

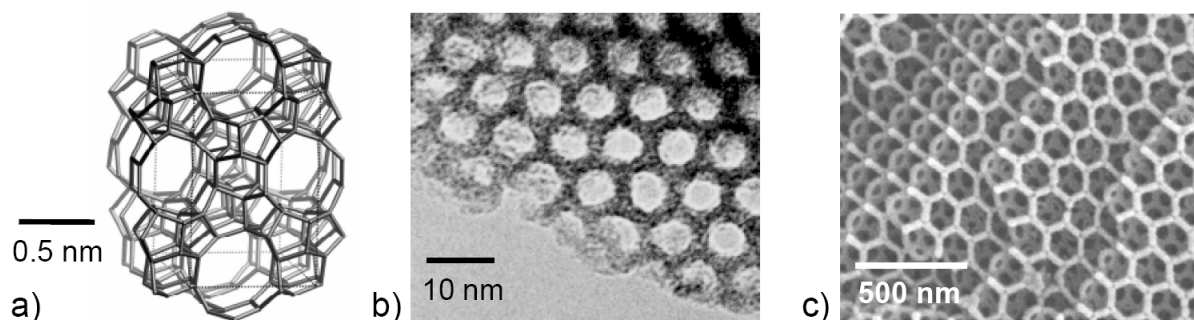
## **2. State of the art**

### **2.1. General aspects on porous solids**

Porous materials have long been of interest in industrial fields as catalytic supports in heterogeneous catalysis, in chemical separation and as adsorbents [14]. Many different types of porous materials have been used in these applications, ranging from carbons to zeolites. For example, the zeolite ZSM-5 is used as a catalyst for conversion of natural gas to gasoline, zeolites A and X are used in detergents to soften water by removal of calcium and magnesium ions via ion exchange. Porous silica gels are used in filtration, chromatography, and thermal and acoustic insulation, and as desiccants [15]. They each have a certain range of practical use dictated by the size, shape and selectivity of the pores in the material, and a distinct manner of preparation to produce the required pore structure. This diversity of applications encourages exploration also of other fields for the use of porous materials.

Porous materials are distinguished according to their adsorption properties and categorized by their pore size resulting from it. According to the IUPAC definition [16] porous solids are divided into 3 classes depending on their pore size (Figure 2.1):

- microporous (with pore sizes  $< 2$  nm),
- mesoporous (2-50 nm), and
- macroporous materials ( $> 50$  nm).



**Figure 2.1:** Examples for the a) microporous (zeolite ZSM-5 after [19]), b) mesoporous (SBA-15 after [17]), and c) macroporous (titania inverse opal after [18]) materials.

The most widely used microporous materials are zeolites with well-defined pore geometries. Zeolites are crystalline aluminosilicas with 133 known frameworks [19]. The pores are highly monodisperse and have a fixed directionality within the crystal. The pores in these systems have often a character of cages and connection tubes. The uniformity of the channels in zeolitic systems means that they are extremely selective adsorbents for small molecules of particular geometries and sizes and so make highly selective catalytic supports and adsorbents. Due to the pore sizes comparable to those of the molecules, zeolites are also called molecular sieves. Other related compounds usually possess similar structures with different framework compositions, such as aluminumphosphates  $\text{AlPO}_4$  [20]. One optical application of molecular sieves is their use as photoswitchable materials [21]. Here, the photo-induced trans-cis isomerization of azobenzene in molecular sieves was found leading to the change of the birefringence after irradiation.

The narrow range of available pore sizes and the relatively small cross-section of those pores restrict the size of molecules that can enter the pores to access catalytic or adsorption sites. This limits their use in applications which involve larger organic molecules. Larger pore sizes are especially required for heavy oil cracking and catalytic conversion of large molecules, separation media, or as a host for bulky molecular species.

The pore range of mesoporous materials is, as the Greek prefix *meso* indicates, between micro- and macroporous. Silicate materials with pores in this range include Vycor glass, silica gels, aerogels (supercritical drying of wet gels [10]), xerogels (air-dried gels) and various types of etched membranes. Porous silica gels are generally

prepared via sol-gel methods (see next Chapter), in which molecular or colloidal silicate species are dispersed in a solvent and then form a gel. The result of the gelation upon solvent evaporation and silica condensation is the formation of pores. The silica walls in these materials are amorphous with no long-range order.

Other mesoporous materials include modified layered materials, such as pillared smectic clays and layered double hydroxides, as well as porous glasses, which consist of a bicontinuous pore system. Mesoporous materials can have different morphologies like particles, membranes, monoliths, fibers, and thin films [14].

Ordered macroporous materials have been actively explored as so-called photonic crystals or photonic band gap (PBG) materials [22, 23]. Photonic crystals are solids with periodicity of the dielectric constant in the range of the wavelength of light. They will be described in more detail in one of the next Chapters. One example of natural photonic crystals are opals [24], which are composed of ordered arrays of spherical silica particles with macropores between them.

## 2.2. The sol-gel method

The sol-gel method [10] is a synthetic process that allows the production of ceramic or glassy materials through the formation of a *sol* starting from a solution of precursors, the condensation of the *sol* into a *gel*, and finally the removal of the solvent.

A *sol* is defined as a colloidal suspension of solid particles in a liquid [10]. The dispersed phase is so small, in the range of 1-1000 nm, that the gravitational forces are negligible and interactions are dominated by short-range forces, such as van der Waals attraction and surface charges. The inertia of the dispersed phase is small enough that it exhibits Brownian motion.

A *gel* can be defined as a substance that contains a continuous solid skeleton enclosing a continuous liquid phase [10]. A gel can also be described as a polymeric molecule with macroscopic dimensions so that it extends throughout the solution.

The *gel point* is the time (or degree of reaction) at which the last bond is formed that completes this giant molecule.

The sol can be produced starting both from organic or inorganic precursors, and the whole process can be conducted at room temperature and ambient pressure. It is noteworthy about this method that the solid state can be reached at low temperature starting from a solution. This feature greatly expands the possibility to create new materials or to improve their properties. It becomes possible to synthesize materials under conditions that are not possible in the usual preparation of metal oxides (i.e. chemical vapor deposition) where high temperatures are required.

The sol-gel process of many molecular precursors is characterized by different sub-processes:

- hydrolysis of the precursors
- condensation
- drying
- sintering

Any of these phases has a big influence on the properties of the resulting material and the great number of variables involved makes the control of the whole process still very empirical. Therefore a detailed knowledge of the chemical mechanisms, which permits to control the properties of the final amorphous material at a molecular scale and to synthesize defined structures, is a great challenge.

### 2.2.1. Hydrolysis

The formation of the sol occurs from the hydrolysis reaction of the precursors in the solution, which are usually metal alkoxides because they react readily with water [10]. The general formula for the alkoxide class is:  $M(OR)_n$ , where the number of alkoxide groups  $n$  depends on the central atom  $M$ . The compound  $Si(OC_4H_9)_4$  (tetrabutoxysilane) also belongs to this class. This class of compounds is used because a hydroxyl ion becomes attached to the metal atom in the hydrolysis reaction:



The reaction involves a nucleophilic attack of the oxygen contained in water molecule to the central atom M, followed by a proton transfer from H<sub>2</sub>O to an alkoxy group –OR, and the exit of an alcohol molecule ROH [10].

Often a catalysis is necessary because of the slow reaction rate of the hydrolysis process, as is the case when M = Si. The catalyst can be both, an acid and a base. Acids serve to protonate negatively charged alkoxide groups and alkaline conditions produce strong nucleophiles via deprotonation of hydroxo ligands [10]. The hydrolysis reaction rate is influenced also by the kind of precursors chosen, because of the different steric hindrance of the alkyl groups. The bigger the alkyl group, the more crowded is the nucleus M, and the slower the hydrolysis will be. Furthermore the longer the chain, the weaker the inductive effects on the central atom, and the slower will be the substitution reaction.

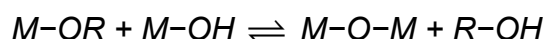
A great role is also played by the solvent used, because of the difference in polarity, dipole moment and availability of labile protons that influence the rate of the hydrolysis and condensation reactions. Together with the hydrolysis reaction, in an alcoholic solution, two other reactions can occur: the reverse reaction, or re-esterification, and the transesterification, in which an alcohol molecule displaces an alkoxide group to produce another alcohol molecule.



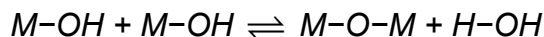
### 2.2.2. Condensation

The condensation process takes place as soon as some hydrolyzed precursor molecules are present in the solution, and it occurs at the same time as the hydrolysis, depending on the quantity of water and catalyst present in solution. The condensation reaction builds a metal-oxygen-metal bridge and can follow two different schemes:

Alcoxolation (alcohol condensation):



Oxolation (water condensation):



with the removal of the protonated species as either alcohol or water. This process leads to the formation first of oligomers and then of macromolecules, whose dimensions and characteristics depend on the reaction conditions used.

The way in which the inorganic polymer grows depends also on the functionality  $f$  of the precursor, or on the number of oxygen bridges that can be bound to the central atom. Silicon has for example a functionality  $f = 4$ , but it can be decreased by chemical modification (i.e.  $\beta$ -diketones, carboxylic acids or other chelating ligands). When the functionality is more than 2, the chain will grow with crosslinks to build a three dimensional network.

### 2.2.3. Drying

The drying process is the first step from the gel to the final solid material, and it occurs with a contraction of the gel's volume and a stiffening of its structure. Drying of gels can be divided into two stages [25]: a constant rate period and a falling rate period. During the constant rate period, mass transfer is limited by convection away from the gel surface, whereas during the falling rate period, mass transfer is limited by the permeability of the gel.

The evaporation of the liquid from the gel surface increases the vapor-solid interface. For this reason the liquid flows from the bulk of the gel to the surface, to cover the dried surface. Because of the evaporation the liquid cannot cover the whole surface without the creation of a meniscus on the pore surface. The capillary force exerted by the liquid causes the contraction of the solid phase, until the radius of the meniscus is equal to the radius of the pore. At this stage the shrinkage proceeds at a constant rate, and the contraction of the solid phase is equivalent to the volume of the evaporated liquid.

After this point the evaporation of the liquid continues moving the liquid-vapor interface towards the bulk of the solid phase leaving a dry solid. This contraction is irreversible, because of the further condensation of the unreacted hydroxyl or alkoxy groups that proceeds during the shrinkage process any time that two groups approach enough to react and form a new Si-O-Si bridge.

The drying of the gel produces anyway a pressure gradient in the liquid phase, which leads to differential shrinkage of the network. If the external part shrinks faster than the internal one, tensile stresses arise that tend to fracture the network. The formation of cracks is energetically favorable because at either side of the crack the material can contract more freely. To avoid this phenomenon, a slow evaporation rate of the solvent is required. The aging of the gel also reduces the risk of fractures, because it helps to strengthen the network, especially if it is still in presence of water and catalyst.

#### **2.2.4. Temperature treatments: calcination, crystallization and sintering**

In the template-assisted synthesis, where the organic template is a central structure around which a network forms, the cavity is created after the removal of the template. The removal of the organics is usually done in a heat treatment called calcination. In this method the as-synthesized materials are usually heated with slow heating rates such as 1°C/min for several hours. Often one or two temperature plateaus are included, where the sample is kept at constant temperature for some time.

Most gels are amorphous, even after drying or low temperature treatment, but some of them crystallize when heated at required temperature. If the objective of the processing is to produce a pore-free ceramic, it is necessary to heat the gel to a high enough temperature to cause sintering. Sintering is a process of collapse of pores driven by surface energy [10].

### **2.3. Ordered mesoporous materials**

Ordered mesoporous materials have characteristics of both sol-gel glasses and zeolites. They contain ordered uniform pore systems similar to those of the microporous zeolites, but the pores are larger, allowing larger molecules to diffuse inside. The walls, however, are made up of amorphous silica, similar to that found in xerogels. Ordered mesoporous inorganic materials are synthesized by using surfactant molecules as structure-directing templates around which inorganic species can polymerize. In the simplest form, a surfactant is used that forms liquid

crystal phases and a silica precursor that interacts with the surfactant micelles and forms a continuous solid network [26, 27]. The porosity is obtained by the removal of the surfactant through calcination, liquid extraction, or other techniques.

The field of research of surfactant-templated inorganic materials has started to grow rapidly since the discovery of the ordered molecular sieve MCM-41 (Mobil Composition of Matter No 41) by a Mobil company research group in 1992 [28]. This structure consists of close-packed cylinders of surfactant ordered in 2D hexagonal phase with a  $p6mm$  symmetry. Beside this most common structure, other phases such as the  $la3d$  cubic (MCM-48) and the lamellar (MCM-50) one were reported in this publication as well. In this initial work only alkaline-catalyzed preparations and materials were involved. In acid-catalyzed preparations using molecular surfactants various structures have been synthesized and named after the city Santa Barbara, SBA-1 ( $Pm3n$  cubic phase), SBA-2 ( $P6_3/mmc$  3D hexagonally packed spherical micelles) and SBA-3 ( $p6mm$  2D hexagonally packed cylinders) [29]. Other surfactant templated materials are disordered materials with a wormlike network of channels (KIT-1 [30] and MSU-1 [31]) and ordered non-ionic alkyl-EO<sub>x</sub>-templated materials, e.g. SBA-11 ( $Pm\bar{3}m$  cubic phase) and SBA-12 ( $P6_3/mmc$  3D hexagonal) [32]. Pinnavaia and his coworkers were the first who demonstrated a neutral templating route by using nonionic surfactants [33]. In order to create materials with larger pore sizes these nonionic amphiphilic triblock copolymers have been used in acidic synthesis, e.g. SBA-15 ( $p6mm$  2D hexagonal) [34] and SBA-16 ( $Im\bar{3}m$  cubic cage structure) [32].

## 2.4. Mechanisms of mesopore self-assembly processes

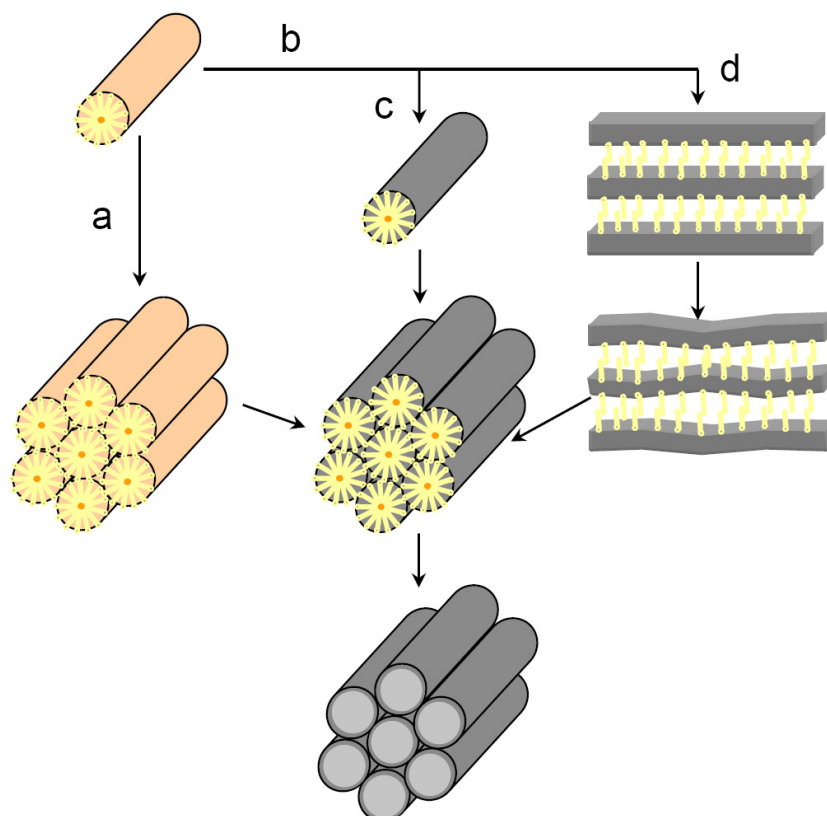
Amphiphilic surfactant molecules or polymers composed of hydrophobic and hydrophilic parts are typical molecules that organize into supramolecular assemblies. In aqueous solution above the critical micelle concentration (cmc), surfactants assemble into micelles that maintain the hydrophilic parts of the surfactant in contact with water while shielding the hydrophobic parts within the micellar interior. As the surfactant concentration further increases, the micelles order themselves into hexagonal, cubic, lamellar, or other mesophases [35].



The surfactant phase, which forms in an ordered mesophase material, depends upon the relative concentrations of surfactant and the inorganic species, although this is not the only factor. The surfactant organization may be described by reference to the packing parameter  $g = V / a \cdot \ell$ , where  $V$  is the volume of hydrocarbon chain,  $a$  the head-group area and  $\ell$  the maximum effective chain length [36]. Spherical aggregates contain the largest area per head group.

A reaction mechanism for the molecular interaction between an inorganic material and a surfactant head group was first proposed by Beck et al. [26] and is called “liquid crystal templating” (LCT). It proposes that the structure of the channel systems in these mesoporous materials is determined by the surfactant aggregation behavior, contrary to the condensation of the silica around the template molecule for zeolites. They proposed two alternative pathways, in which either the liquid-crystal phase is intact before the silica species are added (Figure 2.2, a), or the addition of the silica results in the ordering of the subsequent silica-encased surfactant micelles (Figure 2.2, b). In this case silica anions coated the surface of surfactant micelles, which then self-ordered to form the hexagonal phase observed in the final product, and silica condensation occurred to freeze in this structure. Some groups have reported the formation of a lamellar silica-surfactant phase in the early stages of preparations, which subsequently formed hexagonal phase materials [27, 37, 38, 39]. A “charge density matching” reaction scheme (Figure 2.2, c) has been proposed in which surfactant monomers or micelles in solution become coated with silica oligomers. Probably, the charge on these oligomers causes the surfactant micelle to alter shape during ion-exchange process.

The two processes, the coating of the micelle and the self-assembly of the mesophase, occur on similar time scales. With the subsequent silica condensation, the inorganic charge density decreases. Since low charge densities are necessary to stabilize the structure, the head-group area per surfactant molecule may increase and may drive phase changes, e.g. from lamellar to hexagonal. Incompletely condensed silica walls are flexible enough to undergo this transition.



**Figure 2.2:** Schematic diagram for the formation of MCM-41 with different suggested mechanisms: a) cast of the pre-existing surfactant liquid crystal phase, b) formation of silica-coated surfactant species which form either micelles that agglomerate to form arrays (c) or a lamellar phase which converts into the final hexagonal phase (d). Grey color indicates the coating of the micelle head groups with silica oligomers. The final porous material is obtained upon calcination.

According to other studies, the subsequent formation of the hexagonal phase does not occur as a direct transformation but proceeds via the dissolution of the lamellar phase followed by crystallization of the hexagonal phase [40]. Cheng et al. [41] proposed a different pathway (Figure 2.2, d), where the silica anion first reacts with the pre-existing surfactant micelle, enabling rods of silicated surfactant species to be formed and self-assemble directly into the hexagonal phase, analogously to the pathway b).

The final porous material is obtained by removal of the surfactant through calcination, solvent extraction or UV-ozone treatment [15]. Further stabilization of the silica network is also achieved with the calcination.

Hexagonally ordered mesoporous silica structures with large uniform pore sizes up to 30 nm have been obtained in the synthesis class SBA-15 [34] by use of the triblock copolymer poly (ethylene oxide) – *block* – poly (propylene oxide) – *block* – poly (ethylene oxide) (PEO-PPO-PEO) as a structure-directing agent. The assembly of mesoscopically ordered silica by dilute poly (alkylene oxide) triblock copolymers in acid media likely occurs by the pathway b) in Figure 2.2 that involves a combination of electrostatic and hydrogen-bonding interactions [34].

## 2.5. Synthesis of mesoporous silica thin films

Thin films are highly interesting because of their great range of potential applications in molecular detection, separation, environmental science, medicine, catalysis, optics, opto-electronics, and other still evolving fields. The development with the highest application promise by far is the use of mesoporous silica films as low- $k$  materials [11]. This development seems to be commercially viable, since IBM has fabricated films on the basis of a silsesquioxane precursor with  $k \leq 2.2$  [42, 43]. Mesoporous thin films can be synthesized from solution precursors in two main ways:

- by an aerogel or xerogel process [44] in which random porosity is introduced by controlled gelation and removal of a solvent; and
- by a surfactant-templating process in which the pores are formed by removal of the surfactant. These films are usually fabricated in a spin-coating or a dip-coating process.

### 2.5.1. Spin-coating

The first attempt to create a continuous surfactant-silica mesostructured film was made by spin-coating [45]. In this work, partially hydrolyzed tetramethoxysilane (TMOS) in acid solution (pH = 3) and a solution of an alkyltrimethylammonium bromide ( $C_n$ TAB,  $n$ : carbon number in the alkyl chain) were mixed and the solution was spin-coated on a glass substrate and dried in air at 100°C to remove the solvent and to complete the condensation of the silica. Transparent thin films were formed with thicknesses controlled by spin rate. However, films thicker than 1  $\mu\text{m}$

started to peel off from the substrate. X-ray diffraction (XRD) pattern of these films showed two peaks indicating a layered structure organized parallel to the substrate. Solvent evaporation was proposed as the driving force for organization of the  $C_n$ TAB into lamellar aggregates, which were then ‘frozen-in’ by the continuing condensation of the surrounding silicate. However, it was not commented whether the structure collapsed after calcination, which is what one would expect for the true lamellar structure.

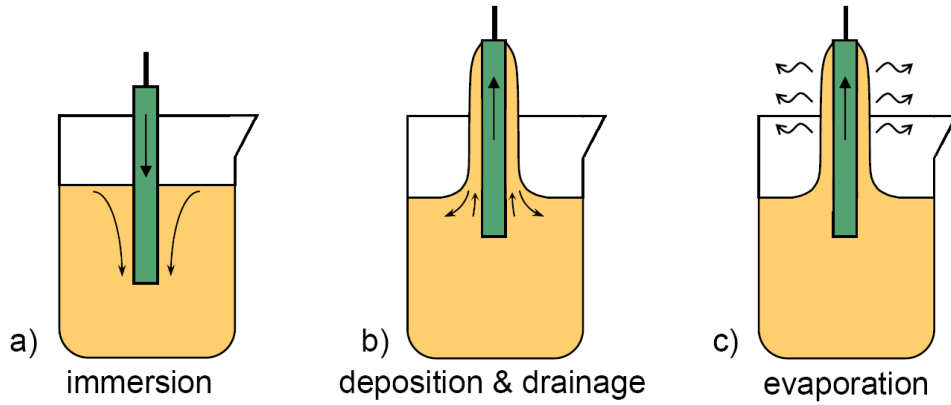
Transparent mesoporous films with hexagonal and cubic symmetries have also been synthesized using cetyltrimethylammonium ( $C_{16}$ TACl) [46]. When the relative ratio of the TMOS to  $C_{16}$ TACl is less than 2.3 a lamellar mesostructure was formed, which collapsed upon calcination. On the contrary, hexagonal mesostructured materials were preferentially formed, when the ratio was greater than 2.5. The TMOS to  $C_{16}$ TACl was increased to 8 in order to obtain a thin film with a cubic  $Pm3n$  mesostructure.

Disordered mesophase silica films have also been prepared using polyoxyethylene ether surfactants in an acidic solution of pre-hydrolyzed TEOS. The dielectric constant of these films after calcination was very low, less than 2.2. A conductive oriented silica mesostructured film can be synthesized by a dye bound surfactant (11-ferrocenylundecylammonium bromide) in a spin-coating method [47]. Spin-coated  $C_{16}$ TAB-silica films with a 3D hexagonal mesostructure ( $P6_3/mmc$  space group) were prepared from a prehydrolysed TEOS in an acidic (pH = 1.25) water-ethanol mixture [48], where  $C_{16}$ TAB was ultrasonically dissolved.

### 2.5.2. Dip-coating

As an alternative to spin-coating, dip-coating is performed with substrates being drawn from a precursor solution and allowed to drain to a particular thickness. Film thickness is controlled by evaporation rates of the solvent and by the viscosity of the coating solution more directly than for spin coating.

The dip-coating process can theoretically be divided into these stages: immersion, deposition and drainage, and evaporation [10] as it is shown in Figure 2.3. These stages can also be mixed, as it happens with volatile solvents like alcohols or THF, where the evaporation process starts directly after the start-up.



**Figure 2.3:** Sol-gel dip-coating process modified after [10] with the stages: a) immersion, b) deposition and drainage and c) evaporation.

If the viscosity of the liquid  $\eta$  and the withdrawal speed of the substrate  $v$  are high enough to lower the curvature of the meniscus, the thickness of the deposited film  $d$  is that one that balance the viscous friction (proportional to  $\eta v/d$ ) and the gravity force ( $\rho g v$ ). It follows the formula [25]:

$$d = c(\eta \cdot v / \rho \cdot g)^{1/2} \quad (2.1)$$

where  $c$  is a constant which depends on the liquid used.

On the other side, when the withdrawal speed of the substrate and the viscosity are not high enough, as often happens under the experimental conditions usually used in sol-gel processes, the balance depends on the friction, the gravity force, and on the liquid-vapor surface tension  $\sigma_{LV}$ . This leads to the Landau-Levich relation [49]:

$$d = 0.94(\eta \cdot v / \sigma_{LV})^{1/6} (\eta \cdot v / \rho \cdot g)^{1/2} \quad (2.2)$$

In both relations the thickness of the film characteristically depends on the withdrawal speed. The faster the substrate speed, the thicker the film and the greater the overlap between the deposition and drying stages. Slower withdrawal speed allows more time for the solution to drain and produce thinner films.

The structure of the forming film is also influenced by the precursor used and by the evolution of the system during drying. The dilute solution is concentrated at the surface of the substrate owing to evaporation. The concentration of the species in

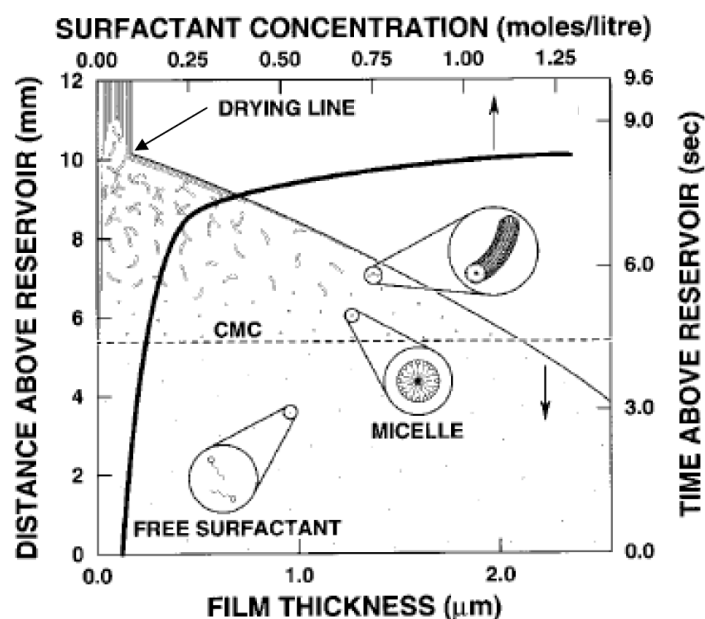
solution increases rapidly, decreasing the distance between oligomers and clusters eventually present and promoting a rapid condensation of such species.

At the gel point the forming network prevents the solution from flowing down, including it into the gel film formed on the surface of the substrate. During the extraction phase there is a competition between the evaporation of the solvent, which causes shrinkage of the film, and the condensation process, which strengthens the structure of the network and counteracts to this shrinkage. This competition permits a modulation of the film structure controlling the withdrawal speed or the atmosphere in which the film is extracted.

There is very often a critical thickness, beyond which the film cracks as a consequence of the differential shrinkage between the interface of the film with air and with the substrate [25].

In an early report of the formation of a silica-surfactant film by dip-coating [50] dipping solutions were prepared using prehydrolysed TMOS at pH = 3 in water, C<sub>16</sub>TAB or Triton-X-100 surfactant and a Coumarin-153 or Pyrene dye as fluorescent probes. The observed energy transfer kinetics of the probe molecules were consistent with a layered system of alternating surfactant bilayer and silica layers (about 10 Å thick).

In continuous films made by dip-coating from a dilute acidic solution of prehydrolysed TEOS in water-ethanol solution with addition of C<sub>16</sub>TAB surfactant [51], the evolution of the mesophase was observed in situ. A lamellar → cubic → hexagonal pathway was driven by continuing silica condensation during calcination. Cross-sectional TEM on the 2D hexagonal mesophase showed ordered regions at the interfaces parallel to the substrate and to the solution-air interface, with a disordered region of wormlike micellar structures sandwiched in between. A formation mechanism was suggested that involved the cooperative self-assembly of surfactant-silica micelles at the air-solution and substrate-solution interfaces (pathway c in Figure 2.2) at an early stage of deposition at or below critical micelle concentration (cmc). A scheme of the film cross-section is shown in Figure 2.4. It was proposed that the ordered regions grow toward the centre of the film as the surfactant concentration increases with evaporation. This formation process was later called evaporation-induced self-assembly and has been investigated especially for ionic surfactants as templates [35, 52].



**Figure 2.4:** Steady-state film thinning profile established during dip-coating with initial surfactant concentration  $c_0 < c_{mc}$  (after [51]). Surfactant concentration increases with distance above the reservoir surface. The vertical axes represent distance above the reservoir surface and the corresponding time. The surfactant concentration was calculated from the thickness profile assuming no surfactant volatility.

The formation of large-pore hexagonally ordered films with the non-ionic triblock copolymer template Pluronic P123 ( $EO_{20}PO_{70}EO_{20}$ ) and of cubically ordered films with Pluronic F127 ( $EO_{106}PO_{70}EO_{106}$ ) have been reported by Zhao et al. [53]. The films were deposited from prehydrolysed TEOS in acidic ethanol-water solutions where the majority component was ethanol. This synthesis system was investigated in detail by Alberius et al. stating that the chemical composition determines the film structure, which can be predicted by using water/alcohol/surfactant phase diagrams [54]. They have prepared continuous, transparent films with thicknesses of 200-600 nm.

### 2.5.3. Other methods of film growth

Cast films are those in which the synthesis solution is merely dropped onto a substrate and left to solidify [55, 56]. This method results in much thicker films, which are similar to monoliths. These films show optical birefringence.

Surfactant silica films can develop spontaneously at an interface submerged in the synthesis solution, e.g. from an acidic synthesis medium on to hydrophilic mica substrates [57] or hydrophobic graphite surfaces [58]. It is believed that the polymerization of a pre-organized liquid-crystal surfactant/silica assembly located at the surface directs the nucleation and growth of the mesoporous silica film. Such films can be grown without a solid substrate at the air-water interface [59]. It was shown that the mesoscopic order within the film grown at the air-water interface develops through a 'disorder to order transition' [60].

In a different approach to producing greater preferential organization of the mesostructured channels in surfactant-templated films grown on substrates [61] a continuous flow cell was used to impose a shear field upon the precursor solution, resulting in elongation of the ordered domains as well as preferential alignment within those domains in addition to the ordering effects of the substrate.

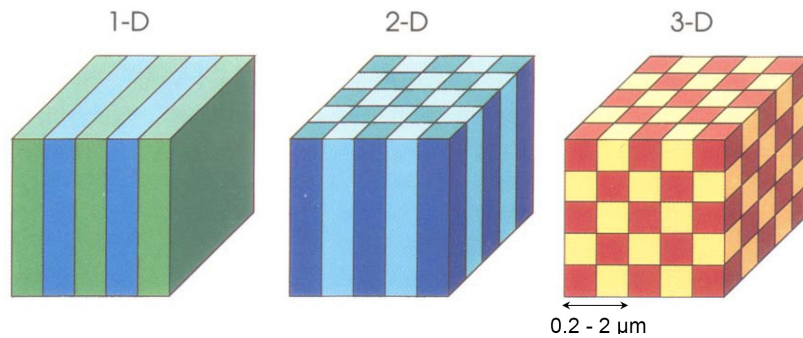
The first MCM-41 films consisting of oriented macroporous tubules with pores perpendicular to the substrate have been prepared using pulsed laser deposition and a series of post-hydrothermal treatments [62]. Another application of the principle of surfactant templating to create mesoporous thin films is the electrodeposition method [63].

## **2.6. Ordered macroporous materials: Photonic crystals**

Photonic crystals (PhCs) are materials that have a periodic variation in refractive index on a length scale that is comparable to the wavelength of light. The term crystal is known from solid state physics and points to the analogy between electronic crystals, investigated in solid state physics, and photonic crystals, investigated in electrodynamics. The periodic potential of the nuclei in semiconductors can lead to electronic band gaps, regions of energy where no allowed electron level exists. Analogously, PhCs exhibit a photonic band gap (PBG), a frequency range where the light cannot propagate through the structure [22, 23]. The periodicity of dielectrics with high refractive index contrast is necessary for the appearance of band gaps.



Photonic crystals can be categorized into one-, two-, and three-dimensional (Figure 2.5). In one-dimension such structures can be made by stacking alternating layers of different refractive index on top of each other. The interesting feature of such a multilayer is that it displays high reflectivity for light, of which the wavelength matches the periodicity of the Bragg reflector (one-dimensional photonic crystal).



**Figure 2.5:** Schematic illustration for one-, two-, and three-dimensional photonic crystals after [65].

Two-dimensional photonic crystals may be realized by fabricating regular arrays of pillars or by etching a regular pattern of holes in a substrate. These materials received a lot of attention because of their possible use in integrated optics, where they might be used to control and manipulate the flow of light in an essentially planar optical chip [64]. A goal of such devices is to make integrated circuits that combine both electronic functions and optical functions. Photonic crystal slabs are built from a layered structure that consists of a high refractive index film sandwiched inside a low refractive index medium therefore confining the light normal to the slab plane by total internal reflection. Bands are sometimes referred to as “air band” and “dielectric band”, distinguished by the localization of the modal power in analogy to the “conduction band” and “valence band” above and below the fundamental gap [65].

Most proposals for devices based on two-dimensional photonic crystals use a defect mode. Such a defect is made when the lattice is changed locally. As a result, light with a frequency inside the band gap can now find local state, i.e. position of the defect in the crystal. It is however still impossible for light to propagate in the surrounding photonic crystal material. By careful engineering of these defects,

structures have been proposed to guide light around sharp corners and to realize add-drop filters [66].

Another important application is the use of the so called superprism effect [67]. Close to the band gap, in which the light cannot propagate, solutions of Maxwell's equations exist that form a standing wave pattern. Frequencies very close to this bandedge have an enormous dispersion. A slight variation in frequency makes an enormous difference in the group velocity; that is the speed at which energy propagates through the crystal. One can use this dispersion to distinguish different frequencies of light. This can be of importance for many applications including telecommunication. For telecommunication, optical fibers are used that are superior over electrical cable because of their much larger bandwidth. However, to effectively use this bandwidth, devices are needed that can distinguish between different frequencies (each frequency that can be distinguished corresponds to a communication channel).

There is a variety of ways of making 2D photonic crystals, many of which have been adapted from the silicon microelectronics industry: electron beam lithography and reactive ion etching [68], anodic etching and growth [69], or vertical selective oxidation [70]. The “aspect ratio” of a 2D PBG material is defined as the ratio of the sample depth (vertical direction) to the lattice constant (transverse direction) [71]. In the field of 2D PhC slab waveguides [72], sol-gel methods are discussed sometimes, but for the practical realization of the systems, sputtered inorganic layers or spin-coated polymers have been preferred up to now. One example for the 2D photonic crystal is a slab waveguide perforated by a periodic array of air holes. The light propagates horizontally by interaction with the holes and all PhC effects occur in the slab plane. The refractive index contrast between core and substrate / superstrate determines the slope of the light line and therefore decisively influences the vertical radiation losses. In waveguide heterostructures with a relatively small refractive index contrast a deep etching into the substrate is required to limit propagation losses [73]. Large vertical index contrast raises the light line above the waveguide modes. Such PhC should guide the light without loss, except for residual adsorption and scattering.

One example for the 3D photonic crystal is a self-organized photonic crystal, such as an opal. An opal consists of a regular, hexagonal arrangement of nearly

spherical balls of amorphous silica. Other self-organized structures include colloidal photonic crystals formed from monodisperse polystyrene particles. They can be used as templates for the formation of regular arrays of titania, zirconia or alumina matrices with open-pore structures [74, 75]. The polystyrene template is then infiltrated with the metal alkoxide precursors that are typically used in sol-gel chemistry, and then removed upon calcination, resulting in a macroporous structure with a hexagonal pattern of spherical holes. One example of such inverse opals is a  $\text{TiO}_2$  inverse opal with skeleton structure [76].

## 2.7. PZT films and photonic crystals

A field of strong interest is the incorporation of active materials into the PhCs [77]. They can be switchable, nonlinear optical, or amplifying and can be incorporated as guests or as constituent of the PhC itself. The second way ensures high densities but requires solving the structuring problem for these active materials. For example, electro-optic PhCs would be very interesting. However, no material with high electro-optic coefficients and a possibility for structuring in PhCs has been identified up to now. Poled polymer films are one possibility to achieve such systems; however they could suffer under stability problems and the relatively small refractive index of the polymers. Inorganic ferroelectric materials represent an interesting alternative, but they are very difficult to be structured. Here, the sol-gel approach can be very useful because it offers a number of tuning possibilities. Lead zirconate titanate (PZT) films are ferroelectric and may represent a step towards inorganic electro-optical PhCs.

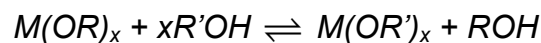
PZT is a ternary system of lead oxide ( $\text{PbO}$ ), zirconia ( $\text{ZrO}_2$ ) and titania ( $\text{TiO}_2$ ). Stoichiometrically it can be described as  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ , with  $0 < x < 1$ . Natural PZT crystallizes in a perovskite structure ( $\text{ABO}_3$ ) named after the mineral perovskite ( $\text{CaTiO}_3$ ) [78]. The symmetry centers of positive and negative charges in the primary cell do not overlap and a dipole is formed leading to the ferroelectricity. For the piezoelectric applications PZT on the phase boundary between the tetragonal and the rhombohedral structure is usually used ( $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ ). The growing of the PZT single crystals is constricted due to diffusion losses of  $\text{PbO}$  during growing and

often cracking during the phase transition from paraelectric to ferroelectric in the cooling stage. Therefore, PZT has found industrial application primarily as a polycrystalline ceramic material [78].

PZT thin films can be fabricated by two main classes of processes, physical deposition processes, such as RF magnetron sputtering [79], laser ablation [80], ion-beam sputtering [81], or solid-phase epitaxy [82], and chemical-based methods, such as metal organic decomposition [83] or metal organic chemical vapor deposition MOCVD [84, 85].

Sol-gel techniques for PZT [86, 87, 88, 89, 90, 91, 92] belong to the chemical processes. The sol-gel method for deposition of films involves the following steps after [93]:

- *Sol preparation:* In this step, the precursors are dissolved in a suitable solvent to form the sol. The precursors have the desired metal ions present as alkoxides or as inorganic salt prior to dissolution. Because of their good solubility and availability zirconium-n-propoxide, zirconium-n-butoxide, titanium-isopropoxide, and titanium-n-butoxide are usually used. As a lead precursor lead-acetate-trihydrate, lead-2-ethylhexanoate or lead-nitrate is favored, because lead-alkoxides are less stable. Although other alcohols have also been utilized, the solvent 2-methoxyethanol ( $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$ ) is most extensively used in the chemical synthesis of perovskite materials. Methoxyethanol lowers the hydrolysis sensitivity of starting reagents in the alcohol-exchange reaction [78]:



where OR is a reactive alkoxy group and OR' is the less reactive methoxyethoxy group.

Zirconium and titanium metal alkoxide react fast with water and alcohol leading to the formation of precipitates or gels, and this hinders the formation of hetero metallic complexes. Chelating ligands, such as acetylacetone (acac) are added, on the one hand also to lower the hydrolysis sensitivity, and on the other to adjust the reaction velocity of the educts to each other.

At this stage, the viscosity of the sol needs to be adjusted prior to gelation so that the deposited film will be dense and uniform. The prepared sol can be deposited on a substrate by spin-, dip-, or spray-coating techniques.

- *Gel formation:* Fluid sol transforms to a semi-rigid solid as a result of the polymerization of different groups present in the sol. The gel formation is determined by the rate of hydrolysis, condensation or polymerization. In the case of colloidal gels, the gelation is determined by electrostatic or steric interactions among various groups present in the sol.

- *Film formation:* The thin gelled film obtained after deposition is subjected to heat treatment for crystallization. The heat treatment can include two temperature plateaus, where the sample is kept at constant temperature for some time, one for film drying and one for removal of organic additives. Due to reactivity of the gel, the film crystallizes at much lower temperatures compared to other deposition techniques. The sol-gel technique is used to lower the process temperature, to control the chemical composition and to synthesize metastable materials, but films with good conformal coverage and selective deposition are difficult to achieve [93]. Also, the chance of contamination of the films is very high due to the presence of undecomposed groups in the gel.

Rapid thermal annealing (RTA) has been sometimes used in electronic device fabrication [93]. The method involves crystallization of the film by heating at a faster rate, holding for short time intervals at the annealing temperature, followed by rapid cooling. The short processing time involved in the crystallization inhibits the unwanted reactions such as dopant diffusion, interface reactions and phase transformations. It has also been applied for the preparation of the better quality PZT films [94, 95].