinate, gives the pore volume. The parameter c is a constant, which depends on the pore shape and equals 1.155 in the hypothesis of pores modeled as hexagonal prisms or 1.213 in the case of pores modeled as circular cylinders. The pore wall thickness b can be evaluated from the pore size w and the unit cell parameter a obtained from XRD ($b = a - w$).

3.3.4 Measurements

The N₂ sorption measurements were performed on an ASAP 2010 (Micromeritics). Prior to the measurement, the calcined samples were activated under vacuum for 5h at 200°C for the silica based mesoporous materials, for > 12 h at 200°C for mesoporous zirconia samples, and for > 12 h at 150°C for titania based samples. The measurements are performed at 77K using a static-volumetric method. The empty volume is measured with helium gas.

3.4 Electron microscopy

Electron microscopes are instruments that use a focused beam of electrons to examine objects on a very fine scale. This examination gives information on topography (surface features and texture), morphology (shape and size of particles), composition, and crystallographic data (structural arrangements).

3.4.1 Transmission electron microscopy (TEM)

Transmission electron microscopy provides images of very small structures, and allows separation down to the Ångström scale depending of the equipment. A transmission electron microscope works much like a slide projector. A beam of electrons, instead of light for the projector, is shined through the sample (specimen) and parts of it are transmitted and projected as a sharp image on a fluorescent screen. Scattered or diffracted electrons from the samples form the image contrast. The wavelength of the electron beam applied limits the resolution of the microscope. The high energy electron beam provided in high voltage microscope systems allows to reach the domain of the structural resolution, where the resolution distance is in the range of the unit cell size. At present, high resolution electron microscopy (HREM) may enable separation at a quasi-atomic length scale (1-2 Å). Because the interaction of the electron beam and the specimen is decisive for the formation of the structural image, high resolution microscopy requires preferentially very thin specimens, so that the image is formed mostly via coherent interactions (low chromatic aberration).¹³

The transmission electron microscopy images of the mesoporous silica samples were obtained in this work with a Hitachi HF 2000 transmission electron microscope operated at 200 keV, which was equipped with a cold field emission source. Calcined samples have been used, and were mounted on carbon films which were fixed on copper grids. These investigations were performed at the MPI für Kohlenforschung, Mülheim an der Ruhr, by Bernd Spliethoff. For the TEM observations performed on as-synthesized and calcined porous zirconium oxophosphates, the samples were first dispersed in ethanol (99.9 vol.%) using the ultrasonic method where the suspension was subsequently dropped onto a carbon microgrid. High-resolution electron microscopy observations were performed with a 400keV electron

microscope (JEM-4000EX) in the group of Prof. Terasaki by Dr. Zheng Liu at the Japan Science and Technology Corporation (CREST) and Department of Physics, Tohoku University, Sendai, Japan.

3.4.2 Electron diffraction (ED)

Electron diffraction and transmission electron microscopy are combined to study crystalline or periodic materials. The results gained from both techniques are complementary, since the formation of an image and diffraction are intimately related. The image of a specimen obtained on a screen or a photographic film by TEM is formed by scattered or diffracted electrons. By varying the focus mode of the projection system of the electron microscope, one can obtain either an image or an diffraction pattern on the screen or film. In imaging mode, one generates either a bright field image or a dark field image depending on the position of the microscope objective aperture (*contrast aperture*). In the dark field image, only the beams corresponding to a selective reflection hkl contribute to the image formation. The dark field imaging allows to work in *diffraction mode* with the formation of an electron diffraction pattern, when a selected area aperture is used instead of an objective aperture. The aperture is used to define the area from which a diffraction pattern is formed in a TEM specimen. The resulting pattern contains information about the phases present (lattice spacing) and sample orientation. The electron diffraction pattern can be described as a plane section of the diffracted lattice in the reciprocal space, and Bragg's fringes can be indexed.

The electron diffraction patterns were obtained during the TEM investigations carried out in Prof. Terasaki's group.

3.4.3 Scanning electron microscopy (SEM)

Scanning electron microscopy is widely employed to observe the surface of bulk samples and is also used to determine the size and shape of particles. A beam of electron is scanned across the sample, ionization occurs near the surface, backscattered and secondary electrons produced can exit the sample and be examined. The image is then formed sequentially on a screen. The resolution of the SEM reaches 10-20 Å for high performance equipments. Due to

shading and the composition dependent yield of secondary electrons, topographical and materials contrast is obtained.

The morphology of mesoporous silica obtained from a two phase acidic system was analyzed using a Hitachi S-3500N scanning electron microscope by Hans-Joseph Bongard at the MPI für Kohlenforschung. The microscope was operated at 5 or 25 keV. The samples were coated by a 10 nm layer of gold.

3.5 Solid-state nuclear magnetic resonance (NMR)

Basically, nuclear magnetic resonance (NMR) is the study of the properties of molecules containing magnetic nuclei by applying a magnetic field and observing the frequency of a resonant electromagnetic field. If a nucleus has a spin quantum number $I > 0$, it possesses a magnetic moment with constant magnitude and $2I+1$ different possible orientations relative to an axis. When locally a magnetic field is applied to a sample, the energies of the nuclear spins and their orientations may change and a net magnetization is induced. The orientations of the spin vectors are then changed by the effect of a radiofrequency (rf) field applied at a frequency in the resonance condition. The frequency of the applied rf field, which modifies the nuclear spins, depends of the electronic structure around each nucleus of interest. Since the electronic structure of an atom is largely influenced by its chemical environment, the frequency of the field is different for nuclei in different chemical environments. This resonance frequency is commonly expressed in terms of *chemical shift*, which is related to the difference between the resonance frequency of a nucleus in the compound of interest and that in a reference material.

In the case of solids, NMR is complementary to XRD and affords information on the structural and chemical local environment of atoms. Solid-state NMR is a powerful method for the characterization of the amorphous framework of mesoporous materials, and facilitates the study of the organization of micellar aggregates or organic molecule confined in an inorganic matrix. However, compared to NMR spectra recorded in solution, a lower resolution is generally observed with broad linewidths. The broad linewidth for solids originates from the interactions of the spins of the nuclei with the surrounding lattice. These interactions are either direct dipole-dipole magnetic interactions between neighboring nuclear spins, anisotropy of the chemical shift arising from orientation of the static molecule, or

quadrupolar interactions when $I > 1/2$. A technique reducing the linewidth in spectra to perform high resolution solid-state NMR is the magic-angle-spinning method (MAS). The dipole-dipole interactions and the chemical shift anisotropy show a $1-3\cos^2\theta$ dependence. The “magic angle” is the angle at which $1-3\cos^2\theta = 0$, and corresponds to $\theta = 54.74^\circ$. The sample is spun at high speed at the magic angle relatively to the applied magnetic field. Rapid motion at this angle averages all dipole-dipole interactions and chemical shift anisotropy to zero.

Experimentally, the ^1H and ^{13}C MAS NMR spectra were recorded by Dr. Bodo Zibrowius at the MPI für Kohlenforschung on a Bruker Avance 500WB spectrometer operating at a proton resonance frequency of 500 MHz. A 4 mm MAS probe with spinning speeds up to 15 kHz was used. For the ^1H NMR measurements a 90° pulse of 4.2 μs and a repetition time of 10 s (8 scans) were used. For ^{13}C CP NMR a proton 90° pulse of 3.8 μs and contact times between 0.5 and 2 ms were applied. The chemical shifts were referenced to neat TMS.

3.6 FTIR-spectroscopy with a probe molecule

Infrared absorption spectroscopy allows the detection of transitions between different vibrational states, and gives information about energy level separations. The nature of chemical bonds, their strength, and elemental data about the atoms involved can be determined. Of particular interest in heterogeneous catalysis is the use of infrared spectroscopy with probe molecules for the characterization of the acidity of porous materials. The acidity of porous zirconium oxide-sulfates and zirconium oxo-phosphates was evaluated by monitoring pyridine adsorption as probe molecule with infrared spectroscopy. This method enables to distinguish Lewis and Brønsted acid sites and hydrogen bonding interactions.

The IR spectra of adsorbed pyridine were collected on a Nicolet 560 FTIR spectrometer equipped with a MCT detector. The samples were pressed from powder (using the same weight of powder for each sample corresponding to 10 mg/cm^2) and used as circular pressed pellets 25 mm in diameter. An *in situ* cell allowed evacuation (ca. 3×10^{-6} mbar), heating, and the dosing of pyridine vapor to the sample. Each sample was heated to 200°C for 12 hours under vacuum to remove adsorbed water prior to the adsorption of pyridine. The sample was

cooled to 140°C and spectra of the unexposed sample pellet taken. For acidity measurements, the sample was exposed to 4 mbar of pyridine vapor at 140°C and then evacuated.

The experiments were carried out in collaboration with Dr. Stuart J. Thomson at the Max-Planck-Institut für Kohlenforschung.

3.7 Literature

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4 Thermal behavior and structural properties

4.1 Mesoporous materials based on silica

The first candidates for *in situ* investigation of the removal of the templating species are materials which are synthesized under alkaline conditions (MCM-41 and MCM-48). Acid prepared mesostructures such as SBA-3 and SBA-15 will then be discussed. All materials described in this section are synthesized according to published standard procedures. The calcinations were performed at 550°C for 5 hours in all cases.

The physicochemical parameters of the materials described in this section are summarized in the appendix part in Table 8.1 and Table 8.2.

4.1.1 Materials synthesized under alkaline conditions

The mesophase formation under alkaline conditions is based on cooperative electrostatic interactions between negatively charged oligomeric silicate species and positively charged surfactant molecules. In general, one considers the mesostructured silica network obtained under alkaline conditions to contain significant amounts of negative charges.

4.1.1.1 MCM-41 (*Grün* synthesis)¹

MCM-41-type materials were all prepared within 2 hours according the method described by Grün et al.² The synthesis is based on the use of TEOS (0.05 mol) as the silicon source, with ammonia (0.14 mol) as the catalyst and an aqueous solution of surfactant ($6.6 \cdot 10^{-3}$ mol in 120 g H₂O). *n*-Alkytrimethylammonium bromides of different alkyl chain lengths with $n_c = 12$ -18 were used as template. The original *Grün* synthesis was modified in 1999³ and Si-MCM-41 samples with apparent increased structural order were achieved by aging the materials in the mother liquor at 90°C for 7 days. *n*-Alkytrimethylammonium bromides can be substituted by

an equimolar amount of n-hexadecylpyridinium chloride (cetylpyridinium chloride, CPCI) for an alternative MCM-41 synthesis. The as-synthesized materials are subsequently dried at 90°C overnight.

Ex situ X-ray diffraction results

The standard reference material is MCM-41 synthesized in the presence of cetyltrimethylammonium bromide ($n_c = 16$) as the template, denoted CTAB/MCM-41. The $d(100)$ -spacing of the well-resolved hexagonal p6m phase prior to calcination is ca. 4.05 nm, giving a unit cell constant at $a_{\text{as-made}} = 4.68$ nm. After the removal of the template, the hexagonal phase is retained. The $d(100)$ reflection is however shifted to about 3.55 nm, resulting in $a_{\text{calcined}} = 4.1$ nm, which corresponds to a lattice shrinkage of about 12%. (Figure 4.1a).

Figure 4.1: **a)** Comparative X-ray diffraction patterns of a conventional MCM-41 sample (red) and MCM-41 after aging at 90°C for a week (black). Both samples are calcined. **b)** N₂ sorption isotherms at 77 K obtained on a conventional MCM-41 sample (open symbols) and MCM-41 after aging at 90°C for a week (solid symbols). Both samples are calcined for 5 hours at 550°C.

The unit cell constant $a_{\text{as-made}}$ for a CTAB/MCM-41 aged at 90°C for 7 days increases slightly with $d(100) = 4.2$ nm and $a = 4.85$ nm. In contrast, however, the lattice shrinkage upon thermal treatment is substantially reduced. The $d(100)$ of the calcined sample aged at 90°C is 4.15 nm with $a_{\text{calcined}} = 4.79$ nm, indicating a lattice shrinkage of only 1-2 %. This fact suggests that materials obtained after an aging period have a higher thermal stability. Furthermore, the diffraction pattern obtained on a material aged for several days seems to exhibit a better resolution with a higher signal to noise ratio compared to MCM-41

synthesized at room temperature. Assuming a same volume of matter for the X-ray preparation, one may suggest a higher degree of order and/or a larger coherent scattering domain size. The N₂ sorption isotherms in Figure 4.1b show that capillary condensation steps are present in both cases. The position of the capillary condensation step is shifted to higher relative pressures for the aged MCM-41 material, indicating a larger pore size, in agreement with the XRD data. Furthermore, the aged sample presents a steeper increase during the capillary condensation suggesting a narrower pore size distribution. The adsorption capacity and surface area are comparable.

In situ X-ray diffraction

The development of the XRD pattern as a function of temperature for a Si-MCM-41 sample is shown in Figure 4.2. An initial change occurs up to 250°C with an increase of all reflection intensities. The intensity of the (100) reflection immediately increases strongly up to 250°C, while those of the (110) and (200) reflections start increasing only after the system has reached 200°C. Following this, the intensities of the reflections at higher 2 theta values grow at a faster rate and reach their maxima at 300°C.

Figure 4.2: Representative XRD patterns stack plot of Si-MCM-41 obtained from the *Grün* synthesis under alkaline conditions. Shown are subsequent XRD patterns as the material is calcined up to a temperature of 550°C, held at this temperature for 5 hours and cooled to room temperature (RT).¹

From 300°C changes are less pronounced; the intensity of the (100) reflection reaches its maximum at 550°C, and all the intensities remain unchanged while the sample is kept for 5 hours at 550°C. The measurements taken during the cooling process show a decrease of the (100) reflection intensity when the sample is cooled below 350°C, with no strong variation for the (110) and (200) reflections.

Figure 4.3 shows the evolution of the maximum intensities of the reflections at low angles recorded for a conventional Si-MCM-41 and illustrates the evolution of the d -spacings during the calcination. The top graph shows clearly a three step evolution for the (100) reflection (room temperature- 250°C, 250°C-550°C, cooling process). One can note that the $d(100)$ -spacing value follows approximately the same temperature dependence. The $d(100)$ is reduced by ca. 0.45 nm, predominantly prior to 350°C. The faster increase of the (100) intensity below 200°C relative to the higher order reflections is confirmed. In addition, the scattering intensity for the higher order reflections reaches a maximum at 350-400 °C, before decreasing linearly (bottom graph). The same evolution of the d -spacings of the higher order reflections is observed.

The general strong increase in intensity appearing in XRD with the increasing temperature is due to the increasing scattering contrast between the pore walls and the inside of the pores, caused by the burning out of the templating organic species. The relative intensities of the low angle reflections are very dependent on the distribution of matter in the pores.^{4,5} Selective removal and redistribution of surfactant fragments in the pores could therefore lead to the different growth rates of the individual reflections. In addition, marked differences in the relative intensities between the reflections at low angles are expected, depending largely on the ratio of the wall thickness to the pore diameter. Recent works on simulations of XRD pattern allow precise investigation of the influence of matter distribution in the unit cell on the diffraction pattern. Hammond et al.⁴ could explain the dramatic change in the X-ray scattering that occurs upon removal of the template from MCM-41 by using a lattice model with hexagonal channels and a different scattering form factor for the wall and the matter in the channel. They proved that the (100) intensity increase upon calcination arises from different phase cancellation between scattering from the wall and the pores. Therefore, once the template is removed from the pore region, the effect of this phase cancellation is reduced, leading to an enhanced scattering intensity. In addition, the presence of molecules bonded to the inorganic surface within the pores, and the surface roughness may also induce strong variation in scattering contrast at low angle.⁶ During the cooling process, a slight loss in scattering intensity is observed, indicating a loss of scattering contrast. This effect is

reversible, since heating the sample leads to the recovery of the intensity, and it can be attributed to physisorbed water condensed in the pores.

Figure 4.3: Evolution of the reflection intensities (solid symbols) of CTAB/MCM-41 as a function of temperature (calcination at 550°C for 5 h). Also plotted are the d -spacing values (open symbols) of the respective reflections. The red symbols show the evolution of the reflections of MCM-41 aged at 90°C. The red dashed line are linear fits of the d -spacings. **Top:** evolution of the (100) reflection. **Bottom:** evolution of the (110) and (200) reflections. The connecting black solid lines are used as guide for the eye.

The thermal behavior of the sample aged at 90°C shows a similar evolution of the reflection intensities observed in general for all reflections according to the three step process as

described for the conventional material. From the graph, the remarkable stability of the mesophase treated at 90°C is evidenced. The sample aged at 90°C shows only a small *d*-spacing shift (0.1 nm) to lower values, mostly between room temperature and 150°C, as physisorbed water is removed. It is interesting to note that the relative intensity ratios of low angle reflections observed for the final material at room temperature are different for a material that has been aged at 90°C. The average ratio (100) : (110) is approximately 3 for aged MCM-41 samples whereas it is 5 for non-aged MCM-41 samples. Such effects may be related to the ratio between wall thickness and size of the pore. These observations are likely attributed to the larger pore size, which results from a lower lattice shrinkage during the thermal treatment. It is reasonable to propose that the lower shrinkage of the unit cell of an aged MCM-41 is a result of a better wall polymerization.⁷ The increased thermal stability and structural order are achieved since hydrolysis of the silicon source and further condensation of the inorganic network are enhanced during the aging period performed in the mother liquor, leading to higher cross-linking of the inorganic species making up the walls.⁸ On the other hand, the expulsion of electrolytes and surfactant molecules may play an additional role in the packing of the surfactant and the condensation of the mesophase.^{9,10} One has to keep in mind, however, that depending on the synthesis conditions, undesired structural degradation and loss of pore uniformity could occur upon prolonged hydrothermal treatment at high temperatures, due to re-hydrolysis and dissolution of the framework.¹¹

TG-DTA/MS

The TG-DTA results (Figure 4.4) show that three main processes take place upon heating CTAB/MCM-41, in agreement with Zhao et al.¹² At temperatures below 150°C, physically adsorbed water is removed. The following stage occurs between 150°C and 350°C and corresponds to the decomposition of the organics. Finally, an additional weight loss is measured at higher temperatures up to 600°C, often assigned to dehydroxylation of silanol and residual coke combustion.

In parallel to our *in situ* XRD studies, the TG-DTA/MS data reveal that the mechanism of removal of the template involves three steps. An initial endothermic step between 150°C and 250°C is caused by the elimination of the trimethylamine head group, via Hofmann degradation, which leads to a hydrocarbon chain ($m/z = 26, 41, 42, 55, 69$). During this step (below 250°C), 46% of template is removed by evaporation of the alkene resulting from the Hofmann degradation. Keene et al.¹³ used sample controlled thermal analysis (SCTA) coupled

with a mass spectrometer to carefully eliminate the organic surfactant and study *in situ* the evolved gases during the thermal decomposition of the template. They found hexadecene to be the major evolved product in this range of temperatures, confirming the elimination of the trimethylamine and the formation of the alkene by Hofmann degradation. They obtained additional evidence for the presence of hexadecane by collecting the intermediate evolved species during calcination, and further characterizing them by GC/MS, and ^1H and ^{13}C NMR. The MS curve of trimethylamine $m/z = 59$ and the corresponding imminium species $m/z = 58$, which is probably formed in the mass spectrometer, shows that the other Hofmann product also leaves the materials at this stage. The second step in the TG-DTA is exothermic and takes place in the temperature range of 250°C to 300°C . Several fragments assigned to shorter chain lengths ($m/z = 15, 26, 41, 42$) appear in this interval accompanied with early oxidation processes producing CO_2 ($m/z = 44$), NO_2 ($m/z = 30, 46$), and H_2O ($m/z = 18$). Heating MCM-41 samples from 250°C to 300°C removes an additional 21% of the template. One can propose that this step, corresponding in the XRD to a less pronounced increase in intensity, results from a successive carbon chain fragmentation or decomposition, with early oxidation of different fragments. Here, some cracking reactions on the hydrocarbon chain occur. Finally, the major part of the oxidation occurs between 300°C and 350°C (peak centered at $330^\circ\text{C} \pm 2^\circ\text{C}$) and converts the remaining organic components (18%) to carbon dioxide, water, and probably residual carbonaceous species. During these two oxidation steps, molecular fragments with $m/z = 59$ and $m/z = 58$ are also detected. The successive oxidation occurring in the pores does not seem to strongly affect the mesostructure, as the XRD pattern does not vary significantly. The intensities increase slowly as the template is burnt and reach a maximum before the template removal has been completed. The presence of a peak in the trace assigned to the imminium form of the trimethylamine ($m/z = 58$) at about 330°C suggests that amine groups are involved in stronger interactions with the inorganic framework and are therefore removed only at higher temperatures.

After the oxidation processes up to 350°C have been completed, about 15% of the organics remain in the material up to higher temperature, namely 600°C , according to the TG measurement. That indicates that the template removal is not complete at 350°C and requires additional heating to 550°C for several hours, which is in agreement with the XRD data. The template residues are probably carbonaceous species since only small quantities of water are produced from Si-OH condensation beyond 350°C . The exact nature of the remaining species above 350°C is not yet clear. It is possible that carbon chains and amine species reassemble together in the mesopores to build very stable polymeric species or coke. Such species are

more difficult to oxidize than the C_xH_y fragments and require higher temperatures and longer treatment times to be removed.

Figure 4.4: TG-DTA/MS measurements performed on a conventional Si-MCM-41 (5°C/min under air up to 800°C). Below are presented the TGA data with a dashed line and the DTA curve with a solid line. Above are plotted the evolution curves of various molecular species recorded from the MS measurements with temperature.¹

Much work has been focused on coke formation in porous materials, namely zeolites.¹⁴⁻¹⁶ It has been determined that coke is not a uniform adsorbate, but a complex mixture of carbonaceous species resulting from condensation and oxidation reactions. The carbonaceous deposits consist of a variety of polyaromatics and polyaliphatic compounds having a wide range of boiling points. They are not necessarily homogeneously distributed in the material and can be located within the pores and on the external surface. A rough distinction can be made between the more mobile residues or physisorbed products termed as soft cokes desorbing at lower temperatures and the more bulky carbonaceous species termed as hard cokes contributing to a weight loss at high temperatures.¹⁵ The formation and the nature of coke are strongly dependent on the temperature and the properties of the porous material. In our case, we assume that rather bulky carbonaceous species remain in the pores up to 600°C. However, the presence of carbon in a thermally even more stable phase such as graphite cannot be excluded. A reaction scheme is proposed for the processes which leads to complete template removal from the pure Si-MCM-41 material (Figure 4.5).

Figure 4.5: Reaction scheme for the process leading to complete removal of the template from MCM-41.¹

The removal of the template from mesostructured samples of MCM-41 aged 7 days at 90°C proceeds via the same reaction scheme. The thermal resistance of the aged materials is however higher. Furthermore, a lower amount of surfactant is contained in the as-synthesized mesophase (Table 4.1).

Effects of the surfactant chain length

All materials synthesized with $n_c = 12-18$ exhibit XRD patterns showing a well-resolved hexagonal mesophase indexed to the $p6m$ space group. As expected, the interplanar distance $d(100)$ increases with increasing alkyl chain length. The unit cell size and pore size of the calcined materials are found to be determined by the alkyl chain length of the cationic surfactant used (Table 8.1 and 8.2). The *in situ* XRD results obtained for materials synthesized with alkylammonium bromide surfactants having alkyl chains with $n_c = 12, 14$ and 18 are apparently similar to the ones obtained with $n_c = 16$. A decrease of the distance d is observed for all samples predominantly before 300°C similar to that observed with C16-MCM-41. The scattering intensities of all reflections increase progressively at different growth rates as the template species are burnt out of the porous channels. If one looks closely to the early stages of the heating process at temperatures below 300°C, one can observe variations in the growth rates with dependence on the surfactant chain length (Figure 4.6).

Figure 4.6: Log_{10} plot of the intensities of the low angle reflections during the heating ramp for materials synthesized in the presence of alkylammonium surfactants with $n_c = 12-18$.

The results strongly suggest that the growth rate in scattering intensity for materials synthesized with shorter surfactant chains might be lower. One could attribute the more rapid growth in intensity during the heating ramp observed for C18-MCM-41 to the larger pore sizes compared to a relatively constant wall thickness, leading to higher scattering contrast upon removal of organics from the inside of the pores.

The TG-DTA/MS measurements performed on these materials show that the weight loss is found to increase as the alkyl chain of the surfactant increase (see Table 4.1). This fact could be attributed to an increasing size and molecular weight¹⁷ of the micellar aggregates relative to the amount of inorganic matter that is embedding the templating species. The observed lower amount of organics contained in the material after aging may result from re-dissolution of some of the template in the mother liquor and/or expulsion of template molecules upon the course of the condensation. A general trend is that the proportion of organics removed at lower temperature (between 150°C and 260°C) seems to be reduced with increasing surfactant chain length. On the other side, the relative fraction of organics that undergo subsequent decomposition and oxidation reactions at higher temperatures increases. This effect is particularly marked for C18TAB/MCM-41. However, it remains unclear whether it is caused by a lower yield of the Hofmann degradation in favor to oxidation processes, or by mass transfer limitations of the larger organic species produced by the elimination.

Samples	25-110°C (%)	110-265 °C (%)	265-305 °C (%)	305-395°C (%) (μV/mg) ^a	395-1000°C (%)	total mass loss (%)
C12-MCM-41	3	24	5	3 (0.5)	4	39
C14-MCM-41	3	24	6	5 (0.6)	5	43
C16-MCM-41	2	21	9	8 (0.8)	6	46
C18-MCM-41	3	19	10	9 (1.10)	7	48
C14-MCM-41 aged	4	21	6	4 (0.7)	4	39
C16-MCM-41 aged	2	19	7	7 (0.9)	5	40
C18-MCM-41 aged	3	17	10	9 (1.2)	6	45

Table 4.1: Mass losses recorded by thermogravimetry for MCM-41 samples synthesized with surfactants having different chain lengths (mass losses below 110°C attributed to physisorbed water). ^a Energy released associated with the main DTA exothermic peak.

To facilitate the comparison, the weight change derivatives can be calculated from the weight change curves measured in TG (Figure 4.7). The decomposition/desorption of the cationic surfactant gives rise to pronounced peaks in the weight change derivatives at 150-400°C. In all cases, the peaks indicate three temperature ranges for the decomposition of the template, corresponding to the stepwise process. An additional broader peak appears at about 550°C, increasing in intensity with the alkyl chain length increasing.

Figure 4.7: Weight change derivatives of MCM-41 synthesized with alkyltrimethylammonium surfactants with increasing carbon chain length. C12, C14 and C16-MCM-41 are shifted for clarity by 1.8, 1.2 and 0.6 %/°C, respectively. The dashed line indicates the limit temperature (250°C) between Hofmann elimination and oxidation.

In Figure 4.8 are plotted various molecular species recorded during TG/MS, that are attributed to the carbon chain of the surfactant ($m/z = 26, 42, 55$) and the trimethylammonium head group ($m/z = 59$) of the different MCM-41 samples. This figure shows the decrease of the fraction of the organic chain removed at lower temperatures relative to the fraction removed during decomposition and oxidations at higher temperatures. This effect is particularly marked for smaller molecular fragments. Furthermore, the fragments $m/z = 59$ attributed to the trimethylammonium headgroup of the surfactants are detected at lower temperatures for the longer chains surfactants. Interestingly, the plots obtained for the C18-MCM-41 show an additional second step or shoulder in the lower temperatures range in the MS traces. This new step is probably caused by surfactant molecules involved in different types of surface interactions with the inorganic framework.

The Hofmann degradation is possibly favored by longer chains and a higher interaction of longer chain surfactants with the silica surface. Hence, the temperature at which the Hofmann degradation starts may decrease. Furthermore, it has been proposed that the temperature of the thermodesorption of alkyltrimethylammoniums is likely governed by their decomposition temperature, and the temperature at which the decomposition products are removed, and not only by the molecular weight of the template.¹⁸ Therefore, it is possible that larger alkene molecules remained partially blocked within the inorganic matrix until reaching the oxidation temperature ranges.

Figure 4.8: Plots of various molecular species recorded with MS on C12, C14, C16 and C18-MCM-41 (from top to bottom) and their evolution with temperature.

Effect of the surfactant head group

The nature of the interaction between the head group of the surfactant and the silica surface seems to play a crucial role in directing the processes involved in the removal of the surfactant. The influence of the surfactant headgroup might be probed by changing the nature of the polar headgroup. Khushalani et al.¹⁹ demonstrated first that MCM-41 could also be synthesized in the presence of cetylpyridinium chloride (CPCl) as the template. It is believed that the CPCl/MCM-41 mesophase formation is possible according to the S^+I^- route because this surfactant is cationic, and has a similar aggregation number and CMC value to CTACl which is often used. However, CPCl allows also for variation in the charge density at the headgroup. In addition, it is suggested that the micellar aggregates formed during the synthesis exhibit an increased rigidity compared to other alkylammonium surfactants and that the interaction between the pyridyl ring of the surfactant and silica is stronger. Therefore, it is likely that the removal of the surfactant species upon thermal treatment could proceed differently.

Figure 4.9: XRD patterns stack plot of MCM-41 obtained from the *Grün* synthesis with CPCl as template. Shown are subsequent XRD patterns as the material is calcined up to a temperature of 550°C, held at this temperature for 5 hours and cooled to room temperature.

The XRD patterns stack plot of MCM-41 obtained from the *Grün* synthesis with CPCI is shown in Figure 4.9. The $d(100)$ value measured for the as-synthesized materials is ca. 3.9 nm, comparable to CTAB/MCM-41. The XRD patterns indicate that the reflections observed at low angles are narrower and with a higher signal to noise ratio than CTAB/MCM-41, in agreement with the literature statements.^{3,19} From the developing XRD patterns, it is seen that the scattering intensities of all reflections at low angles remain constant up to 250°C, which suggests no drastic changes in the distribution of matter in the pores and/or low contrast variation between pore walls and the inside of the channels. From 250°C, all intensities increase drastically, with the (100) reflection increasing at a slightly higher growth rate, reaching their maxima at the calcinations plateau of 550°C. From 550°C, the intensities remain constant until the cooling starts where variations in contrast are again observed, due to water adsorption. The higher order reflections (110), (200), and (210) are retained after calcination. In graph 4.10 are illustrated the evolution of the reflection intensities and the respective values of the d -spacings. The simultaneous increase in intensity of all reflections is observed after 250°C. The comparison with CTAB/MCM-41 emphasizes the different behavior. The first noticeable decrease in d -spacing occurs up to 250–300°C. Subsequently, a second observable shrinkage is measured between 500°C and the first hour at 550°C.

Figure 4.10: Evolution of the reflections intensities of CPCI/MCM-41 as a function of temperature (calcination at 550°C for 5 h). Also plotted are the d -spacing values of the respective reflections (open symbols). Represented with a cross-dashed line is the intensity of (100) of CTAB/MCM-41 as reference.

The TG-DTA/MS data recorded on CPCI/MCM-41 are depicted in Figure 4.11. The first stage is the removal of the physisorbed water. It is followed by the main conversion of the template species between ca. 180°C and 450°C which is a 2-step process (200-300°C and 300-450°C). During this stage, only exothermic peak are detected, suggesting oxidative decomposition and burning out of the organic species. The major exothermic process takes place between 290°C and 420°C (centered at $340 \pm 2^\circ\text{C}$), similar to CTAB/MCM-41. The total mass loss recorded on the mesophase synthesized with CPCI is comparable to that of CTAB/MCM-41. However, the removal of the template occurs differently as highlighted by the comparative curves in Figure 4.10 and 4.11. The presence of the fragment assigned to the pyridyl head group ($m/z = 79$) appearing around 250°C suggests that the surfactant molecule is first decomposed into two species, probably via an elimination-type reaction or cracking. However, a significantly lower amounts of the carbon chain species are detected at this temperature range in relation to the high fraction evolved at higher temperatures. At this step, only 24% of the surfactant species are removed (11% in weight loss). This may explain the modest growth rate of the XRD reflections intensity. Subsequently, 44% of the organic template (20% in weight loss) are removed during the main oxidation step between 300-450°C with a relatively high energy release ($-1.8 \mu\text{V}/\text{mg}$). This process is accompanied by the simultaneous increase of all reflection intensities in XRD (Figure 4.12).

It seems that the major part of the surfactant is removed by exothermic decomposition and oxidation processes, likely increasing the production of coke during the calcination. The CPCI/MCM-41 sample studied here contains about 15 % of carbonaceous species after the main oxidation reaction ($> 450^\circ\text{C}$), which is substantially higher than the amount estimated for CTAB/MCM-41 (Table 4.1). These carbonaceous species represent ca. 33 % of the organics. The residual species are converted to CO_2 at temperatures between 450°C and 550°C, resulting in an additional shrinkage of the hexagonal lattice (Figure 4.14), with an additional X-ray scattering intensity increase. The major difference with CTAB/MCM-41 is the lower weight loss occurring during elimination and larger amounts of coke produced. The carbonaceous residues are however readily removed (soft coke) to yield complete template removal. It seems that the pyridinium headgroup surfactant undergoes Hofmann elimination less readily than the trimethylammonium headgroup surfactant does.

Figure 4.11: TG-DTA/MS measurements performed on a CPCI/MCM-41 mesophase. Below are presented the TGA data with a dashed line with its 1st derivative curve (gray curve), and the DTA curve with a solid line. Above are plotted molecular species recorded from the MS and their evolution with temperature.

4.1.1.2 MCM-48 (cubic $Ia\bar{3}d$ phase)

In comparison to MCM-41, the synthesis of MCM-48 is more difficult. However, high quality MCM-48 is obtained following the hydrothermal method described by Fröba et al.²⁰ using TEOS (0.02 mol) as the silicon source, and CTAB (0.013 mol) as the template in the presence of KOH (0.01 mol) and water. As-synthesized materials were isolated after 3-5 days of hydrothermal treatment at 115°C. The high quality of all as-made MCM-48 samples obtained (Figure 3.1) is suggested by the presence of at least 8 reflections in the XRD patterns.²¹ The average $d(221)$ value is 3.97 nm for the as-synthesized material ($a_{\text{as-made}} = 9.73$ nm). After calcination, the reflections are shifted to higher 2 theta angles, $d(211) = 3.37$ nm giving $a_{\text{calc.}} = 8.25$ nm, and their intensities are increased in comparison with the as-synthesized material. The contraction of the unit cell upon calcination is about 15%, and the well ordered structure is retained.

Figure 4.12: XRD patterns stack plot of CTAB/MCM-48 obtained by hydrothermal synthesis with CTAB as template and TEOS as silicon source. Shown are subsequent XRD patterns as the material is calcined up to temperature of 550°C, held at this temperature for 5 hours and cooled to room temperature.

The *in situ* XRD patterns stack plot obtained on MCM-48 (Figure 4.12) shows the same scattering intensity behavior as that of MCM-41. All intensities increase drastically as the

calcination proceeds resulting from changes in scattering contrasts. The (211) and (220) reflections increase at a higher growth rate than the higher order reflections due to a different distribution of matter inside the pores. From 300°C, changes in intensity are less pronounced. The result shows the good thermal stability of the 3-D cubic structure during calcination. The graph depicted in Figure 4.13 shows the marked decrease in d -spacing observed predominantly below 250°C during the heating ramp. The evolution of the interplanar distance $d(211)$ and the intensity of the reflections approximately follow a 3 step process. With respect to the XRD results, one can assume that the mechanism of the removal of the surfactant from MCM-48 is identical to that described for CTAB/MCM-41.

Figure 4.13: Graph showing the evolution of the reflections intensities of MCM-48 as a function of temperature (calcination at 550°C for 5 h). Also plotted is the evolution of $d(211)$ (open symbols).

Figure 4.14 shows the TG-DTA/MS measurements performed on C16TAB/MCM-48. The results are very similar to those of MCM-41. The stepwise decomposition of the template occurs from 150°C to 400°C. This stage corresponding to the decomposition processes of the templating species and their thermodesorption represents about 45 % in mass loss, which is comparable to the data reported by other authors (ca. 40-45%).^{18,22} The step attributed to the Hofmann degradation of the surfactant (150-250°C) represents a weight loss of 26%, which is similar to that of the MCM-41 mesophases synthesized with short chain C12TAB and C14TAB. Conversely, the successive oxidation steps involve weight losses more comparable to those of C16TAB/MCM-41. The main oxidation peak is centered at $325 \pm 2^\circ\text{C}$. From 400°C, changes provoked in the structure and scattering contrast are due mostly to the

removal of the residual carbonaceous species (ca. 7%), and the release of a low amount of water due to condensation of silanols. The organic content is shown to be higher than that estimated previously for the hexagonally ordered mesostructured silica mesophases, with a total weight loss of ca. 56%, consistent with a higher void volume for the 3-D structure. One can conclude that the 3-D open structure has no marked effects on the processes responsible for the removal of the template by thermal treatment.

Figure 4.14: TG-DTA/MS measurements performed on an as-synthesized MCM-48 mesophase. Below are the TGA data with a dashed line with its 1st derivative curve (gray curve), and the DTA curve with a solid line. Above are plotted various molecular species recorded from the MS with temperature.

4.1.2 Materials synthesized under acidic conditions ($S^+X^-T^+$)

4.1.2.1 SBA-3²³

The synthesis of SBA-3 is carried out in strongly acidic aqueous solutions below the pH of the isoelectric point of silica. Under these conditions, halide ions X^- mediate the interaction between the surfactant and positively charged oligomeric inorganic species ($S^+X^-T^+$) through weak hydrogen bonding forces which ensure the assembly of the mesophase. Silica mesophases synthesized under acidic conditions have different composition, pore structure, wall thicknesses, and adsorption properties compared with samples obtained by alkaline routes.^{23,24} During the polymerization process, the protons associated with the silica species are excluded until a neutral inorganic framework remains. Hence, the framework charge is neutral or slightly positive.

As-synthesized SBA-3 is obtained at room temperature by slow addition of TEOS (0.096 mol) to an aqueous acidic solution of CTAB (0.012 mol) according to the standard procedure.²³ The XRD pattern shows the low angle reflections indexed to a hexagonal $p6m$ mesophase (see Figure 3.4) with $d(100) = 3.94$ nm ($a_{as-made} = 4.55$ nm). After calcination at 550°C for 5 hours, $d(100)$ decreased to 3.18 nm ($a_{calc.} = 3.67$ nm), indicating a large lattice shrinkage of 19 %.

In situ XRD results

Figure 4.15 shows the development of the XRD pattern during calcination of SBA-3. All the intensities of the low angle reflections start increasing simultaneously at a temperatures above 250°C. From 250°C, the growth rate is high, with strong variations in the scattering intensity. The intensities reach their maxima at temperatures close to the calcination plateau. During the remaining part of the process of the calcination, no drastic changes occur. The decrease in intensity observed during the cooling stage is attributed to the adsorption of water which slightly decreases the scattering contrast between walls and pores. Another feature is the higher $I(100) : I(110)$ intensity ratio compared to that observed for MCM-41. This diffraction effect is likely caused by the differences in wall thickness observed when comparing both materials.²⁴

Figure 4.15: XRD patterns stack plot of SBA-3. Shown are subsequent XRD patterns as the material is calcined up to 550°C, held for 5 hours and cooled to room temperature.

Figure 4.16: Graph showing the evolution of the reflection intensities of SBA-3 as a function of temperature (calcination at 550°C for 5 h). Also plotted are the d -spacing values of the respective reflections (open symbols). Represented with a cross-dashed line is the intensity of the (100) reflection of CTAB/MCM-41 as reference.

The graph showed in Figure 4.16 illustrates the changes of the intensities of the low angle reflections combined with the evolution of the interplanar distances $d(100)$, $d(110)$ and $d(200)$ as a function of temperature. The d -spacings of the hexagonal mesophase decrease slightly below 150°C due to the removal of physisorbed water. The system remains then mostly unchanged until 250°C where all intensities drastically increase accompanied by a marked decrease in d -spacing. The d -spacing shift occurs between 250°C and 350°C. Following this, no further lattice contraction is detected, indicating a relatively rapid process of decomposition or thermodesorption of the template. The comparison with the evolution of the (100) intensity of MCM-41 illustrates the different nature of the decomposition process responsible for the removal of the template.

TG-DTA/MS

The TG-DTA/MS data (Figure 4.17) show that the template decomposition is a 3-step process in a narrow temperature range. After the desorption of the physically adsorbed water (1%), an endothermic process is recognized between 180°C and 260°C, (centered at $239 \pm 2^\circ\text{C}$), which, however, has not been discussed before. A marked heat effect and a large weight loss (25%) are observed. During this step evaporation of HCl and H₂O from the mesophase initially takes place. This is followed by evaporation of the surfactant head group fragment ($m/z = 59$) and some carbon chain fragments ($m/z = 42, 55$). It has to be noted that about half of the mass losses (25 %) is measured during this first endothermic step, resulting in a surprisingly modest increase in X-ray scattering contrast. It is followed by an exothermic process (260-300°C), corresponding to 10 % in weight loss, likely attributed to a decomposition and an early oxidation step. The main exothermic process with the higher energy release takes place between 300°C and 400°C (centered at $337 \pm 2^\circ\text{C}$), where the weight loss is 11%. Here, the strong increase of all intensities at the same growth rate is very likely caused by the rapid removal of organics from the inside of the pores. The two exothermic successive oxidation processes occur with release of a large amount of CO₂ and smaller fragments of the carbon chain. The oxidation processes are then completed by coke combustion and water removal at higher temperature. Above 400°C, the weight loss of 9 % corresponds to the combustion of carbonaceous species at 450°C-550°C and water losses via condensation of silanol groups, and at 600°C to high temperature condensation of remaining silanols. The total weight loss measured for SBA-3 is about 55%.

Figure 4.17: TG-DTA/MS measurements performed on as-synthesized SBA-3. Below are presented the TGA data with a dashed line with its 1st derivative curve (gray line), and the DTA curve with a solid line. Above are plotted various molecular species recorded from the MS and their evolution with temperature.

Two main processes are evidenced: 1) low temperature endothermic removal of HCl, water and parts of the surfactant species with no strong structural change, and 2) oxidation and combustion at higher temperature, leading to rapid scattering contrast variations and contraction of the hexagonal mesophase. It is, however, questionable whether the first process could be assigned to the Hofmann degradation observed for MCM-41 since the *in situ* XRD results do not show the same drastic contrast variation and differences in growth rate. Furthermore, the neutral silica framework is less favorable for the base catalyzed Hofmann elimination of the trimethylamine headgroup. Terminal silanol groups are protonated so that the bulk composition of SBA-3 and MCM-41 made with the same surfactant are distinctly different in hydrogen and halide ion content, as supported by the TG/MS results. In addition to the different chemical composition, one has to consider at least two other factors which might influence the thermal behavior of the hexagonal mesophase synthesized under acidic conditions: 1) thicker silica walls are suggested for SBA-3 materials compared to those of MCM-41, 2) the probable presence of disordered micropores in the inorganic framework walls. The evolution of the scattering intensity of the low angle reflections is governed by the contrast between the walls and the inside of the pores, whereas the TG profiles depend on the compositions and the interaction between the matrix and the included species. The removal of the template from as-synthesized SBA-3 is governed by the size of the surfactant species relative to the size of the honeycomb mesopores and framework micropores, and the strength of the interaction between the template and the solid. The presence of microporosity within the walls may induce perturbation in the scattering contrast and a different phase cancellation behavior is expected since the scattering density of the walls is not constant.

Effects of solvent extraction

To reduce the damage caused by the removal of the template by thermal treatment and reduce the cost of the synthesis of mesoporous materials, non-destructive solvent extraction techniques have been developed. For mesoporous material obtained according the S⁺T route, the templating species interact strongly with the inorganic framework via charge-balancing ionic interactions. The destruction of this kind of interaction is rather difficult to achieve by solvent extraction alone. However, in the acid synthesized mesophase the surfactant cationic charge is balanced by a halide ion, which allows the template to be removed by solvent extraction without providing an exchangeable cations.²³

Extraction was therefore performed in pure boiling ethanol according the method proposed by Tanev et al.²⁵ The solvent extraction was carried out twice, with a sample to extraction media ratio of 1g/150ml, and subsequent washing with ethanol. The TG-DTA measurements performed on the extracted sample show a remaining total weigh loss of ca. 10-13%, indicating a removal of ca. 75-80% of the template by the extraction. Therefore, the removal of the residual template species still requires subsequent calcination.

Figure 4.18: XRD patterns stack plot of SBA-3 obtained after extracted in pure ethanol. Shown are subsequent XRD patterns during the calcination.

Figure 4.19: *d*-spacings of SBA-3 during calcination of an as-synthesized sample (black plots) and an extracted sample (red plots).

The $d(100)$ of the hexagonal mesophase of the extracted sample is 3.81 nm, with $a_{\text{extracted}} = 4.40$ nm, indicating a lattice contraction of 3%. Figure 4.18 shows the development of the XRD patterns during calcination at 550°C for 5 hours of SBA-3 after extraction in pure boiling ethanol. The constant intensities of the low angle reflections supports the notion that a large amount of organics has been removed from the pores. This confirms also that the change in intensity observed previously are due to contrast variations. Figure 4.19 shows that the hexagonal lattice of the material after extraction undergoes linear shrinkage from 250°C up to the end of the calcination plateau whereas the *d*-spacings of the as-synthesized SBA-3 mesophase without extraction decrease strongly in a rapid step at 250-300°C. The $d(100)$ of the extracted mesophase is 3.3 nm after calcination, indicating a lower shrinkage of ca. 14% compared to a non-extracted sample. The regular large shrinkage observed for the extracted sample suggests that the exothermic reactions with high energy release are not necessarily responsible for the lattice contraction. Nevertheless, high heat effects may enhance this contraction effect since the effective temperature of the sample might be substantially higher than the oven temperature.

4.1.2.2 SBA-15

SBA-15 is synthesized according to the acidic synthesis route using PEO-PPO-PEO* triblock copolymers of the Pluronic-type as structure directing agents.^{26,27} SBA-15 was prepared with TEOS as the silicon source and EO₂₀-PPO₇₀-EO₂₀ (P123) as the template in an aqueous HCl solution.

Figure 4.20: XRD patterns stack plot obtained for SBA-15. Shown are subsequent XRD patterns as the material is calcined up to 550°C, held at this temperature for 5 hours and cooled to room temperature. The low signal to noise ratio is due to a measurement set up with small receiving and divergence slits. Inset shows an alternative detailed measurement focused on the region of the higher order reflections.

Calcined SBA-15 exhibits reflections indexed to the $p6m$ hexagonal space group at very low angles, $d(100) = 9.65$ nm indicating a very large unit cell with $a = 11.10$ nm. The position of the reflections of the hexagonal phase at very low angle render the *in situ* XRD measurement difficult to realize due to the configuration of the sample holder set up, and may induce large experimental errors. To allow a measurement, the set up has been changed from automatic divergence slit, as was used so far, to a fixed slit configuration. Furthermore, due to the large signal caused by the primary beam at very low angle, the developing *in situ* XRD patterns are

* PEO and PPO stand for polyethylene oxide chains and polypropylene oxide chains, respectively.

corrected by subtraction of the background measured with the empty Pt/Rh band. Figure 4.20 illustrates the development of the XRD patterns during calcination. Such *in situ* experiments are presented for the first time in the case of a SBA-15 mesophase. Regarding the XRD results shown in this figure, only small scattering contrast variation are observed for the reflections.

Figure 4.21: Graph showing the evolution of the reflections intensities of SBA-15 as a function of temperature (calcination at 550°C for 5 h). Also plotted are the *d*-spacing values of the respective reflections (open symbols).

The graph shown in Figure 4.21 indicates a relatively linear shrinkage of the hexagonal lattice occurring between 200°C and 450°C. The lattice shrinkage is accompanied with irregular variations of the scattering intensities for the (100) reflection. This might be due to the limit of the accuracy of the sample holder set up in the reflection geometry at angles below $1^\circ 2\theta$. However, the (110) reflection seems to increase rapidly between 150°C and 250°C, then reaching its maximum (see also inset in Figure 4.20). The *d*(100) of calcined SBA-15 is 8.54 nm, indicating a lattice shrinkage of about 14%. From the TG-DTA/MS (Figure 4.22) one can conclude that the template removal from an as-synthesized SBA-15 sample consists of three main stages. After the removal of physisorbed water (4%) below 150°C in an endothermic process, the exothermic decomposition of the organic template takes place in one step between 150°C and 250°C with a weight loss of 42 %. During this exothermic step (DTA peak centered at $169 \pm 2^\circ\text{C}$), all fragments assigned to block-copolymer fragments ($m/z = 42, 58, 74$), HCl ($m/z = 37$), water and CO_2 are detected simultaneously in the MS. This step could correspond to the increase in scattering contrast observed for the (110) reflection.

Between 250°C and 400°C, a subsequent weight loss of 10% is measured, with an exothermic peak maximum at 317±2°C, assigned to the removal of water and residual carbonaceous species ($m/z = 18$ and $m/z = 44$). The total weight loss measured is about 56%, as reported before.²⁶⁻²⁸ The first major step is the complete decomposition and combined combustion of the organics. During this step, part of the organic template is converted into carbonaceous species. The temperature of this decomposition process is lower than the temperature at which the pure P123 decomposes (about 210°C),²⁷ and substantially lower than the oxidative decomposition temperature observed for the cationic surfactants (see 4.1.1). The subsequent broader step corresponds to the removal of coke by combustion, and to the dehydroxylation of silanols. In this second step, a peak appears at about 315°C where more water is released, with traces of HCl. Surprisingly, the corresponding intensities of the low angle reflections are lower. Of note is that the condensation of silanol to form siloxane has been generally suggested to occur at higher temperatures in the case of mesophases synthesized with cationic surfactants (400-600°C).^{12,29}

The removal of the template is shown to be very different than that of MCM-41 or SBA-3 synthesized with low molecular weight surfactants. The high molecular weight non-ionic template is removed at a much lower temperature. The inorganic framework seems to catalyze the thermal decomposition and oxidation of the block copolymer in the presence of oxygen, since the decomposition is strongly delayed under nitrogen.²⁸

The behavior of the scattering contrast is strongly dependent on the structure of the walls and the size of the pores. In other terms, the scattering power depends on the electron density contrast between the different moieties of the unit cell. It has been recently demonstrated that the large mesopores of SBA-15 are accompanied by disordered micropores located within the silica pore walls, providing connectivity between the ordered large-pore channels.³⁰⁻³² The presence of complementary micropores in the walls may influence the scattering density of the frameworks. As the distribution of matter in the micropores in the walls and the mesopores is temperature dependent, unexpected contrast behavior might take place with possible phase cancellation.

Figure 4.22: TG-DTA/MS measurements performed on P123/SBA-15. Below are presented the TGA data with a dashed line and the DTA curve with a solid line. Above are plotted various molecular species recorded from the MS measurements and their evolution with temperature.

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4.2 Mesostructured materials based on titanium oxide

4.2.1 Hexagonally ordered titanium oxo-phosphate¹

Porous hexagonally ordered titanium oxides can be synthesized with cationic structure directing agents and with titanium alkoxides as the inorganic precursors.¹ These systems are based on a titanium sulfate-surfactant composite mesophase and analogous titanium oxo-phosphates obtained after a post-treatment with phosphoric acid.

Synthetically, the approach is based on titanium isopropoxide ($2.2 \cdot 10^{-2}$ mol) added to an aqueous solution of sulfuric acid (0.5 M) as the inorganic precursor, and *n*-alkyltrimethylammonium bromide ($6.6 \cdot 10^{-3}$ mol) with $n_c = 16$ and 18, in aqueous solution ($r_{\text{surfactant/Ti}} = 0.3$), following the method given by Blanchard et al.¹ The synthesis is performed at room temperature. The alternative use of $\text{Ti}(n\text{-OPr})_4$ or $\text{Ti}(n\text{-OBu})_4$ shows similar results. The wet titanium sulfate composite mesophases are subsequently aged at room temperature in an aqueous solution of phosphoric acid (0.5 M) for 8 hours. This post-synthetic treatment is used to improve the thermal stability of the titania based mesostructures,¹⁻³ since the direct calcination of the un-phosphated samples always results in a collapse of the structure. Upon phosphatation, a better condensation in the inorganic framework is achieved and the sulfate groups are replaced by more thermally stable phosphate groups.¹

4.2.2 Thermal behavior of the titania-based mesophase⁴

The samples are formally denoted $\text{TiO}_x(\text{PO}_4)_y/\text{CnTAB}$ ($n_c=16,18$). All *ex situ* XRD measurements performed on the as-synthesized samples $\text{TiO}_x(\text{PO}_4)_y/\text{C16TAB}$ and $\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$ show a hexagonal phase with $p6m$ symmetry. The $d(100)$ value is 4.2 nm for materials synthesized with C16TAB and 4.62 nm for C18TAB, giving a unit cell with $a = 4.85$ nm and 5.33 nm, respectively, in good agreement with the published data.¹ Upon calcination, a large contraction of the network is observed in both cases, with lattice shrinkages of 25- 33 %, depending on the calcination temperature.

In situ XRD results

Previous studies indicated that the temperature treatments lead to an incomplete calcination at 350°C, or to a partially collapsed structure at 400°C.¹ The possibility of pore blocking was considered in the case of $\text{TiO}_x(\text{PO}_4)_y$ synthesized with C16TAB. Figure 4.23 shows typical X-ray patterns obtained during the calcination of a titanium oxo-phosphate mesophase synthesized with an ionic surfactant (C18TAB) in the temperature range up to 400°C. Upon reaching this temperature, it was maintained for 3 hours. Subsequently, the samples were cooled down to room temperature. A similar procedure was performed with fresh starting materials to a temperature of 350°C.

Figure 4.23: XRD patterns stack plot obtained from a titanium oxo-phosphate synthesized with C18TAB and calcined at 400°C for 3 hours (heating and cooling processes). As is shown in the figure the d -spacings for the material decrease as the calcination proceeds and remain constant during the cooling stage.⁴

The same behavior was observed for materials from $\text{TiO}_x(\text{PO}_4)_y/\text{C16TAB}$ and $\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$ systems, with the expected greater d -spacing and reflection intensities for the material made with the longer chain surfactant (Figure 4.24). The intensity of the (100) reflection reaches a maximum at 300°C in all cases and then decreases when reaching the

final calcination temperature. When the calcination is performed at 400°C, a stronger variation of the intensities is observed (Figure 4.24a). It is interesting to note that after the first hour of calcination, changes are less pronounced in all cases. No further variations are observed until the samples are cooled to below 200°C, where a drastic decrease of the (100) reflection intensity occurs. This effect is stronger when the calcination is performed at 400°C. This phenomenon is always reversible.

Figure 4.24: **a)** Graph showing the evolution of the reflection intensities of $\text{TiO}_x(\text{PO}_4)_y/\text{C16TAB}$ and $\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$ materials as a function of temperature (calcination at 400°C for 3 hours). **b)** d -spacing variations of $\text{TiO}_x(\text{PO}_4)_y/\text{C16TAB}$ and $\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$ materials as a function of temperature. Shown in detail is the expanded plot for the (100), (110), and (200) reflections of a $\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$ material. **c)** Graph showing the evolution of the reflection intensities for the same materials as a function of temperature (calcination at 350°C for 3 hours). **d)** d -spacing variations for the same materials as a function of temperature.⁴

The evolution of the $d(100)$ for both materials is shown Figure 4.24b and 4.24d. Above 250°C, the structures drastically shrink, the d -spacings reach their lowest values at 400°C with shifts of 0.7 nm (350°C) and 1 nm (400°C). In addition, the (110) and (200) reflections are lost. No further variation is observed, the last significant shift always occurs during the first hour of calcination.

TG-DTA/MS

The TG-DTA/MS graph (Figure 4.25) is very different compared to the one observed for basic Si-MCM-41. A first strong exothermic step, corresponding to 40% of the leaving compounds (20% in weight loss), appears between 250°C and 350°C (centered at 295°C $\pm 2^\circ\text{C}$). All hydrocarbon chain fragments, as well as NO, H₂O, CO₂, and trimethylamine fragments are detected in this temperature interval. It is followed by a second broad exothermic step corresponding to a large release of carbon dioxide between 350°C and 500°C. Also, some sulfur dioxide is released at these temperatures. This step is accompanied with a final weight loss of about 28% (55% of the leaving compounds). When the titania sulfate composite is treated with phosphoric acid, one might expect the total exchange of the sulfate groups by more thermally stable phosphate, but from these measurements it seems that a small amount of sulfate remains in the system, as shown by TG-DTA/MS experiments.

	calcined at 350°C	calcined at 400°C
TiO _x (PO ₄) _y /C16TAB	8-9 % H ₂ O 5-6% C _x H _y (500 & 800°C)	11-12% H ₂ O no C _x H _y
TiO _x (PO ₄) _y /C18TAB	9 % H ₂ O 5-6% C _x H _y (500°C)	13-14% H ₂ O no C _x H _y

Table 4.2: Water and coke content (% of the total weight) in titanium oxo-phosphate materials calcined at 350°C and 400°C, synthesized with C16TAB or C18TAB.⁴

To check the water contents of the materials, TG-DTA/MS measurements were carried out on the calcined samples. A significant amount of adsorbed water is measured between room temperature and 200°C. The results are shown in Table 4.2. As expected, the water content is important and is shown to be higher in the 400°C case, with a slightly larger amount for TiO_x(PO₄)_y/C18TAB. The calcination is incomplete at 350°C, as hydrocarbon chains fragments are still detected by MS (5-6%). In the case of TiO_x(PO₄)_y/C16TAB, these traces of hydrocarbon fragments appear at 500°C and 800°C, and may be accompanied by low amounts of H₂O and NO-species (low signal to noise ratio).

Figure 4.25: TG-DTA/MS measurements performed on a $\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$ material ($5^\circ\text{C}/\text{min}$ under air up to 900°C). Below are presented the TGA data with a dashed line and the DTA curve with a solid line. Above are plotted various molecular species recorded from the MS measurements and their evolution with temperature.⁴

Thermal stability

The thermal stability of mesoporous titanium oxo-phosphate was tested under air. A calcined $\text{TiO}_x(\text{PO}_4)_y$ sample (350°C) obtained with C18TAB was heated stepwise up to 1000°C with the high temperature XRD chamber. A heating rate of $10^\circ\text{C}/\text{min}$ was applied.

Figure 4.26: **a)** XRD patterns stack plot obtained with a titanium oxo-phosphate sample calcined at 350°C for 3 hours, during heating up to 1000°C ($10^\circ\text{C}/\text{min}$). **b)** *In situ* wide angle XRD patterns obtained on the same material during heating up to 1000°C .

As depicted in Figure 4.26a, the material shows a relatively poor thermal stability compared to that observed for mesoporous silicas under the same temperature conditions.* The hexagonal phase collapses above 500°C , and disappears completely beyond 600°C . The wide angle XRD results show that the material remains essentially amorphous up to 750°C . The presence of phosphate in the inorganic framework delayed the crystallization to denser titania phases.¹ At 800°C crystallization occurs leading to a mixture of different titania phases and probably titanium oxide phosphate $(\text{TiO})_2\text{P}_2\text{O}_7$. The crystallization process is accompanied by

* Calcined mesoporous silica materials such as MCM-41 from the *Grün* synthesis route exhibit a good thermal stability with the hexagonal mesophase retained up to 900°C .

an exothermic peak at ca. 795°C as revealed by TG-DTA (with 10°C/min), with no weight loss. The TG-DTA measurements carried out on as-synthesized (Figure 4.25) show this process to appear at 765°C (with 5°C/min). At 850°C, some intermediate phases vanish and the fractions of titania with anatase and rutile structures increase.

4.2.3 Improvement of the calcination procedure

The current calcination protocols described for the titania oxo-phosphate lead either to the incomplete removal of the template, with the presence of carbonaceous species blocked in the porous network (ca. 5wt.%) or to partial collapse of the structure and loss of nitrogen adsorption capacity.¹ The results presented proved that the heating ramp of the calcination between 250°C and 350°C is the main temperature range where dramatic structural changes occur. Therefore, a possible way to reduce the effects of the rapid removal of the template, with subsequent shrinkage and damage caused by overheating (combustion), is the introduction of supplementary plateaus during the heating ramp with slow heating rate. (0.5°C/1min).

Figure 4.27: N_2 isotherms obtained at 77K on titanium oxo-phosphates calcined according to different protocols (see text). **a)** $\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$. **b)** $\text{TiO}_x(\text{PO}_4)_y/\text{C16TAB}$. The red and blue dashed lines indicate the adsorption capacity measured by Blanchard et al.¹ for both $\text{TiO}_x(\text{PO}_4)_y$ calcined at 350°C and 400°C, respectively.

For this, 3 protocols were tested: 1) 1 hour at 250°C, 3 hours at 350°C, 2) 1 hour at 250°C, 2 hours at 350°C, 1 hour at 400°C, and 3) 2 hours at 250°C, 2 hours at 350°C, 2 hours at 450°C. The heating ramps were 0.5°C/min in all cases. The nitrogen sorption measurements

performed on $\text{TiO}_x(\text{PO}_4)_y/\text{C16TAB}$ and $\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$, indicate clearly higher adsorption capacity when protocol 1 is applied. Protocol 2 and 3 allows the use of higher calcination temperatures for the calcination of $\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$, leading to better removal of the coke species while conserving the mesoscopic order (Table 4.3). The results of the calcinations performed according to the 3 new protocols compared to the previously reported data are summarized in Table 4.3. The lowest lattice shrinkage is observed with protocol 1, showing a lattice constant decrease of about 20%.

	$\text{TiO}_x(\text{PO}_4)_y/\text{C16TAB}$			$\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$			$\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$		
calcination	$r_{\text{C16TAB/Ti}} = 0.3$			$r_{\text{C18TAB/Ti}} = 0.3$			$r_{\text{C18TAB/Ti}} = 0.225$		
protocols	a	$N_{2 \text{ ads.}}$	V_p	a	$N_{2 \text{ ads.}}$	V_p	a	$N_{2 \text{ ads.}}$	V_p
	[nm]	[cm ³ /g]		[nm]	[cm ³ /g]		[nm]	[cm ³ /g]	
350°C ¹	3.3 (6) ^b	120	0.18	4.1 (6)	170	0.25	-	-	-
1 (350°C) ^a	3.6 (7)	165	0.24	4.25 (8)	197	0.28	4.15 (7)	217	0.30
2 (400°C) ^a	3.4 ^c (3)	47	0.05	4.1 (2.5)	158	0.22	3.9 (2)	192	0.26
3 (450°C) ^a	3.3 ^c (1.5)	13	0.01	3.9 (1)	127	0.18	3.8 (<1)	145	0.21

Table 4.3: Unit cell parameters a obtained for $\text{TiO}_x(\text{PO}_4)_y/\text{C16TAB}$ and $\text{TiO}_x(\text{PO}_4)_y/\text{C18TAB}$ after different calcination procedure assuming a hexagonal phase, and maximum adsorption capacity $N_{2 \text{ ads.}}$ and pore volume V_p measured by nitrogen sorption. ^a Maximal temperature in the protocol of calcinations. ^b In brackets is the weight percentage (%) of carbonaceous species estimated by TG. ^c Low signal to noise ratio indicative of structural collapse.

Of note is that the weight losses attributed to carbonaceous species observed for materials synthesized with C16TAB take place mostly at the temperature when crystallisation occurs (>760°C). That fact strongly supports the assumption that the coke species are blocked in the smaller channel systems. Conversely, the presence of coke in the materials does not seem to prevent large nitrogen sorption in the porous titanium oxo-phosphate, which could suggest that the carbonaceous species are located on the pore walls. Solid state NMR experiments were carried out to substantiate the nature of the coke. Figure 4.28 shows the ¹³C NMR spectra recorded on $\text{TiO}_x(\text{PO}_4)_y/\text{C16TAB}$ after calcination according to protocol 1. Despite the low amount of carbon detected, one can observe two main signals. The signal at 110-150 ppm could be attributed to highly condensed sp² carbon containing species, and the higher signal at about 165 ppm may be corresponding to “C=N”-type species. One may suggest thus

that the residual parts of the headgroup form more condensed species, very likely located at the inorganic surface.

Figure 4.28: ^{13}C CP MAS NMR spectrum of $\text{TiO}_x(\text{PO}_4)_y/\text{C16TAB}$ after calcination at 350°C for 3 hours with an intermediate step at 250°C for 1 hour.

Figure 4.29: XRD pattern of calcined titanium oxo-phosphate (C18TAB), with $r=0.025$ (protocol 1). Inset shows the corresponding N_2 sorption isotherm.

Furthermore, reducing the initial surfactant to the titanium precursor ratio ($r = 0.225$) seems to result in calcined materials with the highest adsorption capacity and higher stability of the hexagonally ordered structure upon calcination (Table 4.3 and Figure 4.29).

4.2.4 Solvent extraction

Solvent extraction was performed in attempt to remove the template via a non-destructive method as proved for other titania-based mesoporous materials.^{5,6} The samples were added to either pure ethanol at reflux for 2 hours (procedure repeated twice), or to solutions of HCl (1ml of HCl 0.5M, 1M, 2M in 100ml ethanol). The sample to extraction media volume ratio was 1 g / 200ml. The results of the extraction carried out with $\text{TiO}_x(\text{PO}_4)_y/\text{C16TAB}$ are listed in Table 4.4. The unit cell parameters measured from XRD are given when the hexagonal phase is retained. The use of pure boiling ethanol for 2 hours as done previously (4.1.3) with SBA-3 leads to the removal of ca. 8% of the template.

[HCl] in	1 hour	12 hours	1 hour	2 hours
C ₂ H ₅ OH	25°C	25°C	80°C	80°C 2x
No HCl	-	-	-	8 % (4.4)
0.5 M	15 % (4.3)	19 % (4.2)	42 % (3.8) ^a	-
1 M	33 % (4.0)	48 % (3.9) ^a	72 % (-) ^b	-
2 M	57 % (3.8) ^a	79 % (-) ^b	-	-

Table 4.4: Percentages of surfactant removal from TiO_x(PO₄)_y/C16TAB via the solvent extraction method, estimated from TG (20°C/min). In brackets is noted the respective unit cell parameters in nm. Note that $a = 4.85$ nm for an as-synthesized sample. ^a Low signal to noise ratio. ^b Complete collapse of the hexagonal mesophase.

This suggests that the interactions between the surfactant and the inorganic framework are stronger than the hydrogen bonding and weak electrostatic interactions considered for the S⁺X⁻T⁺ route proposed for APM-type silica materials.⁷ As a result, counterions are needed in the extraction media to achieve the ion exchange of the alkylammonium surfactant. However, only small amounts of templating species could be removed by extraction (max. 33%) without the destruction of the hexagonal phase. Furthermore, the TG/MS experiments performed under air on extracted samples with a heating rate of 20°C/min indicate generally the release of hydrocarbon species up to 400°C, water up to 450°C, and CO₂, in two steps, up to 600°C and between 710°C and 880°C. Hence, subsequent calcination remains necessary to remove the residual organics. However, the calcination according to protocol 1 of TiO_x(PO₄)_y/C16TAB extracted with a solution of 1M HCl for 1 hour at room temperature, leads to a XRD pattern with low signal to noise ratio, with $a = 3.38$ nm assuming a hexagonal phase. In conclusion, one may consider that it is not possible to remove the template from the titanium oxo-phosphate by chemical extraction without dramatic degradation of the mesophase.

4.2.5 Literature

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4.3 Mesostructured and porous materials based on zirconium oxide

Mesostructured materials based on zirconium oxides are obtained by the self-assembly of a zirconium sulfate-alkylammonium mesophase. By controlling the amount of sulfate in the framework or with the substitution of sulfate by the more stable phosphate, thermally stable porous solids result after removal of the template. The development of these mesoporous materials based on zirconia has been the main topic of the dissertation thesis of Dr. Ulrike Ciesla (Frankfurt am Main, 1997). The synthesis procedures and detailed structural and chemical characterizations of the hexagonal phases were reported at that time, and can be found elsewhere.¹⁻³ Furthermore, the mesophase formation of the zirconium-sulfate surfactant composites ($\text{Zr}(\text{SO}_4)/\text{CnTAB}$) was investigated in our group by Lindén et al.,⁴ as a function of surfactant chain length, temperature and salt concentration.

4.3.1 Zirconium oxide-sulfate⁵

Ex situ XRD results

Zirconium oxide-sulfate materials have been developed by controlling the $\text{SO}_4^{2-}/\text{Zr}$ ratio, assuming that decreasing the amount of sulfate groups can improve the thermal stability. Zirconium oxide-sulfate is synthesized according to the hydrothermal method developed by Ciesla et al.,^{2,3} and C16TAB or C18TAB were used as templates. 70wt% $\text{Zr}(\text{OC}_3\text{H}_7)_3$ in propanol (typically 0.0128 mol) was used as the zirconium precursor, which was added at room temperature to an acidic aqueous solution (HCl) of the surfactant (typically $6.87 \cdot 10^{-3}$ mol). After dissolution, $(\text{NH}_4)_2(\text{SO}_4)$ in water is added with the amount of salt depending on the molar ratio of sulfate to metal desired. The resulting solution is then heated for 3 days at 90°C. Compounds synthesized with a $\text{SO}_4^{2-}/\text{Zr}^{4+}$ ratio of 1.2 show well resolved XRD patterns with three reflections indicating a highly ordered hexagonal phase. Several *ex situ* XRD measurements were performed to study the evolution of the hexagonal mesophases of $\text{ZrO}_x(\text{SO}_4)_y/\text{C16TAB}$ and $\text{ZrO}_x(\text{SO}_4)_y/\text{C18TAB}$. The XRD measurements (Figure 4.30) show the crucial dependence on the calcination temperature. At 500°C the structure seems to partially collapse and the well ordered mesophase is lost. A drastic decrease of the intensities is observed and the (100) reflection is shifted to a lower 2 theta value. The reflections at

higher 2 theta values vanish. Typically, a contraction of the unit cell of about 35% takes place upon calcinations at 500°C for 5 hours. However, if the calcination is performed at 550°C for 5 hours, a new intensity appears at smaller angles.

Figure 4.30: XRD patterns of a $\text{ZrO}_x(\text{SO}_4)_y/\text{C18TAB}$ material with $\text{SO}_4^{2-}/\text{Zr}^{4+} = 1.2$ as-made and calcined for 5 hours at 500°C and 550°C, respectively. Presented above is the expanded region from 27.0° to 34.0° 2 theta for the latter material showing the presence of tetragonal and monoclinic zirconia.⁵

Furthermore, the diffraction pattern measured at higher angles shows reflections of monoclinic and tetragonal crystalline zirconium oxide. From line broadening it could be estimated that the tetragonal particles are of sizes from 7 nm to 8 nm and the monoclinic species from 8 nm to 9 nm.⁺ This phenomenon of crystallization is independent of the $\text{SO}_4^{2-}/\text{Zr}^{4+}$ ratio and is observed for materials synthesized with C16TAB as well as with C18TAB. Only differences in the tetragonal to monoclinic phase ratio of the reflections can be seen depending on the amount of sulfate and surfactant chain length.

⁺ The crystallite sizes were evaluated using the *single line size/strain* Fourier analysis procedure from the STOE WinXPow software package. Due to the overlapping of the reflections, the values are not precise, but can be used to identify trends.

In situ XRD results

In situ high temperature XRD measurements, up to 500°C and 550°C, respectively, were carried out. Figure 4.31a and Figure 4.31b show the patterns obtained for the calcination of the mesophase (synthesized with a $\text{SO}_4^{2-}/\text{Zr}^{4+}$ ratio of 1.2 using C18TAB as surfactant) in the temperature ranges from room temperature to 550°C and 500°C, respectively.

Figure 4.31: **a)** XRD patterns stack plot obtained from a $\text{ZrO}_x(\text{SO}_4)_y/\text{C18TAB}$ with $\text{SO}_4^{2-}/\text{Zr}^{4+} = 1.2$ and calcined at 550°C for 5 hours. **b)** XRD patterns stack plot obtained for the same material calcined at 500°C for 5 hours. In detail is shown the decrease in scattering intensity observed during the cooling process between 150°C and room temperature. *d*-spacing values reported in the figures are given in nm.⁵

Upon reaching their maxima, these temperatures were maintained for 5 hours. In both cases the hexagonal mesophase is retained up to 350°C, where the reflections intensities are at a maximum. The strong increase in intensity observed takes place 50°C higher than in the case of titania. Following this, a strong *d*-spacing shift from 4 nm to 3 nm is observed for the (100) reflection. At 550°C the system collapses quickly and a low angle intensity below 2° (2 theta) is observed after 3 hours. At 500°C the system remains stable, but a decrease in intensity, a strong *d*-spacing shift, and the loss of the higher order reflections are observed. Upon cooling from 500°C to 150°C, no further changes are noticed for the (100) reflection intensity. Below 150°C, a decrease of intensity caused by water condensed in the pores is then observed (Figure 4.31b).

Measurements carried out on systems based on C16TAB as the templating agent show the same behavior. The *ex situ* measurements have shown that calcination at 550°C leads to zirconia with monoclinic and tetragonal crystalline phases. Thus, the *in situ* XRD data suggest that the small angle intensity growth observed in this case is due to low angle scattering caused by the presence of smaller particles. The estimated sizes of these particles appear to be smaller than those of tetragonal and monoclinic zirconia obtained by transforming amorphous precipitates by thermal treatment.⁶ The sulfate containing zirconium oxides obtained might therefore prove to be interesting for catalytic processes.^{7,8}

TG-DTA/MS

Figure 4.32 shows a typical TG-DTA/MS performed on a zirconium oxide-sulfate mesophase, with a $\text{SO}_4^{2-}/\text{Zr}^{4+}$ ratio of 1.2. As shown, the process of template removal is similar to that of the titanium systems. For the case of zirconium, however, the processes occur at slightly higher temperatures: a strong exothermic peak is measured at 356°C ±2°C and the energy released in this oxidation seems to be lower than that observed for titania (Figure 4.26).

Accompanied with the drastic decrease of the *d*-spacing and the initial sharp increase in reflection intensities in the XRD pattern (Figure 4.31), the processes involved generally lead to a loss of order in the mesophase or even to structural collapse. After the first oxidation, the remaining species are probably carbonaceous species and sulfate which are converted to CO₂ and SO₂. Peaks corresponding to *m/z* = 18, assigned to water, and *m/z* = 26 (C₂H₂⁺) from coke species can be detected. Three distinct steps in the sulfur dioxide evolution can be observed by TG-DTA/MS (Figure 4.32). The steps can be attributed to sulfate groups located in the interface between the surfactant and the inorganic framework and sulfate located within

the framework, respectively. The amounts of sulfate corresponding to each of these steps were estimated graphically by the integral intensities of the different MS signals assigned to SO_2 fragments ($m/z = 48, 64$). Table 4.5 summarizes the evaluated percentages in sulfate amount (approximations).

	$\text{ZrO}_x(\text{SO}_4)_y / \text{C16TAB}$	$\text{ZrO}_x(\text{SO}_4)_y / \text{C18TAB}$	$\text{ZrO}_x(\text{PO}_4)_y / \text{C18TAB}$
1 st SO_2 step (320-370°C)	6% (± 0.1)	7% (± 0.6)	19% (± 2)
2 nd SO_2 step (390-600°C)	86% (± 0.9)	86% (± 1.9)	81% (± 2)
3 rd SO_2 step (600-700°C)	8% (± 0.8)	7% (± 1.2)	-----

Table 4.5: Evolution of the sulfate contents in zirconium oxide-sulfate and zirconium oxo-phosphate materials at different temperature steps. Sulfate to zirconium ratio of 1.2 for $\text{ZrO}_x(\text{SO}_4)_y$ and 2 for $\text{ZrO}_x(\text{PO}_4)_y$ prior to phosphatation. Mean percentages estimated graphically (peak areas). Note that the absolute sulfate content is not the same for the different samples.⁵

The thermal stability of the calcined zirconium oxide-sulfate material was tested by heating the sample stepwise up to 1000°C, while XRD patterns were simultaneously recorded. A sample synthesized with $\text{SO}_4/\text{Zr} = 1.2$ and C18TAB was selected for the experiment. The heating protocol is similar to that applied to titanium oxo-phosphate in chapter 4.2, with a heating rate of 10°C/min. It turns out that the porous hexagonal network collapses very rapidly at 600°C. The denser phase of crystalline tetragonal zirconia particles forms directly at 650°C, which corresponds to the observed weight loss at 645°C with the release of SO_2 . The tetragonal phase is stabilized up to 1000°C. Subsequent crystallization in the monoclinic phase occurs upon cooling down to room temperature, resulting in a mixed phase.

Furthermore, attempts to remove the template were made with the solvent extraction method employed in chapter 4.2. However, the low amount of surfactant extracted without damaging the mesophase leads to the same conclusions as made for titanium oxo-phosphates. This suggests relatively strong electrostatic surfactant-inorganic framework interactions.

Figure 4.32: TG-DTA/MS measurements performed on $\text{ZrO}_x(\text{SO}_4)_y/\text{C18TAB}$ with $\text{SO}_4^{2-}/\text{Zr}^{4+} = 1.2$ ($5^\circ\text{C}/\text{min}$ under air up to 900°C). Below are presented the TGA data with a dashed line and the DTA curve with a solid line. Above are plotted various molecular species recorded from the MS measurements and their evolution with temperature.⁵

4.3.2 Zirconium oxo-phosphate⁵

Following the same procedure which was applied to titania mesophases, the zirconium sulfate mesophases can be post-treated with phosphoric acid to improve their thermal stability.^{2,3} Note that the results presented here focus on the zirconium oxo-phosphate materials synthesized with C18TAB, but can be extended to C16TAB as well. Experimentally, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (0.0128 mol) was used as the inorganic precursor, which was added at room temperature to an aqueous solution of C18TAB ($6.87 \cdot 10^{-3}$ mol). After 2 hours stirring, the mixture was heated at 90°C for 3 days. After this, the white solid was post-treated with phosphoric acid (0.5 M) at room temperature for 6 hours to yield the zirconium oxo-phosphate-surfactant composite. The unit cell parameter obtained by XRD of the hexagonal phase is $a = 5.38$ nm. Typically, the calcination of the as-synthesized mesophase was performed at 500°C for 5 hours with a heating rate of 1°C/min. The shrinkage of the hexagonal lattice was about 23 %, with $a_{\text{calc.}} = 4.1$ nm

In situ XRD results

Figure 4.33: XRD patterns stack plot obtained from a $\text{ZrO}_x(\text{PO}_4)_y/\text{C18TAB}$ materials calcined at 550°C for 5 hours. d -spacing values reported in the figures are given in nm.⁵

Upon calcination, this material does not exhibit the drastic phase changes observed for the zirconium oxide-sulfate materials. The intensity of the (100) reflection reaches a maximum at 350°C and then slowly decreases until the temperature reaches 500°C (Figure 4.33). A small *d*-spacing shift occurs up to 300°C, then the structure shrinks dramatically, and the *d*-spacing changes from 4.4 nm at 300°C to 3.5 nm at 550°C. No further strong decrease of the intensities or *d*-spacing shifts are observed, and the water adsorption upon cooling seems to be relatively low. The higher order reflections are observable until 500°C. However, the loss of higher order reflections is also observed if the sample is held at 500°C for prolonged periods of time. Nevertheless, when the calcination is performed at 500°C with a slow heating ramp rate (0.5°C/min), higher signal to noise is observed in the XRD pattern.

TG –DTA/MS

The TG-DTA/MS results (Figure 4.34) are similar to those observed on non-phosphated materials and titania systems. A single step decomposition, representing the oxidation of the surfactant, is observed between 300°C and 360°C (centered at 336 °C ±2°C), followed by a second broad exothermic step corresponding to the release of carbon dioxide and, subsequently, sulfur dioxide (20% of weight loss). Small peaks corresponding to $m/z = 18$, assigned to water, and $m/z = 26$ ($C_2H_2^+$) are also detected. It is interesting to note that the SO₂ step observed above 600°C for the zirconium oxide-sulfate (Figure 4.32) is now missing. Moreover, the second SO₂ step appears to be smaller. This difference in sulfate contents is also revealed by a change in weight loss above 550°C.

Thermal stability

The composition of the walls of zirconium oxo-phosphate calcined at 500°C was shown to be mainly $4 ZrO_2 \cdot P_2O_5 (+ SO_4)$.¹ The thermal stability of the material was tested by heating the sample stepwise up to 1000°C. The heating protocol is similar to that applied to titanium oxo-phosphate in chapter 4.2. The experiment shows that the material collapses progressively up to 750°C with the decrease of the scattering intensities, suggesting a higher thermal stability compared to the other materials described in section 4.2 and 4.3.1. Above 750°C, the hexagonal phase disappears. The wide angle XRD measurements performed on the same materials under similar conditions indicate that the framework remains essentially amorphous

until reaching 950°C where crystallization into $\text{Zr}_3(\text{PO}_4)_4$ and additional $\text{Zr}_2\text{O}(\text{PO}_4)_2$ and/or zirconium oxide phases occurs.

Figure 4.34: TG-DTA/MS measurements performed on a $\text{ZrO}_x(\text{PO}_4)_y/\text{C18TAB}$ material (5°C/min under air up to 900°C). Below are presented the TGA data with a dashed line and the DTA curve with a solid line. Above are plotted various molecular species recorded from the MS and their evolution with temperature.⁵

4.3.3 Porous mesostructured zirconium oxo-phosphate with cubic ($Ia\bar{3}d$) symmetry

Well-ordered 3-D porous networks with large pores and high surface areas can present very attractive features as supports or hosts for active species, flow and transport technologies, delivery and release, separation techniques, and catalysis. Especially for diffusion of reactants within the structure, a 3-D channel structure is expected to have advantages over a 2-D hexagonal one.⁹⁻¹² The desire to create porous materials combining such acid-base properties and the advantages of a well-defined 3-D structure led to the synthesis of a cubic $Ia\bar{3}d$ mesoporous zirconium oxo-phosphate analog.¹³ However, in the initial studies it had not been possible to remove the template without structural collapse.

4.3.3.1 As-synthesized cubic zirconium oxo-phosphate

The addition of an aqueous solution of zirconium sulfate to an aqueous solution of N-benzyl-N,N-dimethyloctadecylammonium chloride (C18BDAC) leads to the rapid formation of a zirconium sulfate-surfactant composite mesophase. The mesostructured material obtained under acidic conditions is then hydrothermally aged and subsequently post-treated with an aqueous solution of phosphoric acid, following the method described previously.²

The synthesis is derived from the method described by Ciesla et al.¹ The reactants molar ratio was $Zr(SO_4)_2 : C18BDAC : H_2O = 1 / 0.27-0.80 / 477$. In a typical synthesis, 3.04 g ($6.87 \cdot 10^{-3}$ mol) of surfactant was dissolved in 85 g of distilled water at 35°C. To this mixture, a solution of 4.55 g of zirconium sulfate (0.0128 mol) dissolved in 25 g of H_2O was added at once. A precipitate formed instantaneously and the mixture was left under stirring for 2 hours. The mixture was transferred to a polypropylene bottle and stored for 3 days at 90°C, under static conditions. After cooling, the mixture was filtered and washed with 50 ml of distilled water. The solid collected was then added to an aqueous solution of 100 ml of H_3PO_4 (0.5 M) and stirred for 5 hours at room temperature. The resulting product was filtered, washed with 100 ml of distilled water and dried overnight in air at 90°C. Samples were isolated at intermediate stages during the synthesis procedure. Additionally, the synthesis batches were scaled-up by a factor of 3 for selected surfactant to zirconium sulfate ratios for testing purposes; these samples are denoted (B).

The XRD patterns presented in Figure 4.35 show the reflections corresponding to the bicontinuous cubic $Ia\bar{3}d$ material. The diffractograms were recorded after the synthesis mixture had been stirred for two hours, with subsequent measurements performed periodically at different synthesis stages. A pure bicontinuous cubic phase is obtained rapidly at room temperature and no intermediate phase was detected in the time range investigated (Figure 4.35).

Figure 4.35: XRD patterns recorded for cubic zirconium oxide-based mesophases at different synthesis stages. **a)** Wet after 2 hours of synthesis. **b)** After a following drying period at 90°C. **c)** Wet after aging 3 days at 90°C. **d)** After ageing 3 days at 90°C dried at 90°C. **e)** Wet zirconium oxo-phosphate obtained after phosphatation. **f)** Zirconium oxo-phosphate dried at room temperature. **g)** Zirconium oxo-phosphate dried at 90°C overnight.

The X-ray diffraction pattern recorded for a wet sample before hydrothermal treatment shows 6 reflections that can be indexed clearly to a $Ia\bar{3}d$ phase (Figure 4.35a). Compared to a silica based cubic mesophase, the reflections appearing at approximately 4° 2 theta are only poorly

resolved. Due to the low signal-to-noise ratio, no further attempts to index the higher 2 theta reflections were made. However, the analogy to the silica based cubic mesophase MCM-48¹⁴ suggests that the material is cubic with a space group $Ia\bar{3}d$. For hydrothermally treated and phosphated samples, $d(211)$ and $d(220)$ remain constant for the wet samples and dried ones, respectively. Upon drying, d -spacing shrinkage of ca. 0.15 nm is observed in all cases (Figure 4.35). The unit cell parameter measured from the (211) reflection of the uncalcined dried material is generally about $a = 9.85$ nm for as-synthesized materials. Only reflections within $2-8^\circ 2\theta$, which are due to the ordering of the pores, are observed. This indicates that no condensed crystalline phases are present.

The hydrothermal treatment is carried out at 90°C for 3 days to achieve a material that is expected to be thermally and mechanically much more stable. Although an improvement of the long range ordering upon aging at 90°C had been reported for the hexagonal zirconium sulfate equivalent mesophase,⁴ the thermal aging results in the case of the cubic mesophase in a decrease of the higher order reflections resolution (Figure 4.35c). No variation in d -spacing or phase transition could be observed. The previous studies showed that the zirconium sulfate-surfactant composite mesophase is not thermally stable and that template removal by calcination leads to structural collapse. An efficient stabilizing method was described based on a post-synthetic treatment with phosphoric acid which replaces the sulfate groups by more thermally stable phosphate groups within the framework. After cooling and filtering, the sample is treated with an aqueous solution of phosphoric acid. The cubic mesophase with $Ia\bar{3}d$ symmetry is retained after phosphatation as shown in Figure 4.35e. However, a slightly less well-resolved XRD pattern finally results after drying (Figure 4.35g).

In order to study surfactant effects, the initial surfactant to zirconium sulfate molar ratio (r) was varied from 0.81 to 0.27. An observable trend is that samples with higher surfactant to zirconium ratio exhibit a cubic structure with better resolved XRD reflections (see representative examples in Figure 4.36a). This might suggest that higher initial amounts of surfactant used leads to better structural order. However, differences in wall thicknesses, size of the scattering domains or variations in surface roughness could also explain the different resolutions.¹⁵ The XRD results obtained on the as-synthesized mesophases are listed in Table 8.3. No significant variation in d -spacing was observed on $d(211)$ of ca. 4 nm. The sample synthesized with $r = 0.27$ exhibits a less well-resolved XRD pattern that can not be clearly indexed as cubic $Ia\bar{3}d$. In comparison, a sample synthesized with $r = 0.40$ without the

hydrothermal aging period at 90°C shows a substantially larger d -spacing value (4.22 nm). However, the XRD pattern of this sample indicates a rather disordered mesophase which may not correspond strictly to the cubic $Ia\bar{3}d$ space group. Scaling-up the synthesis batch results in improved materials in terms of structure and thermal stability.

Figure 4.36: XRD patterns obtained on cubic zirconium oxo-phosphate synthesized with initial surfactant to zirconium sulfate ratios of $r = 0.67$, 0.54 and 0.40 . The samples were obtained from the scaled-up batches (B). **a)** Dried as-synthesized template containing samples. **b)** Calcined samples (3 hours at 300°C and 3 hours at 500°C). The inset is the expanded region from 8° to 32° 2θ for the same materials.

Transmission electron microscopy has been shown recently to be a powerful tool to characterize in detail 3-dimensional porous solids and full structure solution can be

achieved.¹⁶⁻¹⁸ The cubic $Ia\bar{3}d$ symmetry is confirmed by high-resolution electron microscopy (HREM). Figure 4.37 shows a typical HREM image and electron diffraction (ED) pattern of an as-prepared sample with $r = 0.54$. Despite the relatively low resolution of the X-ray diffraction pattern, the HREM image (Figure 4.37a) reveals domains of highly-ordered mesostructure.

Figure 4.37: a) Typical HREM image and electron diffraction (ED) pattern of as-prepared sample (B) with $r = 0.54$. a) HREM image taken along the $[111]$ axis. b) Electron diffraction pattern. c), d) Fourier diffractograms obtained from the HREM images in the rectangular areas labeled by 1 and 2, respectively.

In the ED pattern (Figure 4.37b), one can observe only diffuse rings indicating that the wall structure of the as-prepared sample is amorphous, *i.e.* the inorganic framework is composed of amorphous zirconium oxo-phosphate species. Figure 4.37c and 4.37d, which are Fourier diffractograms obtained from the HREM images at the areas labeled by 1 and 2, suggest that the material is commensurate with the $Ia\bar{3}d$ symmetry. The very weak reflections of (110) type, which are forbidden for $Ia\bar{3}d$, are not genuine, but induced by multiple-scattering effects as the crystal contains a heavy element, Zr, and the specimen is thick. All peaks in powder XRD are indexed by this symmetry. As a whole, we can conclude that the crystal has $Ia\bar{3}d$ symmetry. The image in area 2 looks like the two-dimensional, layered type of mesoporous material. However, we can observe weak reflections in Figure 4.37d showing that this area corresponds to the $Ia\bar{3}d$ phase but slightly tilted off relative to domain 1 along the $-12-1$ axis keeping the same lattice fringe of $-12-1$. It is to be noted that the length scales in reciprocal space are different for Figure 4.37b and Figure 4.37c-d, which are suitable for observing atomic scale ordering and for meso-scale ordering, respectively.

Figure 4.37 indicates that the architecture of the zirconium oxo-phosphate surfactant mesophase synthesized in presence of N-benzyl-N,N-dimethyloctadecylammonium ions is characteristic of the cubic $Ia\bar{3}d$ phase. Furthermore, the other as-prepared samples synthesized with different surfactant to zirconium molar ratios show the same results.

4.3.3.2 Removal of the template

Figure 4.38 shows the TG-DTA/MS measurement performed on the cubic zirconium sulfate-surfactant mesophase with $r = 0.54$, being the standard sample. The zirconium sulfate-surfactant mesophase was shown to collapse upon thermal treatment between 250°C and 300°C, resulting in an amorphous material with no long range order. From the TG curve, a total weight loss of 75% is measured for a sample not hydrothermally treated. After aging, the weight loss decreases to 70%. After water desorption, 3 major steps in the DTA are observed corresponding to exothermic processes. In parallel, 3 distinct steps are observed in the MS for the CO_2 and SO_2 traces. About 25% of the sample mass is lost in the first oxidation step, with a large release of hydrocarbon, H_2O , CO_2 and SO_2 . A second oxidation step, which results in a higher energy release occurs around 500°C where carbonaceous species, water and SO_4^{2-} are removed (about 40% in weight loss). Finally, a small step is observed at 610 °C (5%), where only CO_2 and SO_2 are detected. Samples measured after hydrothermal treatment

display different TG/MS profiles. These samples exhibit a decreased relative ratio between the first mass loss step and the second, and a decrease of the first CO₂ and SO₂ peaks relative to the second ones is observed.

	8.59 mmol	6.87 mmol	5.15 mmol
Surfactant amount	$r = 0.67$	$r = 0.54$	$r = 0.40$
Total mass loss	57 %	54 %	48 %
lattice shrinkage	3.43 –3.48 nm	2.90 nm	2.27-2.45 nm

Table 4.6: Mass losses measured on the as-prepared dried cubic mesophases for different initial amounts of surfactant and extent of lattice shrinkage upon template removal.

Figure 4.38 shows the results of TG-DTA/MS measurements performed on the zirconium oxo-phosphate surfactant mesophase. The TG and DTA curves are very similar to the that of the hexagonal zirconium oxo-phosphate mesophases. The total weight loss is reduced to 53% after phosphatation. Only two exothermic steps are observed.

The first step corresponding to the total conversion of hydrocarbon species occurs with high energy release. The weight loss is comparable to the one observed for the non-phosphated samples (20-25%). It is followed by a second broad exothermic step with lower energy release corresponding to release of carbon dioxide and, subsequently, sulfur dioxide. Compared to the non-phosphated sample, the weight loss is reduced in this second step to about 25%. The final SO₂ release observed above 550°C for the zirconium sulfate mesophase is not seen in the phosphated samples. Furthermore, a difference is observed in the temperature for the release of the surfactant head group (below 300°C), consisting of benzyl-dimethylammonium, compared to the carbon chain which appears at slightly higher temperature (320°C).

Figure 4.38: TG-DTA/MS measurements performed on a zirconium sulfate cubic mesophase with $r = 0.54$ before phosphatation ($5^{\circ}\text{C}/\text{min}$ in air). Below are presented the TGA data with a solid line and the DTA curve with a dashed line. The gray lines correspond to a sample prior to hydrothermal treatment. Above are plotted molecular species detected in the MS. Solid lines are the fragments obtained for a sample before hydrothermal treatment. Dashed lines correspond to fragments measured on a sample hydrothermally aged. The gray and black arrows indicate intensity variations for the peaks observed in the SO_2 traces ($m/z = 48$ and 64) before and after hydrothermal treatment, respectively.

Figure 4.39: TG-DTA/MS measurements performed on an as-prepared cubic zirconium oxo-phosphate with $r = 0.54$ ($5^{\circ}\text{C}/\text{min}$ in air). Below are shown the TGA data with a solid line and the DTA curve with a dashed line. Above are plotted various molecular species detected in the MS measurement and their evolution with temperature.

The experiments suggest that scaling-up of the synthesis batch seems to produce materials with higher thermal stability. The following will therefore focus on materials obtained under such conditions. Figure 4.36a and 4.36b show the XRD patterns recorded for scaled-up samples synthesized with different surfactant to zirconium sulfate ratios before and after calcination, respectively. Increasing the initial surfactant amount resulted in a slight increase in the structural ordering. However, after calcination a reverse tendency is observed. The structure shrinks drastically in all cases and the (220) reflection appears as a shoulder. No higher order reflections can be detected. Furthermore, the presence of a shoulder below the (211) reflection is observed. This might be due to low-angle scattering caused by small amorphous nanoparticles. This is supported by the very broad signals with low signal to noise ratio observed at higher 2 theta angles for all calcined samples (Figure 4.36b inset).

The weight losses measured for the same samples with $r = 0.67$, 0.54 , and 0.40 are listed in Table 4.6. A sample synthesized with $r = 0.67$ contains 57% of organics, and undergoes the largest lattice shrinkage with 3.48 nm. A lower amount of template incorporated within the mesophase results in lower shrinkage upon thermal treatment.

Figure 4.40: **a)** XRD patterns stack plot obtained during *in situ* XRD from a cubic zirconium oxo-phosphate synthesized with $r = 0.40$ (heating ramp $1^\circ\text{C}/\text{min}$). **b)** Plot representing the d -spacing and the (211) reflection intensity as a function of time and temperature ($\circ$ $d(211)$ -spacing, $\blacksquare$ intensity of the reflections).

The sample with $r = 0.40$ seems therefore to be the more thermally stable one. The result of an *in situ* X-ray diffraction measurement during calcination performed on this sample is shown in Figure 4.40a. In an attempt to reduce the strong effect of the first exothermic step occurring

when the template is oxidized, the sample was calcined for 3 hours at 300°C followed by 3 hours at 500°C, since the heating ramp has a critical effect on the mesostructure. From the developing XRD patterns a strong increase in intensity of all reflections up to 300°C is observed, due to removal of the organics from the pores. Slight variations in intensity that accompany the template removal at higher temperature are most likely associated with modifications in structure coherency or possible thermal expansion effects. No indications of phase transformation are observed during the thermal process. The high order reflections vanish around 450°C. The simultaneous evolution of the $d(211)$ value can be divided into 4 temperature-dependent periods (Figure 4.40b). The $d(211)$ value decreases as the calcination proceeds and remains constant during the cooling stage. Upon cooling from 150°C to room temperature, a strong reversible decrease in reflection intensity is observed. Calcination performed at higher temperature (550°C) seems to diminish this effect. The reversible decrease of intensity can be attributed to the adsorption of water. This evolution of the cubic mesophase is also representative of other samples. However, for other samples larger d-spacing shifts and stronger intensity variations might occur.

4.3.3.3 Structure and properties of porous cubic zirconium oxo-phosphate

Template-free products were obtained after calcination in a box furnace in air for 5 hours at either 500°C or 550°C, or for 3 hours at 300°C followed by 3 hours at 500°C. The samples after calcination are further characterized by TEM, XRD and N₂ sorption. Figure 4.41 shows a typical HREM micrograph and electron diffraction (ED) pattern obtained for a calcined sample (B) synthesized with $r = 0.54$. Although the X-ray diffraction patterns recorded for calcined materials are poorly resolved, the HREM image (Figure 4.41a) reveals again domains of highly ordered mesostructure. The EM image presented is consistent with the $Ia\bar{3}d$ symmetry proposed and shows clearly the uninterrupted channels along the $[111]$ axis corresponding to pores in projection. In the electron diffraction pattern (Figure 4.41b) one can observe diffuse electron diffraction rings, indicating that the walls remain essentially amorphous after calcination and could at most consist of very small nanoparticles. This is also supported by the absence of wide-angle reflections in the XRD pattern. Figure 4.41c is the Fourier diffractogram obtained from the HREM image at the labeled rectangle area.

It suggests that the zirconium oxo-phosphate material is commensurate with the $Ia\bar{3}d$ symmetry also after calcination. Therefore, Figure 4.41 gives the evidence that the cubic $Ia\bar{3}d$ mesostructure is retained after the removal of the template by thermal treatment. Samples (B) with $r = 0.40, 0.54$ and 0.67 investigated by EM show similar well-resolved cubic domains.

Figure 4.41: Typical HREM image and electron diffraction (ED) pattern of a sample (B) with $r = 0.54$ after calcination for 3 hours at 300°C and 3 hours at 500°C . **a)** HREM image taken along the $[111]$ zone axis. **b)** Electron diffraction pattern. **c)** Fourier diffractogram obtained from the HREM image in the labeled rectangular area.

The structural and physical properties of calcined materials synthesized with increasing surfactant to zirconium ratios are reported in Table 8.3. The XRD data of materials calcined at 500°C give lattice parameters ranging from about 6.1 to 7.4 nm. When $r = 0.67$, a pronounced decrease of the d -spacing down to 2.59 nm is measured, the lattice parameter being $a = 6.34$ nm. For $r = 0.40$, $d(211)$ of the calcined sample is 3.04 nm, the resulting lattice parameter is $a = 7.45$ nm. In conclusion, one can see that decreasing the amount of surfactant results in materials having larger lattice parameter. Therefore, the amount of surfactant used seems to have a direct influence on the thermal stability of the materials. Note that the lattice parameters measured after template removal are still substantially smaller than the ones reported for conventional calcined Si-MCM-48 ($a = 8.4\text{--}10.2$ nm)^{19,20} which are commonly synthesized with a C16 chain surfactant, indicating substantially smaller pore sizes. Calcination performed at 550°C for $r = 0.40$ resulted in a larger shrinkage of the structure with $a = 7.10$ nm.

Figure 4.42a shows N₂ sorption isotherms recorded for the samples with $r = 0.67$, 0.54, and 0.40. The isotherms are similar to Type I isotherms characteristic for microporous materials. They correspond to pore sizes in the upper micropore range or lower mesopore range. Therefore, the surface area cannot be evaluated accurately from BET calculations, and one has to be careful with the interpretation of the results. The data are given as *equivalent BET* and may only be used to underline tendencies (Table 8.3). The total nitrogen adsorption capacity decreases rapidly with increasing the surfactant to zirconium sulfate ratio (see Table 8.3). The shape of the isotherm obtained when $r = 0.40$ may suggest slightly larger pores in agreement with the larger lattice parameter. In Figure 4.42b, isotherms obtained for different calcination programs are depicted. Also represented as a reference is a typical isotherm measured for the hexagonally ordered zirconium oxo-phosphate.

The highest adsorption capacity is measured for the sample calcined with a plateau at 300°C. Calcination performed at 550°C leads to a Type I isotherm with a lower adsorbed volume. Finally, the cubic zirconium oxo-phosphate clearly shows a lower adsorption volume than its hexagonal counterpart. The step at lower relative pressure measured for the cubic material indicates clearly a smaller pore size.

Figure 4.42: N₂ sorption isotherms of porous cubic zirconium oxo-phosphate materials obtained from scaled-up batches (B). **a)** Isotherms of samples with $r = 0.67$, 0.54 and 0.40 . **b)** Isotherms measured for $r = 0.40$ and for different calcination protocols.

4.3.3.4 Evaluation of the acidity by pyridine sorption measurements

The IR spectra of adsorbed pyridine are shown in Figure 4.43a. The figure details spectra of three samples taken at a temperature of 140°C and a pyridine vapor pressure of 0.01 mbar. The samples measured were two $r = 0.40$ samples calcined at 500 °C and 550 °C, and one $r = 0.54$ sample calcined at 500 °C. The peak assignments for the spectra of adsorbed pyridine are detailed in Table 4.7.²¹

H-bonded (cm ⁻¹)	Lewis Acidity (cm ⁻¹)	Brønsted Acidity (cm ⁻¹)
1400-1447	1447-1460 1488-1503	1485-1500 1540
1580-1600	1580 1600-1633	1640

Table 4.7: IR peak assignment for adsorbed pyridine.²¹

In terms of relative peak intensities, the largest Brønsted : Lewis (B : L) peak ratio, determined using the ratio of the 1540 cm⁻¹ (B) and the 1446 cm⁻¹ (L) peak, was observed in the 0.54 sample. A comparison of the two $r = 0.40$ samples calcined at 500°C and 550°C, respectively, shows a relative increase in Brønsted acidity with increasing temperature. However, when plotted against each other on an absolute absorbance scale, the sample calcined at 550 °C shows a significant decrease in intensity of both Brønsted- and Lewis-adsorbed pyridine compared to its 500 °C counterpart. This observation is consistent with both N₂ adsorption measurements and powder XRD measurements which proved a decrease in void volume and a loss of reflection intensity in the $r = 0.40$ sample at the higher calcination temperature, respectively. Both these factors, combined with the obvious decrease in the number of acid sites, show that temperatures above 500 °C result in an inferior material. The IR spectra of the samples prior to pyridine loading (Figure 4.43b) show the ν_{O-H} region (3000-3600 cm⁻¹) as a broad band. However, in the $r = 0.40$ sample, sharp and well defined peaks were observed at 3749 and 3660 cm⁻¹. These bands are assigned to surface terminal Zr-OH groups and bridging hydroxyl species, respectively.²² From the spectrum it is clear that bridging hydroxyl groups are prominent in this sample, but are significantly reduced upon

heating to 550 °C. It follows that the synthetic conditions for producing the bridged species are reliant on the amount of surfactant used and the temperature of calcination.

Figure 4.43: **a)** The figure details spectra of three samples (B) taken at a temperature of 140 °C and a pyridine vapor pressure of 0.01 mbar. Top $r = 0.40$ (500°C), middle $r = 0.40$ (550°C), bottom $r = 0.54$ (500°C). Offset is to help for clarity. **b)** The OH stretching region prior to pyridine adsorption. Top $r = 0.40$ (500°C), middle $r = 0.40$ (550°C), and bottom $r = 0.54$ (500°C). Offset is to help for clarity.

4.3.4 Literature

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4.4 Comparative discussion

4.4.1 Removal of the template

The high stability of Si-MCM-41 obtained from the basic synthesis is evident. In the first part, we have described the different steps on which the template removal is based: an endothermic evaporation of hexadecene and trimethylamine resulting from the Hofmann degradation, followed by the cracking reaction of the remaining hydrocarbon chains and, subsequently, the oxidation of the organics, the process being completed by coke combustion beyond 350°C. Here, two specific behaviors are clearly distinguished, implying the presence of template molecules involved in two different types of interactions within the pores and with the silica surface. The successive processes involved in complete removal of the template from a MCM-41 type mesostructure are represented schematically in Figure 4.44 which illustrates also the variation in matter distribution in the inside pores responsible for different Bragg X-ray scattering contrasts. One can suggest that the Hofmann degradation is catalyzed by the Si-MCM-41 framework, since it does not occur on the zirconia and titania phases.

Figure 4.44: Schematic representation of the stepwise process involved in the removal of the alkylammonium template from Si-MCM-41 and Si-MCM-48. (evaporation of hexadecene via Hofmann degradation (150°C-250°C), followed by successive decomposition and oxidations (250°C-350°C) and subsequent coke combustion).

The first step of the template decomposition via Hofmann degradation is confirmed for all MCM-41 samples synthesized with *n*-alkyltrimethylammonium surfactants and MCM-48, with however, different proportions of the organics involved in the temperature dependent processes. The use of surfactants with different chain length underlines the effects of the surfactant-surface interactions and to a lower extent, the probable role of the pore size on the thermal desorption of the decomposed organics. Possible mass transfer limitations for the diffusion of larger hydrocarbon species may be suggested. The temperature at which the different alkylammonium surfactants are removed may serve to probe the strength of the interactions considered. Furthermore, the exchange of the surfactant trimethylammonium headgroup for a pyridinium group stresses the determining influence of the interactions of the polar headgroup and the inorganic surface during thermal treatment. Materials synthesized following the acidic route show different behaviors depending on the type of template employed. Despite having thicker walls, the materials obtained via the acidic synthesis route show the highest lattice shrinkage, which may be related to the nature of the framework walls. Moreover, the microporous nature of the walls seems to greatly influence the XRD scattering contrast behavior and the processes of the thermal desorption of the organics. The SBA-15 framework catalyzes the oxidation of the block copolymer template species at low temperatures.

The mechanism of template removal from transition metal oxide mesophases follows a different model. The template removal occurs in two oxidation steps. The surfactant is at first degraded by an exothermic oxidation reaction. In all cases, about half of the organic content is removed during this step, and the remaining organics are converted into carbonaceous species (coke). This template decomposition is always accompanied with a strong coke formation during the oxidation and cracking of the hydrocarbon chain with a high energy release. The process involved in the conversion of the template is quick, the surfactant seems to remain relatively intact up to 240-270°C, with the trimethylamine head group still bound to the carbon chain, as no elimination of the head group or evaporation of the hydrocarbon chain was observed. One could speculate, hence, that the transition metal oxide framework catalyzes template oxidation at this temperature. The second step is the conversion of the carbonaceous species and sulfate groups, it occurs over a broad range of temperatures and represents 23% to 28% of the weight loss. The small production of water measured in some cases around 450°C may be due to the combustion of some residual short hydrocarbon chains ($m/z = 26$) contained in coke (or soft coke), or late condensation of hydroxyl groups within the inorganic framework. The coke removal from the transition metal oxides appears to be

different from that observed for MCM-41. This can be due to the high amount of carbonaceous deposits and the shape and size selectivity of the transition metal oxide hosts, since the pores of the materials are smaller. Furthermore, the intensities of the main exothermic peaks measured in DTA between 290°C and 360°C are shown to be different for each material. The intensity appears to be very high in the case of titania (3.4 $\mu\text{V}/\text{mg}$), indicating a very strong exothermic reaction (Figure 4.25). The signal is measured at 1.5 and 2 $\mu\text{V}/\text{mg}$ for the zirconia based compounds (Figure 4.38, 4.39), and the lowest value is obtained with Si-MCM-41 at ca. 0.8 $\mu\text{V}/\text{mg}$ (Figure 4.4). Here, titania is shown to be the best hydrocarbon oxidation catalyst, with the reaction occurring at lower temperatures. Furthermore, the titania framework seems to catalyze the formation of carbonaceous species, which are also located on the pore surfaces.

Figure 4.45: Schematic representation of the one step process of template combustion catalyzed by the transition metal based framework. High coke amounts are generally produced.

Specifically, in the case of titania, calcination performed at 350°C is shown to be incomplete, with 5-7% of residual hydrocarbon species (Table 4.2) assuming an incomplete oxidation. Calcination performed at 400°C leads to complete template removal, but the structural order is strongly affected. The great release of CO₂, without pronounced water production, clearly suggests the total combustion of the coke species. For a system with small pores, resulting from general shrinkage of the structure, some pore blocking occurs. As the broad oxidation peak is centered at 400°C, a longer treatment or a higher calcination temperature may be necessary to unblock the pores, but such treatments lead to structural collapse due to the low thermal stability of the titania. The main fact appearing upon cooling is the reversible variation in X-ray reflection intensity observed between 150°C and room temperature. This is

due to the presence of a significant amount of adsorbed water inside the channels (Table 4.2), since mesoporous titanium oxides tend to be more hydrophilic than conventional Si-MCM-41. Water condensation in the pores decreases the scattering contrast, and thus leads to decreased intensities of the reflections. Zirconium based materials show the same type of behavior as mesoporous titanium oxides. The two successive exothermic oxidation processes result in the loss of the highly ordered structure. The evolution of the zirconium oxide-sulfate structure depends strongly on the temperature used to calcine the materials, the low thermal stability of the sulfate groups in the framework being responsible for these drastic changes. More thermally stable materials have been achieved by post-treatment with phosphoric acid. The calcination can be performed up to 550°C allowing a better template removal. The different SO₂-evolution steps observed in the TG experiments for zirconium based materials can be attributed to sulfate groups located in the interface between surfactant and inorganic framework and sulfate located within the framework, respectively. It can be assumed that the phosphate groups mostly replaced the sulfate groups located within the inorganic framework, based on the higher coordination ability of phosphate with zirconium. These intra-framework species represented about 10% of the total sulfur content (Table 4.5). This small amount, however, seems to be crucial for the loss the structural integrity, since replacement by phosphate groups leads to a structure stabilization. All the as-synthesized zirconium based materials described here contain sulfate groups, which provide to our systems acidic properties that can be compared with sulfated zirconia.^{1,2} However, the high temperature calcination (> 500°C) necessary to achieve complete coke removal leads to the loss of these active sulfur species. Li et al.³ have studied the coke removal from sulfated zirconia in catalytic processes using TGA/FT-IR. They have shown that the coke removal treatment between 450°C and 650°C leads to the loss of the catalytically active sulfur species, as SO₂ coinciding with CO₂ was evolved. A selective removal of the coke by burning in O₂ at lower temperatures was proposed to retain the catalytic activity. Our zirconium oxide-sulfate systems show similar features in TG-DTA/MS. It is, thus, possible that a selective calcination below 450°C in O₂ would result in catalytically active, mesoporous zirconia with high sulfate contents. Conversely, calcination tests performed on the titania and zirconia based materials with the heating ramp applied under flowing nitrogen, followed by subsequent flushing of air, was proved to be unsuccessful to remove the template.

Finally, it should be noted that the various chemical steps occurring within the mesopores of the different materials imply the presence of different interactions between the pore walls and the surfactant. The surfactant can be present as a framework charge balancing ion, but also

with a separate counterion. These two situations should lead to different reactivities of the surfactant molecules. The properties of the metals seem to control the characteristic of the template removal via different oxidation reactions and decomposition reactions or cracking. The presence of oxygen inside the pore channels is, in any case, the key to a complete template removal.

4.4.2 Cubic zirconium oxo-phosphate

The results in 4.3.3 show that it is possible to synthesize in a simple manner a zirconium oxide based mesoporous material that exhibits the attractive cubic $Ia\bar{3}d$ bicontinuous structure. The use of N-benzyl-N,N-dimethyloctadecylammonium chloride as structure directing agent in water enables the synthesis of a mesophase being structurally analogous to MCM-48. The zirconium sulfate mesophase is therefore also analogous to the lyotropic liquid crystal cubic $Ia\bar{3}d$ phase found in the water-CTAB system.⁴ It is possible to explain the structure of the cubic mesophase obtained by the packing parameter for micelle formation,⁵ although the packing parameter concept has originally been developed for dilute systems only. The formation of inorganic-organic composite mesophases is considered to be controlled by similar structural constraints observed for typical surfactant liquid-crystal phases. Therefore, size, shape and charge of surfactants are crucial structure directing parameters with the packing parameter depending strongly on the volume fraction of surfactant chains.⁶ Surfactants such as hexadecyl- or octadecyltrimethylammonium halides enable preferentially the synthesis of hexagonal mesophases. When such systems have organic additives or hydrocarbon chains located in the region between the head group of the surfactant and the hydrophobic core, the volume fraction of the surfactant chains increases substantially. Micellar aggregates with a slightly lower curvature result and the cubic $Ia\bar{3}d$ structure can be favored.⁷ The synthesis of the zirconium sulfate mesophase under acidic conditions using N-benzyl-N,N-dimethylalkylammonium chloride as a template follows the same principle. The N-benzyl-N,N-dimethyloctadecylammonium ion might be considered as a trimethyloctadecylammonium ion with solubilized benzene molecules anchored to the ammonium head group. The benzene groups are located in the hydrophobic core of the micelle, leading to an increase of the effective volume of the hydrophobic tail. These packing effects together with electrostatic driving forces for self-assembly generate the bicontinuous

cubic structure at low pH. The one-pot synthesis requires an aging period at 90°C in order to achieve a more stable material. This procedure might substantially increase the stability of the structure. During this hydrothermal treatment no phase change occurred, in contrast to what could be observed in some cases for the hexagonal analogues.⁸ The observed decrease of the first CO₂ and SO₂ peaks relative to the second ones in the TG/MS traces after hydrothermal treatment is probably due to the expulsion of surfactant molecules and sulfate groups from the mesophase.* This may result in some decrease in the ionic strength within the material, affecting the surfactant packing parameter in the organic-inorganic mesophase and the framework condensation process. However, it is not clear whether this phenomenon plays an important role in the stabilization of the cubic mesophase. The zirconium sulfate surfactant mesophases show a large organic template content with more than 65-70% of weight loss before 500°C. The strong oxidation processes of the organic chains and the high content in thermally unstable sulfate species account for the structural collapse. A subsequent efficient post-treatment with phosphoric acid is the key step to generate a material stable upon thermal treatment. This phosphatation step occurs without phase transformations in contrast to previous reports on zirconia mesophases.⁹ Regarding the XRD results on the different as-prepared phases, it turns out that the surfactant to zirconium ratio range, where the cubic Ia $\bar{3}$ d mesophase with a well resolved diffraction pattern is obtained, is rather narrow between $r = 0.40$ and $r = 0.67$. Within this r range, it seems that increasing the surfactant amount leads to sharper and better resolved reflections. Comparable observations were made previously on hexagonal zirconium oxide and niobium oxide phases.^{10,11}

The removal of the template has been successfully achieved upon controlling the temperature program and using a very slow heating rate. The amount of organic material is reduced substantially during phosphatation and the sulfate groups are partly replaced by thermally stable phosphate groups. From this, the exothermic effects of template oxidation on the overall structure are possibly reduced significantly and the framework is efficiently stabilized. Moreover, reduction of the amount of template incorporated by diminishing the initial amount used or upon hydrothermal restructuring seems to enhance the rigidity of the mesostructure. Indeed, a clear relationship between the surfactant proportion and the stability of the materials upon calcination is observed. However, the d -spacing of the as-prepared zirconium oxo-phosphate surfactant mesophases is not influenced by the amount of surfactant initially added,

* This difference in CO₂ and SO₂ peaks ratios between the material prior and after hydrothermal treatment, respectively, is also observed for the hexagonal zirconium sulfate-surfactant mesophase.

even if the materials with lower surfactant to zirconium ratio contain less surfactant as shown by the TG experiments. This would indicate a larger proportion of inorganics, which points toward thicker framework walls. On the other hand, a mesophase synthesized with low surfactant amounts could also consist of less compact micellar inorganic-surfactant aggregates. The stronger deterioration of materials obtained with higher surfactant content could either result from lower thermal stability of thinner walls or from higher local heating caused by the burning of more organic substances. Furthermore, compared to a system based on a trimethylalkylammonium halide template (4.3.2, Figure 4.34), the decomposition of the surfactant with the head group leaving at lower temperature suggests different interactions between the benzyl-dimethylammonium head group and the inorganic framework. Shrinkage of the structure and partial loss of long range ordering are phenomena usually observed for transition metal-based mesophases, caused by relatively low thermal stability, incomplete condensation and redox processes occurring within the structure during calcination. Nevertheless, the porous cubic zirconium oxo-phosphates described in this work exhibit fairly well-ordered structures and interesting chemical and physical properties. The best results in terms of organization of the porous material and adsorption capacity were obtained with surfactant to zirconium sulfate ratios between $r = 0.40$ and $r = 0.54$. Beyond $r = 0.54$ the structure undergoes dramatic shrinkage or collapses, showing very low nitrogen adsorption capacities. Below $r = 0.40$, the presence of another phase cannot be excluded. The high quality of the $r = 0.40$ material corresponds to the highest concentration of bridging OH-group as found by pyridine adsorption detected by IR spectroscopy, although the sample synthesized with $r = 0.54$ has a higher B : L ratio. Whether these differences are an effect of different charge compensations, packing parameter at different concentrations, or caused by higher surface energies of smaller pores is unclear as yet.

The porous zirconium oxo-phosphate has a cubic structure with the space group $Ia\bar{3}d$. The electron microscopy images taken show the uninterrupted channels along the [100] and [111] axis corresponding to pores in projection. Along the [110] axis no channel can be observed, only contrast variations are seen due to changes in electron density of the walls in projection. The presence of a $p6m$ hexagonal phase is excluded. Calcination performed at 300°C for 3 hours, followed by 3 hours at 500°C seems to be the most suitable protocol for the removal of the template. At higher temperatures, the structure is more damaged and shrinkage is larger. A plateau in the temperature program seems to be useful for optimal structure preservation. The samples exhibit Brønsted as well as Lewis acid properties. The sample with $r = 0.54$ has the highest B : L ratio of the samples measured by pyridine adsorption, but the $r = 0.40$ (500°C)

sample has clearly more Brønsted acidic bridging OH groups. This sample also has the highest pore volume and thermal stability and shows the least lattice shrinkage upon calcination. It is at present not clear why $r = 0.40$ induces these effects. It might be due to optimum charge compensation at this ratio or to optimal surfactant packing.

Moreover, the differences in long range ordering between a cubic and a hexagonal zirconium oxo-phosphate sample does not seem to play a major role during the thermal treatment of both materials. In both cases, the amorphous nature of the inorganic framework and the similar compositions lead to comparable thermal behavior based on identical inorganic matrix-surfactant interactions.

4.4.3 Literature

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5 Influence of co-surfactants on the properties of mesostructured silica¹

Pronounced swelling of the organic moiety of the mesostructure can be achieved by solubilizing hydrophobic additives inside the core of the aggregates.^{2,3} Recently, other means of affecting both the phase behavior and the *d*-spacing of mesoscopically ordered silicates were described by adding either short-chain *n*-alcohols,⁴ *n*-amines⁵ or polar benzene derivatives⁶ as co-surfactants to a conventional MCM-41 synthesis. The addition of *n*-alcohols to the synthesis results in a complex phase behavior and occasionally up to three co-existing phases were observed.⁴ The phase evolution was hexagonal, swollen hexagonal and lamellar with increasing alcohol content. Addition of *n*-amines, on the other hand, resulted in a marked decrease in the *d*-spacing of the hexagonal phase for short chain amines, while an alcohol-like phase evolution was observed for medium-chain length amines.⁵

5.1 Syntheses

The synthesis procedure is derived from the synthesis developed by Grün *et al.*⁷: 2.4 g of CTAB were dissolved in 120 g of deionized water with stirring and the co-surfactant (R-OH or R-NH₂, respectively) was added. After complete homogenization, 10ml of the ammonia solution was added. The solution was then heated at 35°C and 9.4 g of TEOS were added. The molar composition was H₂O/NH₃/CTAB/TEOS/R-NH₂ or R-OH = 157/3/1.5/1/*x*. A white precipitate formed after about 90 s. The mixture was stirred at 35°C for one hour, the solid recovered by filtration and then dried 8 h at 90° C, before being calcined at 550° C in air for 5 h (heating ramp 1°C/min). The co-surfactant to CTAB molar ratio was varied between 0.1 and 15 depending on the co-surfactant. The pH of the solution before the addition of TEOS was 11.7 – 12.4, depending on the amine concentration, and the pH measured before isolating the product was 10.7 - 11.5.

5.2 Alcohol as co-surfactant

An example of the evolution of the diffractogram with increasing the OcOH/CTAB ratio is shown in Figure 5.1. The d -spacing of the hexagonal phase increases slightly with increasing OcOH content and a co-existing lamellar phase is gradually developing. Finally, a purely lamellar phase is observed. A hexagonal to lamellar transition over an intermediate range where the two phases co-exist was observed for all n -alcohols studied when increasing the alcohol to surfactant ratio.

Figure 5.1 X-Ray diffraction patterns of mesostructured silica synthesized with increasing OcOH/CTAB molar ratio.¹

As for OcOH, a slight swelling of the hexagonal phase was also observed upon addition of the other n -alcohols studied and this effect was more pronounced as the chain length of the alcohol increased. The d -spacing of the lamellar phase increased linearly with increasing chain length of the alcohol, as shown in Figure 5.2. The amount of co-surfactant required to induce the hexagonal to lamellar transition decreased with increasing number of carbon atoms in the alcohol chain, as also shown in Figure 5.2. For methanol and ethanol, previous studies had shown a decrease of the d -spacing of the organic-inorganic hexagonal composite mesophases when increasing the alcohol/CTAB ratio. Here, the addition of methanol results in a decrease of the d -spacing by about 1 Å when adding 50 moles of MeOH per mole of CTAB. The co-solvent effect of the short chain alcohol inducing a decrease in the CTAB aggregation number would account for this observation. However, the effects observed in the present study occur at much lower additive concentrations and therefore a co-surfactant effect rather than a co-solvent effect of the additives has to be assumed in order to explain the results. It has early been suggested and recently shown that the building blocks for the silicate-surfactant mesostructure are probably silicate oligomers/polymers onto which surfactant ions adsorb.

Figure 5.2: Left axis: observed d -spacing of the ▼ lamellar and ■ hexagonal phase as a function of hydrocarbon chain length of the alcohol. Right axis: Δ alcohol/CTAB molar ratio needed for the formation of the pure lamellar phase as a function of hydrocarbon chain length of the alcohol.¹

The polyelectrolyte-surfactant complexes subsequently self-assemble to form the silicate-surfactant mesophase, which is able to solubilize large amounts of semi-polar and hydrophobic substances.^{3,4} The slight swelling of the hexagonal mesophase at low alcohol/CTAB ratio and the subsequent transition to the lamellar phase upon further addition of alcohol follows the direction of decreasing interfacial curvature. An increase of the d -spacing of the organic-inorganic lamellar mesophase is observed upon increasing the alcohol chain length. This can be attributed to an increase of the amphiphilic bilayer thickness of the surfactant portion of the lamellar phase with increasing the alcohol chain length, as previously observed for ternary CTAB/alcohol/water systems.⁹ The amount of co-surfactant required to induce the hexagonal to lamellar transition is decreasing with the number of carbon atoms in the chain of the co-surfactant, which reflects the higher water solubility of the short chain alcohol as well as increased hydrophobic interactions between the surfactant alkyl chains. The absence of an intermediate cubic phase is similar to ternary CTAB/alcohol/water systems.^{8,9} Furthermore, the solubilities of HeOH and OcOH in the hexagonal phase formed in water/CTAB solutions are 0.4 mole and 0.3 mole per mole of CTAB, respectively,^{8,9} which are in fair agreement with the upper stability limits of the hexagonal composite mesophase evaluated in this work; 0.5 and 0.1 mole per mole of CTAB for HeOH and OcOH, respectively. However, it should be emphasized that the bulk/micelle and bulk/composite aggregate partition coefficients of the co-surfactants may differ substantially. Furthermore, there is strong evidence that the bulk/composite aggregate partition coefficients are also strongly dependent on the degree of silicate condensation.^{3,4}

5.3 Amine as co-surfactant

While the addition of alcohol to the synthesis resulted in either an increase in the d -spacing of the hexagonal phase or a transition to the lamellar phase, the effect of amine addition was quite different. The effect of addition of butylamine was investigated for BuNH₂/CTAB molar ratios as high as 15. Increasing the BuNH₂/CTAB ratio resulted in a gradual decrease of the d -spacing of the hexagonal mesophase (see Figures 5.3 and 5.4) up to BuNH₂/CTAB = 12. For higher BuNH₂/CTAB ratios the d -spacing remained almost constant. The mesophase obtained for high BuNH₂/CTAB ratio still possesses long-range order, as highlighted by the presence of high order reflections. However, some loss of order upon BuNH₂ addition is evident, as

shown by the decrease in the relative intensity of the (200) reflection and a relative broadening of the (110) reflection. A transition to a lamellar phase was not observed. The N_2 sorption isotherms shown in Figure 5a show the decrease of the pore diameter upon increasing the $BuNH_2/CTAB$ ratio. A fully reversible type IV isotherm characteristic of the MCM-41 type materials was obtained in the absence of $BuNH_2$. The steep increase due to the filling of the mesopores occurred at $p/p_0 \approx 0.25 - 0.35$. The addition of 4.2 mole of $BuNH_2$ per mole of CTAB resulted in a shift of the steep increase toward lower values ($p/p_0 \approx 0.14 - 0.25$), indicating a decrease of the pore diameter. For $BuNH_2/CTAB = 12$ a type I isotherm was obtained, characteristic for microporous materials. The adsorbed volume decreased only slightly with increasing $BuNH_2/CTAB$ ratio, indicating that the pore walls are thinner in the presence of $BuNH_2$.

Figure 5.3: XRD patterns of silica-surfactant mesophases synthesized with increasing amine/CTAB ratio (numbers on top of the XRD patterns). **Left:** addition of butylamine. **Right:** addition of hexylamine.¹

The pore diameter, w_d , and the wall thickness, calculated according to the relation

$$w_d = cd \sqrt{\frac{\rho V_p}{1 + \rho V_p}}, \quad (3.3.3)$$

show that an increase of the BuNH₂/CTAB ratio results in a dramatic decrease of the pore diameter, but also in a slight decrease of the wall thickness (Figure 5.6). The slight decrease in the silicate wall thickness in the presence of BuNH₂ can be rationalized by changes in the silicate chemistry due to the increase in pH of the synthesis solution by protonation of the amine. One has to note that no wall thinning is observed if amines that do not undergo protonation under the synthesis conditions are used.⁶ The addition of HeNH₂ or OcNH₂ induced a slight increase of the d -spacing of the hexagonal mesophase at low amine/CTAB ratio in a similar way as observed for the alcohols. Furthermore, a transition to a lamellar phase occurred with increasing HeNH₂/CTAB or OcNH₂/CTAB ratios.^{4,5}

Figure 5.4: Variation of the d -spacing of the as-synthesized hexagonal mesophase as a function of the amine/CTAB ratio : Δ addition of butylamine, O addition of hexylamine.¹

However, a decrease of the d -spacing of the mesophase is observed at intermediate HeNH₂/CTAB ratio, similar to that observed for BuNH₂/CTAB, as shown in Figure 5.4. The decrease in the d -spacing occurred at slightly lower amine/CTAB ratios for HeNH₂ than for BuNH₂. This decrease in the d -spacing was not observed for OcNH₂/CTAB. The d -spacings

and unit cell parameters a measured for materials synthesized with HeNH_2 are reported in Table 8.4. The decrease of the size of the hexagonal unit cell upon HeNH_2 addition is also confirmed for calcined samples. After calcination the sample with $\text{HeNH}_2/\text{CTAB} = 4.5$ exhibits no low angle XRD reflection of an ordered mesophase, due to collapse of the lamellar phase. The effect of HeNH_2 is intermediate to that observed for BuNH_2 and OcNH_2 , respectively, in that the d -spacing is first increased, then decreased and finally a transition to the lamellar phase was observed, over an intermediate amine/CTAB range where the two phases coexist, with increasing HeNH_2 content (Figure 5.3 and 5.4).

Figure 5.5: **a)** N_2 sorption isotherms of mesoporous MCM-41 materials synthesized without additional amine (■) and with $\text{BuNH}_2/\text{CTAB}$ ratios = 4.2 (●) and 12 (▲). (solid symbols denote adsorption, open symbols denote desorption). **b)** N_2 sorption isotherms of mesoporous MCM-41 materials synthesized for several $\text{HeNH}_2/\text{CTAB}$ ratios. Solid symbols correspond to a conventional MCM-41 without hexylamine addition.¹

The results of the N_2 sorption measurements performed on the same samples are also summarized in Table 8.4. For materials with pores in the lower mesopore size range the textural parameters extracted from sorption experiments are not very precise but can be used to compare series of samples. The N_2 sorption isotherms are presented in Figure 5.5b. They show a gradual decrease in adsorbed volume with increasing $\text{HeNH}_2/\text{CTAB}$ up to 2.5. This is accompanied with a slight decrease in pore sizes, w_d evaluated from the geometrical calculation based on the primary mesopore volume V_p and the d -spacing of the hexagonal mesophase. In the limit of this approximation, one may consider the variations in pore diameter at low $\text{HeNH}_2/\text{CTAB}$ ratio to be consistent with the XRD data. The addition of 3.4

mole of HeNH_2 per mole of CTAB resulted in a large decrease in volume adsorbed and a steep increase at $p/p_0 \approx 0.2$ is hardly observed. For $\text{HeNH}_2/\text{CTAB} = 4.5$ a type I isotherm was obtained, indicative of microporosity. In the range of $\text{HeNH}_2/\text{CTAB}$ ratios investigated, the reduced amount in physisorbed N_2 volume could be caused by a smaller specific surface area due to a growing fraction of lamellar material. The step at lower relative pressure observed for high $\text{BuNH}_2/\text{CTAB}$ ratios (Figure 5.5a), indicating smaller pores, does not occur with hexylamine, since large amounts of this amine solubilized in the micelles induce a phase transition. The resulting lamellar material collapses upon template removal. However, a significant N_2 adsorption is still measured.

Figure 5.6: The unit cell parameter *a* (left axis) and the pore wall thickness (right axis) as a function of the $\text{BuNH}_2/\text{CTAB}$ ratio.¹

Since the solubilization behavior of amines and the alcohols of the same chain length in aqueous isotropic solutions of CTAB are quite similar,¹⁰ the amines must be able to interact with the silicate and/or the surfactant in an additional way. Furthermore, there is a strong dependence on the amine chain length, which also should be accounted for. The pK_a value for primary amines is around 10.7,¹¹ which is close to, but lower, than the pH-values at which the synthesis was carried out ($\text{pH}_{\text{initial}} = 11.7 - 12.4$, $\text{pH}_{\text{final}} = 10.7 - 11.5$ depending on the amine concentration, no change in pH was observed upon addition of OcNH_2). However, when the amine is solubilized within a cationic surfactant aggregate, the effective pK_a value will

decrease, *i.e.* the amine is protonated to a lower degree in the micelle compared to the bulk.¹² Effectively the protonation degree of amine solubilized in the CTAB micelles is negligible. Free amines are known to have a strong specific interaction with silica in the pH range of 10–11,¹³ which closely corresponds to the pH-window where the synthesis was carried out. Furthermore, the amine does not have to be protonated in order to be able to adsorb to the silicate, as shown for aromatic amines with lower pK_a -values.⁶

One can therefore postulate that the amines compete with the surfactant for the polymeric silicate species⁵ and may form hydrogen-bonds with silicate hydroxyl groups.¹⁴ Therefore, there are at least two distinctly different means by which the amine could be incorporated in the CTAB-silicate mesophase. The amine could act as a co-surfactant like alcohols of similar chain lengths and mainly be solubilized by the composite aggregates or it could directly be adsorbed to the silicate polymer and co-adsorb with the CTAB through hydrogen-bonding to silanol groups. The former would result in an increase in the d -spacing while the latter would cause a decrease in the d -spacing of the composite structure due to a decrease in the hydrocarbon volume. The different types of interactions involving amine molecules in surfactant micellar aggregates are schematically represented in Figure 5.7. Which one of these pathways is dominant is governed by the concentration of bulk amine, which is governed by the bulk/micelle partition. $BuNH_2$ is completely soluble in water and should therefore be able to interact with silica in the bulk while $OcNH_2$ is preferentially solubilized by the CTAB micelles due to its much lower water solubility and would mainly act like an alcohol, in agreement with the observations. $HeNH_2$ exhibits an intermediate behavior. However, both effects could be active at the same time. The concentration dependant effect of the hexylamine can be explained by an inversion in the balance between the two competing effects of amine interaction, adsorption and solubilization. Since most of the $HeNH_2$ is solubilized in the CTAB micelles, the concentration of free $HeNH_2$ will be low at low values of the $HeNH_2/CTAB$ ratio. Therefore, a similar behavior to that of $OcNH_2$ is observed: The concentration of free $HeNH_2$ is too low to compete with CTAB for the silicate. However, as more $HeNH_2$ is added, the concentration of free amine will increase to a point where competitive adsorption occurs. It should be noted that the concentration of $HeNH_2$ needed to compete with the CTAB for the silicate is lower than that needed for $BuNH_2$, since it is well known that the affinity for interfaces increases strongly with increasing chain length of the

adsorbate. The transition from a shrunk, hexagonal mesophase to a lamellar one is then induced by the increased hydrophobic interactions of the amine alkyl chain with CTAB alkyl-chains upon addition of more HeNH_2 .

Figure 5.7: Schematic representation of the hypothesis of different interactions involving amines in surfactant micellar aggregates. The amine molecules which interact as co-adsorbant may be in the protonated form, this is however not necessary for interaction.¹

To specify the interaction between the amine added to the solution and the silicate species, additional investigations with focus on the hexylamine case were carried out. The hypothesis of amine molecules involved in several distinct interactions should be confirmed by characterizing the species included in the materials. This can be done by performing TG-DTA measurements coupled with mass spectrometry on as-prepared samples in order to determine the extent of hexylamine incorporation into the silicate-surfactant mesostructure and whether several interactions are observed or not. A typical plot recorded for fragments resulting from hydrocarbon chains (C_xH_y , with $m/z = 42$ and 55) and its evolution with temperature is shown in Figure 5.8. Also represented are the traces recorded for the chosen molecular species for an amine-free MCM-41 as a reference. Compared to a conventional amine-free MCM-41, the addition of HeNH_2 results in a new peak, appearing between 140°C and 190°C . This peak is

attributed to the carbon chain of the HeNH_2 . When the amount of HeNH_2 was increased to a ratio of $\text{HeNH}_2/\text{CTAB} = 2.5$, the amine peak intensity increases relatively to the peaks assigned to the surfactant. One can see that in the case of a longer chain fragment such as $m/z = 55$, the ratio of the peak corresponding to the fraction of the surfactant that is removed via Hofmann degradation (150-250°C) decreases, compared to the surfactant fraction that is oxidized at higher temperatures (see chapter 4.1). This might be due to the exchange of surfactant molecules against shorter chain molecules. This would result in a lower amount of CTAB molecules involved in the interactions that facilitate the Hofmann elimination.

Figure 5.8: TG/MS measurements performed on HeNH_2 -containing silica mesophases with $\text{HeNH}_2/\text{CTAB}$ ratio of 1, 2, 3.4 and 4.5) and, as references, on conventional Si-MCM-41 (heating rate of 5°C/min under air). Shown are the plots recorded from the MS measurements for the following carbon chain molecular species : **a)** $m/z = 42$ corresponding to a C_3H_6^+ fragment and **b)** $m/z = 55$ corresponding to a C_4H_7^+ fragment), and their evolution as a function of temperature. The arrows onto the MS traces indicate peaks assigned to hexylamine species.¹

As the TG/MS traces are relatively similar to those of amine-free MCM-41, one can suggest that the mesophases consist of mixed $\text{CTA}^+/\text{HeNH}_2$ (or HeNH_3^+)-silicate assembly organized in a shrunk hexagonal mesostructure, as represented in Figure 5.7, in agreement with the XRD and N_2 sorption data. When the amine/CTAB molar ratio exceeds 2.5, the amine peak increases substantially, accompanied by a large increase of the ratio of the species eliminated at temperatures below 250°C . Furthermore, the amine peak is broadened towards lower temperatures, indicating that the templating molecules may be involved in different types of interactions. In addition, a second weaker peak appears as a shoulder, also assigned to HeNH_2 . It can be detected at slightly lower temperatures (120°C - 140°C). At a ratio of 3.4, the mesophase is a mixture of a shrunk hexagonal phase and a lamellar phase, resulting in significant differences in fragments traces. This is again a result of the balance between the two possible roles of the HeNH_2 in the synthesis as a co-surfactant or competing with CTAB for adsorption sites onto the silicate. At high $\text{HeNH}_2/\text{CTAB}$ ratio, the mesophase consists of an increasing fraction of micelles with solubilized HeNH_2 , based on favorable hydrophobic interactions. The additional organics incorporated in the developing lamellar mesophase play in this case mainly a co-surfactant role. They will be removed at lower temperatures, since they are not co-adsorbed to the silicate.

$\text{HeNH}_2/\text{CTAB}$	Weight loss 120-190 $^\circ\text{C}$	Weight loss above 100°C
0	3 %	45.5 %
1	6.5 %	45.5 %
2	7 %	46.5 %
2.5	7 %	46.0 %
3.4	11.5 %	48.5 %
4.5	9.5 %	47.0 %

Table 5.1: Weight losses measured for different $\text{HeNH}_2/\text{CTAB}$ ratios, obtained by thermogravimetry. The hexylamine is considered to appear in the range of temperatures between 120°C and 190°C .¹

The weight losses measured in the range of temperatures where the amine is evolved are given in Table 5.1. The total mass loss, measured beyond 100°C, is about (47 ± 1.5) wt% for all samples. The relative amount of amine contained in the samples generally increases with increasing amine/CTAB ratio. However, the maximum mass loss is measured for the sample with $\text{HeNH}_2/\text{CTAB} = 3.4$ with about 12%. This is due to the coexistence of two phases, a shrunk hexagonal phase containing large amounts of (protonated) amine species and the lamellar one. The highest amount of HeNH_2 in the solid (evaluated from mass loss and peak areas) represents about 25% of the leaving species. One should note that these amounts are much lower than the ones introduced initially. The difference in temperature observed for the amine release upon increasing the amine content and the variations in amounts of amine in the solid may be related to different fractions of HeNH_2 solubilized as a co-surfactant in the hexagonal and lamellar mesophases and different proportions of protonated HeNH_2 species co-adsorbed to the silicate.

However, since the TG-DTA/MS technique did not allow precise amine localization and characterization, solid state NMR experiments on the inorganic-organic composite mesophases for the different ratios were additionally performed. One can expect this technique to provide valuable informations on the molecules solubilized in the micellar aggregates and the ones directly interacting with the silica surface. If the hypothesis of co-adsorption is valid, one might distinguish several peaks assigned to amine molecules, having different chemical shifts depending on their environment. First, detailed NMR experiment can determine if different amine products are effectively present in the materials. In addition, correlations between inorganic and organic species may appear.

To characterize the organic species within the silica mesophase at the different HeNH_2 to CTAB ratios, ^1H MAS NMR and ^{13}C CP MAS NMR spectra were measured (Figure 5.9 and 5.10) of an amine-free sample and samples synthesized in the presence of HeNH_2 . The ^1H NMR spectra obtained on amine-free MCM-41 and HeNH_2 containing samples are depicted in Figure 5.9. The ^1H chemical shifts are summarized in Table 5.3. The spectrum of the amine-free MCM-41 shows 4 resonance lines. Results of recent NMR investigations on aqueous CTAB solutions¹⁵ and silica-CTAB mesophases¹⁶ ease the assignment of these lines. The broad resonance observed at 5.7 ppm is assigned to adsorbed water. The line at 3.26 ppm is mainly caused by the protons (**1'**) of the methyl groups attached to the surfactant head group. Note, that for the mesophases, the signal of the protons (**1**) located on the methylene

carbon in α position, which is observed in a solution of CTAB at 3.42 ppm,¹⁵ cannot be resolved from that of the head groups protons. The intense line at about 1.3 ppm corresponds to the superposition of the signals of the alkyl chain methylene protons (**2-15**). Finally, the protons located on the terminal methyl (**16**) give rise to the line at 0.88 ppm (Table 5.2).

Figure 5.9: ^1H MAS NMR spectra of MCM-41 with $\text{HeNH}_2/\text{CTAB}$ ratios = 0, 1, 2, 2.5, 3.4, 4.5 (from bottom to top). MAS frequency: 14 kHz.¹

The addition of HeNH_2 results in a significant broadening and low-field shift (6.2 ppm for $\text{HeNH}_2/\text{CTAB} = 1$ up to 6.6 ppm for $\text{HeNH}_2/\text{CTAB} = 4.5$) of the line assigned to the adsorbed water. This finding can be attributed to the exchange of the protons from water molecules and protons of the (protonated) amine head group. The ^{13}C CP MAS NMR spectra of the same samples are shown in Figure 5.10. The ^{13}C chemical shifts observed for

CTAB/MCM-41 are listed in Table 5.4. The spectrum of the amine-free sample shows 8 well-resolved lines. The most intense one stems from the superposition of the resonance lines of the methylene carbons **C5** to **C13**. The broad low-field shoulder of the line at 23.3 ppm (**C15**) can be assigned to the **C2** carbon.

HeNH ₂ /CTAB	Adsorbed water (+ ammonium)	Head group + 1	Methylene chain	-CH ₃ tail
0	5.7	3.26	1.30	0.88
1	6.2	3.26	1.30	0.88
2	6.4	3.26	1.30	0.88
2.5	6.3	3.26	1.30	0.88
3.4	6.6	3.26	1.32	0.92
4.5	6.6	3.26	1.32	0.93

Table 5.2: ¹H Chemical shifts of CTAB/MCM-41 mesophases containing different amounts of additional hexylamine.¹

The assignment for the **C2** to **C4** carbons is in line with the results of a very recent NMR study on the influence of counterions on the solubilization of benzene in CTA surfactants¹⁵ as well as a detailed study on chemical shifts in tetraalkylammonium halides.¹⁷ One can not see any evidence for the various differing assignments in a couple of recent papers on the characterization of MCM-41-type materials¹⁸⁻²⁰ and intercalation compounds.²¹ The better resolution in the ¹³C NMR spectra compared to recently published data for similar materials¹⁸⁻²⁰ is attributed mainly to a more precise setting of the magic angle and optimized conditions (power, offset) for the proton decoupling, and only to a minor extent to the higher magnetic field and the higher spinning speeds applied. ¹³C CP MAS NMR spectra taken on a 300 MHz spectrometer with a spinning speed of 4 kHz gave almost the same resolution for CTA⁺.

The addition of HeNH₂ leads to an apparent line broadening for the methylene resonances of CTA⁺ that is caused by the superposition with the methylene resonance lines of HeNH₂. In the spectrum of the sample with HeNH₂/CTAB = 4.5 (Figure 5.10), three additional lines in the respective region can clearly be seen. No attempt is made to assign these lines to the

individual carbon atoms of HeNH_2 . In accord with the growing amount of HeNH_2 in the synthesis, the intensity of the broad line between 39 ppm and 44 ppm caused by the **C1** atom of HeNH_2 increases. This indicates the presence of increasing amounts of this co-surfactant in the mesophase. Even further evidence can be obtained from the observed splitting of the lines for the methyl tail groups in the $\text{HeNH}_2/\text{CTAB}$ region from $\text{HeNH}_2/\text{CTAB} = 1.0$ to 2.5.

Figure 5.9: ^{13}C CP MAS NMR spectra of the same samples as in Fig. 9. On the right, expansions of the region of the methyl group lines are depicted. MAS frequency: 10 kHz, contact time: 1 ms, repetition time: 10 s, 2000 scans.¹

The low-field line is assigned to the methyl group in HeNH_2 . The down-field shift of more than 0.2 ppm with respect to the line of the CTA^+ methyl group can be attributed to a higher

degree of trans conformation of the short C_6 chains between the long C_{16} chains in the micelles of the hexagonal mesophase. In a detailed study on the solubilization of alcohols and amines in CTAB micelles¹⁰ a low-field shift of up to about 1 ppm was observed for the resonance line of the methyl group of HeNH_2 solubilized in the micelle with respect to that of the free molecule. This finding was explained by a more extended conformation of the alkyl chains when solubilized into CTAB micelles. Higher $\text{HeNH}_2/\text{CTAB}$ ratios lead to lamellar phases, where no splitting between the lines of the methyl groups in HeNH_2 and CTA^+ is observed. Very recently, a splitting into four resolved lines over a range of 2.2 ppm has been reported for the tail methyl group in solid CTACl .²⁰ This splitting has also been discussed in terms of trans and gauche conformations. Therefore, the line splitting observed for the methyl groups of the alkyl chains can be regarded as further evidence for the incorporation of HeNH_2 into the supramolecular surfactant portion of the hexagonal mesophase.

	CH_3 , head	C_1	C_2	C_3	C_4	$C_5\text{-}C_{13}$	C_{14}	C_{15}	C_{16}
δ / ppm	54.1	67.1	23.6	27.0	30.2	30.7	32.7	23.3	14.4

Table 5.3: Assignment of the ^{13}C NMR lines observed for CTAB/MCM-41.¹

In conclusion, the NMR results confirm the incorporation of the hexylamine in the surfactant-silica mesophase. The amount of amine incorporated increases with increasing $\text{HeNH}_2/\text{CTAB}$ ratio. Therefore, one can state that the d -spacing of the mesophase and the pores size decrease with increasing amine incorporation in agreement with the XRD and sorption data. So far, the NMR experiments could not differentiate between inclusion of the hexylamine as a co-surfactant in the micellar aggregates or a co-adsorption with the silicate surface. However, one can exclude an unique co-surfactant effect since it would result in a swelling of the mesophase. Furthermore, the effects of the increasing amount of amine incorporated make also a possible co-solvent role of the hexylamine very unlikely. Although the definitive evidence of amine molecules involved in competitive interactions with the silica surface is not proved, one may consider the NMR observations as strongly encouraging results, pointing towards chemical mechanisms other than swelling and well-known co-surfactant effects.

5.4 Literature

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6 Hierarchically organized mesostructured silica fibers¹⁻³

Self-assembly enables the single-step processing of complex structures in mesostructured solids, and may offer the possibility to grow devices in large arrays or supports with elaborated structures or micro-scaled patterns. An important step for electronic or optical application of porous materials was the development of film and fiber processing techniques for mesoporous materials of the MCM-41 and SBA-type families.⁴ To achieve this, simultaneous control of the structural parameters on the nanometer scale and the morphology on the micrometer scale are required. This is of particular interest for optical devices,⁵⁻⁷ for which the organization of the materials on different length scales is decisive.

6.1 Synthesis and properties

Synthesis of the mesostructured silica fibers

The spontaneous growth of hexagonal phase mesoporous silica fibers was originally reported in 1997⁸ and later modified to produce highly-quality homogeneous fibers.⁷ The synthesis of mesostructured fibers under acidic condition is highly flexible. It is possible to use various silicon sources, surfactants and additional oils. The molar composition of the initial aqueous synthesis mixture was: 100 H₂O : 0.0246 alkytrimethylammonium halide : 2.92 HCl, which was prepared with stirring. CH₃(CH₂)₁₅N(CH₃)₃Br (CTAB), CH₃(CH₂)₁₃N(CH₃)₃Br (C14TAB) or CH₃(CH₂)₁₅N(CH₃)₃Cl (CTACl) were used as cationic surfactants. Typically, 0.375 mmol of a silicon source reagent was added to 15 g of the aqueous surfactant solution in a closed 20 ml glass vessel without stirring. The syntheses were performed at room temperature. Different silicon alkoxides were studied as silica precursors. If additional oil was used, the silicon source was dissolved in the oil before the addition to the aqueous solution. (C₄H₉O)₄Si (TBOS) was used without any additional oil and the addition of the silica source to the aqueous solution leads to a separation into 2 phases, with the silicon reagent forming a thin layer on the top of the aqueous phase. The spontaneous growth of the fibers was typically observed in the water phase after 2 days. After 7 days, the fibers were removed from the

solution using a net to collect them, and dried in air. $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ (TEOS) was mixed with either *n*-hexane, CCl_4 , mesitylene or toluene. The same amount of TEOS (0.375 mmol) was dissolved in 3.75 ml, 1.5 ml, 0.750 ml and 0.375 ml of oil. The mixture was then added to the aqueous solution and left under quiescent conditions. In the case of CCl_4 , the aqueous solution was added drop-wise to the silicon precursor solution, since here the aqueous phase is at the top. In all syntheses, spontaneous growth of fibers was observed in the water phase within 24 hours. A solid thin layer forms at the interface between the two phases. In the present work, it will be referred to as a “solid film”. The fibers obtained from the TEOS-based systems were removed from the synthesis batch after 7 days, and dried at room temperature for 4 days. Alternatively, $(\text{C}_3\text{H}_7\text{O})_4\text{Si}$ (TPOS), (0.375 mmol), either without or in *n*-hexane (0.375 ml, 0.75 ml, 1.5 ml) or in CCl_4 (0.075 ml, 0.375 ml, 0.75 ml, 1.5 ml) was used as silica precursor. Generally, solid products were observed in the aqueous phase and at the interface within times ranging from 3 days to several weeks. The fibers obtained from a TPOS/hexane mixture were usually removed after 15 days and dried at room temperature for 4 days. In the case of CCl_4 , the fibers were removed after 6 weeks. The template free fibers were obtained by calcination in a box furnace in air at 500°C for 8 hours

6.1.1 Tetrabutoxysilane (TBOS) as silicon precursor

When $(\text{C}_4\text{H}_9\text{O})_4\text{Si}$ (TBOS) is used as the silicon source, long homogeneous fibers are obtained with thicknesses ranging from submicron to 40 μm . (see Figures 2.11 and 6.1a-b). The yield of the solid products is ca. 1.75 ± 0.10 mg per g of aqueous solution. Based on X-ray diffraction and electron microscopy, the fibers have been determined to have a hexagonally ordered mesostructure of cylindrical aggregates with a lattice constant $a_{\text{as-made}}$ of about 4.7 nm (Figure 6.1c). The XRD diffraction patterns of as-synthesized fibers show a typical hexagonal mesophase with up to four reflections. The intensity ratio of the (110) reflection to the (200) reflection is unusually high in comparison to that observed for MCM-41 or SBA-3. This effect may be attributed to a different wall thickness in comparison to conventional mesostructured silica powders. The fibers obtained have a well-defined pore environment, and show order on different length scales. The fibers are perfectly ordered on the nanoscale and are very homogenous on the micrometer scale. The fibers can be calcined, and nitrogen sorption measurements indicate that the fibers exhibit high surface area and large adsorption capacity,

comparable to other acid prepared mesostructured materials (Figure 6.1d). Upon calcination at 500°C for 8 hours, a lattice shrinkage of 11% is observed with $a_{\text{calc.}} = 4.2$ nm (Figure 6.1c). The lattice shrinkage is significantly smaller than that of powder SBA-3 samples (16-18%), which suggests a relatively higher thermal stability.

Figure 6.1: a-b) SEM images of mesoporous silica fibers obtained from a 2 phase acidic system with TBOS as silicon source; c) XRD pattern of as-synthesized and calcined mesoporous silica fibers; d) N₂ sorption isotherms measured on mesoporous fibers (pH=0) calcined at 500°C for 8 hours, and a reference SBA-3 material.

The removal of the template from the mesostructured silica fibers can be investigated by *in situ* techniques as described in chapter 4. The XRD patterns stack plot shown in Figure 6.2 obtained during the calcination of fibers at 500°C for 8 hours resembles the XRD pattern developments observed for SBA-3. No difference in the evolution of the ratio $I(100) : I(110)$ is evidenced. However, a faster growth rate is observed for the intensity of all low angle reflections compared to SBA-3, as illustrated in Figure 6.3, with the scattering intensity

increasing at temperatures as low as 200°C. Furthermore, a lower d -spacing decrease is seen within the temperature range of interest (200–350°C).

Figure 6.2: XRD patterns stack plot of mesostructured silica fibers synthesized under acidic conditions with TBOS as silicon source ($\text{pH} = 0$). Shown are subsequent XRD patterns as the material is calcined up to temperature of 500°C, held at this temperature for 8 hours and cooled to room temperature.

From 300°C, no significant variation in intensity is observed until the fiber sample is cooled down to room temperature. TG-DTA/MS measurements were carried out on samples of mesoporous silica fibers under the same conditions applied to powder SBA-3 samples. The weight losses recorded for SBA-3 and MSF are listed in Table 6.1. The MS profiles measured for mesostructured silica fibers are usually very similar to those obtained for SBA-3. However, a marked decrease in weight loss of 5% is observed in the range of temperatures between 200–300°C for the mesoporous fibers. The remaining weight changes are identical. This indicates a lower amount of organics in the fibers mesophase. Therefore, the more rapid growth of the intensity above 200°C for fibers may be related to a different distribution of the organic contained in the mesophase, and/or from a probable different arrangement of the hexagonal structure with respect to wall thickness and pore shape.

Figure 6.3: Graph showing the evolution of the reflections intensities (open symbols) of MSF sample (blue plots) and a reference SBA-3 as a function of temperature during the heating ramp up to 500°C. Also plotted are the d -spacing values of the respective reflections (solid symbols). The connecting lines are used as guide for the eye.

Materials	35-110°C	110-285°C	285-375°C	375-900°C	Total >110°C
MSF	2	27	13	10.5	50.5
SBA-3 powder	0.5	32	13	10.5	55.5

Table 6.1: Weight losses measured for mesostructured silica fibers and powder samples obtained from the acid synthesis route.

The higher thermal stability of the mesoporous silica fibers compared to a conventional SBA-3 powder is verified by heating the samples stepwise from 500°C to 1000°C. In Figure 6.4, the XRD patterns of both materials measured *ex situ* after this thermal treatment are shown. The p6m hexagonal pattern is retained only in the fiber case. Conversely, the structure of SBA-3 is drastically altered.

Figure 6.4: XRD patterns of mesoporous silica fibers and a SBA-3 powder measured *ex situ* after heating up to 1000°C.

Similar mesostructured silica fibers were obtained with TBOS as silicon source, by using an equivalent amount of $\text{CH}_3(\text{CH}_2)_{13}\text{N}(\text{CH}_3)_3\text{Br}$ (C14TAB) or $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Cl}$ (CTACl). These fibers exhibit similar XRD characteristics as those synthesized with CTAB (Figure 6.5a). The use of a shorter chain surfactant leads to materials with smaller d -spacing values (3.7 nm), with a smaller pore size as suggested by the sorption data, and lower adsorption capacity. (Figure 6.5b). Furthermore, in all syntheses described above the fibers were prepared from a surfactant solution at $\text{pH} = 0$. However, mesoporous fibers can also be synthesized at a higher pH of 0.5 by decreasing the HCl concentration. The fibers present the same properties as the ones synthesized at lower pH , allowing similar further use. No substantial change in the structure and morphology could be observed, however, the growth process is slower, and the yield is slightly lower (1.1 mg per g). Upon calcination, however, a substantially larger lattice shrinkage is observed (ca. 25%) for the fibers synthesized at $\text{pH} = 0.5$ with $a_{\text{calc.}} = 3.54$. The N_2 sorption isotherm shows a similar adsorption capacity with a shift of the capillary condensation step to lower relative pressure, which suggests smaller pore sizes (Figure 6.5b). The lower concentration in HCl is likely responsible for a lower degree of condensation of the inorganic framework, inducing a larger contraction of the mesophase upon thermal treatment. Even though the decrease of the electrolytes concentration, which reduces the ionic strength of the solution, does not substantially alter the growth in fiber morphology, the sol-gel polymerization process seems to be less favored.

Figure 6.5: a) XRD pattern of different silica fiber mesophases, synthesized with C16TAB and C14TAB; b) N₂ sorption isotherms obtained for various mesoporous silica fibers samples (calcination at 500°C for 8 hours).

Internal structure

At the time of the original synthesis, it was stated that the fibers consist of hexagonally organized channels oriented parallel to the fiber axis, as it is suggested for SBA-15 based fibers^{9,10} and other fibers.^{11,12} However, further investigations suggested that this hypothesis is incorrect. All the spontaneously grown silica fibers are strongly birefringent.^{2,7} The birefringence profiles found showed a volcano-hill shape instead of a constant behavior which would be expected for a

Figure 6.6: TEM image of TBOS based-mesoporous silica fibers perpendicular to the fiber axis. The arrow indicates the direction of the fiber axis.²

homogenous material with hexagonally ordered channels running parallel to the axis. This result excluded that the fiber could consist of homogeneously arranged channels running parallel to the fiber axis. Transmission electron microscopy was used to confirm the conclusions based on the analysis of the birefringence.^{2,13,14} Figure 6.6 shows a TEM micrograph of a fiber sample synthesized with TBOS. A hexagonal channel pattern can only be observed in a viewing direction perpendicular the fiber axis. The hexagonal ordering is only visible near the fiber edges where the smaller thickness of the specimen allows structural contrast to be seen. This observation was made along the whole fiber, on every fiber. The

fibers synthesized with TBOS in the absence of additional oil were then convincingly shown to exhibit a circular inner architecture, consisting of hexagonally organized channels running circularly around the fibers axis,¹³ with the center of the fiber regarded as a decisive structure-controlling element.

6.1.1 Other silicon sources

After the investigation of the TBOS-based fibers it was still unclear whether all the mesoporous silica fibers obtained from a two-phase acidic system have the same circular internal pore arrangement that has been evidenced for the TBOS-based synthesis. Since changes in silica source and the addition of oil are expected to affect the kinetics of the reaction and the nucleation process, the materials obtained could present diverse hierarchical structures. To investigate whether the circular structure is observed for a larger range of synthesis conditions, the nature of the silicon alkoxides reagents has been systematically changed and various additional oils were added to tune the system.

Figure 6.7: Schematic representation of the synthesis for static two-phase acidic systems. **a)** TEOS in hexane, **b)** TEOS in CCl₄.¹

The more slowly reacting TBOS employed previously forms fibers without the use of additional oil. Conversely, synthesis studies have been carried out with tetraethoxysilane (TEOS) and tetrapropoxysilane (TPOS) as silica sources in presence of hexane, CCl_4 and trimethylbenzene. These systems separate into two phases as schematically shown in Figure 6.7. The presence of oil allows the growth of fibers in systems with silicon sources such as TEOS, that hydrolyze quickly in an aqueous environment.

As intermediate situation between TEOS and TBOS, pure TPOS and TPOS diluted with different oils have been investigated as well. In all systems studied, the fiber growth starts in the region close to the interface of the aqueous and organic phases. Depending on the conditions, highly transparent fibers with thicknesses ranging from submicrons to $40\text{ }\mu\text{m}$ were obtained in the aqueous phase, within times ranging from some hours to several weeks. Examples of the products collected from various systems are shown in Figure 6.8. Generally, one can observe among the synthesis products different proportions of long homogeneous fibers, shorter fibers with variable thickness, flat elongated solids, and small circular particles. Fibers with a length ranging from a few microns up to several millimeters can be found. One can note that the syntheses performed in the presence of CCl_4 produce very similar products (Figure 6.8). As this oil has a higher density than water, these experiments make a decisive role of gravity in the fiber growth mechanism very unlikely.

Systems	No oil	0.375ml ^a	0.75 ml ^a	1.5 ml ^a	3.75 ml ^a
TEOS/hexane	52	56	65	65	80
TEOS/ CCl_4	76 ^b	78	59	54	47
TPOS/hexane	90	90	45	25	-
TPOS/ CCl_4	65 ^b	30	30	10	-

Table 6.2: Percentage (%) of fibers obtained in different systems. ¹ The whole synthesis product consists of fibers and small particles. The percentages of both products in the sample were estimated statistically from overview SEM pictures taken after 7 days of synthesis for the TEOS-based systems, after 15 days for the TPOS/hexane systems and after 6 weeks for TPOS/ CCl_4 systems. A grid (16 columns x 12 lines) was overlaid on each representative SEM micrograph and the shape of the each solid particle observed at the grid line intersections was registered. The error of the ratio determination is estimated to $\pm 10\%$. ^a Amount of additional oil. ^b Synthesis performed with 0.075 ml CCl_4 .

Figure 6.8: Typical SEM images of synthesis products: **a-b)** TEOS in hexane (0.375 ml/3.75 ml); **c-d)** TEOS in CCl_4 (0.375 ml/3.75 ml); **e-f)** TPOS in hexane (no oil/1.5 ml); **g-h)** TPOS in CCl_4 (0.075 ml/1.5 ml). Left pictures: low additional oil volume; right pictures: high oil volume as indicated.¹

Depending on the amount and the nature of the oil, the ratio of fibers to other morphologies varies (Table 6.2). A general trend is that the syntheses with additional oil lead to thin fibers and a relatively high content of small circular particles (sometimes called gyroids). A solid film at the phase boundary was always observed. The average fiber thickness was found to be in the range from 2 μm to 10 μm for TEOS in hexane, and from 1 μm to 6 μm for TEOS in CCl_4 . The fiber synthesis carried out with pure TEOS as the precursor leads to a very low total yield of mesostructured products (most of the silica formed is amorphous), with 50% of the mesostructured products consisting of fibers. By adding hexane to TEOS, the proportion of long homogeneous fibers increases as already observed previously.⁸ In a sample where only 0.375 ml of hexane was added to TEOS (Figure 6.8a), about 55% of the product is composed of fibers, whereas in a sample with 3.75 ml of hexane (Figure 6.8b), the amount of fibers increases to about 80%.

Also CCl_4 as oil allows the synthesis of fibers. However, the dependence of the fiber fraction on the oil content was found to be opposite (Table 6.2). The percentage of fibers in the samples, where only 0.375 ml of CCl_4 were added, is about 80% (Figure 6.8c). This percentage drops down to about 45% with addition of 3.75 ml of CCl_4 (Figure 6.8d). In addition, the products with CCl_4 as oil showed separated regions containing large quantities of small particles mixed with other domains containing primarily fibers. In the case of TPOS, the quantity of fibers collected increases with the concentration of the silica source. Scanning electron micrographs of fibers obtained from TPOS in hexane and CCl_4 are shown in Figure 6.8e-h. Here, only very concentrated TPOS or pure TPOS lead to the formation of long homogeneous silica fibers. At high oil contents, small circular particles are predominantly formed. The average fiber thickness ranges from 5 up to 40 μm for syntheses using hexane or pure TPOS, the fibers obtained with the TPOS/ CCl_4 silicon source show diameters between 2 and 10 μm .

Interestingly, materials with peculiar morphologies can be generated in 2-phase acidic systems with the addition of trimethylbenzene (mesitylene) to TPOS as the silicon source. Figure 6.9 shows representative SEM images of the solids collected from these systems. As can be seen, short cylindrical particles with large thickness are obtained with the addition of 0.375 or 0.75 ml of mesitylene to TPOS. The fiber-like solids seem to consist of tight stacking of discoids. At larger oil volume, large irregular particles with no particular shape are obtained.

Figure 6.9: SEM images of solids obtained in a system based on TPOS. **a)** with 0.375 ml; **b)** with 0.75 ml of mesitylene.

The fibers are always formed in the aqueous phase, irrespective whether CCl_4 , hexane or other organics are used as the additional oil. This means that the fibers can be formed either above the phase boundary or below. It can therefore be concluded that gravity is not the key factor in controlling fiber growth.

6.2 Growth kinetics

The addition of CCl_4 to TEOS leads to an interesting system with respect to the arrangement of the phases, and it is also very suitable for kinetic analysis since one can easily observe various stages of the fiber growth directly by eye.

Figure 6.10 describes the macroscopic evolution of the TEOS in CCl_4 system which is very similar also for the other systems. In all cases, an induction period occurs before a visible layer of solid products is formed. The more concentrated the silicon source the shorter the induction time. In the case of addition of 0.375 ml of oil, the induction time is about 15 minutes. If 3.75 ml are added the induction time reaches 2 hours. The results of the kinetic studies carried out on the TEOS/ CCl_4 system are reported in Table 6.3. The phenomenological layer growth velocity v_D was determined via the equation $v_D = 0.5 D_{\max} / (t_{1/2} - t_{\text{ind}})$, where $D_{\max}$ is the maximum thickness of the product layer obtained from Figure 6.11. The growth rate of the mass of products r_m has been determined from the fitted straight lines in Figure 6.12. The

yield (mass of products divided by the mass of synthesis solution) was measured after 7 days of synthesis. It has an error of about 0.05 mg/g due to the product removal procedure.

Figure 6.10: Temporal evolution of a static two-phase acidic system using TEOS in CCl₄ as silica source.¹

The second stage is the growth of a dense layer of solid products above the organic phase (Figure 6.13a). This layer consists preferentially of small particles with some very small fibers present among them (Figure 6.13c). The layer reaches a maximum thickness of about 4 mm where it is stable in a third stage before becoming irregular. In the meantime, a solid film appears at the phase boundary. The solid products form a stable layer in the solution with a thickness which can be directly measured with a ruler. Alternatively, the mass of solid products has been determined. For this, a synthesis batch was filtered and rinsed with 10 ml of heptane. After this, the filter paper together with the solid products was calcined. The product consists of SiO₂ which was weighted. Figure 6.11 shows the thickness of the layer of solid products as a function of time. It can be seen that the more oil is added, the longer the layer remains stable. In the thickness growth period, the growth velocity seems to be constant. However, since many factors could influence this velocity, this is very difficult to interpret. Nevertheless, extrapolation of the growth curve to a thickness of zero allows determination of

the induction time which was found to increase with increasing dilution. Alternatively, the total mass of solid products can be measured. This reveals that the reaction rate of solid formation $r_m = \frac{dm}{dt}$ increases with TEOS concentration in stage II of the growth process, as can be seen in Figure 6.12.

Systems	Induction time t_{ind} (min)	Half layer growth time $t_{1/2}$ (min)	v_D (mm/h)	r_m (mg/h)	Yield in solution + film (mg/g)
TEOS in 0.375 ml CCl_4	10 ± 5	25 ± 5	2.3 - 4.5	2.2	$0.10 + 2.15$
TEOS in 0.75 ml CCl_4	30 ± 5	50 ± 5	2.4 - 4.0	1.5	$0.43 + 1.96$
TEOS in 1.5 ml CCl_4	50 ± 5	85 ± 5	2.6 ± 0.4	0.72	$0.86 + 1.57$
TEOS in 3.75 ml CCl_4	110 ± 5	160 ± 5	2.4 ± 0.4	0.21	$0.74 + 1.40$

Table 6.3: Growth kinetics for the system based on TEOS in CCl_4 .¹

Figure 6.11: Thickness of the dense layer of solid products observed in stage II and III of the synthesis for the TEOS/ CCl_4 systems as a function of time.¹

Figure 6.12: Mass of solid products obtained after calcination for the same systems as a function of time. The arrow indicates the appearance of the solid film at the interface. Two straight lines were fitted to the data points: a horizontal line averaging the data points before the appearance of visible solid products and a linear rise fitting the data points after the appearance of solid products till the appearance of the solid film disturbing the mass determination.¹

The fourth stage of the fiber growth is a period during which the aqueous phase slowly turns turbid (Figure 6.13b), leading to the final stage where visible long fibrous objects appear. The same observations are made when TEOS is mixed with hexane. However, the processes are faster in the TEOS/hexane system and thus more difficult to analyze. The use of TPOS slows down all processes. Very long homogeneous fibers are also found in this system. When TPOS in hexane is used as the silicon reagent, reaction times up to 2 weeks are needed. Addition of CCl_4 slows down the reaction rate even more drastically. In this latter case, the presence of CCl_4 delays the fiber growth to a time scale ranging from 2 to 4 weeks. However, the same stages in the fiber growth as in the TEOS case are again observed, with very long induction times (several days) and the subsequent presence of a dense layer of solid products during a much longer time (2 weeks). Figure 6.13 shows images of the same synthesis batch obtained during the fibers synthesis at different synthesis stages in the case of a TEOS/ CCl_4 system.

Figure 6.13: **a)** Synthesis batch in a TEOS/ CCl_4 system at stage II; **b)** Synthesis batch in a TEOS/ CCl_4 system at stage IV; **c)** Optical microscope image of the dense layer of solid particles observed above the oil phase. The image shows a drop of dispersion taken from the layer.

6.3 Generalization of the internal structure

The XRD diffraction patterns (Figure 6.14a-d) show, in all cases, the typical hexagonal mesophase with up to four reflections. For the TEOS based systems (Figure 6.14a-b), the d -spacing is not strongly affected by increasing the amount of oil added to the system. The $d(100)$ value is observed in the range of 4.25 nm to 4.3 nm and 4.26 nm to 4.37 nm when hexane and CCl_4 are used, respectively, which is equal within the experimental error (Figure 6.15). These values recorded for the TEOS systems are slightly higher than the d -spacings measured for fibers obtained with TBOS as the silicon source (4.1 nm). Furthermore, it

should be noted that the structural ordering for products obtained with TEOS in hexane is substantially increased by increasing the amount of additional oil. A high quality hexagonal structure is observed with 3.75 ml of hexane. This fact suggests that longer reaction times lead to more perfectly ordered structures.

Figure 6.14: XRD recorded for dried mesostructured fibers: **a)** Materials obtained from TEOS in hexane; **b)** from TEOS in CCl_4 ; **c)** from TPOS in hexane; **d)** from TPOS in CCl_4 .¹

The XRD measurements performed on materials obtained from the TPOS-based system show the opposite effect (Figure 6.14c-d). The well-resolved hexagonal mesophases are observed only at very low oil content. When larger amounts of oil are added to the TPOS reagent, the XRD patterns recorded are different. In the case of hexane addition, the signal to noise ratio decreases, suggesting the presence of amorphous products. Also, an increase of the d -spacing is observed by increasing the amount of hexane. The $d(100)$ value increases from 4.15 nm up to 4.4 nm with an oil volume of 1.5 ml (Figure 6.15). The swelling effect is even more pronounced for the CCl_4 system. Figure 6.14d shows the XRD diffractograms recorded for fibers from the TPOS/ CCl_4 system after 6 weeks of reaction. The hexagonal mesophase observed is substantially swollen with CCl_4 and has $d(100)$ values up to 5.15 nm. However, a well ordered mesophase is formed only at low CCl_4 concentrations. At high CCl_4 volumes (1.5 ml CCl_4 and higher), the growth of solids is very slow and the XRD patterns recorded do not show the well resolved hexagonal phase. No fibers have been found among the synthesis products.

Figure 6.15: $d(100)$ spacing for the different systems investigated as a function of volume of added oil. The d -spacing of the sample synthesized with pure TBOS is around 4.1 nm.¹

When TEOS or TPOS is used without any additional oil, the lattice parameter is comparable to that observed with TBOS, with a $d(100)$ spacing of 4.1-4.2 nm. However, the lattice parameters of hexagonal mesophases obtained from TEOS and TPOS in the presence of oil

can be substantially larger than the lattice parameters measured with fibers from syntheses performed without additional oil. The TEOS-based system is only slightly swollen compared to the pure systems with no significant dependence on the oil concentration. On the other hand, the addition of either hexane or CCl_4 to TPOS leads to a large increase of the d -spacing values, and a clear dependence on the amount used can be observed. The influence of oil addition to MCM-41-type materials has already been described in the first publications¹⁵ and has recently been investigated in detail under alkaline conditions.¹⁶ Swelling can be induced even after assembly of the mesophase, as long as the silicate framework is sufficiently flexible due to incomplete condensation. This could be one factor which helps to explain the swelling effects observed in this study: the more hydrophobic and bulky the substituents of the silicon precursor the slower the hydrolysis rate. Therefore, TEOS forms a rigid framework more rapidly than TPOS and TBOS. The mesophase obtained with TEOS has thus less time to incorporate sufficient amounts of oil to result in a detectable lattice expansion. Since oil is supplied from the interface, it is released slowly to the aqueous phase and thus gradually incorporated in the micelles. Structures formed early, such as the products from the TEOS system, will therefore be swollen to a much lower extent than structures formed after several days.

The powder XRD measurements show only the local hexagonal pore arrangement, but they cannot reveal the internal architecture of the fibers as micrometer scale objects. TEM investigations give insight into this architecture if a clear correlation exists between the viewing direction in TEM and the macroscopic fiber shape, as was demonstrated. Therefore, the TEM pictures can be correlated with TEM overview pictures. The TEM pictures (Figure 6.16) show the presence of a hexagonal array of channels. Since the viewing direction is clearly perpendicular to the fiber axis, as shown in the overview, the channels must be running perpendicularly to the fibers axis. This observation is fully reproducible along the whole fiber. It allows two interpretations: the channels can be closed-off rings or helices. Since the channels can be seen on both edges of the fiber simultaneously (Figure 6.16d), only a very small pitch angle of a helix is possible, if the structure is helical instead of consisting of closed-off rings. Spirals with increasing diameter have been excluded by further electron microscopy studies where microtomed fibers were investigated.¹³ The X-ray diffraction and electron microscopy observations are in agreement with the detailed study of the internal fiber structure performed for the TBOS system. Fibers with the same internal structure have been formed from several different two-phase systems. The internal architecture of the fibers obtained in strongly acidic medium is independent of the silica source: the addition of oil to

either TEOS or TPOS does not change the internal ordering of the channels running perpendicular to the fiber axis.

Figure 6.16: TEM pictures of the edge of mesoporous fiber synthesized with different silica sources: **a)** TEOS in CCl_4 ; **b)** TEOS in hexane; **c)** TPOS in CCl_4 ; **d)** TPOS in hexane. The hexagonal ordering is visible near the fiber edges for all samples. The arrows indicate the direction of the fiber axis. In the TPOS/hexane case, pictures obtained simultaneously on both sides of a fiber are shown.¹

One can, therefore, conclude that fibers obtained from TEOS and TPOS with various additional oils have the same internal circular structure observed previously using TBOS as the silicon reagent. Therefore, the circular internal structure can be now regarded as a general property of mesostructured fibers obtained in static systems under acidic conditions. This corrects the former statement⁸ given for fibers from a TEOS-in-oil system, where the channels were described as running parallel to the fibers axis. In this paper the assignment of the TEM pictures to the viewing direction was probably incorrect. Because of the surprising circular architecture which seems to appear generally, former ideas on fiber formation mechanisms have to be re-considered again. For all fibers collected, the high degree of order is confirmed by transmission electron microscopy and the hexagonally ordered channels are found to run perpendicularly to the fiber length axis, whirling around the fiber center. This suggests that all the fibers obtained from the two-phase acidic system under static conditions follow the same mechanism of formation. Despite the identical internal architecture, the different systems described lead to different fractions of various morphologies. The coexistence of different macroscopic shapes and their very similar internal architecture point to a strongly related formation mechanism.

6.4 Possible mechanism of fiber formation

The processes by which curved shapes and fibers form have attracted much interest.¹⁷⁻²¹ It has been recently proposed that the well-defined shapes could be initiated by topological defects^{17,18} and that the shape and length of the mesoporous silica products depend strongly on the silica supply and on the self-assembly of the silica and surfactant at the two phase interface.²² These suggestions are of a general nature and a good starting point for experiments aimed at a better insight into the nucleation processes on a molecular level, but they are not directed towards an explanation of the circular architecture of the fibers.

We therefore proposed a hypothesis for a mechanism that could help to understand the fiber growth processes.² We suggested that the basis for the fiber formation is a hypothetical circular seed. The origin of the circular seeds could be explained by the following multi-step formation process:

1. Formation of a low number of long micelles by a slow aggregation process,
2. Spontaneous bending of the rod-shaped micelles leading to loops,
3. Restructuring of the loop-shaped micelles to tight coils by lowering of the surface energy.

These nanoscopic coils will further grow by addition of new micelles. Around this seed more and more worm-shaped micelles can coil. The possible formation of loop-shaped micelles is known for oligomeric surfactant phases in conventional oil-in-water systems.²³ In addition, the seed will grow in length direction by consumption of spherical micelles which have a high concentration in the solution through the whole synthesis. Finally, elongated circular solids will precipitate in the aqueous phase. As the well-shaped small particles accompanying the fibers have probably a similar internal structure, they are likely formed by a related formation mechanism, where less perfect seeds lead to these shapes instead of fibers.

The formation of a high fraction of well-developed fibers seems to require a delicate balance of a sufficiently low rate of hydrolysis and silica condensation and a sufficient flexibility of the micelles to adapt to a homogeneous fiber. Pure TEOS forms silica too rapidly and the available time is too short for the formation of well developed homogeneous macroscale structures. Pure TBOS forms the most perfect fibers, and the synthesis time is the longest. The

more rapidly reacting silicon sources can be slowed down by dilution, but on the expense of oil incorporation (swelling), which makes the initial micelles less flexible. In addition, micelle size will vary over the course of the synthesis due to increasing amounts of oil solubilized in the aqueous phase. Both factors lead to a more error prone assembly of the micelles to larger scale objects, resulting in a higher fraction of small particles. The higher irregularity of the structures formed under such conditions is also apparent in the noisier and less resolved diffraction patterns for the TPOS system with increasing oil concentration. The addition of oil to the different systems has the tendency to inhibit the longitudinal growth of homogenous fibers, and to favor the occurrence of new morphologies among the synthesis products, such as very compressed short fibers, thinner circular units, or hollow solids.

6.5 Hollow mesoporous silica fibers: tubules by coils of tubules³

Hollow fibers or nanotubes have attracted much attention because of their possible applications and for being an example of hierarchically organized matter. Three different kinds of surfaces may play a role in these materials: firstly, the outer surface, secondly, the inner surface of the central fiber cavity and thirdly, the internal surface of the fiber wall, if the wall consists of a porous material. All three of these surfaces can be functionalized differently and can act together in an integrated chemical system. Several reports have appeared on hollow fibers and tubular morphologies.²⁴⁻²⁷ Hollow fibers of amorphous silica or titania have been prepared by organic supramolecular templating,²⁴⁻²⁷ inorganic salt templating²⁸ or via electrochemical deposition in a polymer mold.²⁹ Zirconia nanotubes have been obtained by a templating method using multi-walled carbon nanotubes.³⁰ However, all these hollow fibers did not present a very high degree of structural ordering of the walls. In addition, there are some reports on oxidic nanotubes exhibiting partially ordered walls of some nanometer thickness.³¹ In the literature on mesoporous materials, the directed or the spontaneous formation of hollow fibers have also been described.^{32,33} For these materials, a highly ordered pore system within the tube wall lies in-between the inner and outer tube surface, possibly connecting the interior and the exterior of the tubes. One may also speculate that there is an inherent connection between the mesopores of the walls and the tubular morphology. This points to the question of the formation mechanism of tubular morphologies which differs between various described systems. One possible procedure for the production of hollow

fibers is the use of nanoscopic “templates” to form a hole inside the fibers as used for non-porous fibers. Another strategy is based on spontaneous hole formation mechanisms, such as the folding of ordered mesostructures proposed for the formation of “tubules within a tubule”.²¹ This mechanism is assumed to lead to a highly directed channel architecture of the hollow fibers obtained in the basic pH range.

In the acid-based synthesis of mesostructure silica fibers described in this chapter, hollow fibers are found. However, their exact structural nature and their relation to the solid fibers and other synthesis products that simultaneously form, remain unclear so far. The aim of the current section is therefore to show (i) that the hollow fibers synthesized in a quiescent acidic solution have the same circular internal channel architecture as have the full fibers, (ii) that hollow fibers are directly intergrown with bulky fibers, (iii) that the diameter of the central hole is variable, and (iv) that the hole is empty after synthesis. These arguments exclude a template-induced hole formation as well as a folding mechanism, and are pointing towards a novel singularity-fluctuation process leading to hole formation in the fiber center. The fiber center must be regarded as a singularity of the highly ordered mesostructure of the fiber. This singularity can change its properties and affects thereby the fiber morphology.

In all synthetic systems investigated so far, a significant proportion (estimated to be up to 10%) of hollow fibers has been observed among the products. Hollow fibers were found in products from syntheses carried out with different precursors, different surfactants and at different levels of acidity, although hollow fibers are more easily observed for thinner fibers. Examples of hollow fibers are depicted in Figure 6.17. The TEM pictures show hollow fibers obtained in syntheses based on TEOS in either CCl_4 or hexane, with the inner radius ranging from 200 to about 500 nm. Every synthesis batch contained hollow fibers with a range of outer and inner diameters. Apart from the fact that the TEM pictures show the inner hole of a number of fibers, they reveal also the channel architecture of the fibers. As described in detail in previous papers, the observation of the fiber edge is a clear indicator for the channel orientation. Here it is found that the channels are whirling around the fiber axis since a hexagonal pattern becomes visible in a viewing direction perpendicular to the fiber axis (Figure 6.17c). Therefore, hollow fibers have the same internal structure as solid ones. The channels can form a helix or closed-off ring structures, since both possibilities are consistent with the TEM pictures. However, since the hexagonal ordering of the channels is visible on both sides of a hollow fiber from the same viewing direction, a possible helix can only have a very low pitch height.

Figure 6.17: TEM pictures of hollow mesoporous silica fibers obtained with different silicon sources: **a)**, **b)** and **c)** with TEOS/ CCl_4 ; **d)** with TEOS/hexane. The light fiber center results from the hollow morphology. For every silicon source a proportion of hollow fibers has been found. At the fiber edges (shown in the insets) it becomes visible that the fibers consist of channels running in a circular direction around the fiber axis.³

The inner diameter of the hollow fibers is variable as shown in Figure 6.17 and ranges from a minimum of about 50 nm up to a maximum of about 1 μm . The most frequently observed hole diameter, as measured by TEM, is around 400 nm. The hole diameter differs for different fibers and also for different positions along one fiber. This is visible for example in Figure 6.17b. These observations of wide spread inner diameter and variable diameter along the fibers are the first arguments to exclude the hypothesis of some kind of macro-hole forming template. The hierarchical structure of a fiber with a hollow center is schematically represented in Figure 6.18.

Figure 6.18: Schematic representation of the different hierarchy levels in hollow ordered mesostructured silica fibers.³

To investigate the formation of holes in the fiber center by template effects, the fibers have been checked directly after the synthesis without calcination. By scanning electron microscopy (SEM) it was detected that there are a number of fibers with a center that is empty already before calcination. The SEM pictures shown in Figure 6.19 show examples of as-prepared fibers coated with a 10 nm thick gold film. Normally this technique delivers a reliable information on the surface topology and we interpret, therefore, the dark areas in the fiber center which occur on some fibers, as being holes. The picture has been selected from a larger number of micrographs showing essentially the same features. Most of the fibers appear solid at their end faces. Together with the arguments presented above, a formation of the hole in the center by supramolecular templates, such as a surfactant assembly, can be excluded. In addition, some other products of the synthesis are visible on Figure 6.22: a very thick fiber with steps in the diameter, small worm-like particles and bigger particles with straight and curved edges. The most typically by-product of the fibers are, however,

Figure 6.19: SEM of as-synthesized hollow fibers (obtained from a TEOS/ CCl_4 silica source). The fibers are hollow before template removal.³

rotationally symmetric particles (gyroids). The optical microscopy allows a larger overview over the whole fiber length. With this technique, larger-diameter inner holes are easily visible. However, this technique reveals that in nearly all the fibers, the inner hole ends somewhere in the fiber. Therefore, these fibers consist of hollow and completely solid parts. An example for this is shown in Figure 6.20.

Figure 6.20: Optical picture of a Rh6G-doped fiber obtained from a TBOS silica source. It is typical that a hollow fiber is connected to a solid fiber as shown in this picture.³

Moreover, there are a number of fibers containing more than one hollow part divided by solid fiber parts. Fibers with a central hole along the whole length are rarely observed and most probably are fragments of longer fibers. It is reasonable to assume that all the hollow fibers are connected to solid fibers. This extends the statement above, that the hollow center has a variable radius, to the degenerated radius value zero. Since the hollow and the solid fibers seem to be always intergrown, the conclusion seems to be justified that one fiber type is growing out of the other. As the major part of the fibers are exclusively solid, only these fibers can be the initial products of the synthesis. The hole must thus arise from a solid fiber as result of a “defect” in the growth process. As for ordinary crystals, the condensation of the micelles to the hexagonal mesostructure of the fiber can also be accompanied with various defects or disturbances from the ideal structure. In circular systems (“circulites”³⁴), a number of specific defects can occur if the defects are connected to the central singularity. Since the central singularity controls the structure of the entire system, even a minor change in the central region could affect the whole arrangement. To date, little is known about the exact growth process of the fibers but some theoretical possibilities can be discussed. In the case of a diffusion-controlled fiber growth, a hole – which is statistically formed in the center – will

have a very low chance to close again because the precursor species can no longer reach the fiber center which is now inside the fiber. The resulting, yet morphologically disturbed structure, still remains perfect in its symmetry; missing only one macroscopic part (the central hole). This is not a defect in the crystallographic sense but a disturbance of the ideal fiber morphology.

Another mechanism, which might play a role, can be associated with a too rapidly growing fiber center. Most likely, the fibers consist of layers of helices³⁴ which end in the fiber front edges. The fiber front edges grow much more rapidly than the cylindrical fiber side face. The diameter of one particular helix of this arrangement is determined by the ensemble of the other helices. Now, if the most inner helix could speed-up its growth process occasionally, its diameter would no longer be determined by the other helices. Its radius might increase by a small value and furthermore force the other helices to do the same. This procedure would result in a macroscopic hole and a structure with a slightly disturbed helical symmetry and a little thicker fiber diameter.

Both proposed mechanisms are based on the fluctuations of the growth of the central singularity which seems to be an unknown principle for inner hole formation up to now. They are inherently connected with the circular architecture of the fibers.

6.6 Literature

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7 Conclusions and perspectives

The thermal behavior of the surfactant in the mesostructured systems has been analyzed, and the processes involved have been ascertained. The high temperature XRD chamber was proven to be a suitable tool in analyzing details of the thermal evolution of the MCM-41-type mesophase. The investigations have shown that the behavior of C16TAB or C18TAB in the mesoporous materials is different for different framework composition. The removal of the surfactant, in the case of Si-MCM-41 or Si-MCM-48, occurs in a stepwise mechanism. Particularly, the XRD studies show the changes in scattering contrast, observed for the low angle reflections, occurring when the template is removed. The TG-DTA/MS experiments show that the removal of the surfactant follows 3 steps: an initial evaporation up to 250°C, based on the Hofmann degradation, involving half of the total organic mass, hydrocarbon chain decomposition at 250-300°C, and, finally, oxidation between 300°C and 350°C. Differences in scattering contrasts and chemical reactions involved are observed for mesoporous silicas synthesized under other conditions, which highlight the role of the silica-surfactant interfaces.

Titanium and zirconium oxides show very different features during the surfactant removal. No endothermic process was observed. The organic components are decomposed in a strong exothermic oxidation step between 250°C and 400°C, depending on the oxide materials, and the well ordered hexagonal structure is generally lost. The reflection intensities decrease and the structure drastically shrinks. A second oxidation step above 350°C is assigned to the release of CO₂ and SO₂ produced from the combustion reaction of coke and decomposition of the remaining sulfate. The oxidation process occurs with a higher energy release than that observed for Si-MCM-41. Furthermore, the materials adsorb a significant amount of water below 150°C, which leads to decreased reflection intensities in the XRD pattern. A strong influence of the amount of sulfate on the thermal behavior could be shown for the zirconium based materials. The substitution of framework sulfate groups by phosphate groups allowed to produce more thermally stable materials. In addition, the use of different plateaus and slow heating rates during the heating ramp in the calcination protocols seem to afford a better control of the surfactant removal. With this respect, a careful control of the synthesis conditions and the removal of the template allowed the synthesis of a porous cubic zirconium oxo-phosphate showing a very well developed cubic Ia $\bar{3}$ d structure. The cubic structure inferred from XRD is confirmed for the template free materials by direct observation using

HREM which enables precise structure assignment. The porous zirconium oxo-phosphate described is therefore one of the first transition metal-based analogues of MCM-48-type materials. The zirconium oxo-phosphate exhibits a total nitrogen gas adsorption capacity of up to 130 cm³/g and has a pore volume of up to 0.20 cm³/g, with pore sizes reaching the upper micropore range. Pyridine sorption followed by IR spectroscopy shows that the samples contain both Brønsted and Lewis acid sites, the concentrations of which depend on the synthesis parameters.

In the present study, it was also demonstrated that the use of co-surfactants in the synthesis of mesoscopically ordered silicate-surfactant materials is a promising mean of affecting important material properties, such as the pore diameter and the phase behavior, while maintaining a high degree of long-range ordering. With the right choice of co-surfactant, the pore diameter can be increased or decreased in a controlled manner, without the need for adjustments of other synthesis parameters. While addition of alcohol or long-chain amines to the system led to large swelling and subsequent transition from hexagonal to lamellar mesophase, with addition of either BuNH₂ or HeNH₂ at low HeNH₂/CTAB ratios, one can decrease the *d*-spacing and pore size of the hexagonal mesophase in a very tunable way. In this latter case, the different effects observed may arise from interactions between the amine and the silicate, possibly through hydrogen bonding or direct ionic interactions. The specification of these interactions requires, however, additional investigations based on syntheses involving different types of amine molecules (benzylamine, ethyl-hexylamine, triethylamine and pyridine, for example) or amides. Further NMR and TG-DTA/MS experiments should be performed to provide the needed supplementary insights. Furthermore, the use of co-surfactants and swelling agents to tune the structural properties of mesostructured materials is currently extended to non-siliceous mesostructured and mesoporous materials. In particular, the synthesis of large pore mesoscopic titanium oxo-phosphate and zirconium oxo-phosphate has been recently achieved by using organic swelling agents. For instance, the *d*-spacings of hexagonal phases titania and zirconia were almost doubled in size with the addition of trimethylbenzene.

The high degree of order of all the mesostructured silica fibers synthesized was confirmed by transmission electron microscopy. The hexagonally ordered channels were found to run perpendicularly to the fiber length axis, in a circular manner around the fiber center. Therefore, the circular internal structure can be now regarded as a general property of

mesostructured fibers obtained in static system under acidic conditions. This suggests that all fibers obtained from the two-phase acidic system under static conditions follow the same mechanism of formation. The circular architecture of the fibers points to a completely new growth mechanism which still needs to be understood in detail. With this respect, subsequent dynamic light scattering investigation of the early stages of the reaction may provide useful information.

Furthermore, it was demonstrated that the fibers are always formed in the aqueous phase, irrespective whether CCl_4 , hexane or other organics are used as the additional oil. Therefore, gravity is not the key factor in controlling fiber growth. By changing the amount of additional oil and by varying the type of precursors, the ratios of different shapes can be tuned and the kinetics of the fiber growth can be influenced. The fiber growth process can be divided into five experimentally well-separated stages with tunable kinetics, starting with an induction period followed by different growth stages of visible solid products. In addition, mesoporous silica fibers presenting a hollow center are one of the regular products of a slow acidic two-phase synthesis. They show variable inner radius and possess a circular internal channel architecture isomorphous to solid fibers. The mechanism for the formation of the hollow fibers is likely based on spontaneous hole formation by growth disturbances of solid fibers. This can be regarded as a novel singularity-fluctuation mechanism for internal hole formation. Mesoporous silica fibers are promising new materials due to their hierarchical structure and processability. One could suggest that the fibers system may allow a variability as provided by the self-assembly processes, by incorporation of heteroatoms such as Al or Ti in the inorganic framework or by changing the type of structure directing agent. Another large potential of the mesoporous fibers to be envisaged is their use as support on which metal oxides or metal cluster could be deposited for instances, or even more challenging, the use of the silica fibers as a mold for a replication of the porous structure to generate mesoporous carbon or titania based fibers.

8 Appendix

8.1 Structural and physical properties of the mesostructured silicas

Materials	$a_{\text{as-synthesized}}$ (nm)	$a_{\text{calcined (550°C)}}$ (nm) (%) ^a	I(100) : I(110) as-synthesized	I(100) : I(110) calcined (RT)
C12-MCM-41	3.73	3.51 (6)	5	6
C14-MCM-41	4.17	3.82 (8)	2.5	3
C16-MCM-41	4.64	4.16 (10)	4.5	5
C18-MCM-41	5.25	4.80 (9)	6.5	5
C14-MCM-41-aged	4.35	4.15 (4)	8.5	7.5
C16-MCM-41-aged	4.75	4.6 (3)	4.5	3
C18-MCM-41-aged	5.46	5.15 (5)	5	3.5
CPCI/MCM-41	4.45	3.95 (11)	4.5	5
MCM-48	9.60	8.33 (13)	4.5 ^b	8 ^b
SBA-3	4.53	3.73 (18)	5.5	12
SBA-3 extracted	4.40	3.8 (14)	5.5	7.5
SBA-15	11.42	9.86 (14)	21 ^c	12

Table 8.1: Results of the *in situ* XRD investigations carried out on different silica mesophases. ^a Lattice contraction (%). ^b Ratio (211) : (332). ^c A large experimental error has to be considered which makes this value uncertain.

Materials	BET surface area ^a (m ² /g)	Pore volume V_p (cm ³ /g)	Pore size $w_{\text{BJH des.}}$ (nm)	Pore size w_d (nm)	b_{BJH} $a-w_{\text{BJH}}$ (nm)	b_d $a-w_d$ (nm)
C12-MCM-41 ^b	1035	0.51	2.06	2.55	1.45	0.96
C14-MCM-41	1100	0.61	2.12	2.89	1.7	0.93
C16-MCM-41	1130	0.78	2.47	3.31	1.7	0.85
C18-MCM-41	995	0.79	2.90	3.83	1.9	0.97
C14-MCM-41-aged	910	0.57	2.32	3.10	1.85	1.05
C16-MCM-41-aged	1010	0.80	2.82	3.67	1.8	0.93
C18-MCM-41-aged	1015	0.85	3.62	4.16	1.55	0.99
CPCI/MCM-41	995	0.58	2.24	2.96	1.7	0.99
MCM-48	1175	0.72	2.16	-	-	-
SBA-3 550°C ^c	1470	0.65	2.04	2.86	1.7	0.87
SBA-15 ^c	630	0.67	5.17	7.61	4.7	2.25

Table 8.2: Physico-chemical parameters observed for the calcined materials, obtained by nitrogen physisorption. ^a Average BET surface area. ^b Limit of the BET equation accuracy. ^c The presence of microporosity in the silica walls makes the use of the BET equation and the *t*-plot method likely inaccurate resulting in discrepancies.

8.2 Structural and physical properties of zirconium oxo-phosphate with cubic (Ia3d) structure

r	$d(211)$ as made (nm)	$d(211)$ cal. (nm)	a cal. (nm)	Total ads. Volume (cm ³ /g)	Surface area <i>eq. BET</i> ^a (m ² /g)	Pore volume ^b (cm ³ /g)
0.80	4.00	2.48	6.07	21	64	0.03
0.67	4.02	2.59	6.34	47	149	0.07
0.67 (B)	4.01	2.55	6.27	19	56	0.03
0.67 (B) plateau ^c	4.01	2.58	6.32	52	164	0.08
0.59	4.02	2.66	6.52	55	173	0.08
0.54	3.95	2.72	6.66	54	168	0.08
0.54 plateau ^c	3.95	2.76	6.76	79	251	0.12
0.54 (B)	4.04	2.88	7.05	75	239	0.11
0.54 (B) plateau ^c	4.04	2.90	7.10	87	280	0.13
0.48	4.06	2.88	7.05	99	321	0.15
0.46	4.05	2.85	6.98	91	292	0.13
0.42	4.04	2.96	7.25	115	377	0.17
0.40 no aging	4.22	3.11	7.62	76	232	0.11
0.40	4.00	3.00	7.35	127	417	0.19
0.40 (B)	3.97	3.02	7.40	123	399	0.18
0.40 (B) plateau ^c	3.97	3.04	7.45	133	432	0.19
0.40 (B) 550°C ^d	3.97	2.90	7.10	105	337	0.15
0.27	3.90 ^e	3.03 ^e	7.42 ^e	139	450	0.20

Table 8.3: Structural and adsorption properties of cubic zirconium oxo-phosphate synthesized with different surfactant to zirconium ratios. Samples denoted (B) correspond to scaled-up batches. ^a The BET surface area has no reliable physical meaning for the materials described herein. It is described as BET equivalent surface area and used to compare series of samples. ^b Pore volume measured from a *t*-plot curve. The linear fit is performed with Harkins & Jura statistical thickness in the range of 0.6 to 1.2 nm. ^c Calcination performed with a plateau at 300°C for 3 hours, followed by a step at 500°C for 3 hours. ^d Calcination temperature. ^e No clear structural assignment possible.

8.3 Structural and physical properties of MCM-41 synthesized in the presence of hexylamine as co-surfactant

HeNH ₂ /CTAB	$d(100)$ as-made (nm)	$d(100)$ cal. (nm)	a cal. (nm)	Surface area ^a (m ² /g)	Pore Volume ^b (cm ³ /g)	Pore size ^c w_d (nm)
0	4.09	3.75	4.33	1128 (536)	0.78	3.38
1	4.06	3.67	4.24	1103 (539)	0.77	3.30
2	3.95	3.62	4.18	1100 (517)	0.73	3.22
2.5	3.93	3.52	4.06	1054 (480)	0.69	3.09
3.4	3.6 / 2.87 ^d	3.28	3.79	986 (334)	0.48	2.65
4.5	– / 3.02 ^d	–	–	738 (264)	0.34	–

Table 8.4: Summarized properties of MCM-41 synthesized in presence of different amounts of hexylamine.

^a BET surface area. In parentheses is the total N₂ volume adsorbed (cm³/g). ^b V_p primary mesopore volume obtained from the t -plot (Harkins & Jura thickness range 0.8-1.2 nm). ^c Pore size calculated with V_p from the geometrical model described in chapter 3.3.3. ^d d -spacing of the lamellar phase, which collapses upon calcination.

8.4 Chemical reagents employed

Ammonia 33%	Riedel de Haen
Ammonium sulfate > 99 %	Fluka
N-benzyl-N,N-dimethyl-octadecylammonium chloride monohydrate 90%, <i>remainder</i> C16 compound	Aldrich
Butanol 99%	Aldrich
Butylamine 99%	Aldrich
Carbon tetrachloride 99%	Riedel de Haen
Dodecyltrimethylammonium bromide (C12TAB) 99%	Aldrich
Ethanol 99%	Overlack
Heptane > 99%	Haltermann
Hexadecyltrimethylammonium bromide (C16TAB)	Aldrich
Hexadecyltrimethylammonium chloride 25% in water (CTAC)	Aldrich
Hexadecylpyridinium chloride hydrate 98% (CPCI)	Aldrich
Hexane	Hanf & Nelles
Hexanol 99%	Aldrich
Hexylamine 99%	Aldrich
Hydrochloric acid 37%	Reininghaus-Chemie
Octadecyltrimethylammonium bromide (C18TAB)	Aldrich
Octanol 99%	Aldrich
Octylamine 99%	Aldrich
Phosphoric acid 85%	Riedel de Haen
Pluronic P123	BASF
Potassium hydroxide 85%	Reininghaus-Chemie
Sulfuric acid 96%	Reininghaus-Chemie
Tetrabutoxysilane >97% (TBOS)	Fluka
Tetradecyltrimethylammonium bromide 99% (C14TAB)	Aldrich
Tetraethoxysilane 98 % (TEOS)	ACROS
Tetrapropoxysilane 97% (TPOS)	Lancaster
Titanium <i>n</i> -butoxide 99%	Aldrich

Titanium <i>n</i> -propoxide 98%	Aldrich
Titanium isopropoxide pract.	Fluka
Trimethylbenzene 97 % (TMB)	Aldrich
Zirconium propoxide 70%wt in <i>n</i> -propanol	Aldrich
Zirconium sulfate 99%	Alfa

8.5 List of the publications

1. “Evolution of Mesoporous Materials during the Calcination Process: Structural and Chemical Behavior” F. Kleitz, W. Schmidt, F. Schüth, *Microporous Mesoporous Mater.* **44-45** (2001) 95.
2. “Untersuchung von Wirt-Gast-Beziehungen an mikro- und mesoporösen Materialien mittels TG/DTA-MS-Kopplung” F. Kleitz, W. Schmidt, in “*Gekoppelte Techniken in der Thermischen Analyse*“ E. Kapsch, M. Hollering, Eds., SKT, 2001, 159-168.
3. “Mesoporous Silica Fibers: Internal Structure and Formation” F. Marlow, F. Kleitz, *Microporous Mesoporous Mater.* **44-45** (2001) 671.
4. “Mesoporous Silica Fibers: Synthesis, Internal Structure and Growth Kinetics” F. Kleitz, F. Marlow, G.D. Stucky, F. Schüth, *Chem. Mater.* **13** (2001) 3587.
5. “Hollow Mesoporous Silica Fibers: Tubules by Coils of Tubules” F. Kleitz, U. Wilczok, F. Schüth, F. Marlow, *Phys. Chem. Chem. Phys.* **3** (2001) 3486.
6. “Influence of Co-surfactants on the Properties of Mesostructured Materials” F. Kleitz, J. Blanchard, B. Zibrowius, F. Schüth, P. Ågren, M. Lindén, *Langmuir* in press.
7. “Synthesis and Characterization of Mesoscopically Ordered Surfactant/Co-surfactant Templated Metal Oxides” T. Czuryrzkiewicz, J. Rosenholm, F. Kleitz, M. Lindén, *Stud. Surf. Sci. Catal.* (Proceedings of Feza 2002) submitted.
8. “Porous Mesostructured Zirconium oxo-phosphate with Cubic ($Ia\bar{3}d$) Symmetry” F. Kleitz, S.J. Thomson, Z. Liu, O. Terasaki, F. Schüth, *Chem. Mater.* submitted.

Additional publication

9. “Drug Release from Biodegradable Silica Fibers” T. Czuryrzkiewicz, J. Ahvenlammi, P. Korteso, M. Ahola, F. Kleitz, M. Lindén, J.B. Rosenholm, *J. Non-Cryst. Solids* in press.

Curriculum vitae

Freddy Kleitz

born October the 24th 1972
in Saverne (France)

Scholar education

1976-1983	primary school, Saverne
1983-1987	junior high school, Saverne
1987-1990	senior high school, Saverne
	final exam: Baccalauréat D (science)

Undergraduate university education

1990-1996	Université Louis Pasteur, Strasbourg, France
June 1993	D.E.U.G. in Chemistry
June 1994	Licence in Chemistry (BSc.)
June 1995	Maîtrise in Chemistry
	Dissertation theme: " <i>Synthesis and study of nucleosides modified in position 3'</i> ", with Dr. J.-F. Biellmann, Laboratoire de Chimie Organique Biologique, Université Louis Pasteur, Feb. 1995 - May 1995
June 1996	D.E.A. in Transition Metal Chemistry and Molecular Engineering (MSc.)
	Dissertation theme: " <i>Study of palladium/tantalum carbenes: synthesis and reactivity.</i> ", with Dr. M. Pfeffer (CNRS), Laboratoire de Synthèses Metallo-Induites, Université Louis Pasteur, Sept. 1995 – July 1996

Civil service

1996-1997	Assistant at the Institut Universitaire de Formation des Maîtres d'Alsace (Academic Institute For Teachers Education), Strasbourg
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Research activities

1997-1998	Research assistant: " <i>Synthesis of carbon-carbon bonds within the coordination sphere of palladium</i> ", under the direction of Pr. J. Dupont, Laboratório de Síntese Assimétrica, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil
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Promotion

Since November 1998 at the Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany, under the direction of Prof. Ferdi Schüth (Abteilung für Heterogene Katalyse). Dissertation title: "*Ordered mesoporous materials: template removal, frameworks and morphology*"