Alkene Epoxidation with Silsesquioxane based Chromium and Titanium Catalysts

Proefschrift

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“Forty-two”

The Hitchhiker’s Guide to the Galaxy,
by Douglas Adams
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Chapter 1

General introduction and the scope of this thesis

Abstract: An introduction is given on liquid phase epoxidation reactions. Various catalysts in general and titanium catalysts in particular are discussed together with the reaction mechanisms involved. In relation to industrial, silica based catalysts, silsesquioxanes are introduced and their use as ligands for (epoxidation) catalysts is discussed. In addition, the usefulness and the methodology for immobilizing homogeneous catalysts are presented. Finally, the general scope for this thesis is outlined.

1.1 Catalytic epoxidation

Alkenes, either derived from natural resources or generated as products of the chemical industry, are found in great abundance in the realm of organic molecules. One of the most useful transformations of alkenes is epoxidation (Scheme 1.1). By epoxidation, two adjacent carbon atoms are functionalized while either of these two adjacent carbons is activated towards nucleofílic attack, which makes the resulting epoxides useful and versatile intermediaries in organic chemistry. Furthermore, in asymmetric synthesis the epoxidation reaction is attractive since it can produce two chiral carbons in one step.¹

Scheme 1.1: Schematic representation of the epoxidation of an alkene.

Due to increasing environmental demands, the use of classical stoechiometric oxidants for achieving this reaction is no longer optional. In order to make the process cleaner, safer and more efficient, the use of catalysts is mandatory.²
The first example of a liquid phase catalytic oxygen transfer dates back to 1936. The so-called Milas reagents\(^3\) were formed by reaction of transition metal oxides with a solution of \(\text{H}_2\text{O}_2\) in \textit{tert}-butanol resulting in soluble inorganic peracids. These catalysts were mainly used for the vicinal dihydroxylation of olefins, but with certain metaloxides, e.g. \(\text{MoO}_3\) or \(\text{WO}_3\), selective epoxidation was observed. From that point on, a great deal of effort has been put into development of transition metal based catalysts, both homogeneous and heterogeneous, for the selective epoxidation of a broad range of olefins.\(^4\)

Based on the key intermediate involved in the oxygen transfer step, the metal catalyzed oxidations can be divided into two categories.\(^5\) The first one involves a peroxometal, while the second one involves an oxometal pathway. Molybdenum, vanadium and titanium catalyzed epoxidations are agreed to proceed via a peroxometal pathway.\(^6\) Oxometal species, on the other hand, are generally accepted as the reactive intermediaries in catalytic epoxidations with selenium,\(^7\) ruthenium,\(^8\) osmium\(^9,5b\) and chromium.\(^10\)

![Scheme 1.2: Peroxo versus oxometal pathways in catalytic epoxidation reactions.](image)

### 1.2 Titanium based epoxidation catalysts

Both heterogeneous as well as homogeneous titanium-catalysts have been extensively studied for their use in liquid phase catalytic epoxidation reactions. The best-known homogeneous catalyst is the Sharpless catalyst,\(^11\) which is able to epoxidize allylic alcohols with enantiomeric excesses over 95\%, using \textit{tert}-butyl hydroperoxide (TBHP) as the oxidizing agent. The catalyst is prepared \textit{in-situ} from an optical active tartrate and a titanium(IV)alkoxide. The active catalyst, however, is not sufficiently stable to be stored over longer periods of time and is very sensitive to water. Catalysis should be performed in
rigorously dried aprotic solvents and even molsieves are employed during catalysis to remove trace amounts of water present.

The most successful heterogeneous liquid phase epoxidation catalysts are the Shell catalyst\textsuperscript{12} and Titanium Silicalite 1 (abbreviated as TS-1).\textsuperscript{13} Table 1.1 provides a comparison of the characteristics of these catalysts.

The Shell catalyst was patented in 1971 by Shell Oil and is industrially used for the epoxidation of propene using an organic peroxide. This titanium(IV) silicon dioxide catalyst is prepared by impregnating silica with TiCl$_4$ or an organo-titanium compound, followed by calcination. Removing the residual Bronsted acid Si-OH groups with an organic silylating agent results in particularly effective catalysts.\textsuperscript{14} Interestingly the catalyst has been reported to leach catalytically inactive titanium species during the initial stages of the epoxidation reaction after which the catalyst becomes truly heterogeneous.\textsuperscript{14b} The catalyst is quite unique in that it is heterogeneous, unlike other supported metal oxides, e.g. MoO$_3$ and V$_2$O$_5$ supported on SiO$_2$ or other inert carriers, which owe their catalytic activity to soluble metal species which rapidly leach from the support.\textsuperscript{15} Initially the structure of the active site has been suggested to be an isolated siloxy bonded titanyl species, but later studies, which also concerned zeolitic systems, suggest that the truly active site is more like a tripodally or tetrapodally attached titanium.\textsuperscript{16} (Scheme 1.3)

\begin{center}
\textbf{Scheme 1.3: Alkene epoxidation catalyzed by a four coordinated Ti(IV) site.}
\end{center}

TS-1 is an ordered crystalline microporous structure, which was first patented by Enichem in 1983.\textsuperscript{13} Below a titanium content of 1 – 2 wt\%, isolated titanium sites are incorporated as part of the MFI lattice. The catalyst is especially known for its ability to use aqueous hydrogen peroxide as the oxidant for the epoxidation of small alkenes.\textsuperscript{16a-b,17} Although water is known to seriously retard epoxidation reactions, the hydrophobicity of the
pores ensures a very low water content around the catalytic titanium centers, enabling this remarkable feature of the catalyst. The small pore size of the zeolite structure (about 6 Å) allows shape selective catalysis, but on the other hand, restricts the reaction to small alkenes only, which can be seen as a major drawback of the catalyst.

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<td>Ti incorporation</td>
<td>Several Ti siloxy sites; from monopodal to tetrapodal</td>
<td>Isomorphous replacement of T-atom sites</td>
</tr>
<tr>
<td>Substrate size</td>
<td>No limitations with regard to substrate size</td>
<td>Micropores of 5.6 Å diameter impose severe limitations</td>
</tr>
<tr>
<td>Oxidant</td>
<td>Limited to organic peroxides</td>
<td>Aqueous hydrogen peroxide</td>
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It is generally accepted that four coordinated titanium sites, which have reacted with hydrogen peroxide to form titanium hydroperoxo species, form the active sites of TS-1. The nature of the solvent, provided it is small enough to enter the pores, was found to have a major influence on reactivity and product selectivity during oxidations on TS-1. Clerici et al postulated a five-membered cyclic species, in which a protic molecule, ROH, stabilizes the titanium-peroxo complex through hydrogen bonding. Which oxygen of the titanium-peroxo complex is transferred is still a subject of debate. While Clerici and Ingallina, on basis of steric arguments, argue that the attack most likely takes place at the oxygen furthest away from Ti, others disagree on basis of computational calculations.

![Figure 1.1: Some proposed methanol stabilized transition structures for epoxidation by hydrogen peroxide on a Ti(IV) site incorporated in TS-1.](image-url)
1.3 Use of peroxides

Currently, there is much interest in substituting processes that use pollutant oxidants with more environmentally friendly ones. Besides properties like price and ease of handling, which cannot be neglected, the choice of oxidant is largely dependent on two factors; the nature of the corresponding by-product and the active-oxygen content. The former property is most important in context of environmental considerations, while the latter one influences the productivity of the process. In this respect, molecular oxygen is a very attractive choice. However, in liquid phase oxidations, the free radical nature of the reaction restricts its applicability to a rather small number of simple petrochemicals.

For the catalytic epoxidation of olefins, organic peroxides and hydrogen peroxide are being used as single oxygen donors. Although organic peroxides are generally much more active as oxidants than hydrogen peroxide, they are more expensive and the active oxygen content is rather low. The epoxidation reaction generates stoechiometric amounts of corresponding alcohols, which in most cases are quite easily recycled via a reaction with hydrogen peroxide, but this process requires at least two extra separation and one extra reaction steps.

Hydrogen peroxide, with respect to active oxygen content (47%) and the nature of by-products (only water!), seems to be the oxidant of choice in catalytic liquid phase epoxidations. However, the inherent co-production of water poses some serious difficulties. Most transition metal catalysts are very sensitive to water, which causes them to leach their active metal. In case the catalyst is stable, water has a serious retarding effect on the epoxidation reaction, making the search for new environmentally friendly, effective epoxidation catalysts a challenging one.

1.4 Heterogenization of homogeneous catalysts

An important factor to consider when choosing a catalytic system is whether to choose for homogeneous or heterogeneous catalysts. The advantages for homogeneously catalyzed reactions, in which the catalyst is in the same phase as the reactants, are high activity and selectivity at mild reaction conditions. Another important factor is the relative ease of
characterization of the well-defined active sites, which makes tuning of the catalysts possible. Unfortunately, ease of recovery and thermal stability, properties that homogeneous catalysts generally lack, are considered very important by industry. This results in the overall use of heterogeneous catalysts, which do possess these handling properties, in industrial bulk processes. However, homogeneous catalysts are still used in small scale manufacturing of fine specialty chemicals, in which the cost of catalysts are relatively irrelevant.

To combine the advantages of both homogeneous and heterogeneous catalysts, heterogenization of active stable and well-defined homogeneous catalysts can be considered. This way the high activity, selectivity and good definition of the homogeneous catalysts can be preserved while combining them with the ease of recovery from the reaction mixture. The most common immobilization techniques used for this purpose include grafting or tethering, physical entrapment, ship in bottle synthesis and supported liquid phase catalysis.

Grafting is an immobilization technique in which the host material becomes a ligand for the active metal complex by reaction of a metal with surface groups, e.g. silanol groups, of the host. In tethering the surface groups of the host react with one of the ligands of the metal complex. This way the active metal center remains equal to the homogeneous case.

Using a mesoporous hosts or polymers, it is possible to physically entrap a homogeneous catalyst. In this immobilizing technique the host is synthesized around the homogeneous catalyst. Sufficient large pores should ensure the diffusion of reactants and products to and from the trapped catalysts. However, if the mesoporous structure is too fragile or prone to swelling with solvent, leaching of the complex out of the host material will prove to be a major problem.

A special type of physical entrapment is the ship-in-the-bottle catalyst. The idea of this immobilization is that the starting materials of the metal complex are able to diffuse inside the host material, usually a cage like zeolite structure, but as soon as the complex is formed, it should be too large to leave the pores of the host. This results in a heterogeneous catalyst in which the catalytic complex is sterically and physically trapped inside its host.

In supported liquid phase immobilization is the catalytic complex dissolved in a very thin solvent layer, supported on a mesoporous host. Catalysis takes place at the interface between this phase and another immiscible liquid phase, containing the reactants.
1.5 Silsesquioxanes

Silsesquioxane is the official IUPAC\textsuperscript{27} name for (polycyclic) compounds consisting of silicon and oxygen. The first description of these compounds, also called sferosiloxanes or silsesquioxanes (the name used throughout the rest of this thesis), dates from 1946. Scott\textsuperscript{28} reported a methylsilsesquioxane, and although he was unable to completely characterize the compound, he concluded that its structure-formula should be \( [\text{CH}_3\text{SiO}_{3/2}]_{2n} \), in which \( n \) is an integer. A decade later, the structures were completely characterized with the help of X-ray diffraction on the single crystals.\textsuperscript{29}

Silsesquioxanes are easy to obtain via hydrolytic condensation of cycloalkyltrichlorosilane in a water/aceton mixture, a method that has been known since 1965.\textsuperscript{30} The most common products obtained by this method are shown in the picture below.

![Figure 1.2: Products obtained by the kinetic hydrolytic condensation of cycloalkyltrichlorosilanes.](image)

Starting from cyclohexyltrichlorosilane the hydrolytic condensation results in products a, b and c (Fig. 1.2). Products c and d can be obtained by using cycloheptyltrichlorosilane. A disadvantage of this synthesis is, that dependent on the preferred product, the synthesis lasts for 2 to 36 months. Interestingly, when using cyclopentyltrichlorosilane, the synthesis-time can be decreased to a few days, but unfortunately, the silsesquioxanes b and d cannot be obtained in this manner.\textsuperscript{31}

The presence of hydroxyl functionality in incompletely condensed silsesquioxanes results in several interesting applications of these silsesquioxanes. One important application is the modeling of hydroxylized silica-surfaces.\textsuperscript{32} The structural resemblance becomes
obvious when the structure of silsesquioxane e from Fig. 1.2 is compared to known (calculated) SiO$_2$-morphologies (Fig. 1.3).

![Figure 1.3: (a) ORTEP plot of R$_7$Si$_7$O$_9$(OH)$_3$ viewed down the pseudo-C$_3$ axis. (b) ORTEP plot of idealized (111)-octahedral face of β-cristobalite. (c) ORTEP plot of idealized (001) rhombohedral face of β-tridymite.](image)

Beside the structural resemblance of silsesquioxanes to silica, also their electronic features are quite similar. Unlike siloxane and alkoxy ligands, which are electron donating, both silsesquioxanes and silica are electron withdrawing.$^{33}$ Not surprisingly, many transition metal complexes containing silsesquioxane silanolate ligands have been reported over the last decade. Not only are these complexes synthesized as analogs for transition metals on silica but also increasingly are they studied with their direct use as catalysts in mind. Metal containing silsesquioxanes have been reported for alkene polymerization,$^{34}$ alkene methathesis$^{35}$ as well as active catalysts for alkene epoxidation.

The first titanium silsesquioxane known for its catalytic activity in epoxidation reactions is the titanium silsesquioxane complex (e-C$_3$H$_{11}$)$_7$Si$_7$O$_{12}$Ti(η$^5$-C$_5$H$_5$)$_{32c,36}$ This remarkable stable complex was found to effectively and selectively catalyze alkene epoxidations using TBHP as the oxidizing agent.$^{37}$ Similar tridentate ligated silsesquioxane titanium complexes with the general formula [TiR{(e-R')$_7$Si$_7$O$_{12}$}] (R = alkyl, cycloalkyl, alkylaryl, alkoxy, aryloxy, siloxy, amido and hydroxy; R' = cyclopentyl, cyclohexyl or cycloheptyl) were later synthesized$^{38}$ and also claimed in a Shell patent as active epoxidation catalysts using TBHP.$^{39}$ In analogy to titanium on silica also bidentately bonded and monodentately bonded silsesquioxane titanium complexes$^{38a,40}$ were reported and tested on catalytic activity for the epoxidation of alkenes using organic peroxides. Although catalytically active, monodentately bonded titanium silsesquioxanes proved to be unstable during epoxidation reactions in organic media containing anhydrous TBHP,$^{37}$ proving that, in
order to obtain stable catalysts, the titanium should be at least bidentately bonded to the silsesquioxane ligands.

1.6 Scope of this thesis

The purpose of this thesis is the development of new catalysts for the liquid phase epoxidation of alkenes with aqueous hydrogen peroxide. Special attention was paid to the use of silsesquioxane-ligated catalysts throughout this thesis. The choice for these ligands was based on the fact that these silsesquioxane compounds may model the supports of important industrial catalysts as the Shell catalyst and TS-1. Throughout this thesis, we place emphasis on catalyst stability and activity in protic media since we regard this as a first requirement for successful applications involving hydrogen peroxide.

In chapter 2 we start with the synthesis and use of chromium silsesquioxane and siloxane based catalysts. Due to instability of these catalysts during epoxidation and the problems associated with the use of chromium in general, we changed our focus to titanium silsesquioxane based catalysts, a choice validated by the already known successful homogeneous and heterogeneous epoxidation catalysts.

In chapter 3, several known and new titanium silsesquioxane complexes were synthesized and tested. This resulted in general guidelines for the required dentacity of the silsesquioxane ligands and the influence of the presence of water during epoxidation.

Chapter 4 deals with the synthesis of a new homogeneous titanium silsesquioxane cluster compound that was found to be the first active, silsesquioxane based, and somewhat bio-inspired, catalyst for the epoxidation of the ‘easy substrate’ cyclooctene with aqueous hydrogen peroxide as the oxidant.

Chapters 5 and 6 are related to catalyst immobilization. Chapter 5 deals with testing of homogeneous titanium silsesquioxane catalysts immobilized in MCM-41, mesoporous molecular sieves, by wet impregnation. The usability of this type of heterogeneous catalysts, on which our group reported earlier, was further elucidated.

Finally, chapter 6 deals with the modification of silsesquioxane ligands, which enabled us to chemically bind a titanium silsesquioxane complex to polysiloxane polymers. The resulting catalytic ensembles were found to be active epoxidation catalysts for the epoxidation
of several different alkenes using aqueous hydrogen peroxide; compared to TS-1 the reaction scope is expanded.

References

12 Shell Oil, British Pat. 1 249 079, 1971.
27) IUPAC-rule D-6.6

Chapter 2

Chromium based oxidation catalysts: Synthesis, structural characterization and stability of a bimetallic chromium(VI) siloxane complex

Abstract: The synthesis and characterization of a new bimetallic chromium(VI)siloxane complex, \([\text{Cr} (=\text{O})_2 \{\text{OSiPh}_2 \text{O}\}_2]\), \(1\), are described, together with chromium silsesquioxane complexes, \([\{(\text{R})_7 \text{Si}_7 \text{O}_{11} \{\text{OSiMe}_3 \} \text{CrO}_2\}]\), \(2\) \(a\), \(R = \text{c-C}_5\text{H}_{11}\); \(2\) \(b\), \(R = \text{c-C}_6\text{H}_{11}\). All chromium complexes were tested on stability and catalytic activity for the homogeneous liquid phase epoxidation of alkenes with TBHP and a comparison was made with the catalytic activity of \(\text{CrO}_3\). The results indicate that all siloxy-chromium compounds investigated are unstable under epoxidation conditions, causing leaching of a chromium species that is responsible for the observed catalytic activity. During epoxidation, this leached out, \(\text{Cr}(\text{VI})\) species, is gradually converted to an inactive \(\text{Cr}(\text{III})\) species. These results led to the conclusion that the relative expensive chromium siloxane and silsesquioxane complexes are impractical catalysts for liquid phase epoxidations.

2.1 Introduction to important chromium based catalysts and reagents

Chromium supported on silica is being used as a catalyst for the coordinative polymerization of ethene.\(^1\) Well-known examples of industrially used systems are the Phillips catalyst, essentially \(\text{CrO}_3\) on \(\text{SiO}_2\) or \(\text{Al}_2\text{O}_3\), and the Union Carbide system which is prepared from \((\eta^5\text{-C}_5\text{H}_5)_2\text{Cr}(\text{II})\) and \(\text{SiO}_2\).\(^2\) In addition, well-characterized homogeneous model systems for heterogeneous ethene polymerization catalysts containing chromium have been reported. These include oxo alkyls of \(\text{Cr}(\text{IV})\) and \(\text{Cr}(\text{V})\),\(^3\) and a constrained geometry chromium(III) alkyl complex.\(^4\) Recently, Theopold et al. reported the first chromium based catalysts that are capable of polymerizing \(\alpha\)-olefins.\(^5\)
Besides its widely known use in polymerization catalysis, chromium is also extensively used in oxidation chemistry. In synthetic organic chemistry, oxidations are of fundamental importance and these are commonly carried out using large excesses of chromium\textsuperscript{6} or manganese reagents.\textsuperscript{7} Not only form the colloidal metal residues a problem during reaction and workup of the desired oxidation products but they also lead to considerable amounts of waste that is environmentally undesired in modern production processes. This is especially true for chromium, which is considered carcinogenic at any of its oxidation states\textsuperscript{8} and therefore deserves extra care in waste control.

In order to enhance the efficiency of (ep)oxidation reactions with regard to energy and material consumption and hereby to diminish the amounts of waste per kilogram desired product, methods have been developed to use only a catalytic amount of the metal reagent in combination with an appropriate oxidant. In case of chromium this led to reports on the catalytic use of \( \text{CrO}_3/\text{TBHP} \), \( \text{CrO}_3/\text{H}_5\text{IO}_6 \), chromium salen complexes, \( \text{CrAPO-5/TBHP} \) and chromium silicalite molecular sieves.\textsuperscript{13}

This chapter reports on the synthesis and molecular structure of a siloxane chromate ester, \([\text{Cr}(=\text{O})\{\text{OSiPh}_2\text{O}\}]_2\), that is surprisingly easy to synthesize. In order to test the suitability of this new complex as an epoxidation catalyst, stability and epoxidation tests were performed. Comparisons were made with the silsesquioxane complex \([(\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{11}\{\text{OSiMe}_3\}\text{CrO}_2]\), a chromate ester reported by Feher et al.,\textsuperscript{14} and a similar chromate ester \([(\text{c-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{11}\{\text{OSiMe}_3\}\text{CrO}_2]\). It was found that due to leaching, the relatively expensive chromium siloxane and silsesquioxane complexes are impractical catalysts for liquid phase epoxidations.

### 2.2 Results

#### 2.2.1 Synthesis and reactivity of a siloxane chromate ester

The formation of the yellow bimetallic chromium(VI) complex \([\text{Cr}(=\text{O})\{\text{OSiPh}_2\text{O}\}]_2, 1\), proceeds surprisingly smooth in near to quantitative yields via the reaction of \(1,1,3,3\)-tetraphenyldisiloxane-1,3-diol, \(\text{Ph}_2\text{Si(OH)OSi(OH)Ph}_2\), with chromium trioxide in carbon tetrachloride at room temperature (Scheme 2.1, step \(i\)).
Complex 1 can be easily crystallized from hot carbon tetrachloride, affording 1 as air and water stable yellow crystals that only start to thermally decompose at ca. 180°C. Related siloxy complexes of the type \([(\text{t-Bu})_3\text{Si-O}]_2\text{M(=O)}_2\) (M = Cr, Mo) were also reported to have good thermal stabilities and resistance to hydrolysis.\(^{15}\) The entire synthesis and storage of 1, however, should be performed in the dark since the complex is, both as a solid and in solution, somewhat light sensitive.

The chromium silsesquioxanes \([\text{[c-C}_5\text{H}_9]_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{CrO}_2], \text{2a, and } [\text{[c-C}_6\text{H}_{11}]_7\text{Si}_7\text{O}_{11}(\text{OSiMe}_3)\text{CrO}_2], \text{2b, which are somewhat related to 1, were prepared using a synthesis method described by Feher et al.}^{14}\) (Scheme 2.2).
An alternative attempt to synthesize the chromium complex 1 starting from diphenylsilanediol instead of its condensation product 1,1,3,3-tetraphenyldisiloxane-1,3-diol, failed. In this case, the diol did not react at room temperature over a period of several days while at prolonged reflux in CCl₄, hexaphenylcyclotrisiloxane was formed in ca. 30% yield. Under these conditions, formation of the cyclotrisiloxane also occurs in the absence of CrO₃.

With coordinating solvents as pyridine or tetrahydrofuran, the chromium complex 1 forms unstable adducts (Scheme 2.1, step iv). This adduct formation can be easily observed by $^{29}$Si NMR. When pyridine or tetrahydrofuran is added to a dichloromethane solution of 1, the $^{29}$Si resonance of 1 at $\delta$ -31.91 directly shifts to higher field, resp. -40.36 or -39.61 ppm. Due to the instability of these adducts, attempts to isolate them failed, as a result of their decomposition, substantial amounts of hexaphenylcyclotrisiloxane are formed. The reaction of 1 with methanol also seems to give, initially, an adduct but in this case rapid decomposition takes place in which the 1,1,3,3-tetraphenyldisiloxane-1,3-diol used for the synthesis of 1 is formed back (Scheme 2.1, step v).

The photochemical decomposition of 1 has been investigated in some detail by $^{29}$Si NMR [79.5 MHz, 298K, CH₂Cl₂, 0.02 M Cr(acac)₃] (Scheme 2.1, step iii). Dichloromethane solutions of 1, turn black when exposed to daylight in the course of about an hour. The chromium-free siloxanes that result from this decomposition are hexaphenylcyclotrisiloxane together with octaphenylcyclotetrasiloxane in a 4:1 ratio resp.; the yield of these siloxanes is ca. 75%.
2.2.2 Solid state structure of \([Cr(=O)\_2\{(OSiPh\_2)_2O\}_2]\)

To obtain an unambiguous assignment of the structure of chromium complex 1, which could not be made on the basis of spectroscopic data alone, an X-ray structure of this compound was determined. Suitable crystals were obtained from a hot tetrachloromethane solution of 1 that was allowed to cool slowly to 20°C.

Crystal data and numerical details of the structure determination are given in table 2.1. Neutral atom scattering factors and anomalous dispersion factors were taken from ref 16. All calculations were performed with SHELXL93\(^{17}\) and the PLATON\(^{18}\) package (geometrical calculations and illustrations) on a DEC-5000 cluster.

The crystal structure of 1 consists of one discrete centrosymmetric dinuclear molecule in a triclinic unit cell. An ORTEP drawing of 1, along with the adopted numbering scheme is shown in Fig. 2.1; selected bond angles are given in table 2.2.

Table 2.1. Experimental data for the X-ray diffraction study of \([Cr(=O)\_2\{(OSiPh\_2)_2O\}_2]\), 1.

<table>
<thead>
<tr>
<th>compound</th>
<th>C(<em>{48}H</em>{40}Cr_{2}Si_{4}O_{10})</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol wt</td>
<td>993.17</td>
</tr>
<tr>
<td>cryst system</td>
<td>triclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P1 (No. 2)</td>
</tr>
<tr>
<td>a, b, c (Å)</td>
<td>9.4843(5), 10.5514(7), 13.3024(9)</td>
</tr>
<tr>
<td>α, β, γ (deg)</td>
<td>111.568(5), 107.088(5), 95.951(5)</td>
</tr>
<tr>
<td>V (Å(^3))</td>
<td>1149.30(14)</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
</tr>
<tr>
<td>D(_{calc}) (g cm(^{-3}))</td>
<td>1.435</td>
</tr>
<tr>
<td>F(000)</td>
<td>512</td>
</tr>
<tr>
<td>μ (cm(^{-1}))</td>
<td>6.4</td>
</tr>
<tr>
<td>cryst size (mm)</td>
<td>0.15 x 0.40 x 0.40</td>
</tr>
<tr>
<td>θ(<em>{min}), θ(</em>{max})</td>
<td>1.77, 27.50</td>
</tr>
<tr>
<td>radiation</td>
<td>Mo Kα (graphite-monochr), 0.71073 Å</td>
</tr>
<tr>
<td>tot. data</td>
<td>11160</td>
</tr>
<tr>
<td>tot. unique data</td>
<td>5259</td>
</tr>
<tr>
<td>final R1 {(Σ(</td>
<td>F_o</td>
</tr>
<tr>
<td>wR2 {(Σ[(w(F_o^2 - F_c^2)^2)/Σ(w(F_o^2))^2)]^{1/2}}</td>
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</tr>
<tr>
<td>S {(Σ[w(F_o^2 - F_c^2)^2]/(n - p))}^{1/2}</td>
<td>1.041</td>
</tr>
</tbody>
</table>
Figure 2.1: Structure of $[\text{Cr}(=\text{O})_2\{\text{OSiPh}_2\text{O}\}]_2$, I, in the crystal; ORTEP drawing with 50% probability ellipsoids. *a* Indicates symmetry operation $2 - x, 1 - y, 1 - z$.

Table 2.2. Selected Bond Lengths (Å) and Angles (deg) for $[\text{Cr}(=\text{O})_2\{\text{OSiPh}_2\text{O}\}]_2$, I.

<table>
<thead>
<tr>
<th>Bond lengths (Å)</th>
<th></th>
<th>Bond angles (°)</th>
<th></th>
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<tr>
<td>$\text{Cr}(1)-\text{O}(1)$</td>
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<td>$\text{O}(1)-\text{Cr}(1)-\text{O}(4)$</td>
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</tr>
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<td>$\text{Cr}(1)-\text{O}(4)$</td>
<td>1.579(2)</td>
<td>$\text{Cr}(1)-\text{O}(1)-\text{Si}(1)$</td>
<td>146.89(14)</td>
</tr>
<tr>
<td>$\text{Cr}(1)-\text{O}(5)$</td>
<td>1.568(2)</td>
<td>$\text{O}(1)-\text{Cr}(1)-\text{O}(5)$</td>
<td>109.90(11)</td>
</tr>
<tr>
<td>$\text{Cr}(1)-\text{O}(2a)$</td>
<td>1.7242(19)</td>
<td>$\text{Cr}(1)-\text{O}(1)-\text{O}(2a)$</td>
<td>110.27(9)</td>
</tr>
<tr>
<td>$\text{Cr}(1)-\text{O}(4)$</td>
<td></td>
<td>$\text{O}(1)-\text{Cr}(1)-\text{Si}(1)$</td>
<td>110.90(11)</td>
</tr>
<tr>
<td>$\text{Cr}(1)-\text{O}(5)$</td>
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<td></td>
<td>$\text{Si}(1)-\text{O}(3)-\text{Si}(2)$</td>
<td>169.25(13)</td>
</tr>
<tr>
<td>$\text{Cr}(1)-\text{O}(5)$</td>
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<td>$\text{Si}(1)-\text{O}(3)-\text{Si}(2)$</td>
<td>108.33(10)</td>
</tr>
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<td>$\text{Si}(1)-\text{O}(3)-\text{Si}(2)$</td>
<td>106.14(11)</td>
</tr>
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<td>$\text{O}(1)-\text{O}(3)$</td>
<td>169.25(13)</td>
<td>$\text{Si}(1)-\text{C}(1)-\text{C}(7)$</td>
<td>107.15(11)</td>
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<td>$\text{Cr}(1)-\text{O}(5)$</td>
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<td>$\text{Cr}(1)-\text{O}(5)-\text{Si}(2)$</td>
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<td>146.39(11)</td>
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<tr>
<td>$\text{O}(2)-\text{Si}(2)$</td>
<td>169.25(13)</td>
<td>$\text{Cr}(1)-\text{O}(5)-\text{Si}(2)$</td>
<td>114.14(10)</td>
</tr>
<tr>
<td>$\text{O}(2)-\text{Si}(2)$</td>
<td></td>
<td>$\text{Cr}(1)-\text{O}(5)-\text{Si}(2)$</td>
<td>114.14(10)</td>
</tr>
<tr>
<td>$\text{C}(19)-\text{Si}(2)$</td>
<td>114.14(10)</td>
<td>$\text{Cr}(1)-\text{O}(5)-\text{Si}(2)$</td>
<td>114.14(10)</td>
</tr>
<tr>
<td>$\text{C}(19)-\text{Si}(2)$</td>
<td>114.14(10)</td>
<td>$\text{Cr}(1)-\text{O}(5)-\text{Si}(2)$</td>
<td>114.14(10)</td>
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</tbody>
</table>
2.2.3 Catalytic epoxidation and catalyst stability

The stability in oxidizing, protic media was investigated for the siloxane complex, 1, and the silsesquioxane complexes 2a and 2b. In a typical experiment, a drop (0.05 mL) of a TBHP-solution (1.8 M in n-hexane) was added to an NMR-tube containing a solution of the investigated chromium complex (50 mg) in CDCl$_3$ (0.5 mL). The mixture was allowed to react for four hours at 50°C after which an NMR-analysis of the mixture was made. $^1$H-NMR clearly showed the reappearance of peaks assigned to the starting materials, i.e. siloxane or silsesquioxane silanol, indicating that under epoxidation conditions chromium leaches from the complexes. Epoxidation tests with chromium complexes 1, 2a and 2b confirmed the observations about the instability of the siloxy-chromium bond under epoxidation conditions as mentioned above.

The first catalytic experiments were performed in stirred 1.5 mL batch reactors, which were kept at 50°C. A solution containing equimolar amounts (1.8 mmol) of cyclooctene and tert.-butyl hydroperoxide (TBHP) in n-hexane (1.0 mL) was added to an amount of chromium complex, either 1 or 2, (corresponding to 1 mol% of chromium). After 24 hours all reaction mixtures had turned to green suspensions, which might be assigned to chromium(III)oxide, and had deactivated. Conversions of the alkene to epoxide were determined by $^1$H NMR and GC. In all cases, selectivities towards epoxide were above 95 % (table 2.3).

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>time [hours]</th>
<th>Conversion$^b$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>blanco (no catalyst)</td>
<td>16.5</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>[Cr(=O)$<em>2$]</em>{2}(OSiPh$_2$)$_2$O]$_2$</td>
<td>15.5</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>[(c-C$_5$H$_9$)$_7$Si$<em>7$O$</em>{11}$(OSiMe$_3$)CrO$_2$]</td>
<td>15.5</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>[(c-C$<em>6$H$</em>{11})_7$Si$<em>7$O$</em>{11}$(OSiMe$_3$)CrO$_2$]</td>
<td>15.5</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>CrO$_3$</td>
<td>16.5</td>
<td>80</td>
</tr>
</tbody>
</table>

$^a$n-hexane as solvent at 50°C with an alkene to peroxide ratio of 1 and 1 mol% of chromium.

$^b$Conversion is based on cyclooctene

In order to distinguish between catalytic activities of the chromium complexes and the reference CrO$_3$, a second set of catalytic tests were performed using twice the amount of TBHP and different alkenes. The conversions and selectivities of the reactions were measured after one, three and 24 hours.
Table 2.4. Epoxidation of alkenes with TBHP, catalyzed by 2a and CrO$_3$$^a$.

<table>
<thead>
<tr>
<th>alkene</th>
<th>time [h]</th>
<th>Conversion$^b$ [%]</th>
<th>Selectivity$^c$ [%]</th>
<th>Conversion$^b$ [%]</th>
<th>Selectivity$^c$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexene</td>
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<td>51</td>
<td>19</td>
<td>50</td>
<td>23</td>
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<td></td>
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<td></td>
<td>24</td>
<td>60</td>
<td>13</td>
<td>56</td>
<td>17</td>
</tr>
<tr>
<td>cyclooctene</td>
<td>1</td>
<td>57</td>
<td>&gt;95</td>
<td>59</td>
<td>&gt;95</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>73</td>
<td>&gt;95</td>
<td>73</td>
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<tr>
<td></td>
<td>24</td>
<td>81</td>
<td>&gt;95</td>
<td>80</td>
<td>&gt;95</td>
</tr>
<tr>
<td>1-octene</td>
<td>1</td>
<td>14</td>
<td>31</td>
<td>11</td>
<td>55</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>24</td>
<td>28</td>
<td>16</td>
<td>19</td>
<td>30</td>
</tr>
<tr>
<td>styrene</td>
<td>1</td>
<td>31</td>
<td>34</td>
<td>35</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>47</td>
<td>29</td>
<td>47</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>58</td>
<td>27</td>
<td>56</td>
<td>26</td>
</tr>
</tbody>
</table>

$^a$ in n-hexane as solvent at 50°C with an alkene to peroxide ratio of ½. $^b$ Conversion of alkene, calculated as (conversion$[t=t] = 100\% \times (\text{substrate}[t=0] − \text{substrate}[t=t]) / (\text{substrate}[t=0])$. $^c$ Selectivity towards epoxide, calculated as (selectivity$[t=t] = 100\% \times (\text{epoxide}[t=t]) / (\text{substrate}[t=0] − \text{substrate}[t=t])$.

Epoxidation tests using aqueous hydrogen peroxide instead of TBHP showed a rapid decomposition of the hydrogen peroxide to molecular oxygen within 10 minutes resulting in high pressure buildups together with complete lack of conversion of cyclooctene towards the epoxide.

2.3 Discussion

2.3.1 Structure of [Cr(=O)$_2${(OSiPh)$_2$O}]$_2$

The X-ray structure analysis shows 1 to be a dinuclear tetracoordinate chromium species, [Cr(=O)$_2${(OSiPh)$_2$O}]$_2$. In this structure, each of two dianionic disiloxanediolate ligands binds to two chromium dioxo units, generating an unique twelve-membered metallacyclic fragment (Fig. 2.2) with pseudo chair type conformation.

The chromium dioxo functionalities in 1 are incorporated in a remarkably close-packed ligand array involving the phenyl groups of the siloxanes and the pseudo equatorial chromium oxo functions (Fig. 2.3). In the solid state structure intramolecular contacts are present between O(5a)...C(6) [3.412(3) Å], and O(5a)...C(24a) [3.395(3) Å].
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Figure 2.2: View at the pseudo chair type conformation of the twelve-membered metallacyclic fragment present in the structure of 1.

The tetrahedral coordination of the metal centers in 1 is near perfect. As expected, the Cr=O bond lengths of both chromium oxo functions [1.568(2) and 1.579(2) Å] are substantially shorter than those present in the chromium siloxy units [Cr-O-Si: both 1.724(2) Å]. In 1, the two similar terminal Cr=O bond distances are close to those derived for CrO₂Cl₂ [1.577(2) Å]¹⁹ as well as to the Cr=O distances found in the silsesquioxane complex,⁷ᵃ [(c-C₆H₁₁)₇Si₃O₁₁(OSiMe₃)Cr(=O)₂], [1.557(5) and 1.574(4) Å]. In addition, there is a good agreement with the Cr=O distances present in the simple siloxy complexes²⁰ Cr(=O)₂Cl(OCPh₃), [1.576(5) and 1.594(5) Å] and Cr(=O)₂(OCPh₃)₂ [1.578(2) Å].

Figure 2.3: Space filling drawing of the chromium dioxo complex 1 showing the crowded coordination sphere around the pseudo equatorial oxo function.
The Si-O distances in the chromium siloxy functions \([\text{O}(1)-\text{Si}(1) = 1.644(2) \, \text{Å}; \text{O}(2)-\text{Si}(2) = 1.657(2) \, \text{Å}]\) are significantly larger than those present in the siloxane unit \([\text{Si}(1)-\text{O}(3) = 1.611(2) \, \text{Å}; \text{Si}(2)-\text{O}(3) = 1.614(2) \, \text{Å}]\). This may be ascribed to a stronger $\pi$-$d\pi$ electron donation of the oxygen lone pairs to the electron deficient chromium center than to the silicon atom. Consistent with this explanation is the finding that in a related low-valent chromium complex, \([\text{Cr}\{\text{OSiPh}_2\text{OSiPh}_2\text{O}\}_\mu-\text{Na(THF)}_2\}_2\] 21, that has a chromium center with formal oxidation state $2^+$ (c.f. $6^+$ for both chromium centers in 1), the Si-O distance in the chromium siloxy unit is shortened to $1.589(6) \, \text{Å}$.

The Si-O distances in the siloxane unit of 1 are typical for configurational unstrained siloxanes, 22 the Si-O-Si angle \([\text{Si}(1)-\text{O}(3)-\text{Si}(2) = 169.25(13)^\circ]\) being rather large. The conformation of siloxane functions, however, is known to be very flexible, thus providing siloxanes with a means to alleviate steric strain arising, for instance, from packing effects in the solid. A nice example of this comes from the X-ray structure of the starting siloxane in the synthesis of 1, \(\text{Ph}_2\text{Si(OH)OSi(OH)Ph}_2\), where the solid state structure comprises of three independent molecules with Si-O-Si angles of $147.8$, $157.0$, and $162.5^\circ$. 23 Lower-end values for related Si-O-Si angles, ranging from $123$-$133^\circ$ are found in a series of spirocyclic complexes of the type \([\text{M}\{\text{OSiPh}_2\text{OSiPh}_2\text{O}\}_\mu-\text{M'(L)}_2\}_2\], reported by Sullivan et al. 24 In 1, as in siloxanes in general, the bond angles around silicon \([105.5(1)-114.1(1)^\circ]\) show only minor deviations from the ideal tetrahedral value.

### 2.3.2 Chromate mediated epoxidation catalysis

Epoxidation experiments with TBHP and cyclooctene (table 2.3) showed the inability of TBHP to epoxidize cyclooctene under mild conditions (50°C) without the addition of a catalyst. The chromium silsesquioxane, 1, and the chromium silsequioxanes, 2, proved to be effective epoxidation catalysts at low concentrations (1 mol% Cr). The complexes were able to selectively epoxidize cyclooctene to form the epoxide in high yields under mild conditions (50°C). After one day, however, all the reaction solutions had gradually changed to greenish suspensions at which point the catalysts were deactivated. This indicates the formation of an catalytically inactive Cr(III) species unable to turn over to Cr(VI). 25

Comparison of CrO$_3$ to [(c-C$_5$H$_9$)$_7$Si$_3$O$_{11}$(OSiMe$_3$)CrO$_2$], 2a, in application as catalyst for different types of alkenes (table 2.4), the similarities in activity and selectivity are quite
striking. These results, combined with the results from the stability tests under epoxidation conditions of complexes 1 and 2 suggest that the active catalyst is not necessarily the chromium-siloxy complex itself but rather a leached out, catalytically highly active chromium(VI)oxide species.

2.4 Conclusions

The chromium(VI)siloxane complex, 1, and the chromium(VI)-silsesquioxanes, 2, effectively catalyze the epoxidation of alkenes using TBHP under mild reaction conditions. However, under oxidizing conditions in the presence of protic compounds the siloxy chromium bonds proved to be unstable, resulting in leaching of the chromium. The leaching of the chromium, and deactivation of the catalysts, possibly due to the gradual formation of a catalytically inactive chromium(III) species, therefore prevents the chromium siloxane, 1, and chromium silsesquioxanes, 2, from being used as reusable liquid phase epoxidation catalysts.

2.5 Experimental Section

General considerations. Solvents were distilled from Na (toluene), K (THF), Na/K alloy (ether, hexanes), or CaH2 (CH2Cl2). NMR solvents were dried over 4 Å molecular sieves (CDCl3). NMR spectra were recorded on a Varian GEMINI 300 and Bruker AC400 spectrometers. Chemical shifts are reported in ppm and referenced to residual solvent resonances (1H, 13C NMR) or external standards (29Si, SiMe4 = 0 ppm). Elemental analyses were carried out at the Organic Department of the Technical University of Eindhoven.

Synthesis. Caution! Chromium(vi) oxide is a cancer suspected strong oxidant; combinations with organic materials may cause explosions.

[Cr(=O)2{(OSiPh2)2O}2]2 (1). A suspension of 1,1,3,3-tetraphenyldisiloxane-1,3-diol26 (7.50 g, 18.1 mmol) and chromium trioxide (2.5 g, 25 mmol) in 100 mL of carbon tetrachloride containing activated 4 Å molsieves was magnetically stirred over night. The resulting voluminous bright yellow suspension was decanted from a residue containing the molsieves together with some dark precipitate. Subsequent removal of the solvent in vacuo and trituration of the residue with hexane (100 mL) afforded 7.33 g (85 %) of yellow powder that was already analytically pure [Anal. Calcd. for C48H40Cr2O10Si2: C, 58.05; H, 4.06. Found: C, 58.44; H, 3.79]. The compound can be crystallized in large block-shaped yellow crystals from hot carbon tetrachloride solutions.
Anal. Calcd. for C_{48}H_{40}Cr_{2}O_{10}Si_{2}: C, 58.05; H, 4.06; Cr, 10.47. Found: C, 58.18; H, 3.83; Cr, 10.45. Mp ~180 °C (dec.).

\[\text{H NMR (400 MHz, CDCl}_3, 23^\circ C, 
\text{TMS): } \delta \text{ 7.52 (d, 2H, Ar o-H), 7.42 (t, 1H, Ar p-H), 7.27 (t, 2H, Ar m-H).} \]

\[\text{13C NMR (100 MHz, CDCl}_3, 23^\circ C, \text{TMS): } \delta \text{ 134.57 (Ar, o-C), 131.99 (Ar, p-C), 130.89 (Ar, m-C), 128.00 (Ar, p-C).} \]

\[\text{29Si NMR (79.5 MHz, CH}_2\text{Cl}_2, 23^\circ C, \text{TMS, 0.02 M Cr(acac)}_3): \delta -31.91. \]

\[\text{[(c-C}_5\text{H}_9\text{)Si}_7\text{O}_{11}(OSiMe}_3\text{)CrO}_2\text{]}(2a). \]

In a typical reaction, a mixture of disilanol 2b (2.00 g, 2.11 mmol), CrO\textsubscript{3} (0.80 g, 8.0 mmol) and MgSO\textsubscript{4} (8.00 g) in CCl\textsubscript{4} (150 mL) was stirred overnight in the dark. Vacuum filtration and evaporation of the volatile material (25 °C, in the dark, 10\textsuperscript{-3} Torr) gave an amorphous orange foam, somewhat photosensitive, in 78.19 % yield.

Structure Determination and Refinement of 1. A transparent, yellow plate shaped crystal was mounted on the top of a glass-fiber (using the inert-oil technique) and transferred to the cold nitrogen stream of an Enraf-Nonius CAD4T diffractometer for data collection at 150K [Rotating anode, 50 kV, 70 mA, graphite-monochromated MoK\textalpha\textsuperscript{a} radiation, \omega\textsuperscript{b}-scan mode; \Delta\omega = (0.64 + 0.35 \tan\theta)^\circ]. Unit cell parameters were determined from a least squares treatment of the SET4 setting angles of 25 reflections with 9.94 < \theta < 14.04°. The unit cell parameters were checked for the presence of higher lattice symmetry.\textsuperscript{18} A total of 11160 reflections were collected and merged into a unique dataset of 5259 reflections (R\textsubscript{int} = 0.0491). Three intensity control reflections, (2 -3 -1, 2 2 2, 3 -3 -2) monitored every hour showed a small decay of 0.8% during the 26.8 hours of X-ray exposure time. The structure was solved with Direct methods (SHELXS-86)\textsuperscript{17} and subsequent difference Fourier analyses. Refinement on F\textsuperscript{2} with all 5259 unique reflections was carried out by full matrix least squares techniques. H-atoms were introduced on calculated positions and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters; H-atoms with isotropic thermal parameters related to the U\textsubscript{eq} of the carrier atoms.

Weights were introduced in the final refinement cycles, convergence was reached at R1 = 0.0381 [calculated for 4166 reflections with Fo > 4\sigma(Fo) ], wR2 = 0.0836 [for all unique reflections], w = 1.0/[ \sigma^2(Fo^2) + (0.0390*P)^2 + 0.58*P ] with P = [ Fo^2 + 2*Fc^2 ] / 3 . A final difference Fourier map shows no features outside the range -0.52 : +0.50 e/Å\textsuperscript{3}.

Acknowledgements

Nicolae Maxim is gratefully acknowledged for his contribution to this chapter.
References


26 Harris, G. I.; *J. Chem. Soc.*, 1963, 5978.
Chapter 3

Synthesis of robust titanium silsesquioxanes and their application in catalytic liquid phase alkene epoxidation involving aqueous media

Abstract: As part of an approach to design new catalysts for the environmentally friendly epoxidation of alkenes with aqueous hydrogen peroxide, several titanium silsesquioxanes were synthesized with various dentacity of silanolate ligation and their stability and reactivity in the presence of water was studied. The bidentate complexes of formula \([R_7Si_7O_9(OSiMe_3)O_2]_2Ti\) (\(R=\) c-C\(_5\)H\(_9\), c-C\(_6\)H\(_{11}\) and c-C\(_7\)H\(_{13}\)) were found to be unstable in the presence of water. The somewhat limited stability of the terdentate Si-O-ligated derivatives R\(_7\)Si\(_7\)O\(_{12}\)Ti-OH in the presence of water indicated that a higher dentacity of Si-O-Ti chelation is important albeit not the only factor. An additional requirement that has to be met involves hydrophobic congestion of the titanium site. This inherent shielding can be achieved by completion of the titanium coordination sphere with a sterically demanding ligand, as present in the cyclopentadienyl complexes R\(_7\)Si\(_7\)O\(_{12}\)Ti(Cp), R\(_7\)Si\(_7\)O\(_{12}\)Ti(\(\eta^5\)-C\(_5\)H\(_4\)(Si(CH\(_3\))\(_3\))) and R\(_7\)Si\(_7\)O\(_{12}\)Ti(\(\eta^5\)-C\(_5\)H\(_3\)-1,3-(Si(CH\(_3\))\(_3\))\(_2\)). These complexes were found to be completely stable in aqueous media.

3.1 Introducing industrially used titanium based epoxidation catalysts; on application and limitation

The use of epoxides as versatile and useful intermediates in organic synthesis has given rise to a high interest in the epoxidation of alkenes in both industry and academia. In the resulting search for non leaching heterogeneous liquid phase oxidation catalysts, a lot of attention is paid to the catalytic performance of the catalysts, rather than looking at the fundamental questions of which properties are responsible for the specific activity of a catalysts. In fact, a lot of catalysts consisting of a metal oxide on an inert carrier owe their
catalytic activity to rapid leaching of the metal from the surface to form active homogeneous catalysts,\(^1\) a fact that the designers of the original catalysts clearly didn’t have in mind. This phenomenon was clearly demonstrated in the previous chapter.

Titanium Silicalite-1\(^2\) (TS-1) and the Shell catalyst\(^3\) (titanium on silica) are two of the most successful members of the family of heterogeneous liquid-phase epoxidation catalysts. The Shell titanium/silica epoxidation catalyst is a highly active catalyst for the industrial epoxidation of propene using an organic peroxide, but only becomes truly heterogeneous after a certain time on stream. Interestingly this catalyst has been reported to leach titanium species, although catalytically inactive,\(^4\) during the initial stages of the reaction. This indicates that the catalysts as synthesized contain several differently anchored titanium sites. Similar catalysts, therefore, that are currently reported as the result of grafting silica\(^5\) or MCM-41 mesoporous silica\(^6\) with titanium derivatives might therefore be only partially heterogeneous when applied in liquid phase oxidation reactions.

The heterogeneous liquid phase catalyst TS-1 is especially known for its ability to epoxidize small alkenes with hydrogen peroxide.\(^7\) The use of hydrogen peroxide is preferred over organic peroxides for two reasons. The first reason is the relatively low cost of hydrogen peroxide. The second reason is that hydrogen peroxide leaves only water as a byproduct.

An inherent property of heterogeneous catalytic systems is the difficulty of studies of the active sites of the catalyst. As such we have studied epoxidations using titanium silsesquioxanes as model catalysts. In these silsesquioxanes, the titanium site is incorporated via spatially oriented siloxy bonds (Ti-O-Si), which structurally resemble surface sites that have been purportedly identified on silica surfaces.\(^8\) Silsesquioxanes also resemble silica surfaces in their electronic features. Unlike siloxane and alkoxy ligands, silsesquioxanes are electron withdrawing, as is the case with silica.\(^9\) These structural and electronic resemblances to silica make silsesquioxanes excellent candidates for modeling silica surfaces.\(^10\) Porous materials have recently been synthesized from silsesquioxane cage precursors,\(^11\) as well as metal containing polymeric derivatives.\(^12\) Currently, several groups are working on titanium silsesquioxanes,\(^13\) and work has been recently published in which titanium silsesquioxanes were shown to be active catalysts for alkene epoxidation. These complexes model monodentately,\(^14\) but also bidentately\(^15\) and terdentately bonded\(^16\) titanium on silica through siloxy chelation. Using silsesquioxane chemistry, even heterogeneous catalysts for the epoxidation of alkenes\(^17\) are being developed.
When designing a titanium-silsesquioxane catalyst for the epoxidation of alkenes, the dentacity of the silsesquioxane ligand is the first important factor that should be taken into account. When we assume a reaction path for the epoxidation, as proposed by Clerici and Sheldon, it is clear that the titanium should be at least bidentately bonded to one silsesquioxane ligand in order to prevent leaching of titanium (Fig. 3.1). This agrees with our earlier work on the importance of the dentacity of the titanium silsesquioxane complexes.

![Figure 3.1: Part of the epoxidation pathway proposed by Clerici and Sheldon in which the peroxide reacts with the titanium site to form an active species for epoxidation.](image)

When using aqueous hydrogen peroxide as the oxidant in alkene epoxidations, two problems are encountered. Both these problems are related to the presence of water during the reaction. The first and most important problem consists of the irreversible hydrolysis of all the siloxy-titanium units in the active sites. This generally results in catalyst deactivation through leaching of catalytically inactive titanium derivatives.

The second problem is caused by the presence of water, which obstructs the active sites of the catalyst and thereby sterically prevents the alkene to react with this site. While the latter problem only gives rise to a decreased activity of the titanium catalyst, the former severely limits the applicability of the catalyst to processes involving rigorously dried media. Since virtually all commercially available sources of hydrogen peroxide and organic peroxides, like the commonly applied tert-butyl hydroperoxide (TBHP), contain water to some extent, the practicality of water unstable epoxidation catalysts may be debated.

Here, the inhibiting effect of water on the catalytic performance of different titanium silsesquioxane complexes is reported. In a series of experiments, the activity of a catalyst in a dry medium to that of a catalyst in a wet medium is compared. To investigate to what extent hydrolysis of the catalyst is responsible for the decrease in activity of the catalyst, studies were also performed in which the catalysts were pretreated with water prior to catalysis.
3.2 Results

3.2.1 Synthesis of titanium silsesquioxane complexes

The complexes \((\text{c-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{TiCp}, \text{1a}, (\text{c-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{Ti}(\text{η}^5\text{-C}_5\text{H}_4\text{-SiMe}_3), \text{2a}, \text{and (c-C}_5\text{H}_9)_7\text{Si}_7\text{O}_{12}\text{Ti}(\text{η}^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_3)_2), \text{3a}, \) are conveniently synthesized by reaction of silsesquioxane \(\text{1a}\) with, respectively, \(\text{CpTiCl}_3\), \((\text{SiMe}_3-\text{η}^5\text{-C}_5\text{H}_4)\text{TiCl}_3\) and \((1,3-(\text{SiMe}_3)-\text{η}^5\text{-C}_5\text{H}_3)\text{TiCl}_3\) in the presence of a base, such as pyridine or triethylamine (Scheme 3.1). The reaction is carried out in dry toluene and under argon, after which the resulting ammonium salts are filtered off and the product is obtained in high purity after evaporating the solvents. The already known titanium complex \((\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}\text{Ti(η}^5\text{-C}_5\text{H}_5), \text{20b}, \text{and the new complexes (c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}\text{Ti(η}^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_3)_2), \text{3b}, \text{and (c-C}_7\text{H}_{13})_7\text{Si}_7\text{O}_{12}\text{Ti(η}^5\text{-C}_5\text{H}_3\text{-1,3-(SiMe}_3)_2), \text{3c}, \) are synthesized in a similar fashion by reaction of silsesquioxane \(\text{1b}\) with, respectively, \(\text{CpTiCl}_3\) and \((1,3-(\text{SiMe}_3)_2-\text{η}^5\text{-C}_5\text{H}_3)\text{TiCl}_3\) and silsesquioxane \(\text{1c}\) with \((1,3-(\text{SiMe}_3)_2-\text{η}^5\text{-C}_5\text{H}_3)\text{TiCl}_3\). NMR-analysis (\(^{13}\text{C}\) and \(^{29}\text{Si}\)) reveals that the \(\text{C}_3\)-symmetry of the silsesquioxane ligands in the new titanium complexes \(\text{1a, 1b, 2a, 3a, 3b and 3c}\) does not change upon reaction.

![Scheme 3.1: synthesis routes to various synthesized cyclopentadienyl ligated titanium-silsesquioxane catalysts.](image-url)
The synthesis of \((c-C_5H_9)_7Si_7O_{12}TiOH, \textbf{4a},\) and \((c-C_6H_{11})_7Si_7O_{12}TiOH, \textbf{4b},\) proceeds via a partial hydrolyzation of, respectively, \((c-C_5H_9)_7Si_7O_{12}TiO^1\text{Pr}\) and \((c-C_6H_{11})_7Si_7O_{12}TiO^1\text{Pr}.\) The latter are synthesized by reaction of \(\text{Ti(O}^\text{i-Pr})_4\) with silsesquioxanes \textbf{1a,} and \textbf{1b} (Scheme 3.2). The titanol silsesquioxanes \textbf{4a} and \textbf{4b} are soluble in THF, from which they are easily crystallized. \(^{29}\text{Si}\) NMR spectroscopy of complexes \textbf{4} in THF reveals the presence of not only the monomeric species, but also the presence of a dimeric species, which gives five signals with a relative intensity of 1:1:2:2:1. The equilibrium between the two forms is highly dependent upon the nature of the silsesquioxane cycloalkylgroups \(R.\) The cyclohexyl complex is for about 60% present as a monomer in THF, observed in \(^{29}\text{Si}\) NMR as two signals (δ -60.31 and –65.31 ppm) with relative intensities of 4:3, whereas the cyclopentyl complex \textbf{4a} mainly consists of the dimeric species. This effect has also been observed Maschmeyer et al.\(^{16}\) for similar methoxy and isoproxy complexes.

\[\begin{align*}
\text{Ti(O}^\text{i-Pr})_4 & \quad \text{R} = c-C_5H_9 (\text{a}), c-C_6H_{11} (\text{b}) \\
\text{H}_2\text{O} & \\
\text{4a-b} & \\
\end{align*}\]

\textbf{Scheme 3.2: Synthesis route of hydroxytitanium silsesquioxanes \((c-C_5H_9)_7Si_7O_{12}TiOH, \textbf{4a,}\) and \((c-C_6H_{11})_7Si_7O_{12}TiOH, \textbf{4b}.\)

Complex \([\{(c-C_5H_9)_7Si_7O_{11)(OSiMe_3)\}]_2\text{Ti}, \textbf{5a}\) is formed by adding \(\text{TiCl}_4\) to a solution of silsesquioxane \(\textbf{IIa},\) in the presence of a base, such as pyridine or triethylamine. Whatever stoichiometry is used for the reaction, the complex \([\{(c-C_5H_9)_7Si_7O_{11}(OSiMe_3)\}]\text{TiCl}_2,\) in which only one bidentate silsesquioxane ligand coordinates to titanium, could never be isolated. Crocker et al.\(^{15}\) were able to isolate a bipodal monosilsesquioxane titanium complex \([\{(c-\]
C_{6}H_{11})_{7}Si_{7}O_{11}[(OSiMe_{3})_{2}Ti\{O^{i}Pr\}]_{2} by stoechiometric reaction of Ti(O^{i}Pr)_{4} with 1 molequivalent of silsesquioxane IIb in THF. Due to the high reactivity of the titanium halide, the reaction of IIa with TiCl_{4} always proceeds to form complex 5a, in which two silsesquioxane ligands are each bidentately coordinated to titanium (Scheme 3.3).

The known complex [(c-C_{6}H_{11})_{7}Si_{7}O_{11}[(OSiMe_{3})_{2}]_{2}Ti, 5b, and the new complex [(c-C_{7}H_{13})_{7}Si_{7}O_{11}[(OSiMe_{3})_{2}]_{2}Ti, 5c, are synthesized in a similar way, and apart from the different R groups in the silsesquioxane ligand, they possess structural and chemical features similar to complex 5a. The presence of only one type of SiMe_{3} as observed by \textsuperscript{1}H, \textsuperscript{13}C and \textsuperscript{29}Si NMR spectroscopy suggests equivalence between the two silsesquioxane ligands. X-ray crystallography confirms this molecular C\textsubscript{2} symmetry in 5 (\textit{vide infra}). Upon reaction with TiL\textsubscript{4} the local symmetry of the silsesquioxane ligands II becomes distorted resulting in seven different signals observed with \textsuperscript{13}C and \textsuperscript{29}Si NMR spectroscopy, which is consistent with the formation of a tetrahedral coordinated titanium silsesquioxane complex.

\[
\text{R} = c-C_{5}H_{9} (a), c-C_{6}H_{11} (b), c-C_{7}H_{13} (c)
\]

\textit{Scheme 3.3: synthesis of the dimeric complexes [(c-C_{5}H_{9})_{7}Si_{7}O_{11}[(OSiMe_{3})_{2}]_{2}Ti, 5a, [(c-C_{6}H_{11})_{7}Si_{7}O_{11}[(OSiMe_{3})_{2}]_{2}Ti, 5b, and [(c-C_{7}H_{13})_{7}Si_{7}O_{11}[(OSiMe_{3})_{2}]_{2}Ti, 5c.}

\textbf{3.2.2. Structural characterization.}

X-ray crystallographic studies were carried out on (c-C_{5}H_{9})_{7}Si_{7}O_{12}Ti(\eta^{5}-C_{5}H_{3}-1,3-(SiMe_{3}))_{2}, 3a, and (c-C_{6}H_{11})_{7}Si_{7}O_{12}Ti(\eta^{5}-C_{5}H_{3}-1,3-(SiMe_{3}))_{2}, 3b. Table 3.1 collects crystal data and refinement parameters for the X-ray diffraction study of both complexes, while average bond distances and angles are collected in table 3.2 and 3.3. ORTEP drawings of 3a and 3b, along with the adopted numbering schemes are shown in Fig. 3.2 and 3.3, respectively. The molecules of 3a, a mononuclear six coordinated titanium complex,
crystallize in the space group P2\textsubscript{1}/c. The coordination sphere of the titanium atom in these three-legged piano stool complexes consists of a $\eta^5$-coordinated 1,3-di-trimethylsilyl-cyclopentadienyl ligand and is completed with three $\eta^3$-bonded siloxy units of the silsesquioxane [O(1), O(4), O(9)]. The siloxy O-Ti distances found in the complex fall within normal range of 1.81 to 1.82 Å and the bond angles and distances for the Si-O framework are not appreciably affected.\textsuperscript{22}

Complex 3\textit{b} crystallizes in a Pbca space group. The solid-state structure of complex 3\textit{b} shows a high similarity to complex 3\textit{a}, which has been described earlier. Complex 3\textit{b} also consists of a mononuclear six-coordinate titanium complex, in which titanium is $\eta^5$-bonded to a 1,3-di-trimethylsilyl-cyclopentadienyl ligand and $\eta^3$-coordinated to three siloxy units of the cyclohexyl-silsesquioxane ligand.
Table 3.1: Experimental data for the X-ray diffraction study of (R)$_2$Si$_7$O$_{12}$-TiCp” 3.

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<th>Compound</th>
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<th>3b</th>
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<tr>
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<td>C$<em>{46}$H$</em>{84}$O$<em>{12}$Si$</em>{9}$Ti</td>
<td>C$<em>{53}$H$</em>{98}$O$<em>{12}$Si$</em>{9}$Ti</td>
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<td>mol wt.</td>
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<td>0.38 x 0.38 x 0.50</td>
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<td>data coll. T [°C]</td>
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<td>-148</td>
</tr>
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<td>cryst. syst.</td>
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</tr>
<tr>
<td>b [Å]</td>
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<td>c [Å]</td>
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<td>27.938(2)</td>
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<tr>
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<td>90</td>
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<tr>
<td>β [deg]</td>
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</tr>
<tr>
<td>γ [deg]</td>
<td>90</td>
<td>90</td>
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<td>V [Å$^3$]</td>
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<td>13524(2)</td>
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<tr>
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<td>F(000)</td>
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<td>5280</td>
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<tr>
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<td>S</td>
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</tr>
<tr>
<td>D$<em>{ρ</em>{fin}}$(max/min) [e/Å$^3$]</td>
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<td>1.17/-0.54</td>
</tr>
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</table>
Figure 3.2: ORTEP plot of 3a showing 50% probability. Isotropically refined carbon atoms are drawn with arbitrary radii. Hydrogen atoms and the cyclopentyl rings on Si(2) and Si(4) have been omitted for clarity. Only one conformation of the disordered trimethylsilyl group on Si(8) is shown.

Table 3.2: Selected bond lengths (Å) and angles (deg) for (c-C$_5$H$_9$)$_7$Si$_7$O$_{12}$TiCp(SiMe$_3$)$_2$ 3a.

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<td>O(1)-Ti(1)-O(4) 102.2(3)</td>
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<td>Ti(1)-O(4)-Si(3) 151.2(4)</td>
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<td>Ti(1)-C(3) 2.392(10)</td>
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<td>Si(4)-C(41) 1.844(8)</td>
<td>Si(4)-C(41) 1.844(8)</td>
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Figure 3.3: ORTEP plot of 3b showing 50% probability. Isotropically refined carbon atoms are drawn with arbitrary radii. Hydrogen atoms and the cyclohexyl rings on Si(2) and Si(4) have been omitted for clarity.

Table 3.3: Selected bond lengths (Å) and angles (deg) for (c-C$_6$H$_{11}$)$_7$Si$_7$O$_7$TiCp(SiMe$_3$)$_2$3b.

<table>
<thead>
<tr>
<th></th>
<th>Bond Lengths</th>
<th>Bond Angles</th>
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<td>Ti(1)-O(4)</td>
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<td>Si(1)-O(2)</td>
<td>1.602(12)</td>
<td>O(1)-Si(1)-O(10)</td>
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Bond Angles

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Bond Angles

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3.2.3 Catalytic epoxidation and catalyst stability

The stability of the different titanium silsesquioxanes with regard to hydrolysis was studied by adding a drop of water (0.05 mL) to a solution of the catalyst (50 mg) in CDCl₃ (0.5 mL). After the mixture was kept sealed at 50°C for two days, it was analyzed by $^{13}$C-NMR spectroscopy. The spectrum obtained was compared to the spectrum of the original complex. In case of a difference between these two, the spectrum of the water-treated catalyst was also compared to that of the silsesquioxane silanol precursor of the used complex. The results of these screening tests are summarized in table 3.4.

Table 3.4: Summary of water stability of several titanium silsesquioxane complexes.

<table>
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<tr>
<th>Entry</th>
<th>Complex</th>
<th>Stability in wet media</th>
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<tbody>
<tr>
<td>1</td>
<td>[(C₅H₉)₇SiO₉(OSiMe₃)O₂]₂Ti (5a)</td>
<td>Not stable*</td>
</tr>
<tr>
<td>2</td>
<td>[(C₆H₁₁)₇SiO₉(OSiMe₃)O₂]₂Ti (5b)</td>
<td>Not stable*</td>
</tr>
<tr>
<td>3</td>
<td>(C₅H₉)₇SiO₂Ti-OH (4a)</td>
<td>Partially stable*⁺⁻</td>
</tr>
<tr>
<td>4</td>
<td>(C₅H₁₁)₇SiO₂Ti-OH (4b)</td>
<td>Partially stable*⁺⁻</td>
</tr>
<tr>
<td>5</td>
<td>(C₅H₉)₇SiO₂Ti-Cp (1a)</td>
<td>Stable</td>
</tr>
<tr>
<td>6</td>
<td>(C₅H₁₁)₇SiO₂Ti-Cp (1b)</td>
<td>Stable</td>
</tr>
<tr>
<td>7</td>
<td>(C₅H₉)₇SiO₂Ti-Cp(SiMe₃) (2a)</td>
<td>Stable</td>
</tr>
<tr>
<td>8</td>
<td>(C₅H₉)₇SiO₂Ti-Cp(SiMe₃)₂-1,3 (3a)</td>
<td>Stable</td>
</tr>
<tr>
<td>9</td>
<td>(C₅H₁₁)₇SiO₂Ti-Cp(SiMe₃)₂-1,3 (3b)</td>
<td>Stable</td>
</tr>
<tr>
<td>10</td>
<td>(C₅H₁₁)₇SiO₂Ti-Cp(SiMe₃)₂-1,3 (3c)</td>
<td>Stable</td>
</tr>
</tbody>
</table>

*After treatment with water, $^{13}$C NMR reveals the presence of the silanol precursor of the complex in the reaction mixture.⁺⁻About 50% hydrolysis to the silanol precursor.

The titanium silsesquioxanes 1-5 were screened as catalysts for activity in epoxidation reactions. The catalytic experiments were performed in stirred 1.5 mL batch reactors, which were kept at 50°C. All experiments were performed using 1 mol% of titanium. For the experiments that were performed in the absence of water, a solution containing equimolar amounts (1.6 mmol) of cyclooctene and tert.-butyl hydrogen peroxide (TBHP) in toluene (1.0 mL) were used. Experiments in wet media refer to similar solutions of cyclooctene and TBHP in toluene / water (1.0 mL, 9:1). Pretreatment of the catalyst involved stirring of the catalyst for 48 h at 50°C in toluene / water (0.4 mL, 3:1) prior to catalysis as described above in the procedure for wet media. Conversions of the alkene to epoxide were determined by $^1$H NMR. In all cases, selectivities were above 95%. 
Table 3.5: Epoxidation of cyclooctene with TBHP in respectively dry and wet media.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>Time (h)</th>
<th>dry medium</th>
<th>wet medium</th>
<th>wet medium with pretreatment</th>
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<td>1</td>
<td>5a</td>
<td>3</td>
<td>55</td>
<td>29</td>
<td>18</td>
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<tr>
<td>2</td>
<td>5b</td>
<td>3</td>
<td>55</td>
<td>30</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>5c</td>
<td>3</td>
<td>41</td>
<td>35</td>
<td>31</td>
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<tr>
<td>4</td>
<td>4a</td>
<td>3</td>
<td>93</td>
<td>84</td>
<td>70</td>
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</tr>
<tr>
<td>6</td>
<td>1a</td>
<td>3</td>
<td>80</td>
<td>69</td>
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<tr>
<td>7</td>
<td>1b</td>
<td>3</td>
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<td>71</td>
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<tr>
<td>8</td>
<td>2a</td>
<td>3</td>
<td>33</td>
<td>27</td>
<td>34</td>
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<tr>
<td>9</td>
<td>3b</td>
<td>3</td>
<td>15</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>10</td>
<td>3c</td>
<td>3</td>
<td>22</td>
<td>12</td>
<td>13</td>
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3.3 Discussion

3.3.1 Activity and stability in epoxidation catalysis

From Table 3.4, it can be concluded that the complexes 5 (entries 1 and 2), which contain bidentate bonding silsesquioxane silanolate ligands, are most easily hydrolyzed. Compounds 4, which contain a terdentate silsesquioxane silanolate ligand (entries 3-10) are more resistant. In addition, from the series of complexes studied, it becomes clear that the presence of a terdentately bonding silsesquioxane ligand does not determine the entire stability of the complex (c.f. entries 3-4 with entries 5-10).

Stability further depends on the ligand that completes the coordination sphere of titanium. If this ligand consists of a cyclopentadienyl (entries 5 and 6) or a substituted cyclopentadienyl function (entries 7 -10), the complex is stable. Complex 4a (entry 3) and 4b (entry 4) having a hydroxy instead of a Cp function are not stable, which could not be predicted from the dentacity of the silsesquioxane alone. The instability of complexes 4a and 4b implies that the acidity of water is high enough to hydrolyze all siloxy-titanium units. For catalytic application in protic media this finding therefore excludes a large group of known titanium silsesquioxane compounds that can be described with the general formula (R)\(_7\)Si\(_7\)O\(_{12}\)Ti-L, in which L stands for an alkyl or alkoxy group. These titanium
silsesquioxanes will react with water to form initially the silsesquioxane titanol complexes, 4, which were shown to hydrolyze slowly. In none of the experiments an influence of the silsesquioxane cycloalkylgroups R on the rate of hydrolysis was noticed.

The catalysts, which were found stable in wet media (entries 5-10), should show a decrease in activity due to two possible effects of water, obstruction and competition. The obstructing effect means that at the time a catalyst has formed an active complex with peroxide, the water coordinates loosely around this peroxo complex and by doing so, the water prevents the alkene from coming close enough to react. Competition can occur between the peroxide and water, which are both able to react with the titanium site. In case water reacts with the titanium site, a non-productive Ti-OH complex is formed.

As a consequence of the results of the stability tests stated in Table 3.4, it is unlikely that the catalysts given in entries 1-4 will be suited for epoxidation reactions in wet media. This limits these catalysts to epoxidation reactions in vigorously dried media. This also implies that it is impossible to use these catalysts successfully in epoxidation reactions involving hydrogen peroxide as the oxygen transfer agent.

Steric hindrance plays an important role when using an anhydrous reaction medium. The results on catalytic epoxidation activity in Table 3.5 show that the complexes in which the titanium is sterically most shielded (entries 8-10) are the least active epoxidation catalysts. Catalysts in which the titanium is easily accessible (entries 4 and 5) are the most active epoxidation catalysts in anhydrous reaction conditions.

The influence of water is visible when using a wet reaction medium for the epoxidation reactions. The general trend shows a decrease in activity of the catalyst when a wet reaction medium is used.

The destructive effect of water on several catalysts is also visible in Table 3.5. As predicted in the section on stability in this report, the complexes 4a, 4b, 5a, 5b and 5c (entries 1-5) show an additional decrease in activity when pretreated with water prior to epoxidation reactions. This clearly shows that water irreversibly hydrolyzes these complexes completely to form catalytic inactive species, which consist of the silanol precursors and catalytic inactive titanium compounds. These results are in agreement with the results given earlier in this report on the stability of the catalysts.
3.4 Conclusions

Of all the titanium silsesquioxane complexes that were synthesized, only the terdentate titanium cyclopentadienyl complexes 1a, 1b and 2a were found to be suitable catalysts for the epoxidation of alkenes in aqueous media. Future research on catalysts using aqueous hydrogen peroxide should concentrate on these titanium silsesquioxanes. The 1,3-substituted cyclopentadienyl complexes 3a and 3b have a too low activity towards epoxidation reactions because of the bulkiness of the cyclopentadienyl ligand on the titanium center.

Terdentate silsesquioxane complexes 4a and 4b, and the bidentate silsesquioxanes 5a, 5b and 5c were irreversibly hydrolyzed by water, which makes these catalysts unsuitable in wet media.

Dentacity of siloxy chelation is the main factor that determines whether a titanium silsesquioxane catalyst is stable in anhydrous media. However, when a wet media for the epoxidation reaction is used, the dentacity is not the only factor that determines the stability of the catalyst. The intramolecular surrounding of the titanium site should be hydrophobic enough to be able to protect this site against irreversible hydrolysis.

3.5 Experimental Section

General considerations. All manipulations with air- or moisture sensitive materials were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were distilled from Na (toluene), K (THF), Na/K alloy (ether, hexanes), or CaH2 (CH2Cl2). NMR solvents were dried over 4 Å molecular sieves (CDCl3). NMR spectra were recorded on a Varian GEMINI 300 and Bruker AC400 spectrometers. Chemical shifts are reported in ppm and referenced to residual solvent resonances (1H, 13C NMR) or external standards (29Si, SiMe4 = 0 ppm). Elemental analyses were carried out at the Organic Department of the Technical University of Eindhoven. Silsesquioxanes (c-C5H9)7Si7O9(OH)3 (Ia), (c-C6H11)7Si7O9(OH)3 (Ib), (c-C7H13)7Si7O9(OH)3 (Ic), (c-C5H9)7Si7O9(OSiMe3)(OH)2 (IIa), (c-C6H11)7Si7O9(OSiMe3)(OH)2 (IIb) and (c-C7H13)7Si7O9(OSiMe3)(OH)2 (IIc) were prepared following literature procedures. TiCl4 (Aldrich) and Ti(OPr)i4 (Acros) were used without further purifications.

(cyclopentyl)Si2O12TiCp (1a). At room temperature a solution of CpTiCl3 (0.35 g, 1.60 mmol) in chloroform (60 mL) was added to a solution of (cyclopentyl)Si2O4(OH)3 (1.43 g, 1.60 mmol) and pyridine (8.5 mL) in chloroform (60 mL). The mixture was stirred over night after which the volatiles were removed in vacuum. Extraction of the remaining white solid with 60 mL of toluene and removal of the solvent of the filtrate
in vacuum afforded 1.71 g (cyclopentyl)$_2$Si$_2$O$_2$TiCp as an amorphous solid. $^1$H NMR NMR (300 MHz, CDCl$_3$, 23°C, SiMe$_3$): δ 6.47 (s, 5H, cyclopentadienyl); δ 1.83-1.65, 1.65-1.38 (m, 56H, CH$_2$-groups of C$_5$H$_5$); δ 1.02-0.83 (m, 7H, CH-group of C$_5$H$_5$). $^{13}$C NMR (100 MHz, CDCl$_3$, 23°C, SiMe$_3$): δ 115.90 (CH-groups of cyclopentadienyl); δ 27.64, 27.43, 27.30, 27.08, 27.02 (s, CH$_2$-groups of C$_5$H$_5$); δ 22.41, 22.32 (s, 1:1, CH-groups of C$_5$H$_5$): $^{29}$Si NMR (79.5 MHz, CHCl$_3$, 0.02 M Cr(acac)$_3$, 23°C, SiMe$_3$): δ - 64.0746, -66.4619, -67.3040 (s, 3:1:3, Si of silsesquioxane cage). Anal. Calcd for C$_{49}$H$_{89}$O$_2$Si$_4$Ti (found): C, 48.75 (48.40); H, 6.96 (6.93).

(cyclopentyl)$_2$Si$_2$O$_2$TiCp(SiMe$_3$)$_2$ (2a). At room temperature, Cp(SiMe$_3$)$_2$TiCl$_3$ (0.68 g, 2.33 mmol) was added to a solution of (cyclopentyl)$_2$Si$_2$O$_2$(OH)$_2$ (2.05 g, 3.34 mmol) in toluene (30 mL). Pyridine (1 mL) was added. The mixture was heated up to 80°C and stirred for two hours. The volatiles were removed in vacuum and the remaining solid was extracted with hexanes (50 mL). Evaporation of the hexanes resulted in (cyclopentyl)$_2$Si$_2$O$_2$TiCp(SiMe$_3$)$_2$ in quantitative yield. Analytical pure (cyclopentyl)$_2$Si$_2$O$_2$TiCp(SiMe$_3$)$_2$ was obtained by layering a toluene solution of the product with acetonitrile. This afforded 1.86 grams of (cyclopentyl)$_2$Si$_2$O$_2$TiCp(SiMe$_3$)$_2$ as colorless crystals (yield 75%). $^1$H NMR NMR (300 MHz, CDCl$_3$, 23°C, SiMe$_3$): δ 6.69, 6.54 (m, 4H, CH-groups of cyclopentadienyl); δ 1.84-1.68, 1.68-1.39 (m, 56H, CH$_2$-groups of C$_5$H$_5$); δ 1.02-0.85 (m, 7H, CH-group of C$_5$H$_5$); δ 0.32 (s, 9H, SiMe$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 23°C, SiMe$_3$): δ 125.65, 124.62, 118.08 (s, 1:2:2, cyclopentadienyl); δ 27.73, 27.39, 27.30, 27.09, 27.03 (s, CH$_2$-groups of C$_5$H$_5$); δ 22.55, 22.31, (s, 1:1, CH-groups of C$_5$H$_5$); δ -0.46 (s, CH$_2$-groups of SiMe$_3$). Anal. Calcd for C$_{49}$H$_{89}$O$_2$Si$_4$Ti (found): C, 48.83 (48.28); H, 7.24 (7.42).

(cyclopentyl)$_2$Si$_2$O$_2$TiCp(SiMe$_3$)$_2$ (3a). At room temperature a solution of Cp(SiMe$_3$)$_2$TiCl$_3$ (0.81 g, 2.23 mmol) in CHCl$_3$ (75 mL) was added to a solution of (cyclopentyl)$_2$Si$_2$O$_2$(OH)$_2$ (2.46 g, 2.81 mmol) in CHCl$_3$ (75 mL) after which 10 mL of pyridine was added. The mixture was stirred over night followed by removal of the volatiles in vacuum. Extraction of the remaining solid with toluene (80 mL) and evaporation of the filtrate to 25 mL followed by a crystallization by careful layering the solution with acetonitrile (25 mL) afforded 2.42 gram of (cyclopentyl)$_2$Si$_2$O$_2$TiCp(SiMe$_3$)$_2$ as colorless crystals. $^1$H NMR NMR (300 MHz, CDCl$_3$, 23°C, SiMe$_3$): δ 6.79 (s, 1H, cyclopentadienyl); δ6.71 (s, 2H, CH of cyclopentadienyl); δ 1.76-1.68, 1.68-1.44 (m, 56H, CH$_2$-groups of C$_5$H$_5$); δ 1.00-0.85 (m, 7H, CH-group of C$_5$H$_5$); δ 0.29 (s, 18H, SiMe$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 23°C, SiMe$_3$): δ 132.90, 130.80 (s, 1:2, CH-groups of cyclopentadienyl), 125.47 (s C-Si-groups of cyclopentadienyl); δ 27.87, 27.35, 27.03 (s, CH$_2$-groups of C$_5$H$_5$); δ 22.78, 22.28, 22.27 (s, 3:1:3, CH-groups of C$_5$H$_5$); δ -0.27 (s, CH$_2$-groups of SiMe$_3$). $^{29}$Si NMR (79.5 MHz, CHCl$_3$, 0.02 M Cr(acac)$_3$, 23°C, SiMe$_3$): δ -64.8484, -67.1692, -68.1550 (s, 3:1:3, Si of silsesquioxane cage). Anal. Calcd for C$_{49}$H$_{89}$O$_2$Si$_4$Ti (found): C, 48.75 (49.06); H, 6.96 (6.86).

(cyclohexyl)$_2$Si$_2$O$_2$TiCp(SiMe$_3$)$_2$ (3b). At room temperature a solution of Cp(SiMe$_3$)$_2$TiCl$_3$ (0.46 g, 1.26 mmol) in CHCl$_3$ (60 mL) was added to a solution of (cyclohexyl)$_2$Si$_2$O$_2$(OH)$_2$ (1.27 g, 1.30 mmol) and 10 mL of pyridine in CHCl$_3$ (60 mL). The mixture was stirred overnight followed by removal of the volatiles in vacuum. Extraction of the remaining solid with toluene (80 mL) and evaporation of the filtrate to ~10 mL
followed by a crystallization by careful layering the solution with acetonitrile (8 mL) afforded 1.32 gram of [(cyclohexyl)Si-O]_2TiCp(SiMe)_2 as colorless crystals (yield 85%).^1^H NMR (300 MHz, CDCl_3, 23°C, SiMe_3): δ 6.80 (s, 1H, cyclopentadienyl); δ 6.69 (s, 2H, cyclopentadienyl); δ 1.76-1.70, 1.25-1.19 (m, 70H, CH_2-groups of C_6H_5); δ 0.77-0.63 (m, 7H, CH-group of C_6H_5); δ 0.29 (s, 18H, SiMe_3).^13^C NMR (100 MHz, CDCl_3, 23°C, SiMe_3): δ 133.48, 130.26 (s, 1:2, CH-groups of cyclopentadienyl); δ 125.51 (s, C-Si-groups of cyclopentadienyl); δ 27.71, 27.57, 27.35, 26.97, 26.77, 26.66 (s, CH_2-groups of C_6H_5); δ 23.82, 23.24, 23.13 (s, 3:1:3, CH-groups of C_6H_5); δ -0.24 (s, SiMe_3): ^29^Si NMR (79.5 MHz, CHCl_3, 0.02 M Cr(acac)_3, 23°C, SiMe_3): δ -66.9903, -69.2925, -70.2685 (s, 3:1:3, Si of silsesquioxane cage). Anal. Caled for C_{35}H_{90}O_{12}Si_5Ti: C, 51.84 (51.85); H, 8.04 (8.13).

[(cycloheptyl)Si-O]_2TiCp(SiMe)_2 (3c). At room temperature, Cp(SiMe_3)_2TiCl_3 (0.66 g, 1.81 mmol) was added to a solution of [(cycloheptyl)Si-O]_2TiCp(SiMe)_2 in THF (50 mL). The mixture was stirred overnight followed by filtration to remove the pyridinium hydrochloride salt. Quenching the remaining clear filtrate with acetonitrile afforded 1.39 g of [(cycloheptyl)Si-O]_2TiCp(SiMe)_2 as an amorphous yellowish solid (Yield 75%). Analytical pure [(cycloheptyl)Si-O]_2TiCp(SiMe)_2 could be obtained by careful layering a toluene solution of [(cycloheptyl)Si-O]_2TiCp(SiMe)_2 with acetonitrile. ^1^H NMR (300 MHz, CDCl_3, 23°C, SiMe_3): δ 6.82 (s, 1H, cyclopentadienyl); δ 6.76 (s, 2H, cyclopentadienyl); δ 1.96-1.63, 1.63-1.21 (m, 84H, CH-groups of C_7H_12); δ 0.87-0.73 (m, 7H, CH-group of C_7H_12); δ 0.30 (s, 18H, SiMe_3).^13^C NMR (100 MHz, CDCl_3, 23°C, SiMe_3): δ 133.46, 130.45 (s, 1:2, CH-groups of cyclopentadienyl); δ 125.52 (s, C-Si-groups of cyclopentadienyl); δ 29.63, 29.41, 28.75, 28.73, 28.62, 28.15 (s, CH_2-groups of C_7H_12); δ 24.70, 23.99 (s, 2:2, CH-groups of C_7H_12); δ -0.15 (s, CH_3-groups of SiMe_3). Anal. Caled for C_{30}H_{82}O_{12}Si_5Ti: C, 54.34 (54.10); H, 8.51 (8.37).

[(cyclopentyl)Si-O]_2Ti(OH) (4a). Titanium(IV)isopropoxide (0.66 g, 2.33 mmol) was added, at room temperature, to a solution of [(cyclopentyl)Si-O]_2Ti(OH) (2.04 g, 2.33 mmol) in THF (50 mL). After five hours, one moleequivalent of water (40 µL, 2.33 mmol) was added. The mixture was stirred overnight followed by an evaporation of the solution to ~15 mL. Heating up the remaining suspension, followed by a slow cooling yielded 0.97 g of [(cyclopentyl)Si-O]_2Ti(OH) as colorless crystals (yield 45%). ^1^H NMR (300 MHz, CDCl_3, 23°C, SiMe_3): δ 1.90-1.63, 1.63-1.39 (m, 56H, CH_2-groups of C_5H_10); δ 1.09-0.91 (m, 7H, CH-groups of C_5H_10); ^13^C NMR (100 MHz, CDCl_3, 23°C, SiMe_3): δ 22.98, 22.46, 22.25 (s, 1:3:3, CH-groups of C_5H_10). ^29^Si NMR (99.3 MHz, THF, 0.02 M Cr(acac)_3, 23°C, SiMe_3): δ -65.93, -66.36, -66.65, -67.18, -67.21 (s, 1:1:2:2:1, Si of dimeric species). Anal. Caled for C_{13}H_{34}O_{13}Si_5Ti: C, 44.85 (44.91); H, 6.88 (6.92).

[(cyclohexyl)Si-O]_2Ti(OH) (4b). Titanium(IV)isopropoxide (0.43 g, 1.52 mmol) was added, at room temperature, to a solution of [(cyclohexyl)Si-O]_2(OH) (1.48 g, 1.52 mmol) in THF (50 mL). After five hours about one moleequivalent of water (30 µL, 1.66 mmol) was added. The mixture for another hour followed by an evaporation of the solution to ~10 mL. Heating up the remaining suspension, followed by a slow cooling yielded 0.92 g of [(cyclohexyl)Si-O]_2Ti(OH) as colorless crystals (yield 60%). ^1^H NMR (300 MHz, CDCl_3, 23°C, SiMe_3): δ 1.98-1.68, 1.68-1.38 (m, 70H, CH_2-groups of C_6H_11); δ 0.98 (m, 7H, CH-groups of C_6H_11). ^13^C NMR
(100 MHz, CDCl$_3$, 23°C, SiMe$_3$): $\delta$ 23.09, 22.98, 22.47 (s, 1:3:3, CH-groups of C$_6$H$_{11}$). $^{29}$Si NMR (99.3 MHz, THF, 0.02 M Cr(acac)$_3$, 23°C, SiMe$_3$): $\delta$ -60.31, -65.31 (s, 4:3, Si of monomeric species); $\delta$ -67.90, -68.14, -69.15, -69.68 (s, 1:1:2:3, Si of dimeric species). Anal. Calcd for C$_{42}$H$_{70}$O$_2$Si$_7$Ti (found): C, 48.71 (49.60); H, 7.59 (7.65).

{(cyclopentyl)$_2$-Si-O$_4$(OSiMe$_3$)$_2$O$_2$}$_2$Ti (5a). At room temperature TiCl$_4$ (0.16 g, 0.84 mmol) was added to a solution of (cyclopentyl)$_2$Si-O$_4$(OSiMe$_3$)(OH)$_2$ (1.03 g, 1.09 mmol) in toluene (50 mL). After addition of pyridine (0.22 mL) the mixture was stirred over night. The suspension was centrifuged and decanted which left a yellowish solid (pyridinium hydrochloride) and an almost colorless solution. The solution was quenched with acetonitrile (200 mL) which yielded 0.92 gram {(cyclopentyl)$_2$-Si-O$_4$(OSiMe$_3$)$_2$O$_2$}$_2$Ti as a white solid. (Yield 87%). $^1$H NMR NMR (300 MHz, CDCl$_3$, 23°C, SiMe$_3$): $\delta$ 1.80 (m, 14H, CH$_2$-groups of C$_6$H$_{10}$); $\delta$ 1.62 (m, 84H, CH$_2$-groups of C$_8$H$_{18}$); $\delta$ 1.01 (m, 28H, CH-groups of C$_5$H$_{11}$); $\delta$ 0.21 (s, 18H, CH$_2$-groups of Si(CH$_3$)$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 23°C, SiMe$_3$): $\delta$ 27.79, 27.65, 27.53, 27.39, 27.09, 26.99 (s, CH$_2$-groups of C$_8$H$_{18}$); $\delta$ 24.36, 23.50, 23.21, 23.12, 23.02, 22.47, 22.35 (s, 1:1:1:1:1:1:1, CH-groups of C$_5$H$_{11}$); $\delta$ 1.93 (s, CH$_2$-groups of Si(CH$_3$)$_3$). $^{29}$Si NMR (79.5 MHz, CHCl$_3$, 0.02 M Cr(acac)$_3$, 23°C, SiMe$_3$): $\delta$ -65.75, -66.27, -66.63, -67.61, -68.59, -68.76, -68.81 (s, 1:1:1:1:1:1, Si of silsesquioxane cage). Anal. Calcd for C$_{78}$H$_{144}$O$_{24}$Si$_{16}$Ti (found): C, 47.07 (46.30); H, 7.48 (7.54).

{(cyclohexyl)$_2$-Si-O$_4$(OSiMe$_3$)O$_2$}$_2$Ti (5b). At room temperature TiCl$_4$ (0.345 g, 1.82 mmol) was added to a solution of (cyclohexyl)$_2$Si-O$_4$(OSiMe$_3$)(OH)$_2$ (3.73 g, 3.57 mmol) in toluene (75 mL). After addition of pyridine (0.72 mL) the mixture was stirred overnight. The suspension was centrifuged and decanted which left a yellowish solid (pyridinium hydrochloride) and an almost colorless solution. The solution was quenched with acetonitrile (200 mL) which yielded 3.47 gram {(cyclohexyl)$_2$-Si-O$_4$(OSiMe$_3$)O$_2$}$_2$Ti in 3 mL of toluene and crystallization by vapor diffusion of acetonitrile into the solution. $^1$H NMR (300 MHz, CDCl$_3$, 23°C, SiMe$_3$): $\delta$ 1.89-1.61, 1.39-1.09 (m, 140H, CH$_2$-groups of C$_6$H$_{11}$); $\delta$ 0.93-0.58 (m, 14H, CH-group of C$_6$H$_{11}$); $\delta$ 0.15 (s, 18H, SiMe$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 23°C, SiMe$_3$): $\delta$ 27.73-27.48, 26.95-26.66 (m, CH$_2$-groups of C$_6$H$_{11}$); $\delta$ 24.96, 24.57, 24.20, 24.19, 23.85, 23.17, 23.15 (s, 1:1:1:1:1:1:1, CH-groups of C$_6$H$_{11}$); $\delta$ 1.99 (s, CH$_2$-groups of SiMe$_3$). $^{29}$Si NMR (79.5 MHz, CHCl$_3$, 0.02 M Cr(acac)$_3$, 23°C, SiMe$_3$): $\delta$ -67.89, -68.20, -68.31, -69.67, -70.76, -70.94, -71.13 (s, 1:1:1:1:1:1, Si of silsesquioxane cage). Anal. Calcd for C$_{90}$H$_{172}$O$_{24}$Si$_{16}$Ti (found): C, 52.30 (51.96); H, 8.14 (8.21).

{(cyclohexyl)$_2$-Si-O$_4$(OSiMe$_3$)SO$_2$}$_2$Ti (5c). At room temperature TiCl$_4$ (0.259 g, 1.37 mmol) was added to a solution of (cyclohexyl)$_2$Si-O$_4$(OSiMe$_3$)(OH)$_2$ (3.03 g, 2.65 mmol) in toluene (75 mL). After addition of pyridine (0.55 mL) the mixture was stirred for 15 minutes. The suspension was filtrated and the volatiles were evaporated until 20 mL. Layering the solution with 10 mL of acetonitrile yielded {(cyclohexyl)$_2$-Si-O$_4$(OSiMe$_3$)SO$_2$}$_2$Ti as a white microcrystalline solid (2.16 g, yield 70%). $^1$H NMR (300 MHz, CDCl$_3$, 23°C, SiMe$_3$): $\delta$ 1.98-1.02 (m, 168H, CH$_2$-groups of C$_8$H$_{18}$); $\delta$ 0.94-0.57 (m, 14H, CH-group of C$_8$H$_{18}$); $\delta$ 0.11 (s, 18H, SiMe$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 23°C, SiMe$_3$): $\delta$ 30.00-29.19, 28.74-27.97 (m,
CH₂-groups of C₇H₁₃); δ 25.59, 25.00, 24.78, 24.62, 24.14, 24.00, 23.72 (s, 1:1:1:1:1:1:1, CH₂-groups of C₇H₁₃); δ 2.01 (s, CH₂-groups of SiMe₃). Anal. Caled for C₁₀₄H₂₀₀O₂₄Si₁₆Ti (found): C, 53.57 (53.27); H, 8.64 (8.58).

Structure determination and refinement of 3a and 3b. X-ray data were collected on an Enraf-Nonius CAD4T rotating anode diffractometer for colorless crystals fixed with polyfluoropolyether-oil on the top of a glass fiber. Accurate cell parameters were derived from the setting angle of 25 well-centered reflections. The unit cell parameters were checked for the presence of higher lattice symmetry. Data were corrected for Lorentz polarization effects. No absorption correction was considered necessary. The structures were solved by automated Patterson methods (DIRDIF-96). Refinement on F² was carried out by full-matrix least-squares techniques (SHELXL-97) on all reflections. The cyclopentyl groups (3a) and the cyclohexyl groups (3b) were heavily disordered. Therefore only the terminal carbon atoms were refined with anisotropical displacement parameters. The other atoms in the rings were refined isotropically. The trimethylsilyl group on Si(8) in the structure of 3a is rotationally disordered and treated with splitted atoms which were isotropically refined. Hydrogen atoms were included on calculated positions, riding on their carrier atoms with fixed isotropic displacement parameters (U = 0.05). Weights were optimized in the final refinement cycles. Neutral atom scattering factors were taken from a literature reference. Geometrical calculations and illustrations were performed with PLATON. Crystal data and details of on data collections and refinement are collected in Table 3.1. Selected geometrical details are listed in Tables 3.3 and 3.4.

Catalytic experiments: Catalytic epoxidation experiments were performed in magnetically stirred 1.5 mL batch reactors, which were kept at 50°C. All experiments were performed using 1 mol% of titanium. Experiments in water-free media were performed using a solution containing equimolar amounts (1.6 mmol) of cyclooctene and tert.-butyl hydrogen peroxide (TBHP) in toluene (1.0 mL). Experiments in wet media refer to similar solutions of cyclooctene and TBHP in toluene / water (1.0 mL, 9:1). Pretreatment of the catalyst with water involved stirring of the catalyst for 48 hours at 50°C in toluene / water (0.4 mL, 3:1) prior to addition of TBHP resulting in the same reaction conditions as described above in the procedure for wet media. Conversions of the alkene to epoxide were determined using ¹H NMR.

References


Chapter 4

Synthesis and structural characterization of silsesquioxane ligated polyoxotitanates; catalytic alkene epoxidation with aqueous H$_2$O$_2$

Abstract: Silsesquioxanes are used as synthetic platforms for the construction of the polyoxometal framework of new polyoxotitanates [(R)$_6$Si$_6$O$_{11}$][Ti($\mu^3$-OH)]$_4$ [R = c-C$_6$H$_{11}$, c-C$_7$H$_{13}$]. These polyoxotitanates proved to be robust catalysts for the epoxidation of cyclooctene using TBHP and to some extent even aqueous hydrogen peroxide. The catalytic results are briefly compared to two other known molecular defined titaniumoxideclusters, [TiO(OSiMe$_3$)(O$_2$P(O$^t$Bu)$_2$)$_4$, and [Ti$_3$(\mu$_3$-O)(\mu$_2$-OH)$_3$(\mu$_2$-HCOO)$_3$(\eta$^5$-C$_5$H$_5$)$_3$]-HCOO$\cdot$2HCOOH.

4.1 Introduction

Polyoxometalates$^1$ and heteropolyacids,$^2$ are emerging as interesting catalysts. The scope of their application may allow for development of a procedure for the epoxidation of alkenes using environmentally friendly oxidants like O$_2$ and H$_2$O$_2$.$^3$ Unfortunately, the synthesis of these materials is often rather empiric and the structural characterizations involved can be difficult.$^4$ As such, further development of successful catalysts from this area of science may need a completely new class of polyoxometalates for which flexible synthetic methods should enable tuning of the size and properties of the oxometal clusters.

In general, the coordination chemistry of titanium alkoxides and their hydrolysis products$^5$ is known to be versatile and a variety of cluster compounds has been reported to result from the partial hydrolysis of alkoxide precursors. Other well defined titanium clusters have been reported,$^6$ but up until now, no reports exist on the catalytic application of these cluster compounds in alkene epoxidations. This may be related to the fact that most of these compounds are known to be unstable in protic media.
Using the silsesquioxanes (c-C₆H₁₁)₆Si₆O₇(OH)₄ and (c-C₇H₁₃)₆Si₆O₇(OH)₄, two novel titanium-hydroxide clusters, [(c-C₆H₁₁)₆Si₆O₁₁][Ti(μ³-OH)]₄, 1a, and [(c-C₇H₁₃)₆Si₆O₁₁][Ti(μ³-OH)]₄, 1b, were synthesized. Both clusters were tested on stability and catalytic activity during the epoxidation of alkenes using both tert-butyl hydroperoxide (TBHP) and aqueous hydrogen peroxide as oxidants.

4.2 Results and Discussion

4.2.1 Synthesis of silsesquioxane polyoxotitanium clusters

The polyoxotitanates [(c-C₆H₁₁)₆Si₆O₁₁][Ti(μ³-OH)]₄, 1a, and [(c-C₇H₁₃)₆Si₆O₁₁][Ti(μ³-OH)]₄, 1b, could be synthesized using different routes. The first route consists of a conventional pyridine assisted metathesis of R₆Si₆O₇(OH)₄, 3, with titanium tetrachloride, performed in toluene. The reaction proceeds fast to form an almost insoluble, possibly polymeric derivative, with the concomitant formation of four equivalents of pyridinium hydrochloride (Scheme 4.1, route i). Hydrolysis of intermediate 2 led to the formation of polyoxotitanate 1.

Scheme 4.1: Two synthesis routes leading to the formation of polyoxotitanate [R₆Si₆O₁₁]₃(TiOH)₄, (1a: R = c-C₆H₁₁ and 1b: R = c-C₇H₁₃)
In order to make the workup of polyoxotitanates 1 easier, a second synthesis route was developed. In this route (Scheme 4.1, route ii) the silsesquioxane 3 reacts with four equivalents of Ti(IV)isopropoxide in THF to form the possibly polymeric intermediate 2. During this reaction, the clear solution containing the precursor silsesquioxane, 3, becomes a suspension from which the intermediate compound, 2, starts to precipitate.

The formed silsesquioxane derivative, 2, is stable in an inert atmosphere and its presumed polymeric structure could not be broken up by adduct formation with, for instance, pyridine or THF. The formation of 2b was followed using $^{13}$C NMR (400 MHz using the characteristic resonances for the silsesquioxane ipso carbons (Fig. 4.1). As the reaction proceeds, the sharp $^{13}$C$_{ipso}$ resonances of ($c$-$C$_7$H$_{13}$)$_6$Si$_6$O$_8$(OH)$_4$, 3b, at $\delta$ 24.2 and 23.8 ppm change within minutes to a broad unresolved pattern ($\Delta$\nu$_{1/2}$ $\sim$ 300 Hz) at $\delta$ 24 ppm.

Although the reaction conditions employed in the synthesis of 2b and the structural characteristics of silsesquioxane 3b might favor its base assisted cyclodehydration to give metal free silsesquioxanes like ($c$-$C$_7$H$_{13}$)$_6$Si$_6$O$_9$, no such complications were observed during these investigations.

Hydrolysis of 2b leads to a surprisingly clean reaction in which polyoxotitanate 1b is formed together with silsesquioxane tetrasilanol 3b as shown in Scheme 4.1. The formation of
the polyoxotitanate 1b has been studied by $^{29}$Si NMR (99.35 MHz, THF) using conditions that were similar to those described for the reaction of tetrasilanol 3b with Ti(O'Pr)$_4$ (Fig. 4.2).

Figure 4.2: $^{29}$Si NMR (99.35 MHz, THF) study on the formation of [(c-C$_7$H$_{13}$)$_6$Si$_6$O$_{11}$][Ti(µ$_3$-OH)]$_4$, 1b, using the patterns of the silsesquioxane compounds. a) tetrasilanol 3b; b) insoluble titanium derivative 2b generated in situ from 3b and Ti(O-i-Pr)$_4$; c) in situ formation of 1b and 3b from 2b by reaction with water.

After addition of four equivalents of water, the precipitate slowly starts to dissolve, and $^{29}$Si NMR investigations clearly show the formation of a pattern of eight separate silicon signals (Fig. 4.2). Two of these signals (δ -58.8 and -67.2 ppm) can immediately be assigned to the precursor silsesquioxane 3b. After addition of additional titanium-isopropoxide to the mixture, these signals disappear leaving only the six signals assigned to the titanium-silsesquioxane 1b. The six signals assigned to the titanium complex are all in a 1 to 1 ratio indicating a total loss of symmetry in the silsesquioxane ligand of the newly formed complex.

Complex 1b can be easily crystallized from acetonitrile layered toluene or from a concentrated THF solution affording 1b as air and water stable colorless crystals that only start to thermally decompose at ca. 250°C.
4.2.2 Structural characterization

Since an unambiguous assignment of the structure of the polyoxotitanate 1b could not be made based on the spectroscopic data alone, the crystal structure of this compound was determined. As in solution, the molecules of 1b show approximate C₃ symmetry in the crystal structure. The crystals also contain disordered solvents molecules, which were interpreted as partially occupied water and toluene positions. The molecular drawing of 1b, along with the adopted numbering scheme is shown in Fig. 4.3; selected bond distances and angles are given in Table 4.1.

Figure 4.3: Molecular structure and labeling scheme of 1b; displacement ellipsoid drawing (50% probability). The cycloheptyl groups and the solvent molecules have been omitted for clarity.
Table 4.1. Selected Bond Lengths (Å) and Angles (deg) for \([((c-C_7H_{13})_6Si_6O_{11})_3[Ti(\mu^3-OH)]_4, 1b.\)

<table>
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<th>Bond Lengths</th>
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<tr>
<td>Ti-Osi</td>
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<td>Ti-O(H)Ti</td>
<td>2.096(4)-2.217(4)</td>
</tr>
<tr>
<td>Si-Oti</td>
<td>1.622(4)-1.637(4)</td>
<td>Si-OSi</td>
<td>1.610(5)-1.655(4)</td>
</tr>
<tr>
<td>Si-C</td>
<td>1.856(6)-1.889(7)</td>
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<tr>
<th>Bond Angles</th>
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<tr>
<td>Ti-O-Ti</td>
<td>104.03(17)-108.01(17)</td>
<td>Si-O-Si</td>
<td>130.6(3)-160.1(3)</td>
</tr>
<tr>
<td>Si-O-Ti</td>
<td>144.6(3)-172.0(3)</td>
<td>O-Si-O</td>
<td>106.7(2)-110.1(3)</td>
</tr>
<tr>
<td>O-Si-C</td>
<td>106.7(2)-114.4(2)</td>
<td>(cis)O-Ti-O</td>
<td>70.36(14)-109.51(17)</td>
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<tr>
<td>(trans) O-Ti-O</td>
<td>150.31(17)-160.74(18)</td>
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</table>

The solid state structure determination shows \([((c-C_7H_{13})_6Si_6O_{11})_3[Ti(\mu^3-OH)]_4, 1b.\) to be a tetranuclear six-coordinated titanium complex with a distorted octahedral geometry of the titanium centers (Fig. 4.3). The central core involves a Ti$_4$(\mu^3-OH)$_4$ cuboid with titanium and hydroxy oxygen atoms occupying alternative vertices (Fig. 4.4). Other clusters, that to some extent resemble the cuboid core present in these silsesquioxane complexes have been reported for the trinuclear \([(CpTi)_3(\mu^2-OH)_3(\mu^3-O)]^+\) core of a formate complex$^7$ and for a series of heterometallic carboxylates of general formula \([Ti_4(\mu^3-O)(OR)_4\{\mu-(CO)_bCo_3(\mu^3-CCO)_2}\}_4].^8\)

The structural element Ti$_4$(\mu^3-OH)$_4$, present in the titanium-silsesquioxane complexes, is somewhat related to that found in the latter compound.

The core cuboid is surrounded by three silsesquioxane tetrasilanolate ligands, resulting in an overall structure that resembles a three bladed propeller for which both enantiomers occur in crystals of 1b. The structure of the central cuboid is distorted which leads to small HO-Ti-OH angles involving the bridging hydroxides [HO-Ti-OH: 70.36(14)–72.73(14)$^6$, Ti-OH = 2.096(4) – 2.217(4) Å]; larger angles of the siloxy O-Ti-O units [SiO-Ti-Osi: 99.20(18)–101.08(18)$^6$, Ti-Osi: 1.797(4)–1.829(4) Å] arise. As a result of different modes of silsesquioxane siloxy coordination, the coordination sphere of one of the titanium centers [Ti(1)] is completed by threefold \eta^1-coordination involving one siloxy unit of each of all three silsesquioxanes [O(5), O(16), O(27)]. The other titanium centers reach saturated coordination by a combination of \eta^1- and additional \eta^2-coordination involving three siloxy units of two different silsesquioxane ligands. As a result, the structure contains one titanium center that is bonded to all three silsesquioxane ligands while the other three titanium centers are each bonded to two out of three silsesquioxanes.
Figure 4.4: Schematic drawing of the Ti₄(µ³-OH)₄ cuboid present in 1b showing the hydrogen bonding of the hydroxide units [O(1)-(3)] with three η¹-coordinating siloxy units [O(6), O(17), O(28)]. The fourth hydroxy unit, situated behind Ti(1) is omitted for clarity.

As observed by IR (Fig. 4.5), the bridging hydroxy units that are attached to Ti(1) via O(1)-(3) are likely to engage in hydrogen bonding with the siloxy oxygen atoms O(6), O(17), O(28) as acceptors (Fig. 4.4). This is reflected in the intramolecular distances of the oxygen pairs O(1)−O(28), O(2)−O(6), and O(3)−O(17) of 2.823(6)–2.858(5) Å. Since all siloxy O-Ti distances found in the structure of 1b are in the normal range of 1.78 to 1.82 Å, the hydrogen bonding does not seem to weaken the incorporation of Ti(1) compared to Ti(2)-(4). A similar analysis for O(4) of the remaining hydroxy unit excludes intramolecular hydrogen bonding.

The characteristics of the titanium hydroxyl units that make up the central core of the complex were investigated using Fourier transformed infrared analysis on a Bruker IFS 113V spectrophotometer equipped with a vacuum cell. For this purpose, a self-supporting wafer was pressed, which was dried under vacuum for half an hour prior to analysis. Investigations of the hydroxyl units of the complex consisted of drying at different temperatures and OH/OD exchange experiments (Fig. 4.5 and 4.6). Acidity of the complex was investigated using CD₃CN adsorption experiments⁹,¹⁰ (Fig. 4.7).

The IR spectrum of a dried sample of 1b (Fig. 4.5) shows a broad and a sharp vibration at 3400 and 3620 cm⁻¹, respectively, that could be assigned to two different types of titanium hydroxide functions. The sharp vibration at 3620 cm⁻¹ is due to an isolated titanium hydroxide unit for which the same value has been reported for [Cp*Ti(OH)(H₂O)]BPh₄·2THF.¹¹ We assign the vibration at 3400 cm⁻¹ to hydroxides that engage in hydrogen bonding (vide infra).
When drying **1b** at 100°C and 10⁻⁶ mbar, a decrease in intensity of the peaks could be observed (Fig. 4.5, graph b), indicating a removal of hydroxides in the core, probably caused by an internal condensation reaction. Exposing this internally condensed sample of **1b** to moist air completely restored the original structure, indicating the condensation to be reversible. A similar observation could be made using TGA. When heating the sample up (1 atm., under air), the sample lost considerable weight above 100°C (weight loss < 1.18 %), however, when the sample cooled down below this temperature again, this weight was recovered by reaction of the condensed complex with water from the air. Successfully repeating this process several times in succession, in combination with the results of the IR, proved the reversible nature of the condensation reaction.

Both types of hydroxyl groups could easily undergo OH/OD exchange at room temperature as was observed by a decrease of the intensity of the peaks in the OH-region and an emerging of corresponding peaks at 2530 cm⁻¹ for hydrogen bonded OD-groups and a small peak at 2666 cm⁻¹ for the isolated OD-groups upon exposure of complex **1b** to D₂O (Fig. 4.6).
Figure 4.6: differential IR-spectra of the polyoxometal 1b, showing the OH/OD exchange [a] Sample dried for 30 minutes at $10^6$ mbar and 100°C. [b] Sample 30 minutes at $10^6$ mbar and 100°C, followed by 30 minutes 18 mbar $D_2O$ at 100°C and dried again at $10^6$ mbar and 100°C. [c] Sample dried for 30 minutes at $10^6$ mbar and room temperature, followed by 30 minutes 18 mbar $D_2O$ at room temperature, and dried again at $10^6$ mbar and room temperature.

Upon condensation of hydroxyl units of the core of the cluster, the complex obtained Lewis acid properties as was shown by adsorption of deuterated acetonitrile (Fig. 4.7). This development of Lewis acidity could easily be explained by the loss of a hydroxyl unit at the cuboid core, leaving a free coordination site around titanium in the core, which accounts for the Lewis acidity of the remaining complex. Without the internal condensation reaction, complex 1b didn’t exhibit any Brønsted or Lewis acidity.
4.2.3 Catalytic epoxidation and catalyst stability

The stability of complex 1b under reaction conditions was examined using NMR studies. During these studies, formation of precursor silsesquioxane, which is indicative of instability, was not observed. Using the guidelines proposed in chapter 3, stating that titanium should be at least terdentately bonded, this is surprising. None of the titanium atoms in the central core is terdentate bonded to any of the silsesquioxane ligands. Three out of the four titanium atoms [Ti(2)-(4)] are bonded bidentate to one of the silsesquioxane ligands and bonded monodentate to another. The fourth titanium [Ti(1)] is even monodentately bonded to all three silsesquioxanes. Although the silsesquioxane ligands are less than terdentately bonded to either one of the four titanium centers, they are tertradentately bonded to the central titanium-hydroxide core, so in order for the silsesquioxane precursor to be formed, four bonds have to be simultaneously hydrolyzed. For a single titanium center to leach out, even six bonds have to be broken, which explains the stability of the complex in protic media according to the stability rules proposed in Chapter 3.
The catalytic epoxidation activity of titanium silsesquioxane complex 1b was examined and although the use of one center silsesquioxane titanium(IV) derivatives as catalysts for the epoxidation of alkenes with organic peroxides has recently been demonstrated,\textsuperscript{12,13} no reports on the catalytic application of titanium cluster complexes could be found in literature. For the purpose of a reference two other known titanium oxide cluster complexes \([\text{TiO(OSiMe}_3(\text{O}_2\text{P(\text{O}}\text{tBu})_2)]_4, 4,\text{ and }\) [Ti$_3$(µ$_3$-O)(µ$_2$-OH)$_3$(µ$_2$-HCOO)$_3$(η$_5$-C$_5$H$_5$)$_3$]-HCOO·2HCOOH, 5,\textsuperscript{7} which exhibit a somewhat related structure to the titanium complexes 1a and 1b, were synthesized and tested on catalytic epoxidation activity (Fig. 4.8).

![Figure 4.8: Titanium oxide cluster complexes \([\text{TiO(OSiMe}_3(\text{O}_2\text{P(\text{O}}\text{tBu})_2)]_4, 4, \) and \([\text{Ti}_3$(µ$_3$-O)(µ$_2$-OH)$_3$(µ$_2$-HCOO)$_3$(η$_5$-C$_5$H$_5$)$_3$]-HCOO·2HCOOH, 5.](image)

Catalytic experiments were carried out in stirred batch reactors (2 mL) that were kept at 50°C. For the epoxidation reaction with TBHP as oxidant, 1 mL of a dried TBHP solution in (1.8 M in either toluene or n-hexane) was added to 1.8 mmol of alkene in the presence of catalyst. Titanium content of the reaction was kept at 1 mol% with regard to the alkene. Samples taken from the reaction mixture were analyzed by GC analysis using a Carlo Erba GC6000 Vega Series 2 equipped with a capillary DB-1 column and a FID. For this purpose, the reaction mixture contains 25 µL of 1,3,5-trimethyl benzene (>98%, Merck) as internal GC standard. Prior to analysis, the samples were filtered, while still warm, through syringe filters of 0.45 µm and diluted with methanol. The results are shown in Table 4.2.
Table 4.2: Conversions and selectivities of the alkene epoxidation reactions with TBHP catalyzed by titanium complexes 1b, 4 and 5.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>n-Hexane</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conversion</td>
<td>Selectivity</td>
</tr>
<tr>
<td></td>
<td>[%]</td>
<td>[%]</td>
</tr>
<tr>
<td>1-cyclooctene</td>
<td>3 80</td>
<td>&gt;95</td>
</tr>
<tr>
<td>2-cyclooctene</td>
<td>24 95</td>
<td>94</td>
</tr>
<tr>
<td>3-cyclohexene</td>
<td>3 73</td>
<td>&gt;95</td>
</tr>
<tr>
<td>4-cyclooctene</td>
<td>24 94</td>
<td>74</td>
</tr>
<tr>
<td>5-cyclohexene</td>
<td>3 5</td>
<td>58</td>
</tr>
<tr>
<td>6-cyclooctene</td>
<td>24 23</td>
<td>62</td>
</tr>
<tr>
<td>7-styrene</td>
<td>3 14</td>
<td>54</td>
</tr>
<tr>
<td>8-1-octene</td>
<td>24 36</td>
<td>49</td>
</tr>
<tr>
<td>9-1-hexene</td>
<td>3 9</td>
<td>89</td>
</tr>
<tr>
<td>10-1-octene</td>
<td>24 24</td>
<td>90</td>
</tr>
<tr>
<td>11-1-hexene</td>
<td>3 3</td>
<td>67</td>
</tr>
<tr>
<td>12-1-octene</td>
<td>24 15</td>
<td>60</td>
</tr>
<tr>
<td>13-2-octene</td>
<td>3 23</td>
<td>90</td>
</tr>
<tr>
<td>14-2-octene</td>
<td>24 48</td>
<td>90</td>
</tr>
</tbody>
</table>

As can be seen in Table 4.2, complex 1b is quite able to catalyze the epoxidation reaction under mild reaction conditions (50°C and 1 mol% Ti). Using complex 1b, cyclooctene and cyclohexene, could be easily converted to the desired epoxides with high selectivities using TBHP. Although these small cycloalkenes are known to be easy to epoxidize, the results give a first impression of the applicability of the complexes as catalysts for the epoxidation reaction. The somewhat more difficult epoxidation reactions of 1-octene
and 2-octene are being catalyzed with excellent selectivities towards the epoxide, while the selectivities for styrene and 1-hexene and cyclododecene drop significantly. Without catalyst present, no conversion could be observed over a period of several days. Also without catalyst, no pressure buildup was observed, indicating an absence or very slow thermal decomposition of the oxidant under these reaction conditions.

In contrast to the results obtained with complex 1b, complexes [TiO(OSiMe₃)(O₂P(O'Bu)₂)]₄, 4, and [Ti₃(μ₃-O)(μ₂-OH)(μ₂-HCOO)₃(η⁵-C₅H₅)]-HCOOH·2HCOOH, 5, hardly showed any catalytic activity at all. In case of complex 5 (Table 4.2, entry 18-20) this was not really surprising, since the complex was almost completely insoluble in any solvent. Although complex 4 is perfectly soluble in the solvents used, catalytic activity for epoxidation reactions is still very low (Table 4.2, entry 15-17). Since the catalytic epoxidation of cyclooctene with an organic peroxide can be seen as a test to predict catalytic activity, the results for complexes 4 and 5 indicate the unsuitability of these complexes as catalysts for liquid phase epoxidation reactions.

A second series of epoxidation experiments were carried out using aqueous hydrogen peroxide as the oxidant to epoxidize cyclooctene and 1-octene. As opposed to the epoxidation reaction with TBHP, the decomposition of oxidant in the reactions with aqueous hydrogen peroxide proved to be a serious problem. Using the same reaction conditions for the reactions with H₂O₂ as for the reactions with TBHP, the reaction vessels became quickly pressurized, and without adequate pressure release, this resulted even in blowing off the caps of the vessels. Analysis of the reaction mixtures after 24 hours showed complex 1b to be able to catalyze the epoxidation of cyclooctene with 50% peroxide efficiency. Complexes 4 and 5 however, only catalyzed the decomposition of peroxide, and no epoxide formation could be observed.

By performing the reaction at 80°C in toluene (750 µl), using an excess of alkene (750 µl) and reducing the amount of added aqueous hydrogen peroxide, a more peroxide-efficient reaction could be observed using titanium silsesquioxane 1b. Using small quantities of hydrogen peroxide, it was possible to selectively epoxidize cyclooctene whereupon a fresh addition of oxidant could start the reaction again after oxidant depletion. However, when using the much less active 1-octene a pressure buildup was still observed and after 24 hours hardly any epoxide was formed after all oxidant had decomposed (Table 4.3).
Table 4.3: Epoxidation of cyclooctene and 1-octene with aqueous hydrogen peroxide catalyzed by polyoxometalate 1b at 80°C.

<table>
<thead>
<tr>
<th>substrate</th>
<th>alkene / oxidant [mol / mol]</th>
<th>time [h]</th>
<th>conversion of oxidant [%]</th>
<th>selectivity to epoxide [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclooctene</td>
<td>50 : 1</td>
<td>1</td>
<td>&gt;95%</td>
<td>&gt;90</td>
</tr>
<tr>
<td></td>
<td>25 : 1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>+1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&gt;95%</td>
<td>&gt;90</td>
</tr>
<tr>
<td></td>
<td>12 : 1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>+1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&gt;95%</td>
<td>&gt;90</td>
</tr>
<tr>
<td>1-octene</td>
<td>50 : 1</td>
<td>24</td>
<td>100&lt;sup&gt;c&lt;/sup&gt;</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

* The ratio was adjusted by adding fresh oxidant to the reaction mixture of the previously listed experiment.  
  <sup>b</sup> The reaction mixture was analyzed on hour after addition of the fresh oxidant.  
  <sup>c</sup> Most of the peroxide is decomposed to oxygen and water.

Although complex 1a hasn’t been tested extensively like complex 1b, the preliminary results of the firsts catalytic experiments indicate a similar catalytic activity as complex 1b in epoxidation reactions with organic peroxides and aqueous hydrogen peroxide as oxidant.

The catalytic behavior when using hydrogen peroxide can be explained by the following reaction scheme 4.2.

![Scheme 4.2: Simplified catalytic cycle for the epoxidation of alkene and decomposition of hydrogen peroxide.](image-url)
When hydrogen peroxide has been activated by the catalyst, it can react in two ways. The first way is presented by route i, the activated oxidant reacts with an alkene to form the desired epoxide. However, this reaction is relatively difficult and thus slow in comparison to the decomposition reaction of the peroxide (route ii). So in order to suppress the decomposition reaction, the oxidant concentration should be kept as low as possible, and the chance for reaction with an alkene should be increased.

In complexes 1a and 1b, the titanium sites are completely surrounded and shielded off by hydrophobic cycloalkyl groups. In order for the peroxide and the alkene to react with the titanium site, they have to enter the cavity in between those cycloalkyl groups. The hydrophobic nature of this cavity, favors the entrance of alkene above peroxide and water. This effect, which reminds of the working of enzymatic systems, keeps the local concentration of water and peroxide very low near the titanium centers and therefore helps to suppress the decomposition of the peroxide. The inability of the monotitanium-silsesquioxanes reported in chapter 3, to epoxidize alkenes using hydrogen peroxide, in contrast to complexes 1a and 1b, might be explained by the absence of these hydrophobic ‘pockets’ around the titanium center. However, when these monotitanium silsesquioxanes are introduced in a sufficient hydrophobic matrix (Chapter 6), these immobilized catalysts are capable of epoxidizing alkenes using aqueous hydrogen peroxide. This leads to the conclusion that the hydrophobic encapsulation of the catalytic titanium centers is the main reason for the observation of catalytic epoxidation activity of alkenes with aqueous hydrogen peroxide.

4.3 Conclusions

The novel polyoxotitanates [(c-\text{C}_6\text{H}_{11})_6\text{Si}_6\text{O}_{11}]_3[\text{Ti}(\mu^3-\text{OH})]_4, 1a, and [(c-\text{C}_7\text{H}_{13})_6\text{Si}_6\text{O}_{11}]_3[\text{Ti}(\mu^3-\text{OH})]_4, 1b, are easy to synthesize, well-defined, soluble titanium clustercompounds that prove to be very stable in protic solvents. Complexes 1a and 1b, could therefore be subjected to experiments involving alkene epoxidation with tert-butyl hydroperoxide (TBHP) and aqueous H_2O_2 (35% in water). As observed during these experiments, complexes 1a and 1b are not only stable in these oxidizing media but also catalyze alkene epoxidation with either oxidizing agent. The cycloalkyl groups of the complexes form organic pockets around the titanium centers. These hydrophobic, enzyme like, pockets keep the water and peroxide concentration around the catalytic titanium center
low and doing so retard the unwanted and relatively fast decomposition of the hydrogen peroxide, enabling the complexes to catalyze the epoxidation of alkenes using aqueous hydrogen peroxide.

4.4 Experimental Section

**General considerations.** All reactions with air- or moisture-sensitive materials were carried out under argon using standard Schlenk techniques. Freshly distilled, dry and oxygen-free solvents were used throughout. The used silsesquioxanes (c-C$_6$H$_{13}$)$_3$Si$_6$O$_4$(OH)$_4$ and (c-C$_6$H$_{13}$)$_3$Si$_6$O$_4$(OH)$_4$ were obtained by synthesis methods described in literature.

$$[(c\text{-}C_6H_{13})_3Si_6O_{11}]_4[Ti(\mu^3\text{-}OH)]_4 \ (1a)$$ A solution of Ti(O-i-Pr)$_4$ (0.40 g, 1.41 mmol) and (c-C$_6$H$_{13}$)$_3$Si$_6$O$_4$(OH)$_4$ (1.25 gram, 1.48 mmol) in THF (25 mL) was briefly brought to reflux and subsequently stirred at room temperature for 0.5 h resulting in the formation of a white suspension. Water (0.028 mL, 1.56 mmol) was added after which the mixture was briefly brought to reflux and subsequently stirred for another half hour at room temperature. Ti(O-i-Pr)$_4$ (0.14 g, 0.49 mmol) was added after which the mixture was briefly brought to reflux followed by addition of (0.009 mL, 0.50 mmol) of water. The reaction mixture was brought to reflux after which the solvent was removed in vacuo. The resulting white solid (1.15 g, 86%) was examined with NMR and consisted almost completely of $$[(c\text{-}C_6H_{13})_3Si_6O_{11}]_4[Ti(\mu^3\text{-}OH)]_4$$ Analytical pure $$[(c\text{-}C_6H_{13})_3Si_6O_{11}]_4[Ti(\mu^3\text{-}OH)]_4$$ was obtained by crystallization of the product from hot THF (3 mL). $^1$H NMR (300 MHz, CDCl$_3$, 23°C, SiMe$_4$): $\delta$ 1.90-1.60 (m, 4H, C$_6$H$_{13}$), 1.40-1.10 (m, 6H, C$_6$H$_{13}$), 0.95-0.70 (m, 1H, $\alpha$-H of C$_6$H$_{13}$). $^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$, 23°C, SiMe$_4$): $\delta$ 28.0-27.2 (m, CH$_2$-groups of C$_6$H$_{13}$), 27.9-26.3 (m, CH$_2$-groups of C$_6$H$_{13}$), 24.13, 23.90, 23.45, 23.22, 23.11, 23.07 (intensity 1:1:1:1:1, CH of C$_6$H$_{13}$-groups).

$$[(c\text{-}C_6H_{13})_3Si_6O_{11}]_4[Ti(\mu^3\text{-}OH)]_4 \ (1b)$$ Route i: At room temperature TiCl$_4$ (0.178 mL, 1.62 mmol) was added to a stirred solution of (c-C$_6$H$_{13}$)$_3$Si$_6$O$_4$(OH)$_4$ (1.13 gram, 1.21 mmol) in toluene (30 mL). Pyridine (0.65 mL, 8 mmol) was added on which a yellow suspension formed. This suspension was heated to 50°C for 2 minutes after which it was allowed to cool to room temperature. Water (0.5 mL) was added and the mixture was stirred over night, filtered in order to remove pyridinium salts after which the filtrate was stripped in vacuo. The resulting white solid was crystallized in air from a mixture of toluene (ca. 20 mL) and acetonitrile (ca. 50 mL) to yield pure microcrystalline 3-C$_6$H$_5$CH$_3$: (0.80 g, 86 %). Anal. calc. for C$_{128}$H$_{238}$O$_{13}$Si$_{18}$Ti$_{14}$C$_{6}$H$_5$CH$_3$: C, 50.96; H, 7.91%. Found: C, 50.77; H, 7.99%.

Route ii: A solution of Ti(O-i-Pr)$_4$ (0.54 g, 1.90 mmol) and (c-C$_6$H$_{13}$)$_3$Si$_6$O$_4$(OH)$_4$ (1.49 gram, 1.60 mmol) in THF (50 mL) was briefly brought to reflux and subsequently stirred at room temperature for 4.5 h resulting in the formation of a white suspension. Water (0.030 mL, 1.7 mmol) was added after which the mixture was briefly brought to reflux and subsequently stirred overnight at room temperature. Ti(O-i-Pr)$_4$ (0.15 g, 0.53 mmol) was added after which the mixture was briefly brought to reflux followed by addition of (0.010 mL, 0.56 mmol) of water. After stirring overnight at room temperature, the solution was concentrated while gradually...
being heated to about 60°C until the onset of precipitation. At this point, the turbid solution was briefly heated further and allowed to slowly cool down to room temperature causing the crystallization of 0.95 g (62%) of 3. These crystals were suitable for an X-ray diffraction experiment. \(^1\)H NMR (300 MHz, CDCl\(_3\), 23°C, SiMe\(_4\)): \(\delta\) 1.90-1.75 (m, 4H, C\(_7\)H\(_{13}\)), 1.59-1.35 (m, 8H, C\(_7\)H\(_{13}\)), 0.91-0.87 (m, 1H, \(\alpha\)-H of C\(_7\)H\(_{13}\)); \(^{13}\)C\{\(^1\)H\} NMR (100 MHz, CDCl\(_3\), 23°C, SiMe\(_4\)): \(\delta\) 30.0-29.39 (m, CH\(_2\)-groups of C\(_7\)H\(_{13}\)), 28.89-27.82 (m, CH\(_2\)-groups of C\(_7\)H\(_{13}\)), 25.61, 24.65, 24.25, 23.95, 23.67 (intensity 1:1:1:1:2, CH of C\(_7\)H\(_{13}\)-groups).

Structure Determination and refinement of 1b. Crystal data for 3. (toluene/water) solvate: [C\(_{126}\)H\(_{238}\)O\(_3\)Si\(_{18}\)Ti\(_4\), 1/5 C\(_7\)H\(_8\), 7/20 H\(_2\)O (fw 3067.12)]; colorless plate, monoclinic, \(P2_1/c\), \(a = 17.2473(4)\) Å, \(b = 51.0761(12)\) Å, \(c = 22.4352(4)\) Å, \(\beta = 127.2874(10)\)°, \(V = 15724.1(6)\) Å\(^3\), \(Z = 4\), \(\rho = 1.296\) g/cm\(^3\) (\(Z = 4\)). A total of 76498 reflections up to a resolution of (\(\sin \theta/\lambda\))\(_{\text{max}}\) = 0.55 Å\(^{-1}\) were collected on a Nonius KappaCCD diffractometer with rotating anode (\(\lambda = 0.71073\) Å) at a temperature of 150 K. 21791 reflections were unique (\(R_{\text{int}} = 0.0598\)). The structure was refined with SHELXL-97 against \(F^2\) of all reflections. The final R-values for the 17437 reflections with \(I > 2\sigma(I)\) were \(R_1 = 0.0780\) and \(wR_2 = 0.2376\). Hydrogen atoms were refined as rigid groups. Cycloheptyl groups were (partially) refined with a disorder model. The positions of the disordered solvent molecules were only partially occupied.

Fourier Transformed Infrared (Ft-IR) spectra were taken at room temperature on a Bruker IFS 113V spectrophotometer equipped with a vacuum cell. Before analyzing, the samples were pressed into self-supporting wafers of about 10 mg and dried at 100°C for 1 hour in vacuum. The spectra from 3000 cm\(^{-1}\) to 4000 cm\(^{-1}\) were linearly baseline corrected.

Catalytic epoxidation tests. Unless noted otherwise, all catalytic experiments were performed in stirred 2 mL batch reactors that were kept at 50°C. Reactions with tert-butyl hydroperoxide were performed using a solution of 1.8 mmol alkene with 1 mL of a dried tert-butyl hydroperoxide solution (1.8 M in toluene or n-hexane, originally 70% in H\(_2\)O, Acros). Reactions with hydrogen peroxide were performed using a solution 750 \(\mu\)l of alkene in 750 \(\mu\)l toluene with 10 \(\mu\)l of aqueous hydrogen peroxide (0.12 mmol, 35 wt % in H\(_2\)O, Merck). Titanium content was kept at 1 mol% with regard to the used alkene. Samples taken from the reaction mixture were analyzed by GC analysis using a Carlo Erba GC6000 Vega Series 2 equipped with a capillary DB-1 column and a FID. For this purpose, the reaction mixture contains 25 \(\mu\)L of 1,3,5-trimethyl benzene (>98%, Merck) as internal GC standard. Prior to analysis the samples were filtered, while still warm, through syringe filters of 0.45 \(\mu\)m and diluted with methanol.

Acknowledgements

Marcel Dinghs is gratefully acknowledged for his contribution to this chapter.
References


Chapter 5

The applicability of physisorption of silsesquioxane based catalysts in MCM-41 carrier materials to produce truly heterogeneous catalysts

Abstract: Industry prefers heterogeneous catalysts for bulk processes due to their ease of handling during workup of the reaction mixtures. The immobilization of epoxidation catalysts of type R_7SiO_{12}Ti-X [R= c-C_5H_9, c-C_6H_{11}; X = OH, Cp] by physisorption inside MCM-41 mesoporous silica was studied. The resulting materials were found to be active catalysts for liquid phase alkene epoxidation with organic peroxides. The degree of catalyst heterogeneity was found to be influenced by very subtle differences in interaction between the pore walls of the MCM-41 material and the impregnated catalyst.

5.1 Introduction

Heterogenization of homogeneous catalytic complexes is an important topic in liquid-phase oxidation catalysis. Ideally, it provides active heterogeneous catalysts, which possess the same active site as their homogeneous counterparts together with the added advantage of catalyst separation by easy filtration. As a result, the catalytic complexes can be reused and do not contaminate the product. Especially methods that allow complex immobilization without chemical modification in a host material are of particular interest. In these cases, no chemical bonds are needed for successful heterogenization and the direct environment of the catalytic site is naturally unchanged. Next to the ease of catalyst preparation, this is of particular importance for applications involving enantioselective catalysis where even small ligand modifications can have a detrimental effect on the enantiomeric excesses reached.

Recently, metal containing silsesquioxanes have been reported as active and stable catalysts in a variety of catalytic transformations. With regard to liquid-phase oxidation catalysis, the previous chapters outlined the catalytic potential of metalla-silsesquioxanes in
alkene epoxidation. One of the contributions to this field relates to the successful immobilization of a titanium(IV) silsesquioxane complex, \((\text{c-C}_6\text{H}_{11})_7\text{Si}_7\text{O}_{12}\text{Ti(Cp)}\), in MCM-41 mesoporous silica and its subsequent use in heterogeneous catalytic epoxidation.\(^2\) Since the heterogenization of the complex is based purely on its physisorption inside the MCM-41 mesopores, an in-depth study to determine which MCM-41 material properties influence the success of catalyst immobilization was undertaken.

In this work, results of immobilization of silsesquioxane-based titanium catalysts in different MCM-41 batches, to produce heterogeneous catalysts for liquid phase epoxidation reaction of alkenes, is studied. Different characterization techniques like thermo gravimetric analysis (TGA), nitrogen adsorption analysis, X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transformed infrared (FT-IR) are used to obtain information about the structural and physical properties of the MCM-41 materials used. The results are then combined to get more information on the applicability of physisorption of silsesquioxane-based catalysts in MCM-41 carrier materials.

5.2 Results

5.2.1 Preparation and characterization of MCM-41 materials

The names of the MCM-41 samples as used in this chapter consist of the abbreviation M41 followed by a code (G#) that refers to the procedure followed for the preparation of the synthesis gel, whereupon G1 refers to the gel composition described in the experimental section of this paper,\(^4\) G2 refers to the synthesis procedure as described in reference 17 and G3 refers to the procedures followed in reference 19). The synthesis temperature in °C is noted as the number following the capital S (S###) and between the brackets is the batch number (#) if different batches have been prepared according to the same procedure. For this study, nine batches of all silica MCM-41 materials were prepared as listed in Table 5.1. This table lists a variety of material properties obtained after calcination at 550°C for 18 hours.
Table 5.1 Material properties of MCM-41 mesoporous silica used in this study

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Pore size [Å]</th>
<th>Surface area [m² / g]</th>
<th>Wall thickness [Å]</th>
<th>Water content [wt%]</th>
<th>Dehydration temp [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M41-G1-S100-#1</td>
<td>27</td>
<td>900</td>
<td>8</td>
<td>16.6</td>
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</tr>
<tr>
<td>2</td>
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<td></td>
<td></td>
</tr>
<tr>
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</tr>
<tr>
<td>4</td>
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<td>28</td>
<td>1000</td>
<td>11</td>
<td>10.5</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>M41-G1-S130-#2</td>
<td>25</td>
<td>1100</td>
<td>13</td>
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<td>1000</td>
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<td>11</td>
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<td>52</td>
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<td>24</td>
<td>900</td>
<td>14</td>
<td>13.0</td>
<td>61</td>
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</table>

*a material properties obtained after calcination at 550°C for 18 hours.

Table 5.1 (Continued)*

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Ordered material [%]</th>
<th>Disordered Material [%]</th>
<th>Amorphous Material [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M41-G1-S100-#1</td>
<td>50-60</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>M41-G1-S100-#2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>M41-G1-S100-#3</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>M41-G1-S130-#1</td>
<td>30-35</td>
<td>30-35</td>
<td>20-25</td>
</tr>
<tr>
<td>5</td>
<td>M41-G1-S130-#2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>M41-G1-S130-#3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>M41-G1-S130-#4</td>
<td>45-55</td>
<td>35-40</td>
<td>5-10</td>
</tr>
<tr>
<td>8</td>
<td>M41-G2-S150-#1</td>
<td>90-95</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>M41-G3-S140-#1</td>
<td>15-20</td>
<td>65-70</td>
<td>15-20</td>
</tr>
</tbody>
</table>

*a material properties obtained after calcination at 550°C for 18 hours.

Although calcination at 550°C for 18 hours was finally employed to remove the organic templates from the as synthesized MCM-41 materials, other temperatures and other removal techniques were briefly investigated as well. Thermo gravimetric analysis was used to verify their effectiveness. In each case, the same batch of MCM-41 material was used (M41-G1-S100-#1). Template extraction was performed with either ethanol or 1M HCl/ethanol. About 10 gram of the as-synthesized MCM-41 material was continuously treated with the solvent (about 300 mL) in a soxhlet setup for two weeks. Next to these continuous extractions, a batch extraction was carried out using 1 g of as-synthesized MCM-41 in 300 mL of 1M HCl/ethanol. Calcination of the as-synthesized MCM-41 materials was performed in a temperature controlled plug flow reactor. About 1.5 g of the as-synthesized material was heated up to the calcination temperature at a rate of 1°C per minute under a continuous Ar-O₂
gas flow containing 80% Argon. After reaching the calcination temperature (either 350 or 550°C), the sample was kept at this temperature for 12 hours. After removal of the templates a TGA analysis was performed to check the amount of organic residue remaining in the treated MCM-41; results are listed in Fig. 5.1 and Table 5.2.

![Figure 5.1: Thermo gravimetric analysis of MCM-41 samples after different template removal techniques: [a] as-synthesized MCM-41 used for each experiment, [b] continuous extraction with ethanol, [c] continuous extraction with 1M HCl in ethanol, [d] batch extraction with 1 M HCl in ethanol (1 gram in 300 g HCl/ethanol), [e] calcination at 350°C, [f] calcination at 550°C.](image)

**Table 5.2: Effectiveness of template removal technique determined by TGA Analysis**

<table>
<thead>
<tr>
<th>entry</th>
<th>technique</th>
<th>Cumulative Weight loss [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>150°C</td>
</tr>
<tr>
<td>1</td>
<td>a - as synthesized MCM-41 material M41-G1-S100-#1</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>Continuous ethanol extraction</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>Continuous HCl / Ethanol extraction</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Batch HCl / Ethanol extraction</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>Calcination at 350°C</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>Calcination at 550°C</td>
<td>2</td>
</tr>
</tbody>
</table>

As synthesized MCM-41 material M41-G1-S100-#1

As can be seen from Table 5.2, the as-synthesized MCM-41 consists of about 60 wt% of organic templates. The total weight loss at 650°C (Fig. 5.1) gives an indication of the amount of organic matter present in the measured samples. After extraction of the MCM-41 with ethanol in a soxhlet setup for two weeks, 28% of the template is removed. Soxhlet extraction of the as-synthesized MCM-41 with a 1M HCl/ethanol solution for two days removes about 46% of the initial present template, while extracting the as-synthesized MCM-
41 by stirring about 1 gram in 300 mL of 1M HCl/ethanol for two days (standard extraction) removes about 80% of the template.

Calcination of the as-synthesized MCM-41 at 550°C for 18 hours in a continuous plug flow reactor of 27 mm internal diameter flushed by an Ar-O₂ gas mixture containing 20 mol% O₂ to remove the templates results in a removal of more than 93% of all the organics. The remaining small amounts of carbon sometimes result in a yellowish color of the remaining solid, which can be removed by treatment of the sample with ozone.²⁰ Calcination up to 350°C results in a brown/black solid still containing 16 wt% of organics, which are removed by calcination at temperatures higher than 500°C. Based on these results, we decided to use calcination at 550°C for 18 hours as the method for template removal throughout this study.

TGA analysis on calcined MCM-41 samples was also performed in order to get information about the hydrophobicity of the MCM-41 materials. In this case, samples were allowed to equilibrate with moisture from air over a period of several days prior to analysis. The weight loss than observed by TGA in the temperature range from 25°C until 150°C is caused by the loss of water that is adsorbed inside the pores. The amount of water and the temperature at which it leaves the pores is indicative of the hydrophilic nature of the sample being analyzed. The results are incorporated in Table 1.1.

All calcined MCM-41 materials were subjected to nitrogen physisorption and XRD analysis. Table 1 lists relevant physical properties of the resulting template free MCM-41 materials. The XRD patterns of both as-synthesized and calcined MCM-41 materials show a sharp (100) peak and three higher order peaks of lesser intensity. Upon calcination, some decrease in intensity of all peaks is observed together with a shift towards higher 2Θ values.

In addition to XRD and nitrogen adsorption measurements, transmission electron microscopy (TEM) was used to obtain information about the morphology and inherent quality of MCM-41 samples.³ The investigations revealed the quality of the MCM-41 materials by giving an indication of the percentages of hexagonally ordered mesoporous material, disordered mesoporous material and amorphous material. The resulting listings on the ratio of ordered / disordered / amorphous material are incorporated in Table 5.1. A graphical example is given in Fig. 5.2 where all phases are present in a particular area.
Figure 5.2: Transmission electron microscope photograph of M41-G1-S130#1 on which all morphologies are visible: [a] hexagonally ordered mesoporous material viewed end-on, [b] hexagonally ordered mesoporous material viewed edge-on, [c] disordered mesoporous material and [d] amorphous material. The scale of the overview photograph is twice the scale of the enlarged areas.

FT-IR-analysis on self-supporting wafers of typical MCM-41 samples [i.e. M41-G1-S100#1, M41-G1-S130#1, M41-G1-S130#1, M41-G2-S150#1 and M41-G3-S150#1] was carried out. The samples were dried at 100°C in vacuum for half an hour prior to analysis. In order to obtain information about type of silanol units and the relative amount of silanol units present in the MCM-41 samples the region between 3000 cm\(^{-1}\) and 4000 cm\(^{-1}\) has been linearly baseline corrected and intensity at 3000 cm\(^{-1}\) has been set to zero. The resulting plots are shown in Fig. 5.3; the hydrogen bridged silanol nests are visible as a broad peak between 3400 cm\(^{-1}\) and 3600 cm\(^{-1}\), while the isolated silanol units are visible as a sharp peak (off scale) at 3740 cm\(^{-1}\).
5.2.2 Physisorption of titanium silsesquioxanes in MCM-41 materials

The known silsesquioxane titanium complexes 1 and 2 (Fig. 5.4) were used for phase immobilization in this study. The cyclopentadienyl complex 2 is a robust complex that is resistant to hydrolysis even in acidic media. In homogeneous alkene epoxidation using organic peroxides as the oxidant, its catalytic activity, however, is modest. Therefore, the immobilization behavior of the titaniumhydroxy complex 1, which was found to be the most active catalyst in such applications, was also studied. In this case, the effect of immobilization on the stability of 1 was studied as well. As was previously reported, 1 has moderate stability in protic media. For instance, 1 was found to slowly hydrolyze (ca. 30% hydrolysis in the course of 3 days at 50°C) in a stirred emulsion of chloroform / water to form silsesquioxane trisilanol (cyclohexyl)₇Si₇O₆(OH)₃ and non-catalytically active titanium species. However, 1 does not hydrolyze or leach titanium under catalytic alkene epoxidation conditions in case care has been taken to ensure anhydrous reaction conditions.
Complexes 1 and 2 were impregnated in the MCM-41 materials by dissolving them in n-hexane and stirring this solution together with dry MCM-41 material overnight. The impregnation could be followed by UV-Vis spectroscopy on the impregnation solution. Both complexes have an intense band at 216 nm assigned to tetrahedral coordinated titanium. Complex 2 also has a second broad band around 310 nm, which corresponds to the cyclopentadienyl chromophore. Upon addition of the dried MCM-41 to a solution with appropriate content of one of these complexes, these UV-Vis bands decrease rapidly (ca. 1h) up to a point were no complex is observed in the impregnation solution anymore. Because of the fast and complete adsorption, the loading of either 1 or 2 can be easily adjusted by varying its total amount in solution. The maximum loading of both complexes is typically 100 mg/g MCM-41 (i.e. 4.3 mg Ti / g MCM-41). For the current investigation impregnations were carried out that resulted in MCM-41 materials containing 1.2 mg Ti / g MCM-41 (25% of maximum load).

5.2.3 Catalyst stability and heterogeneity

Impregnated and dried MCM-41 materials containing 1 or 2 were tested on heterogeneity and stability in a standard epoxidation reaction using cyclooctene and tert.-butyl hydroperoxide (TBHP) at 50°C. In line with previously reported data, selectivity towards the epoxide was high in each test (> 95%).

In order to obtain information about leaching, the reaction mixture was allowed to react in the presence of the catalyst for a limited period (< 2h) during which moderate conversion was reached. At this point the catalyst was filtered off (hot filtration) and the
filtrate was kept at 50°C for another 24 hours to check if any additional conversion occurred. In case the conversion at the moment of filtration is the same as measured after 24h in the filtrate, the catalyst is regarded as heterogeneous. The results of the hot filtration tests are shown in the Table 5.3. For comparison, this table also lists the conversion obtained after 24h in a non-interfered catalytic experiment.

To obtain information about stability of the immobilized catalysts, a sample of each was kept in air at 70°C for about a month. After that period, the catalyst activity was compared to that of a freshly prepared catalyst. From these experiments became clear that only supported catalyst 1 has long time shelf stability.

Table 5.3: Catalyst heterogeneity determined by hot filtration experiments.

<table>
<thead>
<tr>
<th>Support</th>
<th>Leaching</th>
<th>Catalyst</th>
<th>Catalyst</th>
<th>alkene : oxidant : Ti&lt;sup&gt;ab&lt;/sup&gt;</th>
<th>alkene : oxidant : Ti&lt;sup&gt;ac&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TiCp</td>
<td>TiOH</td>
<td>1150 : 1150 : 1</td>
<td>5600 : 250 : 1</td>
</tr>
<tr>
<td>M41-G1-S100#1</td>
<td>low</td>
<td>26-26(62)</td>
<td>6-7(41)</td>
<td>11-12(51)</td>
<td>20-20(99)</td>
</tr>
<tr>
<td>M41-G1-S100#2</td>
<td>low</td>
<td>37-38(69)</td>
<td>5-6(53)</td>
<td>8-9(48)</td>
<td>19-39(91)</td>
</tr>
<tr>
<td>MCM41-G1-S100#3</td>
<td>low</td>
<td>not tested</td>
<td>5-6(24)</td>
<td>not tested</td>
<td>19-22(77)</td>
</tr>
<tr>
<td>M41-G1-S130#1</td>
<td>low</td>
<td>40-41(80)</td>
<td>36-38(75)</td>
<td>38-38(75)</td>
<td>74-81(91)</td>
</tr>
<tr>
<td>M41-G1-S130#2</td>
<td>medium</td>
<td>36-37(74)</td>
<td>30-46(77)</td>
<td>36-52(87)</td>
<td>64-82(91)</td>
</tr>
<tr>
<td>M41-G1-S130#3</td>
<td>medium</td>
<td>40-52(77)</td>
<td>31-39(76)</td>
<td>71-76-88(90)</td>
<td>49-55(90)</td>
</tr>
<tr>
<td>M41-G1-S130#4</td>
<td>medium</td>
<td>37-52(71)</td>
<td>33-40(74)</td>
<td>49-61-84</td>
<td>44-50(84)</td>
</tr>
<tr>
<td>M41-G2-S150#1</td>
<td>high</td>
<td>39-64(75)</td>
<td>27-42(76)</td>
<td>27-45(74)</td>
<td>60-80-89</td>
</tr>
<tr>
<td>M41-G3-S140#1</td>
<td>high</td>
<td>53-89</td>
<td>55-94</td>
<td>not tested</td>
<td>not tested</td>
</tr>
</tbody>
</table>

<sup>a</sup> mol : mol : mol ratio. <sup>b</sup> Unless otherwise specified, filtrations were carried out after 2h for the supported TiCp catalyst and after 1h for the supported TiOH catalyst. Listed data are conversions (%) and are abbreviated as: conv. at filtration – conv. in the filtrate after 24h (conv. of the catalyzed reaction after 24h). <sup>c</sup> Unless otherwise specified, filtrations were carried out after 10 min. for the supported TiCp catalyst and after 5 min. for the supported TiOH catalyst. Listed data are conversions (%) and are abbreviated as: conv. at filtration – conv. in the filtrate after 24h (conv. of the catalyzed reaction after 24h).
5.3 Discussion

5.3.1 Synthesis of MCM-41 materials

Although the pores of MCM-41 materials are relatively uniform, the materials themselves can be regarded as a type of amorphous silica (Fig. 5.5). Since reproducible preparation of amorphous silica requires a very high level of control over many reaction and engineering parameters, it can be expected that, in analogy, reproducible MCM-41 synthesis may meet with complications. As a result, any small change in one of the three steps involved in its synthesis does have an influence on the properties of the final product. Considering this, it can be expected that complications are bound to occur when reproducing results with different batches of MCM-41 material.

Figure 5.5: Schematic representation of the formation of MCM-41 via a liquid crystal templating mechanism.

In order to tailor the structural properties of MCM-41, the preparation of MCM-41 can be divided in three separate steps. By altering conditions in one of these steps, variations in pore sizes, wall thickness and pore hydrophobicity of the prepared MCM-41 are obtained.

The first important part of the synthesis of MCM-41 is the preparation and composition of the synthesis gel. By using different types of surfactants and/or surfactant mixtures it is possible to vary pore sizes.\textsuperscript{4,5,6} Different silica sources can lead to different
cristallinites, and seeding the synthesis gel with calcined small crystallite MCM-41, as part of the silica source needed, has been proposed to produce high quality large crystal MCM-41. Addition of cations like tetra-alkylammonium or sodium have been used to improve hydrothermal stability while addition of alcohols has been reported to enhance reproducibility, shorten reaction times and facilitate easy preparation of large batches. Organo-functionalized MCM-41 can be prepared by addition of various organo-trialkoxy silanes to the synthesis gel, while incorporation of different catalytic metals like titanium and aluminum into the MCM framework is accomplished by addition of the corresponding alkoxy metal compounds.

The second step in the preparation is the actual synthesis step. This part consists of the condensation of the silica in the synthesis gels. By using different gel aging times, synthesis temperatures (ranging from room temperature to temperatures above 150°C), and different synthesis times (ranging from one to several days), the thermal and hydrothermal stability and quality of the final product can be altered as well as variations in channel diameter. Another approach to a fast synthesis route has been reported using a temperature controlled microwave oven to produce crystalline, thermally stable molecular sieve MCM-41 from aged synthesis gels within an hour.

The third and last step consists of the treatment of the as-synthesized MCM-41 to remove the organic templates. The most common way to remove the templates, which are up to 60 wt% of the as-synthesized MCM-41, is using calcination at temperatures of about 550°C for several hours. During the calcination, the cell diameter as found by XRD becomes smaller. Higher calcination temperatures and longer calcination times enhance this effect.

By using ozone, it is possible to remove the surfactants at lower temperatures whereupon the pore sizes during the removal of template are hardly affected. Other techniques, which can be used to remove the surfactants from the MCM-41 are acidic extraction or supercritical fluid extraction.

TGA revealed that as-synthesized MCM-41 contains about 60 wt% of water and organic template (Fig. 5.1 and Table 5.2). The removal of water and template can be divided in four stages of weight loss. The first stage occurs between 25°C and 150°C and is due to the removal of water. The second stage of weight loss is situated in the temperature range of 150°C to 400°C and is the result of decomposition and combustion of organic species such as tetramethylammonium and cetyltrimethylammonium. The third stage is situated at temperatures between 400°C and 530°C and is due to combustion of coke that has been deposited during
the incomplete combustion of organic species in the former stage. The last stage of weight loss occurs at temperatures above 530°C and is caused by condensation reactions of silanol units that are present on the pore walls of the MCM-41 material.

Extraction of the MCM-41 with ethanol in a soxhlet setup is the least successful method of template removal. Even after two weeks of continuous extraction, only 30% of the template is removed. Soxhlet extraction of the as synthesized MCM-41 with a 1M HCl/ethanol solution gives only a small improvement over soxhlet extraction with ethanol, an additional 20% of template is removed, resulting in a MCM-41 material still containing 30 wt% of organic matter (template). Extracting the as-synthesized MCM-41 by stirring about 1 gram in 300 mL of 1M HCl/ethanol for two days (standard extraction) gives the best results in removal of 85% of the template. Although giving the best results compared to other extraction techniques, this method results in too much waste to be applicable on a large scale (300 grams of waste for about 1 gram of material).

Calcination of the as-synthesized MCM-41 to remove the templates gives the overall best results. Calcination does lead to some decrease in pore size (about 10 Å in pore diameter). This can be attributed to the removal of the template that stabilizes the structure in the as-synthesized MCM-41. However, after the template has been removed, the structure is thermally stable to temperatures up to about 650°C after which the structure starts to collapse. Using calcination, over 98% of all the organics are removed, sometimes resulting in a yellowish color of the remaining solid, which can be removed by treatment of the sample with ozone. The calcination temperature needs to be at least 350°C to remove the carbon that is deposited during the initial stages of the calcination. Based on the results of the TGA analysis of the different template removal techniques, MCM-41 samples calcined at 550°C were used for further experiments.

When looking at the results of XRD and nitrogen adsorption analysis (Table 5.1) it seems that a increase in synthesis temperature, when comparing the batches prepared at 100°C (Table 5.1, entry 1, 2 and 3) to batches prepared at 130°C using the same synthesis gel composition (Table 5.1, entry 4, 5 and 6), does increase the reproducibility of properties obtained. However, when looking at the results of the TEM analysis on the samples prepared at 130°C (Table 5.1, entry 2 and 3), there is still a rather big difference in morphology of the samples that looked quite similar analyzed by XRD and nitrogen adsorption experiments.
5.3.2 Catalyst stability and heterogeneity

The heterogenization of complexes 1 and 2 is based on physisorption inside the MCM-41 mesopores only. Previously, it was established that the mesopores should be as hydrophobic as possible.\textsuperscript{2} For this reason the present study is limited to all silica MCM-41 materials only. As confirmed by experiment, aluminum containing MCM-41 materials can be safely expected to have more hydrophilic mesopores and therefore less suitable for the present application. As a result, it is expected that the supported catalysts have better heterogeneity when applied in a more polar reaction medium. This is illustrated by the data presented in Table 5.3 that shows catalytic tests under two conditions. Catalysts have a lower degree of leaching when applied with equimolar amounts of alkene and oxidant. When the amount of the (polar) oxidant is lowered, the degree of leaching increases.

The stability of the impregnated catalyst is dependent on the water stability of the used homogeneous catalysts and in line with observations described in Chapter 3. As the results in section 5.2.3 show, the catalyst 1, which is somewhat water sensitive, is unstable, i.e. slowly decomposes, when impregnated in MCM-41. Epoxidation experiments with impregnated catalysts 1, which have been stored for two months at 70°C show a strong decrease in catalytic activity. On the other hand, impregnated catalyst 2, is completely stable when stored over several months.

A probable cause of the instability of complex 1, inside the pores is the presence of relatively acidic silanol units as part of the pore walls. These silanol units can clearly be seen on the FT-IR spectra of the MCM-41 materials (Fig. 5.3). The region of 3000 cm\textsuperscript{-1} to 4000 cm\textsuperscript{-1} shows two signals, a broad peak around 3500 cm\textsuperscript{-1} and a sharp peak around 3740 cm\textsuperscript{-1}. The former can be assigned to silanol nests and the latter high sharp peak originates from isolated silanol units on the pore walls.

A correlation between physical properties of MCM-41 materials, like pore size, wall thickness, hydrophobicity or morphology, and the leaching behavior could not be found. As can be seen in Table 5.1, all the MCM-41 batches tested have a BET surface area of about 1000 m\textsuperscript{2}/g and a pore size of about 25 Å, which is typical for such materials. The MCM-41 samples that were used to successfully impregnate silsesquioxane based catalyst to form a non-leaching heterogeneous catalyst do not show a different distribution in pore size, BET surface area or wall thickness than those MCM-41 samples that didn’t produce non-leaching heterogeneous catalysts after impregnation. It is therefore not possible to use these properties
to tell whether an MCM-41 sample will be suitable for this impregnation technique to form a non-leaching catalyst. In addition, with the data obtained, it is not possible to find a relation between the morphology of the MCM-41 samples and leaching. Using TEM analysis it was possible to estimate the amounts of ordered, disordered and amorphous material. Although a high amount of ordered material is by definition a good indication of a high quality MCM-41 material, for our purpose this will not guarantee that the material will yield a non-leaching catalyst after impregnation. Even the dehydration temperature and the water content of the MCM-41 samples, measured by TGA (Table 5.2) cannot be used to predict the suitability of the MCM-41 sample for the heterogenization of silsesquioxane-based catalysts based on physisorption.

5.4 Conclusions

Based on the experimental findings presented here, it can be concluded that the heterogenization technique we used, is influenced by very subtle differences in interactions between the pore walls of the MCM-41 and the impregnated catalysts. This interaction cannot be predicted using only one attribute of the MCM-41 like pore-size, wall-thickness, surface area or pore-wall hydrophobicity, but only by a complex combination of all. This leads to the general conclusion that the only way to predict if a specific large batch of MCM-41 is suitable for heterogenization of silsesquioxane-based catalysts using physisorption, is to impregnate a small sample of that batch with the catalyst in mind in order to be able to perform a leach test. The results of this test will determine the suitability of this technique for the entire batch.

Another shortcoming of MCM-41 material is the relative high amount of silanol units present on the pore walls. These silanols are a serious threat to impregnated catalysts if the latter are prone to hydrolysis. MCM-41 is only suitable as carrier material for catalysts that are completely water-stable.

5.5 Experimental Section

General considerations. All reactions with air- or moisture-sensitive materials were carried out under argon using standard Schlenk techniques. Freshly distilled, dry and oxygen-free solvents were used throughout.
The used silsesquioxanes were obtained by synthesis methods described in literature. Catalytic experiments and analysis of reaction products were carried out as previously described. Complexes 1 and 2 prepared as described in Chapter 3.

**Synthesis of MCM-41 materials:**

For the preparation of the different MCM-41 materials, a small variation on the procedures by Beck et al.\(^4\) was used. The exact procedures are stated below.

**Pure-silica MCM-41:** 1.4 g of SiO\(_2\) (Cab-O-Sil M5, Fluka) was added to a solution of 4.2 g TMA-OH (25 wt% in water) and 8.5 g water. This solution was combined with a solution of 6.6 g sodium silicate and 31.1 g of water. Under stirring, 4.8 g of SiO\(_2\) (Cab-O-Sil M5) was slowly added and the resulting gel was stirred for another hour after which the gel was added to a solution of 15.6 g cetyltrimethylammoniumbromide in 105 g of water. The resulting suspension was stirred for another hour.

MCM-41 samples M41-G1-S100 batch 1 to 3 were synthesized by heating the synthesis gel up to 100°C in an oven for 48 hours using polypropylene bottles.

MCM-41 samples M41-G1-S130 batch 1 to 4 were synthesized by heating the synthesis gel up to 130°C for 48 hours using steel autoclaves.

Filtration and washing of the residue with copious amounts of water resulted in a white powder which after drying was analyzed with XRD and TGA, to be as-synthesized MCM-41, still containing up to 60 wt% of organic templates.

**Template removal by calcination.** The organic templates were removed by calcinations in a continuous plug flow reactor of 27 mm internal diameter. For this purpose small amounts of the as-synthesized MCM-41 samples (about 1.5 grams) were heated up to 540°C at a rate of 1°C per minute under a Ar-O\(_2\) gas flow (30 mL per minute) containing 20 mol% O\(_2\). After reaching 540°C the temperature was kept at 540°C for another 12 hours.

**Template removal by extraction.** The organic templates were removed by stirring 1.5 g of the as-synthesized MCM-41 in 450 mL of 2 M HCl solution in ethanol for two days at 70°C.

**Template removal by soxhlet extraction.** About 10 g of MCM-41 (as synthesized) was washed with ethanol in a soxhlet setup for two weeks. The remaining solid (6.47 g) was dried at 70°C.

**Impregnation of catalyst into MCM-41.** The titaniumsilsesquioxane catalysts (containing 1.2 mg of Ti) are dissolved in 50 mL of dry hexanes after which the MCM-41 (1 gram, dried under vacuum) is added. The
suspension is mechanically stirred overnight and filtered. The residue is washed two times with 50 mL of toluene and two times with 50 mL of hexanes. The remaining solid is dried overnight at 70°C.

**Catalytic epoxidation tests.** The catalytic experiments were performed in stirred 1.5 mL batch reactors that were kept at 50°C. All experiments were performed using 60 mg of heterogenized catalysts in sealed vials that were magnetically stirred at 50°C. For the experiments a solution containing equimolar amounts (1.8 mmol) of cyclooctene and the amount of tert-butyl hydrogen peroxide in iso-octane (1.0 mL) corresponding to the ratios given in Table 5.3 were used. Conversions of the alkene to epoxide were determined by GC. In all cases, selectivities were above 95%.

**Characterisation:**

For the nitrogen physisorption analysis all the samples were pretreated just before the measurement in vacuum at 150°C for 30 minutes. The measurements were performed on an ASAP 2000 Micromeritics apparatus using an equilibration interval of 5 seconds and a low pressure dose of 3.00 cm³ g⁻¹ STP. Information about surface area was calculated according to the Brunauer-Emmett-and-Teller method (BET).

X-Ray diffraction (XRD) data were collected on a Rigaku diffractometer using Cu Kα radiation. Diffractograms were taken between 2° and 20°, using a scan speed of 1° per minute. The obtained diffraction patterns were corrected for background, baseline and Kα2 elimination.

Transmission electron microscopy (TEM) was performed using a Philips CM30T electron microscope with an LaB₆ filament as the source of electrons operated at 300 kV. Samples were mounted on a Quantifoil® microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions.

Thermo gravimetric Analysis (TGA) were done on a Shimadzu TGA-50 thermo gravimetric analyzer. Samples (about 10-15 mg) were heated under static conditions in air to 700°C with a rate of 5°C per minute.

Fourier Transformed Infrared (Ft-IR) spectra were taken at room temperature on a Bruker IFS 113V spectrophotometer equipped with a vacuum cell. Before analyzing, the samples were pressed into self supporting wafers of 10 mg and dried at 100°C for 1 hour in vacuum. The spectra from 3000 cm⁻¹ to 4000 cm⁻¹ were linearly baseline corrected.

Gas Chromatographic (GC) analysis of epoxidation reaction mixtures was done on a Carlo Erba 6000 Vega Series 2 equipped with a Flame Ionization Detector (FID) and a DB1 capillary column. Injection temperature was set to 523 K, column temperature to 423 K and detector temperature to 523 K. Prior to analysis the samples were filtered, while still warm, through syringe filters of 0.45 μm and diluted with methanol.
Acknowledgements

Rob Hanssen is gratefully acknowledged for his contribution to this chapter.

References

Chapter 6

Titanium silsesquioxane / 3D-netted polysiloxane based ensembles for the epoxidation of alkenes with aqueous hydrogen peroxide

Abstract: In this chapter the synthesis of two new titanium silsesquioxanes, \((\text{H}_2\text{C}=\text{CH})(\text{c-C}_6\text{H}_{11})_6\text{Si}_7\text{O}_{12}\text{TiX} (2\text{a}, \ X = \text{Cp}, \ 2\text{b}, \ X = \text{O-i-Pr})\) are reported. These robust titanium silsesquioxane complexes are grafted on commercially available linear methylhydrosiloxane dimethylsiloxane copolymers and after that cross-linked by reaction with vinyl-terminated polydimethylsiloxanes. The resulting titanium polysiloxane materials are hydrophobic, 3D-netted polymers that enclose the titanium sites in cavities. After testing of these titanium polysiloxanes on catalytic epoxidation activity, the catalysts proved to be capable of epoxidizing 1-octene, cyclooctene and cyclododecene with aqueous hydrogen peroxide as the oxidant.

6.1 Introduction

Few catalysts have been truly efficient in alkene epoxidation with aqueous hydrogen peroxide. Development of such catalysts is an important goal since with regard to desirability; this oxidant comes only second to oxygen itself.\(^1\) Currently, the best catalyst in this field is the synthetic titanium-containing zeolite, titanium silicalite-1 (TS-1),\(^2\) which is active for a wide range of oxidation reactions, including epoxidation.\(^3\) For TS-1, activity seems to originate from a combination of a robust active Ti(OSi≡)\(_n\) site (\(n = 3,4\)),\(^4\) and its location in a hydrophobic channel or cavity in the MFI structure.\(^5\) The resulting catalytic ensemble prevents poisoning of the active site by water as well as unproductive decomposition of the oxidant.

Homogeneous catalysts with structural elements that are very similar to the active TS-1 site have recently been reported as a series of titanium silsesquioxane complexes.\(^6,7\)
Although some of these were found to be stable in aqueous media (see also Chapter 3), quick catalytic tests with these water stable complexes revealed that none could perform alkene epoxidation with aqueous hydrogen peroxide. It is tempting to ascribe this inability to the lack of a combination of the active titanium site with a suitable hydrophobic environment. The same phenomenon can account for lack of catalytic activity in a study by Sherrington on Ti(IV) grafted polysiloxane networks prepared from silanol rich supports. These materials, showed no activity in alkene epoxidation with 30% aqueous H$_2$O$_2$. Either the presence of residual silanols that make the materials more hydrophilic thus rendering unsuitable catalytic ensembles or the presence of Ti centers with inappropriate structures were probably responsible for this lack of activity with aqueous hydrogen peroxide.

This chapter reports on the synthesis of catalytically active epoxidation catalysts, which consist of titanium silsesquioxanes, which are grafted on a polysiloxane support. By introducing these titanium complexes in the hydrophobic cavities, that are present in the support after cross-linking, it is possible to attain active epoxidation catalysts that use hydrogen peroxide to epoxidize several alkenes including cyclooctene and cyclododecene, substrates that are too large to fit the pores of TS-1.

6.2 Results and Discussion

Vinyl silsesquioxane trisilanol (H$_2$C=CH)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_9$(OH)$_3$, 1, can be easily converted to new titanium silsesquioxane complexes of formula (H$_2$C=CH)(c-C$_6$H$_{11}$)$_6$Si$_7$O$_{12}$TiX (2a, X = Cp, 2b, X = O-i-Pr) by reaction with resp. Cl$_3$TiCp or Ti(O-i-Pr)$_4$. These reactions are similar to those previously described for the related, unfunctionalized silsesquioxane trisilanol (c-C$_6$H$_{11}$)$_6$Si$_7$O$_9$(OH)$_3$. For both new complexes, the $^{13}$C NMR spectra (400 MHz, CDCl$_3$) are particularly informative, showing four peaks of the cyclohexyl methine carbons (ratio 2:1:1:2 for 2a and 1:1:2:2 for 2b) characteristic for C$_2$-symmetric, monomeric silsesquioxane titanium species. Attempts to obtain crystals of 2 suitable for X-ray analysis were unsuccessful thus far.
Scheme 6.1: Vinyl silsesquioxane trisilanol (\(H_2C=CH\)(c-C\(_6\)H\(_{11}\))\_3Si\_2O\_3(OH))\(_3\), 1, and vinyl-bearing titaniumsilsesquioxanes (\(H_2C=CH\)(c-C\(_6\)H\(_{11}\))\_3Si\_2O\_3TiX (2a, X = Cp, 2b, X = O-i-Pr) which result from the reaction of 1 with resp. \(Cl_3TiCp\) or \(Ti(O-i-Pr)\_4\).

Vinyl-bearing metallosilsesquioxanes easily undergo platinum catalyzed hydrosilylation,\(^{11}\) thus for the immobilization of 2, linear methylhydrosiloxane dimethylsiloxane copolymers were chosen as a support. These copolymers are commercially available over a wide range molecular weight and reactive silane content. Both 2a and 2b can be smoothly grafted on these copolymers, followed by cross-linking with vinyl-terminated polydimethylsiloxanes (DMS-V05), also conveniently available, to form brittle organosiliceous materials 3.

Scheme 6.2: Immobilization of 2 in a 3D-netted polysiloxane polymer.

The first step of the hydrosilylation of 2 with methylhydrosiloxane dimethylsiloxane copolymer (HMS-301) can be monitored by \(^1\)H NMR and \(^{13}\)C NMR. Already half an hour after addition of ppm amounts of platinum hydrosilylation catalyst to the reaction mixture of 2 and HMS-301 in deuterated benzene (at the concentrations applied for polymer preparation),
resonances assignable to vinyl groups have disappeared in both $^1$H NMR and $^{13}$C NMR spectra, together with simultaneous changes of the cyclohexyl methine carbon pattern of the silsesquioxanes as observed by $^{13}$C NMR.

Catalytic activity of materials 3 was first studied in epoxidation of cyclooctene with equimolar amounts of tert.-butyl hydroperoxide (TBHP, 1.8 M in iso-octane, 0.33 mol% Ti, 50°C). From these experiments, it is clear that only grafted titanium derivatives yield truly heterogeneous catalysts. After 24 h reaction, 73% and 55% conversion of cyclooctene to cyclooctene epoxide was found for 3a and 3b, respectively, with >95% selectivity. For comparison, a material 4b related to 3b resulting from a known, non-vinyl derivative (c-$C_6H_{11})_7Si_2O_{12}TiO-i$-Pr, that is only physically “trapped” in the polysiloxane, was prepared using the same polymerization procedure as for 3b. For the system 4b, using the same conditions as above, 61% conversion of cyclooctene to cyclooctene epoxide was observed after 24 hours. Hot filtration experiments however, reveal that only materials 3 are truly heterogeneous catalysts, as the epoxidation stops when the polymer is filtered out of the reaction mixture. In case of 4b epoxidation proceeds further after filtration, due to leaching of (c-$C_6H_{11})_7Si_2O_{12}TiO-i$-Pr from the polymer.

![Figure 6.1: Heterogeneous epoxidation of cyclooctene with hydrogen peroxide catalyzed by 2-4. Epoxide yields are based on the amount of peroxide used.](image)

Materials 3 were subsequently tested in catalytic epoxidation of neat cyclooctene with 35% aqueous hydrogen peroxide ($H_2O_2 :$ alkene $= 1 : 4$, 0.33 mol% Ti, 50°C). The results are presented in Fig. 6.1; the reaction scope is discussed below. Epoxide yields are based on the amount of peroxide used. From these experiments, it is clear that only grafted titanium
derivatives yield active catalysts in application with aqueous hydrogen peroxide. As shown in Fig. 6.1 material 4b is less active, than its fully heterogeneous analog 3b, (despite having at least the same Ti content as 3b). The lower catalytic activity of 4b can be easily explained by leaching of (c-C₆H₁₁)₃Si₇O₁₂TiOi-Pr from the polymer. The unsupported complex is inactive in epoxidation of alkenes with H₂O₂ and only results in the unproductive and undesired decomposition of the H₂O₂.

The reaction scope of the most active catalyst 3b was found to include n-alkenes and large cyclic alkenes. For cyclododecene (H₂O₂: alkene = 1:4, 0.33 mol% Ti, 50°C) a maximum epoxide yield of 45% was reached; the remaining part of the peroxide decomposed unproductively to O₂. Catalytic epoxidation with 3b of 1-octene was optimized to 62% yield of epoxide obtained in 1.5 h (H₂O₂: alkene = 1 : 12, 2 mol% Ti, 80°C) resulting in a TOF of ca. 20 mol.(mol Ti)⁻¹.h⁻¹. Reported turnover frequencies for 1-octene epoxidation by TS-1 vary from 4 to ca. 80 mol.(mol Ti)⁻¹.h⁻¹ and generally increase significantly with increasing alkene / H₂O₂ ratios. This is also valid for our systems.

6.3 Conclusions

Grafting of functionalized titanium silsesquioxanes on polysiloxanes provides a way to realize the formation of a truly heterogeneous (polymeric) catalyst that is able to perform epoxidation of several alkenes with aqueous hydrogen peroxide. Clearly, the entire system is capable of outperforming the sum of its parts; it is the synergy between active site and its hydrophobic environment that allows the catalysts presented here, and likewise TS-1, or even metalloenzymes¹² to achieve their desirable performances.

6.4 Experimental Section

**General considerations.** All reactions with air- or moisture-sensitive materials were carried out under argon using standard Schlenk techniques.¹³ Freshly distilled, dry and oxygen-free solvents were used throughout. The silsesquioxane (H₂C=CH)(c-C₆H₁₁)₆Si₇O₉(OH)₃ was obtained by synthesis methods described in literature.⁹
(H₂C=CH)(c-C₆H₃)₄Si₃O₄TiCp (2a): To 2.75 g (3.00 mmol) of (H₂C=CH)(c-C₆H₃)₄Si₃O₄(OH)₃ in 35 mL of toluene was added 0.658 g of CpTiCl₃, followed by addition of 1.5 mL (excess) of dry pyridine. The mixture was stirred for 1 h at room temperature, filtered and the filtrate was concentrated to about 10 mL. After adding 10 mL of acetonitrile, 2a (2.35 g, 76% yield) was isolated as white crystals. ¹H NMR (300 MHz, CDCl₃, 23°C, SiMe₃): δ 6.53 (s, 5 H, C₆H₅) 6.0 (m, 3 H, CH₂=CH₂), 1.75 (m, 30 H, CH₂-C₆H₅), 1.26 (m, 30 H, CH₂-C₆H₅), 0.76 (m, 6 H, CH₃-C₆H₅). ¹³C (¹H) NMR (100 MHz, CDCl₃, 23°C, SiMe₃): δ 134.89 (CH₂-vinyl), 130.97 (s, CH-vinyl), 116.26 (s, CH-C₆H₅), 27.64, 27.57, 27.55, 27.52, 27.11, 26.93, 26.89, 26.83, 26.76, 26.65 (s, CH₂-C₆H₅), 23.43, 23.22, 23.20, 23.15 (s, CH-C₆H₅), ratio 2:1:2:1. ²⁹Si NMR (79.5 MHz, CHCl₃, 0.02 M Cr(acac)₃, 23°C, SiMe₃): δ -66.14, -68.69, -69.33, -69.52 (s, Si-CH, 2:1:2:1 ratio), 78.01 (s, Si-vinyl). Anal. Calcd. (found) for C₄₃H₇₀O₁₂Si₃TiC, 50.26 (50.19); H, 7.26 (7.37).

(H₂C=CH)(c-C₆H₃)₄Si₃O₄TiO-i-Pr (2b): To 2.75 g (3.00 mmol) of (H₂C=CH)(c-C₆H₃)₄Si₃O₄(OH)₃ in 25 mL of hexane was added 0.91 mL (3.00 mmol) of Ti(O-i-Pr)₄. The mixture was stirred at 50°C for 1.5 h and the solvent was evaporated in vacuo, yielding 3.03 g crude white powder. ¹H NMR (300 MHz, CDCl₃, 23°C, SiMe₃): δ 6.06 (m, 2H, CH₂≡C), 5.89 (m, 1H, CH=), 4.62 (m, 1H, CH (CH₃)₂), 1.77 (br m, 30H, CH₂-C₆H₅), 1.27 (m, 36H, CH₂-C₆H₅ and CH₂-OPr), 0.81 (m, 6H, CH₂-C₆H₅). ¹³C (¹H) NMR (100 MHz, CDCl₃, 23°C, SiMe₃): δ 135.69 (s, CH₂-vinyl), 130.03 (s, CH-vinyl), 27.52 (s, CH(CH₃)), 26.88, 26.83, 26.75, 26.70, 26.66 (s, CH₂), 25.65 (s, CH₃, OPr), 23.22, 23.19, 23.14, 23.09 (s, CH, 1:1:2:2 ratio). ²⁹Si NMR (79.5 MHz, CHCl₃, 0.02 M Cr(acac)₃, 23°C, SiMe₃): δ -67.20, -68.60, -69.36, -69.53 (s, Si-CH, 2:1:2:1 ratio), -78.96 (s, Si-vinyl). Anal. Calcd. (found) for C₄₃H₇₀O₁₂Si₃TiC, 48.21 (49.05); H, 7.50 (7.82).

Immobilization of 2a and 2b in polysiloxane (3): 726.9 mg of 1a dissolved in 3 mL of toluene was added to 3.0 g of methylhydrosiloxane-dimethylsiloxane copolymer (HMS-301, Gelest) diluted with 4 mL of toluene and 20 mg of platinum–divinyltetramethyl disiloxane complex in xylene (Gelest). The mixture was stirred at room temperature for 0.5 h, and then 2.40 g of vinyl terminated polydimethylsiloxane DMS-V05 diluted with 3 mL of hexane and 20 mg of Pt-catalyst was added. The reaction mixture was stirred for additional 15 minutes, poured into a Petri plate to evaporate the solvent and cured at 80°C overnight. The brittle polymer was ground, and continuously extracted with diethyl ether for 2 days to remove ungrafted titanium. After filtration and drying 5.1 g polymer 3a was obtained. Anal. Calcd. (found) Ti, 5.5 (5.1 mg/g). The same procedure was applied using 720 mg of 2b to achieve the same initial Ti content (5.5 mg Ti/ g of reacting components) to give 4.8 g of polymer 3b.

Catalytic epoxidation tests. The epoxidation tests were carried out in 2 mL stirred batch reactors, using about 60 mg of 3. For epoxidation with TBHP 1.8 mmol TBHP and 1.8 mmol of cyclooctene in iso-octane was used. Epoxidation with aqueous H₂O₂ was carried out using H₂O₂ (35% aqueous solution) and neat alkene in the molecular ratios specified above. Excess of alkene is used here to suppress unproductive decomposition of H₂O₂ to O₂. Samples taken from the reaction mixtures were analyzed by GC analysis using a Carlo Erba GC6000 Vega Series equipped with a capillary DB-1 column and a FID. For this purpose, all samples contain 25 µL of 1,3,5-trimethyl benzene (>98%, Merck) as GC internal standard. Prior to analysis the samples were filtered, while still
warm, through syringe filters of 0.45 μm and diluted with methanol. Epoxide yields are based on the amount of peroxide used.

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References

Summary

The use of epoxides as versatile and useful intermediates in organic synthesis has induced a high level of interest in their catalytic formation from alkenes, both in industry and in academia. Furthermore, the ever-growing demand for environmentally friendly processes stresses the importance of developing better catalysts in this field. In the current search for robust heterogeneous liquid phase oxidation catalysts, much attention is paid to empiric evaluation of catalytic performance, rather than to fundamental aspects accounting for catalytic activity and catalyst stability. This thesis addresses these fundamental aspects using model systems for industrially used catalysts.

As part of an approach to design new catalysts for the environmentally friendly epoxidation of alkenes with aqueous hydrogen peroxide, a desirable oxidant, several silsesquioxane silanol derivatives were synthesized and converted to silsesquioxane silanolate titanium complexes. The silsesquioxane silanols, which were thus used as ligands, can be regarded as well-defined soluble chunks of silica, suitable for designing precise homogeneous epoxidation catalysts that model some currently used industrial heterogeneous catalysts. By varying the dentacity of silanolate ligation we were able to study both stability and reactivity of the catalysts in the presence of water, which is inevitably present during the epoxidation of alkenes with hydrogen peroxide. This resulted in general rules for stability and reactivity as a function of the dentacity of the silsesquioxane ligands and steric crowding around the titanium site.

Polyoxometalates and heteropolyacids are also emerging as interesting catalysts for the epoxidation of alkenes using oxidants like O$_2$ and H$_2$O$_2$. Unfortunately, the synthesis of these materials is often rather empiric and the structural characterizations involved can be difficult. Two new polyoxotitanates \([((c-C_6H_{11})_bSi_6O_{11})_3[Ti(\mu^3-OH)]_4\) and \([(c-C_7H_{13})_bSi_6O_{11})_3[Ti(\mu^3-OH)]_4\) were synthesized in a relatively easy manner, involving the use of the silsesquioxanes as synthetic platforms for the construction of a polyoxometal framework. The new polyoxotitanates can be used as robust epoxidation catalysts that work to some extent with organic peroxides as well as with H$_2$O$_2$ as the oxidant.

Industry prefers heterogeneous catalysts for bulk processes due to their ease of handling during workup of the reaction mixtures. We therefore researched the possibilities of immobilization of titanium silsesquioxane based catalysts. For this purpose the catalysts were
impregnated in MCM-41, a well-defined large pore silicate. Another approach was made by modifying the silsesquioxane ligands so they could be tethered, via a hydrosilylation reaction, to a commercially available polysiloxane support. The latter method resulted in a catalytic ensemble able to epoxidize alkenes using aqueous hydrogen peroxide, a result that could not be obtained by the homogeneous catalyst prior to immobilization. Interesting analogies with operation of metalloenzymes could be drawn.
Samenvatting

Het gebruik van epoxides als veelzijdige en bruikbare tussenprodukten in organische syntheses heeft gezorgd voor een hoge interesse van de industrie en academische wereld in hun katalytische vorming uitgaande van alkenen. De steeds hoger wordende eisen op milieugebied hebben er tevens voor gezorgd dat er steeds meer vraag is naar milieuvriendelijke processen waarbij steeds meer de nadruk wordt gelegd op het belang van de ontwikkeling van betere katalytische processen. In de huidige zoektocht naar robuuste heterogene vloeistof-fase oxidatie katalysatoren wordt echter meer aandacht besteed aan een empirische evaluatie van de katalytische prestaties, dan aan de fundamentele aspecten die verantwoordelijk zijn voor de katalytische activiteit en stabiliteit van de katalysatoren. In dit proefschrift worden deze fundamentele aspecten aangepakt, gebruik makend van systemen die de industrieel gebruikte oxidatie katalysatoren modelleren.

Een deel van de aanpak om tot de ontwikkeling van nieuwe katalysatoren, voor de milieuvriendelijke epoxidatie van alkenen met waterstofperoxide te komen, werd gevormd door verschillende silsesquioxaan silanol varianten te synthetiseren. Deze werden door reactie omgezet tot chroom- en titaansilsesquioxaan complexen. De silsesquioxaan silanolens die als liganden werden gebruikt kunnen gezien worden als goed gedefinieerde oplosbare silicadeeltjes, die geschikt zijn voor het ontwerp van oxidatie katalysatoren. De hieruit voortgekomen goed gedefinieerde katalysatoren kunnen gebruikt worden voor het modelleren van katalysatoren die in de industrie gebruikt worden. Door het varieren van de dentaciteit van de silanolaat liganden was het mogelijk de reaktiviteit en stabiliteit van de katalysatoren te bestuderen in de aanwezigheid van water, hetgeen onvermijdelijk aanwezig is gedurende de epoxidatie van alkenen met waterstofperoxide. Dit onderzoek resulteerde in een aantal vuistregels voor de stabiliteit en reaktiviteit als functie van de dentaciteit van de silsesquioxaanliganden en sterische blokkering rond het aktieve titaancentrum van de katalysator.

Polyoxometalaten en heteropolyzuren, komen steeds meer op als interessante katalysatoren voor de epoxidatie van alkenen, gebruik makend van oxidanten als zuurstof en waterstofperoxide. Helaas is de synthese van deze materialen nogal empirisch en kan de karakterisatie van deze materialen vaak erg ingewikkeld zijn. Twee nieuwe polyoxotitanaten \([((c-C_6H_{11})_6Si_6O_{11})_3[Ti(\mu^3-OH)]_4\) en \([(c-C_7H_{13})_6Si_6O_{11})_3[Ti(\mu^3-OH)]_4\) werden gesynthetiseerd.
op een relatief simpele manier waarbij silsesquioxanen werden gebruikt als het synthetische platform voor de constructie van het polyoxometal geraamte. Deze nieuwe polyoxometalen kunnen gebruikt worden als robuuste epoxidatiekatalysatoren die tot op zekere hoogte geschikt zijn als epoxidatiekatalysatoren voor gebruik met organische peroxides, alswel met waterstofperoxide als oxidant.

De industrie prefereert heterogene katalysatoren voor bulk processen vanwege het gebruiksgemak tijdens opwerking van de reactiemengsels. Vanwege dit gegeven werden de mogelijkheden onderzocht om op titaan silsesquioxanen gebaseerde katalysatoren te immobiliseren. Voor dit doel werden de katalysatoren geimpregneerd in MCM-41, een goed gedefinieerd silicaliet met grote poriën. Een andere aanpak werd toegepast waarbij het silsesquioxaan ligand werd gedomesticeerd, waardoor het via een hydrosilylatie chemisch gekoppeld kon worden aan een commercieel verkrijgbare polysiloxaan drager. Deze laatste methode resulteerde in een katalytisch ensemble, dat in staat was om alkenen te epoxideren gebruik makend van een waterige waterstofperoxide oplossing, iets wat niet bereikt kon worden met de homogene katalysator voordat deze ge-immobiliseerd was. Dit resultaat laat interessante analogieën zien met de werking van metaalenzymen.
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