SYNTHESIS, CHARACTERIZATION
AND CATALYTIC APPLICATION
OF ZEOLITE TITANIUM BETA

Jan Cornelis van der Waal
Cover:  HREM micrograph showing the channels of zeolite beta.
Magnification 5,600.000x.
SYNTHESIS, CHARACTERIZATION
AND CATALYTIC APPLICATION
OF ZEOLITE TITANIUM BETA

PROEFSCHRIFT

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Jan Cornelis van der Waal

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'And there's the sign, Ridcully', said the Dean. 'You have read it, I assume. You know? The sign which says "Do not, under any circumstances, open this door"?'

'Of course I've read it,' said Ridcully. 'Why d'yer think I want it opened?'

'Er... why?' said the Lecturer in Recent Runes.

'To see why they wanted it shut, of course.'

Terry Pratchett, "Hogfather"
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         - Influence of the water concentration
         - The overall kinetic equation
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</table>
Introduction to zeolites.

Abstract

Zeolites and molecular sieves are crystalline microporous alumino-tectosilicates with an increasing number of applications. Established applications of molecular sieves are in the field of oil refining processes, selective adsorption and ion-exchange. Nowadays zeolites come to the fore as clean, selective and reuseable catalysts in petrochemistry, e.g. in aromatic alkylation. Zeolites are considered to have a high potential for the synthesis of commodities and fine chemicals due to their molecular sized pores. Nevertheless, only a few commercial applications in fine chemical synthesis are known. Based on the essential criteria, extracted from the organic reaction under consideration, some of the potential pitfalls in selecting and screening zeolites as potential catalysts are discussed.
1.1 Zeolites

1.1.1 Structure and properties of zeolites and molecular sieves.

Over 200 years ago the Swedish scientist Crenstedt discovered stilbite,\(^1\) the first of a group of crystalline microporous aluminosilicates. Upon heating the zeolite released occluded water, which gave the materials their general name, zeolite, after the Greek *zeo* (to boil) and *lithos* (stone). A century ago, 18 natural zeolites were known and Damour\(^2\) described the adsorption/desorption properties of water on/from zeolites, followed by Eichhorn’s report on the cation-exchange characteristics.\(^3\) The study of the adsorption and diffusion of organic molecules such as benzene and chloroform, on/in dehydrated zeolites by McBain\(^4\) led to the recognition of the potential of separating molecules by zeolites and hence the name molecular sieves was born.

Nowadays over 40 natural zeolites are known, though the exploration of natural zeolites proved unsuitable for many of the specific industrial applications. In this respect, the pioneering work of the academic Barrer group (Imperial College, London) and the industrial research groups of Union Carbide and Mobil Oil in the USA were essential in the rapid development of the zeolite science. The main focus was on the synthesis of zeolites. Man not only succeeded in producing the natural zeolites on an industrial scale, but also in synthesizing structures not found in nature. In the last 45 years about 100 new structures have been synthesized and characterized. Some of these new zeolites have found practical applications and the spectrum is still expanding.

Zeolites are crystalline aluminosilicates with a framework consisting of SiO\(_4\)- and AlO\(_4\)-tetrahedra (T-atoms), connected via the oxygen atoms at the corner points of the tetrahedron. Zeolites are just a part of the wide variety of silicate structures possible and distinguish themselves from the other classes of silicates in that molecular sized pore - diameters up to 1.0 nm - are present. The other classes of silicates are the dense structures such as \(\alpha\)-quartz, cristobalite, sheet-like structures such as magadiite and kenyanite or the dense cage-like structures such a clathrasils. The connection of two AlO\(_4\)-tetrahedra is not encountered (the Löwenstein rule), thus restricting zeolites to Si/Al molar ratios of \(\geq 1\). Every
Al$^{3+}$ introduces a negative charge which is compensated for by a cation (Figure 1.1). The micropore structure of the zeolites allows the exchange of the cations and the reversible adsorption and desorption of water and other organic molecules. Related to the zeolites are the microporous aluminophosphates (ALPO’s) with a neutral AlO$_2$PO$_2$ building unit.

![Schematic representation of a zeolite and an ALPO](image)

Figure 1.1 Schematic representation of a zeolite (left) and an ALPO (right).

Table 1.1 Pore geometry of zeolites.

<table>
<thead>
<tr>
<th>Channels</th>
<th>Pore geometry</th>
<th>Parallel</th>
<th>Perpendicular</th>
</tr>
</thead>
<tbody>
<tr>
<td>one-dimensional</td>
<td>1 straight</td>
<td>LTL, UTD-1, TON, CIT-5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 straight</td>
<td>MOR</td>
<td></td>
</tr>
<tr>
<td>two-dimensional</td>
<td>1 straight, 1 sinusoidal</td>
<td>MFI</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 straight</td>
<td>MEL, P</td>
<td></td>
</tr>
<tr>
<td>three-dimensional</td>
<td>2 straight, 1 sinusoidal</td>
<td>BEA</td>
<td></td>
</tr>
<tr>
<td>cages + windows</td>
<td>three-dimensional</td>
<td>FAU (X,Y)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>cubic</td>
<td>LTA</td>
</tr>
</tbody>
</table>
Depending on the connection of the T-atoms different zeolite structures can exist. The most common structure-types are the connected cage, the parallel channel and the crossing channel geometry (Table 1.1). The sieving characteristics of zeolites are largely determined by the size of the pore opening. Zeolites are classified by the number of T-atoms in the pore openings of a cage window or channel wall. The small pore zeolites have 8-membered rings (about .45 nm); the medium pore zeolites have 10 membered rings (about .55 nm) and the large pore materials have at least 12 T-atoms in the ring (over 0.7 nm). Figure 1.2 shows an overview of the pore sizes of commonly applied zeolites and some recently developed 14 ring zeolites (UTD-1, CIT-5, over 0.8 nm).5,6

![Figure 1.2](image_url) Pore sizes of silicate and phosphate molecular sieves.
In connection with the structure of the zeolite, the Si/Al ratio determines a number of important properties useful for catalysis, ion-exchange and adsorption. Table 1.2 summarizes the trends of these properties as a function of their initial Si/Al ratio for a number of zeolites. For several zeolites, Si/Al ratios ranging from this initial (minimum) value to infinity can be realized by de-alumination or direct synthesis procedures. An infinite Si/Al ratio for example in silicalite-1 applies to a zeolite with the MFI structure but without Al\textsuperscript{3+} ions in the framework. Silicalite-1 doesn’t meet the definition of a zeolite strictly speaking. The material has no ion-exchange capacity and after activation it has a hydrophobic character.

Table 1.2 Trends in the properties of zeolites as a function of the Si/Al ratio.

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>Si/Al (min.)</th>
<th>A</th>
<th>X</th>
<th>Y</th>
<th>MOR</th>
<th>MFI</th>
<th>Silicalite</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of cations</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
</tr>
<tr>
<td>stability vs. acidic solutions</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
</tr>
<tr>
<td>acid strength zeolite proton</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
</tr>
<tr>
<td>thermal stability</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
</tr>
<tr>
<td>hydrophilic character</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
</tr>
<tr>
<td>hydrophobic character</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
</tr>
<tr>
<td>affinity for polar molecules</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
</tr>
<tr>
<td>affinity for apolar molecules</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
<td>←</td>
</tr>
</tbody>
</table>

What makes molecular sieves and zeolites in particular so special compared to other crystalline inorganic oxides? The answer lays in a combination of specific properties. As mentioned above, zeolites are microporous with uniform pore dimensions, allowing certain molecules to enter whereas others are rejected. Since all tetrahedra of the zeolite framework are exposed to the pore volume, zeolites have a very high surface area compared to non-
porous inorganic solids. Moreover, the surface of a zeolite is not formed by the breakage of crystal bonds but has attained its crystallographic coordination throughout the whole pore system. Furthermore, zeolites exhibit ion-exchange properties which allows them to develop internal acidity by ion-exchanging with ammonium cations, followed by calcination. This opens the way to catalyze organic reactions which require Brønsted acidity.

1.1.2 Application of zeolites in industrial catalysis

Zeolites have found a wide array of applications. Table 1.3 gives a summary of the annual usage of zeolites in 1991. The market for zeolites has been stable for the last decade and these figures can be taken as a guideline for the today’s annual usage. The main application of zeolites is as ion exchangers for detergent formulations: over 800,000 ton a year. When in the early 70’s environmental concern grew with respect to the phosphates applied in detergent formulations, research by Henkel led in 1974 to the introduction of zeolite NaA as an excellent sequestering material for Ca$^{2+}$ and Mg$^{2+}$ ions under high alkalinity. Recently a new zeolite was introduced as a competitor for zeolite NaA. This new zeolite MAP (Maximum Aluminum P, a zeolite related to natural Gismondine) is produced by Crossfield and is thought to have a very flexible framework, allowing fast cation transport through the channels, and a low Si:Al ratio, giving a high ion-exchange capacity.

The use of zeolites as drying agents was one of the first applications which was recognized after their discovery. Nowadays about 40,000 ton of zeolites is used each year as selective drying agents (Table 1.3). The major application is the removal of trace amounts of water from solvents e.g. production of dry ethanol with zeolite KA, also referred to as zeolite 3A. Nowadays, the most commonly used zeolites for removal of water from solvents and gas streams are zeolite KA and the cheaper zeolite NaA (also referred to as zeolite 4A).

Shell and Union Carbide are commercially using zeolite CaA ($\approx$ 4.6 Å, also referred to as zeolite 5A) in the separation of linear paraffins from branched paraffins in their TIP process (Total Isomerization Process, Figure 1.3). In this process the linear C$_5$ and C$_6$ paraffins are first isomerized to the thermodynamic equilibrium whereafter the linear paraffins are selectively adsorbed on zeolite CaA and recycled to the isomerization reactor.
isomerization catalyst of the TIP process is zeolite Pt-H-Mordenite, showing the catalytic potential of zeolites. In this case the zeolite not only serves as a support for the platinum particles but also as a solid-acid catalyst. The TIP process (> 100 plants worldwide) is an excellent example of the versatile nature of zeolites in industrial processes. The demand for new zeolite is, however, modest because of the long service life of the separating and the isomerizing zeolites. The use of zeolites as catalysts (over 100.000 ton annually, Table 1.3) is dominated by FCC cracking of oil feedstocks and to a lesser extent to specialized petrochemical processes, such as the TIP process, hydrocracking, benzene alkylation and the production of para-xylene. FCC is the most important process in oil refining for the production of gasoline components by converting low-value high-boiling feedstocks, e.g. vacuum gasoil and heavier fractions, into lighter products via cracking. The catalyst used is predominantly zeolite USY (partially de-aluminated zeolite Y) sometimes accompanied with small amounts of ZSM-5.

Table 1.3 Estimated annual world production of zeolites in 1991.7

<table>
<thead>
<tr>
<th>Application</th>
<th>Production [ ton year⁻¹ ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion exchange</td>
<td>825.000</td>
</tr>
<tr>
<td>Purification</td>
<td>(natural zeolites)</td>
</tr>
<tr>
<td>Desiccant and Adsorbent</td>
<td></td>
</tr>
<tr>
<td>Catalysis</td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
<td>≈ 500</td>
</tr>
<tr>
<td>Petrochemical, special</td>
<td>≈ 5.000</td>
</tr>
<tr>
<td>Oil refining, FCC cracking,</td>
<td>≈ 95.000</td>
</tr>
</tbody>
</table>
Application of zeolites in the large scale production of intermediates other than alkylbenzenes is still limited. In the synthesis of intermediates only the oxidation of phenol to catechol and hydroquinone with aqueous hydrogen peroxide over titanium containing MFI zeolite (TS-1), the production of tert-butylamine from ammonia and isobutene over zeolite MFI,\(^\text{10}\) the selective conversion of methanol and ammonia to mono- and dimethylamine over modified mordenites\(^\text{11}\) or zeolite Rho\(^\text{12}\) and the hydration of cyclohexene to cyclohexanol are currently performed. Also the near commercialization of the ammonoxidation of cyclohexanone
to cyclohexanone oxime over TS-1 using ammonia and hydrogen peroxide may be mentioned. Zeolites have also found some commercial application in the production of organic fine chemicals, showing that even for relatively small product streams zeolites can be cost effective. Examples include: the synthesis of dichlorotoluenes and of trichlorobenzenes through zeolite catalyzed equilibration and the para-acetylation of anisole with acetic anhydride over zeolite H-beta and H-Y.\textsuperscript{13}

Zeolites certainly will play a role as regenerable, solid acid catalysts, replacing conventional metal chloride and mineral acid catalyzed processes. For example, a comparison of the present industrial process for the preparation of the anti-oxidant 2,4-dihydroxybenzophenone with the zeolite beta catalyzed process developed at the Delft University shows the advantage of the latter process with respect to catalyst usage and waste production.

![Chemical structures]

**Figure 1.4** Industrial process (left) and the Delft-based process (right) for the preparation of 2,4-dihydroxybenzophenone.
1.2 Rational design of zeolites and related materials as catalysts for fine chemicals.

Zeolites are considered to have a high potential as catalysts for the synthesis of fine chemicals. This is due to their uniform and well-defined pore structure, which can increase selectivity by molecular shape selectivity and excellent regenerability. Reviews on the applications of zeolites in organic catalysis have been given by Venuto\textsuperscript{14} and by Hölterich and van Bekkum.\textsuperscript{15} In most cases, the only criterion used in selecting a particular zeolite was the dimensions of its pores. In this paragraph, an attempt is made to stream-line the selection of a particular zeolite(s) as (a) catalyst(s) from the viewpoint of the organic reaction to be performed.

It is, however, good to realize that zeolites also have some drawbacks. They often deactivate rapidly, Turn-Over-Numbers (TON) over 100 are seldom reported when working in the liquid phase, thus requiring frequent regeneration. Furthermore, the reaction rate is usually controlled by diffusion, thus requiring very small particles ($< 1 \mu m$) and high amounts of catalyst for fast conversions. Another important aspect is the limited number of commercially available zeolites. The development and commercialization of new tuned zeolites is too expensive for the small product volumes applied in fine chemical industries.

In the process of selecting a zeolite for a specific organic reaction, it is often useful to look at specific properties of the system itself. These are listed in Table 1.4 together with their relation to the choice of a set of zeolites for screening. The first three criteria mentioned in Table 1.4, the molecular size of reactants and products, the catalytic active site, and the polarity of reactants, products and solvents, are by far the most important ones and their influence on the selection of a particular zeolite will be discussed in more detail. The other criteria are usually less important, though in specific cases they can play an important role, and it is often good to determine their potential impact on a selected zeolite. For example, if the organic reaction is an equilibrium reaction or if a consecutive or a parallel reaction is operative, then shape selectivity is an absolute necessity to obtain high selectivity (see paragraph 2.1 for a detailed discussion).

Under normal working conditions, it is reasonably safe to say that zeolites are thermostable. This can change quite drastically when aggressive chemicals are involved. Water
seems to be a key chemical in this. Most zeolites can easily withstand aggressive chemicals, like HCl, HNO₃, AcOH, amino acids etc. under water-free conditions. When, however, also water is present the zeolite usually degrades gradually, either by amorphesizing or by complete dissolution. Although the zeolite framework itself is quite thermo- and chemostable, this can not always be said of the catalytic active site. Loss of catalytic active sites is often a major problem. This holds especially for the transition metal exchanged or lattice substituted redox molecular sieves where gradual leaching is a serious problem.¹⁶,¹⁷

Table 1.4 Criteria and variables in the selection of zeolites for a particular organic reaction.

<table>
<thead>
<tr>
<th>Characteristic of the reaction</th>
<th>Important variables and tools in relation to choice of zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular size of the reactants, products and of the transitions state(s)</td>
<td>Calculation from models or by computer simulation, Lattice dynamics</td>
</tr>
<tr>
<td>Type of catalytic site required</td>
<td>Acid, Base, Lewis, Redox, Metal complexes and metal(0) clusters</td>
</tr>
<tr>
<td>Polarity and concentration of reactants, products and solvents</td>
<td>Adsorption characteristics on zeolite, Choice of Si/Al ratio and solvent</td>
</tr>
<tr>
<td>Equilibrium or parallel/consecutive reactions</td>
<td>Necessity of shape selectivity, Outer surface passivation</td>
</tr>
<tr>
<td>Reaction conditions</td>
<td>Liquid or gas phase, Powder or extrudate, Mechanical stability, Structured catalyst</td>
</tr>
<tr>
<td>Aggressiveness of chemicals involved</td>
<td>Water in the presence of acids, bases and complexing agents</td>
</tr>
<tr>
<td>Purity of the feed</td>
<td>Poisoning of catalytic site</td>
</tr>
</tbody>
</table>
Chapter 1

A criterion, which is often overlooked, is the purity of the chemicals used. In laboratories usually high grade chemicals are used for the development of new processes, while in a commercial plant technical grade chemicals are used. Even the presence of small amounts of pollutants can sometimes have a significant effect on the catalytic behavior of the zeolite and it is therefore advisable to test also the technical grade chemicals from the beginning when screening zeolites for activity and selectivity.

Table 1.5 lists some of the common impurities found in organic feedstocks and for which catalytic sites they may be detrimental. Two categories can be distinguished, those impurities that reversibly or irreversibly react with the catalytic site under the reaction conditions applied and those that adsorb into the zeolite pores thereby being competitors for the reactants. The latter is a reversible process and can easily be solved by lowering the concentration in the feed sufficiently or in the case of water by applying a proper drying agent prior to use. As to the first group of impurities, it should be noted that poisoning can be temperature dependent. For example, NH$_3$ and amines are in equilibria with the acid site at higher temperatures, consequently zeolites can be used to prepare various amines$^{11,12,18}$ which at first sight would seem inhibitors.

Despite precautions, deactivation of the catalyst occurs often, either by impurities or by other causes such as coke formation or pore plugging with by-products. Careful experimentation has to show the catalyst life-time and the progress of deactivation as a function of time. Since the use of highly purified reagents will not reveal the problem of deactivation by impurities, it is strongly advised to use the chemical feedstocks which will also be applied in the actual chemical plant. If the catalyst deactivates under reaction conditions, an important question to be answered is whether the catalyst can be regenerated. Most commonly this will mean that the zeolite catalyst is heated to at least 400 °C in air to remove inner organic materials by oxidation, whereas for metal-in-zeolites a subsequent reduction step in H$_2$ may be required. Since the oxide framework of the zeolite is quite thermo- and chemostable, this regeneration step usually reverts the deactivated catalyst almost to its original activity. When a more mild reactivation procedure is required three options are:

i) Lowering the oxygen content of the calcination atmosphere.$^{19}$

ii) Building-in an oxidation catalyst (Pd).$^{20}$

iii) Using ozone as the oxidant at relatively low temperatures.$^{21}$
Table 1.5 Common impurities found in reactant feedstocks and their effects in zeolite catalysts.

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Possible interfering interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S and thiols</td>
<td>Formation of metal sulfides or thiolates from metals and metal ions (including those leached from frameworks).</td>
</tr>
<tr>
<td>O₂, H₂O₂ etc.</td>
<td>Irreversible oxidation of the surface of metal clusters.</td>
</tr>
<tr>
<td>Metal ions or H⁺</td>
<td>Exchange of the active metal ions or leaching from framework.</td>
</tr>
<tr>
<td>NH₃ and amines</td>
<td>Neutralization of acid sites at low temperatures.</td>
</tr>
<tr>
<td>H₂O or polar compounds</td>
<td>Selective adsorption by low Si:Al zeolites.</td>
</tr>
<tr>
<td>apolar organics (benzene, alkanes)</td>
<td>Selective adsorption by high Si:Al zeolites.</td>
</tr>
</tbody>
</table>

1.2.1 The molecular dimensions and shape selectivity of the zeolite pores.

The first criterion in the selection of a zeolite as a catalyst for a specific reaction is based on the molecular size of the molecules which have to be adsorbed by and desorbed from the zeolite. The pore dimensions of zeolites and ALPO's range between 3 and 13 Å. In Figure 1.2 the kinetic diameters of some common molecules are shown. Zeolite frameworks are, however, not rigid, but often rather flexible. They can accommodate molecules which would normally be considered to be too bulky. Extreme examples have been reported for the adsorption of 1,3,5-tri-tert-butylbenzene (dimensions: 8.9 Å) and 2,4,6-triethyl-1,3,5-tribromo-benzene (dimensions: 10.5 Å) by zeolite Y (window size: 7.4 Å) at 180 °C, and the adsorption of naphthalene (diameter: 6.0 Å) in the pores of silicalite-1 (pore size: 5.6 x 5.3 Å). As a rough guideline, the size of molecules which can still enter at elevated temperatures, is about 10% larger than the actual crystallographic pore diameter of the zeolite.
In this respect, the use of computer aided docking of molecules in zeolite frameworks is the preferred method since it can account for framework flexibility.

The high expectations of zeolites as selective catalysts for fine chemicals, arise from the uniform, molecular size and distribution of its micropores. This allows more selective reactions paths, due to the restricted spatial confinement of the reaction site. In principle four different types of selectivity can be distinguished:

i) equilibrium shift selectivity.

ii) pore size exclusion shape selectivity. (also called: reactant shape selectivity)

iii) product shape selectivity

iv) transition-state shape selectivity.

Ad (i). The term equilibrium shift shape selectivity is used to describe the application of zeolites as selective adsorbent of one of the product molecules formed in an equilibrium reaction. Examples include acetalization, enamine formation, esterification, transesterification etc. It should be noted that here the zeolite is not used as a catalyst but rather as a non-reactive shape selective adsorbent. The actual catalyst can be a dissolved or suspended chemo-catalyst or an enzyme. For example, in the acetalization of a ketone over the large pore zeolite CeY, the addition of small pore zeolite KA led to an essentially quantitative yield. Zeolite KA shifts the equilibrium towards the ketal by selectively adsorbing the water formed. Here it is important to keep the acid catalyst alive in view of the possibility of ion-exchange between the catalyst and the adsorbent zeolite.

Ad (ii). Pore size shape selectivity, also referred to as ‘reactant selectivity’, takes place when the zeolitic catalyst acts as a molecular sieve and excludes certain molecular sizes and structures from the intracrystalline voids, while other less bulky molecules are able to enter, see Figure 1.5. It is mainly used in the catalytic upgrading of oil feedstocks. In this case the low-value linear alkanes are adsorbed faster and thereby converted faster than valuable bulky alkanes.
Ad (iii). When a zeolite catalyzes a reaction selectively due to product shape selectivity, one usually refers to shifting an equilibrium present inside the cages or at the channel crossings of a zeolite by allowing only the smallest product(s) to escape through the narrower channels or cage openings. The high selectivity is a result of the different diffusivities of the products in the pores of the zeolite, the smallest molecule(s) diffusing faster than the undesired bulky by-products. Since the selectivity is governed by diffusion, it depends amongst other factors on the size of the actual zeolite crystal, larger crystals usually giving better selectivities. High selectivity can only be obtained by constantly withdrawing the desired product from the zeolite pores, shifting the equilibrium essentially completely to the valuable product. The principle is generally restricted to continuous processes.

Various processes are known which rely on product shape selectivity. In the transalkylation of toluene to benzene and xylenes, normally a mixture of all three xylenes is observed. When zeolite H-ZSM-5 is applied as the catalyst, the major xylene observed is the para-isomer. The bulkier ortho- and the meta-isomer are also formed within the pores of the zeolites but diffuse much more slowly out of the catalyst. When they are isomerized to
the 1,4-isomer, can leave the zeolite more easily. As traffic in this zeolite is single file diffusion, the filling should be low and high-temperature gas-phase operation is required. In the ethylation and isopropylation of benzene over MCM-22 highly selective monoalkylation is observed.\textsuperscript{26} Here the cages of the zeolite are assumed to act as microreactors from which only the monoalkylbenzenes escape easily. Another example is the selective production of methylamines from ammonia and methanol. Under normal conditions a mixture of mono-, di- and trimethylamine is formed. However, by engineering the pore opening of the zeolite mordenite used, the catalyst can be tuned to selectively allow the mono- and dimethylamine to escape the pores.\textsuperscript{11} The trimethylamine can only leave the pores of the zeolite when it is converted to the mono- or dimethylamine.

![Figure 1.6](image.png)

**Figure 1.6** Product shape selectivity in the disproportionation of toluene over zeolite H-ZSM-5.

Ad (iv). Transition-state shape selectivity occurs when the spatial demands around the transition states to different products differ such that only certain, most preferably only one, reaction path is possible. The transition state selectivity also applies to undesired consecutive reactions, which can be prevented by the limited pore size of the zeolite. It should be noted here that the reaction has become kinetically determined and selectivities beyond the thermodynamic equilibrium can be obtained.

The preferred orientation of the transition state in the zeolite channel is determined by
the interaction energy between the zeolite walls and the reacting organic molecules in the transition state. The selection of a particular zeolite should be based on this interaction energy and is therefore not so straightforward. The spatial geometry of the preferred transition state will give a good approximation of the pore size required, but catalytic screening of several zeolites is still required. Calculation of the interaction energy of the transition state can in principle be done by computational methods and should provide a better selection criterion of a possible zeolite catalyst. However, these type of calculations are still in their infancy.

As to distinguishing transition-state shape selectivity (iv) from product shape selectivity (iii) the following applies: In the case of transition state shape selectivities, the diffusion of products is not important and the observed selectivity should be independent of the crystal size applied. This allows the use of very small crystals or conglomerates thereof, which have better catalytic properties with respect to internal mass transport phenomena. However, one has to be sure that the reaction is actually limited to the micropores of the catalysts with respect to the potentially catalytically active outer surface of zeolites.59

If one is to consider which of the four possible zeolite induced shape selectivities, viz. equilibrium shift (i), pore size (ii), product (iii) or transition state (iv), would be most desirable in the synthesis of fine chemicals, it should be realized that high selectivity is the main objective. Many reaction types are irreversible, for example oxidations and reductions, and here any shape selectivity based on shifting the reaction equilibria is not usable, viz. (i) and (iii). Also product shape selectivity (ii) is not valid, since usually relatively pure feedstocks are applied. This means that especially catalysis based on transition state shape selectivity (iv) can compete with other highly selective catalysts such as enzymes and organometallic catalysts and has potential in future technologies in the fine chemical areas.

Examples of zeolite-catalyzed reactions exploiting proven transition-state shape selectivity are still rare in literature. A good example of a transition state shape selective reaction has been reported by Creighton et al.27 in the selective reduction of 4-tert-butylcyclohexanone to the corresponding cis-alcohol over zeolite Al-beta (Figure 1.7). The same high selectivity (98 %) to the cis-alcohol in this reaction was also observed by van der Waal et al.28,29 when using a zeolite Ti-beta. In both cases Lewis catalysis is involved and the geometries of the two transition states in connection with the zeolite channel geometry govern selectivity.
Figure 1.7  Transition states for the formation of cis-4-tert-butylcyclohexanol (top) and trans-4-tert-butylcyclohexanol (bottom) in the Meerwein-Ponndorf-Verley reduction of 4-tert-butylcyclohexanone using zeolite beta.

Another example of a transition state shape selective reaction over zeolites is the selective reduction of cinnamaldehyde over platinum in zeolite beta reported by Gallezot et al.\textsuperscript{30} (Figure 1.8). In cinnamaldehyde both the aldehyde group and the C-C double bond can be hydrogenated over a platinum catalyst. The pores of the zeolite, however, directs the
molecule in such a way that only the aldehyde group can approach the Pt surface and is reduced selectively yielding cinnamyl alcohol. This was referred to by Gallezot et al.\textsuperscript{30} as tip-on catalysis, since the zeolite pore forced the reactant to approach the metal cluster by the aldehyde group specifically. A related case is the selective hydrogenation of 1-decene in the presence of trans-5-decene over Pt-beta.\textsuperscript{31}

![Diagram of zeolite catalysis](image)

Figure 1.8  Tip-on catalysis. The selective reduction of cinnamaldehyde to cinnamyl alcohol over platinum clusters in zeolite beta.

Transition state shape selectivity was recently reported by Bhattacharya et al.\textsuperscript{32} in the benzoylation of naphthalene with benzoyl chloride over H-beta. Normally the 2-position of naphthalene is less reactive than the 1-position. Over zeolite H-beta the ratio of the 2-isomer to the 1-isomer was observed to be 4.3. This ratio was found to be independent of the applied benzoyl chloride to catalyst ratio and reaction temperature, which suggests true transition state shape selectivity. It was, however, also dependent on the naphthalene to catalyst ratio, higher ratios giving lower selectivities, which is in favor of product shape selectivity. Similarly, Chu and Chen\textsuperscript{33} reported the selective mono- and dialkylation of naphthalene with 2-propanol to the 2- and 2,6-isomer, respectively, over zeolites H-beta and H-mordenite. Finally we mention the very recently reported combined epoxidation/ring-closure, e.g. the 99% selective formation of 2-hydroxymethyltetrahydrofuran, by treatment of 4-penten-1-ol with H\textsubscript{2}O\textsubscript{2} in the presence of TS-1.\textsuperscript{50}
Figure 1.9  The selective benzoylation (top) en propylation (bottom) of naphthalene over zeolite H-Beta.

1.2.2  The spectrum of catalytically active sites in zeolites

Although the present majority of applications for zeolite catalysts concerns acid and (noble-) metal catalyzed reactions, the scope of possible catalytic sites in zeolites is much wider. A milestone was the discovery of the titanium zeolite TS-1 in the late 1980’s, which expanded the area of zeolite catalysis to redox chemistry. However, zeolites offer an even wider scope of catalytic sites by modifications of framework atoms and introduction of catalytic cations, metal clusters or metal complexes in the zeolite channels. Table 1.6 gives an overview of the possible catalytic sites which can be introduced in the zeolite frameworks or micropores.
<table>
<thead>
<tr>
<th>Type of modification</th>
<th>M</th>
<th>Catalytic site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Framework substitution</td>
<td>Al</td>
<td>Strong Brønsted acid, Lewis acid.</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>Weak Brønsted acid</td>
</tr>
<tr>
<td></td>
<td>Ga, Fe</td>
<td>Moderate Brønsted acid</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>Oxidation catalysis, Lewis acid</td>
</tr>
<tr>
<td></td>
<td>T-Ma</td>
<td>Redox, Lewis acid</td>
</tr>
<tr>
<td>Ion-exchange</td>
<td>Na(^+), K(^+), Cs(^+)</td>
<td>Base</td>
</tr>
<tr>
<td></td>
<td>T-M(^a)</td>
<td>Specific for metal ion (usually oxidations)</td>
</tr>
<tr>
<td></td>
<td>RE(^b)</td>
<td>Strong Brønsted acid upon dehydration</td>
</tr>
<tr>
<td></td>
<td>Zn(^{2+})</td>
<td>Lewis acid</td>
</tr>
<tr>
<td>Metal complexes</td>
<td>Ship-in-a-bottle</td>
<td>Oxidation catalysis</td>
</tr>
<tr>
<td></td>
<td>Chiral complexes</td>
<td>Enantioselective catalysis</td>
</tr>
<tr>
<td>Metal clusters</td>
<td>N-M(^c)</td>
<td>Hydrogenations, Dehydrogenations, Hydrogenolysis, Oxidations, Aromatization</td>
</tr>
<tr>
<td>Oxide clusters</td>
<td>Na(_2)O, Cs(_2)O, CsLaO(_2), Ga(_2)O(_3)</td>
<td>Base catalysis</td>
</tr>
</tbody>
</table>

\(^a\) T-M = Transition Metals; group IIa-IIb metal cations. \(^b\) RE = Rare-Earth metals; lanthanides. \(^c\) N-M = Noble Metal; Pt, Pd, Ru, Rh, Ir etc. also Ni, W.
Framework substituted zeolites

The catalytic activity of zeolites in many reactions is due to the presence of aluminum in the zeolite framework. This aluminum site generates a negatively charged lattice, which is often compensated for after zeolite synthesis with a sodium cation. By ion-exchanging the Na\(^+\) with an NH\(_4^+\), followed by NH\(_3\) removal by calcination the H\(^+\)-form is obtained (Figure 1.10). Acid catalyzed reactions by aluminosilicate zeolites are the most common application in catalysis.

![Figure 1.10  Brønsted acid site in zeolite frameworks with a proton on a bridging Al-O-Si.](image)

The acidity of the proton at the aluminum site is estimated to have a Hammett value ≤ -8.2 for high-silica zeolites.\(^{34}\) From IR spectroscopy evidence has been obtained that the acidic strength of the proton at the aluminum site is strongly dependent on the Si:Al molar ratio of the zeolite.\(^{35}\) The higher the Si:Al molar ratio the stronger the acidity. Maximum acidity is, however, already obtained for Si:Al ratios above 7. To explain this, it has been accepted that the acid strength of a proton at the bridging Al-O-Si group depends on the number of next-neighboring Al atoms.\(^{35}\)

The incorporating of metal other than aluminum in the framework of zeolites is also possible. However, these isomorphously substituted metal atoms should meet certain coordination criteria. Firstly, the metal should be able to adopt a tetrahedral coordination by oxygen atoms. Secondly, they should fit in the lattice. According to Liebau\(^{36}\) the Si-O-Si angles and the Si-O bond length in zeolites can vary between:
1.57 Å < \( d_{(\text{Si-O})} < 1.72 \) Å and 120 ° < \( \angle(\text{Si-O-Si}) < 180 ° \)

In molecular sieves, the \( d_{(\text{Si-O})} \) and \( \angle(\text{Si-O-Si}) \) are correlated in such a way that the average Si····Si distance varies between 3.04 and 3.14 Å.\(^{37,38} \) Obeving this Si····Si variation and assuming the framework flexibility as found by Liebau,\(^{36} \) minimum and maximum values for \( d_{(M-O)} \) of 1.34 and 2.05 Å, respectively, can be calculated. These limits are obeyed by many elements as shown in Table 1.7. Changing the framework metals in zeolites modifies the catalytic properties of the material.

Table 1.7  Metal-oxygen bond length in tetrahedral coordination.

<table>
<thead>
<tr>
<th>M</th>
<th>M-O bond length [Å]</th>
<th>M</th>
<th>M-O bond Length [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^+)</td>
<td>2.00</td>
<td>Al(^{3+})</td>
<td>1.74</td>
</tr>
<tr>
<td>Be(^{2+})</td>
<td>1.65</td>
<td>Ga(^{3+})</td>
<td>1.84</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>2.00</td>
<td>Fe(^{3+})</td>
<td>1.86</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>2.08</td>
<td>Ge(^{4+})</td>
<td>1.77</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>1.95</td>
<td>Ti(^{4+})</td>
<td>1.79</td>
</tr>
<tr>
<td>B(^{3+})</td>
<td>1.47</td>
<td>Zr(^{4+})</td>
<td>2.00</td>
</tr>
</tbody>
</table>

By framework substitution of aluminum(III) with a M(III) atom, the zeolite still retains its acidic character, but the acid strength of the proton is changed significantly. It can be said that boron zeolites have very weak acidic properties\(^{39} \) and gallium and iron zeolites have moderately acidic properties. Boron-substituted zeolite ZSM-5 has found industrial application in the aldehyde-ketone rearrangement of 2-phenylpropanal to phenylacetone.\(^{40} \)
By substitution of the silicon atom by group IIa - VIIa transition metals in all-silica zeolites, catalysts are obtained which have high potential in oxidation chemistry or in Lewis acid catalyzed reactions. Many metals, *e.g.* chromium, germanium, tin, titanium, vanadium and zirconium, have been claimed to be incorporated in zeolite frameworks, especially in the MFI-type framework. However, until now only the incorporation of titanium and that of vanadium have been sufficiently characterized to warrant its presence in all-silica frameworks. Unfortunately vanadium is not strongly bonded and is easily leached by protic solvents. The problem of leaching of the active metal from the framework under liquid-phase conditions has been recognized and appears to apply to most incorporated metals so far, titanium being the exception.

Although possible incorporation of transition metals in silicate frameworks is still open for debate, it has conclusively been shown that many metals, even bivalent metal ions (*e.g.* Co$^{2+}$), can be incorporated in the framework of ALPO's. However, like vanadium in silicalite frameworks, most of these metals gradually leach from the ALPO framework in liquid-phase reactions, thus restricting their applicability to gas-phase reactions. Again, the only exception seems to be titanium, which appears to be stable also in ALPO frameworks.

*Ion-exchanged zeolites*

The most common modification applied to zeolites is by ion-exchange with metal ions. When the counter ions are alkali and earth alkali metals ions, zeolites can be used for base catalysis. Examples include the Meerwein-Ponndorf-Verley reduction of citronellal over alkali-exchanged zeolite X, the side-chain alkylation of toluene with methanol over alkali exchanged X and Y, the conversion of 2-propanol to acetone over alkali-exchanged zeolites X and Y, the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate over Cs-MCM-41 and the industrially relevant synthesis of 4-methylthiazole from SO$_2$, methylamine and acetone on Cs-X (Figure 1.11). For a general review about base catalysis with zeolites see Hölderich and Barthomeuf *et al.*
Upon ion-exchange of zeolites with transition metals catalytic materials are obtained which can be active in reactions specific for the chosen metal cation. Due to the ease of leaching of metal cations, their applicability is limited to gas-phase reactions. Examples of a metal cation catalyzed reaction are the gas-phase conversion of halobenzenes to the corresponding aniline or phenol with ammonia or water over copper exchanged zeolite ZSM-5, Y and beta.\textsuperscript{51} We also mention here the rare-earth metal exchanged zeolite Y (RE-Y), which has acidic properties which are even stronger than the proton acid zeolites, though this is easily spoiled by the presence of small amounts of oxygen containing impurities, water in particular.
Metal complexes in zeolites

The problem of leaching was soon realized and attempts were made to ‘anchor’ the metal cations by constructing complexes inside zeolites that are too bulky to desorb. The use of ligands has the further benefit of tailoring the catalytic activity of the metal cation. Especially the so-called ‘ship-in-a-bottle’-complexes based on bulky ligands such as salen, bipyridyl, porphyrin and phthalocyanine (Figure 1.12), have been widely studied.\textsuperscript{52} The metal-ligand complexes are too large to desorb from the zeolite pores. Recently it was shown that smaller ligands can also be used when they are first anchored to the zeolite framework either by post-synthesis methods\textsuperscript{53} or by direct hydrothermal synthesis.\textsuperscript{54}

![Figure 1.12 Ship-in-a-bottle complex. Iron-phthalocyanine in zeolite Y.](image)

Both types of catalyst have one serious drawback in that the regeneration of the catalyst is very difficult. The organic ligands can not withstand the high calcination temperature usually applied to regenerate zeolite catalysts. Thus these catalysts can only be used once or following washing/drying a few times and discarded thereafter. Industrial application is therefore only possible when the Turn-Over-Numbers are very high, comparable with those of enzymes, \textit{i.e.} over 10,000.

26
Metal clusters in zeolites

Many organic reactions require a metallic catalyst. The zeolite itself is a non-reducible inorganic oxide, but can be used as a support material. The metal is present as very small particles with the same dimensions of the zeolite channel or cage. Due to the small size of the metal particle, usually 5 to 15 Å, they can exhibit different catalytic properties compared with the bulk metal. The metal particles have potential both in reductive and oxidative catalysis. Moreover, on acid zeolites and zeolites with oxidizing properties, they seem to have electron deficient properties.\textsuperscript{55} Most commonly, noble metals are employed for this purpose and such systems have found large scale application in the hydrocracking of oil feeds,\textsuperscript{56} in the isomerization of alkanes (the Shell TIP process\textsuperscript{9}) and the aromatization of alkanes over Pt-Ba-L (Chevron\textsuperscript{56}).

Introduction of metal particles is done \textit{via} a two step method. Firstly, the metal is introduced in the pores of the zeolite as a cationic species by ion-exchange (\textit{e.g.} Pt(NH\textsubscript{3})\textsubscript{4}\textsuperscript{2+}). Special caution has to be taken during this ion-exchange step to attain a homogeneous dispersion of the cations over the zeolite crystal.\textsuperscript{55,57} Careful reduction or oxidation/reduction of the metal cations in the pores of a zeolite yields finely dispersed, nano-sized metal particles. Acidic protons are also formed during this reduction step to counterbalance the zeolite framework, which means that without further treatment these catalysts are bifunctional.

Oxide clusters in zeolites

The introduction of Na\textsubscript{2}O, Cs\textsubscript{2}O, MgO, CaO or CsLaO\textsubscript{2} clusters in zeolites gives rise to basic catalysts with the potential of shape selectivity. However, relatively little is known about the chemistry of base-catalyzed reactions on solid metal oxide clusters in zeolites. Basic clusters can be introduced in two ways. The first approach is only valid for polyvalent cations, which give rise to a hydrolysis reaction (1):
\[ Me^{n+} + H_2O = Me^{(n-1)+}OH + H^+ \] (1)

Upon heating, dehydroxylation occurs, forming dispersed \( M_n/2O \) clusters in the cages of the zeolite. The second approach is by impregnation with solution of salts, e.g. cesium acetate, followed by calcination. The catalytic potential of these materials is somewhat higher than that of the stoichiometric alkali-exchanged basic zeolites (see above), but the materials are often not water-stable.

### 1.2.3 The adsorption characteristics of zeolites.

Equally important in selecting a zeolite for performing in a specific catalytic reaction are the adsorption characteristics of the substrates, products and solvents on the zeolite. For heterogeneous catalysts, a reaction can only take place when the substrate molecules are chemisorbed on the catalytic site. For zeolites this means at least a two-step process: Firstly, the micropores of the zeolite should adsorb the substrate(s), which then travels to the active site and enters chemisorption. Ideally the zeolite should have a polarity similar to that of the substrate, e.i. low Si:Al zeolites for polar substrates and high-silica zeolites for apolar substrates.

It is not always possible to match the polarity of the zeolite with that of the substrates. The three most common pitfalls connected to adsorption are:

\( i) \quad \) The zeolite preferentially adsorbs the solvent applied.

\( ii) \quad \) The zeolite adsorbs product(s) too strong.

\( iii) \quad \) Polarity mismatch between reactants, the zeolite preferentially adsorbs only one of the reactants.

In the case of the preferential adsorption of the solvents (i), the rate and selectivity can be profoundly influenced. Application of a different solvent might solve the problem. Three approaches can be used. The most common approach is to look for a solvent with a correct
polarity with respect to the zeolite and the substrates used. Since changing the solvent can cause problems with solubility of the substrates, one can also look for solvents which are too large to fit in the zeolite pores. A good example of the latter is the use of the bulky 1,3,5-triisopropylbenzene instead of benzene as the solvent. If no solvent is required, also solvent-free procedures can be envisaged.

As already mentioned, high selectivity is the prime target. In rare instances, the internal concentration of one of the reactants is determining the selectivity. When this occurs, it is normally caused by the possibility of reactants to undergo oligo- or polymerization reactions. Since these reactions are usually favored by high reactant concentrations, the use of a non-reacting co-adsorbent (the solvent) can drastically enhance selectivity. Wortel et al. studied the dehydration of 1-(4-methoxyphenyl)ethanol to the corresponding styrene over zeolites CeNaY, CaNaY and H-Y. It was observed that the yield was very high in apolar solvents such as hexane and benzene but that the selectivity was rather low (5%), because the high internal reactant/product concentrations gave rise mainly to dimerization and polymerization reactions. When the solvent was changed to the polar tetrahydrofuran, the yield decreased significantly but the selectivity to the styrene was over 99%. Here the more strongly adsorbing solvent keeps the concentrations of reactant and reactive intermediate low, thereby disfavoring the dimerization and oligomerization reactions.

The problem of polarity mismatch between two or more reactants is more difficult to solve. If the zeolite allows a wide variety in Si:Al ratios, a specific Si:Al ratio may exist which gives the zeolite a polarity in between the two substrates. This is, however, not always possible. Another solution can be the slow addition of the strongest adsorbing substrate to the reaction mixture.

The influence of internal concentrations on the activity and selectivity of a bimolecular reaction is shown by van der Waal et al. in the gas-phase reduction of 4-methylcyclohexanone with secondary alcohols as the reductant over zeolite titanium beta. An optimal 4-methylcyclohexanone-to-alcohol ratio was observed (Figure 1.13) for the activity in accordance with a transition state which brings together both an alcohol and ketone. Selectivity to cis-4-methylcyclohexanol was found to depend heavily on the rate of alcoholysis of products from the catalytic site. The alcoholysis, however, depends only on the internal alcohol concentration. Since zeolite titanium beta is considered to be a hydrophobic zeolite,
the use of apolar alcohol reductants, e.g. cyclohexanol or 2-heptanol, gives high internal concentrations and thus a high selectivity.

Figure 1.13 Conversion (■) and selectivity (▲) to the cis-alcohol in the gas-phase Meerwein-Ponndorf-Verley reduction of 4-methylcyclohexanone as a function of the internal ketone to alcohol ratio (see also Chapter 9).

1.3 Conclusions

Zeolites are a versatile group of catalysts, with a high potential in organic chemical conversion. They owe their catalytic potential to their unique, molecular-sized internal pore structure which allows shape selective reactions and a wide spectrum of catalytic active sites which can be incorporated in the pore structure. In principle four type of shape selectivities can be induced, namely: i) equilibrium shift selectivity; ii) pore size exclusion shape selectivity; iii) product shape selectivity and iv) transition state shape selectivity. For the synthesis of fine chemicals, zeolite catalysts based on transition state shape selectivity have the highest potential in competing with other highly selective catalysts such as enzymes or organometallic catalysts.
Since many of the reactions will be performed in the liquid phase, small zeolite crystals will have to be used to overcome internal diffusion limitations. The possibility of leaching of the active metal component has always to be examined carefully. Adsorption behavior of reactants and products and selection of the solvents are important and sometimes decisive items.

1.4 Scope of this thesis

This thesis deals with the development of a new large pore zeolite catalyst, zeolite titanium beta and its potential in catalytic applications. This includes studies on the synthesis of this new zeolite and related materials, its characterization and its potential use in both oxidative and Lewis acid-catalyzed reactions.

A study of the parameters affecting the synthesis of the related zeolite boron beta using dibenzylidimethylammonium as the template is described in Chapter 2. Based on the observed parameters for the synthesis of zeolite boron beta, predictions can be made as to the synthesis of all-silica zeolite beta. The synthesis and characterization of all-silica zeolite beta using dibenzylidimethylammonium as the template are described in Chapter 3. The synthesis method for all-silica beta failed to produce a zeolite titanium beta due to the thermal instability of the template cation used. By using the new and more stable template cation di(cyclohexylmethyl)-dimethylammonium, the synthesis of zeolite titanium beta was found to be possible.

In Chapter 4 this new synthesis method is described and the characterization of the zeolite obtained is discussed. The use of titanium beta as catalyst is subsequently described. Titanium zeolites are usually tested for application in oxygenation reactions with peroxides as the oxidant. The large pores of zeolite titanium beta, in comparison with the medium pores of the related TS-1, allows the epoxidation of more bulky molecules. Chapter 5 shows the explorative results on the epoxidation of linear alkenes, cyclic alkenes, allylic alcohols and a number of terpenes. Also the influence of solvent type on the catalytic epoxidation are studied. Some of the mechanisms proposed in literature for the epoxidation of alkenes, assume the active interaction of alcohol molecules in the catalytic mechanism. The influence of alcohols is illustrated in Chapter 6. The observed beneficial effect of alcohols is taken as
proof of the active participation in the catalytic mechanism. In Chapter 7 a thorough study on the kinetics of the epoxidation of 1-octene is presented. The observed kinetics are related to possible mass transport limitations, adsorption equilibria of reactants and catalytic epoxidation mechanisms.

The use of zeolite titanium beta as a Lewis-acid catalyst in fine chemical syntheses is illustrated in Chapter 8 in the Meerwein-Ponndorf-Verley reduction of carbonyl compounds and the Oppenauer oxidation of alcohols under liquid-phase conditions. Especially in the reduction of 4-alkylcyclohexanones high selectivities to the thermodynamically unfavored cis-alcohol are observed. Based on the large similarities between zeolite titanium beta and zeolite aluminum beta in these reactions, a mechanism is proposed. The advantage of the titanium containing catalyst is shown by the low by-product formation and allows the application in the gas phase. Chapter 9 deals with a detailed study on the applicability of zeolite titanium beta in gas-phase Meerwein-Ponndorf-Verley reductions and in Oppenauer oxidations. Lower selectivities to the cis-alcohol are observed and based on kinetic experiments performed a mechanism is proposed to explain the differences in selectivities between the gas phase and the liquid phase.
References

Chapter 1


49 W.F. Hölderich, in "Acid-Base Catalysis", (K. Tanabe, H. Hattori, T. Yamaguchi and
Introduction to zeolites

Synthesis of zeolite boron beta using dibenzyl-dimethylammonium as the template.

Abstract

Zeolite boron beta with Si:B ratios between 15 and 40 was synthesized using dibenzyl(dimethylammonium as the template. The obtained zeolite boron beta was characterized using X-ray diffraction, unit-cell contraction, FT-IR, $^{11}$B, $^{13}$C and $^{29}$Si MAS NMR. The incorporation of boron in the zeolite lattice was confirmed by a single peak in the $^{11}$B MAS NMR spectrum at -23.2 ppm and a linear relation between the unit-cell volume and the boron content.

The degradation of the template was studied using pyrolysis-MS, DTG and DTA. The dibenzyl(dimethylammonium cation was found to yield a substantial amount of coke when calcined at 400 to 540 °C in air, which was attributed to the relatively weak benzyl-nitrogen bond. The use of 1% ozone in oxygen at 120 °C followed by a hot acetone wash was found to effectively remove the template with retention of boron in the framework.

The influence of the synthesis temperature, the type of alkali metal, the boron and the template-to-silicon molar ratio on the crystallization and nucleation was investigated. A chemical growth model consisting of three types of sites on the growing zeolite surface was proposed; two of which are structure-determining and one consisting of growth directing groups.
2.1 Introduction

The first high-silica zeolite prepared, was Mobil's zeolite beta by Wadlinger, Kerr and Rosinski\textsuperscript{1,2} in 1967. Since then this zeolite has, to some extent, been overshadowed by subsequently discovered materials, in particular the medium pore MFI type zeolites. In recent years, however, it was fully recognized that zeolite beta is one of the few large-pore high-silica zeolite with a three-dimensional pore structure containing 12-membered ring apertures,\textsuperscript{3-5} which makes it very suitable as a regenerable catalyst in organic reactions.\textsuperscript{6}

Zeolite beta is usually obtained with Si:Al ratios between 10 and 200 using tetraethylammonium (TEA\textsuperscript{+}) as the template.\textsuperscript{1,2} The synthesis of Si:Al ratios higher than 80 is in general rather difficult and only recently Camblor et al.\textsuperscript{7} reported the synthesis of the all-silica analogue using this template. The required synthesis conditions are similar to the first all-silica beta synthesis we reported earlier using dibenzylidimethylammonium (DBDMA\textsuperscript{+}) as the template.\textsuperscript{8} Our interest is also focussed on the preparation of zeolite beta in which aluminum is isomorphously substituted by boron. Such materials can be used as precursor for transition-metal containing zeolites by post-synthesis treatment with volatile metal halides, as reported in literature.\textsuperscript{9-12}

Taramasso et al.\textsuperscript{13} were the first to synthesize zeolite boron beta using tetraethylammonium as the template. Recently de Ruiter et al.\textsuperscript{14} reported that pure zeolite boron beta can only be obtained with Si:B ratios between 8.7 and 10.4, which appeared to correspond to the number of template cations viz tetraethylammonium, in the zeolite framework. Higher Si:B ratios have been mentioned in literature\textsuperscript{15-18} but generally a significant amount of aluminum is also present. In order to obtain higher Si:B ratios, we investigated the use of the dibenzylidimethylammonium cation as a selective template for the synthesis of zeolite boron beta. The dibenzylidimethylammonium cation was first described by Rubin\textsuperscript{19} as a selective template for zeolite beta with relatively high Si:Al ratios. Based on the dependencies of nucleation and crystal growth on the synthesis parameters investigated, a model is proposed which aims to explain some of the underlying processes determining the successful synthesis of zeolite boron beta.

The crystallization of zeolites under hydrothermal conditions is a very complex process.
that is far from being completely understood. In order to study the crystal growth kinetics, the properties of the growing zeolite crystals e.g. crystal size, pore volume and crystallinity must be observed as a function of time. This is usually achieved by sampling and analyzing intermediate products by some macroscopic bulk technique which can distinguish the developing crystalline material from the amorphous starting material. From these measurements, the most basic type of kinetic information, the sigmoidal shaped crystal growth curve (2.1), can be constructed.\textsuperscript{20-24} This type of curve is known as a simplification of the Avrami-Erofeev equation (2.2),\textsuperscript{20,21} though recently Thompson\textsuperscript{22} showed that the use of the Avrami-Erofeev type equations (2.1) and (2.2) is not correct in the description of zeolite growth. The experimental growth curve equation (2.1) usually has a good fit to the Avrami-type equation (2.2) where the constant \( \alpha \) determines whether nucleation (\( \alpha < 4 \)) or crystallization (\( \alpha > 4 \)) is rate-determining.\textsuperscript{25}

\[
Z(t) = 1 - \exp^{-kt^\alpha} \tag{2.1}
\]

\[
Z(t) = 1 - \exp^{-\left(k_4 t^4 + k_5 t^5 + k_6 t^6 + \ldots \right)} \tag{2.2}
\]

Where \( Z(t) \) is the crystal growth (fraction of crystalline material) as a function of the time, \( k \) and \( k_4, k_5 \) etc. are rate constants which are related to the growth rate of germ-nuclei to viable nuclei and \( \alpha \) is a constant.\textsuperscript{21}

The observed growth curve can be divided into an induction and a growth period from which the approximate overall nucleation and crystal growth rates can be calculated.\textsuperscript{20-25} The slope at 50\% of the maximum crystallinity yields the maximum crystal growth rate and the point at which the first crystals appear is usually taken as the induction time. The reciprocal induction time can be used as a measure for the nucleation rate. Using this method, different synthesis experiments can be compared and the effect of reaction variables (e.g. temperature, composition) can be displayed quantitatively. The resulting data should be treated with great caution since they both are combinations of several underlying processes.\textsuperscript{24} As Thompson\textsuperscript{22} already pointed out, this procedure allows only to make semi-quantitative comparisons between series of related experiments.

Several authors\textsuperscript{1,2,8,18,26-36} have reported the influence of various synthesis parameters
on the crystallization of zeolite aluminum beta using tetraethylammonium as the template. A
general three-step description of the processes involved in the crystallization of zeolite
aluminum beta is proposed by Pérez-Pariente et al.:26

i) Initially, an amorphous silica/alumina solid is formed upon mixing the gel.

ii) Subsequently, high-silica aluminosilicate species are formed in solution in a reaction
between the dissolving aluminum and the TEA-silicate species present in the liquid phase.

iii) Finally, at higher temperatures these precursor species condensate towards the zeolite beta
framework.

Important parameters in the TEA-beta synthesis are the alkali cation concentration and
the type of cation used,26-28 the hydroxide concentration,26,28,29 the nature and the amount
of the organic template,1,2,8,18,26-28,30-33 the temperature28,34 and the type of silica source
used.35,36 From these reports it was concluded that the synthesis of zeolite beta required both
the presence of aluminum and sodium. Corma et al.37 showed that the synthesis of zeolite
beta is possible in the absence (< 3 ppm) of alkali metal cations, although the presence of
aluminum or another suitable trivalent metal, e.g. boron or iron, was still necessary. Recently
we reported the synthesis of the all-silica analogue of zeolite beta by using the highly selective
dibenzylidimethylammonium (DBDMA⁺) cation as the template.8

2.2 Experimental

2.2.1 Synthesis of zeolites

Synthesis of zeolite beta was carried out, unless otherwise stated, at 140 °C in 15 ml
polytetrafluoroethylene-lined stainless steel autoclaves under stirred conditions. The autoclaves
were cleaned with 1.0 M NaOH at 80 °C for 24 h. Amorphous silica (Cab-O-Sil M5,
Scintran), tetraethyl orthosilicate (98%, Janssen), boric acid (p.a. Merck), sodium hydroxide
(p.a. Merck), potassium hydroxide (p.a. Merck), cesium hydroxide (25 wt% aqueous solution,
Janssen), silver oxide (99%, Hereaus), benzyl bromide (99%, Janssen), benzyl chloride (98%,
Aldrich) and N,N-dimethylbenzylamine (98%, Janssen) were used as reagents.
Dibenzyldimethylammonium chloride (DBDMA.Cl) was synthesized by slow addition of a stoichiometric amount of benzyl chloride to N,N-dimethylbenzylamine dissolved in acetone. Dibenzyldimethylammonium bromide was synthesized by slow addition of a stoichiometric amount of benzyl bromide to N,N-dimethylbenzylamine dissolved in dichloromethane. In both cases the formation of the quaternary ammonium salt is very exothermic and the addition of the benzyl halide should be slow enough to maintain a gentle reflux. After precipitation of the product by addition of diethyl ether, the quaternary ammonium salt is obtained in a quantitative yield. Subsequently the bromide is converted to the hydroxide by means of silver oxide.

For a typical boron beta synthesis, 0.242 g boric acid was dissolved in 47.2 ml of an aqueous solution containing 3.60 g DBDMA.Cl and 0.47 g sodium hydroxide. To the clear solution 4.62 g silica and 0.25 g beta seeds (5 wt% based on silica, calcined zeolite boron beta Si:B ≈ 20) were added and the resulting gel was aged for at least 24 h, preferably 3 days. The zeolite was crystallized under hydrothermal conditions at 140 °C for 4 days. After crystallization the zeolite was filtered, washed until pH 8, dried and calcined in 1% ozone in oxygen at 120 °C, followed by a hot acetone wash to remove the residual organics. In general, the synthesis gel used had a molar composition of:

\[ x \text{ MOH} : y \text{ DBDMA.Cl} : z \text{ B(OH)}_3 : \text{SiO}_2 : n \text{ H}_2\text{O} \]

where \( x \) was varied from 0.00 to 0.30; The alkali metals used were Na\(^+\), K\(^+\) and Cs\(^+\); \( y \) was varied from 0.1 to 0.5; \( z \) was changed from 0 to 0.10 and \( n \) was varied between 30 and 40.

2.2.2 Characterization of zeolites

Crystallinity and phases formed were determined by X-ray powder diffraction, data were collected on a Philips PW 1840 powder diffractometer using CuK\(\alpha\) -radiation. The intensity of the peak at \( 2\theta \approx 22.5^\circ \) (indexed as 302 for polytype \( \Lambda \))^3 was taken as a measure for crystallinity. The exact position of the reflection at \( 2\theta \approx 43.5^\circ \) (indexed as 600 for polytype \( \Lambda \))^3 was determined using a Guinier-De Wolff camera with quartz as internal standard. The \(^{11}\text{B}\), \(^{13}\text{C}\) and \(^{29}\text{Si}\) MAS NMR measurements were performed on a Varian VXR-400 S 400
MHZ apparatus. Infrared spectra were recorded on a Bruker IFS-60 IR spectrophotometer under the attached FTIR microscope. Differential Scanning Calorimetry (DSC) experiments were recorded on a DSC Gold apparatus of Polymer Laboratories under a flow of dried air. Differential Thermal Gravimetry (DTG) experiments were recorded on a homemade microbalance using air as the oxidant. Chemical analysis of the zeolites was performed on Perkin-Elmer Plasma 40 (ICP-AES) or Perkin-Elmer 110 (AES) instruments. Low pressure argon adsorption isotherms were measured on a Micromeritics ASAP 2000M. Pyrolysis-MS was performed on a VG 70-250 SE.

2.3 Results and Discussion

2.3.1 Characterization

The crystallinity and the composition of the solid materials formed, was determined using XRD (Figure 2.1). The intensity of the strongest peak in the diffractogram of zeolite beta (2θ ≈ 22.5°) was taken as a measure of crystallinity. A fully crystalline zeolite boron beta is obtained exclusively with Si:B ratios between 15 and 40. Outside of this window beta was accompanied by small amounts of impurities (Figure 2.2). The other phases formed are magadite at low Si:B ratios and zeolite ZSM-12 (MTW) and, to a lesser extent, zeolite ZSM-5 and cristobalite at high Si:B ratios. Eapen et al.\textsuperscript{28} reported that in the presence of sodium other crystalline phases also co-crystallize when tetraethylammonium is used as the template for the synthesis of zeolite beta with very high Si:Al molar ratios. The phases formed are ZSM-5 and mordenite. The formation of the large pore ZSM-12 as the predominant impurity over the medium pore ZSM-5 is probably a reflection of the more bulky geometry of the DBDMA\textsuperscript{+} cation compared to the TEA\textsuperscript{+} cation. Close examination of the peak at 2θ ≈ 7.5° in the XRD-diffractogram, indicates that the fault probability as defined by Newsam \textit{et al.}\textsuperscript{4} is independent of the boron content and neither of the two (or three) possible polytypes is crystallized preferentially,\textsuperscript{3-5} as was predicted by Stevens and Cox.\textsuperscript{38} Recently Davis and Lobo\textsuperscript{39} showed that an increased content of polymorph A is possible when a chiral template is employed.
Figure 2.1 XRD-diffactogram of as-synthesized zeolite boron beta (Si:B = 20).

Figure 2.2 Formation of zeolite boron beta as function of the initial Si:B ratio of the gel at 140 °C. (*) indicates the field with magadite as contamination. Gel composition used: Na⁺:Si = 0.15; OH⁻:Si = 0.15; DBDMA.Cl:Si = 0.175; H₂O:Si = 30 - 40; B:Si variable.
Chapter 2

The incorporation of boron in the framework is confirmed by the presence of a single sharp peak at δ -23.2 ppm in the $^{11}$B MAS NMR spectrum (Figure 2.3) and a band around 905 cm$^{-1}$ in the FTIR spectrum (Figure 2.4). Both the peak at δ -23.2 ppm in the $^{11}$B MAS NMR and the IR absorption band at 904 cm$^{-1}$ are assigned to tetrahedrally coordinated boron in a zeolite framework.$^{40-42}$ The intensity of the IR band around 904 cm$^{-1}$ correlates linearly with the boron content (data not shown). Incorporation is further confirmed by a linear relation between the interplanar spacing of the zeolite (calculated for the reflection indexed as 600 for polytype A)$^3$ and the boron content (Figure 2.5). The isomorphous substitution of boron in the zeolite lattice, causes the lattice to contract due to the smaller B-O distance ($d_{B-O}$ = 1.36 Å)$^{43}$ compared to the Si-O distance ($d_{Si-O}$ = 1.59 Å). The contraction of the $a$ axis can be described by equations (2.3) and (2.4).

$$a = a_{All-Si} \cdot (1 + x \cdot \left( \frac{d_{B-O}}{d_{Si-O}} - 1 \right)) \quad 2.3$$

$$a = 12.48 \cdot (1 - 0.126 \cdot x) \quad 2.4$$

wherein $x$ is the fraction of boron in the zeolite. The experimental value of 12.48 for the all-silica zeolite ($x = 0$, equation (2.4)) corresponds to the calculated value of 12.469 reported for polytype A by Higgins et al.$^3$ The small difference is probably caused by the presence of lattice defects in the high-silica materials.$^8$ The observed value of 0.126 corresponds with an average B-O distance of 1.39 Å, which is close to the theoretical value of 1.36 Å$^{43}$ and the values of 1.46 Å reported by Taramasso et al.$^{13}$ and of 1.39 Å reported by Coudurier and Védrine$^{44}$ for borosilicates with the MFI structure.

Care should, however, be taken when interpreting this B-O value. An isotropic expansion in all three directions is assumed in deriving equation (2.3), furthermore the influence of structural defects on the unit-cell volume has been neglected. Marra et al.$^{45}$ have clearly shown that for silicalites with the MFI structure, the presence of defects does affect the unit-cell volume. We have shown already that for the very high Si:B ratios a significant amount of defect sites is present$^8$ and equation (2.3) might be too simple. Furthermore, Jansen et al.$^{46}$ report a different slope of the unit-cell curve as a function of the boron content for the [B]-MFI than Taramasso et al.$^{13}$ and Coudurier and Védrine.$^{44}$ The reported differences in B-O bond length might be linked to the two different coordinations of boron i.e. trigonally or tetrahedrally,$^{40-42}$ in the zeolite framework.

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Figure 2.3 $^{11}$B MAS NMR of as-synthesized zeolite boron beta (Si:B = 21.6).

Figure 2.4 FTIR of zeolite boron beta (Si:B = 21.6). a) as-synthesized; b) ozone-treated and dried at 100 °C.
Figure 2.5 Unit-cell contraction of the a-axis as a function of the boron content in calcined and hydrated zeolite boron beta.

The incorporation of the DBDMA\(^+\) cation as the template cation can be shown by the presence of relatively weak bands in the FTIR spectrum of an as-synthesized zeolite boron beta (see Figure 2.4). The bands around 3029 cm\(^{-1}\), are typical for aromatic \(\nu\) C-H stretching vibrations and the bands around 1481 cm\(^{-1}\) are characteristic for \(\nu\) C=C stretching vibrations of the benzene nucleus. Both are also the strongest bands in the IR-spectrum of pure DBDMA.Cl (data not shown). The very low intensity of the bands which can be assigned to the template molecule is noteworthy, especially if one considers that about 22 wt% of the as-synthesized material consists of the DBDMA\(^+\) template cation.\(^8,38\)

Since both IR bands are not specific for the DBDMA\(^+\) cation but rather for the aromatic ring of the benzyl groups, the as-synthesized zeolite is further characterized by \(^{13}\)C MAS NMR. Figure 2.6 shows the \(^{13}\)C MAS NMR spectra of pure DBDMA.Cl (dissolved in D\(_2\)O) and of the as-synthesized zeolite. Although rather broad signals are obtained for the as-synthesized material, both spectra are similar, confirming that the DBDMA\(^+\) cation is the templating cation. It should be noted that considerable shifts are observed for the benzyl group; the CH\(_2\) shifts from \(\delta\) 70 to 76 ppm, while the four resonances of the six aromatic carbon atoms also seem to shift, though this is more difficult to judge due to the high noise level and broadness of the peaks. The origin of the broadening and the peak shifts is probably due to the confinement of the DBDMA\(^+\) template in the zeolite channels, which hinders the free movement of the cation and forces it in a fixed conformation compared with the
conformational equilibrium in the solution. Molecular Mechanics calculations\textsuperscript{8,38} show that the DBDMA\textsuperscript{+} cation adopts a small twist of both benzyl groups to allow the cation to fit in the zeolite channel (Figure 2.7).

![NMR spectra](image)

Figure 2.6 \textsuperscript{13}C CP MAS NMR of as-synthesized zeolite boron beta containing DBDMA\textsuperscript{+} as the template (a) and \textsuperscript{13}C CP NMR of DBDMA.Cl in D\textsubscript{2}O (\(\delta = 31\) ppm is internal standard) (b).

![Dibenzylidimethylammonium cation](image)

Figure 2.7 Optimal geometry of the dibenzylidimethylammonium cation as determined by molecular mechanics in zeolite beta.
2.3.2 Removal of the template from the zeolite

Compared with aluminum, boron is not so strongly bonded to the zeolite lattice. As reported by Degman et al.\textsuperscript{16} and de Ruiter et al.,\textsuperscript{9,14} boron can easily be removed when a normal air calcination at elevated temperatures (> 400 °C) is applied. De Ruiter et al.,\textsuperscript{14} explained this on the basis of the easy hydrolysis of the acid boron site by water and organic acids formed during calcination. Since we wish to replace the boron by titanium via the post-synthesis method reported by Rigutto et al.,\textsuperscript{10} a detailed investigation of the degradation of the template was conducted to ensure that no boron is removed from the zeolite lattice during calcination.

One way of preventing loss of boron is the use of ammonia instead of oxygen at elevated temperatures. Ammonia has generally a twofold role during the calcination\textsuperscript{9,14,16}.

\textit{i}) It reduces the amount of acidic boron sites by converting them to the stable ammonium form, thus preventing hydrolysis.

\textit{ii}) The basicity of ammonia promotes the Hoffman degradation of a template by abstraction of \(\beta\)-hydrogens, lowering the temperature necessary for complete removal of the template. The DBDMA\textsuperscript{+} cation does, however, not contain any \(\beta\)-hydrogens, eliminating ammonia-assisted Hoffman degradation as a possible degradation route. Upon calcination of a beta sample (Si:B = 21.6) in ammonia at temperatures between 400 and 540 °C the calcined zeolite still contained a large amount of organic material (about 11 and 8 wt\%, respectively, based on the initial amount of zeolite).

To understand the processes which occur during calcination, the degradation of the template was studied by DTG, DSC and pyrolysis-MS. The oxidative degradation of the template in air shows three distinct regions (Figure 2.8). At temperatures below 100 °C (region I) the weight loss is mainly caused by desorption of physisorbed water. The degradation of the template starts at temperatures above 100 °C and a significant weight loss is observed at temperatures between 100 and 380 °C (region II). Since no strong exothermic peak is observed with DSC in the same temperature region, this weight loss must originate from a non-oxidative degradation. At temperatures above 380 °C a strong exothermic signal is observed with DSC, indicating the oxidative removal of the residual organic material. It can also be noted that rather high temperatures (> 600 °C) are necessary to remove all organic material. The total amount of organic materials removed from the zeolite (21 wt\%), corresponds to exactly four DBDMA\textsuperscript{+} cation per unit cell.
The formation of products during the non-oxidative step (region II) can be monitored by using pyrolysis-MS. Figure 2.9 shows the evolution of the five major products, the main product being N,N-dimethylbenzylamine 1, upon heating an as-synthesized zeolite boron beta (Si:B = 21.6) in vacuum to 355 °C. The heterolytic cleavage of the N-methyl bond to N-Methyl-dibenzylamine 2 is observed at temperatures over 270 °C. This clearly indicates that the initial step in region II is the formation of N,N-dimethylbenzylamine and a - presumably surface-bonded - benzyl cation by heterolytic C-N bond cleavage. The surface benzyl cation is very reactive and can alkylate aromatic rings to give benzylated species 3 (Figure 2.10) and eventually coke. To remove these coke-like-species high temperatures and oxygen are required, as is observed by the very low amount of cracked products 4 and 5 and the absence of a strong exothermic peak at temperatures below 380 °C (Figure 2.8). The observed degradation route is harmony with the non-oxidative weight loss as measured by DTG (Figure 2.8). About 50 wt% of the material is removed in this way, predominantly as 1.
Figure 2.9 Evolution of organic species during the non-oxidative degradation of the DBDMA$^+$ template as measured by pyrolysis-MS. 1 N,N-dimethylbenzylamine; 2 N-methylidibenzylamine; 3 dibenzyl species; 4 and 5 unknown (see also Figure 2.10).

The temperature at which the heterolytic cleavage occurs is very low. Weight loss as determined by DTG starts at temperatures slightly above 100 °C (Figure 2.8) and the temperature required as determined by pyrolysis-MS is 190 °C. The discrepancy is mainly caused by the experimental set-up of the mass-spectrometer. In order to monitor the temperature profile, a small sample is fixed in a sealed metal tube, which is subsequently heated in a ceramic oven. The temperature is measured in the oven and it is known that a considerable difference can exist with the actual sample temperature due to heat-transfer effects. Furthermore, it requires a certain pressure in the sealed metal sample holder for products to emerge. The temperatures shown in Figure 2.9 and 2.10 should therefore only be
used as a guide line.

Figure 2.10 Degradation route of dimethyl dibenzylammonium (DBDMA⁺) in zeolite beta during non-oxidative calcination measured via pyrolysis-MS.

Neither oxygen/(air) nor ammonia can be used to remove the DBDMA⁺ template completely from the zeolite with retention of boron in the framework. However, we have found that high temperatures can be avoided by using 1% ozone (O₃) in oxygen at 120 °C followed by a hot acetone wash. Ozone is known to attack aromatic carbon-carbon bonds under mild conditions. This completely removes all organic material with full retention of XRD crystallinity. The presence of a single, sharp peak at δ -23.2 ppm in the ¹¹B MAS NMR (Figure 2.3) and the absence of any significant change in the bulk Si: B ratio as determined by chemical analysis, confirmed that all boron is retained in tetrahedral coordination in the zeolite lattice. Analysis of the materials with ²⁹Si MAS NMR showed a low amount of silanol
groups present at $\delta = -103$ ppm ($Q^3$) for a material with a Si:B ratio of 21.6 (Figure 2.11a). Since this Si:B ratio is close to the stoichiometric incorporation of boron (i.e. 4 DBDMA$^+$ per unit cell$^{8,38}$) most of the template molecules are compensated for by framework boron sites and few defect sites are required. In comparison, the $^{29}$Si MAS NMR of a calcined all-silica zeolite beta (Figure 2.11b) shows a second resonance at $\delta = -103$ ppm ($Q^3$), well separated from the $Q^4$ resonance ($\delta = -108$ to -119 ppm). It is assumed that this signal originates from structural defects already present in the as-synthesized zeolite, probably SiO$^-/SiOH$ pairs which are thought to be necessary for template charge compensation.$^{47,48}$ The observed $Q^3/(Q^3 + Q^4)$ ratio of 0.16 in all-silica beta is not far from the expected value of 0.125, assuming 4 silanol pairs per unit cell (64 atoms, polytype A,$^3$ 4 DBDMA$^+$ molecules$^{8,38}$).

![Figure 2.11](image)

$^{29}$Si MAS NMR of zeolite beta, calcined in 1% ozone in oxygen at 120 °C. a) zeolite boron beta, Si:B = 21.6; b) all-silica zeolite beta. * indicates spinning side-bands

2.3.3 Influence of gel parameters on the crystallization of zeolite boron beta.

- The sodium content

As has been noted by various authors,$^{26-28}$ the presence of sodium or other alkali metal
cations are required for the synthesis of aluminum beta using TEA$^+$ as the template. Pérez-Pariente et al.\textsuperscript{26} noticed a small increase in the induction period and a small decrease in the crystal growth rate when the Na$^+$:Si ratio is changed from 0.136 to 0.236 in the presence of TEA$^+$ as the template. It should be noted that considerable amounts of potassium are also present as impurities in the tetraethylammonium hydroxide solution used (see 3.3.2). As noted by Camblor and Pérez-Pariente\textsuperscript{27} the Na$^+$:K$^+$ ratio has a strong influence on the crystallization kinetics, which makes the data difficult to interpret. This is in contrast to the DBDMA-system. Figure 2.12 shows clearly that on reducing the Na$^+$:Si ratio from 0.3 to 0.01, the crystal growth rate decreases while the induction time increases. However, upon complete elimination of alkali metal ions - less than 6 ppm total alkali metals as determined by ICP/AES - the crystallization of zeolite beta is not stopped. This sharp change in behavior thus indicates that at least two different mechanisms are operating in the formation of zeolite beta using DBDMA$. One mechanism in which sodium plays a significant role (similar to the TEA$^+$ mechanism) and one in which the presence of sodium is detrimental (a postulate for these processes is discussed below).

![Graph showing the influence of sodium on the induction time and maximum crystal growth rate.]

Figure 2.12  Influence of sodium on the induction time (▲) and maximum crystal growth rate (■) of zeolite boron beta (Si:B = 20, T= 140 °C).
Chapter 2

- Other alkali metals

Results reported by Camblor and Pérez-Pariente\textsuperscript{27} have clearly shown that the crystallization as well as the morphology of zeolite aluminum beta using TEA\textsuperscript{+} as the template is strongly dependent on the type of alkali metal ion involved. Similar effects are also known for other zeolites.\textsuperscript{49} However, from the SEM pictures presented\textsuperscript{27} it is not clear whether the zeolite particles are single crystals or agglomerates of very small crystallites. The usefulness of electron microscopic techniques is therefore limited to high resolution electron microscopy (TEM) which can discriminate between the two type of particles. It can be said that different alkali metals in the synthesis gel direct the formation of different types of silicate anions in solution.\textsuperscript{50} Furthermore, the crystal morphology of the zeolite often changes when different alkali metals are used. This is an indication that the presence of these metal ions plays an important role at the growing crystal surface as well.

The crystal growth rate and the induction time of zeolite boron beta using DBDMA\textsuperscript{+} as the template are strongly influenced by the type of alkali cation used. Zeolite beta is still the only phase formed (Si:B ratio of 20 for all experiments). Small but significant differences in the crystal growth rate and the induction period are observed when part of the sodium was replaced by potassium, K\textsuperscript{+}/(Na\textsuperscript{+} + K\textsuperscript{+}) = 0.1. The induction time appears to decrease while the crystal growth rate increases slightly (Figure 2.13). A more pronounced effect is observed upon complete replacement of sodium by potassium or cesium. The crystal growth rate decreases and the induction time increases. SEM analysis of the crystal morphology of the materials obtained showed in all cases spherical particles.

The influence of the type and amount of alkali cation used on the synthesis of zeolite aluminum beta using TEA\textsuperscript{+} as the template, is described by Camblor and Pérez-Pariente.\textsuperscript{27} Similar to our observations, these authors reported that crystal growth is faster in the presence of sodium than potassium. They also observed a synergetic effect for sodium/potassium mixtures, the optimum ratio was found to be at 33% potassium. Based on changes in chemical composition of the liquid and solid phases of the gel, the conclusion was drawn that the relative content of Na\textsuperscript{+} and K\textsuperscript{+} influences the crystallization kinetics by regulating the aluminum level in solution. A simple relationship between aluminum concentration and the
observed rate did not exist, simply because the highest rates were observed at the lowest solubility of both aluminum and silicon species.

![Graph showing crystallinity vs. synthesis time](image)

Figure 2.13  Influence of alkali cation on the crystal growth curve of zeolite boron beta, Si:B$_{gel}$ $\approx$ 20, M$^+$:Si = 0.15, H$_2$O:Si = 40, DBDMA$^+$:Si = 0.175 at 140 °C. ●) Na$^+$; ▲) K$^+$; ■) Cs$^+$ and +) K$^+/(K^+ + Na^+)$ = 0.1.

- The boron over silicon ratio

The formation of zeolite boron beta is strongly dependent on the initial Si:B ratio of the gel. In the case of TEA$^+$ as the template de Ruiter et al.\textsuperscript{14} reported that aluminum-free zeolite boron beta can only be obtained within a narrow Si:B range (8.7 to 10.4) which corresponds to the amount of template molecules incorporated in the zeolite. The boron balances approximately the charge of the occluded template molecules. As can be seen from Figure 2.2, when applying DBDMA$^+$ as the template, the formation of almost pure zeolite boron beta is only possible for Si:B ratios between 15 and 30. These higher Si:B ratios for DBDMA, reflect the larger volume of the DBDMA$^+$ cation compared to the TEA$^+$ cation. As we reported\textsuperscript{8} earlier and was verified by molecular mechanics calculations\textsuperscript{38} exactly four DBDMA$^+$ cations can be incorporated in one unit cell of zeolite beta (64 atoms, polytype A),\textsuperscript{3} i.e. a
Si:DBDMA$^+$ of 16. A preferred B:template close to 1 appears also to be the case for DBDMA$^+$. At Si:B ratios up to 45, zeolite beta is still the predominant phase with small amounts of other denser phases like ZSM-12 and to a lesser extent ZSM-5 and cristobalite. Careful analysis of the evolution of phases formed at an initial Si:B ratio of 120 shows that initially only zeolite beta crystallizes (about 20% crystallinity as determined by XRD) and the formation of other phases starts thereafter. This indicates that initially all boron is used to synthesize a boron beta with a Si:B ratio close to 25, i.e. approaching stoichiometric, whereafter the boron-depleted gel crystallizes further to denser phases.

As we reported earlier, the synthesis of pure zeolite boron beta with Si:B ratios over 30 can only be achieved in the absence of sodium. This suggests that sodium or in general alkali metal ions play an important role in controlling the Si:B ratio of the final product. The preferred Si:B molar ratio is that in which each template molecule is compensated for by a boron site, thus ideally no sodium is incorporated in the as-synthesized zeolite. The beneficial effect of adding sodium to the system (Figure 2.12) shows that the role of sodium should be thought of in terms of facilitating the growth of the zeolite, much as a catalyst would do. A more detailed discussion on the role of boron, the template and sodium is given below when the crystallization mechanism is discussed.

The strong relation between boron and the template, is supported by the effects on the crystal growth rate upon variation of the Si:B ratio in the gel (Figure 2.14). The crystal growth rate drops significantly at a boron content less than 0.04, e.g. Si:B = 19. Thus, zeolite growth only occurs when a boron atom is used to compensate the template cation in the zeolite framework. In contrast, the induction time does not seem to be influenced strongly by the amount of boron present. In other words, the nuclei do not seem to require a boron atom to form. This is curious, considering that a nucleus is usually thought of as a small crystalline entity, already containing at least one template molecule and therefore also containing at least one boron atom, conform the observed relation between boron and template.

Two types of nucleation mechanisms are described in literature:

i) Homogeneous formation of nuclei.

ii) Heterogeneous nucleation on impurities at ppb scale present in the synthesis gel or on the surface of added seeds. Since 5 wt% seeds (based on silica) are used, nuclei are most likely
formed at the surface of the seed crystals via ii. It is mentioned by various authors\textsuperscript{51,52} that in the case of seeding (pre-)nucleation is determined by the total amount of surface added to the synthesis gel rather than by the weight of seeds added. It is therefore likely to assume that the (pre-)nucleation is controlled by processes which take place at the surface of the seed. Since the seeds already contain a sufficient amount of boron, additional boron from the bulk solution may not be required. The observed increase, though small, in the induction period, agrees with the findings of Camblo\textit{r et al.}\textsuperscript{27} who reported a similar behavior for zeolite aluminum beta when TEA\textsuperscript{+} is used as the template.

![Graph](image)

Figure 2.14 Influence of initial boron content on the induction period (▲) and the crystal growth rate (●) of zeolite boron beta, Na\textsuperscript{+}:Si = 0.15, OH\textsuperscript{−}:Si = 0.15, DBDMA\textsuperscript{−}:Si = 0.175 and H\textsubscript{2}O:Si = 40 at 140 °C.

- \textit{The alkalinity}

The influence of the amount of hydroxide on the formation of zeolite boron beta is shown in Figure 2.15. Similar to the effects reported for the TEA\textsuperscript{+} template,\textsuperscript{26-28} the influence is large at low OH\textsuperscript{−}:Si ratios while adding more hydroxide only has a small effect. The hydroxide is usually thought of as a mineralizing agent which dissolves silica and metal oxides. Since the
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boric acid used (pKₐ 9.7) easily dissolves in alkaline media as borate ions (B(OH)₄⁻), this means that at low OH⁻:Si ratios most of the hydroxide is consumed by boric acid (B:Si=0.05), resulting in a decrease of free hydroxide available for synthesis. At high OH⁻:Si ratios the gel is buffered by the high amount of silica species present. Additional hydroxide does not significantly change the pH of the solution.

![Graph showing crystallinity over synthesis time](image)

Figure 2.15 Influence of alkalinity on the crystallization of zeolite boron beta (Si:B = 20 at 140 °C). ▲) OH⁻:Si = 0.075; ●) OH⁻:Si = 0.15; ■) OH⁻:Si = 0.30.

The influence of the OH⁻ concentration on the crystal growth rate has been studied extensively²⁶-²⁸ for TEA⁺ as the template. Pérez-Pariente et al.²⁶ showed that higher alkalinity decreased the induction time and increased crystal growth rate. Upon increasing the OH⁻:Si ratio even further (OH⁻:Si > 0.3), the high alkalinity dissolves the zeolite formed after prolonged heating. At very high OH⁻:Si ratios (> 0.9), the induction time increases again and large amounts of zeolite P are found to co-crystallize with zeolite beta. The authors noted that the increase of alkalinity is achieved by addition of NaOH, though addition of an equal amount of NaCl to the original synthesis mixture does not result in a significant change in the induction time and the crystal growth rate. Both Pérez-Pariente et al.²⁶ and Eapen et al.²⁸ concluded that an optimum OH⁻:Si ratio exists for the TEA-beta system. At low alkalinity the crystallization is too slow, which is caused by the slow dissolution and low concentration of
silicon in solution, but too high OH⁻:Si ratios tend to keep high concentration of silicon species in solution, thus decreasing the amount of nuclei formed, lowering the crystal growth rate and decreasing the overall yield of crystals formed.

- The template concentration

The crystal growth is a function of the template DBDMA⁺:Si ratio of the gel. High template concentrations fasten crystal growth (Figure 2.16). The influence of the DBDMA⁺:Si ratio on the nucleation rate is, however, difficult to determine and open to various interpretations. The differences are a result of different methods in determining the initial induction period. When the slope through the initial points is used, only a small effect on the induction period is observed (Figure 2.16a). If, however, the induction period is determined via extrapolation from the slope at 50% crystallinity (Figure 2.16b), significant differences are found. The first method has the advantage that it uses data points near the actual induction point, but it is lacking the accuracy in the detection of newly formed zeolite crystals due to the high amount of seeds (5 wt%) and the high level of noise.

![Graph](image)

**Figure 2.16** Influence of the initial DBDMA⁺:Si ratio on the growth of zeolite boron beta (Si:B ≈ 20) at 140 °C. ■) DBDMA⁺:Si = 0.10; ▲) DBDMA⁺:Si = 0.175; ●) DBDMA⁺:Si = 0.30. The dotted lines indicate the slope through 50% crystallinity.
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As discussed for the influence of the B:Si ratio, the (pre-)nucleation is likely to be determined by processes which take place at the seed surface. The role of the template molecule at the surface is probably in structure directing the nuclei formed towards the desired zeolitic phase. Unlike boron, see above, no template molecules are present \textit{a priori} at the surface of the calcined seeds. The surface template concentration, and hence the nucleation rate, is a function of the affinity of the template to the surface. The surface displays the geometry of the zeolite channel or at least the mouth of it, which has a high affinity for the template. One of the basic requirements for the chosen template is its excellent fit in the channel geometry of zeolite beta.\textsuperscript{38} This high affinity results in a non-linear relation between the concentration of template at the surface and in the bulk liquid, for example a Langmuir-type adsorption. The number of surface sites on which the template can adsorb, is very small compared to the total amount of template molecules present in solution. It might therefore be assumed that the surface of the seed is almost fully covered with template within the bulk concentration range we investigated, which may explain the small influence of the template concentration on the induction period.

The crystal growth rate on the other hand is strongly dependent on the template concentration. This effect has also been observed by Pérez-Pariente \textit{et al.}\textsuperscript{26} and by Camblor \textit{et al.}\textsuperscript{27} for zeolite aluminum beta and TEA\textsuperscript{+} as the template. These authors conclude that the template has a very important role in the zeolitization process, though they do not give an indication what the exact role of the template could be. It is clear from our results, see the discussion on the influence of the boron content, that one important role of the template is to compensate negative boron framework sites. This indicates that the template sorbed on a framework boron site represents by far the energetically most favorable position, while other non-boron containing framework species, defects for example, are not compensated for by the DBDMA\textsuperscript{+} template molecule so efficiently.

\textit{- The crystallization temperature.}

To study the effect of the temperature on the formation of zeolite beta in the presence of DBDMA\textsuperscript{+} template, the crystallization kinetics are studied in the range 120 - 170 °C by
comparing the extent of crystallization at different synthesis times (Figure 2.17). In all cases zeolite boron beta is the only phase formed. The synthesis time required to obtain fully crystalline materials ranges from 16 h at 170 °C to 130 h at 120 °C, showing the wide applicability of the DBDMA⁺ template. The only drawback of this template is the relative ease of degradation. As can be seen from the DTG of the as-synthesized material (Figure 2.8), the DBDMA⁺ already starts to degrade at temperatures as low as 120 °C. After the hydrothermal crystallization an oil is usually present that consists primarily of N,N-dimethylbenzylamine and benzyl alcohol as determined by GC-MS. The latter compound formed by the reaction of the benzyl cation (Figure 2.10) and water or hydroxide ions present. Despite this gradual hydrothermal degradation of the template cation, the crystallization of zeolite boron beta is not hindered.

![Graph showing crystallinity vs. synthesis time](image)

Figure 2.17 Influence of temperature on the growth of zeolite boron beta with Si:B = 20, Na⁺:Si = 0.15, OH⁻:Si=0.15, H₂O:Si = 30 - 40, DBDMA⁺:Si = 0.175 at +) 170 °C; ▲) 150 °C; □ 140 °C; ● 130 °C; ■ 120 °C.

Normally the nucleation rate is inversely proportional to the induction time and both the nucleation rate and crystal growth rate exhibit first order kinetics. The observed apparent activation energies are 77.4 and 78.6 kJ/mol (Table 2.1), respectively. Thompson and den

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Ouden\textsuperscript{22,24} already showed that the Avrami-Erofeev type equation (2.1) to describe zeolite synthesis has certain shortcomings which do not allow meaningful deductions based on the observed activation energies. It is therefore not possible to deduce reliable mechanistic information, with respect to the lower values found for the activation energies for the TEA\textsuperscript{+} template cation.\textsuperscript{28,34}

Table 2.1 Apparent activation energies for nucleation and crystallization of zeolite beta using DBDMA\textsuperscript{+} and TEA\textsuperscript{+} as the template.

<table>
<thead>
<tr>
<th>Template</th>
<th>Activation Energy [kJ mol\textsuperscript{-1}]</th>
<th>nucl.</th>
<th>crystal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBDMA.Cl + NaOH</td>
<td>77.4</td>
<td>78.6</td>
<td></td>
</tr>
<tr>
<td>TEA.OH + NaOH\textsuperscript{34}</td>
<td>29.3</td>
<td>63.6</td>
<td></td>
</tr>
<tr>
<td>TEA.Br + NaOH\textsuperscript{28}</td>
<td>54.3</td>
<td>45.5</td>
<td></td>
</tr>
</tbody>
</table>

2.3.4 The crystallization mechanism, a tentative model

The crystallization mechanisms of zeolites are complex cooperations of various processes such as hydrodynamics, silica gel reorganization,\textsuperscript{53} hydrolysis and condensation processes,\textsuperscript{54} formation of specific structure in solution around cations,\textsuperscript{54,55} mass-transfer of building units, nucleation and crystallization. Specific chemical aspects of part of the above mentioned processes are difficult to unravel as no characterization technique is available to accurately monitor the organizations of nutrients in the bulk solution to viable nuclei and on the growing crystal surface. Zeolite growth is usually monitored indirectly from the crystallinity by bulk techniques, e.g. XRD, IR, sorption etc., or more accurately by determining the size and shape of crystals by SEM. The latter is restricted to a limited number of syntheses, requiring relatively large crystals with well-defined crystal morphologies, excluding this method for our
synthesis.

Our experiments show that especially the crystal growth rate has two unexpected relations with the boron and the sodium content. As to the boron content, a sharp drop in the crystal growth rate is observed at B/(B + Si) ratios slightly lower than the stoichiometric boron incorporation (Figure 2.14). This stoichiometric incorporation corresponds to a complete template charge compensation by framework boron sites, similar to the results of de Ruiter et al.,\textsuperscript{14} for the incorporation of boron using TEA\textsuperscript{+} as the template. The stoichiometric incorporation of boron (i.e. B:DBDMA\textsuperscript{+} \approx 1) as well as the dependency of the crystal growth rate on the Si:B ratio, suggests that each framework boron site is preferentially compensated for by the organic template cation.

It can be seen from Figure 2.12 that the crystal growth rate decreases with decreasing sodium content. Upon essentially complete elimination of sodium (< 6 ppm) the synthesis does not stop, the crystal growth rate even increases. This would suggest a different crystallization mechanism, vide infra, in the absence of sodium, which is apparently repressed by even very small amounts of sodium. If specific sites at the growing zeolite surface are required, the presence or the absence of sodium in the synthesis mixture could have a strong influence, even in small amounts. Especially during the early stages, when the total zeolite surface, including the seed surface, and thereby the number of specific sites, is comparatively small.

The strong interaction of framework boron sites with the template and the low amounts of sodium required to stop the sodium free mechanism, both indicate that surface-related processes should be considered. We propose that three types of surface groups are possible at the crystal surface (see Figure 2.18), determining via which mechanism the zeolite can crystallize. The three groups are: I a tetrahedral boron site with a delocalized negative charge; II a framework defect site and III a site containing free silanol groups, probably partially deprotonated due to the high alkalinity.

When boron is incorporated in the zeolite lattice (type I), the negative charge can either be compensated for by sodium or template cations. Since the negative charge of the boron site is delocalized over at least four framework oxygens this site is not a very hard Lewis base, thus preferring the soft Lewis acidic template cation over hard Lewis acids, like sodium. The second surface group which is also structure-directing, is the defect site (type II). The SiO\textsuperscript{-}}
group in the defect site is a hard Lewis base and therefore prefers an alkali metal cation as the counter cation. The actual places where new silicate species attach are not at the type I or II sites but at the type III sites. This site consists of terminal Si-O⁻ and silanol groups and is located at the growing zeolite surface. Like the type II site, prefers sodium cations as counter ions. In other words, I and II are in principle used for directing the framework structure during the attachment of new silicon building blocks at site III. The existence of type I - template and the type II - alkali pairs has been shown by Camblo et al.²⁷ for zeolite aluminum beta. The large amount of defects present in zeolite aluminum beta, as observed with ²⁹Si and ²⁷Al MAS NMR and IR, are counter balanced by alkali cations rather than by TEA⁺ in accordance with the proposed model.

![Schematic representation of the three proposed site types](image)

**Figure 2.18** Schematic representation of the three proposed site types at the growing surface of zeolite boron beta (cf. text). Connecting silicon atoms are not shown. The structure directing boron - template site I; the defect - sodium site II; and the growth site III.
Whether or not zeolite beta is formed is determined by the kind of cation which is present at the growing zeolite surface at both I and II. Sodium is not a preferred structure directing cation for the synthesis of zeolite beta while DBDMA$^+$ is. In a typical synthesis with a stoichiometric amount of boron, hardly any II sites exist or they are easily converted to I. High sodium contents are still favorable for the stabilization of III, thereby facilitating crystal growth (see Figure 2.12). Similarly higher template concentrations should also result in faster crystallization by a higher amount of I - template species (see Figure 2.16). In the case of non-stoichiometric syntheses either more or less boron can be present:

- If a surplus of boron is present, the growing surface is covered by the maximum amount of boron allowed. This is a value close to the stoichiometric amount since the boron at the growing surface is only stable when a DBDMA$^+$ cation can also be accommodated. The crystal growth rate is thereby not significantly changed. As is shown in Figure 2.19 for crystallization curves for Si/B=10, 15 and 20 only at the end of crystallization - when the boron content of the gel has increased too much (boron is incorporated less than silicon) - the crystallization of zeolite boron beta is retarded severely. This might be related to a change in type of building units in solution due to the decreasing Si:B ratio in the liquid phase or to an over-crowding of boron on the growing zeolite surface thereby disturbing the strict pre-ordering of the template cations required for zeolite growth.

- At high Si:B ratios, e.g. a shortage of boron, template charge compensation in the growing zeolite has to (partially) proceed via framework defect sites II. During synthesis these sites are, however, preferably compensated for by sodium and not by the template. Zeolite crystallization of zeolite beta therefore stops at these sites and can only continue when they are converted to a type I site by uptake of a boron from the solution. This, however, depletes boron from the synthesis gel as well as produces a zeolite beta phase with a Si:B ratio closer to its stoichiometric incorporation (Si:B $\approx$ 16). The resulting boron depleted gel can crystallize further into other high-silica phases e.g. ZSM-12, ZSM-5 and cristobalite.$^8$
Figure 2.19 Crystal growth curves of zeolite boron beta as a function of boron content in the synthesis gel. + Si:B = 10; ■ Si:B = 15; ● Si:B = 20.

The major principle of our tentative model is that it assumes that the ordering of silicate species takes place at the crystal plane-solution interface. This is mostly based on our observation of a stoichiometric boron incorporation, though it is a generally accepted mechanism for zeolite growth.\textsuperscript{25} The exact ratio suggests that an ordering is present at a certain point. We assume that this ordering does not take place in solution for this would suggest either secondary building units or other ordered silicate species that consist exactly of \approx 16\textsuperscript{34} Si, 1 B and 1 template molecule. The idea of SBU's is frequently mentioned in literature,\textsuperscript{54,55} but no proof of their existence has ever been published. Another option is the clathrate-template model proposed by Zones and Davis.\textsuperscript{56} In this model the template cations are firstly hydrated to form a clathrate structure whereafter the semi-crystalline water framework is exchanged for borate and silicate anions with a precise stoichiometry. In our opinion, this model\textsuperscript{56-58} is more a complementary then a different model \textit{i.e.} it discusses another facet of the chemical processes involved by describing the ordering processes of silicate precursors at the surface. Our model only proposes what kind of chemical conditions are required for zeolite growth to occur not how they specifically grow \textit{via} attachments of silica building units. The identification or even modelling of groups in terms of structure
directing and structure building sites, similar to I, II and III, however, could be a helpful tool in the understanding of the growth of zeolites.

The model can also be used to predict synthesis conditions necessary for the synthesis of zeolite boron beta with high Si:B ratios or even the all-silica analogue. These materials require that a substantial amount of the template cations is compensated for by defects (e.g. type II - DBDMA\(^+\)). Since during synthesis these sites prefer sodium instead of the template, which stops growth or even favors the formation of unwanted phases, a sodium-free synthesis will be necessary. The type II - DBDMA\(^+\) site is not so favorable and thus requires a higher amount of template in the synthesis gel to facilitate its formation. In fact these conditions, sodium free and high template concentrations, are those which we reported\(^8\) for the synthesis of high silicon to boron ratios and the all-silica analogue of zeolite beta.

2.3.5 The nucleation mechanism, a tentative model

One of the challenges in understanding zeolite crystallization, is an accurate description of the nucleation mechanism.\(^{51}\) The scale and degree of organization of nuclei are such that characterization is very difficult for atomic techniques (resolution about 10 ~ 20 Å\(^3\)), like \(^{29}\)Si NMR, and the amount (approximately 10\(^{-8}\) nuclei per gram of silica) makes it unsuitable for quantification via bulk techniques. Two types of nucleation are commonly proposed, homogeneous nucleation and heterogeneous nucleation.\(^{52}\) The issue of homogeneous or heterogeneous nucleation in zeolite synthesis is much debated.\(^{52}\) It has been known since the late 1960’s that adding seed crystals of the desired zeolite phase to a synthesis shortens the time required for zeolite growth.\(^{59,60}\) The mechanism of this rate enhancement has not been clearly delineated, but two cases can be proposed:

\(i)\) the added surface area of the seed crystal results in the more rapid consumption of reagents, reducing supersaturation even to the point of inhibiting the formation of new crystals, or,

\(ii)\) the seeds promote nucleation by some sort of secondary nucleation mechanism on its outer surface.\(^{51}\)

In our case the seeds itself did not grow, suggesting that the second type of nucleation applies.
Since both crystallization and nucleation seem to take place at the surface, we assume that similarities between both mechanisms may exist. If the influence of the various synthesis parameters is correlated with both the crystal growth rate and the reciprocal induction time, similar behavior is found for the sodium content, cation type, hydroxide concentration and temperature dependency and none or little influence on the nucleation is found for the boron content. The influence of the template concentration on the nucleation is not yet clear (paragraph 2.3.3.3). If one has to compare the parameters with each of the sites of the crystallization model (Figure 2.18), it can be seen that the parameters strongest associated with the site types II and III, also seem to have the same influence on the nucleation rate, whereas those for site I, containing only boron and template hardly seem to influence nucleation. In the crystallization model the type I site is associated with a structure directing group, but since the seed is already comprised of the beta framework this function may not be required. On the other hand type III and perhaps also type II are associated with sites on which silicate species can bind. Since the latter is considered a dynamic process, the reversal can also occur. This means that the detachment of small nuclei from the seed crystal surface could be an important step in nucleation.

The formation and detachment of nuclei is like the crystallization mechanism a complex process of both chemical and physical processes. The concentration of chemical nutrients in solution determines the degree of supersaturation and probably the surface concentration of I, II and III species. Beside chemical considerations, the nucleation rate also increases when the number of collisions of particles increases which is a strong function of the temperature, of the hydrodynamics e.g. the viscosity of the gel, and of the number of particles in solution e.g. gel dilution, amount of seeds or the presence of impurities.

We should stress that the site model (Figure 2.18), which takes place on a molecular level, is based on macroscopic measurements, in our case bulk XRD crystallinity. This makes the model nothing more than a proposition for further research, since none of the sites proposed have actually been characterized. Another obvious flaw is the use of the reciprocal induction period as measure for the nucleation rate, as determined from the crystal growth curve. The induction time for example is comprised of various other processes e.g. the time required to heat the gel to the synthesis temperature, the rearrangement of the gel particles, the dissolution rate of precursors and the achievement of supersaturation level. The
observed differences in the induction time might therefore not even be related to the nucleation mechanism.

2.4 Conclusions

Zeolite boron beta can be synthesized using dibenzylimidethylammonium as the template. The optimal Si:B ratios are found to correspond to the amount of template molecules occluded in the zeolite, similar as found for tetaethylammonium. The hydrothermal crystallization can be performed at temperatures between 120 and 170 °C and required 16 to 130 h to reach completion. The boron is incorporated tetrahedrally in the zeolite framework as determined by $^{11}$B MAS NMR, FTIR and unit-cell contraction via XRD. The thermal instability of the template and the facile extraction of boron at high temperatures, requires the use of ozone in oxygen at 120 ° to completely remove the template.

In order to attain higher Si:B ratios, various synthesis parameters were investigated. Based on the dependency of the nucleation and crystal growth rate on the sodium, boron, template and hydroxide to silicon ratio, a model comprised of three site types all located at the growing zeolite surface, is tentatively proposed (Figure 2.18). Two of these, type I and II, are related to directing the structure and whereas type III is used as sites at which a new silica precursor can attach. The model explains the phenomena observed in the synthesis of zeolite boron beta using DBDMA⁺ as the template. The observed stoichiometry between boron and template in the as-synthesized zeolite, is explained by a strong interaction between template molecules and the boron-containing site I during synthesis, while sodium is present at the defect site II. Since sodium cations are not structure directing towards the beta framework, zeolite growth will only occur via the I -DBDMA⁺ site as the building unit. The synthesis conditions for very high Si:B ratios can be predicted by the model. Part of the occluded template needs to be compensated for by defects, i.e. type II. These sites prefer alkali metals over organic template molecules for charge compensation. Absence of alkali ions is therefore required. As reported earlier, the absence of alkali metals is indeed one of the absolute requirements for the synthesis of all-silica zeolite beta.
References

Zeolite Boron Beta

Synthesis of all-silica and of low boron-content zeolite beta.

Abstract

Synthesis of pure zeolite boron beta with Si:B molar ratios from 20 to infinity is realized when dibenzyl(dimethyl)ammonium hydroxide is used as the template. The synthesis conditions required are a template hydroxide to silicon ratio of 0.5 and the absence of alkali metal ions, as predicted by the synthesis model for zeolite beta using dibenzyl(dimethyl)ammonium as the template, described in Chapter 2 of this thesis. After the subsequent removal of the template by ozone at 120 °C, the low amount of water adsorbed by the all-silica zeolite beta shows the increased hydrophobicity compared to zeolite aluminum beta. The all-silica material is further characterized by a high amount of defects in the lattice as determined by FT-IR and $^{29}$Si MAS NMR.
3.1 Introduction

Zeolite beta is the only high-silica zeolite with a three-dimensional pore system with large 12-membered ring apertures,\textsuperscript{1,2} which makes it very suitable as a regenerable catalyst in organic reactions. Moreover zeolite beta exhibits a unique internal Lewis acidity, enabling highly selective catalysis.\textsuperscript{3-7} It was generally believed that the presence of aluminum is essential for the formation of zeolite beta\textsuperscript{8}; and usually the Si:Al molar ratio was claimed to be between 5 and 200.\textsuperscript{9} Recently Rubin obtained zeolite beta with Si:Al molar ratios up to 500, upon synthesis in the presence of triethanolamine.\textsuperscript{10} Our interest is aimed at the synthesis of zeolite boron beta with extremely high Si:B molar ratios, in particular the all-silica analogue. The all-silica zeolite has no importance in catalytic applications due to the absence of catalytic sites, but the material has importance as a reference material and could find use in selective adsorption e.g. removal of small amounts of organic materials from waste water streams. Provided that no chelating agent, such as triethanolamine, is used, such an all-silica synthesis could be further modified to allow direct incorporation of transition metals. In an effort to vary the density of the boron sites, we found the dibenzyldimethylammonium cation (DBDMA, 1), which was reported by Rubin\textsuperscript{11} to be particularly suitable for the synthesis of zeolite beta containing relatively low amounts of aluminum, could serve to make the all-silica form of zeolite beta.\textsuperscript{12}

\[ \text{H}_2\text{C} \overset{\text{N}}{\text{C}} \text{CH}_3 \]

The use of the dibenzyldimethylammonium cation as a specific template for zeolite boron beta is described in Chapter 2. Based on the observations made for the zeolite growth under alkali-rich conditions, a model for the growth of boron beta is proposed. In this model, see Figure 3.1, the growing zeolite surface is thought to consist of three types of sites. Two of these types are used for structure direction and one is used for zeolite growth. In the presence of alkali metal ions, the structure directing site II is preferentially compensated for by alkali metal cations and growth only proceeds via the boron site I compensated by a
template molecule, resulting in Si:B molar ratios close to the stoichiometric value. For an all-silica zeolite no structure directing sites I are possible, *vide infra*, and growth can only occur when the II sites are compensated for by template molecules. Since these sites prefer alkali metal ions over organic template cations, all-silica zeolite beta is only expected to crystallize if no alkali metal ions are present. Moreover a higher template concentration is required to attain a sufficiently high concentration of these II - DBDMA sites.

Figure 3.1 Growth sites on the surface of zeolite beta.

Since we reported the first synthesis of all-silica zeolite beta,\textsuperscript{12} four other methods have been published for the synthesis of all-silica zeolite beta. Three\textsuperscript{13-15} of these new methods have remarkable similarities to our all-silica synthesis. Our all-silica synthesis is characterized by the use of a beta specific template at a high template hydroxide to silicon ratio, by the absence of alkali metal ions and by a relatively high amount of seeds, see further below. The fourth all-silica beta synthesis\textsuperscript{16} is a fluoride synthesis using tetraethylammonium as the
template.

Saxton et al.\textsuperscript{13} used a comparable highly specific template, 4,4'-trimethylene bis (N-benzyl-N-methylpiperidinium) 2, but otherwise similar conditions for the synthesis of an aluminum-free titanium containing zeolite beta. The spatial geometry of the template 2 is the same as for the DBDMA\textsuperscript{+} cation except that it is twice as long. The use of another specific template for the synthesis of an aluminum-free titanium containing all-silica zeolite beta has been reported by van der Waal et al.\textsuperscript{14} The di(cyclohexylmethyl)dimethylammonium 3 cation used is similar to the DBDMA\textsuperscript{+} cation in spatial geometry, but is thermally more stable due to the absence of benzyl groups (see paragraph 2.3.2 in Chapter 2 for a full discussion).

\begin{center}
\includegraphics[width=0.4\textwidth]{template}
\end{center}

Camblor et al.\textsuperscript{17,18} were the first to achieve the incorporation of titanium in beta framework using tetraethylammonium as the template. This synthesis still required the presence of small amounts of aluminum, in accordance with Brunner.\textsuperscript{8} Recently Camblor et al.\textsuperscript{15} showed the synthesis of the aluminum-free titanium containing zeolite beta using the same template. The two syntheses\textsuperscript{15,17,18} are similar in all but the seeding level. The all-silica synthesis requires very high amounts of dealuminated zeolite beta seeds, about 5 wt\% based on silica used, to proceed smoothly whereas no seeds are required when aluminum is present. It should be noted that only about 20 wt\% of the initial silica was converted to the final zeolite. Since the authors state that the seed crystals are also found in the final product, this would suggest that a substantial amount of the obtained zeolite consists of the initial seed crystals added.

The fluoride method, reported by Camblor et al.,\textsuperscript{16,19} also required a high amount of
template, the absence of alkali and a high amount of fluoride instead of hydroxide as the mineralizing agent. The material obtained by the fluoride method differs from the hydroxide methods\textsuperscript{13-15} in that no framework defects are required for template charge compensation\textsuperscript{14} because of incorporated fluoride anions.\textsuperscript{16} The resulting $^{29}$Si MAS NMR spectrum of the calcined material is well-resolved and shows no resonances below 100 ppm indicative of framework defects.

\subsection*{3.2 Experimental}

In a typical synthesis 3.0 g silica (SiO$_2$, Cab-O-Sil M5) was added to a solution containing 6.31 g dibenzyldimethylammonium hydroxide, 35.6 g water, the appropriate amount of boric acid (B(OH)$_3$, Merck) and 0.15 g all-silica beta seeds, giving a molar oxide ratio for the gel of:

$$1 \text{ SiO}_2 : 0.25 (\text{DBDMA})_2 \text{O} : x \text{ B}_2 \text{O}_3 : 38 \text{ H}_2 \text{O}$$

with $x$ in the range of 0 to 0.0125. Table 3.1 gives a summary of the gel compositions used. All gels were seeded with 5 wt\% (based on SiO$_2$) deboronated Al-free zeolite beta (prepared according to de Ruiter et al.\textsuperscript{20}). A 22.55 wt\% aqueous solution of template hydroxide, free of alkali metals, was used, prepared from dibenzyldimethylammonium bromide and silver oxide. The gels were aged for at least three days, after which the initially viscous gel was transformed into a homogeneous, opaque liquid. After hydrothermal crystallization at 135 °C to 140 °C in stirred autoclaves, the as-synthesized zeolite was washed until pH 9, dried and treated with 1\% ozone in oxygen at 110 to 120 °C for 3 h to remove the occluded template.

Crystallinity and phases formed were determined by X-ray powder diffraction on a Philips PW 1830 Diffractometer using CuK$\alpha$ radiation. Unit-cell expansions were determined from the exact position of the peak at 2$\theta$ $\approx$ 43.5°, indexed as 600 for polytype A,\textsuperscript{1} measured with a Guinier-de Wolff camera using quartz as internal standard. Solid-state $^{11}$B and $^{29}$Si MAS NMR measurements were performed on a Varian VXR-400 S 400 MHz. Infrared
measurements were performed on a Bruker IFS-66 FT-IR instrument under the attached microscope. Low pressure argon adsorption isotherms were measured on a Micromeritics ASAP 2000M apparatus. Adsorption experiments were performed on a home-made DTG apparatus. After outgassing the zeolite sample at 400 °C under a flow of dry nitrogen, the zeolite was cooled to 50 °C and subjected to a flow of nitrogen saturated with water or toluene at 0 °C. The total amount of occluded organic materials and volatile inorganics was determined using the same DTG apparatus. The as-synthesized zeolite was heated at a rate of 6 °C/min under a flow of dry air.

Table 3.1 Gel compositions used for the synthesis of zeolite boron beta. Synthesis time and temperature of crystallization were 3 days at 140 °C, or 7 days at 135 °C for samples A1-A5 and B1-B6, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si:B (gel)</th>
<th>OH⁻:Si (gel)</th>
<th>Na⁺:Si (gel)</th>
<th>Q⁺:Si³⁺ (gel)</th>
<th>Si:B zeolite</th>
<th>Relative crystallinity [%]</th>
<th>Beta [%]¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>20.3</td>
<td>0.15</td>
<td>0.15</td>
<td>0.147</td>
<td>21.6</td>
<td>100⁰</td>
<td>100</td>
</tr>
<tr>
<td>A2</td>
<td>31.2</td>
<td>0.15</td>
<td>0.15</td>
<td>0.147</td>
<td>30.8</td>
<td>116</td>
<td>97</td>
</tr>
<tr>
<td>A3</td>
<td>41.4</td>
<td>0.15</td>
<td>0.15</td>
<td>0.147</td>
<td>39.2</td>
<td>97</td>
<td>93</td>
</tr>
<tr>
<td>A4</td>
<td>45.4</td>
<td>0.15</td>
<td>0.15</td>
<td>0.147</td>
<td>n.d.</td>
<td>95</td>
<td>92</td>
</tr>
<tr>
<td>A5</td>
<td>65.7</td>
<td>0.15</td>
<td>0.15</td>
<td>0.147</td>
<td>n.d.</td>
<td>88</td>
<td>84</td>
</tr>
<tr>
<td>B1</td>
<td>40</td>
<td>0.50</td>
<td>0.00</td>
<td>0.50</td>
<td>29</td>
<td>74</td>
<td>100</td>
</tr>
<tr>
<td>B2</td>
<td>80</td>
<td>0.50</td>
<td>0.00</td>
<td>0.50</td>
<td>59</td>
<td>101</td>
<td>100</td>
</tr>
<tr>
<td>B3</td>
<td>120</td>
<td>0.50</td>
<td>0.00</td>
<td>0.50</td>
<td>72</td>
<td>103</td>
<td>100</td>
</tr>
<tr>
<td>B4</td>
<td>200</td>
<td>0.50</td>
<td>0.00</td>
<td>0.50</td>
<td>108</td>
<td>109</td>
<td>92</td>
</tr>
<tr>
<td>B5</td>
<td>400</td>
<td>0.50</td>
<td>0.00</td>
<td>0.50</td>
<td>220</td>
<td>109</td>
<td>92</td>
</tr>
<tr>
<td>B6</td>
<td>∞</td>
<td>0.50</td>
<td>0.00</td>
<td>0.50</td>
<td>&gt;1000⁴</td>
<td>106</td>
<td>&gt;98</td>
</tr>
</tbody>
</table>

¹ Q⁺ = dibenzylidimethylammonium cation (DBDMA), ² Impurities are ZSM-12, ZSM-5, cristobalite and magadiite, see text. ³ Reference zeolite. ⁴ Si:Al > 5000.
3.3 Results and Discussion

3.3.1 Synthesis of zeolite beta

In all cases a fully crystalline zeolite beta was obtained, sometimes accompanied by small amounts of impurities (see Figure 3.2 and Table 3.1). A highly crystalline all-silica zeolite beta was obtained from a sodium-free formulation (sample B6). The crystallization of an all-silica beta is apparently hindered by the presence of sodium ions, which appear to promote the crystallization of unwanted phases. In the presence of sodium ions the major crystalline phase was ZSM-12, accompanied by small amounts of ZSM-5, cristobalite and magadiite; in the absence of sodium ions only a trace of ZSM-12 was formed, which agrees with the observation by Goepper et al.\textsuperscript{21} that the formation of ZSM-12 is enhanced by sodium ions. Using the DBDMA template Rubin\textsuperscript{11} also observed the formation of ZSM-12 at high Si:Al ratios in the presence of sodium cations.

The interpretation of the single crystal X-ray diffractograms as performed by Marler et al.\textsuperscript{22} is consistent with the following model: the framework of zeolite beta is built from identical layers as building units arranged perpendicularly to (001). Neighboring layers are shifted by 6.51 Å along the "c" direction. Each sheet is 90° rotated against its neighbor and shifted by ±1/3 a\textsubscript{o} or by ±1/3 b\textsubscript{o}. These shifts occur in a disordered sequence. Any change in layer sequence does not block the channels in the "c" direction nor change the channel size and dimensionality. In principle three different (hypothetic) ordered "end-members" are possible, called polytype A, B and C.\textsuperscript{1,2,22-24} The framework of as-synthesized zeolite beta can be thought of as a continuous intergrowth of two polytypes (A en B) in a sheet-like manner, schematically represented in Figure 3.3. No synthesis of any pure end-member of zeolite beta has been reported in literature so far, though some success has been obtained by Davis et al.\textsuperscript{25} in using chiral molecules to produce samples with an enriched content of polymorph A. Especially the synthesis of a pure polymorph A would be interesting since it is a chiral zeolite, with potential in chiral catalysis and enantiomeric separations.\textsuperscript{25}
Figure 3.2 X-ray diffractograms of as-synthesized zeolite beta. a) All-silica zeolite beta (sample B6), b) Zeolite boron beta Si:B = 72 (sample B3). (*) Indicates the position of strongest peak (2θ ≈ 20.5) for ZSM-12.

Figure 3.3 Schematic view of the orientation of the faulting of a,b-planes in zeolite beta (see text).
Close examination of the XRD patterns (see Figure 3.2) indicates that the fault probability as defined by Newsam et al.\(^1\) is independent of the boron content and neither of the polymorphs crystallizes preferentially. Molecular mechanics calculations\(^{26,27}\) show that the DBDMA cation is oriented in the straight channels in the "a" and "b" direction. There is no interaction of the template in the "c" direction between different sheets, which explains why no preference for any of the three polymorphs is observed.\(^{27}\)

In contrast to syntheses carried out in the presence of sodium, relatively more boron than silicon is incorporated during the sodium-free syntheses (see Table 3.1). This is probably due to the high alkalinity (OH\(^-\):Si = 0.5), which keeps a relatively large amount of silicon in solution. The efficiency of silicon incorporation in the as-synthesized zeolite is found to vary around 52 % w/w for samples B2 to B6 (see Table 3.2). The efficiency of boron incorporation is very high, which suggests that boron is preferentially incorporated in the zeolite framework. From the crystallization under alkali-rich conditions, see Chapter 2, it is concluded that the occluded template molecules are preferentially compensated for by the boron containing sites, e.g. type I - DBDMA interactions (Figure 3.1). Probably the same also applies to the synthesis of zeolite beta under alkali-free conditions.

Table 3.2 Efficiency\(^a\) of boron and silicon incorporation in zeolite beta under alkali-free conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Efficiency of Incorporation(^a)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Silicon</td>
<td>Boron</td>
</tr>
<tr>
<td>B2</td>
<td>0.57</td>
<td>0.78</td>
</tr>
<tr>
<td>B3</td>
<td>0.49</td>
<td>0.82</td>
</tr>
<tr>
<td>B4</td>
<td>0.47</td>
<td>0.87</td>
</tr>
<tr>
<td>B5</td>
<td>0.51</td>
<td>0.93</td>
</tr>
<tr>
<td>B6</td>
<td>0.53</td>
<td>(\text{--})</td>
</tr>
</tbody>
</table>

\(^a\) Defined as the mass fraction incorporated in the as-synthesized zeolite from the initial gel.
3.3.2 Characterization

In a Differential Thermal Gravimetry experiment (DTG) with zeolite boron beta (sample A1), carried out in dry air, a total weight loss was observed of 21 % (at 700 °C), primarily due to oxidation of the template. This corresponds to 4.0 template ions per 64 T-atoms, in accordance with molecular mechanics calculations.\textsuperscript{26,27} It appeared, however, that after calcination at 400 °C a substantial amount of coke was still present. The higher temperature necessary to remove this coke (> 450 °C), gave rise to a substantial loss of XRD-crystallinity, accompanied by loss of boron. The use of high temperatures can be avoided by calcination in 1% ozone in oxygen at 120 °C followed by a hot acetone wash at room temperature, which was found to completely remove the template with full retention of XRD-crystallinity and boron in the framework, see Chapter 2 for a more detailed discussion on the removal of the DBDMA\textsuperscript{+} cation from the beta framework.

The incorporation of boron in the zeolite framework was confirmed by the presence of a single sharp peak at δ =-23.2 ppm in the \textsuperscript{11}B MAS NMR spectra (Figure 3.4) and a band at 905 cm\textsuperscript{-1} in FT-IR spectra (Figure 3.5a en b).\textsuperscript{28} This was further supported by a linear relation between the interplanar spacing (indexed as 600 for polytype A\textsuperscript{1}) and the boron content. \textsuperscript{11}B MAS NMR and chemical analysis show that boron is fully retained in the framework after the mild ozone treatment. When an as-synthesized all-silica zeolite beta was treated in exactly the same way, a small second resonance at -103 ppm (Q\textsuperscript{3}) well-separated from the Q\textsuperscript{4} resonance (-108 to -119 ppm) is observed in the \textsuperscript{29}Si MAS NMR spectra (Figure 3.6). It is assumed that this signal originates from structural defects already present in the as-synthesized material, probably as SiO\textsuperscript{-} - SiOH pairs which are thought to be necessary for template charge compensation.\textsuperscript{29,30} The observed Q\textsuperscript{3}/(Q\textsuperscript{3}+Q\textsuperscript{4}) ratio of 0.16 is not far from the expected value of 0.125, assuming a template content of 4 molecules per unit cell as found by DTG. The presence of Si-OH groups in the all-silica material is also confirmed by the presence of an absorption band at 960 cm\textsuperscript{-1} in the FT-IR spectrum (Figure 3.5c) Similarly, Cambior et al.,\textsuperscript{15} reported high amounts of defects for all-silica zeolite beta when tetra-ethylammonium hydroxide was used as the template. The formation of defects can be circumvented by using fluoride as the mineralizing agent as shown by Cambior et al.\textsuperscript{16,19}
Figure 3.4 $^{11}$B MAS NMR of as-synthesized zeolite boron beta (sample A1).

Figure 3.5 Infra-red of zeolite boron beta (sample A1) a) as-synthesized; b) ozone-treated and dried at 100 °C; and all-silica beta (sample B6) c) ozone-treated, at room temperature.
Figure 3.6 $^{29}$Si MAS NMR of ozone-treated all-silica beta (sample B6).

The ozone-treated all-silica zeolite had a nitrogen micropore volume of 0.266 ml g$^{-1}$zeolite against 0.25 ml g$^{-1}$zeolite and 0.226 ml g$^{-1}$zeolite reported in literature for zeolite aluminum beta$^{31}$ and zeolite boron beta,$^{20}$ respectively. The low micropore volume of 0.177 ml g$^{-1}$subscript for the high temperature calcined zeolite sample agrees with the observed loss in XRD-crystallinity. The Horvath-Kawazoe plot (Figure 3.7) showed a bimodal pore size distribution with maxima at 5.6 Å and 7.0 Å. The physical meaning is not clear, though the values agree with the description of the channel system by Higgins et al.,$^{1}$ who reported average diameters of 5.5 Å and 7.0 Å for the tortuous and the straight channels, respectively. By contrast, an unimodal pore-size distribution at 6.5 Å is reported by de Ruiter et al.$^{20}$ for zeolite boron beta prepared using TEA$^+$ as the template.

As a measure of hydrophobicity, the sorption of water and toluene on all-silica zeolite beta (an ozone-treated and an air-calcined sample) was measured at 50 °C. In sharp contrast to an H-[Al]-beta (Si:Al = 11.2) the ozone-treated all-silica zeolite hardly adsorbed any water (8 mg g$^{-1}$zeolite vs. 74 mg g$^{-1}$zeolite for an H-[Al]-beta at 50 °C with Si:Al = 11.2) whereas toluene sorption was somewhat higher for the all-silica sample (210 vs. 170 mg g$^{-1}$zeolite at 50 °C). This clearly shows the increased hydrophobic character of the all-silica zeolite. The low adsorption of toluene on the air-calcined all-silica zeolite (170 mg g$^{-1}$zeolite at 50 °C)
compared to the ozone treated sample, agrees with the observed loss in XRD-crystallinity and the decreased nitrogen micropore volume and shows the advantage of the low temperature ozone treatment over conventional high temperature air calcination.

Figure 3.7 Argon Horvath-Kawazoe pore size distribution plot of ozone-treated all-silica beta (sample B6).

3.4 Conclusions

Based on the model for the growth of zeolite boron beta using dibenzyl(dimethylammonium) as the template, as described in Chapter 2, the synthesis of zeolite boron beta with a wide compositional range (Si:B molar ratios of 40 to infinity) is possible under alkali-metal-free conditions and applying relatively high template hydroxide to silicon ratios. Using these synthesis conditions even the synthesis of all-silica beta appeared to be possible. These conditions as a starting point in the synthesis of aluminum- and boron-free titanium containing
zeolite beta analog of the well-known titanium silicalite 1 (TS-1) system.\textsuperscript{32} Recent reports in literature\textsuperscript{13-15} on the synthesis of titanium zeolite beta indeed show that, despite differences in templates used, similar conditions are required for the synthesis of the all-silica zeolite beta or its titanium containing analog. The method is also suitable for the synthesis of well-defined materials with high Si:B molar ratios, which can be used as precursors for transition metal containing materials.\textsuperscript{20,33}

The use of ozone at 110 to 120 °C was found to lead to complete removal the template without loss in XRD-crystallinity. The calcined all-silica material is characterized by a high crystallinity (Figure 3.2), a bimodal poresize distribution in the Horvath-Kawazoe plot (Figure 3.7) with maxima at 5.6 Å and 7.0 Å and an increased hydrophobicity compared to zeolite aluminum beta. The \textsuperscript{29}Si MAS NMR spectrum (Figure 3.6) showed that the interior of the zeolite contains a large amount of defects. These defects were already present in the as-synthesized material and are thought to originate from sites required for template charge compensation in analogy with the site I in our proposed growth model for zeolite boron beta (Figure 3.1).
3.5 References


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Chapter 3


Synthesis and characterization of aluminum-free zeolite titanium beta using a new and selective template.

Abstract

The aluminum-free titanium silicate analogue of zeolite beta was synthesized using di(cyclohexylmethyl)dimethylammonium as the template. The influence of the synthesis conditions was investigated and the formation of highly crystalline zeolite titanium beta appeared to be possible within a narrow chemical and temperature window. The Ti-beta zeolite was characterized using powder-XRD, TEM, SEM, electron diffraction, EDX, UV-Vis, nitrogen adsorption, SAXS and IR. The influence of the external surface on the catalytic activity was determined by catalytic epoxidation experiments using surface sensitive probe molecules.

Evidence was obtained for the isolated incorporation of titanium in the zeolite lattice from UV-Vis and X-ray unit-cell expansion. The UV-Vis spectra showing a single absorption band at 47.000 cm\(^{-1}\) characteristic for fourfold coordinated titanium in a silicate framework. The linear expansion of the unit-cell volume with increasing titanium content corresponds to an average Ti-O bond length of 1.79 Å. EDX showed a homogeneous distribution of titanium over the zeolite framework and the absence of titanium rich phases. The morphology of the crystals is a pillow- or disk-shaped particle with an average diameter of 1.2 μm. Transmission Electron Microscopy (TEM) and the electron diffraction showed that the particles are single beta crystallites. Sometimes a thin amorphous layer or small particles were detected with TEM at the crystal surface. By using 3,5-di-tert-butylphenyl 1-(3-methyl-2-butenyl) ether as a selective bulky probe molecule for external surface titanium sites, it was shown that epoxidation takes place primarily at the titanium sites located in the internal surface of the zeolite.
4.1. Introduction

Since the discovery in 1983 of TS-1, a titanium-containing silicalite-1, by Taramasso et al.\(^1\) much research has been devoted to its synthesis and to its application as an oxidation catalyst for a wide range of oxygenations with hydrogen peroxide. The strength of TS-1 is the combination of isolated tetrahedrally coordinated titanium atoms in a tectosilicate structure and a hydrophobic and acid-free defined environment.\(^2\) An obvious limitation is its pore size of 5.6 x 5.3 Å. Recently various new types of titanium containing molecular sieves and zeolitic materials with large pores have been reported, e.g. Ti-MCM-41\(^3,4\) Ti-ZSM-12,\(^5\) Ti-ZSM-48,\(^6\) TAPSO-5\(^7\) and Ti,Al-beta.\(^8\) Especially the titanium analogue of zeolite beta (Ti-beta) is interesting, since it has a three dimensional structure with channel dimensions of 7.6 x 6.4 Å\(^9\) as well as a hydrophobic interior, provided that aluminum is absent. We have recently shown that it is possible to synthesize all-silica zeolite beta using a more efficient template (dibenzyldimethylammonium, DBDMA\(^+\), 1)\(^10\) than the usually applied tetraethylammonium (TEA\(^+\)) template. The thermal degradation of the DBDMA\(^+\) cation at temperatures above 100 °C under synthesis conditions, makes it not suitable for use in the preparation of Ti-beta. We hereby report the use of di(cyclohexylmethyl)dimethylammonium (DCDMA\(^+\), 2) as a further improved and well-fitting selective template for the titanosilicate analogue of zeolite beta.\(^11\) By applying this new template Ti-beta was synthesized.

![Diagram](image1)

Recently three other articles appeared in which the synthesis of Ti-beta via other methods is described. First, a patent application on an aluminum-free Ti-beta by Saxton et al.\(^12\), applying 4,4'-trimethylene bis(N-benzyl-N-methyl)piperidinium (3) as the template. The use of the "classical" TEA\(^+\) cation as the template has been reported recently by Camblor et
Characterization of Titanium β

but only when a high amount of seeds was present Ti-beta could be obtained. The TEA⁺-Ti-beta contained a high amount of silanol groups, originating mainly from the negatively charged defects required for template charge compensation.

![Chemical Structure](image)

Defect-free materials can be obtained when fluoride instead of hydroxide is used as the mineralizing agent. Blasco et al., also from the Corma group, very recently reported the synthesis of Ti-beta via such a method. The fluoride synthesis of TS-1 is known to yield large crystals with a low amount of defects. Sometimes small particles are formed on the external surface of the zeolite crystals and cannot be excluded that the titanium present in these samples is concentrated in the particles on the external surface. The fluoride synthesis of TS-1 and other titanium zeolites might therefore not be as straightforward as is generally assumed. Furthermore the presence of residual fluoride in these materials is known to have a detrimental effect on the catalytic performance. This residual fluoride strongly binds to the titanium site, preventing the coordination of hydrogen peroxide to the site. This does not have to be a problem since it has been reported that fluoride can be removed quantitatively from titanium-containing all-silica materials by calcination in slightly moist air.

This chapter describes the synthesis of an aluminum-free, titanium-containing zeolite beta using di(cyclohexylmethyl)dimethylammonium as the template and the characterization of the materials obtained. The crystallinity is determined by XRD, electron diffraction and SAXS. The incorporation of titanium in the zeolite framework is studied by UV-Vis, IR, cell-contraction and EDX. The macroscopic properties of the zeolite particles are determined using SEM, nitrogen adsorption. The microscopic properties of the zeolites are investigated using TEM, HREM and electron diffraction. The activity of the outer surface is determined by catalytic epoxidation using a bulky probe molecule having no access to the inner surface.
4.2 Experimental

4.2.1 Template preparation

N,N-dimethyl(cyclohexylmethyl)amine was prepared from cyclohexylmethanol via the tosylate which was prepared by the slow addition of 209.7 g (1.1 mol) p-toluenesulfonyl chloride to a vigorously stirred mixture of 114.2 g (1.0 mol) cyclohexylmethanol and 158 g (2.0 mol, 200 ml) dry pyridine at 2 to 10 °C. After the addition of the tosyl chloride the mixture was allowed to react further for 3 h at 10 °C. Subsequently 200 ml 36 wt% aqueous hydrochloric acid and 600 ml ice were added to the reaction mixture to neutralize the pyridine present and to precipitate the crude tosylate. After filtration the crude tosylate was recrystallized from petroleum ether (bp. 40 - 60 °C) at -18 °C. The solid product was collected by filtration and the adhering petroleum ether removed under vacuum in a desiccator. The yield of tosylate was 221.6 g (0.825 mol).

The tosylate was subsequently converted to the corresponding tertiary amine. To 100 g (0.37 mol) cyclohexylmethyl tosylate in 100 ml N,N-dimethylformamide was added 34.1 g (0.76 mol) aqueous dimethylamine (40 wt%) and the reaction mixture was heated to 50 °C for at least 5 h. The reaction mixture was acidified with hydrochloric acid to separate the unreacted tosylate from the amine, followed by neutralization with sodium hydroxide to rectify the amine. The amine was dried over magnesium sulfate and distilled under reduced pressure (bp. 69 °C at 20 mm Hg). The yield of N,N-dimethyl(cyclohexylmethyl)amine was 44.1 g (0.33 mol), purity >99 % as determined with GC.

Di(cyclohexylmethyl)dimethylammonium bromide (DCDMA.Br) was synthesized from 92.9 g cyclohexylmethyl bromide (0.525 mol, 98%, Aldrich) and 69.5 g N,N-dimethyl(cyclo-

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4.2.2 Zeolite synthesis

In a typical synthesis of Ti-beta, 0.25 g titanium(IV) ethoxide (TEOT, Acrós) was added to 30.0 g of a 19.5 wt% DCDMA.OH aqueous solution and the mixture was stirred until all the TEOT was dissolved. To facilitate the dissolution of the TEOT, 1 ml of H₂O₂ (30 wt% aqueous) was added. To the clear solution 3.0 g Aerosil 200 (Degussa), 0.15 g seeds (all-silica beta¹⁰) and 11.8 g water were added and the gel was aged for at least 24 h until an opalescent gel with low viscosity was obtained. The molar gel composition was:

\[ 1 \text{SiO}_2 : 0.022 \text{TiO}_2 : 0.46 \text{DCDMA.OH} : 38 \text{H}_2\text{O} \]

After hydrothermal crystallization for two weeks at 140 °C the zeolite was filtrated, washed, dried and calcined at 540 °C in air (yield 1.4 g, 45 % silicon incorporation). Synthesis parameters studied were the amount of titanium, template and the presence of seeds. The titanium content was varied between 0 and 0.05, the DCDMA.OH content was varied between 0.15 and 0.50. In absence of seeds, crystallization required 8 weeks to attain full crystallinity.

4.2.3 Catalyst characterization

UV-Vis spectra were recorded on a Varian Cary-1 spectrophotometer using barium sulfate as a reference. FT-IR spectra were recorded on a Bruker IFS 66 photospectrometer under the attached IR-microscope. X-Ray powder diffractograms were recorded on a Philips PW 1840 powder diffractometer using CuKα-radiation. The intensity of the peak at 2θ ≈ 22.5° (indexed as 302 for polytype A, d_{302} ≈ 3.94 Å)⁹ was taken as a measure of crystallinity. The exact position of the reflection at 2θ ≈ 43.5° (indexed as 600 for polytype A) was determined using a Guinier-De Wolf camera with quartz as internal standard. ¹³C MAS NMR and ²⁹Si MAS NMR, ¹³C liquid-phase NMR measurements were performed on a Varian VXR-400 S 400 MHz. Scanning electron microscopy (SEM) was carried out on a Philips XL-20 apparatus. Transmission electron microscopy (TEM) was performed using a Philips CM 30 ST electron microscope with a field emission gun as the source of electrons at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets
of a suspension of the ground sample in ethanol on the grid, followed by drying at ambient conditions. Under the same conditions, elemental analysis was performed using a LINK EDX attached to the TEM. Small Angle X-Ray Scattering (SAXS) spectra of Ti-beta was measured at the Universität Rostock, Mathematisch-Naturwissenschaftliche Fakultät. Chemical analyses of the zeolites were done on a Perkin-Elmer Plasma 40 (ICP-AES) apparatus or on a Perkin-Elmer 110 (AES) apparatus. Determinations of the micropore and mesopore areas and the micropore volume were performed on a Quantachrome Autosorb 6 and calculated according to the BET method.

4.3. Results and discussion

4.3.1 Synthesis of zeolite titanium beta

The possibility to synthesize the all-silica variety of zeolite beta using dibenzyl-dimethylammonium 1 (DBDMA⁺) as the template,¹⁰ opened the way for the synthesis of the TS-1 analogue of zeolite beta. Initial experiments using DBDMA⁺ as the template were unsuccessful due to the thermal instability of this cation at elevated temperatures (T > 100 °C), see Chapter 2 of this thesis. This instability is caused by the relatively weak benzyl-nitrogen bond which breaks heterolytically to yield the relatively stable benzyl cation. In order to increase the thermal stability of the template, it was found that the fully hydrogenated form, di(cyclohexylmethyl)dimethylammonium 2 (DCDMA⁺) is a stable and selective template for the synthesis of aluminum-free titanium containing zeolite beta (Ti-beta). For compound 2 Hoffman degradation is possible, but apparently slow.

Table 4.1 shows the results of six Ti-beta syntheses. Excellent results were obtained with Si:Ti molar ratios between 50 and 80 and a H₂O:Si molar ratio of 38. Higher dilution (H₂O:Si = 97) or high Ti:Si ratios (>600) were found to give materials with lower crystallinity after two weeks. It these cases a prolonged synthesis time was required to obtain highly crystalline materials.
Table 4.1  X-Ray crystallinity and chemical composition of zeolites used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>XRD crystallinity&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Si:Ti gel&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Si:Ti zeolite</th>
<th>Si:Al&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Si:B&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-beta-1</td>
<td>100</td>
<td>54</td>
<td>59</td>
<td>&gt;2600</td>
<td>&gt;1600</td>
</tr>
<tr>
<td>Ti-beta-2</td>
<td>98</td>
<td>80</td>
<td>69</td>
<td>&gt;3000</td>
<td>&gt;1400</td>
</tr>
<tr>
<td>Ti-beta-3</td>
<td>104</td>
<td>50</td>
<td>58</td>
<td>&gt;2500</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ti-beta-4&lt;sup&gt;d&lt;/sup&gt;</td>
<td>e</td>
<td>50</td>
<td>e</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Ti-beta-5</td>
<td>92&lt;sup&gt;f&lt;/sup&gt;</td>
<td>20</td>
<td>47</td>
<td>&gt;3000</td>
<td>&gt;1800</td>
</tr>
<tr>
<td>Ti-beta-6</td>
<td>86</td>
<td>600</td>
<td>287</td>
<td>&gt;2800</td>
<td>n.d.</td>
</tr>
<tr>
<td>Si-beta</td>
<td>71&lt;sup&gt;g&lt;/sup&gt;</td>
<td>$\infty$</td>
<td>&gt;2000</td>
<td>&gt;2500</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

<sup>a</sup> Intensity of Ti-beta-1 is taken as reference for 100% crystallinity.  
<sup>b</sup> Gel composition 1 SiO$_2$ : x TiO$_2$ : 0.46 DCDMA.OH : 38 H$_2$O; 14 days at 140 °C.  
<sup>c</sup> Detection limit of ICP-AES.  
<sup>d</sup> H$_2$O:Si ratio was increased to 97, synthesis time 14 weeks at 140 °C.  
<sup>e</sup> Amount of material was too small to accurately determine crystallinity, zeolite beta is the only phase detected and crystallinity was at least 80%.  
<sup>f</sup> Also ± 10 % MTW present.  
<sup>g</sup> After 6 weeks at 140 °C.

The X-ray diffraction pattern (Figure 4.1) showed that pure zeolite beta was synthesized and small amounts of ZSM-12 (less than 3 %) could only be detected after prolonged crystallization times, which demonstrates the high selectivity of the DCDMA<sup>+</sup> cation as a template for beta type zeolites. ICP-AES of the as-synthesized materials (Table 4.1) confirmed the presence of titanium and the absence of aluminum and boron (Si:Al > 2500; Si:B > 1400). Close examination of the peak at 2θ ≈ 7.5 °, showed that the fault plane, as defined by Newsam et al.,<sup>23</sup> was independent of the Si:Ti molar ratio and that neither of the two polymorphs crystallized preferentially.
Figure 4.1  X-Ray diffractogram of as-synthesized zeolite titanium beta (sample Ti-beta-1).

The relatively high amount of template necessary (template:Si $\approx 0.5$), whereas only a template:Si ratio of 0.0833 is incorporated in the zeolite, and the relatively long synthesis times (2 weeks for a seeded synthesis, about 4 weeks for a non-seeded synthesis) induced us to investigate the influence of the template:Si molar ratio and of the temperature on the crystallization of Ti-beta. Figure 4.2 shows the influence of the template:Si molar ratio and of the temperature on the formation of Ti-beta. It is clear that both parameters have a strong influence on the amount of crystalline material formed. The decreased yields of Ti-beta at higher temperatures and the influence of the DCDMA.OH:Si molar ratio on the yield of crystalline material suggest that the formation of Ti-beta is governed by thermodynamic principles. High template concentrations favour the zeolite formation. At higher temperature the high alkalinity favours dissolution of silica more than the crystallization of the zeolite framework. At lower temperatures, longer synthesis times are required to attain the maximal obtainable crystallinity.
Figure 4.2 Crystallinity as a function of synthesis temperature and template content (2 wt% seeds, 2 weeks synthesis). DCDMA.OH:Si molar ratio $\bullet = 0.5$; $\nabla = 0.35$; $\bullet = 0.25$; $\blacktriangle = 0.15$.

In contrast to the Ti-beta synthesis reported by Camblor et al.\textsuperscript{8} the high hydroxide to silicon ratio does not keep the incorporation efficiency of silicon low. In the present work the incorporation efficiency for silicon ranged from 49 to 56 %, which is significantly higher than the silicon efficiencies of 15 to 20 % when TEA is used as the template.\textsuperscript{8} Very high yields on silicon, near 100%, are reported by Corma et al.\textsuperscript{14} for the fluoride synthesis of Ti-beta, but catalytic results for titanium zeolites prepared in fluoride synthesis mixtures are usually not so good.\textsuperscript{15}

The incorporation efficiency of titanium in the framework is strongly dependent on the initial Si:Ti molar ratio of the gel. At high Si:Ti molar ratios an incorporation efficiency for titanium of 95% is found. At low Si:Ti molar ratios the incorporation efficiency decreases significantly. From Figure 4.3 it can be seen that the maximum amount of titanium which can be incorporated is about 0.025. This corresponds to a Si:Ti molar ratio of about 40, which is about the same ratio as reported in literature\textsuperscript{24} for the maximum incorporation of titanium in TS-1.
Figure 4.3 Influence of the initial molar Ti/(Ti+Si) fraction of the gel on the final Ti/(Ti+Si) fraction in the zeolite.

The $^{13}$C MAS NMR spectrum of the as-synthesized zeolite shows that the resonances of the CH$_3$ and CH$_2$-N groups of the occluded template cation are shifted substantially compared to the dissolved template cations (Figure 4.4, Table 4.2). The CH$_3$ carbon signal shifts from 73.4 ppm to 66.6 ppm, while the CH$_2$-N carbon signal shifts from 52.2 to 43.9 ppm. The position of resonances for the carbons in the ring also seem to shift. The observed shifts can be explained by assuming that the template molecule in the zeolite channel is fixed in the pores of the zeolite channels. Molecular Mechanics calculations (Figure 4.5) show that the DCDMA$^+$ cation adopts a similar position in the beta framework as the DBDMA$^+$ cation (see Figure 2.7 in Chapter 2). Similar to the DCDMA$^+$ cation, shifts in chemical shifts for the $^{13}$C NMR signal of the template cation is also observed for the dibenzyldimethyl cation in zeolite beta channels (see section 2.3.1 of Chapter 2). In both cases the largest shifts are observed for the CH$_2$-N and CH$_3$-N signals
Figure 4.4 \(^{13}\)C NMR of di(cyclohexylmethyl)dimethylammonium. a) \(^{13}\)C MAS NMR of as-synthesized zeolite Ti-beta-2, b) APT \(^{13}\)C NMR of DCDMA.Br in D\(_2\)O.

Table 4.2 \(^{13}\)C NMR chemical shifts for the di(cyclohexylmethyl)dimethylammonium cation in solution (as the bromide) and occluded in the framework of zeolite beta.

<table>
<thead>
<tr>
<th>Carbon atom</th>
<th>(\delta) liquid phase</th>
<th>(\delta) zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td>a CH(_3)-N</td>
<td>73.39</td>
<td>66.57</td>
</tr>
<tr>
<td>b CH(_2)-N</td>
<td>52.21</td>
<td>43.87</td>
</tr>
<tr>
<td>c C-(CH(_2))(_3)</td>
<td>33.39</td>
<td>36.92</td>
</tr>
<tr>
<td>d or e CH(_2) ring</td>
<td>26.85</td>
<td>27.06</td>
</tr>
<tr>
<td>d or e CH(_2) ring</td>
<td>34.37</td>
<td>32.70</td>
</tr>
<tr>
<td>f CH(_2) ring</td>
<td>26.52</td>
<td>27.82</td>
</tr>
</tbody>
</table>
Figure 4.5  Optimal geometry of the di(cyclohexylmethyl)dimethylammonium cation as determined by molecular mechanics in zeolite beta. (Left) view along the $a$-axis of the crystal. (Right) view along the $b$-axis of the crystal.

4.3.2 Incorporation of titanium in the framework.

With comparative EDX chemical analysis of Ti-beta-1, Ti-beta-2 and Ti-beta-3 the location and variation of titanium in the zeolite was determined (Figure 4.6). It was found for all the zeolites tested that the Si:Ti molar ratio is nearly identical over the whole of the zeolite particle (Figure 4.6a) and does not significantly change for different particles of one batch. A number of protrusions and amorphous patches on the outer-surface of Ti-beta-2 were also measured using EDX to determine the titanium content of these particles. The Si:Ti molar ratio in the amorphous patches (Figure 4.6b) and protrusions (Figure 4.6c) was either identical to the bulk Si:Ti molar ratio or no titanium could be detected at all. No protrusions were found which showed high amounts of titanium and no silicon. It is concluded that titanium is homogeneously distributed over the zeolite framework and that no titanium dioxide phases have been formed during synthesis.
The incorporation of titanium can be monitored by the change in the unit-cell volume as a function of titanium content. The basis is that in tetrahedral configuration the Ti-O bond length, $d_{\text{Ti-O}}$, longer is than the $d_{\text{Si-O}}$ (1.76 Å and 1.59 Å, respectively), causing the lattice to expand slightly upon incorporation of Ti.\(^{25}\) The unit-cell volume, $V(x)$, is dependent on the fraction titanium, $x$, in the zeolite according to equation (4.1). The expected variation of unit-cell volume $V(x)$, when replacing $\text{SiO}_4^{2-}$ framework species by $\text{TiO}_4^{2-}$ species, can be calculated under the assumption that each tetrahedron contributes equally to the volume occupancy in the crystal proportionally to $d_{\text{T-O}}^3$, with $d_{\text{T-O}}$ the oxygen T-atom bond distance. For a mixed Ti/Si framework the unit-cell volume $V(x)$ is:
\[ V(x) = V_{all-silica} \left( 1 + x \left( \frac{\frac{d^3_{Ti-O}}{d^3_{Si-O}}}{1} \right) \right) \]  

(4.1)

with \( x \), the fraction of titanium sites, equal to Ti/(Ti+Si).

Since the \( c \)-axis of zeolite beta is disordered, determination of the unit-cell volume is not so easy. We therefore chose to monitor the change in the length of the \( a \)-axis \( L_a(x) \). Formula (4.1) then reduces to equation (4.2). This is, however, only allowed if expansion is isotropic in all directions. Camblo et al.\(^8\) showed that this approach was allowed for Ti,Al-beta and we therefore assume the same for Ti-beta.

\[ L(x) = L_{all-silica} \left( 1 + x \left( \frac{d^3_{Ti-O}}{d^3_{Si-O}} - 1 \right) \right) \]  

(4.2)

As can be seen in Figure 4.7 a linear relation exists between the fraction of titanium in the zeolite beta samples and the length of the \( a \)-axis for the calcined materials. Calculation of the titanium-oxygen bond length from the slope yields a \( d_{Ti-O} \) of 1.79 \( \pm \) 0.06 Å, which is only slightly higher than the values reported for TS-1,\(^{26,27}\) The average \( d_{Ti-O} \) distance in the MFI type zeolite was found to vary between 1.65 and 1.80 Å. The observed \( d_{Ti-O} \) corresponds well to the mean crystallographically determined value of 1.786 Å\(^{28}\) for tetrahedrally coordinated titanium in Ba\(_2\)TiO\(_4\) or CsAlTiO\(_4\) and the theoretically calculated value of 1.80 Å using ab initio quantum mechanical calculations.\(^{29}\) The observed linear expansion of the \( d_{100} \) with the titanium content, the value of 1.79 for the Ti-O bond length and the absence of titanium dioxide phases as shown by EDX, confirmed the incorporation of titanium in the framework of zeolite beta.

Figure 4.7 also shows that the length of the \( a \)-axis hardly changes for the as-synthesized materials. The as-synthesized all-silica material and the Ti-beta samples with very high Si:Ti molar ratios actually have a longer \( a \)-axis than the calcined materials. This suggests that the template is slightly too bulky for the channel geometry of all-silica zeolite beta and the system compensates this by a slight expansion of the zeolite framework. This is also reflected in the longer synthesis times required and the lower XRD crystallinity of very high Si:Ti type materials (Table 4.1). The all-silica synthesis had a XRD crystallinity of only 71%
after six weeks at 140 °C, while fully crystalline materials were obtained within two weeks for Si:Ti molar ratios around 50. The following reasoning might apply. The incorporation of the DCDMA⁺ cation during synthesis apparently causes an expansion of the zeolite framework, which is energetically unfavourable. By incorporating titanium in the zeolite framework, the larger d_{Ti-O} bond length causes a unit-cell expansion, which is used to compensate the required expansion of the framework caused by the DCDMA⁺ template. As can be seen from the expansion of the α-axis (Figure 4.7) the optimal titanium fraction would be about 0.020, which corresponds well with the maximum Si:Ti molar ratio of 40 observed by changing the titanium fraction of the gel (Figure 4.3).

![Graph showing interplanar spacing as a function of titanium content.](image)

Figure 4.7 Interplanar d_{100} spacing (α-axis) of zeolite beta samples as a function of the titanium content. ● = as-synthesized; ■ = calcined.

4.3.3 State of titanium in the zeolite framework

Some direct information on the state of the titanium was obtained from diffuse reflectance UV-Vis charge-transfer spectrophotometry³⁰,³¹ and infrared spectroscopy.³² The incorporation of titanium in the zeolite framework was confirmed by the presence of a strong absorption maximum at 47,000 - 50,000 cm⁻¹ in the UV-Vis spectra (Figure 4.8). This absorption is attributed to tetrahedrally coordinated titanium in a silicate framework.³⁰,³¹ In the presence
of water or 2-propanol the absorption band is shifted towards a lower frequency (45.000 - 48.000 cm\(^{-1}\)), which is generally accepted as an indication for a higher coordination number around the titanium atom, most probably five coordinated. In the case of water a second weak absorption around 36.000 - 40.000 cm\(^{-1}\) is observed. Absorptions below 40.000 cm\(^{-1}\) are usually attributed to octahedral titanium species.\(^{30}\) The absence of an absorption below 30.000 cm\(^{-1}\) in the as-synthesized zeolite confirms the absence of more highly clustered titanium oxide phases.\(^{30}\)

Figure 4.8 UV-Vis of Ti-beta-2 and the effect of hydroxylic compounds. The sample was pre-dried at 200 °C, water and 2-propanol was added to the sample (0.18 g\(_{\text{adsorbate}}\) g\(^{-1}\) zeolite) at room temperature.

Since the discovery of TS-1 by Taramasso \textit{et al.},\(^1\) methods of vibrational spectroscopy have been widely applied to characterize the titanium site in zeolites. In the infrared spectra of titanium zeolites a distinct absorption peak at approximately 960 cm\(^{-1}\) is normally found.\(^{30,33-39}\) The origin of this band is still not elucidated. The absorption at 960 cm\(^{-1}\) in the FT-IR spectra of TS-1 is usually taken as a confirmation of titanium in the zeolite\(^{32}\) although no relation between the intensity of this band and the titanium content or the catalytic activity is observed. Several assignments have been proposed to explain this band. Boccuti \textit{et al.}\(^{30}\) and
Pilz et al.\textsuperscript{33} assigned it to a stretching vibration of a polarized Si-O\textsuperscript{5-}···Ti\textsuperscript{5+} of fourfold coordinated titanium (Figure 4.9a). Camblor et al.\textsuperscript{34} assigned it to Si-O\textsuperscript{−} or Si-OH defects generated by the incorporation of titanium into the framework (Figure 4.9b). Recently Crocker et al.\textsuperscript{40} showed by probing the titanium site with SO\textsubscript{2} that the 960 cm\textsuperscript{-1} band can not be assigned to Ti=O groups as proposed by Sheldon\textsuperscript{41} and Huybrechts et al.\textsuperscript{35} (Figure 4.9c). A recent computational study by Smirnov et al.\textsuperscript{42} showed that the 960 cm\textsuperscript{-1} band can be assigned to a localized Si-O mode of a Si-O···Ti group due to the inequivalence of the Si-O and Ti-O bonds, in line with the assignments given by Boccuti et al.\textsuperscript{30} (Figure 4.9a).

![Diagram showing proposed Titanium sites. a) Fourfold coordinated.\textsuperscript{30,33} b) Defect site\textsuperscript{34} c) Titanyl.\textsuperscript{35,41}](image)

As can be seen in Figure 4.10, both the calcined and the as-synthesized Ti-beta contain a band at 960 cm\textsuperscript{-1}. However, the FT-IR spectrum of calcined all-silica beta also exhibits a strong band around 960 cm\textsuperscript{-1}, characteristic of silanol groups. More surprisingly is the large amount of water present in the calcined material at room temperature. Since the material is essentially aluminum free, it was expected that the material was hydrophobic. Analysis of the Ti-beta-2 sample using $^{29}$Si MAS NMR (Figure 4.11) showed a large signal at δ -98 to -106 ppm, characteristic of Si(OSi)$_3$OH groups. The increase in the intensity of the absorption at 960 cm\textsuperscript{-1} in calcined Ti-beta therefore suggests a large amount of silanol groups to be present, originating from defect sites which are required for template charge compensation during synthesis.\textsuperscript{10} This restriction does not apply to the as-synthesized zeolite Ti-beta in which the silanol absorption band is normally not visible. However, care should be taken since the DCDMA\textsuperscript{+} cation itself has also a weak absorption band at 960 cm\textsuperscript{-1}. The use of infrared techniques is therefore not so straightforward in the characterization of titanium in the
framework of beta type zeolites. The high amount of silanol groups \( \frac{Q^3}{(Q^3 + Q^4) \approx 0.15} \) is probably the cause of the increased hydrophillic character, as shown by the adsorbed water in the IR spectrum of Ti-beta-2 at room temperature (Figure 4.10).

![Figure 4.10 FT-IR of zeolite Ti-beta-2. a) as-synthesized; b) calcined.](image)

Figure 4.10 FT-IR of zeolite Ti-beta-2. a) as-synthesized; b) calcined.

![Figure 4.11 ²⁹Si MAS NMR of calcined zeolite Ti-beta (sample Ti-beta-2).](image)

Figure 4.11 ²⁹Si MAS NMR of calcined zeolite Ti-beta (sample Ti-beta-2).
The coordination around the titanium atom can be determined from the observed Ti-O bond length. The Ti-O bond length is smaller for tetrahedral coordination than for octahedral coordination (1.79 Å and 2.00 Å, respectively). Small Angle X-ray Scattering (SAXS) is a known method for the determination of the coordination number of silicon and titanium and of Si-O and Ti-O distances in amorphous oxides.\textsuperscript{54} Using this technique a reduced diffraction curve $i(q)$ is obtained which, after Fourier-transformation, yields the radial density function $G(r)$ (Figure 4.12). The difference in bond distance of Si-O and Ti-O (1.59 and 1.79 Å, respectively) should be shown by a distinct peak in the $G(r)$ function. Close examination of the $G(r)$ function for Ti-beta-1 shows the presence of maxima at 1.6, 2.7, 3.2 and 4.1 Å, which correspond to the Si-O, O-O, Si-Si and Si-O\textsuperscript{11} distances in zeolite beta, respectively. The presence of a Ti-O band at 1.79 Å, indicative for fourfold coordinated Ti-O species, could not be observed due to the low amount of titanium in the material used (Ti-beta-3, \ensuremath{\approx} 1.6 wt%). The Ti-O peak is probably present under the Si-O peak or is simply not intense enough to show up after the curve fitting procedures. Comparing the $G(r)$ function of the Ti-beta zeolite with that of an amorphous silica, shows an excellent fit in the short distance ordering ($< 4$ Å). The clearer pattern at higher values of $r$ (Å) for Ti-beta-1 is a reflection of the higher ordering of SiO$_4$-units in the zeolite framework compared to that in the amorphous silica.

![Graph](image)

Figure 4.12 Radial density function determined \textit{via} SAXS of a) Ti-beta-3 and b) amorphous silica.
Chapter 4

It is concluded from the UV-Vis and IR spectra and from the EDX analysis that titanium is tetrahedrally incorporated in the zeolite lattice, is accessible for substrates and that no oligomeric titanium oxides are present. The coordination number and position of oxygen atoms around the framework titanium sites could not be established by SAXS. This was due to the low amount of titanium species in the materials used. The method only shows the higher degree of crystallinity of the zeolite in the range of 4 to 10 Å, which is not surprising since zeolites are highly ordered silicates.

4.3.4 Particle size and morphology

A study of the Ti-beta samples by Scanning Electron Microscopy (SEM, Figure 4.13) shows that regular particles with a pillow-shaped morphology are formed. A normal synthesis of zeolite aluminum beta according to Wadlinger et al.,43 using tetraethylammonium as the template, generally yields cauliflower-shaped spheres, which are conglomerates of very small nanocrystallites. Clearly faceted crystals of zeolite beta have a bipyramidal-like structure as shown by Marler et al.,44 Caullet et al.45 and Kunkeler et al.55 applying more specific templates or using fluoride as the mineralizing agent. If large crystals are formed with tetraethylammonium as the template,36 the crystal morphology resembles the bipyramidal form with the exception that the growth in the c-direction is inhibited. The a,b-plane in the middle of the crystal is an almost perfect square.46 SEM pictures of our Ti-beta samples show that the particles are rather flat in the c-direction and have a very rough surface (Figure 4.13, Table 4.3).

For catalytic purposes small crystal sizes are usually preferred in order to eliminate internal diffusion limitations. Van der Pol and van Hooij47 clearly showed by varying zeolite particle size that diffusion limitations are present when TS-1 particles larger than 0.2 μm were used as catalyst for the hydroxylation of phenol. In connection with our study of the reaction kinetics in the epoxidation of alkenes, see Chapter 7 of this thesis, particles of three catalysts were investigated by electron diffraction. The observed electron diffraction patterns (EDP) for
all three catalysts were the same. Figure 4.14a shows a clear spot pattern when the electron beam is directed orthogonal to the flattened part of the crystal. This observed pattern corresponds to the \( h0l \) diffraction pattern with sharp reflections on \( h = 3n \). If the crystal is subsequently tilted over 86° the spot pattern disappears almost completely. The pattern in Figure 4.14b only shows a few spots and a diffuse ring. This pattern corresponds to the \( hkl \) diffraction pattern.\(^{44}\) Apparently the TEM picture in Figure 4.14c corresponds to a view on the \( a,b \)-plane of the crystal, viewed along the \( c \)-axis. The angle of 90° of the corners corresponds to the \( \gamma = 90^\circ \) expected for the 110 plane.\(^{44}\)

![Image](image_url)

a) Ti-beta-1 (Magn. 7,000 x)  
b) Ti-beta-1 (Magn. 20,000 x)

c) Ti-beta-3 (Magn. 5,400 x)  
d) Ti-beta-4 (Magn. 8,200 x)

**Figure 4.13** Scanning electron microscopy (SEM) of various Ti-beta samples, (bar indicates 1 \( \mu \)m). a) Ti-beta-1; b) Ti-beta-1 (enlarged); c) Ti-beta-3; d) Ti-beta-4.
Table 4.3  Crystal size and morphology as determined by SEM for various Ti-beta catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average particle diameter [μm]</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-beta-1</td>
<td>1.30</td>
<td>uniform, pillow-shaped spheres</td>
</tr>
<tr>
<td>Ti-beta-2</td>
<td>1.10</td>
<td>uniform, pillow-shaped spheres</td>
</tr>
<tr>
<td>Ti-beta-3</td>
<td>1.20</td>
<td>pillow-shaped spheres</td>
</tr>
<tr>
<td>Ti-beta-4</td>
<td>4.30</td>
<td>uniform, pillow-shaped spheres</td>
</tr>
</tbody>
</table>

For catalytic purposes a wide range of crystal diameters is preferred as to verify the presence of diffusion limitations (see Chapter 7). As mentioned above, synthesis of zeolite Ti-beta is only possible within a narrow temperature range (135 to 150 °C) and a narrow DCDMA.OH:Si molar ratio (about 0.5), with little variation in both parameters allowed. In order to obtain larger crystals the H₂O:Si molar ratio of the gel was increased from 38 to 97 and no seeds were added. Dilution of a gel suppresses nucleation, generally resulting in larger crystals. The decreased nucleation rate also means that the overall crystallization time increases. It was found that instead of the 4 weeks usually required for a non-seeded synthesis, the synthesis mixture required 14 weeks to crystallize completely. By this method, the average particle diameter had increased to 4.3 μm (Catalyst Ti-beta-4, Table 4.3).

Based on the sharp electron diffraction patterns observed for all three batches (Figure 4.14a), the high regularity of the crystals viewed along the c-axis and the intense and sharp XRD-patterns (Figure 4.1, Table 4.1), it is concluded that zeolite titanium beta is obtained with a well defined morphology of highly crystalline single crystals with dimensions of 1.1 to 1.3 μm and disk- or pillow-shaped morphology. The highly crystalline nature of the materials is also reflected in the High Resolution Electron Microscopy image of sample Ti-beta-2 (Figure 4.15). A regular pattern over a wide area in the a,b-plane is clearly visible, further underlying the excellent templating properties of the DCDMA⁺ cation for beta type materials. The white spots in this highly crystalline part have a periodicity of 12.4 Å, which corresponds well with the average distance of 13.0 Å between the pore openings of zeolite beta in the c-direction as reported by Marler et al.⁴⁴
Figure 4.14  Electron diffraction patterns (EDP, a and b) and transmission electron microscopy (TEM, c and d) of a single zeolite crystal of catalyst Ti-beta-2. a,c) View at the $h0l$ plane of a single crystal; b,d) Same crystal 86° rotated to show the $hk0$ plane.
4.3.5 Catalyst outer-surface properties

Recent literature on the catalytic behaviour of the outer surface of zeolites shows that especially for beta type zeolites the outer surface plays an important role. Three catalysts (Ti-beta-1, Ti-beta-2 and Ti-beta-3), which had the same XRD crystallinity (Table 4.1), similar SEM pictures (Figure 4.13) were investigated using transmission electron microscopy (TEM) and nitrogen adsorption. Close inspection with TEM (Figure 4.16) of the outer-surface of the three investigated catalysis, revealed remarkable differences. Hardly any amorphous material is observed on Ti-beta-1 (Figure 4.16a) while a thin continuous amorphous layer of about 20 to 50 Å is visible on Ti-beta-2 (Figure 4.16b). The surface of the material denoted as Ti-beta-
Characterization of Titanium β

3 is found to have either a thin amorphous layer of 50 to 150 Å (Figure 4.16c) or patches of amorphous material (Figure 4.16d).

Further information about the pores of the catalysts was obtained by N₂-adsorption experiments, from which the micropore volume and area was calculated according to the BET method. All three catalysts had a very low mesopore area (15 to 20 m² g⁻¹ zeolite, Table 4.4) compared to the micropore surface area (about 660 to 680 m² g⁻¹ zeolite, Table 4.4) and a micropore volume of 0.27 to 0.28 cc g⁻¹ zeolite. The low mesopore areas observed further, the high regularity of the HREM micrograph and the well-resolved electron diffraction pattern, confirm that the particles observed with SEM and TEM (Figure 4.13 and 4.16) are most probably single crystals and not agglomerates of smaller crystals. The micropore volumes and micropore areas observed correspond well with those reported in literature for macroporous zeolite α-alumina and all-silica θ. Comparing the micropore characteristics of the titanium beta zeolites with those of a highly macroporous aluminum beta zeolite, which was reported by Kunkeler et al. to consist of large crystals (> 1 μm) with the truncated bipyramidal morphology, also demonstrated the high quality of our materials. We therefore conclude that Ti-beta-1, and also to a lesser extent Ti-beta-2 and Ti-beta-3, consist of well-formed crystals with a small external surface compared to the internal surface.

Table 4.4 Nitrogen adsorption data for Ti-beta samples, determined via the de Boer t-method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Micropore volume [cc g⁻¹ zeolite]</th>
<th>Micropore area [cc g⁻¹ zeolite]</th>
<th>Mesopore area [m² g⁻¹ zeolite]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-beta-1</td>
<td>0.279</td>
<td>687</td>
<td>18</td>
</tr>
<tr>
<td>Ti-beta-2</td>
<td>0.269</td>
<td>661</td>
<td>15</td>
</tr>
<tr>
<td>Ti-beta-3</td>
<td>0.282</td>
<td>662</td>
<td>19</td>
</tr>
<tr>
<td>Si-beta</td>
<td>0.266</td>
<td>673</td>
<td>42</td>
</tr>
<tr>
<td>Al-beta</td>
<td>0.266</td>
<td>656</td>
<td>12</td>
</tr>
</tbody>
</table>

a All-silica beta samples prepared according to van der Waal et al. b Macroporous material, from Kunkeler et al.
Figure 4.16  Transmission electron microscopy (TEM) of the hk0 edge of Ti-beta. a) Ti-beta-1; b) Ti-beta-2; c) and d) Ti-beta-3 at different crystals.
Recently Creighton et al. developed a probe molecule, allyl 3,5-di-tert-butylphenyl ether 4, for the determination of the external surface catalytic activity of large pore zeolites. The spatial geometry of this probe molecule (11.0 x 10.8 x 5.8 Å) is too large to enter the pores of zeolite beta (7.6 x 6.4 Å) and to pass twelve-membered rings of zeolites. Compound 4 is multifunctional in that it can be used for the determination of the amount of outer-surface noble-metal particles via hydrogenation of the allyl ether, or it can probe external Brønsted acid sites by the acid-catalyzed Claisen-rearrangement. TS-1 is known to epoxidize allyl ethers and allyl alcohols. We recently showed the possibility of epoxidizing allylic alcohols over Ti-beta. The allylic functional group of the probe can therefore in principle also be used for testing the external surface epoxidation activity of titanium zeolites. However, as shown in Table 4.5, Ti-beta displays a negligible activity in the epoxidation of the sterically unhindered allyl phenyl ether to glycidyl phenyl ether. This is probably due to the presence of a phenoxy group at the allylic position; the electron withdrawing properties of this group deactivate the C=C double bond for electrophilic epoxidation.

Table 4.5 Determination of the activity of surface of Ti-beta in the epoxidation of alkenes.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>mmol substrate</th>
<th>TOF [mol mol⁻¹ Ti h⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-octene, as-synthesized catalyst</td>
<td>20</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>1-octene, calcined catalyst</td>
<td>20</td>
<td>148</td>
</tr>
<tr>
<td>allyl phenyl ether</td>
<td>5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>allyl 3,5-di-tert-butylphenyl ether 4</td>
<td>5</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>1-(3-methyl-2-butenyl) phenyl ether</td>
<td>10</td>
<td>12.9</td>
</tr>
<tr>
<td>3,5-di-tert-butylphenyl 1-(3-methyl-butenyl) ether 5</td>
<td>11</td>
<td>≈0.5²</td>
</tr>
</tbody>
</table>

²Experimental conditions: 5-20 mmol substrate, 10 mmol H₂O₂ (30 wt% aqueous) in 24 g acetonitrile, 50 mg catalyst Ti-beta-1 at 70 °C. b Ether splitting to the corresponding phenol is observed, approx. 6 mol% after 3h.
Elings et al.\textsuperscript{53} showed that the dimethyl substituted probe molecule 5 can also be used for the determination of external surface acid activity, although the Claisen-rearrangement of 5 is not so straightforward as for the allyl ether 4. Several acid-catalyzed secondary products are easily formed. The addition of electron donating groups to the C=C double bond \textit{i.e.} two methyl groups, enhances the activity towards epoxidation.\textsuperscript{21} Despite the two additional methyl groups, the activity of 1-(3-methyl-2-butanyl) phenyl ether is still rather low (Table 4.5). However, the activity of the bulky probe molecule, 3,5-di-\textit{tert}-butylphenyl 1-(3-methyl-2-butanyl ether) 5, is still an order of magnitude lower. It is therefore concluded that epoxidation by titanium sites occurs predominantly at titanium sites \textit{within} the pores of the zeolite. It also illustrates the wide applicability of the 3,5-di-\textit{tert}-butylphenyl 1-(3-methyl-2-butanyl) ether and of allyl 3,5-di-\textit{tert}-butylphenyl as selective probes for the determination of external surface activity of large pore zeolites.\textsuperscript{48,53}

Another method to determine the outer surface activity of zeolite beta is by comparing the activity of the as-synthesized and the calcined zeolite. The idea is that in the as-synthesized form the template molecules block the internal active sites for catalysis and only the outer-surface active sites can be used. We recently showed \textit{via} this method that the hydration and the isomerization of $\alpha$-pinene take places \textit{within} the pores of zeolite beta.\textsuperscript{57} As can be seen in Table 4.5 the epoxidation of 1-octene is only observed for the calcined material, which further confirms that epoxidation predominantly takes place over titanium sites located \textit{within} the pores of the zeolite.
7.3.6 Catalyst stability

Since the observation that zeolite catalysts, redox molecular sieves in particular, can leach their active metal components, the stability of these catalysts has been questioned. During the oxidation of substrates two major problems can occur:

i) Uncatalyzed "blank" oxidation by hydrogen peroxide or oxygen from the air.

ii) Homogeneous oxidation by catalytically active titanium species leached from the zeolite framework.

Efforts were made to determine the influence of these two effects on the conversion observed (Table 4.6). In the presence of Ti-beta-1, a considerable amount of the corresponding epoxide was formed in the epoxidation of 1-octene in acetonitrile at 70 °C. When no catalyst was added to the reaction mixture, no detectable amount of oxidized products was observed after 3 h. Only after 72 h was a small amount of oxidized products detected, predominantly the products of allylic oxidation 1-octen-3-ol and 1-octen-3-one. The possibility of leached titanium species was tested by removal of the catalyst from the reaction mixture by filtration. When the catalyst was removed from the reaction mixture by a hot filtration, only a very small increase in conversion was observed (from 9.7 % to 9.9% in 3 h, Table 4.6 and Figure 4.17). When the reaction mixture was first allowed to cool to room temperature before the Ti-beta catalyst was filtered, off also no significant increase in conversion was observed (from 9.7% to 9.2% in 3h, Table 4.6 and Figure 4.17). Chemical analysis of the catalyst before and after reaction showed no significant change in the bulk Si:Ti molar ratio of the catalyst. The observed catalytic activity of Ti-beta is therefore related to the framework titanium sites.
Figure 4.17  Leaching experiment in the epoxidation of 1-octene over Ti-beta-1 with aqueous hydrogen peroxide. + Normal reaction; Δ Cold filtration of the catalyst after 1 h; ○ Hot filtration of the catalyst after 1 h.

Table 4.6  Blank and leaching experiments for the catalytic epoxidation of 1-octene at 70 °C with aqueous hydrogen peroxide in acetonitrile as the solvent using Ti-beta-2 as the catalyst.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Time [h]</th>
<th>Conversion [%]</th>
<th>Major products formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blanc reaction</td>
<td>3</td>
<td>&lt; 0.2</td>
<td>1-octen-3-ol, 1-octen-3-one, (1,2-epoxyoctane)&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>72</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>Ti-beta-1, no treatments</td>
<td>1</td>
<td>9.7</td>
<td>1,2-epoxyoctane</td>
</tr>
<tr>
<td>Hot filtration of the catalyst</td>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.7</td>
<td>1,2-epoxyoctane</td>
</tr>
<tr>
<td>after 1 h</td>
<td>2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.5</td>
<td></td>
</tr>
<tr>
<td>Cold filtration of the catalyst</td>
<td>1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.8</td>
<td>1,2-epoxyoctane</td>
</tr>
<tr>
<td>after 1 h</td>
<td>2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.9</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Time after removal of the catalyst. <sup>b</sup> Minor amounts.
4.4. Conclusions

The crystallization of essentially aluminum-free Ti-beta is possible using DCDMA\textsuperscript{+} as the template. Variation in temperature and in the DCDMA.OH:SiO\textsubscript{2} molar ratio indicates that fully crystalline materials can only be synthesized within a narrow synthesis window. At low temperatures (< 135 °C) the crystallization is too slow and long synthesis times are required to obtain fully crystalline materials. At temperatures over 150 °C, fully crystalline materials are not obtained, even after prolonged heating. The latter might be related to the high alkalinity, which favours the dissolution of silicate species.

The successful incorporation of titanium is confirmed by (i) the linear relation of the unit-cell parameters with the titanium content, (ii) the absence of titanium dioxide phases as determined by EDX, (iii) the presence of an absorption band at 960 cm\textsuperscript{-1} in the FT-IR spectrum of the as-synthesized material and (iv) a single absorption peak at 47,000 - 50,000 cm\textsuperscript{-1} in the UV-Vis spectrum, which also confirms the absence of oligomeric titanium species. The confirmation of titanium incorporation of calcined materials via the presence of an absorption band at 960 cm\textsuperscript{-1} in the IR spectrum is not recommended due to the large amount of silanol groups present in high silica beta type zeolites, which also give an absorption around 960 cm\textsuperscript{-1}. The d\textsubscript{Ti-O} bond length is not observed in the radial density distribution plot as determined by SAXS, due to the low amount of titanium present in the materials (< 2 wt%).

Analysis of the highly crystalline material with SEM shows that crystals are obtained with a pillow-shaped morphology and a very rough surface. Closer examination of the outer surface using TEM analysis shows that it has locally a very smooth surface but sometimes an amorphous layer is present. The EDP patterns demonstrate that the particles observed with SEM and TEM are single crystals, which is further confirmed by the low mesoporous surface area (∼ 18 m\textsuperscript{2} g\textsubscript{zeolite},) compared to the micropore surface area (670 m\textsuperscript{2} g\textsubscript{zeolite}).

The small influence of the outer surface on the catalytic rate of epoxidation is determined by the low epoxidation rate for the surface probe molecule 3,5-di-tert-butylphenyl 3-methyl-2-butenyl ether compared to that for the unhindered phenyl 3-methyl-2-butenyl ether. Furthermore, the influence of blank reactions and leaching of active homogeneous titanium species was found to be negligible.
Chapter 4

References

Characterization of Titanium β


121
53 S. Elings, privat communications.
Aluminum-free titanium beta as a selective catalyst in the epoxidation of bulky alkenes.

Abstract

The catalytic potential of aluminum-free zeolite titanium beta (Ti-beta) in the epoxidation of alkenes with aqueous hydrogen peroxide is demonstrated. The Ti-beta catalyst is compared with TS-1, Ti,Al-beta and Ti-MCM-41. The advantage of the larger pore size of Ti-beta was demonstrated by the facile epoxidation of norbornene, in which reaction TS-1 displayed no activity.

In the epoxidation of linear alkenes over Ti-beta two trends were observed. The lower alkenes were epoxidized faster than the higher alkenes and the internal alkenes reacted slightly faster than the terminal alkenes. The catalytic properties of Ti-beta were further investigated in the epoxidation of bulky alkenes such as cyclohexenes and cyclic terpenes. In the epoxidation of methyl-substituted cyclohexenes the reactivity of methylenecyclohexane was twice that of 1-methylcyclohexene, which suggests that steric effects at the titanium site can play a dominant role in determining reactivity of substrates. Electronic effects were found to be more important in the epoxidation of allylic alcohols: more highly substituted alcohols were more reactive, whereas the reactivity of the substrates bearing a terminal double bound was over an order of magnitude lower.

In contrast to TS-1 and Ti-MCM-41, the Ti-beta exhibits Bronsted acidic properties when alcohols are applied as the solvent. This is tentatively explained by the Lewis acid character of the titanium site in Ti-beta, which on coordination of an alcohol yields a Brønsted acid site. The exchange of these Bronsted acidic sites with alkali metal salts, resulted in a linear decrease in activity with cation exchange level. The fully exchanged material showed no activity at all. The use of acetonitrile as the solvent reduced the acid-catalyzed secondary reactions significantly, except for highly activated epoxides or substrates such as camphene oxide and α-pinene, respectively.
5.1 Introduction

Since the discovery in 1983 of TS-1, a titanium containing silicalite with the MFI structure, by Taramasso et al.,\textsuperscript{1} much research has been performed on its synthesis as well as on its application as an oxidation catalyst in a wide range of oxygenations with hydrogen peroxide. The strength of TS-1 is a combination of isolated tetrahedrally coordinated titanium atoms in a silicate structure and a hydrophobic and non-acidic well-defined environment.\textsuperscript{2} An obvious limitation is its pore size of 5.6 x 5.3 Å. Recently various new types of large pore titanium containing molecular sieves have been reported, Ti-MCM-41,\textsuperscript{3,4} Ti-ZSM-12,\textsuperscript{5} TAPSO-5\textsuperscript{6} and Ti,Al-beta.\textsuperscript{7} Especially the titanium analogue of zeolite beta (Ti-beta) is interesting, since it has a three-dimensional pore structure as well as a hydrophobic interior, provided that aluminum is absent. We have recently shown that it is possible to synthesize an all-silica zeolite beta using a more efficient structure-directing template (dibenzylidimethylammonium, DBDMA\textsuperscript{+})\textsuperscript{8} than the usually applied tetraethylammonium template (see Chapter 3). In Chapter 4, the use of di(cyclohexymethyl)dimethylammonium (DCDMA) as a further improved and well-fitting template for the selective synthesis of Ti-beta has been described.\textsuperscript{9}

Since the first report on the incorporation of titanium in the framework of zeolite aluminum beta by Camblor et al.\textsuperscript{7} in 1992, a number of articles by the group of Corma on the catalytic potential of Ti,Al-beta in the epoxidation of alkenes have appeared.\textsuperscript{7,10-13} Only very recently, a number of publications on the catalytic applicability of aluminum-free titanium containing zeolite beta in oxygenation reactions have appeared.\textsuperscript{9,14-17} The presence of aluminum in Ti,Al-beta causes Brønsted acidity, which can lead to acid-catalyzed consecutive reactions as shown in Figure 5.1. This was first shown by Corma et al.,\textsuperscript{10} in the epoxidation of 1-hexene and cyclohexene with aqueous hydrogen peroxide in methanol as the solvent. The major products observed were the glycol monomethyl ether and the glycol, respectively, while the epoxide was the main product over TS-1 and only small amounts of acid-catalyzed secondary products were formed. Two methods are known to decrease the rate of acid-catalyzed secondary reactions. The first involves exchanging the acid proton of the aluminum site with alkali metals. In this way, Sato et al.\textsuperscript{18,19} could effectively neutralize the catalyst with only a small loss in oxygenation activity. Secondly, acid sites can be neutralized
by applying weakly basic solvents, such as acetonitrile, as reported by Corma et al.\textsuperscript{11}

Obviously, the best way to circumvent the acid-catalyzed secondary reactions of the epoxide, which is in most cases the desired product, would be the total elimination of aluminum from the catalyst. Four methods for the direct hydrothermal synthesis of an \emph{aluminum-free} titanium containing zeolite beta (Ti-beta) have been reported so far\textsuperscript{9,14-17} and a detailed description of these synthesis methods is given in Chapter 4. As we reported earlier\textsuperscript{9} and will discuss in this chapter, the titanium site in Ti-beta and TS-1 has Lewis acidic properties which in the presence of alcoholic solvents will generate a mild Brønsted acidic site. This Brønsted acidity is apparently more pronounced for Ti-beta than for TS-1. This was also shown by Camblor \textit{et al.}\textsuperscript{16} The rate of oxirane cleavage of 1,2-hexene oxide in methanol is 4.5 times faster over Ti-beta than over TS-1. For TS-1 alcoholic solvents, methanol in particular, are reported to be the best solvents with high selectivities towards the epoxide.\textsuperscript{20} Saxton \textit{et al.}\textsuperscript{15} also reported similar results \textit{viz.} low epoxide selectivities over Ti,Al-beta when alcoholic solvents are employed.

![Figure 5.1 Epoxidation of alkenes to epoxide and consecutive acid-catalyzed secondary reactions.](image)

Due to the acidity of the aluminum sites, Ti,Al-beta can be considered a bifunctional catalyst, \textit{i.e.} possessing a combination of Brønsted acidic and oxidative sites. For example,
Corma et al.\textsuperscript{12} reported the use of this bifunctionality in the conversion of linalool to cyclic furans and pyrans using TBHP under anhydrous conditions (Figure 5.2). The ratio between the pyrans and the furans was found to be constant during the course of the reaction which was taken as proof that the reaction first involved an epoxidation over the titanium sites, followed by an \textit{in-situ} ring-closure over the acid protons at the aluminum sites.\textsuperscript{12} Similarly Corma et al.\textsuperscript{13} reported the acid-catalyzed intramolecular rearrangement of the epoxide of \(\alpha\)-terpineol over Ti,Al-beta and Ti-MCM-41. Another application of Ti,Al-beta as a bifunctional catalyst has recently been reported by van Klaveren and Sheldon,\textsuperscript{21} who showed the potential of Ti,Al-beta as a catalyst for the one-step conversion of alkenes into aldehydes and ketones. Earlier the one pot two step conversion of styrene to phenylacetaldehyde over TS-1 was reported by Neri and Buonomo,\textsuperscript{22} thereby showing the existence of acidic properties of titanium sites in zeolites.

\begin{equation}
\text{TBHP} \quad \xrightarrow{\text{Ti,Al-beta, CH2Cl2}} \quad \text{H}^+ \quad \xrightarrow{} \quad \text{Product} + \text{Product}
\end{equation}

Figure 5.2 Epoxidation of linalool followed by ring closure using Ti,Al-beta.\textsuperscript{12}

The difference in activity between the medium pore TS-1 and the large pore beta type catalysts has been studied by several groups. Table 5.1. summarizes the literature data of the relative rates of epoxidation of alkenes over Ti-beta and Ti,Al-beta compared to TS-1. The relative activity of Ti,Al-beta compared to TS-1 varies from 0.24 to 0.83 for 1-alkenes, which in all cases is lower than the relative activity of 0.88 observed for the epoxidation of 1-octene over Ti-beta. This wide range of relative activities for Ti,Al-beta is probably caused by the different levels of aluminum in the catalysts used. As shown by Corma \textit{et al.}\textsuperscript{11} the catalytic behavior of Ti,Al-beta is strongly influenced by the adsorption of solvent molecules as well as by the amount of protic aluminum sites. Lower amounts of aluminum in the catalyst, with
the aluminum-free Ti-beta as the limiting case, resulted in higher activities.\textsuperscript{10,11} In general it can be concluded that the activity of the titanium sites in Ti-beta and Ti,Al-beta is only slightly lower than that displayed by TS-1 in the case of linear alkenes.

Table 5.1 Comparison of relative activity of TS-1, Ti-beta and Ti,Al-beta in the epoxidation of alkenes using aqueous hydrogen peroxide taken from literature data and our present work.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Relative reaction rate\textsuperscript{a}</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TS-1</td>
<td>Ti-beta</td>
</tr>
<tr>
<td>1-hexene</td>
<td>1</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.82</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>1</td>
<td>14.0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>80.0</td>
</tr>
<tr>
<td>1-octene</td>
<td>1</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>norbornene</td>
<td>1</td>
<td>71.6</td>
</tr>
<tr>
<td>1-decene</td>
<td>1</td>
<td>0.42</td>
</tr>
<tr>
<td>1-dodecene</td>
<td>1</td>
<td>0.79</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Since the experimental conditions differ widely, only the relative activities are given. \textsuperscript{b} Dry TBHP in 1,2-dichloroethane is used instead of aqueous H\textsubscript{2}O\textsubscript{2}.
Chapter 5

The lower intrinsic activity and the lower selectivity of framework titanium in Ti-beta makes it unfavorable for the epoxidation of linear alkenes compared to TS-1. The potential of the beta type catalysts lays, however, in the epoxidation of substrates which are too bulky to be epoxidized by TS-1. The larger pore apertures of the main channels of zeolite beta, 7.4 x 6.9 Å versus 5.6 x 5.3 Å for TS-1, should allow the epoxidation of relative bulky alkenes such as cyclohexene and norbornene. It is clear from Table 5.1 that for norbornene and cyclohexene Ti-beta and Ti,Al-beta, respectively, are indeed much more active than TS-1.

In this chapter, the catalytic properties of Ti-beta in the epoxidation of alkenes are investigated and compared with those of TS-1, Ti,Al-beta and Ti-MCM-41. The influence of the type of solvent on the activity and selectivity has been studied. The effect of neutralization of the titanium-site by ion-exchange on the catalytic activity is discussed. The catalytic applicability of the Ti-beta as an epoxidation catalyst was tested for four types of alkenes, namely: linear alkenes, cyclic alkenes, terpenes and allylic alcohols.

5.2 Experimental

5.2.1 Catalyst preparation

Zeolite Ti-beta was prepared and characterized according to van der Waal et al.,\textsuperscript{8,14} using di(cyclohexylmethyl)dimethylammonium hydroxide as the template. The catalysts used were Ti-beta-1 with a Si:Ti molar ratio of 59 and Ti-beta-2 with a Si:Ti ratio of 69. Ti,Al-beta was prepared according to Cambier et al.,\textsuperscript{6} chemical analysis showed a Si:Ti molar ratio of 39 and a Si:Al molar ratio of 76. Full characterization of Ti-beta-1 and Ti-beta-2 catalysts is described in Chapter 4 of this thesis. TS-1 was kindly supplied by the van Hooff group, TU Eindhoven (Euro-TS-1, Si:Ti = 59). UV-Vis spectra were recorded on a Varian Cary-1 photospectrophotometer using barium sulfate as a reference. Chemical analysis of the materials was performed on a Perkin-Elmer Plasma 40 apparatus (ICP-AES) or a Perkin-Elmer 110 apparatus (AES). Ti-MCM-41 was prepared according to Corma et al.,\textsuperscript{3} (Si:Ti = 42).
5.2.2 Catalytic reactions

The catalysts were tested in the epoxidation of alkenes (linear alkenes, cyclic alkenes, allylic alcohols and terpenes). To determine the influence of the solvents on the activity of the zeolite catalysts, the epoxidation of 1-octene was performed at 313 K and 333 K, using 23.5 g solvent (methanol, ethanol, 2-propanol, tert-butanol and acetonitrile), 20 mmol alkene and 10 mmol H$_2$O$_2$ (30 wt% aqueous solution); 1,3,5-trisopropylbenzene was used as the internal standard. The reaction was started by the addition of 100 mg catalyst to the reaction mixture.

The determination of the influence of the alkali content on the reactivity of the titanium site of Ti-beta was investigated by the addition of 0.25 mmol alkali metal salt (sodium chloride, sodium acetate, lithium chloride and lithium acetate) to the reaction mixture at 343 K. The reaction mixture contained 24 g acetonitrile as the solvent, 20 mmol 1-octene, 10 mmol H$_2$O$_2$ (30 wt% aqueous solution) and 250 mg 1,3,5-trisopropylbenzene as the internal standard. The reaction was started by the addition of 50 mg Ti-beta-1. Samples were taken at regular intervals and analyzed by GC (CP-Sil-5) and GC-MS.

The influence of the structure of the alkene on its reactivity was studied by the epoxidation of the four groups of substrates, using 24 g acetonitrile as the solvent, 20 mmol substrate, 10 mmol H$_2$O$_2$ (30 wt% aqueous solution) and 50 - 100 mg catalyst at 343 K. Samples were taken at regular intervals and analyzed by GC (CP-Sil-5) and GC-MS.

Chemicals were purchased from Acros (1-hexene, norbornene, 1-octene, 2-octene, trans-5-decene, α-terpineol, camphene, methylenecyclohexane), Aldrich (1-butene-3-ol, cis-2-butene-1-ol, 1-methylcyclohexene, 4-methylcyclohexene, 3-methyl-2-butene-1-ol, 2-methyl-1-propen-3-ol, cis-2-penten-1-ol and 2-propen-1-ol), Baker (methanol p.a., ethanol p.a., 2-propanol p.a.), Fluka (1-heptene), Merck (hydrogen peroxide, 30 wt% aqueous), TCI Japan (3-methylcyclohexene) or kindly donated by Quest Int. UK (α-pinene, β-pinene, R- (+)-limonene). All chemicals used were of the highest purity available and used without further purification.
5.3 Results and discussion

5.3.1 The coordination of solvent molecules to the titanium site

Characterization of the materials obtained was performed by XRD, ICP/AES, diffuse reflectance UV-Vis and FT-IR spectroscopy, see Chapter 4 of this thesis for a full discussion of the Ti-beta's used. XRD measurements showed that essentially pure as-synthesized zeolite beta was obtained, sometimes accompanied by small amounts of ZSM-12 (estimated less than 3 %). The tetrahedral incorporation of titanium in the as-synthesized zeolite Ti-beta framework was investigated by UV-Vis (Figure 5.3) and a linear unit-cell expansion with titanium content was observed (Figure 4.7 in Chapter 4).

![Graph showing UV-Vis spectra of Ti-beta-2 and the effect of the addition of hydroxylic compounds. The sample was pre-dried at 200 °C, water and 2-propanol was added to the sample (0.18 g_adsorbate/g_zeolite) at room temperature.]

Figure 5.3 UV-Vis spectra of Ti-beta-2 and the effect of the addition of hydroxylic compounds. The sample was pre-dried at 200 °C, water and 2-propanol was added to the sample (0.18 g_adsorbate/g_zeolite) at room temperature.
Information on the state of titanium was obtained by UV-Vis spectrophotometry (Figure 5.3). The incorporation of titanium in the zeolite framework is confirmed by the presence of a strong absorption maximum at 47.000 - 50.000 cm\(^{-1}\), which is attributed to tetrahedrally coordinated titanium in a silicate framework. In the presence of water or 2-propanol the band is shifted towards a lower frequency (45.000 - 48.000 cm\(^{-1}\)). This is generally accepted as an indication for a higher coordination number around the titanium atom, most probably five-coordinated. Upon reheating the sample to 200 °C, the absorption band returned to 47.00 - 50.000 cm\(^{-1}\), showing the reversible nature of the 2-propanol coordination. In the case of water a second weak absorption around 36.000 - 40.000 cm\(^{-1}\) is observed. Absorptions below 40.000 cm\(^{-1}\) are usually attributed to isolated octahedral titanium species. The absence of a significant absorption below 36.000 cm\(^{-1}\) confirms the absence of more highly clustered titanium oxide phases.

5.3.2 Solvents effects

The Ti-beta-2 catalyst was first tested in the epoxidation of 1-octene with hydrogen peroxide in methanol as the solvent and compared with TS-1, Ti,Al-beta and Ti-MCM-41. At low temperature (40 °C) Ti-beta (TOF = 0.5 mol mol\(^{-1}\)\(\text{Ti} \cdot \text{h}^{-1}\)), Ti,Al-beta (TOF = 3.6) and Ti-MCM-41 (TOF = 0.4) were hardly active (table 5.2). Only TS-1 exhibited a high activity with an initial turn-over-frequency (TOF) of 27.7 mmol products per mmol titanium per hour. Upon raising the temperature to 60 °C the activity of the large pore materials increased significantly with TOF's of 85.5 and 41.8 mmol products per mmol titanium per hour for Ti-beta and Ti,Al-beta, resp., though TS-1 retained the best catalytic properties with a TOF of 96.8 mmol products per mmol titanium per hour (Table 5.3). It is as yet unclear why Ti-beta has such a low activity in methanol at 40 °C, while at 60 °C its activity is close to TS-1.

It was surprising to find that the aluminum-free Ti-beta-2 gave the glycol monomethyl ether (\(\text{C}_6\text{H}_{13}\text{CH}(\text{OMe})\text{CH}_2\text{OH}\) and isomer, Figure 5.1) as the major product (59 % at 60 °C). The very low amount of aluminum present (Si: Al > 2500) in Ti-beta-2 could not account for the observed acid-catalyzed secondary reactions, suggesting that, unlike the titanium site in
Table 5.2 Catalytic epoxidation of 1-octene at 40 °C in methanol.a

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOFb</th>
<th>Conversion [%]c at 1 h</th>
<th>Conversion [%]c at 5 h</th>
<th>Selectivity to oxygenatesd 1-oct. H₂O₂</th>
<th>Epoxides in products [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-1</td>
<td>27.7</td>
<td>4.1</td>
<td>13.5</td>
<td>93</td>
<td>96</td>
</tr>
<tr>
<td>Ti-beta-2</td>
<td>0.5</td>
<td>-.</td>
<td>-.</td>
<td>98 glycol ether</td>
<td></td>
</tr>
<tr>
<td>Ti,Al-beta</td>
<td>3.6</td>
<td>0.5</td>
<td>2.1</td>
<td>67</td>
<td>53</td>
</tr>
<tr>
<td>Ti-MCM-41</td>
<td>0.4</td>
<td>-.</td>
<td>-.</td>
<td>98 glycol ether</td>
<td></td>
</tr>
</tbody>
</table>

a Experimental conditions: 20 mmol 1-octene, 10 mmol hydrogen peroxide (30 wt% aqueous) and 100 mg catalyst in 24 g methanol. b Initial Turn-Over-Frequency in mol mol⁻¹ Ti⁻¹ h⁻¹. c Based on 1-octene. d After 1 hour reaction, oxygenates observed are the epoxide and the glycol monomethyl ether. e Predominant product, conversion too low to determine the selectivity accurately.

Table 5.3 Catalytic epoxidation of 1-octene at 60 °C in methanol.a

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOFb</th>
<th>Conversion [%]c at 1 h</th>
<th>Conversion [%]c at 5 h</th>
<th>Selectivity to oxygenatesd 1-oct. H₂O₂</th>
<th>Epoxides in products [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-1</td>
<td>96.8</td>
<td>16.0</td>
<td>41.7</td>
<td>84</td>
<td>91</td>
</tr>
<tr>
<td>Ti-beta-2</td>
<td>85.5</td>
<td>11.6</td>
<td>23.8</td>
<td>82</td>
<td>81</td>
</tr>
<tr>
<td>Ti,Al-beta</td>
<td>41.8</td>
<td>6.7</td>
<td>15.9</td>
<td>87</td>
<td>65</td>
</tr>
<tr>
<td>Ti-MCM-41</td>
<td>7.2</td>
<td>1.3</td>
<td>2.9</td>
<td>76</td>
<td>54</td>
</tr>
</tbody>
</table>

a Experimental conditions: 20 mmol 1-octene, 10 mmol hydrogen peroxide (30 wt% aqueous) and 100 mg catalyst in 24 g methanol. b Initial Turn-Over-Frequency in mol mol⁻¹ Ti⁻¹ h⁻¹. c Based on 1-octene. d After 1 h reaction, oxygenates observed are the epoxide and glycol monomethyl ether.
Epoxidation of alkenes

TS-1, the titanium site in Ti-beta has acidic properties, most likely Lewis acidic. A similar result, viz. a low selectivity (about 60 %) towards the epoxide, is also reported by Saxton et al. for an aluminum-free Ti-beta and methanol as the solvent.

The low activity of Ti,Al-beta and Ti-MCM-41 at 40 °C can be explained on the basis of their hydrophilic interior: Ti,Al-beta contains acidic sites and the internal surface of Ti-MCM-41 consists mainly of Si-OH groups. Water, methanol and hydrogen peroxide are strongly adsorbed by these materials and 1-octene is adsorbed probably weakly, thus hindering the catalytic performance. As expected for Ti,Al-beta the products are the glycol monomethyl ethers (cf. Figure 5.1) due to the acidity of the aluminum site.

It is known for zeolite-catalyzed liquid-phase reactions that the choice of the solvent has a crucial effect on the activity and selectivity. The solvent can govern the intraporous concentration of reactants or may participate in the catalytic cycle. The fact that alcohols are the preferred solvents for epoxidation of alkenes using aqueous hydrogen peroxide and TS-1 as the catalyst, is interpreted in terms of electronic effects induced by coordination of a solvent molecule to the catalytic center or by adsorption effects caused by the polar solvent. The influence of the solvent choice on the catalytic activity of Ti-beta-2 was tested by using methanol, ethanol, 2-propanol, tert-butanol and acetonitrile as the solvent at 40 °C. The highest activity was observed for 2-propanol (TOF = 13.5 h⁻¹) while the highest selectivities were observed for acetonitrile and tert-butanol (Table 5.4). The observed solvent effects differ from those reported in literature for TS-1 and Ti,Al-beta, where methanol is the solvent of choice.

Remarkable is the low selectivity towards the desired epoxide for all alcoholic solvents used (less than 36% after 5 h, Table 5.4). We believe that the active titanium site in Ti-beta acts as a Lewis acid, which upon adsorption of an alcohol molecule gives rise to a moderate Brønsted acid. Low selectivities towards the epoxide when applying Ti-beta as the catalyst have also been reported by Saxton et al. and Camblor et al.
Table 5.4 Effect of various solvents on the catalytic activity and selectivity of Ti-beta-2 in the epoxidation of 1-octene with hydrogen peroxide at 40 °C.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>TOF\textsuperscript{b}</th>
<th>Conversion at 1 h [%]\textsuperscript{c}</th>
<th>Selectivity to oxygenates\textsuperscript{d} 1-oct. H\textsubscript{2}O\textsubscript{2}</th>
<th>Epoxides in products [%] 1 h 5 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>0.5</td>
<td>-.-</td>
<td>87 77</td>
<td>glycols\textsuperscript{e}</td>
</tr>
<tr>
<td>ethanol</td>
<td>5.4</td>
<td>0.7</td>
<td>89 51</td>
<td>46 7</td>
</tr>
<tr>
<td>2-propanol</td>
<td>13.5</td>
<td>1.9</td>
<td>67 78</td>
<td>63 24</td>
</tr>
<tr>
<td>tert-butanol</td>
<td>1.7</td>
<td>0.3</td>
<td>89 69</td>
<td>100 36</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>5.4</td>
<td>0.7</td>
<td>100 98\textsuperscript{f}</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Experimental conditions: 20 mmol 1-octene, 10 mmol H\textsubscript{2}O\textsubscript{2} (30 wt% aqueous) and 100 mg Ti-beta-2 in 24 g solvent. \textsuperscript{b} Initial Turn-Over-frequency in mol mol\textsuperscript{-1} Ti h\textsuperscript{-1}. \textsuperscript{c} Based on alkene. \textsuperscript{d} Oxygenates observed are the epoxide and glycol monomethyl ether. \textsuperscript{e} Predominant product, conversion too low to be determined accurately. \textsuperscript{f} Other 2% is the diol.

The coordination of alcohols to the titanium site can be monitored by UV-Vis spectroscopy, which shows an increase in the coordination number for the titanium site by adsorption of 2-propanol (see Figure 5.3) and methanol (not shown). During the reaction, the Brønsted acid site, which is thought to result from alcohol or water coordination, can activate the primary epoxide product by protonation. Pyrolysis-MS of the catalyst after reaction in methanol, revealed a considerable amount of polymeric products. In the case of highly polar solvents, such as methanol and ethanol, the amount of free solvent molecules in the pore system is thought to be low and we propose that polymerization of the epoxide is the predominant reaction path, with subsequent deactivation by pore blocking. Solvents with lower polarity (e.g. 2-propanol) have a higher affinity with the zeolite and thus a higher intraporous concentration. The protonated epoxide can now react with a solvent molecule to give a glycol ether, which can diffuse out of the zeolite channels without deactivating the catalyst. When
the solvent has an even lower polarity (e.g. tert-butanol), the high loading of the zeolite with solvent molecules and bulky tert-butyl monoglycol ethers effectively decreases the rate of reaction.

Interestingly, the use of acetonitrile as the solvent resulted in a high selectivity towards the epoxide (Table 5.4). Corma et al.\textsuperscript{11} already showed that the use of acetonitrile as the solvent could effectively reduce the acid-catalyzed secondary reactions for Ti,Al-beta and ascribed this to the weak basic properties of the acetonitrile molecule, which can effectively neutralize the acidic properties of the catalyst. We therefore assume that the weak basic character of acetonitrile, neutralizes the Brønsted acidic properties of coordinated water molecules on the titanium site.

5.3.3 Neutralization of the acid titanium site

The work of Sato et al.\textsuperscript{18,19} showed that acid-catalyzed consecutive reactions in Ti,Al-beta can be successfully suppressed by exchanging the acidic sites with alkali metal ions. We therefore studied the influence of alkali metals on the activity and selectivity of Ti-beta-1 in the epoxidation of 1-octene with hydrogen peroxide at 70 °C in acetonitrile. As can be seen in Figure 5.4 and Table 5.5 the activity of Ti-beta decreases linearly with the alkali metal content, while the selectivity to epoxide remains constant (about 95%). The materials in which all the protons of titanium sites are exchanged by alkali metal ions \textit{i.e.} M\textsuperscript{+}:Ti \approx 1, as measured by ICP/AES after reaction, showed no activity at all. Since the presence of alkali cations at aluminum sites is not detrimental for the catalytic activity, as shown by Sato et al.,\textsuperscript{18} this suggests that an alkali exchanged titanium site is not active in the epoxidation of alkenes. The decreased activity on addition of sodium salts to TS-1 is also reported by Hutchings et al.\textsuperscript{27} in the epoxidation of allyl alcohol (2-propen-1-ol). Similar to our results obtained for Ti-beta, TS-1 was also found to be almost completely deactivated when sodium carbonate, a strong base, was applied. However, no elemental analysis of the catalyst before or after the reaction was given to show the exchange level of titanium sites.
Table 5.5 The influence of alkali metal salts on the catalytic performance of Ti-beta-1 in the epoxidation of 1-octene in acetonitrile as the solvent at 70 °C.a

<table>
<thead>
<tr>
<th>Salt added</th>
<th>Alkali : Titanium molar ratio after reaction</th>
<th>Initial TOFb [mol mol⁻¹ Ti h⁻¹]</th>
<th>Selectivity to epoxide.c [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>0.00</td>
<td>148</td>
<td>95</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.62</td>
<td>57</td>
<td>94</td>
</tr>
<tr>
<td>CH₃CO₂Na</td>
<td>1.08</td>
<td>&lt;1</td>
<td>e</td>
</tr>
<tr>
<td>LiCl</td>
<td>0.75d</td>
<td>22</td>
<td>93</td>
</tr>
<tr>
<td>CH₃CO₂Li</td>
<td>0.97</td>
<td>&lt;1</td>
<td>e</td>
</tr>
</tbody>
</table>

a Experimental conditions: 20 mmol alkene, 10 mmol H₂O₂ (30 wt% aqueous), 0.25 mmol alkali metal salt and 50 mg Ti-beta-1 in 24 g acetonitrile. b Initial Turn-Over-Frequency in mol mol⁻¹ Ti h⁻¹. c Fraction of epoxides on total amount of oxygenates observed after 3 h. d ICP/AES results showed Li:Ti = 0.47 and Na:Ti = 0.28 e Conversion too low for accurate determination, epoxide is the major product.

Figure 5.4 Activity of Ti-beta-1 as a function of alkali metal (Na, Li) content in the epoxidation of 1-octene with hydrogen peroxide (reaction conditions see Table 5.5).
The almost constant epoxide selectivity observed for all experiments involving alkali metal ion-exchanged catalysts (Table 5.5) suggests that the acid-catalyzed secondary reactions do not proceed via residual acidic aluminum sites (Si:Al > 2500). Conform Sato et al.\textsuperscript{18} an increase in the selectivity should have been observed upon exchanging the residual aluminum sites with alkali metal ions. This supports our interpretation that the titanium site itself has Brønsted acidic properties in the presence of protic molecules, either the alcoholic solvent or the water from the aqueous hydrogen peroxide used.

The problem of acidity and hydropobicity in Ti,Al-beta was soon recognized by the groups of Corma\textsuperscript{7,10-13} and of Sheldon\textsuperscript{18,19} and was attributed to the presence of framework aluminum, restricting the applicability of Ti,Al-beta to bifunctional catalysis, e.g. a combination of oxidative and acidic catalysis as reported by Corma et al.\textsuperscript{12,13} and by van Klaveren and Sheldon.\textsuperscript{21} The problem of acidity has successfully been addressed by Sato et al.\textsuperscript{18,19} by exchanging the acidic sites with alkali metals. High selectivity to the epoxide (87\%) was reported for the lithium-exchanged Ti,Al-beta material.\textsuperscript{18} The overall activity was dependent on the type of cation on the aluminum site; \(H^+ > Li^+ > Na^+ > K^+ > Mg^{2+}\). It seems quite reasonable to ascribe this to an increasing tendency of the cation to make the zeolite more hydrophilic. As shown in Table 5.3 the aluminum-free Ti-Beta has a higher activity (TOF = 85.5 h\textsuperscript{-1}) than the Ti,Al-beta catalyst (TOF = 41.8 h\textsuperscript{-1}), which underlines the benefit of a higher hydrophobicity.

5.3.4 Catalytic epoxidation of alkenes with hydrogen peroxide

In studies on the activity of TS-1 in the epoxidation of alkenes, large differences in activity for different substrates were observed.\textsuperscript{23-25,28-32} The relative reactivity of alkenes was found to depend on the nucleophilicity of the double bond, but steric factors are sometimes dominant.\textsuperscript{28} By contrast, homogeneous epoxidation of alkenes is mainly governed by electronic factors and steric factors have only a minor influence.\textsuperscript{33} The steric factors observed for TS-1 are in part the result of the relatively small pore size (5.6 x 5.3 Å). The pores of TS-1 do not allow the bulky alkenes to enter and may sterically hinder the formation of the transition state.\textsuperscript{30,31}
As is obvious from Tables 5.1, 5.2 and 5.3 the advantage of applying Ti-beta as a catalyst does not lie in the epoxidation of small or linear alkenes, for which TS-1 is the preferred catalyst. The larger pore size of zeolite beta (7.4 x 6.9 Å) should allow the epoxidation of bulkier substrates. For example, cyclohexene can easily enter the pores of beta type zeolites, which is reflected in the facile epoxidation of cyclohexene over Ti,Al-beta (Table 5.1), which is 14 to 80 times faster than over TS-1 (Table 5.1).\textsuperscript{5,10,11} Ti-beta is therefore tested in the epoxidation of linear alkenes (page 142), cyclic alkenes and terpenes (page 144) and allylic alcohols (page 150) in order to investigate the influence of electronic and steric effects on the relative epoxidation activity.

- **Linear alkenes**

The catalytic epoxidation of linear alkenes, viz. 1-hexene, 1-heptene, 1-octene, 2-octene (mixture of cis and trans), trans-4-octene, 1-decene and trans-5-decene, in acetonitrile at 70 °C, shows that Ti-beta is highly active and selective for all alkenes tested (Table 5.6). The highest activity is observed for 1-hexene (TOF = 235 h\textsuperscript{-1}) and the lowest activity for 1-decene (TOF = 127 h\textsuperscript{-1}). Though differences are modest, two trends can be observed for Ti-beta:
i) Lower alkenes are epoxidized faster than the higher alkenes.

ii) Epoxidation of an internal double bond is somewhat faster than that of a terminal double bond.

The relative reactivity of 1-hexene over Ti-beta was found to be 1.8 times higher than that of 1-heptene (Table 5.6). A higher activity for lower 1-alkenes, \textit{i.e.} \( n\text{-C}_n > n\text{-C}_{n+1} \), was also reported by Clerici \textit{et al.}\textsuperscript{28} and Tatsumi \textit{et al.}\textsuperscript{24} for TS-1 when methanol was employed as the solvent. For TS-1, the observed epoxidation of 1-heptene was 2.5 times slower than that of 1-hexene\textsuperscript{28} in accordance with the narrower pore system of TS-1. However, it should be noted that the observed initial TOF for 1-heptene is not in between those of 1-hexene and 1-octene as would be expected. Interpretation of our results (Table 5.6) is therefore not so straightforward.
Epoxidation of alkenes

Table 5.6. The epoxidation of various linear alkenes over Ti-beta-1 in acetonitrile at 70 °C.\(^a\)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Initial TOF ([\text{mol mol}^{-1}\text{Ti} \cdot \text{h}^{-1}])</th>
<th>TON after 3 h. ([\text{mol mol}^{-1}\text{Ti}])</th>
<th>Peroxide efficiency ([%])^d</th>
<th>Selectivity on substrate^e</th>
<th>Epoxide</th>
<th>Diol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-hexene</td>
<td>235</td>
<td>182</td>
<td>94</td>
<td>93</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>1-heptene</td>
<td>129</td>
<td>136</td>
<td>92</td>
<td>93</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>1-octene</td>
<td>148</td>
<td>214</td>
<td>77</td>
<td>88</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>2-octene^b</td>
<td>169</td>
<td>229</td>
<td>78</td>
<td>91</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>4-octene^c</td>
<td>152</td>
<td>208</td>
<td>95</td>
<td>87</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>1-decene</td>
<td>127</td>
<td>135</td>
<td>93</td>
<td>81</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>5-decene^c</td>
<td>159</td>
<td>166</td>
<td>64</td>
<td>90</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Experimental conditions: 20 mmol alkene, 10 mmol aqueous hydrogen peroxide (30 wt% aqueous) and 50 mg Ti-beta-1 in 24 g acetonitrile. \(^b\) mixture of cis and trans alkene. \(^c\) trans isomer only. \(^d\) Defined as mmol oxygenated products observed per mmol of hydrogen peroxide consumed. \(^e\) Minor amounts of the aldehyde (from consecutive epoxide isomerization) were observed in the case of the 1-alkenes.

The location of the double bond is also known to have an influence on the rate of epoxidation.\(^33\) On the basis of inductive effects of alkyl groups on the double bond, a higher intrinsic activity is expected for an internal double bond. In the epoxidation of octenes and decenes (Table 5.6) it is indeed observed that the alkenes bearing a internal double bond react somewhat faster. However, the differences in reactivities between the internal alkenes and the terminal alkenes tested are lower than would be expected purely on the basis of electronic effects known for electrophilic epoxidizing agents.\(^33-35\) For example, 1-octene has a TOF of 148 while for 2- en 4-octene TOF's of 169 and 152 h\(^{-1}\), respectively, are observed. It is therefore assumed that steric factors also play a role, i.e. the accommodation at the Ti-site is more difficult for the internal alkenes. The influence of steric factors on the reactivity of linear alkenes was already shown by Clerici et al.\(^28\) in the epoxidation of butenes using TS-1 as the catalyst. The reactivities observed were: cis-2-butene > 1-butene > trans-2-butene. The relatively low reactivity of the trans-2-butene compared to 1-butene was explained by steric hindrance upon approaching the active Ti-site.\(^28\)

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The higher steric hindrance of internal double bonds compared to terminal double bonds of linear alkenes, was also reported by Creighton et al.\textsuperscript{36} in the hydrogenation of 1-decene and trans-5-decene over platinum clusters in zeolite beta. Here, the effects are more pronounced. Whereas the 1-decene was readily hydrogenated, hydrogenation of the 5-decene proceeded much more slowly. Since the hydrogenation of 5-decene proceeded easily over platinum on carbon or on alumina catalysts, it was concluded that the 5-decene was sterically hindered in approaching the platinum clusters inside the zeolite channels. It should be noted that the platinum clusters are located in the pores of the zeolite, whereas the titanium sites for epoxidation are located in the framework of the zeolite and therefore the alkenes have better access to the catalytic sites.

- Bulky alkenes

To investigate the effect of the pore size, various titanium catalysts, Ti-beta, TS-1, Ti,Al-beta and Ti-MCM-41 were tested in the epoxidation of norbornene with hydrogen peroxide and methanol as the solvent. As shown in Table 5.7, the large pore size of the Ti-beta allows the moderately selective epoxidation of norbornene (56 % to the epoxide). Ti-beta has a higher catalytic activity (TOF = 71.6 h\textsuperscript{-1}) than Ti,Al-beta (TOF 43.7 h\textsuperscript{-1}), TS-1 (no activity) and Ti-MCM-41 (TOF = 28.8 h\textsuperscript{-1}). The major by-product for all catalysts was the diol with minor amounts of the glycol monomethyl ether. The difference in the activity and in the selectivity between Ti-beta and Ti,Al-beta demonstrates where the catalytic potential of the aluminum-free zeolite lies. Though, the Ti-beta is also weakly acidic when alcoholic solvents are used (as discussed in paragraph 5.3.2), the strongly acidic Ti,Al-beta catalyzes the secondary reactions (Figure 5.1) of the epoxide much faster. The lower initial activity per titanium site for the Ti,Al-beta catalyst is most likely caused by the protic aluminum sites, which decrease the hydrophobicity of the zeolite allowing solvent molecules, \textit{viz.} methanol, to be adsorbed preferentially. The low activity of TS-1 in the epoxidation of norbornene can be attributed to the small size of the pores, \textit{i.e.} norbornene is too large to diffuse into the channels of the zeolite. Ti-MCM-41 is active in epoxidation but its activity and selectivity are low,
presumably due to the relatively hydrophilic interior of M41S-type materials \(^{37}\) or to inaccessibility of titanium sites due to incorporation inside the silica walls as described by Oldroyd \textit{et al.}\(^ {38}\).

Table 5.7 Epoxidation of norbornene in methanol at 60 °C.\(^a\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial TOF [mol \text{ mol}^{-1}\text{Ti h}^{-1}]</th>
<th>Conversion at 1 h [%] (^b)</th>
<th>Selectivity to oxygenates(^c)</th>
<th>Epoxide in products [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-1</td>
<td>no reaction</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ti-beta</td>
<td>71.6</td>
<td>13.3</td>
<td>67, 80</td>
<td>56</td>
</tr>
<tr>
<td>Ti,Al-beta</td>
<td>43.7</td>
<td>10.1</td>
<td>57, 64</td>
<td>27</td>
</tr>
<tr>
<td>Ti-MCM-41</td>
<td>28.8</td>
<td>6.7</td>
<td>65, 54</td>
<td>74</td>
</tr>
</tbody>
</table>

\(^a\) Experimental conditions: 20 mmol alkene, 10 mmol aqueous hydrogen peroxide (35 wt% aqueous) and 50 mg Ti-beta-1 in 24 g methanol. \(^b\) Based on norbornene. \(^c\) Oxygenates observed are the epoxide and the glycol monomethyl ether.

In order to further study the ability of Ti-beta to selectively oxidize larger molecules, the epoxidation of norbornene, limonene, \(\alpha\)- and \(\beta\)-pinene, camphene and \(\alpha\)-terpineol in acetonitrile as the solvent were carried out. We reported\(^ {39}\) earlier that zeolite aluminum beta and zeolite boron beta are excellent catalysts for the rearrangement of terpenes, \(\alpha\)-pinene in particular. Since boron zeolites are considered to be very weakly acidic,\(^ {40}\) it was expected that Ti-beta, which also has acidic properties in alcoholic solvents (see paragraph 5.3.1), can catalyze the rearrangements of terpene based substrates. In an attempt to avoid these rearrangement reactions of either substrates or products, acetonitrile was used as a weak basic solvent.

Ti-beta was found to catalyze the epoxidation of norbornene, limonene, camphene and \(\alpha\)-terpineol (Table 5.8). By contrast hardly any conversion of \(\alpha\)- and \(\beta\)-pinene was observed under these conditions. In the epoxidation of R-(+)-limonene (Figure 5.5a) a mixture of both the side-chain and the ring epoxide (in a 55:45 ratio, respectively) was obtained, thereby
showing that Ti-beta does not have a preference for either one of the two double bonds. The major by-products observed in the limonene epoxidation were the two corresponding diols with minor amounts of the side-chain aldehyde. In the epoxidation of camphene, the strained epoxide initially formed isomerizes and the aldehyde is formed essentially as the only product (Table 5.8, Figure 5.5b). Rearrangement of the initially formed epoxide was also observed for the other terpenes. α-Terpineol was found to rearrange to cineol alcohol by an intramolecular reaction between the alcohol and the epoxide group (Figure 5.5c). In the case of α- and β-pinene (data not shown) the epoxidation is very slow (conversion after 1 h < 0.2%) and besides the epoxide a wide variety of by-products were observed, originating both from the pinene itself and from the epoxide formed. The rearrangements of the epoxides from camphene, α-terpineol and α- and β-pinene are all acid-catalyzed, which suggests that the acidic titanium sites are still active even when surrounded by the basic acetonitrile, and can still activate very reactive epoxides or activated C=C double bonds.

Figure 5.5 Epoxidation of bulky substrates with H₂O₂ over Ti-beta-1 in acetonitrile as the solvent. a) limonene, b) camphene, c) α-terpineol.
The results of Table 5.8 show a wide variety in activity for different terpenes tested. Since epoxidation of double bonds using titanium zeolites is considered an electrophilic addition of oxygen to the double bond, it is expected that more highly substituted C=C double bonds are more reactive.\textsuperscript{33-35} From the reactivities of the terpenes studied (Table 5.8) it can clearly be seen that reactivity is not only based on electronic effects. For example, in the epoxidation of limonene the double bond in the ring should react much faster than the side-chain double bond and this is indeed the case in the homogeneously catalyzed epoxidation in solution. The major epoxide formed is, however, the side-chain epoxide (55%) and not the ring-epoxidized product (45%). This suggests that other factors besides electronic effects, most likely steric, contribute to the reactivity of substrates for epoxidation inside Ti-beta.

Table 5.8  Epoxidation of various bulky substrates over Ti-beta in acetonitrile at 70°C.\textsuperscript{a}

<table>
<thead>
<tr>
<th>substrate</th>
<th>Conversion H\textsubscript{2}O\textsubscript{2} after 1 h ( % )</th>
<th>Selectivity to epoxide on substrate H\textsubscript{2}O\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-octene</td>
<td>6.6</td>
<td>88 77</td>
</tr>
<tr>
<td>norbornene</td>
<td>8.0</td>
<td>89 50</td>
</tr>
<tr>
<td>R-(-)-limonene</td>
<td>11.0</td>
<td>79\textsuperscript{b} 53</td>
</tr>
<tr>
<td>camphene</td>
<td>7.2</td>
<td>1 (92)\textsuperscript{c} (67)\textsuperscript{c}</td>
</tr>
<tr>
<td>(\alpha)-terpineol</td>
<td>9.1</td>
<td>43 (12)\textsuperscript{d} 35 (11)\textsuperscript{d}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Experimental conditions: 20 mmol alkene, 10 mmol aqueous hydrogen peroxide (30 wt% aqueous) and 50 mg Ti-beta-1 in 24 g solvent. \textsuperscript{b} Both the side-chain and ring epoxide are formed in a ratio of 55:45 (Figure 5.5a). \textsuperscript{c} Between brackets the selectivity to camphyl aldehyde, formed by an acid-catalyzed secondary reaction of the epoxide (Figure 5.5b). \textsuperscript{d} Between brackets the selectivity to cineol alcohol, formed by an acid catalyzed intramolecular rearrangement (Figure 5.5c).
In order to gain insight in the role of steric effects for Ti-beta, we studied the epoxidation of various alkenes, such as hexene, cyclohexene, heptene, methylenecyclohexane, 1-, 3- and 4-methylenecyclohexene. The large pores of Ti-beta allow the epoxidation of structurally related substrates to study the relation between structure, i.e. position and substitution of the double bond, and the reactivity. As shown in Table 5.9, cyclohexene (TOF = 289) is indeed more reactive than 1-hexene (TOF = 235), as would be expected on the basis of electronic effects. The epoxidation of various cyclohexenes follow the order of activity: methylenecyclohexane > 3-methylcyclohexene > 1-methylcyclohexene > 4-methylenecyclohexene. Based on electronic effects one would expect that 1-methylcyclohexene would be the most reactive and methylenecyclohexane the most unreactive. Since the pores of zeolite beta are sufficiently large to accommodate the substrate and the product epoxide, it is assumed that the hindered formation of the transition state at the titanium site is an important factor in determining the activity for more highly substituted C=C double bonds.

Table 5.9 The epoxidation of various cycloalkenes over Ti-beta in acetonitrile at 70 °C.\(^a\)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Initial TOF [mol mol(^{-1})(_{\text{Ti}}) h(^{-1})]</th>
<th>TON after 3h [mol mol(^{-1})(_{\text{Ti}})]</th>
<th>Peroxide efficiency [%](^b)</th>
<th>Select. to epoxide [%](^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-hexene</td>
<td>235</td>
<td>182</td>
<td>94</td>
<td>92.9</td>
</tr>
<tr>
<td>cyclohexene</td>
<td>289</td>
<td>389</td>
<td>92</td>
<td>86.0 (7.2)</td>
</tr>
<tr>
<td>1-heptene</td>
<td>129</td>
<td>136</td>
<td>92</td>
<td>94.7</td>
</tr>
<tr>
<td>1-methylenecyclohexene</td>
<td>170</td>
<td>182</td>
<td>82</td>
<td>88.0 (7.7)</td>
</tr>
<tr>
<td>3-methylenecyclohexene(^d)</td>
<td>200</td>
<td>242</td>
<td>68</td>
<td>68.3 (24.5)</td>
</tr>
<tr>
<td>4-methylenecyclohexene</td>
<td>152</td>
<td>178</td>
<td>79</td>
<td>91.9 (5.7)</td>
</tr>
<tr>
<td>4-methylenecyclohexene(^d)</td>
<td>157</td>
<td>187</td>
<td>83</td>
<td>74.7 (21.3)</td>
</tr>
<tr>
<td>methylenecyclohexane</td>
<td>328</td>
<td>456</td>
<td>95</td>
<td>&gt;98</td>
</tr>
<tr>
<td>norbornene</td>
<td>179</td>
<td>137</td>
<td>50</td>
<td>&gt;98</td>
</tr>
</tbody>
</table>

\(^a\) Experimental conditions: 20 mmol alkene, 10 mmol hydrogen peroxide (30 wt% aqueous) and 50 mg catalyst in 24 g solvent under N\(_2\)-atmosphere. \(^b\) Peroxide efficiency is based on epoxide, diol and aldehyde or ketone as oxidation products, see text. \(^c\) Selectivity to epoxide, based on total oxidized products. Values in brackets indicate fraction of allylic oxidized products. \(^d\) Epoxidation in the presence of air.
The best known examples of sterically hindered reactions for TS-1 are the oxygenation of cyclohexane and cyclohexene. The rate of oxygenation for both substrates is about two orders lower than for the corresponding linear C₆ hydrocarbon.²⁹,³⁰ The critical dimensions of cyclohexane (4.7 x 6.2 Å) are larger than the pore opening of TS-1 (5.6 x 5.3 Å), and the cyclic hydrocarbons have difficulty in diffusing through the channels.

For the (methyl)cyclohexene substrates allylic oxidation to the corresponding allylic alcohol was also observed in addition to the normal by-products due to acid-catalyzed consecutive reactions. It should be noted that cycloalkenes are readily oxidized by molecular oxygen at the reaction temperature applied,⁴¹-⁴⁴ and the allylic oxidation is thought to proceed through a free radical chain mechanism (Figure 5.6).⁴¹ Initiation occurs via the formation of a radical, usually originating from a peroxide initiator. This reaction is not considered to be catalyzed by titanium, though the titanium site could interfere by the reduction of the initially formed peroxide via epoxidation of an alkene. In a comparative epoxidation of 4-methylcyclohexene under air, i.e. in the presence of oxygen, it was observed that a substantial amount of the corresponding allylic alcohol was formed (21.3 %, Table 5.9). By performing the reaction under a nitrogen atmosphere, the amount of allylic oxidized products was reduced significantly (5.7 %, Table 5.9). Due to the decomposition of hydrogen peroxide to oxygen and water under the reaction conditions used, a complete elimination of the allylic oxidation could not be achieved. No allylic oxidation was observed for methylenecyclohexane and norbornene. For norbornene the formation of a stabilized radical is difficult for steric reasons.

\[
\text{H} \quad \text{R}^* \quad \text{O}_2 \quad \text{O}^* \quad \text{R-H} \quad \text{H} \quad \text{R}^* \\
\text{cyclohexene} \quad \text{cyclohexene} \quad \text{peroxide} \quad \text{alcohol} \quad \text{radical}
\]

Figure 5.6 Free radical chain mechanism of the oxidation of cyclohexene with oxygen.⁴¹
Chapter 5

- Allylic alcohols

The influence of electronic effects of substituents in the epoxidation of alkenes over Ti-beta was further investigated by examination of the activity of electron deficient substrates, allylic alcohols in particular. The allylic alcohols tested were 2-propen-1-ol (allyl alcohol), 1-buten-3-ol, cis-2-buten-1-ol, 2-methyl-1-propen-3-ol, 3-methyl-2-propen-1-ol, and cis-2-penten-1-ol, see Table 5.10. The activity of Ti-beta in the epoxidation of linear allylic alcohols was found to increase with increasing chain length, e.g. cis-2-penten-1-ol > 2-buten-1-ol > allyl alcohol ≈ 1-buten-3-ol, as would be expected on the basis of the type of substituents on the C=C double bond. The observed turn-over-frequency for 2-propen-1-ol (TOF = 18 mol mol\(^{-1}\) Ti h\(^{-1}\)) is an order of magnitude lower than for 1-hexene (Table 5.9, TOF = 235) under similar conditions. This is not surprising, since the presence of an electron withdrawing alcohol group near the C=C double bond is expected to decrease its reactivity for electrophilic oxidations.\(^{33,35}\) An exception is the epoxidation of allylic alcohols using either the homogeneous titanium tartrate complexes, viz. the Sharpless catalyst\(^{45}\) or vanadium-ALPO's\(^{46}\) as the catalysts. The fact that these catalysts show a high activity for the epoxidation of allylic alcohols and a much lower activity for the epoxidation of alkenes, has been ascribed to the coordination of the alcohol group to the titanium or vanadium site, thereby activating the double bond as well as orienting it favorably with respect to the coordinated oxygen transfer agent.

The reactivity of the allylic alcohols can be enhanced by substituting alkyl groups onto the double bond. For example, 2-buten-1-ol (TOF = 119) is far more reactive than 2-propen-1-ol (TOF = 18). As can be seen in Table 5.10, the branched allylic alcohols tested are also relatively easily epoxidized. The overall reactivity for the allylic alcohols follows the trend: trisubstituted > 1,2-disubstituted > 1,1-disubstituted > monosubstituted, which is exactly what would be expected of a sterically non-hindered electrophilic epoxidation mechanism.\(^{28}\) Compared with the cyclohexenes (Table 5.9), no direct indication of steric effects at the titanium site in Ti-beta is observed. This is probably due to the relatively small size of the substrates compared to the cyclohexenes. The major side-reaction observed was not the acid-catalyzed consecutive reaction of the epoxide group (Figure 5.1) but the oxidation of the alcohol group, as was also observed by Tatsumi et al.\(^{47,48}\) for TS-1.

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Table 5.10  The epoxidation of allylic alcohols over Ti-beta-1 in acetonitrile at 70 °C.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Initial TOF\textsuperscript{b} [mol mol\textsuperscript{-1}Ti h\textsuperscript{-1}]</th>
<th>TON\textsuperscript{b} after 3h [mol mol\textsuperscript{-1}Ti]</th>
<th>Peroxide efficiency [ % ]\textsuperscript{c}</th>
<th>Select. to Epoxide [ % ]\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-propen-1-ol (allyl alcohol)</td>
<td>18</td>
<td>42</td>
<td>70</td>
<td>&gt;90\textsuperscript{e}</td>
</tr>
<tr>
<td>1-buten-3-ol</td>
<td>13</td>
<td>27</td>
<td>92</td>
<td>&gt;90\textsuperscript{e}</td>
</tr>
<tr>
<td>cis-2-buten-1-ol</td>
<td>119</td>
<td>128</td>
<td>92</td>
<td>73.9 (23.7)\textsuperscript{f}</td>
</tr>
<tr>
<td>2-methyl-1-propen-3-ol</td>
<td>62</td>
<td>93</td>
<td>62</td>
<td>85 (11)\textsuperscript{f}</td>
</tr>
<tr>
<td>3-methyl-2-buten-1-ol</td>
<td>275</td>
<td>274</td>
<td>68</td>
<td>96.0</td>
</tr>
<tr>
<td>cis-2-penten-1-ol</td>
<td>256</td>
<td>304</td>
<td>79</td>
<td>88.6 (11.4)\textsuperscript{f}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Experimental conditions: 20 mmol alkene, 10 mmol aqueous hydrogen peroxide (30 wt% aqueous) and 50 mg catalyst in 24 g solvent. \textsuperscript{b} TOF and TON are based on the epoxide and triol formed only. \textsuperscript{c} Defined as mmol oxygenated products observed per mmol of hydrogen peroxide consumed. \textsuperscript{d} Selectivity to epoxide, based on total products formed. \textsuperscript{e} Conversion too low to accurately determine the selectivity, epoxide major product. \textsuperscript{f} Value in brackets indicate the fraction of products from the oxidation of the alcohol group.\textsuperscript{47,48,50}

The epoxidation of allyl alcohol (2-propen-1-ol) over TS-1 has been studied extensively by Hutchings \textit{et al.},\textsuperscript{27,49} Tatsumi \textit{et al.}\textsuperscript{47,48} and Bhaumik \textit{et al.}\textsuperscript{50} Similar to Ti-beta, TS-1 was found to be active but the rate of allyl alcohol epoxidation was reported to be an order of magnitude lower than that of 1-hexene epoxidation under similar conditions. The difference between TS-1 and Ti-beta is shown by their relative activities in the epoxidation of more highly substituted allylic alcohols. These were difficult to oxidize over TS-1,\textsuperscript{47,48} while high activities were observed for Ti-beta (Table 5.10). This clearly shows the advantage of the large pores of zeolite Ti-beta compared with the medium sized pores of TS-1 in converting even not-so-bulky substrates.
5.4 Conclusions

The large pore zeolite Ti-beta is an active and selective catalyst for the epoxidation of various alkenes with aqueous hydrogen peroxide. By contrast to TS-1, Ti-beta exhibits acidic properties when alcoholic solvents are used, decreasing the selectivity towards epoxides by promoting the consecutive formation of glycol ethers and polymeric products. Based on the experiments in the presence of alkali metal salts, it is concluded that the very small amount of aluminum present (Si:Al > 2500) does not contribute to the acidity observed. Ion-exchanging the acidic titanium site with alkali metals ions was found to be detrimental for the catalytic properties of the Ti-site. The observed acidity is ascribed to the Lewis acidity of the titanium site in Ti-beta and can be circumvented by using aprotic and weakly basic solvents, e.g. acetonitrile.

Ti-beta is a good catalyst for the epoxidation of linear alkenes, though its activity is slightly lower than that observed for TS-1. The catalytic potential of the large pore zeolite Ti-beta is demonstrated by the facile epoxidation of bulky alkenes like norbornene, methylcyclohexenes and cyclic terpenes and the facile epoxidation of moderately bulky allylic alcohols.

From the higher reactivity of methylenecyclohexane compared to 1-methylcyclohexene, it is concluded that steric effects still play an important role in the actual oxygen transfer reaction. Since the cyclohexenes tested could all easily enter the pores of zeolite beta, this suggests that differences in steric hindrance in the transition states underlie the observed effects. The epoxidation of substrates that can easily rearrange in the presence of weak acids, e.g. camphene, α-terpineol and α- and β-pinene, shows that Ti-beta still has weakly acidic properties despite the presence of a weakly basic solvent. In the epoxidation of allylic alcohols all substrates bearing a terminal, unsubstituted double bond are slowly oxygenated in accordance with literature data for TS-1. The presence of electron-donating alkyl groups at the double bond enhances the activity substantially. Again, the larger pores of Ti-beta allowed the epoxidation of more highly branched allylic alcohols compared to TS-1.
5.5 References

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Epoxidation of alkenes

(1993), L41.

The influence of solvents on the catalytic epoxidation of 1-octene over zeolite titanium beta.

Abstract

The aluminum-free titanium analog of zeolite beta (Ti-beta) was used in the epoxidation of alkenes with aqueous hydrogen peroxide. Ti-beta exhibits Brønsted acidic properties when alcohols are employed as the solvent. This is explained by a Lewis acidic character of the titanium site in Ti-beta, which on coordination of an alcohol yields a mild Brønsted acid site. When alcohol/acetonitrile mixtures are applied as the solvent, a clear maximum in activity was observed at compositions depending on the polarity of the alcohol used. The values for the maximum activities obtained in the 1-octene epoxidation were within the same range for all alcohols tested, suggesting that solvent effects observed are mainly caused by differences in physisorption equilibria. A similar behavior was found for TS-1 in the 2-propanol/acetonitrile system, while Ti,Al-beta did not show a maximum in activity. Based on the observed relation between activity and solvent composition a catalytic intermediate is proposed in which an alcohol as well as a hydroperoxo group is coordinated to a framework titanium atom.
6.1 Introduction

Since the discovery in 1983 of TS-1, a titanium containing silicalite with the MFI structure, by Taramasso et al.\(^1\) much research has been conducted on its synthesis and on its application as an oxidation catalyst for a wide range of oxygenations with hydrogen peroxide as the oxidant. Specific properties of TS-1 are the presence of isolated tetrahedrally coordinated titanium atoms in a well-defined silicate structure and a hydrophobic and acid-free environment.\(^2\) An obvious limitation is its pore size of 5.6 x 5.3 Å. Recently two new types of titanium containing molecular sieves with large pores were reported. Camblor et al.\(^3\) reported the incorporation of titanium in zeolite beta. However, this catalyst contained an unavoidable amount of aluminum, which resulted in unwanted acid-catalyzed secondary reactions. For that reason research has been aimed at obtaining aluminum-free materials. Rigutto et al.\(^4\) avoided the presence of aluminum by gas-phase substitution of framework boron in zeolite boron beta with TiCl\(_4\). Recently four publications concerning the direct hydrothermal synthesis of the aluminum-free titanium analogue of zeolite beta\(^5\)-\(^8\) have appeared.

The titanium analogue of zeolite beta (Ti-beta) is of particular interest, since it combines a three-dimensional structure of large pores with a hydrophobic interior. We found the di(cyclohexylmethyl)dimethylammonium cation (DCDMA\(^+\)) to be a well-fitting template cation for the synthesis of zeolite Ti-beta and showed that Ti-beta is an excellent catalyst in the epoxidation of bulky alkenes, such as norbornene, limonene and α-terpineol.\(^6\) Ti-beta possessed acidic properties when alcoholic solvents were used, which were not caused by residual aluminum in the framework.\(^6\) Similar results, e.g. the formation of glycols when alcoholic solvents were employed, were observed by Saxton et al.\(^5\) and Corma et al.\(^7\)

It is known that the choice of the solvent can have a crucial effect on the activity and selectivity in zeolite-catalyzed reactions.\(^9\),\(^10\) Alcohols are usually the preferred solvents for epoxidation of alkenes using aqueous hydrogen peroxide and TS-1 as the catalyst, which is either interpreted in terms of hindrance by physisorbed solvent molecules in the zeolite channels\(^11\),\(^12\) or by electronic effects of the adsorbed solvent molecule on the catalytically active center.\(^13\),\(^14\) Two different intermediates for the epoxidizing species are proposed.
Huybrechts et al.\textsuperscript{11} and Notari et al.\textsuperscript{12} proposed the Ti(\(\eta^2\)-O\(_2\)) species \(\text{I}\) (Figure 6.1) based on known active peroxo complexes of the group 4-7 transition metals. However, this species \(\text{I}\) cannot adequately explain the observed solvent effects, in particular the beneficial influence of methanol and ethanol. Furthermore, a number of stable titanium peroxo-complexes have been isolated but they were not active as an oxygen transfer reagents in epoxidations. Clerici and Ingallina\textsuperscript{15} interpreted the solvent effects as evidence for the participation of solvent molecules in the catalytic mechanism. These authors formulated a mechanism for TS-1 catalyzed epoxidation which involves a hydroperoxo species \(\text{II}\) (Figure 6.1) rather than the (\(\eta^2\)-O\(_2\))-peroxo species \(\text{I}\). In species \(\text{II}\) both an alcohol and a hydroperoxide are coordinated to the site. Differences in epoxidation activity between various alcoholic solvents are explained by differences in steric hindrance caused by the coordinated alcohol rather than electronic effects.\textsuperscript{11-14}

![Figure 6.1](image) Catalytic sites proposed for the epoxidation of alkenes using TS-1. \(\text{I}\) Ti(\(\eta^2\)-O\(_2\)) species\textsuperscript{11,12}; \(\text{II}\) Hydroperoxo species, including a coordinated solvent alcohol molecule.\textsuperscript{15}

Recently, three studies on the influence of solvents on the catalytic activity of Ti,Al-beta were reported by Sato et al.\textsuperscript{14,16} and Corma et al.\textsuperscript{17} As was observed for TS-1, the activity of Ti,Al-beta decreased along the series methanol > ethanol > 2-propanol > tert-butanol.\textsuperscript{18} However, the relative activity between the solvents for Ti,Al-beta varied less than observed for TS-1. The major products formed were the glycol ethers via acid-catalyzed secondary
reactions (Figure 6.2), which were ascribed to the presence of the acidic aluminum site.\textsuperscript{17}

![Figure 6.2 Epoxidation of alkenes and the acid-catalyzed secondary reactions over titanium containing zeolites.](image)

Sato \textit{et al.}\textsuperscript{14} on Ti,Al-beta showed that the use of 2,2,2-trifluoroethanol as the solvent increased the selectivity towards epoxide significantly which was explained on the basis of a lower strength of the hydrogen bond of 2,2,2-trifluoroethanol with the acidic aluminum site. For methanol in ZSM-5 the group of van Santen has shown with \textsuperscript{1}H MAS NMR that at least six molecules, contacted via hydrogen bonds, are necessary to stabilize the methoxonium ion (CH$_3$OH$_2^+$).\textsuperscript{19} The weaker hydrogen bond strength for 2,2,2-trifluoroethanol, caused by the electron withdrawing CF$_3$ group, causes less alcohol molecules to be involved in the protonated species. For methanol, epoxide cleavage is relatively easy since the extended protonated species takes up a substantial part of the free zeolite volume and acid protons are readily available at all the methanols involved. For 2,2,2-trifluoroethanol the charge is located to a single molecule thus lowering the chance of epoxide cleavage.\textsuperscript{14}

Another explanation given by Sato \textit{et al.}\textsuperscript{14} for the high activity in the presence of 2,2,2-trifluoroethanol, was partial oxidation of the alcohol to trifluoroacetic acid, which can \textit{in situ} form a peracid with hydrogen peroxide. Peracids are known to react readily with alkenes to give the corresponding epoxide. However, the authors did not observe a significant increase
in activity and selectivity in the presence of trifluoroacetic acid\textsuperscript{14}, excluding the peracid pathway.

The use of acetonitrile, a weak base, in the epoxidation of alkenes using Ti,Al-beta, was found to reduce effectively the acid catalyzed secondary reactions\textsuperscript{17}. Moreover, the activity of the catalyst in acetonitrile was significantly higher than for methanol as the solvent. This striking difference between TS-1, for which methanol is by far the best solvent, and Ti,Al-beta was ascribed to the aluminum sites. The aluminum sites strongly adsorb alcohols, thus decreasing the amount of substrates in the zeolite and thereby the activity. Upon using acetonitrile/methanol mixtures, it was observed that the activity showed a minimum when a 34/66 mixture was applied. The selectivity towards the epoxides was, however, very high (>83.5\%) for all solvent mixtures except for the pure methanol solvent, thus showing the neutralizing properties of the weakly basic acetonitrile.

In this Chapter, results on the effect of the applied solvent on the catalytic activity and selectivity of Ti-beta in the epoxidation of 1-octene are presented and interpreted in relation to the catalytic intermediates proposed in literature\textsuperscript{37}. The solvents used are methanol, ethanol, 2-propanol, \textit{tert}-butanol or acetonitrile and mixtures thereof.

\section*{6.2 Experimental}

Di(cyclohexylmethyl)dimethylammonium bromide (DCDMA.Br) was synthesized from cyclohexylmethyl bromide and N,N-dimethyl(cyclohexylmethyl)amine in DMSO at 90 °C overnight (see Chapter 4 for synthesis details). The DCDMA.Br was subsequently converted to the corresponding hydroxide (DCDMA.OH) by silver oxide. For a typical synthesis of Ti-beta, 0.25 g titanium(IV) ethoxide (TEOT) was added to 30.0 g of a 19.5 wt\% DCDMA.OH solution in water and stirred until all the TEO\textsuperscript{T} was dissolved. To the clear solution 3.0 g Aerosil 200 (Degussa), 0.15 g seeds (all-silica beta)\textsuperscript{20} and 11.8 g water were added and the gel was aged for at least 24 h until opalescent gel of low viscosity was obtained. The molar gel composition was:

\[ 1 \text{ SiO}_2 : 0.022 \text{ TiO}_2 : 0.46 \text{ DCDMA.OH} : 40 \text{ H}_2\text{O} \]
After crystallization (14 days at 140 °C) the as-synthesized zeolite (yield 1.4 g, 45 % silicon incorporation) was collected by filtration, washed, dried and calcined at 540 °C in air.

The chemical composition of the materials was determined using ICP/AES on a Perkin-Elmer Plasma II apparatus (ICP) or a Perkin-Elmer 1100 apparatus (AES). UV-Vis spectra were recorded on a Varian Cary-1 UV/Vis spectrophotometer using barium sulfate as the reference. Exact position of the reflection at 2θ ≈ 43.5° (indexed as 600 for polytype A)\(^3\) was determined using a Guinier-De Wolf camera with quartz as internal standard. Full characterization of the Ti-beta materials obtained is described in Chapter 4. The catalysts employed in this Chapter were Ti-beta-1 (Si:Ti = 59) and Ti-beta-2 (Si:Ti = 69). For comparison TS-1 (Si:Ti = 58, kindly donated by M. van Klaveren and synthesized according to the procedure of van der Pol et al.\(^{21}\)), Ti,Al-beta (Si:Ti = 39; Si:Al = 75, prepared according to Corma et al.\(^4\)) and Ti-MCM-41 (Si:Ti = 54, kindly donated by J.P.M. Niederer of the Hölderich group at the RWTH Aachen and synthesized according to the procedure of Cambor et al.\(^{22}\)) were used.

The catalysts were tested in the epoxidation of 1-octene (98 %, Aldrich). Epoxidations were performed at 313 or 343 K, using 23.5 g solvent (acetoneitrile, ethanol, 2-propanol, tert-butanol, 2,2,2-trichloroethanol and mixtures thereof), 100 mg catalyst, 2.24 g 1-octene (20 mmol) and 1.135 g H\(_2\)O\(_2\) (10 mmol, 30 w/w % aqueous solution); 1,3,5-triisopropylbenzene was used as internal standard. Samples were taken at regular intervals and analyzed using GC (CP-Sil-5) and GC-MS.

Chemicals were purchased from Baker (methanol, ethanol, 2-propanol and tert-butanol), Rathbury (acetoneitrile), Aldrich (1-octene and 1,3,5-triisopropylbenzene), Fluka (1,3,5-tri-tert-butylbenzene) and Merck (hydrogen peroxide, 30 wt% aqueous).

6.3 Results and Discussion

6.3.1 Catalyst Characterization

Primary characterization of the Ti-beta materials obtained was performed by XRD, ICP/AES
and UV-Vis spectroscopy. XRD measurements showed that essentially pure zeolite beta had been synthesized, sometimes accompanied by small amounts (less than 3 %) of ZSM-12. ICP/AES of the as-synthesized material confirmed the presence of titanium and the absence of aluminum and boron (Si/Al > 2500; Si/B > 1600). The incorporation of titanium was confirmed by UV-Vis, infrared spectroscopy and lattice cell-expansion, see Chapter 4 for full details. The infrared spectra of the as-synthesized and calcined materials show a band at 960 cm$^{-1}$, indicative of fourfold coordinated titanium in a silicate framework.$^{23,24}$ As we already pointed out,$^{20}$ a strong band at 960 cm$^{-1}$ is also present in the all-silica analogue and infrared is therefore not a suitable characterization method. The incorporation of titanium was confirmed by a linear relation between the unit-cell parameter $a$, determined from the diffraction line indexed as 600 for polytype A and the titanium content in the zeolite (see Figure 4.7 in Chapter 4). The observed expansion corresponds to an average $d_{Ti-O}$ distance of $1.79 \pm 0.06 \text{Å}$, which is close to the average $d_{Ti-O}$ of 1.76 Å observed for TS-1$^{25}$ and 1.764 Å for titanium in tetrahedral coordination in metal oxides.$^{26}$

As we described earlier, the titanium site in Ti-beta has Lewis acidic properties and can bind alcohols through expansion of its coordination sphere.$^{23}$ The state of coordination around the titanium can be obtained from diffuse reflectance UV-Vis. The incorporation of tetrahedral coordinated titanium$^{27,28}$ in the framework of Ti-beta-2 (dried at 200 °C) was confirmed by the presence of a strong absorption maximum at 47.000 - 50.000 cm$^{-1}$ in the UV-Vis spectra (Figure 6.3). In the presence of water or 2-propanol this band is shifted towards a lower frequency (45.000 - 48.000 cm$^{-1}$), which is generally accepted as an indication for a higher coordination number around the titanium atom, most probably five-coordinated. In the case of water a second weak absorption around 36.000 - 40.000 cm$^{-1}$ is observed. Absorptions around 40.000 cm$^{-1}$ are usually attributed to isolated octahedral titanium species.$^{27,28}$ The absence of an absorption below 30.000 cm$^{-1}$ in the calcined zeolite confirms the absence of more highly clustered titanium oxide phases.$^{27}$
Figure 6.3 UV-Vis of Ti-beta-2 and the effect of hydroxylic compounds. The sample was pre-dried at 200 °C, water and 2-propanol were added to the sample (0.18 g/gzeolite) at room temperature.

6.3.2 Influence of type of titanium catalyst

The Ti-beta-2 catalyst (Si:Ti = 69) was tested in the epoxidation of 1-octene with hydrogen peroxide (30 wt% aqueous) and compared with TS-1, Ti,Al-beta and Ti-MCM-41. At low temperature (40 °C) Ti-beta, Ti,Al-beta and Ti-MCM-41 exhibit low activities and only TS-1 exhibits a high activity (Table 6.1). The low activity of the Ti-beta catalysts at 40 °C compared with TS-1, and the tremendous increase in activity by raising the reaction temperature to 60 °C (Table 6.2), is not clear. It was surprising to find that the essentially aluminum-free Ti-beta gave the monomethyglycol ether (C₆H₁₃CH(OMe)CH₂OH and isomer, Figure 6.2) as the major product. As we reported earlier⁶ this implies that, unlike TS-1, the titanium site in Ti-beta has Brønsted acidic properties when alcoholic solvents are applied. In Chapter 5, we already showed by means of pyrolysis-MS that polyglycol formation is an important side-reaction, besides the formation of glycol monoalkyl ethers, when high polar
alcohols are applied as the solvent. Apparently, at low temperatures polymerization is favored over glycol formation, thereby faster deactivating the catalyst. Similar results, viz. a low selectivity towards the epoxide, were reported by Saxton et al.\textsuperscript{5} and Corma et al.\textsuperscript{7} for essentially aluminum-free Ti-beta's.

Table 6.1 Epoxidation of 1-octene at 40 °C in methanol.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF\textsuperscript{b}</th>
<th>Conversion [ % ]\textsuperscript{c} at 1 h</th>
<th>Conversion [ % ]\textsuperscript{c} at 5 h</th>
<th>Selectivity to oxygenates\textsuperscript{d} 1-oct. H\textsubscript{2}O\textsubscript{2}</th>
<th>Epoxides in products\textsuperscript{d} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-1</td>
<td>27.7</td>
<td>4.1</td>
<td>13.5</td>
<td>93</td>
<td>96</td>
</tr>
<tr>
<td>Ti-beta-2</td>
<td>0.5</td>
<td>--</td>
<td>--</td>
<td></td>
<td>glycol ether\textsuperscript{e}</td>
</tr>
<tr>
<td>Ti,Al-beta</td>
<td>3.6</td>
<td>0.5</td>
<td>2.1</td>
<td>67</td>
<td>53</td>
</tr>
<tr>
<td>Ti-MCM-41</td>
<td>0.4</td>
<td>--</td>
<td>--</td>
<td></td>
<td>glycol ether\textsuperscript{e}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Experimental conditions: 20 mmol 1-octene, 10 mmol hydrogen peroxide (30 wt% aqueous) and 100 mg catalyst in 24 g methanol. \textsuperscript{b} Initial Turn-Over-Frequency in mmol\textsuperscript{-1} Ti h\textsuperscript{-1}. \textsuperscript{c} Based on 1-octene. \textsuperscript{d} After 1 hour reaction, oxygenates observed are the epoxide and the glycol monomethyl ether (Figure 6.2). \textsuperscript{e} Predominant product, conversion too low to determine selectivity accurately.

Table 6.2 Epoxidation of 1-octene at 60 °C in methanol.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF\textsuperscript{b}</th>
<th>Conversion [ % ]\textsuperscript{c} at 1 h</th>
<th>Conversion [ % ]\textsuperscript{c} at 5 h</th>
<th>Selectivity to oxygenates\textsuperscript{d} 1-oct. H\textsubscript{2}O\textsubscript{2}</th>
<th>Epoxides in products\textsuperscript{d} [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-1</td>
<td>96.8</td>
<td>16.0</td>
<td>41.7</td>
<td>84</td>
<td>91</td>
</tr>
<tr>
<td>Ti-beta-2</td>
<td>85.5</td>
<td>11.6</td>
<td>23.8</td>
<td>82</td>
<td>81</td>
</tr>
<tr>
<td>Ti,Al-beta</td>
<td>41.8</td>
<td>6.7</td>
<td>15.9</td>
<td>87</td>
<td>65</td>
</tr>
<tr>
<td>Ti-MCM-41</td>
<td>7.2</td>
<td>1.3</td>
<td>2.9</td>
<td>76</td>
<td>54</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Experimental conditions: 20 mmol 1-octene, 10 mmol hydrogen peroxide (30 wt% aqueous) and 100 mg catalyst in 24 g solvent. \textsuperscript{b} Initial Turn-Over-Frequency in mol mol\textsuperscript{-1} Ti h\textsuperscript{-1}. \textsuperscript{c} Based on 1-octene. \textsuperscript{d} After 1 h reaction, oxygenates observed are the epoxide and glycol monomethyl ether (Figure 6.2).
In the case of Ti,Al-beta and Ti-MCM-41 the low activity can be explained on the basis of their hydrophilic interior; Ti,Al-beta contains acid sites and the internal surface of Ti-MCM-41 consists mainly of Si-OH groups. Water, methanol and hydrogen peroxide are strongly adsorbed by these materials and the inner concentration of 1-octene will be very low, thus retarding the catalytic conversion. As expected the primary products for Ti,Al-beta are the glycol ethers due to the acidity of the aluminum site. Upon raising the temperature the activity of all the large pore materials increased significantly, though TS-1 retained the best catalytic properties (Table 6.2).

Next the influence of several solvents on the Ti-beta catalyzed epoxidation of 1-octene with hydrogen peroxide at 40 °C was studied. It is clear from Table 6.3 that methanol and ethanol are not the most suitable solvents for the epoxidation of 1-octene. The most suitable alcoholic solvent was 2-propanol, though the major product for all alcoholic solvents used were the monoglycol ethers rather than the epoxide. Since the materials were essentially free of aluminum (Si:Al > 2500), we assume that the acidity is generated by the titanium-site itself.

Table 6.3  Effect of various solvents on the catalytic activity of Ti-beta-2 in the epoxidation of 1-octene at 40 °C.a

<table>
<thead>
<tr>
<th>Solvent</th>
<th>TOFb</th>
<th>Conversion [ % ]c 1 h 5 h</th>
<th>Selectivity to oxygenatesd 1-oct. H₂O₂</th>
<th>Epoxides in products [ % ] 1 h 5 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>0.5</td>
<td>--.  --.</td>
<td></td>
<td>glycols¹</td>
</tr>
<tr>
<td>ethanol</td>
<td>5.4</td>
<td>0.7  1.1</td>
<td>87  77</td>
<td>46  7</td>
</tr>
<tr>
<td>2-propanol</td>
<td>13.5</td>
<td>1.9  4.1</td>
<td>89  51</td>
<td>63  24</td>
</tr>
<tr>
<td>tert-butanol</td>
<td>1.7</td>
<td>0.3  0.8</td>
<td>67  78</td>
<td>100  36</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>5.4</td>
<td>0.7  1.7</td>
<td>89  69</td>
<td>100  98f</td>
</tr>
</tbody>
</table>

a Experimental conditions: 20 mmol 1-octene, 10 mmol hydrogen peroxide (30 wt% aqueous) and 100 mg Ti-beta-2 in 24 g solvent. b Initial Turn-Over-frequency in mol mol⁻¹ Ti⁻¹ h⁻¹. c Based on 1-octene. d Oxygenates observed are the epoxide and glycol monomethyl ether. e Predominant product, conversion too low to be determined accurately. f Other 2% is the diol.
As we reported earlier\(^6\), we believe that the Brønsted acidity is generated by the coordination of an alcohol to the Lewis-acidic titanium site. The coordination of alcohols to the titanium site can be monitored by UV-Vis which indeed shows an increased coordination number for the titanium site by adsorption of 2-propanol (see Figure 6.3) and methanol (data not shown). As we reported very recently\(^{29}\) Ti-beta is capable of catalyzing the Meerwein-Ponndorf-Verley (MPV) reduction of ketones to the corresponding alcohols. In the MPV reduction both a ketone and an alcohol are coordinated to a Lewis acidic metal ion after which a hydride transfer from the alcohol to the ketone takes place (see Figure 6.4). In our view, this is a further confirmation that the titanium site in Ti-beta has oxophilic Lewis acidic properties, which can lead to a Brønsted acidic character by coordination of protic molecules (i.e. alcohols).

![Diagram](image.png)

Figure 6.4 Proposed catalytic site in the Meerwein-Ponndorf-Verley reduction of ketones with alcohols over titanium sites in Ti-beta.\(^{29}\)

6.3.3 Solvent effects

In order to study the influence of alcohols on the catalytic activity of Ti-beta-2 (Si:Ti = 69), the catalytic activity and performance of Ti-beta using acetonitrile as the solvent while adding various amounts of alcohol as co-solvents was investigated. Both the epoxidation results so far\(^{5,6,7}\) and the recently reported MPV reduction\(^{29}\) suggest that titanium acts as a Lewis acid and can coordinate two oxygen containing molecules. If an alcohol molecule is required in
the catalytic cycle e.g. species II, changes in catalytic activity as a function of the alcohol used and amount of alcohol added are to be expected. The results for the alcohols tested are shown in Figure 6.5.

Upon addition of various amounts of ethanol, 2-propanol, tert-butanol and 2,2,2-trichloroethanol to acetonitrile, the activity of Ti-beta changes depending on the amount and type of alcohol added (Figure 6.5). A clear maximum in activity is visible for all alcohols, indicating that the presence of an alcohol is beneficial for epoxidation. If the alcohol concentration is further increased, the activity decreases again. The maximum attainable activity was found to be almost equal for all the alcohols tested and the position of the maximum was found to be dependent on the polarity of the alcohol used.

![Graph showing the influence of alcohols on initial epoxidation rates of 1-octene in acetonitrile over Ti-beta-2.](image)

**Figure 6.5** Influence of alcohols on the initial epoxidation rates of 1-octene in acetonitrile over Ti-beta-2. • tert-butanol; ▲ 2-propanol; ■ ethanol; ◆ 2,2,2-trichloroethanol. Experimental conditions: 2.24 g 1-octene; 1.14 g H₂O₂ (30 w/w % aqueous); 100 mg Ti-beta in 24 g total solvent at 70 °C.

The increase in activity when small amounts of alcohols were added to the solvent, confirms that alcohols participate actively in the catalytic mechanism. This confirms in our
view that species II, in which an alcohol is coordinated to the Ti-site, is an important intermediate in the catalytic cycle for the epoxidation of alkenes. For species I, the observed effects can only be explained in terms of sorption equilibria of solvents and substrates in the zeolite.

To ascertain that the observed increase in activity when small amounts of alcohols were added, could not be explained solely in terms of competitive sorption effects, e.g. supporting species I as the catalytically active intermediate, insight in the sorption behavior of the catalyst under experimental conditions was required. It is, however, inconvenient to determine the adsorption equilibria for five-component systems. Two-component competitive adsorption experiments with 2-propanol and acetonitrile (Figure 6.6), showed that the Ti-beta catalyst has a slight preference for the alcohol.

![Figure 6.6 Competitive sorption of acetonitrile (●) and 2-propanol (■) onto Ti-beta (500 mg substrates total, 500 mg dry zeolite Ti-beta-2, 25 ml 1,3,5-triisopropylbenzene as non-adsorbing solvent and 1,3,5-tri-tert-butylbenzene as internal standard at 298 K).](image)

If species I would be the predominant intermediate, one would perhaps expect that the observed rate would be dependent on the intraporous 1-octene and hydrogen peroxide concentration only and thus indirectly on the applied solvent via shifts in the adsorption
equilibria. Under the reaction conditions used the zeolite is completely filled and the initial (i.e. no epoxides have been formed) pore-filling of the catalyst can be described by equation (6.1):

\[ V_{zeo} = V_{1-octene} + V_{H_2O_2} + V_{solvent} = Constant \quad (6.1) \]

In which \( V_{zeo} \) is the total free pore volume of the zeolite and \( V_i \) is the volume occupied by component \( i \). The solvent is defined as all components which can be adsorbed but which do not participate in the catalytic mechanism. For the proposed species I, the solvent would consist of water, 2-propanol and acetonitrile. Equation (6.1) can be rewritten to expression (6.2) to show the dependency of the adsorbed volumes of the two active components as a function of the bulk solvent composition.

\[ V_{1-octene} + V_{H_2O_2} = Constant - V_{solvent} \quad (6.2) \]

The volume of the solvent, \( V_{solvent} \) is determined by the adsorbed amount of non-reacting molecules in the zeolite. Since only the bulk concentrations of acetonitrile and 2-propanol were changed and Ti-beta is a hydrophobic zeolite, it is assumed that the absolute change in \( V_{water} \) is comparatively small compared to the total volume of the solvent, \( V_{solvent} \). Therefore, the contribution of \( V_{water} \) on \( V_{solvent} \) was neglected and equation (6.2) reduces further to give equation (6.3):

\[ V_{1-octene} + V_{H_2O_2} = constant - ( V_{ACN} + V_{2-ProOH} ) \quad (6.3) \]

Based on the preference of the Ti-beta zeolite for 2-propanol compared to acetonitrile (Figure 6.6), it can be expected that in a mixture of both solvents, the increase in \( V_{2-ProOH} \) will be greater than the decrease in \( V_{ACN} \). This would suggest that according to equation (6.3), the total volume available for the reactive substrates will decrease continuously with an increasing fraction of 2-propanol in the solvent. This decrease in intraporous 1-octene and hydrogen peroxide concentration is expected to small due to the high affinity of the hydrophobic Ti-beta
for 1-octene. A substantial increase in either $V_{\text{1-octene}}$ or $V_{\text{H}_2\text{O}_2}$ is not very likely. In the case of species I, one would not expect that the rate to show a maximum, since a kinetic rate expression for species I would only depend on $V_{\text{1-octene}}$ and $V_{\text{H}_2\text{O}_2}$. It is therefore concluded that the observed maxima in catalytic activity cannot be caused solely by physisorption. Thus, the alcohol added participates actively in the catalytic mechanism, suggesting species II as one of the major catalytic species (Figure 6.1).

The maximum attainable activity was almost the same for all the alcohols tested (Figure 6.5), suggesting little influence of electronic and steric effects of the coordinated alcohol on the catalytic activity under these conditions. This is surprising, especially for the bulky tert-butanol and 2,2,2-trichloroethanol. On the other hand, Ti-beta was found to catalyze the Meerwein-Ponndorf-Verley reduction of 4-methylcyclohexanone with 2-heptanol as the reducing alcohol. In this reaction both the ketone and the alcohol are coordinated simultaneously at the titanium site, which shows that bulky transition states are feasible within the pores of Ti-beta.

If one compares the position at which the maximum activity is observed with the polarity of the alcohol used, it can be seen that the higher the polarity of the alcohol the higher the percentage alcohol needed in the solvent, i.e. 2,2,2-trichloroethanol > ethanol > 2-propanol > tert-butanol. Since Ti-beta is a hydrophobic zeolite, it is logical to assume that for a more polar solvent molecule a higher bulk solvent concentration is required to reach the same alcohol concentration inside the zeolite channels.

When the alcohol concentration is further increased, the activity decreases again. To explain this phenomenon we assume that the amount of adsorbed alcohol in the pores of the zeolite still increases at higher alcohol concentrations. Two possible phenomena might be used to explain the decrease in activity observed.

i) The additionally adsorbed alcohol could become a barrier, hindering the diffusion of substrates and products as well as decreasing the amount of substrate which can be adsorbed and thereby decreasing the intrinsic reaction rate.

ii) The additional alcohol is in competition with hydrogen peroxide for the second coordination to the titanium site (Figure 6.8, species IV), thus reducing the amount of catalytic intermediate species II.

Note that (ii) is closely related to (i). In order to have an alcohol molecule competing with
hydrogen peroxide for a second coordination at the titanium site (ii), higher concentrations of alcohol in the zeolite are necessary. This is, however, the condition at which effect (i) would also occur.

Some direct proof for (i) or (ii) is given by the adsorption characteristics of 2-propanol/acetonitrile mixtures onto Ti-beta. The maximum activity in the Ti-beta catalyzed epoxidation of 1-octene is observed at approximately 20 wt% 2-propanol added. From the adsorption curve (Figure 6.6), it can be seen that the zeolite has adsorbed about 30 % of its maximum amount of 2-propanol. At 2-propanol fractions higher than 20 wt% more 2-propanol is still adsorbed. Despite this increase in internal 2-propanol concentration, (i) will still only be true if this excess 2-propanol prevents the other substrates from adsorbing. It was, however, difficult to determine the absorption curves for water and hydrogen peroxide, due to their low solubility in the solvent, 1,3,5-triisopropylbenzene. Zeolite Ti-beta is, however, considered to be a hydrophobic zeolite and it is not to be expected that either of the two will be adsorbed preferentially. The hydrophobic zeolite Ti-beta most likely prefers apolar adsorbates such as 1-octene, which was demonstrated by co-adsorption experiments using mixtures of 1-octene and acetonitrile in a bulky solvent (Figure 6.7).

![Figure 6.7 Competitive sorption of acetonitrile (●) and 1-octene (■) onto Ti-beta (500 mg substrates total, 500 mg zeolite Ti-beta-2 (dried at 200 °C), 25 ml 1,3,5-triisopropylbenzene and 1,3,5-tri-tert-butylbenzene as internal standard at 298 K.](image-url)
Figure 6.8 Titanium site with two coordinated alcohols.

From Figure 6.7 it was also observed that under the experimental conditions, i.e. about 10 wt% 1-octene, a considerable amount of the polar acetonitrile was adsorbed by the zeolite. This suggests that zeolite Ti-beta is not as hydrophobic as expected for a nearly all-silica zeolite. This is probably due to the relatively high amount of silanol groups present in these materials. The $^{29}$Si MAS NMR spectrum of calcined Ti-beta (Figure 4.10) showed a considerable amount of silanol groups in accordance with the related all-silica zeolite beta (Figure 3.6), for which we reported that about 16 % of the silicon atoms bear a hydroxyl group.

We concluded that hardly any steric or electronic effect of the coordinated alcohol on the epoxidation activity exists and that the polarity of the alcohol determines the bulk solvent concentration of alcohol at which the maximum activity is attained. It is concluded that the concentration of alcohol in the hydrophobic zeolite is one of the key factors in determining the activity of Ti-beta and possibly of titanium zeolites in general. A certain amount of alcohol in the zeolite channels is necessary to obtain species II but a higher concentration will reduce the activity via either (i) or possibly (ii). The intraporous alcohol concentration is largely determined by the polarity of the alcohol, i.e. the higher the polarity of alcohols the lower their internal concentration. When one would consider this for pure alcoholic solvents, one would expect the most polar alcohol to have the highest activity.

This effect is well known for TS-1, methanol is by far the preferred solvent with decreasing activity in the series methanol > ethanol > 2-propanol > tert-butanol. The picture
is not so clear for Ti-beta due to the higher acidic character compared to TS-1 and the effect of deactivation caused by acid-catalyzed by-products should also be considered. As we reported earlier the two main side-reactions are glycol ether formation by addition of an alcohol molecule and oligomerization of the epoxide. Polymerization leads to a stronger and less reversible deactivation since the monoglycol ethers formed can still diffuse through the zeolite channels whereas the polymers may not. In the case of highly polar alcohols, e.g. methanol and ethanol, the low amount of alcohol in the zeolite caused polymerization of the epoxide, as shown by pyrolysis-MS, and therefore caused a more profound decrease in activity, as can be seen in Table 6.3.

The influence of applying solvent mixtures of 2-propanol/acetonitrile has also been studied for TS-1 and Ti,Al-beta (Figure 6.9). For TS-1 similar behavior as Ti-beta is observed, viz. a maximum at a certain 2-propanol/acetonitrile mixture. However, the maximum activity is found at a higher 2-propanol fraction than observed for Ti-beta. This is probably due to differences in intrinsic hydrophobicities of the two zeolites. Whereas TS-1 is reported to be virtually defect free, the Ti-beta has a considerable amount of silanol groups as shown by $^{29}$Si MAS NMR, (see Figure 4.10 in Chapter 4). The absence of these silanol groups in TS-1, will effect a higher hydrophobicity compared to Ti-beta. Thus, higher bulk 2-propanol concentrations are required to obtain the same internal alcohol concentration in TS-1 compared with Ti-beta.

The initial epoxidation activity for Ti,Al-beta does not show a maximum as a function of the 2-propanol content in the solvent. Comparing the curves for Ti,Al-beta with either TS-1 or Ti-beta immediately shows the effect of aluminum sites. It is apparent that the presence of aluminum Bronsted sites increases the hydrophilicity of the zeolite significantly. Polar solvent molecules are now adsorbed preferentially over apolar substrates, such as the 1-octene used in our experiments. The intrinsic activity of the titanium site in Ti,Al-beta may well be similar to that of Ti-beta: the difference in activity between Ti,Al-beta and Ti-beta is determined by the difference in internal concentrations of solvent and substrate molecules in the zeolite pores. At the experimental conditions used, the rate is reduced by the decreased internal 1-octene concentration due to the high amount of polar solvent molecules adsorbed. Similar results for Ti,Al-beta have also been reported by Corma et al. for the methanol/acetonitrile system.
Figure 6.9 Influence of solvent composition for the 2-propanol/acetonitrile system on the initial epoxidation activity of 1-octene of various catalysts. ▲ Ti-beta; ■ TS-1; ● Ti,Al-beta.

6.3.4 Acid-catalyzed by-product formation as a function of solvent composition.

The coordination of an alcohol or hydroperoxy group to the titanium site results in a Brønsted acid which catalyzes unwanted site reactions (see Table 6.3) such as polyglycol formation, diol formation by reaction with a water molecule, monoglycol ether formation by reaction with an alcohol molecule and rearrangement to aldehydes and ketones. The existence of weak Brønsted acid sites in TS-1 has already been shown by Zecchina et al., who reported the exchangeability of the titanium hydroperoxy site II in TS-1 with bases, e.g. NaOH and NH₃. We have found that the use of the non-protic and slightly basic acetonitrile effectively reduces by-product formation.

The amounts of by-products, predominantly the monoglycol ether at high alcohol contents and the diol and aldehyde at low alcohol contents, were monitored as function of the 2-propanol content. As can be seen clearly from Figure 6.10, the high amount of by-products (73% by-products at 32% $\text{H}_2\text{O}_2$ conversion) for pure 2-propanol could be reduced significantly by the addition of small amounts of acetonitrile (18% by-products at 59% $\text{H}_2\text{O}_2$ conversion).
conversion upon addition of 5 wt% acetonitrile). It has to be noted that the activity also increases. This is probably related to the lower by-product formation since the glycols (and polyglycols) formed tend to plug the pore system, hindering the diffusion of substrates and epoxide through the channels. This implies that the main function of acetonitrile is to reduce the acidity of the catalytic species II by its weakly basic character and not to participate in the catalytic mechanism itself.

Figure 6.10  By-product formation in the epoxidation of 1-octene over Ti-Beta as a function of the fraction (wt%) of 2-propanol in acetonitrile after 3h reaction time at 70 °C.

The question still remains why TS-1 does not show these acidic properties as strongly as Ti-beta does. TS-1 also catalyzes the rearrangement of epoxides when hydrogen peroxide is present but at a rate which is reported to be 4.3 times lower than that of Ti-beta. Furthermore Clerici et al. have shown that it is possible to obtain stable alkali metal containing peroxo complexes of TS-1 by treatment with alkaline hydrogen peroxide solutions.

An answer might be found by considering the possible mechanisms by which an alcohol or water molecule can react with an epoxide. In general, three mechanisms are known in literature:
a) Brønsted acid catalyzed ring opening involves the protonation of the epoxide oxygen, followed by an attack of the alcohol.

b) Lewis acid induced ring opening. Similar to (a) but instead of protonation, a weak coordinative oxygen-metal bond is formed, thus activating the oxirane ring for ring opening.\textsuperscript{36}

c) Base catalyzed ring opening. A hydroxide or alkoxide ion-type nucleophile attacks a carbon atom of the epoxide ring.

All three mechanisms can be rationalized on the basis of reaction of plausible titanium complexes (Figure 6.11, Sites V, VI and VII). The first is related to the acid catalyzed glycol ether formation (a), i.e. the titanium site V generates a Brønsted acid site by coordination of a protic molecule, which subsequently protonates the epoxide. The oxophilic titanium can also directly activate the oxirane ring in a Lewis acidic mechanism VI. A base catalyzed mechanism (c) might consist of an oxirane ring which is attacked by an alcohol or alkoxide coordinated to the titanium site. In the case of titanium zeolites the Ti-site is considered to be a strong Lewis acid, ruling out the possibility of the base catalyzed mechanism VII. It can be noted that the sites V and VII are similar to the proposed epoxidation site II.

![Figure 6.11](https://example.com/figure6.11.png)  
Catalytic mechanisms of glycol monoalkyl ether formation over titanium sites in zeolites.
Chapter 6

A clue to what the mechanism of glycol formation is can be found in the catalytic behavior of Ti-beta during epoxidation itself. We found that the maximal attainable catalytic activity for epoxidation is independent of the coordinated alcohol in species III, and therefore concluded that steric hindrance due to alcohol coordination does not occur in the epoxidation. As can be seen in Table 6.3, selectivity to epoxide increases in the order MeOH < EtOH < 2-PrOH < t-BuOH, indicating that steric hindrance does play a role in glycol and glycol ether formation, e.g. bulky alcohols suppress the formation of by-products. The large pores of Ti-beta may then be responsible for the differences between Ti-beta and TS-1. On the other hand the spatial demand of the Sites VI and VII (three molecules e.g. one alcohol, peroxide and epoxide) is similar to that of the active epoxidation Site II (also three molecules involved e.g. one alcohol, peroxide and alkene), and this makes it difficult to find reasons why glycol ether formation only occurs in Ti-beta and hardly in TS-1. This reasoning makes Sites VI and VII less probable as the active site. We therefore assume that in the case of glycol and glycol ether formation at least one alcohol molecule and a peroxide molecule coordinate to the titanium to form the Brønsted acid site V, while a second alcohol subsequently attacks the protonated epoxide. The observed differences in by-product formation for TS-1 and Ti-beta can be explained by the smaller pore diameter of TS-1 (5.6 x 5.3 Å compared to the 7.4 x 6.9 Å for zeolite beta). The lower amount of acid catalyzed by-products in the case of TS-1 is therefore not due to the absence of the Brønsted acidic sites but rather to a lack of space around the acidic site.

6.4 Conclusions

The crystallization of essentially aluminum-free Ti-beta is possible using di(cyclohexylmethyl)dimethylammonium as the template. The successful incorporation of titanium is confirmed by a single absorption peak at 47.000 - 50.000 cm\(^{-1}\) in the UV-Vis spectrum, which also evidences the absence of oligomeric titanium species and a linear expansion of the crystallographic unit-cell volume with increasing titanium content.

In comparison with TS-1, Ti-beta displays a considerably higher acidity in the epoxidation of alkenes when pure alcohols are used as the solvent, as judged from by-product
formation. The acidity is assumed to originate from an adsorbed alcohol molecule on the catalytically active titanium site, the Ti(IV) lowers the pKₐ of the coordinated alcohol profoundly. When mixtures of acetonitrile and an alcohol are applied as the solvent, the activity of Ti-beta shows a clear maximum at a composition which depends on the polarity of the alcohol (Figure 6.5). The maximum attainable activity is independent of the type of alcohol applied in the mixture, indicating that steric or electronic effects due to the alcohol are absent. The differences in activity observed for the pure alcohols tested are explained on the basis of their polarity, which causes differences in competitive adsorption: the better the alcohol is adsorbed, the lower amount of 1-octene adsorbed and the lower the activity. The solvents effects observed confirm in our view the presence of an alcohol in the catalytic mechanism which would supports species II, originally proposed by Clerici and Ingallina,¹⁵ as the catalytically active site and two catalytic mechanisms of epoxidation can be envisaged based on Site II (Figure 6.12). A second effect which is observed, is the improved selectivity towards epoxides if even small amounts of acetonitrile are present. This is possibly due to the slightly basic nature of acetonitrile, which might effectively neutralize the acidity generated.

The active participation of alcohols in the catalytic mechanism would imply that species II is most likely to be the catalytically active site and species I not. As was already pointed out by Belussi and Rigutto², however, the species II has some major short-comings in that it invokes no specific chemical property of titanium. The role of titanium is that of a neutral, oxyphilic Lewis acid which can coordinate an alcohol and hydrogen peroxide simultaneously. From our results (Figure 6.5) it can be seen that for Ti-beta the maximum attainable activity is independent of the type of alcohol applied, which suggests the absence of steric or electronic effects due to a coordinated alcohol are absent. This seems odd especially in the case of the bulky tert-butanol and 2,2,2-trichloroethanol. We therefore conclude that alcohols do play an important role in the catalytic mechanism of epoxidation, though not necessarily via species II as the active oxygenating species. Further discussion on the nature of the catalytic site and the epoxidation mechanism is given in Chapter 7, where the influence of other kinetic parameters on the observed reaction rate will be discussed.
Figure 6.12  Possible catalytic mechanisms for the epoxidation of 1-octene over site II.
6.5 References

Chapter 6

A kinetic study of the epoxidation of 1-octene over zeolite titanium beta.

Abstract

In a study on the catalytic properties of zeolite titanium beta in the epoxidation of 1-octene, the effects of mass transfer, adsorption and intrinsic chemical kinetic processes were investigated. It was concluded that the influence of external mass transfer limitations in the bulk solution on the observed rate was negligible. The substantial differences between the activation energies of 1-octene epoxidation over different titanium containing zeolites and that for the mesoporous Ti-MCM-41 material, suggested that for the titanium zeolites internal diffusion limitations are present. This was also indicated for Ti-beta by a decrease in activity with an increase of the particle size. From competitive adsorption of acetonitrile and 1-octene it was concluded that the bulk concentrations applied were proportional to the internal concentration in the zeolite.

The observed rate of epoxidation as a function of the bulk concentration of 1-octene and of hydrogen peroxide, could unfortunately equally well be fitted to the proposed kinetic models as to an alternative model assuming diffusion limitations. The observed maximum in activity when the concentration of water was varied, is an indication that water plays an important role in the catalytic mechanism. This maximum in the catalytic activity, suggests that one water molecule is coordinated onto the titanium site in the catalytically intermediate species and that higher hydrated titanium species are not catalytically active. Ti,Al-beta also demonstrated a maximum in the catalytic activity as a function of water content whereas TS-1 did not show a maximum in activity. Similarly, maxima in activity were observed for Ti-beta when various amounts of different alcohols were added to the reaction mixture.

The kinetic data are interpreted in terms of mechanistic models proposed in literature and to a new model. The observed effects are conclusive with the models in which a lattice connected Ti(ROH)(H₂O₂) site is an important intermediate species. The model proposed by
Clerici and Ingallina assume that this Ti(ROH)(H$_2$O$_2$) species is the catalytically active intermediate. Our model for epoxidation reactions assumes that the formation of the catalytic active Ti($\eta^2$-O$_2$) species from the Ti(ROH)(H$_2$O$_2$) is the rate determining step, which at least takes into account the specific d$^0$ chemistry of the Ti(IV) atom.

7.1 Introduction

In the years since the discovery of TS-1 by Taramasso et al.$^1$ much research has been devoted to its application as an oxidation catalyst in various oxygenations using aqueous hydrogen peroxide and the catalytic mechanisms which underlie these reactions.$^{2-4}$ The precise nature of the mechanisms of catalytic oxygenation has as yet not been elucidated. From IR, UV-Vis and EXAFS spectroscopy it was concluded that the titanium site acts as a Lewis acid and can reversibly coordinate molecules such as water, ammonia, hydrogen peroxide and alcohols.$^{5-7}$ It was also demonstrated that the valency of the titanium atom did not change during oxygen transfer reaction and for this reason it was concluded that, in general, titanium catalyzes the oxygenation of hydrocarbons via the activation of a coordinated hydrogen peroxide on the Lewis acidic titanium site.

Several kinetic studies on the oxygenation of hydrocarbons over TS-1, TS-2 and Ti,Al-beta have been published in literature.$^{8-13}$ These studies were aimed at obtaining evidence for the catalytically active sites. The oxygenations studied were the oxidation of alcohols,$^{8,9}$ the oxofunctionalization of alkanes$^{10-12}$ and the epoxidation of alkenes.$^{12,13}$ The oxidation of alcohols with hydrogen peroxide was both investigated by Maspero et al.$^8$ using TS-1 and by Corma et al.$^9$ applying Ti,Al-beta as the catalyst. The results presented by Maspero et al.$^8$ show little influence of the alcohol concentration on the reaction rate. However, the observed order for hydrogen peroxide is somewhat ambiguous. The graphical data presented clearly show a negative order in contradiction with the first to zero order mentioned in the text. A positive order for hydrogen peroxide would be in agreement with the results obtained by Corma et al.$^9$ who also observed first to zero order kinetic behavior in hydrogen peroxide and first order in alcohol concentration. Both authors interpreted their kinetic data with exactly the same catalytic mechanism involving a Ti(ROH)(H$_2$O$_2$) intermediate. The Ti(ROH)(H$_2$O$_2$)
stands for a titanium species in which an alcohol molecule and a hydrogen peroxide molecule are simultaneously coordinated in one way or another. The differences in kinetic orders observed are explained by Corma et al.\textsuperscript{9} by differences in adsorption behavior under the different catalytic conditions used.

The same catalytic intermediate, Ti(ROH)(H\textsubscript{2}O\textsubscript{2}), is also presumed by Khouw et al.\textsuperscript{12} to be the active species in the epoxidation of alkenes and the oxofunctionalization of alkanes using TS-1. In both reactions a zero order kinetic behavior in water is observed in non-alcoholic solvents and even in the absence of water the catalytic activity remains unaltered. We think this is curious, since in non-alcoholic solvents the ROH in the catalytic intermediate is replaced by a water molecule and the amount of water added should definitively influence the observed reaction rate. Similarly, Corma et al.\textsuperscript{9} observed a negative order in the water concentration in the alcohol oxidation catalyzed by Ti,Al-beta, though this was explained by an enhanced competition of water and alcohol for the catalytic site due to the presence of the aluminum sites in the zeolite framework. In a kinetic study on the catalytic epoxidation of allyl chloride using TS-1 reported by Gao et al.,\textsuperscript{13} the observed orders for hydrogen peroxide (first to zero order) and allyl chloride (first order) are similar to those observed by Corma et al.\textsuperscript{9} in the oxidation of alcohols. Fu and Kaliaguine\textsuperscript{11} observed a kinetic order for hydrogen peroxide between one and two in the n-hexane oxofunctionalization in hydrogen peroxide with TS-2 as the catalyst. No correlation between the n-hexane concentration and the observed rate was found. This was explained by suggesting a Ti(H\textsubscript{2}O\textsubscript{2})\textsubscript{2} intermediate as the catalytically active intermediate in the oxofunctionalization of alkanes.\textsuperscript{11}

The large differences in the kinetic orders observed in the kinetic studies, suggest that other factors besides true chemical kinetics might influence the observed activity. The most obvious two are the sorption behavior of the titanium zeolite and the existence of diffusion limitations. TS-1 has - due to its hydrophobic nature - a high preference for apolar molecules, which might explain the zero order behavior often observed for one, usually the most apolar, of the reactants. The possibility of diffusion limitations was suggested by Corma et al.\textsuperscript{9} and Fu and Kaliaguine\textsuperscript{11} based on the observed activation energies of 70 and 78 kJ mol\textsuperscript{-1}, respectively. The existence of internal diffusion limitations in the TS-1 catalyzed hydroxylation of phenol with aqueous hydrogen peroxide was proven by van der Pol et al.\textsuperscript{14} for zeolite particles greater than 0.2 µm by variation of the crystal size. Both Corma et al.\textsuperscript{9}
and Fu and Kaliaguine, however, fully neglect diffusion limitations when they interpret their kinetic data. The large differences in the observed orders suggest that the interpretation of the kinetic measurements for titanium zeolites is not as straightforward as often assumed by these authors.

Discussions on mechanisms in heterogeneous catalysis often rely on analogies with homogeneous systems. The homogeneous system often allows one to do kinetic studies in a straightforward way. In the case of titanium zeolites, it is difficult to find a suitable homogeneous analog, since soluble homogeneous titanium complexes do not catalyze oxidations with aqueous hydrogen peroxide. In general, for heterogeneous catalysts, the observed rate is determined by physical and chemical processes which are interrelated. In broadest terms three processes can be distinguished: transport phenomena, sorption equilibria and the true or intrinsic chemical kinetics. In order to correlate the observed reaction rates with a catalytic mechanism, the effects of the physical processes viz. the transport phenomena and the adsorption equilibria, on the observed rate should be determined or at least estimated.

In this Chapter, the kinetics of epoxidation using aluminum-free Ti-beta are studied and interpreted in terms of these three processes - transport phenomena, sorption equilibria and chemical kinetics - and compared with the kinetic behavior of other titanium containing catalysts. An effort is made to connection the different literature proposals for the mechanism with the observed kinetics.

7.2 Experimental

7.2.1 Materials

Zeolite titanium beta (Ti-beta-1 with Si:Ti = 59; Ti-beta-2 with Si:Ti = 59, Ti-Beta-3 with Si:Ti = 58 and Ti-Beta-4 = 60) were synthesized according to van der Waal et al. Synthesis and characterization of zeolite Ti-beta is described in Chapter 4 of this thesis (the same sample codes are applied). Ti,Al-beta (Si:Ti=39, Si:Al=79) was synthesized according to Camblor et al. and TS-1 was kindly donated by M. van Klaveren (Si:Ti = 58). ICP/AES
was performed a Perkin-Elmer Plasma 40 apparatus (ICP/AES) and a Perkin-Elmer 40 (AES), SEM was performed on a Philips CL-20, TEM was performed on Philips CM 30ST with a field emission gun as the source of electrons at 300 kV. A Ti-MCM-41 sample was kindly donated by J.P.M. Niederer (Si:Ti = 54) of the Hölderich group at the RWTH Aachen.

Chemicals were purchased from Acros (1-octene and 2,2,2-trichloroethanol), Baker (ethanol, 2-propanol and tert-butanol), Fluka (1,3,5-tri-tert-butylbenzene), Mereck (hydrogen peroxide, 30 wt% aqueous) and Aldrich (1,3,5-triisopropylbenzene) and were of the highest purity available.

7.2.2 Adsorption experiments

Sorption experiments of 1-octene and acetonitrile were performed at ambient temperature using 500 mg Ti-beta pre-dried at 200 °C under high-vacuum and a total of 500 mg of adsorbates in 20 ml 1,3,5-triisopropylbenzene as the solvent and 1,3,5-tri-tert-butylbenzene as the internal standard. Samples were taken at regular intervals and analyzed using a CP-52-Carbowax column (50 m, i.d. 0.53 mm).

7.2.3 Catalytic reactions

Epoxidation of 1-octene was performed at 343 K using 24 g acetonitrile as the solvent, and 50 mg catalyst. In a typical experiment, 10 mmol hydrogen peroxide (30 wt% aqueous), 20 mmol 1-octene and about 250 mg 1,3,5-triisopropylbenzene as internal standard were used. For the kinetic experiments, the amounts of 1-octene, hydrogen peroxide and water were varied to determine their influence on the initial epoxidation activity. When required, a 70 wt% aqueous hydrogen peroxide solution was utilized to keep either the water or the hydrogen peroxide concentration constant. Samples were taken at regular time-intervals and analyzed using a CP-Sil-5 GC column (50 m, D.I. 0.53 mm).
Chapter 7

7.3 Results and discussion

7.3.1 Catalyst characterization

Primary characterization of the synthesized zeolites was performed by XRD, ICP/AES and UV-Vis (see Chapter 4). The XRD powder diffractogram showed that essentially pure as-synthesized zeolite titanium beta is obtained, sometimes accompanied by small amounts of ZSM-12 (less than 3%, see Figure 4.1 in Chapter 4). The incorporation of titanium in the as-synthesized zeolite was confirmed by UV-Vis spectroscopy and unit-cell expansion. ICP/AES showed Si:Ti molar ratios of 59, 69 and 58 for Ti-beta-1, Ti-beta-2 and Ti-beta-3, respectively, and also proved that the materials were essentially aluminum-free (Si:Al > 2500).

Recent literature\(^{18}\) on the role of the crystal outer surface in catalytic reactions of zeolites indicates that, especially for beta type zeolites, the outer surface of the crystal can play an important role in the observed catalytic activity. The outer-surface properties of the three Ti-beta samples used, have been studied using Transmission Electron Microscopy (TEM, Fig. 4.16 in Chapter 4). The XRD-crystallinity (Figure 4.1 in Chapter 4), the crystal morphology and the size as determined by Scanning Electron Microscopy (SEM, \(\approx 1.2 \, \mu m\) in diameter, Figure 4.13 in Chapter 4) and the Si:Ti molar ratio were almost identical for the catalysts Ti-beta-1, Ti-beta-2 and Ti-beta-3, while Ti-beta-4 has the same morphology but a significantly larger crystal size (4.3 \(\mu m\)). A close examination of the catalysts with TEM showed remarkable differences (Figure 4.16 in Chapter 4). Hardly any amorphous material was present on the Ti-beta-1 crystals while Ti-beta-3 and to a lesser extent Ti-beta-2 show the presence of a thin amorphous layer or patches of amorphous material. Since an amorphous layer causes an additional diffusion barrier for the substrates and the products to and from the catalysts surface, Ti-beta-1 (Si:Ti = 59, crystal size 1.3 \(\mu m\)) was considered the preferred catalyst for performing kinetic experiments.
7.3.2 Determination of diffusion limitations.

For a reaction to take place it is required that substrates and products move to and from the catalytically active site. Especially in the case of a heterogeneous catalyst, studying the kinetics of a reaction requires knowledge of the influence of mass transport processes on the observed rate. Mass transport limitations can be divided in external and internal diffusion limitations. If mass transport to and from the catalyst particle outer surface is rate determining, it is usually referred to as external diffusion limitation. External diffusion limitation is caused by the slow diffusion of reagents in the bulk of the liquid- or gas-phase to the outer surface of the catalyst. In the case of internal diffusion limitation, the transport of reactant and product molecules in the pores of the catalyst is rate determining.

External diffusion limitations

The external mass transport from the bulk of a liquid- or gas-phase to the external surroundings of the catalyst can be described by the so-called film model. In this model a stagnant layer with a thickness $\delta_v$ along the external surface is assumed to exist. External mass diffusion limitations occur when the transport of substrates and products over this stagnant layer is rate limiting. The importance of external mass transfer limitations is expressed by the second Damköhler number, $Da_H$. The Damköhler number, equation (7.2), is defined as the ratio between the volumetric kinetic rate and the transport rate to the catalyst surface. For first order kinetics, the observed rate, $r_{v}^{obs}$, is a function of $Da_H$ and the volumetric rate constant $k_v$ and can be written as equation (7.1).

\[ r_{v}^{obs} = \frac{k_v}{1 + Da_H} C_A \]
with:

\[ D_{\alpha II} = \frac{k_v}{k_{fA} \alpha'_v} \]  \hspace{1cm} (7.2)

\[ k_{fA} = \frac{D_{eff}}{\delta_v} \]  \hspace{1cm} (7.3)

and

\[ \alpha'_v = \frac{A_p}{V_p} = \frac{6}{d_p} \]  \hspace{1cm} (7.4)

where \( k_v \) is the volumetric rate constant; \( k_{fA} \) the mass transfer coefficient for component A through the stagnant layer; \( D_{eff} \) is the effective diffusion coefficient of the substrate in the bulk solvent; \( C_A \) is the bulk concentration in mol m\(^{-3}\) and \( \alpha'_v \) is the volumetric external surface area in m\(^{-1}\), equation (7.4), and \( k_{fA} \) is defined as the diffusion coefficient divided by the film thickness \( \delta_v \), equation (7.3).

Often \( k_v \) and \( k_{fA} \) are not known and the thickness \( \delta_v \) of the stagnant layer around the catalyst particle is determined with the assumption that external mass transport limitation occurs, e.g. \( D_{\alpha II} \gg 1 \). Equation (7.1) can then be rewritten as equation (7.5) per catalyst volume considered. If the determined \( \delta_v \) is substantially larger than the stagnant layer \( \delta_l \) determined \textit{via} hydrodynamics, external mass transfer limitations can be neglected. Experimentally it is difficult to determine the film thickness \( \delta_v \) for small catalyst particles, but a hypothetical value can be calculated from \( k_{fA} \) \textit{via} equation (7.5). equations (7.3) and (7.4) in equation (7.5), yields the film thickness \( \delta_v \) for spherical particles (equation (7.6)).

\[ r_v^{obs} = \alpha'_v k_{fA} C_A \]  \hspace{1cm} (7.5)

\[ \delta_v = \frac{6 \cdot D_{eff} C_A}{d_p \cdot r_v^{obs}} \]  \hspace{1cm} (7.6)

In the 1-octene epoxidation with hydrogen peroxide using Ti-beta-1 as the catalyst, an initial turn-over-frequency (TOF) of 148 mol\(_{1\text{-octene}}\) mol\(^{-1}\) Ti h\(^{-1}\) was observed, which corresponds to a volumetric rate \( r_v^{obs} \) of 25.8 mol s\(^{-1}\) m\(^{-3}\) at an initial bulk 1-octene concentration \( C_{\text{octene}} \) of 577 mol m\(^{-3}\). The Ti-beta catalyst has an average particle diameter
d_p of 1.3 \mu m, (\alpha'_v = 4.6 \times 10^6 \, m^{-1}) and the diffusion coefficient, D_{effA}, for 1-octene in acetonitrile is estimated to be around $10^{-9}$ \, m$^2$ \, s$^{-1}$. Using equation (7.6), a hypothetical film thickness $\delta_{v,octene}$ in the order of 0.1 m can be calculated. Similar values can be found for hydrogen peroxide. It should be noted that the physical diameter of the reaction vessel used was 0.05 m, which is less than $\delta_v$, making external diffusion limitations unlikely.

The actual thickness of the stagnant fluid layer around the catalyst particle can also be estimated from hydrodynamics.\textsuperscript{20} It can be shown that for a turbulent (e.g. well stirred) solution a laminar, stagnant layer $\delta_i$ around the surface exists. The thickness of this laminar layer $\delta_i$ can be expressed by equation (7.7) as:

$$\delta_i = \frac{2 \eta}{f \rho \langle v_x \rangle}$$

(7.7)

where $\eta$ is the viscosity, $f$ is the friction factor, which is a correction factor for the smoothness of the surface and the turbulence of the liquid phase, and $\langle v_x \rangle$ is the average speed of the liquid in the reaction vessel. The order of $\langle v_x \rangle$ is about 1 m s$^{-1}$. For very rough surfaces (see Figure 4.13 in Chapter 4) and at high Reynolds numbers, the value for $f$ is estimated around 0.075.\textsuperscript{20} For acetonitrile $\eta = 2.44 \times 10^{-4}$ \, kg \, m$^{-1}$ \, s$^{-2}$ and $\rho = 781$ \, kg \, m$^{-3}$, and a laminar film thickness $\delta_i$ can be calculated that is in the order of \mu m. Comparing the $\delta_i$ with the calculated value for $\delta_v$ of 0.1 m, it is clear that the hydrodynamic film thickness is several orders of magnitude lower than the hypothetical limiting stagnant layer $\delta_v$. It is thus concluded that under the experimental conditions used, external diffusion limitations did not occur.

\textit{Internal diffusion limitations}

For many heterogeneous catalyzed reactions, the active site is located in the interior of the catalyst and the reaction on the external surface can be neglected. This is not always the case for zeolites. Certain zeolites, zeolite aluminum beta in particular,\textsuperscript{18} crystallize as conglomerates of very small nanocrystallites (< 100 nm). The outer surface of these
conglomerates can be quite substantial and its catalytic activity cannot be neglected provided the outersurface contains similar active sites as the interior which is not always the case.\(^\text{18}\) The Ti-beta samples used are single crystals (see Chapter 4, paragraph 4.3.4 and 4.3.5) and have low mesopore surface areas (15 to 20 m\(^2\) g\(^{-1}\) zeolite\(^{-1}\)) compared to their micropore surface areas (\(\approx 680\) m\(^2\) g\(^{-1}\) zeolite\(^{-1}\)). By using external-surface probes (paragraph 4.3.5) it was shown that the influence of the outer surface on the observed reaction rate can be neglected for Ti-beta, provided that internal diffusion limitations are not too severe.

If a reaction takes place in the inside of a zeolite, then the reactants have to be transported through the pores of the catalyst to reach the active sites. Due to the small pores of the zeolite channels, internal diffusion limitations often occur in liquid-phase reactions in which case the pores of the zeolite are completely filled with reactants and solvent molecules. A measure for the degree of internal diffusion limitations is given by the effectiveness factor, \(\eta\), of the catalyst used and is defined by equation (7.8).\(^{21-23}\)

\[
\eta = \frac{\text{reaction rate with diffusion limitations}}{\text{reaction rate at external surface conditions}} \quad (7.8)
\]

For a particle with size \(2L\), equation (7.9) for the effectiveness factor \(\eta\) can be derived\(^{19}\):

\[
\eta = \frac{D_{\text{effA}} \frac{dC_A}{dz}}{r_v \frac{obs}{L}} \bigg|_{z=L}
\]

\[
\eta = 36 \frac{D_{\text{effA}} C_A}{r_v \frac{obs}{L}} \bigg|_{z=L}^{2}
\]

where \(D_{\text{effA}}\) is the effective diffusion coefficient of component A in the zeolite, \(dC_A/dz\bigg|_{z=L}\) the concentration gradient at the external surface, \(r_v\) \(\frac{obs}{L}\) the observed rate and \(z\) the linear dimension over the dimensionless length \(L\) of the zeolite catalyst. For spherical particles, \(L = d_p/6\), with \(d_p\) the particle diameter. For values of \(\eta\) close to 1, all active sites of the catalysts are used, \(i.e.\) no diffusion limitations are operative. In this case \(dC_A/dz \bigg|_{z=L}\) can be
approximated by \( C_A/L \) and equation (7.9) reduces to (7.10).

The major problem in applying the above mentioned approach to liquid-phase zeolite catalysis is the accurate determination of the diffusion coefficients of substrates and products in the zeolite pores. In our case the diffusion coefficients \( D_{\text{effA}} \) of 1-octene and hydrogen peroxide in the pores of beta type zeolites have to be known. Since the pores are almost completely filled, it is expected that the diffusion will be relatively slow. According to Moore and Katzer\(^\text{24}\) the diffusivities of molecules in the zeolite pores under liquid-phase conditions can vary between \( 10^{-12} \) and \( 10^{-20} \) m\(^2\) s\(^{-2}\). Van der Pol et al.\(^\text{10,14}\) have calculated the diffusion coefficients for phenol and 2-octanol in TS-1 to be \( 2 \times 10^{-18} \) and \( 3 \times 10^{-17} \) m\(^2\) s\(^{-1}\), respectively, from the effectiveness of various TS-1 samples by varying the crystal sizes of the catalyst. Since 1-octene has a smaller kinetic diameter than phenol and 2-octanol and the pores of Ti-beta are wider than those of TS-1, it can be expected that the effective diffusion coefficient in our system will be somewhat higher. The effective diffusion coefficient \( D_{\text{effA}} \) for 1-octene is estimated to be about \( 10^{-16} \) m\(^2\) s\(^{-1}\) and with a bulk concentration \( C_A \) of 577 mol m\(^{-3}\), a \( d_p \) of \( 1.3 \times 10^{-6} \) m and an observed reaction rate \( r_v^{\text{obs}} \) of 25.8 mol s\(^{-1}\) m\(^{-3}\), a value for the effectiveness factor \( \eta \) of 0.05 can be calculated. This would suggest the presence of internal diffusion limitations. Since the exact value for \( D_{\text{eff}} \) is not accurately known, it is not possible to predict anything conclusive \(\text{via} \) this method, unless the calculated \( \eta \) is either very large or very small (\( \eta > 10^3 \) or \(< 10^{-3} \)).

Though the analysis of diffusion problems in the reaction system by the effectiveness factor \( \eta \) is not very accurate, the low value of 0.05 does suggest that the presence of diffusion limitations cannot be neglected, \( i.e. \) the influence of internal diffusion limitations on the observed reaction rate should at least be considered. If internal mass transfer limitations are present for an \( n^{\text{th}}\)-order irreversible reaction in \( A \), the observed reaction rate can be expressed as equation (7.11)\(^\text{19}\):

\[
r_v^{\text{obs}} = \eta r_v(C_A) = \frac{6}{d_p} \left( \frac{2}{n+1} \right)^{1/2} \left( \frac{k_v}{D_{\text{effA}}} \right)^{1/2} C_A^{n+1} 
\]  

(7.11)

This equation implies that it is not the intrinsic kinetics that are observed, but the so-called disguised or false kinetics. From equation (7.11), it follows that in the case of internal
diffusion limitations:

i) the observed rate \(r_v^{obs}\) is inversely proportional to \(d_p\);

ii) the observed activation energy \(E^{obs}\) equals \((E_{act} + E_{dif})/2\), with \(E_{act}\) being the true activation energy for the chemical reaction and \(E_{dif}\) being the 'activation' energy for diffusion.

iii) the observed reaction order is now \((n+1)/2\)

Experimentally two methods are used to verify the role of internal diffusion limitation, either via (i), measuring the catalytic activity as a function of particle size, \(d_p\), or via (ii) by the determination of activation energy, \(E^{obs}\). The change in the observed reaction order (iii) can in principle also be used, but requires the a priori knowledge of the order in the absence of diffusion limitations. Furthermore, in the (normal) case of a first order reaction, the influence of diffusion limitations on the observed order can be neglected, viz. \((n+1)/2 = 1\) for \(n = 1\), and the presence of diffusion limitations can not be proven via this method.

The activation energy \(E^{obs}\) of a reaction can be determined from the temperature dependance of the rate constant \(k^{obs}\), by what is generally known as the Arrhenius equation (7.12). The logarithm of the rate constant \(k^{obs}\) versus the inverse reaction temperature yields a straight line with a slope of \(-E^{obs}/R\). It can be derived from equation (7.11) that in the case of internal diffusion limitations, the observed activation energy \(E^{obs}\) is the mean value of the real activation energy \(E_{act}\) and the activation energy for the diffusion process \(E_{dif}\). Usually diffusion limitations occur at relatively high reaction temperatures and as a consequence two regions can normally be observed in the Arrhenius plot. At low temperatures the rate is solely determined by kinetics, e.g. \(E_{obs}\) equals \(E_{act}\), and at high temperatures the rate is also governed by diffusion and the observed activation energy will be about \((E_{act} + E_{dif})/2\). Since \(E_{dif}\) is normally distinctly smaller than \(E_{act}\), the observed activation energy at high temperatures is often about half that observed at low temperatures.

\[
k^{obs} = k_0 \times \exp^{-E^{obs}/RT}
\]

(7.12)

Care should be taken when using these theories in the case of zeolites and other microporous materials. Due to the strong sorption of the substrates in the pores of the zeolite,
the $E^{\text{obs}}$ should be corrected for by the heat of absorption $\Delta H_{\text{adsorption}} - \Delta H_{\text{condensation}}$. This occurs especially at lower occupancies and can lower the observed activation energy considerably. Under these conditions the influence of diffusion limitations on the activation energy will be less pronounced than in the case of fully loaded zeolites. From the sorption experiments performed (see below), it was concluded that the zeolite is fully loaded and the influence of the heat of adsorption on the activation energy can be neglected.\textsuperscript{25,26}

In an attempt to prove the existence of internal diffusion limitation by means of the activation energy for Ti-beta, the activation energy was determined for the epoxidation of 1-octene with aqueous hydrogen peroxide in acetonitrile from the initial reaction rate at temperatures between 0 and 70 °C (see Figure 7.1). From the slope of the curve, an effective activation energy of $65.4 \pm 2.7$ kJ mol$^{-1}$ can be calculated. The limited temperature range (0 to 70 °C) over which the reaction rate was measured is too small to show the two regions, as mentioned above, and since no comparable case of homogeneously catalyzed epoxidation of alkenes with aqueous hydrogen peroxide is known, the value for $E_{\text{act}}$ in the absence of diffusion limitations is not known. The interpretation of the observed activation energy is therefore not so straightforward. The $E^{\text{obs}}$ of $65.4$ kJ mol$^{-1}$ is in reasonable agreement with the values reported for the oxidation of alcohols\textsuperscript{9,14} of 70 and 71 kJ mol$^{-1}$ and for the oxofunctionalization of n-hexane\textsuperscript{11} of 78 kJ mol$^{-1}$.

One way to circumvent this problem, is by determination of the activation energy for various titanium catalysts with different pore sizes. Comparison of the activation energy of the epoxidation over Ti-beta-1 with those over TS-1, Ti,Al-beta and Ti-MCM-41 (see Table 7.1), shows that TS-1 exhibits the lowest activation energy, 54.9 kJ/mol. The activation energies for Ti-beta-1 and Ti,Al-beta are slightly higher, 65.4 and 65.0 kJ mol$^{-1}$, respectively. The activation energy for Ti-MCM-41, 106 kJ/mol, is significantly higher than those observed for Ti-beta and TS-1. This is in agreement with the idea that the larger pores of Ti-MCM-41 ($\approx 40$ Å) are less inclined to show internal diffusion limitations. In view of the limited number of observations in the case of Ti-MCM-41, the calculated value of 106 kJ mol$^{-1}$ for the observed activation energy should only be used as a guide value. Nevertheless, the low values for the activation energies of Ti-beta, Ti,Al-beta and TS-1 compared to Ti-MCM-41 indicate strongly that internal pore diffusion limitations in these materials are present. Furthermore, the observed activation energies increase with increasing pore size, which
corresponds well with the idea that the materials with the smallest pores are affected the most by internal diffusion limitations.

![Arrhenius plots for the epoxidation of 1-octene using Ti-beta (▲), Ti,Al-beta (x), TS-1 (■) and Ti-MCM-41 (□) as the catalyst in acetonitrile (20 mmol 1-octene, 10 mmol H₂O₂ (30 wt% aqueous), 50 - 100 mg catalyst and 24 ml acetonitrile).](image)

**Figure 7.1** Arrhenius plots for the epoxidation of 1-octene using Ti-beta (▲), Ti,Al-beta (x), TS-1 (■) and Ti-MCM-41 (□) as the catalyst in acetonitrile (20 mmol 1-octene, 10 mmol H₂O₂ (30 wt% aqueous), 50 - 100 mg catalyst and 24 ml acetonitrile).

**Table 7.1** Activation energy for the epoxidation of 1-octene with hydrogen peroxide over various titanium containing zeolites\(^a\).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pore diameter(s) [Å]</th>
<th>Activation energy [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS-1</td>
<td>5.3 x 5.6</td>
<td>54.9 ± 4.9</td>
</tr>
<tr>
<td>Ti-beta-1</td>
<td>6.5 x 7.4</td>
<td>65.4 ± 2.7</td>
</tr>
<tr>
<td>Ti,Al-beta</td>
<td>6.5 x 7.4</td>
<td>65.0 ± 3.7</td>
</tr>
<tr>
<td>Ti-MCM-41</td>
<td>≈ 36</td>
<td>106 ± 20</td>
</tr>
</tbody>
</table>

\(^a\) For experimental conditions see Figure 7.1.
The second method to determine internal diffusion limitations is by determination of the reaction rate as a function of crystal size. According to equation (7.11) the observed reaction rate should be inversely proportional to the particle diameter in the case of strong internal diffusion limitations. Table 7.2 summarizes the initial activity for four Ti-beta catalysts. Since Ti-beta-1, Ti-beta-2 and Ti-beta-3 all are highly crystalline as determined by XRD and have a similar particle size ($\approx 1.2 \, \mu m$) and morphology (pillow-shaped spheres), the large differences in activity should be ascribed to other factors. Close examination of the crystal-surface using transmission electron microscopy (TEM, Figure 4.16 in chapter 4) clearly reveals that an amorphous layer is present on the crystals of samples Ti-beta-2 and Ti-beta-3, i.e. the lower activity (see Table 7.2) of these materials can be ascribed to surface barrier resistance due to partial blocking of the outer surface.

### Table 7.2
Initial activity of four Ti-Beta batches in the epoxidation of 1-octene with aqueous hydrogen peroxide.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average $d_p$ [( \mu m )]</th>
<th>Initial T.O.F. [mol mol(^{-1}) Ti h(^{-1})]</th>
<th>Thickness of amorphous layer [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-beta-1</td>
<td>1.3</td>
<td>148</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Ti-beta-2</td>
<td>1.1</td>
<td>93</td>
<td>30 - 50</td>
</tr>
<tr>
<td>Ti-beta-3</td>
<td>1.2</td>
<td>69</td>
<td>50 - 120</td>
</tr>
<tr>
<td>Ti-beta-4</td>
<td>4.3</td>
<td>27</td>
<td>not determined</td>
</tr>
</tbody>
</table>

*Experimental conditions: 20 mmol 1-octene, 10 mmol H\(_2\)O\(_2\) (30 wt\% aqueous), 24 mol acetonitrile and 50 mg catalyst at 70 °C.*

In order to determine with confidence the presence of internal diffusion limitations via particle size diameter, a wide range of crystal sizes with a well-defined morphology should be used. As we reported earlier,$^{16}$ the synthesis of Ti-beta using di(cyclohexylmethyl)-
dimethylammonium is only possible within a narrow range of temperature and chemical composition. This, however, also reduces the possibility to direct the zeolite growth during synthesis to crystals with significantly different sizes. A well known method for the synthesis of large zeolite crystals is by diluting the synthesis gel. Dilution of the gel to a Si:H₂O = 100 instead of 40, resulted in a sample with an average particle diameter of 4.3 μm, (denoted as catalyst Ti-beta-4) after 17 weeks instead of the usual 2 weeks for a non-diluted synthesis gel. It is clear from Table 7.2 that Ti-beta-4 has a markedly lower activity than the other catalysts, indicating that internal diffusion limitations are present. However, the scope of particle diameters studied is too small to verify the presence of internal diffusion limitations via this method. Therefore the synthesis of crystals with substantially different particle diameters and methods for dissolving amorphous silica layers are highly recommended.

From the dependency of the initial rate on the particle size (Table 7.2) and the observed activation energies (Table 7.1) for various titanium zeolites, evidence is obtained for the existence of diffusion limitations under the experimental conditions used for the epoxidation of 1-octene. The presence of internal diffusion limitations does, however, influence the observed order of the reaction.¹⁹ From equation (11) it can be derived that for an \(n\)th order reaction, the experimentally determined order in the case of a diffusion limited reaction will be \((n+1)/2\). Except for a first order reaction, a different reaction order will be measured. As we intended to study the kinetics of epoxidation in relation to the catalytic mechanism as proposed in literature, the observed reaction orders cannot simply be used without at least knowing what the contribution of diffusion limitations to the observed reaction order would have been.

### 7.3.3 Adsorption characteristics of Ti-beta.

The rate of a reaction is dependent on the local concentration of substrates at the catalytic site. For zeolites, the catalytic sites are mostly located at the interior surface of the zeolite pore system and the concentration of substrates in the zeolite pores should be used rather than the bulk substrate concentrations. The sorption of substrates in zeolites is dependent on various
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factors, such as pore size diameter and the hydrophobicity/hydrophilicity of the zeolite pore surface. The latter is directly related to the amount of aluminum in the zeolite. An incorporated aluminum atom generates a negative charge which has to be compensated for by a cation in the zeolite pore and hence hydrophilicity is increased. Since the Ti-beta zeolites used are essentially aluminum-free, the catalysts are expected to be hydrophobic. As we reported\(^{27}\) for all-silica beta, a material with similar hydrophobicity properties as Ti-beta, the amount of adsorbed water at 50 °C at a partial water pressure of 0.611 kPa is indeed an order smaller than observed for Al-beta (Si:Al = 11.2).

For heterogeneous catalysts in general, the relation between the internal concentration and the bulk concentration is usually not linear and sorption experiments have to be performed to determine the exact relation between internal and bulk concentration. If non-dissociative Langmuir adsorption isotherms and a fixed internal volume are assumed, the internal concentration of each component can be written as:

\[
[A_i]_i = [A_i]_b N_{zeo} \theta_i \quad (7.13a)
\]

\[
\theta_i = \frac{K_i[A_i]_b}{\left(1 + \sum_j K_j[A_j]_b\right)} \quad (7.13b)
\]

where \([A_i]_b\) is the bulk concentration; \(K_i\) the adsorption constant for component \(i\); \(N_{zeo}\) the available adsorption volume and \(\theta_i\) is the volume fraction occupied by component \(i\). Under the experimental conditions chosen, the adsorption capacity of the zeolite is low (about 13 to 26 mg in view of the amount of catalyst (50 to 100 mg)) compared to the total amount of available sorbates (about 27 g total). It is therefore assumed that the zeolite is fully loaded with reactants, solvents and product molecules \(i.e.\ \sum_i^n K_i[A_i]_b \gg 1\) and equation (7.13) reduces to equation (7.14):

\[
[A_i]_i = \frac{K_i[A_i]_b N_{zeo}}{\sum_j^n K_j[A_j]_b} \quad (7.14)
\]

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In order to investigate what the influence of the bulk 1-octene concentration on the internal sorbate concentration was, a series of competitive adsorption experiments were conducted. The adsorbates chosen were the solvent, acetonitrile, and 1-octene, the most apolar substrate. From the competitive adsorption curves of 1-octene and acetonitrile (Figure 7.2) it can be concluded that the preference of Ti-beta for the apolar 1-octene is indeed higher (though not much) than for the polar acetonitrile, in agreement with the expected hydrophobicity of Ti-beta. Under the experimental conditions used, however, the 1-octene concentration varied between 2.5 and 25 wt% in acetonitrile. From Figure 7.2 it follows that under the experimental conditions used the amount of intra-porous 1-octene and acetonitrile concentrations can be fairly well approximated by a linear relation with their bulk concentration.

![Graph showing competitive sorption of acetonitrile and 1-octene on Ti-beta](image)

**Figure 7.2** Competitive sorption of acetonitrile (●) and 1-octene (■) on Ti-beta (500 mg substrates total, 500 g Ti-beta-2, 25 ml 1,3,5-triisopropylbenzene and 1,3,5-tri-tert-butylbenzene as internal standard at 298 K).

In a typical epoxidation experiment using Ti-beta, the zeolite can adsorb 1-octene, hydrogen peroxide, water and acetonitrile. Except for acetonitrile, they can all participate in the catalytic mechanisms proposed, as discussed below. From the competitive 1-octene/-
acetonitrile adsorption experiments it was already concluded that a linear relation between bulk and intra-porous concentration could be assumed for 1-octene and acetonitrile. Ti-beta is considered to be a hydrophobic zeolite which means that for polar molecules such as water and hydrogen peroxide, the sorption term $K_j \{A_j\}_b$ of equation (7.14) is relatively small and a linear relation between adsorbed amount and bulk concentration can be used as a good approximation.

### 7.3.4 The kinetic results

The epoxidation kinetics of the epoxidation of 1-octene with aqueous hydrogen peroxide in acetonitrile as the solvent were investigated. The interpretation of the kinetic results in terms of mechanistic aspects, however, requires the a priori knowledge of the mechanism. From this mechanism a rate equation can be obtained, which can then be fitted to the kinetic data. Unfortunately the mechanism of epoxidation is not known for titanium zeolites. In section 7.3.7 (p. 209, see below) three possible mechanisms for epoxidation are discussed. These three mechanisms can be used to find expressions for the initial kinetic rates. By assuming an epoxide concentration of zero, assuming a steady state for all equilibria and taking as rate determining step the formation of the epoxide from site III and IV for the hydroperoxy and peroxy mechanism (Figure 7.12 and 7.14, respectively, p. 213 and 215) and the formation of Site I in our own mechanism (Figure 7.15, p. 217), the expressions for the initial kinetic rates can be derived. The separate rate equations for each mechanism are:

$$r_1 = \frac{C_1[H_2O]_2[H_2O_2]_3[alkene]_2}{1+C_2[H_2O]_2+C_3[H_2O]_2[H_2O_2]_2+C_4[H_2O]_2[H_2O_2]_2[alkene]_2+C_5[H_2O]_2^2} \quad (7.15)$$

for the hydroperoxide mechanism (Figure 7.12, p. 213),

$$r_2 = \frac{C_1[H_2O_2]_2[alkene]_2}{1+C_2[H_2O]_2+C_3[H_2O_2]_2+C_4[H_2O_2]_2[alkene]_2} \quad (7.16)$$
for the peroxy mechanism (Figure 7.14, p. 215), and

$$r_3 = \frac{C_1[H_2O]_2 + C_2[H_2O][H_2O_2] + [H_2O_2]_2 + C_5[alkene]_2 + C_6[H_2O][H_2O_2]_2}{1 + C_3[H_2O] + C_4[H_2O][H_2O_2]_2 + C_5[alkene]_2 + C_6[H_2O][H_2O_2]_2 + C_7[H_2O]^2 + C_8[H_2O]_2}$$

(7.17)

for our proposed mechanism (Figure 7.15, p. 217).

Subscript z indicates that the concentration within the zeolite catalyst is to be considered and C_i are combinations of equilibrium constants, reaction rate constants and the number of catalytically active titanium sites.

Since the three kinetic equations (7.15), (7.16) and (7.17) have only three variables, namely the [H_2O_2]_2, [alkene]_2 and [H_2O]_2 concentrations, series of kinetic experiments were conducted in which the effect of the bulk hydrogen peroxide, 1-octene and water concentration on the initial epoxidation rate were determined. It should be noted that in each of the rate equations the intraporous concentrations are used and corrections for the adsorption characteristics of Ti-beta have to be made. However, from the competitive adsorption experiments for acetonitrile and 1-octene it was deducted that a linear relation between internal and bulk concentrations may be assumed as a first approximation.

- Influence of the 1-octene concentration

The amount of 1-octene in the reaction mixture was varied to study the influence on the observed reaction rate. It was observed for Ti-beta that a higher bulk 1-octene concentration resulted in a higher initial reaction rate (Figure 7.3). The theoretical influence of the bulk 1-octene concentration on the observed rate can also be derived for our proposed mechanistic model (Figure 7.15) from equation (7.17) by assuming a constant internal water and hydrogen peroxide concentration and by using the bulk concentration of 1-octene as a first
order approximation of the internal concentration. Equation (7.17) then reduces to expression (7.18).

\[ r_{v}^{obs} = \frac{K_1 [1-octene]_b}{1 + K_1 K_2 [1-octene]_b} \]  

(7.18)

Subscript \( b \) refers to the bulk concentration of 1-octene. It should be noted that by using the same assumptions for the two rate equations (7.15) and (7.16) exactly the same equation will be obtained. It is therefore not possible to distinguish between any of the mechanisms based on the influence of the 1-octene concentration on the initial rate. From equation (7.18) it follows that the true kinetic orders in 1-octene would be first order at low 1-octene concentrations and zero order at high 1-octene concentrations. Since internal diffusion limitations are present, the observed order can vary between first and half order, conform equation (7.11).

The observed initial rate, derived from the slope of products formed at \( t = 0 \) min, as a function of the initial 1-octene concentration is presented in Figure 7.3. If the observed initial rates are fitted to the kinetic equation (7.18), an \( r^2 \) of 0.9684 (dotted line) is obtained. If the influence of diffusion limitations is taken into account, the kinetic order of the reaction at each of the bulk 1-octene concentrations has to be known \textit{a priori}. The complication in modelling diffusion limitations is that the kinetic order can vary from zero to one depending on the 1-octene concentration. However, for kinetic orders close to one the influence of diffusion limitations on the observed order in comparison to the true kinetic order is relatively small. A zero order true kinetic behavior is therefore assumed, changing the overall observed order in 1-octene to half e.g. \( r^{obs} = C_1 \ast [1-oct]_b^{0.5} \), (solid line). The diffusion limited rate equation fits even better (\( r^2 \) of 0.9722). Due to the small number of observations, it cannot be concluded what the dominant process is. Exact determination of the observed order at even higher 1-octene concentration might help to distinguish the dominant process. A zero order would confirm a kinetically determined rate, while an order of a half would ascertain diffusion limitations as the most dominant process. Unfortunately this was not possible due to phase separation of the reaction mixture when 80 mmol of 1-octene ([1-octene]_b = 2.9 mol l\(^{-1}\)) was added.
Figure 7.3 Initial activity (+) of Ti-beta-1 in the epoxidation as a function of the initial 1-octene concentration. (10 mmol H₂O₂ (30 wt% aqueous), 24 g acetonitrile, 44 mmol water and 50 mg catalyst Ti-beta-1 at 70 °C). Solid line: diffusion limitations; dotted line: intrinsic kinetic rate using equation (7.18).

- Influence of the hydrogen peroxide concentration

The influence of the hydrogen peroxide concentration in the presence of water on the initial epoxidation rate was investigated by varying the amount of hydrogen peroxide in the bulk reaction mixture. The amounts of water and 1-octene was kept constant was achieved by applying 70 wt% aqueous hydrogen peroxide if necessary. Similar as observed for 1-octene, higher hydrogen peroxide concentrations were found to be beneficial for a high epoxidation rate (Figure 7.4). The dependency of the true kinetic rate on the bulk hydrogen peroxide concentration for the proposed model can be derived from the overall kinetic rate equation (7.17) and is represented by equation (7.19). Similar to 1-octene, the same dependency on the hydrogen peroxide concentration on the observed rate can be derived for the other two models.
\[ r_{v}^{\text{obs}} = \frac{K_1[H_2O_2]_b}{1 + K_1K_2[H_2O_2]_b} \]  

(7.19)

Similar to 1-octene, the influence of diffusion limitations on the observed kinetics should be taken into account. If the experimental data is fitted to the kinetic equation (7.19) or to a diffusion limited rate (i.e. \( r^{\text{obs}} = C_1[H_2O_2]^{1/2} \)), both the rate equations fitted the data points well (Figure 7.4). The fit of the data with the kinetic rate (dotted line) yielded an \( r^2 \) of 0.9880, while the diffusion limited model has an \( r^2 \) of 0.9401 (solid line). No conclusion could be drawn on the dominant process is, due to the small number of observations and again to the occurrence of phase separation when 40 mmol hydrogen peroxide (1.45 mol l\(^{-1}\)) was added.

Figure 7.4 Initial activity in the epoxidation as a function of the initial hydrogen peroxide concentration. (20 mmol 1-octene, 24 g acetonitrile and 50 mg catalyst Ti-Beta-1 at 70 °C). Solid line : diffusion limitations; Dotted line : intrinsic kinetics using equation (7.19).
- Influence of the water concentration

Since the actual structure of the catalytic site is not known, many models have been proposed.\textsuperscript{27-29} All proposed sites have in common that at one stage they coordinate a peroxide to the titanium site which subsequently transfers one of its oxygen atoms to an alkene. Our proposed catalytic mechanism (Figure 7.15, p. 217) is different in that it tries to explain the observed solvent effects by the coordination of water or alcohol molecules in the catalytic intermediate prior to the rate determining step, similar to the site proposed by Clerici and Ingallina.\textsuperscript{28} Since this model assumes the active participation of water in the catalytic mechanism, the influence of the bulk water concentration on the epoxidation rate was investigated.

From the theoretical rate equation (7.17) for our mechanism, equation (7.20) can be derived for the dependency of the initial rate on the water concentration. A similar equation (7.21) is obtained for the mechanism proposed by Clerici and Ingallina.\textsuperscript{28} The difference is the presence of an additional constant in the nominator, representing the two different pathways for the epoxidation of alkenes (Figure 7.15). The rate equation (7.15) for the mechanism proposed by Huybrechts et al.\textsuperscript{29} and by Notari et al.,\textsuperscript{4} show a dependency in water as expressed in equation (7.22)

\[
r_{obs} = \frac{K_1[H_2O]_b + K_2}{1 + K_1K_3[H_2O]_b + K_1K_4[H_2O]_b^2} \tag{7.20}
\]

\[
r_{obs} = \frac{K_1[H_2O]_b}{1 + K_1K_3[H_2O]_b + K_1K_4[H_2O]_b^2} \tag{7.21}
\]

\[
r_{v}^{obs} = \frac{K_1}{1+K_1K_2[H_2O]_c} \tag{7.22}
\]

For equation (7.20) and (7.21) it is expected that low water concentrations are beneficial for the observed rate, while upon increasing the water concentration firstly a maximum should appear, whereafter the rate is linearly dependent on the reciprocal water concentration. The physical interpretation is that at low water concentrations the fourfold coordinated framework
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titanium site is converted to an active mono-hydrate titanium species and at higher water concentrations this site is further hydrated to form the inactive di-hydrate titanium species (see Figure 7.13 and 7.15). The kinetic rate for equation (7.22) only shows a negative dependency on the water concentration.

Although the existence of internal diffusion limitations will change the observed orders, the curves described by equations (7.20) and (7.21) should most importantly still show a maximum in the observed rate. Interestingly a maximum in activity was indeed observed when approximately 40 mmol water was added to the reaction mixture ([H₂O]₀ ≈ 1.8 mol l⁻¹, Figure 7.5). This increase in activity suggests an active role of water in the catalytic mechanism, though the maximum in activity might also arise from solvent effects as proposed by Romano et al.³⁰,³¹ Similar to 1-octene and hydrogen peroxide, the maximal solubility of water in the reaction mixture is limited due to phase separation at too high water concentration, so the exact behavior of the rate at high water concentrations could not be determined.

![Initial activity in the epoxidation as a function of the water concentration. (20 mmol 1-octene, 24 g acetonitrile and 50 mg catalyst Ti-beta-1 at 70 °C). Added amount of hydrogen peroxide: + 10 mmol H₂O₂; Δ 20 mmol H₂O₂. Fits according to equation (7.20) (———); equation (7.21) (- - -) and equation (7.22) (- - -).](image)

Figure 7.5
- The overall kinetic equation

The fits of the investigated parameters with both the true kinetic model and the completely diffusion limited model for the individual parameters are reasonably good, considering the small number of experimental observations. The best way to distinguish between these two processes would be by determining the initial rate at high concentrations, for this would allow an accurate determination of the observed order at higher concentrations. An observed order close to zero for 1-octene and hydrogen peroxide would then confirm the kinetic model as the major factor, while an order of an half would ascertain a strong influence of diffusion limitations. Unfortunately, it was not possible to use higher concentrations due to phase separation.

Since the errors between the internal diffusion model and kinetic model were found to be small for the individual components, equations (7.15), (7.16) and (7.17) derived for three mechanisms can be used as overall expressions for the catalytic activity. The three rate equations were fitted to the 16 data points total (Table 7.3). The best fit was observed for equation (7.17) with an $r^2$ of 0.981 followed by equation (7.15) with an $r^2$ of 0.976. The low overall fit ($r^2 = 0.503$) of equation (7.16) is solely caused by the inadequate description of the influence of water on the kinetic reaction rate.

Table 7.3 Regression data for the fits of the data with the kinetic equations.

<table>
<thead>
<tr>
<th>Data points</th>
<th>Obtained $r^2$ for fit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Equation (7.15)</td>
</tr>
<tr>
<td>All (16)$^a$</td>
<td>0.976</td>
</tr>
<tr>
<td>1-octene (6)$^a$</td>
<td>0.968</td>
</tr>
<tr>
<td>H$_2$O$_2$ (4)$^a$</td>
<td>0.988</td>
</tr>
<tr>
<td>H$_2$O (5)$^a$</td>
<td>0.903</td>
</tr>
</tbody>
</table>

$^a$ Influence of single component within series of similar experiments, value in brackets indicate the number of data points used.
7.3.5 *Influence of alcohols on the catalytic activity.*

In order to study further the parameters that determine the activity of Ti-beta in the epoxidation of 1-octene, the influence of alcohols on the initial rate was investigated. The possible role of alcohols in the catalytic mechanism was first suggested by Clerici and Ingallina and is assumed to be similar to that of water (see Figure 7.13). The rate is therefore expected to go through a maximum as the alcohol concentration increases. As we reported and discussed in Chapter 6 of this thesis, this is indeed found for Ti-beta-2 (Figure 7.6) and in a less pronounced way for TS-1, for various alcohols tested. The maxima, like the maximum observed for water, indicate that an alcohol molecule is present in the catalytic cycle. It can further be noticed that the position of the maxima is related to the polarity of the alcohol used, more polar alcohols *viz.* ethanol and 2,2,2-trichloroethanol, requiring higher bulk concentration to attain the maximum in epoxidation activity. Since zeolite Ti-beta is considered to be a hydrophobic zeolite, this seems to indicate that the *intraporous* concen-

![Graph](image)

*Figure 7.6* Initial rates in the epoxidation of 1-octene in acetonitrile over Ti-beta-2. Influence of alcohols as co-solvent. • *tert*-butanol; ▲ 2-propanol; ■ ethanol; ● 2,2,2-trichloroethanol. Experimental conditions: 2.24 g 1-octene; 1.14 g H₂O₂ (30 wt% aqueous); 100 mg Ti-beta in 24 g total solvent at 70 °C.
tration of the alcohols is an important factor determining activity. Solvent effects in the bulk solvent as suggested by Romano et al.\textsuperscript{30,31} might be less important. Based on physisorption or competitive adsorption effects it would have been expected that the most apolar alcohol, would be the most beneficial (see Chapter 6 for a full discussion).

A remarkable observation is that the maximum rate observed is equal for ethanol, 2-propanol and \textit{tert}-butanol. This strongly suggests that steric factors hardly play a role at the catalytic site during the oxygen transfer step, which can be taken as an indication of the absence of an alcohol molecule in the catalytically active intermediate. This contradicts the conclusion drawn from the existence of a maximum and the position of the observed maxima that alcohols play an active role in the catalytic cycle for epoxidation.

7.3.6 \textit{Comparison with other titanium zeolites}

Evaluation of the catalytic activity of Ti-beta in the epoxidation of 1-octene, showed that equation (7.17) described the observed kinetics reasonably well. The observed maximum in epoxidation activity when increasing the bulk water concentration suggested that the formation of multiple hydrated titanium species should be avoided. The formation of these titanium species is dependent on the relative amount of free water inside the zeolite which in itself is a function of the hydrophobicity/philicity of the zeolite used and the bulk concentration. The catalytic properties of titanium containing zeolites with different hydrophobicities \textit{e.g.} Ti,Al-beta and TS-1 compared to Ti-beta, were therefore investigated.

The aluminum present in Ti,Al-beta, creates negatively charged framework sites normally compensated for by protons or alkali metal cations. These charged sites prefer polar molecules thus making the zeolite considerably more hydrophilic than Ti-beta. The increased hydrophilicity of Ti,Al-beta is shown by the dependency of the initial rate of the bulk water concentration (Figure 7.7). A maximum in activity is observed at a water concentration lower than observed for Ti-beta and TS-1. Indirectly the increased hydrophilicity is also shown by the dependency of the initial rate on the 1-octene concentration (Figure 7.8). Ti,Al-beta requires higher bulk concentrations of the apolar 1-octene to obtain an activity comparable to that of TS-1 and Ti-beta.
Figure 7.7  Catalytic activity of titanium zeolites as a function of the initial water concentration. Experimental conditions: 20 mmol 1-octene; 10 mmol H$_2$O$_2$, 50 mg catalyst and 24 g acetonitrile at 70 °C. + Ti-beta-1; ○ TS-1; △ Ti,Al-beta.

Figure 7.8  Catalytic activity of titanium zeolites as a function of the initial 1-octene concentration. Experimental conditions: 10 mmol H$_2$O$_2$, 44 mmol H$_2$O; 50 mg catalyst and 24 g acetonitrile at 70 °C. + Ti-beta-1; ○ TS-1; △ Ti,Al-beta.
The dependency of the initial rate on the bulk hydrogen peroxide concentration appears to have a maximum (Figure 7.9) for Ti,Al-beta. The reason for this maximum is not clear. It might be related to the high hydrophilicity of the catalyst; at high bulk hydrogen peroxide concentrations the zeolite is practically filled with hydrogen peroxide. The internal concentration of the other adsorbed components, especially 1-octene, will strongly decrease, thereby decreasing activity.

Figure 7.9  Catalytic activity of various titanium zeolites as a function of the initial hydrogen peroxide concentration. Experimental conditions: 20 mmol 1-octene; 44 mmol H₂O; 50 mg catalyst and 24 g acetonitrile. + Ti-beta; ○ TS-1; △ Ti,Al-beta.

Zeolite TS-1 is, like Ti-beta, a hydrophobic zeolite, and similar kinetic behavior is expected. The major difference between TS-1 and Ti-beta is the amount of defects, e.g. silanol groups, that are present. From the ²⁹Si MAS NMR spectrum of Ti-beta (see Figure 4.11 in Chapter 4) it was found that about 16% of the silicon atoms has a silanol group, also referred to as Q²-sites. On the other hand TS-1 has been reported in literature to be nearly defect-
free. Since the presence of silanol groups, though not as distinctly as the charged aluminum sites, will increase hydrophilicity, TS-1 is expected to have a more pronounced hydrophobic character. This increased hydrophobicity is nicely shown by the dependence of the initial rate on the 1-octene concentration (Figure 7.8). Lower 1-octene concentrations compared to Ti-beta are required in the case of TS-1 to obtain the same internal concentration in the zeolite and thus the same rate.

Interpretation of the catalytic data for water is rather difficult for TS-1. In analogy with equation (7.17), a maximum in the observed rate as function of the water content would be expected. As can be seen from Figure 7.7, this is clearly not the case. This might be explained by the more pronounced hydrophobic nature of TS-1 compared to Ti-beta. It can be seen in Figure 7.8, that at 20 mmol 1-octene added ([1-octene]_b = 0.74 mol l^{-1}), TS-1 has already reached its maximum activity, suggesting a high pore-filling with 1-octene. Due to this high amount of 1-octene adsorbed, the maximal attainable internal water and hydrogen peroxide concentrations are lower relative to those for Ti-beta, since only a small part of the potential adsorption volume remains free for the combined water and hydrogen peroxide. It could be that the internal water concentration in TS-1 never reaches a high enough value to decrease activity by formation of Site V (see p. 217) under the reaction conditions chosen. The assumption that all internal concentrations are proportional to the bulk concentrations is thus probably not correct for TS-1. Nevertheless, equation (7.17) can be used to accurately describe the kinetic behavior of Ti-beta, Ti,Al-beta and TS-1.

7.3.7 The catalytic mechanism of epoxidation

One of the most elusive features of titanium zeolite catalyzed oxygenations is the catalytic mechanism. The actual structure of the oxidizing titanium complex for the epoxidation of alkenes is not yet experimentally proven, though solvent effects for TS-1^{28} and Ti-beta^{32} provide evidence that water and alcohol molecules participate actively in the catalytic mechanism. A kinetic study of the epoxidation of 1-octene over Ti-beta in acetonitrile as the
solvent, see above, also suggests the active participation of water in the catalytic mechanism. Furthermore, the epoxidation occurs with retention of configuration and the activity is dependent on the nucleophilicity of the C-C double bond, indicating a heterolytic nucleophilic oxygen transfer. The solvent effects were interpreted by Clerici and Ingallina\textsuperscript{28} in terms of a simultaneous coordination of a peroxide and an alcohol molecule in the catalytically active oxygenating species (site I, Figure 7.10). However, the observed solvent effects are not universally interpreted as the active participation of alcohols and water in the oxygenating species. The Ti(\(\eta^2\)-O\(_2\)) site II (Figure 7.10) proposed by Huybrechts \textit{et al.}\textsuperscript{29} and Notari \textit{et al.}\textsuperscript{4} was based on analogy with the epoxidation mechanisms known for group 4 - 7 transition metals. Both these mechanisms were tested for consistency with the experimentally determined kinetics.

![Figure 7.10](image)

**Figure 7.10** Catalytic sites proposed for the epoxidation of alkenes using TS-1. I Hydroperoxo species, including coordinated solvent alcohol molecule.\textsuperscript{28} II Ti(\(\eta^2\)-O\(_2\)) species.\textsuperscript{4,29}

An excellent discussion of the mechanism of epoxidation is given by Bellussi and Rigutto.\textsuperscript{34} The study of catalytic mechanisms over TS-1 is severely hampered by the lack of a suitable soluble homogeneous analog capable of epoxidation\textsuperscript{35-37} and the related titanium-on-silica heterogeneous catalyst, which can also catalyze epoxidations with tert-butyl hydroperoxide, also does not offer many clues.\textsuperscript{38} Nevertheless, consensus exists on the following relevant points:
Complexes that catalyze the heterolytic epoxidation of alkenes with peroxides are almost always Lewis acids.

The most effective Lewis acid are high-valent transition metals with an empty d-shell (d^0).

All known peroxo or alkylperoxo complexes of the group 4 - 7 transition metals bind the O_2^{2-} or ROO^- peroxo moiety side-on (η^2-O_2). Epoxidation involves a smooth oxygen transfer by a 1,2-migration of the metal with minimal disruption of the metal-oxygen bonding. Based on frontier-orbital models, the highest activity is expected for metals with an empty d^0-shell.  

A number of stable titanium peroxo complexes is known that contain the η^2-O_2 peroxo ligand, but none of them acts as an oxygen transfer agent.

The M(η^2-O_2) structure is not the only structure which is capable of epoxidation. Organic peracids smoothly epoxidize alkenes by a (somewhat) different mechanism involving a five-membered ring, usually referred to as the "butterfly" transition state.

The solvent effects observed are similar for the homogeneous transition metal catalyzed and the peracid epoxidation: polar solvents enhance the reaction rate, with the exception of strongly coordinating or protic solvents, which slow down or completely inhibit the reaction rate. Except for titanium zeolites, this also applies to homogeneous and heterogeneous catalysis by titanium.

None of the mechanisms suggested per se can adequately explain the solvents effects observed for TS-1. This pertains in particular to the beneficial influence of alcholic solvents.

TS-1 is active in the absence of water or alcohols.

The active species possess Brønsted acidity and ion exchange properties.
The beneficial effects of alcohols, methanol in particular, as the solvent in the epoxidation of alkenes, prompted Clerici and Ingallina\textsuperscript{28} to assume the participation of alcohol molecules in the actual oxygenating complex. In this mechanism both an alcohol or a water molecule and a hydrogen peroxide molecule are coordinated to the Ti-site, which interact with each other to form a peracid-like configuration. The activated hydrogen peroxide of site I can then transfer one of its oxygens to an alkene (complex III, Figure 7.11) in a manner similar to the "butterfly"-mechanism known for peracids. A catalytic cycle based on this mechanism is depicted in Figure 7.12. One additional feature of this mechanism is the presence of the dihydrate Ti-site V. The existence of this species was already reported by Deo \textit{et al.}\textsuperscript{39} Since high internal water concentrations would shift the equilibrium between Site I and V to the diaqua species V (R = H), this would suggest that the presence of water is only beneficial for the reaction at low internal concentrations.

![Figure 7.11](image.png)

**Figure 7.11** The "Butterfly" peracid epoxidation mechanism for Site I.

The Ti(H\textsubscript{2}O)(H\textsubscript{2}O\textsubscript{2}) site I is not generally accepted as the catalytic site. Both Huybrechts \textit{et al.}\textsuperscript{29} and Notari \textit{et al.}\textsuperscript{4} suggested that the active species is the Ti(\eta\textsuperscript{2}-O\textsubscript{2}) species II, rather than the hydroperoxo site I. The site II was based on analogy with epoxidation mechanisms known for group 4 - 7 transition metals, and the observed solvent effects were explained by Romano \textit{et al.}\textsuperscript{30,31} by selective adsorption of substrates by the hydrophobic TS-1. Furthermore Khouw \textit{et al.}\textsuperscript{12} reported that the rate of epoxidation of alkenes in the absence of water is similar to that in the presence of water. Extrapolation of the data for the influence of the bulk water concentration on the epoxidation rate for TS-1 (Figure 7.7), suggests that
Epoxidation Kinetics

Figure 7.12  Possible catalytic mechanism for the epoxidation over titanium zeolites via the Ti(ROH)(H₂O₂) site I proposed by Clerici and Ingallina. R = H or alkyl.
the rate in the absence of water is similar to that in the presence of water. Smooth oxygen transfer in the transition state site IV (Figure 7.13) occurs via a 1,2-shift of the metal.\textsuperscript{35} A catalytic mechanism based on site I is depicted in Figure 7.14. Like in the hydroperoxo mechanism for the Ti(H\textsubscript{2}O)(H\textsubscript{2}O\textsubscript{2}) site (Figure 7.12), a dihydrate species \textit{V} can be assumed to exist. Unlike the "Butterfly" mechanism, however, the presence of water is always detrimental for catalysis by competing with hydrogen peroxide for coordination on the Ti-site.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7.13.png}
\caption{The mechanism of epoxidation via a 1,2-shift of the titanium atom in the Ti(\eta\textsuperscript{2}-O\textsubscript{2}) site.}
\end{figure}

Based on what is known about the epoxidation mechanism of several group IV - VII transition metals with the d\textsuperscript{0} configuration, site \textit{II} would \textit{a priori} be the most likely candidate for the catalytic active intermediate. However, the solvent effects observed show that the role of alcohol and water appears to be essential and not purely based on sorption characteristics of the hydrophobic Ti-beta\textsuperscript{33} and TS-1.\textsuperscript{28} A maximum in the initial epoxidation rate was observed for Ti-beta when the bulk water concentration was increased. Despite the apparent participation of alcohols or water in the catalytic mechanism, the site I is not generally accepted as the catalytic site for a number of reasons. Although this site appears to be able to epoxidize via a mechanism similar to that of oxygen transfer from peracids via the so-called "butterfly" transition state (\textit{III}, Figure 7.11), no specific property of the titanium atom is invoked. The titanium site acts simply as a neutral, oxyphilic Lewis acid. By contrast, zeolites with other Lewis-acid properties such as germanium silicalite-1 do not appear to be very active in epoxidation. It is well known that the d\textsuperscript{0} configuration of many group IV - VII
transition metals enhances their effectiveness in epoxidation reactions compared to other oxyphilic Lewis acids. These metals are able to coordinate a peroxide side-on, similar to site II (Figure 7.12), followed by smooth oxygen transfer via a simultaneous 1,2-migration of the metal with minimal disruption of the metal-to-oxygen bonding in the transition state.\textsuperscript{37}

Figure 7.14 Tentative catalytic mechanism for epoxidation over titanium zeolites involving the Ti(η\textsuperscript{2}-O\textsubscript{2}) oxygenating species as proposed by Huybrechts \textit{et al.}\textsuperscript{29} and Notari \textit{et al.}\textsuperscript{4}
The study of the direct interaction of hydrogen peroxide with the titanium site is of direct interest for catalysis. A limitation in the study of surface (hydro-)peroxo complexes of TS-1 and other heterogeneous titanium catalysts is their low stability at low temperatures. Using UV-Vis spectroscopy, Geobaldo et al.\textsuperscript{7} obtained evidence for the existence of species II by adsorbing aqueous hydrogen peroxide on TS-1. A new absorption band at 26.000 cm\(^{-1}\) appears, which corresponds reasonably well both in wavenumber and in shape with the characteristic wavenumbers for the Ti(\(\eta^2\)-O\(_2\)) group of the TiF\(_5\)(\(\eta^2\)-O\(_2\))\(^{3-}\) anion. For these reason the Ti(\(\eta^2\)-O\(_2\)) site II was proposed as the catalytically active species. It should be noted that a number of titanium(\(\eta^2\)-O\(_2\)) complexes is known, but none of these show any appreciable activity in epoxidation.\textsuperscript{15} However, these complexes are different from Site II in zeolites by the type of ligands around the titanium atom and perhaps in the geometry of the (\(\eta^2\)-O\(_2\)) coordination itself and might not be representative for the TS-1 catalyzed epoxidation.

Since neither of the two sites seems to be fully consistent with the observed catalytic behavior\textsuperscript{34}: Site I lacks a specific character of the titanium atom and Site II cannot explain the beneficial influence of water and alcoholic solvents, we propose a mechanism which comprises both type of sites (Figure 7.15). Based on the electronic properties of the titanium atom we assume that the actual catalytic epoxidation site is II, but that the predominant configuration in which the titanium is present, is site I. Site II is formed from site I by an intramolecular elimination of an alcohol or water molecule, whereafter it can transfer its oxygen atom to an alkene via an electrophilic 1,2-addition (Figure 7.12).

A key step in this new mechanism (Figure 7.15) is the reaction from I to II. This reaction is generally considered to be reversible. If the reverse reaction, \textit{i.e.} formation of I from II, is faster than the epoxidation, then the expression of the intrinsic kinetic rate would have a negative order in alcohol only \textit{i.e.} alcohol inhibition. In other words, higher alcohol concentrations decrease the amount of active II sites by shifting the equilibrium back to the site I. To circumvent this, one has to assume that the epoxidation step is fast compared to the formation of II. In this way, the reverse reaction in the equilibrium is suppressed and the formation of II from I can be considered to be irreversible. The direct formation of II from a H\(_2\)O\(_2\) absorbed on the Ti-site without the coordinated water molecule is also reported in literature to be possible\textsuperscript{12,41}. Khouw et al.\textsuperscript{12} apply a drying agent (MgSO\(_4\)) during TS-1 catalyzed reactions to remove the water formed, while Corma et al.\textsuperscript{40} use dry hydrogen
peroxide in methanol without a water sink and interpret the influence of water on the initial activity of Ti, Al-beta.

Figure 7.15 Proposed catalytic mechanism based on Site II as the catalytic site and Site I as the most abundant site (see text).
Finding a suitable justification for this new mechanism is more difficult. However, noting what Bellussi and Rigutto summarized about what is actually accepted, it is all based on known chemical properties of titanium or known adsorption characteristics of the zeolite. Since these data are insufficient to explain the observed phenomena, we assumed that the zeolite framework itself influences the catalytic cycle. The catalytic intermediates (Figure 7.15) all differ in their coordination around the titanium number, especially the spatial organization of the four framework oxygens differs substantially from site to site. These framework oxygens are, however, strongly hindered in their movement by the relatively fixed zeolite lattice. It is therefore assumed that the energy difference required to convert one site into another is (partly) determined by the amount of energy required to distort the "fixed" lattice oxygen atoms around the titanium site. Apparently, the formation of \( \text{II} \) is more facile via site \( \text{I} \) than directly from a hydrogen peroxide bonded to a framework titanium, though it is not exactly clear why. Since titanium prefers an octahedral coordination, Site \( \text{I} \) will be the most abundant.

7.4 Conclusions

The kinetic properties of zeolite Ti-beta in the epoxidation of 1-octene have been studied to elucidate whether diffusion or kinetic parameters determine the observed rate. External diffusion limitations could be excluded, but strong indications of the existence of internal diffusion limitations in the pores of the zeolite were found based on the observed activation energies and crystal size dependency of the rate. The observed activation energy for Ti-beta was found to be 65.4 kJ/mol which was slightly higher than that observed for TS-1 (54.9) and significantly lower than observed for mesoporous Ti-MCM-41 (106 kJ). Based on the pore size of the materials it would be expected that TS-1 would have most problems with internal diffusion limitations, \( i.e. \) the lowest activation energy and Ti-MCM-41 the smallest problems, \( i.e. \) the highest activation energy. This was indeed found to be the case.

Determination of internal diffusion limitations via variation of the particle diameter was not conclusive due the lack of a sufficiently wide range of particle diameters and a large
variation in activity of batches with similar particle size diameters. The large differences in activity observed were found to correspond to the presence of an amorphous layer around the zeolite crystals as measured by transition electron microscopy (TEM). The bulk crystallinity of all materials as measured by XRD was very high, which shows the potential danger of relying on bulk techniques solely. Determination of internal diffusion limitation from a theoretical basis, yielded an effectiveness factor of 0.05 which seems to suggest that internal diffusion limitations at least partially exist. Since this technique relies heavily on the intrinsic diffusion coefficient, which is difficult to determine for fully filled zeolites, this approach could only be used as an indication for the presence of diffusion limitations.

Since the presence of internal diffusion limitation changes the observed kinetic order of a reaction, care should be taken when interpreting the observed rate in kinetic terms. A catalytic mechanism site has been proposed in which the predominant intermediate is the site I proposed by Clerici and Ingallina\textsuperscript{28} and the catalytically active site is site II as proposed by Huybrechts \textit{et al.}\textsuperscript{29} and Notari \textit{et al.}\textsuperscript{4}. The rate determining step is assumed to be the formation of II from I by an intramolecular hydrolysis. This was explained by assuming that the distortion of the zeolite framework to allow the coordination of the $\eta^2$-O$_2$ peroxy ligand is rate determining. Molecular Mechanics calculations using the Biosym software indicated that the formation of Site II from Site I required the least distortion of the framework. Furthermore, the hydrogen peroxide moiety in Site II is already oriented towards the most favorable coordination site.

Rate equations for this new mechanism (Figure 7.15) and the two mechanisms proposed in literature (Figure 7.13 and 7.14) only show a dependency on three parameters viz. the intraporous 1-octene, the hydrogen peroxide and the water concentrations. Variation of the bulk solvent concentration of the three parameters, showed a good fit with the proposed model and the hydroperoxo mechanism proposed by Clerici and Ingallina,\textsuperscript{28} although the data points also fitted well to a model in which internal diffusion limitation was the predominant process. Poor results were obtained when fitting the data to a model derived form the peroxy mechanism proposed by Huybrechts \textit{et al.}\textsuperscript{29} and Notari \textit{et al.}\textsuperscript{4}.

Especially the dependence on the water concentration showed interesting results. The catalytic activity was found to have a maximum activity. It is assumed that a water molecule is coordinated to the titanium site (species I) to facilitate the formation of the catalytic active
intermediate II, but if too much water is present two water molecules can coordinate thereby decreasing the amount of intermediate species I. Similar results (viz. a maximum in the activity) were also found for various alcohols, see Chapter 6 for details. The catalytic data can, however, be interpreted in a two site mechanism. The model could also be used for the aluminum-containing Ti,Al-beta catalyst, but significant discrepancies were observed for TS-1. The latter could not readily be explained, perhaps differences in adsorption behavior between TS-1 and Ti-beta play a major role.
7.5 References

Zeolite titanium beta: a sand water-resistant catalyst in Meerwein-Ponndorf-Verley-Oppenauer reactions.

Abstract

Aluminum-free zeolite titanium beta was found to be a selective catalyst in the Meerwein-Ponndorf-Verley reduction of carbonyl compounds, 4-alkylcyclohexanones in particular, and in the Oppenauer oxidation of 4-alkylcyclohexanols. 4-tert-Butyl- and 4-methylcyclohexanone were reduced with > 98% selectivity to the cis-alcohols. The high stereoselectivity is explained by transition-state selectivity. A catalytic site is proposed which is similar to the titanium site proposed for epoxidation. The observed enantiomeric excess of 34 % in the reduction of phenylacetone with (S)-2-butanol, indicates a transition state in which both the ketone and the alcohol reactant are coordinated simultaneously to the same titanium atom.

The Ti-beta catalyst shows a high tolerance towards water, but was completely poisoned by pyridine. When compared with an Al-beta catalyst, the Ti-beta showed less by-products during the Oppenauer oxidation, probably due to the absence of Brønsted acid sites.
8.1 Introduction

Zeolite beta is the only high-silica zeolite with a three-dimensional pore system containing large 12-membered ring apertures,\(^1\) which makes it very suitable as a regenerable catalyst in organic reactions. The synthesis of zeolite beta has been systematically studied since the material was discovered by Wadlinger \textit{et al.}\(^2\) Despite its early discovery in 1967,\(^2\) research reports concerning the application of zeolite beta in organic conversions long remained relatively scarce. In recent years, because of its structural characteristics, zeolite beta was successfully used in Friedel-Crafts type reactions of benzene and functionalized aromatics\(^3\)-\(^5\) and in the hydration and isomerization of bulky alkenes, \textit{e.g.} \(\alpha\)-pinene.\(^6\) The alkylation of benzene is already in industrial practice. Camblor \textit{et al.}\(^7\) found zeolite titanium aluminum beta to be a promising catalyst in various oxygenations using hydrogen peroxide. Due to its bifunctionality two-step reactions, \textit{e.g.} epoxidation/isomerization or epoxidation/ring closure, are possible over this catalyst. The synthesis of the aluminum-free analog of zeolite beta appeared to be possible by using more selective templates.\(^8\) Recently we reported the synthesis of an aluminum free titanium zeolite beta by further improvement of the template.\(^9\)

The Meerwein-Ponndorf-Verley reduction of carbonyl compounds and the Oppenauer oxidation of alcohols, together denoted as MPVO reactions, are recognized and practiced in the fine chemicals industry as highly selective reactions. Thus, C=C double bonds, C-halogen bonds and nitro groups are not attacked. In MPV reductions a secondary alcohol is the hydrogen donor whereas in Oppenauer oxidations a ketone is the hydrogen acceptor. It is generally accepted that MPVO reactions proceed \textit{via} a complex in which both the carbonyl and the alcohol are coordinated to the same Lewis acid metal ion. The reaction then proceeds by a hydride transfer from the alcohol to the carbonyl group.\(^10\) Usually metal alkoxides derived from secondary alcohols, \textit{e.g.} Al(OiPr)_3, are used as homogeneous catalysts in reductions and metal \textit{tert}-butoxides in oxidations.

As has been reported by Bourgeat-Lami \textit{et al.},\(^11\) the aluminum in the framework of zeolite beta can exist in the normal zeolitic four-coordination and in partially hydrolyzed forms without losing the connection to the zeolite framework. Part of these different aluminum-sites in beta exhibit Lewis acidic properties. Accordingly, Creighton \textit{et al.}\(^12\)
recently reported the use of zeolite beta in the stereoselective MPV reduction of 4-\textit{tert}-butylcyclohexanone (Figure 8.1). In an FT-IR study of the applied aluminum beta zeolites, Creighton et al.\textsuperscript{13} acquired convincing evidence that the observed catalytic activity is related to aluminum atoms which are only partially bonded to the framework and possess Lewis-acidic properties.

\begin{center}
\includegraphics[width=0.8\textwidth]{figure8.1.png}
\end{center}

Figure 8.1 Reduction of 4-\textit{tert}-butylcyclohexanone to the corresponding \textit{cis}- and \textit{trans}-alcohol.

The use of homogeneous Lewis acid titanium complexes in MPVO reactions was reported by Li et al.\textsuperscript{14}, \textit{i.e.} Ti(OR),\textsubscript{4} (R= Et, iPr, n-Bu), TiCl,\textsubscript{4} (as precursor) and Cp\textsubscript{2}Ti(OPh),\textsubscript{2} were used as catalysts for homogeneous MPVO reactions. Ti(OiPr),\textsubscript{4} was found to give the best catalytic activity, but it was also observed that catalytic amounts of Ti(OiPr),\textsubscript{4} did not reduce cycloalkanones. By using an aluminum-free zeolite titanium beta (Ti-beta) in the epoxidation of alkenes, we have shown that Ti-beta has acidic properties when alcoholic solvents are employed.\textsuperscript{9} This indicates that the titanium site in beta exhibits Lewis acidity. The use of TS-1, a medium pore titanium containing zeolite, as a Lewis acid catalyst has been reported for the Michael reaction of silyl enol ethers with \textalpha,\textbeta-unsaturated carbonyl compound\textsuperscript{15} and the Mukaiyama aldol reaction\textsuperscript{16}. In this chapter the MPV reduction of ketones and aldehydes and the Oppenauer oxidation of alcohols using Ti-beta as the catalyst is discussed.
8.2 Experimental

8.2.1 Materials

Zeolite aluminum beta (Al-beta) with a Si:Al molar ratio of 11.2 was synthesized according to Wadlinger et al.\textsuperscript{2} In a typical preparation 12.2 g sodium aluminate (NaAlO\textsubscript{2}) was dissolved in 110 g aqueous tetraethylammonium hydroxide (40 wt\% TEAOH). To the clear solution 291.6 g Ludox LS (30 wt\% colloidal silica) was added and the resulting gel was hydrothermally crystallized at 150 °C for 6 days. After cooling and filtration the zeolite was washed, dried and calcined at 540 °C. Titanium beta (Ti-Beta-2; Si:Ti = 69, see Chapter 4 for the full characterization) was synthesized according to van der Waal et al.\textsuperscript{9} using di(cyclohexylmethyl)dimethylammonium hydroxide as the template. The zeolite was activated at 540 °C to remove the occluded template. Ti-MCM-41 (Si:Ti = 54) was kindly donated by J. Niederer (RWTH Aachen). All-silica beta (Si:Al > 2500; Si:Ti > 2000) was prepared according to van der Waal et al.\textsuperscript{8}

Chemicals were purchased from Aldrich (S)-2-butanol, 2- and 4-tert-butylcyclohexanone, 2- and 3-methylcyclohexanone and titanium isopropoxide), Baker (cyclohexanone, 2-butanol, and 2-propanol), Jansen (cyclopentanone) and Merck (aluminum isopropoxide). The commercial 4-tert-butylcyclohexanol (Aldrich) was a mixture of both the trans- (70 wt\%) and cis-alcohol (30 wt\%). Pure cis-4-tert-Butylcyclohexanol (> 95 wt\%) was prepared by the MPV-reduction of 4-tert-butanol according to Creighton et al.\textsuperscript{12} using Al-beta as the catalyst. The solvents used were dried over zeolite KA to remove trace amounts of water present.

X-Ray powder diffractograms were recorded on a Philips PW 1830 powder diffractometer using CuK\textalpha radiation. UV-Vis spectra were recorded on a Varian Cary-1 spectrophotometer using barium sulfate as a reference. Chemical analysis of the catalysts was performed on a Perkin-Elmer Plasma 40 (ICP-AES) or a Perkin-Elmer 110 (AES) apparatus.
8.2.2 Catalytic reactions

The reductions of ketones were performed under stirring in refluxing 2-propanol (25 ml, 82 °C) using 2.5 mmol of the appropriate ketone (2- and 4-tert-butylcyclohexanone, 2-, 3- and 4-methylcyclohexanone, cyclohexanone or cyclopentanone) and 1,3,5-tri-tert-butylbenzene as internal standard. As the catalyst either 0.5 g zeolite, activated at 540 °C, or 0.25 mmol metal alkoxide, Al(OiPr)_3 or Ti(OiPr)_4, was used. Samples were taken at regular intervals and analyzed by GC using a Chrompack CP Wax 52 CB column (50 m, i.d. 0.53 mm) and by GC-MS.

The oxidations of 4-tert-butylcyclohexanol were performed under stirring in butanone (25 ml, 85 °C) using a 1:1 cis:trans mixture of the alcohols (2.5 mmol of each isomer) and 1,3,5-tri-tert-butylbenzene as internal standard. As the catalyst either 0.5 g zeolite, activated at 540 °C, or 0.25 mmol metal alkoxide was used. Samples were taken at regular intervals and analyzed as described above.

The enantioselective reduction of 1-phenylacetone was performed in refluxing (S)-2-butanol (5 ml, 99 °C) using 0.5 mmol of the ketone, 100 mg Ti-beta and 1,3,5-tri-tert-butylbenzene as internal standard. Samples were analyzed by GC using a chiral G-TA cyclodextrin column (40 m, i.d. 0.25 mm). The optical rotation of the reaction mixture was determined with a Perkin-Elmer 241 polarimeter with a sodium lamp after removal of the solvent.

8.3 Results and Discussion

8.3.1 Catalyst Characterization

As we reported earlier, Ti-beta exhibits Brønsted acidic properties in the epoxidation of alkenes using aqueous hydrogen peroxide when alcoholic solvents were employed. This was explained on the basis of Lewis acidic properties of the tetrahedrally coordinated titanium atom, which on coordination with alcohols gives moderate to weak Brønsted acid sites. Some
direct information on the state of the titanium can be obtained from the diffuse reflectance UV-Vis spectra of calcined Ti-beta and from the effects of the adsorption of water and 2-propanol. The presence of a strong absorption maximum at 47,000 - 50,000 cm\(^{-1}\) (see Figure 8.2) confirms that in the calcined material all titanium is incorporated in tetrahedral positions. Upon adsorption of either water or 2-propanol a shift to lower wavenumbers occurs, which indicates a higher coordination number around the titanium atom, most probably five.\(^{9,17}\) A full characterization of the Ti-beta catalyst is given in chapter 4 of this thesis.

![UV-Vis spectra of Ti-beta](image)

**Figure 8.2** UV-Vis spectra of Ti-beta. The sample was pre-dried at 200 °C, then allowed to cool down, whereafter water or 2-propanol was added to the sample (0.18 g/g\(_{\text{zeolite}}\)) at room temperature.

8.3.2 *Titanium catalyzed Meerwein-Ponndorf-Verley reduction*

Since the MPVO reactions can generally be catalyzed by Lewis acids, Ti-beta and various other titanium containing materials were tested in the reduction of 4-tert-butyleyclohexanone (Figure 8.1). As can be seen from Table 8.1, Ti-beta is indeed able to catalyze the MPV reduction, although with a lower TOF than observed for Al-beta. Other heterogeneous titanium containing materials, *i.e.* Ti-MCM-41 (Al-free), rutile (TiO\(_2\)) and TiO\(_2\)-deposited-on-
silica\textsuperscript{18}, were found to be completely inactive in the MPV reduction. The high selectivity of Ti-beta towards the thermodynamically less favorable \textit{cis}-alcohol, which is the isomer of industrial relevance,\textsuperscript{19} and the non-reactivity of the titanium isopropoxide, indicate that the reaction takes place over framework titanium and not over leached titanium species. This further confirms our belief that the titanium site in Ti-beta has considerable Lewis acidic properties.

Table 8.1 MPV reduction of 4-\textit{tert}-butylcyclohexanone over some titanium containing catalysts in refluxing 2-propanol.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TOF\textsuperscript{d} [mol \text{ mol}^{-1} \text{ Ti h}^{-1}]</th>
<th>Conversion [%]\textsuperscript{e}</th>
<th>Selectivity \textit{cis} : \textit{trans}\textsuperscript{e}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-beta (69)\textsuperscript{b}</td>
<td>2.26</td>
<td>64.9</td>
<td>98 : 2</td>
</tr>
<tr>
<td>Ti(OLPr)\textsubscript{4}\textsuperscript{c}</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Ti-MCM-41 (66)\textsuperscript{b}</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>TiO\textsubscript{2} on SiO\textsubscript{2}</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Al-beta (11.2)\textsuperscript{b}</td>
<td>&gt;12</td>
<td>100.0</td>
<td>95 : 5</td>
</tr>
<tr>
<td>Si-beta</td>
<td></td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Experimental conditions: 2.5 mmol ketone, 0.5 g catalyst, 25 ml 2-propanol, 100 mg 1,3,5-tri-\textit{tert}-butylbenzene as internal standard at 82 °C. \textsuperscript{b} Values in brackets indicate either Si:Ti or Si:Al ratios. \textsuperscript{c} 0.25 mmol catalyst used. \textsuperscript{d} Initial turn-over-frequency in mol ketone per mol titanium or aluminum per hour. \textsuperscript{e} Conversion and selectivity after 6 h reaction; no dehydration occurs and the alcohols are the only products observed.

The possibility of using titanium-containing zeolites as Lewis-acid catalysts was further tested by the MPV reduction of cyclopentanone over Ti-beta as well as over the medium pore titanium containing zeolite TS-1. Ti-beta was found to be active (11.0 % conversion after 6
h, Table 8.2), while no reduction products could be detected for TS-1 even after 24 h. The inactivity of TS-1, may well be caused by spatial constrictions in the narrow pores (5.6 x 5.3 Å). Ti-MCM-41, a mesoporous titanosilicate with 40 Å pores, and TiO2-deposited-on-SiO2 18 could not catalyze the reduction of 4-tert-butylcyclohexanone (see Table 8.1). It should be noted that Al-MCM-41 is active in the MPV-reduction of 4-tert-butylcyclohexanone, but its activity is more than an order of magnitude lower than that of Al-beta. It might therefore be that Ti-MCM-41 is also active but similar to Al-MCM-41 has an activity which is over an order of magnitude lower than that of Ti-beta. This activity might not be sufficient to show a detectable amount of products after 6 h.

Until now it seems that the Lewis acidic nature of the titanium site and the coordination of ligands towards higher coordination numbers is unique for zeolite beta. An analogy may be seen with the reversible interconversion of framework tetrahedral and octahedral aluminum species as recently reported by Bougeat-Lami et al.11 for zeolite beta, which strongly suggests that the properties of the titanium site are related to the framework topology of zeolite beta.

8.3.3 The catalytic site

In the homogeneous system using titanium alkoxides, Li et al.14 proposed that the reaction proceeds via a five coordinated titanium transition state 1 (Figure 8.3). The UV-Vis spectra (Figure 8.2) and the catalytic behavior of Ti-beta in the epoxidation of alkenes9 indicate that alcohols can be coordinated onto the Ti-site to give a higher coordinated species 2. Upon replacement of the silanol group by a carbonyl group the transition state 3, similar to the homogeneous system, is obtained. Creighton et al.12 also proposed that the initial formation of an aluminum alkoxide group is necessary for MPVO reactions to take place. We therefore suggest that the five-coordinated titanium species 2 and 3 are the active intermediates in the Ti-beta catalyzed MPVO reactions.
Creyghton et al.\textsuperscript{12} explained the very high stereoselectivity in the Al-beta catalyzed 4-\textit{tert}-butylcyclohexanone reduction towards the thermodynamically less favored \textit{cis}-alcohol on the basis of transition-state selectivity. It can be seen in Figure 8.4 that, taking the zeolite pores into account, the transition states leading to the \textit{cis} and \textit{trans}-alcohol differ substantially in spatial requirements. The transition state leading to the \textit{cis}-isomer is aligned with the zeolite channel while that leading to the \textit{trans}-alcohol occupies a more axial position. Even with smaller alkyl groups than \textit{tert}-butyl at the 4-position or with alkyl groups on other positions in the ring, selectivity to the axial alcohol product prevails. Thus in the reduction of 4-, 3- and 2-methylcyclohexanone the thermodynamically less favored products, the \textit{cis}-, \textit{trans}- and \textit{cis}-alcohol, respectively, were the major products (Table 8.2). It is therefore proposed that the cycloalkane ring itself is already a structure-directing group, favoring an equatorial attack of the donor hydride to give an axial alcohol group. When a 4-alkyl group is present, the selectivity is further enhanced towards \textgtwentyfive{} \% \textit{cis}-alcohol formation. In the case of 2-methylcyclohexanone a low activity and a \textit{cis} : \textit{trans} ratio of 60:40 were observed. This is probably due to the close proximity of the methyl group to the catalytic site, which distorts the favorable \textit{cis}-transition state, leading to a lower selectivity and activity. Moreover, the even more bulky 2-\textit{tert}-butylcyclohexanone could not be reduced at all under the present conditions.
Table 8.2 MPV reduction of cyclic ketones over Ti-beta-2.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Substrate</th>
<th>TOF\textsuperscript{b} [mol \text{ mol}^{-1}\text{Ti h}^{-1}]</th>
<th>Conversion [%\textsuperscript{c}]</th>
<th>Selectivity (cis : trans\textsuperscript{c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclopentanone</td>
<td>0.46</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>cyclohexanone</td>
<td>0.80</td>
<td>26.9</td>
<td></td>
</tr>
<tr>
<td>2-methylcyclohexanone</td>
<td>0.28</td>
<td>8.8</td>
<td>60:40</td>
</tr>
<tr>
<td>3-methylcyclohexanone</td>
<td>0.74</td>
<td>25.8</td>
<td>30:70\textsuperscript{d}</td>
</tr>
<tr>
<td>4-methylcyclohexanone</td>
<td>1.04</td>
<td>33.7</td>
<td>99: 1</td>
</tr>
<tr>
<td>2-\textit{tert}-butylecyclohexanone</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>4-\textit{tert}-butylecyclohexanone</td>
<td>2.26</td>
<td>64.9</td>
<td>98: 2</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Experimental conditions: 2.5 mmol ketone, 0.5 g Ti-beta-2, 25 ml 2-propanol, 100 mg 1,3,5-tri-\textit{tert}-butylbenzene as internal standard at 82 °C. \textsuperscript{b} Initial turn-over-frequency in mol ketone per mol titanium per h. \textsuperscript{c} Conversion and selectivity after 6 h reaction. \textsuperscript{d} Note that the trans-isomer of 3-methylcyclohexanol contains an axial OH in the preferred configuration, whereas in the cis-isomer both substituents are equatorially positioned.

The catalytic activity of Ti-beta in MPVO reactions is not restricted to the reduction of cyclic ketones. Linear ketones could also be reduced selectively, except when a bulky group is present next to the carbonyl group, \textit{e.g.} acetophenone. This is probably caused by steric repulsion, as discussed above for 2-methyl- and 2-\textit{tert}-butylecyclohexanone. In the reduction of aldehydes, acetals were usually observed as the major product and only small amounts of alcohols were detected. Although the acetal is in equilibrium with the aldehyde, the amount of free aldehyde in the zeolite is apparently too low for a fast MPV reduction. The formation of acetals from aldehydes and not from ketones suggests that Ti-beta has Brønsted acidic properties in the presence of alcohols, in accordance with the observed epoxide cleavage in alcoholic solvents\textsuperscript{9}. Apparently, the acid sites have a weak to moderate acidic character since stronger acids are usually required for the formation of acetals from ketones\textsuperscript{20}, which was not observed.

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Figure 8.4 Transition states for the formation of $\textit{cis}$-$\textit{4-tert}$-butylcyclohexanol (top) and $\textit{trans}$-$\textit{4-tert}$-butylcyclohexanol (bottom) in the straight channels of zeolite beta.$^{13}$
8.3.4 Enantioselective MPV reductions

The synthesis of chiral compounds is of considerable interest in the preparation of pharmaceuticals and agrochemicals. Zeolites are promising catalysts for fine chemical synthesis, and some extraordinary shape selectivities are known already, though until so far not in chiral catalysis. The framework of zeolites consists of tetrahedrally coordinated SiO$_4^-$ units and in case of four inequivalent neighboring SiO$_4^-$ units, these sites are inherently chiral. This was first recognized for polytype A of zeolite beta$^{21-24}$, but nowadays it has been recognized that many zeolites have chiral centers. No pure chiral zeolite has been reported so far.$^{19}$ Though Davis et al.$^{25}$ have reported the synthesis of zeolite beta which is chirally enriched in polytype A. Optical activity can also be induced by using chiral reducing alcohols. The simultaneous coordination of both a pro-chiral ketone and a chiral alcohol in the MPV transition-state should in principle allow the enantioselective reduction of non-symmetrical ketones when optically active alcohols are employed.

The reduction of the prochiral phenylacetone in refluxing (S)-2-butanol using Ti-beta as the catalyst gave the corresponding alcohol in an enantiomeric excess of 34 % e.e. after 77% conversion in 20 days. Similar e.e.'s were obtained when Al-beta was used as the catalyst, while only an e.e. of 4.2 % for aluminum isopropoxide was observed.$^{26}$ The observed chiral induction confirms that the proposed mechanism (site 3, Figure 8.3) for the heterogeneous MPVO is analogous to the homogeneous MPVO mechanism,$^{1,14}$ where both alcohol and ketone are coordinated simultaneously to a Lewis acidic metal ion. The small positive rotation of the reaction mixture after removal of the excess (S)-2-butanol, proved the preferred formation of the (S)-(+) -1-phenyl-2-propanol enantiomer.$^{27}$ The formation of the (S)-enantiomer can be explained by assuming a preferential orientation of the bulky benzyl group of the phenylacetone in relation to the spatially smaller methyl group of the (S)-2-butanol in the transition state, as shown in Figure 8.5. The relatively low e.e. of 34 % is probably due to the direction of the bulky benzyl group compared to the side-groups of the alcohol. In the MPVO transition state all groups are pointed away from each other, thereby reducing the steric interaction. This effect is described in detail by Cram et al.$^{28}$
Introduction of optical activity via this method has been reported for homogeneous aluminum alkoxide based catalysts by various authors.\textsuperscript{29-32} Doering \textit{et al.}\textsuperscript{29} have tested (S)-2-butanol as the reductant in the MPV reduction of 3-methyl-2-heptanone and observed an e.e. of 22\% at 60 \% conversion over aluminum-(S)-2-butoxide as the catalyst. Furthermore Menicagli \textit{et al.}\textsuperscript{30} reported very low e.e.’s while using the primary alcohol (S)-2-methyl-1-butanol as the reductant. The low optical induction has been attributed to the fact that the position of the alcohol group and the chiral center in (S)-2-methyl-1-butanol do not coincide. It should be noted that none of these homogeneous methods resulted in e.e.’s higher than the 34 \% observed for the beta zeolites. High e.e.’s (>90 \%) are therefore not to be expected using this method for the introduction of optical activity by zeolite catalysts.

\textit{8.3.5 Competitive reduction of cyclic ketones}

The influence of the hydrophobicity of the catalyst can also be visualized by the competitive reduction of mixtures of ketones. The reduction of an equimolar mixture of cyclohexanone, 4-methylocyclohexanone and 4-\textit{tert}-butylcyclohexanone over Ti-beta or Al-beta (Table 8.3),
showed that the most apolar substrate, \textit{viz.} 4-\textit{tert}-butylcyclohexanone, was reduced fastest on the hydrophobic Ti-beta and slowest on the less hydrophobic Al-beta. In order to obtain some further understanding, competitive adsorption experiments with an equimolar mixture of 4-
\textit{tert}-butylcyclohexanone, 4-methylcyclohexanone and cyclohexanone over Ti-beta and Al-beta were performed (Table 8.4). The 4-
\textit{tert}-butylcyclohexanone adsorbed slightly better in Ti-beta when compared to 4-methylcyclohexanone which in turn was slightly better adsorbed than cyclohexanone. For Al-beta the opposite order was found. Therefore, the observed reactivities appear to correlate with the concentration of ketones in the zeolite.

Table 8.3 Competitive reduction of an equimolar mixture of cyclohexanone, 4-methylcyclohexanone and 4-
\textit{tert}-butylcyclohexanone in 2-propanol over Ti-beta and Al-beta.\(^8\)

<table>
<thead>
<tr>
<th>Substrate mixture</th>
<th>Ti-beta (59)</th>
<th>Al-beta (11.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOF(^b)</td>
<td>Conversion(^c)</td>
</tr>
<tr>
<td>cyclohexanone</td>
<td>0.6</td>
<td>18.6</td>
</tr>
<tr>
<td>4-methylcyclohexanone</td>
<td>0.9</td>
<td>28.2</td>
</tr>
</tbody>
</table>
| 4-
\textit{tert}-butylcyclohexanone | 1.4          | 43.5           | 0.7        | 88.2            |

\(^8\) Reaction conditions: 2.5 mmol of each ketone, 0.5 g catalyst, 25 ml 2-propanol, 100 mg 1,3,5-tri-
\textit{tert}-butylbenzene as internal standard at 82 °C. Al-beta was calcined at 480 °C to obtain a lower initial activity.\(^13\)

\(^b\) Initial turn-over-frequency in mol ketone per mol titanium or aluminum per h. \(^c\) After 6 h reaction.
Table 8.4 Competitive adsorption of 4-tert-butylcyclohexanone, 4-methylcyclohexanone and cyclohexanone on zeolite Ti-beta and Al-beta.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Substrate</th>
<th>adsorbed amount on Ti-beta [ mg g\textsuperscript{-1} zeolite ]</th>
<th>adsorbed amount on Al-beta [ mg g\textsuperscript{-1} zeolite ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-tert-butylcyclohexanone</td>
<td>101</td>
<td>74</td>
</tr>
<tr>
<td>4-methylcyclohexanone</td>
<td>87</td>
<td>81</td>
</tr>
<tr>
<td>cyclohexanone</td>
<td>73</td>
<td>88</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Experimental conditions: equimolar mixture of ketones (1 mmol each), 500 mg zeolite pre-dried at 450 °C in 20 ml 1,3,5-triisopropylbenzene as the solvent at room temperature.

8.3.6 By-product formation in the Oppenauer oxidation

The most important side reactions in MPVO reactions are the acid catalyzed aldol condensation and acetalization. Ketones are somewhat less prone than aldehydes to give acetals. Aldol products are usually formed during the Oppenauer oxidation when surplus ketone or aldehyde is used as oxidizing agent and solvent. In the zeolite beta catalyzed Oppenauer oxidation (see Table 8.5) of a 1 : 1 mixture of cis- and trans-4-tert-butylcyclohexanol, both Ti-beta and Al-beta selectively convert the cis-alcohol, which is ascribed to spatial restrictions of the transition states in the zeolite channel, in analogy with the MPV reduction of the corresponding ketone. In this way, MPVO reduction and oxidation are in harmony as to the high transition-state selectivity. The low amount of by-products formed when Ti-beta is used as a catalyst clearly shows another advantage of the titanium system over Al-beta. This is probably caused by the much weaker Brønsted acidity of the alcohol coordinated to the titanium site (site 2, Figure 8.3), compared with the strong H\textsuperscript{+}-acidity of the aluminum sites in Al-beta which can easily catalyze the aldol condensation.
Table 8.5  Competitive Oppenauer oxidation of cis- and trans-4-tert-butylcyclohexanol with butanone as the oxidant.\(^a\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion [%](^b) of cis-alcohol</th>
<th>Conversion [%](^b) of trans-alcohol</th>
<th>Byproducts [mg](^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-beta</td>
<td>52.1</td>
<td>4.6</td>
<td>22.4</td>
</tr>
<tr>
<td>Al-beta</td>
<td>98.6</td>
<td>47.3</td>
<td>317.3</td>
</tr>
<tr>
<td></td>
<td>49.4(^d)</td>
<td>5.7(^d)</td>
<td>63.8(^d)</td>
</tr>
<tr>
<td>Ti(OiPr)(_4)</td>
<td>6.1</td>
<td>12.9</td>
<td>22.7</td>
</tr>
<tr>
<td>Al(OiPr)(_3)</td>
<td>5.3</td>
<td>7.4</td>
<td>56.5</td>
</tr>
</tbody>
</table>

\(^a\) Experimental conditions: 2.5 mmol alcohol each of a 1:1 mixture of cis and trans, 82 °C, 25 ml butanone, 0.5 g zeolite or 0.25 mmol metal alkoxide as catalyst.\(^b\) After 6 h reaction time.\(^c\) Total amount of by-products formed after 6 h as determined from the peak areas in the GC chromatogram, predominantly aldol condensates originating from butanone and dehydrated products thereof.\(^d\) After 15 min reaction time.

8.3.7 Poisoning tests

The commonly used MPVO catalysts consist of metal alkoxides which are easily hydrolyzed to inactive (hydr)oxides in the presence of water. Similarly, in the proposed heterogeneous mechanisms, alkoxide groups play an important role.\(^1,12,13,33,34\) The use of hydrophobic heterogeneous materials, high silica zeolites in particular, could be favorable. As shown in Table 8.6, Ti-beta hardly looses activity in the presence of 1 vol% water, while for the two aluminum containing catalysts the activity drops significantly. The low decrease in activity in the case of Ti-beta can be explained by the hydrophobic interior of the nearly all-silica zeolite. As we reported earlier, the sorption capacity for water of all-silica beta at 50 °C is low (about 8 mg water g\(^{-1}\) zeolite compared to 74 mg g\(^{-1}\) zeolite for Al-beta).\(^8\) It is therefore expected that hardly any water, hindering the formation of the water-sensitive titanium alkoxide group, enters the zeolite. Although it is much more inclined to adsorb water on the cationic H\(^+\) site, zeolite Al-beta still has a considerable hydrophobic character. The catalytic MPV site, as proposed by Creighton et al.,\(^12\) consists of an aluminum alkoxide intermediate,
similar to the titanium isopropoxide in our transition states 2 and 3 (Figure 8.3), which are water sensitive. Apparently, the higher amount of water in Al-beta reduces the amount of the catalytic active aluminum isopropoxide sites much more than in the case of Ti-beta.

Upon addition of a strong Lewis base (pyridine) the activity of both Al-beta and Ti-beta is reduced to zero. In case of Al-beta this can be explained by the formation of a pyridinium cation by protonation of pyridine or the coordination of the amine directly onto Lewis acid sites. In principle, the same reasoning applies to Ti-beta. The amine can either add directly to the titanium atom or deprotonate the Brønsted acidic silanol group of site 2 (Figure 8.3). The latter phenomenon (deprotonation of the Brønsted acidic silanol group) is most likely. From the UV-Vis spectra (Figure 8.2) it can be seen that alcohols coordinate easily to the Lewis acid titanium site to give higher coordinated species e.g. site 2. Furthermore, titanium is a hard Lewis acid, preferring hard Lewis bases (oxygen-containing bases such as alcohols or ketones) over pyridine, which is an intermediate Lewis base.

Table 8.6 Influence of water and pyridine on the catalytic activity of Ti-beta, Al-beta and Al(OiPr)_3 in the MPV reduction of 4-tert-butylcyclohexanone.

<table>
<thead>
<tr>
<th></th>
<th>Initial TOF [mol mol(^{-1}\text{Me h}^{-1})](^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no addition</td>
</tr>
<tr>
<td>Ti-beta (59)</td>
<td>2.26</td>
</tr>
<tr>
<td>Al-beta (11.2)</td>
<td>&gt;12</td>
</tr>
<tr>
<td>Al(OiPr)_3</td>
<td>&gt;12</td>
</tr>
</tbody>
</table>

\(^a\) Experimental conditions: 2.5 mmol ketone, 0.5 g zeolite or 0.25 mmol Al(OiPr)_3, 25 ml 2-propanol, 100 mg 1,3,5-tri-tert-butylbenzene as internal standard at 82 °C, 0.25 ml water or pyridine was added to the reaction mixture. \(^b\) Initial turn-over-frequency in mol ketone per mol titanium or aluminum per hour. \(^c\) 0.50 ml instead of 0.25 ml water was added to the reaction mixture.
8.4 Conclusions

Ti-beta was found to be an active catalyst for the Meerwein-Ponndorf-Verley (MPV) reduction of ketones and the Oppenauer oxidation of the alcohols. High stereoselectivity is observed in the MPV reduction 4-\textit{tert}-butylcyclohexanone. The high stereoselectivity to the \textit{cis}-alcohol is explained on the basis of a restricted transition state similar as the explanation given for Al-beta [12,13]. The observed chiral induction in the reduction of prochiral ketones when an optical active alcohol was used as the reductant, confirms that the proposed mechanism\textsuperscript{9,33,34} for the heterogeneous MPVO is analogous to the homogeneous MPVO mechanism,\textsuperscript{1,14} where an alcohol and ketone are coordinated to a Lewis acidic metal atom. The catalytic potential of Ti-beta compared to Al-beta and metal alkoxides is shown by its high tolerance towards water. Furthermore, the lower Bredsted acidity of Ti-beta reduces the formation of aldol products from ketone solvents and makes it a more suitable catalyst for the Oppenauer oxidation due to the reduced. Neither TS-1 nor Ti-MCM-41 was found to be able to reduce ketones, which restricts the MPV reaction over titanium containing zeolites to Ti-beta, so far.

In the competitive reduction of cyclohexanone, 4-methylcyclohexanone and 4-\textit{tert}-butylcyclohexanone, Ti-beta has the highest activity for 4-\textit{tert}-butylcyclohexanol while Al-beta has the highest activity for cyclohexanone. From the complementary competitive adsorption experiments it is observed that Ti-beta has the highest affinity for 4-\textit{tert}-butylcyclohexanone while Al-beta has the highest affinity for cyclohexanone. This in accordance with the hydrophobic nature of Ti-beta and the hydrophilic nature of Al-beta. The observed activity of the two zeolites seems therefore related to the internal concentration of the ketone in the zeolite.

The Lewis acidic properties of titanium sites in zeolite beta show analogy with the remarkable dynamic behavior of aluminum in zeolite beta\textsuperscript{11} and seem to be caused by the framework topology of zeolite beta. The Lewis-acidic and moderate to weak Bredsted acidic properties of the large pore Ti-beta upon adsorption of alcohols make it a potentially interesting catalyst for various Lewis-acid catalyzed reactions.
8.5 References


26 Private communication from E.J. Creighton. See also S.D. Ganeshie, E.J. Creighton and H. van Bekkum, internal report.


The gas-phase Meerwein-Ponndorf-Verley reduction of 4-methylcyclohexanone and Oppenauer oxidation of 4-methylcyclohexanol over zeolite titanium beta.

Abstract

Aluminum-free zeolite titanium beta was tested in the gas-phase Meerwein-Ponndorf-Verley reduction of 4-methylcyclohexanone with various alcohols as the hydrogen donors and the Oppenauer oxidation of 4-methylcyclohexanol with acetone as the oxidant. A high selectivity towards the thermodynamically unfavorable cis-4-methylcyclohexanol was observed, which is ascribed to transition-state selectivity in the straight channels of zeolite beta. In the gas phase, the observed selectivity to the cis-alcohol is significantly lower than in the liquid phase. A kinetic study of the gas-phase reaction was conducted to resolve the origin of the observed differences in selectivity.

Based on kinetic and adsorption experiments, it is concluded that the concentration of alcohol reductant in the zeolite is an important parameter in determining selectivity. More hydrophobic alcohols or higher alcohol partial pressures give rise to an increased selectivity to the cis-alcohol product. From the sorption experiments it was concluded that this is due to a higher internal concentration of the alcohol reductant in the hydrophobic zeolite. The observed selectivities and activities are consistent with a mechanism in which the alcohol is not only the hydrogen donor but is also required to remove the cis-alcohol product formed from the catalytic site by alcoholysis, before consecutive reactions can occur.

The excellent catalytic properties of titanium beta were shown by the high MPVO activity in the presence of water. No significant loss in selectivity and activity was observed after 35 regeneration cycles at 480 °C in air. Even the presence of N-bases, e.g. ammonia, is not detrimental though higher reaction temperatures are required.
9.1 Introduction

The Meerwein-Ponndorf-Verley reduction of carbonyl compounds and the Oppenauer oxidation of alcohols, together denoted as MPVO reactions, are highly selective reactions. For instance other reducible groups such as C=C double bonds and C-halogen bonds, are not attacked. In MPV reductions a secondary alcohol generally forms the reductant while in Oppenauer oxidations a ketone acts as the oxidant. It is generally accepted that MPVO reactions proceed via a complex in which both carbonyl and alcohol are coordinated to a Lewis acid metal ion, after which a hydride transfer from the alcohol to the carbonyl group occurs (Figure 9.1). Usually, aluminum sec-alkoxides are used as homogeneous catalysts in reductions and aluminum tert-butoxides in oxidations.

![Figure 9.1 The Meerwein-Ponndorf-Verley-Oppenauer reaction.](image)

Zeolites are crystalline microporous metal oxides which have potential as regenerable heterogeneous catalysts in various organic reactions. Because of their unique microporous structures, zeolites are especially promising in the field of shape-selective catalysis. Only a few examples of the use of zeolites in MPVO reactions have been reported so far. The reactions were carried out in the gas phase over zeolites A, X and Y, exchanged or impregnated with alkali or alkaline-earth cations or in the liquid and gas phase over beta type zeolites. Shape-selectivity in gas-phase reactions was observed by Shabtai et al. in the conversion of citronellal over zeolite X. It was shown that selectivity could be tuned by the size of the exchanged metal ion. In NaX there was enough space for the substrate to perform an intramolecular ring closure to isopulegol, whereas over CsX reduction to the linear citronellol was observed. Similar steric effects were also observed for various other substrates.

Recently Creighton et al. reported the use of zeolite beta in the MPVO reduction of 4-tert-butylenecyclohexanone. The high selectivity towards the thermodynamically less favored
cis-alcohol, which is the industrially relevant isomer,\textsuperscript{10} is explained by a restricted transition-state for trans-alcohol formation around a Lewis-acidic aluminum in the zeolite pores (Figure 9.2). When using an aluminum-free zeolite, titanium beta (Ti-beta) in the epoxidation of alkenes, we have shown that the titanium site has acidic properties when alcoholic solvents are employed.\textsuperscript{11} This was ascribed to the Lewis-acidic character of titanium in the zeolite framework. As we reported very recently,\textsuperscript{8,12} Ti-beta is found to be an excellent catalyst in MPVO reactions with a tolerance for water. In a preliminary report on the possibility of gas-phase MPVO reactions over zeolite beta based catalysts, we noted significant changes in selectivity compared to the liquid-phase experiments.\textsuperscript{9} In the gas-phase a lower selectivity towards the cis-alcohol and dehydration of the alcohols formed were observed.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure9.2.png}
\caption{Transition states in the MPV reduction of 4-tert-butylcyclohexanone. Transition state leading to the cis-alcohol (top, aligned with channel wall) and trans-alcohol (bottom, axially oriented to channel wall).}
\end{figure}

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The remarkable differences in selectivity between the liquid- and gas-phase reactions induced us to study the gas-phase reaction in more detail. Kinetic measurements have been employed to study the effect of the intra-zeolitic alcohol-reductant concentration, which could be influenced by changing the alcohol used or by applying different partial pressures of the alcohol, on the activity and the selectivity. Based on the observed effects, a catalytic mechanism is proposed and a dual role of the alcohol reductant is suggested.

9.2 Experimental

Aluminum-free zeolite titanium beta (Ti-beta-1) was synthesized according to van der Waal et al.\textsuperscript{8,11} using di(cyclohexylmethyl)dimethylammonium hydroxide (DCDMA.OH) as the template. The synthesis and the characterization of the material (Ti-beta-1) used are described in full in Chapter 4. Elemental analysis showed a Si:Ti molar ratio of 59 and EDX confirmed the absence of oligomeric titanium dioxide phases. Zeolite aluminum beta (Al-beta, Si:Al = 11.2) was prepared according to Wadlinger et al.\textsuperscript{13}

The competitive adsorption experiments were performed in 1,3,5-triisopropylbenzene (10 g) as the solvent with 1,3,5-tri-\textit{tert}-butylbenzene as the internal standard. For the experiments with various alcohols, 50 µl of the appropriate alcohol, 50 µl 2-propanol and 100 mg zeolite titanium beta, pre-dried at 200 °C, were added to the solvent. For the competitive adsorption experiments with 4-methylcyclohexanone (4-Me-ONE), 50 µl 4-methylcyclohexanone (0.35 mmol) and 3.5 mmol of the appropriate alcohol were used. This molar ratio of 1:10 is similar to the conditions used in the gas-phase experiments. All samples were analyzed after attainment of the adsorption equilibria and analyzed by GC on a CP-52-Carbowax column (50 m, i.d. = 0.53 mm).

The gas-phase MPVO reactions were performed at 85 to 400 °C in a fixed-bed continuous down-flow reactor with an internal diameter of 7 mm, operated at atmospheric pressure under plug flow conditions. All auxiliary tubing was maintained at 200 °C to prevent condensation of products. The catalyst, Ti-beta or Al-beta (0.30 g), was diluted with 1.20 g α-quartz powder and pressed to pellets which were subsequently crushed and sieved to particles with a diameter of 0.7 - 1.0 mm. Reactant mixtures were pumped, via an evaporator,
into a stream of preheated carrier gas (usually nitrogen) by means of a motor-driven syringe pump. The gas flow, unless otherwise stated, contained 10 vol.% 2-propanol (Baker p.a.) and 1 vol.% of 4-methylcyclohexanone (4-Me-ONE, Acros, 98%). The total gas flow was typically 50 ml/min, the molar gas flow of 4-Me-ONE and products was 2.04 $10^{-5}$ mol/min (WHSV = 2.9 gtotal gcat$^{-1}$ h$^{-1}$, GHSV = 1.56 $10^{3}$ h$^{-1}$). Other alcohols tested were 1-propanol (Baker p.a.), 1-butanol (Acros, 99%), 2-butanol (Baker p.a.), 1-pentanol (Acros, 98%), 2-pentanol (Acros, 99%), 3-pentanol (Fluka), 2-heptanol (Fluka), cyclopentanol (Acros, 99%) and cyclohexanol (Baker), under similar conditions as described for 2-propanol. Samples of the reactor effluent were taken regularly by means of an autosampler and analyzed by an on-line GC equipped with a CP-Sil-19 column (50 m, i.d = 0.53 mm). The temperature-programmed reactions were performed by continuously raising the reactor temperature at 12 °C h$^{-1}$.

9.3 Results

9.3.1 Catalyst characterization

Primary characterization of the Ti-beta-1 catalyst used was performed by X-ray diffraction (XRD), UV-Vis and Scanning Electron Microscopy (SEM). After hydrothermal synthesis, the XRD diffractogram showed that a fully crystalline material was obtained with less than 2 % impurities. The incorporation of tetrahedral titanium in the zeolite framework was confirmed by the presence of a single absorption band at 47.000 - 50.000 cm$^{-1}$ in the UV-Vis spectrum (See Figure 4.8 in Chapter 4). The absence of absorption bands at lower frequencies in the UV/Vis spectrum also confirmed the absence of oligomeric titanium dioxide particle. Analysis of the zeolite crystal size and morphology with SEM (Figure 4.11 in Chapter 4) demonstrated a uniform distribution of disk-shaped particles with a diameter of 1.3 μm.
9.3.2 Gas-phase MPVO reactions

From an industrial point of view, gas-phase reactions are often preferred due to their ease of operation. Comparing the Ti-beta and Al-beta catalyst in the gas-phase reduction of 4-methylcyclohexanone (Figure 9.3), showed that the titanium-based catalyst has a considerably lower rate of deactivation. The higher deactivation rate of zeolite Al-beta is probably caused by the higher acidity of the protic aluminum site compared to the non-protic titanium site. From the liquid-phase experiments, it was concluded that the major by-products are the acid-catalyzed aldol condensation products from two ketone molecules.\(^8\) In the gas phase, the formation of non- or very slowly desorbing aldol condensates formed from two 4-Me-ONE molecules probably plugs the pores of the zeolite thereby deactivating the catalyst.

Two important differences between the gas-phase and liquid-phase reactions were observed over Ti-beta. The most striking is the changed selectivity towards the cis-alcohol. Under liquid-phase conditions a selectivity of 99 % at 85 °C towards the cis-alcohol was observed, while in the gas-phase at 100 °C over Ti-beta-1 initially only 51 % cis-alcohol was obtained (Figure 9.3).\(^8,9,12,14\) Furthermore, the dehydration of the alcohols formed to 4-methylcyclohexene (4-Me-ENE) was a major consecutive reaction in the gas-phase, while not even a trace of dehydrated products could be detected in the liquid-phase reductions. The somewhat higher temperature of 100 °C, compared with 85 °C for the liquid-phase experiments, could not explain this behavior. Decreasing the temperature to 85 °C of the gas-phase experiment over Ti-beta-1 still resulted in a cis-4-Me-OL selectivity of 63 % and a 4-Me-ENE selectivity of approximately 15 % (see Figure 9.12, to be discussed later in this Chapter).\(^9\)

In order to investigate the formation of the alkene from the alcohol and to gain more insight in the kinetics of product formation, the gas-phase Oppenauer oxidation of 4-methylcyclohexanols was studied. Since 4-Me-ENE can be formed via dehydration of either of the two stereoisomeric alcohols formed, both alcohols were tested separately in the Oppenauer oxidation at 100 °C, using acetone as the oxidant (see Figure 9.5). The dehydration of the trans-alcohol only occurred on a very limited scale (Figure 9.5b) whereas dehydration of the cis-alcohol was an important side-reaction.
Figure 9.3  The gas-phase MPV reduction of 4-methylcyclohexanone with 2-propanol at 100 °C over a) Ti-beta-1 and b) Al-beta. ■ = conversion; □ = cis-4-Me-OL; x = trans-4-Me-OL; ○ = 4-Me-ENE.
The dehydration of the cis-alcohol yields as the only product 4-methylcyclohexene (4-Me-ENE) while no 1- or 3-methylcyclohexene isomers are observed at low temperatures. This can be understood in terms of an E2-elimination (Figure 9.4) of cis-alcohol on the titanium site. In this mechanism, both the axial alcohol group and an axial hydrogen atom at the β-position are removed simultaneously without the formation of a carbenium intermediate. Molecular modelling of the most favorable coordination of the cis-alcohol on the catalytic site (see Figure 8.4 in Chapter 8) shows that none of the two available axial hydrogen atoms is in close vicinity to zeolite framework oxygen atoms. We therefore assume that the intraporeous alcohol molecules act as base, possibly polarized by interaction with the zeolite framework as shown in Figure 9.4. The 4-ME-ENE formed can further isomerize over Brønsted acid sites to the more stable 1-methylcyclohexene (1-Me-ENE) at higher temperatures.⁹

![Figure 9.4 Proposed mechanism for the formation of 4-Me-ENE via E2-elimination of cis-4-Me-OL.](image)

It was further observed that the cis-alcohol (Figure 9.5a) is easily oxidized to the corresponding ketone, while the trans-alcohol showed a much lower activity. This is in accordance with the transition-states assumed for liquid-phase MPVO reactions (Figure 9.2, see also Figure 8.4 in Chapter 8). It was also observed that both alcohols isomerized, which reaction most likely proceeds via the MPVO transition-state.
a) Oxidation of cis-4-Me-OL

b) Oxidation of trans-4-Me-OL

Figure 9.5 The gas-phase Oppenauer oxidation of the 4-methylcyclohexanols with acetone over Ti-beta-1 at 100°C. a) cis-4-Me-OL and b) trans-4-Me-OL. ■ = conversion; ● = cis-4-Me-OL; x = trans-4-Me-OL; ▲ = 4-Me-ONE. □ = 4-Me-ENE.
Figure 9.6 Reaction scheme for the MPV reduction of 4-Me-ONE.

Comparing the deactivation of the Ti-beta-1 catalyst in the reduction of 4-methylcyclohexanone (from 51 to 32 % conversion, Figure 9.3) and the oxidation of cis-4-methylcyclohexanol (from 42 % to 19 % conversion, Figure 9.5a) shows that deactivation is more pronounced during oxidative conditions. This is probably caused by the fact that the acetone being present in a higher amount, can easily form aldol condensates or oligomers plugging the zeolite channels and inhibiting access to the micropore system.

9.3.3 Kinetic experiments.

The kinetics of the 4-Me-ONE/2-propanol system have been investigated in order to acquire insight into the mechanism of consecutive product formation from cis-4-Me-OL, viz. the alkene and the trans-alcohol. The influences of the contact time, the substrate partial pressures, the ratio of 4-Me-ONE to 2-propanol and the type of alcohol reductant have been studied. Due to the limitations in the experimental setup, the conversion usually exceeded the threshold value for differential plug flow conditions and exact determination of kinetic constants could not be performed. Additional information could also be obtained from the adsorption behavior of the Ti-beta catalyst used, in relation to the observed conversions and selectivities.
- Variation of the contact time at constant substrate partial pressure

The influence of the contact time at constant substrate partial pressure on the activity and selectivity of Ti-beta-1 was investigated. The results are shown in Figure 9.7 and are in accordance with the reaction scheme in Figure 9.6. A steady increase in the selectivities to the trans-4-Me-OL and 4-Me-ENE by-products with contact time is observed, while the selectivity to cis-4-Me-OL shows a corresponding decrease. The cis-alcohol is formed initially, whereafter it can be converted to the trans-alcohol or the alkene. The increase in conversion with the reciprocal gas flow as a measure of the contact time indicates that the surface reaction and not the desorption of the products from the zeolite into the gas phase is the rate-limiting step. The increase in conversion further shows that the reversible MPVO reaction has not reached its equilibrium and that kinetically determined rates are measured. At high contact time the trans-alcohol selectivity is seen to decrease somewhat, probably due to the increased alkene formation which is an irreversible process.

![Graph showing conversion and selectivity vs contact time](image)

**Figure 9.7** Effect of the contact time under constant partial pressure of reactants on the selectivity and the activity of the MPV reduction of 4-Me-ONE with 2-propanol at 100 °C over Ti-beta-1. The contact time is defined here as the reciprocal gas flow. ■ = Conversion; ○ = cis-4-Me-OL; x = trans-4-Me-OL; □ = 4-Me-ENE
- *Influence of the partial pressure*

In order to investigate the influence of the sorption equilibrium in the zeolite pores on the activity and selectivity, experiments were conducted in which the substrate partial pressure, at a constant 4-Me-ONE/2-propanol molar ratio of 1:10, was varied at constant contact time. For each partial pressure measurement a separate run was performed using freshly calcined Ti-beta-1 catalyst. As shown in Figure 9.8, the effect of increasing the partial pressure is a sharp reduction in the conversion, indicating a strong inhibiting effect of one or both of the substrates. At the same time, the selectivity to the *cis*-4-Me-OL increased from 13 to 72 %, while that for 4-Me-ENE decreased from 81 to 14 %. Since the alkene is believed to be formed by dehydration of the *cis*-alcohol *via* an E2 mechanism,⁹ the fact that high partial pressures are required to attain a high selectivity to *cis*-4-Me-OL suggests that a high internal concentration of either one of the reactants, *i.e.* 4-Me-ONE or 2-propanol, in the zeolite acts either to facilitate the desorption of the *cis*-alcohol from the catalytic site before dehydration can occur or to a kinetic suppression of the alkene formation. When seen on an absolute scale (mol h⁻¹) the conversion increases with partial pressure of the reactants; *i.e.* the turn-over-frequency increases. Therefore, a change in selectivity is related to an intrinsic change in the catalytic performance of the active site.

During the experiments at low partial pressures, it was further observed that the GC analysis of the gas-stream showed initially no 4-methylcyclohexanone or products derived thereof. They could only be detected after a time on stream which was found to correspond roughly with the time required to load the zeolite almost fully with 4-methylcyclohexanone. On the other hand, 2-propanol was always detected. This suggests that under the experimental conditions the zeolite is predominantly filled with 4-methylcyclohexanone and its products irrespective of the partial pressures applied. This can be explained by the hydrophobic character of the Ti-beta catalyst,¹⁶ which preferentially adsorbs the less polar 4-Me-ONE over the more polar 2-propanol. Since the internal 4-Me-ONE concentration does not change significantly with changing partial pressure, the observed effect of the partial pressure on the activity and selectivity should be ascribed to differences in the internal concentration of 2-propanol.
Figure 9.8 Influence of the partial pressure on the selectivity and activity in the MPV reduction of 4-Me-ONE with 2-propanol at 100 °C over Ti-bet-1. ■ = Conversion; ● = cis-4-Me-OL; x = trans-4-Me-OL; □ = 4-Me-ENE

It is not surprising that it is the alcohol concentration which has a significant effect on the catalytic performance. It is well known for the MPVO reactions that the alkoxy intermediate formed may leave the complex via an alcoholysis reaction in which a proton is abstracted from a second adsorbed alcohol molecule. The increased selectivity to the cis-alcohol is therefore ascribed to an increased alcoholysis reaction, removing the cis-4-Me-OL from the catalytic site, rather than to a suppression of the dehydration reaction.

To further investigate the influence of the internal alcohol concentration on the selectivities, the partial pressure of 2-propanol in the feed was varied from 1 to 50 vol% at constant partial pressure of 4-Me-ONE (1 vol%) and constant contact time. The selectivity towards the cis-alcohol increases substantially at higher partial pressures of 2-propanol (Table 9.1). It can be seen from Table 9.1 that, at the highest 2-propanol partial pressure, the cis-4-Me-OL selectivity tends towards the high values observed in the liquid phase. It was noted that the activity also increases with higher partial pressures of 2-propanol, thus confirming that the intra-porous 2-propanol concentration is an important parameter in the kinetic expression.
Chapter 9

It should be noted that at low 2-propanol pressures, the deactivation of the catalyst is much more severe than at higher partial pressures, which suggests that also for a high catalyst stability the presence of 2-propanol near the catalytic active center is necessary to inhibit the aldol condensation of 4-Me-ONE.⁹

Table 9.1 Influence of the partial pressure of 2-propanol on the selectivity and activity of Ti-beta-1 at a constant 4-Me-ONE pressure of 1 vol% at 100 °C.

<table>
<thead>
<tr>
<th>2-Propanol pressure [ vol % ]</th>
<th>Conversion [ % ]</th>
<th>Selectivity to cis-4-Me-OL [ % ]&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Selectivity to 4-Me-ENE [ % ]&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15&lt;sup&gt;b&lt;/sup&gt;</td>
<td>16</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>21&lt;sup&gt;b&lt;/sup&gt;</td>
<td>22</td>
<td>39</td>
</tr>
<tr>
<td>10</td>
<td>36</td>
<td>60</td>
<td>24</td>
</tr>
<tr>
<td>50</td>
<td>68</td>
<td>81</td>
<td>7</td>
</tr>
<tr>
<td>liquid-phase&lt;sup&gt;c&lt;/sup&gt;</td>
<td>(33.7)</td>
<td>97</td>
<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> After 6 h on stream. <sup>b</sup> Strong deactivation of the catalyst was observed. <sup>c</sup> See Chapter 8 and van der Waal et al.⁸ for details.

Our kinetic experiments with 2-propanol suggest that a high selectivity could be achieved if the cis-alcohol formed could be removed from the catalytic site before isomerization to the trans-alcohol or dehydration to the alkene could occur. The desorption of the cis-alcohol, via alcoholsysis of the cis-alkoxide intermediate formed, can be enhanced greatly by a high internal alcohol concentration in the zeolite pores. The function of the alcohol is thus not only to serve as a hydrogen donor, but also to release the cis-alcohol from the catalytic site (see Figure 9.9 for the reaction-cycle).
Gas-phase MPVO reactions
- The influence of different alcohol reductants

From the kinetic experiments with 2-propanol as the reductant, it was concluded that a high internal alcohol concentration in the zeolite is important to obtain a high selectivity towards the preferred cis-alcohol. Even at the high molar ratio of 2-propanol to 4-Me-ONE of 50:1 only 81 % cis-alcohol was observed (Table 9.1). The relatively low selectivity in the gas-phase reductions using 2-propanol is probably caused by the hydrophobic nature of the Ti-beta catalyst. Ti-beta prefers to adsorb 4-Me-ONE instead of 2-propanol under the reaction conditions used. In order to test further whether the internal alcohol concentration directs selectivity, other secondary alcohols with a higher hydrophobicity were tested (Table 9.2). Indeed, the selectivity towards cis-4-Me-OL increased with increasing aliphatic chain-length of the alcohol, in accordance with the above idea.

Table 9.2  Conversion and selectivity in gas-phase MPV reduction of 4-Me-ONE with secondary and cyclic alcohols at 100 °C.\(^a\)

<table>
<thead>
<tr>
<th>Reducing Alcohol</th>
<th>(\Delta H_f^0) [kJ/mol](^b)</th>
<th>Conversion [%](^c)</th>
<th>Selectivity to cis-4-Me-OL [%](^c)</th>
<th>Selectivity to 4-Me-ENE [%](^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-propanol</td>
<td>70.0</td>
<td>36</td>
<td>60</td>
<td>24</td>
</tr>
<tr>
<td>2-butanol</td>
<td>69.3</td>
<td>67</td>
<td>72</td>
<td>11</td>
</tr>
<tr>
<td>2-pentanol</td>
<td>67.9</td>
<td>88</td>
<td>84</td>
<td>6</td>
</tr>
<tr>
<td>2-heptanol</td>
<td>n.a.</td>
<td>34</td>
<td>95</td>
<td>-</td>
</tr>
<tr>
<td>cyclopentanol</td>
<td>64.4</td>
<td>71</td>
<td>92</td>
<td>1</td>
</tr>
<tr>
<td>cyclohexanol</td>
<td>77.0</td>
<td>53</td>
<td>95</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Experimental conditions: 1 vol% 4-Me-ONE, 10 vol% alcohol in nitrogen, total gas flow 50 ml/min and 0.3 g Ti-beta-1 in 1.2 g quartz at 100 °C. \(^b\) From Pedley et al.\(^{17}\) \(^c\) After 6 h on stream.

The activity of various alcohols is also determined by their reduction potential, \(\Delta H_f^0\). The reduction potential is defined here as the difference in heat of formation between the
alcohol and the corresponding carbonyl compound, *i.e.* it represents the ease of hydrogen abstraction. Since all secondary alcohols tested (Table 9.2) have similar reduction potentials (≈ 70 kJ mol⁻¹), the observed differences in activity must originate from the adsorbed amount of alcohol. High internal alcohol concentrations probably facilitate the reaction by a faster regeneration of the catalytic site. However, when the reducing alcohol approaches the polarity of the 4-Me-ONE, as is the case for 2-heptanol, cyclopentanol and cyclohexanol, the amount of alcohol adsorbed is interfering with the amount of 4-Me-ONE adsorbed, thereby limiting the reaction rate.

To test the assumption of alcoholysis being both the rate and selectivity determining step, isomeric alcohols with similar polarity but different reduction potentials were applied. These alcohols are expected to adsorb quite similarly under the experimental condition used. If the rate-determining step is the alcoholysis of the initially formed *cis*-alcohol from the catalytic site *via* the coordination of a second reductant alcohol, selectivity should hardly change for isomeric alcohols. Equal internal alcohol concentrations will result in approximately equal probabilities of *cis*-alkoxide removal and, thus, roughly the same selectivity. Therefore, 1-propanol, 1-butanol and 1-pentanol were compared with the corresponding 2-isomers as the reductant alcohol. From Table 9.3 it can be seen that nearly identical selectivities were indeed obtained from both isomers of a pair, thereby confirming that it is the internal concentration of alcohols that largely determines the selectivity towards the *cis*-alcohol.

The reactivity of the alcohol is determined by its reduction potential. Since the MPVO reaction is an equilibrium reaction, the choice of reductant strongly influences the amount of *cis*-alkoxide on the titanium site in the MPVO reduction step.¹ The general influence of the reduction potential on the catalytic activity can be demonstrated by plotting the activity of all alcohols tested against their reduction potential (Figure 9.10). A clear decrease in activity is observed with increasing reduction potential. The large spread in activities observed is caused by differences in sorption characteristics, as discussed above for the secondary alcohols (Table 9.2). This would, however, suggest that the achievement of the MPVO equilibrium is relatively fast compared with the desorption of the *cis*-alcohol from the catalytic active site. Thus, the fraction of *cis*-4-Me-OL alkoxide groups on the catalytic site is determined by thermodynamics and the observed rate and selectivity are a reflection of the alcoholysis rate of the product-alkoxide with a another solvent alcohol molecule, *e.g.* 2-propanol.
Table 9.3  Initial selectivity and activity in the gas-phase MPV reduction as a function of the reduction potential and polarity of the alcohol reductant applied.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Reducing Alcohol</th>
<th>$\Delta H_f^\circ$ [kJ/mol]</th>
<th>Conversion [%]\textsuperscript{d}</th>
<th>Selectivity to cis-4-Me-OL [%]\textsuperscript{d}</th>
<th>Selectivity to 4-Me-ENE [%]\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-propanol</td>
<td>87.3\textsuperscript{b}</td>
<td>$\approx$1</td>
<td>60</td>
<td>22</td>
</tr>
<tr>
<td>2-propanol</td>
<td>70.0\textsuperscript{b}</td>
<td>36</td>
<td>60</td>
<td>24</td>
</tr>
<tr>
<td>1-butanol</td>
<td>79.7\textsuperscript{c}</td>
<td>9</td>
<td>74</td>
<td>13</td>
</tr>
<tr>
<td>2-butanol</td>
<td>69.3\textsuperscript{b}</td>
<td>67</td>
<td>72</td>
<td>11</td>
</tr>
<tr>
<td>1-pentanol</td>
<td>84.3\textsuperscript{b}</td>
<td>14</td>
<td>85</td>
<td>6</td>
</tr>
<tr>
<td>2-pentanol</td>
<td>67.9\textsuperscript{b}</td>
<td>88</td>
<td>84</td>
<td>6</td>
</tr>
<tr>
<td>3-pentanol</td>
<td>73.8\textsuperscript{c}</td>
<td>75</td>
<td>80</td>
<td>8</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Experimental conditions: 1 vol% 4-ME-ONE, 10 vol% alcohol, gas flow = 50 ml min\textsuperscript{-1} at 100 °C. \textsuperscript{b} From Pedley et al.\textsuperscript{17} \textsuperscript{c} From Cox.\textsuperscript{18} \textsuperscript{d} After 6 h on stream.

Figure 9.10  The activity of Ti-beta in the MPV reduction of 4-Me-ONE at 100 °C as a function of the reduction potential, $\Delta H_f^\circ$, of the alcohol used. A dotted line has been added as a guide for the eye.
9.3.4 Competitive sorption experiments

To investigate the differences in adsorption between the secondary alcohols used, competitive sorption experiments were performed. From the results, presented in Table 9.4, it can be seen clearly that the increased chain length of the higher alcohols causes an increased preference in adsorption over 2-propanol, which is in accordance with the hydrophobic character of zeolite titanium Beta already mentioned.

Table 9.4 Competitive adsorption characteristics of alcohol/2-propanol mixtures in Ti-beta.\(^a\)

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Volume fraction alcohol [ % ](^b)</th>
<th>Total adsorbed volume [ml/g(_{zeo})]</th>
<th>Adsorbed volume 2-propanol [ml/g(_{zeo})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-butanol</td>
<td>56</td>
<td>0.196</td>
<td>0.086</td>
</tr>
<tr>
<td>2-pentanol</td>
<td>61</td>
<td>0.209</td>
<td>0.082</td>
</tr>
<tr>
<td>2-heptanol</td>
<td>84</td>
<td>0.247</td>
<td>0.039</td>
</tr>
<tr>
<td>cyclopentanol</td>
<td>69</td>
<td>0.239</td>
<td>0.077</td>
</tr>
<tr>
<td>cyclohexanol</td>
<td>78</td>
<td>0.244</td>
<td>0.053</td>
</tr>
</tbody>
</table>

\(^a\) Experimental conditions: 50 µl 2-propanol, 50 µl of alcohol and 100 mg Ti-beta (=25 µl pore volume)\(^16\) in 10 ml 1,3,5-triisopropylbenzene at room temperature. \(^b\) Balance is 2-propanol.

In order to show that, especially in the case of the higher alcohols, competitive sorption with 4-methylcyclohexanone also starts to play a role, the sorption characteristics of the secondary alcohols were measured relative to 4-methylcyclohexanone. In a series of competitive sorption experiments, the molar ratio between alcohol and 4-Me-ONE was kept constant, \(i.e.\) 10:1, similar to the experimental conditions used in the gas-phase experiments.
From Table 9.5 it can be seen clearly that the higher alcohols are more strongly adsorbed. It should be noted that these are liquid-phase adsorption experiments at room temperature; they can therefore only be used as an indication of the sorption patterns under the catalytic gas-phase conditions. Nevertheless, if the conversion and selectivity of the related gas-phase experiments are plotted against the alcohol to 4-Me-ONE ratio determined in the liquid phase, it is observed that selectivity increases with an increasing internal alcohol concentration and that the conversion shows a maximum (Figure 9.11). In our view this further confirms that the high selectivity observed for the higher alcohols originates from the higher internal alcohol concentrations. The decrease in the observed conversions at high internal alcohol to 4-Me-ONE ratios, is probably due to a decreased 4-Me-ONE concentration in the zeolite.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Volume fraction alcohol [%]</th>
<th>Internal molar ratio alcohol : 4-Me-ONE</th>
<th>Total adsorbed volume [ml /g_{zeo}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-propanol</td>
<td>55</td>
<td>2.24</td>
<td>0.215</td>
</tr>
<tr>
<td>2-butanol</td>
<td>69</td>
<td>3.36</td>
<td>0.238</td>
</tr>
<tr>
<td>2-pentanol</td>
<td>74</td>
<td>4.34</td>
<td>0.248</td>
</tr>
<tr>
<td>2-heptanol</td>
<td>85</td>
<td>5.52</td>
<td>0.251</td>
</tr>
<tr>
<td>cyclopentanol</td>
<td>78</td>
<td>4.74</td>
<td>0.249</td>
</tr>
<tr>
<td>cyclohexanol</td>
<td>82</td>
<td>5.25</td>
<td>0.243</td>
</tr>
</tbody>
</table>

* Experimental conditions: 3.5 mmol alcohol, 0.35 mmol 4-methylcyclohexanone (50 µl) and 100 mg Ti-beta (≈25 µl pore volume) in 10 ml 1,3,5-trisopropylbenzene at room temperature. * Relative volume fraction of alcohol adsorbed, balance is 4-methylcyclohexanone.
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![Graph showing selectivity vs. Alcohol : 4-Me-ONE molar ratio in the zeolite](image)

**Figure 9.11** The conversion of 4-Me-ONE and the selectivity to *cis*-4-Me-OL in the gas-phase MPV reduction as a function of the internal alcohol to 4-Me-ONE ratio, determined by liquid-phase adsorption experiments (see Table 9.5). ■ = Conversion; ▲ = Selectivity to *cis*-4-Me-OL.

9.3.5 *Influence of temperature, water and ammonia*

In a further study of the factors influencing the selectivity, the effects of temperature and of the presence of water or ammonia on the selectivity to the *cis*-alcohol were investigated. The influence of the reaction temperature was determined by raising the reactor temperature continuously at a rate of 12 °C h⁻¹. It was observed that the selectivity to the *cis*-alcohol decreases at higher temperature (Figure 9.12). Initially the amount of *trans*-alcohol increases at the expense of the *cis*-alcohol, but at higher temperatures the dehydration to 4-methylcyclohexene becomes the major reaction. This is in accordance with the proposed reaction mechanism (Figure 9.9) in which the thermodynamically more favored *trans*-alcohol is formed reversibly and the alkene is formed irreversibly from the *cis*-alcohol in a consecutive reaction. At still higher temperatures (> 200 °C) the 4-methylcyclohexene is subsequently isomerized to the more stable 1-methylcyclohexene.
Figure 9.12  Temperature-programmed gas-phase MPV reduction of 4-Me-ONE with 2-propanol over Ti-beta-1. Temperature increment was 12 °C h⁻¹. ■ = conversion; ● = cis-4-Me-OL; x = trans-4-Me-OL; □ = 4-Me-ENE; + = 1-Me-ENE.

The commonly used MPVO homogeneous catalysts consist of metal alkoxides, which are easily hydrolyzed to inactive (hydr)oxides in the presence of water.¹ In the mechanisms proposed for the heterogeneously catalyzed reactions, initially formed surface alkoxide groups are also reported to be the active sites.¹⁰ Since these surface-alkoxide groups can also be hydrolyzed easily, the presence of water in the feed stream is usually avoided. As can be seen from Figure 9.13, the presence of water is not detrimental to the activity of Ti-beta in the gas-phase MPV reduction of 4-methylcyclohexanone. The temperature at which a ketone conversion of 50% is measured in the presence of water (2.7 vol %), viz. 112 °C, is nearly identical to the temperature required for 50% conversion in the absence of water (108 °C, Figure 9.12). This is in accordance with the high tolerance for water of Ti-beta, as reported for the liquid-phase reductions,⁸¹² which is ascribed to the hydrophobic interior of Ti-beta.
Figure 9.13 Temperature programmed MPVO reduction of 4-Me-ONE with 2-propanol over Ti-beta in the presence of 2.7 vol% water. Temperature increment was 0.2 °C/min. ■ = conversion; • = cis-4-Me-OL; x = trans-4-Me-OL; □ = 4-Me-ENE; ▲ = 1-Me-ENE.

Although water has almost no influence on the catalytic MPVO activity, the selectivity towards the cis-alcohol increased from 63 % to 87% at 85°C upon addition of water to the feed stream. This enhanced selectivity in the presence of water can be ascribed to either:

i) a kinetic suppression of an irreversible dehydration in a manner similar to the alcoholysis by alcohols, or

ii) to a change in the alcohol-alkene equilibrium due to the higher amount of water present.

In the case of a shift in equilibrium, it should be possible to hydrate and oxidize alkenes with ketones in the presence of water via alcohols formed in situ. In an attempt to oxidize cyclohexene with acetone in the presence of water, no conversion to cyclohexanol and cyclohexanone was observed between 85 and 400 °C. It is therefore concluded that under the experimental conditions used, 4-methylcyclohexene is formed irreversibly from the cis-alcohol. The increased selectivity towards alcohols should therefore be ascribed to a suppression of the
dehydration, most likely via hydrolysis of the surface Ti-cis-alkoxide complex as described for alcoholysis by 2-propanol (Figure 9.9).

For the liquid-phase reactions at 85 °C, we reported that small amounts of a strong base, e.g. pyridine, completely poisoned the catalyst.\textsuperscript{2} It can be seen from Figure 9.14 that in the presence of 2.66 vol% ammonia higher temperatures are required to reduce the 4-methyl-cyclohexanone. These higher temperatures are required for the desorption of ammonia from the catalytically active site. The relatively low temperature of 305 °C at which 50 % conversion is observed, suggests that the ammonia is not bonded to a strong acidic site. Since the strong Brønsted-acidic aluminum sites in zeolite beta desorb ammonia above 400 °C,\textsuperscript{19} this confirms that the MPVO reactions proceed via the titanium sites and not via any residual framework aluminum sites (Si:Al > 2500). This is consistent with the inactivity of the all-silica analogue of zeolite beta\textsuperscript{8} which has a Si:Al ratio similar to Ti-beta.\textsuperscript{16} In the presence of ammonia no isomerization of 4-Me-ENE to 1-Me-ENE occurred even not at a temperature of 400 °C, suggesting that this isomerization requires strong Brønsted acid-sites, most probably the residual aluminum sites (Si:Al > 2500). The aluminum originates from slight contaminations of the Si- and Ti-sources used in the preparation of Ti-beta.

![Temperature programmed MPVO reduction of 4-Me-ONE with 2-propanol over Ti-beta in the presence of 2.66 vol% ammonia. Temperature increment was 0.2 °C/min. ■ = conversion; ○ = cis-4-Me-OL; x = trans-4-Me-OL; □ = 4-Me-ENE; ▲ = 1-Me-ENE.](image)

Figure 9.14  Temperature programmed MPVO reduction of 4-Me-ONE with 2-propanol over Ti-beta in the presence of 2.66 vol% ammonia. Temperature increment was 0.2 °C/min. ■ = conversion; ○ = cis-4-Me-OL; x = trans-4-Me-OL; □ = 4-Me-ENE; ▲ = 1-Me-ENE.
9.3.6 Catalyst stability and regenerability

As was already shown in Figures 9.5a and 9.12, Ti-beta exhibits a low deactivation rate in the reduction of 4-methylcyclohexanone and a significantly higher deactivation rate in the oxidation of cis-4-methylcyclohexanol. In both cases, however, frequent regeneration of the catalyst will be necessary. Catalyst stability was therefore tested by regeneration at 480°C in air after each run. No significant loss in activity per gram of catalyst, selectivity or product distribution was observed, after 35 and 50 consecutive runs. Similar results were also obtained for the Ti-beta used in liquid-phase reductions; after regenerating the Ti-beta catalyst 5 times, the same initial catalytic activity per gram of catalyst was observed.

4. Conclusions

Ti-beta is found to be an excellent catalyst for MPVO reactions under gas-phase conditions. Remarkable differences exist between the liquid- and gas-phase reactions at otherwise similar temperatures. Under liquid-phase conditions, a very high selectivity in the reduction of 4-substituted cyclohexanones towards the commercially desired cis-alcohols was observed. In the gas phase, the selectivity to the cis-alcohol is significantly lower than under liquid-phase conditions, but still above the thermodynamically expected value. In addition dehydration of the alcohol product to the corresponding alkene is an important side-reaction for the gas-phase reaction, while no alkenes were observed in the liquid phase.

In a kinetic study, the parameters affecting activity and selectivity were investigated and a mechanistic model was derived. The selectivity to the desired cis-alcohol was found to be determined by the internal alcohol concentration in the zeolite. High partial pressures of 2-propanol in the feed stream or the use of more strongly adsorbing alcohols, e.g. cyclohexanol or 2-heptanol, were found to increase the selectivity towards the cis-alcohol significantly. This was explained by an increase in the rate of cis-alcohol removal from the catalytic site by accelerated alcoholysis, before consecutive reactions can take place. Consecutive reactions were also found to be suppressed by co-feeding water in the reactant
stream. The water probably enhances the selectivity by an increased hydrolysis rate of the cis-alkoxide intermediate in a manner similar to that described for alcoholysis.

The activity of the Ti-beta catalyst depends both on the adsorption characteristics and the reduction potential of the alcohol used. Although a high internal alcohol concentration is favorable for a high activity by regenerating the catalytic site via accelerated alcoholysis, too high an internal alcohol concentration tends to decrease the activity by reducing the amount of 4-methylcyclohexanone adsorbed. The activity was also found to correlate with the reduction potential of the alcohol reductant used. Alcohols with low reduction potentials, e.g. secondary alcohols, were found to be much more active than alcohols having high reduction potentials, e.g. primary alcohols.

Based on the observed relations, a catalytic pathway is proposed in which the ketone is first reduced to the corresponding cis-alcohol by an MPVO type mechanism, following which the cis-alkoxide intermediate can undergo either:

i) desorption from the titanium site via alcoholysis or hydrolysis,

ii) reversible isomerization to the trans-alcohol via an MPVO mechanism, or

iii) irreversible dehydration via an E2-elimination mechanism.

The potential of zeolite titanium beta in the gas-phase Meerwein-Ponndorf-Verley and Oppenauer reactions was shown by the high resistance to water and ammonia and the excellent stability as shown by multifold regeneration without loss of activity.
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References

Summary

Zeolites and molecular sieves are microporous materials with an increasing number of applications. Nowadays zeolites come to the fore as clean, selective and recyclable catalysts in petrochemistry, e.g. in aromatic alkylation. Although zeolites have found wide-spread application as catalysts in the production of bulk chemicals, especially in the petro-chemical industries, few examples exist for the production of fine-chemicals. In Chapter 1, the development of zeolite catalysts for fine chemicals is discussed. Based on the requirements of the organic reaction, some of the potential pitfalls in selecting and screening zeolites as potential catalysts are discussed.

The other Chapters (2-9) focus on zeolite titanium beta, with respect to the development of a synthesis procedure, its characterization and the catalytic application of this new large pore material.

Chapter 2 describes the synthesis and characterization of zeolite boron beta using dibenzylidimethylammonium as the template. Characterization using X-ray diffraction, unit-cell contraction, FT-IR spectroscopy, $^{11}$B, $^{13}$C and $^{29}$Si MAS NMR of the materials obtained showed that pure zeolite boron beta could be obtained with Si:B ratios between 15 and 40. The incorporation of boron in the zeolite lattice was confirmed by a single peak in the $^{11}$B MAS NMR at -23.2 ppm and a linear relation between the unit-cell volume and the boron content.

The influence of the synthesis temperature, the type of alkali metal, the boron- and template-to-silicon ratio on the crystal growth rate and nucleation time were investigated. Upon decreasing the sodium content of the gel, the crystal growth rate decreased and the nucleation time increased. However, on complete elimination of sodium from the gel, the crystal growth rate increased and the nucleation time decreased significantly. This strongly suggests the existence of at least two crystallization mechanisms. Furthermore, a sharp decrease in the crystal growth rate at a silicon-to-boron ratio slightly above stoichiometrical was observed. Based on our findings a crystal growth model consisting of three type of sites on the growing zeolite surface is proposed; two of which are structure-directing and one directing the growth of the zeolite walls.
Chapter 3 reports on the synthesis of all-silica zeolite beta. Based on the growth model for zeolite boron beta of Chapter 2, the synthesis conditions for the preparation of an all-silica zeolite beta can be predicted. The synthesis conditions required are a high template hydroxide-to-silicon ratio and the absence of alkali metal ions (less than 6 ppm), which is consistent with the growth model for zeolite boron beta. The all-silica zeolite beta is characterized by a high amount of defects as determined by FT-IR and $^{29}$Si MAS NMR and an increased hydrophobicity compared to zeolite aluminum beta.

Chapter 4 deals with the synthesis and characterization of the aluminum-free zeolite titanium beta (Ti-beta) by using a new template molecule, di(cyclohexylmethyl)-dimethylammonium. The influence of the synthesis conditions was investigated and showed that highly crystalline Ti-beta is only possible within a narrow chemical and temperature window.

The Ti-beta was characterized using XRD, TEM, SEM, EDP, EDAX, UV-Vis, nitrogen adsorption, SAXS and FT-IR. Catalytic experiments were performed to verify the contribution of the external surface to the epoxidation activity. Evidence for the isolated incorporation of fourfold-coordinated titanium in the zeolite framework was obtained by the presence of a single absorption band at 47,000 cm$^{-1}$ in the UV-Vis spectrum and a linear expansion of the unit-cell volume with the titanium content. From the linear expansion of the unit-cell volume an average $d_{\text{Ti-O}}$ bond length of 1.79 Å can be calculated, which corresponds well with the Ti-O bond lengths reported in literature for TS-1 and TS-2.

The morphology of the crystals is a pillow- or disk-shaped particle with an average diameter of 1.2 μm. Transmission Electron Microscopy (TEM) and electron diffraction (EDP) showed that these particles are single crystalline entities, though sometimes a thin amorphous layer was observed on the crystal surface. By using 3,5-di-tert-butylphenyl 1-(3-methyl-2-butenyl) ether as a selective probe molecule for the external surface titanium sites, it was shown that epoxidation takes place primarily at the titanium sites located in the micropores of the zeolite.

Chapter 5 discusses the catalytic potential of Ti-beta in the epoxidation of alkenes with aqueous hydrogen peroxide as the oxidant and acetonitrile as the solvent. The advantage of the large pore size of Ti-beta is demonstrated by the facile epoxidation of the bicyclic norbornene, in which reaction the medium pore zeolite TS-1 showed no activity. The catalytic
properties of Ti-beta are further investigated in the epoxidation of linear alkenes, bulky alkenes, such as cyclohexenes and cyclic terpenes, and electron deficient alkenes such as allylic alcohols.

In the epoxidation of methyl-substituted cyclohexenes the reactivity of methylenecyclohexane is twice that of 1-methylocyclohexene, which suggests that steric effects at the titanium site can play a dominant role in determining reactivity of substrates. That electronic effects also play an important role is shown by the epoxidation of allylic alcohols. For example, the epoxidation rate for 2-propen-1-ol (allyl alcohol) is two orders lower than that for 1-hexene. More highly substituted allylic alcohols are found to be more reactive, whereas the reactivity of substrates bearing a terminal double bond is over an order of magnitude lower.

Chapter 6 reports on the effects of solvent choice on the epoxidation rate of 1-octene with aqueous hydrogen peroxide over Ti-beta. Ti-beta exhibits Brønsted acidic properties when alcohols are employed as the solvent. This is explained by a Lewis acidic character of the titanium site in Ti-beta, which on coordination of an alcohol yields a weakly/mild Brønsted acid site. The use of the weakly basic acetonitrile as the solvent was found to suppress the acid catalyzed secondary reactions almost completely. When alcohol/acetonitrile mixtures are applied as the solvent, a clear maximum in activity was observed at compositions depending on the polarity. The increase in activity at low alcohol concentrations suggests the active participation of alcohol in the catalytic mechanism. The values for the maximum activities obtained in the 1-octene epoxidation are within the same range for all alcohols tested, suggesting that the solvent effects observed are mainly caused by differences in physisorption equilibria due to polarity of the alcohol. A similar behavior is observed for TS-1 in the 2-propanol/acetonitrile system, while Ti,Al-beta did not show a maximum in activity. Based on the observed relation between activity and solvent composition, a catalytic intermediate is proposed in which an alcohol and a hydroperoxy group are coordinated to a framework titanium atom.

Chapter 7 deals with the kinetics of 1-octene epoxidation. The influence of both physical and kinetic processes are investigated and compared with those obtained for Ti,Al-beta and TS-1. The substantial differences between the activation energies of 1-octene epoxidation over different titanium zeolites compared to that for the mesoporous Ti-MCM-41
material, suggests that internal diffusion limitations are present when applying the zeolite catalysts.

The observed rate of epoxidation as a function of the bulk concentration of 1-octene and of hydrogen peroxide, can equally well be fitted to the proposed kinetic models as to an alternative model assuming diffusion limitations. The observed maximum in activity when the bulk water concentration is varied, suggests that at least one water molecule is coordinated onto the titanium site in a catalytic intermediate species and that higher coordinated titanium sites are not catalytically active.

The kinetic data are interpreted in terms of mechanistic models proposed in literature and in terms of a new model. The observed effects are in agreement with models in which a lattice-connected Ti(H₂O)(H₂O₂) species is an important intermediate species, which is in line with the Ti(ROH)(H₂O₂) species proposed in literature. Our model for the epoxidation assumes that the formation of the catalytically active Ti(η²-O₂) species from the Ti(H₂O)(H₂O₂) is the rate determining step, rather than that the Ti(H₂O)(H₂O₂) species itself is the oxygenating species.

Chapter 8 reports on the use of Ti-beta as a new and shape-selective catalyst in liquid-phase Meerwein-Ponndorf-Verley-Oppenauer reactions. In the reduction of 4-tert-butyl- and 4-methylcyclohexanone selectivities of over 98% to the corresponding cis-alcohol were observed. The high stereoselectivity is explained by transition-state selectivity in analogy with zeolite aluminum beta. The observed enantiomeric excess of 34 % in the reduction of phenylacetone with (S)-2-butanol, indicates a transition state in which both the ketone and the alcohol reactant are coordinated simultaneously to the same titanium atom.

The Ti-beta catalyst shows a high tolerance towards water, but is completely poisoned by pyridine. When compared with an Al-beta catalyst, the Ti-beta shows less by-products during the Oppenauer oxidation, probably due to the absence of strong Brønsted acid sites.

Chapter 9 describes a kinetic study of Ti-beta as a catalyst for the gas-phase Meerwein-Ponndorf-Verley reduction of 4-methylcyclohexanone with various alcohols as the hydrogen donors and the Oppenauer oxidation of 4-methylcyclohexanol with acetone as the oxidant. The excellent catalytic properties of Ti-beta are shown by the high activity in the presence of water. No significant loss in selectivity and activity was observed after 35 regeneration steps at 480 °C in air and even the presence of N-bases, e.g. ammonia, is not
Summary

detrimental though higher reaction temperatures are required for conversion.

Large differences in selectivity between the gas- and the liquid-phase MPV-reduction were observed. Based on kinetic and adsorption experiments, it is concluded that the concentration of alcohol reductant in the zeolite is an important parameter in determining selectivity. More hydrophobic alcohols or higher alcohol partial pressures gave rise to an increased selectivity to the cis-alcohol product. From sorption experiments it is concluded that this is due to a higher internal concentration of the alcohol. The observed selectivities and activities are consistent with a mechanism in which the alcohol is not only the hydrogen donor but is also required to remove the cis-alcohol product formed from the catalytic site by alcoholysis, before consecutive reactions can occur.
Samenvatting

Zeolieten en moleculaire zeven zijn microporeuze materialen met een toenemend aantal industriële toepassingen en zijn in de aardolieraffinage niet meer weg te denken als katalysatoren en selectieve adsorbentia. Zeolieten worden steeds meer gebruikt als schone, selectieve en regenereerbare katalysatoren in de petrochemie, bijvoorbeeld in de alkylering van aromaten. Er zijn slechts weinig voorbeelden bekend van het gebruik in de synthese van fijnchemicaliën. In Hoofdstuk 1, wordt de ontwikkeling van zeolietkatalysatoren voor fijnchemicaliën besproken. Op basis van de gewenste organische reactie kan men enige voorwaarden formuleren teneinde mogelijke valkuilen in het screenen en selecteren van een potentiële zeolietkatalysator te omzeilen.

De andere Hoofdstukken (2-9) richten zich vooral op zeoliet titanium-beta, met name de ontwikkeling van een syntheseprocedure, de karakterisering van het materiaal en de katalytische toepassing van dit nieuwe materiaal.

Hoofdstuk 2 beschrijft de synthese en karakterisering van zeoliet borium-beta waarbij gebruik is gemaakt van dibenzylidimethylammonium als het templaat-molecuul. De karakterisering is gedaan met Röntgen-diffactie, eenheidscel-contractie, FT-IR spectroscoorie en $^{11}$B, $^{13}$C en $^{29}$Si MAS NMR. Goed gedefinieerde, zuivere zeoliet borium-beta kan verkregen worden met een silicium:borium verhoudingen tussen 15 en 40. De inbouw van borium in het rooster van de zeoliet werd bevestigd door de aanwezigheid van één enkele piek in het $^{11}$B MAS NMR bij -23.2 ppm en een lineaire relatie tussen het eenheidscel-volume en de hoeveelheid borium.

De invloed van de synthesetemperatuur, het type alkali-kation, de borium:silicium en templaatsilicium verhouding op de kristalgroeisnelheid en de nucleatietijd werden bestudeerd. Verlaging van de natrium:silicium verhouding in de synthesezegel blijkt de kristalgroeisnelheid af te laten nemen en de nucleatietijd toe te laten nemen. Echter in complete afwezigheid van natrium in de gel nam de kristalgroeisnelheid weer toe en de nucleatiesnelheid juist af. Dit wijst er sterk op dat er minimaal twee kristallisiatiemechanismen mogelijk zijn. Daarnaast
Samenvatting

blijkt dat voor een borium:silicium verhouding net boven de stoichiometrische verhouding, de kristalgroeiensnelheid een scherpe afname vertoont. Op basis van de gevonden relaties wordt een groeimodel voor zeoliet borium-beta voorgesteld uitgaande van drie type sites aan de groeiende zeolietwand; twee van deze sites bepalen wat de structuur van de zeoliet wordt terwijl de derde bepaalt hoe de zeolietwand groeit.

Hoofdstuk 3 behandelt de synthese van all-silica zeoliet beta. Op basis van het in hoofdstuk 2 kunnen de synthesecondities voor de bereiding van een all-silica zeoliet worden voorspeld. De gevonden condities zijn een hoge templaat-hydroxide:silicium verhouding en de afwezigheid van alkali-kationen (minder dan 6 ppm) in overeenstemming met het groeimodel voor zeoliet borium-beta. De all-silica zeoliet wordt gekenmerkt door een groot aantal defecten, bepaald met FT-IR en $^{29}$Si MAS NMR, en een toegenomen hydrofobiciteit in vergelijking met zeoliet aluminium-beta.

Hoofdstuk 4 beschrijft de synthese en karakterisering van aluminium-vrije zeoliet titanium-beta (Ti-beta) door gebruik te maken van een nieuw templaat-molecuul, di(cyclohexylmethyl)dimethylammonium. De invloed van de synthesecondities is bestudeerd en er is gevonden dat de synthese van hoogkristallijn Ti-beta alleen binnen een nauw chemisch en temperatuur-venster mogelijk is.

De Ti-beta is gekarakteriseerd met behulp van XRD, TEM, SEM, EDP, EDAX, UV-Vis, stikstofadsorptie, SAXS en FT-IR. Tevens zijn er katalytische experimenten gedaan om de bijdrage van het buitenoppervlak in de epoxidatie-activiteit vast te stellen. Bewijs voor de geïsoleerde inbouw van viervoudig-gecooordeerde titaniumatomen in het rooster van de zeoliet is verkregen door de aanwezigheid van een enkele absorptieband bij 47.000 cm$^{-1}$ in het UV-Vis spectrum en een lineaire expansie van het eenheidscelvolume met de titanium fractie. Uit de helling van de eenheidscelexpansie kan een gemiddelde d$_{Ti-O}$ bindingsafstand van 1.79 Å worden berekend, welke in overeenstemming is met de in de literatuur gevonden waarden voor TS-1 en TS-2.

De vorm van de kristallen is een kussenvormig deeltje met een gemiddelde diameter van 1.2 μm. Transmissie Electronen Microscopie (TEM) en Electronen-Diffractie (EDP) laten zien dat deze deeltjes bestaan uit een continue kristallijn fase, hoewel soms een dunne amorfe laag werd waargenomen aan het oppervlak van het kristal. Door gebruik te maken van 3,5-di-tert-butylphenyl-1-(3-methyl-2-butenyl)ether als selectieve, omvangrijke probe voor
katalytische titaniumcentra op het buitenoppervlak, kon worden vastgesteld dat de epoxidatie vrijwel volledig plaatsvindt in de microporiën van de zeoliet.

**Hoofdstuk 5** bespreekt de toepassing van Ti-beta in de epoxidatie van alkenen met waterig waterstofperoxide als oxidant en acetonitril als oplosmiddel. Het voordeel van de "large pore" zeolite Ti-beta (7.4 Å) blijkt uit bijv. de gemakkelijke epoxidatie van norborneen, terwijl de "medium pore" zeoliet TS-1 (5.4 Å) ten opzichte van deze bicyclische reactant geen activiteit vertoont. De katalytische eigenschappen van Ti-beta zijn verder bestudeerd in de epoxidatie van lineaire alkenen, ruimtelijk grote alkenen, zoals cyclohexenen en cyclische terpenen, en electron-deficiënte alkenen, zoals allylalcoholen.

In de epoxidatie van methyl-gesubstitueerde cyclohexenen is de reactiviteit van methyleencyclohexaan tweemaal zo groot als die van 1-methylcyclohexeen, hetgeen erop wijst dat sterische effecten op de titaniumcentra een dominante rol spelen. Dat electronische effecten ook een belangrijke rol spelen, is verder aangetoond bij de epoxidatie van allylalcoholen. Bijvoorbeeld, de orde grootte van de epoxidatiesnelheid voor 2-propen-1-ol (allylalcohol) is twee ordes lager dan die voor 1-hexeen. Hoger substitueerde allylalcoholen zijn reactiever, terwijl de reactiviteit van substraten met een eindstandige dubbele binding een orde lager is.

**Hoofdstuk 6** behandelt de effecten van oplosmiddelkeuze op de epoxidatiesnelheid van 1-octeen met waterig waterstofperoxide over Ti-beta. Ti-beta blijkt Brønsted-zure eigenschappen te bezitten als alcoholen worden toegepast als oplosmiddel. Dit wordt verklaard door het Lewis-zure karakter van de titanium-centra in Ti-beta, welke door coördinatie van een alcohol transformeren tot een mild Brønsted-zure site. Het gebruik van het zwak basische acetonitril als oplosmiddel onderdrukt de zuur-gekatalyseerde volgreacties vrijwel volledig. Als alcohol/acetonitril mengsels worden toegepast als oplosmiddel, wordt een maximum in de activiteit waargenomen bij een samenstelling welke afhangt van de polariteit van de alcohol. De toename in activiteit bij lage alcoholconcentraties suggereert de actieve deelname van een alcoholmoecuul in het katalytische mechanisme. De gevonden waarden voor de maximum activiteiten in de 1-octeen epoxidatie zijn hetzelfde voor alle geteste alcoholen, hetgeen erop wijst dat er geen sterische effecten zijn.

Vergelijkbaar gedrag is ook gevonden voor TS-1 in het 2-propanol/acetonitril systeem, terwijl Ti,Al-beta een minimum in activiteit laat zien. Op basis van de gevonden relatie tussen
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activiteit en de samenstelling van het oplosmiddel wordt een katalytisch intermediair voorgesteld waarin een alcohol en een hydroperoxogroep gelijktijdig aan een titaniumatoom bevestigd zijn.

**Hoofdstuk 7** bestudeert de kinetiek van de 1-octeen-epoxidatie. De invloed van zowel fysische als kinetische processen is onderzocht en vergeleken met die verkregen voor Ti,Al-beta en TS-1. De verschillen tussen de activeringsenergieën voor de 1-octeen-epoxidatie over verschillende titanium-zeoliën en die voor het mesoporeuze Ti-MCM-41 materiaal, wijzen op de aanwezigheid van interne diffusielimitering in de zeolietkatalysatoren.

De waargenomen reactiesnelheid als functie van de bulkconcentraties van 1-octeen en van waterstofperoxide, kan evengoed worden "gefit" aan de voorgestelde kinetische modellen als aan een alternatief model dat slechts diffusielimitering aannemt. Het maximum in de activiteit als de waterconcentratie wordt gevarieerd, duidt erop dat op zijn minst één watermolecuul gecooördineerd is aan het titanium-atoom in een intermediair deeltje en dat verdere hydratatie van de titanium-site tot niet-katalytisch-actieve centra leidt.

De kinetische gegevens zijn geïnterpreteerd met de epoxidatiemechanismen die zijn voorgesteld in de literatuur en met een nieuw model. De waargenomen effecten zijn in overeenstemming met modellen waarin een roostergebonden Ti(H$_2$O)(H$_2$O$_2$) deeltje een belangrijk intermediair is, hetgeen overeenkomt met het Ti(ROH)(H$_2$O$_2$) intermediair voorgesteld in de literatuur. Ons eigen model neemt echter aan dat de vorming van het katalytische actieve Ti(η$_2$-O$_2$) intermediair uit Ti(H$_2$O)(H$_2$O$_2$) de snelheidsbepalende stap is, in plaats van te veronderstellen dat de Ti(H$_2$O)(H$_2$O$_2$) zelf het epoxiderend deeltje is.

**Hoofdstuk 8** beschrijft het gebruik van Ti-beta als nieuwe en vormselectieve katalysator in vloeistoffase Meerwein-Ponndorf-Verley-Oppenauer reacties. In de reductie van 4-tert-butyl- en 4-methylcyclohexanon worden selectiviteiten van meer dan 98% naar de corresponderende *cis*-alcohol waargenomen. De hoge stereoselectiviteit wordt verklaard door transition-state selectiviteit naar analogie met zeoliet aluminium-beta. De waargenomen enantiomere inductie van 34 % e.e. in de reductie van fenylaceton met (S)-2-butanol, wijst op een transition state waarin zowel het keton als de alcohol gelijktijdig zijn gecoördineerd aan een titaniumatoom.

De Ti-beta katalysator heeft een hoge tolerantie voor water, maar wordt volledig vergiftigd door pyridine. In vergelijking met een Al-beta katalysator, vertoont Ti-beta minder

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bijproducten in de Oppenauer-oxidatie van alcoholen, hetgeen waarschijnlijk is toe te schrijven aan de afwezigheid van sterk zure Brønsted-plaatsen.

In **Hoofdstuk 9** wordt een kinetische studie beschreven van Ti-beta als katalysator voor de gasfase Meerwein-Ponndorf-Verley-reductie van 4-methylcyclohexanon met verschillende alcoholen als de waterstofdonor en de Oppenauer-oxidatie van 4-methylcyclohexanol met aceton als de oxidant. De excellentie katalytische eigenschappen van Ti-beta blijken uit de hoge activiteit in aanwezigheid van water. Geen significant verlies in selectiviteit en activiteit werd waargenomen na 35 regeneratie-cycli bij 480 °C aan de lucht en zelfs de aanwezigheid van N-basen, zoals ammonia, is niet schadelijk, hoewel een hogere reactietemperatuur noodzakelijk is.

Grote verschillen in de selectiviteit tussen de gas- en de vloeistoffasereductie zijn waargenomen. Op basis van kinetische en adsorptie-experimenten, is geconcludeerd dat de concentratie van de reducerende alcohol in de zeoliet een belangrijke parameter is die de selectiviteit bepaalt. Hydrofobere alcoholen of hogere alcohol-partiaaldrukken resulteren in een toename van de selectiviteit naar de cis-alcohol. Uit adsorptie-experimenten wordt geconcludeerd dat dit wordt veroorzaakt door een toegenomen interne concentratie van de alcohol in de zeoliet. De waargenomen selectiviteiten en activiteiten zijn in overeenstemming met een mechanisme waarin de alcohol niet alleen de waterstofdonor is maar ook noodzakelijk is om de cis-alcohol van het katalytische centrum te verwijderen via een alcoholyse, voordat volgreacties kunnen plaatsvinden.
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Publications and oral presentations

Publications:


- E.J. Creyghton, J. Huskens, J.C. van der Waal and H. van Bekkum, "Meerwein-Ponndorf-


**Oral Presentations:**

- J.C. van der Waal, M.S. Rigutto and H. van Bekkum, "Solvent effects in the epoxidation of 1-octene over Ti-beta", SON Katalyse, Lunteren, the Netherlands, januari 1996.


- J.C. van der Waal, "Zeolites in Catalysis", series of invited lectures at the Tianjin Institute of Chemical Industry, Tianjin, China, july 1997.

Curriculum Vitae


Op 1 mei 1993 ving het promotie-onderzoek aan bij het Laboratorium voor Organische Chemie en Katalyse van de Technische Universiteit Delft onder begeleiding van Prof.dr.ir. H. van Bekkum op de synthese, karakterisering en toepassing van zeoliet titanium-beta. De resultaten van dit onderzoek zijn beschreven in dit proefschrift.

De auteur zal vanaf mei 1998 werkzaam zijn als postdoc in de groep van Chris John en Ian Maxwell van het Shell Research and Technology Centre in Amsterdam.