Synthesis and functionalization of mesoporous silica and its application as a support for immobilized metal catalysts

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Synthesis and Functionalization of Mesoporous Silica and its Application as a Support for Immobilized Metal Catalysts

A dissertation submitted to the

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Zusammenfassung


Die Benzylchloridgruppe wurde substituiert mit dem Ziel einen immobilisierten EDTA-Liganden zu erzeugen. Die Methode beinhaltete drei weitere Modifikationschritte an der Oberfläche des funktionalisierten Materials. Wegen unvollständig
ablaufenden Reaktionen während der einzelnen Schritte war es nicht möglich, den gewünschten Liganden herzustellen.


Summary

Immobilization of molecular homogeneous catalysts is a promising approach to combine the advantages of heterogeneous and homogeneous catalysts. One way to achieve immobilization is to bind ligands covalently to support surfaces and to use these ligands to complex metal ions. This was the chosen procedure in this work.

Mesoporous silica materials were used as a solid support. Materials of the desired quality are not yet commercially available. Therefore, they were synthesized. The processes during the syntheses were followed spectroscopically. The insight gained helped to develop a methodology to synthesize mesoporous M41S materials with any pore diameter in the range of 3 to 10 nm. These materials with narrow pore size distributions, large specific surface areas and pore volumes are ideal supports for the immobilization of molecular catalysts.

The immobilization of homogeneous catalysts was mostly performed in two steps. First, the silanol groups on the surface of the mesoporous M41S materials were reacted with silane compounds. After this functionalization of the surface, the silica material is covered with the organic residue of the silane compound. In this way functionalization with benzylchloride and 3-aminopropyl-groups was achieved. Both species can be used as a linker for further surface modifications to obtain ligands for catalytically active metal ions.

The benzylchloride was substituted to prepare an EDTA-like ligand. The method involved three further modification steps after the surface functionalization with benzylchloride. Because of incomplete conversion of each of these steps the desired immobilized ligands could not be prepared.

The M41S, functionalized with 3-aminopropyl groups on its surface, was used for coupling reactions with natural amino acids via amide bonds. This approach worked well and was implemented with an automated peptide synthesizer. Histidine and
glutamic acid were immobilized in order to prepare very simple mimics of the MMO enzyme, which is able to hydroxylate hydrocarbons very selectively. The immobilized amino acids were treated with iron salts and a specific complexation was observed. These heterogeneous biomimetic catalysts were tested for cyclohexane oxidation with $\text{H}_2\text{O}_2$. They were active at very mild conditions, but the selectivity implied that the reaction mechanism differs from that in the enzyme.

Alternatively, ligands with silane substituents were synthesized first and then bound covalently to the silica surface. These immobilized ligands were used to complex manganese and ruthenium ions. These materials were tested as catalysts for styrene epoxidation with several oxidants. The materials were active but mainly due to the leaching of metal ions into the reaction solution.
Chapter 1

Introduction

"A substance able to increase the rate of a chemical reaction without itself being consumed or changed by the reacting chemicals is called a catalyst. The action of a catalyst is called catalysis." [1]

"Catalysts may be gases, liquids, or solids. In homogeneous catalysis, the catalyst is molecularly dispersed in the same phase (usually gaseous or liquid) as the reactants. In heterogeneous catalysis the reactants and the catalyst are in different phases, separated by a phase boundary. Most commonly heterogeneous catalysts are solids and the reactants are gases or liquids” [1]

The homogeneous or heterogeneous nature of a catalyst has a big influence on the scientific approach of research in the two fields and also on the ongoing processes during catalysis. Homogeneous catalysts are normally molecular species that can be characterized in detail with spectroscopic techniques as NMR and MS. Structure - activity relationships can be derived from exact structure analysis and catalytic tests. Heterogeneous catalysts are often non crystalline solids. The catalytically active sites must be on the surface of the solid otherwise they would not be in contact with the gas or liquid. For these two reasons it is often very difficult to evaluate the exact structure of the catalytically active site in heterogeneous catalysts.

On the other hand, process design is normally much easier with heterogeneous catalysts. Since they are in a separate phase they can easily be separated from the
reaction mixture and it is much easier to implement continuous processes with heterogeneous catalysts. Already that shows that the advantageous properties of homogenous and heterogenous catalysts should be combined. One way to do that is to immobilize well defined molecular catalysts on the surface of an inert support, in other words to heterogenize a homogeneous catalyst.

1.1 Mesoporous silica supports

The inert support that is used for heterogenization of catalytically active species should fulfill the following requirements:

- it should not influence or harm the structure of the catalytically active species
- it should be easy to immobilize the species on the surface of the support
- it should be chemically and mechanically stable under reaction conditions
- it should have a large specific surface area accessible to the reaction media
- it should have a particle size and shape that allows filtration
- it should be non toxic and cheap to produce and dispose of

Porous silica material is one class of materials that fulfills all these requirements. Silicas are chemically inert but allow irreversible surface modification by reaction of the surface silanol groups. They are very stable under many reactions conditions. They can be prepared by different methods with surface areas up to 1300 m²/g, while maintaining good particle morphology. Finally they can be synthesized from cheap natural feedstocks and are not an environmental hazard.

Silica is a compound of silicon and oxygen (SiO₂) and can be crystalline or amorphous. Quartz is the most abundant crystalline form of silica. All crystalline and amorphous silicas have in common that they consist of three-dimensional networks of SiO₄ tetrahedra (Fig. 1.1). It is clear that many secondary structures can be constructed from these units.

The specific surface of crystalline quartz is very small because only a very small fraction of the silicon and oxygen atoms can be accessed from a surrounding media. The vast majority is inside the crystal. Therefore quartz is not suited as a support for heterogeneous catalysts. The fraction of atoms on the external surface and thereby the specific surface area can be enlarged by decreasing the particle size. This method is limited by the fact that very small particles are difficult to handle
1.1. MESOPOROUS SILICA SUPPORTS

Figure 1.1: SiO$_4$ tetrahedra and possible modes of connectivity.

and to filter. Therefore the only possibility to combine large specific surface areas with a practical particle size is given by porous materials. Porous materials can be imagined as micrometer-sized sponges.

An important characteristic of porous materials is the diameter of the pores. Silica materials with any defined pore diameter down to 0.3 nm can be prepared. Since the pore diameter is very important for the use of a porous silica as support, porous materials are often classified on the base of their pore diameter. IUPAC defined [2] the following three classes of porous materials (Fig. 1.2):

- pore diameter $< 2$ nm $\rightarrow$ microporous materials
- $2$ nm $\leq$ pore diameter $\leq 50$ nm $\rightarrow$ mesoporous materials
- pore diameter $> 50$ nm $\rightarrow$ macroporous materials

In Figure 1.2 the pore diameter of three representative classes of silica materials with micro-, meso- and macropores are depicted. Zeolites have micropores. They are crystalline and have therefore very well defined pore diameters. Silica gel with macropores is purely amorphous and its pores vary considerably in diameter. Mesoporous silicas are in between these two materials, both in pore diameter and in distribution of pore diameters. Well ordered mesoporous silica materials are promising
supports for catalysts because they have pores that are large enough to immobilize molecular catalysts (e.g. metal complexes) and still the uniformly sized tunable pores have the potential to induce shape selectivity or hydrophobicity in the local environment of the active center.

1.2 M41S materials

Well ordered mesoporous silica materials were first synthesized in 1992 [3, 4]. The so called M41S materials are prepared with micelles of quaternary ammonium detergents as template (Fig. 1.3). The amphiphilic hexadecyl-trimethylammonium chloride or bromide is used as template (Fig. 1.4). The micelles form in the presence of molecular silicate species. During several hours up to several days at elevated temperatures (typically 100°C) the silicate species condense and form an organic-inorganic mesophase. In the final step the organic material is removed at high temperature (above 500°C) (so called calcination), or with template extraction in an organic solvent.

Depending on the amount of template different organic-inorganic mesophases form [4, 5]. With increasing relative amounts of detergent molecules hexagonal, cubic and lamellar (Fig. 1.5) organic-inorganic mesophases form. The hexagonal phase is re-
1.2. M41S MATERIALS

![Diagram of M41S material formation](image)

**Figure 1.3:** Formation of M41S materials.

![Hexadecyl-trimethylammonium detergent](image)

**Figure 1.4:** Hexadecyl-trimethylammonium detergent.

ferred to as MCM-41, the cubic phase as MCM-48 and the lamellar phase as MCM-50.

The nature of these phases was determined by means of XRD. Even though M41S silica materials are not crystalline the pores are ordered and give characteristic reflections in the low angle range of XRD (Fig. 1.6). After the removal of the template from the hexagonal mesophase an MCM-41 material with straight cylindrical pores is obtained. The hexagonal honeycomb arrangement of mesopores in MCM-41 can be seen in TEM (Fig. 1.7). The cubic MCM-48 material has a three-dimensional pore system after the removal of the organic template. Both materials have very large specific surface areas ($\sim 1000 \ \text{m}^2/\text{g}$) and pore volumes (0.5 - 1.0 cm$^3$/g). The lamellar MCM-50 does not give any ordered porosity after the removal of the template because the sandwich-like structure collapses.

Besides the geometry of the channel system, also the pore diameter of M41S material can be varied. Two methods were used to achieve that. Already in the first publication [4] the non-amphiphilic mesitylene was used to expand or swell the organic template and thereby enlarge the pore diameter. The so-called swelling agents are incorporated in the hydrophobic core of the templating micelles. Pores with diame-
CHAPTER 1. INTRODUCTION

Figure 1.5: Organic-inorganic phases of M41S materials.

Figure 1.6: XRD of hexagonal MCM-41.

ter up to 10 nm can be prepared with this method [6]. The problem is that swelling allows more flexibility to the templating micelles. Therefore pores with ordered pore diameters, but no well-ordered phase symmetry are obtained.

Alternatively the length of the hydrophobic tail of the amphiphilic detergent molecules (Fig. 1.4) can be varied to adjust the pore diameter to a certain value. The use of alkyl-trimethylammonium detergent molecules with C8 - C18 hydrocarbon chains enables the synthesis of hexagonally ordered MCM-41 materials with pore diameters between 1.5 and 4 nm [7]. However, this concept can not be extended further. Cylindrical templating micelles can only be formed if the ratio of the volume of hydrophobic tail and the area of the polar head group of an amphiphilic molecule is within a certain range [8].
1.3 Other ordered mesoporous materials

The names of microporous and mesoporous silica materials contribute a problem. They can not easily be used as a description of the structure. They were chosen by the institution which discovered the respective material. Thus codes MCM-41, MCM-48 and MCM-50 mentioned before stand for Mobil Composition of Matter 41, 48 and 50. The numbers are just consecutive identifiers that were given to these materials. A problem is that, even though these three materials are structurally related (as their codes imply), the material MCM-22 for example has nothing in common with the other three materials. Even worse is that there are materials which are almost identical to MCM-41 but have completely different codes. Therefore the literature of the field is difficult to understand or even confusing if the reader is not up to date.

The following sections intend to give an overview of the most important mesoporous materials that were described since 1990.

**FSM-16**

This material is structurally very similar to MCM-41. It was discovered independently by a Japanese group [9] shortly before the M41S class of materials. The main difference is that it is prepared from crystalline kanemite as silicon source. The sheet silicate is intercalated with surfactants of the alkyltrimethylammonium type. The 16 in the code indicates the number of C atoms in the surfactant tail.
KSW-2
This material was prepared by the same Japanese group as FSM-16 [10]. It is also prepared with kanemite and alkyltrimethylammonium surfactants. The difference is that slightly acidic conditions are used. The obtained material has ordered straight square-shaped one-dimensional channels.

HMS
This material has similar pore characteristics as MCM-41. It is prepared from non-ionic tertiary amine detergents [11]. The structure is less ordered than in MCM-41. One advantage of this material is that the organic template can be easily extracted.

KIT-1
This material was described by a group at the Korean advanced Institute of science and Technology [12]. The material is prepared with cationic detergents, sodium silicate solution and salts. It structurally resembles HMS.

LMU
The material LMU was described by a Group at the Ludwigs Maximilian Universitaet in Muenchen [13]. The material is prepared with micelles of cationic detergents as template. The structure has no defined phase symmetry but the material has pore characteristics comparable with MCM-41.

MSU-X
These materials with wormlike structure were discovered at Michigan State University [14]. The materials are prepared with non-ionic polyethylene-oxide (PEO) micelles as template at neutral pH. The pore diameter can be varied with the temperature during the synthesis.

SBA-15
This material was discovered at university of Santa BArbara [15]. The material is prepared with non-ionic amphiphilic triblock copolymer micelles as template under acidic reaction conditions. The material has a well defined hexagonal symmetry. The specific surface areas and specific pore volumes are somewhat smaller than of M41S materials, but the pore walls are thicker. Therefore also the mechanical and hydrothermal stability of these materials are better. The pore diameters can be
varied between 5 and 20 nm by varying the synthesis temperature (between 30 and 90°C) and the template.

**MCF**

The synthesis of this material is derived from the synthesis of SBA-15 [16]. The abbreviation stands for MesoCellular Foams. The templating micelles are enlarged by adding an organic swelling agent (mesitylene) to the triblock copolymer. The pore system consists of three-dimensional interconnected spherical compartments. Pore openings up to 20 nm could be prepared.

**FDU-1**

This material was found at FuDan University [17]. The material is prepared with amphiphilic triblock copolymers in acidic synthesis conditions. The material has a cubic symmetry and pore diameters up to 12 nm.

**HOM**

This class of materials was first described in 2003 [18]. The code stands for Highly Ordered Mesoporous silica. The non-ionic Brij 56 (C_{16}H_{33}(OCH_2CH_2)_{10}OH) surfactant is used as template. By variation of the reaction temperature and the amount of template hexagonal, cubic and lamellar phases were prepared.

### 1.4 Functionalization of mesoporous silica supports

Silica materials are often used as supports for the heterogenization of catalysts. Besides classical impregnation (e.g. with metal cations) the silanol groups on the surface can react with silane compounds with leaving groups (Fig. 1.8). Since the character of the silica surface changes due to these reactions this process is referred to as functionalization.

Often used leaving groups for surface functionalization are chlorides (Cl\textsuperscript{-}) [19], silazanes (N-SiR\textsubscript{3}) [19] and alkoxy groups (OR\textsuperscript{-}) [20]. Chlorosilane and disilazane compounds are very reactive. Therefore water has to be excluded during functionalization reactions with these compounds. That makes these reactions synthetically rather demanding. Furthermore, adsorbed water on the surface of silica materials has to be removed prior to functionalization. Often this is done under high vacuum at elevated temperatures (100°C - 400°C). Under these severe conditions not only physisorbed water is removed from the silica surface but neighboring silanol groups
condense and form siloxane bridges (Fig. 1.9). Therefore the number of reactive silanol groups is reduced during this treatment, which leads to a low loading of functional groups after the functionalization reaction.

Alkoxysilanes are much less reactive than chlorosilanes and disilazanes. Water does not have to be removed prior to functionalization. On the contrary, it was shown that small amounts of water improve the surface functionalization reaction without inducing unwanted overreaction [20,21]. Therefore higher molar loadings of functional groups on the silica surfaces are possible with that method. It is possible to cover the silica surface completely.

As a result alkoxysilanes are mainly used for functionalization of mesoporous silica materials. Furthermore they can also be used for so-called one pot syntheses of organic functionalized molecular sieves (OFMS) [22–24]. These materials are prepared by adding alkoxysilanes to the syntheses of template directed mesoporous silica materials. That is an alternative to the classical method to synthesize the mesoporous silica support first, followed by the functionalization of the surface.

Disadvantages of the classical two step method are:

- It is more elaborate because it involves more reaction steps.
- The pore diameter is further decreased during functionalization.
Advantages of the classical two step method are:

- The templating micelles of the mesoporous material can be removed by calcination. During a calcination already functionalized organic groups would be decomposed. A calcination has the advantage that really all template is removed and that the silica framework becomes more stable.

- Only the surface of the mesoporous material is functionalized. In a one pot procedure functional groups are also incorporated into the framework.

- The two separate synthesis steps allow much more flexibility in either step. Phase symmetry and pore diameter in the synthesis of the mesoporous silica and the nature as well as the loading of the functional group can be varied independently.

Since, in our view, the advantages of the classical two step method (in particular its higher flexibility) outweigh the disadvantages this method was chosen for all the functionalization reactions performed in this study.
Chapter 2
Characterization Methods

2.1 Nitrogen physisorption

Nitrogen physisorption is probably the most important characterization method in this work. The measurement of gas adsorption is a relatively easy procedure. The data evaluation, however, relies on models of the adsorption processes. Since the models do not always apply for the system under investigation, the data derived from nitrogen physisorption measurements always have to be questioned. Therefore the data evaluation methods that were used in this work are discussed in detail. For the discussion of adsorption processes, adsorbent, adsorbate and adsorptive were differentiated (Fig. 2.1).

2.1.1 Isotherms

The most widely used gas adsorption measurement for the characterizing of the surfaces of solid materials is nitrogen physisorption. To obtain accurate adsorption measurements the amount of adsorbed gas should be high and the temperature constant. Therefore nitrogen physisorption measurements are often performed at liquid nitrogen temperature (-195.8°C = 77.35 K). The amount of adsorbed gas is measured at different pressures. The measurement is performed volumetrically. Calibrated volumes of gas are added to a sample tube that is immersed in liquid nitrogen with a known amount of sample. The amount of adsorbed gas can be calculated from the measured pressure difference in the sample tube after the addition of a known volume. If amounts of adsorbed gas are plotted against the pressure the so called isotherm is obtained (Fig. 2.2). According to conventions the volume of adsorbed gas is expressed as cm³ at 0°C and 1 atm (10¹³ Pa) per g of adsorbent material. The pressure is displayed as relative pressure p/p₀, where p is the actual pressure in the sample tube and p₀ is the saturation pressure of the adsorptive at
the temperature of the measurement. In a measurement with nitrogen as adsorptive at liquid nitrogen temperature $p_0$ is 1 atm.

Normally not only the adsorption of gas is measured but also the desorption. The desorption is measured in the same way, but by removing known volumes of gas instead of adding them. In some isotherms adsorption occurs at higher pressures than desorption is observed (as in Fig. 2.2). This phenomenon is called hysteresis or an irreversible isotherm. Possible reasons for this effect will be discussed later. The points taken during the adsorption are referred to as adsorption branch and the points measured during desorption as desorption branch.

The nitrogen physisorption isotherm is the plot of the measured data. It gives qualitative information about the specific surface area, the specific pore volume as well as about pore dimensions and pore size distribution. Ways to obtain quantitative values for these parameters will be discussed later. As mentioned before deriving quantitative information requires models, which makes the obtained values sometimes questionable. During data evaluation, the isotherms themselves are the first thing to be checked. They should always be reported along with the derived data, such as specific surface areas and pore volumes. Since all isotherms are normalized to volume adsorbed per g of solid material they can always be used to compare any of the mentioned properties of a solid material with the properties of another one.
2.1. NITROGEN PHYSIOSORPTION

Figure 2.2: Nitrogen physisorption isotherm measured at liquid nitrogen temperature (-195.8°C).

Statements of the form: "The pore size distribution of solid A is broader than that of solid B." can thereby be made on the base of isotherms.

To facilitate the interpretation of the isotherms the shape of six physisorption isotherms was defined by IUPAC (Fig. 2.3) [25].

- Type I isotherms are typical for microporous materials with relatively small external surface areas (as zeolites).

- Type II isotherms are observed if unrestricted layer by layer adsorption is possible as in the case of macroporous and non-porous materials.

- Type III and V isotherms are very uncommon. They are only observed if the adsorbent-adsorbate interaction is very weak (as between some polymers and nitrogen).

- Type IV isotherms are typical for mesoporous materials. They normally show hysteresis. Most of the isotherms presented in this work are of this type.

- Type VI isotherms are special cases. They were added for completeness.

Type IV isotherms were observed in this work. Therefore the processes that cause the observed features of a type IV isotherm are discussed in more detail (Fig. 2.4).
Figure 2.3: Isotherm types according to IUPAC definition [25]. Very general assignment of porous nature: type I - microporous material, type II - macro- or non-porous material, type III - macro- or non-porous material with weak adsorbent-adsorbate interactions, type IV - mesoporous materials, type V - mesoporous material with weak adsorbent-adsorbate interactions, type VI stepwise adsorption at very homogeneous surfaces.

Figure 2.4: Adsorption and desorption processes in mesopores and their influence on features of type IV isotherms: (a) monolayer adsorption, (b) layer by layer adsorption, (c) beginning of capillary condensation, (d) capillary condensation, (e) adsorption at the external surface area, (f) beginning of capillary desorption, (g) capillary desorption, (h) layer by layer desorption.
2.1. NITROGEN PHYSISORPTION

At very low pressures monolayer adsorption occurs. Since the adsorption on the bare solid surface is energetically very favorable (in terms of heat of adsorption) the isotherm rises fast in this range (Fig. 2.4a). At increasing pressures layers of adsorbate are adsorbed on top of each other. As long as this so-called multilayer adsorption goes on the isotherm is linear (Fig. 2.4b). In ordered mesoporous materials the multilayer adsorption reaches a state where additional adsorptive molecules do not interact with a flat layer of adsorbate any more but with a curved surface. The adsorption on curved surfaces is more favorable. That can be expressed mathematically with the so-called Kelvin equation (eq. 2.1, \( p/p_0 \) is the relative vapor pressure over a curved surface, \( \gamma \) is the surface tension, \( \nu^l \) is the molar volume of the liquid and \( r_k \) is the radius of curvature).

\[
\frac{p}{p_0} = \exp\left(-\frac{2\gamma \nu^l}{r_k \cdot RT}\right)
\] (2.1)

According to that equation, the relative vapor pressure over a concave surface is lower than the relative vapor pressure over a flat surface. That effect induces the filling of mesopores (Fig. 2.4c+d) at relative pressures that are characteristic for the diameter. The environment for the adsorbate in filled mesopores is comparable with the liquid state. Therefore this process is referred to as capillary condensation. Capillary condensation in small pores starts at lower pressures than in large pores. A broad capillary condensation step in the isotherm comes from mesopores with a broad distribution of diameters. A very narrow capillary condensation step is observed if very many mesopores of identical size are filled simultaneously. These characteristics of type IV isotherms are very informative and allow qualitative interpretation.

Once the mesopores are filled only multilayer condensation at the external surface can occur (Fig. 2.4e). The volumes adsorbed at these pressures are a direct measure for the total mesopore volume of a material (i.e. the volume that was adsorbed until all pores were filled). If the desorption branch of the isotherm is also measured the same processes are observed while removing the adsorbate (Fig. 2.4f-h).

The phenomenon of hysteresis that is often observed in isotherms of mesoporous materials is still under debate. The shape of the hysteresis may give some hints about the pore geometry of the investigated material (Fig. 2.5). H1 hysteresis was often observed in the presented study. One (but not the only) possible reason for this hysteresis is the shape of the so called meniscus at the pressure where capillary condensation or desorption occur (Fig. 2.6). If multilayer adsorption goes on in a straight cylindrical pore, the free space inside the pore is a cylinder whose diameter decreases. If the critical pressure is reached this cylindrical meniscus is filled.
Figure 2.5: Hysteresis types according to IUPAC definition [25]. Very general assignment of porous nature: H1 - typical for type IV isotherms, H2 - characteristic for "ink-bottle" pores, H3 + H4 - slit pores.

During desorption, however, the pores are filled with adsorbate and if adsorbate is removed from the pore openings a spherical meniscus forms. Because the curvature of this meniscus is higher than in the cylindrical meniscus (eq. 2.1) the desorption is delayed. The isotherms of materials with straight cylindrical mesopores always have a hysteresis if the pore diameter is big enough to allow the formation of a meniscus. In the case of nitrogen physisorption at liquid nitrogen temperature hysteresis loops are only observed at relative pressures (p/p₀) larger than 0.42 because at smaller relative pressures no meniscus can be formed. Therefore the isotherms of MCM-41 materials do not show hysteresis, even though they have straight cylindrical pores. Hysteresis loops do also occur in mesoporous materials with pore geometries other than cylinders. Then the pore geometry can also influence the shape (i.e. the type of hysteresis loops) or the difference between adsorption and desorption branch.

2.1.2 Specific surface area (BET method)

For the determination of the specific surface area of silica materials the BET method is standard. The method was established by Brunauer, Emmet and Teller [26]. The model on which it is based assumes that the heat of adsorption on the naked adsorbent surface is different from the heats of adsorption of all successive layers (which are assumed to be identical). In spite of this simplification, reliable and reproducible values of specific surface areas are obtained with the BET method.

In the BET method the isotherm is linearized with the so called BET equation (eq. 2.2, Vₐ is the adsorbed volume at a p/p₀, Vₘ is the volume adsorbed in a monolayer and C is an empirical constant that is related to the difference between the heat of adsorption on the naked surface (E₁) and on the following layers (Eₙ) eq. 2.3).
2.1. NITROGEN PHYSISORPTION

Figure 2.6: Cylindrical meniscus observed during adsorption in straight cylindrical pore and spherical meniscus observed during desorption from straight cylindrical pore.

\[
\frac{p}{V_A(p_0 - p)} = \frac{1}{V_m + C} + \frac{C - 1}{V_m + C} \times \frac{p}{p_0}
\]

\[
C \approx e^{\frac{E_L - E_H}{kT}}
\]  

(2.2)  

(2.3)

The BET plot is obtained by plotting \(p/(V_A(p_0 - p))\) against \(p/p_0\). As long as only multilayer adsorption occurs it is linear. From the slope (\(s = (C-1)/(V_m\times C)\)) and the intercept (\(i = 1/(V_m\times C)\)) of this straight line \(V_m\) and \(C\) can be derived. With \(V_m\) and the area of a single adsorbate particle on a certain surface (16.2 Å² with N₂ as adsorptive on silica surfaces) the specific BET surface area can be calculated.

If data points where condensation in mesopores occurs are included in surface determination with the BET method too large specific surface areas are obtained. To avoid that, data points in the relative pressure range \(0.02 < p/p_0 < 0.2\) were used in this work for the calculation of BET surface areas.

Before relying on BET values one should always check if, (1) the BET plot is linear, (2) \(C\) (that is always determined) is not negative nor larger than 200 and (3) that the weight of the analyzed sample is correct.
2.1.3 Specific pore volumes

The specific pore volumes were determined with two different methods. In the first it is assumed that all pores are filled at a relative pressure \( p/p_0 = 0.97 \). From the volume adsorbed at that pressure the pore volume was calculated directly. This very simple method gives correct results if (1) the investigated material has a low external surface area and (2) no macropores are present that cause condensation in this pressure range.

Since both requirements are fulfilled in ordered mesoporous materials this method was mostly used.

Alternatively, a more sophisticated approach based on the so-called t-plot method [27] was used. This method was developed for the characterization of the porosity of a material. In the so-called t-plot the measured adsorbed volumes are plotted against the statistical layer thickness \( t \) (Fig. 2.7).

The statistical thickness is specific for the combination of an adsorptive (\( N_2 \) in these cases), the temperature and an adsorbent (silica in these cases). In this work the statistical thickness was calculated with the semi-empirical formula of Harkins and Jura [28].
2.1. **NITROGEN PHYYSISORPTION**

The specific pore volume is calculated from the intercept of the straight line that is drawn through the second linear region of the t-plot (Fig. 2.7). From the slope of this line a value for the external surface area can also be calculated.

### 2.1.4 Pore diameter distributions and average pore diameters

Deriving quantitative values for mesopore diameters from nitrogen physisorption data is a matter of debate in the field, as can be seen from the fact that several methods are still in use. In this work two different methods were used. The BJH method [29] and the BdB-FHH method [30].

**BJH Method**

Although this method was developed for cylindrical pores, it is by far the most widely used for all kind of mesopores. The method was developed by Barret, Joyner and Halenda [29]. In the BJH approach the filled pores are taken as starting point. From that point the emptying of the pores with decreasing relative pressure is evaluated to obtain a pore diameter distribution. That is done incrementally. For each increment the pore diameter of pores emptied in that increment is calculated with the Kelvin equation (eq. 2.1).

From this value and the difference of adsorbed volumes before and after the increment the volume of emptied pores of the respective diameter range is calculated. Since the pores are not completely emptied but the multilayer that is characteristic for a certain relative pressure remains on the inner surface of the pore the calculations are corrected for that effect. This method is normally applied to both the adsorption and desorption branch of a nitrogen physisorption isotherm. The maximum of BJH pore size distributions calculated from the adsorption and the desorption are referred to as average BJH adsorption and BJH desorption pore diameter hereafter. Although one may quarrel about the absolute values, BJH distributions and diameters are correct in a relative sense. Therefore they were mostly used in this study. Mesopores with 8 nm BJH pore diameter, for example, are surely larger than mesopores with 4 nm BJH pore diameter. But the real diameter does not have to be 8 or 4 nm because the assumptions of the Kelvin equation (eq. 2.1) are not fully fulfilled in small mesopores.

**BdB-FHH Method**

The BdB-FHH method [30] is not fundamentally different from the BJH method. It was originally developed by Broekhoff and de Boer [31,32] and simplified later with
the equation of Frankel, Halsey and Hill [30]. It is also based on the Kelvin equation. The main difference is that the BdB-FHH method is corrected for the effect that the thickness of an adsorbed layer on a curved surface is larger than on a flat surface. Therefore average pore diameters determined with the BdB-FHH method are larger than those determined with the BJH method.

The BdB-FHH method was used in Chapter 4 because it was shown [30] that this method produces identical values for the pore diameter from both the adsorption and desorption branch of the isotherm if the pores are cylindrical. Pores with larger compartments interconnected with smaller ones give, however, larger BdB-FHH pore diameters for the adsorption than for the desorption. Therefore the BdB-FHH method allows to characterize the pore geometry of mesopores. In that part of this work it was important to decide wether pores were cylindrical or consisted of larger compartments interconnected by smaller ones.

2.1.5 Experimental procedures

Nitrogen sorption measurements were performed at liquid nitrogen temperature with a TriStar 3000 apparatus of Micromeritics. The analysis procedure is fully automated and operates with the static volumetric technique. 50 - 100 mg of sample were measured. The reproducibility of the measurements was very good, with a maximal error between two BET surface area measurements of 2%.

Prior to the measurement the samples were degassed for at least 4 h at 10 Pa. If this pressure was not reached the degassing was prolonged. Pure silica materials were degassed at 400°C. Functionalized materials with organic material bound to the surface of the silica were degassed at 80°C.

Argon sorption that was performed in one case (Chapter 4 / Fig. 4.2) was performed with an ASAP 2010 apparatus of Micromeritics at liquid nitrogen temperature. The relative pressure \( p/p_0 \) in the argon isotherm is the ratio of the equilibrium vapor pressure and the saturation vapor pressure for the gas-solid equilibrium at liquid nitrogen temperature.

2.2 X-Ray powder diffraction

2.2.1 Theory

X-Ray powder diffraction or powder XRD is a well established method for the identification of ordered phases. Beside the symmetry also unit cell dimensions and changes thereof can be followed with powder XRD.
2.2. X-RAY POWDER DIFFRACTION

The diffraction of X-rays is observed because their wavelength is in the same range as distances between atoms in solid materials. If the materials are ordered constructive interference between scattered X-rays occurs. To record a powder XRD with a Bragg-Brentano device the powder is placed in a plate and the monochromatic X-ray source and the detector are moved over the sample plane in a way that the whole 2Θ range is scanned (Fig. 2.8).

In the XRD pattern the intensity (in counts per second cps) is plotted against the angle 2Θ (e.g. Fig. 1.6). The symmetry of the solid can be seen from the position and the relative intensity of the obtained reflections.

Since the walls of mesoporous materials are amorphous and only the arrangement of the pores induce the regularity in the solid, reflections in powder XRD are only obtained in the range: 0.5 < 2Θ < 10°.

In mesoporous materials the average distance between pores (pore diameter plus pore wall) can be calculated from the position of the first reflection according to Bragg’s law (eq. 2.4) (n is the order of reflection and λ is the wavelength of the X-Ray).

\[ d = \frac{n\lambda}{2 \times \sin\Theta} \] (2.4)

Figure 2.8: Geometry of Bragg-Brentano diffractometer.
2.2.2 Experimental procedure

Powder XRD patterns were measured with a D5000 Siemens powder diffractometer with Bragg-Brentano geometry in the range of 0.5 to 10° 2θ with steps of 0.01° and a step time of 4 s. The CuKα transition was used as X-Ray source (λ = 1.5406 Å).

2.3 NMR

2.3.1 Theory

Liquid (Chapter 5) and solid state NMR (Chapters 7, 8 and 9) were used to follow changes in synthesis reaction mixtures and to characterize solid materials. ¹H NMR spectra were recorded of liquid phases whereas ²⁹Si and ¹³C NMR was measured in the solid state.

NMR spectra of solids have very broad signals that are difficult to interpret. The interactions that cause the broadening can be minimized with “magic angle spinning” MAS. The sample holder (so called rotor) with the solid material is tilted by an angle of 54.74° against the magnetic field and rotated. The faster the rotation of the rotor the more the broadening of the NMR peaks is reduced. The possible improvement of the quality of NMR by MAS is reached when the spinning speed equals the broadening interaction (in Hz). For many samples, however, that would require very high spinning speeds that are not possible yet.

The chemical shifts of peaks in solid state ¹³C and ²⁹Si NMR spectra were used for characterization of solid materials. For ¹³C the chemical shifts from the liquid state could be used for peak assignments [33]. In ²⁹Si NMR spectra Qⁿ (Qⁿ = Si(OSi)ₙ(OH)₄₋ₙ, n=2-4) and Tᵐ (Tᵐ = RSi(OSi)ₘ(OR)₃₋ₘ, m=1-3) were assigned according to Figure 2.9.

2.3.2 Experimental Procedure

The experimental parameters of the ¹H NMR spectra recorded of liquid phases are described in Chapter 5.

Solid state MAS NMR spectra were recorded using a Bruker AMX 400 spectrometer operating at 9.4 T. That magnetic field corresponds to 100.61 MHz for ¹³C and 79.49 MHz for ²⁹Si.

¹³C was measured with CP-MAS in a 4 mm rotor with a spinning speed of 10 kHz. A flip angle of 3 μs was used with a 5 s recycle delay.

²⁹Si was measured with HPDEC in a 7 mm rotor with a spinning speed of 5 kHz. A high-power decoupling pulse sequence (HPDEC) with an r.f. pulse length of 2.5 s
2.4. SAXS

SAXS measurements were performed at the "Institute of Biophysics and X-ray Structure Research" at the Austrian Academy of Sciences in Graz. SAXS allows to follow changes in phase symmetry and unit cell dimensions in forming organic inorganic mesophases.

Small-angle X-ray measurements were performed on a Hecus System-3 SAXS camera (Hecus X-ray Systems, Graz, Austria) with block-slit collimation, operated at a Seifert ID-3003 (Seifert, Ahrensburg, Germany) generator (50 kV/40 mA) with Cu anode. Samples were investigated in a thermostated quartz capillary (1 mm i.d.) cuvette at 20°C. For the SAXS measurements during the synthesis process, the sample cell was connected to a syringe and filled directly from the synthesis gel. The required amount was about 100 μl. The SAXS measurements at different stages of the synthesis procedure lasted 15 min.
2.5 IR

FT-IR spectra were recorded on a Bio-Rad Excalibur FTS 3000 IR spectrometer equipped with an MCT detector at a resolution of 4 cm\(^{-1}\). Samples were measured as self-supporting pellets after 1 h treatment at 200°C in a flow of He in a stainless steel cell equipped with CaF\(_2\) windows. The treatment was performed to remove adsorbed water. For comparison of peak intensities the spectra were normalized to an identical intensity of the Si-O-Si overtone at 1860 cm\(^{-1}\). If structurally substantially different materials were compared the normalization was done with the weight of the self supporting pellet.

2.6 UV

Diffuse reflectance UV-Vis spectra of the Fe exchanged materials were measured on a Cary 400 UV-Vis spectrometer equipped with a Praying Mantis sample stage from Harrick. BaSO\(_4\) was used as a reference. Even though the background was measured independently of the sample the measurements were always performed in double beam mode to compensate for instabilities.

2.7 TEM

Transmission electron microscopy (TEM) was performed on a Philips CM30 electron microscope (super twin lens, point resolution 0.2 nm, operated at 300 kV). Samples were suspended in ethanol and deposited on a holey carbon foil.

2.8 Total organic carbon

The total organic carbon (TOC) analysis was performed on a Shimadzu TOC-5050A apparatus using samples obtained by diluting the aqueous phases of the synthesis gels by a factor of 12.

2.9 C, H, N, F, Cl and S contents in solid materials

These measurements were performed in the elementary analysis service of ETH. Organic elementary analysis (CHN) was performed on a LECO CHN-900 apparatus. The organic material in a sample of 2 mg of functionalized M41S was combusted at 1000°C in a flow of He with O\(_2\) and the amounts of evolving CO\(_2\), H\(_2\)O and N\(_2\) were used to calculate the content of C, H and N. Each measurement was repeated.
twice. The S content was measured on a LECO CHNS-932 apparatus. The amount of evolving SO$_2$ was used to calculate the content of S. The amount of F and Cl were determined with ion chromatography.

### 2.10 AAS

The iron content of the Fe-exchanged materials was determined by atomic absorption spectrometry with a Varian SpectrAA 220FS instrument. The instrument was equipped with a D$_2$-lamp for background correction. A Co, Cu, Cr, Fe, Mn, Ni UltrAA multi hollow cathode lamp was used. An acetylene / air flame was used for atomization. The Fe containing materials were dissolved with HF. The procedure involved the following steps:

1. Take the empty weight of a 25 ml plastic flask.
2. Add around 10 mg of solid material to the flask and take exact weight.
3. Add 1-2 ml of demineralized water to wet the solid and flush it from the walls of the flask.
4. Add 1 ml of HF (40% in water) with the micropipette.
5. Add 2 ml of HNO$_3$ (2.5 M in water). Close flask with lid.
6. Let the solid material dissolve over night.
7. Fill to 25 ml with demineralized water.
8. Take the weight of the full flask and calculate the weight of the stock solution.

From such a stock, solutions for measurements were prepared by dilution to Fe concentrations between 0.5 and 1.0 mg/l. To prevent precipitation of dissolved Fe, dilutions were made with a 0.05 M HNO$_3$ solution. Quantification was done with a calibration curve (standards with 0.25, 0.5 and 1.0 mg/l). The standard solutions were prepared by dilution of a 1000 mg/l solution (Fluka) with 0.05 M HNO$_3$. The accuracy of the Fe contents determined with this method is 5%. The method allowed the determination of Fe contents as low as 0.1 wt%.
Chapter 3

A Mechanistic Explanation of the Formation of High Quality MCM-41 with High Hydrothermal Stability

3.1 Introduction

Pure silica MCM-41 has potential as support in catalysis and as sorbent for separation. Due to the amorphous structure of the pore walls, mesoporous MCM-41 materials can vary considerably in pore characteristics and hydrothermal stability depending on the synthesis procedure. Parameters that influence the quality are the nature of the templating surfactant [34] and the silica precursor [35–37]. Water glass is the cheapest and therefore most used silica precursor in industrial production of zeolites. It was also used in this work. Further synthetic parameters that strongly influence the quality of the MCM-41 material are the pH and the ionic strength of the synthesis gel [34,38–41]. By adding acids or salts to the gel during synthesis, materials with remarkably improved pore characteristics and stability were obtained. The effect was explained by the higher degree of condensation of the silicate framework which leads to less structural collapse in the subsequent calcination step. As a result materials with exceptional pore characteristics as well as improved hydrothermal stability are obtained. These properties are the key for any application of these interesting materials. The influence of different procedures for adding acid during the synthesis and two different silicate precursors were tested for the synthesis of pure silica MCM-41. The systematic variation of these parameters brought new insight into the processes that occur during synthesis. The hydrothermal stability was tested with steaming and water treatment of the calcined materials.
3.2 Experimental

3.2.1 Synthesis procedure

Ryoo et al. [38] and Lindlar et al. [6] showed that the addition of acetic acid is a crucial step in the synthesis of both pure silica MCM-41 and Al-MCM-41. To synthesize about 8 g of calcined MCM-41 material a clear template solution of 22.3 g hexadecyltrimethylammonium chloride solution (25 % in water, HTMA-Cl, Fluka) was used. Separately, a silicate mixture was prepared from 28.4 g of a sodium silicate solution (water glass, 27 % SiO₂, 8 % Na₂O in water, Merck extra pure), 0.75 g Cab-osiil M5 (Fluka) and 49.3 g demineralized water. The silicate mixture was stirred for 15 min. The synthesis gel was obtained by adding the silicate mixture to the template mixture and stirring vigorously for another 60 min. The molar composition of the gel was always 1 SiO₂ / 0.260 Na₂O / 0.124 HTMA-Cl / 33.4 H₂O. The synthesis mixture was filled into a PTFE bottle, the bottle was closed and the mixture was aged at 100°C for 96 h in an oven. The only variations between different syntheses were the batch of sodium silicate solution of the same manufacturer and the amount as well as the procedure of acetic acid addition. In one procedure of acid addition the pH of the synthesis gel was adjusted to different values between 10.2 and 10.8 after 24, 48 and 72 h of synthesis. This procedure is referred to as repeated pH adjustment hereafter. For a pH adjustment the synthesis gel was cooled to a temperature between 29 and 30°C (pH temperature dependent). The pH of the gel was lowered to the desired value by titration with acetic acid (100 %, Scharlau). In the second procedure a certain volume of acetic acid was added to the synthesis gel all at once after 24 h. This procedure is referred to as addition of a fixed amount of acid. As will be reported later the best materials were obtained after the addition of 2.65 ml for the described batch size, which gave a molar ratio of 1 SiO₂ / 0.3 AcOH in the synthesis gel. After 96 h of synthesis, the gel was filtered and washed with 2 l of demineralized water and 0.5 l of ethanol. The product was dried over night at 50°C in an evacuated oven and subsequently calcined in flowing air by heating at 5°C/min to 120°C (3 h dwell time) followed by 1°C/min to 540°C (4 h dwell time).

3.2.2 Hydrothermal stability

To test the hydrothermal stability, calcined MCM-41 materials were steamed at a temperature of 500°C and refluxed in water. For the steaming a gas mixture of helium and water (300 mbar partial pressure) with a total flow of 30 ml/min was used. A bed of 60 mg MCM-41 inside a glass tube (i.d. 4 mm) was treated with
this gas stream and heated to 500°C for 6 h. For the water treatment 200 mg of MCM-41 was dispersed in 10 ml of demineralized water and heated to reflux for 4 h. The water treated material was recovered by filtration.

3.3 Results

A series of MCM-41 materials synthesized by repeated pH adjustment to different pH values showed that the optimal pH is lower than was reported before [38,41] under these synthesis conditions. The pore characteristics of the materials are summarized in Table 3.1. The total pore volume and the average BJH diameter constantly increased when decreasing the pH to 10.2. The pH could not be adjusted reliably to values below 10.2, because it was no longer possible to stir and homogenize the gel. Alternatively, some syntheses were performed with the addition of fixed amount of acetic acid after 24 h of synthesis. This procedure was justified by the fact that the amounts required to adjust the pH after 48 and 72 h were small in relation to the first adjustment. The procedure with one addition of acid has the advantage that only one manipulation is required during the synthesis and that the addition of a fixed amount of acetic acid, rather than titration, improves the reproducibility of the synthesis. The amounts of acetic acid used for repeated pH adjustment and the addition of fixed amounts are summarized in Table 3.1, for the described batch size. The total amounts of acetic acid used for adjusting the pH to values from 10.8 to 10.2 increased from 1.7 to 2.8 ml.

The pore characteristics in Table 3.1 show that the addition of 2.65 ml of acetic acid after 24 h of synthesis yielded the best pore characteristics of all the MCM-41 materials. Fig. 3.1 depicts the nitrogen adsorption isotherm of this material. Adding 3 ml of acetic acid decreased the pore volume and surface area. Furthermore, adding acid at the beginning of the synthesis, i.e. before the aging period, or a shorter aging period led to materials with poorer pore characteristics.

Since the pore characteristics derived from the nitrogen adsorption measurements do not give a complete picture of the structural order of MCM-41, XRD patterns of as synthesized and calcined materials, obtained from adjusting the pH to 10.8 and adding 2.65 ml acetic acid (Fig. 3.2), were collected. The patterns of the as synthesized materials, obtained by adjusting the pH to 10.8 in the course of the synthesis, changed after calcination, as described previously for MCM-41 [38,40]. The intensity and resolution of the reflections decreased, whereas the position of the reflections shifted to higher 2Θ values. The shift in the (100) reflection was about 0.22°, which indicates a considerable decrease in the unit cell dimension during
Table 3.1: Pore characteristics of materials synthesized by repeated pH adjustment to different values or by addition of fixed amounts of acid

<table>
<thead>
<tr>
<th>Acetic acid treatment</th>
<th>Acid addition 24/48/72 h [ml]</th>
<th>Pore vol. ( \text{cm}^3/\text{g} )</th>
<th>BJH pore diam. [nm]</th>
<th>BET surface [m(^2)/g]</th>
<th>Wall thickn. [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH adj. 10.8</td>
<td>1.1/0.4/0.2</td>
<td>0.65</td>
<td>2.3</td>
<td>1025</td>
<td>2.2</td>
</tr>
<tr>
<td>pH adj. 10.6</td>
<td>1.2/0.5/0.3</td>
<td>0.68</td>
<td>2.4</td>
<td>945</td>
<td>2.1</td>
</tr>
<tr>
<td>pH adj. 10.4</td>
<td>1.5/0.6/0.4</td>
<td>0.78</td>
<td>2.6</td>
<td>990</td>
<td>n.m.</td>
</tr>
<tr>
<td>pH adj. 10.2</td>
<td>1.8/0.6/0.4</td>
<td>0.81</td>
<td>2.9</td>
<td>1003</td>
<td>n.m.</td>
</tr>
<tr>
<td>Add. of fix</td>
<td>2.65/0/0/0</td>
<td>0.83</td>
<td>2.9</td>
<td>1012</td>
<td>2.1</td>
</tr>
<tr>
<td>Add. of fix</td>
<td>3.0/0/0</td>
<td>0.71</td>
<td>2.9</td>
<td>907</td>
<td>2.1</td>
</tr>
<tr>
<td>Add. of fix</td>
<td>2.65/0/0/0/0</td>
<td>0.73</td>
<td>2.7</td>
<td>933</td>
<td>n.m.</td>
</tr>
<tr>
<td>Add. of fix</td>
<td>2.65/0/0</td>
<td>0.71</td>
<td>2.7</td>
<td>931</td>
<td>n.m.</td>
</tr>
<tr>
<td>Add. of fix</td>
<td>2.65/0/0/0</td>
<td>0.73</td>
<td>2.6</td>
<td>948</td>
<td>2.2</td>
</tr>
</tbody>
</table>

\(^a\) calculated from t-plot
\(^b\) pore wall thickness is equal to \( a_0 - BJH \) pore diameter \( (a_0 = d_{100} \ast 2/3) \)
\(^c\) immediate addition of acetic acid without aging the gel
\(^d\) gel aged for totally 72 h (instead of 96 h)
\(^e\) second batch of sodium silicate solution with smaller silicate species

calcination. Another important feature of the XRD pattern of the calcined material is the increased intensity at 2\(\Theta\) angles smaller than 2. This indicates that some of the pore walls of this MCM-41 collapse during calcination thus creating larger pores, which give rise to reflections in this very low-angle range. Thus the instability during calcination seems to be the cause of the poorer pore characteristics of this material synthesized with repeated pH adjustment.

The material synthesized by adding 2.65 ml acetic acid after 24 h of aging behaved differently. The intensity as well as the resolution of the reflections increased after calcination (patterns presented in Fig. 3.2 as recorded without magnification). This indicates that structural order was not lost during the calcination of this material. The fact that the reflections in the XRD pattern of the calcined material were more intense than those of the as synthesized material does not, however, necessarily indicate a better structural order. The removal of the templating micelle during the calcination step empties the pores and, thus, leads to a better contrast for the XRD measurements. The shift in the (100) reflection position was only 0.08°. The results clearly show that our new method of acid treatment leads to a MCM-41 material with exceptional pore characteristics as well as high structural order.

A sodium silicate solution was the main silica precursor for all the syntheses described here. After repeating some of the syntheses, it was found that two batches of sodium silicate solution from the same manufacturer led to different materials.
Further investigation of these effects showed that the two batches of sodium silicate solution had very similar elemental compositions but a slightly different viscosity. This difference is a consequence of different degrees of dissolution or oligomerization of the silicate species present. The batch of sodium silicate solution with the higher viscosity (350 P) consisted of larger silicate species than the less viscous batch (145 P). In one set of syntheses two identical MCM-41 synthesis gels were prepared using the two batches of silicate solution in parallel. After 24 h of aging, 2.65 ml acetic acid were added to both gels, as described above. Table 3.1 and Figure 3.2 show the differences in the pore characteristics and XRD patterns of these two materials. The material prepared from the sodium silicate solution with the larger silicate species had a sharper XRD pattern and a higher pore volume, BJH average pore diameter and BET surface area. The difference seems small, but it led to a large difference in the hydrothermal stability of the materials. The hydrothermal stability of calcined MCM-41 was tested on the one hand in the gas phase, by exposing it to steam at 500°C, and, on the other hand, in the liquid phase by refluxing in water at 100°C. Table 3.2 and Figure 3.3 show the pore characteristics and nitrogen adsorption isotherms of the materials prepared from the two batches of sodium silicate solution after the hydrothermal treatments.
Figure 3.2: XRD pattern of MCM-41: (a) material synthesized by adjusting the pH to 10.8 (the calcined is pattern offset for better visibility), (b) material synthesized by addition of 2.65 ml acetic acid to the synthesis mixture, (c) material synthesized by addition of 2.65 ml acetic acid to the synthesis mixture made from sodium silicate solution with smaller silicate species.
Figure 3.3: Nitrogen isotherms of different materials after different treatments to test hydrothermal stability: (1) MCM-41 synthesized with addition of a fixed amount of acid using a sodium silicate solution with large silicate species, (2) MCM-41 synthesized with addition of a fixed amount of acid using a sodium silicate solution with small silicate species, (3) MCM-41 synthesized with pH adjustment to 10.8 using a sodium silicate solution with large silicate species; (a) as calcined, (b) after steaming at 500°C for 6 h and (c) after refluxing in water for 4 h.
Table 3.2: Structural damage to MCM-41 materials upon steaming at 500°C and treatment in boiling water

<table>
<thead>
<tr>
<th>Acetic acid treatment</th>
<th>Treatment to test hydrothermal stability</th>
<th>Pore volume [cm$^3$/g]</th>
<th>BET surface area [m$^2$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Add. of 2.65 ml acid calcined</td>
<td></td>
<td>0.83</td>
<td>1012</td>
</tr>
<tr>
<td>Add. of 2.65 ml acid $^b$</td>
<td></td>
<td>0.73</td>
<td>948</td>
</tr>
<tr>
<td>pH adj. 10.8</td>
<td></td>
<td>0.65</td>
<td>1025</td>
</tr>
<tr>
<td>Add. of 2.65 ml acid steamed at 500°C</td>
<td></td>
<td>0.69</td>
<td>905</td>
</tr>
<tr>
<td>Add. of 2.65 ml acid $^b$</td>
<td></td>
<td>0.31</td>
<td>566</td>
</tr>
<tr>
<td>pH adj. 10.8</td>
<td></td>
<td>0.28</td>
<td>608</td>
</tr>
<tr>
<td>Add. of 2.65 ml acid refluxed in water</td>
<td></td>
<td>0.70</td>
<td>917</td>
</tr>
<tr>
<td>Add. of 2.65 ml acid $^b$</td>
<td></td>
<td>0.18</td>
<td>540</td>
</tr>
<tr>
<td>pH adj. 10.8</td>
<td></td>
<td>0.53</td>
<td>844</td>
</tr>
</tbody>
</table>

$^a$ calculated from t-plot

$^b$ batch of sodium silicate solution with smaller silicate species

The sample prepared by repeated pH adjustment to 10.8 is also included for comparison. The material with the best pore characteristics and XRD pattern after calcination, i.e. the material prepared by addition of a fixed amount of acid and using the sodium silicate with the large species, exhibited excellent hydrothermal stability. Its pore volume decreased only slightly during the treatment with steam or boiling water. The material synthesized with addition of a fixed amount of acid but using the small silicate species and the material synthesized with repeated pH adjustment showed rather large decreases in both the pore volume and the surface area, i.e. they were less stable. Note that the material synthesized by repeated pH adjustment was more stable during water treatment, whereas the stability of these two materials was about the same during steaming. We attribute this difference to the use of the sodium silicate solution with the large silicate species in the synthesis with the repeated pH adjustment. This shows clearly that both the appropriate acid treatment during the synthesis and the size of the silicate species in the sodium silicate solution influence the pore characteristics and the hydrothermal stability of MCM-41 materials. It is surprising that a different batch of sodium silicate solution from the same manufacturer but with somewhat smaller silicate species has such a strong effect on the hydrothermal stability of MCM-41 material.

Since the hydrothermal stability of MCM-41 materials was often related to the wall thickness of the pores [35,36] we estimated these values for some of our samples. As can be seen in Table 3.1 very similar wall thicknesses were obtained for all materials.
3.4 DISCUSSION

This observation shows that the pore wall thickness is not the explanation for the better hydrothermal stability in this case.

3.4 Discussion

The mechanism of MCM-41 formation has been investigated intensively in recent years [42–46]. In-situ SAXS measurements showed that the formation of a hexagonally ordered silicate surfactant mesophase is very fast when TEOS is the silica precursor [43]. A hexagonal diffraction pattern appeared only a few minutes after TEOS was added to the synthesis mixture. With increasing synthesis time, the reflections gradually shifted to larger 2θ angles. This was ascribed to a contraction of the hexagonal phase due to condensation between the silicate surfactant micelles. If fused silica is used as a silica precursor, the process of mesophase formation takes much longer. In-situ EPR measurements with spin-probe molecules showed that the fraction of cylindrical silicate/surfactant micelles in the synthesis mixture increased only slowly [42]. Initially, the formation of a disordered phase was observed, which was then consumed at the expense of the ordered hexagonal phase. The process lasted several days at a synthesis temperature of 50°C. Considering both the information about the mechanism of MCM-41 synthesis and the influence of acid addition on the sol-gel chemistry of the system [47], the positive effect of acid addition on the long-range order and the hydrothermal stability of MCM-41 materials can be explained as follows. From the data presented in ref. [42] it is assumed that, after 24 h of aging, a hexagonal silicate surfactant phase is formed in our syntheses. However this phase is neither fully ordered nor fully condensed (Fig. 3.4, stage (b)). The acid treatment shifts the polymerization/depolymerization equilibrium of the silicate species to a higher degree of condensation (Fig. 3.5). It helps to close the silica-wall around the micelle and to strengthen it by the formation of covalent Si-O-Si bonds. As a second effect, lowering the pH leads to protonation of the negatively charged silicate species, thus reducing the electrostatic repulsion between the micelles. This facilitates the approach and the condensation of the micelles. The consequences of these two effects are depicted in stage (c) of Figure 3.4.

The acid treatment also reduces the amount of charge-compensating Na\(^+\) ions, which remain in the framework of the MCM-41 material. Upon protonation, Si-O-Na\(^+\) units become Si-OH silanol groups. Adjacent silanol groups will condense at the high temperatures of calcination by elimination of water. In this way, the structural order of the MCM-41 can improve during the calcination step, if the acid treatment is appropriately applied.
Figure 3.4: Schematic representation of the proposed mechanism of MCM-41 formation. (a) template and silicate mixture before mixing, (b) hexagonal surfactant silicate mesophase formed from positively charged surfactant molecules and silicate oligomers carrying multiple negative charges, (c) partial protonation of silicate species facilitated approach and condensation between the template-silicate agglomerates to form a well ordered surfactant silicate mesophase, (d) removal of the detergent by calcination and further condensation between adjacent silicate species.

Figure 3.5: Shift in polymerization/depolymerization equilibrium of silicate species.
In conclusion, acid treatment favors the formation of covalent Si-O-Si bonds within and between the silica walls of the mesostructure during both synthesis and calcination. This strengthening of the silica walls leads to the observed improvement in the long-range ordering and hydrothermal stability.

The acid treatment was most effective when applied after 24 h of aging the synthesis gel. This effect can also be explained by the model proposed above. In-situ EPR measurements have shown [42] that the formation of ordered micelles takes about 24 h, if a polymeric silica precursor is used. In fewer than 24 h there is a disordered phase present together with the hexagonal MCM-41 phase. Thus, if the acid treatment is applied at an early stage of the synthesis, a structure with a low degree of ordering is "cemented" and a material with poorer pore characteristics and hydrothermal stability is obtained. In our synthesis the initial 24 h of aging enable the system to form an ordered phase before the acid treatment. After the acid addition the formation of the mesophase is completed in the following 72 h as a result of the condensation between the silicate micelles, as far as thermodynamics allows it.

Others have described an improvement in the quality of MCM-41 after adding a salt rather than an acid to the synthesis gel [39]. Additional salt cations decrease the electrostatic repulsion between the negatively charged micelles in the same way as protons. Nevertheless, salt cations do not shift the degree of condensation between adjacent silicate species and silanol groups, which can condense further during calcination, do not form. This aspect seems to be of major importance because more salt cations will remain in the framework, which leads to materials, which are thermally and hydrothermally less stable.

Considering these mechanistic explanations of the enhancement of MCM-41 by acids or salts and the mechanism of the formation of the template-silicate agglomerates, [42,44,46] a complete picture of the mechanism of the formation of MCM-41 materials results (Fig. 3.4).

Another observation, also described by others [35–37,48], is the influence of the silicon source on the pore characteristics and hydrothermal stability of MCM-41. We found that the pore characteristics and, in particular, the hydrothermal stability of MCM-41 were better when a batch of sodium silicate solution with larger silicate species was used. Cassiers et al. reported that both the thermal and the hydrothermal stability of MCM-41, prepared from fumed silica, was better than that of similar materials prepared from TEOS as the silica precursor [36]. Igarashi et al. showed that MCM-41 prepared from water glass is more stable under humid conditions than a comparable material prepared from TEOS as silica precursor [35]. The sodium
silicate solution, which yielded the better MCM-41 in our experiments, contained the larger silicate species. The same is valid to a greater extent for the fumed silica compared to TEOS. In the synthesis of Silicalite-1 too, a correlation between the particle size of the silica precursor and the size of the obtained nanocrystals was observed [49]. Increasing the size of the silicate species in the silica precursor can of course improve MCM-41 to a certain extent only, because the species cannot be too large for steric reasons. This steric effect probably explains the reverse trend in the quality of MCM-41 when two fumed silicas with different particle sizes were used [37]. The reason for the improvement of the structural order and hydrothermal stability when a silica precursor consisting of larger silicate species could be that the larger species contain more Si-O-Si bonds and thereby induce better resistance against structural breakdown during calcination and hydrothermal treatment.

3.5 Conclusions

The subtle variation of acid treatments during the course of the synthesis shows that the optimum method of preparing pure silica MCM-41 from sodium silicate solution is the addition of an appropriate amount of acetic acid all at once after 24 h of synthesis. The acid treatment improves the condensation and coagulation between the silicate species during the synthesis and thereby improves the quality of the final MCM-41. The quality of MCM-41 also depends strongly on the silica precursor. A source with larger silicate species results in a material with better pore characteristics and excellent hydrothermal stability. A correlation was observed between the pore characteristics, as revealed by nitrogen physisorption and XRD, and the hydrothermal stability. The materials with the best pore characteristics were also hydrothermally most stable.
Chapter 4

The Effect of the Hydrophobicity of Aromatic Swelling Agents on Size and Shape of Templating Micelles of Mesoporous M41S Silicas.

4.1 Introduction

Mesoporous materials can vary considerably in their pore characteristics depending on the synthesis procedure. Relevant characteristics for the mentioned applications are pore geometry, pore diameter, pore size distribution, pore volume, and specific surface area. In addition, the adaptation of the pore size to a certain application is also very important. The size of the pores in mesoporous materials can be altered by different methods. Since the discovery of M41S the templates were swelled by means of organic additives [4]. Substituted aromatic compounds [4, 6, 50-52], alkanes [52, 53], amines [54] or mixtures of two different swelling agents [50, 51, 53] have been described as suitable swelling agents. By swelling, ordered M41S materials with average pore diameters up to 10 nm could be prepared [4, 6]. The mesopores of SBA-15, which are synthesized under acidic conditions with a non-ionic template, could also be enlarged by swelling with substituted aromatic compounds [16].

A comparison of the swelling effect of different aromatic compounds revealed that the bulkier aromatic swelling agents led to the formation of mesoporous materials with smaller pore diameters [50, 51, 53]. This is counterintuitive. We therefore decided to have a closer look at this phenomenon by systematically studying the swelling of M41S templates by five different aromatic compounds. Unfortunately, the
characterization of the materials is not straightforward and hardly any well-defined structure can be observed with XRD. The increase of the dimension of a template micelle is accompanied by an increase in structural disorder. Still many of the M41S materials prepared with swelled templating micelles show narrow pore diameter distributions derived from physisorption measurements and exhibit some degree of order in transmission electron micrographs. A combination of TEM, XRD, SAXS, and physiosorption is therefore used in this study to elucidate the pore structure.

4.2 Experimental

To synthesize about 4 g of calcined, purely siliceous mesoporous M41S material, a gel was prepared as follows. The template mixture consisted of 12.9 g hexadecyltrimethylammonium chloride solution (25 % in water, HTMA-Cl, Fluka), 0.8 g dodecyltrimethylammonium bromide (DTMA-Br, Fluka), a varying amount of benzene (Fluka), mesitylene (Fluka), 1,3,5-triisopropylbenzene (TiPB, Fluka), 1,3,5-triethylbenzene (TEB, Fluka), 1,3,5-tri-tert-butylbenzene (TtBB, Lancaster) or mixtures of mesitylene and TiPB (Fig. 4.1 and Table 4.1), and 12.1 g demineralized water. The mixture was stirred for 30 min in a 100 ml PTFE bottle. Separately, a silicate mixture was prepared from 18.9 g of a sodium silicate solution (27% SiO$_2$, 8% Na$_2$O in water, Merck extra pure), 0.5 g Cab-osil M5 (Fluka), and 18.6 g demineralized water. The silicate mixture was stirred for 15 min. The synthesis gel was obtained by adding the silicate mixture to the template mixture and stirring vigorously for another 60 min. The molar composition of the gel was 1 SiO$_2$ / 0.262 Na$_2$O / 0.109 HTMA-Cl / 0.040 DTMA-Br / 31.5 H$_2$O. The swelling agent / SiO$_2$ ratio (SA/SiO$_2$) varied between 0 and 2.2 (Table 4.1). Syntheses with a SA/SiO$_2$ ratio of 0.72 were described previously [6,51] for the synthesis of mesoporous materials prepared with mesitylene, TiPB, and mixtures thereof. To facilitate comparison this value of SA/SiO$_2$ is referred to as 100 %. Smaller and larger SA/SiO$_2$ ratios are expressed as percentages of this reference value (Table 4.1). The PTFE bottle was closed with a lid and heated to 100°C for 96 h in an oven. After 24, 48, and 72 h the gel was removed from the oven and cooled to a temperature between 25 and 30°C. The pH of the cooled gel was lowered by addition of 0.82, 0.38, and 0.19 ml of acetic acid (100%, Scharlau) after 24, 48, and 72 h of aging for the described batch size. The obtained pH value after each acid addition was 10.6. ±/− 0.2. The addition of defined amounts of acid rather than titration to a certain pH leads to a much better reproducibility because the temperature dependence of the pH does not interfere [55]. The total addition of acetic acid gave a molar ratio AcOH/SiO$_2$
4.3. Results

4.3.1 Identical molar amounts of different aromatic swelling agents

Mesoporous M41S materials were synthesized from gels with identical molar compositions but with different aromatic compounds (Fig. 4.1) as swelling agents (BEN 100, MES 100, TiPB 100, TEB 100, and TtBB 100 in Table 4.1). After calcination all gels except the one prepared with benzene gave materials with uniform mesopores. The nitrogen sorption isotherms of the four ordered mesoporous materials together with the BdB-FHH pore size distributions are presented in Fig. 4.2. The isotherms and the pore characteristics calculated thereof (Table 4.2) show that with the larger swelling molecules mesoporous materials with smaller pores are formed. The average pore size diameter decreased with decreasing total pore volume. This effect is not due to a structural collapse occurring during the calcination step: The XRD pattern (Fig. 4.3) before and after calcination show the same features. During calcination a small shift towards higher 2θ values occurred. This is a normal effect for mesoporous silicas due to further condensation inside the pore wall at the elevated temperatures of the calcination, which causes a contraction of the unit cell. With benzene as swelling agent only non-porous silica was obtained after the calcination. The XRD pattern (Fig. 4.3 BEN 100) of the as synthesized material indicated the presence of a lamellar phase with a d-spacing of around 3 nm. Lamellar organic-inorganic phases collapse during calcination and do not give any porosity [5].
Table 4.1: Amounts of used aromatic swelling agents (structures see Fig. 4.1)

<table>
<thead>
<tr>
<th>swelling agent</th>
<th>relative molar amount [%] (^a)</th>
<th>weight (^b) [g]</th>
<th>molar ratio (\text{SA}/\text{SiO}_2) (^c)</th>
<th>material identifier</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>100</td>
<td>5.3</td>
<td>0.72</td>
<td>BEN 100</td>
</tr>
<tr>
<td>mesitylene</td>
<td>0</td>
<td>0</td>
<td></td>
<td>no swelling</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.6</td>
<td>0.15</td>
<td>MES 20</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>4.1</td>
<td>0.36</td>
<td>MES 50</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>6.1</td>
<td>0.54</td>
<td>MES 75</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>8.1</td>
<td>0.72</td>
<td>MES 100</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>12.2</td>
<td>1.09</td>
<td>MES 150</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>16.2</td>
<td>1.45</td>
<td>MES 200</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>24.3</td>
<td>2.17</td>
<td>MES 300</td>
</tr>
<tr>
<td>TEB</td>
<td>100</td>
<td>10.9</td>
<td>0.72</td>
<td>TEB 100</td>
</tr>
<tr>
<td>TiPB</td>
<td>5</td>
<td>0.7</td>
<td>0.04</td>
<td>TiPB 5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1.4</td>
<td>0.07</td>
<td>TiPB 10</td>
</tr>
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<td></td>
<td>20</td>
<td>2.8</td>
<td>0.14</td>
<td>TiPB 20</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>4.1</td>
<td>0.22</td>
<td>TiPB 30</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>5.5</td>
<td>0.26</td>
<td>TiPB 40</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>6.9</td>
<td>0.36</td>
<td>TiPB 50</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>10.4</td>
<td>0.54</td>
<td>TiPB 75</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>11.0</td>
<td>0.58</td>
<td>TiPB 80</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>13.8</td>
<td>0.72</td>
<td>TiPB 100</td>
</tr>
<tr>
<td>TtBB</td>
<td>100</td>
<td>16.6</td>
<td>0.72</td>
<td>TtBB 100</td>
</tr>
<tr>
<td>mesitylene/TiPB</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>series 1</td>
<td>75/10</td>
<td>6.1/1.4</td>
<td>0.61</td>
<td>Mix 75/10</td>
</tr>
<tr>
<td></td>
<td>50/20</td>
<td>4.1/2.8</td>
<td>0.51</td>
<td>Mix 50/20</td>
</tr>
<tr>
<td></td>
<td>25/30</td>
<td>2.0/4.1</td>
<td>0.39</td>
<td>Mix 25/30</td>
</tr>
<tr>
<td>series 2</td>
<td>80/20</td>
<td>6.5/2.8</td>
<td>0.72</td>
<td>Mix 80/20</td>
</tr>
<tr>
<td></td>
<td>60/40</td>
<td>4.9/5.5</td>
<td>0.72</td>
<td>Mix 60/40</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>3.2/8.3</td>
<td>0.72</td>
<td>Mix 40/60</td>
</tr>
<tr>
<td></td>
<td>20/80</td>
<td>1.6/11.0</td>
<td>0.72</td>
<td>Mix 20/80</td>
</tr>
</tbody>
</table>

\(^a\) to facilitate comparison, the molar ratio swelling agent/\(\text{SiO}_2\) = 0.72 was defined as 100%

\(^b\) needed for the described batch size

\(^c\) SA: swelling agent
4.3. RESULTS

Figure 4.2: Nitrogen sorption isotherms (shifted to higher adsorbed volumes for better visibility) and BdB-FHH pore size distributions calculated from the adsorption and desorption branch of the isotherms for a cylindrical pore geometry: Mesitylene swelled (MES 100, shifted by 1200 cm$^3$/g), TiPB swelled (TiPB 100, shifted by 800 cm$^3$/g), TEB swelled (TEB 100, shifted by 400 cm$^3$/g), TtBB swelled (TtBB 100, grey isotherm: measured with argon as adsorptive at 77 K).

Table 4.2: Pore characteristics of mesoporous materials prepared with identical molar amounts of different aromatic swelling agents (SA/SiO$_2$ = 0.72).

<table>
<thead>
<tr>
<th>swelling agent</th>
<th>$D_{BdB-FHH}$~$^a$ adsorption [nm]</th>
<th>$D_{BdB-FHH}$~$^b$ desorption [nm]</th>
<th>tot. pore vol. t-plot [cm$^3$/g]</th>
<th>BET surface [m$^2$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesitylene</td>
<td>10.0</td>
<td>9.7</td>
<td>2.65</td>
<td>1180</td>
</tr>
<tr>
<td>TEB</td>
<td>6.7</td>
<td>3.7</td>
<td>1.58</td>
<td>1051</td>
</tr>
<tr>
<td>TiPB</td>
<td>6.7</td>
<td>5.5</td>
<td>1.43</td>
<td>986</td>
</tr>
<tr>
<td>TtBB</td>
<td>4.2</td>
<td>4.5 $^c$</td>
<td>1.06</td>
<td>995</td>
</tr>
</tbody>
</table>

$^a$ BdB-FHH average pore size calculated from adsorption branch  
$^b$ BdB-FHH average pore size calculated from desorption branch (assuming cylindrical geometry)  
$^c$ artefact caused by the forced closure of the nitrogen isotherm
Figure 4.3: XRD pattern of as synthesized and calcined materials prepared with a template swelled with identical molar amounts of: benzene (BEN 100), mesitylene (MES 100), TiPB (TiPB 100), TEB (TEB 100), and TtBB (TtBB 100).
### 4.3. RESULTS

Table 4.3: Organic content of freshly synthesized M41S materials with identical molar amounts of different aromatic swelling agents derived from elementary analysis.

<table>
<thead>
<tr>
<th>Swelling Agent</th>
<th>C (^a) [wt%]</th>
<th>N (^b) [wt%]</th>
<th>C(_{det}) (^c) [wt%]</th>
<th>C(_{sw}) (^d) [wt%]</th>
<th>Ratio C(_{sw})/nC (^e)</th>
<th>TOC [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesitylene</td>
<td>33.4</td>
<td>0.7</td>
<td>11</td>
<td>22.4</td>
<td>2.5</td>
<td>1.32</td>
</tr>
<tr>
<td>TEB</td>
<td>44.4</td>
<td>0.74</td>
<td>11</td>
<td>33.4</td>
<td>2.8</td>
<td>n.d.</td>
</tr>
<tr>
<td>TiPB</td>
<td>46.8</td>
<td>0.55</td>
<td>8</td>
<td>38.8</td>
<td>2.6</td>
<td>1.27</td>
</tr>
<tr>
<td>TtBB</td>
<td>55.4</td>
<td>0.55</td>
<td>8</td>
<td>47.4</td>
<td>2.6</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

\(^a\) total carbon content (detergent + aromatic swelling agents)

\(^b\) nitrogen content (from cationic detergent)

\(^c\) carbon assigned to detergent by: 

\[ C_{det} = \text{wt\% N} \times 15.6 \]

(15.6 is the C/N weight ratio in the HTMA-Cl, DTMA-Br detergent mixture used in the synthesis)

\(^d\) carbon assigned to swelling agent, 

\[ C_{sw} = C - C_{det} \]

\(^e\) nC = number of carbon atoms in the swelling agent, 

\[ C_{sw}/nC \] gives a measure for the relative molar amounts of swelling agent in the freshly synthesized materials

All other XRD patterns do not exhibit any features that could be assigned to a well-defined phase.

The content of organic C, H, and N directly after the filtration was measured for all organic-inorganic mesophases (Table 4.3). The total carbon content in the freshly synthesized material increased in the sequence mesitylene < TEB < TiPB < TtBB with increasing molar mass of these swelling agents. The constant ratio between the wt\% of carbon assigned to a swelling agent and its molar mass proves that the molar composition of the freshly synthesized M41S materials was the same for all swelling agents. Furthermore the total organic content (TOC) of the aqueous phase of some of the synthesis gels was measured (Table 4.3). Their very low organic content showed that virtually all organic template molecules remained in the organic-inorganic mesophase after the synthesis. Incomplete incorporation of the organic template can therefore be ruled out and the decrease of the pore volume by increasing the size of the swelling molecule must lie in different manner of micelle formation with the different swelling agents.

The nitrogen sorption isotherms and XRD patterns of the materials prepared with TiPB and TEB as swelling agents were very similar. Therefore only materials prepared with TiPB as swelling agent were investigated further. To complete the characterization of the materials with ordered mesopores (i.e. the ones prepared with mesitylene, TiPB, and TtBB as swelling agents), TEM micrographs of all three were recorded (Fig. 4.4). All three have the same sponge-like appearance but differ in the size of their pore openings. The sizes of the openings agree well with the values...
derived from nitrogen sorption measurements. From nitrogen physisorption, XRD, and TEM it can be concluded that these materials have ordered pores with narrow distributions, although no clear long-range order could be identified.

The nitrogen sorption measurements show that the materials differ not only by the size of their pores. The hysteresis loop in the isotherm of the material prepared with mesitylene as swelling agent (Fig. 4.2, MES 100) is of type H1, indicating a cylindrical or rod-like geometry of the pores. The BdB-FHH method gave quite similar average pore diameters for the adsorption and the desorption branch of the isotherm (Table 4.2), which supports the assumption that the pores have a rod-like geometry. The hysteresis loop of the material prepared with TiPB (Fig. 4.2, TiPB 100) is more of type H2 and the average pore diameter calculated from the desorption branch is smaller than that from the adsorption branch (Table 4.2). According to Lukens et al. [30] this indicates a pore geometry of larger compartments interconnected by smaller windows, as it is observed in MCF materials (mesostructured cellular foams) [16]. Note that a pore model with spherical pore geometry would be more appropriate for analyzing the pore size distribution of this material. Nevertheless cylindrical pore geometry was assumed for all calculations, to facilitate comparison between materials and to give a measure for the non cylindrical character of the pores in a specific material. The average pore diameters calculated from the adsorption branch are, however, independent of the assumed pore geometry and are therefore correct for all materials.

The hysteresis loop of the material prepared with TtBB as swelling agent (Fig. 4.2, TtBB 100) is a good example for the forced closure at relative pressures of 0.43 when nitrogen is used as an adsorptive at 77 K. The very sharp maximum in the BdB-FHH pore size distribution at 4.5 nm calculated from the desorption branch is an artefact caused by this forced closure of the isotherm [56,57]. This is supported by the argon sorption measurement that was performed at 77 K. The point of closure of the hysteresis is lower when argon is used \( (p/p_0 = 0.38) [56,57] \). Because the argon isotherm shows exactly the same feature with a forced closure of the hysteresis loop at the characteristic pressure for argon, the real pore diameter of the mesopores that are controlling the desorption must be substantially smaller than the pore diameter corresponding to the forced closure of the hysteresis loop, i.e. 3.9 nm [56]. The same effect of forced pore closure is probably responsible for the second maximum in the BdB-FHH distributions calculated of the desorption branch of the materials prepared with TiPB and TEB as swelling agents. In summary, the isotherms show a trend from rod-like pores to a pore system of larger compartments interconnected
4.3. RESULTS

Figure 4.4: TEM of calcined M41S materials prepared with a template swelled with identical molar amounts of: mesitylene (MES 100), TiPB (TiPB 100), TtBB (TtBB 100).
with smaller windows when going from mesitylene to more hydrophobic swelling agents as TiPB, TEB, and TtBB.

Also the XRD patterns exhibit some differences (Fig. 4.3). The shoulder of the main reflection at larger 2θ values becomes more and more pronounced from mesitylene to TtBB. In the pattern of the material prepared with TtBB this shoulder has a broad local maximum. From the much larger width of this shoulder as compared to the main reflection, one can infer that this does not represent a second-order reflection. It can rather be attributed to an independent, secondary correlation maximum representing smaller layer spacing or pore diameter.

### 4.3.2 Varying amounts of mesitylene and TiPB as swelling agent

An alternative way to change the pore volume and pore diameter is to vary the molar amount of the swelling agent [52]. This method was applied to further investigate the influence of the amount and nature of the organic swelling agent on the resulting pore size.

A mesoporous material without any aromatic swelling agent was prepared together with materials with relative molar amounts of mesitylene in the range of 20-300% (MES 20 - MES 300) and with TiPB in the range of 5 - 100 % (TiPB 5 - TiPB 100). The pore characteristics derived from nitrogen sorption measurements are shown in Table 4.4. The material prepared without any swelling additive showed the typical pore characteristics of MCM-41. All materials except the one with a very small amount of mesitylene as swelling agent gave mesoporous materials with increased pore volumes and pore diameters. Generally, the materials prepared with mesitylene as swelling agent had slightly larger BET surface areas than those prepared with TiPB. An increase of the mesopore volume was always associated with a relative increase in average pore diameter. Therefore only pore volumes are mentioned hereafter as a means of expressing the degree of swelling observed for a certain material. The largest pore volumes, which could be achieved with mesitylene and TiPB were 3 cm³/g and 1.5 cm³/g respectively. Both swelling agents led to a point of saturation where additional swelling agent did not increase the pore volume any more (Table 4.4 and Fig. 4.5). With mesitylene this saturation was reached at a relative molar amount that was 5 times larger (200 %) than with TiPB (40 %) (Table 4.4).

The nitrogen sorption isotherms of the materials with the maximal degree of swelling (Fig. 4.6) show the same general features as those shown in Figure 4.2. Elemental analysis showed that all organic material was retained in the solid material even after the saturation of template swelling was reached (Table 4.3). Therefore it
### 4.3. RESULTS

Table 4.4: Pore characteristics of mesoporous materials prepared with different molar amounts of mesitylene and TiPB as swelling agents.

<table>
<thead>
<tr>
<th>Swelling Agent Material Identifier</th>
<th>(D_{B4B-FHH}) Adsorption</th>
<th>(D_{B4B-FHH}) Desorption</th>
<th>Total Pore Vol. (t-plot)</th>
<th>BET Surface</th>
<th>SAXS (^b) Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>no swelling</td>
<td>2.8</td>
<td>3.1</td>
<td>0.82</td>
<td>1098</td>
<td></td>
</tr>
<tr>
<td>Mesitylene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MES 20</td>
<td>3.8</td>
<td>4.3</td>
<td>0.59</td>
<td>949</td>
<td></td>
</tr>
<tr>
<td>MES 50</td>
<td>6.6</td>
<td>7.0</td>
<td>1.04</td>
<td>942</td>
<td></td>
</tr>
<tr>
<td>MES 75</td>
<td>7.9</td>
<td>8.2</td>
<td>2.20</td>
<td>1125</td>
<td></td>
</tr>
<tr>
<td>MES 100</td>
<td>10.1</td>
<td>10.1</td>
<td>2.67</td>
<td>1124</td>
<td>881 (1119)</td>
</tr>
<tr>
<td>MES 150</td>
<td>10.1</td>
<td>10.2</td>
<td>2.89</td>
<td>1145</td>
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</tr>
<tr>
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<td>11.3</td>
<td>3.10</td>
<td>1117</td>
<td></td>
</tr>
<tr>
<td>MES 30</td>
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<td>10.2</td>
<td>2.77</td>
<td>1106</td>
<td></td>
</tr>
<tr>
<td>TiPB</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiPB 5</td>
<td>3.2</td>
<td>4.2</td>
<td>0.86</td>
<td>942</td>
<td></td>
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<tr>
<td>TiPB 10</td>
<td>3.7</td>
<td>4.4</td>
<td>0.91</td>
<td>912</td>
<td></td>
</tr>
<tr>
<td>TiPB 20</td>
<td>5.0</td>
<td>4.8</td>
<td>1.14</td>
<td>986</td>
<td>839 (1024)</td>
</tr>
<tr>
<td>TiPB 30</td>
<td>6.1</td>
<td>5.0</td>
<td>1.26</td>
<td>936</td>
<td></td>
</tr>
<tr>
<td>TiPB 40</td>
<td>6.7</td>
<td>5.7</td>
<td>1.52</td>
<td>1090</td>
<td>1008 (1239)</td>
</tr>
<tr>
<td>TiPB 50</td>
<td>6.6</td>
<td>5.5</td>
<td>1.39</td>
<td>983</td>
<td></td>
</tr>
<tr>
<td>TiPB 75</td>
<td>6.8</td>
<td>5.7</td>
<td>1.49</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>TiPB 80</td>
<td>6.6</td>
<td>5.5</td>
<td>1.49</td>
<td>998</td>
<td>864 (1067)</td>
</tr>
<tr>
<td>TiPB 100</td>
<td>6.7</td>
<td>5.5</td>
<td>1.43</td>
<td>986</td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>series 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mix 75/10</td>
<td>9.2</td>
<td>9.3</td>
<td>2.34</td>
<td>1055</td>
<td></td>
</tr>
<tr>
<td>Mix 50/20</td>
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<td>8.2</td>
<td>2.26</td>
<td>1094</td>
<td></td>
</tr>
<tr>
<td>Mix 25/30</td>
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<td>6.8</td>
<td>1.85</td>
<td>1058</td>
<td></td>
</tr>
<tr>
<td>series 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mix 80/20</td>
<td>8.3</td>
<td>8.6</td>
<td>2.52</td>
<td>1103</td>
<td></td>
</tr>
<tr>
<td>Mix 60/40</td>
<td>7.8</td>
<td>7.3</td>
<td>2.17</td>
<td>1103</td>
<td></td>
</tr>
<tr>
<td>Mix 40/60</td>
<td>6.6</td>
<td>6.4</td>
<td>1.95</td>
<td>1106</td>
<td></td>
</tr>
<tr>
<td>Mix 20/80</td>
<td>6.2</td>
<td>5.5</td>
<td>1.73</td>
<td>1101</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) see Table 4.1

\(b\) specific inner surface area \(S_i\) calculated with \(s = 2.2 \text{ g/cm}^3\) (values in brackets were calculated with \(s = 1.65 \text{ g/cm}^3\)
Figure 4.5: Range of pore volume (a), and average pore diameter (b) achievable with pure TiPB, pure mesitylene and mixtures of both as swelling agent in this system.
4.3. RESULTS

Figure 4.6: Nitrogen sorption isotherms: (MES 200) maximal pore volume and pore diameter with mesitylene as swelling agent, (TiPB 40) maximal pore volume and pore diameter with TiPB as swelling agent.

is assumed that the excess aromatic molecules not incorporated into the organic-inorganic mesophase are located on the surface of M41S particles in microsized droplets. They do not serve as template for mesoporous materials and collapse already during the drying of the material.

4.3.3 SAXS investigation in the course of the synthesis

Comparison of benzene, mesitylene, and TiPB as swelling agents

Synthesis gels with benzene (BEN 100), mesitylene (MES 100), and TiPB (TiPB 40) as swelling agent were investigated with SAXS in the course of the syntheses. The maximal degree of swelling was larger when mesitylene instead of the larger aromatic compounds was used (Table 4.4). Therefore, syntheses with 100 % relative molar amount of benzene and mesitylene and 40 % relative molar amount of TiPB were compared. The SAXS patterns of all three gels directly after mixing looked very similar (Fig. 4.7a).

The patterns were consistent with a disordered hexagonal symmetry. They only differed in the d-spacing decreasing from benzene to mesitylene to TiPB (Table 4.5). After the first 24 h of thermal treatment at 100°C the SAXS patterns look completely
Figure 4.7: Small-angle X-ray curves I(h) in log-log representation, uncorrected for collimation effects, of synthesis gels with 100% relative molar amount of benzene (BEN 100), mesitylene (MES 100), and 40% relative molar amount of TiPB (TiPB 40): (a) directly after mixing the silicate and the template mixture, (b) after 24 h of thermal treatment at 100°C, (c) after 96 h of thermal treatment at the end of the synthesis.
Table 4.5: Phase symmetry, correlation lengths, and internal surface areas of M41S mesophases prepared with benzene, mesitylene, and TiPB as swelling agent at different stages of the synthesis.

<table>
<thead>
<tr>
<th></th>
<th>benzene (BEN 100)</th>
<th>mesitylene (MES 100)</th>
<th>TiPB (TiPB 40)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sym</td>
<td>corr.</td>
<td>int.</td>
</tr>
<tr>
<td>length</td>
<td>[nm]</td>
<td>[m²/ml]</td>
<td></td>
</tr>
<tr>
<td>mixed</td>
<td>hex</td>
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<td>5720</td>
</tr>
<tr>
<td>24 h</td>
<td>lam</td>
<td>4.8</td>
<td>4720</td>
</tr>
<tr>
<td>96 h</td>
<td>lam</td>
<td>4.2</td>
<td>3120</td>
</tr>
<tr>
<td>calc</td>
<td>-</td>
<td>11.2</td>
<td>2920</td>
</tr>
</tbody>
</table>

---

4.3. RESULTS

The SAXS data show that the formation of the organic-inorganic mesophase was completed within the first 24 h of thermal treatment. The additional 72 h of synthesis were, however, necessary to complete the silica condensation and to obtain stable mesoporous materials after the calcination [6,55].
Table 4.6: Phase symmetry, correlation length, and internal surface area of M41S mesophases with varying amount of mesitylene and TiPB as swelling agent after 24 h of synthesis at 100°C.

<table>
<thead>
<tr>
<th>symmetry</th>
<th>correlation length</th>
<th>internal surf. area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[nm]</td>
<td>[m²/ml]</td>
</tr>
<tr>
<td>200 % MES</td>
<td>un. d.</td>
<td>13.6</td>
</tr>
<tr>
<td>100 % MES</td>
<td>un. d.</td>
<td>12.6</td>
</tr>
<tr>
<td>50 %MES</td>
<td>un. d. + lamellar</td>
<td>9.8 ± 5.5</td>
</tr>
<tr>
<td>80 % TiPB</td>
<td>un. d.</td>
<td>8.5</td>
</tr>
<tr>
<td>40 % TiPB</td>
<td>un. d.</td>
<td>8.6</td>
</tr>
<tr>
<td>20 % TiPB</td>
<td>un. d.</td>
<td>7.7</td>
</tr>
</tbody>
</table>

- un. d. = undefined ordered mesophase
- internal surface area parameter from SAXS, including the volume fraction factor

Varying amounts of mesitylene and TiPB as swelling agent

Three gels with 50 %, 100 %, and 200 % relative molar amount of mesitylene were prepared (MES 50, MES 100, and MES 200) and SAXS patterns were recorded after 24 h of thermal treatment at 100°C (Fig. 4.8a). This point of the synthesis was chosen because the earlier experiments had shown that the formation of the phases was completed at that stage. For the material with 50 % relative molar amount of mesitylene two phases can be identified: one broad reflection at low q-values with a correlation length of 9.2 nm, and a lamellar phase with one relatively narrow reflection with a higher order reflection and a d-spacing of 5.5 nm. A clear indication that the second phase in this material is lamellar is the fact that it disappears during the calcination of the material. After the calcination (Fig. 4.8b) only the broad reflection with a correlation length of 8.3 nm can be identified. The materials prepared with 100 % and 200 % relative molar amount of mesitylene exhibit only one broad reflection but differ slightly in the correlation length (Table 4.6). The material prepared with 200 % mesitylene has a larger correlation length both after 24 h of thermal treatment and after the calcination of the materials.

Analogously to the above experiments with mesitylene, the same approach was taken with three gels with 20 %, 40 %, and 80 % relative molar amount of TiPB as swelling agent (TiPB 20, TiPB 40, and TiPB 80). The SAXS patterns after 24 h of thermal treatment (not shown) of all three synthesis gels look similar. The only difference is that the material with 20 % relative molar amount has a smaller correlation length than the other two (Table 4.6). The reflections of the material with 40 % and 80 % relative molar amount of TiPB appear at almost identical q-values i.e. no additional
Figure 4.8: Small-angle X-ray curves I(h) in log-log representation, uncorrected for collimation effects, of synthesis gels with 200 % (MES 200), 100 % (MES 100), and 50 % (MES 50) relative molar amount of mesitylene: (a) after 24 h of thermal treatment at 100°C, (b) after calcination of the organic-inorganic mesophase at 540°C.
swelling occurred if the amount of TiPB as swelling agent was doubled from 40 % to 80 %.

Specific inner Surface area

Specific inner surface areas (Table 4.4) and internal surface areas (Tables 4.5 and 4.6) were estimated from the decay of the SAXS patterns [58]. The development of the internal surface areas in synthesis gels with benzene, mesitylene, and TiPB as swelling agent (Table 4.5) shows that all three gels follow the same general features. The area decreased from the beginning throughout the whole synthesis and the calcination due to the condensation of the silica species. The identical values of the internal surface areas of synthesis gels with varying amounts of mesitylene and TiPB after 24 h of thermal treatment at 100°C (Table 4.6) also show that all gels follow the same pattern of phase evolution.

4.3.4 Mixtures of mesitylene and TiPB

Swelling the templating micelles with mesitylene alone could be used to prepare mesoporous materials with pore diameters in the range of 7-11 nm and large pore volumes (Fig. 4.5). TiPB as swelling agent gave materials with pore diameters in the range of 3-6 nm. Mixtures of the two swelling agents can be used to close the gap in pore diameter while maintaining large pore volumes. In one series of syntheses (Series 1 in Table 4.1) the materials with 100 % relative molar amount of mesitylene and 40 % of TiPB were chosen as the endpoints of mixtures. Mixtures were prepared by linearly decreasing the molar amount of mesitylene while simultaneously increasing the molar amount of TiPB (Fig. 4.5 and Table 4.4). In the other series (Series 2 in Table 4.1), the total amount of swelling agent was fixed to 100 % relative molar amount and the ratio of mesitylene/TiPB was varied. In both series the pore diameters could be adjusted to any value between 6 and 10 nm. In the range between 6 and 8 nm the pore volume of these materials was larger than in the case where pure mesitylene was used as swelling agent (Fig. 4.5). Thus, by using mesitylene, TiPB, or mixtures thereof any desired pore diameter between 4 and 11 nm could be obtained. Even though these M41S materials have no highly ordered mesopores they have larger specific surface areas and larger pore volumes than SBA-15 [15] and FDU-1 [59] materials.
4.4 Discussion

Benzene and 1,3,5-trialkylsubstituted aromatic compounds with methyl, ethyl, isopropyl, and tert-butyl substituents were tested as swelling agents for the template of M41S syntheses. Thereby the influence of both the increasing size and hydrophobicity of the aromatic swelling agent could be evaluated. The hydrophobicity of the aromatic compound, which increases in the order benzene < mesitylene < TiPB < TtBB proved to control the mesophase formation. The trends observed in nitrogen sorption, XRD, and SAXS are as follows: The average pore diameter of the final mesoporous material decreased with increasing hydrophobicity of the aromatic swelling agent. Together with the average pore diameter also the pore volume decreased. The pore geometry changed from a rod-like shape in the case of mesitylene to a more spherical shape with higher surface curvature with TiPB, TEB, and TtBB as swelling agent. The maximal degree of swelling decreased with increasing hydrophobicity of the aromatic swelling agent, due to the saturation of the micelles at lower SA/SiO2 ratios.

XRD and SAXS showed the formation of a lamellar phase for benzene as swelling agent. Small amounts of mesitylene gave a mixture of a lamellar phase and a phase with rod-like micelles. Large amounts of mesitylene led exclusively to a phase with rod-like templating micelles. For the more hydrophobic swelling agents the shoulder of the first reflection in the XRD and the SAXS pattern became more pronounced, which indicates the formation of a different phase. Globally, XRD and SAXS showed a trend from a lamellar to a rod-like and finally to a globular phase as the hydrophobicity of the swelling agent increased. This is in good agreement with the change of a rod-like to a spherical pore geometry deduced from the nitrogen sorption data.

Shape and size of a micelle are determined by the counterplay of the electrostatic repulsion of the surfactant head groups, the surface tension, which tries to minimize the surface area, and the tendency of the system to achieve a close packing of the hydrocarbon chains. In the absence of swelling agent the balance between the electrostatic repulsion of the cationic head groups and the close packing of the hydrocarbon chains leads to the formation of rodlike (cylindrical) micelles [4]. When benzene is added to the system it is incorporated near the cationic head groups and in the so-called palisade layer of the micelle [60–63]. It reduces the electrostatic repulsion between the head groups by screening and increases the volume of the hydrocarbon layer. A lamellar phase is formed (Fig. 4.9). Mesitylene has a lower tendency to be incorporated near the cationic head groups [53,61–65]. The micelle increases its curvature and becomes rodlike (Fig. 4.9). Since mesitylene is incorporated in the palisade layer as well as in the core of the micelle (at higher
concentrations), the curvature of these rodlike micelles remains low. The micelles can grow to large pore volumes and pore sizes. TEB, TiPB and TtBB have no tendency any more to be incorporated between the hydrocarbon chains. They only reside in the core of the micelle (Fig. 4.9). In order to increase the packing of the hydrocarbon chains, the curvature of the micelle has to increase. As a result, globular structures are formed. They cannot be swelled to large pore diameters because that would decrease the curvature, which is energetically not favored. Mesitylene leads to the largest degree of swelling because it can be incorporated in the core as well as in the palisade layer of the micelles and thereby stabilizes large micelles with low curvature.

The reason for the preferential location of benzene (near the head groups), mesitylene (in the palisade layer and in the core), TiPB, TEB and TtBB (only in the core) in the micelle is the hydrophobicity of the aromatic compounds, which increases from benzene to TtBB. The shape of the molecules may also play a role. It may be more difficult to incorporate the more spherical molecule TtBB between the straight hydrocarbon chains than to incorporate benzene or mesitylene.

The concept of changing the shape and the size of pores by adjusting the hydrophobicity of the swelling agent can not only be applied to cationic micelles in the synthesis of M41S, but can also be extended to other systems. An example is the transformation from a cylindrical pore system of SBA-15 to a spherical pore system in MCF when mesitylene is added as a swelling agent to the non-ionic block.
Figure 4.10: Nitrogen sorption isotherms of materials with 50 % relative molar amount of aromatic swelling agent (25/30 mixture of mesitylene and TiPB, pure mesitylene and pure TiPB).
copolymer template. This model also explains why, in a certain range of pore sizes, mixtures of mesitylene and TiPB lead to higher pore volumes than the pure compounds (Fig. 4.10). The material prepared with 25 % and 30 % relative molar amount of mesitylene and TiPB had about the same average pore diameter and hysteresis shape as the material that is prepared with 50 % relative molar amount of pure mesitylene. On the other hand the pore volume was twice as big. The reason is that a two-phase system was formed with 50 % relative molar amount of mesitylene, where one phase was lamellar and collapsed during the calcination. The role of the TiPB in the swelling agent mixture is to increase the micelle surface curvature to an extent that the formation of a lamellar phase is prevented.

4.5 Conclusions

Swelling of cationic surfactant micelles with varying amounts of TiPB (1,3,5-triisopropyl-benzene), mesitylene or mixtures thereof enabled the synthesis of M41S materials with any pore diameter between 3 and 11 nm. The materials exhibit narrow pore size distributions, large specific surface areas and pore volumes. The comparison of benzene, mesitylene, TEB (1,3,5-triethylbenzene), TiPB, and TtBB (1,3,5-tri-tert-butylbenzene) revealed that pore diameters decreased with increasing size of the swelling molecule. The only exception is benzene, which induces the formation of a lamellar phase that collapses during calcination. Mesitylene induces the formation of rod-like micelles, whereas the more hydrophobic swelling agents TEB, TiPB, and TtBB form globular micelles, which yield a pore system of large compartments interconnected by smaller openings in the calcined material. Since these globular micelles cannot accommodate large amounts of swelling agent, small pore sizes and pore volumes are obtained with TEB, TiPB, and TtBB. The reason for the different shapes and sizes of the micelles is the preferred locus of the aromatic compounds in the micelle. The more hydrophobic the swelling agent, the higher is its tendency to be incorporated only in the core of the micelle. Therefore the more hydrophobic swelling agents induce a transition towards micelle geometries with larger surface curvature. Mesitylene is the best swelling agent because it is distributed between core and palisade layer of the micelle and thereby stabilizes large micelles of low curvature.
Chapter 5

Solubilization of Aromatic Molecules in Templating Micelles of Mesoporous Silicas followed by $^1$H NMR

5.1 Introduction

In the previous chapter the effect of aromatic swelling agents on the pore geometry and pore size of mesoporous M41S materials was described. Benzene and 1,3,5-trisubstituted aromatic compounds were used as swelling agents. The characterization of the final products and SAXS measurements in the course of the synthesis showed that the nature and the amount of swelling agent influenced both the size and the geometry of the templating micelles and pores of the final M41S material. It was observed that the surface curvature of the templating micelle increased together with the hydrophobicity of the aromatic swelling agent. Based on NMR [64] and UV [62] results of others this effect could be rationalized with the locus of incorporation of the aromatic swelling agent in the templating micelle. It was proposed that benzene and substituted aromatic molecules distribute according to their polarity between the highly nonpolar core and the relatively polar interfacial region of the hexadecyl-trimethyl-ammonium-bromide micelles in water. Calorimetric measurements of an aqueous solution of tetradecyl-trimethyl-ammonium-bromide showed that benzene decreases the micelle curvature [61]. Simultaneously a transition of the micelles from a spherical to a rod-like geometry was observed. The transformation of rod-like tetradecyl-trimethyl-ammonium-bromide micelles to spherical micelles as a consequence of the addition of both aliphatic and aromatic compounds was also described [60]. Here a $^1$H NMR investigation of the distribution of aromatic
molecules in the silica-surfactant micelles of M41S synthesis gels is reported. Goal of the study was to provide direct evidence for the locus of incorporation of the aromatic molecules in the real synthesis mixture.

## 5.2 Experimental

Mesoporous pure silica M41S materials were synthesized by thermal treatment of a gel with sodium silicate solution, cationic quaternary ammonium surfactants (C\textsubscript{16} and C\textsubscript{12} chains), organic swelling agent and water for 96 h at 100°C in a sealed Teflon vessel, as described in the previous chapter. The nature and the amount of the aromatic swelling agent SA (benzene, mesitylene, 1,3,5-triisopropylbenzene (TiPB), and 1,3,5-tri-tert-butylbenzene (TtBB)) were varied while keeping all the other parameters constant. In the standard recipe a molar ratio of SA/SiO\textsubscript{2} = 0.72 was used [6]. For simplicity, this relative molar amount of swelling agent was defined as 100%. Smaller and larger SA/SiO\textsubscript{2} ratios are expressed by the corresponding values in percent (Table 5.1).

Fifteen syntheses of mesoporous materials were performed and monitored in situ with \textsuperscript{1}H NMR. Samples from the synthesis gel were taken at different stages of the

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### Table 5.1: Amounts of aromatic swelling agents employed.

<table>
<thead>
<tr>
<th>swelling agent</th>
<th>relative molar amount, %</th>
<th>molar ratio SA/SiO\textsubscript{2}\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>no swelling</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>benzene</td>
<td>5</td>
<td>0.04</td>
</tr>
<tr>
<td>mesitylene</td>
<td>20</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>1.45</td>
</tr>
<tr>
<td>TiPB \textsuperscript{b}</td>
<td>5</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.58</td>
</tr>
<tr>
<td>TtBB \textsuperscript{c}</td>
<td>5</td>
<td>0.04</td>
</tr>
</tbody>
</table>

\textsuperscript{a} SA: swelling agent

\textsuperscript{b} TiPB: 1,3,5-trisopropylbenzene

\textsuperscript{c} TtBB: 1,3,5-tri-tert-butylbenzene
synthesis procedure. For all measurements the synthesis gel was cooled to ambient
temperature and stirred for at least 15 min before the sample was taken. A Wilmad
coaxial insert capillary (1 mm OD) was filled with synthesis gel and was introduced
into an ordinary 5 mm NMR tube with TMS in deuterated chloroform (CDCl₃) as
external standard. ¹H NMR spectra of the synthesis gels were recorded on a Bruker
AVANCE 500 at ambient temperature (¹H frequency 500.13 MHz, ¹H recycle de-
lay 2.7 s). At the end of the syntheses, the gels were filtered. The as synthesized
material was dried, calcined and characterized with nitrogen sorption. All materi-
als showed pore characteristics comparable to those prepared without the removal
of small amounts of gel for ¹H NMR measurements in the course of the synthesis.
The formation of silica-surfactant micelles in these synthesis systems is rather slow
since sodium silicate is used as the silica source. The ¹H NMR measurements lasted
10 min which is fast compared to the 96 h total synthesis time. In addition the
¹H NMR spectra were recorded at ambient temperature whereas the temperature of
the thermal treatment was 100°C. Therefore, it can be safely assumed that the syn-
thesis mixtures change only to a very small extent during the NMR measurements.
This was verified by repeating some of the measurements, no differences could be
observed. The sedimentation of the silica particles during the measurements was
very slow and did not interfere.

5.3 Results

5.3.1 No aromatic swelling agents

For the peak assignment an aqueous solution of the two quaternary ammonium salts
with the same concentration as used in the syntheses was measured (Fig. 5.1).
The two surfactants differ only in the length of the hydrophobic chain. Without any
swelling agent or silicate present one obtains a clear solution with sharp ¹H NMR
signals. The chemical shifts of the peaks were very close to those of a similar solution
measured in D₂O [66].

When the template and the silicate were mixed to obtain the synthesis mixture, a
white precipitate formed immediately. From that point the synthesis mixture was a
homogeneous white gel throughout the synthesis. The effect of the gel formation on
the ¹H NMR spectrum of the quaternary ammonium template can be seen in the
spectrum of a synthesis mixture recorded after stirring the gel for 60 min (Fig. 5.2a).
Because all ¹H NMR spectra of the synthesis gels were recorded with an external
reference of TMS in CDCl₃, they all showed the following sharp signals coming from
the external reference: CHCl₃ impurity at 7.26 ppm, water impurity at 1.50 ppm,
HDO at 1.54 ppm, and TMS at 0.00 ppm. Directly after mixing the synthesis gel, the quaternary ammonium species could be identified by three very broad peaks in the $^1$H NMR spectrum (Fig. 5.2a). One peak with a maximum at 3.09 ppm can be assigned to the protons bound to the carbon atoms next to the nitrogen atom. The signal at 1.21 ppm comes from the protons in the middle of the hydrophobic chain of the surfactant molecule. The signal with a maximum at 0.85 ppm can be assigned to the CH$_3$ groups at the end of the hydrophobic chain. In addition to these three very broad peaks, two very weak but sharp signals were observed at 1.26 ppm and 0.88 ppm. They are most probably caused by a small fraction of the quaternary ammonium salt that is still dissolved in the aqueous phase of the synthesis gel. The chemical shift of these two signals was slightly lower than those in the aqueous solution (Fig. 5.1), because the synthesis gel has a higher ionic strength. The reason for the broadening of the peaks of the cationic quaternary ammonium species in the synthesis gel is the binding of negatively charged silicate oligomers and polymers to the quaternary ammonium cations. The large S$^+$I$^-$ units have a low mobility and are partly insoluble [46]. After 24 h of synthesis (Fig. 5.2b), the proton peaks of the quaternary ammonium species were broadened into the baseline. This is due
to the condensation between adjacent silicate species and the actual formation of the solid organic-inorganic mesophase during these first 24 h of synthesis. No more peak maxima could be identified in the spectra. On the other hand, a new and relatively sharp signal at 1.85 ppm appeared in the spectrum recorded after 24 h of synthesis and also in the subsequent $^1$H NMR spectra recorded in the course of the synthesis. This signal comes from the methyl group of the acetic acid which is added to the synthesis mixture after 24 h. The addition of acid was shown to improve the stability of this kind of mesoporous materials [6,55]. The acid proton of the acetic acid was not visible because it exchanges rapidly with the water in the synthesis mixtures. Until the end of the synthesis (Fig. 5.2c) the $^1$ NMR spectrum of this synthesis gel did not change significantly any more.
5.3.2 Identical amounts of benzene, mesitylene, TiPB, and TtBB as swelling agents

The same peaks of the quaternary ammonium salts and the acetic acid as described above were also observed in all the syntheses performed with aromatic swelling agents. In the following, only the evolution of the peaks ascribed to the aromatic swelling agents are discussed. In general, the signals of the aromatic swelling agents were sharper than those of the surfactant molecules. This is a consequence of the fact that the swelling agents are more mobile than the surfactant molecules, which are bound to the silicate by ionic bonds. The differences between the chemical environments of the four aromatic swelling agents could be best seen in materials with very small SA/SiO₂ ratios, i.e. 5 % relative molar amount of each swelling agent. Figures 5.3 and 5.4 show the ¹H NMR spectra of the respective gels before and after 96 h of thermal treatment at 100°C respectively. In the case of benzene, the aromatic protons were clearly visible in the gel before the thermal treatment. After 96 h at 100°C, no signal for the aromatic protons could be identified any more. This indicates that the benzene was immobilized in the templating micelle, causing a broadening of its NMR signal. The broad signal disappeared in the baseline. In the case of mesitylene, the peak of the aromatic protons was strongly diminished after 96 h of thermal treatment, but could still be identified. 90 % of its intensity was lost in the baseline, as in the case of benzene. The same effect was observed for the aliphatic protons of the mesitylene molecule. At the end of the synthesis all spectra showed a broad shoulder at the low field side of the water signal. The intensity of the shoulder strongly decreased when D₂O was used as a solvent instead of H₂O (Fig. 5.5). Therefore, the shoulder is ascribed to water incorporated in the cationic palisade layer of the silica-surfactant micelles.

With TiPB as swelling agent no loss of ¹H NMR signal intensity was observed after 96 h of thermal treatment, i.e. no intensity was lost in a broadened peak. Each of the three resonances at 6.65 ppm (aromatic protons), 2.62 ppm (C-H of the isopropyl group), and 1.01 ppm (CH₃ of the isopropyl group) could be deconvoluted into a narrow signal at higher chemical shift and a broader signal at a lower chemical shift. The broader signal had a relative intensity of about 40 %. A similar situation was found in the spectrum of TtBB after 96 h of thermal treatment: Each peak consisted of two overlapping signals. The separation of the two signals was larger than in the case of TiPB. The one at lower chemical shifts was also broader and accounted for 10 % of the intensity. The signal intensities of TiPB and TtBB increased from the spectrum measured after mixing the synthesis gel to the spectrum measured after 96 h of thermal treatment (compare Figs. 5.3 and 5.4). This is ascribed to the low
5.3. RESULTS

Figure 5.3: $^1$H NMR spectra of synthesis mixture with 5 \% relative molar amount of varying aromatic swelling agent after 60 min of stirring (before the thermal treatment). Benzene (BEN 5), mesitylene (MES 5), TiPB (TiPB 5), TtBB (TtBB 5).
Figure 5.4: $^1$H NMR spectra of synthesis mixture with 5% relative molar amount of varying aromatic swelling agent after 96 h of thermal treatment at 100°C. Benzene (BEN 5), mesitylene (MES 5), TiPB (TiPB 5), TtBB (TtBB 5).
solubility of these compounds. TtBB is a solid at ambient temperature and was still undissolved after 60 min of stirring the synthesis gel.

5.3.3 Varying amounts of mesitylene and TiPB as swelling agent

$^1$H NMR spectra of synthesis gels with varying amounts of mesitylene (Fig. 5.6) and TiPB (Fig. 5.7) as swelling agent were recorded after 96 h of thermal treatment at 100°C. When the relative molar amount of mesitylene increased, the peaks were shifted to higher field (Table 5.2). In all the spectra only one signal of the aromatic protons could be identified. On the other hand, all materials prepared with TiPB as swelling agent showed a splitting of all three proton resonances into two or more distinct signals, as already mentioned above. The chemical shift of the most intense TiPB resonance was not changed by the variation of the amount of TiPB.

It was mentioned above that with 5% relative molar amount of mesitylene only a very small peak could be observed. Most of the mesitylene in this material was incorporated and immobilized between the aliphatic surfactant chains causing a severe broadening of the $^1$H NMR signal, so that it could not be identified any more. If the amount of mesitylene was increased, a larger fraction of the original amount
Figure 5.6: $^1$H NMR spectra of the aromatic and water region of synthesis mixtures with varying relative molar amounts of mesitylene after 96 h of thermal treatment at 100°C (MES 200, MES 100, MES 50, MES 20, and MES 5).
5.3. RESULTS

Figure 5.7: $^1$H NMR spectra of the aromatic and water region of synthesis mixtures with varying relative molar amounts of TiPB after 96 h of thermal treatment at 100°C (TiPB 80, TiPB 40, TiPB 30, TiPB 20, and TiPB 5).
Table 5.2: Chemical shifts of the predominant peaks in the $^1$H NMR spectra after syntheses with varying amounts of mesitylene and TiPB as swelling agents.

<table>
<thead>
<tr>
<th>rel. molar amount of swelling agent [%]</th>
<th>aromatic H</th>
<th>aliphatic H (2 $^a$)</th>
<th>aliphatic H (3 $^a$)</th>
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<td>$^b$</td>
</tr>
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<td>MES 50</td>
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<td>1.89</td>
<td>$^b$</td>
</tr>
<tr>
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<td>2.03</td>
<td>$^b$</td>
</tr>
<tr>
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<td>2.11</td>
<td>$^b$</td>
</tr>
<tr>
<td>pure mesitylene $^c$</td>
<td>6.63</td>
<td>2.16</td>
<td>$^b$</td>
</tr>
<tr>
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<td>0.94</td>
</tr>
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<td>2.53</td>
<td>0.94</td>
</tr>
<tr>
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<td>2.54</td>
<td>0.95</td>
</tr>
<tr>
<td>TiPB 20</td>
<td>6.60</td>
<td>2.54</td>
<td>0.95</td>
</tr>
<tr>
<td>TiPB 5</td>
<td>6.65</td>
<td>2.62</td>
<td>1.01</td>
</tr>
<tr>
<td>pure TiPB $^c$</td>
<td>6.85</td>
<td>2.78</td>
<td>1.19</td>
</tr>
</tbody>
</table>

$^a$ labelled as in Fig. 5.3

$^b$ only one aliphatic proton

$^c$ as a reference

could be detected at the end of the synthesis. Also a decrease of the chemical shift of the aromatic protons was observed. Both effects are due to an increasing amount of mesitylene molecules that have an aromatic environment. The reason for the smaller chemical shifts of the species in such an aromatic environment is the change in magnetic susceptibility compared to the environment with aliphatic surfactant chains. At 50 % relative molar amount of mesitylene the chemical shift remains almost constant, indicating that with larger amounts of swelling agent the average chemical environment of the mesitylene did not change any more. The chemical shift of all the peaks of the TiPB in the templating micelles was very similar for all investigated amounts of TiPB as swelling agent. This clearly indicates that the change from a less aromatic environment to one with more aromatic character did not occur if TiPB was used as swelling agent. Already very small amounts of TiPB are incorporated in the core of the micelle where nests with aromatic character form. Although TiPB has an aromatic environment in the core of the micelle, the chemical shift is smaller than in a pure TiPB solution (Table 5.2). The resonance of mesitylene in materials with large amounts of swelling agent showed the same shift to higher fields with respect to the pure compound. The reason for this effect must be the magnetic susceptibility of our synthesis gels, which are more diamagnetic than
the pure aromatic solutions. The signal around 7 ppm that appeared when larger amounts of TiPB swelling agent were used is assigned to TiPB species between the aliphatic chains of the surfactant molecules.

5.4 Discussion

It is known that benzene is incorporated into the palisade layer of micelles of quaternary ammonium surfactants [60–62], whereas aromatic compounds with more hydrophobic substituents tend to reside in the hydrophobic core of the micelle [53, 61–64]. Our NMR data show that this is also valid for silica-surfactant $S^+I^-$ micelles: A comparison of Fig. 5.3 and 5.4 shows that the initially rather sharp $^1H$ NMR resonance of benzene disappeared in the course of the synthesis. In the previous chapter it was found that benzene as swelling agent leads to the formation of a lamellar organic-inorganic mesophase. A lamellar phase can only be advantageous for this system if the surface curvature of the organic template is decreased by the incorporation of the benzene between the cationic head groups of the surfactant molecules. The reasons for the observed decrease of surface curvature as a consequence of the incorporation of the benzene might be the reduction of the electrostatic repulsion between the cationic head groups of the micelles or a change in charge matching between the cationic micelle and the anionic silicate species [63]. The incorporation of the benzene molecules between the surfactant molecules bound to the growing silica polymers leads to a strong reduction of their mobility. This would cause a severe broadening of the benzene signal similar to the broadening of the signals of the surfactant species. This is in agreement with the experimental observation. We conclude that with increasing synthesis time an increasing fraction of the benzene was immobilized in the organic-inorganic mesophase, near the cationic head groups. At the end of the synthesis, the incorporation into the surfactant layer was complete, since the NMR peak of the mobile benzene had completely disappeared.

The same was observed if mesitylene was used as a swelling agent, but to a smaller extent: The $^1H$ NMR peaks of mobile mesitylene did not disappear completely at the end of the synthesis (Fig. 5.4). The residual peaks are attributed to mesitylene molecules that still possess some mobility. Their chemical shift is relatively large because these molecules feel the aliphatic chains and the polarizing environment of the cationic head groups of the surfactant molecules. Both effects lead to a shift of the signals to lower field. The shift of mesitylene in cyclohexane for example is 0.4 ppm larger than in pure mesitylene. The majority of the mesitylene molecules, however, did not give rise to a detectable NMR resonance because they are trapped
between the aliphatic chains of the surfactant. The driving force for incorporation of mesitylene into the surfactant layer was smaller than in the case of benzene.

In the case of TiPB the intensity of the relatively sharp peaks originating from the mobile species was retained. No broadening of the signals which could be attributed to molecules immobilized in the surfactant layer was observed. With TtBB relatively sharp signals could only be identified at the end of the synthesis. Two components could be identified in the spectra of TiPB and TtBB. This indicates that two different environments, which both allow some mobility, are populated. The predominant signal is attributed to swelling molecules in the core of the micelle. The other signal, which is broader and occurs at smaller shifts, could not be unequivocally assigned.

The following two hypotheses could explain this signal: (1) TiPB/TtBB molecules are located between the aliphatic chains of the surfactant molecules. The reason for the smaller chemical shift of TiPB/TtBB molecules in this position is the polarizing effect of the water that is occluded in the palisade layer of the micelle if such small amounts of swelling agent are used. (2) The formation of ordered domains (e.g. π-stacking) of the aromatic compounds in the core of the micelle.

The discussion above referred to the spectra measured in synthesis mixtures containing 5% swelling agent. If the amount of the swelling agent mesitylene was increased, a decrease in the chemical shifts of the one species could be observed. This is due to an increasing amount of mesitylene in the aromatic environment in the core of the micelle. The chemical shifts of the main species of the TiPB in the templating micelles were very similar for all investigated amounts of TiPB as swelling agent (Table 5.2).

By combining these findings the following conclusion can be drawn: The TiPB is under no conditions immobilized in the surfactant shell in a way that severe line broadening would occur. The fact that the chemical shifts of the main TiPB signal did not change as a function of the amount of this swelling agent indicates that these molecules are exclusively incorporated in the core of the micelle or in positions where an exchange of the molecules is still possible. Mesitylene is incorporated in both the surfactant shell and the core of the micelle. At low amounts of swelling agent most of the mesitylene is immobilized in the surfactant shell, but at high concentrations a fast exchange between the molecules in the core and in the shell of the micelle takes place.

The \(^1\)H NMR spectra of the synthesis gel without aromatic swelling agent (Fig. 5.2) show that the signals of the surfactant molecules are severely broadened during the first 24 h of synthesis. This is due to the formation of an organic-inorganic mesophase where the surfactant molecules are ionically bound to the solid silicate.
5.5. CONCLUSIONS

The broadening does not change any more during further synthesis. This shows that all surfactant molecules are incorporated in the solid organic-inorganic mesophase after 24 h of synthesis. The broadening of the signals of small amounts of benzene and mesitylene as swelling agent followed exactly the same pattern (Fig. 5.4). This is in good agreement with the results of the SAXS measurements in the previous chapter where it was shown that mesophases do not change much after the first 24 h of synthesis. This supports the mechanistic model that the mesophase is formed within the first 24 h of synthesis and that the last 72 h are necessary to strengthen the silicate network by further condensation between adjacent silicate units.

5.5 Conclusions

The $^1$H NMR data show that benzene is located preferentially near or between the head groups of the surfactant molecules. Mesitylene is distributed between the core and the shell of the micelle, whereas 1,3,5-triisopropylbenzene and 1,3,5-tri-tert-butylbenzene reside exclusively in the core of the micelle. The preferred locus of these swelling agents in the templating micelles for the M41S synthesis follows the same trend as in purely aqueous surfactant solutions. This different location of the swelling agent within the micelle explains the change in geometry of the silica-surfactant micelles described in the previous chapter. By incorporating benzene close to the head groups of surfactant molecules, it reduces the surface curvature, which leads to a lamellar structure. Mesitylene has a lower tendency to adsorb near the head groups. The curvature of the micelle surface is therefore larger and cylindrical pores are obtained. Yet, the ability of mesitylene to exchange between the core and the shell of the micelles allows the stabilization of the micelles with very low curvature and large internal volume. Large pore volumes and pore sizes can be obtained. 1,3,5-triisopropylbenzene resides exclusively in the core of the micelle. As a result, the curvature of the micelle has to increase and a transition to a spherical micelle is observed.
CHAPTER 5. $^1$H NMR DURING $M_{41S}$ FORMATION
Chapter 6

Functionalization of Silica Surfaces with Aromatic Compounds and Trimethylsilane

6.1 Introduction

The surface of silica materials can be functionalized with various organic groups by treatment with the respective silane component [67–69]. This methodology is often referred to as grafting. Silanol groups react thereby with chloro- or alkoxy-organosilanes (Fig. 6.1). Silanes with one, two or three leaving groups are common. In this study silanes with three alkoxy leaving groups were mostly used. The possible modes of surface modification are depicted in Figure 6.1.

The availability of the silanol groups on the surface determines whether the grafted silicon atom is bound via one, two or three silicon-oxygen bonds. It is still not clear which is the predominant mode under a certain condition. The grafted silicon atoms are denoted as T\(^1\) (RSi(OSi)(OR'))\(_2\), T\(^2\) (RSi(OSi)(OR'))\(_2\) (OR') and T\(^3\) (RSi(OSi)(OR'))\(_3\) sites, respectively, where R is the organic moiety and R’ is an alkyl-group or a H atom. Depending on the silane, the specific surface area of the silica and the available number of surface silanol groups organic loadings of 0.2–5 mmol/g of solid can be obtained. Because many silanes are commercially available silica surfaces can be functionalized with a broad variety of organic groups. If ordered mesoporous silica materials as M41S or SBA-15 are used for functionalization by grafting of silanes both the average pore diameter and the specific surface area are decreased during this process. To a certain extent this effect is expected because the walls of the materials become thicker.

The functionalization with phenyl, benzylchloride and trimethylsilyl groups is described in this chapter.
6.2 Experimental

6.2.1 Functionalization with phenyl-groups

M41S materials functionalized with phenyl-groups were synthesized with a procedure that was based on a method originally described by Feng et al. [20] and slightly modified in our group [21,51] using phenyltrimethoxysilane (see PTMS in Fig. 6.2) as the grafting reagent. The procedure always included the same steps. Prior to synthesis the mesoporous M41S material was refluxed in water (25 ml per g of solid) for 60 min. After the water treatment the material was collected by filtration with a glass fritt (porosity 4) and washed with benzene or toluene. The wet material was suspended in benzene or toluene (100 ml per g of solid) and the majority of the remaining water in the M41S material was removed during 2 h of azeotropic distillation (1-4 ml water removed per g of solid).

After cooling to ambient temperature the PTMS grafting reagent (19 mmol or 4 ml per g of solid) was added to the slurry. This mixture was stirred over night (14 - 20 h). In some experiments the solid was filtered off the reaction mixture with unreacted alkoxysilane and dispersed in fresh solvent. This step is referred to "intermediate filtration". The terminal step of the functionalization reaction was refluxing the reaction mixture for 1 h. The final product was collected by filtration and washed.

Figure 6.1: Functionalization of silica materials with silane compounds.
with isopropanol. In some experiments a Soxlett-extraction was performed at this stage. The functionalized material was placed in a Soxlett filter and treated with a 2:1 diethylether : acetonitrile mixture for 24 h. The final material was dried in an evacuated oven at 50°C.

### 6.2.2 Functionalization with benzylchloride-groups

**Functionalization "with water treatment"**

M41S materials functionalized with benzylchloride groups were synthesized with three different procedures. The most used one was similar to the one described for phenyl groups (see 6.2.1). The only differences were that (p-chloromethyl)phenyltrimethoxysilane (see CMPTMS in Fig. 6.2) was used as grafting reagent instead of PTMS and that 5 ml (19 mmol) of grafting reagent were used per g of support. This method is referred to as functionalization "with water treatment" hereafter.

**Functionalization "after equilibration in humid atmosphere"**

Alternatively, benzylchloride-functionalized materials were prepared following two procedures that were based on methods reported by Maciel et al. [19,70].
In the first method the mesoporous material was stored in a humid atmosphere (saturated with water at room temperature) for at least a week in order to generate silanol groups on the surface. Then some of the water was removed with high vacuum treatment ($10^{-1}$ mbar) at different temperatures. The rest of the procedure was as the one "with water treatment" described before. This method is referred to as functionalization "after equilibration in humid atmosphere" hereafter.

**Functionalization "with chlorosilane"**

For the third method another grafting reagent was used to generate benzylchlo-
rside moieties. Instead of the trimethoxysilane group as linker between silicic sur-
face and the organic groups trichlorosilane substituted with a benzylchloride was
used as grafting reagent. To use (p-chloromethyl)phenyltrichlorosilane (CMPTCS
in Fig. 6.2) water had to be excluded from the functionalization reaction to prevent
hydrolysis and polymerization of the trichlorosilane moiety. Prior to the synthesis
the mesoporous material was dried under high vacuum at 400°C for 4 h. The dried
material was suspended in dry toluene (70 ml per g of solid). Then the CMPTMS
grafting reagent was added (3.5 ml or 13 mmol per g of solid). The slurry was
heated to 70°C for 2 h. The solid was filtered and washed with toluene, followed by
acetone. The final product was dried under vacuum at 50°C. This third method is
referred to as functionalization "with chlorosilane" hereafter.

**6.2.3 Functionalization with trimethylsilane-groups**

Mesoporous materials with trimethylsilane moieties covalently bound to their surface
were prepared by using a procedure that was described by Anwander et al. [71] using
1,1,1,3,3,3-hexamethyldisilazane (see HMDS in Fig. 6.2) as the grafting reagent. The
mesoporous starting material was dried under high vacuum at 400°C for 24 h and
suspended in dry hexane (40 ml per g of solid). Then HMDS was added (1 ml per
g of solid) and the reaction mixture was stirred for 24 h at room temperature. The
functionalized product was filtered, washed with hexane and dried in an evacuated
oven at 50°C.
6.3 Results and discussion

6.3.1 Properties of phenyl-functionalized materials

Phenyl grafted mesoporous M41S materials were characterized by nitrogen physisorption measurements, elementary analysis and IR. Data from physisorption and elementary analysis are collected in Table 6.1.

The two materials that were prepared with benzene with identical experimental parameters (G16 and G40 in Table 6.1) show the reproducibility of this method. Almost identical BET surface areas were obtained. Pore volume and average BJH pore diameter differed only slightly. It was found that the pore volumes are much more sensitive to changes in the accessibility of the pores upon functionalization than the BET surface areas. Materials with larger pore volume and average BJH pore diameter also showed a smaller carbon content in organic elementary analysis. The influence of this factor can be seen from the pore characteristics of a material that was prepared with toluene as solvent instead of benzene (G39 in Table 6.1). A slightly larger carbon content led to a significant decrease in pore volume, BET surface area and average BJH pore diameter. Toluene was tested as a solvent because it is less hazardous than benzene. The reason why toluene led to a higher organic content than benzene is that the azeotropic distillation is less efficient, i.e. more adsorbed water is left on the surface after distillation in toluene. If more water is left in the mesopores after the azeotropic distillation the water can induce an oligomerization of the silanes and lead to pore blocking. Adjusting the right amount of water in the M41S support by azeotropic distillation is therefore crucial for the
success of the functionalization. A small amount must, however, remain in the pores in order to hydrolyze the alkoxysilanes (Fig. 6.3). The silanol groups (Si-OH) of the hydrolyzed silanes react much faster with the silica surface than the methoxysilane groups (Si-OCH₃) [72].

The question arises if it is more desirable to have a material with high organic loading and poorer pore characteristics or the opposite. The fact that a phenyl-functionalized material prepared in benzene as solvent (G16 in Table 6.1) showed complete stability against boiling water shows that the silicic surface is fully covered by the organic layer and thereby protected against water. Otherwise the water would hydrolyze the silica from areas which are not functionalized.

In order to prevent overreaction of trialkoxysilane with the solid the intermediate filtration and redispersion in fresh solvent was performed prior to the refluxing step. The material prepared in this way (G37 in Table 6.1) showed clearly superior pore characteristics and smaller organic loading than a material that was prepared identically but omitting the intermediate filtration (G39 in Table 6.1).

The reason for the positive effect of the intermediate filtration on the quality of the functionalized material lies in the refluxing step that is performed afterwards. This refluxing step is considered as final strengthening of the already bound silane species (Fig. 6.4) by condensation of unreacted -OH or -OCH₃ groups. If the intermediate filtration is omitted, H₂O which is formed during the condensation of -OH groups can hydrolyze present alkoxysilanes and thereby improve their reactivity. That can cause an oligomerization of unreacted silanes and cause pore blocking.

The Soxlett extraction that was performed in some functionalization reactions (e.g. G37 sox in Table 6.1) did not change the surface characteristics or the organic loading of the functionalized materials. Two conclusions can be drawn from that: (1) Pore characteristics can not be improved after the functionalization reaction with that method. (2) The functionalized material is very stable against organic solvents. That shows that silicon oligomers (if there are any) do not dissolve in the solvent and that surface bound groups are stable.
A comparison of the nitrogen isotherms of the parent M41S and the PTMS functionalized materials that were prepared in benzene and toluene (G16 and G37 in Fig. 6.5) as solvent shows that the functionalization in benzene gives the material with slightly better pore characteristics (i.e. specific surface area, total pore volume and average pore diameter), but the difference is small.

For these reasons the method with toluene as solvent, an “intermediate filtration” and no further treatment after the refluxing step (as used for the synthesis of G37 in Table 6.1) was used as standard method hereafter.

The IR spectrum of the parent M41S material (Fig. 6.6) shows broad silanol bands above 3000 cm$^{-1}$ and remaining template (below 3000 cm$^{-1}$) that was not removed during the calcination. A band assignment [73] is given in Table 6.2.

The IR of the phenyl-functionalized material (G16 in Fig. 6.6) shows the characteristic bands of the aromatic ring (Table 6.3) and quite a lot of bridged silanol groups. This shows that with phenyl by far not all available silanol groups on the surface...
react with the alkoxy silane reagent. The reason is most probably the incomplete hydrolysis of the trimethoxysilane (characteristic bands observed in the IR, Fig. 6.6 and Table 6.3).

### 6.3.2 Properties of benzylchloride-functionalized materials

Benzylchloride functionalized materials were synthesized by three different methods (see 6.2.2). For two of the methods different experimental parameters were tested. Data obtained from nitrogen adsorption measurements and elementary analysis are collected in Table 6.4.

The comparison of the three procedures shows that functionalization of M41S materials ”with water treatment” yields a material with a carbon content over 20 wt%. Functionalization, after the parent M41S materials were equilibrated in a humid atmosphere, yields materials with a carbon content around 15 wt%. Both methods cause rather large but comparable loss of surface area and pore volume. The third method, the functionalization ”with chlorosilane”, gave a material with a very low carbon content, but very high accessible surface area and pore volume. These properties are advantageous if the surface does not have to be functionalized completely.
Figure 6.6: IR spectra of parent M41S and phenyl-functionalized M41S materials
### Table 6.3: IR band assignment of phenyl-functionalized material (G16)

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<tr>
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<th>Assigned Species</th>
<th>Wavenumbers [cm(^{-1})]</th>
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<td>Arom. ring vibration</td>
</tr>
</tbody>
</table>

\(a\) one bridge; \(b\) two bridges; \(c\) unsubstituted methoxy-group of silane; \(d\) rest of template; \(e\) benzene fingers; \(f\) Si substituted C atom; \(g\) quadrant I; \(h\) quadrant II

### Table 6.4: Properties of benzylchloride-functionalized mesoporous materials

<table>
<thead>
<tr>
<th>Material procedure (^a)</th>
<th>Method (^b)</th>
<th>BET Surf. [m(^2)/g]</th>
<th>Total pore vol. [cm(^3)/g]</th>
<th>Avg. BJH [nm]</th>
<th>C cont [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent</td>
<td></td>
<td>1080</td>
<td>2.64</td>
<td>7.5</td>
<td>0.2</td>
</tr>
<tr>
<td>G6 water trea. benz</td>
<td></td>
<td>284</td>
<td>0.37</td>
<td>4.3</td>
<td>22.5</td>
</tr>
<tr>
<td>G9 eq. hum. at. no HV</td>
<td></td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>18.3</td>
</tr>
<tr>
<td>G10 eq. hum. at. 24h HV@RT</td>
<td></td>
<td>245</td>
<td>0.20</td>
<td>2.9</td>
<td>14.8</td>
</tr>
<tr>
<td>G12 eq. hum. at. 6h HV@150</td>
<td></td>
<td>350</td>
<td>0.29</td>
<td>3.8</td>
<td>n.m.</td>
</tr>
<tr>
<td>G7 chlorosilane 24h HV@400</td>
<td></td>
<td>965</td>
<td>1.94</td>
<td>6.4</td>
<td>1.6</td>
</tr>
</tbody>
</table>

\(a\) water trea.: functionalization "with water treatment," eq. hum. at.: functionalization "after equilibration in humid atmosphere," chlorosilane: functionalization "with chlorosilane"; \(b\) benz: benzene as solvent; no HV: no high vacuum treatment at all; HV@RT: high vacuum treatment (10\(^{-1}\) mbar) at room temperature; HV@XXX: high vacuum treatment at XXX°C; \(c\) calculated from the desorption branch of the isotherm.
Table 6.5: Comparison of phenyl and benzylchloride-functionalized materials

<table>
<thead>
<tr>
<th>Material</th>
<th>org. group</th>
<th>BET surf. [m²/g]</th>
<th>tot. pore vol. [cm³/g]</th>
<th>pore diam. des. BJH [nm]</th>
<th>pore diam. ads. BJH [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>parent</td>
<td>no org. group</td>
<td>1080</td>
<td>2.64</td>
<td>7.5</td>
<td>8.8</td>
</tr>
<tr>
<td>G16</td>
<td>phenyl</td>
<td>659</td>
<td>1.37</td>
<td>6.0</td>
<td>6.4</td>
</tr>
<tr>
<td>G8c</td>
<td>benzylchloride</td>
<td>330</td>
<td>0.37</td>
<td>3.8</td>
<td>3.8</td>
</tr>
<tr>
<td>G12c</td>
<td>benzylchloride</td>
<td>350</td>
<td>0.29</td>
<td>3.3</td>
<td>3.3</td>
</tr>
<tr>
<td>G7d</td>
<td>benzylchloride</td>
<td>965</td>
<td>1.94</td>
<td>6.4</td>
<td>7.0</td>
</tr>
<tr>
<td>G4e</td>
<td>mix. of groups</td>
<td>452</td>
<td>0.68</td>
<td>4.7</td>
<td>4.4</td>
</tr>
</tbody>
</table>

* a from the desorption / adsorption branch of the isotherm
* b "with water treatment"
* c "after equilibration in humid atmosphere"
* d "with chlorosilane"
* e 1:4 molar ratio of CMPTMS and PTMS "with water treatment"

### 6.3.3 Comparison between phenyl and benzylchloride functionalization

Pore characteristics of representative materials obtained by functionalization with phenyl and benzylchloride moieties and a mixture thereof are compared in Table 6.5. It can be seen that the loss in specific surface area, total pore volume and average pore diameter is much more pronounced in benzylchloride-functionalized materials. The comparison of nitrogen physisorption isotherms of materials functionalized "with water treatment" with phenyl and benzylchloride moieties (Fig. 6.7) shows this effect very clearly.

The losses in pore volumes during the benzylchloride functionalization are about 30% larger. One reason for this is the larger size of the benzylchloride moiety in comparison with the phenyl moiety. To estimate if this effect accounts for the whole loss of pore diameter, surface area and pore volume, a calculation of the expected decrease of pore diameter for both organic moieties was used for further interpretation (see Fig. 6.8). This calculation is based on the assumption of straight cylindrical pores in the starting material. That assumption is not correct for the mesoporous materials used for these functionalization reactions but the results can be used to check the pore characteristics roughly.

The pore diameter obtained with the BJH method for the phenyl-functionalized material (e.g. G16 in Table 6.5) is around 6 nm. This is in good agreement with the calculated value (Fig. 6.8) of 6.4 nm. For the benzylchloride-functionalized material (e.g. G8c in Table 6.5) the BJH pore diameter values are around 4 nm.
Figure 6.7: N\textsubscript{2}-physisorption isotherm of phenyl and benzyl chloride-functionalized ("with water treatment") M41S materials

Figure 6.8: Calculation: decrease of pore diameter (molecular dimensions of surface bound phenyl and benzyl chloride calculated from known bond length)
6.3. RESULTS AND DISCUSSION

Table 6.6: Calculated and measured loss of specific surface area and pore volume for characteristic phenyl- and benzylchloride- grafted materials

<table>
<thead>
<tr>
<th>Material</th>
<th>loss of surf. [%] calculated</th>
<th>measured loss [%] BET</th>
<th>loss of pore vol. [%] calculated</th>
<th>measured loss of pore vol. [%] t-plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>G16</td>
<td>20</td>
<td>41</td>
<td>36</td>
<td>55</td>
</tr>
<tr>
<td>G8c</td>
<td>24</td>
<td>69</td>
<td>42</td>
<td>83</td>
</tr>
</tbody>
</table>

which is remarkably smaller than the calculated value of 6.2 nm. So the loss of average pore diameter during the functionalization with benzylchloride moieties is larger than expected. Based on the expectations for the average pore diameter after functionalization reactions one can also calculate expected values for the loss of specific surface area and pore volume.

The surface area $A_z$ of a cylinder (eq. 6.2) is the product of its circumference $U$ (eq. 6.1) and its length $h$. $d$ is the diameter of the cylinder.

$$U = d \times \pi \quad (6.1)$$

$$A_z = U \times h \quad (6.2)$$

The volume $V$ of cylinder (eq. 6.4) is the product of its circular area $A$ (eq. 6.3) and its length $h$.

$$A = \frac{d^2}{4} \times \pi \quad (6.3)$$

$$V = A \times h \quad (6.4)$$

With these geometrical formulas it is possible to calculate the loss of surface area and pore volume due to a certain functionalization for a single cylindrical pore. The relative loss of specific surface area and pore volume of mesoporous materials is the same as the relative loss of a single cylindrical pore if the number of pores does not change during the grafting reaction. If one applies this concept using the expected decrease of pore diameter (Fig. 6.8), expected losses of specific surface area and pore volume can be calculated for materials functionalized with phenyl and benzylchloride moieties. Calculated and measured losses of specific surface area and pore volume are listed in Table 6.6.

Comparing the calculated and the measured data for both phenyl- and benzylchloride-functionalized material it is clear that the losses are underestimated for all materials. This is a consequence of the oversimplified model of cylindrical pores.
Nevertheless the discrepancies between calculated and measured values are much more pronounced for the benzylchloride-functionalized material. The same trend was observed for the loss of average pore diameter. All these findings lead to the conclusion that the huge loss of surface area and pore volume of the benzylchloride-functionalized material is not only due to the larger size of the organic group but to a certain extent due to an unwanted polymerization or oligomerization (Fig. 6.9) that occurs during grafting and that causes pore blocking.

The grafting reagents used for functionalization with phenyl and benzylchloride could both undergo vertical oligomerization. Only CMPTMS that was used for the functionalization with benzylchloride can undergo horizontal oligomerization. Therefore horizontal oligomerization must be responsible for the unexpected big difference in pore characteristics between the two functionalized materials.

This explanation is further supported by the pore characteristics of the material that was functionalized with a mixture of phenyl and benzylchloride groups (G4 in Table 6.5). The loss in porosity due to the functionalization reaction is between those of the functionalization reactions with only phenyl or benzylchloride.
Table 6.7: Properties of trimethylsilane-functionalized mesoporous materials

<table>
<thead>
<tr>
<th>Material</th>
<th>method</th>
<th>BET surf. area</th>
<th>total pore vol.</th>
<th>av. BJH diam.</th>
<th>cont. of C</th>
<th>EA [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>parent</td>
<td></td>
<td>1080</td>
<td>2.64</td>
<td>7.5</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>G5</td>
<td>after drying</td>
<td>727</td>
<td>1.51</td>
<td>5.9</td>
<td>8.5</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) calculated from the desorption branch of the isotherm
\(^b\) as described by Anwander et al. [71]

6.3.4 Properties of trimethylsilane-functionalized materials

Pore characteristics of trimethylsilane-functionalized materials and organic loading are listed in Table 6.7. The surface area, pore volume and pore diameter decrease as a consequence of the functionalization reaction, but only to a small extent. Trimethylsilane functionalized materials were originally prepared with HMDS as grafting reagent in order to estimate the number of silanol groups on the surface of the mesoporous material available for grafting reaction [71]. The amount of reacted silanol groups is calculated from the carbon content (measured by classical elementary analysis) of the functionalized material. Applying this method gives an amount of 2.5 mmol/g (or 1.25 -Si(CH\(_3\))\(_3\) per nm\(^2\)) grafted moieties on the used mesoporous material. This amount of grafted silane moieties corresponds to the amount of silanol groups available for this grafting reaction. This is in good agreement with the values Anwander et al. found [71]. This value is specific for the conditions that were used for the grafting of trimethylsilane moieties. In the grafting reactions performed with different trimethoxysilanes after water treatment of the mesoporous material, the amount of available silanol groups is much larger than in the case of trimethylsilane grafting where the mesoporous material was dried at 400°C for 24 h. Unfortunately it is not clear which mode of surface modification (Fig. 6.1) is predominant under certain functionalization conditions. So it can not be said if a trialkoxysilane is reacting with one, two or three surface silanols. Therefore one can not derive the amount of silanol groups that were originally available from the amount of grafted silane groups if the functionalization "with water treatment" is performed.
Chapter 7

Functionalization of Silica Surfaces with Mixtures of 3-Aminopropyl and Methyl Groups

7.1 Introduction

An organic group which is often used for functionalization is 3-aminopropyl. A primary amine is a good ligand for metal ions and can therefore serve as sorbent in waste water treatment [74, 75] or can immobilize catalytically active transition metal ions [76–78]. Furthermore the nucleophilic primary amine can be used as linker between the silica surface and any organic species with a leaving group for a nucleophilic substitution reaction [79–84] or serve as solid base catalyst [79, 85–88]. Mesoporous materials functionalized with 3-aminopropyl groups can either be prepared by co-condensation of 3-aminopropyl-trialkoxy silane with a silica precursor (typically TEOS) [89, 90] or by post synthetic grafting on the surface of a mesoporous silica support [20]. An important advantage of post synthetic grafting is that the mesoporous silica can be calcined to remove all template. The calcination stabilizes the silica framework. Moreover, the synthesis of the support and the functionalization are independent, which allows more flexibility in both procedures. Therefore functionalization by post synthetic grafting was investigated in this study.

As mentioned before, silica materials functionalized with 3-aminopropyl groups have diverse potential applications. Still these materials often suffer from poor hydrothermal stability in humid environment or aqueous solutions. The reason is that all silica-based materials tend to hydrolyze under basic conditions. Therefore 3-aminopropyl-functionalized silica materials are often not stable enough for technical processes. One approach to overcome this limitation is to functionalize the silica surface with a second group which protects the surface against unwanted hydrolysis. It was re-
ported for example that a silica surface, that was functionalized with a mixture of chloropropyl and methyl groups, was hydrothermally more stable than materials functionalized with chloropropyl alone [91]. We therefore functionalized mesoporous M41S materials with mixtures of 3-aminopropyl and methyl groups (Fig 7.1). This methodology also allows to adjust the amount of active 3-aminopropyl species on the surface. This is especially important for applications in which a defined chemical environment on the surface is more important than the maximal number of functional groups, as is often the case in heterogeneous catalysis. The functionalization method presented hereafter was developed from the method described by Feng et al. [20] and our group [21].

7.2 Experimental

7.2.1 Functionalization "with water treatment"

A pure silica M41S material (see chapter 4) with well ordered mesopores was used as support for all described functionalization reactions. Functionalization reactions were performed with (3-aminopropyl)trimethoxysilane (APTMS) and methyltrimethoxy-silane (MTMS) as reactive species (Fig 7.1).

Prior to functionalization the mesoporous M41S material was refluxed in water (25 ml per g of support) for 1 h. After the water treatment the material was collected by filtration and washed with toluene (20 ml/g). The wet material was suspended in toluene (100 ml/g) and the majority of the remaining water was removed during 2 h
of azeotropic distillation (~2.5 ml/g). After cooling to ambient temperature pure APTMS (3.6 ml/g), MTMS (2.8 ml/g) or both silanes were added to the slurry. In the latter case MTMS was added before APTMS. The total amount of silane was kept constant at 19 mmol of reactive silane per g of support. Mixtures of APTMS and MTMS are identified by the molar ratio of the silanes in the reaction mixture. For example, 1 g of support with APTMS / MTMS 1:5 was reacted with 0.7 ml (3.2 mmol) APTMS and 2.2 ml (15.8 mmol) MTMS. The mixture was vigorously stirred for 14 h at room temperature. Then the solid was filtered off, redispersed in fresh toluene (100 ml/g) and refluxed for 1 h. The solid was collected by filtration and washed with isopropanol (20 ml/g). The functionalized material was dried at 50°C in an evacuated oven. This method is referred to functionalization "with water treatment" hereafter.

7.2.2 Functionalization "after drying"

Alternatively M41S material was functionalized with a method that was described by Alcon et al. [83] also using (3-aminopropyl)trimethoxysilane as the grafting reagent. Prior to synthesis the mesoporous M41S material was dried at high vacuum at 400°C for 18 h. The dried material was placed in a "Schlenk"-flask while excluding air with a stream of nitrogen. Dry toluene (100 ml per g of solid) and the APTMS grafting reagent were added (5 ml or 26 mmol per g of solid) to the flask. The flask was closed with a septum and stirred at room temperature for 24 h. The final product was collected by filtration and washed with dry toluene followed by technical toluene. The final material was dried in an evacuated oven at 50°C. This method is referred to functionalization "after drying" hereafter.

7.2.3 Test of hydrothermal stability

The hydrothermal stability of the functionalized materials was tested by refluxing 200 mg of material in 20 ml of demineralized water for 2 h. After the treatment the material was collected by filtration and dried at 50°C in an evacuated oven. The degree of structural collapse was tested with N₂ physisorption.
Table 7.1: Properties of mesoporous materials functionalized with 3-aminopropyl.

<table>
<thead>
<tr>
<th>Material method</th>
<th>BET surf. area [m²/g]</th>
<th>total pore vol. [cm³/g]</th>
<th>av. BJH diam. [nm]</th>
<th>cont. of C [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>parent</td>
<td>1080</td>
<td>2.64</td>
<td>7.5</td>
<td>0.2</td>
</tr>
<tr>
<td>G63 water trea</td>
<td>619</td>
<td>1.41</td>
<td>6.4</td>
<td>10.6</td>
</tr>
<tr>
<td>G19 after drying</td>
<td>700</td>
<td>1.57</td>
<td>6.7</td>
<td>9.7</td>
</tr>
</tbody>
</table>

*a* calculated from the desorption branch of the isotherm

*b* parent M41S material, see Chapter 4

### 7.3 Results and discussion

#### 7.3.1 Properties of materials functionalized with 3-aminopropyl with different methods

3-Aminopropyl functionalized materials were synthesized by two different methods. Data obtained from nitrogen physisorption and elementary analysis are collected in Table 7.1.

As observed on the benzylchloride functionalized materials (see 6.3.2) drying of the M41S parent material prior to the functionalization instead of water treatment gives materials with lower organic loading, and more accessible surface area.

#### 7.3.2 Properties of materials functionalized with 3-aminopropyl, methyl groups or mixtures of the two groups

All materials functionalized with 3-aminopropyl and methyl groups alone or with both groups (Table 7.2) show that an increasing fraction of MTMS in the functionalization reaction mixture gives materials with first constant and then increasing values for the total pore volume, average BJH pore diameter and BET surface area. Simultaneously the content of carbon and nitrogen goes down. This is not surprising because the methyl moiety is smaller in size and has only one carbon atom. However, the increase in porosity and the decrease of organic loading are not linear. There is a step in both properties when going from the materials with mixed functionalized groups to the material with pure MTMS functionalization. This observation becomes more clear when the molar loadings of the 3-aminopropyl and methyl groups are calculated from the organic loading (Table 7.3).

These data also show that the material which is functionalized with 3-aminopropyl groups alone has a smaller molar loading of organic groups than the materials with a mixture of 3-aminopropyl and methyl groups bound to their surfaces. Furthermore,
7.3. RESULTS AND DISCUSSION

Table 7.2: Pore characteristics and organic loading of M41S materials functionalized with pure 3-aminopropyl and methyl moieties or with mixtures of both functionalities.

<table>
<thead>
<tr>
<th>Material</th>
<th>APTMS: MTMS&lt;sup&gt;a&lt;/sup&gt;</th>
<th>BET surf.</th>
<th>tot. pore vol.</th>
<th>av. BJH&lt;sup&gt;b&lt;/sup&gt;</th>
<th>C&lt;sup&gt;c&lt;/sup&gt;</th>
<th>H&lt;sup&gt;c&lt;/sup&gt;</th>
<th>N&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[m²/g]</td>
<td>[cm³/g]</td>
<td>[nm]</td>
<td>[wt%]</td>
<td>[wt%]</td>
<td>[wt%]</td>
<td></td>
</tr>
<tr>
<td>G63 APTMS&lt;sup&gt;d&lt;/sup&gt;</td>
<td>619</td>
<td>1.41</td>
<td>6.4</td>
<td>10.6</td>
<td>2.8</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>G67 1:5</td>
<td>618</td>
<td>1.45</td>
<td>6.2</td>
<td>9.7</td>
<td>2.8</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>G65 1:10</td>
<td>606</td>
<td>1.42</td>
<td>6.3</td>
<td>9.0</td>
<td>2.5</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>G58 1:20</td>
<td>635</td>
<td>1.43</td>
<td>6.2</td>
<td>7.8</td>
<td>2.3</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>G60 1:50</td>
<td>652</td>
<td>1.55</td>
<td>6.4</td>
<td>6.6</td>
<td>1.9</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>G61 1:100</td>
<td>662</td>
<td>1.52</td>
<td>6.5</td>
<td>6.3</td>
<td>2.0</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>G62 MTMS&lt;sup&gt;d&lt;/sup&gt;</td>
<td>796</td>
<td>1.90</td>
<td>6.9</td>
<td>3.9</td>
<td>2.0</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> molar ratio of APTMS and MTMS reagent in functionalization reaction mixture
<sup>b</sup> calculated from the desorption branch of the isotherm
<sup>c</sup> from organic elementary analysis
<sup>d</sup> functionalized with single compound

Table 7.3: Molar loading of M41S materials functionalized with pure 3-aminopropyl and methyl moieties or mixtures of both functionalities (values calculated from Table 7.2).

<table>
<thead>
<tr>
<th>Mat.: APTMS: MTMS&lt;sup&gt;a&lt;/sup&gt;</th>
<th>C&lt;sup&gt;b&lt;/sup&gt;: N&lt;sup&gt;c&lt;/sup&gt;</th>
<th>methyl load&lt;sup&gt;c&lt;/sup&gt;</th>
<th>tot. load&lt;sup&gt;d&lt;/sup&gt;</th>
<th>3AP:methyl&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mat.:</td>
<td>C: [mmol/g]</td>
<td>N: [mmol/g]</td>
<td>methyl load: [mmol/g]</td>
<td>tot. load: [mmol/g]</td>
</tr>
<tr>
<td>G63 APTMS</td>
<td>8.8</td>
<td>2.7</td>
<td>-</td>
<td>2.7</td>
</tr>
<tr>
<td>G67 1:5</td>
<td>8.1</td>
<td>1.9</td>
<td>2.5</td>
<td>4.4</td>
</tr>
<tr>
<td>G65 1:10</td>
<td>7.6</td>
<td>1.5</td>
<td>3.1</td>
<td>4.1</td>
</tr>
<tr>
<td>G58 1:20</td>
<td>6.5</td>
<td>0.7</td>
<td>4.4</td>
<td>5.0</td>
</tr>
<tr>
<td>G60 1:50</td>
<td>5.5</td>
<td>0.4</td>
<td>4.2</td>
<td>4.6</td>
</tr>
<tr>
<td>G61 1:100</td>
<td>5.3</td>
<td>0.2</td>
<td>4.6</td>
<td>4.8</td>
</tr>
<tr>
<td>G62 MTMS</td>
<td>3.2</td>
<td>0.1</td>
<td>3.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

<sup>a</sup> molar ratio in functionalization reaction mixture
<sup>b</sup> also loading of 3-aminopropyl groups
<sup>c</sup> molar surface loading of methyl groups = mmol/g C - (3 * mmol/g N)
<sup>d</sup> mmol/g N + mmol/g methyl
<sup>e</sup> 3-aminopropyl (3AP) : methyl group ratio on the surface of the support = mmol/g N : mmol/g methyl
Table 7.3 shows that 3-aminopropyl is always overrepresented on the surface of materials with both functionalities. The data show that the presence of 3-aminopropyl together with methyl groups increases the degree of surface functionalization. These observations can be rationalized with the following model of the functionalization process: The basic APTMS reacts faster with the silanol groups on the surface of the M41S material because it is able to accelerate its own hydrolysis (Fig. 7.2).

That explains why the ratio of 3-aminopropyl to methyl groups bound to the surface is always larger than the ratio of APTMS / MTMS in the reaction mixture. Since also the loading of methyl groups is larger in materials with mixed functionalization than in the material with methyl alone it must be concluded that the 3-aminopropyl also enhances the hydrolysis of MTMS. In addition, the higher loadings of the materials functionalized with both 3-aminopropyl and methyl groups are due to the smaller size of the methyl group. The methyl group can fill gaps between 3-aminopropyl groups and profit from the presence of adjacent silane groups for further condensation reactions on the surface of the support. Therefore the materials with both 3-aminopropyl and methyl groups bound to their surface have the highest molar loading of functional groups.

These ideas are supported by $^{29}$Si MAS NMR (Fig. 7.3) and IR spectroscopy (Fig. 7.6). The NMR spectra (Fig. 7.3) of the materials with pure 3-aminopropyl and methyl functionalization show two important differences: (1) The intensity of the $Q^3$ species near 100 ppm is much higher in the methyl-functionalized material. (2) $T^1$ and $T^2$ organosilane species around 55 ppm are predominant in the methyl-functionalized material whereas mainly $T^2$ and $T^3$ species are found in the 3-aminopropyl-functionalized material. The first observation shows that the reactivity of the surface silanol groups towards MTMS is small (if used alone), presumably because only a fraction of the methoxy groups is hydrolyzed in that case. The distribution of the $T$ sites confirms that. The high intensity of $T^1$ and $T^2$ species after functionalization with
Figure 7.3: $^{29}$Si MAS NMR spectra of M41S materials functionalized with pure APTMS (pure 3-aminopropyl), 1:20 mix APTMS:MTMS (1:20 molar ratio of APTMS:MTMS in the functionalization reaction mixture) and pure MTMS (pure methyl).
MTMS alone can be ascribed to \( \text{CH}_3\text{-Si(O)}\text{Si(OCH}_3\text{)}_2 \) and \( \text{CH}_3\text{-Si(O)}\text{Si(OCH}_3\text{)}_2 \) groups, i.e. to methylsilanes that were not completely hydrolyzed. With APTMS, on the other hand, at least two methoxy groups were hydrolyzed (no T1) and therefore condensed with neighboring silicon atoms.

The material functionalized with a mixture of APTMS and MTMS shows the same features as the APTMS silica, i.e. a low concentration of Q3 and high concentration of T2 and T3 species. Both indicate a high degree of condensation of the silanes with the silica surface and / or with each other. The NMR data therefore support the idea that the presence of an amine during the functionalization enhances the hydrolysis and condensation of APTMS itself, but also of MTMS.

To complete the picture of the functionalized materials IR spectra were recorded (Figs. 7.5 - 7.6). The mesoporous M41S support was included for comparison. A detailed band assignment is given at the end of this chapter.

The spectrum of the material functionalized with methyl-groups alone (Fig. 7.4) shows a higher concentration of H-bridged silanol species than the starting silica material. These silanol groups were formed during the water treatment prior to the functionalization reaction. The other prominent features of the IR spectrum are four C-H stretching bands below 3000 cm\(^{-1}\) and a C-H deformation band at 1411 cm\(^{-1}\). The spectrum of the material functionalized with 3-aminopropyl-
groups alone (Fig. 7.5) shows less silanol species than the spectrum of the methyl-functionalized material, in agreement with $^{29}$Si MAS NMR. It confirms that more silanol groups on the surface of the silica support react with APTMS than with pure MTMS. In addition, the spectrum of APTMS-functionalized silica exhibits two broad N-H stretching bands above 3000 cm$^{-1}$, a very broad and intense feature between 3000 and 2000 cm$^{-1}$, which is caused by stretching vibrations of H-bonded NH$_2$ and NH$_3^+$ groups, and an N-H deformation vibration at 1595 cm$^{-1}$. The series of spectra of the material with methyl groups alone to the material with 3-aminopropyl groups alone (Fig. 7.6) shows that the characteristic features of the methyl groups decrease in intensity while the features of the 3-aminopropyl species become more and more pronounced. The very broad feature between 3000 and 2000 cm$^{-1}$, which was assigned to H-bonded NH$_2$ and NH$_3^+$ species, increases very slowly in intensity. In the materials prepared with APTMS / MTMS ratios of 1:100, 1:50 and 1:20 the feature between 3000 and 2000 cm$^{-1}$ is rather low indicating that not much H-bonding between NH$_2$ - moieties or between NH$_2$ and silanol groups is possible in these materials. It indicates that the 3-aminopropyl and methyl groups are randomly distributed on the surface of the support and that the distance between two adjacent 3-aminopropyl groups is too large for H-bonding in these materials. When the density of 3-aminopropyl groups increases (as in the case of the materials
Figure 7.6: IR spectra of M41S materials functionalized with pure 3-aminopropyl and methyl moieties or mixtures of both functionalities. M41S support: mesoporous silica support without functionalization, pure APTMS: pure 3-aminopropyl, pure MTMS: pure methyl, 1:X: molar ratio of APTMS:MTMS in the functionalization reaction mixture, * shifted to higher absorbance for better visibility.
prepared with APTMS / MTMS ratios of 1:10, 1:5 and with pure APTMS functionalization), H-bonding between the amines becomes more and more probable and the broad feature between 3000 and 2000 cm\(^{-1}\) more and more pronounced. Also the bands of the silanol species continuously lose intensity when the amount of 3-aminopropyl groups increases due to the catalytic activity of the amine groups on the hydrolysis and condensation of silanes. In summary, the body of data shows that the mixing of APTMS and MTMS allows a continuous variation of the concentration of surface bound amine groups. The ratio of 3-aminopropyl / methyl groups on the surface of the functionalized material, is, however, always larger than in the functionalization reaction mixture. The amine groups are evenly distributed over the silica surface.

3-Aminopropyl functionalized material was also characterized with \(^{13}\text{C}\) CP-MAS NMR (Fig. 7.7). The three signals come from the three carbon species present in the 3-aminopropyl group.
Table 7.4: Structural loss of functionalized M41S materials after 2 h of refluxing in water.

<table>
<thead>
<tr>
<th>Mat.: MTMS</th>
<th>APTMS</th>
<th>tot pore vol. $^a$ [cm$^3$/g]</th>
<th>lost pore vol. [%]</th>
<th>BET surf. $^a$ [m$^2$/g]</th>
<th>lost surf. area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G63</td>
<td>APTMS</td>
<td>0.91</td>
<td>35</td>
<td>297</td>
<td>53</td>
</tr>
<tr>
<td>G67</td>
<td>1:5</td>
<td>1.08</td>
<td>25</td>
<td>366</td>
<td>41</td>
</tr>
<tr>
<td>G65</td>
<td>1:10</td>
<td>1.12</td>
<td>21</td>
<td>424</td>
<td>33</td>
</tr>
<tr>
<td>G58</td>
<td>1:20</td>
<td>1.17</td>
<td>18</td>
<td>442</td>
<td>30</td>
</tr>
<tr>
<td>G60</td>
<td>1:50</td>
<td>1.55</td>
<td>0</td>
<td>619</td>
<td>5</td>
</tr>
<tr>
<td>G61</td>
<td>1:100</td>
<td>1.55</td>
<td>+2</td>
<td>664</td>
<td>0</td>
</tr>
<tr>
<td>G62</td>
<td>MTMS</td>
<td>1.75</td>
<td>8</td>
<td>827</td>
<td>+4</td>
</tr>
</tbody>
</table>

$^a$ after 2 h of treatment in boiling water (values before see Table 7.2)

7.3.3 Hydrothermal stability of materials functionalized with 3-aminopropyl, methyl groups or mixtures of the two groups

The hydrothermal stability is a very important property of functionalized silica materials. In the case of 3-aminopropyl functionalization this is especially important because these materials often suffer from poor stability because of the basicity of their functional group. Therefore all functionalized materials were treated in boiling water for 2 h. The observed losses in total pore volume and BET surface area are compiled in Table 7.4. The nitrogen physisorption isotherms of some functionalized materials before and after this hydrothermal treatment are shown in Figure 7.8.

The material with only 3-aminopropyl moieties on the surface shows a rather poor hydrothermal stability. The reason is the fast hydrolysis of the silica in the presence of an amine. The hydrothermal stability improves by decreasing the amount of 3-aminopropyl bound to the silica surface. This is on the one hand due to a decreased basic character inside the pores of the functionalized materials but also because the silica surface is protected from hydrolysis when hydrophobic methyl groups are present together with 3-aminopropyl groups. The influence of that effect can be seen from the fact that the materials with very small amounts of 3-aminopropyl on their surface (1:50 and 1:100 in Table 7.3) show better hydrothermal stability than the material functionalized with only methyl groups. The reason is that the molar loading is larger (Table 7.3) and the connectivity between silicon atoms of the silica and the silane is higher (Fig. 7.3) when mixtures of APTMS and MTMS are used for functionalization reactions.
Figure 7.8: Nitrogen physisorption isotherms of functionalized materials before and after 2 h of treatment in boiling water. Pure APTMS: pure 3-aminopropyl, APTMS:MTMS 1:100: molar ratio in the functionalization reaction mixture 1:100, pure MTMS: pure methyl.
7.3.4 Conclusions

The grafting of mixtures of APTMS and MTMS on the surface of M41S silicas enables the synthesis of materials with an adjustable amount of 3-aminopropyl groups bound to their surface. The control of the 3-aminopropyl loading is important for application of these materials as supports for the immobilization of metal complexes, stationary phases in chromatography and base catalysts. The methodology is not specific for mesoporous M41S silica but can be applied to any porous or non-porous silica support. The presence of APTMS in the functionalization reaction leads to some unexpected effects: The amine group base-catalyzes the hydrolysis of its own trialkoxysilane group as well as the hydrolysis of other trialkoxysilanes such as MTMS. As a result, (i) the 3-aminopropyl moieties are always found in a higher concentration on the surface of the functionalized material than in the reaction mixture and (ii) higher total loadings of organosilanes on the silica surface are achieved than in the absence of APTMS. The latter result is important because the complete coverage of the silica surface with organosilanes strongly improves the stability of the material against hydrolysis. The same effect should be found in mixtures of APTMS with other silanes.
Detailed IR band assignment of materials functionalized with 3-aminopropyl and methyl groups

Table 7.5: IR band assignment of methyl-functionalized material

<table>
<thead>
<tr>
<th>wavenumbers [cm(^{-1})]</th>
<th>assigned species</th>
<th>wavenumbers [cm(^{-1})]</th>
<th>assigned species</th>
</tr>
</thead>
<tbody>
<tr>
<td>3620</td>
<td>H - bonded SiO-H(^a)</td>
<td>1961</td>
<td>overtone of Si-O-Si st</td>
</tr>
<tr>
<td>3505</td>
<td>H - bonded SiO-H(^b)</td>
<td>1865</td>
<td>overtone of Si-O-Si st</td>
</tr>
<tr>
<td>2975</td>
<td>asymmetric C-H(_3) st</td>
<td>1641</td>
<td>overtone of Si-OH st</td>
</tr>
<tr>
<td>2954</td>
<td>asymmetric C-H(_3) st(^c)</td>
<td>1465</td>
<td>C-H(_3) def(^c)</td>
</tr>
<tr>
<td>2919</td>
<td>symmetric C-H(_3) st</td>
<td>1411</td>
<td>C-H(_3) def</td>
</tr>
<tr>
<td>2851</td>
<td>symmetric C-H(_3) st</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) one bridge \(^{b}\) two bridges \(^{c}\) unsubstituted methoxy group

Table 7.6: IR band assignment of 3-aminopropyl-functionalized material

<table>
<thead>
<tr>
<th>wavenumbers [cm(^{-1})]</th>
<th>assigned species</th>
<th>wavenumbers [cm(^{-1})]</th>
<th>assigned species</th>
</tr>
</thead>
<tbody>
<tr>
<td>3635</td>
<td>H - bonded SiO-H(^a)</td>
<td>1963</td>
<td>overtone of Si-O-Si st</td>
</tr>
<tr>
<td>3430</td>
<td>H - bonded SiO-H(^b)</td>
<td>1851</td>
<td>overtone of Si-O-Si st</td>
</tr>
<tr>
<td>3365</td>
<td>asymmetric N-H(_2) st</td>
<td>1647</td>
<td>overtone of Si-OH</td>
</tr>
<tr>
<td>3298</td>
<td>symmetric N-H(_2) st</td>
<td>1595</td>
<td>N-H def</td>
</tr>
<tr>
<td>3170</td>
<td>overtone of N-H def</td>
<td>1552</td>
<td>symmetric N-H(_3)(^+) def</td>
</tr>
<tr>
<td>3200-2000</td>
<td>N-H st(^c)</td>
<td>1470</td>
<td>C-H(_2) def(^d)</td>
</tr>
<tr>
<td>2932</td>
<td>asymmetric C-H(_2) st</td>
<td>1447</td>
<td>C-H(_2) def(^e)</td>
</tr>
<tr>
<td>2922</td>
<td>asymmetric C-H(_2) st</td>
<td>1410</td>
<td>C-H(_2) def(^f)</td>
</tr>
<tr>
<td>2883</td>
<td>symmetric C-H(_2) st</td>
<td>1390</td>
<td>C-H(_2) wag</td>
</tr>
<tr>
<td>2798</td>
<td>asymmetric C-H(_2) st(^d)</td>
<td>1352</td>
<td>C-H(_2) wag</td>
</tr>
<tr>
<td>2762</td>
<td>symmetric C-H(_2) st(^d)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) one bridge \(^{b}\) two bridges \(^{c}\) H-bonded and protonated amine species \(^{d}\) CH\(_2\)-group bound to NH\(_2\)-group \(^{e}\) middle CH\(_2\)-group \(^{f}\) CH\(_2\)-group bound to Si
Chapter 8

Surface Chemistry on Functionalized Materials

8.1 Introduction

The surface functionalization of silica materials with organic groups was described in the previous chapters. The resulting materials are often further modified by exploiting the chemical activity of the functional group. Reactions that the molecular compound can undergo in solution can often also be performed at the solid liquid interface of the functionalized material. An example for this kind of modification is the oxidation of thiol groups on the surface of an MCM-41 material with hydrogen peroxide [92] to obtain a solid acid catalyst with sulfonic acid groups on its surface. The chloride of a benzylchloride group is a fairly good leaving group, which can be substituted by different nucleophiles in an $S_N1$ reaction. The reason for this property of the benzylchloride group is the fact that the carbocation intermediate is stabilized by delocalization of the positive charge in the aromatic ring. The mild conditions and irreversibility of this reaction make benzylchloride a good starting point to obtain different organic molecules covalently bound to silicic supports. The phenyl moiety of the benzylchloride induces a hydrophobic character that may be an advantage in applications such as catalysis and chromatography.

8.2 Experimental

8.2.1 Nucleophilic substitution of chlorine in benzylchloride

Two different substitution reactions of functionalized benzylchloride were performed using ethylene diamine and ammoniumsulfite as nucleophiles (Fig 8.1).
Ethylenediamine substitution with benzylchloride was performed according to a procedure that was described for the substitution of chlorine in benzylchloride with piperazine in liquid phase [93].

Benzylchloride functionalized material (preparation see Chapter 6.2.2) was suspended in ethanol (100 ml per g of solid) and stirred. Pure ethylenediamine (2 ml per g of solid) was added and the mixture was heated to 65°C for 30 min. Then the reaction mixture was cooled to ambient temperature and the solid was collected by filtration. The collected solid material was washed with technical ethanol and water and dried in a evacuated oven at 50°C.

To synthesize a solid acid the benzylchloride was treated with a aqueous ammoniumsulfite solution.

Benzylchloride functionalized material was suspended in water (100 ml per g of solid) and ammoniumsulfite solution (34% in water) was added (10 ml per g of solid). Subsequently the reaction mixture was refluxed for 3 h. The product was filtered, washed with water and ethanol and dried in an evacuated oven at 50°C.

8.2.2 Formation of EDTA-like ligands

Starting from ethylenediamine-substituted solid material (see above) the same procedure as for the synthesis of EDTA was followed [94] (Strecker-reaction) (see. Fig 8.2).
8.3. RESULTS AND DISCUSSION

The reaction consists of two consecutive steps. In the first step nitriles bound to the ethylenediamine moiety by a CH₂-group are generated. Then the nitriles are hydrated to get the acid groups.

Material with ethylenediamine-substituted benzylchloride was suspended in a 1:1 mixture (volumetric) of water and tert.-butanol (30 ml per g of solid) in a three necked flask. Two dropping funnels were mounted to the flask. One was loaded with a 3:2 mixture of formaldehyde (37% in water) and water (15 ml per g of solid). The other dropping funnel was loaded with sodiumcyanide (70 mg/ml) in a solution of NaOH (0.1 M in water) (15 ml per g of solid). The formaldehyde and sodiumcyanide solutions were added dropwise to the reaction mixture over a period of 30 min. Then the reaction mixture was refluxed for 24 h. The product was filtered and washed with water (2 l per g of solid). The product was dried in an evacuated oven at 50°C.

To hydrate the nitriles, the solid was dispersed in water (100 ml per g of solid) and the pH was adjusted by titration with concentrated sulfuric acid to a value around 1. The mixture was refluxed for 3 h, followed by filtration, washing with water and drying of the sample in an evacuated oven at 50°C.

8.3 RESULTS AND DISCUSSION

8.3.1 Properties of materials after substitution of benzylchloride

Benzylchloride functionalized mesoporous M41S silica was used as substrate for nucleophilic substitution with ethylenediamine. An overlay of nitrogen physisorption
isotherms of mesoporous M41S material and materials after functionalization with benzylchloride, after substitution with ethylenediamine and after the reactions to prepare the EDTA-like ligands are compared.

One of the two benzylchloride-functionalized starting materials had a very low loading of organic groups and therefore very high surface area before substitution. That is only possible if the surface of the silica support is not completely functionalized as is the case if functionalization is performed "with chlorsilane". The material obtained after substitution (F2a in Table 8.1) of that material lost almost all of its specific pore volume. This indicates that the porous structure of this material collapsed during the substitution reaction with ethylenediamine in ethanol, due to hydrolysis of the not completely covered mesoporous silica under the basic reaction conditions. The material that was functionalized "with water treatment" did not degrade further during substitution with ethylene diamine (F1a in Table 8.1). The reason is that the silica was covered completely by organic groups that protected the silica from hydrolysis during the substitution reaction. That shows a dilemma of functionalized materials. If the loading of functional groups is low, a material
Table 8.1: Specific pore volumes, C, N, Cl and S content of substituted benzylchlo-
ride functionalized materials

<table>
<thead>
<tr>
<th>Material subst. with</th>
<th>tot. pore vol.</th>
<th>C $^a$</th>
<th>N $^a$</th>
<th>Cl $^a$</th>
<th>S $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[cm$^3$/g]</td>
<td>[wt%]</td>
<td>[wt%]</td>
<td>[wt%]</td>
<td>[wt%]</td>
</tr>
<tr>
<td>F1a $^b$ ethylenediamine</td>
<td>0.37 (0.31 $^d$)</td>
<td>22.6 (22.5 $^d$)</td>
<td>2.5</td>
<td>3.6 (7.0 $^d$)</td>
<td>0.05</td>
</tr>
<tr>
<td>F2a $^c$ ethylenediamine</td>
<td>0.53 (1.90)</td>
<td>4.7 (1.6 $^d$)</td>
<td>0.6</td>
<td>n.m. (1.3 $^d$)</td>
<td>0.05</td>
</tr>
<tr>
<td>F1b $^b$ ammoniumsulfite</td>
<td>0.32 (0.31)</td>
<td>18.5</td>
<td>0.5</td>
<td>4.4</td>
<td>0.9</td>
</tr>
<tr>
<td>F2b $^c$ ammoniumsulfite</td>
<td>1.05 (1.90)</td>
<td>1.6</td>
<td>0.15</td>
<td>n.m.</td>
<td>0.15</td>
</tr>
</tbody>
</table>

$^a$ from organic elementary analysis

$^b$ starting material functionalized "with water treatment" with CMPTMS (G6 in Table 6.4)

$^c$ starting material functionalized "with chlorosilane" with CMPTCS (G7 in Table 6.4)

$^d$ functionalized parent material

with very high accessible surface is obtained. However, an incomplete coverage of the silica surface may lead to structural degradation during subsequent reactions. Therefore the degree of surface coverage always has to be adjusted to the following reaction steps.

Furthermore it can be seen that the Cl content decreases whereas the N content increases during the substitution with ethylenediamine as one would expect. Nevertheless about 50% of the originally found Cl is present after substitution, indicating that the substitution is not complete. This ethylenediamine substitution step is a fast reaction if performed between dissolved molecules. Therefore the reason for the incomplete substitution of the immobilized benzylchloride must be the vertical poly-
merization discussed in chapter 6.3.3 that occurs during functionalization. That undesired reaction blocks the access to some of the benzylchloride groups during substitution.

The same general pattern was observed during the substitution with ammoniumsul-
fite. The sulfite substitution on the material that was functionalized "with chlorosil-
ane" (F2b in Table 8.1) degraded severely during substitution reaction and had a very low sulfur loading afterwards. Also in this case the reason was that the uncovered silica surface was hydrolyzed in the aqueous solution what led to a structural decay and a loss of functional groups. The substitution of the material with a fully covered surface (F1b in Table 8.1) induced no loss and gave a material with almost 1 wt% of sulfur. Therefore it can be said that the desired substitution to obtain a solid acid worked but was not complete as observed before.
8.3.2 Properties of EDTA-like ligands

Several attempts were made to obtain the desired EDTA-like ligands from ethylenediamine-substituted benzylchloride-functionalized M41S material. The desired ligand could not be synthesized because of the following problems. The benzylchloride functionalization causes a large loss of surface area and pore volume and prevents access to some reactive groups as discussed above. Nevertheless the substitution with ethylenediamine proceeds to a considerable extent to the desired product as concluded from organic elementary analysis (Table 8.1). This is supported by $^{13}$C CP-MAS NMR (Fig. 8.4)

The generation of the nitriles, which is the next step towards the wanted EDTA like ligands can neither be confirmed nor denied on the base of the $^{13}$C CP-MAS NMR spectra. The problem that has prevented the generation of the EDTA like ligands is that the hydrolysis of the nitriles to carboxylic acid groups in acidic aqueous medium can not be achieved. An explanation for this is the hydrophobicity of the pores that hinders the acidic watery solution to access the nitrile groups.
Figure 8.4: $^{13}$C CP-MAS NMR: Benzylchloride functionalized M41S: BnCl functionalized, after substitution with ethylenediamine: substituted (* mark signals of the solvent (ethanol)), after reactions to generate EDTA like ligands: EDTA like lig.
Chapter 9

Mn and Ru Complexes Immobilized on Mesoporous MCM-41 and M41S Molecular Sieves as Catalysts in Styrene Epoxidation

The experiments presented in this chapter were performed in collaboration with Andrea Cecchetto. The chapter is also part of his Ph.D. thesis.

9.1 Introduction

One of the most important current topics in catalysis is the development of efficient and environmentally friendly catalysts for epoxidation reactions. In homogeneous catalysis several systems have been developed for the epoxidation of different substrates [95–97]. A very interesting family of catalysts has been studied by Jacobsen [98] and Katsuki [99]. Jacobsen catalysts use a Mn(III) chiral salen complex that combines oxygen and nitrogen donors. These catalysts use either iodosylbenzene [98] or commercial bleach [100] as the stoichiometric oxidant and they represent one of the most enantioselective non-enzymatic alkene epoxidation catalysts.

In spite of the high activity, the application of homogeneous catalysts is affected by several problems, particularly the decomposition or degradation of the catalyst following a variety of pathways such as autooxidation, ligand decomposition, reaction with impurities [101] or formation of β-oxo bridged dimers [102]. In addition, from a practical point of view, homogeneous catalysts are more difficult to separate from the products than heterogeneous ones. Therefore one of the challenges
in green chemistry, is to develop highly selective heterogeneous catalysts, which use environmentally friendly oxidants such as H$_2$O$_2$, O$_2$ or air. Several heterogeneous catalysts found industrial application in the epoxidation reaction in gas phase or in liquid phase. Examples are the gas phase oxidation of ethylene over Ag catalysts and a titania based catalyst developed by Shell for propylene epoxidation [103].

A way to combine the advantage of heterogeneous and homogeneous catalysis is to immobilize the transition metal complex on a solid support. This can combine the high activity of a homogeneous complexes with the easy separation of the heterogeneous complex. Moreover it can prevent the formation of $\mu$-oxo bridged dimers. Mesoporous silicas are interesting support materials for the immobilization of homogeneous catalysts because of their high surface area and rather narrow pore size distributions. It was shown that the confined space in a mesopore can, in certain cases, enhance the selectivity in catalytic conversions with immobilized complexes [81, 104–107]. Several examples for the immobilization of homogeneous catalysts in ordered mesoporous silicas (MCM-41) have been reported in the last few years [80, 82, 83, 108–112]. Most of these studies employed salen, similar Schiff-base or bipyridine ligands. They are based on nitrogen donors, which can stabilize high valence metal ions and are not extremely sensitive towards oxidation. In the present work a new method to prepare Mn and Ru complexes anchored on MCM-41 and M41S is reported. Inspired by earlier work [83, 113], a new type of ligand, with an amide and a pyridine group, was chosen. The catalytic properties in the epoxidation of styrene were evaluated. Particular attention was paid to the problem of leaching that often affects this kind of catalysts. Manganese and ruthenium were chosen as active metal centers because they are known as efficient catalyst for oxidation reaction, in particular epoxidation [114–116].

9.2 Experimental

9.2.1 Preparation

Mesoporous MCM-41 and M41S supports, and the organic ligands were synthesized separately. In the first method (self-assembly in Fig. 9.1) the ligand was first immobilized on the mesoporous support. The obtained material was used for the complexation of Ru and Mn by contact with a solution of the metal salt. The complex self-assembled inside the pores of the mesoporous support. The second method, (grafting in Fig. 9.1), involves the preparation of the metal-complex as first step followed by the grafting in the pores of the support.
Figure 9.1: Strategy for immobilization of metal complexes on MCM-41 and M41S.
9.2.2 Synthesis of immobilized complexes

All syntheses of ligands and complexes were carried out under N$_2$ atmosphere. All the solvents were dried before use. DMF and CH$_3$OH were dried on molecular sieve. THF was distilled from a solution of sodium benzophenone and used immediately after distillation. MCM-41 and M41S were dried overnight at 120°C and 10$^{-1}$ mbar before grafting reactions. This functionalization method (see section 7.2.2) was chosen here instead of the standard method with "water treatment" prior to the grafting reaction (see section 7.2.1) because oligomerization of these silanes with large functional groups would cause severe pore blocking immediately. Anyway it was shown (see section 7.3.1) that the differences in molar loading between the two tested functionalization methods is not much if the immobilized species contains basic amine groups as it is the case here.

MCM-41 (see Chapter 3) with an average BJH mesopore diameter of 2.9 nm and M41S (see Chapter 4) with an average BJH mesopore diameter of 7.8 nm were prepared as presented before.

Ligand immobilized on M41S (1)

1 g (8.1 mmol) of picolinic acid was added to 3 ml of thionyl chloride and left 30 min at room temperature under N$_2$ atmosphere. The green mixture was refluxed 3 h in a dry environment and cooled to room temperature. The thionyl chloride was removed and 20 ml of dry THF were added to the remaining solid. The solution was cooled to 0°C and 0.89 ml (4.08 mmol) of 3-(2-aminoethylamino)-propyl-trimethoxy-silane and 2.5 ml of triethylamine were added dropwise. The pasty reaction mixture was stirred for 30 min at 0°C and then stirred at room temperature for 6 h. 2 g of previously dried M41S was added to the mixture and stirred over night under N$_2$ atmosphere. The precipitate was filtered off and the solid was washed with methanol and Soxlet extracted with CH$_3$CN over night. The final material was dried at 60°C under vacuum.

Elemental analysis C$_{17}$H$_{19}$N$_{4}$O$_2$ : Found C 16.11%; H 2.5%; N 4.48% (C$_{17}$H$_{31}$N$_{4}$). IR (cm$^{-1}$): 1658, 1630 (C=O st.), 1531 (CO-NH st). $^{13}$C CP-MAS NMR δ (ppm) 168 (C=O), 148.6 (C$^1$ and C$^5$ Py), 135.9 (C$^3$ Py), 123.3 (C$^2$ and C$^4$ Py), 49.5(NCH$_2$CH$_2$N), 39 (CH$_2$CH$_2$N), 21.6 (CH$_2$CH$_2$N), 9.4 (Si-CH$_2$).

Ligand immobilized on MCM-41 (2)

The same procedure as for the preparation of (1) was used to prepare the same ligand supported on MCM-41.
9.2. EXPERIMENTAL

Elemental analysis $C_{17}H_{19}N_{4}O_{2}$: C 14.47%; H 2.39%; N 3.92% ($C_{17.2}H_{34}N_{4}$). IR (cm$^{-1}$): 1658, 1634 (C=O st), 1527 (CO-NH st). $^{13}$C CP-MAS NMR δ (ppm) 163 (C=O), 148.1 (C$^1$ and C$^5$ Py), 137.5 (C$^3$ Py), 123.01 (C$^2$ and C$^4$ Py), 49 (NCH$_2$CH$_2$N), 38.4 (CH$_2$CH$_2$N), 21.5 (CH$_2$CH$_2$N), 9.3 (Si-CH$_2$).

**Ru complex on M41S by self-assembly (3)**

The ruthenium complex immobilized on M41S was prepared by suspending 250 mg of (1) in 10 ml of ethanol and adding 50 mg of $\text{RuCl}_3$$^n\text{H}_2\text{O}$. The suspension was stirred for 2 days at room temperature. The solid was filtered off and washed with ethanol.

Metal content: 7.6% Ru. M/L=1.15 (M/L metal / ligand ratio). Elemental analysis $C_{17}H_{19}N_{4}O_{2}$: Found C 13.3%; H 2.3%; N 3.6% ($C_{16.5}H_{34}N_{4}$). IR (cm$^{-1}$): 1622 (C=O st), 1595 (CO-NH st).

**Ru complex on M41S by grafting (4)**

An amount of 400 mg (3.25 mmol) of picolinic acid was added to 1.5 ml of thionyl chloride and stirred 30 min at room temperature. The mixture was refluxed 3 h and cooled to room temperature. The thionyl chloride was removed and 10 ml of dry THF were added to the remaining solid. The solution was cooled to 0°C. Then 0.35 ml (1.62 mmol) 3-(2-aminoethylamino)-propyl-trimethoxy-silane and 0.5 ml of triethylamine were added dropwise. The pasty reaction mixture was stirred for 30 min at 0°C and then stirred at room temperature for 6 h. 400 mg of $\text{RuCl}_3$$^n\text{H}_2\text{O}$ dissolved in 30 ml of solvent (1:2 THF:CH$_3$OH) were added dropwise to this mixture and stirred over night. Then 0.9 g of previously dried M41S was added to the mixture and the mixture was left over night under N$_2$ atmosphere. The precipitate was filtered off and the solid was washed with methanol and Soxlet extracted with CH$_3$CN over night. The remaining solid was dried at 60°C under vacuum.

Metal content 3.8% Ru. M/L = 0.92. Elemental analysis $C_{17}H_{19}N_{4}O_{2}$: Found C 8.38%; H 2.17%; N 2.27%; Cl 6.07% ($C_{17.3}H_{53.5}N_{4}Cl_4$). IR (cm$^{-1}$): 1618 (C=O complex st.), 1591 (CO-NH st).

**Mn complex on MCM-41 by grafting (5)**

An amount of 1 g (8.1 mmol) of picolinic acid was added to 3 ml of thionyl chloride and stirred for 30 min at room temperature. The mixture was refluxed 3 h and cooled to room temperature. The thionyl chloride was removed and 20 ml of dry DMF were added to the solid. The solution was cooled to 0°C. Then 0.89 ml (4.1 mmol) of 3-(2-aminoethylamino)-propyl-trimethoxy-silane were added dropwise followed by
600 mg NaH (3x 200 mg). The reaction mixture was stirred for 30 min at 0°C and then at room temperature for 6 h. Then 503 mg of MnCl₂ (4.0 mmol) were added, followed by 2 g of previously dried MCM-41. The mixture was stirred over night. The precipitate was filtered off and the solid was washed with methanol and Soxlet extracted with CH₃CN over night. The resulting solid was dried at 60°C under vacuum.

Metal content 6.17% Mn. M/L = 2. Elemental analysis C₁₇H₁₉N₄O₂ : Found C 11.58%; H 1.33%; N 3.01% (C₁₇H₂₃N₃O₂). IR (cm⁻¹): 1657, 1627 (C=O st.), 1594 (CO-NH st).

Mn complex on M41S by grafting (6)

The same procedure as above was used to prepare a solution of the Mn-ligand-complex. Then 2 g of previously dried M41S were added and stirred overnight. The precipitate was filtered off and the solid was washed with methanol and Soxlet extracted with CH₃CN overnight. The resulting solid was dried at 60°C under vacuum.

Metal content 5.4% Mn. M/L = 1.8. Elemental analysis C₁₇H₁₉N₄O₂: Found C 11.41%; H 3.19%; N 3.22% (C₁₇H₅₇N₄O₂). IR (cm⁻¹): 1652, 1629 (C=O st), 1539 (CO-NH st).

9.2.3 Epoxidation of styrene

All materials were tested in the epoxidation of styrene using tert-butyl-hydroperoxide (TBHP, 5.6 M in nonane), H₂O₂ (30 wt% in H₂O) and iodosylbenzene (PhIO) as oxidants. The reactions were carried out in a 10 ml round flask equipped with magnetic stirrer. A flask was charged with 0.4 ml of styrene (3.5 mmol) and either 0.89 ml of TBHP (5 mmol) or 0.52 ml of H₂O₂ (5 mmol) in 5 ml of CH₃CN. Then 50 mg of the solid catalyst was added and stirred at 50°C for 24 h. The reaction was periodically analyzed by GC using toluene as external standard. A HP1 column (25 m x 0.32 mm ID, 0.52 mm film thickness) was employed for separation and a flame ionization detector for detection.

To check for leaching of the transition metal ions into solution the test proposed by Lempers and Sheldon was used [117]: After 1 h of reaction, the catalyst was filtered off at the reaction temperature and the solution was left to react further with periodic sampling in order to check the substrate conversion.

For the reactions with PhIO, 25 mg catalyst were suspended in 2.5 ml of CH₂Cl₂ and 0.21 ml of styrene (1.8 mmol) were added. 400 mg of PhIO (1.8 mmol) was
9.3. RESULTS AND DISCUSSION

Table 9.1: Pore characteristics and organic loading of the support and the immobilized ligands, Ru- and Mn-complexes.

<table>
<thead>
<tr>
<th></th>
<th>pore vol.: [cm³/g]</th>
<th>BET surf.: [m²/g]</th>
<th>C cont.: [wt%]</th>
<th>N cont.: [wt%]</th>
<th>Cl cont.: [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>parent MCM-41</td>
<td>0.7</td>
<td>1075</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ligand on MCM-41 (2)</td>
<td>0.3</td>
<td>606</td>
<td>14.5</td>
<td>3.9</td>
<td>n.m.</td>
</tr>
<tr>
<td>Mn on MCM-41 gr (5)</td>
<td>0.25</td>
<td>431</td>
<td>11.4</td>
<td>3.1</td>
<td>0.8</td>
</tr>
<tr>
<td>parent M41S</td>
<td>2.64</td>
<td>1080</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ligand on M41S (1)</td>
<td>1.5</td>
<td>682</td>
<td>16.2</td>
<td>4.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Mn on M41S gr (6)</td>
<td>0.9</td>
<td>335</td>
<td>11.4</td>
<td>3.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Ru on M41S gr (4)</td>
<td>1.6</td>
<td>753</td>
<td>8.4</td>
<td>2.3</td>
<td>6.1</td>
</tr>
<tr>
<td>Ru on M41S sa (3)</td>
<td>1.0</td>
<td>576</td>
<td>13.3</td>
<td>3.6</td>
<td>n.m.</td>
</tr>
</tbody>
</table>

a see Chapter 3
b gr = grafting metal complex, sa = self assembly inside pores
c see Chapter 4

then added in small portions over 5 min and the whole mixture was left to react for 2 h at room temperature under magnetic stirring.

9.3 Results and discussion

9.3.1 Characterisation of materials

More than 90% of the surface of MCM-41 and M41S is internal. Therefore immobilized complexes or ligands are almost exclusively bound in the pores of the support material and not on its external surface. Since ligands and complexes are rather bulky, large pore sizes should be advantageous for the immobilization. In Table 9.1 the pore characteristics and the organic loading of the supports and the functionalized materials are compared. It shows that there is surprisingly little difference in the loading of the pure ligand on MCM-41 or M41S.

If the molar loadings (Table 9.2) of the ligands are compared it becomes clear that the ligand density is the same in MCM-41 and M41S materials, namely ~ 0.6 molecules/nm² of support. In other words, the ligand occupies on average 1.7 nm², which is in reasonable agreement with the size of the molecule. The ligand loading was low compared to the concentration of silanol groups on the surface, which are available for grafting (2.4 mmol/g [71]). For steric reasons not all the surface OH-groups can react with the linker. Therefore it can be safely assumed that the alternative grafting method with a water treatment (see section 7.3.1), prior to the
Table 9.2: Ligand and metal loading of the immobilized ligands and Ru- and Mn-complexes.

<table>
<thead>
<tr>
<th>Ligand or Metal</th>
<th>Ligand Loading [mmol/g]</th>
<th>Metal Load [species/nm²]</th>
<th>Metal Load [%]</th>
<th>M/L a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand on MCM-41 (2)</td>
<td>0.9</td>
<td>0.61</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn on MCM-41 gr b (5)</td>
<td>0.7</td>
<td>0.44</td>
<td>4.6 / 6.2</td>
<td>1.5 / 2.0</td>
</tr>
<tr>
<td>Ligand on M41S (1)</td>
<td>1.1</td>
<td>0.57</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn on M41S gr (6)</td>
<td>0.7</td>
<td>0.37</td>
<td>5.4</td>
<td>1.7</td>
</tr>
<tr>
<td>Ru on M41S gr (4)</td>
<td>0.5</td>
<td>0.25</td>
<td>3.8</td>
<td>0.9</td>
</tr>
<tr>
<td>Ru on M41S sa (3)</td>
<td>0.8</td>
<td>0.43</td>
<td>7.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

a molar metal/ligand ratio

Surface reaction, that leads to somewhat larger molar loading, would not increase the surface loading in this functionalization reaction where the steric bulks of the immobilized ligand is the limiting factor and not the number of available silanol groups on the surface. Even lower loadings than for the pure ligands were obtained when the whole complex was grafted onto the mesoporous support. This is attributed to lower flexibility of the complex and/or its higher polarity and therefore lower affinity to the rather apolar pore wall. Pore volumes and surface areas decreased upon grafting, but a complete blocking of the pores did not occur even with the MCM-41 support.

The grafting of complexes or ligands takes place by reaction of the trimethoxysilane-linker R-Si(OCH₃)₃ with free Si-OH groups on the surface of the MCM-41 and M41S materials. The presence of the typical bands of the CH₃-stretching vibrations at 2950 and 2890 cm⁻¹ in the IR spectra of the grafted samples showed that some CH₃ groups were still present after grafting, i.e. not all the methoxy-groups had reacted with surface silanols. The C/N ratios found in elementary analysis indicate, on the other hand, that the fraction of unreacted methoxy groups must be very small: the C/N ratio of the original ligand molecule is 5.0 (SiC₂₀H₂₈N₄O₅). It is expected to decrease to 4.25 (SiC₁₇H₁₉N₄O₂) if all methoxy groups were removed. Experimental values were between 4.2 and 4.4, i.e. close to the fully reacted ligand.

¹³C CP-MAS NMR and IR were used to characterize the immobilized ligands. The ¹³C CP-MAS NMR spectra of (1) and (2) were recorded at three different spinning speeds (5, 10 and 12 kHz) in order to attribute all the peaks without side band interferences. The ¹³C NMR evidences the presence of the carbonyl group of the ligand at 168 ppm. All the signals of the aromatic and aliphatic parts of the organic molecule could be assigned. The IR spectra of the non coordinating ligands on MCM-41 (2)
3. RESULTS AND DISCUSSION

Figure 9.2: IR spectra of ligand-MCM-41 (2) and Mn-MCM-41 gr (5).

Figure 9.3: IR spectra of ligand-M41S (1) and Ru-M41S gr (4).
Figure 9.4: Structures of amide moiety.

(Fig. 9.2) and M41S (1) (Fig. 9.3) show two bands at 1665 and 1635 cm$^{-1}$, which are due to the C–O stretching vibration of the secondary and tertiary amide group, respectively. The assignment of the lower frequency vibration to the tertiary amide group is based on the observation that a N-propyl-picolinamide ligand showed only one C=O vibration at 1660 cm$^{-1}$. The sharp band at 1534 cm$^{-1}$ is due to the C-N stretching vibration coupled with the N-H bending vibration of the secondary amide group (the so-called amide II band) [73]. The two bands at 1591 and 1570 cm$^{-1}$ as well as the pair at 1464 and 1437 cm$^{-1}$ are ring stretching-vibrations of pyridine.

The grafted Mn-complex on MCM-41 shows some distinctly different features (Fig. 9.2). The pyridine ring vibrations at 1464 and 1437 cm$^{-1}$ are split, the two others at 1591 and 1570 cm$^{-1}$ strongly gained in intensity. Both observations indicate that pyridine is involved in the complexation. Also the C=O stretching vibrations gained in intensity, but most of the intensity shifted to lower wavenumbers, i.e. 1635 cm$^{-1}$. The amide II band broadened. If complexation occurred via C=O a marked shift of the C=O stretching vibration to lower wavenumbers would be expected, accompanied by a shift of the amide II band to higher wavenumbers (Fig. 9.4): The resonance form with the C=N double bond and the C-O single bond gains in importance.

Since none of this was observed, complexation of Mn probably occurs via the nitrogen atom of the amide group. In that case an increase of the C=O stretching vibration would be expected (more double bond character), but conjugation with the aromatic ring can change that situation.

The IR spectrum of the Mn-complex on M41S was similar to the one shown in Figure 9.2, but less resolved. The IR spectrum of the Ru-complex on M41S (Fig. 9.3) was completely different from that of the Mn-complex. None of the original bands of the ligands remained after complexation with Ru. The C=O stretching vibration shifted to 1622 cm$^{-1}$. The original amide II band shifted and was covered by other bands, while the pyridine signal at 1595 cm$^{-1}$ gained in intensity [118]. The shift of the C=O and the CO-NH vibration strongly indicate complexation via the carbonyl group. The broadening of the aromatic ring vibrations indicates that also pyridine
is involved in the complexation. Note that the intensity of the C=O stretching vibrations decreased due to the lower loading of complex (4) compared to material (1) in Figure 9.3, and not because of a decrease of the absorption coefficient. The spectrum of the Ru-complex prepared by self-assembly inside the pores was identical to the one shown in Figure 9.3, but more intense, due to the higher loading.

9.3.2 Structure of complexes

The ligand N,N'-bis(2'-pyridine-carboxyamide)-1,2-ethane can coordinate metals with many variations both in the geometry and the metal/ligand ratio. Several possibilities are presented in Figure 9.5 [83]. For the Ru-complexes, elemental analysis showed a metal/ligand ratio close to 1.0 (Table 9.2). The FT-IR spectra indicated that complexation of Ru occurred via the carbonyl group and the pyridine ring: the shift of the carbonyl band of the secondary amide to lower frequency, the disappearance of the original amide II band and the intensification of the pyridine ring vibrations support that idea. In case of the tertiary amide group it is less clear whether complexation occurs via the carbonyl group or the amide nitrogen. Complexation via pyridine and the tertiary nitrogen (Fig. 9.5 b) should slightly increase the frequency of the C=O vibration [73]. Since this was not observed in the FT-IR
spectra, a complexation via both carbonyl groups seems more likely, i.e. a structure as shown in Figure 9.5 a.

The self assembly of Mn complexes was less straightforward. The attempt to complex Mn with the immobilized ligands in MCM-41 and M41S (analogous to sample (3)) led to very low metal loadings (less than 1% of Mn). Better results were obtained by preparing the complex in a first step, then grafting it on the support. With this methodology, surprisingly high metal/ligand ratios close to 2.0 were obtained. The IR spectra (Fig. 9.2) indicate that Mn is ligated by the pyridine and amide N-atoms. Although ligation by the carbonyl group is the more common mode of complexation it does not seem to prevail in our samples since the C=O stretching vibration was not markedly shifted. The IR spectra and the M/L ratio close to 2 suggest a complexation as shown in Figure 9.5 c, i.e. two Mn atoms are bound by the two pyridine and amine groups of the ligand. Since the metal/ligand ratio was a bit lower than 2, this structure probably exists in a mixture with the structure shown in Figure 9.5 d, where one Mn atom is bound to the four nitrogen atoms of the ligand. In that structure the Mn is not coordinatively saturated. Due to the very low Cl/Mn ratios observed in elemental analysis, the remaining ligands are probably not Cl (as confirmed by the absence of Cl to Mn LMCT bands in the UV-Vis spectra, not shown), but hydroxy groups, which replaced the Cl anions due to use of the strong base NaH in the preparation of the complex. Overall the Mn-complexes are certainly less well defined than their Ru analogues.

9.3.3 Catalytic activity

All the catalysts were tested in styrene epoxidation. The results are summarized in Table 9.3. Reactions carried out using the catalyst and H₂O₂ (30 wt%) gave mainly decomposition of the peroxide. The water/acetonitrile solution easily leaches the metal into solution, and particularly manganese quickly decomposes the peroxide. Less coordinating systems were used, i.e. a solution of TBHP (70%) in nonane with either CH₂Cl₂ or CH₃CN as solvents. With CH₂Cl₂ at 40°C no reaction took place. With CH₃CN at 50°C a detectable activity was observed with all the catalysts. The two main reaction products were the epoxide and benzaldehyde, formed by cleavage (Fig. 9.6).

The Mn complexes gave higher yields of epoxide, but the selectivity was only moderate. The preparation method of the complex (grafting vs. self-assembly) and the pore size of the support material (MCM-41 vs. M41S) did not strongly affect the catalytic properties. This is not surprising since the leaching tests showed that the catalytic activity was to a large extent due to metal ions leached in solution (see
Table 9.3: Activity in styrene oxidation. Reactions with TBHP were carried out at 50°C in CH₃CN, reactions with PhIO in CH₂Cl₂ at room temperature.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>oxidant</th>
<th>react. time</th>
<th>aldehyde [yield %]</th>
<th>epoxide [yield %]</th>
<th>select. b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru on M41S sa (3)</td>
<td>TBHP</td>
<td>1</td>
<td>7 / -</td>
<td>6 / -</td>
<td>31 / -</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>13 / 13</td>
<td>9 / 4</td>
<td>40 / 24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td>27 / 16</td>
<td>12 / 7</td>
<td>31 / 30</td>
</tr>
<tr>
<td>Ru on M41S gr (4)</td>
<td>TBHB</td>
<td>1</td>
<td>6 / 0</td>
<td>5 / 0</td>
<td>45 / -</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>9 / 11</td>
<td>7 / 6</td>
<td>44 / 35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td>29 / 20</td>
<td>19 / 9</td>
<td>31 / 31</td>
</tr>
<tr>
<td>Mn on MCM-41 gr (5)</td>
<td>TBHB</td>
<td>3</td>
<td>13 / 11</td>
<td>12 / 9</td>
<td>48 / 42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td>17 / 16</td>
<td>21 / 13</td>
<td>55 / 45</td>
</tr>
<tr>
<td>Mn on M41S gr (6)</td>
<td>TBHB</td>
<td>3</td>
<td>10 / 9</td>
<td>6 / 6</td>
<td>37 / 40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td>32 / 23</td>
<td>19 / 11</td>
<td>37 / 32</td>
</tr>
<tr>
<td>Ru on M41S sa (3)</td>
<td>PhIO</td>
<td>2</td>
<td>9</td>
<td>3</td>
<td>27</td>
</tr>
<tr>
<td>Ru on M41S gr (4)</td>
<td>PhIO</td>
<td>2</td>
<td>8</td>
<td>3</td>
<td>25</td>
</tr>
<tr>
<td>Mn on MCM-41 gr (5)</td>
<td>PhIO</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn on M41S gr (6)</td>
<td>PhIO</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

a activity of catalyst / activity of the solution, hot filtered after 1 h of reaction
b epoxide / (epoxide + aldehyde)

Figure 9.6: Reaction scheme of the oxidation of styrene.
yields and selectivities in Table 9.3). In order to avoid the leaching of the metal a less coordinating system and milder reaction conditions were chosen (room temperature): With CH$_2$Cl$_2$ as solvent and PhIO as oxidant, the Mn catalysts did not show any catalytic activity. The Ru catalysts however converted styrene to epoxide and aldehyde already at room temperature, with a similar selectivity as with the TBHP oxidant. In this case the filtered solution did not show any catalytic activity. Also the pure support materials MCM-41 and M41S did not lead to any reaction. Similar homogeneous ruthenium catalysts showed better activity and selectivity than the heterogeneous catalysts described here [119]. There are also examples of homogeneous Mn catalysts for which good results in the epoxidation of styrene using PhIO have been reported [120,121].

9.4 Conclusions

Mn and Ru complexes with pyridine-carboxamide ligands have been incorporated in MCM-41 and M41S mesoporous silica using two different methodologies. The complexes were prepared outside the mesoporous material and then grafted inside the channels of the support or the ligand was covalently bound in the mesoporous material and the metal complex self-assembled inside the pores. Both preparation methods were successful and lead to high metal loadings of the mesoporous materials. Characterization by IR spectroscopy showed that the ligands bind Ru mainly via its carbonyl group while complexation of Mn occurred mainly via the nitrogen atoms of the pyridine ring and the amide group. The materials were active in the epoxidation of styrene, but activity and selectivity were not as good as those reported for homogeneous Mn and Ru complexes. With strongly coordinating solvents or oxidants, Ru and Mn leached into solution and the leached ions were responsible for a large part of the catalytic activity. This indicates that the ligand, although capable of immobilizing a high concentration of metal on the support, is not suited for imparting a high stability of the complex under these reaction conditions. Under milder reaction conditions, however, no leaching was observed and the heterogeneous Ru-catalyst showed some activity.
Chapter 10
Biomimetic Iron Catalysts

10.1 Introduction

Several metalloproteins and enzymes have carboxylate-bridged diiron clusters in their active site [122]. The most prominent of these are hemerythrin, ribonucleotide reductase and methane monooxygenase (MMO). Especially methane monooxygenase has attracted much attention over the last decade because it is able to selectively oxidize methane to methanol [123–125]. Preparing molecular analogues of defined carboxylate-bridged iron clusters is, however, very difficult [126,127]. One reason is that iron tends to form large clusters in aqueous solutions. Furthermore, even very simple mimics of active centers of enzymes do not self assemble easily but often require enormous synthetic efforts [126,127]. Variations of properties of homogeneous biomimetic complexes are often limited by the synthetic feasibility. Finally a medium where the biomimetic complex together with the substrate and oxidant is soluble enough has to be found. We believe that heterogeneous immobilized mimics of carboxylate-bridged metalloproteins have the potential to overcome these problems. Furthermore, heterogeneous systems are also advantageous for separation and reuse.

If one wants to mimic the active site of a metal enzyme the best ligands are the amino acids present in the enzyme. In the case of MMO histidine and glutamic acid amino acids serve as ligands for the binuclear iron cluster. The most convenient method to immobilize amino acids is to form amide bonds with surface bound amine groups (Fig. 10.1). Amine functionalized materials can be prepared by several methods, e.g. grafting the commercially available 3-aminopropyl-trimethoxysilane on silica surfaces or co-condensation of the same trimethoxysilane with a silica precursor (typically TEOS) [23, 75, 89, 128]. If porous silica supports are used for surface functionalization the hydrophobic character inside the pores can be adjusted by
glutamic acid \* R = \begin{align*}
&\text{H} \\
&\text{O} \\
&\text{H} \\
&\text{CH}_2 \\
&\text{OH}
\end{align*}

histidine \* R = \begin{align*}
&\text{H} \\
&\text{N} \\
&\text{H} \\
&\text{C} \\
&\text{N} \\
&\text{H}
\end{align*}

silica

side chain protection of amino acids

Figure 10.1: Immobilization of amino acids on the surface of functionalized silica material.
co-functionalization with other species as described in chapter 7. The molar ratio between the two functional groups could be easily adjusted by varying the ratio of the respective silanes during the functionalization reaction. Thereby well-ordered mesoporous materials with a decreasing density of 3-aminopropyl and simultaneously an increasing hydrophobic character inside the pores were obtained. The potential to vary the hydrophobic character of the local environment of immobilized catalytically active sites may also be a very important advantage over homogeneous systems because it is known that the hydrophobic local environment of the active site of many enzymes is very important for the catalytic activity [129]. In the case of MMO for example the active Fe cluster is close to a hydrophobic pocket which is responsible for the binding of the substrate.

The big advantage of using amine-functionalized silica materials as starting point for amino acid immobilization is that it can be automated with a peptide synthesizer. The amine-functionalized silica can be used instead of polystyrene resins as solid phase for automated peptide synthesis. Standard procedures and commercially available reagents can be used. This methodology allows the fast synthesis of large libraries of immobilized mimics of MMO or any other protein. The resulting amino acid-carrying silica material can be treated with metal salts and used as catalyst for liquid or gas phase reactions. The stepwise procedure that involves functionalization of any silica surface, immobilization of amino acids and the exchange of these ligands with metals is extremely flexible and can be varied on each stage. This is a clear advantage over the co-condensation of amino acid-carrying silanes with silica precursors in one step [130].

10.2 Experimental

10.2.1 Immobilization of amino acids

A functionalized pure silica M41S material with well-ordered mesopores was used as support for immobilization of amino acids. The parent silica material had an average BJH pore diameter of 8.0 nm, a specific BET surface area of 1100 m²/g and a specific pore volume of 2.6 cm³/g. Experimental details of the synthesis of this mesoporous M41S material were presented in chapter 4. The described methodology is not, however, specific for this silica material. It can also be performed with other mesoporous silica materials or commercially available silica products. The silica surface was functionalized with mixtures of 3-aminopropyl and methyl groups, as described in detail in chapter 7. By varying the ratio of (3-aminopropyl)trimethoxysilane (APTMS) and methyl-trimethoxysilane (MTMS) in the functionalization reaction mixture materi-
als with different concentrations of surface bound 3-aminopropyl groups were prepared. The following ratios of 3-aminopropyl / methyl groups on the surface of the functionalized materials were obtained: 1:1, 1:2, 1:6, 1:10, 1:20. These ratios are used hereafter to identify the functionalized material that was used for immobilization of amino acids.

The immobilization of amino acids was performed by solid phase peptide synthesis, using a ABI 433 A peptide synthesizer (Applied Biosystems) [131] and standard HBTU/HOBt/NMP activation protocols for Fmoc chemistry (FastMoc protocol, Applied Biosystems) [132](Fig. 10.2). Amino acid side chains were protected as Glu(OtBu) and His(Trt) (Fig. 10.1). After drying the materials with immobilized amino acids the side chains were deprotected by shaking in trifluoroacetic acid (20 ml per g of solid) for 30 min in the presence of scavengers (water 5% (v/v), triisopropylsilane 1% (v/v)). The solid was collected by filtration with a glass frit. After deprotection the solid was shaken for 15 min in a pyridine solution (20% (v/v) in ethanol) and collected by filtration. This washing cycle was repeated 5 times. Finally the same cycle was performed 2 times with pure ethanol. The deprotected and washed solid was dried in ambient atmosphere. Codes identifying the used
10.3. RESULTS AND DISCUSSION

Functionalized starting material and the immobilized amino acid of all prepared materials are included in Table 10.1. The M41S support, a functionalized material with a 3-aminopropyl / methyl ratio of 1:1 and all materials with immobilized amino acids on their surface were exchanged with Fe (II) in aqueous solution. For that purpose about 200 mg of solid material was dispersed in 20 ml of demineralized water in a flask. The dispersion was degassed for 5 min with simultaneous vigorous stirring and bubbling N₂. 200 mg of ammonium-iron(II)-sulfate hexahydrate (Mohr Salt (NH₄)₂[Fe(SO₄)₂]) was added. The flask was closed with a septum. The colorless solution was stirred for 60 min. After the exchange the solid was collected by filtration and dried in air.

10.2.2 Oxidation of cyclohexane

All Fe exchanged materials were tested as catalyst for cyclohexane oxidation with H₂O₂ as oxidant. The oxidation reactions were carried out in 10 ml glass flasks that where sealed with glass lids. 4 ml acetonitrile was placed in the flask and degassed with bubbling N₂ for 2 min. Then 100 μmol cyclohexane and 110 μmol H₂O₂ (35% in water) were added. The reaction was started by adding 50 mg of catalyst. The reaction mixture was degassed with N₂ for another 30 s in order to remove dissolved O₂. The flasks were closed and stirred for 1.5, 6 or 24 h in an oil bath at 30°C. After that the reaction mixture was analyzed with gas chromatography (HP 5890 Series II, HP-1 column with a FID detector). 1-pentanol was added as internal standard for quantification. Peaks were assigned with the addition method. The degree of H₂O₂ decomposition was checked by titration with KMnO₄.

10.3 Results and discussion

10.3.1 Characterization

Functionalized materials with both 3-aminopropyl and methyl groups on their surfaces were used as support for all immobilizations of amino acids (Fig. 10.1). The advantages of materials with mixed functionalization over materials with only 3-aminopropyl on their surface are: (1) They are hydrothermally more stable. (2) A larger fraction of the amine groups is in its free form. Protonation of the amine functionality by unreacted silanol groups on the surface of the silica or H-bonding between adjacent amine groups decreases their reactivity towards amino acids. IR confirmed that materials with mixed functionalization had a much smaller fraction of protonated and H-bonded amine-groups on their surface (see section 7.3.2). (3) The
Table 10.1: Pore characteristics, changes in C and N loading and F contents of functionalized M41S materials with immobilized amino acids.

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[cm³/g]</td>
<td>[m²/g]</td>
<td>[wt%]</td>
<td>[wt%]</td>
<td>[wt%]</td>
</tr>
<tr>
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<td>472</td>
<td>2.4</td>
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<tr>
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<td>1.5</td>
<td>3.7</td>
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<tr>
<td>His on 1:6</td>
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<td>0.9</td>
<td>1.4</td>
<td>1.9</td>
</tr>
<tr>
<td>His on 1:10</td>
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<td>649</td>
<td>-0.6</td>
<td>0.8</td>
<td>0.7</td>
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<tr>
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<td>690</td>
<td>-1.7</td>
<td>0.4</td>
<td>0.5</td>
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<tr>
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<td>2.8</td>
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<td>0.5</td>
<td>1.3</td>
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<tr>
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<td>591</td>
<td>0.4</td>
<td>0.6</td>
<td>0.3</td>
</tr>
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<td>0.4</td>
</tr>
<tr>
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<td>607</td>
<td>-2.3</td>
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<td>0.2</td>
</tr>
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<td>3.8</td>
<td>1.6</td>
<td>3.0</td>
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<tr>
<td>Glu+His on 1:1 *</td>
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<td>478</td>
<td>2.4</td>
<td>1.2</td>
<td>3.8</td>
</tr>
</tbody>
</table>

---

*a* code e.g. Glu on 1:1: glutamic acid immobilized on functionalized material with 3-aminopropyl / methyl ratio of 1:1

*b* increase observed during immobilization of amino acids: wt% after immobilization - wt% before immobilization (values of starting materials given in Table 7.2)

*c* immobilized in the given sequence: 1. Glu, 2. His

*d* treated with a 1:1 mixture of glutamic acid and histidine during the same cycle
variable density of the amine species on the surface allows to vary the amount of immobilized amino acids on the solid. Thereby also the average distance between two immobilized amino acids can be varied.

Histidine and glutamic acid were immobilized on functionalized materials with molar 3-aminopropyl / methyl group ratios of 1:1, 1:2, 1:6, 1:10 and 1:20. Pore characteristics derived from N$_2$ physisorption of all these materials are compiled in Table 10.1. All materials preserved high specific BET surface areas and pore volumes after immobilization of histidine, glutamic acid, and combinations thereof. The materials with higher surface loading of 3-aminopropyl loose more pore volume because more amino acid is immobilized on the surface. The increase of the C and N content is listed in Tables 10.1 and 10.2. All materials experienced an increase in N loading during the immobilization of amino acids. The increase was larger for histidine which has three nitrogen atoms compared to only one in the case of glutamic acid. Within a series of histidine or glutamic acid immobilized on functionalized silicas with decreasing 3-aminopropyl loadings, the largest increase of N content during immobilization is observed for the 1:2 and 1:6 starting materials. The reason is that in the material with a higher 3-aminopropyl loading (1:1 in Table 10.2) less amine groups are free for reaction with the amino acids, due to H-bonding. In the materials with lower 3-aminopropyl loadings (1:10 and 1:20 in Table 10.2) on the other hand the amount of amine species is too small. The C content shows a similar pattern, but an additional effect is observed. In the materials with small molar loadings of 3-aminopropyl the C content decreases during immobilization of amino acids. The reason is that unreacted methoxy-groups of methyl-trimethoxysilane functionalization agent are hydrolyzed during the immobilization procedure and removed from the material. Fluorine is found after the immobilization of amino acids because trifluoroacetic acid is used as reagent to deprotect the side groups of the immobilized amino acids. The fact that all materials with histidine have higher F contents indicates that CF$_3$COO$^-$ acts partly as a counterion for protonated imidazole rings of histidine. The rest of the CF$_3$COO$^-$ is present as counterion of protonated 3-aminopropyl groups that are present on the surface of all materials. After the exchange with Fe(II) no F was found on the materials any more, showing that the CF$_3$COO$^-$ anions were replaced during metal exchange.

To characterize the chemical state of the immobilized species on the surface of the materials with immobilized amino acids IR spectroscopy was used. After the immobilization of both histidine and glutamic acid a decrease of the N-H deformation vibration at 1595 cm$^{-1}$ of the free amine occurs (Fig. 10.3). At the same time the two characteristic bands for amide-groups appear around 1670 and 1550 cm$^{-1}$. 
Table 10.2: Changes of molar C + N loadings, pore volumes and Fe loadings after immobilization of amino acids and exchange with Fe(II).

<table>
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<tr>
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<td>1.06</td>
<td>0.8</td>
</tr>
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<td>His on 1:2</td>
<td>2.5</td>
<td>1.3</td>
<td>1.19</td>
<td>0.3</td>
</tr>
<tr>
<td>His on 1:6</td>
<td>0.9</td>
<td>1.2</td>
<td>1.32</td>
<td>0.2</td>
</tr>
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<td>His on 1:10</td>
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</tr>
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<td>1.50</td>
<td>0.2</td>
</tr>
<tr>
<td>Glu on 1:1</td>
<td>2.0</td>
<td>0.3</td>
<td>1.09</td>
<td>0.5</td>
</tr>
<tr>
<td>Glu on 1:2</td>
<td>1.8</td>
<td>0.4</td>
<td>1.22</td>
<td>0.1</td>
</tr>
<tr>
<td>Glu on 1:6</td>
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<td>0.5</td>
<td>1.35</td>
<td>0.1</td>
</tr>
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</tr>
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<td>Glu on 1:20</td>
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<td>0.1</td>
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<tr>
<td>Glu-His on 1:1</td>
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<td>1.4</td>
<td>0.93</td>
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<tr>
<td>Glu+His on 1:1</td>
<td>2.4</td>
<td>1.0</td>
<td>1.09</td>
<td>0.5</td>
</tr>
</tbody>
</table>

\( ^a \) molar C loading normalized to the weight of the silica support:

\[
\text{wt\% C incr.} \times \frac{10}{12} / \left( \frac{100 - \text{wt\% C + wt\% H + wt\% N}}{100} \right)
\]

\( ^b \) molar N loading normalized to the weight of the silica support:

\[
\text{wt\% N incr.} \times \frac{10}{14} / \left( \frac{100 - \text{wt\% C + wt\% H + wt\% N}}{100} \right)
\]

\( ^c \) M41S material functionalized with 3-aminopropyl / methyl 1:1, treated with iron for comparison.
10.3. RESULTS AND DISCUSSION

Figure 10.3: IR spectra of immobilized amino acids. Parent 1:1: functionalized starting material with 3-aminopropyl / methyl 1:1, histidine: histidine immobilized on parent functionalized material (His on 1:1 in Table 10.1), glutamic acid (Glu on 1:1), Glu-His seq. (Glu-His on 1:1), Glu+His mix. (Glu+His on 1:1), * shifted to higher absorbance for better visibility.

That shows that the free amine reacted with the amino acid and formed the amide. The very broad features above 3000 cm\(^{-1}\) are due to the immobilization of amino acids. They are characteristic for zwitterionic amino acids [73]. Both materials with immobilized amino acids show a band around 1700 cm\(^{-1}\) which is characteristic for carboxylic acid groups. On the materials with immobilized glutamic acid this band is (partly) caused by the carboxylic acid of the side chain. In the case of immobilized histidine, however, this band must come from the trifluoroacetic acid that is still present at that stage. Also the material with immobilized glutamic acid contains some trifluoroacetic acid in addition to the carboxylic acid side chain. That is probably the reason why that band of the spectrum is not resolved and more intense. A detailed band assignment is given at the end of this chapter. The material with a sequence of glutamic acid and histidine (Glu-His seq. in Fig. 10.3) and the material where the two amino acids were mixed and immobilized both at the same time (Glu+His mix. in Fig. 10.3) show the combination of features observed in the materials with only one kind of immobilized amino acid. The comparison of the series of spectra of materials with immobilized histidine (Fig. 10.4) shows that the characteristic amide bands and the broad N-H stretching bands (around 3200 cm\(^{-1}\))
are the most intense in the material with 3-aminopropyl / methyl 1:2. This is in agreement with the N and C increases found in elementary analysis (Table 10.1). The same trend can be seen in the comparison materials with immobilized glutamic acid (Fig. 10.5).

The immobilized amino acids were then used to complex Fe(II) in aqueous solution. The porosity of amino acid-functionalized materials was not affected by the ion exchange with Fe(II) salt (Table 10.2). This is noteworthy because mesoporous silica materials often suffer from instability towards hydrolysis in aqueous environment. Materials with immobilized histidine generally had larger iron loadings than materials with glutamic acid. Interestingly the highest iron loading is not obtained for the highest amino acid loading (Table 10.2). The iron loading increases with increasing 3-aminopropyl / methyl ratios. The reason must be that the complexation involves both the amino acids and neighboring amine groups. The concentration of amine groups increases in a series of materials from for example His on 1:20 to His on 1:1, because only a fraction of the amines react with the amino acid. The material with a sequence of histidine and glutamic acid (Glu-His on 1:1) gave the largest iron loading. This suggests that the iron complex is formed with the two amino acids and that the surface amine groups do not participate in that case. For comparison the
mesoporous silica support was also exchanged with Fe(II) salt. It suffered a severe structural decay and gave only a very low iron loading. The functionalized material (funct. 1:1 in Table 10.2) could complex a high concentration of iron. The brownish color of the sample indicates, however, that the complexation was unspecific and that large iron oxide clusters were formed.

The comparison of the infrared spectra after the treatment with the spectra before the exchange (Fig. 10.6) shows some interesting differences between the immobilized amino acids. The spectra of the material with immobilized histidine before and after Fe treatment have two remarkable differences. The N-H stretching bands are broadened and shifted to lower wavenumbers by more than 25 cm$^{-1}$ after the iron treatment. That indicates strong electron donation of the lone pair of the amine group to the iron cation. The amine groups are ligands of the complexed iron in the case of immobilized histidine. The second difference concerns the region between 1800 and 1450 cm$^{-1}$. The band at 1720 cm$^{-1}$ which was assigned to the carbonyl group of the trifluoroacetic acid disappears. This is due to the mentioned removal of this trifluoroacetic acid during the iron exchange in aqueous solution. The C=O stretching band is shifted to lower wavenumbers by 10 cm$^{-1}$ and in addition a shoulder at even lower wavenumbers appears. The CHN vibration does not shift.
Figure 10.6: IR spectra of immobilized amino acids before and after treatment with Fe. Histidine (His on 1:6), glutamic acid (Glu on 1:6). These two materials are presented because they have the highest loading of amino acid.

This indicates that the lone pairs of the C=O group of the amide act as ligands in the complexation of the iron cations. A possible iron complexation mode of the material with immobilized histidine is depicted in Figure 10.7. The shoulder of the C=O stretching band could be explained with a fraction of Fe(II) that is not complexed with the amine of the imidazole ring (as depicted in Fig. 10.7) but only with the free amine of the amino acid. As mentioned before, the other ligands of Fe(II) are neighboring amines on the surface and water (not depicted in Fig. 10.7 for clarity).

The spectra of the materials with immobilized glutamic acid are less affected by the complexation with iron. The stretching vibrations of the amine group are not shifted at all. It can be concluded that the amine groups in this material are hardly involved in iron complexation. Also the 1800 - 1450 cm\(^{-1}\) range shows less changes. The C=O band of trifluoroacetic acid disappears. The overlaid C=O bands of the carboxylate group of the side chain and the amide are both slightly shifted to lower wavenumbers. The CHN vibration of the amide is shifted to larger wavenumbers by 3 cm\(^{-1}\). This indicates that the carboxylate groups of the carboxylic acid side chain and of the amide group are involved in the complexation of the iron cations in that case. A possible iron complexation mode of the material with immobilized
glutamic acid is depicted in Figure 10.7. The structures proposed in Figure 10.7 are just possibilities that explain the changes in the IR spectra before and after iron exchange. It is clear that with immobilized ligands not just one complex structure is present. As mentioned neighboring amine species are most probably also involved in iron complexation and moreover also two neighboring immobilized amino acids could be involved. The IR spectra of the materials with a sequence of glutamic acid and histidine and a mixture of these two amino acids showed a combination of the features observed for the immobilized single amino acids after iron exchange (Fig. 10.8).

UV spectra give information about the environment of the iron complexed with immobilized amino acids. The comparison of the UV spectra before and after Fe treatment (Fig. 10.9) show that two bands at 40000 cm⁻¹ and 44500 cm⁻¹ appear after the iron treatment. Both are ligand-to-metal charge transfer transitions. The strong absorption at higher energies, which is already found before the iron treatment, is due to the organic ligands. The iron complexation of the material with histidine shows an additional interesting feature. The absorption of the organic groups is shifted to higher energies after the Fe treatment. This indicates that the aromatic imidazole moiety donates electron density to the metal, as was postulated on the basis of IR. The UV spectra of the Fe-amino acid complexes differ
Figure 10.8: IR spectra of immobilized amino acids before and after treated with Fe. Glu-His seq. (Glu-His on 1:1), Glu+His mix. (Glu+His on 1:1).
Figure 10.9: UV spectra of immobilized amino acids before and after treatment with Fe. Histidine (His on 1:1), glutamic acid (Glu on 1:1). Inset: Fe(II) on parent 1:1.
fundamentally from the species formed on the amine-functionalized material (inset of Fig. 10.9). The Fe treated parent materials shows bands at 20000 and 30000 cm\(^{-1}\) characteristic for clustered iron species [133]. From these findings it can be concluded that the complexation in the materials with immobilized histidine and glutamic acid the complexation is very specific and that mainly isolated iron species are present. The same is also valid for the materials with histidine and glutamic acid immobilized together (not shown).

**10.3.2 Catalytic test**

Cyclohexane oxidation was performed with all described materials with 24 h reaction time. Some reactions were repeated for 1.5 and 6.5 h reaction time. All tested materials had reasonable activities at the reaction temperature of 30°C. A blind test without catalyst gave no reaction products and no oxidant decomposition. None of the Fe containing materials gave complete oxidant decomposition after 24 h of reaction as confirmed with titration of H\(_2\)O\(_2\). Due to the limited volume of the reaction mixture accurate titration of H\(_2\)O\(_2\) was not possible, so that no statement about effectivity of the oxidant can be made.

A comparison of TOF values for the formation of cyclohexanol and cyclohexanone (Table 10.3) shows that no general trend between the amount of Fe and the activity of the catalyst can be made. For the materials with immobilized histidine the TOF values are constant for materials with high loadings of immobilized amino acids (His on 1:1, 1:2 and 1:6 in Table 10.3) and decrease rapidly as soon as the density of immobilized amino acids goes down. For the materials with immobilized glutamic acid it is exactly the opposite. There the highest TOF was obtained for the material with the lowest amount of immobilized glutamic acid (Glu on 1:20 in Table 10.3). It seems that a higher concentration of immobilized histidine on the surface is advantageous for the catalytic activity whereas it is the opposite with immobilized glutamic acid. That proves that the chemical environment, namely the nature of the ligands and the proximity between two active sites, strongly influences the activity. The low selectivity towards the alcohol and the high activity of the support treated with Fe indicate, however, that the reaction mechanism involves free radical reactions and is not truly biomimetic.

The four materials with histidine (His on 1:1), glutamic acid (Glu on 1:1), and both histidine and glutamic acid (Glu+His and Glu+His on 1:1) immobilized together on the same functionalized materials were investigated in more detail. They show comparable activities and selectivities after 24 h of reaction. At shorter reaction times, however, big differences appear (Fig. 10.10). For all four materials the selectivity
### Table 10.3: Cyclohexane oxidation activity of Fe-exchanged materials with immobilized amino acids. 24 h reaction time.

<table>
<thead>
<tr>
<th>Fe material</th>
<th>tot. prod.(^a):</th>
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<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td>[μmol]</td>
<td>CyOL</td>
<td>CyON</td>
<td>sel.(^d):</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>([10^{-6} \text{ s}^{-1}])</td>
<td>([10^{-6} \text{ s}^{-1}])</td>
<td>[% CyOL]</td>
<td></td>
</tr>
<tr>
<td>no catalyst</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>M41S support</td>
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<td>4.04</td>
<td>28</td>
<td></td>
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<tr>
<td>funct. 1:1</td>
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<td>0.89</td>
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<td></td>
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<td>0.74</td>
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</tr>
</tbody>
</table>

\(^a\) total amount of formed products: μmol cyclohexanol + μmol cyclohexanone

\(^b\) turn over frequency of cyclohexanol:

\[ \text{TOF CyOL} = \frac{\text{mol cyclohexanol}}{\text{mol Fe} \times \text{s reaction time}} \]

\(^c\) turn over frequency of cyclohexanone:

\[ \text{TOF CyON} = \frac{\text{mol cyclohexanone}}{\text{mol Fe} \times \text{s reaction time}} \]

\(^d\) selectivity towards cyclohexanol:

\[ \text{sel} = \frac{\mu \text{mol cyclohexanol}}{\mu \text{mol cyclohexanol} + \mu \text{mol cyclohexanone}} \]

\(^e\) catalyst recycled and reused under identical reaction conditions
Figure 10.10: Conversion of cyclohexane oxidation reaction vs. time. Histidine (His on 1:1), glutamic acid (Glu on 1:1), Glu-His seq. (Glu-His on 1:1), Glu + His mix. (Glu+His).
towards the alcohol increases with reaction time, but the increase is larger for the three materials with immobilized glutamic acid (alone or together with histidine). The material with immobilized histidine alone shows severe deactivation. The three materials that contain glutamic acid are initially less active. Together with the finding that the highest activity was found for the material with a very small amount of immobilized glutamic acid this might suggest that a small amount of glutamic acid eventually together with other amino acid could give a catalytically promising system.

10.3.3 Conclusions

The presented automated immobilization procedure enabled us to prepare a small library of very simple heterogeneous MMO mimetic catalysts. The method is very fast and reliable. The catalytic tests showed activity under very mild conditions. Both the nature of the immobilized amino acid as well as its surface density had an influence on the catalytic activity. These findings are very encouraging and are a starting point for further optimization. The stepwise procedure allows very easy adaptation and optimization of the support, the nature of the functional groups on the support, the immobilized amino acids and the complexed metal. Therefore this approach can not only be used to prepare heterogeneous mimics of carboxylate bridged metalloproteins but simple functional models of any protein.
Detailed IR band assignment of materials with immobilized histidine and glutamic acid

Table 10.4: IR band assignment of immobilized histidine (His on 1:1 in Table 10.1), Spectra (Fig. 10.3).

<table>
<thead>
<tr>
<th>Wavenumbers $[\text{cm}^{-1}]$</th>
<th>Assigned Species</th>
<th>Wavenumbers $[\text{cm}^{-1}]$</th>
<th>Assigned Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>3650</td>
<td>H - bonded SiO-H $^a$</td>
<td>1865</td>
<td>Overtone of Si-O-Si st</td>
</tr>
<tr>
<td>3425</td>
<td>H - bonded SiO-H $^b$</td>
<td>1715</td>
<td>Acid C=O st $^d$</td>
</tr>
<tr>
<td>3365</td>
<td>Asymmetric N-H$_2$ st</td>
<td>1668</td>
<td>Amide C=O st</td>
</tr>
<tr>
<td>3315</td>
<td>Symmetric N-H$_2$ st</td>
<td>1547</td>
<td>Amide CHN vib</td>
</tr>
<tr>
<td>3104</td>
<td>Overtone of C=O st</td>
<td>1552</td>
<td>Symmetric N-H$_3^+$ def</td>
</tr>
<tr>
<td>3200-2000</td>
<td>N-H st $^c$</td>
<td>1495</td>
<td>C-F$_3$ vib $^d$</td>
</tr>
<tr>
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<td>C-H$_2$ def $^e$</td>
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<td>C-H$_2$ def $^g$</td>
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<td>C-H$_2$ wag</td>
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$^a$ One bridge $^b$ Two bridges $^c$ H-bonded and protonated amine species $^d$ Trifluoroacetic acid $^e$ CH$_2$ bound to N $^f$ Middle CH$_2$-group $^g$ CH$_2$-group bound to Si

Table 10.5: IR band assignment of immobilized glutamic acid (Glu on 1:1 in Table 10.1), Spectra (Fig. 10.3).

<table>
<thead>
<tr>
<th>Wavenumbers $[\text{cm}^{-1}]$</th>
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<th>Wavenumbers $[\text{cm}^{-1}]$</th>
<th>Assigned Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>3650</td>
<td>H - bonded SiO-H $^a$</td>
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<td>Overtone of Si-O-Si st</td>
</tr>
<tr>
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<td>H - bonded SiO-H $^b$</td>
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<td>C-H$_2$ def $^e$</td>
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<td>N-H st $^c$</td>
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<td>C-H$_2$ def $^f$</td>
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<tr>
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</tr>
</tbody>
</table>

$^a$ One bridge $^b$ Two bridges $^c$ H-bonded and protonated amine species $^d$ Side group and trifluoroacetic acid $^e$ CH$_2$ bound to N $^f$ Middle CH$_2$-group $^g$ CH$_2$-group bound to Si
Bibliography


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Curriculum Vitae

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**Chapter 7:**
"Functionalization of Silica Surfaces with Mixtures of 3-Aminopropyl and Methyl Groups.”
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Chem. Mat., submitted for publication

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M. Luechinger, A. Kienhöfer, G. D. Pirngruber
Manuscript in preparation
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