2 Template-Directed Synthesis of Structured Materials

2.1 Introduction - History

The design and synthesis of porous materials is a current challenge in solid-state chemistry. For many applications, the precise control of pore dimensions is the limiting factor. A porous material of good quality should provide the following properties [1]:

- A narrow pore size distribution,
- A readily tunable pore size in a wide range.

In addition, high chemical, thermal, hydrothermal and mechanical stabilities as well as appropriate particle size, high surface area and pore volume are required.

Depending on the predominant pore size, the solid materials are classified by IUPAC rules as [2]:

- microporous: pore size < 2 nm,
- mesoporous: 2 nm $<$ pore size < 50 nm,
- macroporous: pore size > 50 nm.

At present time, applications for macroporous compounds are relatively limited due to their low surface area and large non-uniform pores. In contrast, micro- and mesoporous materials, generally called nanoporous materials, are very suitable for size-specific applications in catalysis and separation [3].

The most famous class of microporous compounds are zeolites. Zeolites are naturally occuring or synthetic highly crystalline aluminosilicates with the general chemical formula $[M_{x/n}(AlO_2]_x \cdot [SiO_2]_y \cdot mH_2O$ [4]. Usually, synthetic zeolites are prepared under hydrothermal conditions from aluminosilicate gels or solutions, containing metal (alkali or alkaline earth cations) or organic ions (e. g. tetraalkyl ammonium ions) or molecules (e. g. amines) as templates. Zeolites exhibit an extremely narrow pore size distribution and the pore sizes (3 to 13 Å) reflect the template dimensions [5]. The role of the ions and molecules acting as templates is not understood completely. They direct the formation of a specific zeolite framework during the crystallization of the growing zeolite crystals during hydrothermal treatment. In addition, larger organic template molecules may also have a space-filling effect that inhibits the crystallization of thermodynamically more stable nonporous phases [6]. It is obvious, searching mesoporous materials, a zeolite-like synthesis with larger templating agents should also lead to larger pore sizes. With this strategy, it should be possible to transfer the specific advantages of zeolites, i. e. their crystallinity and sharply defined pore sizes, from the micro- to the mesoporous regime. But for a long time, all the attempts to enlarge the pore size distinctly beyond the 13 Å limit failed.

The break-through came in 1992, when researchers of Mobil Oil Research and Development presented a new concept in the synthesis of large pore silicates [7,8]. The template is no longer a single organic molecule or metal ion, but rather a regular liquid-crystalline arrangement of tenside molecules formed by self-assembly. These new materials, called M41S, are characterized by pore diameters that can be adjusted in the wide range between 15 Å and 100 Å. The pore size distribution is nearly as sharp as that of conventional, zeolite-type materials. After calcination at 500°C to burn off the template molecules, a material with extremely high surface area was obtained. Of particular interest is MCM-41, which has hexagonally-packed cylindrical pore channels containing surface areas greater than 1200 m^2/g and uniform pore sizes that can be tailored from 20 to 100 Å in diameter. In addition to the hexagonal form, also cubic (MCM-48) and layered (MCM-50) phases were obtained [9].

It was proposed, that a liquid crystal templating mechanism is operative in the synthesis of these mesoporous materials [7,8]. Typically, long-chain quaternary ammonium ions $C_nH_{2n+1}(CH_3)_3N^+$ (n=8-16) were used as surfactants. These ions are known to form micelles or liquid crystal phases in aqueous solutions, thus, the silicate or aluminosilicate species condense and polymerize around the hydrophilic parts of the surfactant aggregates to form the walls of the porous solid, at the same time enclosing the template molecules. The liquid crystal template mechanism is strongly supported both by the fact, that the alkyl chain length n of the template influences the pore size and that cubic and layered crystallisation products corresponding to cubic and lamellar liquid crystal phases were found.

But further studies provided evidence, that no pre-existing liquid crystal phase is required for the formation of M41S silicates. Instead, a dynamic model, the cooperative templating mechanism, has been proposed [10-13]. The basic idea is that the inorganic species promote the formation of the liquid crystal phase below the critical micelle concentration. Prior to the addition of the inorganic precursor, the surfactant molecules are in a dynamic equilibrium of different forms of micelles and single molecules. Upon the addition of the inorganic species, an inorganic-organic mesophase is formed. The polymerizing inorganic precursor leads to a continous change of the charge density at the surfactant-inorganic interface, thus, the system responds by steadily re-arranging the mesophase morphology. As a consequence, each surfactant can act as a template for the formation of several different mesostructures, depending on the reaction conditions [10].

2.2 The Sol-Gel Process

The conventional synthesis of ceramic materials involves the direct reaction of a mixture of powders. For these solid state reactions, high temperature and small particle sizes are needed to provide high mobility of the reactants and maximum contact surface between the particles. Several difficulties have to be considered: Thermodynamic factors often prevent, that metastable phases are obtained, control over the size and morphology of solid particles is almost impossible, the stoichiometry is difficult to reproduce, impurities of reactants, poor chemical homogeneity and the formation of undesirable phases.

In the field of ceramics, chemistry has two major roles. It has to provide not only methods for the synthesis of novel ceramics, but also techniques for the fabrication of these materials into useful shapes. Thus, new synthesis methods have been developed [14,15].

Among these chemical methods like coprecipitation (formation of intermediate precipitates with the correct stoichiometry), reactions in molten salts (molten salts as solvent), hydrothermal techniques, polymer pyrolysis (synthesis of a polymeric compound, which is then fabricated into a shape and pyrolysed to the ceramic), topochemical and ion-exchange reactions, especially sol-gel processes have been extensively studied [16-24]. Starting from molecular precursors, an oxide network is obtained via inorganic polymerization reactions. Since these reactions occur in solution, sol-gel processing broadly describes the synthesis of inorganic oxides by wet chemistry methods. Compared to the conventional powder route, sol-gel processes allow a better control from the molecular precursor to the final product, offering possibilities in the tailoring of materials which result in high purity, high homogenity, low temperature preparations, size and morphological control of the particles, and the opportunity for the preparation of new crystalline and non-crystalline solids.

In general, the sol-gel procedure (**Fig. 2.1**) consists of the following steps [25]:

1. Preparation of a homogeneous solution either by dissolution of metal organic precursors in an organic solvent that is miscible with water, or by dissolution of inorganic salts in water.
2. Converting the homogeneous solution to a sol by treatment with a suitable reagent (pure water or water with either HCl, NaOH or NH_4OH).
3. Aging: The sol changes into a gel by self-polymerization.
4. Shaping the gel to the finally desired form (thin films, fibers, spheres…).
5. Converting (sintering) the shaped gel to the desired ceramic material generally at temperatures around 500°C.

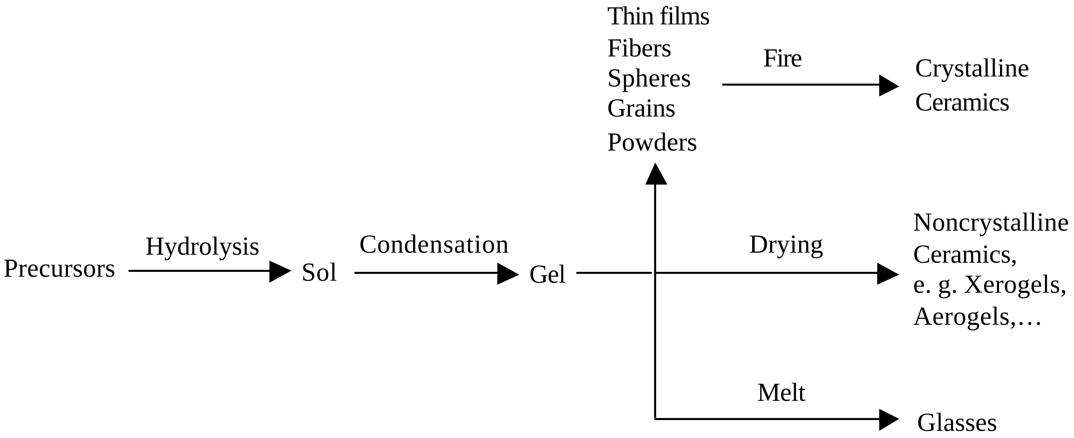

Fig. 2.1: General proceeding in the sol-gel synthesis of ceramic materials.

The most important step in this route is the formation of an inorganic polymer by hydrolysis reactions, i. e. the transformation of the molecular precursor into a highly crosslinked solid. Hydrolysis leads to a sol, a dispersion of colloidal particles (solid particles with diameters of 1-100 nm) [18] and condensation forms a gel, an interconnected, porous network filled with a liquid phase. This transformation is called the sol-gel transition [21]. During removal of the pore liquid under hypercritical conditions, the network does not collapse and aerogels [26] are produced. When the pore liquid is removed by evaporation under normal conditions, shrinkage of the pores occurs and a xerogel is formed.

One of the highly attractive features of the sol-gel process is the possibility to obtain the final ceramic materials in different forms like fibers, coating, spheres, irregular aerogels and others by the control of the process conditions (cf. **Fig. 2.1**).

The sol-gel processes can be classified into two different routes depending on the nature of the precursors: a) the precursor is an aqueous solution of an inorganic salt or b) a metal organic compound [16].

The inorganic route involves the formation of condensed species from aqueous solutions of inorganic salts by adjusting the pH, by increasing the temperature or by changing the oxidation state. But this method has several disadvantages. The aqueous chemistry of transition metal ions can be rather complicated because of the formation of a large number of oligomeric species, depending on the oxidation state, the pH or the concentration. The role of the counter anions, which are able to coordinate the metal ion giving rise to a new molecular precursor with different chemical reactivity towards hydrolysis and condensation, is almost impossible to predict. These ions can influence the morphology, the structure and even the chemical composition of the resulting solid phase. Also the removal of these anions from the final metal oxide product is often a problem. In addition, the formation of a gel rather than a precipitate from inorganic precursors is a very complicated process [16] depending on pH, concentration, addition mode, order of mixing the reactants, temperature, chemical composition of the aqueous solution and even the geometry of the reaction vessel plays a role.

In order to avoid all these problems, in many cases metal alkoxides are used for the preparation of metal oxides [27-29]. Metal alkoxides are strongly preferred as precursors, because they are soluble in organic solvents providing high homogenity, they can easily be converted to the corresponding oxide, they are nearly known for all elements [25,30-33]. The disadvantages are that only a few are commercially available and that they are in general very expensive.

The sol-gel process involving metal alkoxides is normally based on hydrolysis and condensation reactions. These nucleophilic reactions can be described as the substitution of alkoxy ligands by hydroxylated species XOH as follows [16]:

$$M(OR)_z + y\,XOH \xrightarrow{-\,y\,ROH} [M(OR)_{z-y}(OX)_y] \xrightarrow{\Delta T} MO_x\,,$$

where X stands for hydrogen (hydrolysis), a metal atom (condensation), or even an organic or inorganic ligand (complexation). Finally, heat treatment of the wet gel results in the formation of the corresponding metal oxide. In this step, the amorphous network is first dried and then solidified.

Chemical aspects play an important role in studying and controlling the sol-gel process. The chemical reactivity of metal alkoxides towards hydrolysis and condensation depends mainly on the electronegativity of the metal atom, its ability to increase the coordiantion number, the steric hindrance of the alkoxy group, and on the molecular structure of the metal alkoxides (monomeric or oligomeric) [16]. The amount of added water in the hydrolysis step and how the water is added, determines, whether the alkoxides are completely hydrolyzed or not and which oligomeric intermediate species are formed. Additional parameters are the polarity, the dipole moment, and the acidity of the solvent [20]. So the large amount of different reaction parameters as well as the simultanous occurrence of hydrolysis and condensation reactions, still prevents reliable methods to control completely the sol-gel transformation.

2.3 Structured Metal Oxides and Organic-Inorganic Composites

The principle of template synthesis has already been known since the sixties. But in the last few years the interest increased rapidly because of surprising discoveries in the field of supramolecular chemistry. The progress in the synthesis of supramolecular assemblies is strongly connected with the introduction of template ions or molecules. The template acts as a structure-directing agent favoring the connection of the decisive bond. As guest, the metal ion or the molecule coordinates a ligand or host molecule, which is thereby brought into a suitable conformation for the formation of a specific product [34].

For the synthesis of mesoporous media, long-range ordered molecular arrays were used as templates instead of single molecules. The concept is based on the self-assembly of surfactants into micelles or into lyotropic liquid crystal phases with highly symmetric architectures [35]. Upon addition of a precursor molecule, condensation and polymerization at the surfactant-precursor interface gives rise to the corresponding organic-inorganic composite, i.e. the structure phase of the template assembly is imprinted on the inorganic framework. One important point in the preparation of such mesostructures is the adaption of the template headgroup to that of the inorganic precursor. Several different interactions at the interface between the organic and inorganic phase are possible [36]: i) ionic interactions, ii) hydrogen bonding and, iii) covalent bonds.

Cationic surfactants were used for the structuring of negatively charged inorganic species, and vice versa. Interestingly, also organic-inorganic combinations with identically charged partners are possible, but then a counter-charged ion has to mediate the mesostructure. Mesostructures can also be formed without participation of charged building units. Using neutral template molecules, the interaction at the organic-inorganic interphase can either occur through hydrogen bonds or covalent connections.

In 1992, researchers at Mobil Research and Development Corporation reported the exciting discovery of the novel family of molecular sieves called M41S [7,8]. Many research groups all over the world since exploited this technique of supramolecular templating to produce not only mesoporous silicate and aluminosilicate materials but also mesostructured metal oxides [1,3,36-38,91]. The extension of this liquid-crystal templating mechanism into the field of transition metal oxide synthesis represented a major step forward towards tailoring catalytic, electronic and magnetic properties of these redox-active materials.

Since one of the most important aspects in the synthesis of mesoporous materials is the interaction at the interface between organic and inorganic phase, three basic models were proposed (**Fig. 2.2**). The *charge matched templating approach* is based on the compensation of the ionic charges between the surfactant head groups and the inorganic species. Hydrogen-bonding and van der Waals interactions are present between non-charged organic surfactants and inorganic precursor, leading to the *neutral templating approach*. The *ligand-assisted templating approach* used ligation of the surfactant head group directly to the metal alkoxide prior to hydrolysis and condensation [38].

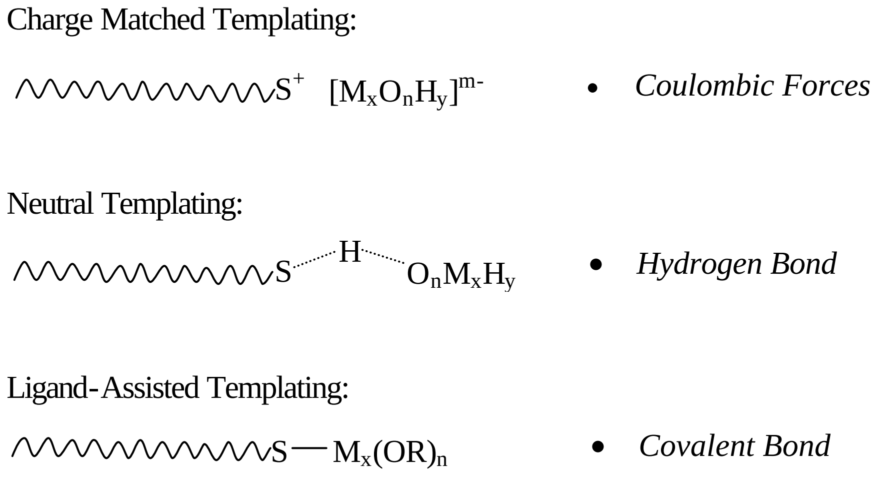

Fig. 2.2: A schematic overview of the three liquid crystal templating models [39].

The first reports on the preparation of non-silica based mesostructures were published in 1994 by Stucky and co-workers [10,11,40]. Both, cationic and anionic surfactants were used in the presence of water soluble inorganic species. Control of the charge, geometry, and association of the molecular inorganic species in solution by adjusting the pH, cosolvent, counterions, and temperature opened the possibility to direct the formation of a particular phase [11]. But the materials obtained, except antimony, tungsten, and lead oxides, formed rather lamellar than hexagonal phases, and they were all thermally unstable and collapsed upon surfactant removal.

Many attempts have been made to apply this charge density matching approach for the synthesis of mesostructured metal oxides. Unfortunately, the use of methods based on electrostatic interactions generally met limited success, because most of the obtained phases were lamellar and thermally unstable. Both, lamellar phases as well as the three dimensional structures did not withstand any surfactant removal technique. One possible reason for the lack of stability is the low degree of condensation of the inorganic walls.

So the next step forward involved a neutral templating route for the preparation of mesoporous molecular sieves, based on hydrogen-bonding interactions and self-assembly between neutral surfactants and neutral inorganic precursors. Pinnavaia and co-workers used primary amine templates [41] or polyethylene oxide surfactants [42] and alkoxides as precursors for the synthesis of mesoporous silicates and mesoporous alumina [43]. In contrast to electrostatic templating pathways, the use of neutral templates allows for the facile recovery of the template by simple solvent extraction or evaporation methods.

A further extension in the field of template-directed synthesis of transition metal oxides followed in 1995, when Ying and co-workers introduced the ligand-assisted templating approach, based on the dative coordinate bond interactions between the template molecules and the inorganic precursor units [3,38,39,44-46].

In general, the procedure involves selective hydrolysis and condensation of metal alkoxides, chemically linked to a long-chain amine surfactant molecule prior to the hydrolysis step. It is important, that the surfactant-precursor bond is strong enough to resist hydrolysis, but at the same time allowing easy chemical removal without damage to the mesostructure after aging. The formation mechanism is still not fully understood, since it does not require preformed micelles. It is unclear, how and at what stage of the synthesis self-assembly occurs [45]

These new family of mesoporous transition metal oxide molecular sieves, termed M-TMS1 (M=Nb, Ta, Ti, Zr), has remarkable thermal stabilities, consist of a high surface area and hexagonally packed array of inorganic tubules [38]. By varying the synthesis parameters like surfactant-to-metal ratio or surfactant chain length, also layered and cubic phases were achieved [39]. In addition, short-chain amines [47] or templates with a second hydrophilic functional group can be applied to generate microporous transition metal oxides with pore sizes of less than 20 Å [48].

The big limitation of the ligand-assisted templating approach is the fact, that up to now only the synthesis of mesoporous metal oxides was possible by starting from transition metal alkoxides and amine template molecules. Covalent bonding to atoms like oxygen and sulfur is still to be developed.

The syntheses of these mesoporous non-silica materials were carried out generally in aqueous solutions, using metal alkoxides or inorganic salts as precursors and low molecular weight surfactants for the assembly of the mesostructures. Recently, a new, generalized method for the synthesis of large-pore mesoporous metal oxides with semicrystalline frameworks was published by Stucky and co-workers [49,50]. Compared to the pore sizes of the M41S materials (15-100 Å) and M-TMS1 (20-40 Å), the novel material exhibits large pores up to 140 Å. Amphiphilic poly(alkylene oxide) block copolymers were used as structure-directing agents and inorganic salts, rather than alkoxides, as precursors. The special feature of this procedure is the use of the inorganic precursors in predominantly nonaqueous media. Metal chlorides were reacted with an alcohol solvent to form metal-oxygen-chlorine networks [50]. The calcined samples showed no detectable chlorine, the inorganic walls only consist of metal and oxygen. It is proposed, that the mechanism combines block copolymer self-assembly with complexation of the inorganic species [49].

Since the template-directed synthesis is a rapidly growing field, a lot of different structured metal oxides and inorganic-organic composites were reported since 1992. **Table 2.1** gives a selected overview of metal oxides synthesized with organic template molecules. Alumina and silica, as well as metal oxo phosphates, metal oxo sulfates, metal sulfides, and mixed metal oxides are not listed.

Table 2.1: Template-structured metal oxides and inorganic-organic hybrid materials.

Metal oxide	Precursor	Template	Mesostructure	Literature
Antimony (V) oxide	$K[Sb(OH)_6]$	Quaternary alkylammonium salts	Cubic and hexagonal	[11]
	Antimony(III) n-butoxide	Polystyrene spheres	Macroporous	[51]
Chromium oxide	$K_2Cr_2O_7$	Quaternary alkylammonium salts	Lamellar	[52]
	CrO_3	Quaternary alkylammonium salts	Lamellar	[53]
Hafnium oxide	$HfCl_4$	Amphiphilic poly(alkylene oxide) block copolymers	Large-pore mesoporous	[49] [50]
Iron oxide	$FeCl_2 \cdot 4H_2O$	Hexadecylsulfonic acid	Maybe hexagonal, but unstable	[40]
	Fe(II) and Fe(III) salts	Sodium n-alkyl sulfates	Lamellar	[54]
	$FeCl_3$	Sodium n-alkyl sulfates	Lamellar	[55]
	Iron(III) ethoxide	Polystyrene spheres	Macroporous and bulk material	[51]
Lead oxide	$Pb(NO_3)_2$	Alkyl sulfonates	Hexagonal and lamellar	[11]
	$Pb(NO_3)_2$	Hexadecylsulfonic acid	Hexagonal and lamellar	[40]
Manganese oxide	$Mn(OH)_2$	Quaternary alkylammonium salts	Mesoporous	[56]
Molybdenum oxide	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Quaternary alkylammonium salts	Lamellar	[40]
	Molybdenum(V) ethoxide	Dodecylamine	Toroids	[57]
	$Na_2MoO_4 \cdot 2H_2O$ or H_2MoO_4	Quaternary alkylammonium salts	Lamellar	[58]
	Molybdic acid	Carbon nanotubes	Nanotubes	[59]
	Na_2MoO_4 or H_2MoO_4	Quaternary alkylammonium salts	Lamellar	[60]
	H_2MoO_4	Carbon Nanotubes	Nanorods and nanotubes	[94]
Niobium oxide	Niobium ethoxide	Primary amines	Mesoporous	[44] [45]
	$NbCl_5$	Amphiphilic poly(alkylene oxide) block copolymers	Large-pore mesoporous	[49] [50]
	Niobium ethoxide	Diamines	Microporous	[48]
	Niobium ethoxide	Short-chain amines	Microporous	[47]
	$K_4Nb_6O_{17}$	Tetra-n-butylammonium hydroxide/MgO	Porous	[61]
	Niobium ethoxide	Tetradecylamine	Mesoporous	[62]
	Niobium ethoxide	Long-chain alkyl amines with salt water	Macroporous	[90]
	$K_4Nb_6O_{17}$	Tetra-n-butylammonium hydroxide	Tubules	[93]

Rhenium dioxide	Methyltrioxo-rhenium(VII)	Long-chain alkylamines	Nanostructured	[63]
Ruthenium oxide	$RuCl_2$	Carbon nanotubes	Nanorods and nanotubes	[94]
Tantalum oxide	Tantalum ethoxide	Primary amines	Mesoporous	[39]
	$TaCl_5$	Amphiphilic poly(alkylene oxide) block copolymers	Large-pore mesoporous	[49] [50]
Titanium oxide	Titanium isopropoxide	Tetradecylphosphate	Mesoporous	[64]
	$TiCl_4$	Amphiphilic poly(alkylene oxide) block copolymers	Large-pore mesoporous	[49] [50]
	Titanium isopropoxide	Dodecyl phosphate	Mesoporous	[62]
	$TiCl_4$	Sodium dodecyl phosphate or Cetyltrimethylammonium bromide	Lamellar	[65]
	Titanium alkoxides	Tetramethylammonium hydroxide	Nanocrystals with different morphologies	[66]
	Titanium butoxide	Monodispersive polystyrene particles	Nanoporous	[67]
	Titanium isopropoxide	Alumina membrane	Tubules and fibers	[68]
	Titanium isopropoxide	Chitosan	Mesoporous	[69]
	Titanium isopropoxide	Polyacrylic acid	Mesoporous	[70]
	Titanium isopropoxide	Cetyltrimethylammonium bromide and ethylene glycol	Mesoporous	[71]
	Titanium isopropoxide	None	Nanotubes	[72] [73]
	Titanium ethoxide	Polystyrene spheres	Macroporous	[51]
	Titanium isopropoxide	Long-chain alkyl amines	Mesoporous	[89]
	Titanium isopropoxide	Trans-(1R, 2R)-1,2-Cyclohexanedi-(11-aminocarbonylundecylpyridinium)-hexafluorophosphate	Hollow fibers	[92]
	Titanium isopropoxide	Octadecylamine	Wormhole-like mesopores	[95]
	Titanium ethoxide	Block copolymer	Mesoporous	[96]

Tungsten(VI) oxide	$(NH_4)_6H_2W_{12}O_{40}$	Quaternary alkylammonium salts	Hexagonal	[11]
	$(NH_4)_6H_2W_{12}O_{40}$	Quaternary alkylammonium salts	Predominantly hexagonal	[40]
	WCl_6	Amphiphilic poly(alkylene oxide) block copolymers	Large-pore mesoporous	[49] [50]
	H_2WO_4	Quaternary alkylammonium salts	Keggin clusters	[60]
	WCl_6	Alumina membrane	Fibrils	[68]
	Sodium metatungstate	Cetyltrimethylammonium hydroxide	Keggin clusters	[74]
	Tungsten(V) ethoxide	Polystyrene spheres	Macroporous	[51]
Vanadium oxide	Sodium metavanadate	Carbon nanotubes	Nanotubes	[59]
	V_2O_5	Quaternary alkylammonium salts	Lamellar	[60]
	Ammonium vanadate	Cetyltrimethylammonium chloride	Hexagonal and lamellar	[75]
	Vanadium isopropoxide	Dodecylamine	Hexagonal and lamellar	[76]
Yttrium oxide	$Y(NO_3)_3 \cdot 6H_2O$	Sodium dodecyl sulfate	Hexagonal and lamellar	[77]
Zirconium oxide	$ZrCl_4$	Amphiphilic poly(alkylene oxide) block copolymers	Large-pore mesoporous	[49] [50]
	Zirconium propoxide	Cetyltrimethylammonium bromide	Mesoporous	[78]
	Zirconyl chloride octahydrate	Cocamidopropyl betaine	Hexagonal	[79]
	$ZrOCl_2$	Sodium hexadecanesulfonate	Lamellar	[80]
	Zirconium propoxide	Carbon nanotubes	Nanotubes	[81]
	Zirconium sulfate	Long-chain primary amines or quaternary ammonium salts	Hexagonal and lamellar	[82]
	Zirconium sulfate	Amines and ammonium salts	Hexagonal and lamellar	[83]
	Zirconium alkoxides	Long-chain carboxylic acids	Meso- and microporous	[84]
	Zirconium propoxide	Many anionic and neutral amphiphiles	Hexagonal and lamellar	[46]
	$ZrOCl_2 \cdot 8H_2O$	Cetyltrimethylammonium chloride	Mesoporous	[85]
	Zirconium isopropoxide	Dodecylamine	Lamellar - hexagonal - cubic	[86]
	Zirconium propoxide	Many anionic surfactants	Mesoporous	[87]
	$ZrOCl_2 \cdot 8H_2O$	Cetyltrimethylammonium chloride	Mesoporous	[88]
	Zirconium n-propoxide	Polystyrene spheres	Macroporous	[51]

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