A STUDY ON
TITANIUM-SILICALITE-1
AND
RELATED SYSTEMS
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RELATED SYSTEMS

proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus, prof. ir. K.F. Wakker
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een commissie, aangewezen door het College van Dekanen,
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Patricia Jane Kooyman

geboren te Amsterdam
doctorandus in de chemie
Dit proefschrift is goedgekeurd door de promotor, 
prof. dr. ir. H. van Bekkum
I want to live, I want to grow
I want to see, I want to know
I want to share what I can give
I want to be, I want to live

John Denver
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Cover design by J. van der Put.

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CHAPTER 1

A GENERAL INTRODUCTION ON TITANIUM, ITS OXIDES, ITS MINERALS AND ITS USE IN CATALYSIS

1.1. INTRODUCTION

Titanium is the 22\textsuperscript{nd} element in the Periodic Table of the elements. Its atomic weight is 47.90. Titanium is a transition- or d-metal of group 4, and its electron configuration is 2-8-10-2. To obtain noble-gas configuration, titanium has to become 4+, which it readily does. However, also 3+ and 2+ oxidation states are possible. Titanium is the ninth most abundant element in the earth's crust, where it is the fourth most abundant structural element.\textsuperscript{1} Titanium is found incorporated in many minerals, of which the most abundant is ilmenite, FeTiO\textsubscript{3}. Mineable deposits are also found of rutile (tetragonal TiO\textsubscript{2}) and perovskite (CaTiO\textsubscript{3}). Other frequently encountered titanium-containing minerals are anatase (another form of tetragonal TiO\textsubscript{2}), brookite (rhombic TiO\textsubscript{2}), sphene or titanite (CaTiSiO\textsubscript{5}) and geikielite (MgTiO\textsubscript{3}).

As a metal, that is in oxidation state +0, titanium has a very high strength-to-weight ratio, which gives the metal and its alloys many uses in air- and spacecraft technology. Like aluminium metal, titanium metal is covered with a thin, inert layer of its oxide, which makes the metal very resistant to all sorts of chemical treatment. This film is insoluble, easily repairable by small amounts of water, and non-porous in many chemical environments, but the corrosion rate is very high where this surface layer is broken. Titanium metal is often used in the construction of vessels or other components of chemical plants for processes that use corrosive or otherwise aggressive reagents.

The principal use of titanium, TiO\textsubscript{2} as a white pigment in paints, is due to the specific whiteness and chemical stability of TiO\textsubscript{2}. The market for TiO\textsubscript{2} pigment was 3.0 million tonnes per annum in 1992.
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Both titanium metal and TiO₂ are produced on a commercial scale from FeTiO₃- or TiO₂-containing ores. It is also possible to produce a titanium-containing slag (> 70% TiO₂) by removing the ferrous content from ilmenite-type ores.

Two main processes are used: the chlorination process for high-grade ores (> 60 % TiO₂) and the sulfate route for lower grade ores.

The sulfate route is used to convert ilmenite to TiO₂:

\[ \text{FeTiO}_3 + 5 \text{H}_2\text{O} + 2 \text{H}_2\text{SO}_4 \rightarrow \text{TiOSO}_4 + \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \]

The iron sulfate precipitates after concentration and cooling. The TiOSO₄ is obtained as an aqueous solution, which is heated to 90°C to give precipitated hydrated titanium oxide, which is calcined at 1000°C to TiO₂:

\[ \text{TiOSO}_4 + 2 \text{H}_2\text{O} \rightarrow \text{TiO(OH)}_2 + \text{H}_2\text{SO}_4 \]

\[ \text{TiO(OH)}_2 \rightarrow \text{TiO}_2 + \text{H}_2\text{O} \]

In the chlorination process TiO₂ is converted to TiCl₄ by reaction with solid carbon and chlorine gas, above 800°C and slightly above atmospheric pressure:

\[ \text{TiO}_2 + 2 \text{C} + 2 \text{Cl}_2 \rightarrow 2 \text{CO} + \text{TiCl}_4 \]

Alternatively, CO can be used as the reducing reagent.
The titanium tetrachloride is either oxidized to the dioxide or reduced to the metal:

\[ \text{TiCl}_4 + \text{O}_2 \rightarrow \text{TiO}_2 + 2 \text{Cl}_2 \]

\[ \text{TiCl}_4 \rightarrow \text{Ti} + 2 \text{Cl}_2 \]

The Cl₂ gas can be recycled.
Yields are better in the chlorination process, but raw materials are more expensive for the chlorination process than for the sulfate process.

1.2. Titanium dioxide

The three most abundant oxides of titanium are rutile (tetragonal), anatase (tetragonal) and brookite (rhombic). In all these forms of TiO₂, titanium is octahedrally coordinated by oxygen. Table 1.1 lists the Ti-O bond lengths for these oxides.
### General Introduction

**TABLE 1.1. Ti-O distances in the most abundant mineral forms of TiO₂.**

<table>
<thead>
<tr>
<th>form of TiO₂</th>
<th>coord number</th>
<th>Ti coord¹</th>
<th>shortest Ti-O (Å)</th>
<th>longest Ti-O (Å)</th>
<th>average Ti-O (Å)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>rutile</td>
<td>6</td>
<td>oct</td>
<td>1.947</td>
<td>1.982</td>
<td>1.959</td>
<td>2</td>
</tr>
<tr>
<td>anatase</td>
<td>6</td>
<td>oct</td>
<td>1.937</td>
<td>1.934</td>
<td>1.934</td>
<td>3</td>
</tr>
<tr>
<td>brookite</td>
<td>6</td>
<td>dist oct</td>
<td>1.863</td>
<td>2.052</td>
<td>1.960</td>
<td>2</td>
</tr>
</tbody>
</table>

¹) oct = octahedral; dist = distorted.

![Crystal habit of natural anatase](left) and rutile (right). 
Taken from ref. 4.

The minerals rutile, anatase and brookite are usually coloured red-brown to black. Although in all three structures each oxygen atom is bonded to three titanium atoms, these stuctures are different in that the octahedrons are connected to each other in different ways. In rutile, two edges of each octahedron are shared. The crystal habit of rutile is usually prismatic with bipyramidal short ends (see Fig. 1.1). Rutile’s specific density is 4.2 - 4.4, its hardness 6.0 - 6.5. In brookite, the octahedra share three edges. In anatase, the octahedra share four edges. The crystal habit is usually bipyramidal for anatase, as shown in Figure 1.1. The hardness of anatase is 5.5 - 6.0 with a specific density of 3.8 - 4.0. Anatase can transform irreversibly to rutile by heating above a certain threshold temperature. At
atmospheric pressure, this transition temperature can vary from 400 - 1200°C, depending on grain size, atmosphere and nature and amount of impurities. The specific density of brookite is 3.9 - 4.2 at a hardness of 5.5 - 6.0. The crystal habit is not as well-defined as with the two tetragonal forms of TiO$_2$, but very often platelets are found.

1.3. Titanium-containing minerals

There are numerous minerals that contain titanium (see eg appendix 1.1), but the structure of only part of them is known. In this section, we will take a look at the coordination of titanium in some selected minerals. Ti-O bond lengths and Ti-O coordination of some well-known titanium-containing minerals will be discussed, and we will focus on some of the natural titanium-containing silicates (especially those that, apart from Ti, Si and O, do not contain too many other elements).

TABLE 1.2. Ti-O distances in six-coordination: non-silicates.

<table>
<thead>
<tr>
<th>mineral</th>
<th>coord no</th>
<th>Ti-O coord$^1$</th>
<th>shortest Ti-O (Å)</th>
<th>longest Ti-O (Å)</th>
<th>average Ti-O (Å)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgTiO$_3$</td>
<td>6</td>
<td>dist oct</td>
<td>1.735</td>
<td>1.956</td>
<td>1.846</td>
<td>5</td>
</tr>
<tr>
<td>CaTiO$_3$</td>
<td>6</td>
<td>oct</td>
<td>1.952</td>
<td>1.963</td>
<td>1.956</td>
<td>6</td>
</tr>
<tr>
<td>perovskite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeTiO$_3$</td>
<td>6</td>
<td>dist oct</td>
<td>1.874</td>
<td>2.089</td>
<td>1.982</td>
<td>7</td>
</tr>
<tr>
<td>ilmenite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$ oct = octahedral; dist = distorted.

Six-coordinated titanium

Titanium is most likely to be found in six-coordination, where the oxygens surround the titanium as a (distorted) octahedron. For most minerals, the distances
found differ somewhat depending on the sample and the method used. We have tried to summarise some representative data in Tables 1.2 and 1.3.

**TABLE 1.3. Ti-O distances in six-coordination: silicates.**

<table>
<thead>
<tr>
<th>mineral</th>
<th>coord no</th>
<th>Ti-O coord</th>
<th>shortest Ti-O (Å)</th>
<th>longest Ti-O (Å)</th>
<th>average Ti-O (Å)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaTiSiO$_5$</td>
<td>6</td>
<td>oct</td>
<td>1.847</td>
<td>2.033</td>
<td>1.953</td>
<td>8</td>
</tr>
<tr>
<td>titanite / sphene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaTiSi$_3$O$_9$</td>
<td>6</td>
<td>oct</td>
<td>1.968</td>
<td>1.968</td>
<td>1.968</td>
<td>9</td>
</tr>
<tr>
<td>benitoite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb$_2$TiSi$_3$O$_9$</td>
<td>6</td>
<td>oct</td>
<td>1.973</td>
<td>1.973</td>
<td>1.973</td>
<td>10</td>
</tr>
<tr>
<td>Na$_2$Ti$_2$Si$_2$O$_9$</td>
<td>6</td>
<td>dist</td>
<td>1.820</td>
<td>2.181</td>
<td>1.988</td>
<td>11</td>
</tr>
<tr>
<td>ramsayite / lorenzenite</td>
<td></td>
<td>oct</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_2$TiSi$_3$O$_9$</td>
<td>6</td>
<td>oct</td>
<td>2.005</td>
<td>2.005</td>
<td>2.005</td>
<td>6</td>
</tr>
<tr>
<td>Na$_6$MnTiSi$<em>6$O$</em>{18}$</td>
<td>6</td>
<td>oct</td>
<td>2.007</td>
<td>2.007</td>
<td>2.007</td>
<td>12</td>
</tr>
<tr>
<td>kazakovite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_5$Ti$_2$(Si$_2$O$_7$)(PO$_4$)O$_2$</td>
<td>6</td>
<td>oct</td>
<td>1.825</td>
<td>2.159</td>
<td>1.981</td>
<td>13</td>
</tr>
<tr>
<td>lomonosovite</td>
<td>6</td>
<td>oct</td>
<td>1.889</td>
<td>2.203</td>
<td>2.033</td>
<td></td>
</tr>
<tr>
<td>Na$_2$TiSi$_2$O$_6$</td>
<td>6</td>
<td>oct</td>
<td>1.971</td>
<td>2.105</td>
<td>2.046</td>
<td>14</td>
</tr>
<tr>
<td>pyroxene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) oct = octahedral; dist = distorted.

**Five-coordinated titanium**

Titanium is also found in five-coordination. Table 1.4 lists some of the natural silicates in which titanium is found in five-coordination, and their Ti-O distances. The usual coordination for five-coordinated titanium is a regular square pyramid.
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TABLE 1.4. Ti-O distances in five-coordination.

<table>
<thead>
<tr>
<th>mineral</th>
<th>coord no</th>
<th>Ti-O coord</th>
<th>shortest Ti-O (Å)</th>
<th>longest Ti-O (Å)</th>
<th>average Ti-O (Å)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$_2$TiSi$_2$O$_8$ fresnoite</td>
<td>5</td>
<td>pyram</td>
<td>1.634</td>
<td>2.001</td>
<td>1.928</td>
<td>15</td>
</tr>
<tr>
<td>id</td>
<td>5</td>
<td>pyram</td>
<td>1.980</td>
<td>2.007</td>
<td>2.002</td>
<td>16</td>
</tr>
<tr>
<td>Na$_2$TiSiO$_5$</td>
<td>5</td>
<td>pyram</td>
<td>1.695</td>
<td>1.990</td>
<td>1.931</td>
<td>17</td>
</tr>
</tbody>
</table>

1) pyram = regular square pyramidal.

Four-coordinated titanium

As will be explained in chapter 2 of this thesis, titanium is sometimes assumed to be present in tetrahedral coordination in zeolites. As this fact is believed by some and disputed by others, it is useful to take a look at the occurrence of tetrahedral titanium in other materials. Table 1.5 lists all the tetrahedral configurations we have been able to find.

A calculation of a hypothetic Ti(OH)$_4$ tetrahedron using the Hartree-Fock direct SCF method and GAMESS-UK software,$^{18,19}$ kindly performed by Dr. A.J.M. de Man at our laboratory, gives a Ti-O distance of 1.800 Å. A similar Si(OH)$_4$ tetrahedron, orthosilicic acid, is frequently being studied by theoretical chemists.$^{20,21}$ A review by Sauer$^{20}$ lists about 15 values for the Si-O bond length in orthosilicic acid, all from different papers. However, the results obtained by different authors show only slight variety: all data range from 1.60 to 1.66 Å. A paper by Gibbs$^{21}$ claims the Si-O bond length in orthosilicic acid to be 1.65 Å. All these values are significantly lower than the Ti-O bond length of 1.80 Å, indicating that it might be difficult to incorporate titanium tetrahedrally into a silicate framework.
TABLE 1.5. Ti-O distances in four-coordination.

<table>
<thead>
<tr>
<th>Material</th>
<th>Coord no</th>
<th>Coord type</th>
<th>Shortest Ti-O (Å)</th>
<th>Longest Ti-O (Å)</th>
<th>Average Ti-O (Å)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba₂TiO₄</td>
<td>4</td>
<td>tetrah</td>
<td>1.629</td>
<td>1.819</td>
<td>1.710</td>
<td>22</td>
</tr>
<tr>
<td>Id</td>
<td>4</td>
<td>tetrah</td>
<td>1.788</td>
<td>1.817</td>
<td>1.802</td>
<td>23</td>
</tr>
<tr>
<td>Id</td>
<td>4</td>
<td>tetrah</td>
<td>1.766</td>
<td>1.836</td>
<td>1.808</td>
<td>24</td>
</tr>
<tr>
<td>Id</td>
<td>4</td>
<td>tetrah</td>
<td>1.799</td>
<td>1.836</td>
<td>1.819</td>
<td>23</td>
</tr>
<tr>
<td>Id</td>
<td>4</td>
<td>tetrah</td>
<td>1.797</td>
<td>1.831</td>
<td>1.820</td>
<td>23</td>
</tr>
<tr>
<td>Ni₂₄₂Ti₀.₇₄Si₀.₀₅O₄</td>
<td>4</td>
<td>tetrah</td>
<td>1.823</td>
<td>1.823</td>
<td>1.823</td>
<td>25</td>
</tr>
<tr>
<td>Defect spinel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca₃Fe₂Si₁.₅₈Ti₁.₄₂O₁₂</td>
<td>4</td>
<td>tetrah</td>
<td>1.744</td>
<td>1.744</td>
<td>1.744</td>
<td>26</td>
</tr>
<tr>
<td>Synthetic garnet</td>
<td>6</td>
<td>oct</td>
<td>1.988</td>
<td>1.988</td>
<td>1.988</td>
<td></td>
</tr>
</tbody>
</table>

1) tetrah = tetrahedral; oct = octahedral.

1.4 Titanium in catalysis

Apart from serving as a catalyst support (TiO₂) in heterogeneous catalysis, titanium complexes, halides and oxides can be the active phase in both homogeneous and heterogeneous catalysis. Perhaps the best known example is the use of TiCl₃ in the Ziegler-Natta polymerisation of small olefins.

Homogeneous catalysis

Like other transition metal complexes, liquid or soluble titanium complexes can be active and selective catalysts for several oxidation reactions. The best known example is the selective asymmetric epoxidation of allylic alcohols, using t-butyl hydroperoxide (TBHP) as the oxidising agent, together with a chiral bidentate ligand (eg RR or SS diethyl tartrate). In this so-called "Katsuki-Sharpless-reaction" (named after its discoverers, T. Katsuki and K.B. Sharpless), one enantiomer of the ep-
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oxides is formed selectively (e.g. up to 95%). Usually a requirement is that the TBHP / allylic alcohol ratio is around 0.6, and that a zeolite (NaA) is added as a drying agent. The reactions usually are very fast, so that they can be performed at temperatures of -20 to 0°C. The homogeneous catalyst is prepared in situ by adding 1 equivalent of tartrate to a tetra-alkoxy titanium compound, according to:

\[ \text{Ti(OR)}_4 + \text{tartrate} \rightarrow \text{Ti(tartrate)(OR)}_2 + 2 \text{ROH} \]

A detailed mechanism for the catalytic reaction has been advanced by Sharpless et al.\textsuperscript{27}

Tetra-alkoxy titanium compounds serve as catalysts in industrial esterifications.\textsuperscript{28} For example in the preparation of dialkyl phthalates, a Ti(RO)\textsubscript{4} compound is used. Although these catalysts are less active than the acidic catalysts conventionally used in these reactions, and somewhat higher reaction temperatures are required, their selectivity is better, resulting in for example decreased dialkyl ether formation.\textsuperscript{28}

**Heterogeneous catalysis: catalyst support material**

Titanium dioxide is a so-called "reducible oxide".\textsuperscript{29} This means that in a reducing environment, (part of) the TiO\textsubscript{2} will be reduced to TiO\textsubscript{x}, 1 < x < 2, which gives it special properties in some oxidation catalysts. In these catalysts, the titania (titanium dioxide) is often used as a catalyst support material. However, the specific surface area of titania is rather low (< 20 m\textsuperscript{2}/g), whereas a high surface area is a requirement for good catalyst support materials. This drawback can be overcome by coating a high-surface material, like silica, with titania. The resulting catalyst support material has the high surface area of the silica, and the reducible oxide properties of the titania.\textsuperscript{30} Also, methods are being developed to synthesise high surface area titania.\textsuperscript{31}

The application with the widest practical possibilities is the use of titania as support material for vanadia catalysts.\textsuperscript{32} For example, for the selective catalytic reduction of NO with NH\textsubscript{3}, VO\textsubscript{x}/TiO\textsubscript{2} and even more so VO\textsubscript{x} on TiO\textsubscript{2}-coated SiO\textsubscript{2} not only have good activity and selectivity, but these systems also are much more
resistant to poisoning by SO₂ than comparable VOₓ/Al₂O₃ systems. Titania-supported vanadium oxide catalysts are also used for the selective oxidation of various organic compounds with molecular oxygen, like the oxidation of o-xylene to phthalic anhydride, oxidative dehydrogenation of isopropanol to acetone, oxidation of methanol to formaldehyde and ammoxidation of aromatics.

Another application of titania as catalyst support material is for group 8 metals. These catalysts are prepared by impregnating the titania with a metal salt, which is subsequently reduced, usually with H₂, to the pure metal. When using a reducible oxide as support material, the reduction temperature is very important, as only after HTR (high temperature reduction) above ca. 450°C, the special properties of these oxides come into effect. During HTR, part of the titania support is reduced to TiOₓ species, which migrate to cover part of the metal particles. This phenomenon is known as the SMSI (strong metal-support interaction) effect. This SMSI effect is mainly beneficial to syngas reactions. Structure-insensitive reactions like (de)hydrogenation reactions are practically unaffected by the use of reducible oxides as catalyst support materials, whereas structure sensitive reactions like hydrogenolysis are inhibited by the SMSI effect.

Wismeijer et al. reported that Ru/TiO₂ is more active and selective in the hydrogenation of citronellal to citronellol than Ru/SiO₂. It is very likely that this effect is due to promoting TiOₓ species covering part of the Ru surface.

Heterogeneous catalysis: active phase

As far as we know, there are few reports on using pure TiO₂ as the active phase in ordinary heterogeneous catalysis. One report claims the selective direct hydroxylation of phenol to dihydroxybenzenes with hydrogen peroxide, using high-surface (100 - 300 m²/g) TiO₂ as the catalyst. The activities reported are high (up to 98% hydrogen peroxide conversion) with moderate yields of hydroxylated aromatic (up to 40%). The high-surface material is prepared by hydrolysing titanium compounds, followed by a low-temperature calcination.

The catalytic systems studied in this thesis are all heterogeneous catalysts, containing both silicon and titanium oxides. Titanium can be incorporated into crystalline silica or deposited on both amorphous and crystalline silica (SiO₂), as
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will be discussed in this thesis.

TiO$_x$ supported on amorphous silica is used in a commercial process for the epoxidation of olefins with organic hydroperoxides. The catalyst is prepared by reacting TiCl$_4$ (from n-heptane solution) with surface Si-OH groups, followed by hydrolysis and calcination. Thus, catalysts are prepared containing up to a monolayer of TiO$_x$. The epoxidation reaction is industrially performed to epoxidise propene (Shell Styrene-Monomer-Propylene-Oxide (SMPO) process) using ethyl-benzene hydroperoxide. However, this catalyst is also active using t-butyl hydroperoxide.

Another commercial process, the selective hydroxylation of phenol to dihydroxybenzenes with hydrogen peroxides, uses a special system as the catalyst: titanium-silicalite-1 or TS-1. Section 2.2.c of this thesis gives a review of the literature available concerning the catalytic properties of TS-1, which is a good catalyst for various selective oxidation reactions using aqueous hydrogen peroxide as the oxidising agent.

A very promising field using TiO$_2$ as the active phase is as a photocatalyst. TiO$_2$ is a semiconductor which can be activated by light, giving a separated pair of an electron ($e^-$) and a hole ($h^+$). These species can be used directly as the driving force for chemical reactions, or they can be transferred to other catalysts (which are deposited on the TiO$_2$) which can subsequently assist a chemical reaction. An already rapidly growing area of practical application is in the purification of water and air from (organic) contaminants. In this process, the contaminants are oxidised to CO$_2$ and H$_2$O. Another promising process on which a lot of research is being conducted at the moment is the direct utilisation of sunlight to produce environmentally-friendly fuel. In this process, water is decomposed to H$_2$ and O$_2$ on TiO$_2$.

Alternatively, the energy provided by the sunlight is used directly to reduce CO$_2$ in the presence of water, yielding various organic products, like formic acid, formaldehyde and methanol. Although yields are still low (about 1% of the incident sunlight energy is converted to products), the direct activation of sunlight is the example of sustainable energy, and it is bound to receive increased attention from scientists working in all kinds of fields, especially catalysis.
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Chapter 1

18) M. Dupuis, D. Sprangler and J. Wendolowski, NRCC Software Catalog, Vol. 1, Program No. QC01 (GAMESS).


*) References marked with * were not consulted directly, but through CRYSTIN, Crystal Structure Information System (Release 2.52), Hundt and Sievers, University of Bonn. The number in brackets is the reference number in CRYSTIN.
APPENDIX 1.A. NATURAL TITANIUM-CONTAINING SILICATES

An overview restricted to natural silicates containing titanium and not too many other elements. If there are two references, the structure of the mineral is known and can be found in the second reference. Alphabetically, from Mineral Reference Manual, E.H. Nickel and M.C. Nichols.

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<td>Ferrokaersute</td>
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### Appendix

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<td>(Na,Ca)(Na,Mn)\textsubscript{2} (Sr,Ba)\textsubscript{2}Ti\textsubscript{3} (Si\textsubscript{5}O\textsubscript{7})\textsubscript{2}(O,OH,F)\textsubscript{4}</td>
<td>Am.Min. 27 (1942) 397 Sov.Phys.Dokl. 28 (1983) 206</td>
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Natural Ti-silicates

Penk-vilksite $\text{Na}_4\text{Ti}_2\text{Si}_6\text{O}_{22}.5\text{H}_2\text{O}$ Am.Min. 60 (1975) 340

Perrierite $(\text{Ca,Fe,Fe})_4$ Am.Min. 63 (1978) 499
$(\text{Mg,Fe})_2(\text{Ti,Fe})_3$ Am.Min. 59 (1974) 1277
$O_8(\text{Si}_2\text{O}_7)_2$ ---

Rhönite $\text{Ca}_2(\text{Fe,Mg,Ti})_6$ Am.Min. 70 (1985) 1211
$(\text{Si,Al})_6O_{20}$ ---

Rinkite $(\text{Na,Fe})_3(\text{Ca,Fe})_4$ Am.Min. 43 (1958) 795
$\text{Ti}_4(\text{Si}_2\text{O}_7)_2(\text{O,F})_4$ Acta Cryst. B27 (1971) 1277

Rosenbuschite $(\text{Ca,Fe})_4\text{TiZr}$ Dana's System 6th (1892) 374
$(\text{Si}_2\text{O}_7)_2(\text{F,OH})_4$ Struc.Repts. 28 (1963) 254

Schorlomite $\text{Ca}_3(\text{Ti,Fe})_2$ Dana's Textb. 4th (1932) 596
$[((\text{Si,Fe})_4\text{O}_9)_3$ Phys.Chem.Min. 13 (1986) 198

Seidozerite $(\text{Na,Fe})_4\text{MnTiZr}$ Am.Min. 44 (1959) 472
$(\text{Si}_2\text{O}_7)_2(\text{O,OH})_2$ Struc.Repts. 23 (1959) 472

Shcherbakovite $\text{NaK}(\text{Ba,K})\text{Ti}_2$ JCPDS 8-1101
$(\text{Si}_2\text{O}_7)_2$ ---

Sogdianite $\text{KNa}(\text{Li,Al})_3$ Am.Min. 54 911969) 1221
$(\text{Fe,ti},\text{Zr})\text{Si}_{12}\text{O}_{36}$ Sov.Phys.Cryst. 19 (1974) 460

Strontiochevikinite $(\text{Sr,Fe})_4\text{La}_4\text{Fe}$ Am.Min. 69 (1984) 1192
$(\text{Si}_2\text{O}_7)_2(\text{OH})_2$ ---

Tadzhibite $\text{Ca}_3(\text{Fe,Al})_2$ Am.Min. 56 (1971) 1838
$(\text{Ti,Fe})_4\text{B}_4$ Min.Abstr. 83M/4211
$\text{Si}_4\text{O}_{22}$ ---

Taramellite $\text{Ba}_4(\text{Fe,Ti})_4\text{B}_2$ Am.Min. 70 (1985) 217
$(\text{Si}_8\text{O}_{27})_2\text{Cl}_x$ ---

Tienshanite $\text{KNa}_3\text{Ba}_6\text{Ca}_2\text{Mn}_6$ Am.Min. 53 (1968) 1426
$\text{Ti}_8\text{B}_12\text{Si}_{13}\text{O}_{12}\text{OH}_2$ Min.Abstr. 79-2103

Tinkasite $\text{K}_2\text{Na}(\text{Ca,Mn})_2\text{Ti}_4\text{Si}_{10}\text{OH}_2$ Am.Min. 50 (1965) 2098
$\text{Si}_{10}\text{OH}_2$ Acta Cryst. B36 (1980) 259

Tisinalite $\text{H}_2\text{Na}_2(\text{Mn,Fe})_2\text{Ti}_4\text{Si}_{16}(\text{O,OH})_18$ Am.Min. 66 (1981) 219
$\text{H}_2\text{O}$ ---

Tityanclino-humite $(\text{Mg,Fe})_9\text{Si}_4\text{O}_{24}(\text{O,OH})_2$ Zapiski Vsesoyuznogo Mineralogicheskogo
$\text{O}_{18}$ Obschestva 117 (1988) 675

Titanite $\text{CaTiSiO}_5$ Am.Min. 58 (1973) 43
Am.Min. 61 (1976) 878
Am.Min. 61 (1976) 238

Titanantarmellite $\text{Ba}_4(\text{Ti,Fe,Mg})_4\text{B}_2$ Am.Min. 69 (1984) 358
$\text{Si}_8\text{O}_{27}\text{SO}_3\text{Cl}_x$ ---

Tranquillityite $\text{Fe}_4\text{Ti}_3(\text{Zr,Y})_2$ Am.Min. 58 (1973) 140
$\text{Si}_4\text{O}_{24}$ ---

Traskite $\text{Ba}_4\text{Fe}_2\text{Si}_4\text{O}_{54}\text{Cl}_{13}.7\text{H}_2\text{O}$ Am.Min. 50 (1965) 1500
Min.Abstr. 78-202
### Appendix

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<td>$Na_2TiNb_2(Si_2O_7)_2$</td>
<td>Sov.Phys.Cryst. 29 (1984) 403</td>
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<td>$O_{26}.(H_2O,K)_2$</td>
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### Important non-Si-containing Ti minerals:

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<td>$Fe_2Ti_3O_9$</td>
<td>Nature 211 (1966) 179</td>
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<td>Dana’s System 7th (1944) vol.1 p.554</td>
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CHAPTER 2

SYNTHETIC TITANIUM-CONTAINING ZEOLITES

2.1. INTRODUCTION

In this chapter the state-of-the-art concerning titanium-containing zeolites will be described. The literature available up to May 1993 will be critically reviewed, and the backgrounds for the scope of this thesis will be discussed. Additionally, literature data on the methods used throughout this thesis to characterise the materials are discussed. Apart from reasonably common physical characterisation methods like X-ray diffraction and Infra-red spectroscopy, some less common characterisation methods and the standard catalytic test reactions employed will be discussed.

2.1.a. ZEOLITES AND MOLECULAR SIEVES

The term "zeolite" was first introduced by Cronstedt,\(^1\) who found that a certain mineral, stilbite, started "to boil" when heated. Furthermore, the "boiling stone", "zeolithos" in Greek, could be hydrated again and subsequently would boil again when heated, demonstrating one of the many useful properties of zeolites: reversible selective adsorption.

The zeolites form a subclass of the family of tectosilicates. Strictly speaking, zeolites are crystalline alumino-silicates, of which the three-dimensional crystal framework consists of corner-sharing \(\text{Si}_4\) and \(\text{Al}_4\) tetrahedra, as depicted in Figure 2.1. Si and Al are the so-called "T-atoms". The Si/Al ratio is always at least one. Structure-related materials, like alumino-phosphates, ferro-, boro-, gallo-, germano- and titanio-silicates and all-silica materials, should strictly be referred to as "molecular sieves". However, especially the metallo-silicates are often also referred to as zeolites. Frequently both terms are used interchangeably.

The term "molecular sieve" was introduced by McBain\(^2\) and stems from the ability of the materials to distinguish between (organic) molecules differing in size. The three-dimensional structure of the materials contains micropores and channels
of specific dimensions. Molecules smaller than those dimensions can enter the structure and be adsorbed, whereas larger molecules cannot enter the structure and thus pass through a bed of the material essentially unretarded. In this respect, also some amorphous carbon materials should be referred to as molecular sieves, because they can selectively adsorb (organic) molecules up to a certain size.

Figure 2.1. Tetrahedral building blocks forming zeolitic frameworks.

Zeolitic frameworks are not really rigid, and especially at higher temperatures the shape and dimensions of the pore mouth openings and of the channels are somewhat flexible. Thus, always a certain margin has to be taken into account when considering which molecules can enter a specific zeolitic structure. In general, the kinetic diameter of the molecule under consideration has to be smaller than the pore mouth opening for the molecule to be able to enter the zeolitic structure.

The pore diameters of zeolitic and molecular sieve materials are generally 3 - 14 Å, although recently materials with pores up to 100 Å have been synthesised (see eg ref 3).

If we take a closer look at alumino-silicates, we see that the zeolite framework bears a negative charge, the charge surplus being -1 per aluminium atom, due to the formal charge on aluminium being +3, on silicon +4 and on oxygen -2. This surplus charge has to be compensated for by cations being present in the zeolite channels. These cations, counter-ions, are exchangeable, making zeolites materials
that can easily be modified. Zeolites with relatively low Si/Al ratios, like A, X, Y, and MOR are commercially synthesised with Na\(^+\) as the counter-ion. Other common counter-ions are K\(^+\), NH\(_4\)\(^+\) and H\(^+\), but also divalent (eg Ca\(^{2+}\)) and sometimes trivalent ions (eg lanthanides) can be used.

If H\(^+\) is the counter-ion, the material is often referred to as a solid acid, and can act as a Brønstedt catalyst for many organic reactions. With Na\(^+\) it can be used as an ion-exchanger, for example to remove Mg\(^{2+}\) and Ca\(^{2+}\) from water, like zeolite Na-A in present-day European detergent formulations. The counter-ion also affects the pore diameter, and can thus be used to modify adsorption properties.

If Fe\(^{3+}\), B\(^{3+}\) or Ga\(^{3+}\) are present as T-atoms instead of Al\(^{3+}\), different catalytic properties are obtained, mostly due to the H\(^+\) ions having a different intrinsic acidity. However, the acidity of the acid sites can also be regulated somewhat by changing the amount of sites per unit cell, which is related to the amount of trivalent T-atoms per unit cell. The more sites per unit cell, the weaker the acidity per site.

If Ti\(^{4+}\) or other tetravalent ions are present as T-atoms, the catalytic properties of the material are not due to the counter-ions; there are no counter-ions because there is no surplus charge. Thus, the catalytic properties stem directly from the incorporated tetravalent T-atom. All-silica materials are generally rather inert with respect to catalysis. Further details about zeolites and molecular sieves are available in a number of good textbooks.\(^4,5\)

2.1.b. ZEOLITE SYNTHESIS

Zeolites are usually synthesised by heating a so-called synthesis gel to 100 - 180°C in an autoclave, a solid stainless steel reactor that can be closed air-tight and that can withstand the pressure build-up that results from heating the aqueous gel. Often a Teflon insert is used, to prevent the steel of the autoclave from being corroded by the often strongly basic reaction mixture. The gel generally consists of water, a silicon source (eg fumed silica or a silica sol like Ludox), an aluminium (or other metal) source (eg a water soluble metal salt or a hydrolysable organo-metallic compound), and a source of mineralising agent. For high-silica zeolites and
Chapter 2

ALPO's, a so-called templating agent or template is also added. The template serves as a structure-directing agent around which the zeolite framework crystallises. Frequently quaternary ammonium ions are used as templates, like tetrapropylammonium (TPA⁺) which is an excellent template for the MFI structure. The synthesis gel very often has a high pH (11 - 14), which can be accomplished for example by adding the template as an aqueous solution of its hydroxide, and/or by adding some other source of OH⁻ ions, like NaOH, KOH or NH₄OH. In the high pH range, the OH⁻ ions serve as the so-called mobilising agent, that is they help to solubilise the building blocks so that these can form the zeolitic structure.

F⁻ can be used as the mobilising agent for zeolite synthesis⁶,⁷ instead of OH⁻. Thus, by adding for example NH₄F.HF or diluted HF to a synthesis mixture instead of an OH⁻ source, it is possible to prepare a synthesis gel with a pH of around 7. This can be very beneficial if (one of) the T-atoms easily form(s) insoluble hydroxides, as is the case with Ti.

2.1.c. THE MFI STRUCTURE

A material with the MFI (Mobil five) structure was first described in a Mobil patent.⁸ This patent claimed the synthesis of a crystalline microporous aluminosilicate with Si/Al ratios higher than 10, denoted as ZSM-5 (short for Zeolite-Socony-Mobil-5). Later, an all silica analogue, silicalite-1⁹ was reported. Nowadays, many structural analogues of MFI are known, containing various T-atoms next to Si.¹⁰

MFI belongs to the "pentasil" family of zeolites. The main secondary building unit (built up from tetrahedra) is the pentasil unit (see Fig. 2.2.a). Pentasil units can be combined to form chains (see Fig. 2.2.b), and these chains are combined to form the MFI structure (Fig. 2.3). In the resulting structure, two intersecting channel systems are present, one set of straight channels and one of sinusoidal channels (see Fig. 2.4). Both channel systems have pore mouth openings consisting of 10 T-atoms, measuring 5.6 * 5.3 Å for the straight channels, and 5.1 * 5.5 Å for the sinusoidal channels. The channel intersections form almost spherical cavities with a diameter of about 7.8 Å. A unit cell of the MFI structure contains 96 T-atoms, 192
O-atoms and 4 channel intersections.

Figure 2.2. The pentasil unit (a) and the chains formed from pentasil units (b).

Figure 2.3. The MFI structure.  Figure 2.4. The channel system of the MFI structure.
Chapter 2

Zeolite ZSM-5 in its H-form has developed towards an important industrial catalyst in, amongst others, ethylbenzene production. Compared to conventional ethylbenzene production processes (using eg AlCl₃ or BF₃-on-alumina), important waste reductions are achieved when using H-ZSM-5.

2.2. TITANIUM-SILICALITE-1

Since the discovery by Taramasso et al.¹¹ at ENIchem, Italy, that titanium can be incorporated into the MFI structure in such a way as to obtain a material that can catalyse selective oxidation reactions using aqueous hydrogen peroxide as the oxidising agent, many research groups have published on these kind of systems. The discovery has attracted such extensive attention because selectively using the relatively cheap (35% technical solution: US $ 0.245 per lb as of April 1993) aqueous hydrogen peroxide as the oxidising agent means that no environmentally undesirable waste products are formed, the residue from the hydrogen peroxide being water. Furthermore, using a zeolitic system opens numerous opportunities with respect to the shape-selectivity and the regenerability of the catalyst.

2.2.a. THE CHARACTERISATION OF TS-1

Infra Red Spectroscopy

Undoubtedly, the most striking difference reported between silicalite-1 and titanium-silicalite-1 is the additional absorption band in the IR spectrum of TS-1 at around 960 cm⁻¹ (see Fig. 2.5). In the early papers by research scientists at ENIchem¹¹,¹² this band was reported to be at 950 or 970 cm⁻¹. However, in most recent papers¹³,¹⁴,¹⁵ it is reported to be at 960 cm⁻¹, and this is now the position at which it is generally accepted to be located.¹⁶

Although there is still a lot of debate as to the exact assignment of this IR absorption band, it is generally accepted to be indicative of titanium associated with the zeolitic structure. The 960 cm⁻¹ IR absorption band has been assigned to an Si-O-Ti vibration arising from Ti as a true T-atom (see Scheme 2.1.), as well as to a Ti=O (titanyl group) vibration of a sort of "hydrolysed" form of titanium in the zeolite
Figure 2.5. The IR spectra of a) silicalite-1; b) titanium-silicalite-1.

framework (see Scheme 2.2).\(^\text{15}\)

However, it is likely that the 960 cm\(^{-1}\) IR band arises from the Si-OH groups accompanying a titanyl group. The assignment of the 960 cm\(^{-1}\) band to an Si-OH vibration has recently been confirmed by Corma et al.\(^\text{17}\) for Ti-BEA (see also section 2.3.b.), and it is very likely that the same assignment is valid for TS-1.

Scheme 2.1. Ti as a true T-atom in TS-1.

Scheme 2.2. Ti as a "hydrolysed" T-atom in TS-1.

It is possible to calculate the expected IR frequency of an Si-OH or a Ti-OH vibration. However, the accuracy of these kind of calculations still needs to be improved, and that is considered to be outside the scope of this thesis.
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The IR equipment used for recording the spectra reported in this thesis is a Bruker IFS 66 FT-IR spectrometer. For samples pressed into KBr wafers, the spectra are recorded from 4000 to 400 cm\(^{-1}\) in the transmission mode, 128 scans per measurement. For selected crystals placed on top of a thin flake of KCl, spectra are calculated from 500 or 1000 scans per measurement via a microscope, either in transmission or absorption mode, from 4000 to 600 cm\(^{-1}\). For both methods, spectral resolution is better than 8 cm\(^{-1}\).

X-Ray Diffraction

![X-ray diffractograms](image)

Figure 2.6. The X-ray diffractograms of Silicalite-1 (a) and Titanium-Silicalite-1 (b).
Synthetic Ti-zeolites

The X-ray diffractograms of silicalite-1 and TS-1 are very similar (see Fig. 2.6). The main difference lies in the fact that some reflections, which are double reflections for silicalite-1, are single reflections for TS-1. This is interpreted as a change in symmetry at room temperature from monoclinic (pseudo-orthorhombic) for silicalite-1 to orthorhombic for TS-1.

The structure of MFI-type zeolites is, at room temperature, either monoclinic or orthorhombic, depending on the type and amount of non-Si T-atoms, and on the presence of adsorbates. For adsorbate-free materials, the transition temperature monoclinic to orthorhombic lies at 80°C for pure silicalite-1 (only Si as T-atoms). For Al$^{3+}$ containing MFI with a Si/Al ratio of 400, the transition temperature is lowered to 22°C, and with Si/Al < 220 it is below 0°C. B$^{3+}$ containing MFI with a Si/B ratio of 25 is orthorhombic at room temperature, indicating that the monoclinic-orthorhombic transition temperature is below 20°C. However, the incorporation of Ge$^{4+}$ in the MFI structure leads to a rise in transition temperature. This temperature increases linearly with increasing incorporation of Ge$^{4+}$, reaching 238°C for a sample with Si/Ge = 2. Considering these results, one would expect that if Ti$^{3+}$ is incorporated into the MFI framework, also the monoclinic - orthorhombic transition temperature would increase above the value of 80°C found for all-silica MFI. However, for TS-1 the transition temperature is lower, as already at room temperature the structure is orthorhombic. This is a strong indication that titanium is not incorporated into the structure as a true +4 T-atom, but gives rise to some kind of distortion of the MFI framework.

Another difference is that the interplanar distances are slightly greater for TS-1 than for silicalite-1, due to the Ti-O bond length (1.8 Å, see Chapter 1 of this thesis) being somewhat greater than the Si-O bond length (1.578 Å). An increase in unit cell volume can be calculated from the increase in interplanar distances, and the increasing cell volume with increasing titanium content is sometimes used as a proof of the incorporation of titanium as T-atoms.

X-ray diffractograms reported in this thesis were recorded using a Philips PW 1840 powder diffractometer with Cu-Kα radiation.
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Laser Raman Spectroscopy

To our knowledge, only one substantial report concerning Laser Raman Spectroscopy (Raman in short) study on TS-1 is available. Figure 2.7 shows the Raman spectra found for silicalite-1 and for two samples of TS-1.

![Raman Spectra Chart]

Figure 2.7. The Laser Raman spectra of a) silicalite-1; b) and c) TS-1. Data from ref 21.

For TS-1 (spectrum b) an additional band is observed with respect to silicalite-1 (spectrum a) at around 970 cm\(^{-1}\). This band is weak and rather broad, and it is assigned to homogeneously distributed TiO\(_x\) species. However, when a TS-1 is synthesised which contains more titanium (spectrum c), extra bands due to TiO\(_2\) (anatase) appear in the spectrum, at around 640 and 515 cm\(^{-1}\). This technique is rather sensitive: even small amounts of TiO\(_2\) can be detected, making it a useful method to study TS-1 and related materials.

Raman data presented in this thesis were kindly collected by Dr. B. Sulikowski at the Institute of Catalysis and Surface Science, Polish Academy of Sciences, Krakow, Poland. The spectra are recorded in the region 1200 - 200 cm\(^{-1}\) on a Nicolet 800 spectrometer using a power of 0.1 - 1 W. The laser used is a Neody-
nium laser: Nd : YAG, CVI Laser Corporation, model C-95, with radiation at 1.046 μm. Signals are detected using a Germanium detector, and spectra are calculated by Fourier Transformation of 500 - 2000 scans. All spectra are corrected for white light and for background due to Rayleigh scattering. Spectral resolution is better than 8 cm⁻¹.

**UV-Vis Spectroscopy**

Using UV-Vis - DRS (Diffuse Reflectance Spectroscopy), bulk TiO₂ (anatase) can be detected. The generally accepted considerations²² are that isolated framework Ti(IV) in tetrahedral coordination gives rise to a charge-transfer band at 48,000 cm⁻¹; isolated Ti in octahedral coordination gives a signal at 42,000 cm⁻¹; and bulk Ti (IV) in octahedral coordination gives a strong band of which the absorption edge is at 30,500 cm⁻¹. Thus, when bulk TiO₂ is present, the signals due to the two isolated Ti(IV) species are lost in the intense anatase signal. The UV-Vis spectra of anatase, TS-1 (with tetrahedrally isolated Ti(IV)) and silicalite-1 are depicted in Figure 2.8.

![UV-Vis Spectra](image)

**Figure 2.8.** UV-Vis spectra of a) silicalite-1; b) TS-1; c) anatase. Data from ref. 16. KMF = Kubelka-Munk Function.
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The UV-Vis spectra presented in this thesis were kindly recorded by Mr. J. Klaas, Universität Bremen, Germany, on a Varian Cary 4 with a Praying Mantis diffuse reflectance accessory from Starna, using the two canal mode. The spectral band width is 4 nm, the data point distance 1 nm. The size of the light spot is 1 - 2 nm, scan speed 120 nm/min and integration time 0.5 s. BaSO₄ was used as the standard reference material, and if necessary the samples were diluted with BaSO₄ to obtain F(R) < 1.5 in the Kubelka-Munk function.

2.2.b. THE SYNTHESIS OF TS-1

Direct synthesis

The main problem encountered in the direct synthesis of TS-1 is the premature precipitation of TiO₂, which is such a chemically inert compound that the titanium contained in it will not be incorporated into the zeolite framework during zeolite synthesis.

OH⁻

In the early patents and publications of the group of Taramasso, the TS-1 synthesis gel is obtained by controlled hydrolysis of a mixture of TEOS (tetraethyl orthosilicate, Si(OC₂H₅)₄) and the titanium analogue of that compound, TEOT (Ti(OC₂H₅)₄).¹¹ The hydrolysing liquid is a solution of the template tetrapropylammonium hydroxyide (TPAOH) in water. In this way it is hoped that the homogeneous distribution of the Ti-compound in the Si-compound will stabilise the titanium and thus prevent TiO₂ precipitation. According to the first publications, the crystallisation takes about 10 days at 175°C. However, recently Van der Pol and Van Hooff have published a more detailed investigation into various factors affecting the synthesis of TS-1, and they concluded that a synthesis time of 2 days is sufficient to obtain the maximum yield of crystalline material.²³ Earlier, Notari of ENIchem²⁴ reported that a synthesis time of 3 hr produces TS-1 with the preferred crystal size of 0.2 - 0.3 μm, however in that case "repeated washings are necessary to remove non-framework TiO₂", indicating that the maximum level of crystallisation has not yet been reached. Research workers from the group of Ratnasamy (Pune, India)
argued that this synthesis method can be improved by using titanium compounds which hydrolyse at about the same speed as the Si(OC₂H₅)₄, like Ti(O-n-C₃H₇)₄ or Ti(O-n-C₄H₉)₄.²⁵,²⁶ They also report that it is beneficial to dissolve both the silicon and the titanium compounds in isopropyl alcohol prior to mixing them.

Another method of providing a homogeneous mixture of the SiOₓ and the Ti building blocks is by hydrolysing Ti(OC₂H₅)₄ to a white gelatinous precipitate (presumably TiO₂₋ₓ(OH)ₓ₂), and dissolving this precipitate to form an orange-coloured peroxytitane solution with the aid of hydrogen peroxide before adding the template solution and a silica sol (eg Ludox) as the silicon source.¹¹ Huybrechts et al.²⁷ compare the physicochemical and catalytic properties of samples of TS-1 obtained through these two synthesis procedures. They find that in the method using hydrolysis of a mixture of TEOS and TEOH, the Si/Ti ratio in the TS-1 is always equal to that in the synthesis mixture. At higher titanium contents (Si/Ti < 65), part of the titanium is present in the samples as TiO₂. However, when the synthesis method using peroxytitane is employed, the titanium content of the sample does not exceed Si/Ti = 65, even if the synthesis mixture has Si/Ti = 30.

In all ENIchem papers it is stressed that the synthesis mixture should be free from alkali metal ions, as TS-1 resulting from alkali-containing synthesis gels performs poorly in catalytic oxidations with H₂O₂. El Hage - Al Asswad,²⁸ however, reports that samples of TS-1, synthesised from sodium-containing gels, do show good catalytic properties, provided that the sodium present in the samples is removed by multiple exchange with hydrochloric acid. El Hage-Al Asswad²⁸ also reports that TS-1 synthesised using NaOH + TPABr only has a shoulder at 970 cm⁻¹ in the IR spectrum, whereas TS-1 synthesised using TPAOH has a strong absorption band at 970 cm⁻¹. Later, similar results were reported by Bellussi et al.²⁹

It is not always necessary to obtain a homogeneous fluid synthesis gel. In one report, Padovan et al.³⁰ investigate the synthesis of TS-1 via impregnation to incipient wetness of amorphous silica with a solution of a Ti-compound and TPAOH obtained by dissolving Ti(O₁C₃H₇)₄ in isopropyl alcohol, followed by addition of aqueous TPAOH and subsequent heating at 80°C to remove the alcohol. As the synthesis time at 175°C is increased from 1 to 5 to 10 hr, the crystallinity of the samples increases from 10 to 60 to 95%. In the product the Si/Ti ratio is higher
than in the starting synthesis mixture, indicating that titanium is not easily incorporated into the zeolite framework. However, after a synthesis time of 15 or 20 hr, the crystallinity of the samples does not increase any further, whereas the titanium content does increase. Simultaneously, a charge transfer band appears in the UV-Vis spectrum in the 35,000 - 37,000 cm\(^{-1}\) region. This band is positioned in between the band at 48,000 cm\(^{-1}\) that is found for pure TS-1 and the one at 30,500 cm\(^{-1}\) for octahedral titanium in anatase. This leads the authors to the conclusion that subsequent to the formation of the maximum amount of TS-1 (when all the silica present has been transformed to TS-1), titanium is deposited as extra-framework TiO\(_2\). In another report\(^{31}\), Padovan et al. describe the synthesis of TS-1 via impregnation to incipient wetness of an amorphous mixture of SiO\(_2\) and TiO\(_2\) with an aqueous solution of TPAOH. However, the materials obtained are only characterised by their X-ray diffractogram, IR spectrum and catalytic activity for the liquid phase ammoximation of ketones.

\[ F^- \]

To our knowledge, the first reports in the open literature to mention Ti-containing zeolites synthesised using F\(^-\) as the mineralising agent were published almost simultaneously by Guth et al.\(^{32}\) and by Shilun et al.\(^{33}\) in 1989. Subsequently it wasn’t until 1992 that the next non-patent publication on this subject appeared, by Sulikowski and Klinowski.\(^{34}\) In the mean time, Guth et al. applied for numerous patents.\(^{35,36}\) For this kind of TS-1 synthesis the silica source is usually fumed silica. The titanium source can be TiO\(_2\) (anatase or rutile) dissolved in concentrated (40 - 50%) HF,\(^{34,35}\) Ti(OC\(_4\)H\(_9\))\(_4\),\(^{35}\) H\(_2\)TiF\(_6\)\(^{36}\) or TiF\(_3\) (see also chapter 4 of this thesis). In some instances\(^{34,35}\) small particles are formed on the external surface of the zeolite crystals. It is not unlikely that most of the titanium present in these samples is concentrated in the particles on the external surface, indicating that this synthesis procedure for TS-1 is not as straightforward as is generally assumed. Additional effort is required to elucidate the factors determining the formation of these particles (see also chapter 4 of this thesis).
Secondary synthesis

In secondary synthesis of titanium-containing zeolites, first a Ti-free zeolite is synthesised, which is treated with a titanium compound later on. Thus, the titanium is incorporated into an already existing zeolite framework. Using this approach, other T-atoms (e.g. Al) have to be removed prior to or simultaneous with the Ti-incorporation.

The first workers to report on the secondary synthesis of a Ti-containing ZSM-5 (we cannot properly call it TS-1 because the material also contains Al) were Skeels and Flanigen. Amongst other zeolites, they treated NH$_4^+$ exchanged ZSM-5 with a slurry of (NH$_4$)$_2$TiF$_6$ in water at 100°C. Based on XRD and sorption data, they conclude that the structure of the zeolite is entirely retained. The materials show some dealumination, and titanium is indeed found in the samples after the (NH$_4$)$_2^-$ TiF$_6$ treatment, although for the titanium-treated ZSM-5 samples no 960 cm$^{-1}$ IR band is observed.

A few years later, Kraushaar and van Hooff report on the synthesis of TS-1 through gas-phase TiCl$_4$ treatment of dealuminated ZSM-5 at 450°C. According to the authors, the resultant material is true TS-1, because all the aluminium present in the ZSM-5 had been removed by dealumination with aqueous HCl prior to TiCl$_4$ treatment, the Si/Al ratio increasing from 50 to 2000.

Using gaseous TiCl$_4$ at various temperatures, Ferrini and Kouwenhoven treated several types of Al-containing zeolites, including ZSM-5. Their data obtained on ZSM-5 are summarised in Table 2.1.

The authors comment that, as the Si/Al ratio does not decrease upon TiCl$_4$ treatment, either substituted Al remains in the structure as extra-framework Al or the reaction with TiCl$_4$ is not a substitution of Al in T-sites but a reaction with -OH groups. They take the change in unit cell volume as a proof of the incorporation of Ti in T-sites. The small decrease in measured BET surface area ($N_2$ sorption data) is attributed to a loss in crystallinity. However, this is not supported by the XRD data, which show that all samples are fully crystalline. More likely, the decrease in $N_2$ sorption capacity is due to pore blocking, probably by TiO$_x$ species reacting with -OH groups near the pore entrances, as TiCl$_4$ has been shown to be too large to enter the MFI structure at temperatures up to 350°C.
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TABLE 2.1. TiCl₄ treated ZSM-5 samples from ref 39.

<table>
<thead>
<tr>
<th>sample</th>
<th>T TiCl₄-treatment °C</th>
<th>BET surface area m²/g</th>
<th>Si/Ti ratio</th>
<th>Si/Al ratio</th>
<th>volume of unit cell Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5 start.mat.</td>
<td>-</td>
<td>390</td>
<td>2800</td>
<td>25</td>
<td>5367</td>
</tr>
<tr>
<td>A</td>
<td>200</td>
<td>360</td>
<td>36</td>
<td>25</td>
<td>5415</td>
</tr>
<tr>
<td>B</td>
<td>400</td>
<td>360</td>
<td>42</td>
<td>25</td>
<td>nd</td>
</tr>
<tr>
<td>C</td>
<td>500</td>
<td>370</td>
<td>58</td>
<td>25</td>
<td>nd</td>
</tr>
</tbody>
</table>

Carati et al.⁴¹ did not only treat (non-dealuminated) ZSM-5 with gaseous TiCl₄, but also silicalite-1 and boron-containing silicalite-1. At 400°C they found that the aluminium content of the ZSM-5 does not decrease upon TiCl₄ treatment, whereas the boron content of the B-silicalite-1 does decrease. However, as more titanium is present than boron has been removed in the [B]-silicalite-1 samples after TiCl₄ treatment, and as two peaks are found in the XPS spectra of these samples (one for a TS-1-like titanium species and one for a TiO₂-like species), the authors conclude that only part of the titanium is incorporated as T-atoms; the rest is deposited as extra-framework TiO₂. From their results they speculate that TiCl₄ cannot diffuse freely into the zeolitic channels, which is in agreement with the work of de Ruiter et al.,⁴⁰ who conclude that TiCl₄ is too bulky to diffuse into zeolites with the MFI structure at 350°C.

TS-1 as it is synthesised cannot be used as a catalyst, because its pores are blocked by the occluded template. The template can be removed by calcination in air, usually overnight at at least 450°C. It is important to raise the temperature slowly, to prevent the formation of hot spots due to the sudden decomposition / combustion of the template, which might damage the zeolite framework.
2.2.c. CATALYTIC APPLICATIONS OF TS-1

TS-1 has received extensive attention as a catalyst because of its outstanding ability to catalyse various organic oxidations with aqueous hydrogen peroxide.

The hydroxylation of phenol

Using TS-1 as the catalyst and aqueous hydrogen peroxide as the oxidising agent, phenol is hydroxylated selectively to dihydroxybenzenes. Only the ortho- and para-isomers are formed, and no tri- or higher hydroxybenzenes are formed. However, the dihydroxybenzenes formed are further oxidised in a slow consecutive step to the corresponding quinones (see scheme 2.3), and the products can oligomerise consecutively to the so-called "tarry by-products". The overall reaction equation is depicted in scheme 2.3.

![Diagram of hydroxylation of phenol](image)

Scheme 2.3. The hydroxylation of phenol.

Classically, dihydroxybenzenes are produced either via the aniline process (scheme 2.4) or via the p-diisopropylbenzene process (scheme 2.5). Both processes are multi-step and produce a lot of by-products, inorganic salts in the case of the aniline process, and organic by-products in the case of the p-diisopropylbenzene process. In the latter case, the iso-propylbenzene side-products can be recycled, whereas the acetone formed in the final reaction step can be sold, be it at a low price.
Scheme 2.4. The aniline process for producing dihydroxybenzenes.

Scheme 2.5. The p-diisopropylbenzene process for the production of dihydroxybenzenes.
The text reads:

Around 1980, several processes were developed based on the hydroxylation of phenol with aqueous hydrogen peroxide. These processes all use different catalysts and are compared in Table 2.2.

### Table 2.2. Processes for the hydroxylation of phenol with aqueous hydrogen peroxide. Data from ref 42.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>HClO₃, H₃PO₄</th>
<th>Fe⁺⁺/Co⁺⁺</th>
<th>TS-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol conversion (%)</td>
<td>5</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>H₂O₂ eff (%)</td>
<td>70</td>
<td>50</td>
<td>70</td>
</tr>
<tr>
<td>Dihydroxybenzene selectivity (%)</td>
<td>90</td>
<td>80</td>
<td>90</td>
</tr>
<tr>
<td>o/p ratio</td>
<td>1.4</td>
<td>2.3</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Apart from the high H₂O₂ efficiency and dihydroxybenzene selectivity, the ENichem process using TS-1 as the catalyst has the advantage of a relatively high phenol conversion, which decreases recycling streams. From a comparison of the selectivities and yields of the three processes, Notari argues that with TS-1 as the catalyst neither a radical mechanism (as in the Fe⁺⁺/Co⁺⁺ process) nor a mechanism via peroxonium ions (as in the acid-catalysed process) prevails. In analogy with TiO₂/SiO₂ amorphous catalysts, a mechanism via a titanyl group and titanium peroxo-compounds (see scheme 2.6) is proposed.

![Scheme 2.6. Proposed active site in TS-1.](image-url)
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Simultaneously, the decomposition of hydrogen peroxide on two adjacent titanium sites is explained (see scheme 2.7).

![Diagram](image)

Scheme 2.7. The precursor system for the decomposition of H$_2$O$_2$ on adjacent Ti-sites.

It is argued that, due to the homogeneous distribution of Ti in TS-1, hydrogen peroxide decomposition is prevented. Moreover, due to reaction taking place inside the zeolite pore system, tar formation is believed to be suppressed through "restricted transition state shape selectivity". Kraushaar and van Hooff$^{43}$ come to the conclusion that the presence of extra-framework TiO$_2$ not only leads to decomposition of hydrogen peroxide, but also to increased tar formation. However, recently Popa et al.$^{44}$ have applied for a patent for using high-surface TiO$_2$ as a catalyst for the hydroxylation of phenol with aqueous hydrogen peroxide, indicating that it is not really the TiO$_2$ which is detrimental to the catalytic performance.

Van Santen$^{45}$ suggests a different mechanism for the decomposition of hydrogen peroxide on TiO$_2$. From the schematic drawing of this mechanism, as shown in Scheme 2.8, it is clear that the presence of two adjacent Ti-sites is not a requirement for the decomposition of hydrogen peroxide. All that is required is an atom that can bind one H-atom (or ion) and release it again. It is feasible that an O-atom from for example a Ti-O-Si bond plays this part as well, so that hydrogen peroxide can be decomposed on one single titanium site.

Thangaraj et al.$^{46}$ published a study on the effect of the variation of several parameters on the hydroxylation of phenol with aqueous hydrogen peroxide, using TS-1 as a catalyst. They found that at catalyst ratios lower than 0.1 g of catalyst per g of phenol, both conversion and selectivity depend on the amount of catalyst present. However, from our own (non-published) data it can be concluded that the
critical minimum ratio is 0.01 g of catalyst per g of phenol. At catalyst ratios higher than 0.1 g of catalyst per g of phenol, Thangaraj et al.\textsuperscript{46} find that the hydrogen peroxide conversion after 6 hr of reaction stabilises at 80%, with the product ratio hydroquinone: catechol: p-benzoquinone = 47: 53: 0, whereas at lower hydrogen peroxide conversion significant amounts of p-benzoquinone are found. Also, when the hydrogen peroxide conversion is low due to other factors (reaction temperature, type of solvent used) significant amounts of p-benzoquinone are found. Unfortunately, the authors do not take into account that when both hydroquinone and hydrogen peroxide are injected into a GC evaporation chamber, a large portion of the hydroquinone is oxidised to p-benzoquinone. Thus, the large amounts of p-benzoquinone found at low hydrogen peroxide conversion might be due to undesired reactions in the GC injection chamber instead of to catalyst performance. Such oxidation in the GC injection chamber is also supported by the fact that the higher the hydrogen peroxide conversion, the lower the amount of benzoquinone and the higher the amount of hydroquinone found. The authors ascribe this to a reduction reaction of p-benzoquinone to hydroquinone, which is unlikely in the presence of the strong oxidant hydrogen peroxide.

Probably the same phenomenon, the oxidation of hydroquinone in the GC injection chamber, disturbs the data found by Tuel et al.\textsuperscript{47} Although they do not report whether p-benzoquinone is found, the authors state that during the early
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stages of the batch-wise reaction (when hydrogen peroxide conversion is low) catechol formation prevails over hydroquinone formation, whereas during later stages hydroquinone formation prevails over catechol formation. The formation of catechol is ascribed to external surface sites, which become more and more poisoned as the reaction proceeds, whereas hydroquinone is formed on sites inside the zeolite pores. However, it is more likely that both isomers are formed with a constant ratio throughout the reaction, the hydroquinone being oxidised in the GC injection chamber in the early stages of the reaction when hydrogen peroxide conversion is low. The reaction of hydroquinone to p-benzoquinone during the GC analysis has now been confirmed by van der Pol et al.\textsuperscript{48} By comparing GC data to HPLC data of the same samples, they prove that the hydroquinone concentration decreases significantly and the p-benzoquinone concentration increases proportionally when a reaction mixture containing substantial amounts of hydrogen peroxide is injected into a GC, whereas the catechol concentration does not decrease. Apparently catechol is more difficult to oxidise than hydroquinone.

In the paper by Thangaraj et al.\textsuperscript{46} a significant solvent effect is reported, with 2-butanone and acetonitrile showing a slower (factor two) hydrogen peroxide conversion than acetone and methanol. It is also reported that an increase in the phenol / H\textsubscript{2}O\textsubscript{2} ratio leads to an increase of the hydrogen peroxide efficiency, defined as \{H\textsubscript{2}O\textsubscript{2} used to hydroxylate / H\textsubscript{2}O\textsubscript{2} converted\}, of the reaction. Although the authors don’t comment on this, it is to be expected that the dihydroxybenzenes formed are prone to further oxidation to benzoquinones, which can subsequently be polymerised to tarry by-products, probably using hydrogen peroxide. Thus, the higher the phenol / H\textsubscript{2}O\textsubscript{2} ratio, the smaller the amount of undesired by-products formed through further oxidation of the dihydroxybenzenes, and the higher the hydrogen peroxide efficiency.

Huybrechts et al.\textsuperscript{49} compare the catalytic performance of TS-1 samples obtained through different synthesis methods. Apart from four different direct synthesis samples, they also consider samples obtained through treatment of ZSM-5 (Si/Al=50) with gas-phase TiCl\textsubscript{4} and with an aqueous solution of (NH\textsubscript{4})\textsubscript{2}TiF\textsubscript{6}. The authors conclude that the IR band at 960 cm\textsuperscript{-1} is a necessary, though not sufficient, condition for good catalytic performance. Two of the direct synthesis samples and
the sample obtained through (NH₄)₂TiF₆ treatment do not show the 960 cm⁻¹ band in the IR spectrum, and they do not give appreciable conversions in the reactions tested (phenol hydroxylation, hexane oxyfunctionalisation and 1-octene epoxidation). The sample obtained through TiCl₄ treatment does show an IR band at 960 cm⁻¹ and it also shows catalytic activity. The remaining two direct synthesis samples show a more intense 960 cm⁻¹ IR absorption, accompanied by a better catalytic performance. However, in chapters 4 and 5 of this thesis proof is presented that the 960 cm⁻¹ IR absorption band is not necessary for phenol hydroxylation activity.

In another paper, Huybrechts et al.²⁷ compare the physicochemical and catalytic properties of two sets of TS-1 samples obtained through two different direct synthesis methods. Using the controlled hydrolysis of a mixture of TEOS and TEOH (samples denoted as "TSEx1"), it is found that the Si/Ti ratio in the TS-1 is always equal to that in the synthesis mixture. However, from IR, UV-Vis and H₂O₂ decomposition data, the authors conclude that at Si/Ti ratios lower than 65, part of the Ti is present as TiO₂. When samples denoted as "TSEx2" are prepared using peroxytitanate as the titanium source and silica sol as the silica source, the lowest Si/Ti ratio obtained in the samples is 55, even if the Si/Ti ratio in the synthesis mixture is 32. Thus it is suggested that in the "TSEx2" samples Ti is only incorporated as true T-atoms. However, in the hydroxylation of phenol the catalytic performance of the "TSEx1" samples is better than that of the "TSEx2" samples. The authors ascribe this fact to the presence of substantial amounts of aluminium in the "TSEx2" samples (Si/Al=300), the aluminium being introduced into the synthesis mixture with the silica sol. It is argued that the presence of aluminium would poison the phenol hydroxylation activity. However, Ferrini and Kouwenhoven³⁹ reported that various titanium-free aluminium-containing zeolites, including H-Y and ZSM-5, do show catalytic activity in the hydroxylation of phenol. Thus, there must be some other (and as yet unidentified) reason for the high phenol hydroxylation activity of the "TSEx1" samples as compared to the "TSEx2" samples. One possible explanation is that the titanium in "TSEx1", which is not incorporated as T-atoms, forms a very disperse phase of TiOₓ on the external surface of the TS-1 crystals, this TiOₓ linked to (titanium)silicalite-1 being an active phase for the hydroxylation of phenol.
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Van der Pol et al.\textsuperscript{50} report a pronounced particle size effect for the hydroxylation of phenol with TS-1, smaller particles being more active than larger particles. This implies that external surface or outer shell reactions might play an important role. On the contrary, Tuel et al.\textsuperscript{47} calculate the same activity per titanium atom for differently sized particles of TS-1, from which they conclude that the influence of the crystal size on the activity is negligible. However, in chapters 4 and 5 of this thesis it is found that titanium deposited on the external surface of various zeolites and silicas from $\text{TiF}_3$/HF aqueous solution or from $\text{TiCl}_4$ shows catalytic activity for phenol hydroxylation, indicating that whenever present, external surface $\text{TiO}_x$ species affect catalytic performance. Thus, one is inclined to conclude that the samples synthesised by van der Pol et al.\textsuperscript{50} contain external surface $\text{TiO}_x$, whereas those of Tuel et al.\textsuperscript{47} contain only T-site titanium. However, as both van der Pol et al.\textsuperscript{50} and Tuel et al.\textsuperscript{47} use the same synthesis method as Huybrechts et al.\textsuperscript{27}, and both groups\textsuperscript{50,47} incorporate more titanium than Huybrechts et al.\textsuperscript{27} do for "TSEX1", one would expect similar results from the experiments of van der Pol et al.\textsuperscript{50} and of Tuel et al.\textsuperscript{47}

From discrepancies in the literature like the ones mentioned here, it is clear that in order to understand the synthesis and catalytic properties of titanium-containing zeolites, much more study is required.

In the work reported here, the hydroxylation of phenol was performed in a three-necked glass vessel, using an oil bath for heating. Usually, 10 g of phenol and 1 g of internal standard (IS, pentafluorobenzoic acid) were dissolved in 32 g of methanol (methanol serves solely as a solvent, its oxidation being much slower than the hydroxylation of phenol). A 0.5 ml sample of this mixture was taken for analysis of the starting phenol / IS ratio, then 100 mg of the catalyst was added. The mixture was heated to reflux (about 80°C) before 5.0 ml of 30% $\text{H}_2\text{O}_2$ in water (Merck, p.a.) was added dropwise over a period of 10 min. In the course of time (usually every 30 or 60 min), 0.5 ml samples were withdrawn from the reaction mixture for analysis. Samples were filtrated through 0.45 μm FP-Vericel membrane filters (Gelman Sciences, Ann Arbor, MI, USA) to remove the catalyst and thus halt the reaction. Samples were analysed for organics using HPLC analysis on a 5 μm Nucleosil C18 column measuring 150 * 4.6 mm, using a mixture of volume ratio MeOH : $\text{H}_2\text{O}$ :
THF : TFA = 13.5 : 85.5 : 1.0 : 0.02 as the eluent (TFA = trifluoroacetic acid) at 1.0 ml / min. UV-detection at 240 nm was used. Hydrogen peroxide conversion was analysed using iodometric titration. This is an indirect titration, in which first hydrogen peroxide reacts with a surplus quantity of iodide:

$$\text{H}_2\text{O}_2 + 2 I^- + 2 \text{H}^+ \rightarrow I_2 + 2 \text{H}_2\text{O}$$

Then the amount of iodine formed is determined by titration with sodium thiosulfate solution:

$$I_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 2 I^- + \text{S}_4\text{O}_6^{2-}$$

For colourless solutions, the orange-coloured iodine serves as an indicator. If necessary, 1 ml of a solution of 0.5 % starch in 1 % aqueous KI is used as an indicator. With iodine the starch has a dark blue colour, due to $I_3^-$ inclusion, whereas it is colourless when no iodine but only iodide is present.

The titration is performed by weighing 0.2 - 1 g of reaction mixture into an Erlenmeyer flask containing 20 ml of water, 5 ml of 1 M aqueous $\text{H}_2\text{SO}_4$, 1 g of KI and 2 drops of a 3 % aqueous solution of (NH$_4$)$_6$Mo$_7$O$_{24}$, which serves as a catalyst for the reaction between hydrogen peroxide and iodide. This mixture is titrated with 0.100 N aqueous sodium thiosulfate.

The hydroxylation of other aromatic compounds has also been reported.$^{12}$ Toluene, ethylbenzene, anisole and all three isomers (o,m,p) of cresol are hydroxylated with selectivities (based on hydrocarbon conversion) of 80 - 90%. The selectivity reported in the same paper for phenol hydroxylation is 90 - 95%.

**The oxyfunctionalisation of n-hexane**

Alkanes (paraffins) are chemically inert, and with the strongly oxidising reagents required to oxidise them, it is very difficult to perform the oxidation selectively. However, with TS-1 and aqueous hydrogen peroxide, saturated organic compounds can be selectively oxidised at secondary and tertiary C-positions under relatively mild conditions to their alcohols and subsequently to their ketones. Thus, n-hexane (as a model compound) can be selectively oxidised to a mixture of 2-hexanol, 3-hexanol, 2-hexanone and 3-hexanone, according to the reaction pathways given in scheme 2.9, using methanol as a solvent. Occasionally more than one functional group per molecule is found.
Scheme 2.9. The TS-1 catalysed oxyfunctionalisation of n-hexane.

Although Tatsumi et al.\textsuperscript{51} were the first to report on the oxyfunctionalisation of alkanes using TS-1 and \( \text{H}_2\text{O}_2 \) in the open literature, their results were limited to a TON for n-hexane of 35 mol per mol Ti. However, before the paper by Tatsumi et al.\textsuperscript{51} was published, Huybrechts et al.\textsuperscript{52} had submitted a paper on the same subject to a different journal. Their results are much better than those reported by Tatsumi et al., with TON's for n-hexane > 1,000. After reading the aforementioned papers, Clerici of ENIchem decided to publish a paper on the same subject in the open literature,\textsuperscript{53} as obviously ENIchem's earlier Italian patent application\textsuperscript{54} had not been noticed by research groups working on TS-1.

Although Clerici\textsuperscript{53} claims his oxyfunctionalisation experiments were performed at 55°C at atmospheric pressure, Huybrechts et al.\textsuperscript{52} perform their experiments at 100°C, which means that with the methanol used as solvent, experiments have to take place in an autoclave. Our own experiments (not published) show that at 55°C extremely long reaction times (at least 3 days) are required to obtain detectable quantities of products, whereas at 100°C in an autoclave 3 to 24 hours (depending on which catalyst is used) is sufficient to obtain 50 - 100% hydrogen peroxide conversion and good yields.

Regio-selectivities found by various authors differ significantly. For n-hexane oxyfunctionalisation, Clerici\textsuperscript{53} reports a 2/3 product ratio of 2.6, whereas Huybrechts et al.\textsuperscript{52} find this ratio to be just over 1. One is inclined to think that this
difference in selectivity is due to the different reaction temperatures used by both groups, but our own results (see also chapter 7) at 100°C (the temperature used by Huybrechts et al.) show a 2/3 product ratio of 2.5, that is, the same as that reported by Clerici at 55°C. The statistical 2/3 product ratio for n-hexane is 1, as it has 2 C-2 and 2 C-3 positions. Besemer\textsuperscript{55} reports that for reaction of n-hexane with free OH\textsuperscript{-} radicals, the 2/3 product ratio is 0.91. The much higher ratio found by Clerici and by our group indicates that with TS-1 and H\textsubscript{2}O\textsubscript{2} this reaction does not proceed through free OH\textsuperscript{-} radical attack. Huybrechts et al.\textsuperscript{52} give a tentative mechanism (see scheme 2.10) for the oxyfunctionalisation of alkanes with TS-1 and hydrogen peroxide, analogous to stoichiometric alkane oxidation with vanadium peroxo complexes.

\[
\begin{array}{cccc}
O & O & O* & O \\
\text{Ti} & \text{Ti} & + & \text{H-CR} \\
& & \text{Ti} & \text{Ti} \\
& & \text{OH} & \text{OH} \\
& & \text{Ti} & \text{Ti} \\
& & \text{HO-CR} & \text{HO-CR}
\end{array}
\]

Scheme 2.10. Oxyfunctionalisation mechanism as proposed by Huybrechts et al.\textsuperscript{52}

However, Tatsumi et al.\textsuperscript{56} propose a different (and more feasible) mechanism (see scheme 2.11).

\[
\begin{array}{ccc}
H & H & \text{C} \\
\text{Ti} & \text{Ti} & \text{Ti} \\
O & O & O \\
\rightarrow & \rightarrow & \rightarrow \\
\text{H}_2\text{O} & \text{O} & \text{H} \\
\text{O} & \text{C} & \text{H}
\end{array}
\]

Scheme 2.11. Oxyfunctionalisation mechanism as proposed by Tatsumi et al.\textsuperscript{56}

The selective oxidation of alcohols

Some time before it was discovered that TS-1 can catalyse the oxyfunctionalisation of alkanes to alcohols and subsequently to ketones, the selective oxidation of
alcohols to carbonyl compounds, using TS-1 and hydrogen peroxide, was already being studied, though not as intensively as aromatic hydroxylation. ENIchem workers were the first to claim the selective formation of carbonyl compounds (aldehydes or ketones). However, when oxidising primary alcohols, the aldehydes formed can undergo consecutive oxidation to carboxylic acids, which in turn can give esters by reaction with unreacted alcohol. Thus, in order to obtain sufficient selectivity, it is necessary to work with alcohol : H₂O₂ ratios significantly higher than one.

The ammoximation of ketones

The most important ketone to be ammoximated is cyclohexanone (see scheme 2.12), as the product cyclohexanone oxime can undergo Beckmann-rearrangement to ε-caprolactam, the monomer for nylon-6 synthesis. Using TS-1, aqueous hydrogen peroxide and aqueous ammonia, cyclohexanone is ammoximated at 60°C in the liquid phase, without additional solvent. Probably ammonia is oxidised to hydroxylamine first, which subsequently reacts with cyclohexanone.

![Scheme 2.12. The ammoximation of cyclohexanone.](image_url)

It was already known that cyclohexanone could be ammoximated in the gas-phase, using molecular oxygen and ammonia gas, and amorphous silica as a catalyst. TS-1 was also tested for the gas-phase reaction, but both activity and selectivity are lower for TS-1 than for amorphous SiO₂.

The TS-1 catalysed ammoximation of cyclohexanone combined with the zeolite (SAPO) catalysed Beckmann-rearrangement of the oxime forms a promising possibility for a salt-free manufacture of the nylon-6 monomer, as in present-day
processes substantial amounts of ammonium sulphate are formed as a waste product.

*The epoxidation of olefins*

The epoxidation of olefins with TS-1 and aqueous hydrogen peroxide at temperatures of 20 - 80°C has been reported. Epoxidation experiments were first performed in autoclaves, thus under a pressure > 1 atm., and under conditions using excess olefin with respect to H₂O₂. Methanol or acetone is used as a solvent. Hydrogen peroxide conversions are high, reaching about 90% conversion in 1-2 hr. Selectivities for the desired epoxide are 80-90% for propylene, 98% for 2-butene and around 60% for 1-octene. Small amounts of epoxide ring-opening products are generally found, both due to reaction with water and with solvent. Recently, Clerici and Ingalla from ENIchem published an extensive report in the open literature on the epoxidation of olefins. In this paper, the epoxidation reaction is performed at -5 to 45°C in a glass vessel under nitrogen. Selectivities based on hydrogen peroxide are high: around 90%. Activities are also high, but only for linear olefins (in relation with the accessibility of the zeolite framework and with diffusion rates): for 1-hexene, 88% hydrogen peroxide conversion is reached in 70 min at 25°C, whereas for cyclohexene at the same temperature only 9% hydrogen peroxide conversion is measured after 90 min. Methanol is used as the solvent.

Van Santen proposes a mechanism for the epoxidation of olefins by hydrogen peroxide and catalysed by TS-1. This mechanism (see Scheme 2.13) involves only a change in coordination number of the Ti atom; its valency does not change during the catalytic reaction.

In patents Clerici and Bellussi describe a method to selectively epoxidise the cis- and trans-isomers of olefins in a mixture. By working with excess olefin, the cis-isomer is first epoxidised selectively, and after separation of the cis-epoxide, the remaining trans-isomer is epoxidised by again adding hydrogen peroxide.
Scheme 2.13. The epoxidation of olefins with hydrogen peroxide on TS-1, as proposed by van Santen.\textsuperscript{45}

Olefins containing a second oxidisable group are usually epoxidised selectively, the second oxidisable group remaining unoxidised,\textsuperscript{13} although for branched molecules which are sterically hindered near the double bond, the selectivity towards epoxidation is lower.\textsuperscript{65}

Altogether, TS-1 is a versatile catalyst for selective oxidation reactions with hydrogen peroxide, and new reactions are still discovered regularly.

2.3. OTHER TITANIUM-CONTAINING ZEOLITES

Although TS-1 is the zeolitic titanium-containing structure about which most data are available, recently also other titanium-containing zeolitic structures have been reported.
2.3a. TITANIUM-SILICALITE-2

A titanium-containing silicalite with the MEL (ZSM-11) structure, usually denoted as TS-2 or tsiil-2, was first described by Bellussi et al.\textsuperscript{61} at ENIChem, Italy in 1989. The template used for most MEL syntheses is tetrabutylammonium (TBA). As for TS-1, an extra IR absorption band with respect to non-titanium-containing MEL at around 960 cm\textsuperscript{-1} was observed, accompanied by an increase in unit cell parameters due to the Ti-O bond length being greater than the Si-O bond length. These observations are interpreted as proof of the incorporation of Ti into the zeolite framework.

As the structures of both TS-1 and TS-2 belong to the pentasil family and thus are somewhat alike (see Table 2.3), similar catalytic properties are expected.

**TABLE 2.3. Comparison of MFI and MEL structures.**

<table>
<thead>
<tr>
<th>material</th>
<th>largest pore opening</th>
<th>dimensionality</th>
<th>channel configuration</th>
<th>no. of T-atoms/uc</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFI</td>
<td>5.6 * 5.3 Å</td>
<td>3</td>
<td>straight \perp sinusoidal</td>
<td>96</td>
</tr>
<tr>
<td>MEL</td>
<td>5.4 * 5.3 Å</td>
<td>3</td>
<td>straight \perp straight</td>
<td>96</td>
</tr>
</tbody>
</table>

Scientists from the group of Ratnasamy (Pune, India) have frequently published on catalytic experiments using TS-2 as the catalyst.\textsuperscript{66,67,68,69,70,71,72} In the hydroxylation of phenol\textsuperscript{71} an increase in both activity and selectivity with increasing Ti content is reported, although the values obtained for TS-2 are lower than those reported for TS-1 by the people from ENIChem.\textsuperscript{42} As with TS-1, tar formation decreases when an excess amount of phenol with respect to H\textsubscript{2}O\textsubscript{2} is present in the reaction mixture. The product distribution (o/p ratio around 1) is the same as that reported for TS-1.

TS-2 was also found to be an active catalyst for the oxyfunctionalisation of paraffins. Reports have been published on n-hexane\textsuperscript{69} and cyclohexane.\textsuperscript{70} In the
selective oxidation of n-hexane, TS-2 is a little less active than TS-1, and although the ratio of 2- and 3- oxygenates is the same for TS-1 and TS-2, with TS-2 more multiple oxygenated products and lactones are formed. The oxyfunctionalisation of cyclohexane on TS-2 is 5 - 10 times slower than that of n-hexane, indicating (reactant) shape selectivity. However, TOFs (number of cyclohexane molecules converted per Ti atom per second) of up to $4.5 \times 10^{-3}$ were reported, with selectivities (based on cyclohexane conversion) of 70 - 95 %. For this reaction the performance of TS-1 is only slightly better than that of TS-2.

The liquid phase ammoximation of cyclohexanone to cyclohexanone oxime with aqueous ammonia and hydrogen peroxide is another reaction that has been studied by the group of Ratnasamy. Although fumed silica (which is known to be a good catalyst for the gas phase ammoximation of cyclohexanone with NH$_3$ and O$_2$) and silicalite-2 give high conversions of cyclohexanone, the main product formed on these catalysts is peroxy dicyclohexylamine, a product of a coupling reaction. TS-2 however shows good activity (up to 85% cyclohexanone conversion when the TS-2 has the low Si/Ti ratio of 27), the main product being cyclohexanone oxime (selectivities of up to 80% are reported). In the same paper, attempts to perform the ammoximation of some other substances are reported, with various degrees of success. Benzaldehyde and 2-butanone give high conversions and selectivities, acetophenone gives moderate conversion with high selectivity, and benzophenone gives hardly any conversion with only moderate selectivity. The low activity towards benzophenone ammoximation is ascribed to it being too large to diffuse into the zeolitic pore system easily. Although no Beckmann rearrangement (to $\epsilon$-caprolactam) of the formed cyclohexanone oxime is reported in the liquid phase ammoximation, an entire publication appeared on the vapour phase Beckmann rearrangement using, amongst others, TS-2 as the catalyst. TS-2 was compared with silicalite-2, ZSM-11, amorphous (fumed) silica and Al-TS-2, and it turned out to be the best catalyst tested. In another publication, TS-1 is tested for its performance in this reaction. For TS-1 twice the amount of catalyst is used under otherwise similar reaction conditions. Both conversion and selectivity are higher for TS-1 than for TS-2. Furthermore, TS-1 deactivates slower than TS-2.

Thus, although catalytic properties are rather similar for TS-1 and TS-2, generally
TS-1 is the more active, selective and stable catalyst of the two.

2.3.b. TITANIUM-BEA

To our knowledge, so far only one research group has published on the direct synthesis of titanium-containing material with the framework of BEA.\textsuperscript{74,75,76} This group, Corma et al., is working on a material which also contains aluminium, and since no method is known for the direct synthesis of all-silica BEA, it will not be feasible to directly synthesise aluminium-free Ti-BEA. A study concerning a two-step synthesis procedure for essentially Al-free Ti-BEA is presently in progress in our laboratory. The Si/Al ratio of the direct-synthesis Ti-BEA first reported by Corma et al. is about 50, and the Si/Ti ratio ranges from 30 to 60.\textsuperscript{74,75} The material is tested for its catalytic properties in the oxyfunctionalisation of cyclohexane and cyclo-
dodecane. The results of the catalytic tests are compared to those obtained with TS-1 as the catalyst, but unfortunately no comparison with non-titanium-containing BEA is given. Ti-BEA is reported to exhibit a higher activity than TS-1. No regio-
selectivity is possible with the molecules investigated, but with Ti-BEA more ketones are formed than with TS-1.

In their most recent paper, Corma et al.\textsuperscript{76} report a Ti-BEA with Si/Ti ratios as low as 20 and containing very little aluminium (Si/Al = 125). However, the most titanium-rich and aluminium-poor samples are not fully crystalline. Furthermore, the samples are calcined at 550°C, which might be too high for the BEA structure.\textsuperscript{77} The samples are tested in several oxidation reactions with aqueous hydrogen peroxide. As a reference sample Euro-TS-1 is used, a "standard" TS-1 sample prepared by Van Der Pol and Van Hooff of Eindhoven University of Technology. In the oxyfunctionalisation of n-hexane, at 100°C in an autoclave and using acetone as the solvent, the activity of TS-1 is about 10 times that of Ti-BEA. For cyclo-
hexane oxyfunctionalisation, the activities are practically the same. For the epoxidation of olefins, TS-1 is generally more selective than Ti-BEA, which gives very high selectivities to undesired epoxide ring-opening reactions. For linear olefins (1-
hexene and 1-dodecene) TS-1 is the more active catalyst, whereas for cyclohexene and cyclooctene Ti-BEA is more active, proving the expected better accessibility.
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of the BEA structure.

Several methods have been described to incorporate titanium into the BEA structure via secondary synthesis, mostly analogous to the secondary synthesis of TS-1. Chen et al. \(^{78}\) briefly describe the treatment of zeolite Beta and of B-BEA (containing both Al and B as T-atoms next to Si) with TiCl\(_4\) at 350°C. Unfortunately they do not give any data on the elemental composition and only little data on the characterisation of the resulting materials; they subject the samples to ion-exchange treatment before measuring only the cation exchange capacity, NH\(_3\)-TPD and cyclohexane sorption capacity.

Ferrini and Kouwenhoven\(^ {39}\) use TiCl\(_4\) at 250°C to incorporate titanium into zeolite H-Beta. Again no elemental analysis is given, but the resulting material is tested as a catalyst for the hydroxylation of phenol. It is reported that zeolite H-Beta is a much more active catalyst than the TiCl\(_4\) treated H-Beta, a fact on which the authors hardly comment. However, as one of the current commercial processes for producing dihydroxybenzenes is based on an acid-catalysed reaction of phenol with hydrogen peroxide,\(^ {42}\) it is not really surprising that the H-form of a zeolite (commonly referred to as a "solid acid") shows catalytic activity for this reaction. The deactivation upon TiCl\(_4\) treatment might then be explained by reaction of TiCl\(_4\) with the acidic OH groups, resulting in extra-framework / framework-associated TiO\(_x\) species instead of the desired Al-replacement. The Ti atoms are not sufficiently isolated to form active "TS-1 like" catalytic sites. The fact that the total surface area of the H-Beta decreases from 630 to 530 m\(^2\)/g upon TiCl\(_4\) treatment indicates that pore-blocking occurs, probably due to the TiO\(_x\) deposited inside the zeolitic channel system. As the pore openings of the BEA structure are substantially larger than those of the MFI structure (largest pore dimensions 7.6 * 6.4 Å for BEA vs 5.6 * 5.3 Å for MFI), TiCl\(_4\) diffusion into the BEA structure is feasible, whereas for the MFI structure this is less likely.\(^ {40}\)

In our laboratory, this problem is approached by first synthesising aluminium-free B-BEA, followed either by deboronation and subsequent occupation of the vacancies by reaction with a titanium-compound, or by direct boron substitution using a titanium-compound.
2.3.c. ETS-4 AND ETS-10

Although they are not zeolites in the sense of consisting solely of tetrahedrons as primary building units, the titano-silicates ETS-4 and ETS-10\textsuperscript{79} are microporous crystalline solids with uniform pores. Their pore dimensions are similar to those of zeolites. Like zeolites, ETS-4 and ETS-10 are synthesised under hydrothermal conditions from an alkaline synthesis gel, although no organic templating agents are required. Thus, no activation treatment to remove occluded, pore-blocking organic material, is necessary after synthesis. The frameworks of ETS-4 and ETS-10 consist of SiO\textsubscript{4} tetrahedra and TiO\textsubscript{6} octahedra, connected through corner-sharing oxygen atoms. For ETS-4, the Si/Ti ratio is 2.5, for ETS-10 4.5. As the TiO\textsubscript{6} octahedron bears an excess charge of -2, charge-balancing counter-ions are present in these structures. As for zeolites, these counter-ions can be exchanged fairly easily, and the type of counter-ion present affects the effective pore diameter. Thus, Ca-ETS-4 has an effective pore diameter of 4 Å, whereas the as-synthesised Na/K form does not adsorb SO\textsubscript{2}, which has an effective diameter of 3.8 Å. As-synthesised Na/K-ETS-10 has an effective pore diameter of 8 Å. Although Kuznicki et al.\textsuperscript{79} give some data on ion-exchange and on the adsorption of various organics (benzene, o-xylene, triethylamine), as yet no catalytic data are available.

2.4 REFERENCES

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45) R.A. van Santen, Theoretical Heterogeneous Catalysis, World Scientific, Singapore (1991), Ch. 4.


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CHAPTER 3

TS-1 SYNTHESISED IN OH\textsuperscript{-} MEDIUM

3.1. INTRODUCTION

Zeolites are very often synthesised in a strongly basic environment (pH 10 - 14), in which OH\textsuperscript{-}-ions act as the so-called "mineralising agent". The OH\textsuperscript{-}-ions complexate the T-atom building blocks, so they are solubilised from the gel and transported to the growing zeolite framework. In the case of the MFI structure, which is the structure type of TS-1, TPA (tetrapropylammonium) serves as the structure-directing "template" around which the T-atom building blocks form the zeolite framework.

Originally, TS-1 was synthesised using TEOS (tetraethyl orthosilicate, Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}) as the silicon source and the titanium analogue of that compound, TEOT (Ti(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}) as the titanium source.\textsuperscript{1} Also, other titanium sources were used, like TPOT (tetratropyl orthotitanate, Ti(O\textsuperscript{0}C\textsubscript{3}H\textsubscript{7})\textsubscript{4}),\textsuperscript{1} Ti\textsuperscript{4}POT (teta-isopropyl orthotitanate, Ti(O\textsuperscript{0}C\textsubscript{3}H\textsubscript{7})\textsubscript{4}\textsuperscript{1}) and TBOT (tetrabutyl orthotitanate, Ti(O\textsuperscript{0}C\textsubscript{4}H\textsubscript{9})\textsubscript{4}).\textsuperscript{2} It was also reported that the addition of isopropyl alcohol during the preparation of the synthesis gel is beneficial.\textsuperscript{2} Sometimes hydrogen peroxide is added as a titanium-complexating agent.\textsuperscript{1}

In this chapter, the synthesis of TS-1 using OH\textsuperscript{-} as the mineralising agent is studied. Apart from the synthesis method, the source of titanium, the Si/Ti ratio and the synthesis time are varied. The resulting materials are characterised using elemental analysis (Inductively Coupled Plasm - Atomic Emission Spectroscopy, ICP-AES), X-ray diffraction, IR spectroscopy, and the hydroxylation of phenol as a catalytic test reaction.

3.2. EXPERIMENTAL

The synthesis of TS-1

Samples denoted as TEOT1 - TEOT5 were synthesised using TEOS as the silicon source and TEOT as the titanium source.\textsuperscript{1} The required amounts of TEOS
(Janssen Chimica) and TEOt (Tioxide UK Ltd.) were weighed and mixed together under nitrogen, as especially tetra-alkyl orthotitanium compounds are very sensitive to hydrolysis by moisture, even from air. The mixture was stirred for 10 min at room temperature, and subsequently cooled to 0°C under nitrogen. When the mixture had cooled down completely, the required amount of cold (0°C) 1 M aqueous TPAOHi (CFZ Zaltbommel, containing up to 1000 ppm K and 300 ppm Na) was added dropwise and with vigorous stirring. The mixture was kept under nitrogen until half of the required amount of TPA-OH solution had been added. When all the TPA-OH had been added, the mixture was slowly heated to 80°C under stirring, to evaporate the ethanol formed from hydrolysis of the silicon- and titanium-compounds. The mixture was stirred at 80°C for half an hour before the required amount of extra water was added slowly. The mixture was heated at 175°C in a Teflon-lined stainless steel 40 ml autoclave for at least 11 days. The product was filtered to separate it from the mother liquor, washed three times with warm water, dried at 120°C and calcined overnight in air in a muffle furnace at 450°C, to remove incorporated TPA. Table 3.1 lists the synthesis parameters of the samples of TEOt.

<table>
<thead>
<tr>
<th>sample</th>
<th>TEOt (mg)</th>
<th>TEOS (g)</th>
<th>TPA-OH 1 M (g)</th>
<th>H2O (g)</th>
<th>time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOt1</td>
<td>21</td>
<td>3.7</td>
<td>7.8</td>
<td>24.9</td>
<td>26</td>
</tr>
<tr>
<td>TEOt2</td>
<td>41</td>
<td>3.4</td>
<td>6.6</td>
<td>25.2</td>
<td>22</td>
</tr>
<tr>
<td>TEOt3</td>
<td>62</td>
<td>2.5</td>
<td>6.2</td>
<td>20.0</td>
<td>11</td>
</tr>
<tr>
<td>TEOt4</td>
<td>65</td>
<td>2.1</td>
<td>6.0</td>
<td>23.5</td>
<td>22</td>
</tr>
<tr>
<td>TEOt5</td>
<td>199</td>
<td>3.7</td>
<td>8.4</td>
<td>24.8</td>
<td>23</td>
</tr>
</tbody>
</table>

Samples denoted as TPOT1 - TPOT4 were synthesised following the procedure described for the TEOt samples, but using TPOT (Tioxide) as the titanium source.
The synthesis parameters of the TPOT samples are listed in Table 3.2. The synthesis gel prepared for sample TPOT2 was divided into three roughly equal parts, which were autoclaved for various periods of time, yielding samples TPOT2a, 2b and 2c.

The sample denoted as T<sup>1</sup>POT was prepared as described above for the TEOT samples, but using T<sup>1</sup>POT (TiO<sub>2</sub>) as the titanium source. The synthesis parameters of this sample are listed in Table 3.2.

### TABLE 3.2. Synthesis parameters TPOT and T<sup>1</sup>POT samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>TPOT (mg)</th>
<th>TEOS (g)</th>
<th>TPA-OH 1 M (g)</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O (g)</th>
<th>time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPOT1</td>
<td>18</td>
<td>2.4</td>
<td>6.4</td>
<td>25.2</td>
<td>43</td>
</tr>
<tr>
<td>TPOT2a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>32</td>
</tr>
<tr>
<td>TPOT2b</td>
<td>106</td>
<td>7.0</td>
<td>15.3</td>
<td>50.3</td>
<td>25</td>
</tr>
<tr>
<td>TPOT2c</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>TPOT3</td>
<td>92</td>
<td>3.2</td>
<td>7.1</td>
<td>25.0</td>
<td>11</td>
</tr>
<tr>
<td>TPOT4</td>
<td>505</td>
<td>3.6</td>
<td>7.1</td>
<td>25.1</td>
<td>27</td>
</tr>
<tr>
<td>T&lt;sup&gt;1&lt;/sup&gt;POT</td>
<td>204</td>
<td>4.4</td>
<td>10.0</td>
<td>40.0</td>
<td>19</td>
</tr>
</tbody>
</table>

Samples denoted as prop1 - prop3 were prepared by dissolving TPOT and dry TPABr (CFZ Zaltbommel) in about 15 ml of dry isopropyl alcohol<sup>2</sup> under nitrogen, to which solution TEOS was added under nitrogen and stirring. After cooling down to 0°C, cold TPAOH 1 M aqueous solution was added dropwise with vigorous stirring and under nitrogen until half of the required amount of TPAOH had been added. When all the TPAOH had been added, the mixture was additionally stirred for 10 min before slowly heating to 80°C to evaporate the alcohols. The temperature was maintained at 80°C for half an hour before the required amount of extra water was added. The resulting synthesis gel was autoclaved at 175°C in a Teflon-
Chapter 3

lined stainless steel autoclave. The synthesis parameters are listed in Table 3.3.

A sample denoted as IMP was prepared by Mrs. C. Ferrini (ETH Zürich) according to EP 311,983, by impregnating a mixture of amorphous TiO₂ and SiO₂ (Grace, No. 1, Type I) with aqueous TPAOH and autoclaving the synthesis gel thus obtained for 4 days in a stirred stainless-steel autoclave at 150°C.

<table>
<thead>
<tr>
<th>sample</th>
<th>TEOT (mg)</th>
<th>TPABr (mg)</th>
<th>TEOS (g)</th>
<th>TPA-OH 1 M (g)</th>
<th>H₂O (g)</th>
<th>time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>prop1</td>
<td>16</td>
<td>240</td>
<td>2.3</td>
<td>5.0</td>
<td>24</td>
<td>29</td>
</tr>
<tr>
<td>prop2</td>
<td>74</td>
<td>210</td>
<td>2.4</td>
<td>4.8</td>
<td>24</td>
<td>12</td>
</tr>
<tr>
<td>prop3</td>
<td>282</td>
<td>240</td>
<td>2.3</td>
<td>5.0</td>
<td>24</td>
<td>28</td>
</tr>
</tbody>
</table>

A sample of "Euro-TS-1", the standard TS-1 material synthesised by van der Pol and van Hooff of Eindhoven University of Technology, was also tested for its performance in the hydroxylation of phenol.

Phenol hydroxylation

The catalytic test reaction, the hydroxylation of phenol with aqueous hydrogen peroxide, was performed as described in detail in chapter 2 of this thesis, using 10 g of phenol, 5.0 ml of 30% hydrogen peroxide, 1 g of pentafluorobenzoic acid (internal standard), 32 g of methanol as a solvent and 100 mg of catalyst. The reaction was performed at reflux, about 80°C.

3.3. RESULTS AND DISCUSSION

According to powder X-ray diffraction, all samples reported here are crystalline and of the MFI structure. Tables 3.4 - 3.6 summarise the results of the synthesis experiments, and Figure 3.1 gives the relation between the Si/Ti ratio of the synthesis gel and that of the samples.
Generally speaking, the Si/Ti ratio of the samples is lower than that of the synthesis gel (i.e., the titanium content of the samples is higher than that of the gel). Several explanations for this phenomenon are possible. For one of these explanations, the titanium might be incorporated into the zeolitic framework more easily than the silicon, possibly as some kind of octahedrally coordinated species which is connected to the zeolite framework via one or two oxygen bridges. A more feasible explanation might be that the titanium is less soluble than the silicon, in which case the formation of domains or crystals of $\text{Ti}_x\text{O}_y$ is to be expected. The fact that the yields of the syntheses are always substantially lower than 100% does not help to distinguish whether one of the aforementioned explanations is the correct one.
Table 3.4. Synthesis results TEOt samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Ti gel¹</th>
<th>time (days)</th>
<th>cryst. yield²</th>
<th>crystal size (µm)</th>
<th>Si/Ti sample³</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOt1</td>
<td>190</td>
<td>26</td>
<td>50</td>
<td>30</td>
<td>80</td>
</tr>
<tr>
<td>TEOt2</td>
<td>90</td>
<td>22</td>
<td>23</td>
<td>35</td>
<td>41</td>
</tr>
<tr>
<td>TEOt3</td>
<td>45</td>
<td>11</td>
<td>40</td>
<td>1</td>
<td>34</td>
</tr>
<tr>
<td>TEOt4</td>
<td>36</td>
<td>22</td>
<td>53</td>
<td>40</td>
<td>11</td>
</tr>
<tr>
<td>TEOt5</td>
<td>.20</td>
<td>23</td>
<td>71</td>
<td>4</td>
<td>7</td>
</tr>
</tbody>
</table>

1) Calculated from quantities of TEOS and TEOt employed.
2) Synthesis yield = (grams of product isolated / theoretical maximum) * 100%.
3) Bulk elemental value determined using ICP-AES.

Table 3.5. Synthesis results TPOT and TPOT samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Ti gel¹</th>
<th>time (days)</th>
<th>cryst. yield²</th>
<th>crystal size (µm)</th>
<th>Si/Ti sample³</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPOT1</td>
<td>180</td>
<td>43</td>
<td>54</td>
<td>40</td>
<td>125</td>
</tr>
<tr>
<td>TPOT2a</td>
<td>90</td>
<td>32</td>
<td>88</td>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>TPOT2b</td>
<td>90</td>
<td>25</td>
<td>88</td>
<td>1</td>
<td>70</td>
</tr>
<tr>
<td>TPOT2c</td>
<td>50</td>
<td>18</td>
<td></td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>TPOT3</td>
<td>50</td>
<td>11</td>
<td>29</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>TPOT4</td>
<td>10</td>
<td>27</td>
<td>70</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>TPOT²</td>
<td>50</td>
<td>19</td>
<td>68</td>
<td>60</td>
<td>35</td>
</tr>
</tbody>
</table>

1) Calculated from quantities of TEOS and TPOT or TPOT employed.
2) Synthesis yield = (grams of product isolated / theoretical maximum) * 100%.
3) Bulk elemental value determined using ICP-AES.
TABLE 3.6. Synthesis results prop samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Ti gel(^1)</th>
<th>time (days)</th>
<th>cryst. yield(^2)</th>
<th>crystal size (μm)</th>
<th>Si/Ti sample(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>prop1</td>
<td>195</td>
<td>29</td>
<td>89</td>
<td>1</td>
<td>275</td>
</tr>
<tr>
<td>prop2</td>
<td>45</td>
<td>12</td>
<td>64</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>prop3</td>
<td>11</td>
<td>28</td>
<td>84</td>
<td>20</td>
<td>12</td>
</tr>
</tbody>
</table>

1) Calculated from quantities of TEOS and TPOT employed.
2) Synthesis yield = (grams of product isolated / theoretical maximum) * 100%.
3) Bulk elemental value determined using ICP-AES.

Tables 3.7 - 3.10 give the results of the phenol hydroxylation reactions. Unless otherwise stated, the results are those obtained after 6 hr of reaction.

TABLE 3.7. Phenol hydroxylation results TEOH samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Ti(^1)</th>
<th>H(_2)O(_2) yield(^2)</th>
<th>TON(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOH1</td>
<td>80</td>
<td>28 (3.5 hr)</td>
<td>650</td>
</tr>
<tr>
<td>TEOH2</td>
<td>41</td>
<td>6 (5 hr)</td>
<td>75</td>
</tr>
<tr>
<td>TEOH3</td>
<td>34</td>
<td>15</td>
<td>150</td>
</tr>
<tr>
<td>TEOH4</td>
<td>11</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>TEOH5</td>
<td>7</td>
<td>36</td>
<td>80</td>
</tr>
</tbody>
</table>

1) Bulk elemental value determined using ICP-AES.
2) (moles of dihydroxybenzenes formed after 6 hr (unless otherwise stated) of reaction / moles of H\(_2\)O\(_2\) added) * 100%.
3) moles of dihydroxybenzenes formed / moles of Ti present.
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TABLE 3.8. Phenol hydroxylation results TPOT and T1POT samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Ti1</th>
<th>H2O2 yield2</th>
<th>TON3</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPOT1</td>
<td>125</td>
<td>53 (4 hr)</td>
<td>2000</td>
</tr>
<tr>
<td>TPOT2a</td>
<td>90</td>
<td>13</td>
<td>350</td>
</tr>
<tr>
<td>TPOT2b</td>
<td>70</td>
<td>68</td>
<td>1400</td>
</tr>
<tr>
<td>TPOT2c</td>
<td>60</td>
<td>36 (3.5 hr)</td>
<td>650</td>
</tr>
<tr>
<td>TPOT3</td>
<td>20</td>
<td>8</td>
<td>50</td>
</tr>
<tr>
<td>TPOT4</td>
<td>7</td>
<td>41</td>
<td>100</td>
</tr>
<tr>
<td>T1POT</td>
<td>35</td>
<td>44</td>
<td>450</td>
</tr>
</tbody>
</table>

1) Bulk elemental value determined using ICP-AES.
2) (moles of dihydroxybenzenes formed after 6 hr (unless otherwise stated) of reaction / moles of H2O2 added) * 100%.
3) moles of dihydroxybenzenes formed / moles of Ti present.

TABLE 3.9. Phenol hydroxylation results prop samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Ti1</th>
<th>H2O2 yield2</th>
<th>TON3</th>
</tr>
</thead>
<tbody>
<tr>
<td>prop1</td>
<td>275</td>
<td>51 (3.5 hr)</td>
<td>4100</td>
</tr>
<tr>
<td>prop2</td>
<td>15</td>
<td>21</td>
<td>100</td>
</tr>
<tr>
<td>prop3</td>
<td>12</td>
<td>53</td>
<td>200</td>
</tr>
</tbody>
</table>

1) Bulk elemental value determined using ICP-AES.
2) (moles of dihydroxybenzenes formed after 6 hr (unless otherwise stated) of reaction / moles of H2O2 added) * 100%.
3) moles of dihydroxybenzenes formed / moles of Ti present.
TABLE 3.10. Phenol hydroxylation results IMP and EURO-TS-1 samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Ti sample(^1)</th>
<th>crystal size (μm)</th>
<th>H(_2)O(_2) yield(^2)</th>
<th>TON(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMP</td>
<td>80</td>
<td>5</td>
<td>31</td>
<td>725</td>
</tr>
<tr>
<td>Euro-TS-1</td>
<td>60</td>
<td>0.2</td>
<td>48</td>
<td>850</td>
</tr>
</tbody>
</table>

1) Bulk elemental value determined using ICP-AES.
2) (moles of dihydroxybenzenes formed after 6 hr of reaction / moles of H\(_2\)O\(_2\) added) * 100%.
3) moles of dihydroxybenzenes formed / moles of Ti present.

For all hydroxylation experiments, the ratio of the para- to ortho-products is much higher than the value of 1 reported in the literature.\(^4\) To calculate the H\(_2\)O\(_2\) yield, the amounts of para- and ortho-products were added up.

Generally, the lower the titanium content (the higher the Si/Ti ratio) of the samples, the higher the TON is per titanium site. This indicates that only small amounts of titanium incorporated into silicalite-1 are required to obtain catalytic activity. It is possible that for the samples with a higher titanium content, only part of the titanium participates in the catalytic reaction, in which case the part of the titanium which does participate in the catalytic reaction has a TON of the same order of magnitude as the titanium in samples with a low titanium content.

Concerning the samples obtained through different synthesis methods, apparently the performance in the hydroxylation of phenol is better for the prop and T\(^{OPT}\) samples than for the TEO\(_T\) and TP\(_T\) samples. This is in accordance with literature data,\(^2\) where especially the prop synthesis was reported to result in high-quality TS-1.

Figures 3.2 - 3.6 give the IR spectra of the samples, measured as KBr tablets.
Figure 3.2. IR spectra of a) TEOT1; b) TEOT2; c) TEOT3; d) TEOT4; e) TEOT5.
Figure 3.3. IR spectra of a) TPOT1; b) TPOT3; c) TPOT4.
Figure 3.4. IR spectra of a) TPOT2a; b) TPOT2b; c) TPOT2c.
Figure 3.5. IR spectrum of sample TiOPT.
Figure 3.6. IR spectra of a) prop1; b) prop2; c) prop3.
Table 3.11 lists the ratio of the 960 cm\(^{-1}\) IR band to the 550 cm\(^{-1}\) band for all samples. The ratio of the 960 cm\(^{-1}\) to the 550 cm\(^{-1}\) IR band is 0.405 for Euro-TS-1 and 0.390 for IMP.

**TABLE 3.11. 960/550 cm\(^{-1}\) IR band ratio.**

<table>
<thead>
<tr>
<th>Si/Ti sample</th>
<th>TEO T</th>
<th>TPO T</th>
<th>T(^1)PO T</th>
<th>prop</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.217</td>
<td>0.528</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.615</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td>0.910</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>0.864</td>
<td></td>
<td></td>
<td>0.814</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td></td>
<td></td>
<td>0.624</td>
</tr>
<tr>
<td>41</td>
<td>0.707</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>0.500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td>0.414</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.632</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>0.432</td>
<td></td>
<td></td>
</tr>
<tr>
<td>125</td>
<td></td>
<td>0.471</td>
<td></td>
<td></td>
</tr>
<tr>
<td>275</td>
<td></td>
<td></td>
<td></td>
<td>0.273</td>
</tr>
</tbody>
</table>

The 960 cm\(^{-1}\) IR band is said to be characteristic of tetrahedral framework titanium species\(^1\), whereas the IR band at 550 cm\(^{-1}\) is characteristic for the MFI structure. Thus, the ratio of these two bands should be an indication of the amount of titanium present in the samples. However, although the amount of titanium present in the samples depends on the amount of titanium present in the synthesis gel (see Fig. 3.1), the ratio between the 960 and 550 cm\(^{-1}\) IR bands does not show a dependence on the amount of titanium present in the samples. This means that
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either the 960 cm\(^{-1}\) band is not directly related to tetrahedral framework titanium, or
that only part of the titanium in our samples is present as tetrahedral framework
species. Apparently, there is no relation between the 960 / 550 cm\(^{-1}\) IR band ratio
and the catalytic performance of the samples.

3.4. CONCLUSIONS

The synthesis of TS-1 in OH\(^{-}\) medium is indeed improved by the addition of
isopropanol as a solvent during the preparation of the synthesis gel, as was
reported by Thangaraj and Srivasanker.\(^2\) Although the titanium content of the
samples of TS-1 depends on the titanium content of the synthesis gel, in general
the titanium content of the TS-1 is higher than that of the synthesis gel. There is no
relation between the titanium content of the samples of TS-1 and their 960 / 550
cm\(^{-1}\) IR band ratio, nor is there a relation between the catalytic performance of the
samples in the hydroxylation of phenol and the 960 / 550 cm\(^{-1}\) IR band ratio.
Generally, the lower the titanium content of the samples, the higher the TON is per
titanium site.

3.5. REFERENCES

   123.
4) B. Notari, in: Chemistry of microporous crystals, eds. T. Inui, S. Namba and
CHAPTER 4

TITANIUM INCORPORATED INTO ZEOLITES AND SILICAS FROM TiF₃

4.1. INTRODUCTION

In this chapter, systems obtained through direct synthesis of TS-1 in a fluoride medium, as well as through the deposition of Ti from TiF₃ on various zeolites and silicas are discussed.

Zeolites are usually synthesised in a strongly basic environment, where OH⁻-ions are the mobilising agent for the anionic silicate and aluminate species that form the zeolite structure. However, Guth et al.¹,² have synthesised zeolites and boron-containing silicates by using F⁻-ions as the mobilising agent. The advantage of this synthesis method is the possibility to work at moderate or even low pH. In this study a titanium-containing silicalite, TS-1, was synthesised by using F⁻ as the mobilising agent and TiF₃ as the titanium source. Although titanium is mentioned by Guth et al.,² hardly any data on the exact synthesis conditions, characterisation and catalytic properties of the materials are given. TiF₃ was chosen as the titanium source, because it is one of the few titanium compounds that do not react immediately with water to form the highly stable TiO₂, which is incorporated into the zeolite framework only with great difficulty.

This chapter also reports on the preparation and catalytic properties of materials obtained by surface treatment of various zeolites and silicas with TiF₃ in the liquid phase and in the presence of HF.

4.2. EXPERIMENTAL

Synthesis

The synthesis of the sample denoted as TS-1-F was performed analogous to that described by Guth et al.¹ for aluminium-containing silicalite. Thus, 21.92 g of
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SiO₂ (Degussa Aerosil 200), 2.04 g of NH₄F·HF, 11.64 g of TPABr (tetrapropylammonium bromide) and 213.6 g of H₂O were stirred together until a homogeneous mixture resulted (24 to 60 hrs). Then the TiF₃ was added, and after a further 1 to 2 hrs of stirring the mixture was autoclaved at 180°C for 23 days, yielding almost 20 g of crystals. To remove incorporated TPA, the crystals were calcined at 400°C for 3 days.

For comparison, a sample denoted as TS-1-OH was prepared according to a procedure described in the patent literature.³ The details of this synthesis method are described in chapter 3 of this thesis, where this material is denoted as sample "IMP".

Samples of various zeolites and silicas (both crystalline and amorphous) were treated with TiF₃ in the following manner: First, a solution was made by dissolving 0.5 g TiF₃ in 0.2 g of 40% HF and 10 ml of water at 60°C. When all the TiF₃ had been dissolved, another 50 ml of water was added, resulting in solution "A". Then, 0.5 g of the zeolite or silica was autoclaved for 90 min at 180°C with 0.25 to 5.0 ml of this solution and an amount of water to obtain a total liquid volume of 25 ml. After cooling to room temperature, the samples were filtrated, washed thoroughly with water and dried overnight at 120°C. These samples will be denoted as stated in Table 4.1.

Characterisation

The samples were characterised using several physico-chemical characterisation methods, which are described in detail in chapter 2 of this thesis.

The catalytic activity of the samples for the hydroxylation of phenol was tested, following the procedure described in chapter 2 of this thesis, using 10 g of phenol, 32 g of methanol (as a solvent), 1 g of internal standard, 5.0 ml of 35% aqueous hydrogen peroxide and 100 mg of catalyst. The reaction temperature was about 80°C.

The catalytic activity for the oxyfunctionalisation of n-hexane was tested in
stirred, Teflon-lined autoclaves of 25 ml total volume, in which 10 ml of methanol (as a solvent), 1.0 ml of n-hexane, 0.80 ml of 30% aqueous hydrogen peroxide and 20 mg of catalyst were mixed together before placing the autoclave in a pre-heated oven at 100°C. At the desired reaction time, the autoclave was taken out of the oven and cooled to room temperature quickly by placing it in a strong flow of air. After filtration of the catalyst, hydrogen peroxide conversion was determined using standard iodometric titration, and products were determined using GC analysis of a portion of the homogeneous reaction mixture, to which toluene had been added as a GC standard.

TABLE 4.1. Notation of TiF₃/HF treated samples

<table>
<thead>
<tr>
<th>notation</th>
<th>sample description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti/S-1</td>
<td>Solution &quot;A&quot; treated silicalite-1, synthesised in F⁻ medium</td>
</tr>
<tr>
<td>Ti/CRI</td>
<td>Solution &quot;A&quot; treated cristobalite, M006 SCR Sibelico</td>
</tr>
<tr>
<td>Ti/CFU</td>
<td>Solution &quot;A&quot; treated amorphous silica, Chromatografiegel type C-569, Chemische Fabrik Uetikon</td>
</tr>
<tr>
<td>Ti/Sh</td>
<td>Solution &quot;A&quot; treated amorphous silica spheres, diameter ca 2 mm, Shell</td>
</tr>
<tr>
<td>Ti/Y</td>
<td>Solution &quot;A&quot; treated zeolite H-Y, obtained from AKZO, Si/Al = 2.5</td>
</tr>
<tr>
<td>Ti/BEA</td>
<td>Solution &quot;A&quot; treated zeolite H-Beta, obtained from Exxon, Si/Al = 35</td>
</tr>
<tr>
<td>Ti/MFI</td>
<td>Solution &quot;A&quot; treated zeolite H-ZSM-5, synthesised according to the method described by Argauer and Landolt,⁴ Si/Al = 22</td>
</tr>
</tbody>
</table>
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4.3. RESULTS AND DISCUSSION

Characterisation

**TS-1-OH:** The X-ray diffractogram of this zeolite confirms the structure to be that of silicalite-1 (all-silica MFI). The IR spectrum of this zeolite shows an absorption band to be present at 960 cm\(^{-1}\). This band is said to be indicative of Ti incorporated into the zeolite framework. Furthermore, it is said that this band is necessary to obtain catalytic activity in selective oxidation reactions with aqueous hydrogen peroxide. However, we have shown that this is not the case,\(^5\) and that materials containing Ti and SiO\(_2\) can show good catalytic properties for selective oxidation reactions with aqueous hydrogen peroxide without showing the IR absorption band at 960 cm\(^{-1}\).

Figure 4.1. SEM micrographs of TS-1-F (left, enlargement 2400 times) and Ti/S-1_A, (right, enlargement 2000 times, see table 4.2).

**TS-1-F:** SEM micrographs (Fig. 4.1) show the TS-1-F to consist of well-formed elongated prismatic crystals, covered with small particles. The crystals are about
35 \mu m long, the diameter of the particles is about 1 \mu m.

Powder X-ray diffraction does not show any extra lines in the pattern as compared to that of ordinary silicalite. The IR spectrum does not show an absorption band at 960 cm\(^{-1}\). EDX measurements show the small particles to contain Ti, whereas using this method, no Ti is detected on the remaining part of the external surface of the crystals. This can be seen clearly from Figure 4.2, which shows the EDX line-scan titanium signal across the indicated line.

![Figure 4.2. SEM micrograph of TS-1-F and EDX line-scan, Ti signal, measured along the indicated line.](image)

The BET surface area of the TS-1-F is 405 m\(^2\)/g and the pore volume 90 ml*NTP/g. For silicalite-1 these values are 425 and 95, respectively, indicating that
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neither the small particles on the external surface, nor any other surface or pore
mouth deposits are blocking the pores of the zeolite strucuture. In the Raman
spectrum of this sample (shown in Fig. 4.3), apart from the silicalite bands also a
weak and broad band at 970 cm\(^{-1}\) is observed, characteristic of homogeneously
distributed TiO\(_x\).\(^6\) Additionally, bands at 636 and 514 cm\(^{-1}\) show that part of the
titanium is present as anatase.

Ti/S-1: As can be seen from SEM micrographs (Fig. 4.1) the silicalite, syn-
thesised in F\(^-\) medium and (after calcination to remove the template) treated with
TiF\(_3\)/HF, is covered with small particles, which seem to be similar to those found
on TS-1-F. Neither the X-ray diffractogram nor the IR spectrum show differences
before and after TiF\(_3\)/HF treatment. For these samples also, according to EDX
measurements, the Ti seems to be concentrated in the small particles on the
external surface. It cannot be excluded that additional Ti is present on the surface,
formed for example by reaction of surface SiOH groups with TiF\(_3\). The BET
surface area and the pore volume for this sample are 405 m\(^2\)/g and 91 ml \(\!*\)
NTP/g, respectively. These values correspond with those for the untreated
silicalite-1 (425 m\(^2\)/g and 90 ml \(\!*\) NTP/g), indicating that pore-blocking does not
occur upon TiF\(_3\)/HF treatment. The Raman spectrum of a sample of Ti/S-1 is
shown in Figure 4.3. This spectrum indicates that anatase is formed. Due to the
many small peaks in the region 1100 - 900 cm\(^{-1}\), it cannot be concluded whether
or not also homogeneously distributed TiO\(_x\) is present.

Considering the formation of these particles in direct synthesis using TiF\(_3\) as
well as in post-synthesis treatment of silicalite-1 with TiF\(_3\)/HF, we think they might
be formed during the cooling of the autoclave before the sample is isolated, when
the remaining dissolved Ti is deposited, most probably as TiO\(_2\). In the direct
synthesis there are probably several kinds of Ti-incorporation mechanisms. In one
of these, Ti is incorporated in the zeolite crystals during crystal growth, possibly
as T-atoms. Then, probably during the cooling period of the autoclave before the
crystals are isolated, Ti that is still present in solution is deposited on the external
Figure 4.3. Raman spectra of a) silicalite-1; b) TS-1-F; c) Ti/S-1.
surface of the crystals. Although we cannot detect it with EDX analysis, we cannot exclude that a TiO$_x$ structure similar to one or a few monolayers is formed on the silicalite crystal surface in between the TiO$_2$ particles. Possibly these mechanisms all operate simultaneously.

In the post-synthesis treatment with TiF$_3$/HF, apart from the external deposition of TiO$_x$ as described above, it might also be possible to titanate the internal surface of the zeolite channels, for example by reaction with silanol groups.

Figure 4.4. Raman spectra of a) SiO$_2$ CFU; b) Ti/CFU.

While this work was in progress, Sulikowski and Klinowski\textsuperscript{7} published a paper on a similar F$^-$ TS-1 synthesis, using rutile or anatase (TiO$_2$) dissolved in concentrated (40%) HF as the titanium source. Although the authors don't comment on
it, the well-formed elongated prismatic crystals of their samples are also covered with small particles, very similar to those we find. With X-ray diffraction, traces of "unreacted" rutile or anatase are detected. However, this might also include TiO₂ which was deposited as proposed above.

**Ti/CRI and Ti/CFU:** Neither SEM, IR nor XRD show changes before and after treatment with TiF₃/HF for these two sets of samples. The Raman spectra of the amorphous silica CFU and of a sample of Ti/CFU are depicted in Figure 4.4. The sample of Ti/CFU contains small amounts of anatase and of homogeneously distributed TiOₓ.

![Graph](image)

**Figure 4.5.** Relation between the amount of solution "A" added to the silicas and the amount of Ti found in the samples.
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Ti/Sh: Because of the size of the silica spheres (diameter about 2 mm) and the unknown influence of grinding, no XRD or IR data were obtained. With SEM no changes could be detected before and after TiF₃/HF treatment. According to ICP analysis, these silica spheres do not contain titanium prior to TiF₃/HF treatment.

Although all the TiF₃/HF treated SiO₂ samples contain titanium (see Table 4.2 and Fig. 4.5), with SEM no particles were observed on the external surface of the CFU, CRI and Sh samples. However, we have shown that upon treating amorphous silica (CFU) as well as silicalite-1 in the gas-phase at 450°C with TiCl₄, titanium-containing particles are formed on the external surface of the samples.⁵

![Graph](image)

Figure 4.6. Relation between the amount of solution "A" added to the zeolites and the amount of Ti found in the samples.

From the Raman spectra available (Figs. 4.3 and 4.4), it can be concluded that apart from a homogeneously distributed TiOₓ phase, also anatase is present in

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the TiF$_3$/HF-treated samples discussed so far. The particles of anatase on the solution "A" treated samples are probably too small to be detected using XRD, IR and even SEM in some cases.

**Ti/Y and Ti/Beta:** The IR spectra of these zeolites before and after TiF$_3$/HF treatment are identical, as are the XRD diffractograms. Due to the very small particle sizes of these samples, no conclusive SEM data could be obtained.

**Ti/MFI:** The IR spectra of these samples do not show any differences before and after TiF$_3$/HF treatment. Neither do the X-ray diffractograms or the SEM micrographs. However, elemental analysis (see Table 4.3 and Fig. 4.7) shows that the more of solution "A" is added, the more the MFI dealuminates. Also, the treatment of the MFI with diluted HF only (see Table 4.3) results in some dealumination.

![Graph](image)

Figure 4.7. Relation between the amount of solution "A" added to the zeolites and the amount of Al found in the samples.
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As can be seen from Figure 4.6, the amount of Ti present in the samples depends linearly on the amount of solution "A" that was added to the samples, except for zeolite Y. Strikingly, all the zeolites studied here (Beta, Y and ZSM-5) are dealuminated upon TiF₃/HF treatment. The more of solution "A" is added to 0.5 g of these zeolites, the more aluminium is extracted (see also Table 4.3). This can be seen clearly from Figure 4.7.

Catalysis

Hydroxylation of phenol

The results obtained in the phenol hydroxylation experiments are summarised in Tables 4.2 and 4.3. As can be seen, all the titanated samples, as well as both direct synthesis samples, show catalytic activity for the hydroxylation of phenol with aqueous hydrogen peroxide. Most measurements show good reproducibility. Included in Table 4.3 are the results obtained when using the non-titanated zeolites as catalysts, as well as data for the zeolites that were treated with diluted HF (ie solution "A" but without the TiF₃): 5 ml of diluted HF and 20 ml water were autoclaved with 0.5 g of zeolite at 180°C for 90 min, when only slight dealumination of the materials is observed. The zeolites are dealuminated to a higher extent when not only diluted HF but also TiF₃ is present, indicating some kind of interaction between the zeolitic framework and the TiF₃/HF solution.

Both samples obtained through direct synthesis (TS-1-OH and TS-1-F) show good activity and efficiency. As can be seen, many of the titanated silica samples show comparable activities and efficiencies. The samples of zeolite Y and some of the BEA samples show very high H₂O₂ conversion rates, and some of them also show a high efficiency. There does not really seem to be a relation between the amount of Ti present in the samples and the catalytic properties for this reaction.
TABLE 4.2. Hydroxylation of phenol. Direct synthesis and TiF$_3$/HF treated silica samples, data after 6 hr of reaction.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Ti$^1$</th>
<th>H$_2$O$_2$ conv$^2$</th>
<th>efficiency$^3$</th>
<th>TON$^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-1-OH</td>
<td>80</td>
<td>56</td>
<td>55</td>
<td>725</td>
</tr>
<tr>
<td>TS-1-F</td>
<td>70</td>
<td>39</td>
<td>47</td>
<td>375</td>
</tr>
<tr>
<td>Ti/S-1_A</td>
<td>21</td>
<td>39</td>
<td>24</td>
<td>60</td>
</tr>
<tr>
<td>Ti/S-1_B</td>
<td>95</td>
<td>24</td>
<td>16</td>
<td>100</td>
</tr>
<tr>
<td>Ti/S-1_C</td>
<td>360</td>
<td>56</td>
<td>42</td>
<td>2500</td>
</tr>
<tr>
<td>Ti/CRI_A</td>
<td>37</td>
<td>27</td>
<td>40</td>
<td>125</td>
</tr>
<tr>
<td>Ti/CRI_B</td>
<td>145</td>
<td>14</td>
<td>46</td>
<td>275</td>
</tr>
<tr>
<td>Ti/CRI_C</td>
<td>850</td>
<td>27</td>
<td>11</td>
<td>725</td>
</tr>
<tr>
<td>Ti/CFU_A</td>
<td>88</td>
<td>43</td>
<td>53</td>
<td>600</td>
</tr>
<tr>
<td>Ti/CFU_B</td>
<td>220</td>
<td>43</td>
<td>48</td>
<td>1300</td>
</tr>
<tr>
<td>Ti/CFU_C</td>
<td>625</td>
<td>43</td>
<td>47</td>
<td>3700</td>
</tr>
<tr>
<td>Ti/CFU_D</td>
<td>900</td>
<td>88</td>
<td>77</td>
<td>17800</td>
</tr>
<tr>
<td>Ti/CFU_E</td>
<td>1500</td>
<td>82</td>
<td>39</td>
<td>1100</td>
</tr>
<tr>
<td>Ti/Sh_A</td>
<td>84</td>
<td>78</td>
<td>53</td>
<td>1000</td>
</tr>
<tr>
<td>Ti/Sh_B</td>
<td>280</td>
<td>26</td>
<td>37</td>
<td>800</td>
</tr>
<tr>
<td>Ti/Sh_C</td>
<td>900</td>
<td>76</td>
<td>41</td>
<td>8200</td>
</tr>
</tbody>
</table>

1) bulk molar ratio as determined by ICP-AES.
2) % H$_2$O$_2$ converted after 6 hours of reaction.
3) (mole dihydroxybenzenes formed / mole H$_2$O$_2$ converted) * 100%.
4) mole dihydroxybenzenes formed / mole Ti present.
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TABLE 4.3. Hydroxylation of phenol. TiF₃/HF treated zeolites, data after 6 hr of reaction.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Al ¹</th>
<th>Si/Ti ¹</th>
<th>Si/(Al+Ti) ¹</th>
<th>H₂O₂ conv ²</th>
<th>eff³</th>
<th>TON Ti⁴</th>
<th>TON Ti+Al⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>2.3</td>
<td>-</td>
<td>2.5</td>
<td>98 (2 hr)</td>
<td>42</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>HF/Y</td>
<td>2.2</td>
<td>-</td>
<td>2.2</td>
<td>9</td>
<td>8</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>Ti/Y_A</td>
<td>2.7</td>
<td>12</td>
<td>2.2</td>
<td>94 (4 hr)</td>
<td>55</td>
<td>250</td>
<td>50</td>
</tr>
<tr>
<td>Ti/Y_B</td>
<td>2.4</td>
<td>43</td>
<td>2.3</td>
<td>47</td>
<td>46</td>
<td>400</td>
<td>20</td>
</tr>
<tr>
<td>Ti/Y_C</td>
<td>2.8</td>
<td>165</td>
<td>2.8</td>
<td>96 (3 hr)</td>
<td>32</td>
<td>2000</td>
<td>30</td>
</tr>
<tr>
<td>Ti/Y_D</td>
<td>2.3</td>
<td>600</td>
<td>2.3</td>
<td>97 (3 hr)</td>
<td>35</td>
<td>8500</td>
<td>30</td>
</tr>
<tr>
<td>Ti/Y_E</td>
<td>2.3</td>
<td>725</td>
<td>2.3</td>
<td>97 (3 hr)</td>
<td>35</td>
<td>10300</td>
<td>30</td>
</tr>
<tr>
<td>BEA</td>
<td>35</td>
<td>-</td>
<td>35</td>
<td>96</td>
<td>21</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td>HF/BEA</td>
<td>46</td>
<td>-</td>
<td>46</td>
<td>13</td>
<td>9</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>Ti/BEA_A</td>
<td>120</td>
<td>49</td>
<td>35</td>
<td>72</td>
<td>23</td>
<td>250</td>
<td>175</td>
</tr>
<tr>
<td>Ti/BEA_B</td>
<td>77</td>
<td>n.d.</td>
<td>(&lt;77)</td>
<td>52</td>
<td>53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti/BEA_C</td>
<td>46</td>
<td>320</td>
<td>40</td>
<td>64</td>
<td>52</td>
<td>3200</td>
<td>400</td>
</tr>
<tr>
<td>Ti/BEA_D</td>
<td>37</td>
<td>550</td>
<td>35</td>
<td>96</td>
<td>38</td>
<td>6000</td>
<td>375</td>
</tr>
<tr>
<td>Ti/BEA_E</td>
<td>34</td>
<td>650</td>
<td>32</td>
<td>67</td>
<td>38</td>
<td>5000</td>
<td>250</td>
</tr>
<tr>
<td>MFI</td>
<td>22</td>
<td>-</td>
<td>22</td>
<td>26</td>
<td>5</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>HF/MFI</td>
<td>29</td>
<td>-</td>
<td>29</td>
<td>20</td>
<td>2</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Ti/MFI_A</td>
<td>38</td>
<td>63</td>
<td>24</td>
<td>10</td>
<td>4</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Ti/MFI_B</td>
<td>28</td>
<td>93</td>
<td>22</td>
<td>21</td>
<td>1</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Ti/MFI_C</td>
<td>24</td>
<td>130</td>
<td>20</td>
<td>16</td>
<td>3</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>Ti/MFI_D</td>
<td>25</td>
<td>350</td>
<td>23</td>
<td>31</td>
<td>1</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>Ti/MFI_E</td>
<td>21</td>
<td>600</td>
<td>20</td>
<td>19</td>
<td>3</td>
<td>100</td>
<td>3</td>
</tr>
</tbody>
</table>

1) bulk molar ratio as determined by ICP-AES; n.d. = not determined.
2) % H₂O₂ converted after 6 hours of reaction.
3) (mole dihydroxybenzenes formed / mole H₂O₂ converted) * 100%.
4) mole dihydroxybenzenes formed / mole Ti present.
5) mole dihydroxybenzenes formed / mole Ti + mole Al present.
For samples with Ti-containing particles on the external surface this is to be expected, because not all the Ti present in these particles is exposed to the reaction mixture. Although a general trend seems to be that a decreasing amount of Ti present in the samples gives rise to a lower activity and efficiency, the samples with a low Ti content (a high Si/Ti ratio) show a surprisingly high activity, with TON as high as 18000 molecules of product formed per titanium site. This indicates that only very small quantities of Ti connected to Si are required to catalyse this reaction. Blank hydroxylation experiments using the non-titanated silicas or TiO$_2$ show that none of these materials has significant activity. However, the non-titanated aluminium-containing zeolites do show some (MFI), modest (BEA) or high (Y) activity with low (MFI), modest (BEA) or high (Y) efficiency. The activity of these samples is due to the acidic sites, that is H$^+$ ions as charge-balancing cations. Although the general opinion is that bulk TiO$_2$ can only decompose hydrogen peroxide without using it for selective oxidation reactions, recently Popa et al.$^8$ applied for a patent for the preparation of high-surface TiO$_2$ (100 - 300 m$^2$/g) and its use in the hydroxylation of phenol with aqueous hydrogen peroxide. For the catalytic reaction, high activities are claimed (up to 90% hydrogen peroxide conversion) accompanied by moderate selectivities (up to 40%). It is possible that, by coating a silica carrier with TiO$_x$ as described above, a similar high-surface species is prepared which accounts for at least part of the catalytic activities observed.

Oxyfunctionalisation of n-hexane

Table 4.4 gives some results obtained regarding the oxyfunctionalisation of n-hexane using the samples of TS-1 obtained through direct synthesis. More detailed data on this reaction, using both conventional and microwave heating techniques, can be found in chapter 7 of this thesis.
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TABLE 4.4. Oxyfunctionalisation of n-hexane.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Ti$^1$</th>
<th>$\text{H}_2\text{O}_2 \text{ conv}^2$</th>
<th>2-hexanol$^3$</th>
<th>3-hexanol$^3$</th>
<th>2-hexanone$^3$</th>
<th>3-hexanone$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-1-OH</td>
<td>80</td>
<td>100</td>
<td>12.6</td>
<td>6.5</td>
<td>14.2</td>
<td>2.1</td>
</tr>
<tr>
<td>TS-1-F</td>
<td>70</td>
<td>81</td>
<td>5.3</td>
<td>1.3</td>
<td>1.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

1) bulk molar ratio as determined by ICP-AES.
2) % $\text{H}_2\text{O}_2$ converted after 24 hours of reaction.
3) % product formed/ $\text{H}_2\text{O}_2$ converted; corrected by factor 2 for 2- and 3-hexanone.

It seems that the systems obtained through post-synthesis treatment with TiF$_3$/HF do not give products, although some $\text{H}_2\text{O}_2$ conversion is measured (usually 5 - 15%). As the TS-1-OH shows a much better activity and efficiency for this reaction than the TS-1-F, which certainly contains some extra-framework Ti (in the particles on the external surface) and probably some framework Ti, the oxyfunctionalisation of n-hexane might be a better test reaction for these kind of systems than is the hydroxylation of phenol.

4.4. CONCLUSIONS

Using simple titanation methods to synthesise samples containing both SiO$_2$ and Ti, materials can be produced that are active and selective catalysts in the hydroxylation of phenol with aqueous hydrogen peroxide. However, to characterise TS-1 and related systems for their catalytic activity in selective oxidation reactions using aqueous hydrogen peroxide as the oxidising agent, the oxyfunctionalisation of n-hexane is a better test reaction than the hydroxylation of phenol.
4.5. ACKNOWLEDGMENTS

The authors would like to thank Mrs. C. Ferrini, ETH Zürich, Switzerland, for synthesising the TS-1-OH, and Mrs. F. van Looij, RU Utrecht, The Netherlands, for the EDX measurements. Dr. B. Sulikowski, Polish Academy of Sciences, Krakow, Poland, is gratefully acknowledged for measuring the Raman spectra and helping out with their interpretation.

4.6. REFERENCES


CHAPTER 5

TITANIUM INCORPORATED INTO ZEOLITES AND SILICAS FROM TiCl₄

5.1 INTRODUCTION

Kraushaar and van Hooff¹ reported that TS-1 can be synthesised by titanation of
dealuminated MFI. These authors report that ordinary aluminium-containing MFI
can be dealuminated by three-fold treatment with 1 N aqueous hydrochloric acid at
80°C. Thus, the Si/Al ratio of their material increases from 50 to 2000. The dealumi-
nated MFI is subsequently treated with TiCl₄ vapour at 400 - 500°C, and it is
claimed that titanium is incorporated into T-sites that have been vacated by
aluminium. The authors report that the infrared spectrum of the titanated material
shows the absorption band at 970 cm⁻¹, which is supposed to be indicative of
titanium incorporation,² and an increase of the unit cell parameters, measured
using powder X-ray diffraction, due to the Si-O-Ti bond length being greater than
the Si-O-Al and Si-O-Si bond lengths. In another paper,³ the same authors report
that the catalytic hydroxylation of phenol with aqueous hydrogen peroxide is a
suitable test reaction for titanium-containing zeolites: if extra-framework titanium
dioxide is present, mainly tarry by-products and hardly any dihydroxybenzenes are
formed. However, recently Popa et al.⁴ applied for a patent, claiming the selective
hydroxylation of phenol to dihydroxybenzenes with aqueous hydrogen peroxide,
using high-surface TiO₂ as the catalyst.

Apart from TS-1, other titanium-containing SiO₂ systems are known to be good
catalysts for selective oxidation reactions,⁵ mainly epoxidation reactions using
organic hydroperoxides as the oxidising agent. In a commercial process, viz. the
epoxidation of propene with phenylethyl hydroperoxide, a titanium-on-amorphous-
silica serves as the catalyst. High selectivity and hydroperoxide efficiency have
been reported. It seemed worthwhile to establish whether this type of catalyst is
also able to catalyse selective oxidation reactions using aqueous hydrogen perox-
ide as the oxidising agent. Moreover, the question arises whether crystalline silica
might induce special catalytic oxidation properties in supported titanium species.
Chapter 5

In this chapter, the synthesis method for TS-1 as described by Kraushaar and van Hooff, through gas-phase TiCl$_4$ treatment of dealuminated ZSM-5, is investigated. Not only "dealuminated" ZSM-5 and silicalite-1, but also other zeolites and amorphous silica are treated with TiCl$_4$ in the gas-phase. However, our samples of ZSM-5 did not dealuminate as easily as those of Kraushaar and van Hooff, see chapter 6 of this thesis. Also, silicalite-1 and amorphous silica are treated with TiCl$_4$ in n-heptane solution, as described for a commercial titanium-on-amorphous-silica catalyst. The resulting materials are characterised using several physico-chemical characterisation techniques, as well as the hydroxylation of phenol with aqueous hydrogen peroxide as a catalytic test reaction.

5.2 EXPERIMENTAL

When synthesised using an organic templating agent, the zeolitic materials were calcined in air at least 500°C for at least 8 hr prior to TiCl$_4$ treatment, to remove incorporated organic material.

![Scheme 5.1. The gas-phase reactor. 1) Source of N$_2$; 2) mass-flow-controller; 3) drying unit; 4) recoilvessel; 5) saturator with TiCl$_4$; 6) bypass; 7) titanium reactor tube; 8) fluid-bed oven; 9) temperature controller with thermocouple; 10) recoilvessel; 11) vessel with NaOH solution.](image)

Gas-phase TiCl$_4$ treatment

1 g of zeolite or silica was loaded into a titanium reactor tube, with a diameter of 1 cm. The reactor tube (7 in scheme 5.1) was inserted into the fluid-bed oven (6) and dry nitrogen gas was led through the reactor continuously at 30 ml/min. First
the flow of nitrogen was led through the bypass (5) and the reactor was heated to 450°C with a rate of 1°/min. To remove adsorbed water, the reactor temperature was kept at 450°C for at least 6 hr before the nitrogen was led through the saturator (4) filled with TiCl₄. The saturator was kept at room temperature. The flow of TiCl₄/N₂ was usually led through the reactor for two hours at 450°C. To remove excess TiCl₄, the reactor was flushed for two hours with pure nitrogen at the reaction temperature before cooling down slowly to room temperature. The flow of nitrogen was not switched off before the reactor had cooled down completely. The samples did not undergo any further treatment, but were stored in air.

Liquid-phase TiCl₄ treatment

This method was only performed using aluminium-free samples: silicalite-1 and amorphous silica, following the method described for the preparation of a commercial catalyst.⁵ The zeolite or silica was refluxed in n-heptane (about 100 ml per gram of sample) at around 95°C until all the water present had been removed azeotropically. Then the TiCl₄ was added as a solution in n-heptane, and the mixture was refluxed overnight. Water (5 - 10 ml) was added and the mixture was refluxed until no more HCl gas evolved. The n-heptane was evaporated or decanted, and the sample was washed with water, dried in air at 120°C and usually calcined in air at 500°C.

Materials

The material denoted as SiO₂ is an amorphous silica for chromatography, type C-569, BET surface area 450 m²/g, obtained from Chemische Fabrik Uetikon, Switzerland.

Silicalite-1 (aluminium-free MFI) was synthesised in our laboratory according to various synthesis procedures. Materials denoted as SSG were synthesised according to a method described by Sand and Ghamami.⁶ Thus, solution "A" was prepared by mixing 209 g of Ludox HS-40 silica sol, 185 g of 25 wt% aqueous NH₃ and 100 g of water. Solution "B" was prepared by mixing 31.5 g of tetrapropylammonium bromide, 100 g of water and 75 g of 25 wt% aqueous NH₃. Solutions A and B were combined under vigorous stirring, and the resulting gel was placed in a
Chapter 5

Teflon-lined stainless steel autoclave after overnight stirring. The autoclave was placed in a pre-heated oven at 170°C for one week. The crystals were separated from the mother liquor by filtration, washed thoroughly with water, dried in air at 120°C and calcined in air at 500°C. Materials denoted as SGK were synthesised according to a method described by Guth et al. for aluminium-containing MFI, by omitting the aluminium addition step. Thus, 22 g of Aerosil 200 fumed silica, 2 g of NH₄F.HF, 12 g of tetrapropylammonium bromide and 215 g of water were stirred together until a homogeneous mixture resulted (usually 2 - 4 days). The synthesis mixture was placed in a Teflon-lined stainless steel autoclave at 175°C for three weeks. The crystals were filtrated, washed thoroughly with water, dried in air at 120°C and calcined in air at 500°C.

Samples of zeolite MFI (ZSM-5) were synthesised in our laboratory according to the method described by Argaer and Landolt. A solution "A" was prepared by dissolving 40.1 g Aerosil 200 (amorphous SiO₂) in 209.5 g 40% TPAOH in water. To obtain a solution, it is necessary to heat the mixture to about 100°C under stirring. Solution "B" was obtained by dissolving the appropriate amount of NaAlO₂ in 72.3 g water, and was stirred into solution "A". The resulting gel was autoclaved at 150°C for six days.

Zeolites H-Y and H-BEA were obtained from Akzo and Exxon, respectively.

A sample of TS-1, synthesised by direct synthesis using OH⁻ as the mineralising agent, was prepared according to a procedure described by Padovan et al. in the patent literature. See chapter 3 of this thesis for a detailed description of this synthesis (sample IMP).

Phenol hydroxylation

The hydroxylation of phenol was performed as described in detail in chapter 2 of this thesis, using 100 mg of catalyst, 10 g of phenol, 5.0 ml of 30% aqueous H₂O₂, 32 g of methanol as a solvent and 1 g of pentafluorobenzoic acid as internal standard. The reaction was performed at reflux, about 80°C.
5.3 RESULTS AND DISCUSSION

Ti/SiO\textsubscript{2} samples

Using SEM, XRD and IR, no changes in the SiO\textsubscript{2} samples could be detected before and after treatment with TiCl\textsubscript{4} in n-heptane. With EDX analysis, no titanium could be detected on the external surface of these Ti/SiO\textsubscript{2}\textsuperscript{lq} samples. This indicates that the titanium, which is detected with ICP-AES analysis (bulk chemical analysis) is distributed homogeneously on the external surface of the samples, at least within the detection limits of the characterisation methods employed.

![Raman spectra](image)

Figure 5.1. The Raman spectra of a) SiO\textsubscript{2}; b) Ti/SiO\textsubscript{2}\textsuperscript{lq}, Si/Ti = 16.

The Raman spectrum of a sample of Ti/SiO\textsubscript{2}\textsuperscript{lq} with Si/Ti = 16 is shown in Figure 5.1, together with the spectrum of the SiO\textsubscript{2}. From the Raman spectrum it can be concluded that the sample of Ti/SiO\textsubscript{2}\textsuperscript{lq} contains small amounts of anatase (shoulders at 638, 512 and 399 cm\textsuperscript{-1}), rutile (peaks at 614 and 451 cm\textsuperscript{-1}) and homogeneously distributed titanium (broad peak at 965 cm\textsuperscript{-1}).
Figure 5.2. UV-Vis spectra of a) SiO$_2$; b) Ti/SiO$_2$$_{aq}$, Si/Ti = 130; c) Ti/SiO$_2$$_{aq}$, Si/Ti = 16.

Figure 5.3. SEM pictures of Ti/SiO$_2$$_{aq}$ (left, enlargement 600 times) and Ti/S-1$_{aq}$ (right, enlargement 300 times).
Figure 5.2 shows the DRS UV-Vis spectra of SiO$_2$ and of two samples of Ti/-SiO$_2$$_4^{1,4}$ with Si/Ti ratios of 130 and 16. These spectra show that in the sample with the lowest amount of titanium present, the titanium is distributed homogeneously without the formation of bulk TiO$_2$, whereas the titanium-rich sample does contain bulk TiO$_2$, as can be deduced from the absorption edge of this sample starting at about 30,500 cm$^{-1}$.

However, the anatase and rutile particles are too small to be detected by XRD, SEM or EDX. For the liquid-phase TiCl$_4$-treated samples with higher Si/Ti ratios (containing less titanium) it is very likely that most of the titanium is present as homogeneously distributed TiO$_x$ species on the external surface of the samples.

The gas-phase treated SiO$_2$ samples show small particles to be present on their external surface (see Fig. 5.3). Although they could not be detected using XRD, these particles seem to be crystalline.

![UV-Vis spectra](image)

**Figure 5.4.** UV-Vis spectra of a) SiO$_2$; b) Ti/SiO$_2$.

The IR spectra do not show any differences between the TiCl$_4$-treated SiO$_2$ and the starting material SiO$_2$ either. With EDX analysis, it can be seen that titanium is
Chapter 5

concentrated in these particles. The DRS UV-Vis spectra of SiO$_2$ and of a sample of Ti/SiO$_2^{\,g}$ (Si/Ti = 16) (shown in Fig. 5.4) indicate that the gas-phase TiCl$_4$-treated sample does contain bulk TiO$_2$.

![UV-Vis spectra graph](image)

Figure 5.5. UV-Vis spectra of a) silicalite-1; b) Ti/S-1$^{\,g}$; c) Ti/S-1$^{\,l}$. 

Ti/S-1 samples

SEM examination of the Ti/S-1$^{\,g}$ samples, obtained from silicalite-1 treated with gaseous TiCl$_4$ at 450°C, shows small particles to be present on the external surface of the silicalite crystals (see Fig. 5.3), similar to those observed on the Ti/SiO$_2^{\,g}$ samples. Although these particles seem to be crystalline, they could not be detected using XRD: the X-ray diffractogram of silicalite-1 is identical to that of the Ti/S-1$^{\,g}$ samples. The IR spectra of the samples do not show additional features to that of silicalite-1, either. However, using EDX analysis a concentration of titanium in these particles on the external surface can be clearly seen. According to EDX analysis these particles do not contain silicon or chlorine. Although oxygen cannot be detected using EDX analysis, it is most likely that these particles consist
of an oxidic titanium phase. The UV-Vis spectrum of a sample of Ti/S-1\textsuperscript{9} (Fig. 5.5) shows that both bulk TiO$_2$ and homogeneously distributed TiO$_x$ are present (absorption around 30,000 and 38,000 cm$^{-1}$, respectively).

For the liquid-phase TiCl$_4$-treated samples of silicalite-1, no differences could be detected before and after TiCl$_4$ treatment using XRD, IR or SEM. De Ruiter et al.$^{10}$ have demonstrated that TiCl$_4$ cannot enter the MFI structure at temperatures up to 350°C, indicating that at the low temperature employed here (95°C), the TiCl$_4$ will only react with external surface OH groups. The UV-Vis spectrum of Ti/S-1\textsuperscript{10}, shown in Figure 5.5, indicates that some bulk TiO$_2$ is formed, as the absorption starts around 30,000 cm$^{-1}$.

The results of the phenol hydroxylation test reaction are listed in Table 5.1 for the aluminium-free samples. For comparison, a sample of TS-1 is also listed in this table.

The pure silicas do not show catalytic activity; only traces of hydrogen peroxide are decomposed and no products are detected. The bulk TiO$_2$ (Degussa P25) does not show catalytic activity: no products are formed, and no hydrogen peroxide is decomposed at all. This is not in accordance with what is reported in the literature, where Kraushaar and van Hooft$^1$ claim that bulk TiO$_2$ present in samples of TS-1 is detrimental to the catalytic selectivity because hydrogen peroxide is rapidly decomposed on bulk TiO$_2$. On the other hand, Popa et al.$^4$ claim that high-surface TiO$_2$, obtained via a special synthesis procedure, is in itself a good catalyst for the hydroxylation of phenol with aqueous hydrogen peroxide. However, the TiO$_2$ employed in the present study is a low-surface material (10 m$^2$/g), which might explain why no activity at all is found.

For the gas-phase TiCl$_4$-treated samples, the trend seems to be that with decreasing titanium content the catalytic activity decreases and the selectivity increases, indicating that only small amounts of titanium or TiO$_x$ connected to SiO$_2$ are required to catalyse the hydroxylation of phenol. The most striking feature of the TONs listed in Table 5.1 is that the lower the titanium content of the samples is, the higher the TON per titanium site is.
TABLE 5.1. Elemental analysis and phenol hydroxylation; aluminium-free samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Ti(^1)</th>
<th>H(_2)O(_2) conv(^2)</th>
<th>eff(^3)</th>
<th>TON(^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>-</td>
<td>2</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>SSG</td>
<td>-</td>
<td>3</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>-</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti/SiO(_2)(^g)</td>
<td>16</td>
<td>100</td>
<td>5</td>
<td>25</td>
</tr>
<tr>
<td>Ti/SSG(^g)</td>
<td>660</td>
<td>28</td>
<td>84</td>
<td>4500</td>
</tr>
<tr>
<td>Ti/SSG(^g)</td>
<td>200</td>
<td>46</td>
<td>48</td>
<td>1300</td>
</tr>
<tr>
<td>TS-1</td>
<td>80</td>
<td>56</td>
<td>55</td>
<td>725</td>
</tr>
<tr>
<td>Ti/SiO(_2)(^{liq})</td>
<td>16</td>
<td>13</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>Ti/SiO(_2)(^{liq})</td>
<td>130</td>
<td>24</td>
<td>20</td>
<td>175</td>
</tr>
<tr>
<td>Ti/SGK(^{liq})</td>
<td>120</td>
<td>77</td>
<td>57</td>
<td>1500</td>
</tr>
<tr>
<td>Ti/SGK(^{liq})</td>
<td>150</td>
<td>83</td>
<td>50</td>
<td>1800</td>
</tr>
</tbody>
</table>

1) bulk molar ratio as determined by ICP-AES.
2) % H\(_2\)O\(_2\) converted after 6 hours of reaction.
3) (moles of dihydroxybenzenes formed / moles of H\(_2\)O\(_2\) converted) * 100%.
4) moles of dihydroxybenzenes formed / moles of Ti present.

The samples of silicalite-1 treated with TiCl\(_4\) in the liquid phase show activities that are higher than that of the TS-1 sample, accompanied by comparable selectivities. The TONs of all the TiCl\(_4\) treated S-1 samples are much higher than the TON found for TS-1. The Ti/SiO\(_2\)\(^{liq}\) samples show both lower activities, selectivities and TONs, indicating that the presence of the MFI framework is beneficial to the catalytic properties of these kinds of systems. However, it can be concluded that the commercial titanium-on-amorphous-silica catalyst is also somewhat active using hydrogen peroxide instead of organic peroxide as the oxidising agent.
Aluminium-containing zeolites

Samples of three well-known zeolites, MFI, Y and BEA, all containing aluminium, were treated with TiCl₄ in the gas-phase. For zeolites MFI and BEA, the TiCl₄ treatment temperature was 450°C. However, the stucture of zeolite Y collapsed at that temperature to amorphous material, so zeolite Y was treated with TiCl₄ at 300°C, maintaining the crystallinity.

Neither IR, XRD nor SEM show any differences in all of these samples before and after TiCl₄ treatment, but from ICP-AES (bulk chemical analysis) it is clear that titanium is present in the samples after the treatment (see Table 5.2).

### TABLE 5.2. Elemental analysis and phenol hydroxylation; aluminium-containing samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Ti¹</th>
<th>Si/Al¹</th>
<th>Si/(Ti+Al)¹</th>
<th>H₂O₂ conv²</th>
<th>eff³</th>
<th>TON⁴</th>
<th>TON⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFI</td>
<td>-</td>
<td>22</td>
<td>22</td>
<td>26</td>
<td>5</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>MFI</td>
<td>125</td>
<td>23</td>
<td>19</td>
<td>30</td>
<td>10</td>
<td>110</td>
<td>15</td>
</tr>
<tr>
<td>BEA</td>
<td>-</td>
<td>35</td>
<td>35</td>
<td>96</td>
<td>21</td>
<td>-</td>
<td>200</td>
</tr>
<tr>
<td>BEA</td>
<td>35</td>
<td>35</td>
<td></td>
<td>55</td>
<td>23</td>
<td>130</td>
<td>70</td>
</tr>
<tr>
<td>Y</td>
<td>-</td>
<td>2.5</td>
<td>2.5</td>
<td>98 (2 hr)</td>
<td>42</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>Y</td>
<td>7.4</td>
<td>2.5</td>
<td></td>
<td>96</td>
<td>58</td>
<td>135</td>
<td>45</td>
</tr>
</tbody>
</table>

1) bulk molar ratio as determined by ICP-AES.
2) % H₂O₂ converted after 6 hours of reaction.
3) (molës dihydroxybenzenes formed / moles H₂O₂ converted) * 100%.
4) moles dihydroxybenzenes formed / moles Ti present.
5) moles dihydroxybenzenes formed / moles Ti + Al present.

Of the aluminium-containing titanium-free samples, surprisingly the BEA and Y show high activities and efficiencies, whereas the MFI is significantly less active and
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efficient. Upon gas-phase TiCl₄ treatment, the BEA and Y samples show a much lower activity and a slightly higher efficiency, whereas the MFI shows about the same activity with a somewhat higher efficiency. The high activity of the titanium-free samples of BEA and Y could be due to acid activity, as one of the commercial processes for the hydroxylation of phenol with hydrogen peroxide is based on an acid-catalysed process.¹¹ However, one would expect the titanium-free but aluminium-containing MFI to show reasonable activity, too, as it also contains acid sites. Unfortunately, it is not clear why the different zeolite structures show such varying activities. The reason for the decrease in activity of the zeolites BEA and Y and the increase of activity of the MFI might be explained by keeping in mind that the TiCl₄ cannot enter the pore system of MFI (even at high temperatures),¹⁰ whereas the larger pores of BEA and Y are accessible for TiCl₄. Thus, it may be possible that TiCl₄ reacts with active acid sites inside the BEA and Y framework, thereby changing the activity from acidic to a titanium site with a lower activity but a higher efficiency. It is even feasible that small clusters of an oxidic titanium phase are formed inside the pores of these zeolites. For the MFI one would expect the TiCl₄ to react only with external surface OH groups, and as can be seen from Table 5.2, the activity and efficiency are only slightly affected by the TiCl₄ treatment.

5.4. CONCLUSIONS

For the aluminium-free samples of amorphous or crystalline (silicalite-1) SiO₂, treatment with TiCl₄ in the gas-phase leads to a concentration of titanium in oxidic particles on the external surface, whereas liquid-phase TiCl₄ treatment leads to a more homogeneous distribution of the titanium on the external surface. For these systems, the catalytic activity for the hydroxylation of phenol with aqueous hydrogen peroxide not only depends on the titanium content, but also on the structure of the SiO₂ support used. With decreasing titanium content the TON per titanium site increases dramatically, indicating that only small amounts of titanium or TiOₓ connected to SiO₂ are required to obtain catalytic activity. Although the systems based on amorphous SiO₂ show catalytic activity for the hydroxylation of phenol, the presence of the crystalline SiO₂ silicalite-1 has a greatly enhancing effect on
both activity and selectivity. The presence of an IR absorption band at 960 cm\(^{-1}\) is not a requirement for obtaining good catalytic performance in the hydroxylation of phenol with aqueous hydrogen peroxide.

For the aluminium-containing systems studied here, it seems that the acid activity is relatively high, which results in the total catalytic activity decreasing upon gas-phase TiCl\(_4\) treatment. However, for the MFI structure, which is not easily accessible for TiCl\(_4\), the catalytic properties with regard to the hydroxylation of phenol do not change much upon TiCl\(_4\) treatment.

5.5 REFERENCES

CHAPTER 6

ON THE DEALUMINATION OF ZSM-5

6.1. INTRODUCTION

Generally, the less framework aluminium acidic sites a unit cell of a zeolite framework possesses, the stronger the acidity per site is. Thus, by controlling the Si/Al ratio of the zeolite framework, the acidic catalytic properties of the zeolite can be influenced. However, many types of zeolites (eg BEA, MOR and the industrially important zeolite Y) cannot be synthesised directly in a high-silica form. These zeolites have to be dealuminated using a post-synthesis treatment. Although it is well known that most zeolites can be dealuminated without seriously affecting the crystal structure of the materials, not many types of zeolites have been studied systematically for their behaviour under acid dealumination conditions. The most commonly used dealumination methods are the so-called steaming treatment (in which the zeolite is heated to high temperatures, eg 500°C, in a flow of water vapour) and treatment with gaseous SiCl₄, also at elevated temperatures. Many papers have been published on the behaviour of zeolite Y under these treatments, mainly because the resulting material, "USY", shows enhanced catalytic cracking properties, which is of great interest to the petroleum industry. However, using either of the aforementioned treatments, zeolites are obtained that contain less framework Al species than the parent materials, but few framework vacancies (silanol nests). This is due to direct substitution of Si for Al in the SiCl₄ treatment, and to the "T-jump mechanism" in steaming. Due to the T-jump mechanism, during steaming also mesopores are created. Less frequently used dealumination techniques include reaction with chelating agents like EDTA, reaction with aqueous (NH₄)₂SiF₆ and reaction with F₂ gas.

When synthesising MFI containing other T-atoms than Al (eg Ti, Fe, B, Ga, V), materials are obtained showing various useful catalytic properties, depending on the T-atom incorporated. However, as the direct incorporation of some transition metals (eg Ti) into the MFI framework is not very feasible, it can be beneficial to
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follow a secondary synthesis route: dealuminate Al-MFI with a relatively low Si/Al ratio via acid treatment to create silanol nests, then insert the desired transition metal into the silanol nests, creating TM-MFI.

In a paper on the incorporation of Ti into ZSM-5 via dealumination and subsequent TiCl₄ treatment, Kraushaar and Van Hooff² report that the Si/Al ratio of their ZSM-5 sample increases from 50 to 2000 upon three-fold treatment with 1 N HCl at 80°C. However, other authors³,⁴ report that similar treatments at the boiling point of the HCl solution give only moderate dealumination of the ZSM-5 under study. Although not all authors give the method according to which their ZSM-5 samples were synthesised, the question arises whether the synthesis method of ZSM-5 is important in the resistance of the material to acid dealumination. Thus, we have synthesised various samples of ZSM-5 according to different synthesis methods, and we have studied the results of treating these samples of ZSM-5 with varying concentrations of different acids and the results of changing the temperature of the acid treatment.

In the discussion, data available from the literature concerning the acid dealumination of Al-MFI will be considered, and an overview of the literature data will be given.

6.2. EXPERIMENTAL

Materials: Synthesis of ZSM-5

Samples denoted as ARL-N were synthesised according to the original patent method, described by Argauer and Landolt⁵, N indicating the Si/Al ratio in the resulting material. Typical features of this synthesis method are the high TPA/Si (TPA = tetrapropylammonium cation, the most commonly used template for ZSM-5 synthesis) and H₂O/Si ratios employed. Thus, a solution "A" was prepared by dissolving 40.1 g Aerosil 200 (amorphous SiO₂) (Degussa) in 209.5 g 40% TPAOH in water (CFZ Zaltbommel). To obtain a solution, it is necessary to heat the mixture to about 100°C under stirring. Solution "B" was obtained by dissolving the appropriate amount of NaAlO₂ (ICN Pharmaceuticals) in 72.3 g water, and was stirred into solution "A". The resulting gel was autoclaved at 150°C for six days.
Sample **SSG-40** was synthesised according to a method described by Sand and Ghamami.⁶ 105 g Ludox AS-40 (Du Pont), 127 g 25% NH₃ in water, 16 g TPABr (CFZ Zaltbommel) and 2.86 g aluminium isopropoxide (Janssen Chimica) were mixed to a homogeneous mixture, which was autoclaved at 180°C for two weeks.

Sample **CHA-15** was synthesised according to a method described by Chang et al.⁷ by making a solution "A" of 150 g Ludox HS-40 and 100 g 1.3 % TPABr in water, and a solution "B" by dissolving 8.65 g NaOH in 11 g H₂O and subsequently slowly adding 6 g sodium aluminate. Then solution "B" was stirred into solution "A", and the resulting gel was autoclaved for three days at 175°C.

Sample **KR-38** was synthesised according to the method used by Kraushaar and van Hooff⁸ by first making three solutions: solution "A" by dissolving 12 g NaOH and 30 g Cab-O-Sil (amorphous SiO₂) (the Cabot Company) in 90 g of water; solution "B" by dissolving 3.4 g Al₂(SO₄)₃·18H₂O and 24.0 g TPABr in 74.3 g 4 N H₂SO₄; solution "C" by dissolving 14.7 g NaCl in 45.3 g water. Then, starting with solution "C", solution "B" and about 3/4 of the total amount of solution "A" were added simultaneously under vigorous stirring. The pH was set at 3 by adding a little bit more of solution "A", and the mixture was stirred for two hours. The pH was then set at 9 by adding the remaining part of solution "A" and a little bit of NaOH whilst stirring, and the mixture was autoclaved at 160°C for three days.

The X-ray diffractograms and the IR spectra of all ZSM-5 samples synthesised show them to be pure MFI. Prior to the dealumination experiments, all samples were calcined in air in a muffle furnace at at least 500°C overnight, to remove incorporated TPA. The samples are expected to be mainly in the protonic form.

**Acid treatment**

The samples of ZSM-5 were treated with different mineral acids at different temperatures in order to remove aluminium from the framework. Threefold treatment with 100 ml of 1 N aqueous acid per gram of zeolite, for at least half an hour, was used. The zeolite was placed in the reaction vessel with the acid solution and heated to the desired temperature. The desired temperature was maintained for the amount of time indicated, after which the source of heat was turned off and the suspension was left to settle. The acid solution was decanted, fresh acid solution
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was added and the whole procedure was repeated. After the third heating period, the suspension was not left to settle and decanted, but filtrated, and the zeolite was washed thoroughly with water. Samples were dried overnight at 120°C in air. Up to 100°C the dealumination experiments were performed in a stirred round bottom glass vessel; at temperatures higher than 100°C a Teflon-lined stainless steel autoclave (not stirred) was used.

$^{27}$Al MAS NMR

$^{27}$Al NMR spectra were recorded on a Varian VXR-400 S spectrometer, using magic angle spinning and a Doty probe. 1 M aqueous Al(NO$_3$)$_3$ was used as an external standard. Acquisition time was 0.3 s with an acquisition delay of 0.3 s. The number of datapoints was 16000, and the pulse width was 1.5 μs, to correspond with a flip angle < 15°.9

6.3. RESULTS AND DISCUSSION

Table 6.1 lists the results of the dealumination experiments with different aqueous mineral acids at 80°C. 1 N H$_2$SO$_4$ and 1 N HBr do not give dealumination at all, whereas 1 N HCl leads to only slight dealumination.

<table>
<thead>
<tr>
<th>acid</th>
<th>conc</th>
<th>time (hr)</th>
<th>Si/Al init</th>
<th>Si/Al final</th>
<th>temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3*0.5</td>
<td>ARL-44</td>
<td>53</td>
<td>80</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>1 N</td>
<td>3*0.5</td>
<td>ARL-44</td>
<td>43</td>
<td>80</td>
</tr>
<tr>
<td>HBr</td>
<td>1 N</td>
<td>3*0.5</td>
<td>ARL-44</td>
<td>42</td>
<td>80</td>
</tr>
</tbody>
</table>
Table 6.2 gives the dealumination results for various samples of ARL with different Si/Al ratios, using threefold 0.5 hr treatment with 1 N HCl at 80°C. Although Si/Al ratios show a slight increase, it cannot be said that dealumination is efficient.

<table>
<thead>
<tr>
<th>acid</th>
<th>conc</th>
<th>time (hr)</th>
<th>Si/Al init</th>
<th>Si/Al final</th>
<th>temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3*0.5</td>
<td>ARL-11</td>
<td>14</td>
<td>80</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3*0.5</td>
<td>ARL-18</td>
<td>25</td>
<td>80</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3*0.5</td>
<td>ARL-44</td>
<td>53</td>
<td>80</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3*0.5</td>
<td>ARL-63</td>
<td>69</td>
<td>80</td>
</tr>
</tbody>
</table>

TABLE 6.2. Dealumination of ZSM-5 (ARL) with different Si/Al ratios.

Apparently, hardly any dealumination is achieved in these experiments. However, we have to take into account that the acid dealumination procedure comprises two stages. In the first stage, aluminium is removed from its tetrahedral framework position and becomes octahedrally coordinated inside the zeolitic pore structure. Thus after this first stage the bulk Si/Al ratio does not change, even though the framework Si/Al ratio can change significantly. In the second stage (which can occur almost simultaneous with the first stage, and does not require different reagents), the octahedrally coordinated Al(H₂O)₆³⁺ species diffuses out of the zeolitic pore system and into the surrounding solution. During this second stage the bulk Si/Al ratio decreases, whereas the framework Si/Al ratio does not change. Possibly after 0.5 hr at 80°C the aluminium has indeed been extracted from the framework, but is still present inside the pores of the zeolite. If this is the case, a decrease of the bulk Si/Al ratio would be expected upon prolonged acid treatment or upon increasing the temperature of the acid treatment, as in both cases the total diffusion of the octahedrally coordinated aluminium species is expected to be more complete.
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However, prolonging the 1 N HCl treatment at 80°C from 3 * 0.5 hr to 3 * 24 hr does not lead to a significantly higher degree of dealumination, as can be seen from Table 6.3.

TABLE 6.3. Dealumination of ZSM-5 (ARL-18 and -22) using different reaction times.

<table>
<thead>
<tr>
<th>acid</th>
<th>conc</th>
<th>time (hr)</th>
<th>Si/Al init</th>
<th>Si/Al final</th>
<th>temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3 * 0.5</td>
<td>ARL-18</td>
<td>25</td>
<td>80</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3 * 1</td>
<td>ARL-18</td>
<td>24</td>
<td>80</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3 * 1</td>
<td>ARL-22</td>
<td>23</td>
<td>80</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3 * 2</td>
<td>ARL-18</td>
<td>26</td>
<td>80</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3 * 6</td>
<td>ARL-18</td>
<td>25</td>
<td>80</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3 * 24</td>
<td>ARL-22</td>
<td>29</td>
<td>80</td>
</tr>
</tbody>
</table>

Using higher reaction temperatures, as listed in Table 6.4, does not lead to a significantly higher degree of dealumination, either.

TABLE 6.4. Dealumination of ZSM-5 (ARL-44) using different reaction temperatures.

<table>
<thead>
<tr>
<th>acid</th>
<th>conc</th>
<th>time (hr)</th>
<th>Si/Al init</th>
<th>Si/Al final</th>
<th>temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3 * 0.5</td>
<td>ARL-44</td>
<td>53</td>
<td>80</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3 * 0.5</td>
<td>ARL-44</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3 * 0.5</td>
<td>ARL-44</td>
<td>43</td>
<td>125</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3 * 0.5</td>
<td>ARL-44</td>
<td>48</td>
<td>160</td>
</tr>
</tbody>
</table>
Figure 6.1. $^{27}$Al MAS NMR spectra of ARL-22 a) starting material; b) after 3 * 1 hr acid treatment; c) after 3 * 24 hr acid treatment.
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Although the experiments at 125 and 160 °C were performed without stirring, and thus the material may have been dealuminated a little bit less than it would have been with stirring, these results show that even at 160 °C dealumination is not significant.

Solid-state $^{27}$Al-NMR can discriminate between tetrahedral (framework) and octahedral (non-framework) Al species. Both species give NMR signals at distinctly different chemical shifts. Figure 6.1 shows the $^{27}$Al MAS NMR spectra of the sample ARL-22 before and after threefold treatment with 1 N HCl for 1 and 24 hr. From these spectra it is clear that the starting material contains only tetrahedrally coordinated aluminium (signal at 54 ppm), whereas both acid treated samples contain approximately the same ratio of tetrahedrally to octahedrally coordinated aluminium. Moreover, only a small part of the aluminium is coordinated octahedrally in the acid treated samples (signal at 0 ppm). From these NMR spectra we can conclude that although some aluminium is extracted from the framework upon acid treatment, dealumination is not very efficient, and dealumination efficiency does not increase upon prolonging the acid treatment from 3 * 1 hr to 3 * 24 hr.

As all samples obtained using the ARL synthesis method did not show significant dealumination, samples of ZSM-5 obtained using different synthesis methods were treated with 1 N aqueous HCl. However, if we compare the results of dealumination experiments on materials synthesised through different synthesis methods (listed in Table 6.5), we see that none of these materials is easily dealuminated.

TABLE 6.5. Dealumination of ZSM-5 obtained through different synthesis methods, using 1 N HCl.

<table>
<thead>
<tr>
<th>acid</th>
<th>conc</th>
<th>time (hr)</th>
<th>Si/Al init</th>
<th>Si/Al final</th>
<th>temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3*2</td>
<td>SSG-40</td>
<td>42</td>
<td>80</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3*1</td>
<td>CHA-15</td>
<td>16</td>
<td>80</td>
</tr>
<tr>
<td>HCl</td>
<td>1 N</td>
<td>3*1</td>
<td>KR-38</td>
<td>40</td>
<td>80</td>
</tr>
</tbody>
</table>
Figure 6.2. $^{27}$Al MAS NMR spectra of SSG-40 a) starting material; b) after 3 * 2 hr acid treatment.

The $^{27}$Al MAS NMR spectra of sample SSG-40 before and after threefold 2 hr treatment with 1 N HCl are shown in figure 6.2. The acid treated sample shows
only a very small signal at 0 ppm, indicating that practically no aluminium is removed from the framework. If we take a closer look at data available in the literature, summarised in Table 6.6, we find many contradictory results, ranging from good dealumination to hardly any dealumination at all.

**TABLE 6.6. Literature data; dealumination of ZSM-5.**

<table>
<thead>
<tr>
<th>synthesis method</th>
<th>dealumination treatment</th>
<th>T (°C)</th>
<th>Si/Al init</th>
<th>Si/Al final</th>
<th>from ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>KR</td>
<td>3 * 1 N HCl&lt;sup&gt;1&lt;/sup&gt;</td>
<td>80</td>
<td>50</td>
<td>2000</td>
<td>2,8</td>
</tr>
<tr>
<td>Mostowicz</td>
<td>5 hr 1.25 N HCl</td>
<td>bp</td>
<td>40</td>
<td>120</td>
<td>3,10</td>
</tr>
<tr>
<td>Mostowicz</td>
<td>2 hr 1.25 N HCl</td>
<td>bp</td>
<td>40</td>
<td>93</td>
<td>3,10</td>
</tr>
<tr>
<td>Grose</td>
<td>2*18 hr 4N HCl</td>
<td>60</td>
<td>15</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
<td>ARL</td>
<td>3*1 hr 1N HCl</td>
<td>95</td>
<td>94</td>
<td>106</td>
<td>4</td>
</tr>
<tr>
<td>ARL</td>
<td>2*18 hr 4N HCl</td>
<td>60</td>
<td>11</td>
<td>15</td>
<td>11</td>
</tr>
<tr>
<td>Plank</td>
<td>48 hr 4 N HCl</td>
<td>50</td>
<td>18</td>
<td>21</td>
<td>12</td>
</tr>
<tr>
<td>?</td>
<td>0.5 N HCl&lt;sup&gt;1&lt;/sup&gt;</td>
<td>80</td>
<td>22</td>
<td>25</td>
<td>13</td>
</tr>
</tbody>
</table>

<sup>1</sup> reaction time not specified.

Krausshaar and van Hooff<sup>2</sup> are the only authors to report almost 100% dealumination upon treating ZSM-5 with 1 N HCl. However, even using the synthesis method they use,<sup>8</sup> we can not reproduce their dealumination efficiency, as can be seen from Table 6.5, sample KR-38. The <sup>27</sup>Al MAS NMR spectra of this material before and after acid treatment are shown in figure 6.3. From these spectra it is clear that the material KR-38 is very resistant to acid treatment, as the signal for octahedrally coordinated aluminium is very small after acid treatment.
Figure 6.3. $^{27}$Al MAS NMR spectra of **KR-38** a) starting material; b) after 3 * 1 hr acid treatment.

Using Mostowicz’ synthesis method and boiling 1.25 N HCl, reasonable dealumination has been achieved.$^3,^{10}$ Moreover, in that case the degree of dealumination
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increases with increasing acid treatment period.\textsuperscript{3,10} However, the majority of the literature data as well as the data of the present work show that the acid dealumination of ZSM-5 is not as feasible as one would be inclined to think.

6.4. CONCLUSIONS

The acid dealumination of zeolite ZSM-5 is not as straightforward as it seems to be. Apparently no dealumination is found when using aqueous HBr or H\textsubscript{2}SO\textsubscript{4}, and hardly any dealumination is found when using aqueous HCl. The temperature or the period of time of the acid treatment do not influence the extent of dealumination, nor do the Si/Al ratio of the samples or the synthesis method according to which the samples were obtained.

6.5. REFERENCES

8) Prof. J.H.C. van Hooff, private communication.

CHAPTER 7

ZEOLITE CATALYSIS USING MICROWAVE HEATING.

7.1. INTRODUCTION

Recently, domestic microwave ovens have been introduced to chemical laboratories as an alternative heating tool to conventional conductive heating methods.\textsuperscript{1,2} Rate enhancement of reactions and of digestion of samples for analysis are the main features of this technique, and these are mainly due to temperature and pressure effects. However, in various catalytic organic reactions using microwave heating, apart from rate enhancement also increased selectivity or increased catalyst stability have been observed.\textsuperscript{3}

The microwave region of the electromagnetic spectrum, 300 MHz - 300 GHz, lies between the infrared and radio frequencies. Domestic microwave ovens generally operate at 2.45 GHz (12.2 cm). Microwave dielectric heating is based on the ability of some liquids and solids to transform electromagnetic energy into heat. This ability is expressed in the dissipation factor, $\tan \delta$. The higher $\tan \delta$, the better the dissipation of microwave radiation energy. Microwave energy absorbed by molecules with a high $\tan \delta$ as rotation energy, resulting in a "wobbling" of the molecules, through which the absorbed energy is converted to kinetic energy. Solvated ions and counter-ions in zeolites start to "wobble" to and fro, directly converting the microwave energy to kinetic energy. The kinetic energy thus generated can be passed on to other (non-microwave absorbing) molecules through common interactions, resulting in a rise in temperature of the entire reaction mixture.

Reaction vessels that are to be used with microwave heating should be constructed from microwave transparent materials: $\tan \delta$ should be low (up to about 0.002). Table 7.1 lists the dissipation factors for some common microwave transparent materials.

For ions in solutions, the dissipation factor increases with increasing concentration.
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TABLE 7.1. Dissipation factors of some common microwave transparent materials.4

<table>
<thead>
<tr>
<th>material</th>
<th>tan δ (×10⁻⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon (PFA, FEP, PTFE)</td>
<td>2.1</td>
</tr>
<tr>
<td>polyethylene (LD, HD)</td>
<td>2.2 - 2.3</td>
</tr>
<tr>
<td>PVC</td>
<td>3.2</td>
</tr>
<tr>
<td>Glass (quartz, SiO₂)</td>
<td>3.8 - 4.1</td>
</tr>
<tr>
<td>Glass (borosilicate)</td>
<td>3.7 - 4.8</td>
</tr>
</tbody>
</table>

Polar molecules are microwave absorbing, and thus alcohols and water can be heated rapidly by microwave radiation. It should be noted that only mobile polar substances are heated using microwave radiation, and that non-polar molecules are microwave transparent. Metals are totally reflective, microwave radiation is not able to pass through metals or to heat them. However, microwave radiation can be absorbed and emitted again by metals, like an antenna.

One thing that has to be kept in mind when using microwave heating is the tendency of liquids to be superheated, although the degree to which a liquid is superheated depends on several factors, like the amount of dissolved gases and impurities, and the roughness of the surface of the container in which the liquid is placed. Table 7.2 lists some common solvents, their dissipation factors and the temperatures to which they can be easily superheated.

TABLE 7.2. Dissipation factors of some common solvents.

<table>
<thead>
<tr>
<th>solvent</th>
<th>tan δ</th>
<th>bp (°C) conventional</th>
<th>T easily reached in microwave</th>
<th>superheating above bp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>0.157⁵</td>
<td>100</td>
<td>104,⁶ 110⁷</td>
<td>4, 10</td>
</tr>
<tr>
<td>methanol</td>
<td>0.640²</td>
<td>65</td>
<td>84⁶</td>
<td>19</td>
</tr>
<tr>
<td>ethanol</td>
<td>0.250²</td>
<td>79</td>
<td>103⁵</td>
<td>24</td>
</tr>
</tbody>
</table>
Microwave catalysis

Recently, a study on the microwave heating of zeolites indicated that the heating rates of zeolites are dependent on the composition of the zeolite (eg type of charge-balancing counter-ions). Microwave heating of zeolite synthesis mixtures, as studied in our laboratory, showed very promising results. Using short synthesis times, batches of crystals with a sharp particle size distribution can easily be obtained.

As nowadays microwave radiation is used more frequently both in the laboratory and in industry, some studies on its effect on heterogeneous catalysis have been reported. For example, Gutierrez et al. report on the solvent-free rearrangement of pinacol adsorbed on samples of montmorillonite with various counter-ions. From their results, summarised in Table 7.3, it is clear that microwave heating can have a greatly enhancing effect on the catalytic performance. The effect observed in this reaction is substantial acceleration. However, the temperature of the samples was not measured in the microwave experiments, and it is possible that the temperature of the samples heated using microwave radiation is substantially higher than the 100°C of the samples heated conventionally, in which case at least part of the acceleration is due to a pure reaction temperature effect.

<table>
<thead>
<tr>
<th>M(^{n+})</th>
<th>yield of pinacolone conventional heating 15 hr 100°C</th>
<th>yield of pinacolone microwave heating 15 min 450W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>5 %</td>
<td>38 %</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>2 %</td>
<td>23 %</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>30 %</td>
<td>94 %</td>
</tr>
<tr>
<td>Cr(^{3+})</td>
<td>99 %</td>
<td>98 %</td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td>98 %</td>
<td>99 %</td>
</tr>
</tbody>
</table>

1) Reaction conditions: 100 mg Montmorillonite and 20 mg pinacol mixed intimately in an unsealed Pyrex glass reaction vessel.
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In the present paper we also report on the use of microwave heating in heterogeneous catalysis. Our reactants are in the liquid phase, the zeolitic catalyst is a solid-phase material. The reaction studied is the oxyfunctionalisation of n-hexane using aqueous hydrogen peroxide as the oxidising agent and TS-1 (titanium-silicalite-1) as the catalyst.

Using TS-1 as a catalyst and aqueous hydrogen peroxide as the oxidising agent, n-hexane can be converted to a mixture of 2- and 3-hexanol and 2- and 3-hexanone\(^{12}\) (see Scheme 7.1).

![Scheme 7.1. The oxyfunctionalisation of n-hexane.](image)

In this study, both conventional and microwave heating are applied.

7.2. EXPERIMENTAL

Using conventional heating techniques, the oxyfunctionalisation of n-hexane is suitably performed in a Teflon-lined stainless steel autoclave, which is placed in a pre-heated metal oven, in which the metal of the oven is in direct contact with three sides of the autoclave. When employing microwave heating, an all-Teflon (PTFE) autoclave is used. Methanol is used as a solvent. The exact reaction conditions are listed in Table 7.4.
### TABLE 7.4. Reaction conditions n-hexane oxyfunctionalisation.

<table>
<thead>
<tr>
<th></th>
<th>conventional heating</th>
<th>microwave heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>autoclave total volume</td>
<td>25 ml</td>
<td>100 ml</td>
</tr>
<tr>
<td>catalyst</td>
<td>20 mg</td>
<td>80 mg</td>
</tr>
<tr>
<td>methanol</td>
<td>10 ml</td>
<td>40 ml</td>
</tr>
<tr>
<td>n-hexane (Baker, Z.A.)</td>
<td>1.0 ml (7.68 mmoles)</td>
<td>4.0 ml (30.72 mmoles)</td>
</tr>
<tr>
<td>30% H₂O₂ (Merck, p.a.)</td>
<td>0.80 ml (7.84 mmoles)</td>
<td>3.20 ml (31.36 mmoles)</td>
</tr>
<tr>
<td>temperature</td>
<td>100°C</td>
<td>100°C</td>
</tr>
</tbody>
</table>

The microwave equipment employed in this work is a Gerling Moore microwave generator equipped with an S-band WR-284 wave guide, operating in the TE₁₀ mode (see Scheme 7.2).

![Scheme 7.2. Schematic drawing of the microwave set-up; 1) variable power microwave generator; 2) flexible waveguide; 3) E-H-field tuner; 4) all-teflon autoclave.](image-url)
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The experimental set-up is similar to that described by Graef et al.\textsuperscript{13} A continuously variable power with a maximum of 2500 W can be applied; the microwave source operates at 2.45 GHz. An all-Teflon (PTFE) autoclave of 2.2 cm inner diameter was used, placed in the wave-guide via a shielded hole of 3 cm inner diameter. The temperature was measured by positioning an earth-connected thermocouple in the liquid phase but outside the microwave cavity.

The catalyst used, Euro-TS-1, was obtained from Dr. van der Pol, Eindhoven University of Technology. Euro-TS-1 is the result of the first attempt to synthesise a "standard" TS-1 catalyst that can be used as a reference sample by anyone studying TS-1. The material was received "as synthesised", meaning that the organic templating material TPA (tetrapropylammonium), used as a structure-directing agent during synthesis, was still present in the zeolitic channel system, blocking the pores for reactants. To remove the template, the material was calcined in air in a muffle furnace at 500°C overnight prior to use. The Si/Ti ratio of the TS-1 calcined material was 60 as determined using ICP-AES (Inductively Coupled Plasma - Atomic Emission Spectroscopy) analysis.

The suspension of the catalyst in the otherwise homogeneous reaction mixture is stirred. For both conventional and microwave heating blank reactions, without the addition of catalyst, were performed. Products are determined using GC analysis, for which toluene is used as GC standard, added after reaction; H\textsubscript{2}O\textsubscript{2} conversion is monitored using iodometric titration.

A sample of TS-1-F, obtained through direct synthesis using F\textsuperscript{-} instead of OH\textsuperscript{-} as the mineralising agent (see chapter 4 of this thesis), was also used as a catalyst for the oxyfunctionalisation of n-hexane. The Si/Ti ratio of this sample is 70.

Adsorption experiments were performed using the TS-1-F, by refluxing the zeolite in the liquid (or solution) for a few minutes, cooling to room temperature and evaporating excess liquid at ambient conditions. Selected crystals were placed under the IR microscope on a thin flake of KCl, and adsorbed species were studied by taking the IR absorption spectrum in transmission through a crystal. The IR equipment used was a Bruker IFS 66 FT-IR spectrophotometer. Spectra were calculated from 500 or 1000 scans, with a resolution better than 8 cm\textsuperscript{-1}.

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7.3. RESULTS AND DISCUSSION

Catalytic experiments

As can be seen from Tables 7.5 and 7.6 and Figure 7.1, the hydrogen peroxide conversion rate is much higher when using microwave heating than when using conventional heating. However, when using conventional heating, the efficiency of the reaction based on hydrogen peroxide conversion is higher than when using microwave heating. Apparently, more hydrogen peroxide is decomposed when using microwave heating.

TABLE 7.5. TS-1 catalysed n-hexane oxyfunctionalisation using microwave heating.

For reaction conditions see Table 7.4.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>H₂O₂ conv</th>
<th>H₂O₂ conv¹</th>
<th>y² 2-ol</th>
<th>y² 3-ol</th>
<th>y² 2-one</th>
<th>y² 3-one</th>
<th>H₂O₂ eff²</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank⁴ 3</td>
<td>52 %</td>
<td>16.31</td>
<td>0.07</td>
<td>0.03</td>
<td>0.06</td>
<td>0.06</td>
<td>2.1 %</td>
</tr>
<tr>
<td>0.5</td>
<td>12 %</td>
<td>3.76</td>
<td>0.94</td>
<td>0.67</td>
<td>0</td>
<td>0</td>
<td>42.8 %</td>
</tr>
<tr>
<td>1</td>
<td>34 %</td>
<td>10.66</td>
<td>2.04</td>
<td>1.04</td>
<td>0.54</td>
<td>0.01</td>
<td>39.2 %</td>
</tr>
<tr>
<td>1.5</td>
<td>41 %</td>
<td>12.86</td>
<td>2.82</td>
<td>1.43</td>
<td>0.44</td>
<td>0.10</td>
<td>41.4 %</td>
</tr>
<tr>
<td>3</td>
<td>92 %</td>
<td>28.85</td>
<td>3.66</td>
<td>2.05</td>
<td>2.15</td>
<td>0.38</td>
<td>37.3 %</td>
</tr>
</tbody>
</table>

1) mmoles of H₂O₂ consumed.
2) mmole of product formed.
3) efficiency = (mmoles of -ols formed + 2 * mmoles of -ones formed / mmoles of H₂O₂ converted) * 100 %.
4) no catalyst added.

Upon subjecting a sample of TS-1 to microwave radiation (400 W) for 25 min, its temperature did not rise significantly. In view of the data presented in Table 7.1, it is assumed that the zeolite, which consists mainly of SiO₂, is essentially transparent to microwave radiation. This means that in the catalytic experiments the reaction mixture is heated through absorption of microwave radiation by the solvent (metha-
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and some water from the hydrogen peroxide solution), the hydrogen peroxide and the products in the bulk liquid and in the adsorbed phase. The zeolite is heated indirectly through the temperature rise of the reaction mixture.

TABLE 7.6. TS-1 catalysed n-hexane oxyfunctionalisation using conventional heating. For reaction conditions see Table 7.4.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>H$_2$O$_2$ conv</th>
<th>H$_2$O$_2$ conv$^1$</th>
<th>y$^2$ 2-ol</th>
<th>y$^2$ 3-ol</th>
<th>y$^2$ 2-one</th>
<th>y$^2$ 3-one</th>
<th>H$_2$O$_2$ eff$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank$^4$ 24</td>
<td>0 %</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0 %</td>
<td>0</td>
<td>trace</td>
<td>trace</td>
<td>0</td>
<td>0</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>3</td>
<td>32 %</td>
<td>2.51</td>
<td>0.63</td>
<td>0.36</td>
<td>0.09</td>
<td>0.02</td>
<td>48.2 %</td>
</tr>
<tr>
<td>6</td>
<td>57 %</td>
<td>4.47</td>
<td>1.14</td>
<td>0.60</td>
<td>0.51</td>
<td>0.07</td>
<td>64.9 %</td>
</tr>
<tr>
<td>15</td>
<td>99 %</td>
<td>7.76</td>
<td>1.34</td>
<td>0.88</td>
<td>1.37</td>
<td>0.18</td>
<td>68.6 %</td>
</tr>
</tbody>
</table>

1) mmoles of H$_2$O$_2$ consumed.
2) mmoles of product formed.
3) efficiency = (mmoles of -ols formed + 2 * mmoles of -ones formed / mmoles of H$_2$O$_2$ converted) * 100 %.
4) no catalyst added.

The blank experiment (ie without catalyst) using conventional heating does not give any hydrogen peroxide conversion, whereas the blank experiment using microwave radiation does give significant hydrogen peroxide conversion (although only small amounts of products). Although some would readily ascribe this difference to a "microwave effect" related to direct activation of the hydrogen peroxide, this is not very feasible. As the activation energy for dissociation of the O-O bond in a free H$_2$O$_2$ is 2.4 * 10$^{-19}$ J, and the energy of a photon of microwave radiation at 2.45 GHz is 1.623 * 10$^{-24}$ J, the direct activation of hydrogen peroxide by the microwave radiation employed is highly improbable. Although the influence on the activation energy for dissociation of adsorbing hydrogen peroxide onto TS-1 is not
known, it is very unlikely that this activation energy is decreased by more than 2 orders of magnitude upon adsorption. Moreover, as only the average temperature of the reaction mixture outside the microwave cavity is measured, it is also possible that the temperature of the reaction mixture inside the microwave cavity is somewhat higher than the temperature measured by the thermocouple. It might be possible that part of the hydrogen peroxide is decomposed on the thermocouple, as hydrogen peroxide can be decomposed on most metals. However, an experiment using silicalite-1 as the "catalyst" does not give any products, nor appreciable hydrogen peroxide conversion (about 5%). This is not in accordance with the blank reaction (without catalyst), where 52% of the hydrogen peroxide is decomposed. One is inclined to think that silicalite-1 somehow stabilises the hydrogen peroxide.
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When TS-1 is present, a substantially larger part of the converted hydrogen peroxide is used to oxidise the n-hexane. This might be due to selective adsorption of n-hexane and hydrogen peroxide on the internal and / or external surface of the TS-1.

Comparing the absolute yields of products between the microwave and conventionally heated reaction (listed in Table 7.7) at the same reaction time, it seems that the microwave heated reaction gives higher absolute amounts of products. However, as also the hydrogen peroxide conversion is much higher in the microwave heated reaction, it must be kept in mind that the efficiency of the microwave heated reaction is substantially lower than the efficiency of the conventionally heated reaction.

TABLE 7.7. Difference in absolute yields between microwave and conventional heating.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>(y^1) 2-ol</th>
<th>(y^1) 3-ol</th>
<th>(y^1) 2-one</th>
<th>(y^1) 3-one</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.51</td>
<td>0.26</td>
<td>0.14</td>
<td>0.003</td>
</tr>
<tr>
<td>3</td>
<td>0.29</td>
<td>0.15</td>
<td>0.45</td>
<td>0.08</td>
</tr>
</tbody>
</table>

1) mmole of product formed in microwave heated reaction - 4 * mmole of products formed in conventionally heated reaction.

Using conventional heating, an induction period of about 1 hr is observed. It might be possible that this induction period coincides with the period needed for the reaction mixture to reach the reaction temperature of 100°C. Although Clerici\(^{14}\) claims that the oxyfunctionalisation of n-alkanes can be performed at 55°C, our own experiments at that temperature indicate that reaction times of three or more days are necessary to obtain detectable amounts of products. Apparently, the reaction does not proceed at temperatures much lower than 100°C.

Tables 7.8 and 7.9 give the product distribution and the ratio of 2- to 3-oxygenated products found for microwave and conventional heating, respectively.
### TABLE 7.8. TS-1 catalysed n-hexane oxyfunctionalisation using microwave heating.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>( H_2O_2 ) conv</th>
<th>total(^1) 2-prod</th>
<th>total(^1) 3-prod</th>
<th>ratio 2/3 prod(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank 3</td>
<td>52 %</td>
<td>0.13</td>
<td>0.09</td>
<td>1.44</td>
</tr>
<tr>
<td>0.5</td>
<td>12 %</td>
<td>0.94</td>
<td>0.67</td>
<td>1.40</td>
</tr>
<tr>
<td>1</td>
<td>34 %</td>
<td>2.58</td>
<td>1.05</td>
<td>2.46</td>
</tr>
<tr>
<td>1.5</td>
<td>41 %</td>
<td>3.26</td>
<td>1.53</td>
<td>2.13</td>
</tr>
<tr>
<td>3</td>
<td>92 %</td>
<td>5.81</td>
<td>2.43</td>
<td>2.39</td>
</tr>
</tbody>
</table>

1) mmoles of -ol formed + mmoles of -one formed.
2) mmoles of 2-products formed / mmoles of 3-products formed.

### TABLE 7.9. TS-1 catalysed n-hexane oxyfunctionalisation using conventional heating.

<table>
<thead>
<tr>
<th>time (hr)</th>
<th>( H_2O_2 ) conv</th>
<th>total(^1) 2-prod</th>
<th>total(^1) 3-prod</th>
<th>ratio 2/3 prod(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank 24</td>
<td>0 %</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>32 %</td>
<td>0.72</td>
<td>0.38</td>
<td>1.89</td>
</tr>
<tr>
<td>6</td>
<td>57 %</td>
<td>1.65</td>
<td>0.67</td>
<td>2.46</td>
</tr>
<tr>
<td>15</td>
<td>99 %</td>
<td>2.71</td>
<td>1.06</td>
<td>2.56</td>
</tr>
</tbody>
</table>

1) mmoles of -ol formed + mmoles of -one formed.
2) mmoles of 2-products formed / mmoles of 3-products formed.

Although the statistical ratio of 2/3 products is 4/4, if the oxyfunctionalisation reaction proceeds solely through an \( \text{HO}^- \) radical mechanism, the 2/3 substitution ratio is expected to be 0.91.\(^{15}\) The ratio found for the blank reaction using micro-
wave heating is 1.44, and we may assume that in that run essentially only reaction through free HO· radicals occurs. Although hydrogen peroxide conversion is over 50 %, only small amounts of products are formed in the blank reaction using microwave heating. When TS-1 is added, not only does the total product yield increase dramatically, but also the 2/3 product ratio increases, indicating that the hydrogen peroxide is not (only) activated through free radical formation, but (also) in a different way, presumably in interaction with the catalyst.

If we compare the 2/3 product ratios obtained when using microwave heating to those obtained using conventional heating, we see that generally this ratio is lower for microwave heating, indicating a larger contribution of the free radical mechanism as compared to conventional heating. Again, this could be due to a higher temperature reached in the microwave reaction.

In the literature concerning the oxyfunctionalisation of alkanes, so far two reaction mechanisms have been proposed. Huybrechts et al.\textsuperscript{12} propose a mechanism via the formation of a titanium-peroxo radical, as depicted in Scheme 7.3.

\begin{equation}
\text{O} \quad \text{O} \quad \text{O} \quad \text{OH} \quad \text{Ti} = \text{O} \\
\text{Ti} \quad \text{Ti} \quad \text{Ti} \quad \text{Ti} \quad \text{HO-CR} \\
\end{equation}

Scheme 7.3. Oxyfunctionalisation mechanism as proposed by Huybrechts et al.\textsuperscript{12}

Tatsumi et al.\textsuperscript{16} propose a concerted mechanism:

\begin{equation}
\text{H} \quad \text{H}_2\text{O} \\
\text{Ti} \quad \text{Ti} = \text{O} \\
\end{equation}

Scheme 7.4. Oxyfunctionalisation mechanism as proposed by Tatsumi et al.\textsuperscript{16}
Adsorption measurements

In order to get an idea of the adsorbed mixture during catalytic oxidation experiments, some adsorption experiments were undertaken. These experiments were performed using the TS-1-F (crystal size 30 μ), because the crystals of Euro-TS-1 are too small (0.15 μ) to use them in the IR microscope set-up. TS-1-F is expected to be a bit more hydrophobic than Euro-TS-1.

Figure 7.2. IR spectra of a) TS-1-F; b) TS-1-F refluxed in methanol.
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Figure 7.2 shows the IR spectra of TS-1-F and of TS-1-F refluxed in methanol. These spectra show that methanol is not adsorbed in TS-1-F. TS-1-F is probably too hydrophobic to adsorb methanol.

The IR spectra of TS-1-F refluxed in demineralised water and in 30% aqueous hydrogen peroxide are shown in Figure 7.3. As expected, water is not adsorbed in the hydrophobic TS-1-F.

![Figure 7.3. IR spectra of TS-1-F refluxed in a) water; b) 30% H₂O₂.](image)

Wavenumbers cm⁻¹
However, hydrogen peroxide is slightly adsorbed, indicating it to be less polar than water or methanol.

In Figure 7.4 the spectra of TS-1-F refluxed in n-hexane, 30% aqueous hydrogen peroxide and in the n-hexane oxyfunctionalisation reaction mixture are shown. n-Hexane is easily adsorbed in TS-1-F, as is to be expected, as n-hexane is non-polar and TS-1-F is very hydrophobic. Furthermore, the cross-section of n-hexane in its all-trans conformation is about 4.8 Å, which is substantially smaller than the maximum accessible diameter of the pores of the MFI structure of 5.5 Å.

If we study the IR spectrum of TS-1-F refluxed in the reaction mixture, we see that somehow molecules containing hydroxyl groups now are adsorbed in TS-1-F. This may be due to a synergism in adsorption between n-hexane (which is also adsorbed from the reaction mixture) and hydrogen peroxide. If n-hexane and hydrogen peroxide are adsorbed in TS-1 simultaneously, then reaction between the two should be enhanced, as is indeed found in the catalytic experiments. However, if we study the IR spectra of TS-1-F refluxed in n-hexanol (Fig. 7.5.a), practically no absorption in the -OH region is observed. The same is valid for TS-1-F refluxed in a mixture of n-hexane and 30% hydrogen peroxide (Fig. 7.5.b) and for a mixture of n-hexane and methanol (Fig. 7.5.c). Thus, cautiously our conclusion is that all the components of the reaction mixture are necessary to obtain the synergism in adsorption of n-hexane and - presumably - hydrogen peroxide.
Figure 7.4. IR spectra of TS-1-F refluxed in a) n-hexane; b) 30% H$_2$O$_2$; c) n-hexane oxyfunctionalisation reaction mixture.
Figure 7.5. IR spectra of TS-1-F refluxed in a) 2-hexanol; b) n-hexane + 30% H₂O₂; c) n-hexane + methanol.
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7.4. CONCLUSIONS

The reaction rate of the oxyfunctionalisation of n-hexane with hydrogen peroxide using TS-1 as a catalyst can be greatly enhanced by using microwave heating, albeit at a substantially lower reaction efficiency. IR data of adsorbed species on TS-1 synthesised in a fluoride medium show that only in the case of contacting the TS-1 with the total oxyfunctionalisation reaction mixture a synergism of adsorption is found between n-hexane and hydrogen peroxide. With the 2/3-product selectivity data available, no definite statement can be made as to which of the two oxygenation reaction mechanisms proposed in literature is the most likely mechanism to operate in reality.

7.5. ACKNOWLEDGEMENTS

Dr. A. Arafat is acknowledged for his cooperation in conducting the microwave experiments. The author would like to thank Ir. G.C.A. Luijkx and Dr. A.J.M. de Man for valuable discussions.

7.6. REFERENCES

5) J.R. White, Trans. IMPL 1 (1973) 40.


EPILOGUE

GENERAL REMARKS

For the characterisation of titanium-silicalite-1, perhaps the most important point of discussion is the assignment of the IR band at around 960 cm\(^{-1}\). Although many authors readily ascribe this band as due to some vibration directly related to the presence of titanium at a T-site, several alternative interpretations remain possible. Apart from the suggested Ti=O vibration, assignment to an Ti-OH vibration is encountered in the literature. However, also assignment to an Si-OH vibration would make sense.

One would expect to find a relation between the 960 cm\(^{-1}\) IR band and the 970 cm\(^{-1}\) Raman band found in TS-1 samples, as both bands should be due to the same vibration. The Raman band is generally ascribed to "homogeneously distributed" TiO\(_x\) species, however without specifying the coordination and valency of the titanium. Among the samples studied in this thesis, there are quite a few which do not show the IR band, but which do show a weak Raman band, along with the catalytic properties for the hydroxylation of phenol which are generally said to be related to the presence of the IR band. However, as both IR and Raman spectroscopy are rather sensitive to parameters like the particle size of the sample, small variations in absorption between the two methods are expected.

For vanadium-silicalite-1, also an IR and a Raman band at about 960 cm\(^{-1}\) have been reported. This is another indication of the assignment to Ti=O or V=O not being the correct one, as this vibration for V is expected at around 1000 cm\(^{-1}\). Furthermore, a weak Raman band at 970 cm\(^{-1}\) is found for silicalite-1, probably due to Si-OH vibrations of framework defects. Another explanation might be an Si-O\(^{\delta-}\) -- Ti\(^{\delta+}\) vibration.

In this thesis, several methods have been studied for the direct synthesis of TS-1. Using the OH\(^{-}\) synthesis, the source of titanium seems to have some effect on the catalytic performance of the resulting material. Using tetra-isopropyl orthotitana-
Epilogue

te as the titanium source, samples are obtained which show a better performance in the hydroxylation of phenol than the samples obtained using tetra-n-propyl orthotitanate or tetra-ethyl orthotitanate. Moreover, adding isopropyl alcohol during the preparation of the synthesis gel also results in materials which show improved catalytic performance.

Materials synthesised using F⁻ as the mineralising agent and TiF₃ as the source of titanium, have a large part of the titanium concentrated in small, seemingly crystalline, particles on the external surface of well-formed elongated prismatic (titanium-)silicalite-1 crystals. However, the catalytic performance in the hydroxylation of phenol is of the same order of magnitude as that of "ordinary" TS-1, indicating that the presence of "bulk" TiO₂ is not as detrimental to the catalytic properties of the materials as has been claimed in the literature.

Upon treatment of (titanium-free) silicalite-1 with TiF₃ dissolved in diluted hydrofluoric acid, also titanium-containing particles are formed on the external surface of the crystals, which are very similar to those formed in the direct synthesis using F⁻ as the mineralising agent.

The secondary synthesis method described by Kraushaar and van Hooff, involving the treatment of dealuminated ZSM-5 with TiCl₄ in the gas-phase at elevated temperatures (450°C), could not be reproduced. This might have been partly due to the stability of our samples of ZSM-5, which would not dealuminate at all. Even when reproducing the ZSM-5 synthesis that Kraushaar and van Hooff used for their experiments, no dealumination using aqueous hydrochloric acid could be achieved. Another explanation could be that the TiCl₄ is simply too bulky to enter the MFI structure. De Ruiter proved that at 350°C TiCl₄ does not enter the MFI structure, even though at elevated temperatures the zeolite framework is somewhat flexible. The gas-phase TiCl₄ treated silicalite-1 showed small, titanium-containing particles on the external surface of the crystals, which were similar to those observed on the TiF₃/HF treated samples and on the F⁻ direct synthesis samples. In accordance with the catalytic results obtained for the F⁻ samples, the catalytic performance for the hydroxylation of phenol of the gas-phase TiCl₄ treated samples of silicalite-1 was good. However, gas-phase TiCl₄ treated amorphous
silica showed similar titanium-containing particles to be present on the external surface, and although these samples showed a high rate of decomposition of hydrogen peroxide, some phenol hydroxylation products were also formed. For the materials with small particles on the external surface, only part of the titanium is exposed to the reaction mixture. Thus, the activity per exposed titanium-site is even higher than the value obtained from the calculation per titanium atom present.

When using another form of SiO₂ (crystobalite) as a carrier material for TiOₓ species (by treating the SiO₂ with aqueous TiF₃/HF), systems were obtained which showed some activity for the hydroxylation of phenol with reasonable selectivities. Even liquid-phase TiCl₄ (n-heptane solution) treatment of silicalite-1 and amorphous silica gave active materials. Again in this case the samples based on silicalite-1 were better catalysts than those based on amorphous silica, indicating that the structure of the silica does somehow affect the catalytic properties of the resulting materials. The MFI structure seems to be beneficial to the titanium-related catalysis.

Results obtained with another catalytic test reaction, the oxyfunctionalisation of n-hexane, show that this reaction is probably able to discriminate between different titanium sites, as most of the post-synthesis titanium treated samples show only poor catalytic performance, whereas the performance of the direct synthesis samples is much better. The samples of TS-1 obtained through F⁻ synthesis, containing small particles of TiO₂ on the external surface, show a poorer performance in this reaction than the OH⁻ synthesis samples.

Using microwave heating for the catalytic oxyfunctionalisation of n-hexane, overall increase in reaction rate was observed, however accompanied by a loss of selectivity. Most probably the increase in reaction rate is due to a higher heating rate, higher reaction temperature and thus higher pressure. The method requires accurate measurement of temperature and pressure to ascertain whether this is truly the case.
SUMMARY

This thesis concerns titanium-containing zeolites and related systems. Apart from the synthesis and characterisation of the aforementioned systems, their catalytic properties with respect to some model reactions are evaluated. Practically all materials obtained are tested as catalysts for the hydroxylation of phenol with aqueous hydrogen peroxide. Additionally, several samples are evaluated as catalysts for the oxyfunctionalisation of n-hexane, also with hydrogen peroxide.

CHAPTER 1: A general introduction on titanium, its oxides, its minerals and its use in catalysis.

The occurrence of titanium in nature is discussed. Apart from the abundant forms of titanium dioxide, several other titanium-containing minerals are described. In particular the coordination of titanium in these minerals along with the Ti-O bond lengths are studied. Next to a brief discussion of the main applications of titanium, its use in heterogeneous catalysis is discussed extensively.

CHAPTER 2: Synthetic titanium-containing zeolites.

An extensive review of the literature is given, focusing on TS-1. Synthesis, characterisation and catalytic properties are discussed. Unfortunately, data reported by different research groups are very often not in accordance with each other.

CHAPTER 3: TS-1 synthesised in OH⁻ medium.

The classical direct synthesis method for TS-1, using OH⁻ as the mineralising agent, is studied. The source of titanium, the Si/Ti ratio and the synthesis time are varied. Although the titanium content of the samples depends linearly on the titanium content of the synthesis gel, no relationship can be found between the titanium content and the catalytic activity of the samples. The ratio of the 960/550 cm⁻¹ IR bands is not related to the catalytic activity, either. Generally, the lower the titanium content of the sample, the higher the TON is per titanium site.
CHAPTER 4: Titanium incorporated into zeolites and silicas from TiF₃.

The direct synthesis of TS-1 using F⁻ as the mineralising agent is studied. TiF₃ is used as the source of titanium. TiF₃ dissolved in diluted hydrofluoric acid is used for the post-synthesis treatment of various zeolites. Also, amorphous silica and cristobalite (a dense crystalline silica) are treated with TiF₃/HF. All samples obtained contain titanium, and for the TiF₃/HF treated samples the titanium content depends linearly on the amount of titanium added to the samples. Surprisingly, the samples based on silicalite (both direct synthesis and post-synthesis treatment) show small particles to be present on their external surface, along with good performance for the hydroxylation of phenol. According to the Raman spectra, these particles on the external surface probably consist of anatase (TiO₂). The oxyfunctionalisation of n-hexane does discriminate between direct synthesis samples (which show modest performance) and post-synthesis treated samples (which hardly show activity).

CHAPTER 5: Titanium incorporated into zeolites and silicas from TiCl₄.

A literature procedure for the incorporation of titanium into dealuminated ZSM-5 could not be reproduced. Apart from the TiCl₄ probably being too bulky to enter the MFI structure, our samples of ZSM-5 could not be dealuminated following the literature procedure.

Various zeolites and silicas (both crystalline and amorphous) are treated with TiCl₄ in the gas-phase at temperatures up to 450°C. For the silicas, this results in the formation of small particles on the external surface, probably consisting of anatase (TiO₂). The silicas are also treated with TiCl₄ from a solution in n-heptane at 95°C, probably resulting in mono-layer like TiO₂ species. The samples based on silicalite-1 show reasonable to good performance for the hydroxylation of phenol, whereas only the liquid-phase treated amorphous silica shows modest performance. The zeolites themselves show reasonable to good performance for the hydroxylation of phenol before TiCl₄ treatment. However, after TiCl₄ treatment their performance has decreased somewhat.
CHAPTER 6: On the dealumination of ZSM-5.

Samples of ZSM-5 with different Si/Al ratios and obtained via several synthesis methods are treated with aqueous HCl, following a method frequently used in the literature. Results in the literature range from almost complete dealumination to no dealumination at all. None of the samples studied here are more than slightly dealuminated.

CHAPTER 7: Zeolite catalysis using microwave heating.

The oxyfunctionalisation of n-hexane using TS-1 as a catalyst is studied using both conventional and microwave heating techniques. Using microwave heating, the reaction rate is greatly enhanced, albeit with a simultaneous loss of selectivity.
SAMENVATTING

EEN STUDIE AAN TS-1 EN AANVERWANTE SYSTEMEN

Dit proefschrift gaat over titaan-bevattende zeolieten en aanverwante systemen. Naast de synthese en karakterisering van deze systemen worden hun katalytische eigenschappen voor enkele modereacties besproken. Van alle verkregen materialen worden de eigenschappen getest als katalysator voor de hydroxylering van fenol met waterstof peroxide. Enkele van de monsters worden ook getest als katalysator voor de oxyfunctionalisering van n-hexaan, ook met waterstof peroxide.

HOOFDSTUK 1: Een algemene inleiding over titaan, haar oxid, haar mineralen en haar toepassingen in de katalyse.


HOOFDSTUK 2: Synthetische titaan-bevattende zeolieten.

De beschikbare literatuur wordt uitgebreid besproken, waarbij de nadruk ligt op TS-1. Gekeken wordt naar de synthese, de karakterisering en de katalytische eigenschappen. Jammergenoeg zijn de gegevens die door verschillende onderzoeksgroepen worden gemeld vaak met elkaar in tegenspraak.

HOOFDSTUK 3: TS-1 gesynthetiseerd met behulp van OH^.

De klassieke synthesemethode voor TS-1 wordt bestudeerd. Hierbij wordt OH^ gebruikt als complexerend agens. De titaanbron, de Si/Ti verhouding en de synthetetijd worden gevarieerd. Hoewel het titaangehalte van de monsters recht evenredig is met het titaangehalte van de synthesgel, is er geen verband tussen het titaangehalte van de monsters en hun katalytische activiteit. De verhouding van de 960/550 cm^-1 IR banden van de monsters geeft ook geen verband met de
Samenvatting

katalytische activiteit. In het algemeen geldt dat hoe lager het titaangehalte van een monster is, hoe hoger de activiteit per titaan atoom is.

HOOFDSTUK 4: Titaan aangebracht op zeolieten en silicas via TiF₃.

De directe synthese van TS-1, met F⁻ als complexerend agens, wordt bestudeerd. TiF₃ wordt gebruikt als titaanbron. TiF₃ opgelost in verdun HF wordt gebruikt om verschillende zeolieten en silicas na te behandelen. Alle verkregen monsters bevatten titaan, en voor de TiF₃/HF behandelde materialen is het titaangehalte rechtstevenredig met de hoeveelheid toegevoegde TiF₃/HF oplossing. De op silicaliet gebaseerde monsters hebben kleine deeltjes op het externe oppervlak en zijn goede katalysatoren voor de hydroxylering van fenol. Met Raman spectroscopie is te zien dat deze deeltjes waarschijnlijk bestaan uit TiO₂. De oxyfunctionalisering van n-hexaan kan wel onderscheid maken tussen monsters verkregen via directe synthese en via nabehandeling.

HOOFDSTUK 5: Titaan aangebracht op zeolieten en silicas via TiCl₄.

Verschillende zeolieten en silicas worden met gasvormig TiCl₄ behandeld bij 450°C. Voor de silicas resulteert dit in de vorming van kleine deeltjes op het externe oppervlak, die waarschijnlijk bestaan uit TiO₂. De silicas worden ook bij 95°C behandeld met TiCl₄ opgelost in n-heptaan, waarschijnlijk resulterend in een monolaag-achtige structuur van TiOₓ. De monsters gebaseerd op silicaliet zijn redelijke tot goede katalysatoren voor de hydroxylering van fenol, terwijl alleen het vloeistof-fase behandelde amorfe silica enige acitviteit heeft. De zeolieten hebben zelf al een redelijke tot goede katalytische activiteit, die echter minder wordt na behandeling met TiCl₄.

HOOFDSTUK 6: De dealumining van ZSM-5.

Monsters ZSM-5 met verschillende Si/Al verhoudingen en verkregen via verschillende synthesemethoden worden behandeld met zoutzuur, zoals in de literatuur regelmatig wordt beschreven. De resultaten in de literatuur variëren van zeer goede tot bijna geen dealumining. Geen van de hier bestudeerde monsters vertoonde enigerlei dealumining.
Samenvatting

HOOFDSTUK 7: Zeoliet katalyse met microgolfverwarming.

De oxyfunctionalisering van n-hexaan met TS-1 als katalysator wordt bestudeerd. Daarbij worden het gebruik van conventionele en microgolf verwarmingstechnieken vergeleken. Met microgolfverwarming is de reactiesnelheid veel groter, terwijl de selectiviteit lager is.