Modification and Catalytic Application of Zeolite Beta

Paul Kunkeler
cover: It is science, but not as we know it
Modification and Catalytic Application
of
Zeolite Beta

Proefschrift

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Tampert.
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1. INTRODUCTION

1.1 Objectives and justification

In the production of fine chemicals, Brønsted acids like hydrochloric and sulfuric acid, and Lewis acids like AlCl₃, are widely employed as catalysts [1]. Unfortunately, these catalysts have several serious drawbacks which originate from their aggressive nature and the necessity to neutralise the acids which in turn results in the production of inorganic waste that needs to be discarded. Furthermore, classical acid-catalysed reactions often give rise to undesired by-products. In view of the growing awareness for the environmental impact of chemical processes and the resulting legislation, reduction of waste streams is needed. Therefore, the development of new catalytic processes employing selective heterogeneous catalysts for the production of fine chemicals is desired.

The Dutch Institute for Catalysis Research (NIOK) subsidises the catalysis research efforts conducted at national universities and gives impetus to the development of more environmentally benign and more efficient chemical production processes. The research projects subsidised by NIOK are specifically aimed at meeting the present needs of industry; an advisory board in which major chemical companies participate selects the research frameworks. NIOK, therefore, encourages a greater collaboration between the academic world and industry.

The research described in this thesis was conducted with NIOK sponsorship and formed part of a joint investigation into heterogeneously catalysed routes to amines at the Universities of Twente (aliphatic amines) and Delft (aromatic amines). Initially, zeolites were expected to be the catalysts of choice. It rapidly became clear, however, that the synthesis of aromatic amines was in several cases unsuited to catalysis by zeolites, owing to the fact that many of the reactions proceed via intermediates of the imine type, which under reaction conditions oligomerise leading to fouling and deactivation of the catalysts. Investigations into the reasons for this led to a broadening of the scope of the research. A particular focus was on the synthesis, modification and characterisation of zeolite Beta, a zeolite with potential as selective catalyst. The Beta materials were tested in selected reactions, both in the liquid and the gas-phase. The design and building of specific equipment to perform the modifications and catalytic testing constituted an important part of the research efforts.
1.2 Catalysis

Fine chemicals, besides being produced in far smaller amounts than bulk chemicals, often contain more than one functional group, which makes them more susceptible towards high temperatures and consecutive reactions. This has important consequences for the choice of the catalyst and the reaction conditions to be employed. Low reaction temperatures and working under liquid-phase conditions are usually necessary for the more complex molecules. Selectivity becomes important as well; we can distinguish chemo-, regio- and stereoselectivity:

*chemoselectivity* is the selective conversion of one functional group in the presence of other different functional groups within the same molecule, *regioselectivity* is defined as the selective conversion of a functional group in the presence of other groups of the same type, and *stereoselectivity* indicates the production of one stereoisomer in excess over another.

The latter type of selectivity can be subdivided into *cis/trans, diastereo-* and *enantioselectivity*. Especially enantioselectivity is of increasing importance in the pharmaceutical industry.

It is important to note that the conversion and the selectivity of a chemical reaction are determined to a large extent by the properties of the reactants themselves and the conditions under which the reaction takes place i.e. thermodynamic considerations should be taken into account. The effect of a catalyst compared to the thermally induced reaction, should be thoroughly investigated before any statement is made about alteration of the selectivity due to the catalyst alone. For example, if a catalyst permits the use of lower reaction temperatures, then the thermodynamics of the system change accordingly and the lower reaction temperature itself may alter the product distribution.

In the past, solid acids have not gained much attention for use as catalysts in fine chemicals production due to the lack of selectivity and activity. In contrast, solid acid catalysts like silica-alumina's and zeolites play an important role in the oil refineries and in petrochemical industry e.g. in catalytic cracking of oil fractions (FCC) in hydroisomerisation (TIP process). Solid acids have many advantages over classical acid catalysts: they are more safe and easier to handle, less corrosive and can be easily separated from the reaction mixture by filtration or used in fixed-bed continuous-flow reactors. Equally important, many solid acids can be easily regenerated and reused. These latter characteristics make them in principle ideally suited to reduce the waste streams generated by classical processes, provided the question of selectivity and
activity can be solved. Among the solid acids the zeolites constitute an important group with high potential as selective acid catalysts [2-8].

1.3 Zeolites

Zeolites are crystalline aluminosilicates with precisely defined, uniform micropore structures [9]. The presence of channels and/or cages within the zeolite is an intrinsic feature of the structure and finds its origin in the specific organisation of the building blocks. Formally, the framework consists of SiO$_4^-$ and AlO$_4^-$tetrahedra linked to each other via the shared oxygen atoms at the corners of the tetrahedra. The connection of two AlO$_4$-tetrahedra is not encountered (Löwenstein rule) which imposes a maximum molar Si/Al ratio of $\geq 1$. Effectively, the zeolite consists of SiO$_2$ and AlO$_2^-$ and the negative charge of the latter is compensated for by a cation. This cation can be readily exchanged for other cations using aqueous solutions; thus, zeolites can be applied as ion-exchangers, the ion-exchange capacity depending upon the amount of aluminium present. Upon thermal decomposition of ammonium-exchanged zeolites, the Bronsted acidic form is obtained. Direct proton exchange using mineral acids is usually not employed in order to prevent degradation of the zeolite framework by hydrolysis.

Although sensitive to the combination of water and acid and/or water and high temperatures (steam), zeolites are relatively inert to many chemicals and are thermally and mechanically stable. Spent zeolite-based catalysts, being fouled by organic deposits, can therefore easily be regenerated by an air burn-off at sufficiently high temperatures e.g. $>500\, ^\circ$C.

The zeolite pore apertures are in the size range of approximately 3 to 9 Å, while internally larger cages (up to approx. 12 Å for FAU and even 18 Å for MWW see Table 1) can be present, depending on the type of zeolite. These pore sizes enable zeolites to discriminate between molecules on size basis; in other words, zeolites display molecular sieving characteristics and therefore belong to the type of solids known as molecular sieves. According to the pore access, the zeolites are classified as small pore, medium pore and large pore zeolites, containing 8-, 10- and 12-membered oxygen ring apertures, respectively. Recently, also two 14-membered oxygen ring zeolites were discovered. The pore system can be uni-dimensional, with parallel channels or two or three-dimensional, with interconnected channels and/or cages [9]. In Table 1 some characteristics of the pore structure of various zeolites are presented.
Table 1. Properties of selected zeolites with potential as catalyst. Data from reference [10] and [11].

<table>
<thead>
<tr>
<th>Zeolite (code)</th>
<th>Pore dimens.</th>
<th>Ring aperture (nr. of O-atoms)</th>
<th>Access diameter (Å)</th>
<th>Crossing or cage diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5 (MFI)</td>
<td>3</td>
<td>10-10</td>
<td>$5.3 \times 5.6$</td>
<td>7.8</td>
</tr>
<tr>
<td>Mordenite (MOR)</td>
<td>1 (2)**</td>
<td>12-8</td>
<td>$6.5 \times 7.0$</td>
<td>-</td>
</tr>
<tr>
<td>Beta (BEA)</td>
<td>3b</td>
<td>12-12</td>
<td>$7.6 \times 6.4$</td>
<td>12.5</td>
</tr>
<tr>
<td>L (LTL)</td>
<td>1</td>
<td>12</td>
<td>7.1</td>
<td>-</td>
</tr>
<tr>
<td>Faujasite (FAU)**</td>
<td>3</td>
<td>12</td>
<td>7.4</td>
<td>12.8</td>
</tr>
<tr>
<td>MCM-22 (MWW)</td>
<td>2</td>
<td>10-10</td>
<td>$5.5 \times 4.0$</td>
<td>$7.1 \times 7.1 \times 18.2$</td>
</tr>
</tbody>
</table>

a) Zeolite Mordenite contains ‘side-pockets’ branching from the main channels.
b) The perpendicular channels in zeolite Beta are interconnected and these connections constitute the third pore dimension ($5.5 \times 5.5$ Å).
c) Zeolite Faujasite is subdivided into zeolite X (Si/Al=1-1.5) and Y (Si/Al ≥ 2.5).

Due to the internal pore system and the fact that each tetrahedrally coordinated silicon and aluminium atom (T-atom) is exposed to the pore system, zeolites have large specific surface areas. Depending on the type of zeolite, values of approx. 700 m²/g are common of which the contribution of the internal surface is the most significant. However, as will be explained, the contribution of the external surface cannot be ignored.

1.4 Zeolites as (acid)catalysts

The combination of the Si/Al ratio and the pore structure of a particular zeolite determines a number of properties important for its initial selection as a potential (acid) catalyst. Primarily dependent on the Si/Al ratio are the hydrophilicity/hydrophobicity balance, the number and strength of the acid sites, and the thermal stability; the last, together with hydrophobicity and acid-site strength, in general increase with Si/Al ratio.

**Determination of the acid strength and the acid-site density**

For application as acid catalysts, quantitative determination of the acidity would be desirable. There have been many attempts to determine the acid strength of the (bridging) hydroxyl groups and also their number [3,12-14]. The adsorption strength of various basic molecules, such as ammonia, is measured by techniques including temperature programmed desorption (TPD) and thermogravimetric analysis (TGA) and also infrared spectroscopy [12]. The latter technique is able – through pyridine
adsorption – to distinguish between Lewis and Brønsted sites. For TPD, difficulties arise due to the interference of diffusion phenomena with the chemical desorption process, which have important consequences. One of them is the difficulty to make a distinction between physically and chemically adsorbed ammonia, since ammonia desorbs over a broad temperature range owing to its adsorption being both physical (van der Waals and by H-bonding) and chemical (in protonated form), as was explained by Farneth et al. [15] for H-ZSM-5 samples. Also, the temperature at which the desorption curve passes through a maximum depends very much on the experimental conditions, thereby making a distinction between physically and chemically adsorbed ammonia even more difficult. Additionally, the ammonia base adsorbs on Lewis sites as well, making it difficult to titrate only the Brønsted acid sites using NH$_3$-TPD. Deconvolution of the NH$_3$-TPD curve can sometimes be applied [16].

To overcome these problems, isopropylamine has been used as a base with a double function. According to Farneth et al. [15], application of isopropylamine TPD/TPR has several advantages: amine molecules in excess of one amine/Al desorb unreacted at lower temperatures, leaving a stoichiometric adsorption complex following which the thermolysis products propene and ammonia desorb at a higher, well defined temperature that depends much less on the experimental conditions. Another advantage of the use of isopropylamine as a probe for heterogeneous acid-site densities is that the temperature-programmed decomposition occurs only at Brønsted sites, not at Lewis sites [17]. By measuring the amount of propene and ammonia evolved, the quantity of acid sites in the (weighed) sample can be determined. This, however, has only been shown for a specific H-ZSM-5 sample (Si/Al=80). A crucial point is, again, the reliability of the assumption that, at a certain point, a stoichiometric adsorption complex between base and acid is established, with a much higher activation energy for dissociation than the activation energy required for desorption of the physically adsorbed base molecules. This gap between the activation energies is necessary to obtain the required distinction between chemically and physically adsorbed molecules. As was shown by Drago et al. [18] this energy gap is small due to the fact that intraporous diffusion is an activated process with activation energies approaching the energies for desorption. Thus, a clear distinction between chemically and physically adsorbed molecules is difficult to detect using TPD, which renders the determination of the number of acid sites doubtful. The interference of diffusion phenomena with desorption also negatively influences the determination of the acid-strength.
Curiously, although many researchers have attempted to obtain an acidity scale [19,20], the actual predictive value for catalysis is limited. Firstly, most techniques for measuring the acidity are performed under conditions not present during a catalytic reaction. Secondly, the zeolite acts as a ‘solid solvent’ which affects each adsorbed molecule in a different way [5]. The simple fact that an adsorbed molecule may be under strain will already influence its susceptibility towards reaction. Since each different molecule will experience a different stress (within the same type of zeolite) and therefore displays a different reactivity, a satisfactory ‘molecule insensitive’ acidity scale cannot be obtained.

In conclusion, to test whether a certain classical acid-catalysed reaction can be catalysed by a certain zeolite, one has to bear in mind the parameters mentioned before and finally the actual experiment should be performed since a reliable acidity scale is not available. The outcome can be surprising since in some cases zeolites are able to catalyse a reaction normally only accessible using super-acid media [21-23].

Shape selectivity

The unique feature possessed by zeolites is their pore structure, which gives rise to the possibility of shape-selective catalysis: the confinement of the pores may exert a spatial influence on reactants, products and the transition state in between, as depicted in Figure 1, in which three types of selectivity are symbolised.
Figure 1. The three possible shape-selectivities for a zeolite catalysed reaction.
Chapter 1

Reactant selectivity is based on the molecular sieving properties of the zeolite, larger molecules being excluded from access to the pore system. Since, however, neither the zeolite framework nor the organic molecules are rigid, molecules with kinetic diameters somewhat larger (~10%) than the crystallographically determined pore-size of the zeolite can be admitted, sometimes accompanied by a crystallographic phase-transition of the zeolite [24-26]. When employing relatively pure starting materials, such as in laboratory research, this type of selectivity is usually not of concern but can be valuable in industrial processes where reactant mixtures are employed.

Transition state selectivity can occur when in parallel reactions the transition states (TS) leading to different products differ in volume. The reaction path with the more space demanding transition state is then retarded or even inhibited when the required space for the TS is not available (dashed line in Figure 1). This type of selectivity is also known as restricted TS selectivity [27]. A more subtle form of TS selectivity is the preferential stabilisation of one TS over another, for example due to a specific interaction between the reacting molecule and the pore-wall [28]. TS selectivity results in kinetically determined product distributions. TS selectivity also applies to consecutive reactions.

Product selectivity is a diffusion based selectivity and can be valuable in case of an equilibrium reaction; then, the pore system acts as a micro-reactor with a selective leak for the smaller molecules thus pulling the reaction to completion [29-31]. This may lead to non-thermodynamically determined product selectivities. 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. Pore-mouth narrowing techniques (see below) can be used to increase the selectivity towards the smallest molecule. This is e.g. applied in the industrial preparation of mono- and dimethylamine from ammonia and methanol. Trimethylamine is too bulky to escape from the pore interior and re-enters the equilibrium. In the case of irreversible reactions, products formed which are too large to escape remain trapped in the cages or channel crossings and may be converted to coke, leading to deactivation by pore plugging.

In the case of TS selectivity, the product selectivities are independent of the internal diffusion of the products and therefore are independent of the zeolite crystal size. This allows the use of very small crystals, which display more favourable internal mass transport phenomena than larger crystals.

It should be emphasised that the above mentioned shape-selectivities are only possible if the catalysed reaction is indeed taking place within the zeolite pore-system. If the zeolite contains sites active for the reaction under study both at the internal- and external surface, then the catalysed reaction may take place predominantly at the external surface, where no internal diffusions nor spatial limitations exist i.e. no
possibilities for shape-selectivity. Several researchers have addressed this problem and various methods have been developed to quantify the contribution of the external surface; below, an overview is given on this important subject.

As mentioned, the hydrophobicity / hydrophilicity of the zeolite is also a parameter of interest in the selection of a zeolite as a catalyst since it, too, determines the adsorption characteristics of the material. To allow a sufficient filling of the zeolite pores with reactants, the zeolite framework should have a polarity similar to that of the substrates i.e. low Si/Al zeolites for the more polar substrates and high Si/Al zeolites for the more apolar substrates. In the case of two substrates with different polarities this may cause a difficulty; the zeolite will adsorb one of the reactants preferentially thereby retarding the reaction [21,32]. There are several options to overcome this problem: when the 'polarity mismatch' is not too large, a solution may be to apply an excess of the less strongly adsorbing substrate, since the intra-porous substrate concentration depends on the external concentration. In case of liquid-phase reactions, slow addition of the more strongly adsorbing substrate to the reaction mixture containing the less strongly adsorbing substrate is also a possible solution [21].

For reactions conducted in the liquid-phase the solvent may add an additional requirement; when the solvent (usually present in excess) is adsorbed preferentially, the internal substrate concentration may become so low that the reaction is severely retarded [33]. However, actually, preferential adsorption of the solvent can sometimes be used to reduce polymerisation reactions of the reactants and to reduce undesired consecutive reactions of products formed, since the solvent reduces the internal concentration of both reactants and products [33].

Not only the substrates, but also the resulting products will usually be adsorbed to different extents. Ideally, the products should be adsorbed less strongly than the substrates; this will favour a continuous flow of reactants in and products out [34]. If, however, the products are adsorbed more strongly, the zeolite may become saturated with products and eventually deactivates.

The most fundamental solution to the adsorption-related difficulties is the selection of a zeolite with a specific Si/Al ratio such that its polarity is between those of substrate and product. This option, however, is not often possible since few zeolite families permit the variation of the Si/Al ratio over a wide range. Post-synthesis treatments to modify the external surface may, in certain cases, offer a solution, as discussed below [9,35].
1.5 Role and modification of the external surface

Characterisation methods employing bulky probe molecules

In order to make use of the valuable property of shape selectivity, it is essential that the reaction takes place predominantly within the internal pore structure of the zeolite and not at its external surface. Some zeolites, notably Beta [36], are known to have extensive and reactive external surfaces which can contribute substantially to the overall reaction. For the unambiguous characterisation of a zeolite-catalysed reaction it is necessary to be able to quantify the contributions of the internal and external surfaces. This can be achieved by employing probe molecules in the form of model substrates with dimensions too large to penetrate the pores; in this case any observed reaction can only be the result of external-surface activity. Care needs to be taken with the selection of a suitable probe molecule; the pore diameter does not represent a suitable threshold molecular diameter, since molecules 20% larger than this diameter are easily admitted. The rate of the reaction catalysed by the external surface can be determined to provide a measure of its reactivity [37], or the surface-probe interaction can be studied by spectroscopic methods such as IR [12,38], UV-vis [39], TGA [40] and TPD [41]. From a catalytic point of view, the first method gives more direct information on the catalytic contribution of the external surface to the total catalytic activity and is therefore preferred. An overview of the various catalytic test methods is given below, each with its own characteristics. Most papers referred to deal with coating of the zeolites’ exterior and the subsequent characterisation of the external surface activity.

For the study, in the petroleum refining industry, of acid-catalysed cracking reactions at high temperatures (270-450 °C) under continuous-flow gas-phase conditions, 1,3,5-tri-tert-butyl- and 1,3,5-tri-isopropylbenzene (TTBB and TIPB, respectively, see Figure 2) were used as probe molecules [42-46]. Both are much larger (11.0 × 11.0 × 6.3 Å for TTBB and 9.2 × 9.2 × 5.0 Å for TIPB, CPK models) than the pore-mouth of 12-ring aperture zeolites and can therefore (at first sight) be used to study the external surface activity of the zeolites Faujasite, Mordenite and Beta. Given the high temperature and the results obtained in ref. [26] doubt should be expressed to the assumed non-accessibility of the zeolite pores for these molecules.
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Figure 2. 1,3,5-tri-tert-butylbenzene (TTBB) and 1,3,5-tri-isopropylbenzene (TIPB).

To test the external activity of medium pore zeolites, especially ZSM-5, comparable molecules such as 1,3-di-isopropylbenzene (cracking at 400 °C) [47] and 1,2,4-trimethylbenzene (isomerisation to 1,3,5-trimethylbenzene at 450 °C) [46] were also applied.

Interpretation of the results is complicated by the use of high temperatures, which often result in fast deactivation due to coke formation. Therefore, only the initial reaction rate can be used in the activity determination. However, an extremely active zeolite catalyst may deactivate so rapidly that the initially determined activity is much lower than the actual initial activity; accidently, it may be concluded that the catalyst is less externally active than other zeolite samples tested. Determination of the amount of coke deposited is then necessary, e.g. by Thermal Gravimetric Analysis (TGA). Other disadvantages are the less well defined reaction paths and the possibilities for consecutive reactions.

More sensitive probe molecules which allow the use of lower temperatures have also been employed. An example is the acid catalysed dehydration of cyclohexanol into cyclohexene performed under continuous-flow gas-phase conditions at 120 °C and atmospheric pressure [48], see Figure 3. Unfortunately, the researchers used it for determining the external surface contribution of Mordenite with pore apertures large enough to allow adsorption of the molecule. Thus, the probe molecule is not specific enough for an accurate measurement.

Figure 3. Dehydration of cyclohexanol to cyclohexene.
Chapter 1

For the determination of the external activity of ZSM-5 and ZSM-5 layers on supports (composite materials) the dehydration of 3,3-dimethyl-2-butanol as probe molecule was developed by van der Puil [49], see Figure 4. This reaction can take place on mild Brensted or Lewis acid sites, while cracking of the molecule was only observed for the strong Brønsted acidic catalysts. Thus, the product distributions gave additional information on the composite materials prepared. Reactions were carried out in a batch-wise gas-phase micro-reactor at 175 °C under atmospheric pressure.

\[
\begin{align*}
\text{3,3-dimethyl-2-butanol} & \xrightarrow{\text{H}_2\text{O}} \text{3,3-dimethyl-1-butene} + \text{2,3-dimethyl-2-butene} \\
\end{align*}
\]

**Figure 4.** Dehydration of 3,3-dimethyl-2-butanol into 3,3-dimethyl-1-butene and consecutive isomerisation into 2,3-dimethylbutenes.

Additionally, the isomerisation of 2,4,4-trimethyl-1-pentene (Figure 5) was used to verify the results obtained with the dehydration reaction of 3,3-dimethyl-2-butanol and the cracking of 1-heptene [49]. Here, also, cracking was only observed in the presence of strong acid sites.

\[
\begin{align*}
\text{2,4,4-trimethyl-1-pentene} & \xrightarrow{\text{mild acid sites}} \text{2,4,4-trimethyl-2-pentene} \\
\text{2,4,4-trimethyl-1-pentene} & \xrightarrow{\text{strong acid sites}} \text{Cracking} \\
\end{align*}
\]

**Figure 5.** Isomerisation of 2,4,4-trimethyl-1-pentene.

In order to be able to study the external activity of 12-ring aperture zeolites under the mild conditions employed in fine-chemical synthesis, Creighton et al. [37] developed a bulky molecule which is capable of acting as probe for both Brønsted acid (Claisen rearrangement: isomerisation) and double bond hydrogenation sites (Pt dispersed on the zeolites' exterior), see Figure 6. The isomerisation reaction is conducted under liquid-phase conditions at a temperature of 80 °C using benzene as the
Solvent. An advantage is the use of standard, inexpensive equipment and the absence of uncontrolled side-reactions leading to deactivation. The probe molecule is not commercially available but its synthesis has been published [37].

**Figure 6.** Allyl 3,5-di-tert-butylphenyl ether; Claisen rearrangement and hydrogenation.

From this basic system a number of valuable probe molecules can be generated. A closely related probe molecule was developed by Creighton et al. to test the external Lewis acidity of zeolites by performing a Meerwein-Ponndorf-Verley (MPV) reduction with the molecule depicted in Figure 7 [27].

**Figure 7.** Reduction of 1-(3,5-di-tert-butylphenoxy)propan-2-one into 1-(3,5-di-tert-butylphenoxy)propan-2-ol using 2-propanol as the reductant.
2-Propanol is used as reductant and as solvent. Most important observation was the incapability of zeolite Beta to catalyse the MPV reduction of this bulky molecule while smaller ketones were reduced under identical conditions.

Two other test reactions used to study the external surface activity, but which do not rely on a bulky probe molecule, are mentioned here also: first the acylation of 2-methoxynaphthalene with acetic anhydride [36] and second the isopropylation of naphthalene [48,50,51]. These reactions are of commercial importance and are not based on a specific molecule probing the external surface but rather on the selectivity of the reaction to the smallest or most linear product (= the most desirable product) originating from an intraporous occurring reaction. Actually, many reactions can be chosen since catalysing an industrially relevant reaction in a shape-selective way is the ultimate goal.

In Figure 8 the acylation of 2-methoxynaphthalene using acetic anhydride is shown. It was applied to test the external activity of zeolite Beta based on the assumption that the selectivity towards the more linear product 2-acetyl-6-methoxynaphthalene would increase when the zeolite Beta was pretreated in such a way as to reduce the external activity. The external surface was expected to catalyse this reaction in a non-shape-selective manner and the reaction products should initially be present in the kinetically determined ratio, i.e. an excess of the 1-acetyl-2-methoxynaphthalene product, and finally in the thermodynamically determined ratio i.e. an excess of the 6-acetyl-2-methoxynaphthalene product (the most stable isomer). The researchers stated that only the 6-acetyl-2-methoxynaphthalene product could escape from the zeolite Beta pore system and that the 1-acetyl-2-methoxynaphthalene product (the kinetic isomer), once formed inside the pore system, would be converted into the other isomer [36]. However, no correlation whatsoever was found between the pretreatment of the external surface of zeolite Beta and the observed selectivity. A possible explanation may be the influence of the calcination procedure on the presence of Lewis acidic aluminium atoms in zeolite Beta [52]: classically, the reaction is catalysed using Lewis acids like AlCl₃. Also the assumptions made with respect to the sorption behaviour of the zeolite and the reaction products, which were based on consideration of the pore dimensions only (see above), are probably not sufficient to predict with any accuracy the zeolite catalysed reaction path. Furthermore, the acetic acid formed as by-product will adsorb strongly on the catalyst thus inhibiting the reaction. Therefore, this reaction is not very valuable to study the influence of various pretreatments on the external activity of zeolite Beta.
Figure 8. Acylation of 2-methoxynaphthalene using zeolite Beta as the catalyst, acetic anhydride as the acylation agent and chlorobenzene as the solvent under reflux conditions.

The isopropylation of naphthalene using propene in an autoclave (Figure 9) is based on the same principle as the acylation of 2-methoxynaphthalene. Reduction of external activity should in principle lead to a preferential production of the linear product 2,6-diisopropynaphthalene (2,6-DIPN) [48,50,51].

Figure 9. Isopropylation of naphthalene with propene.
Chapter 1

Post-synthesis treatments

A method of eliminating the contribution of the external surface is to render it inactive by a passivation treatment. Partial surface passivation can also be employed in order to fine-tune a chosen catalyst system by, for example, reducing the pore-entrance diameter. A number of options are available, depending on the effect desired. It should be noted, however, that each post-synthesis treatment influences several parameters and, therefore, the resulting new material should be carefully examined to investigate if it still meets the criteria for the reaction to be catalysed. In Table 2 an overview is given of various post-synthesis treatments and the way they affect the zeolite properties.

Silica-coating by Chemical Vapour Deposition (CVD) or Chemical Liquid Deposition (CLD) is often employed to reduce both the pore-mouth opening and the amount of acid sites at the external surface. A comprehensive overview is given by Vansant [35]. Also the group of Niwa has been very active in the field of silica-coating of zeolites [53]. Possible precursors for a silica-coating are tetra(m)ethyl-orthosilicate (TMOS or TEOS) and SiCl₄, but many more silicon compounds can be used. The coated material can be used as such or the material can be calcined, after which the silicon oxide form is obtained. To a lesser extent other oxide coatings, e.g. germanium oxides, are used as well [4754-56].

Sometimes the zeolite can be overgrown by an all-silica analogue of the zeolite resulting in a hydrophobic and more inert external surface [41,57]. The specific pore structure will then be maintained.

Extraction of aluminium from the zeolite framework can be performed by using aqueous solutions of nitric and/or hydrochloric acid at room temperature or at elevated temperatures. The use of chelating compounds such as EDTA [58] and oxalic acid [42] has also been reported. Selective removal of the outer framework aluminium atoms ideally results in a zeolitic material that does not display any external activity together with full retention of the properties of the micropores. In contrast, overall dealumination alters the properties significantly, but can be valuable in catalyst preparation as was shown recently for Mordenite by Dow Chemical in a series of patents [59-63]. It was claimed by the researchers that the parent uni-dimensional Mordenite was 'opened up' by the acid treatments resulting in a so-called 3-Dimensional Dealuminated Mordenite (3-DDM). It should be noted that the procedure described by the Dow researchers is complex and parameters like the nature of the initial material, the temperature at which dealumination is performed and the calcination steps in between the various dealumination steps are likely to affect the final state of the Mordenite based catalyst.
**Introduction**

**Table 2.** Various post-synthesis modification methods, the effect on the zeolite itself and the resulting change in catalytic properties. (for references, see text)

<table>
<thead>
<tr>
<th>Modification method</th>
<th>Effect on zeolite material</th>
<th>Effect on catalytic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>external coating of zeolite crystals</td>
<td>• micropores not affected</td>
<td>• decrease / inhibition non-shape-selective reactions: higher selectivity</td>
</tr>
<tr>
<td></td>
<td>• pore-mouth narrowing</td>
<td>• increased diffusion barrier: lower reaction rate and possibly higher selectivity</td>
</tr>
<tr>
<td></td>
<td>• covering external sites</td>
<td></td>
</tr>
<tr>
<td>treatment of template-occluded zeolite with mild acidic solutions / chelating agents</td>
<td>• external dealumination: decrease of external acid sites</td>
<td>• decrease / inhibition non-shape-selective reactions: higher selectivity</td>
</tr>
<tr>
<td></td>
<td>• micropores not affected</td>
<td></td>
</tr>
<tr>
<td>treatment of template-free zeolite with strong mineral acid solutions</td>
<td>• bulk dealumination: overall higher Si/Al ratio</td>
<td>• preferential sorption more apolar molecules</td>
</tr>
<tr>
<td></td>
<td>• increased hydrophobicity</td>
<td>• less active sites: lower reaction rate</td>
</tr>
<tr>
<td></td>
<td>• decrease of active sites</td>
<td>• better access to micropores: higher reaction rate</td>
</tr>
<tr>
<td></td>
<td>• increased acid strength</td>
<td>• higher acid strength: higher reaction rate, possibly increase consecutive reactions</td>
</tr>
<tr>
<td></td>
<td>• increased thermal stability</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• partial collapse of structure</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• formation of mesopores</td>
<td></td>
</tr>
<tr>
<td>steaming (high temperature hydrolysis)</td>
<td>• bulk dealumination: overall higher Si/Al ratio</td>
<td>• preferential sorption more apolar molecules</td>
</tr>
<tr>
<td></td>
<td>• increased hydrophobicity</td>
<td>• higher acid strength: higher reaction rate, possibly increase consecutive reactions</td>
</tr>
<tr>
<td></td>
<td>• increased acid strength</td>
<td>• new sites: new reactions possible</td>
</tr>
<tr>
<td></td>
<td>• increased thermal stability</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• partial collapse of structure</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• formation of Lewis acidity</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 1

The effects of steaming have been most extensively investigated for zeolite Y [9]. The material resulting after steam-treatment is known as Ultra Stable Y or USY and is an important Fluid Catalytic Cracking (FCC) catalyst.

However, the precise effects of steaming are still not clearly understood due to limitations of the current techniques. Especially $^{27}$Al-NMR, in principle a very powerful technique, is complicated due to the large quadrupole coupling of the aluminium nucleus (S=5/2). Although dealumination occurs, the nature of the resulting extra-framework aluminium (EF-Al) is not known. It seems that EF-Al can act as a Lewis acid itself, but also that it is able to increase the Brønsted acidity of nearby bridging Si-OH-Al. The combination of Lewis acidity and Brønsted acidity can also affect the reactivity of an adsorbed molecule; when it is polarised by the Lewis acid it may become more (or less) susceptible towards the Brønsted acid [64]. In these cases, reactions may be catalysed which before the treatment were not subject to catalysis, either due to the absence of Lewis acidity or due to the absence of very strong acid sites. Thus, often, steaming enhances the activity significantly. Besides the formation of EF-Al, it has also been reported that mobile siliceous species are created at places were dealumination is accompanied by partial loss of the zeolite structure [9]. These mobile siliceous species may react with the framework at places (silanol nests) were aluminium has been removed without local structural collapse resulting in a more stable framework. However, it seems paradoxical that loss of structural integrity should result in a more stable framework. To explain this, one has to assume that, within a certain type of zeolite structure, some crystallographic positions are more favourable to be occupied by aluminium atoms than others. Removal of aluminium from certain positions then may lead to local structural collapse while removal at other positions would not damage the framework. Insertion of silicon at these latter positions will anneal the structure and stabilise it towards further degradation.

Another external-surface inertisation method is based on the selective poisoning of the external acid sites by the use of bulky bases such as triphenyphosphine and triphenylamine [37,43,65,66], which has proven to be very selective in some cases. However, it limits the reusability of the catalyst system and is unsuitable for application at higher temperatures. Furthermore, the applied base may react with the reactants / products and may degrade. An interesting variation is the use of BaO as solid base in a physical mixture with the zeolite sample [67].
1.6 Zeolite Beta (BEA)

A major part of the research described in this thesis is focussed on zeolite Beta: synthesis, characterisation and various modifications to either reduce the external activity [68] or to influence the Lewis acidity by changing the geometry of the framework aluminium atoms [52]. Therefore, a brief description of zeolite Beta is given here to introduce some aspects of this zeolite which currently receives a lot of attention [69].

Zeolite Beta (BEA) was first synthesised in 1967 by Wadlinger et al. at the Mobil Corporation [70]. It was the first high-silica zeolite discovered with a three-dimensional pore system consisting of 12-ring apertures. Nowadays, the zeolite can be synthesised in a wide range of Si/Al ratios (4.5 to \(\infty\)) and thus the number of acid sites as well as the hydrophobicity can be tuned [71-76]. The application of templates other than tetrachylammonium has contributed largely to the synthesis of the all-silica (Si/Al = \(\infty\)) analogue [74,77]. Besides the aluminium containing zeolite Beta also boron- [78,79], iron- [80] and titanium- [81-84] containing analogues have been reported and very recently also zirconium Beta [85] was reported. However, *isomorphous* framework substitution is not always rigorously proven [85,86].

Zeolite Beta is an intergrowth of two or three polymorphs, named A, B and C, and therefore the framework is disordered along the [001] plane [73,87]. Polytypes A and B contain 9 unique tetrahedral framework positions (T-sites) whereas polytype C is reported to contain 32 unique T sites. All three polytypes possess two mutually perpendicular 12-ring channel systems which are both perpendicular to [001]. The elliptically shaped channels (7.6 \(\times\) 6.4 Å) are straight. The tortuous third channel runs parallel with the [001] direction and is circularly shaped (\(\phi = 5.5\) Å). Interestingly, if the A-polymorph is synthesised in a pure form then a chiral zeolite Beta is obtained which in principal offers the possibility of a chiral shape-selective catalyst [87-89]. However, this has not been achieved yet [90]. In Figure 10 the framework of zeolite Beta is displayed; the channel system is shown filled.

Finally it may be mentioned that zeolite Beta samples generally display a relatively large outer surface. Values up to 80 m²/g have been reported. See for further information on zeolite Beta crystals Chapter 3 of this thesis.
Figure 10. Framework of zeolite Beta in which the pore system has been made visible.
1.8 References

52. See Chapter 4 of this thesis.
68. See Chapter 3 of this thesis.
Chapter 1

2. CATALYTIC SYNTHESSES OF AROMATIC AMINES: A REVIEW

ABSTRACT

The most important manufacturing processes for aniline and other bulk arylamines are based on the continuous catalytic hydrogenation of nitro compounds, employing heterogeneous copper, nickel or platinum-group metals. For more complex amines produced on a smaller scale, homogeneous catalysis with its greater possibilities for chemo- and regioselective hydrogenation is increasingly the method of choice.

A newer alternative process of increasing importance for aniline and phenylenediamines is the nucleophilic amination of phenols. The catalytic amination of haloarenes has also been employed commercially. Amination processes also find application in the production of pyridines and pyrroles.

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2.1 INTRODUCTION

A survey is presented of catalytic routes to aromatic amines. These include the hydrogenation of nitroarenes and the amination of phenols, haloarenes and others. Also covered are amination routes to pyridines and pyrroles.

Rather than attempting to provide comprehensive coverage of such a broad area, a selection has been made by placing emphasis on aspects that are the subject of recent or current research attention. For other topics, citations to secondary literature such as reviews, monographs and reference works are given where these provide recent overviews. For published work from Japan and other Asian countries, English language publications have generally been relied on.

2.2 ARYLAMINES

The arylamines include a number of bulk organic chemicals, including aniline itself, diphenylamine and the phenylenediamines. The aniline derivative bis (4-aminophenyl)methane, produced by condensation with formaldehyde, and the toluenediamines are intermediates in the manufacture of isocyanates and polyurethanes.

Aromatic amination is conducted on scales ranging from the large-scale, continuous production of the above industrial products to the small-scale batch manufacture and laboratory synthesis of large numbers of substituted derivatives.

For the production of aniline and other bulk arylamines, catalytic hydrogenation of nitroarenes has long displaced the traditional Bechamp reduction employing iron and hydrochloric acid. To a lesser extent, the amination of chlorobenzenes has also been employed, while in recent years catalytic amination of phenols has become an important commercial process. These alternatives are summarized in Scheme 1.

While heterogeneous catalysts are employed in large-scale processes, a growing literature attests to the importance of homogeneous catalysis for smaller scale synthetic applications. For speciality products, aryl nitroso compounds or hydroxylamines may form alternative starting materials.
Scheme 1. Industrial routes to aniline

Catalytic hydrogenation of nitroarenes

Nitroarenes, conventionally produced by nitration with mixed nitric / sulfuric acids, form the starting materials for many arylamine processes. It may be noted that the substitution of an acid zeolite for the sulfuric acid has recently been announced [1].

The nitro group is one of the most easily hydrogenated functional groups and the choice of catalysts is therefore wide. For aniline production, many catalysts offering high activity and selectivity are available and the choice for a particular commercial process will reflect technological considerations of stability/regenerability, mechanical strength, susceptibility to poisons and cost. In an organic synthesis in which several possible products may be obtained by the hydrogenation of a polyfunctional starting material, the selectivity to the desired product is likely to determine the choice of catalyst.
Chapter 2

Heterogeneous catalysis

Useful summaries of the catalysts and processes employed in commercial production of aniline and other bulk arylamines are provided in standard reference works [2a,2b,3,4a]. An important consideration in designing a process for the hydrogenation of a nitro compound is the high exothermicity of the reaction (approx. 550 kJ/mol in the liquid phase), requiring attention to heat removal. Another is the fact that some catalysts may be poisoned by nitro compounds, necessitating the use of a reactor in which the concentration of starting material is minimized, such as a continuous stirred-tank reactor (CSTR) operated at high conversion [3].

For the production of aniline, numerous processes are in commercial operation; catalysts include supported copper, cobalt, palladium and nickel. The latter two may require the addition of inhibitors to prevent ring hydrogenation as a consequence of their higher activity. Vapour-phase processes employ either fixed-bed or fluid-bed reactors; copper on silica is typically employed as catalyst [2b]. Vapour-phase processing is also employed for other volatile products, such as the toluidines and xylidines. Instead of hydrogen, natural gas may be used for nitrobenzene hydrogenation, as demonstrated by Bayer workers employing methane/water and copper chromite catalyst [5].

Aniline is also manufactured by liquid-phase processes. The same catalysts may be employed as for vapour-phase processing, with nickel in either supported or Raney form. Recent patents to Mitsui Toatsu claim the use of a palladium catalyst, inhibited with zinc salts, in a CSTR in which the heat of reaction is removed by continuously distilling off the aniline product and water [6,7]. For less volatile products, only liquid-phase processing is appropriate. An example is the production of 1-aminonaphthalene by hydrogenation of 1-nitronaphthalene using a nickel catalyst [2c].

Solvents employed for liquid-phase hydrogenation include lower alcohols, N-methylpyrrolidone and liquid ammonia [2a]. Water may be employed in suitable cases, though the low solubility of hydrogen may cause difficulty, as described for the nickel-catalyzed hydrogenation of nitronaphthalenesulfonic acids [8].

In addition to the traditional supported-metal catalysts and Raney metals, catalysts prepared by the chemical anchoring of metal complexes to support materials are described, although their application remains limited to laboratory work. Examples include a silylaminepalladium(II) complex attached to montmorillonite clay [9] and macroporous organometallic polymers containing palladium [10]. Palladium supported on a borohydride exchange resin is claimed to be active under mild conditions and to hydrogenate the nitro group selectively in the presence of other reducible substituents [11]. Numerous examples of nitro compound hydrogenation by anchored Group VIII
metal complexes on organic polymers and on silica and other oxides are collected in the recent monograph of Chalonet al. [12].

For certain synthetic purposes, nitroso compounds, rather than nitroarenes, form the starting materials for amine preparation. Since these are intermediates in the hydrogenation of nitroarenes, catalysts employed for the latter, such as palladium, are suitable [13].

Halo and diamino derivatives

Numerous aniline derivatives are also prepared by the hydrogenation of the corresponding nitro compound. These include alkyl-, acyl-, hydroxy-, alkoxy-, nitro- and haloanilines [3]. When the substituent group is also reducible, catalyst selection may present interesting challenges. An example is provided by the hydrogenation of 2,4-dinitroaniline, in which the 4-nitro group is selectively hydrogenated over Pt/C in acidic solution [14,15], while rhodium in the presence of ammonia and in DMF as the solvent is selective for the 2-nitro group [16] (see Scheme 2).

![Scheme 2. Regioselective hydrogenation of a single nitro group in a dinitro compound.](image)

Numerous other examples of chemo- and regio-selectivity are collected in a recent survey [17].

Diamines, such as the commercially important 2,4- and 2,6-diaminotoluenes and the phenylenediamines, are produced by the hydrogenation of dinitro compounds. For the diaminotoluenes, numerous processes involving palladium and nickel catalysts in CSTR or fixed-bed reactors are known [3]. The activity of palladium is enhanced by various metallic promoters. Recently, the promoting effect of iron alloyed with palladium has been studied [18]; it is proposed that the iron improves the dispersion of the metal phase and also facilitates the transfer of hydrogen to the adsorbed dinitrotoluene.
Choice of solvent is also important: for the hydrogenation of dinitrotoluenes with Raney nickel, the use of tetrahydrofuran is claimed to improve the product selectivity by eliminating by-products formed from the alcohol solvents commonly employed [19].

Extensive studies to elucidate the mechanism and reaction kinetics of the hydrogenation of 2,4-dinitrotoluene (2,4-DNT), the most important isomer for toluene diisocyanate production, have recently been conducted [20-22]. The catalyst employed was 5% Pd/C. The multistep reaction sequence resembles the Haber mechanism for the hydrogenation of nitrobenzene. Janssen et al. identified two parallel reaction pathways, proceeding via the two aminonitrotoluenes, as shown in Scheme 3 below.

The hydrogenation of the para-nitro group of 2,4-DNT proceeds via a hydroxylamine intermediate, stable enough for 4-hydroxylamino-2-nitrotoluene to be isolable from the reaction mixture at partial conversion. Neri et al., working under different conditions (atmospheric pressure), showed that the hydrogenation product of this intermediate, 4-amino-2-nitrotoluene, is also directly formed from 2,4-DNT in a third parallel pathway [20].

The same catalysts employed for the dinitrotoluenes are used to hydrogenate 1,3-dinitrobenzene in the production of m-phenylenediamine. The o- and p-isomers are obtained by the hydrogenation, over a palladium catalyst, of the corresponding nitroanilines, which are themselves produced by the amination of the chloronitrobenzenes [2d]. Margitfalvi et al. have reported the preparation of o-phenylenediamine from 4-chloro-2-nitroaniline, employing a Pd catalyst for simultaneous nitro-group hydrogenation and Cl removal. The stabilized, ionic Pd catalyst was prepared by a surface-anchoring reaction involving initiation of the surface [23]. A patent to Máthe et al. discloses the use of high-dispersion Pd/C for the catalysis of this reaction on the pilot-plant scale [24].
Scheme 3. Mechanism of 2,4-dinitrotoluene hydrogenation over 5% Pd/C, according to Neri et al. [20] and Janssen et al. [21,22].

Where a halogen-containing product is the goal, dehalogenation becomes a side reaction needing to be suppressed. For sensitive materials such as 4-bromonitrobenezene, lower temperatures and/or pressures are used and catalysts employed are typically palladium inhibited with sulphur, lead or bismuth, or Raney nickel with thiocyanate [2a]. Phosphorus compounds are applied as selectivity enhancing additives in the hydrogenation of 3-chloronitrobenezene over Pd/C [25]. Recent examples of inhibitors employed with Pt/C catalyst include the use of formamidine salts to achieve yields of 94-97% in the hydrogenation of 1-chloro-2,4-dinitrotoluene [26,27], and of iron oxide and an amine for hydrogenating 3,4-dichloronitrotoluene [28]. Other systems claimed
Chapter 2

to hydrogenate nitro (and nitroso) compounds selectively, without hydrogenolysis of
halo substituents also present, are tungsten carbide [29] and sulfided nickel and
molybdenum hydrotreating catalysts [30].

Bamberger rearrangement

Phenylhydroxylamines undergo the acid-catalyzed Bamberger rearrangement to
p-aminophenols. Since the hydrogenation of a nitroarene proceeds via a
phenylhydroxylamine intermediate, a nitro compound may, under suitable conditions,
be hydrogenated to yield an aminophenol rather than the amine product. This elegant
variation is employed in the production of several crop-protection chemicals and
pharmaceutical intermediates.

For the preparation of 4-aminophenol from nitrobenzene, sulfuric acid is
typically employed, with Pt/C as the catalyst giving the lowest production of aniline by-
product. Further suppression of aniline results from inhibition of the catalyst with
sulphur compounds [31]; 4-aminophenol selectivities from nitrobenzene were 85% in
the presence of 2-thiophene-carboxylic acid, compared with 74% without sulfur
modifier. It is claimed that pretreating the sulfuric acid with hydrogen peroxide also
leads to a selectivity improvement [32]. Alternative acid systems such as
trifluoromethanesulfonic acid in acetic acid [33] and phosphinic acid (with Pd/C
 catalyst) [34] are also described. Improvements in reaction rate and yield are claimed
from operating under phase-transfer conditions [35,36]. The fungicide intermediate, 2,3-
4-amino-dichlorophenol may be produced, in 75-80% yield, from 2,3-dichloro-
nitrobenzene employing Pt/C catalyst and sulfuric acid in aqueous acetone [8] (see
Scheme 4).

\[
\text{NO}_2 \quad \text{Cl} \quad \text{H}_2, \text{Pt/C} \quad \text{Cl} \quad \text{H}_2\text{SO}_4 (\text{aq}), \text{acetone} \quad \text{NHOH} \quad \text{Cl} \quad \text{Bamberger} \quad \text{rearrangement} \quad \text{NH}_2 \quad \text{Cl} \quad \text{OH} \quad \text{Cl}
\]

Scheme 4. Hydrogenation with rearrangement of 2,3-dichloronitrobenzene [8].

Tungsten carbide is also suitable for use under Bamberger conditions, the
hydrogenation of nitrobenzene in sulfuric acid giving 4-aminophenol in 58% selectivity
at 99% conversion, compared with hydrogenation without acid which gave 95% aniline at complete conversion [29].

The use of methanolic sulfuric acid yields p-anisidines (methoxy anilines) from nitrobenzenes, instead of 4-aminophenol [37]. This forms the basis of a process for p-anisidine, commercialised by Mitsui Toatsu [38].

Homogeneous catalysis in nitroarene hydrogenation

As in the case of heterogeneous catalysis, the choice of homogeneous catalysts capable of hydrogenating nitro compounds with high activity and selectivity is very wide. Although homogeneous catalysts are unlikely to displace heterogeneous for continuous production, the greater opportunities for selectivity tuning, and the often mild operating conditions, make homogeneous catalysis attractive for small-scale and synthetic applications involving multifunctional starting materials.

The range of variables influencing selectivity in homogeneous catalysis includes the metal, the ligand, the solvent, and reaction conditions such as pH, temperature and pressure. As in the case of heterogeneous catalysis, Group VIII metals, particularly iron, cobalt, ruthenium, rhodium and palladium are frequently employed for the hydrogenation of nitro compounds [12,39]. In a recent example, dinuclear ruthenium complexes [RuL(CO)₂Cl]₂, where L = a nitrogen ligand such as 2-phenylpyridine, were shown to be effective catalysts for the selective hydrogenation of a variety of nitroarenes [40]. No hydrogenolysis of Cl took place in the case of 2-chloro-6-nitrotoluene substrate. The actual catalytic species was proposed to be the solvent adduct of the monomeric complex into which the dimer dissociates.

Hydrogenation using water gas

The combination of the homogeneous water-gas shift reaction (WGSR) and nitro-group hydrogenation (see Scheme 5 below) provides an alternative technique for arylimine preparation [12,39,41]. The catalysts are typically carbonyl complexes of iron, ruthenium and rhodium, employed in strongly basic solutions in order to facilitate nucleophilic attack on the coordinated CO. Both homogeneous and phase-transfer systems are employed. Advantages of this method include the use of environmentally benign, water-based solvents. Also, for substituted arylimines, new synthetic possibilities arise from the fact that the intermediate monohydride complexes, formed via the reaction of a CO ligand, may differ, in their reactivity to other reducible groups in the nitroarene substrate, from the dihydrides formed from the same precursor complexes with dihydrogen.
Scheme 5. Combined WGSR and nitroarene hydrogenation.

In an extensive series of publications, Nomura et al. have developed active and highly selective catalysts for the hydrogenation of nitroarenes, based on rhodium and ruthenium carbonyls such as Rh₄(CO)₁₂, Rh₆(CO)₁₆, Rh(CO)₃(acac) and Ru₆(CO)₁₅ [42]. Ligands employed include mono- and bidentate phosphines [43] and amines [44]. The catalysts are active under ambient conditions and are capable of hydrogenating 1-nitroanthraquinone to 1-aminoanthraquinone with high selectivity [45].

Catalysts based on Ru₆(CO)₁₅ with ligands such as triethylamine are found not only to be inactive for other reducible substituents such as cyano and carbonyl in the nitroarene substrates, but also not to hydrogenate substrates such as benzonitrile, phenylacetylene and acetophenone [44]. Such exclusive nitro group selectivity, together with the fact that no free hydrogen from the WGSR is detected at the end of these reactions, has led Nomura to propose a new type of reaction mechanism [45]: an intramolecular hydrogen transfer between a metal nitrene, formed via a cyclic adduct of metal carbonyl species and nitroarene, and hydride (see Scheme 6 below). The same may hold for the catalyst Rh₄(CO)₁₂ with 9,10-diaminophenanthrene [46].
Scheme 6. Proposed mechanism of nitrobenzene reduction with CO/H₂O and Ru₃(CO)₁₂/NEt₃ catalyst [45].

Skupinska et al. showed that the catalyst system PdCl₂/Fe₂O₃/FeCl₃/pyridine, employed for the reductive carbonylation of nitro compounds to isocyanates and urethanes, rapidly gives an almost quantitative yield of aniline from nitrobenzene in the presence of water [47]. With the activity further enhanced by iodine employed as promotor, the less active 2,4-dinitrotoluene similarly gave 2,4-diaminotoluene in high yield.

Another system for the carbonylative reduction of nitrobenzene in aqueous alkaline solutions has been described by Macho et al. [48,49]. The catalysts are sulfur compounds such as COS and H₂S and the selectivity to the arylamine product is improved by the addition of vanadium(V) compounds.

Transfer hydrogenation

While hydrogen is invariably employed in bulk processing, transfer hydrogenation offers an alternative when pressure equipment and hydrogen handling facilities are unavailable. Lower aliphatic alcohols and formates are typically employed as hydrogen-transfer agents [12,50] (see Scheme 7).
Scheme 7. Transfer hydrogenation with formate [50]

Transfer hydrogenation with homogeneous catalysts furnishes a further valuable synthetic method for the selective hydrogenation of nitroarenes having other reducible substituents, since the chemoselectivity obtained with a given catalyst may differ, depending on whether direct or transfer hydrogenation is employed. Watanabe et al. have shown, for example, that RuCl₂(PPh₃)₃ with HCOOH as hydrogen donor gives the corresponding aniline derivatives from nitrobenzenes with methyl, methoxy and chloro substituents; 2-methylaniline, for example was obtained in 96% selectivity at 99% conversion [51]. However, with 4-nitroacetophenone, direct hydrogenation is required to obtain 4-aminoacetophenone as product, since transfer hydrogenation with HCOOH selectively reduces the carbonyl group (see Scheme 8). Ruthenium has also been employed by Ben Taleb and Jenner, who showed that Ru₅(CO)₁₂ promoted by tertiary amines was effective for the transfer hydrogenation of nitroarenes using methyl formate as donor [52].

Scheme 8. Chemoselectivity in hydrogenation of 4-nitroacetophenone with [RuCl₂(PPh₃)₃] [51].
The use of hydrazine as reductant may be favoured when it is desired to stop the reaction at an intermediate stage. Yun et al. demonstrated that the hydrogenation of nitrobenzene, with hydrazine monohydrate and a nickel/zinc catalyst, could either be halted at the azobenzene stage or continued to aniline, depending on whether nickel nitrate or chloride were used as catalyst precursor [53]. Boothroyd and Kerr employed N,N-dimethylhydrazine and FeCl₃ catalyst to give anilines in high yields from nitroanilines such as 4-nitrophenol [54].

Transfer hydrogenation with heterogeneous catalysts is also employed. Conventional hydrogenation catalysts such as nickel or palladium are applicable, but the use of magnesium oxide with alcohol transfer agents is claimed by Kijenski et al. [55]. Hydrazine may also be used as reductant [2a]; in a recent application Hoechst workers obtained 3-chloroaniline in 96% yield from 3-chloronitrobenzene using hydrazine and Pd/C catalyst [56]. The toxicity of hydrazine, however, is disadvantageous.

Wiener et al. investigated the transfer hydrogenation of nitroarenes with Pd/C catalyst and formate salt donors. A mechanism involving the successive adsorption of nitroarene, formate anion and water on a single catalytic site was proposed [50]. The use of 4-vinylcyclohexene as donor, with Pd/C catalyst, has recently been reported [57].

Cervilla et al. have demonstrated an interesting example of transfer hydrogenation employing a molybdenum catalyst as model for a nitroreductase enzyme. The dioxomolybdenum (VI) complex is intercalated within a hydrotalcite-like layered double hydroxide to give an active catalytic system for the reduction of nitrobenzene to aniline using thiophenol as hydrogen-transfer agent [58].

**Nucleophilic amination reactions**

Nucleophilic amination of substituted benzenes is an important reaction for the production of both aniline and its derivatives. Although a range of starting materials can be employed [2a], only phenols and chlorobenzene have been employed in large-scale production processes. The use of aniline or its derivatives instead of ammonia provides a route to diphenylamines.
Chapter 2

**Phenols and phenolic ethers**

The catalytic amination of phenol (see Scheme 1) is the newest of the several commercial processes for the bulk production of aniline [3] and is operated in Japan (Mitsui Petrochemical) and the USA (Aristech). A lively account of the impact of this process on the established aniline market is given by Szmant [59a]. From \( m \)-cresol, \( m \)-toluidine is produced by an analogous process [4a]. A comparison of the aniline process economics with the traditional nitrobenzene hydrogenation route was provided by Gans [60]. One of the significant economic advantages of this process is claimed to be the outstanding catalyst stability.

Mechanistically, it is the tautomeric ketone form of phenol which can be considered as susceptible to nucleophilic attack by ammonia. This will be enhanced by coordination of the oxygen to a Lewis acid such as Al(III).

The original Halcon/Scientific-Design aniline-from-phenol process employed a proprietary solid-acid catalyst, based on silica-alumina [2b]. By-products in the process include di- and triphenylamines and carbazole.

The substitution of ammonia by aniline forms the basis of a process to diphenylamine [3]. The phenol-to-aniline process can also be modified to produce diphenylamine by recycling aniline to the reactor inlet [61].

In addition to silica-alumina, alternative oxide catalysts have been proposed, based on magnesium, boron and titanium oxides, with co-catalysts including cerium, vanadium and tungsten [4a]. Niobium oxide is claimed in a patent to Tosoh Corp. [62]. Other catalysts include fluorided alumina [63] and silica, impregnated with aluminium hydride and calcined [64].

Alumina as catalyst has been proposed to reduce problems of selectivity and stability loss associated with more strongly Lewis-acidic systems. The use of a \( \gamma \)-alumina with a highly specific pore-size distribution of 3-9 nm is claimed to improve stability [65], while alumina from calcined bayerite is claimed to reduce isomerization in the production of aniline derivatives [66].

Acid zeolites such as HZSM-5 [67,68] have also been claimed for the amination of phenols. The use of ZSM-5 suppresses the heavy by-products obtained (see above) with amorphous catalysts, owing to its specific pore size (0.55 nm). However, at high contact times, 2-methylpyridine is formed from aniline in a consecutive reaction in which ammonia is involved [69]; alkylanilines also undergo this reaction [70]. Zeolite Beta (BEA) is also active for phenol amination and its use is claimed to give very low diphenylamine formation [71].

Warawdekar and Rajadhyaksha investigated the amination of phenol and anisole (methoxybenzene) over NaY and HNaY zeolites and NaY exchanged with calcium,
chromium and copper [72]. For phenol amination the highest activity was found for the most acidic catalysts, HNaY and CuNaY. A mechanism involving the participation of both cations and protons was proposed.

**Dihydroxybenzenes**

The amination of phenols has been extended to dihydroxybenzenes, now available from the modified Hock process from diisopropylbenzenes, thus providing an alternative to the traditional multistep routes to phenylenediamines via nitro compounds. Much of the activity in this area is in Japan, where this process is employed in the manufacture of the valuable intermediate m-aminophenol by Sumitomo and by Mitsui Chemical Co. [38] (see Scheme 9).

\[ \text{OH} \quad \xrightarrow{\text{NH}_3 / \text{Mo cat.}} \quad \text{OH} \quad \xrightarrow{473K} \quad \text{NH}_2 \]

**Scheme 9.** Mitsui process for amination of resorcinol

Processes that have been described include vapour-, aqueous- and solvent-phase variants. For the vapour-phase reaction, oxides of Mo, W, Ga and Zn, and phosphoric acid on silica have been claimed [73]. Reactions in aqueous ammonia employ salts such as ammonium molybdate [74] and the phosphates of Fe, Ni or Zn [73]. For the solvent case, a recent development is the use of zeolites and montmorillonite clays in toluene or xylene [75].

An example of the application to an alkylaminophenol is the amination of resorcinol (1,3-dihydroxybenzene) with butylamine and phosphoric acid catalyst as the first step in the preparation of the di-N-butyl derivative [76].

In an analogous way, the amination of hydroquinone, with ammonia or alkylamines, yields p-aminophenol and its N-alkyl derivatives. Catalysts patented for this process by Mitsui include zeolite H-USY treated with ammonium fluoride [77] and the phosphates of Ti, Zr or Hf [78]; in the latter case, co-feeding phenol was essential to obtain a high selectivity of 78% at 93% conversion.

In the above processes further reaction leads to the formation of diamine by-products. Under appropriate conditions diamines become the main products; for
example, hydroquinone can also be fully aminated to yield \( p \)-phenylenediamine [2d]. A patent to Mitsui Petrochemical claims the use of aq. ammonia and Pd/C catalyst in the presence of cyclohexanone to give \( p \)-phenylenediamine in 50% selectivity at 73% conversion [79].

**Haloarenes**

The amination of halobenzenes not possessing nitro or other activating groups requires a catalyst. The catalyzed reaction of chlorobenzene with ammonia is the third process to have been employed commercially for the production of aniline [2a] (see Scheme 1). Dissolved copper salts such as the 'Nieuwland catalyst', CuCl/NH\(_4\)Cl, were employed [4a].

Halide exchange is also employed in the preparation of aniline derivatives. Examples are the manufacture of \( p \)-nitrodiphenylamine from \( p \)-nitrochlorobenzene and aniline and of \( N \)-phenyl-\( p \)-phenylenediamine from \( p \)-chloronitrobenzene and aniline, both processes employing copper salts as catalysts. Copper salts are also employed in the preparation of \( o \)- and \( p \)-phenylenediamines by amination of the corresponding dichlorobenzenes. An example involving a bromine compound is the amination of \( p \)-bromofluorobenzene over cuprous oxide to give \( p \)-fluoroaniline in 91% yield [80].

Heterogeneous catalysis of halobenzene amination offers the advantages of simplified product/catalyst separation and waste reduction. Following incidental reports of the use of zeolitic catalysts for this reaction, a systematic investigation was conducted by Burgers [81]. In a screening comparison of various metal-ion-exchanged zeolites for the gas-phase amination of chlorobenzene, copper was confirmed as the most active and selective metal. When different Cu-zeolites were compared, the order of initial activity was found to be \( Y \gg L \gg M O R > B E A > Z S M-5 \), which roughly parallels the increasing silica/alumina ratio. It was suggested that the higher surface polarity of the low-silica zeolites is responsible for the higher activity [82].

40
The principal by-products obtained are benzene and diphenylamine. Interesting selectivity differences between the various zeolites were observed. The lowest benzene and diphenylamine, and thus the highest aniline selectivity, were obtained with ZSM-5 and mordenite. This shape-selective advantage is lost as the pore size is increased, zeolite L giving increased diphenylamine yield, though benzene formation remained low. The still larger-pore materials BEA and Y gave substantially increased benzene but the diphenylamine selectivity, instead of increasing further, was once again found to be low (see Figure 1). The proposed explanation of these trends was that benzene is formed, not via simple hydrodehalogenation of chlorobenzene by hydrogen formed from ammonia decomposition, but principally from the decomposition of heavy condensation products.

![Figure 1](image)

**Figure 1.** Amination of chlorobenzene over various Cu-exchanged zeolites: influence of increasing pore diameter on (by-)product distribution [81].

The various zeolites were also found to differ strongly in stability, the large-pore zeolites BEA and Y showing the most rapid deactivation during operation. The most stable operation was found at 400 °C and two separate deactivation regimes were recognized, coke formation being the principal cause of activity loss at temperatures above 400 °C and accumulation of by-products at lower temperatures. All the catalysts were found to be fully regenerable by means of a simple calcination at 450 °C.
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The active site in these catalysts is considered to be the Cu(I) ion. The reduction of the as-synthesized Cu(II) zeolite, prepared by ion-exchange, to the active Cu(I) form by ammonia generates protons by charge compensation and catalysts formed in this way will be Brensted acidic. To study the effect of this acidity, a Cu-mordenite prepared in this way was compared with a non-acidic Cu-MOR prepared by impregnation with CuCl₂, followed by ammonia reduction [83]. It was found that the activity of the acidic catalysts is higher than that of the non-acidic. This, coupled with the fact that the rate of chlorobenzene amination is higher than that of bromobenzene [84], i.e. opposite to the order observed in the case of homogeneous catalysis, leads to the suggestion that the rate-determining step is the decomposition of, or the elimination of HX from, the copper-product complex, which is mediated by H⁺.

Copper mordenite was also found to be active for the amination of the chlorotoluenes [83]. The extension of the reaction to dichlorobenzenes would represent an alternative to the hydrogenation of the dinitro compounds [2d] for the production of diamines. However, the catalysts Cu-mordenite and Cu-L proved inactive for the transformation of p-dichlorobenzene to p-phenylenediamine [83] although other copper catalysts may be employed, for example CuO [85] and copper salts in aq. ammonia [3].

Other arene starting materials

The direct amination of benzene and other arenes has been named by James F. Roth as one of "ten challenges that typify the present needs of industrial catalysis" [86]. However, rather less progress appears to have been made in this area than with the direct amination of olefins, which has been commercialized by BASF for the production of tertbutylamine from ammonia and isobutene. Du Pont developed the use of oxide catalysts such as ZrO₂-promoted Ni/NiO to give aniline from benzene and ammonia with high selectivity of 97%, though at a low benzene conversion of 13% [4a,87]. A catalyst reoxidation step is necessary to maintain the catalytic cycle. Aniline itself can be aminated to phenylenediamines [88] and toluene to toluenediamines [89].

A more recent example is the production of small amounts of aniline (2%) and phenol (4%) from benzene (at 6% conversion) and aq. ammonia, employing a copper / calcium phosphate catalyst [90].
Indirect methods, involving the use of hydroxylamine salts or reductive amination, are also known [41]. A recent example of the latter is the amination of toluene by sodium amide, catalyzed by Rh/C and other hydrogenation catalysts [91].

An interesting Monsanto process for p-phenylenediamine provides an example of a more environmentally acceptable route than existing processes which generate chlorine-containing waste streams [92]. The starting material, nitrobenzene, reacts in the first step with benzamide, in the presence of a base and molecular oxygen, to give 4-nitrobenzanilide. This compound, with methanolic ammonia, regenerates benzamide and yields p-nitroaniline, which is catalytically hydrogenated to p-phenylenediamine. Formally, the reaction sequence is a nucleophilic substitution of NH$_2$ for aryl hydrogen (see Scheme 10).

A final example of the use of copper to effect a formal nucleophilic amination is the reaction of benzoic acid and alkylbenzoic acids to (alkyl)anilines under ammonia pressure, employing homogeneous copper compounds, as described by Arzoumanidis and Rauch [93]. Substitution proceeds via ortho-attack of coordinated amide (see Scheme 11). The process would seem mechanistically related to the Dow process for converting benzoic acid to phenol under Cu-catalysis (operated by DSM in the Rotterdam area).
Scheme 10. Monsanto route to p-phenylenediamine [92]
Scheme 11. Proposed mechanism for benzoic acid amination [93].

The decarboxylation is accompanied by reduction of Cu(II) to Cu(I), which may be reoxidized by atmospheric oxygen. So far, it has not proved possible to combine these two steps to achieve a truly catalytic cycle.

Diarylaminics

The use of aniline or a derivative, instead of ammonia, leads to the formation of diarylaminics from anilines, phenols or halobenzenes [3]. The self-condensation of aniline with acid catalysts forms the basis of manufacturing processes for diphenylamine. Heterogeneous catalysts such as alumina may be used, but high temperatures are required, resulting in coke formation. A patent to Uniroyal [94] claims that the use of a suitable large-pore alumina enables the temperature to be lowered from above 450 °C to around 400 °C.

Mechanistically, the situation is analogous to the amination of phenol; aniline in its imine form is subject to nucleophilic attack by a second aniline molecule.

The use of zeolites HNaY and rare-earth exchanged REY for the self-condensation of aniline was studied by Warawdekar and Rajadhyaksha [95]. Interesting observations were the maximum activity of HNaY at an intermediate level of exchange and the negative temperature dependence of the reaction. As in the case of the phenol-to-aniline reaction, a mechanism involving both cations and protons was proposed.
2.3 HETEROCYCLICS

Pyridine and derivatives

In this section, catalytic amination reactions leading to pyridines are discussed. Cyanide cyclization and aniline rearrangements yielding these compounds form the subject of an article in reference [96] and are not included here. Compounds containing more than one hetero-atom have also not been included in this overview.

The growing demand for pyridine and its derivatives, traditionally products of coal-tar distillation, by the fine-chemicals industry has led to the development of synthetic methods for their production. Several amination processes for pyridine itself and its alkyl derivatives are commercially operated [2e,4b,59b]. In Japan, pyridine and 3-picoline are manufactured from acrolein and ammonia (see Scheme 12).

\[
2 \text{CH}_2=\text{CHCHO} + \text{NH}_3 \rightarrow \begin{array}{c}
\text{CH}_3 \\
\text{N}
\end{array} + \begin{array}{c}
\text{N} \\
\end{array}
\]

Scheme 12. Pyridine and 3-picoline from acrolein.

The niacin (pyridine-3-carboxylic acid) intermediate 2-methyl-5-ethylpyridine is obtained from acetaldehyde and aqueous ammonia using ammonium acetate as catalyst (see Scheme 13). Acetaldehyde and ammonia react in the gas-phase, over silica-alumina catalyst containing proprietary promoters, to give 2- and 4-picolines, while pyridine and 3-picoline are produced in a gas-phase process from acetaldehyde and formaldehyde (see Scheme 13).
Scheme 13. Pyridine and derivatives from acetaldehyde.

In a developmental process of Nippon Steel the two most important derivatives, 2-picoline and 2-methyl-5-ethylpyridine, are produced from ethylene and ammonia, using as catalyst an ammoniacal palladium solution with a copper redox system to generate in situ acetaldehyde [4b] (see Scheme 14).

Scheme 14. Alkylpyridines from ethylene.

Acetone and furfuryl alcohol also represent potential commercial feedstocks for pyridines via amination processes [59b] and many other starting materials have been
Chapter 2

described. Crotonaldehyde [97] and acetylene [98] have been investigated by Russian workers. The use of ethanol is discussed at more length below.

Catalysis development for the amination of aldehydes, ketones and alcohols to pyridines, and in particular the investigation of zeolitic catalysts, represents a very active area of research. The suitability of pentasil-type zeolites for this application was demonstrated by Mobil workers [99]. The results described below are from gas-phase experiments at atmospheric pressure and temperatures in the range 350-450 °C.

Pyridines from aldehydes and ketones

For the amination of acetaldehyde alone, which yields predominantly 2- and 4-picolines, Chang and Lang showed ZSM-5 zeolite to be superior in activity to amorphous catalysts and in stability to mordenite. The highest selectivity of 13% to the desired 2-picoline was obtained with cadmium-modified ZSM-5 [99]. Picolines are also obtained in high yield from propylene glycol, when HZSM-5 is employed [100].

Faujasite zeolites have been used to catalyse this reaction by Roy et al. Cadmium gave improvements in this case also, but the highest activity was found with silica-alumina modified with ZnO, which gave a yield of 70% [101,102].

In contrast to the amination of acetaldehyde alone, the inclusion of formaldehyde and/or methanol in the feed yields pyridine as the main product, together with 3-picoline [97]. Adjustment of the product distribution is demonstrated in a process modification of Feitler and Wetstein employing a pentasil-type zeolite catalyst, containing also kaolin and amorphous silica-alumina, and a ternary aldehyde mixture containing acetaldehyde, formaldehyde and propionaldehyde [103,104]. A pyridine/picolines molar ratio of 0.55 was obtained, at a 66% selectivity to total pyridine bases, compared with a ratio of 2.2 without propionaldehyde.

Modifications of ZSM-5 with palladium [105], thallium [106] or both thallium and palladium [107] are claimed to increase the pyridine selectivity. A systematic comparison of various zeolites and silica-alumina was conducted by Sumitomo workers [108,109]. The highest pyridine selectivity was obtained with HZSM-5. Thallium and other modifiers such as lead, cobalt and zinc were found to be beneficial and both the total pyridines yield (76-81%) and the pyridine selectivity were found to be maximized by the use of Tl-ZSM-5 with intermediate Si/Al ratios in the 30-120 range.
The amination of acetaldehyde/formaldehyde has also been studied over the zeolite MCM-22; the product distribution is qualitatively similar to that obtained with ZSM-5 [110].

The amination of acetone over HZSM-5 leads to the formation of dimethylpyridines (lutidines) and more highly alkylated derivatives [99]. Different zeolites were compared in the reaction of acetone and methanol with ammonia by Van der Gaag et al. [111]. With HZSM-5, the selectivity to 2,6-lutidine was found to increase with the Si/Al ratio; by co-feeding water, the selectivity could be increased to around 20%. No activity was shown by silicalite catalyst (all-silica ZSM-5) showing that the presence of acid sites is required. Very low activity was shown by mordenite, which has a low Si/Al ratio of 6-7. The introduction of $^{13}\text{C}$-labelled methanol yielded 2,6-lutidine with $^{13}\text{C}$ exclusively at the 4-position (see Scheme 15). This is consistent with mechanisms proceeding via methyl vinyl ketone or imines formed from acetone or its condensation products but does not permit of an unambiguous assignment.

Scheme 15. 2,6-lutidine from acetone/methanol.

A recent paper of Rama Rao et al. compares various zeolites and amorphous catalysts in the amination of acetone/formaldehyde/methanol mixtures [112]. As in the example above, with HZSM-5 zeolites the 2,6-lutidine selectivity (and also the 2-picoline selectivity) increased with Si/Al ratio, but fell again at the highest Si/Al of 280. At acetone conversions of 50-60%, 2-picoline yields of 30-47% were obtained. A lead-promoted silica-alumina was higher in activity than that of any of the unmodified HZSM-5 catalysts, but gave a product mix containing much more 2,6-lutidine and less 2-picoline. The modification of ZSM-5 with lead gave the most active catalyst tested.
Still more highly alkylated pyridines have been prepared via the reaction of acrolein with alkanals such as butanal, employing pentasil-type zeolites. The major products were 3-ethylpyridine and 3-picoline [113]. Acrolein and formaldehyde, together with acetaldehyde or propionaldehyde, were aminated using CdO/silica-alumina catalyst. Acetaldehyde gave chiefly pyridine (50%), with 3-picoline as main by-product (22%) [114], while propionaldehyde yielded principally 3-picoline (57%) and some 3,5-lutidine (13%).

**Pyridines from alcohols**

Van der Gaag et al. showed that pyridine, together with 2- and 4-picolines as minor products, could be obtained by the oxidative amination of ethanol, in selectivities approaching 50%, using HZSM-5 catalyst [116] (see Scheme 16). No pyridine was obtained in the absence of oxygen. Co-feeding water was found to have a positive effect on both pyridine selectivity and catalyst stability. A mechanism proceeding via oxidation of ethanol to acetaldehyde was proposed. LeFebre showed zeolite Nu-10 to also be an effective catalyst for the reaction, giving a maximum of 80% (alkyl)pyridines. In further mechanistic studies the involvement of both acetaldehyde and formaldehyde, formed by radical fragmentation from ethanol, was invoked to explain the preponderance of pyridine itself among the products [117].

![Scheme 16. Pyridine and picolines from ethanol.](image)

Kulkarni et al. achieved the non-oxidative amination of ethanol over HZSM-5 catalysts by incorporating formaldehyde in the feed, thereby eliminating yield losses through carbon dioxide formation [118]. Pyridine yields of 20-40%, with 10-25% picolines were obtained. The reaction is proposed to proceed via the formation of ethylamine, which dehydrogenates to an imine; the reaction of two molecules of this with formaldehyde produces pyridine, while the condensation of three molecules of imine gives picolines.
The non-oxidative amination of ethanol is also effected using a heteropoly acid catalyst supported on γ-alumina [119]. This system yields 2- and 4-piclines with >55% selectivity at 94% alcohol conversion.

For the amination of tetrahydrofurfuryl alcohol, Choi et al. employed palladium on various carriers and identified carrier acidity and the palladium loading and dispersion to be the critical factors determining the pyridine selectivity [120]. The highest selectivities were obtained with γ-alumina carrier and a Pd particle size of 3-4 nm.

Pyrrole and derivatives

Pyrroles may be manufactured by the amination of furans and butynediol [21] with ammonia or amines. Solid acids such as silica-alumina and zeolites, and also transition-metal catalysts, are employed. Recent developments by BASF workers include the production of pyrrole, in up to 86% selectivity at complete conversion, from 1,4-dimethoxytetrahydrofuran [121], over acid catalysts including a borosilicate zeolite, and of 1-methylpyrrole from 2-butene-1,4-diol and methylamine employing a copper catalyst [122]. See Scheme 17.

Scheme 17. Pyrrole and derivatives by amination reactions.

Martin and Lücke employed HZSM-5 to obtain 2-methyl- and 1,2-dimethylpyrrole in almost quantitative selectivity at 40 and 70% 2-methylfuran conversions with ammonia and methylamine, respectively [123].
2.4 CONCLUSIONS; FUTURE TRENDS

Manufacturers of aromatic amines, in common with others in the chemicals industry, are increasingly required to reduce the environmental impact of their processes and to increase their feedstock and energy efficiency. The replacement of traditional operations involving dissolving metal reductions and acidic reagents by catalytic processes is an effective way to reduce waste streams and achieve these goals and, as has been shown above, catalytic processes already dominate this branch of the industry. It is to be expected that producers of aniline and other bulk products will continue to improve their proprietary technology; such evolutionary improvements are seldom reported in the literature, however. Nevertheless, in the absence of the introduction of revolutionary technology, such as the direct amination of benzene, which would have an impact comparable to that of the phenol-to-aniline process, progress in the future is likely to continue to be of this kind.

With regard to smaller-scale production, the increasing sophistication of homogeneous catalytic systems can be expected to enable further improvements in the selectivity to multifunctional amines, for example those containing other reducible groups. Although homogeneous catalysts are at a disadvantage compared with heterogeneous, with respect to product and catalyst recovery, the use of new phase-transfer and biphasic systems will make the use of homogeneous catalysts increasingly practicable and enable their potential for selectivity tuning to be realised.

The emphasis in current work on processes, such as hydrogen-transfer and CO/H₂O reductant systems, which frequently employ benign solvent systems such as aqueous ethanol, reflects the trend to reduce the use of environmentally unacceptable solvents. It is likely that alternatives for processes involving chlorine-containing intermediates, where the final product does not contain chlorine, will continue to be actively sought.
### Glossary of trivial names and abbreviations

<table>
<thead>
<tr>
<th>Term</th>
<th>Description</th>
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<tbody>
<tr>
<td>acac</td>
<td>acetylacetonato (2,4-pentanedione anion)</td>
</tr>
<tr>
<td>acrolein</td>
<td>2-propenal</td>
</tr>
<tr>
<td>anisidine</td>
<td>methoxyaniline</td>
</tr>
<tr>
<td>anisole</td>
<td>methoxybenzene</td>
</tr>
<tr>
<td>BEA</td>
<td>zeolite Beta</td>
</tr>
<tr>
<td>cresol</td>
<td>methylphenol</td>
</tr>
<tr>
<td>CSTR</td>
<td>continuous-flow, stirred-tank reactor</td>
</tr>
<tr>
<td>furfuryl alcohol</td>
<td>2-(hydroxymethyl)-furan</td>
</tr>
<tr>
<td>lutidine</td>
<td>dimethylpyridine</td>
</tr>
<tr>
<td>MOR</td>
<td>zeolite mordenite</td>
</tr>
<tr>
<td>niacin</td>
<td>nicotinic acid; pyridine-3-carboxylic acid</td>
</tr>
<tr>
<td>picoline</td>
<td>methylpyridine</td>
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<tr>
<td>resorcinol</td>
<td>1,3-dihydroxybenzene</td>
</tr>
<tr>
<td>REY</td>
<td>rare-earth Y zeolite</td>
</tr>
</tbody>
</table>
2.5 REFERENCES


59. H. Szmant, "Organic Building Blocks of the Chemical Industry" John Wiley & Sons, New York etc., 199, 1989; (a) Ch. 9, (b) Ch. 10.
63. L.A. Cullo, World Pat. 91/01293 (1991) to Aristech Chemical Corp.
66. A.A. Schutz and L.A. Cullo, World Pat. 9,305,010 (1993) to Aristech Chemical Corp.
80. A.A. Bazzi and E.B. Inskip, World Pat. 93/03002 (1993) to Mallinckrodt Specialty Chemicals Co.
88. E.N. Squire, *German Pat.* DE 2114255 (1971) to Du Pont de Nemours and Co.
89. E. N. Squire, *German Pat.* DE 2114254 (1971) to Du Pont de Nemours and Co.


3. MEASUREMENT AND PASSIVATION OF THE CATALYTIC ACTIVITY OF THE EXTERNAL SURFACE OF ZEOLITE MORDENITE AND BETA

ABSTRACT

The external surface acidity of the zeolites Mordenite and Beta can be selectively passivated by means of an amorphous silica-coating prepared from tetraethyl orthosilicate (TEOS) by Chemical Liquid Deposition. This coating is permeable, thus leaving the inner pore system accessible to reactants. A prerequisite for obtaining an effective coating on zeolite Beta is the use of relatively large, well formed crystallites, the microcrystalline mass afforded by the Wadlinger procedure giving poor results. Selective dealumination of the external surface in order to reduce the surface acidity could not be achieved. The inertization was measured by using a recently developed surface-sensitive probe molecule. The silica-coated zeolites can be regenerated several times without destroying the inert shell.

Part of this work was done in collaboration with Dr. J.A. Elings and has appeared in his PhD. Thesis; it was also presented at the 12th IZC, Baltimore, USA, 1998. The results obtained using zeolite Beta and the silica-coating technique were published in Microporous Mater. 11 (1997) 313-323.
3.1 INTRODUCTION

As a result of their uniform micropore systems, zeolite catalysts are capable of shape-selective catalysis, most commonly observed with acid-catalysed reactions [1,2]. The zeolite surface accessible to reactants comprises a large internal surface (the micropore system) and a smaller external surface (i.e. outside the micropores). For strictly shape-selective catalysis to occur, only the micro-pore system is of interest. The more accessible active (acid) sites at the external surface need to be minimized if it is desired to exploit fully the shape-selective property of the micropores. A further incentive to neutralize the external acid sites is that they may also promote the formation of undesirable coke-like products which can cause deactivation by inhibiting access to the micropores [3]. It should be noted that the zeolite external surface may show selectivity of its own, in the form of pore-mouth induced selectivity or as a result of its acid strength.

In order to use solely the zeolite pores for catalysis it is necessary to be able to make a distinction between the internal and external surface activity. Several research groups have addressed this problem [4-15].

In our own group, attention is focused on zeolite catalysed reactions for the synthesis of fine chemicals. Especially the 3-dimensional large pore zeolite Beta has proved to be a valuable catalyst for several reactions [16-21]. For the study of the mechanisms of these reactions, it would be desirable to be able to distinguish between reactions occurring in the micropores, with the possibility of shape selectivity, and those at the external surface. For zeolite Beta only a few publications have appeared that are concerned with the external surface and modifications thereof [12,14,21]. Recent reports indicate that the external surface activity of Beta can be extremely high [4,12]. The use of a bulky probe molecule for distinguishing the internal and external surface contribution has recently been described [4,14]. In a further approach to the problem described here, we attempted to prepare a zeolite Beta with a totally deactivated external surface while leaving the inner pore system unaffected and accessible.

Several post-synthesis modifications can be applied to reduce the external activity of zeolites, see also Chapter 1. These include dealumination with the aid of acids or complexing agents [14,22-24], poisoning by bases too bulky to penetrate the micropores [4,10,13] and covering the surface by a permeable coating e.g. amorphous silica [8,9,25-31].

The deposition of thin silica layers by Chemical Vapour (or Liquid) Deposition (CVD/CLD) from tetraalkyl orthosilicates or alkylchlorosilanes is usually employed as a pore size engineering technique, intended to improve the shape selective properties by narrowing the pore entrances. The methods have been applied to mostly zeolites ZSM-5
and Mordenite [8,9,25,30,31]. Silica-coated Mordenite is used in the amination of methanol, where a reduction in the formation of trimethylamine has been observed after pore-mouth narrowing [31]. These procedures simultaneously passivate the external acid sites. When trialkylchlorosilanes are used under water-free conditions, a monolayer is obtained (only one trialkylsilyl group per active site) whereas the use of tetraalkyl orthosilicates generally leads to a thicker layer, depending on the amount of substrate employed and on the small amounts of water present (in the zeolite pores and solvent in the case of CLD). The use of trimethylchlorosilane necessitates the use of template-occluded zeolite samples to prevent internal silylation since its small size enables it to diffuse readily into the pore system. For the more bulky (~9.5 Å) tetraethyl orthosilicate (TEOS) dissolved in a suitable solvent, this is less critical and calcined zeolite samples can be used.

Another option to reduce the contribution of the external surface is the synthesis of larger crystals which have intrinsically a smaller (external) surface area per unit mass. Much research has been devoted to zeolite Beta synthesis and several reports mention the influence of the synthesis conditions on the crystal size [32-40]. However, it is sometimes unclear whether the crystal size reported is actually referring to a single crystal or to a microcrystalline aggregate [16,33]. A consequence of both silica deposition and increase in crystallite size will be a greater diffusional barrier (higher Thiele modulus).

In this chapter, we report on both the synthesis of relatively large Beta crystals, referred to as macrocrystalline zeolite Beta, and the deposition of a silica layer by means of the CLD technique using TEOS and trimethylchlorosilane, applied to both micro- and macrocrystalline preparations of zeolite Beta. Previous to the work performed with zeolite Beta, dealumination and silica-coating procedures were investigated using zeolite Mordenite (a unidimensional, 12-ring aperture zeolite). Based on the results obtained with Mordenite the possibilities for zeolite Beta were explored. When the synthesis of macrocrystalline Beta was achieved, more clarity into the processes of dealumination and silica-coating were obtained.
3.2 EXPERIMENTAL

Zeolite synthesis

Tetraethylammonium hydroxide (TEA-OH) (20 wt%) solution, trimethylchlorosilane and tetraethyl orthosilicate (TEOS) were obtained from Janssen Chimica. Sodium aluminate (41 wt% Na₂O, 54 wt% Al₂O₃) was supplied by Riedel-de Haën. NaCl and NaOH were obtained from Baker Chemical. Aerosil 200 from Degussa was used as silica source.

Macrocryalline zeolite Beta was prepared according to the method described by Sun et al. [36], modified by the use of Aerosil as single silica source (Sun et al. apply both aerosil and sodium silicate as silica source). The gel had a molar composition of:

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>TEA-OH</th>
<th>Na₂O</th>
<th>H₂O</th>
<th>NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>132</td>
<td>16 or 24</td>
<td>36</td>
<td>1500</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

The template solution was diluted with the water and the NaOH and NaCl were added. Under vigorous stirring the silica was added, followed by a solution of sodium aluminate in a little water. Stirring was continued for at least three hours. The gel obtained was transferred to a Teflon-lined autoclave and heated under autogeneous pressure to 140 °C for three days. The as-synthesised (a.s.) material, denoted (a.s.)Beta1, was recovered by filtration, washed thoroughly with water until the filtrate attained pH=7 and subsequently calcined in air with a temperature program derived from published DSC measurements [32,41]: ambient to 200 °C (ramp 1 °C/min), 200 to 370 °C (ramp 0.2 °C/min), 370 to 500 °C (ramp 0.5 °C/min), 500 to 540 °C (ramp 1 °C/min), 10h at 540 °C, finally cooling down by 6 °C/min to ambient temperature again. This was done to avoid internal hot spots (possibly leading to the formation of cracks) generated by oxidative decomposition of the template and the accompanying water formation.

Ammonium exchange was performed once overnight at room temperature with an aqueous 0.1 M NH₄NO₃ solution. The Beta sample thus obtained is denoted (NH₄)Beta1 and the material obtained from this by activation at 450 °C is denoted (H)Beta1. For comparison, a batch of microcrystalline zeolite Beta was prepared via the Wadlinger synthesis [42], denoted (a.s.)Beta2. From this, (NH₄)Beta2 and (H)Beta2 were obtained in an analogous manner.

Zeolite NaMor (Si/Al=7.3, Na/Al=0.9, S_{BET}=460 m²/g) was supplied by PQ-zeolites. Threefold ammonium exchange (1h each) using 0.1 or 1M NH₄NO₃ solutions followed by activation at 450 °C transformed the materials into the acid form.
Post-synthesis modifications

Dealumination procedures

Mordenite samples. Severe dealumination of zeolite Mordenite was performed according to a patent by Dow Chemical [43]. NaMor (30g) was stirred for 0.5h in 300 ml 1M HCl at room temperature. After filtration and washing with water the sample was subsequently treated with a 6M HNO₃ solution under reflux conditions for 2h. Filtration and rinsing with water followed by calcination at 400 °C for 10h resulted in a highly siliceous mesoporous material which is referred to as 3-Dimensional Dealuminated Mordenite (3-DDM).

The influence of the ammonium exchange procedure on both the external activity and the aluminum content was investigated by performing ion-exchange experiments at room temperature and 80 °C and by the use of 0.1 and 1 M NH₄NO₃ solutions.

Beta samples. Template-occluded zeolite Beta was subjected to a severe dealumination treatment by heating the sample in 5 M aqueous nitric acid at 80 °C for 3.5h [44] and to a milder treatment by stirring the sample in 2 M aqueous oxalic acid (100 ml per g of template-occluded zeolite Beta) at 70 or 90 °C for 1h according to a Mobil patent [14].

Very mild dealumination procedures using Na₂H₂EDTA and H₂EDTA were performed using 0.025 M solutions (100 ml per g of template-occluded zeolite) at room temperature. After the treatments the samples were recovered by filtration, thoroughly washed with water and calcined in three steps (ambient-450 °C in air (ramp 1 °C/min, 6h at final temperature), followed by an ozone calcination at 120 °C and subsequently to 450 °C again).

silica-coating

Method a: a suspension of a sample of (H)-zeolite sample was stirred in (molecular sieve KA dried) hexane (or benzene), to which a solution of TEOS (0.2 g per g of zeolite) in hexane (or benzene) was added. Stirring was continued for one or three hours after which the zeolite was recovered by filtration and washed with hexane (or benzene) to remove excess of TEOS. The Mordenite samples, after calcination, are denoted (H)Mor-3a-ben and (H)Mor-3a-hex, respectively. The Beta samples, after calcination, are denoted (H)Beta1-1a and (H)Beta1-3a and (H)Beta2-3a, respectively. Based on the results obtained with Mordenite (see below), only hexane was used as the solvent in the coating procedure applied to the Beta samples.

Method b: (a.s.)Beta1 or (a.s.)Beta2 (dried at 190 °C, 10 Torr) were treated at room temperature with an excess of pure trimethylchlorosilane. Subsequent evaporation of the
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excess of reagent in a dry nitrogen stream resulted in very apolar materials which repelled water. After calcination (as described above), ammonium exchange and activation (at 450 °C), these materials are denoted (H)Beta1-b and (H)Beta2-b, respectively.

Method c: an activated (H)-zeolite sample was treated at room temperature with an excess of trimethylchlorosilane, either pure or dissolved in hexane or benzene. Subsequent evaporation of the excess of reagent in a dry nitrogen stream resulted in very apolar materials which repelled water.

Characterization

Elemental analyses were performed on a Perkin-Elmer 1100 flame-AAS. Nitrogen physisorption measurements were performed on a Quantachrome Autosorb 6B Automated Gas Sorption System, in the partial pressure range of p/p₀ = 0.01-0.09. S BET -areas were calculated according to ASTM D 3663-92. Powder diffraction data were obtained on a Philips PW 1840 using Cu-Kα radiation, in the range of 2θ = 5-50 °. SEM micrographs were taken on a Philips XL-20 microscope using 25 KeV. TEM micrographs were obtained with a Philips CM 30 ST electron microscope equipped with a field emission gun operated at 300 kV. NH₃-TPD measurements were run on a Micromeritics TPD/TPR 2900 equipped with a TCD. The sample (~60 mg) was activated at 450 °C (ramp 10 °C/min) in a flow of helium following which NH₃ was adsorbed at 110 °C. Desorption was monitored at a temperature ramp of 10 °C/min from 110 °C to 450 °C.

Catalytic testing

External surface

External surface activity per weight of material was measured using the conversion rate of the bulky allyl 3,5-di-tert-butylphenyl ether (11.0×10.8×5.8Å) as described in [4]. This ether undergoes an acid-catalysed Claisen rearrangement followed by an acid-catalysed cyclization. In the test 1 g of activated catalyst is added to a solution of 1 g of the bulky ether dissolved in 100 ml benzene. The reaction mixture is stirred under reflux conditions.

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Figure 1. External surface sensitive probe molecule. Claisen rearrangement followed by cyclization.

Internal surface

The accessibility and activity of the internal surface of zeolite Beta was measured by performing Meerwein-Ponndorf-Verley (MPV) reductions of 4-tert-butylcyclohexanone (2.5 mmol) with isopropanol (25 ml) as the hydrogen donor, under reflux conditions. This reaction was proven to be catalysed by internal Lewis acid sites only, as was shown by Creighton et al. [16]. Before each catalytic run, all Beta samples (200 mg) were activated at 450 °C (ramp 1 °C/min) in air for 6 h.

3.3 RESULTS AND DISCUSSION

Dealumination procedures

a. Mordenite samples. Upon severe dealumination of Mordenite (1M HCl followed by 6M HNO₃ leading to a bulk Si/Al ratio of 38) the outer-surface activity is vanished completely, i.e. no conversion of the probe molecule was observed even after 4h. This is a slight improvement on the results obtained earlier, when only the nitric acid step was performed without the preceding hydrochloric acid step resulting in a bulk Si/Al=33 and a conversion of 7% after 3h [4]. The nitrogen $S_{BET}$ measurement shows an increase in the total surface area from 460 m$^2$/g (H-Mor) to 500 m$^2$/g for the 3DDM sample due to the increase (~ doubling) in the mesopore area.

However, it is clear that this drastic treatment is not surface specific and alters many parameters such as the amount of active sites, the hydrophobicity and of course the texture of the material.
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The effect of a different ammonium exchange procedure should not be underestimated. It is well known that dealumination of Mordenite occurs easily even during ion-exchange with ammonium [45]. At room temperature their seems to be no effect of the ammonium concentration but at higher temperature a distinct increase in the probe conversion rate is observed for the 1M NH₄NO₃ exchanged sample and a remarkable lower activity in case of the 0.1 M NH₄NO₃ exchanged sample (see Figure 2). Removal of aluminum at higher temperature is likely to occur as well as the formation of mesopores. This can lead to an increase in the external surface area and accessibility for the probe molecule. The lower external activity for the 0.1 M NH₄NO₃ / 80 °C exchanged sample is not understood.

![Conversion vs Time Graph](image)

**Figure 2.** Influence of the concentration and temperature of the ammonium exchange procedure on the external activity of (H)Mor samples. Between brackets the Si/Al ratio and the N₂-BET surface area (in m²/g) are given.

b. Beta samples. For a batch of microcrystalline zeolite Beta it was found that the dealumination procedure using EDTA did not have any influence on the probe conversion rate; the activities were equal and very high (complete conversion within 90 min). Treatment of microcrystalline zeolite Beta with oxalic acid (ox.ac) at 90 °C surprisingly increased the external activity while dealumination at 70 °C left the material unaltered to the probe molecule (see Figure 3). These findings are in contrast to the Mobil patent [14] in which a selective dealumination of the external surface of zeolite Beta was claimed (claim: 49% reduction of external surface activity as determined by the cracking of 1,3,5-tri-tert-butylbenzene). Severe dealumination of template-occluded microcrystalline zeolite Beta using nitric acid resulted in an increase of the outer-surface activity as well, also related to an increase in the mesopore area [46].

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Figure 3. The influence of post-synthesis treatments on the external Brønsted acid activity of microcrystalline zeolite Beta. Between brackets the Si/Al ratio and the N₂-BET surface area (in m²/g) are given. (ox.ac.= aqueous oxalic acid treatment at 70 or 90 °C) Results from reference [46].

Better results, see Figure 4, were obtained with oxalic acid (90 °C) and the use of a batch of macrocrystalline zeolite Beta (see below for its characterisation). Actually, the results are even better than claimed by the Mobil workers. The bulk Si/Al ratio increased with 25% from Si/Al=11.6 to 14.3. Unfortunately, when using another batch of macrocrystalline Beta, reproduction proved to be difficult. Although much less active, essentially the same phenomenon was observed as with the microcrystalline samples i.e. after the oxalic acid treatments the outer surface activity increased. This leads us to conclude that the possibility of dealuminating zeolite Beta is batch dependent. Crystal-size and deposition of debris on the external surface during synthesis may have influenced the dealumination process. When debris has been deposited, an oxalic acid (ox.ac.) treatment may remove this thereby exposing the catalytically active crystal surface to the probe molecules causing an increase in reaction rate. When debris is absent the oxalic acid treatment may extract aluminium from the crystals exterior thus achieving the desired reduction in external acidity.

However, there still is a residual contribution of the outer-surface to the total acidity even when the external dealumination was successful.
Figure 4. The influence of an aqueous oxalic acid treatment on the external activity of macrocrystalline zeolite Beta (see also Figure 6). For comparison a microcrystalline Beta sample with an identical Si/Al ratio is displayed. Between brackets the Si/Al ratio and the N$_2$-BET surface area (in m$^2$/g) are given.

Silica-coating, Mordenite samples

Method a: Both the treatment of (H)Mor with TEOS in benzene and in n-hexane drastically reduced the external acidity, with hexane being the most suitable solvent (Figure 5 [46]). The lower effectiveness of silica-coating using benzene as the solvent is probably related to a stronger adsorption of benzene to the external silanol groups thus hindering the reaction with TEOS.

Method c: Silica-coating of the (H)Mor sample with pure trimethylchlorosilane (monolayer-coating) proved to be less effective in reducing the external activity: a reduction of 45% (conversion parent material: 98% in 3h, silica coated: 53% in 3h) was observed.
Measurement and Passivation of the Catalytic Activity of...

Figure 5. The effect of silica-coating on the external activity of Mordenite using TEOS in benzene (-ben) or hexane (-hex) as the solvent. Note that the (H)Mor sample is much more active due to an exchange procedure using 1M NH₄NO₃ at 80 °C for 24h. Results from reference [46].

Based on the good results obtained in these preliminary investigations for Mordenite, we expected to be able to passivate the outer-surface of zeolite Beta by TEOS treatment as well. However, this turned out to be less straightforward as is described below.

Preparation and characterization of macrocrystalline zeolite Beta

The preparation of macrocrystalline zeolite Beta according to the modification described by Sun et al. [36] was found preferable to other published methods [32,39] because of its reproducibility, as was found in preliminary studies. The use of one single silica source instead of two (Aerosil and sodium silicate solution) as described by Sun et al. suppressed the formation of zeolite Mordenite, which usually appeared as a by-product. When performed on a 50 ml scale, zeolite Beta was obtained without other (XRD-detectable) phases (see Figure 6).
Figure 6. Powder diffractogram of a batch of macrocrystalline zeolite Beta (as synthesised) crystallized in a 50 ml autoclave. The SEM micrograph (insert) shows uniformly-sized crystallites and a contamination, probably Mordenite (see below).

For the catalytic experiments it was desirable to have a larger batch of macrocrystalline zeolite Beta available. Therefore the synthesis was scaled up to a 300 ml autoclave. However, when using this autoclave, small amounts of Mordenite were detected (by its XRD pattern) as contaminant. Probably, the mixing of the large amount of synthesis gel and the heating of the larger autoclave are less homogeneous and result in an increased formation of Mordenite. Dividing the large amount of gel over several smaller autoclaves still resulted in Mordenite formation to a larger extent than when only a small amount of gel was prepared. The simple propeller-shaped mixer used to stir the visqueous gel may have resulted in improper mixing. Thus, when possible, this synthesis should be carried out on a small scale. By increasing the relative amount of TEA-template from '16' to '24' the Mordenite inducing effect by the presence of sodium can be reduced a little. For the work described here, one batch of macrocrystalline material was prepared in a 300 ml autoclave; the small amount of Mordenite present was not detrimental.

The synthesis gel is characterized by a relatively high Si/Al ratio, a large amount of sodium and highly diluted conditions. Generally it is known that dilution of a synthesis gel results in a slower nucleation rate and thus in the formation of larger crystals. The role of the high amount of sodium is less clear, since it is known that sodium cations actually accelerate the formation of nuclei. The formation of Mordenite as a by-product is likely
due to the presence of this large amount of sodium; sodium acts as a template for the formation of Mordenite.

A representative SEM micrograph of the (NH$_3$)Beta1 sample (prepared in a 300 ml autoclave), shows the presence of regularly shaped crystals with a truncated square-bipyramidal morphology (Figure 7). The average size is approximately 2 μm but the particle size is not uniform. The largest crystals shown in Figure 7 are 3 μm. Twinned crystals were not observed with SEM. No differences were observed between the a.s. samples and the calcined samples. Also, the silica-coating procedures did not change the appearance of the crystals under the scanning electron microscope, as compared to the parent samples.

![Figure 7. SEM micrograph of the (NH$_3$)Beta1 sample. The bar indicates 2 μm.](image)

The elemental analyses presented in Table 1 show that the macrocrystalline Beta samples (Beta1 etc.) have a much lower Si/Al ratio than the initial synthesis gel, indicating that Al is preferentially incorporated. The sodium content in the (a.s.)Beta1 sample is also higher than in the (a.s.)Beta2 sample.

No significant differences were found between the silica-coated and parent samples concerning the Si/Al ratio; it is therefore concluded that only a very small amount of silica has been deposited. As to the origin of the water required to hydrolyse TEOS, we think that residual water, which is present in the TEOS applied or released from the zeolite (as described in ref. [33]), is the main source. As no special precautions were taken to exclude water from the reaction mixture, water entering from the atmosphere may also contribute.
Table 1. Elemental analyses and nitrogen sorption data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al ratio</th>
<th>Na/Al ratio</th>
<th>$S_{BET}$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a.s.) Beta1</td>
<td>10.4</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>(H) Beta1</td>
<td>11.4</td>
<td>0.01</td>
<td>671±18</td>
</tr>
<tr>
<td>(a.s.) Beta2</td>
<td>11.6</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>(H) Beta2</td>
<td>11.6</td>
<td>0.01</td>
<td>699±8</td>
</tr>
<tr>
<td>(H) Beta1-1a</td>
<td>11.6</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>(H) Beta1-3a</td>
<td>11.6</td>
<td>0.02</td>
<td>640±18</td>
</tr>
<tr>
<td>(H) Beta2-3a</td>
<td>11.6</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>(H) Beta1-b</td>
<td>11.4</td>
<td>0.01</td>
<td>675±19</td>
</tr>
<tr>
<td>(H) Beta2-b</td>
<td>11.6</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>

a: TEOS-coated (Method a)
b: trimethylchlorosilane-coated (Method b)

The nitrogen sorption data presented in Table 1 show that the $S_{BET}$ areas of the (H)Beta1, (H)Beta1-3a and (H)Beta1-b samples are equal within the error limits, thereby confirming that the silica layer is permeable to nitrogen. The absence of hysteresis in the adsorption/desorption isotherms (not shown) for these samples indicates the absence of mesopores; this points to a material that is not composed of microcrystalline aggregates, which is in accordance with the SEM micrographs. For the microcrystalline (H)Beta2 sample hysteresis was found, from which a mesopore surface area of ca. 4% of the total surface area was calculated.

The powder diffraction pattern of the (a.s.)Beta1 sample (Figure 8) is much better resolved than that of the (a.s.)Beta2 sample (Figure 9), indicating extended long range ordering. After calcination of the samples the diffraction lines are seen to have been broadened to some extent. A small amount of Mordenite is present in sample (a.s.)Beta1, as can be concluded from the reflection marked with an asterisk ((a.s.)Beta1 stems from a 300 ml autoclave synthesis).
Figure 8. Powder diffraction patterns of the as-synthesised (lower) and calcined (upper) macrocrystalline Beta1 samples. The asterisk indicates a Mordenite impurity.

Figure 9. Powder diffraction patterns of the as-synthesised (lower) and calcined (upper) microcrystalline Beta2 samples.
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Crystal surface

Electron diffraction analysis revealed that the Beta1 material is comprised of single- and / or internally-twinned crystals. Sharp diffraction spots also proved the absence of micro-crystalline aggregates, which will give diffraction rings rather than spots. TEM micrographs of the (NH₄)Beta1 sample (Figure 10) show the exterior of the crystals to be very smooth and the typical Beta facets on top of the truncated octahedra can be imaged. The crystal edges of the (H)Beta1-3a sample (Figure 11) have a more rounded appearance and are covered with an amorphous layer. Its thickness is between 20-30 nm.

Figure 10. TEM micrograph of the (NH₄)Beta1 sample showing a very smooth crystal surface.
**Figure 11.** TEM micrograph of the (H)Beta-3a sample showing the crystallites to be covered with an amorphous silica layer. (The arrow points to the interface between the crystalline material and the amorphous silica layer.)

NH$_3$-TPD measurements presented in Figure 12 show the pore system of the parent ((H)Beta1) and silica-coated ((H)Beta-3a) samples to be also readily accessible to ammonia. The ammonia desorption curves are very similar and indicate the presence of strong acid sites in both samples.
Figure 12. NH$_3$-TPD curves of the parent (H)Beta1 and the silica-coated (H)Beta1-3a sample. Ramp rate 10 $^\circ$/min, indicated by the straight line.

External activity

The conversion rates of the bulky probe molecule (Figure 13 and 14) show that the (H)Beta1 sample has a significantly lower activity than the (H)Beta2 sample, as is to be expected on the basis of the external surface areas. After silica-coating by the TEOS technique, the activity of (H)Beta1 is reduced to ca. 10% of the initial activity (measured after 30 min) for the (H)Beta1-1a sample and to 0% for the (H)Beta1-3a sample. The complete external inactivity (no conversion after 4 h) was retained after repeated regeneration of the (H)Beta1-3a sample by filtration and calcination in air. In contrast, the activity of (H)Beta2-3a showed little decrease in activity as a result of silica-coating by the TEOS technique, as compared to the parent (H)Beta2. Silica-coating with trimethylchlorosilane (samples (H)Beta1-b and (H)Beta2-b) proved to be less effective for both macro- and microcrystalline samples. Possible explanations may be the destruction of the monolayer during calcination by oxidative decomposition of the template and the accompanying water formation. Also the impossibility of thorough water removal from the template-occluded zeolite without template destruction may be an explanation. To test this latter assumption, the experiments were repeated using calcined zeolite Beta (Method c). However, silica-coating of calcined (H)Beta samples with trimethylchlorosilane (pure or dissolved in a solvent) did also not result in any reduction of the external acidity of the Beta samples; by contrast, Method c applied to (H)Mor did result in a decrease of the external acidity as was reported above. As mentioned in the introduction, trimethylchlorosilane (TMCS) may readily diffuse into the pores of 12-ring aperture zeolites and potentially react with internal acid sites as well.
**Figure 13.** External activities for the Beta1 samples modified according to Method a and b.

**Figure 14.** External activities for the Beta2 samples modified according to Method a and b.
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The MPV reduction of 4-tert-butylicyclohexanone with isopropanol fulfills several criteria for verifying that the silica-coating on zeolite Beta does not narrow the pore entrances to such an extent that reactants are unable to enter (and products to leave) the micropore system. The reaction displays a high selectivity to GC-detectable products, a clear shape selectivity and the ketone and its alcohol products are relatively large. The conversion rates of 4-tert-butylicyclohexanone in the MPV reduction with isopropanol for the parent and modified macrocrystalline Beta samples are shown in Figure 15.

![Conversion rates graph](image)

**Figure 15.** Conversion rates of 4-tert-butylicyclohexanone (2.5 mmol) in the MPV reduction with isopropanol (25 ml, reflux conditions) for the Beta1 samples (200 mg).

Upon silica-coating (samples (H)Beta1-3a and (H)Beta1-b) the conversion rate is reduced substantially but indicates that the pore system is still accessible for reactants as large as 4-tert-butylicyclohexanone. Sample (H)Beta1-1a is more active than sample (H)Beta1-b; extrapolating the external surface measurements to accessibilities the opposite was expected. It should be noted, however, that the activity of zeolite Beta in the MPV reduction strongly depends on the sample preparation, especially the calcination procedure (temperature and number of times of activation) [47]. Therefore, the change in activity will be related mainly to the silica layer as extra barrier, but not completely. Finally we note that in the MPV reduction the total selectivity to alcohols was usually >95% with a cis-alcohol stereoselectivity of >95% in full agreement with the results on non-silica coated Beta [16,47]. Thus, the silica-coating does not block the pore-entrances, not for nitrogen and ammonia and also not for a molecule as large as 4-tert-butylicyclohexanone.
3.4 CONCLUSIONS

Zeolite Beta with a completely deactivated external surface was obtained by coating the parent H-Beta with a thin (20-30 nm) amorphous silica layer grown from TEOS by the CLD method. This layer is permeable, thus leaving the inner pore system accessible for reactants to enter and products to leave. This coating is also robust; the material can be regenerated without losing its passivating shell. A prerequisite for obtaining an effective coating is the use of macrocrystalline Beta samples. An explanation for the difference in effectiveness of the silica-coating may be the extremely rough surface of microcrystalline zeolite Beta limiting the possibilities for silica-coating. Destruction of the silica layer deposited on the microcrystalline aggregates during calcination by uneven thermal expansion may also be a contributing factor. It was found that the silica-deposition technique is superior to selective dealumination of the external surface in terms of reduction of the external acidity.

The externally deactivated zeolite Beta is an excellent catalyst for the MPV reduction of 4-tert-butylenol to cis-4-tert-butylenol. Its potential as highly shape-selective catalyst in acid-catalysed reactions is still under investigation.

Zeolite Mordenite with an external surface almost completely inactive towards the bulky probe molecule allyl 3,5-di-tert-butylphenyl ether can be prepared by coating the parent H-Mor with a silica layer grown from TEOS by the CLD method. This is in accordance with existing literature on silica-coating of zeolite Mordenite samples.

ACKNOWLEDGEMENT

Dr. Patricia Kooyman of the National Centre for High Resolution Electron Microscopy is thanked for performing the TEM measurements.
3.5 REFERENCES

Measurement and Passivation of the Catalytic Activity of... 

47. See Chapter 4 of this thesis.
4. ZEOLITE BETA: THE RELATIONSHIP BETWEEN CALCINATION PROCEDURE, ALUMINIUM CONFIGURATION AND LEWIS ACIDITY

ABSTRACT

Zeolite Beta was calcined under a variety of carefully controlled conditions to study the influence of (hydro-) thermal treatments on the catalytic activity of zeolite Beta in the Lewis acid catalysed Meerwein-Ponndorf-Verley reduction of ketones. The activity of (H)Beta can be increased by several orders of magnitude by mild steaming. The catalytic activity of the materials following re-activation can be reduced again by adsorption of ammonia followed by an induction period. For these changes, an explanation is offered in terms of Lewis acidic framework aluminium atoms which undergo a recersible change of configuration depending on the ligands present, rather than becoming extra-framework aluminium. FT-IR, \(^{29}\)Si and \(^{27}\)Al MAS NMR spectroscopy were applied to investigate the changes induced by the (hydro-) thermal procedures.

The contents of this Chapter are accepted for publication in J. Catal. (1998).
4.1 INTRODUCTION

Zeolite Beta, a 12-ring aperture (7.6×6.4Å) three-dimensional high-silica zeolite, currently receives much attention as a potential catalyst in numerous reactions [1]. Besides its Bronsted acidic properties it displays Lewis acidity as well. Interestingly, this Lewis acidity is believed not to be solely generated by extra-framework aluminium species, as is known for USY samples [2], but can also be displayed by framework aluminium atoms in a non-tetrahedral environment.

Several studies point to the flexibility of the coordination sphere of the aluminium atoms in zeolite Beta [3-8]. Besides tetrahedrally coordinated framework aluminium, octahedrally coordinated framework aluminium has been proposed, consisting of an aluminium connected with four bonds to the framework, one water molecule and a hydronium ion [3-6]. The amount of these types of aluminium was shown to depend on the pre-treatment of zeolite Beta and on the water content [3,6]. FTIR and $^{29}$Si and $^{27}$Al MAS NMR were applied to study the changes induced by various calcination conditions (shallow vs. deep-bed [4]), temperature treatments and interactions with molecules like ammonia, pyridine, benzene, n-hexane and water [7]. Also the influence of cations such as Na$^+$, K$^+$, NH$_4^+$ and protons on the state of the aluminium atoms was investigated [3]. Based on the reported results it was concluded that framework aluminium adopts a tetrahedral symmetry when protons are not the charge-compensating cations. Aluminium atoms, which have adopted another coordination symmetry but are still connected to the framework, can revert to their tetrahedral coordination sphere by ion-exchange with cations like Na$^+$ and K$^+$ and by adsorption of ammonia [3]. Extra-framework aluminium (EF-Al) has been reported to be formed during high temperature treatments of protonic zeolite Beta and was reported to be readily removed by applying aqueous nitric acid solutions [3]. The nature of the EF-Al has not been explained in detail.

As was shown recently, zeolite Beta is a highly stereoselective catalyst for the Lewis acid catalysed Meerwein-Ponndorf-Verley (MPV) reduction of ketones using a secondary alcohol as the reductant [9]. In the reduction of 4-tert-butylcyclohexanone, for example, a mixture of isomeric cis- and trans-4-tert-butylcyclohexanols is formed. While homogeneous and most heterogeneous Lewis catalysts give the thermodynamically most stable trans-4-tert-butylcyclohexanol with a selectivity of 70-90%, zeolite Beta produces the commercially desired cis-4-tert-butylcyclohexanol (a fragrance chemical intermediate) with >95% selectivity. Clearly, Lewis sites are present in zeolite Beta. The absence of Lewis-acidic metal ions as the charge compensating cations indicates coordinatively unsaturated aluminium atoms as the only possible
candidates [10]. Both Jia et al. [4] and Beck et al. [5] mention that framework aluminium atoms in a non-tetrahedral coordination may exhibit Lewis acidic properties.

The catalytic activity of zeolite Beta for the MPV reaction was shown to depend strongly on the calcination method (shallow or deep-bed [4]), on the calcination temperature and on the number of calcination steps. A deep-bed, high temperature calcination resulted in a more active catalyst. Repeated calcination further enhanced the activity without loss of selectivity and a correlation between the calcination method and the IR-data was observed [9]. The nature and the formation of the active site has not been resolved as yet. For the MPV reduction, Creyghton et al. [9] proposed a five-coordinated framework Al in which both the alcohol and ketone are simultaneously coordinated to the Al atom. No explanation for the correlation between the calcination procedure and the formation of the active sites was given at that time. A deeper insight into the formation of Lewis sites in zeolite Beta is therefore desired. Also, it seems logical to assume that the way of pre-treatment will influence the catalytic behaviour of zeolite Beta in several other Lewis acid catalysed reactions, e.g. Friedel Crafts reactions [11,12].

Based on $^{27}$Al MAS NMR studies on zeolite H-Y and the steamed H-USY [2], various aluminium configurations have been proposed. Interpretation of $^{27}$Al NMR data, however, is complicated by the quadrupole moment of the aluminium nucleus (I=5/2) causing quadrupole broadening. Also, not all the aluminium present in a sample might be detected by NMR techniques [3,13] Besides NMR techniques, XAFS has also been performed on these materials [14]. Besides tetrahedral framework aluminium and octahedral extra-framework aluminium (EF-Al), several other species (neutral or cationic) have been proposed including penta-coordinated EF-Al [15] and distorted tetrahedral EF-Al [2]. Earlier, Gilson et al. [16] reported on the possible existence of penta-coordinated Al in several aluminosilicates, including zeolites. Also Chen et al. [17] have reported on the coordination number of aluminium and the related Lewis acidity in aluminas. Interestingly, for AlPO$_4$-5, a microporous aluminophosphate with a neutral framework, it was reported that part of the framework aluminums could undergo a reversible transition from tetrahedral to octahedral coordination upon hydration [18]. The octahedrally coordinated aluminums are still connected to the (phosphate) framework by four bonds and have two additional coordinating water molecules. Penta-coordinated framework aluminium was also detected and was assumed to have only one coordinating water molecule.
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In the present work the influence of the calcination procedure on the catalytic activity of zeolite Beta in the MPV reduction of ketones was investigated in more detail. The Lewis acid catalysed MPV reaction seems to be an ideal test reaction for studying the changes induced by the (hydro) thermal treatments: the activity is highly dependent on the calcination or activation procedure of zeolite Beta and the extremely high stereoselectivity offers additional information about the catalytic active site. Furthermore, due to the mild reaction conditions (neutral pH, 82 °C), no modifications of the catalyst during a catalytic run are expected, except for the formation of the actual active site. To rule out any influences of the template removal on the catalytic activity, the ammonium form of zeolite Beta was prepared from the as-synthesised material in such a way that partial dealumination of the framework was prevented. This ammonium-Beta was used as the starting material for all subsequent (hydro-) thermal treatments. Instead of the poorly defined, inhomogeneous deep-bed calcination procedure, all additional treatments were performed using a well-defined shallow calcination bed while varying the atmosphere above the zeolite sample. Hot-spots and auto-steaming [6], intrinsically related to deep-bed calcination procedures under an oxidative atmosphere, will be prevented in this way, thus permitting a more reproducible calcination method.

Both microcrystalline and macrorystalline Beta samples were used to study the influence of the crystal size on the pre-treatments and to investigate whether the phenomena observed were the same for batches prepared by different synthesis procedures. Based on the combined results of FTIR, $^{29}$Si and $^{27}$Al (MQ) MAS NMR and the catalytic experiments, a mechanism is proposed which accounts for the effects observed as a function of the pre-treatment.
4.2 EXPERIMENTAL

Zeolite synthesis

Tetraethylammonium hydroxide (TEA-OH) (20 wt%) solution and tetraethyl ortho-silicate (TEOS) were obtained from Janssen Chimica. Sodium aluminate (41 wt% Na₂O, 54 wt% Al₂O₃) was supplied by Riedel-de Haën. NaCl and NaOH were obtained from Baker Chemical. Aerosil 200 from Degussa was used as the silica source.

Macrocrystalline zeolite Beta (Beta1, ~2µm) was prepared according to Kunkeler et al. [19] and microcrystalline zeolite Beta (Beta2) was prepared via the Wadlinger synthesis [20]. The as-synthesised materials were carefully washed with water until the filtrate attained pH 7 (pH-paper). Subsequently, the materials were washed once with a 0.025 M Na₂H₄EDTA solution at room temperature to remove possible debris formed during cooling of the synthesis mixture. Dealumination of the external surface by this treatment is unlikely as we reported recently [21]. X-ray powder diffraction confirmed that with both syntheses zeolite Beta was obtained. The macrocrystalline Beta material contained some Mordenite as contamination, as reported earlier [19].

Calcination procedure (template removal)

The calcination steps were performed using a horizontally mounted glass tube, which essentially represents a larger version of the tube shown in Figure 1. The as-synthesised materials (10 g) were first calcined under a pure ammonia atmosphere from ambient temperature to 400 °C (ramp 1 °C/min, 6 h at final temperature) after which the material appeared white to the eye. Subsequently, the samples were sodium-exchanged overnight using a 1M NaCl solution (100 ml / g zeolite) under reflux conditions. The thus obtained sodium-Beta’s were further calcined at 120 °C in an oxygen atmosphere containing approx. 1% ozone, followed by a third calcination step at 400 °C (ramp 1 °C/min, 6 h at final temperature) in an oxygen atmosphere. The calcined sodium Beta’s were transformed into their ammonium forms by three-fold ion-exchange with an 0.1 M NH₄NO₃ solution at room temperature.

Activation method and sample coding

Activation of small amounts (100-200 mg) of the ammonium forms of zeolite Beta was conducted in a small glass tube mounted horizontally in a tubular oven. A nitrogen gas stream (atmospheric pressure), either dried or saturated with a water partial pressure of 4.2 kPa, was led over the Beta sample. The samples were spread-out equally, thus obtaining a shallow calcination bed, see Figure 1.
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Figure 1. Experimental set-up for small-volume sample activation. Length tube approx. 10 cm, Ø 20 mm. The sample was positioned in the middle of the oven. The open end of the oven was closed by a quartz-wool plug.

The heating rate was set to 1 °C/min for all experiments. The water vapour pressure was regulated by a thermostatted condenser at 30.0 °C above an evaporator containing boiling water, through which nitrogen (30 ml/min) was fed via a glass-frit (water partial pressure at 30.0 °C = 4.2 kPa). When the sample had spent the prescribed time at the ceiling temperature it was allowed to cool down to 200 °C. The water vapour was switched off and replaced by a dry nitrogen stream one hour prior to a catalytic run, to ensure that a dry (H)Beta sample was used.

Each sample has been given a code which indicates the conditions of the activation procedure: the ceiling temperature in °C, the time at the ceiling temperature in hours (h), days (d) or weeks (w) and whether the atmosphere was dry or contained water vapour (w30) e.g. (H)Beta1 450(6h)w30.

Characterization

Elemental analyses were performed on a Perkin-Elmer 3000 DV ICP-OES. Nitrogen physisorption measurements were performed on a Quantachrome Autosorb 6B Automated Gas Sorption System, in the partial pressure range of p/p₀ = 0.01-0.09. S_BET areas were calculated according to ASTM D 3663-92. Powder diffraction data were obtained on a Philips PW 1840 apparatus using Ni-filtered Cu-Kα radiation, in the range of 2θ = 5-50°. SEM micrographs were taken on a Philips XL-20 microscope using 25 KeV. Transmission FT-IR spectra of the microcrystalline Beta2 samples were recorded on an FT-IR spectrophotometer equipped with a flow-cell enabling the spectra to be taken at
different temperatures and atmospheres, including vacuum. The samples were pressed to a
self supporting wafer and activated at 450 °C (heating rate 10 °C/min) under vacuum for
half an hour prior to data acquisition at 50 °C. Diffuse reflectance FT-IR (DRIFT) spectra
of the micro- and macrocrystalline Beta samples were collected on a Nicolet Magma 550
apparatus, equipped with a flow-cell enabling the spectra to be taken at different
temperatures under a nitrogen atmosphere. $^{13}$C and $^{29}$Si MAS NMR spectra were recorded
using a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5 mm Solids
MAS Probe (sf=5 kHz), and $^{27}$Al MAS NMR spectra were recorded on a Bruker DMX-
300 spectrometer (7.1T, sf=12.4 kHz). TMS was used as external standard for the $^{13}$C
and $^{29}$Si nuclei, and an Al(NO$_3$)$_3$ solution was used as the external reference for the $^{27}$Al
spectra. Deconvolution and integration of the $^{29}$Si peaks was performed to be able to
calculate the relative contributions of the various species and the framework Si/Al ratio
according to the formula: Si/Al = ($\Sigma$ 0.25-n-I$_n$)$^{-1}$, where I$_n$ is the relative intensity of the
SiO(Al)$_n$ peak (n=0 to 4). The samples were pre-saturated with water (desiccator at RT)
 prior to data collection. For the $^{27}$Al MAS spectra a 0.7 μs excitation pulse was used at
an rf-field strength of 42 kHz. The recycle delay was 0.25 s. It was checked that these
conditions are appropriate to ensure quantitative analysis of the spectra (i.e. all
aluminium atoms in the sample will be visible in the NMR spectra). For the $^{29}$Si spectra
a $\pi$/6 pulse: 3.0 μs and a 10 s delay were used, which was found to be an adequate
compromise between acquisition- and relaxation times.

Catalytic testing

Meerwein-Ponndorf-Verley (MPV) reductions of 4-tert-butylycyclohexanone (2.5
mmol) with 2-propanol (50 ml, zeolite-3A-dried, reflux) as the hydrogen donor were
performed in a 100 ml three-necked round-bottom flask using 200 mg of catalyst and
1,3,5-tri-tert-butybenzene (1 mmol) as internal standard (see Figure 2). Cis- and trans-
4-tert-butylycyclohexanol were formed as the only products in a ratio of 94:6 to 98:2.
Samples were taken regularly and analysed by a GC equipped with a CP-52-Carbowax
column (50 m, i.d.=0.53, nitrogen carrier gas) and FID. Before each catalytic run, the Beta
samples were activated under the conditions as discussed below. Activated samples were
carried in the activation tube to the reaction vessel under ambient atmosphere.
4.3 RESULTS AND DISCUSSION

The method of template removal from the as-synthesised zeolite and subsequent activation procedures influence the final condition of the material and thus the catalytic performance. Contradictory results obtained by independent researchers may be caused by the inadequate description of the experimental conditions, in particular those during the calcination (template removal) and subsequent temperature treatments [7,8]. Therefore, the heating rate, the time the samples spend at the ceiling temperature and the atmosphere under which the calcination and activation procedures were performed, are mentioned explicitly.

Due to the difficulty of pressing self-supporting wafers of the macrocrystalline Beta1 samples, only microcrystalline Beta2 samples were used for the transmission FT-IR measurements. Diffuse reflectance FT-IR was used for both Beta1 and Beta2 samples.

For the interpretation of the IR data, we rely predominantly on the publication of Kiricsi et al. [7]. According to these researchers, five types of hydroxyl groups can be distinguished by IR spectroscopy: bridging, Brønsted acidic Si-OH-Al (3605 cm\(^{-1}\)), OH groups attached to extra-framework Al (3660-3680 cm\(^{-1}\)), internal silanol groups (3730 cm\(^{-1}\)), terminal silanol groups (3745 cm\(^{-1}\)) and OH attached to an Al (3782 cm\(^{-1}\), the so called Very High Frequency band [4]). This Al-OH (VHF) band is referred to as a transient species by Kiricsi et al. [7], as an unusual aluminium site associated with the framework by Beck et al. [5] and as an aluminium species still connected to the framework by Jia et al. [4] in accordance with the earlier proposal of Bourgeat-Lami et al. [3]. Clearly, it is still unknown what the exact nature of this species is.
Calcination of the as-synthesised Beta zeolites

In order to avoid dealumination of the framework, template removal from the as-synthesised Beta samples was performed under an ammonia flow at a maximum temperature of 400 °C [9,22]. The template degrades via a Hoffman type mechanism, assisted by the ammonia base, towards ethene and triethylamine, which molecules can desorb as such, and the counterion role of TEA is taken over by ammonium. Formation of water is precluded by the absence of oxygen. According to Bourgeat-Lami et al. [3] ammonium cations prevent the formation of octahedrally coordinated aluminium. Sodium exchange after the first calcination step was applied to prevent dealumination during the second and third calcination step [3]. Three-fold ammonium exchange was performed to prepare the (pre-acid) ammonium form of zeolite Beta.

Octahedrally-coordinated aluminium was absent in the materials thus obtained as was concluded from the $^{27}$Al MAS NMR spectra (not shown) of the as-synthesised, the sodium-exchanged and the ammonium forms which showed only a single symmetrical peak centered at 56 ppm. The $^{29}$Si MAS NMR spectra (Figure 3) remained unaltered as well, showing broad overlapping bands at $-98$ ppm (Si(OSi)$_3$(OAl)$_2$, relative area = 0.9%), $-105$ ppm (Si(OSi)$_4$(OAl)$_1$ or Si(OSi)$_3$(OH)$_1$, r.a. = 32.4%) -111 ppm and -115 ppm (both attributed to Si(OSi)$_4$, r.a. = 55.6% and 11.1%) [4,23]. From the data of the (NH$_3$)Beta1 sample a framework Si/Al ratio of 11.7 was calculated, in good correlation with the wet-analysis data (Table 1).

The IR spectra of the hydroxyl region of the in situ activated Betal and Beta2 samples (see Figure 4, lower spectrum) showed absorptions for Brønsted acidic Si-OH-Al (3605 cm$^{-1}$) and silanol groups (3747 cm$^{-1}$) super-imposed on a broad absorption band (3700-3000 cm$^{-1}$) [3,4,7]. Compared to the microcrystalline sample, the macrocrystalline Betal showed less silanol groups, likely due to the smaller external surface area and consequently less terminal silanol groups.

These parent materials were further modified by the application of additional (hydro-) thermal treatments.
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### Table 1. Composition and surface areas of the Beta samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al ratio</th>
<th>Na/Al ratio</th>
<th>S(_{\text{BET}}) (m(^2/g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a.s.)Beta1</td>
<td>10.4</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>(Na)Beta1</td>
<td>11.4</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>(NH(_4))Beta1</td>
<td>11.6</td>
<td>0.01</td>
<td>660 ± 12</td>
</tr>
<tr>
<td>(a.s.) Beta2</td>
<td>11.6</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>(Na)Beta2</td>
<td>11.6</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>(NH(_4))Beta2</td>
<td>11.6</td>
<td>0.01</td>
<td>687 ± 8</td>
</tr>
<tr>
<td>(H)Beta1 450(6h)w30</td>
<td>11.6</td>
<td>0.01</td>
<td>635 ± 15</td>
</tr>
<tr>
<td>(H)Beta1 550(10h)w30</td>
<td>11.6</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>(H)Beta1 550(3d)w30</td>
<td>11.6</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>

#### Figure 3. \(^{29}\text{Si}\) MAS NMR spectra of the as-synthesised, sodium-exchanged and ammonium-exchanged (macrocrystalline) Beta1 samples.
Activation of the NH₄-Beta samples

To simulate deep-bed calcination conditions but without the temperature inhomogeneities (hot-spots [4]), the atmosphere above the sample was saturated with a water partial pressure of 4.2 kPa thus enabling controlled hydrolysis (mild steaming) of Si-O(H)-Al bonds in the framework, forming silanol groups and Al species with a coordination geometry differing form the tetrahedral framework Al-atoms. These aluminium species, or some of them, are believed to be the active centers in the MPV reaction. We thus assume that the water normally liberated during deep-bed oxidative calcination procedures is the main cause of the formation of aluminium species active in the MPV reaction. Liberation of water by the annealing of silanol nests may also contribute [24]. In a deep-bed, the water formed will spend more time in the zeolite sample than in a shallow-bed and consequently has an increased chance to get involved in hydrolysis (auto-steaming). On a smaller scale, this may also be important for the effect of the primary crystallite size, a large crystal retaining water longer during activation than a small crystal, while during steaming a large crystal may limit the intraporous supply of water necessary for hydrolysis. This may result in less MPV active sites when compared to the microcrystalline sample treated in a similar way. The effect on the catalytic activity will also depend on whether all possible active sites will be reached by the reactants to the same extent. It is likely that for larger crystallites the available micropore volume is not used as efficiently as the micropore volume of the smaller crystals. Activation under dry conditions may result in some auto-steaming when water is liberated at high temperatures from hydroxyl nests. These are known to be abundant in zeolite Beta because of the stacking faults present in the structure [25].

Creyghton et al. [9] showed that any water present during the MPV reaction has a detrimental effect on the catalyst system. Therefore, the steam-treated (H)Beta samples were flushed with dry nitrogen for one hour at 200 °C prior to the catalytic run.
**Figure 4.** Transmission FT-IR spectra of the hydroxyl region of the (H)Beta2 samples. Prior to data acquisition the samples were activated *in vacuo* at 450 °C for 0.5 h.
Catalytic activity as a function of the pre-treatment

Protons as the charge compensating cations are essential for the catalytic activity since Beta samples with a Na/Al ratio of 1.0 proved to be completely inactive. It was observed that samples with a Na/Al ratio of <1 are active, even when only 6% of the cations were protons. Since protons are not assumed to be the active site for the MPV reaction their presence seems to be essential in the formation of the active site, which points to the simultaneous formation of silanol groups with the formation of the active site. (N.B. Na⁺ cations prevent the formation of octahedrally coordinated aluminium upon heating.)

To ascertain that the combination of the activation procedure and catalytic testing indeed gave reproducible results and that the differences observed between different activation procedures were significant, we subjected several Beta samples of the same batch to the same activation procedure and tested their catalytic activity. The deviation in the initial activities was within ~2%.

Effect of activation temperature

Activation at 450 °C under dry conditions for 1 h results in barely active catalysts, see Figure 5 and Figure 6. Raising the ceiling temperature to 550 °C increases the activity significantly for the microcrystalline Beta sample (Figure 5) but not for the macrocrystalline sample (Figure 6). As was to be expected on basis of the crystal sizes, the activities of the macrocrystalline Beta samples are lower.

The temperature effect observed for the microcrystalline sample may indicate that the formation of the active sites for the MPV reaction has a high activation energy and/or that silanol groups from hydroxyl nests are consumed and water is liberated (see below). (N.B. the heating rate of 1 °C/min will cause a sample activated at a ceiling temperature of 550 °C actually to be activated 100 min longer (450 °C<Temp.<550 °C) than the sample activated at 450 °C.)

Effect of water during activation

The effect of the presence of water during activation at 450 °C and 550 °C on the catalytic activity of the zeolite Beta samples becomes apparent from Figure 5 and Figure 6. Clearly, water has a profound influence and leads to a drastic increase of the catalytic activity. Formation of the precursor for the MPV active sites is thus strongly dependent on the availability of water. The combination of a high temperature and the presence of water results in very active Beta samples. The assumption that template-
removal under oxidative conditions in a deep-bed configuration leads to auto-steaming and enhanced activity therefore seems correct.

![Conversion Graph](image)

**Figure 5.** Conversion of 4-tert-butylcyclohexanone vs. time. The effect of water vapour during activation at 450 and 550 °C on the catalytic activity of microcrystalline Beta2 samples.

For both micro- and macrocrystalline samples the activity could be enhanced further by increasing the time of steam activation (6 h or 10 h vs. 1 h) as is shown in Figure 7 for the Beta2 samples. At 450 °C, an increase of the activation time from 6 to 10 h does not result in a pronounced increase in activity, while for the samples activated at 550 °C the activities became so high that differences could not be observed any longer under the reaction conditions applied. The same trend was observed for the macrocrystalline samples using the DRIFT technique.
Figure 6. Conversion of 4-tert-butylcyclohexanone vs. time. The effect of water vapour during activation at 450 and 550 °C on the catalytic activity of macro-crystalline Beta1 samples.

To examine whether a plateau or a maximum for the activity exists depending on the time of activation, three steam-activated active Beta1 samples were tested with half the amount of catalyst (100 mg) and a doubled amount of reactants (5 mmol ketone and 100 ml 2-propanol). The samples tested were: (H)Beta1 550(10h)w30, (H)Beta1 550(3d)w30 and (H)Beta1 550(1w)w30. The latter two samples showed under the standard reaction conditions conversions of 100% within 5 min with a cis-alcohol selectivity of 98%. This suggests that the zeolite has become very stable towards further hydrolysis, at least at 550 °C. The XRD pattern, however, had almost completely vanished indicating that the long-range ordering had diminished (Figure 8). From Figure 9 it becomes clear that a plateau in the catalytic activity is approached when the Beta sample has been steamed for three days at 550 °C; steaming for one week does not increase the activity much more. This indicates that the maximum amount of aluminium that can be transformed into a MPV active site has been reached. A turnover number (TON) of 19 (mol/molₐ) was reached in 1 min for the most active sample. Note, however, that not all the aluminums present will be transformed into an active site and consequently the actual TON per active aluminium will be higher.
Figure 7. Conversion of 4-tert-buty1cyclohexanone vs. time. The influence of the time (h) of activation at 450 and 550 °C in the presence of water on the catalytic activity of microcrystalline Beta2 samples.

Figure 8. Powder diffractogram of (NH₄)Beta1 (upper) and (H)Beta1 550 (3d)w30 (bottom).
**Zeolite Beta: The Relationship between ...**

![Figure 9](image)

**Figure 9.** Conversion of 4-tert-butylcyclohexanone vs. time. Effect of catalyst activation time. Reaction conditions: 100 mg zeolite (H)Beta1, 5 mmol ketone and 100 ml 2-propanol under reflux conditions.

**Reversibility of the catalytic activity**

As described in the introduction, some framework aluminium atoms in Beta can undergo a reversible transformation from tetrahedral to octahedral coordination. To examine whether the formation of the MPV active site could also be reversed by the adsorption of ammonia, (H)Beta1 450(6h)w30 samples were catalytically tested before and after admission of ammonia at 100 °C [3]. Prior to the catalytic run the ammonia was again removed at 450 °C (under nitrogen flow) to obtain the protonic form. As a reference, one sample was only cooled down and exposed to the ambient atmosphere for 1h, in order to verify whether ambient water at RT already reduces the amount of active sites. It is known that the presence of water influences the aluminium coordination [3,6].

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Table 2. Influence of ammonia adsorption and induction time on the catalytic activity of (H)Beta 450(6h)w30. (standard reaction conditions)

<table>
<thead>
<tr>
<th>Sample treatment</th>
<th>Conversion (%) after 6h</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H)Beta 450(6h)w30</td>
<td>49</td>
</tr>
<tr>
<td>(H)Beta 450(6h)w30 + ambient + 450(1h)</td>
<td>38</td>
</tr>
<tr>
<td>(H)Beta 450(6h)w30 + NH₃ 100(1h) + 450(1h)</td>
<td>27</td>
</tr>
<tr>
<td>(H)Beta 450(6h)w30 + NH₃ 100(4d) + 450(1h)</td>
<td>18</td>
</tr>
</tbody>
</table>

From Table 2 it becomes clear that the adsorption of ammonia results in a decrease of the number of active sites. This decrease is more pronounced when the induction time is extended from 1 h to 4 days. However, not all the active sites disappear within 4 days: the sample still displayed a higher activity than the (H)Beta 450(1h) sample (the least active sample, see Figure 6). Exposure of an activated sample to the ambient atmosphere for 1 h, followed by a short activation to remove the water adsorbed, also reduces the activity although less effectively than when ammonia had previously been absorbed. These results support the idea of a Lewis-acidic framework aluminium whose coordination sphere can undergo a change of coordination depending on the ligands present.
IR study

The effect of mild steaming can be made clearly visible with IR spectroscopy, see Figure 4. Upon steaming the bridging OH peak (3605 cm\(^{-1}\)) decreases, while the silanol peak (3745 cm\(^{-1}\)) increases. Furthermore, two new absorptions arise: a broad one around 3660-3680 cm\(^{-1}\) and a clear peak at 3782 cm\(^{-1}\) (VHF). These four absorptions are super-imposed on a very broad band spanning 3700-3000 cm\(^{-1}\). It is believed that this broad absorption stems from the presence of hydroxyl nests \((\text{SiOH})_4\) created by imperfections of the lattice [3,4,7]. The intensity seems to be decreased for the (H) Beta2 550(3d)w30 sample, which might indicate that some hydroxyl nests are repaired and that siliceous species formed during the steaming process have been inserted. This may result in a more silica-rich framework which is less susceptible towards further hydrolysis; this seems to be in agreement with the plateau in the catalytic activity. The latter sample also shows a sharpening of the small peak at 3666 cm\(^{-1}\). For the macrocrystalline Beta1 samples identical results were obtained using the DRIFT technique.

The decrease of the amount of bridging hydroxyls can be explained by breaking of the Si-OH-Al bond into a SiOH group, with concomitant increase of the 3745 cm\(^{-1}\) band, and formation of an aluminium connected to three framework silicon atoms and coordinating a water ligand. Further hydrolysis may result in an aluminium species connected to the framework by two remaining bonds and bearing a hydroxyl group which is responsible for the VHF band [7]. Another explanation for the decrease of the 3605 cm\(^{-1}\) band may be the replacement of the charge-compensating proton by a cationic EF-Al species [26] (upon steaming a peak appears at 3666 cm\(^{-1}\) which is ascribed to EF-Al species) although its nature is unclear [7].
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$^{29}$Si and $^{27}$Al MAS NMR study

The $^{27}$Al MAS NMR spectrum of the Betal sample following the short activation procedure (450(1h)dry) (see Figure 10, bottom) is distinctly different from the ($\text{NH}_4$)Betal spectrum (single line at 56 ppm). (N.B. before the NMR measurements all samples were hydrated.) A peak around 0 ppm becomes visible which is ascribed to octahedrally coordinated Al (Oh-Al). As discussed in the introduction, it is now believed that this Oh-Al is still connected to the framework [3-8] instead of being extra-framework Oh-Al as is usually proposed for USY [2]. This is also confirmed by our $^{29}$Si MAS NMR data: upon activation (450(1h)dry) the spectrum (Figure 11, bottom) did not change, indicating that no changes took place in the environments of the silicon atoms, in other words, dealumination of the framework did not occur. From this, it can be directly concluded that the Oh-Al visible in the $^{27}$Al NMR spectra of the 450(1h)dry samples cannot be extra-framework aluminium. Since the catalytic activity for the 450(1h)dry samples is very low, this indicates that Oh-Al is not involved in the MPV active site, in accordance with Creighton et al. [9]. The reversal of the Oh-Al back to Td-Al was shown by the treatment of the sample with ammonia. Indeed, after 4d at 100 °C, no Oh-Al signal is present in the $^{27}$Al-NMR spectrum in agreement with the results obtained by Bourgeat-Lami et al. [3].

The $^{27}$Al NMR spectrum of the (H)Betal 550(3d)w30 sample (see Figure 10) shows a decrease of the octahedral peak (0 ppm) and a broadening of the tetrahedral peak (60 ppm). Preliminary results obtained with the newly developed $^{27}$Al MQ MAS NMR technique [27,28], which enables the determination of the quadrupole interactions, show the 60 ppm peak to be build up of (at least) two contributions: the normal framework non-distorted tetrahedrally coordinated aluminium and a distorted tetrahedrally coordinated aluminium (see Figure 12). This distorted tetrahedrally coordinated aluminium is absent in the parent (H)Betal 450(1h)dry sample (see Figure 13). Thus, steaming causes some aluminium atoms previously able to attain an octahedral coordination to adopt a distorted tetrahedral geometry.

Note: First, the quadrupole coupling constants are determined using the $^{27}$Al MQ MAS NMR technique. Then, the $^{27}$Al MAS NMR spectra are recorded with the parameters as mentioned in the Experimental section. To obtain quantitative data, the loss of information in the time between the excitation-pulse and the acquisition of the FID ('dead-time') is accounted for by inter-polation of the FID to $t=0$ using the previously determined quadrupole coupling constants. In this way, the very fast relaxation of aluminium atoms in a distorted environment is compensated for, thus obtaining quantitative spectra, i.e. without invisible aluminium.
Figure 10. $^{27}$Al MAS NMR spectra of Beta1 samples: lower spectrum dry activated at 450 °C, upper spectrum steam activated at 550 °C. Prior to data-acquisition both samples were hydrated.

Figure 11. $^{29}$Si MAS NMR spectra of Beta1 samples: lower spectrum dry-activated at 450 °C, upper spectrum steam-activated at 550 °C.
Figure 12. $^{27}$Al MQ MAS NMR spectrum of the (H)Beta1 550(3d)w30 sample. The part of the ~60 ppm signal that is not symmetrical around the diagonal indicates the presence of distorted tetrahedrally coordinated aluminium in the sample.
Figure 13. $^{27}$Al MQ MAS NMR spectrum of the (H)Beta 450(1h)dry sample. The signals are symmetrical around the diagonal indicating the presence of non-distorted tetrahedrally (~60 ppm) and octahedrally (~0 ppm) coordinated aluminium atoms in the sample.
The $^{29}$Si MAS NMR spectrum of the (H)Beta1 550(3d)w30 sample shows a clear decrease of the -105 ppm peak and a sharpening of the -115 ppm peak (assigned to Si(OSi)$_3$), see Figure 11. The framework Si/Al ratio calculated is 34 indicating that dealumination occurred and EF-Al must be present, whatever its nature. $^{29}$Si CP MAS NMR showed that the (remaining) -105 ppm peak has a contribution from silanol groups and consequently the calculated Si/Al value is a minimum value. The $^{29}$Si MAS NMR spectrum of the (H)Beta1 550(1w)w30 sample was identical and a possible progress in the dealumination could not be observed. The sharpening of the -115 ppm peak might indicate a decrease of the anisotropy of the Si-atom under study. Presumably, the next nearest neighbour (NNN) shell becomes deficient in aluminium and, under the conditions applied (high temperature and steam), siliceous species may fill up the vacancies in the framework thus creating a more isotropic environment for the Si(OSi)$_3$ [29]. These siliceous species are assumed to be created during structural collapse of the framework at positions where severe dealumination has taken place. This structural loss also becomes clear from the XRD patterns (see Figure 8) of the severely steamed samples, which show decreased long-range ordering. This is especially pronounced for the macrocrystalline samples, which show initially a highly resolved diffraction pattern [19]. The insertion of silicon species into the framework will have a stabilising effect towards further hydrolysis which is in agreement with the catalytic plateau observed.
Proposal for the precursor for the MPV active site

Creyghton et al. observed a correlation between the calcination method and the IR spectra of the Beta samples [9]. Especially the appearance and the increase of the 3782 cm⁻¹ (VHF) peak with the increase of the catalytic activity was clear. Concomitantly the 3605 cm⁻¹ peak (Si-OH-Al) decreased and the 3745 cm⁻¹ peak (silanol groups) increased. Our IR data, based on dry- and steam-activated zeolite Beta samples, support these observations. It is obvious that water is essential during the activation of zeolite Beta to create a (partially) hydrolysed aluminium species that functions as the precursor for the MPV active site.

An important question to be answered is: 'can the catalytic activity be due to the presence of extra-framework aluminium species?' We think not. In this respect, it is essential to mention that aluminium-free titanium Beta is also active in the MPV reaction and displays an almost identical cis-alcohol selectivity (98%) [30-32]. It seems logical to assume that there are analogies between the active sites in titanium Beta and aluminium Beta. The titanium Beta catalyst could be regenerated up to 100 times without any change in the activity and the selectivity. Additionally, the UV-Vis spectrum showed that the titanium remained in tetrahedral coordination in the zeolite framework after regeneration. In our view, this proves that the active titanium sites are framework atoms [31,32] Extrapolating this to aluminium Beta suggests that the catalytically active aluminium species is also part of the framework. The reduction of the catalytic activity upon adsorption of ammonia supports the idea of a Lewis acidic framework aluminium site as well.

Formation of large amounts of alumina species from a high-silica zeolite such as Beta is not expected. Furthermore, if aluminium-rich phases were present and catalytically active, they would be expected to display an activity and stereo-selectivity that resembles USY or amorphous silica-alumina (ASA) samples (10% cis-alcohol) [9]. Cationic EF-Al species which act as charge compensators are not confined to the zeolite pores and can also be present at the external surface. The high stereo-selecitivity and the fact that the external surface proved to be catalytically inactive for the MPV reaction [9] points to a reaction occurring in the internal pore system.

If EF-Al (present in steamed samples) is the active species, then a reduction of the catalytic activity should be observed after removal of the EF-Al. To test whether EF-Al could be removed selectively by applying an 0.01 M HNO₃ aqueous solution as described by Bourgeat-Lami et al. [3], a steamed (H)Beta 1 450(6h)w30 sample was subjected to an acid wash at RT; as a reference an unsteamed (H)Beta 1 450(1h)dry sample was given the same treatment. Both samples proved to be catalytically inactive (conversion after 24h: 3%) and the elemental analysis gave identical Si/Al ratios of 30. The XRD of both samples was deteriorated indicating a loss of long-range ordering and
the N₂-BET analysis showed a reduction of the surface area to 500 m²/g (-160 m²/g) for both samples; mesopores were not detected. Clearly, EF-Al was not removed selectively and we were unable to make a distinction between framework and non-framework aluminium.

The presence of extra-framework species becomes indirectly apparent by the cis-4-tert-butylcyclohexanol selectivity. As reported by Creighton et al. [9], the cis-alcohol selectivity can be increased from 95% up to 99% by partially (~60%) replacing the protons by large cations (K⁺, Rb⁺, Cs⁺). It was suggested that the large cations limited the available micropore volume to such an extent that the formation of the bulky trans-alcohol was even more suppressed. We observed that the more active zeolite Beta samples (steam-activated) displayed cis-alcohol selectivities of up to 98%, whereas the less active samples (dry activated) gave 94% cis-alcohol selectivities. We therefore propose that in steamed Beta samples extra-framework species act in a manner analogous to that exerted by large alkali cations in Beta.

Taking all the above into consideration, we propose a partially hydrolysed framework aluminium as the precursor for the catalytic active species, as indicated in Figure 14. Based on the very high stereo-selectivity we think that only one type of aluminium site is responsible for the catalytic activity. Only a part of the aluminiums present will undergo the transformation, presumably those which are in framework positions under strain e.g. are part of a four-ring in the structure (in Beta five four-rings are connected in an S-shape).

Upon heating, ammonia is released and the remaining proton is transferred to another oxygen. At this point the framework becomes deformable; if instead of the ammonium ion a metal-cation was present, the aluminium would be locked into its tetrahedral coordination. The presence of some water may facilitate the breaking of a Si-OH-Al bond, forming a silanol group and an aluminium connected to three framework silicon atoms and bearing a water molecule. The aluminium atom probably inverts its coordination geometry upon the coordination of water. Instead of being 'buried' within the larger oxygen framework atoms it is now exposed into the zeolite pore and thus becomes available to other ligands like water or reactants. If the heating (activation) is stopped at this point and water is adsorbed at room temperature, an octahedrally coordinated framework aluminium may be formed and observed by ^{27}Al MAS NMR. On the other hand, if ammonia is adsorbed, the process may be reversed by an equilibrium shift and finally only tetrahedral aluminium will exist. When the heating is continued and some water is present in the pores (to maintain water adsorbed on to the
aluminium) then an Al-O-Si bond may be hydrolysed and a new tetrahedrally coordinated aluminium species forms which bears the hydroxyl group vibrating at 3782 cm\(^{-1}\) (VHF). This species was also suggested by Kiricsi et al. as a possible explanation for the observed VHF band [7]. Formation of this new aluminium species will result in a decrease of the amount of aluminium able to attain an octahedral coordination and thus in a decrease of the Oh-Al peak in the \(^{27}\)Al MAS NMR spectrum (Figure 10). We mention again that the NMR data were obtained on hydrated samples and therefore differ from the actual catalyst. From Table 2 it is seen that absorption of ambient water at room temperature already reduces the catalytic activity which suggests that some active sites are annihilated, possibly by an equilibrium shift towards octahedral aluminium. Therefore, the \(^{27}\)Al MAS NMR spectrum of the (H)Beta1 550(3d)w30 sample may indicate more octahedral aluminium to be present than in the actual catalyst.

Upon reaction of this new aluminium species with 2-propanol, an Al-isopropoxide species is formed which will act as the initial catalyst in the MPV reaction (Al(OiPr)\(_3\)) is an MPV catalyst [9]). Coordination of the ketone to the Al-isopropoxide species initiates the MPV reaction-cycle. Subsequent hydride transfer, acetone elimination and finally alcoholysis of the product alcohol and concomitantly regeneration of the active site complete the reaction-cycle, as was proposed recently by van der Waal et al. [32], see Figure 15. The presence of water (as contaminant) in the reaction mixture may (besides the above mentioned) reverse the formation of the isopropoxide species or may prevent the ketone to coordinate, thus inhibiting the reaction [9].
Figure 14. Proposed mechanism for the formation of the catalytically active site (Al-isopropoxide species) in zeolite Beta for the MPV reduction. The dashed line represents the pore-wall with the left side being the empty pore.
Figure 15. Proposed MPV reaction scheme starting with an aluminium-alkoxide species in zeolite Beta.

The nature of the EF-Al remains unclear although it is unlikely to be an octahedrally coordinated species since the steamed samples show a decreased 0 ppm peak intensity. A possible explanation may be the formation of a distorted, tetrahedrally coordinated EF-Al from tetrahedral framework aluminium atoms. The presence of various tetrahedrally coordinated aluminium species makes identification by NMR techniques difficult. Currently, we are extending the (2D) NMR investigations [33]. Also XANES is currently applied to obtain more insight into the various coordination geometries of the aluminium atoms.
4.4 CONCLUSIONS

The catalytic activity of zeolite Beta in the stereoselective Meerwein-Ponndorf-Verley reduction of ketones using secondary alcohols as reductant can be tuned by appropriate pre-treatment. During activation, water is essential to obtain an active catalyst. On the basis of IR, NMR and the catalytic data a partially hydrolysed framework aluminium is proposed as the precursor for the active site. The formation of the initial catalytic site from the precursor is thought to be a lattice attached aluminium-isopropoxide species; its formation can be easily reversed when water is present in the reaction mixture, thus explaining the sensitivity of the reaction towards water. We assume that EF-Al species are present as catalytically inactive species although, by their size, they reduce the amount of trans-alcohol formed in a manner analogous to that previously described for large alkali cations.

Since the specific aluminium site has not been observed unambiguously by either IR or NMR techniques, an additional research employing other techniques seems required to observe the Al-species directly. Currently, EXAFS / XANES is being used [34]. Preliminary results indicate that (NH₄)Beta₁ contains only tetrahedrally coordinated aluminium and upon heating under vacuum, octahedrally coordinated aluminium is formed. When ammonia is again adsorbed the octahedrally coordinated aluminium atoms revert quantitatively to the tetrahedral coordination, which is in full agreement with the $^{27}$Al NMR results. The steamed (H)Beta₁ 550(3d)w30 sample did also contain octahedral aluminium but upon adsorption of ammonia not all the aluminium atoms reverted to the tetrahedral coordination.

The observed phenomena may not be restricted to zeolite Beta alone; for example, the catalytic activity of MCM-22, which under reaction conditions identical to the MPV reaction catalyses the reductive etherification of 4-tert-butylcyclohexanone [35], might also be susceptible to the calcination procedure.
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4.5 REFERENCES

1. J.C. Jansen, E.J. Creighton, S.L. Njo, H. van Koningsveld and H. van Bekkum, 
   3659.
Chapter 4

27. A.P.M. Kentgens, J.A. van Bokhoven, A.L. Roest and D.C. Koningsberger, to be published.
33. J.A. van Bokhoven, A.P.M. Kentgens, P.J. Kunkeler, H. van Bekkum and D.C. Koningsberger, to be published.
34. J.A. van Bokhoven, results obtained at Daresbury Synchrotron Facility, personal communication.
5. THE ZEOLITE CATALYSED CLAISEN REARRANGEMENT OF N-ALLYLANILINE AND THE DIRECT SYNTHESIS OF N-ALLYLANILINE FROM ANILINE AND ALLYL ALCOHOL IN THE GAS PHASE

ABSTRACT

The aromatic amino-Claisen rearrangement (AACR) of N-allylaniline to 2-allylaniline has been performed under gas-phase conditions at 200 °C employing various solid acid catalysts. The selectivity towards 2-allylaniline, and the consecutive cyclized product 2-methylindoline, is predominantly determined by the number and strength of the acid sites. From the catalysts examined, zeolite Beta proved to be the most active. In the direct gas-phase synthesis of N-allylaniline from aniline and allyl alcohol, the formation of N-propylaniline is an important side reaction. A mechanism is proposed which accounts for the formation of N-propylaniline and the strong deactivation observed.

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5.1 INTRODUCTION

The [3,3]-sigmatropic rearrangement of vinyl and allyl ethers, known as the Claisen rearrangement, is a useful method for regiospecific carbon-carbon bond formation. The reaction has been extensively studied both from mechanistic and synthetic points of view [1-3]. By contrast, the nitrogen analogue of the Claisen-rearrangement, the amino-Claisen rearrangement or 3-aza-Cope rearrangement, has received much less attention due to several limitations including the need of temperatures as high as 250-280 °C. Under these conditions, N-allylamines tend to undergo thermal decomposition accompanied by tar formation, as was reported for N-allylaniline [4], the simplest aromatic N-allylamine. The first recorded example of an (aromatic) amino-Claisen rearrangement was the thermally induced rearrangement of N-allyl-1-naphthylamine into 2-allyl-1-naphthylamine at 260 °C (see Figure 1). Following a thorough kinetic investigation on the Claisen rearrangement of allyl ethers, the researchers successfully predicted the smooth rearrangement for this amine compound [5].

![Figure 1](image)

**Figure 1.** The first recorded example of a thermally induced amino-Claisen rearrangement: N-allyl-1-naphthylamine into 2-allyl-1-naphthylamine at 260 °C [5].

They concluded that the energy of the cyclic transition state is lowest when the allyl/vinyl moiety is coplanar with the aromatic ring. In aromatic allylamines more energy is required to bring about coplanarity than in allyl ethers, since the nitrogen atom bears a hydrogen atom. Inhibition of the rotation of the amino hydrogen atom also leads to a more negative activation entropy. The difficulty of the occurrence of the amino-Claisen rearrangement for N-allylaniline could now be explained: the activation energy for the thermally induced rearrangement was estimated to be 40 kcal/mol and, together with the negative activation entropy, would therefore require very high temperatures. At these temperatures, decomposition, with a positive entropy, becomes dominant.

Several years later also non-aromatic amine systems were found which underwent the thermally induced rearrangement smoothly [6]. It is mentioned here that
the reported amino-Claisen rearrangements were performed in sealed tubes to prevent exposure to the atmosphere.

Catalysts often permit the occurrence of an aromatic amino-Claisen rearrangement (AACR) that is thermally inaccessible. Lewis acids, like anhydrous ZnCl₂, AlCl₃, and TiCl₄, were applied in stoichiometric amounts with varying success [1,7-9]. The most efficient and generally applicable Lewis acid catalyst reported to date is BF₃-diethyl etherate e.g. N-allylaniline rearranged to 2-allylaniline in 73% yield with BF₃-OEt₂ in refluxing p-xylene, compared with 40% using ZnCl₂ [1,10].

Brønsted acids have also been used extensively to promote the AACR [1]; the rearrangement is then often followed by cyclisation to yield indolines and, after (in situ) dehydrogenation of the latter, indoles [11-13]. Thus, the AACR and subsequent cyclisation of aromatic allylamines offers a means for the synthesis of aromatic cyclic amines. In Figure 2 the AACR of N-allylaniline followed by cyclisation into 2-methylindoline is shown. Cyclisation towards a six-membered ring, resulting in 1,2,3,4-tetrahydroquinoline, is less likely but has been observed in some cases.

![Figure 2](image_url)

**Figure 2.** Amino-Claisen rearrangement of N-allylaniline followed by cyclisation. The asterisk indicates the inversion of the allyl group.

The coordination of the nitrogen to a Lewis acid or the formation of an ammonium ion induces a positive charge which accelerates the reaction; the lowered activation enthalpy being a consequence of charge delocalization in the transition state and inhibition of nitrogen lone pair delocalization in the ground state [1,8]. Electron-withdrawing groups within the molecule itself also facilitate the rearrangement [10]. A detailed mechanism is given in Figure 3, which also explains the decomposition to anilines and concomitant intermolecular allyl transfers via a Friedel-Crafts type reaction.
Figure 3. Mechanism of the Brønsted acid catalysed amino-Claisen rearrangement according to [1]. \( R_1 \) and \( R_2 \) are alkyl groups or hydrogens.

A disadvantage of the above mentioned catalysts is that they are not recyclable. Recently, however, zeolites H-Beta and H-Mordenite were reported as heterogeneous catalysts for the Claisen rearrangement of allyl phenyl ethers using benzene as the solvent [14,15] and in the photo-Claisen rearrangement of allyl phenyl ether with H-ZSM-5 [16]. Besides easy separation of the catalyst from the reaction mixture, these catalysts can be regenerated by a simple calcination. In an attempt to use these zeolites as catalysts under similar conditions in the AACR of N-allylaniline, we only obtained a trace amount of 2-allylaniline. Application of higher boiling solvents (e.g. replacement of benzene by \( p \)-xylene) did not result in an increased conversion of N-allylaniline; probably the amine interacts too strongly with the acid sites thus making desorption difficult at these temperatures. However, as will be described in this chapter, the use of higher temperatures under continuous-flow vapour-phase conditions is a new and interesting method for performing the AACR of N-allylaniline. At the same time, the work-up procedure is significantly simplified as no catalyst and solvent separation is needed.

The preparation of N-allylamines, \textit{via} classical routes, involves the condensation reaction between a halo-allyl reactant (e.g. allyl bromide) and the amine [5]. As side product HX (e.g. HBr) is formed in equimolar amounts, which needs to be neutralised, resulting in an undesirable salt production. Clearly, this is not a very efficient synthesis.
Also the selectivity to the mono N-alkenylated product is difficult to control. Attempts to improve the selectivity towards the mono N-alkenylated product using zeolites have been undertaken for p-nitroaniline [17].

Newer homogeneously catalysed routes to allylamines have appeared very recently; for example the Fe(II,III) mediated allylic N-functionalization of alkenes by aryloxyxylamines [18]. Also the Mo(VI) peroxo complex-catalysed allylic amination of alkenes by aryldimethyl sulfates as the oxidant has been reported [19]. The chemoselective allylation of imines in the presence of aldehydes via a palladium catalysed allylstannane reaction is a totally different approach [20]. However, by-product formation is substantial for these routes and for the latter two examples expensive reactants as well as stoichiometric or even excess amounts of 'catalyst' need to be used.

Both from a practical and environmental point of view, it is desirable to seek for an alternative. An interesting example of the modern approach is the vapour-phase N-methylation of 4(5)-methylimidazole with methanol over H-ZSM-5, H-Y and H-Beta zeolites [21]. Classical routes employed methyl halides or dimethyl sulfate, both being toxic and corrosive, and more than a stoichiometric amount of a strong base was needed. Besides easy product recovery and less aggressive reactant handling, the zeolite-based systems additionally offer regioselectivity. In the methylation over (H)Beta and (H)ZSM-5, 1,4-dimethylimidazole was the predominant product while zeolite (H)Y was selective towards the 1,5-dimethylimidazole isomer. However, it was mentioned explicitly that the different selectivities found were not due to pore-induced restrictions but rather to the difference in acidity between the zeolites; strongly acidic but non-microporous catalysts gave results identical to (H)Beta and (H)ZSM-5.

Returning to N-allylaniline, the direct selective amination of aniline with allyl alcohol is an option. Then, the only side-product is water, which is non-toxic and needs not to be neutralised. Interestingly, heterogeneously catalysed condensation reactions employing aniline and simple alcohols like methanol and ethanol have already been examined by various research groups [22-25]. Alkylation of aniline with methanol, either in the aromatic ring or at the nitrogen atom, catalysed by acidic and basic zeolites has been reported to depend on several parameters such as the temperature, acid or base strength of the catalysts and the molar ratio of the reactants. Relatively low temperatures (~250 °C) favour N-alkylation, whereas higher temperatures favour ring-alkylation, either by direct alkylation or by rearrangement of N-alkylated anilines. Also medium strength acids and bases are preferred for N-alkylation while strong acids will give predominantly ring-alkylation. The use of allyl alcohol as nitrogen alkylating agent was reported very recently by Göbölös et al. in the allylation of ammonia [26]. It should be noted, however, that the use of higher alcohols (i.e. higher than methanol) increases the
chance that dehydration of the alcohol becomes an important side-reaction, especially when acidic catalysts are used. The ease of dehydration increases going from a primary to a secondary alcohol and the use of high temperatures will also facilitate dehydration. When the acid sites are occupied by the nitrogen base, dehydration may be suppressed. On the other hand, too strong adsorption of the base will hinder desorption and consequently the reaction will be retarded.

In perspective of the above mentioned AACR of N-allylaniline, it would be interesting to synthesize N-allylaniline directly from aniline and allyl alcohol (as depicted in Figure 4) and subsequently convert it into 2-allylaniline via the AACR of N-allylaniline. When the 2-allylaniline is cyclized, this might become a new route towards 2-methylindoline. Dehydrogenation of the latter product opens the way towards the synthesis of substituted indoles, see also Chapter 6.

\[
\begin{align*}
\text{aniline} & \quad + \quad \text{allyl alcohol} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{N-allylaniline}
\end{align*}
\]

**Figure 4.** Direct synthesis of N-allylaniline from aniline and allyl alcohol.

Compared with saturated alcohols, allyl alcohol is more reactive due to the resonance stabilization of the allyl cation. On the other hand, allyl alcohol contains two functional groups thus making it a difficult reagent for selective alkylation; two aromatic molecules may react with one allyl alcohol molecule resulting in diarylpropanes [27]. Other side reactions that may occur are self-condensation of allyl alcohol towards diallyl ether and dehydrogenation of allyl alcohol forming acrolein and hydrogen [28]. The potential catalyst for the direct condensation between aniline and allyl alcohol should preferably not catalyze the formation of acrolein since then the aniline present will, via a Michael-type and enamine type condensation, react with acrolein resulting in (non-desorbing) polymers which will deactivate the catalyst. According to the results of Hutchings and Lee [28] on the reaction products from the self-condensation of allyl alcohol, basic faujasites (LiNaY, NaY, KNaY and Cs-NaY) may have potential: they show low acrolein formation and are active in the self-condensation of allyl alcohol towards diallyl ether. They might therefore also be active in the condensation between different types of molecules like allyl alcohol and aniline.
In this chapter the application of zeolites and amorphous silica-alumina in the synthesis of 2-allylaniline and 2-methylindoline from aniline and allyl alcohol via N-alkenylation and subsequent AACR is described.

5.2 EXPERIMENTAL

Reactants and products

N-allylaniline (NAA) (95% purity) was obtained from Acros. Allyl alcohol (AA) was supplied by Fluka. Aniline (A) was purified by distillation prior to use (colourless liquid). 2-Allylaniline (2AA) and N-propylaniline (NPA) were obtained by column chromatography (silica gel, eluent: hexane/ethyl acetate = 9:1) from the combined condensates of several reaction runs and analysed by $^1$H-NMR and GC-MS. N-propylaniline was also obtained via the direct condensation of aniline with 1-propanol using silica-alumina as the catalyst at 160 °C in the vapour-phase reactor (mol ratio aniline:1-propanol = 1:3). 2-Methylindoline (2MIE), 2-methylindole (2MIL) and 1,2,3,4-tetrahydroquinoline (THQ) were purchased from Aldrich.

Characterisation

(bp = base peak, Bp = boiling point)

N-allylaniline (NAA); $^1$H-NMR: 3.77 ppm (doublet, ArNH-CH$_3$), 5.16 ppm and 5.28 ppm (both doublet of quartets, N-CH$_2$-CH=CH$_2$), 5.96 ppm (multiplet, N-CH$_3$-CH=CH$_2$), 6.96 ppm (mono-substituted aryl ring pattern). (El) MS: m/z = 77, m/z = 106 (bp), m/z = 132 and m/z = 133 (mol. mass). Bp: 218 °C.

2-allylaniline (2AA); $^1$H-NMR: 3.35 ppm (doublet, Ar-CH$_3$-CH=CH$_2$), 5.05 and 5.07 ppm (both doublet of quartets, Ar-CH$_2$-CH=CH$_2$), 5.90 ppm (multiplet, Ar-CH$_3$-CH=CH$_2$), 6.90 ppm (o-substituted aryl ring pattern). (El) MS: m/z = 77, m/z = 106, m/z = 118, m/z = 132 and m/z = 133 (mol. mass, bp).

N-propylaniline (NPA); $^1$H-NMR: 0.95 ppm (triplet, ArN-CH$_2$CH$_2$CH$_3$), 1.65 ppm (multiplet, ArN-CH$_2$CH$_2$CH$_3$), 3.10 ppm (triplet, ArN-CH$_2$CH$_2$CH$_3$) and 7.00 ppm (mono-substituted aryl ring pattern). (El) MS: m/z = 77, m/z = 106 (bp) and m/z = 135 (mol. mass).

2-methylindoline (2MIE); $^1$H-NMR: 1.20 ppm (doublet, -CH$_3$), 2.55 ppm (doublet of doublets), 3.05 ppm (doublet of doublets), 3.90 ppm (multiplet) and 6.90 ppm (o-substituted aryl ring pattern). (El) MS: m/z = 91, m/z = 118 (bp) and m/z = 133 (mol. mass). Bp: 228 °C.
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2-methylindole (2MIL); \( ^1\)H-NMR (Aldrich): 2.3 ppm (singlet, -CH\(_3\)), 6.15 (singlet) and 7.2 ppm (o-substituted aryl ring pattern). (EI) MS: \( \text{m/z} = 130 \) (bp) and \( \text{m/z} = 131 \) (mol. mass). Bp: 273 °C.

1,2,3,4-tetrahydroquinoline (THQ); \( ^1\)H-NMR (Aldrich): 1.9 ppm (multiplet), 2.75 ppm (multiplet), 3.25 ppm (multiplet), 6.4 (dd), 6.6 (dd) and 6.9 (o-substituted aryl ring pattern). (EI) MS: \( \text{m/z} = 118 \), \( \text{m/z} = 132 \) (bp) and \( \text{m/z} = 133 \) (mol. mass). Bp: 249 °C.

Catalysts

Zeolite Beta was synthesized according to the Wadlinger procedure [29]. After calcination in air at 540 °C for 10 h, the material was ion-exchanged once using 0.1 M aqueous NH\(_4\)NO\(_3\) at room temperature to obtain the pre-acid ammonium form, or it was ion-exchanged overnight using 1 M aqueous sodium or potassium chloride to obtain the corresponding metal-ion exchanged sample. The procedure for the ammonia calcination of the a.s. Beta sample is described in Chapter 4. This sample was sodium exchanged using 1M aqueous NaCl to obtain a Na/Al ratio of 1.0.

Mordenite (NaMor) was kindly donated by PQ-zeolites. Threefold ammonium exchange using 0.1 M aqueous NH\(_4\)NO\(_3\) at room temperature was applied to obtain the pre-acid ammonium form, see also Chapter 3. Dealuminated mordenite (3-DDM) was prepared according to a patent of Dow Chemical [30], see also Chapter 3.

The Zn(II)-exchanged Faujasites were obtained by ion-exchanging overnight the parent NaX and NaY using 0.2 M aqueous ZnCl\(_2\) at room temperature.

Amorphous silica-alumina (ASA, HA-HPV-707) was kindly donated by AKZO-Nobel. USY was kindly provided by the Shell Research and Technology Centre Amsterdam.

Activation of the catalysts was performed within the reactor tube in a dry nitrogen flow. When only water needed to be removed, the activation temperature did not exceed 200 °C. To obtain the acid form of the ammonium exchanged zeolites a higher activation temperature of 400 °C was employed. For the amorphous silica-alumina samples two different activation procedures were applied to influence the amount of Lewis-sites [31].
Vapour-phase reactor

The fixed-bed continuous down-flow reactor consisted of a vertically mounted borosilicate glass tube (7 mm i.d.) heated by a fluidized bed oven. To be able to run the reactor under plug-flow conditions, the catalysts were pelletized and subsequently crushed and sieved to collect the particles in the range of 0.7-1.0 mm. One gram of catalyst was used to obtain a sufficiently high catalyst bed. To exclude influences of metallic components (tubing, connectors etc.) and oxide-phases present on these components, all auxiliary reactor parts were made of glass and heated externally to ca. 200 °C to prevent condensation of reactants and products. The reactant mixtures were pumped into a stream of pre-heated carrier gas (nitrogen) by means of a motor-driven syringe pump or a HPLC pump. All reactions were run under atmospheric pressure. Usually 1 vol.% of N-allylaniline or aniline and allyl alcohol was used in a total gas stream of 50 ml/min (1.22 mmol/h per g_cat). The AACR reactions were performed at a temperature of 200 °C, the condensation reactions between aniline and allyl alcohol were performed in the range of 140-200 °C. Products were collected in a water-cooled condensation vessel and analysed by GC-MS. Samples of the reactor effluent were taken regularly by an on-line autosampler and analyzed by a GC equipped with a CP SIL-19 CB column (50 m, 0.53 mm i.d., N2 carrier gas) and FID (selectivity = mol product formed per mol reactant converted). In Figure 5 the vapour-phase reactor is displayed schematically.
Figure 5. Schematic diagram of the 'all-glass' vapour-phase reactor used.

_N.B. 1._ To prevent back-mixing and turbulent flow in the catalyst bed, the following conditions for plug-flow have to be obeyed [32]: \( L/d_p > 50 \) (\( L \) = height of the catalyst bed and \( d_p \) = diameter of the catalyst particles) and \( 6 < D/d_p < 10 \) with \( D \) = diameter of the catalytic bed, which, in this case, equals the diameter of the reactor tube (7 mm). The particle diameter was between 0.7 - 1.0 mm, and 1 g of catalyst was usually sufficient to obtain a bed-height of approx. 50 mm.

_N.B. 2._ GC analysis of larger amines is difficult; apolar columns are often not suited, while polar columns cannot be brought to high enough temperatures to assure removal of all components, such as heavy by-products. Moreover, amines, and especially imines, are often sensitive to high temperatures at which they start to decompose. The column applied here is therefore a compromise: it has a medium polarity and can be heated to 300 °C which is high enough. This is essential since no filter is present between the gas-stream from which the samples are taken and the GC column.
5.3 RESULTS AND DISCUSSION

Performing the AACR of N-allylaniline under continuous vapour-phase conditions has several advantages such as easy recovery of products and catalyst and the possibility to influence the amount of consecutive products by changing the contact times. A consequence of working under vapour-phase conditions is the limitation to relatively volatile components.

An overview of the investigated catalysts with their compositions and activation temperatures is given in Table 1.

Table 1. Catalyst compositions as determined by flame AAS and activation temperatures.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Si/Al</th>
<th>Na/Al</th>
<th>K/Al or Zn/Al₂</th>
<th>activation (°C, min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Beta</td>
<td>11.6</td>
<td>0.06</td>
<td></td>
<td>400, 30</td>
</tr>
<tr>
<td>Na-Beta-A</td>
<td>11.6</td>
<td>0.96</td>
<td></td>
<td>200, 30</td>
</tr>
<tr>
<td>Na-Beta-B</td>
<td>11.6</td>
<td>1.02</td>
<td></td>
<td>200, 30</td>
</tr>
<tr>
<td>K-Beta</td>
<td>11.6</td>
<td></td>
<td>0.89</td>
<td>200, 30</td>
</tr>
<tr>
<td>Na-Y</td>
<td>2.4</td>
<td>0.94</td>
<td></td>
<td>200, 30</td>
</tr>
<tr>
<td>Na-X</td>
<td>1.3</td>
<td>1.00</td>
<td></td>
<td>200, 30</td>
</tr>
<tr>
<td>H-Na-Y</td>
<td>2.7</td>
<td>0.20</td>
<td></td>
<td>400, 30</td>
</tr>
<tr>
<td>USY</td>
<td>20</td>
<td></td>
<td></td>
<td>200, 30</td>
</tr>
<tr>
<td>Zn-Na-Y</td>
<td>2.4</td>
<td>0.35</td>
<td>0.72</td>
<td>200, 30</td>
</tr>
<tr>
<td>Zn-Na-X</td>
<td>1.3</td>
<td>0.30</td>
<td>0.76</td>
<td>200, 30</td>
</tr>
<tr>
<td>Na-Mor</td>
<td>6.8</td>
<td>0.90</td>
<td></td>
<td>200, 30</td>
</tr>
<tr>
<td>H-Mor</td>
<td>6.8</td>
<td>0.02</td>
<td></td>
<td>400, 30</td>
</tr>
<tr>
<td>3-DDM</td>
<td>38</td>
<td>0.02</td>
<td></td>
<td>200, 30</td>
</tr>
<tr>
<td>HA-HPV-707</td>
<td>•</td>
<td></td>
<td></td>
<td>#</td>
</tr>
</tbody>
</table>

- Amorphous Silica-Alumina (ASA), 25 wt% Al₂O₃ on silica.
# 200°C, 30 min or 480°C, 120 min, see text.
Chapter 5

Amino-Claisen rearrangement of N-allylaniline

To test whether the Lewis or Brønsted acid sites are the most important sites for the AACC, the catalysts were pretreated in various ways to influence the amount of these sites; see Table 1. Zeolite Beta was calcined in air or ammonia to influence the amount of Lewis sites. Also different cations (Na or K) were introduced. Zeolites NaX and NaY were ion-exchanged with Zn\(^{2+}\) to introduce Lewis acidity and to compare the selectivities with the classical ZnCl\(_2\) catalyst. Zeolite Mordenite was dealuminated to 'open up' the uni-dimensional structure to improve access to the micropores (see also Chapter 3). The (non-microporous) HA-HPV-707 was activated at different temperatures to vary the amount of Lewis sites (see below); it also served as a comparison with the zeolites to test whether the micropores actually offer an advantage for this reaction [21].

In Table 2 the selectivities are listed for the AACC of N-allylaniline at 4h on stream at a temperature of 200 °C. Lower temperatures resulted in heavy fouling due to condensation of the reactant and its corresponding products.

The catalysts can be divided by the type of sites present: i) weak Brønsted (acidic hydroxyl groups) and Lewis sites and ii) strong Brønsted and Lewis sites. Overall, the strong Brønsted catalysts (marked with an asterisk) are the most active. Interestingly, the activity (and the related selectivity) for the amorphous silica-alumina's depends heavily on the pretreatment; a dry, high temperature activation (480 °C, 120 min) results in a far more active catalyst than an activation at 200 °C for 30 min. Clearly, the amount of active sites is substantially increased. It was reported that a higher activation temperature results in partial dehydroxylation of the surface, thereby converting Brønsted sites into Lewis sites [31].

In view of the results described in Chapter 4 on the activation procedure of zeolite Beta, it was investigated whether the pretreatment of zeolite Beta had an impact on the catalytic performance in the AACC of N-allylaniline. For the sodium-exchanged Beta samples, sample A prepared by air-calcination (Na/Al=0.96) and sample B by ammonia calcination (Na/Al=1.02), it was expected that sample A would show a higher activity than sample B, due to the presence of Lewis-acidic aluminum sites. The air-calcined and potassium-exchanged Beta sample (K/Al=0.89) was expected to be more active than both sodium-exchanged samples. However, all three Beta samples showed the same activity, stability and selectivity. A possible explanation may be that the presence of Lewis-acidic sites becomes of less importance when (strong) Brønsted sites are also present.
Table 2. Results of the solid-acid-catalysed vapour-phase AACR of N-allylaniline. Conversions and selectivities to the main products (4h T.O.S.). Conditions: 1 % NAA in 50 ml N₂/min (1.22 mmol/h per g_cat.), 200 °C. Selectivity (%) = mol product formed per mol reactant converted, bar (-) indicates no trace detected.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>2AA (%)</th>
<th>2MIE (%)</th>
<th>A (%)</th>
<th>conversion (%)</th>
<th>conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4h T.O.S.</td>
<td>2h / 6h T.O.S.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-Beta *</td>
<td>30</td>
<td>55</td>
<td>2</td>
<td>100</td>
<td>100 / 99</td>
</tr>
<tr>
<td>Na-Beta-A</td>
<td>62</td>
<td>3</td>
<td>7</td>
<td>33</td>
<td>75 / 24</td>
</tr>
<tr>
<td>Na-Beta-B</td>
<td>65</td>
<td>7</td>
<td>8</td>
<td>32</td>
<td>75 / 24</td>
</tr>
<tr>
<td>K-Beta</td>
<td>63</td>
<td>7</td>
<td>9</td>
<td>41</td>
<td>70 / 24</td>
</tr>
<tr>
<td>Na-Y</td>
<td>54</td>
<td>-</td>
<td>7</td>
<td>60</td>
<td>63 / 48</td>
</tr>
<tr>
<td>Na-X</td>
<td>68</td>
<td>5</td>
<td>5</td>
<td>81</td>
<td>90 / 75</td>
</tr>
<tr>
<td>H-Na-Y *</td>
<td>65</td>
<td>15</td>
<td>1</td>
<td>90</td>
<td>100 / 50</td>
</tr>
<tr>
<td>USY *</td>
<td>53</td>
<td>9</td>
<td>5</td>
<td>60</td>
<td>80 / 52</td>
</tr>
<tr>
<td>Zn-Na-Y</td>
<td>50</td>
<td>0</td>
<td>&lt;1</td>
<td>5</td>
<td>30 / &lt;1</td>
</tr>
<tr>
<td>Zn-Na-X</td>
<td>25</td>
<td>8</td>
<td>10</td>
<td>28</td>
<td>90 / &lt;1</td>
</tr>
<tr>
<td>Na-Mor</td>
<td>74</td>
<td>-</td>
<td>2</td>
<td>32</td>
<td>58 / 30</td>
</tr>
<tr>
<td>H-Mor *</td>
<td>66</td>
<td>4</td>
<td>2</td>
<td>72</td>
<td>93 / 50</td>
</tr>
<tr>
<td>3-DDM *</td>
<td>60</td>
<td>7</td>
<td>4</td>
<td>12</td>
<td>40 / &lt;1</td>
</tr>
<tr>
<td>ASA act. 200 °C *</td>
<td>44</td>
<td>-</td>
<td>11</td>
<td>32</td>
<td>57 / 31</td>
</tr>
<tr>
<td>ASA act. 480 °C *</td>
<td>57</td>
<td>15</td>
<td>5</td>
<td>89</td>
<td>96 / 84</td>
</tr>
</tbody>
</table>

* strong Brønsted acid (after activation)

(2AA = 2-allylaniline, 2MIE = 2-methylindoline, 2MIL = 2-methylindole, A = aniline, ASA = HA-HPV 707)

The proposed Lewis acidic aluminum in zeolite Beta, see Chapter 4, coordinates a Brønsted acidic hydroxyl group. The acid strength of this hydroxyl group is still a matter of debate: some researchers report it to be far more acidic than silanol groups [33], others, however, think of it as being less acidic than a silanol group [34]. Then, the three catalysts will only differ in the amount of Brønsted sites present and, thus, be effectively equal. The (H)Beta sample, containing the highest amount of Brønsted sites (Na/Al=0.06), is the most active catalyst, see also Figure 6. The very high external surface acidity of zeolite Beta will contribute to the high activity [35]. The decrease in activity and selectivity to 2-methylindoline (2MIE) with concomitant increase in 2-allylaniline (2AA) selectivity, up to 86%, is explained by catalyst deactivation:
deposition of heavy, non-desorbing compounds leaves few active sites available for the consecutive cyclisation of 2-allylaniline to 2-methylindoline. Despite its high activity, the degradation to aniline is low. A small amount of dehydrogenated 2-methylindoline, 2-methylindolc (2MIL), was also observed.

Notes:
1. Selectivities to products resulting from consecutive reactions are related to the conversion, and thus indirectly to the deactivation [32].
2. The strength of adsorption depends on both the structure of reactants and products and the catalyst; thus, a basic reactant will adsorb strongly on an acidic catalyst. The relatively low basicities of aniline (pKb=9.37) and N-allylaniline (pKb=9.83) are therefore an advantage. Also the indole and indoline system are weak bases. However, heavier (e.g. transalkylated, see introduction) products adsorb more strongly and the catalyst may become partly deactivated.
3. Transalkylation is indirectly observed via the detection of aniline as by-product, which can desorb from the catalyst.

The Zn$^{2+}$-exchanged Faujasites appear to deactivate fast combined with a low selectivity to 2-allylaniline, especially for the ZnNaX sample. The introduced Zn$^{2+}$ actually decreases the activity compared to the parent sodium form, possibly due to pore-narrowing and consequently slowing down the intra-zeolitic diffusion. The activity for the NaX sample (Na/Al=1.00) must be solely due to the mildly acidic silanol groups. The Na-Y sample (Na/Al=0.90) surprisingly shows a lower activity which is even combined with a lower 2-allylaniline selectivity. The strongly acidic H-Na-Y sample showed, as was to be expected, a high initial activity combined with an increased selectivity towards the ring-closed product, 2-methylindoline. Again, as was observed with the strongly acidic zeolite Beta, aniline selectivity (and thus transalkylation) was low.

The Brønsted acidic mordenite (H-Mor) is, in line with the other catalysts, more active than the parent sodium form (Na-Mor). The dealuminated mordenite (3-DDM) is much less active, probably due to the higher Si/Al ratio and thus less Brønsted acid sites. However, the reduction in activity is less than would be expected on basis of the reduction of the number of acid sites alone: the more open structure of the material increases the diffusion rate and thereby partly compensates the loss of Brønsted acid sites. Also, the material has become more hydrophobic which probably increases the sorption of the reactant.
All the catalysts suffer from severe deactivation and the spent catalysts are found to be slightly coloured. TGA of a sample of completely deactivated ZnNaX sample showed it to contain 30 wt.% of deposited material.

No specific advantage of the use of zeolites was observed, merely the presence and number of strong Brønsted sites determines the activity and thereby the selectivity.

![Conversion and selectivity graph]

**Figure 6.** Conversion and selectivities in the AACR of N-allylaniline catalysed by zeolite (H)Beta at 200 °C. (2AA = 2-allylaniline, 2MIE = 2-methylindoline, 2MIL = 2-methylindole)
Direct condensation between aniline and allyl alcohol

With two reactants, aniline and an alcohol, and at the lower temperatures required, it did not prove possible to obtain sufficiently reliable GC data for other than semi-quantitative conversions to be obtained, while instead of product selectivities, molar percentages (normalised to 100%) in the product stream are given. This nevertheless proves sufficient to provide insights into these condensation reactions between aniline and alcohols higher than methanol in the gas-phase. Note that the actual product selectivities will be lower than the percentages given since in all experiments deactivation was significant.

![Graph](image)

**Figure 7.** Catalytic behaviour of HA-HPV-707 (activated at 200 °C) at 170 °C in the condensation of aniline (1%) and allyl alcohol (1%) in nitrogen as the carrier-gas (50 ml/min). AA = allyl alcohol, A = aniline, NAA = N-allylaniline, 2AA = 2-allyl-aniline, NPA = N-propylaniline, THQ = 1,2,3,4-tetrahydroquinoline, NMA = N-methylaniline, NEA = N-ethylaniline.

Preliminary results on the condensation of aniline and allyl alcohol showed that indeed N-allylaniline is formed, although much lower temperatures than required for the AACR (200 °C) are necessary to avoid the formation of too many by-products, especially di-alkylated aromatics (mol.mass=173) and partially hydrogenated
compounds (several compounds with mol. mass =175 have been observed with MS). Also N-methylaniline (NMA) and N-ethylaniline (NEA) were observed at higher temperatures, see Figure 7 and 8. Desorption becomes difficult at low temperatures and the activity drops accordingly.

From the catalysts examined (see Table 1), HA-HPV-707 and zeolite (H)Beta have the highest potential with widely differing selectivities; the basic faujasites mentioned before (NaY, KY and CsNaX) proved to be inactive or deactivate at a very high rate. When using HA-HPV-707 as the catalyst, the main side-product is N-propylaniline (NPA), which becomes the major product at increasing time on stream (see Figure 7, 9 and 10).

![Chemical Reaction Diagram](image_url)

**Figure 8.** Catalytic behaviour of (H)Beta at 170 °C in the condensation of aniline (1%) and allyl alcohol (1%) in nitrogen as the carrier-gas (50 ml/min). AA = allyl alcohol, A = aniline, 2AA = 2-allylaniline, 2MIE = 2-methyl-indoline, NPA = N-propylaniline, 2MIL = 2-methylindole.
Figure 9. Catalytic behaviour of HA-HPV-707 (activated at 200 °C) at 140 °C in the condensation of aniline (1%) and allyl alcohol (1%) in nitrogen as the carrier-gas (50 ml/min). AA = allyl alcohol, A = aniline, NAA = N-allylaniline, NPA = N-propylaniline, THQ = 1,2,3,4-tetrahydroquinoline.

The (increasing) formation of N-propylaniline (NPA) as by-product in the condensation of aniline and allyl alcohol using HA-HPV-707 as the catalyst is noteworthy and has been investigated in more detail. The reaction between 1-propanol and aniline using HA-HPV-707 as the catalyst at 140 °C was insignificant; only at approximately 160 °C the formation of N-propylaniline (as the sole product) became substantial. Still higher temperatures increased the conversion as well as the formation of propene and di-alkylated products (GC-MS). From this, it was concluded that a reaction pathway via the formation of 1-propanol could be excluded.
Figure 10. Catalytic behaviour of HA-HPV-707 at 140 °C in the condensation of aniline (1%) and allyl alcohol (1%) in nitrogen as the carrier-gas (100 ml/min). AA = allyl alcohol, A = aniline, NAA = N-allylaniline, NPA = N-propylaniline.

Since (noble) metals were absent in the catalysts (and no hydrogen was present in the gas-stream), reduction of the terminal double bond of N-allylaniline seems unlikely. This was confirmed by feeding a 1:1 mixture of N-allylaniline and allyl alcohol over HA-HPV-707 as the catalyst at 140 °C: although alklylation products were detected, no formation of N-propylaniline was observed. The use of a partially deactivated HA-HPV-707 catalyst, previously used in an aniline / allyl alcohol experiment, did not lead to any N-allylaniline reduction.

Therefore, another H-donor was assumed to explain the formation of N-propylaniline; allyl alcohol itself might be operative giving acrolein upon oxidation. (Note that allyl alcohol conversion always exceeded that of aniline.) This might also explain the observed catalyst deactivation: reaction of aniline with acrolein gives a reddish polymeric substance by condensation and Michael additions. Indeed, all deactivated catalysts were red-coloured. This is further supported by the observation that HA-HPV-707 catalyses the formation of acrolein with increasing time on stream when allyl alcohol is the only reactant; this was also reported by Hutchings and Lee for the Brønsted acidic catalysts [28]. However, these authors did not observe/report the formation of 1-propanol so it was concluded that H₂(g) was formed which could not be
detected with the FID of the GC used. Since the acrolein selectivity is a function of the
time on stream it can be assumed that the sites active for hydrogen-transfer have to be
created by materials deposited or other sites present on the catalyst surface need to be
deactivated first before products from (de)hydrogenation reactions can evolve. It was
reported by Munson et al. [36], that the reaction of allyl alcohol-1\textsuperscript{13}C over (strongly
acidic) H-ZSM-5 led to rapid polymerization whereas the (mildly acidic) CsHXM only
gave 1,3 'isotope scrambling'. Extrapolating this, it may be assumed that the stronger
acid sites are poisoned first, whereas the remaining weaker acid sites are able to
catalyse isomerisation and (de)hydrogenation reactions.

In a separate experiment to test whether allyl alcohol can function as reductant in
the MPV reaction [37], employing cyclohexanone and HA-HPV-707 as the catalyst at
140 °C in the gas-phase, it was found that allyl alcohol indeed reduces cyclohexanone
forming acrolein and cyclohexanol, respectively.

Possibly, N-propylaniline is formed by a hydrogen transfer reduction of the
corresponding imine, which is formed by condensation of aniline with propanal.
Propanal may be formed by isomerisation of allyl alcohol. Liquid-phase homogeneously
catalysed reduction of imines with 2-propanol has been reported [38]. We therefore
propose the following mechanism for the formation of N-propylaniline in the gas-phase
condensation between aniline and allyl alcohol, see Figure 11.
Figure 11. Proposed mechanism for the formation of N-propylaniline and the observed deactivation in the gas-phase condensation of aniline and allyl alcohol over acidic catalysts.
Chapter 5

Isomerisation of allyl alcohol results in propanal. Condensation of propanal with aniline gives N-propyldiene-benzene amine, which upon reduction transforms to N-propylaniline (NPA). The acrolein formed may react with aniline resulting in a polymeric substance.

Interestingly, the N-propylaniline (NPA) production is much less when zeolite (H)Beta is used as the catalyst (see Figure 8, 12 and 13). Presumably, the Brønsted function is more dominant here: (H)Beta produces more consecutive products (stemming from N-allylaniline (NAA) which is formed initially) than HA-HPV-707, see Figure 8 and 12. Shortening the contact time reduces the amount of consecutive products, as can be seen in Figure 13. The selectivity to N-allylaniline increases further when the catalyst deactivates and less sites become available for the consecutive reactions.

Figure 12. Catalytic behaviour of (H)Beta at 140 °C in the condensation of aniline (1%) and allyl alcohol (1%) in nitrogen as the carrier-gas (50 ml/min). (AA = allyl alcohol, A = aniline, NAA = N-allylaniline, 2AA = 2-allylaniline, 2MIE = 2-methyl-indoline, NPA = N-propylaniline)
Figure 13. Catalytic behaviour of (H)Beta at 140 °C in the condensation of aniline (1%) and allyl alcohol (1%) in nitrogen as the carrier-gas (100 ml/min). (AA = allyl alcohol, A = aniline, NAA = N-allylaniline, 2AA = 2-allylaniline, 2MIE = 2-methylindoline, NPA = N-propylaniline)

5.4 CONCLUSIONS

The combination of a vapour-phase fixed-bed flow-reactor and the amino-Claisen rearrangement offers an example of the potential of heterogeneous catalysts for the production of fine chemicals. H-Beta displays the best performance for the aromatic amino-Claisen rearrangement of N-allylaniline, the simplest aromatic amine. Amorphous silica-alumina shows potential for the allylic N-functionalization of aniline due to the mild acidity, although side reactions still cause a rapid deactivation of the catalyst. Interestingly, the main side-product is N-propylaniline which presumably stems from the reduction of N-propyldiene-benzene amine. Allyl alcohol probably functions as the H-donor molecule giving acrolein which polymerizes with aniline causing the observed catalyst deactivation. The zeolites examined suffer from severe deactivation, probably caused by pore-plugging by polymeric molecules.
5.5 REFERENCES

37. See Chapter 4 of this thesis.
6. ZEOLITE CATALYSED REGIOSELECTIVE SYNTHESIS OF 2,3- SUBSTITUTED INDOLES

ABSTRACT

The use of zeolites as shape-selective catalysts in the Fischer Indole Synthesis was investigated. The condensation of phenylhydrazine with a non-symmetrical ketone results in a hydrazone which upon cyclisation can give two isomeric indoles. Based on the assumption that the steric demands of the intermediates differ, an influence of the zeolite pores was expected. It was found that in certain cases a higher selectivity to the less space-demanding isomer was obtained, especially on zeolite Beta. However, the results obtained on one set of indole isomers could not be extrapolated to another set of indole structures. Furthermore, a high contribution from the non-shape-selective external zeolite surface is suspected, thus limiting the potential of the zeolites as shape-selective catalysts.
6.1 INTRODUCTION

The indole nucleus is present in many biologically active molecules. Examples include plant growth regulators, proteins and pharmaceuticals. The selective synthesis of indole derivatives therefore constitutes an important area of drug research. A versatile method for synthesising substituted indoles is the well known Fischer Indole Synthesis (FIS) \[1\]. It consists of a condensation of a phenylhydrazone and a ketone towards a phenylhydrazone followed by a Brønsted- or Lewis-acid catalyzed tautomerization to an enehydrazone. This enehydrazone tautomer undergoes a fast \([3,3]\)-sigmatropic rearrangement followed by elimination of ammonia yielding the indole product. A detailed reaction mechanism is described in refs. \([2]\) and \([3]\). (the reader is referred to Robinson \([4]\) for a comprehensive review on the Fischer Indole Synthesis)

As shown in Scheme 1, the use of non-symmetrical ketones will result in two isomeric enehydrazone tautomers and hence in two isomeric indoles.

\[
\begin{align*}
&\text{R}_1\text{CH}_2\text{C}=\text{CH}_2\text{R}_2 \\
&\text{+} \\
&\text{NHNNH}_2 \\
\rightarrow &\text{phenylhydrazone (E+Z)} \\
\rightarrow &\text{R}_1\text{CH}_2\text{C}=\text{CH}_2\text{R}_2 \\
&\text{NH} \\
\rightarrow &\text{R}_1\text{CH}_2\text{C}=\text{CH}_2\text{R}_2 \\
&\text{NH} \\
\rightarrow &\text{R}_2\text{CH}_2\text{C}=\text{CH}_2\text{R}_1 \\
\rightarrow &\text{R}_1\text{CH}_2\text{C}=\text{CH}_2\text{R}_2 \\
&\text{NH} \\
\rightarrow &\text{R}_2\text{CH}_2\text{C}=\text{CH}_2\text{R}_1 \\
&\text{NH}
\end{align*}
\]

**Scheme 1.** Reaction steps in the Fischer Indole Synthesis.

In the case of *methylalkylphenylhydrazones (R \(_1\)=H)* e.g. obtained from phenylhydrazone and phenylacetone \([5]\) or isopropyl methyl ketone \([6]\) it was reported that the distribution of the two possible indole isomers depends on the kind, the concentration, and the excess of Brønsted acid catalyst used \([5,6]\). An increase of the concentration and/or excess of acid enhanced the formation of the 2-substituted 3-H-indole isomer. The investigators explained this by assuming a change in the reaction mechanism from monoprotonation of the phenylhydrazone (in the case of weak or diluted strong acids) to double protonation in the case of concentrated strong acids \([4,6]\). The subsequent elimination of the protons by an E1 or an E2 mechanism, would account for the differences found. However, an E2 mechanism seems unlikely in a strongly acidic reaction mixture. Furthermore the mechanism does not explain the differences found between different
kinds of acids. Especially polyphosphoric acid gives in certain cases a remarkably high selectivity towards the 2-substituted 3-H-indole isomer [4,5]. An acid strength relationship as exemplified above was not reported for other non-symmetrical alkylphenylhydrazones.

Despite claims made for PCl₅ [7], Lewis acids as catalysts do not exert any systematic influence on the regioselectivity; the distribution of the indole isomers is mainly determined by the structure of the phenylhydrazone as was shown by Prochazka and Carlson [8]. As already summarized by Robinson [4], attempted prediction of the direction of ambiguous indolizations of ketone arylhydrazones must include consideration of the relative steric strain in the two possible enehydrazones involved and the relative steric hindrance in their subsequent reaction as well as consideration of the stabilization effected by multiple alkyl substitution of the double bond of the enehydrazine tautomer.

Therefore, to be able to prepare indoles selectively from non-symmetrical ketones by means of the Fischer synthesis it is necessary to apply a more dedicated catalyst or (if possible) to separate the phenylhydrazone E/Z isomers and use a catalyst for the tautomerization / rearrangement without affecting the E or Z configuration [9]. However the combination of a simple one-pot reaction with a selective and recyclable heterogeneous catalyst would be advantageous.

Prochazka et al. [10] recognized that the spatially restricted reaction environment of zeolite pores can be an effective catalytic tool for influencing the ratio of indole isomers formed since the two indoles differ in bulkiness. As the most striking example, the authors reported that the use of mordenite as a catalyst led to the selective formation of 2-benzyl-3-methylindole from phenylhydrazine and 1-phenyl-2-butanone, whereas according to the same report only 2-ethyl-3-phenylindole was formed when the reaction was performed in acetic acid. In attempts carried out at our laboratory to reproduce those findings mixtures of both isomers were invariably obtained. As was reported by Rigutto et al. [11] molecular sieves possessing a one-dimensional channel system such as mordenite were ineffective in altering the indole isomer ratio. By contrast the three-dimensional zeolites H-Na-Y and H-Beta were able to alter the isomer ratio significantly with H-Beta showing the highest preference of formation of the less bulky isomer 2-benzyl-3-methylindole.

In view of the continuing interest in the use of zeolites as shape-selective catalysts in fine chemical synthesis [12], a more detailed study on the zeolite catalyzed Fischer Indole Synthesis was undertaken. Our main interest was to identify the parameters which determine the selectivity when zeolites are used as catalysts in the Fischer Indole Synthesis. Parameters of interest were the strength and concentration of the acid sites and the geometric structure of the zeolites, by which steric constraints are imposed on the reactants, intermediates, transition states and products. The contribution of the external surface was also investigated. Since the indole products do not interconvert, product selectivity as a result of the pore system is unfavourable since then the pores will be
plugged by the bulky non-desorbing indole isomer and only non-shape selective catalysis on the external zeolite surface remains. Therefore a restricted transition state (RTS) based selectivity is aimed at. On the basis of adsorption data of the isomeric indoles from 1-phenyl-2-butanone and phenylhydrazine Rigutto et al. [11] suggested that this is the most likely selectivity-determining mechanism.

**Choice of reference**

3-Heptanone was selected as reference ketone on the basis of the following criteria: the availability of a reliable and reproducible GC-analysis (amines, imines and hydrazones often cause great difficulties during GC-analysis) of the indole mixtures [4,7,10], no methyl alkyl ketone and no possibilities for conjugation in the transition state or indole product as this might play a dominating role in the TS [4]. Furthermore, the difference between the indole isomers at the 3-positioned substituent (methyl or propyl, see Scheme 2.) is large enough to effect a different interaction with the zeolite lattice (as was calculated with the computer program Delphi and checked by adsorption experiments).

The computer programs Delphi [13], MM3 [14] and BIOSYM were used to calculate the relative differences in steric energies and heats of formation between the two possible indole isomers.

![Scheme 2](image)

**Scheme 2.** The two possible indole isomers from 3-heptanone and phenylhydrazine with molecular dimensions (CPK models) in Å.
Zeolite Catalysed Regioselective Synthesis of Indoles

6.2 EXPERIMENTAL

Materials

Phenylhydrazine and the ketones were obtained from Aldrich and used as received. The solid acid catalysts used were: amorphous silica-alumina (ASA) HA-HPV-707 (gift from AKZO-Nobel Amsterdam, 25wt% Al₂O₃ on silica), NaY (Si/Al=2.4), zeolite Beta (synthesised according to Wadlinger et al., Si/Al=12 [15]), zeolite Mordenite (Si/Al=6.2), MCM-41 (Si/Al=15, prepared by K.R. Kloetstra) and HPA (H₃PW₁₁O₄₆). The appropriate calcination (max. 450 °C), NH₄⁺-exchange and activation (max. 450 °C) procedures were followed to obtain acidic dehydrated materials. XRD and flame-AAS were used to characterise the materials. Polyphosphoric acid (PPA) was made from 6 g P₂O₅ and 4 g 85% H₃PO₄.

Reaction procedure

In 50 g of p-xylene were dissolved 10 mmol of ketone and 10 mmol of phenylhydrazine. This solution was stirred for 30 min while heating to 140 °C (reflux) to allow quantitative formation of the phenylhydrazone. A continuous dry nitrogen flow was maintained to prevent air-oxidation. The activated catalyst (0.5 g) was added to the reaction mixture as a suspension in p-xylene. Samples were taken at regular intervals and analysed by GC/GCMS using a CP Sil-5 CB capillary column combined with an appropriate temperature program. 1,3,5-tri-isopropylbenzene or 1,3,5-tri-tert-butylbenzene was used as internal standard for GC analysis. It was assumed that the GC detector (FID) had the same sensitivity for both indole isomers.

Mineral acid catalyzed reactions were performed using (trifluoro)acetic, sulfuric or (poly)phosphoric acid under reflux conditions or at 140 °C. For each run 10 mmol of reactants were used under solvent-free conditions. After quenching and neutralising the reaction mixture the products were extracted with an organic solvent, dried (Na₂SO₄) and analysed by GC/GCMS.

Adsorption experiments with 2-ethyl-3-propylnindole and 2-butyl-3-methylindole

An A/B indole-isomer mixture, obtained by silica column chromatography using hexane as eluents, was used for the adsorption measurements. The first and last column fractions containing each isomer separately (98% GC-purity) were used for ²H-NMR identification and proved to be in accord with GCMS measurements. NMR data for the bulky isomer 2-ethyl-3-propyl-indole: ²H-NMR, triplet (-CH₂CH₂CH₃) 0.945 ppm, triplet (-CH₂CH₃) 1.25 ppm, multiplet (-CH₂CH₂CH₃) 1.64 ppm, triplet (-CH₃CH₂CH₃) 2.66 ppm,
Chapter 6

quartet (\(-\text{CH}_2\text{CH}_3\)) 2.72 ppm, and NH 7.65 ppm. MS (m/z): 143, 158 (bp), 187 (mol.mass). For the linear 2-butyl-3-methylindole isomer: \(^1\)H-NMR, 0.94 ppm (t, -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 1.40 ppm (m, -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 2.21 ppm (s, -\text{CH}_3), 2.65 ppm (m, -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3), 2.70 ppm (t, -\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3). MS (m/z): 144 (bp), 187 (mol.mass).

Competitive adsorption experiments were performed at RT in a glass apparatus similar to that described by Choudary et al. [16]. Approximately 200 mg of H-Beta or H-Na-Y was activated in a sample tube, connected with the sorption chamber, at 450 °C for 3h in vacuo (heating rate 1 °C/min). After cooling to room temperature the zeolite was introduced into the sorption chamber, and the vacuum line was closed. At t=0, 0.54 mmol (0.1 g) of a mixture of A and B indoles (bulky:linear = 42:58) together with a known amount of bulky internal standard (approximately 60 mg 1,3,5-tri-tert-butylbenzene) dissolved in 20 ml 1,3,5-tri-isopropylbenzene (also incapable of entering the zeolite pores under the conditions applied) was introduced rapidly into the sorption chamber. The vacuum was released and stirring started. Samples were withdrawn from the reaction mixture at suitable time intervals and analysed by GC.

Note: Owing to the intractability of the hydrazones, formed from the ketones and phenylhydrazine, on the GC column, reliable conversion data could not be obtained. The selectivities given in this chapter are therefore based on the peak-area ratios of the indole products obtained at complete conversion, which required less than one hour for homogeneously catalysed reactions and ca. 6h in the case of heterogeneous reactions. During the reactions the indole product ratios were constant, since the isomers do not interconvert.

The analysis is further complicated by the similarity of the indole isomers, which make separation difficult even on a modern capillary GC-column. From the indole systems examined, the analysis of the 3-heptanone/phenylhydrazine based system was critical but reliable. Using an apolar column (CP Sil-5), the separation between the bulky indole isomer, the corresponding hydrazone and the linear indole isomer was just feasible.
Post synthesis external surface modification of zeolite Beta

To minimise the contribution of the external surface of zeolite Beta (where no spatial constraints exist) efforts were undertaken to reduce the amount or activity of acid sites on this surface in several ways, see chapter 3 for a complete overview. External surface dealumination procedures were performed with as-synthesised zeolite Beta (template still present). In one procedure 10g of Beta was stirred in 340 ml 0.025M Na₂H₂EDTA or H₂EDTA solutions at RT. After filtration the samples were washed three times with water until pH=7. All Beta samples were pre-calcined in air at 450 °C followed by calcination in 1% O₃ in O₂ at 120 °C and finally for two hours at 450 °C in oxygen. In this way the template molecules were removed completely without using temperatures as high as 550 °C. This calcination procedure renders the crystal structure of Beta better intact. (The thorough investigation of zeolite Beta described in chapters 3 and 4 was performed after the research described in this chapter and consequently the knowledge gained from that was not available).

6.3 RESULTS AND DISCUSSION

As shown in Scheme 2 both indoles from 3-heptanone have a 3-positioned substituent. Although no methylalkylphenylhydrazone is obtained in this reaction the indole isomer ratio from 3-heptanone is slightly but clearly influenced by using Brønsted acids with different strength and/or in excess, as can be seen from Table 1. Clearly the mono / diprotonation model does not hold here. A possible explanation may be the concomitant increase in solvent polarity of the system together with the increasing acidity. These parameters will play an important role in the stabilisation of intermediates or transition states.

As shown in Table 2 the three-dimensional zeolites H-Na-Y and H-Beta have a large impact on the isomer ratio. H-Na-Y gives rise to a small preference for the bulky isomer. Zeolite Beta is the most selective heterogeneous catalyst for the synthesis of the linear isomer. The sorption data (Table 3) are in accordance with this observation although the total adsorption (at room temperature) is remarkably low. The use of Beta with a lower concentration of acid sites (higher Si/Al) or the use of boron Beta (lower intrinsic acidity) does not have a pronounced effect on the isomer ratio.

Treatment of zeolite beta with complexing agents like Na₂H₂EDTA or H₂EDTA to reduce outer surface activity proved to be ineffective [17] and consequently did not increase the amount of linear product. Inactivation of the outer surface of zeolite Beta by other means e.g. poisoning with triphenylphosphine proved to be ineffective as well, i.e. under the reaction conditions applied. The deposition of silica layers by CLD on large
crystals of zeolite Beta resulted in a reduction of the external activity as tested with the method described in chapter 3.

**Table 1.**
Ratio of indole isomers (A:B) as function of acid strength and concentration of the catalyst. (ratio denotes catalyst/reactant mol ratio)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A:B</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic acid</td>
<td>31:69</td>
</tr>
<tr>
<td>CF₃COOH (1:1)</td>
<td>33:67</td>
</tr>
<tr>
<td>10% H₂SO₄ (1:1)</td>
<td>37:63</td>
</tr>
<tr>
<td>10% H₂SO₄ (5:1)</td>
<td>39:61</td>
</tr>
<tr>
<td>80% H₂SO₄ (5:1)</td>
<td>45:55</td>
</tr>
<tr>
<td>97% H₂SO₄ (5:1)</td>
<td>48:53</td>
</tr>
<tr>
<td>PPA</td>
<td>47:53</td>
</tr>
</tbody>
</table>

_A (bulky) and B (linear) according to Scheme 2._

**Table 2.**
Ratio of indole isomers (A:B) over various heterogeneous acid catalysts. (p-xylene, 140 °C)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A:B</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Mor</td>
<td>43:57</td>
</tr>
<tr>
<td>H-Na-Y</td>
<td>53:47</td>
</tr>
<tr>
<td>HA-HPV (SiO₂/Al₂O₃)</td>
<td>38:62</td>
</tr>
<tr>
<td>H-MCM-41 (Si/Al=15)</td>
<td>38:62</td>
</tr>
<tr>
<td>HPA (H₃PW₁₁O₄₀)</td>
<td>43:57</td>
</tr>
<tr>
<td>H-Beta, parent (Si/Al=10)</td>
<td>27:73</td>
</tr>
<tr>
<td>H-Beta, Na₃H₂EDTA treated</td>
<td>26:74</td>
</tr>
<tr>
<td>H-Beta, H₄EDTA treated</td>
<td>30:70</td>
</tr>
<tr>
<td>H-Beta, oxalic acid treated</td>
<td>24:76</td>
</tr>
<tr>
<td>H-Beta (Si/Al=45)</td>
<td>25:75</td>
</tr>
<tr>
<td>H-boron Beta (Si/B=10)</td>
<td>23:77</td>
</tr>
</tbody>
</table>

**Table 3.** Sorption of 2-ethyl-3-propyldindole (A, bulky) and 2-butyl-3-methylindole (B, linear) from 1,3,5-tri-isopropylbenzene at room temperature. (200 mg zeolite, 100 mg of a 42:58 indole mixture (A and B), 20 ml solvent)

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Channel system (Å)</th>
<th>Total indoles sorbed (wt.%)</th>
<th>Ratio of indoles sorbed (A:B) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Na-Y</td>
<td>7.4 × 7.4</td>
<td>30</td>
<td>36:64</td>
</tr>
<tr>
<td>H-Beta</td>
<td>7.6 × 6.4</td>
<td>7.7</td>
<td>28:72</td>
</tr>
</tbody>
</table>

* as determined by GC analysis. Sorption on the internal or external surface cannot be distinguished by this method.

To obtain insight into the scope of the zeolite catalyzed FIS a methyl alkyl ketone, phenylacetone (=1-phenyl-2-propanone), was tested. The results are presented in Table 4. For comparison the relevant data for the indoles obtained from phenylhydrazine and 1-
phenyl-2-butanone and 3-heptanone, respectively, are given as well together with the
calculated thermodynamical ratios at 140 °C. (product identification by GC/MS)

Table 4. Comparison of three different ketones as to the ratio of indole isomers
(bulky:linear)

<table>
<thead>
<tr>
<th>catalyst</th>
<th>1-phenyl-2-butanone</th>
<th>1-phenyl-2-propanone</th>
<th>3-heptanone</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetic acid</td>
<td>75:25</td>
<td>100:0</td>
<td>31:69</td>
</tr>
<tr>
<td>PPA</td>
<td>n.d.</td>
<td>59:41</td>
<td>47:53</td>
</tr>
<tr>
<td>H-Na-Y</td>
<td>50:50</td>
<td>100:0</td>
<td>53:47</td>
</tr>
<tr>
<td>H-Beta</td>
<td>25:75</td>
<td>100:0</td>
<td>26:74</td>
</tr>
<tr>
<td>HA-HPV</td>
<td>71:29</td>
<td>100:0</td>
<td>38:62</td>
</tr>
<tr>
<td>thermod. eq.</td>
<td>3:97</td>
<td>5:95</td>
<td>69:31</td>
</tr>
</tbody>
</table>

Formation of the linear 2-benzyl-3-H-indole by the Fischer Indole Synthesis with
phenylacetone was only observed with polyphosphoric acid [5] and not at all with zeolite
Beta although it resembles 2-benzyl-3-methylindole, the linear indole isomer obtained
from 1-phenyl-2-butanone (see Scheme 3), in bulkiness. If the production of the linear
isomer would be solely based on a suppression of the formation of the bulky isomer, then
the trends in the selectivities in the FIS for 1-phenyl-2-propanone and 1-phenyl-2-
butanone should be comparable. This is not the case. Thus, the observed selectivities in
the 1-phenyl-2-butanone system, and also in the 3-heptanone system, are assumed not to
be determined by intraporous restricted TS i.e. the reactions take place at the external
surface as we know now from Chapter 3. An alternative explanation may be that the
intermediate enehydrazine tautomer corresponding to the linear 2-benzyl-3-H-indole has
an unfavourable terminal double bond compared with an intermediate with a favourable
internal double bond leading to the bulky 2-methyl-3-phenylindole isomer. In the case of
1-phenyl-2-butanone both intermediate enehydrazines possess an internal double bond.
This observation, however, is catalyst independent. If the presence of the terminal double
bond in the phenylacetone enehydrazine intermediate is dominating the product
selectivity, then the question arises why this is not the case for the PPA catalysed system
as well. Interestingly, the selectivity to the linear 2-benzyl-3-H-indole isomer could be
increased to 76% when the PPA was made from 9 g P₂O₅ and 1 g of 85% phosphoric acid.
Clearly, the reaction path of the FIS is more complex than assumed initially.
Scheme 3. Indole isomers from 1-phenyl-2-propanone and 1-phenyl-2-butanone. Dimensions (Length × Height × Thickness (Å)) obtained from CPK models. (The length has been measured between the most distant points in the molecule, the height was determined at the indole unit and the thickness is determined by the benzene ring.)

Calculations indicate that the (linear) 2-benzyl-3-H-indole is the most stable isomer by ca. 10 kJ/mol. Also the enehydrazine tautomer leading to the linear isomer is calculated to be ca. 6 kJ/mol lower in energy. For the linear indole isomers obtained from 1-phenyl-2-butanone and 4-phenyl-2-butanone (no experimental data available) the values are ca. 12 kJ/mol in preference of the linear isomer. For 3-heptanone the bulky indole isomer A was calculated to be the most stable by ca. 2.7 kJ/mol. Comparison with Table 4 shows that a large discrepancy exists between calculated stabilities and experimentally obtained data which indicates that the reaction is kinetically controlled and solvent effects are important. Adsorption experiments showed that zeolite Beta has a preference for
sorbing the linear 2-benzyl-3-H-indole isomer over the bulky 2-methyl-3-phenylindole isomer (ratio 73:27 at a total sorption of 9.5 wt% at RT) which proves that in this case sorption experiments with the reaction products are not representative for distinguishing between RTS selectivity and product selectivity.

Macrocristalline zeolite Beta, with a more favourable internal / external surface area ratio, proved to be as selective as microcristalline zeolite Beta. When the externally passivated (i.e. silica-coated) macrocristalline zeolite Beta [17] was used as the catalyst in the Fischer synthesis using 3-heptanone, 1-phenyl-2-butanone and phenylacetone respectively, no conversion whatsoever was observed, even after 24h. This supports the idea that the external zeolite surface is actually the catalytic centre.

6.4 CONCLUSIONS

Zeolites H-Na-Y and H-Beta are active and recyclable heterogeneous catalysts in the Fischer Indole Synthesis. In certain cases zeolite H-Beta is effective in producing the linear indole isomer in excess. Although tempting to explain the preference for the linear product as arising from an intraporous occurring reaction, leading to a restricted transition state, we conclude, also concerning the results of Chapter 3, that the external surface is actually the place where the catalytic activity resides. Thus the selectivity observed is presumably due to adsorption in a preferential conformation onto the outer surface of zeolite Beta. This might also explain the very low selectivity (0 %) towards the linear indole isomer in the Fischer Indole Synthesis using phenylacetone and phenylhydrazine as the reactants, whereas the use of 1-phenyl-2-butanone leads to a significant amount (75%) of the linear isomer. In the case of phenylacetone the substantial energy difference between the two ene-intermediates (conjugated internal vs. terminal double bond) will play a role. Anyway, prediction of selectivities of zeolite catalysed reactions on zeolite-pore-dimensions alone is unreliable. This finding was the basis for the thorough investigation of zeolite Beta, regarding both its external activity and its Lewis acidity, as described in the Chapters 3 and 4 of this thesis.
Chapter 6

6.5 REFERENCES

17. See Chapter 3 of this thesis.
7. THE LEWIS ACID CATALYSED REARRANGEMENT OF $\alpha$-PINENE OXIDE TO CAMPHOLENIC ALDEHYDE

ABSTRACT

Zeolite titanium Beta is found to be an effective catalyst for the industrially relevant rearrangement of $\alpha$-pinene oxide to campholenic aldehyde, giving selectivities of up to 89 % in the liquid phase. In the gas phase, up to 94 % selectivity is obtained at conversions above 95 %, which exceeds the best values obtained with homogeneous Lewis-acid catalysts. The selectivity obtained is profoundly influenced by the solvent or co-adsorbate applied.

The research described in this Chapter has been published in *Catal. Lett.* 53 (1998) 135.
7.1 INTRODUCTION

Several recent publications have reported on the Lewis acidic character of micro- and mesoporous materials. Besides USY, examples include zeolite Beta [1] and the titanium and zirconium containing hexagonal mesoporous silica's (Ti/Zr-HMS) [2]. Very recently the Lewis-acid activity of aluminium-free zeolite titanium Beta (Ti-Beta) was demonstrated by van der Waal et al. in the epoxidation of alkenes [3] and in the Meerwein-Ponnordorf-Verley reduction of 4-tert-butylocyclohexanone to the corresponding cis-alcohol with high stereoselectivity [4].

Campholenic aldehyde is an important intermediate in the synthesis of several sandalwood fragrances, which constitute an important growth area in perfumery fine chemicals. Earlier work, in our group, on the acid-catalyzed rearrangement of α-pinene oxide showed the potential of solid Lewis acids to promote the selective formation of campholenic aldehyde [5]. In general, Brønsted acids give maximum selectivities of 55 %, while Lewis acids, especially the zinc halides, can give selectivities as high as 85 %. Recently, Hölderich et al. [6] reported a selectivity to campholenic aldehyde of 78 % by using a carefully prepared H-USY zeolite at low reaction temperatures of around 0 °C. These authors claimed that the high selectivity observed was a result of well-dispersed Lewis acid sites in a nearly all-silica matrix.

Since the selective production of campholenic aldehyde appears to be favoured by Lewis acids, these materials have been tested as catalyst in the rearrangement of α-pinene oxide. The low active-site concentration of these materials suggests that they may be beneficial for reactions involving highly reactive molecules prone to (bi-molecular) consecutive reactions.

7.2 EXPERIMENTAL

Materials

Ti-Beta was synthesised according to the method of van der Waal et al. [3] with a Si / Ti ratio of 59, a N₂-BET surface of 687 m² g⁻¹ and a particle diameter of 1.2 μm (as determined by SEM). α-Pinene oxide (97%) was obtained from Aldrich. Campholenic aldehyde was kindly provided by Quest International.

Ti-HMS and Zr-HMS were prepared according to Tuel et al. [2]. ZnNaX was prepared by ion-exchange of NaX (10 g) once with a 250 ml 0.2 M solution of Zn(NO₃)₂ at 90°C followed by filtration and rinsing with water. Macrorcrystalline
(H)Beta and silica-coated macrocrystalline (H)-Beta (externally passivated) were synthesised according to Kunkeler et al. [7]. Amorphous silica alumina (ASA, HA-HPV-707) was a gift from AKZO-Nobel Amsterdam. H-USY was kindly provided by Shell Amsterdam. TiO₂ on SiO₂ was prepared by reacting TiCl₄ in hexane with amorphous silica and subsequent calcination. Prior to a catalytic run the catalysts were activated in air at 450 °C for 1h.

Methods

Catalytic experiments

Liquid-phase experiments were conducted at 70 °C in a thermostatted double-wall glass reactor. The reaction mixture consisted of 25 ml of the appropriate solvent, 4.22 g (27.8 mmol) of α-pinene oxide, 250 mg 1,3,5-tri-isopropylbenzene as the internal standard, and 50 mg of the catalyst. The initial rate has been calculated after the first 10 minutes of each experiment. Samples of the reaction mixture were taken periodically and analysed using a GC equipped with a CP Sil-5 CB column (50 m, 0.53 mm i.d., N₂-carrier gas) and FID. The initial injection temperature was 50 °C which was subsequently increased to 250 °C with 50 °C/min. to prevent thermal decomposition of reactants and products. The products were analysed during two isothermal periods at 120 and 150 °C. Retention times were determined using pure samples.

Vapour-phase reactions were performed at atmospheric pressure using a fixed-bed down-flow reactor consisting of a borosilicate glass tube (7 mm i.d.) heated by a fluidised-bed oven at 90 and 100 °C. To be able to run the reactor under plug flow conditions, the catalysts were pelletized and subsequently crushed and sieved to collect the particles in the size-range of 0.7-1.0 mm. One gram of catalyst was used to obtain a sufficiently high catalyst bed. In case of Ti-Beta as the catalyst, 0.3 g Ti-Beta (83 µmol Ti) was diluted with 1.2 g quartz powder/Aerosil before pelletizing etc. To exclude influences of metallic components (tubing, connectors etc.), all auxiliary reactor parts were made of glass and heated externally to prevent condensation of reactants and products. Reactant mixtures were pumped into a stream of preheated carrier gas (nitrogen) by means of a motor-driven syringe pump or a HPLC pump. The gas flow (50 ml min⁻¹) contained 1 vol. % α-pinene oxide (1.22 mmol/h) and 10 vol. % of an inert co-adsorbate in nitrogen as the carrier-gas. Products were collected in a cooled condensation vessel and analysed by GC-MS and by 2D ¹H and ¹³C NMR after purification. Samples of the reactor effluent were taken regularly by an on-line autosampler and analysed by a GC equipped with a CP Sil-19 CB column (50 m, 0.53 mm i.d., N₂-carrier gas) and FID. (See Chapter 5, Figure 5)
Chapter 7

Characterization

Elemental analyses were performed on a Perkin-Elmer 1100 flame-AAS and on an ICP-AAS. Nitrogen physisorption measurements were performed on a Quantachrome Autosorb 6B Automated Gas Sorption System, in the partial pressure range of \( p/p_0 = 0.01-0.09 \). \( S_{\text{BET}} \)-areas were calculated according to ASTM D 3663-92. Powder diffraction data were obtained on a Philips PW 1840 using Ni-filtered Cu-K\( \alpha \) radiation, in the range of \( 2\theta = 5-50^\circ \). SEM micrographs were taken on a Philips XL-20 microscope using 25 KeV. \(^1\)H, \(^13\)C and NOE-NMR were performed on a Varian VXR-400-S for the identification of campholenic aldehyde.

NMR identification of campholenic aldehyde (=2,2,3-trimethyl-3-cyclopentene-1-acetaldehyde)

To identify 2,2,3-trimethyl-3-cyclopenteneacetaldehyde (campholenic aldehyde) from the 2,2,4-trimethyl-3-cyclopenteneacetaldehyde isomer, NMR analysis was performed. A close look on both structures (see Figure 1) reveals that one dimensional \(^1\)H or \(^13\)C NMR will not be able to distinguish the structures from each other. Therefore, NOE, \(^1\)H and \(^13\)C NMR were applied. Only the 2,2,3-trimethyl isomer will have a Nuclear Overhauser Effect since here all three methyl groups are in close proximity; this was confirmed experimentally.

\(^13\)C-NMR (ppm relative to TMS): 203.01, 148.01, 46.95, 45.15, 44.25, 35.56, 25.66, 20.05 and 12.62. Comparison with an authentic sample of campholenic aldehyde provided by ICI/Quest International showed that campholenic aldehyde prepared by Ti-Beta catalysed isomerisation of \( \alpha \)-pinene oxide was indeed identical.

2,2,3-trimethyl-3-cyclopentene-1-acetaldehyde (campholenic aldehyde)

2,2,4-trimethyl-3-cyclopentene-1-acetaldehyde

Figure 1. The two possible aldehyde isomers from the isomerisation of \( \alpha \)-pinene oxide.
7.3 RESULTS AND DISCUSSION

The rearrangement of α-pinene oxide is believed to be initiated by the coordination of the epoxide oxygen atom to a Lewis (or a Brønsted) acidic centre thereby inducing ring opening of the epoxide followed by subsequent or concerted alkyl shifts (Figure 2) [5]. It is assumed that this mechanism also holds for solid Lewis acid catalysts. Furthermore, the unique molecular-sized pore structure of the zeolites may enhance selectivity by space-confinement as was shown in the reduction of 4-tert-butylcyclohexanone [4].

![Figure 2. Proposed mechanism for the isomerisation of α-pinene oxide by a Lewis acid (here represented by a Ti atom connected to a zeolite framework) into campholenic aldehyde.](image)

For a comparison with the micro- and mesoporous Lewis-acidic materials studied, several other solid catalysts were tested as well. These include Zn" exchanged zeolite X (NaX as reference), an amorphous silica alumina (HA-HPV-707, 25 wt% Al₂O₃ on SiO₂) and TiO₂ on SiO₂. The catalyst compositions and nitrogen BET surface areas are given in Table 1.
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Table 1. Catalyst compositions and N\textsubscript{2}-BET-surface areas

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Si / M</th>
<th>Cation / Al</th>
<th>S\textsubscript{BET}(m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-Beta</td>
<td>Si/Ti=59</td>
<td>&gt;2500</td>
<td>687±8</td>
</tr>
<tr>
<td>Ti-HMS</td>
<td>Si/Ti=77</td>
<td></td>
<td>602±4</td>
</tr>
<tr>
<td>Zr-HMS</td>
<td>Si/Zr=77</td>
<td></td>
<td>517±6</td>
</tr>
<tr>
<td>(H)Beta, microcrystalline</td>
<td>Si/Al=11.6</td>
<td>Na / Al = 0.01</td>
<td>699±8</td>
</tr>
<tr>
<td>(Na)Beta, microcrystalline</td>
<td>Si/Al=11.6</td>
<td>Na / Al = 1.02</td>
<td></td>
</tr>
<tr>
<td>(H)Beta, macrocrystalline</td>
<td>Si/Al=11.4</td>
<td>Na / Al = 0.01</td>
<td>671±18</td>
</tr>
<tr>
<td>(H)Beta, silica-coated</td>
<td>Si/Al=11.6</td>
<td>Na / Al = 0.02</td>
<td>640±18</td>
</tr>
<tr>
<td>NaX</td>
<td>Si/Al=1.3</td>
<td>Na / Al = 1.0</td>
<td></td>
</tr>
<tr>
<td>ZnNaX</td>
<td>Si/Al=1.3</td>
<td>Na/Al = 0.3 Zn/Al\textsubscript{2} = 0.76</td>
<td></td>
</tr>
<tr>
<td>H-US-Y</td>
<td>Si/Al=20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HA-HPV-707</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO\textsubscript{2} / SiO\textsubscript{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Liquid-phase experiments

Initially, the catalysts were tested using 1,2-dichloroethane as the solvent. It rapidly became clear (Table 2) that Ti-Beta displayed the best overall performance in terms of campholenic aldehyde selectivity and activity. As was to be expected, the Bronsted acidic catalysts show a low campholenic aldehyde selectivity. The silica-coated macrocrystalline zeolite (H)Beta (externally passivated) proved to be as selective as the uncoated material. The NaX zeolite was completely inactive.

The effects of various solvents on the activity and selectivity in the Ti-Beta catalysed isomerisation have been extensively investigated, since the co-adsorption of the solvent into the micropore system of Ti-Beta will greatly influence the intraporous α-pinene oxide concentration. Since α-pinene oxide can give undesired bi-molecular or polymerisation reactions, low intraporous concentrations are thought to be preferred for high yields of campholenic aldehyde. The hydrophobic nature of Ti-Beta [3] will cause it to preferentially adsorb less polar molecules over more polar molecules. Apolar solvents are expected to be adsorbed strongly, thus giving a low intraporous α-pinene oxide concentration and vice versa. However, when the solvent molecules are preferentially adsorbed (i.e. over the reactant) the reaction will be retarded. In Table 3 the dipole moments, dielectric constants and boiling points of the solvents applied have been summarised.

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The Lewis acid catalysed rearrangement of...

Table 2. Catalyst activities and selectivities for the conversion of α-pinene oxide into campholenic aldehyde in the liquid-phase (1,2-dichloroethane (DCE) as solvent).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>conversion (%) α-pinene oxide (TON)*</th>
<th>initial rate (mmol / min)</th>
<th>Selectivity (%) Camph. aldehyde #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-Beta</td>
<td>29 (576)</td>
<td>0.108</td>
<td>81</td>
</tr>
<tr>
<td>Ti-HMS</td>
<td>20 (397)</td>
<td>0.052</td>
<td>37</td>
</tr>
<tr>
<td>Zr-HMS</td>
<td>9 (179)</td>
<td>0.025</td>
<td>42</td>
</tr>
<tr>
<td>(H)Beta, microcryst.</td>
<td>32 (643)</td>
<td>0.125</td>
<td>53</td>
</tr>
<tr>
<td>(Na)Beta, microcryst.</td>
<td>6 (119)</td>
<td>0.018</td>
<td>68</td>
</tr>
<tr>
<td>(H)Beta, macrocryst.</td>
<td>16 (318)</td>
<td>0.075</td>
<td>53</td>
</tr>
<tr>
<td>(H)Beta, sil.coated</td>
<td>17 (339)</td>
<td>0.023</td>
<td>53</td>
</tr>
<tr>
<td>NaX</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnNaX</td>
<td>15 (298)</td>
<td>0.020</td>
<td>43</td>
</tr>
<tr>
<td>(H)US-Y</td>
<td>68 (1350)</td>
<td>0.388</td>
<td>56</td>
</tr>
<tr>
<td>HA-HPV</td>
<td>80 (1589)</td>
<td>0.398</td>
<td>52</td>
</tr>
<tr>
<td>TiO₂ / SiO₂</td>
<td>16 (318)</td>
<td>0.060</td>
<td>42</td>
</tr>
</tbody>
</table>

Conditions: 25 ml DCE, 27.8 mmol α-pinene oxide, 50 mg catalyst, 70 °C. conversion without catalyst less than 1%.

* after 24h; values in brackets denote total Turn Over Numbers

# selectivities determined at low (<10%) conversion are less reliable.

Table 3. Selected solvent properties arranged by an increasing dielectric constant.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dipole moment (Debie)</th>
<th>Dielectric constant</th>
<th>Boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>0.00</td>
<td>2.02</td>
<td>80.7</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>0.45</td>
<td>2.21</td>
<td>101.3</td>
</tr>
<tr>
<td>benzene</td>
<td>0.00</td>
<td>2.28</td>
<td>80.1</td>
</tr>
<tr>
<td>di-iso-propyl ether</td>
<td>1.22</td>
<td>3.88</td>
<td>68.5</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>1.54</td>
<td>5.62</td>
<td>132.0</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>0.70</td>
<td>10.36</td>
<td>83.4</td>
</tr>
<tr>
<td>butanone</td>
<td>2.76</td>
<td>18.51</td>
<td>80.0</td>
</tr>
<tr>
<td>2-propanol</td>
<td>1.66</td>
<td>19.20</td>
<td>82.2</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>3.44</td>
<td>37.50</td>
<td>81.6</td>
</tr>
</tbody>
</table>
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As can be observed from Table 4, the solvent employed has indeed a major impact on the selectivity, activity and stability of the Ti-Beta catalyst. The low selectivities in the case of the polar solvents 2-propanol and butanone are most likely a result of:

\( i \) the transformation of the Lewis acidic Ti-site into a Brønsted acid site by the coordination of alcohols [3] and

\( ii \) products resulting from the reaction of the solvent with \( \alpha \)-pinene oxide, as was deduced from GC-MS measurements. We mention here also the unexpected reaction of \( \alpha \)-pinene with ketones such as butanone [8].

Table 4. Catalytic activity of Ti-Beta as a function of the solvent applied

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion (%)*</th>
<th>Initial rate (mmol / min)</th>
<th>Selectivity (%)#</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>4 (79)</td>
<td>0.036</td>
<td>83</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>45 (849)</td>
<td>0.083</td>
<td>68</td>
</tr>
<tr>
<td>benzene</td>
<td>35 (695)</td>
<td>0.110</td>
<td>55</td>
</tr>
<tr>
<td>di-isopropyl ether</td>
<td>16 (318)</td>
<td>0.095</td>
<td>68</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>6 (119)</td>
<td>0.042</td>
<td>72</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>29 (576)</td>
<td>0.108</td>
<td>81</td>
</tr>
<tr>
<td>butanone</td>
<td>72 (1430)</td>
<td>0.079</td>
<td>42</td>
</tr>
<tr>
<td>2-propanol</td>
<td>100 (1986)</td>
<td>0.076</td>
<td>33</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>7 (139)</td>
<td>0.308</td>
<td>89</td>
</tr>
</tbody>
</table>

Conditions: 25 ml DCE, 27.8 mmol \( \alpha \)-pinene oxide, 50 mg catalyst, 70 °C. conversion without catalyst less than 1%.

* after 24h; values in brackets denote total Turn Over Numbers
# selectivities determined at low (<10%) conversion are less reliable.

When an apolar solvent such as cyclohexane is applied, a very low initial reaction rate and conversion are observed. In contrast, acetonitrile, the most polar solvent tested, gives the highest initial rate but the catalyst deactivates rapidly, resulting in a conversion of only 7% after 24 h. In view of the hydrophobic character of Ti-Beta, the intraporous \( \alpha \)-pinene oxide concentration is expected to be the highest for polar solvents, this indicates that the initial rate is dependent on the intraporous \( \alpha \)-pinene oxide concentration. When this is high, however, consecutive reactions with other \( \alpha \)-pinene oxide molecules will be facilitated, resulting in a faster catalyst deactivation. An optimal intraporous \( \alpha \)-pinene oxide concentration thus exists, leading to high activity and selectivity and good catalyst
stability. Under the experimental conditions chosen, 1,2-dichloroethane proved to be the most suitable solvent, with a selectivity of 81% and a TON of 576. A similar reaction case in which the choice of a proper solvent leads to a low intraporous reactant concentration is the dehydration of 2-phenylethanol and 4-substituted derivatives over zeolite HY [9].

Vapour-phase reactions

In heterogeneous catalysis vapour-phase conditions are often preferred due to their ease of (continuous) operation. It was recently shown that Ti-Beta is an excellent catalyst for the vapour-phase reduction of 4-methylcyclohexanone via the MPV reaction [4]. In the corresponding liquid-phase MPV reduction, both Ti-Beta and Al-Beta could be used as highly shape-selective catalysts, but, in the vapour phase, the strong Brønsted acidity of Al-Beta causes rapid deactivation, leaving only Ti-Beta as an option for vapour-phase conditions [4].

The absence of a solvent when working under vapour-phase conditions will strongly increase the intraporous α-pinene oxide concentration. This will lead to a decreased campholenic aldehyde selectivity, since from the liquid-phase experiments it was concluded that the intraporous α-pinene oxide concentration should be kept low to suppress consecutive (polymerisation) reactions. From the first entry of Table 5 for pure α-pinene oxide, it can be seen that the campholenic aldehyde selectivity is indeed only 63%, combined with a fast deactivation of the catalyst within 5 h. A competitive inert co-adsorbate may be added to the reactor feed to control the intraporous α-pinene oxide concentration in an analogous way to that achieved by variation of the solvent in the liquid phase. The ratio co-adsorbate / reactant will usually be lower than the ratio solvent / reactant in the liquid phase. Therefore, more hydrophobic co-adsorbates can be used which would cause the catalyst to be almost completely filled with solvent under liquid-phase conditions and consequently retard the reaction; this is illustrated by the entry for cyclohexane in Table 4 and Table 5. When an appropriate co-adsorbate is chosen, a very high selectivity to campholenic aldehyde (94%) can be obtained, even at complete conversion (TOF ≥ 15 mol mol⁻¹ h⁻¹) of α-pinene oxide, as shown in Table 5. 1,2-Dichloroethane is again found to be a very suitable co-adsorbate, although its undesirable environmental impact provides an incentive to seek alternatives. It was found that the use of the more eco-friendly alkanes as the co-adsorbates also results in very high campholenic aldehyde selectivities of >85%; methylcyclohexane and 1,4-dimethylcyclohexane are found to be particularly effective. The use of the somewhat more bulky 1,3- and 1,2-dimethylcyclohexane, however, leads to a reduction in selectivity.
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It is possible that the intraporous diffusion coefficients for the bulky dimethylenecyclohexanes are lower than for the linear alkanes, leading to a slower diffusion of reactants and products. The resulting increased residence time of \( \alpha \)-pinene oxide and products in the internal pore system may result in an increased probability of bimolecular reactions and consequently to reduction of the maximum attainable campholenic aldehyde selectivity. This is supported by GC-MS measurements, which show the formation of several products with molecular mass 304, corresponding to dimers of \( \alpha \)-pinene oxide or isomers. The high conversions obtained with the present experimental set-up make it unsuitable for studying the possible differences in sorption behaviour and/or kinetic effects caused by the addition of co-adsorbates. It is possible that, at lower conversions, even higher selectivities may be observed than in the present work. Unfortunately, a reduction of the Ti-Beta content of the catalyst bed from the current 20 wt\% to 10 and 2.5 wt\% actually resulted in a decrease of the selectivity with decreasing Ti-Beta content. This is probably due to the presence of impurities in the quartz and silica (Aerosil 200) which were used as binder and contaminations from the press used in pelletizing. The influence of these impurities becomes more pronounced when less Ti-Beta is present.

The possible participation of the product in the production of heavy condensate was tested by feeding campholenic aldehyde over a freshly calcined catalyst. However, no formation of products was observed and the catalyst remained colourless. This indicates that dimerization of campholenic aldehyde cannot be a cause of deactivation. When the feed was changed to a mixture of \( n \)-heptane and \( \alpha \)-pinene oxide, without prior regeneration of the catalyst, the rearrangement occurred with the same selectivity (87\%) and conversion (100\%) as when no campholenic aldehyde had previously been fed. It appears that intraporous \( \alpha \)-pinene oxide is the most likely molecule to be implicated in the heavy-ends formation and in the catalyst deactivation despite its low intraporous concentration.
**The Lewis acid catalysed rearrangement of...**

**Table 5.** α-Pinene oxide conversion and campholenic aldehyde selectivity as a function of the co-adsorbate and the time on stream in the vapour-phase experiments

<table>
<thead>
<tr>
<th>co-adsorbate</th>
<th>initial conversion (%)</th>
<th>campholenic aldehyde initial selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>95 (36)(^a)</td>
<td>63 (25)(^a)</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>95 (95)(^a)</td>
<td>90 (70)(^a)</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>95 (^b)</td>
<td>94 (^b)</td>
</tr>
<tr>
<td>benzene</td>
<td>100 (82)(^a)</td>
<td>88 (81)(^a)</td>
</tr>
<tr>
<td>n-heptane</td>
<td>100 (100)(^a)</td>
<td>88 (85)(^a)</td>
</tr>
<tr>
<td>n-octane</td>
<td>100</td>
<td>89</td>
</tr>
<tr>
<td>n-nonane</td>
<td>100</td>
<td>88</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>100</td>
<td>85</td>
</tr>
<tr>
<td>methylocyclohexane</td>
<td>100</td>
<td>93</td>
</tr>
<tr>
<td>1,2-dimethylocyclohexane</td>
<td>100</td>
<td>76</td>
</tr>
<tr>
<td>1,3-dimethylocyclohexane</td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>1,4-dimethylocyclohexane(^c)</td>
<td>100</td>
<td>92</td>
</tr>
</tbody>
</table>

_Conditions:_ 0.3 g Ti-Beta (83 µmol Ti), gas flow 50 ml min\(^-1\), 1 vol. % α-pinene oxide (1.22 mmol/h) and 10 vol. % co-adsorbate in nitrogen, 90 ºC.

\(^a\) Values in brackets denote the conversion and the selectivity after 5 h on stream.

\(^b\) Due to the swelling of "O"-rings in the reactor system no long term data could be collected with 1,2-dichloroethane as the co-adsorbate

\(^c\) _cis / trans_ mixtures

In an extended vapour-phase experiment, using n-heptane as the co-adsorbate at 90 ºC, it was observed that the catalyst deactivates linearly (after 6h time on stream, the conversion drops below 100%). The campholenic aldehyde selectivity decreases steadily. Heavier products (GC-MS: MW= 304) were also detected with increasing time on stream. After termination of the run, the reactor tube was found to be heavily fouled by condensation products and the spent catalyst bed was black, indicating that at 90 ºC product desorption is severely hindered. Raising the reaction temperature to 100 ºC eliminated the condensation of heavy products, while maintaining essentially the same selectivity to campholenic aldehyde (88% to 79% in 16h). In Figure 3 the conversion and selectivity (_n_-heptane as the co-adsorbate, 100 ºC) as a function of the time on stream are displayed, showing the linear decrease in activity and selectivity. Furthermore, after termination of the run the catalyst was only slightly coloured and hardly any condensates
were detected inside the reactor. The most likely cause of the deactivation appears to be the accumulation of undesorbed dimeric and heavier oligomers.

It is noteworthy that operation at these industrially practicable temperatures appears possible with Ti-Beta, while for other catalysts low temperatures are required for high selectivity [6]. Complete regeneration of the catalytic activity (up to 100 times) could be achieved by calcination at 480 °C.

![Conversion vs. Time](image)

**Figure 3.** Selectivity to campholenic aldehyde and conversion of α-pinene oxide as a function of the time on stream. Conditions: Ti-Beta (20 wt% in quartz), 100 °C, 1 vol.% α-pinene oxide and 10 vol.% n-heptane in nitrogen, 50 ml/min total gas stream.

Other catalysts tested under gas-phase conditions included the Ti-HMS, Zr-HMS, ZnNaX and H-US-Y materials. The Ti-HMS, Zr-HMS and ZnNaX all showed a campholenic aldehyde selectivity of 50-60% at an initial conversion of 90-100% using n-heptane as the co-adsorbate. Compared to the liquid-phase experiments (Table 2) the selectivities are higher but still far below the selectivities obtained with Ti-Beta. Feeding α-pinene oxide without the co-adsorbate to ZnNaX did not result in a loss of selectivity or activity; ZnNaX is a very hydrophilic material and will therefore not adsorb n-heptane preferentially over α-pinene oxide. The intraporous α-pinene oxide concentration will therefore not be influenced. Unexpectedly, the H-US-Y sample showed no formation of campholenic aldehyde at all.
7.4 CONCLUSIONS

Titanium-Beta proved to be an excellent catalyst for the rearrangement of $\alpha$-pinene oxide to campholenic aldehyde in both the liquid- and vapour-phase. This is mainly attributed to the presence of isolated, well-dispersed titanium sites in a Brønsted acid free silica matrix. The very high selectivities observed for Ti-Beta, even at temperatures as high as 100 °C, in contrast to other Lewis-acid catalysts, are proposed to be due to transition-state shape-selectivity induced by the pore structure of the zeolite. The competitive adsorption of inert molecules plays also a major role in the selectivity and the choice of solvent also depends on the type of reactor employed; in a gas-phase reactor alkanes are preferred but when alkanes are applied as a solvent in liquid-phase experiments they lead to an inactive system due to a too high intra-porous concentration of the solvent in the hydrophobic catalyst.

Since $\alpha$-pinene oxide may be obtained by oxidation of $\alpha$-pinene using Ti-Beta as the oxidation catalyst [3], Ti-Beta may be a promising catalyst for the direct synthesis of campholenic aldehyde from $\alpha$-pinene employing an inexpensive oxidant. However, it is necessary to avoid the use of aqueous reaction mixtures (e.g. aqueous H$_2$O$_2$) or alcoholic solvents, if a high selectivity towards campholenic aldehyde is to be achieved.
7.5 REFERENCES

b) P.J. Kunkeler, B.J. Zuurdeeg, J.C. van der Waal, J.A. van Bokhoven, D.C.
   Koningsberger and H. van Bekkum, J. Catal., accepted for publication, see also
   Chapter 4 of this thesis.
   Pays-Bas 111 (1992) 432.
   353.
7. P.J. Kunkeler, D. Moeskops and H. van Bekkum, Microporous Mater. 11 (1997) 313,
   see also Chapter 3 of this thesis.
SUMMARY

The research described in this thesis is focused on the synthesis, modification, characterisation and catalytic application of zeolites, in particular zeolite Beta. In the Introduction (Chapter 1) the basic principles behind zeolites and their use in heterogeneous catalysis are explained.

Initially, the PhD research was aimed at the direct synthesis of cyclic aromatic amines using zeolites as shape-selective catalysts. In Chapter 2 an overview is given of the current available catalytic routes towards aromatic amines.

A thorough investigation of the catalytic contribution of the external surface to the total catalytic activity of the zeolites Mordenite and Beta is described in Chapter 3. The external activity has been quantified using a surface sensitive probe-molecule. For both zeolites an effective silica-coating procedure has been developed which reduces the external surface activity to a minimum. For zeolite Beta it was found that the crystal size and morphology have a large influence on the effectiveness of the coating procedure, larger well-formed crystals being beneficial. The silica-coating is permeable thus leaving the inner-pore system accessible to reactants. Potentially, the silica-coated zeolite Beta can be used as a highly shape-selective acid catalyst.

The often peculiar behaviour of zeolite Beta in various acid-catalysed reactions urged us to investigate the Lewis-acidic properties of this zeolite in more detail. Chapter 4 describes the calcination and activation steps applied to this zeolite to influence the amount of Lewis-acidic aluminium atoms. It was found that steaming results in a modified zeolite Beta which is extremely active in the Lewis acid catalysed Meerwein-Ponndorf-Verley reduction of 4-tert-butylocyclohexanone. Based on FT-IR, $^{27}$Al and $^{29}$Si MAS NMR spectroscopy a mechanism is proposed in which framework aluminium atoms invert their geometry in such a way that they point into the zeolite pores and become available to reactants as a Lewis acidic site.

In Chapter 5 the heterogeneously catalysed aromatic amino Claisen rearrangement of N-allylaniline is presented, which offers a route towards cyclic aromatic amines. After the rearrangement of N-allylaniline at 200 °C in the gas-phase, 2-allylaniline is obtained. Cyclisation of the latter compound produces 2-methylindoline, which can be dehydrogenated in a separate step to 2-methylindole. It was found that the number and strength of the acid sites of the zeolite-catalyst applied determines the selectivity under continuous-flow gas-phase conditions rather than the pore-structure of the catalyst.

The influence of the zeolite pore-structure on the zeolite catalysed Fischer indole synthesis is described in Chapter 6. Upon condensation of phenylhydrazine and a non-symmetrical ketone a hydrazone is formed. Cyclisation of the hydrazone releases
Summary

ammonia and results in two isomeric indoles. It was found that the indole product ratio not only depends on the solid-acid catalyst used, but is also influenced by the strength of the homogeneous acid-catalysts used. Therefore, other parameters than the confinement exerted by the zeolite pores are equally important and thus the indole product ratio is not satisfactorily predicted by the pore-structure and pore-size of the zeolite alone.

Zeolite titanium Beta is found to be an effective catalyst for the industrially relevant rearrangement of α-pinene oxide to campholenic aldehyde, giving selectivities of up to 89% in the liquid phase. In the gas phase, up to 94% selectivity is obtained at conversions above 95%, which exceeds the best values obtained with homogeneous Lewis-acid catalysts. The selectivity obtained is profoundly influenced by the solvent or co-adsorbate applied.
SAMENVATTING

Het onderzoek beschreven in dit proefschrift is gericht op de synthese, modificering, karakterisering en katalytische toepassing van zeolieten, in het bijzonder zeoliet Beta. In de inleiding (Hoofdstuk 1) worden de beginselen van zeolieten en hun gebruik in de heterogene katalyse beschreven.

Het oorspronkelijke onderzoeksvoorstel was gericht op de katalytische synthese van cyclische aromatische aminen, waarbij zeolieten als mogelijke vorm-selectieve katalysator kunnen optreden. In Hoofdstuk 2 wordt een overzicht gegeven van de huidige stand van zaken op het gebied van de katalytische productie van deze verbindingen.

Een uitgebreid onderzoek naar de ongewenste (niet vorm-selectieve) katalytische bijdrage van het buitenoppervlak van de zeolieten Mordeniet en Beta wordt beschreven in Hoofdstuk 3. De Bronsted-zure activiteit van het externe oppervlak werd gekwantificeerd met behulp van een oppervlakte-gevoelig testmolecul. Door het gebruik van een silica-coating techniek kon voor beide onderzochte zeolieten een sterke reductie van de externe oppervlakte activiteit worden bereikt, terwijl het binnenoppervlak van de zeolieten, de poriestructuur, bereikbaar en onaangetast bleef. Voor zeoliet Beta bleek de kristalgrootte van doorslaggevende invloed te zijn op het welslagen van de silica-coating techniek. Door de inertisering van het buitenoppervlak van de zeolieten neemt de kans op werkelijk vorm-selectieve katalyse sterk toe.

Het vaak onvoorspelbare gedrag van zeoliet Beta in verschillende zuur-gekatalyseerde reacties leidde tot een gedetailleerd onderzoek naar de Lewis zure eigenschappen van deze zeoliet en de relatie met de calcineringsmethode. Hoofdstuk 4 beschrijft de nauwkeurig gecontroleerde calcinerings- en activerings-stappen welke de coordinatietoestand van de aluminiumatomen in zeoliet Beta beïnvloeden. De activiteit van zeoliet Beta in de Lewis zuur-gekatalyseerde Meerwein-Ponndorf-Verley reductie van 4-tert-butylecyclohexanon bleek sterk verhoogd te kunnen worden door het zeoliet-materiaal te stomen. Op basis van informatie verkregen uit FT-IR, 27Al en 29Si MAS NMR spectroscopie wordt een mechanisme voorgesteld waarbij tetraëdrisch gecoördineerde rooster-aluminiumatomen via een paraplu-inversie hun geometrie zodanig veranderen dat ze de zeolietporie insteken en als Lewis-zuur centrum bereikbaar worden voor reactanten.

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1 "... zeoliet Beta, dat is een raar ding ...", H. van Bekkum, promotor.
Samenvatting

In Hoofdstuk 5 wordt de heterogene zuurgekatalyseerde aromatische ammino-
Claisen-omlegging (isomerisatie) van N-allylaniline beschreven wat een mogelijke
route naar cyclische aromatische aminen is. De isomerisatie van N-allylaniline bij 200
°C in de gasfase levert 2-allylaniline. Ringsluiting van dit product geeft 2-
methylindolinedione, dat in een aparte stap gedehydrogeneerd kan worden tot 2-
methylindoool. Selectiviteiten naar 2-allylaniline en 2-methylindolinedione bleken voor-
namelijk bepaald te worden door het aantal en de sterkte van de zure sites aanwezig op
de katalysator en niet door de (micro)poreestructuur van de gebruikte katalysator.

De mogelijke invloed van zeoliet-microporiën op de productdistributie in de
zeoliet-gekatalyseerde Fischer indoolsynthese wordt beschreven in Hoofdstuk 6.
Condensatie van fenylhydrazine met een asymmetrisch keton geeft een hydrazon. Ringsluiting onder afspilting van ammoniak kan leiden tot de vorming van twee isomere
indolen. De matrix waarin deze reactie plaatsvindt (oplosmiddel, pH) heeft een grote
invloed op de productdistributie. Hiermee vergeleken was de invloed van de vast-zure
catalysatoren, waaronder zeolieten, klein. Voor de zeolietkatalysatoren bleek tevens de
bijdrage van het katalytisch actieve, maar niet vorm-selectieve buitenoppervlak groot.
De indool-productdistributie kan daarom niet worden voorspeld door alleen naar de
zeoliet-poreestructuur te kijken.

De isomerisatie van α-pineenoxide naar Kamfooleenaldehyde gekatalyseerd door
het mild Lewis-zure zeoliet Titanium-Beta wordt beschreven in Hoofdstuk 7. Een zeer
hoge selectiviteit naar Kamfooleenaldehyde (93%) werd bereikt omdat de Lewis zure
centra (de titaniumatomen in het zeolietrooster) geïsoleerd in een silica-matrix zitten
terwijl Brønsted-zure centra volledig afwezig zijn. De binnenconcentratie van α-
pineenoxide dient laag gehouden te worden om polymerisatie te voorkomen. Dit werd
gerealiseerd door een juiste keuze van oplosmiddel (bij vloeistoffase-reacties) en van
co-adsorbaat (bij de gasfase-reacties).
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LIST OF PUBLICATIONS


CURRICULUM VITAE


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