Adsorption effects in acid catalysis by zeolites

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Adsorption Effects in

Acid Catalysis by Zeolites

PROEFSCHRIFT

ter verkrijging van de graad doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr. M. Rem, voor een commissie aangewezen door het College van Dekanen in het openbaar te verdedigen op woensdag 29 januari 1997 om 16.00 uur

door

ANNEMIEKE VAN DE RUNSTRAAT

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Druk: Universiteitsdrukkerij, Technische Universiteit Eindhoven.

Runstraat, van de, Annemieke

Trefwoorden: kinetics / kinetiek; modelling / modellering


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Introduction

1.1. Hydro-isomerization

Public awareness and concern about the environment have been growing during the last decade. This resulted in legislation by the governments restricting allowable levels of pollutants in exhaust emissions. At the same time the oil refining industry had to meet increasing fuel demands by modern combustion engines. Recently, a letter about trends and constraints of the European refining industry was published.

The combustion efficiency, cold start properties and knock resistance of a fuel can be expressed in a factor known as the Research Octane Number (RON). Modern engines require fuels with a RON between 92 and 100. This demand cannot be met by the petroleum fraction as distilled and therefore the octane rating must be upgraded. In the past this was done using lead compounds such as tetra-ethyllead and tetra-methyllead. These lead compounds are now banned since they are toxic to humans and animals and they poison the catalytic exhaust gas converters that are nowadays compulsory in many countries in the world. Another way to upgrade the RON is by adding benzene and other aromatics. However, the legislation about allowable contents of these compounds in fuel is also getting increasingly strict.

An alternative way to increase the octane rating of gasoline is through isomerization of linear to branched alkanes. Figure 1.1. shows the equilibrium concentration of hexanes and their RON value in parentheses as a function of temperature. From this figure it is clear that there exists a considerable incentive to isomerize n-hexane to its isomers at low temperature. The process involved is often referred to as hydro-isomerization.
Chapter 1

Figure 1.1. Equilibrium concentration of hexanes

Nowadays, there are over 25 sites operating the Total Isomerization Process (TIP) and more than 75 units of the related Penex Process\(^7\). TIP is a combination of Shell's Hysomer process and Union Carbide's ISOSIV process\(^6\). The Hysomer process is carried out using a Pt/HMOR catalyst and performs the hydro-isomerization of a mixture of n-pentane and n-hexane. It operates at 250 °C and a hydrogen pressure of 10-30 bar.

The ISOSIV process separates unreacted normal paraffins from their isomers by selectively adsorbing them on zeolite CaA (pressure swing adsorption). After desorption (by applying vacuum) the n-alkanes are recycled.

Figure 1.2. Total Isomerization Process (TIP)

1.2. Why hydro-isomerization?

The low deactivation rate of hydro-isomerization was the reason that it was chosen as a model reaction to study adsorption effects in acid catalysis in stead of cracking. Narbeshuber already
found the cracking of light hydrocarbons to be adsorption driven. Such a stable catalyst is needed to study the reactions under true steady state conditions. It means, however, involving a noble metal function, thus increasing the complexity of the reaction mechanism.

Hexane was chosen since it possesses a low cracking rate and it has two mono- and two di-branched isomers. Normal alkanes with more than six carbon atoms crack much faster than pentane and hexane. The explanation for this phenomenon is given in Chapter 2. The modelling of the reaction is less complex when cracking can be excluded. The modelling of the isomerization itself can thus be more elaborate. Since pentane has only one isomer, it is more interesting to study a reactant producing more products with different selectivities.

1.3. Zeolites

Zeolites are crystalline alumino-silicates with a three-dimensional porous structure. This structure is formed by connecting aluminium and silicon atoms, the so-called T-atoms, by oxygen atoms. By varying the way in which these T-atoms are connected many different zeolite structures are possible. Typical pore diameters range between 4 and 12 Å. This is comparable to the size of hydrocarbons (typically 4 to 7 Å). Therefore, zeolites and related structures (Alumino-phosphates) are also referred to as molecular sieves. By replacing a silicon(IV) by an aluminium(III) atom a negative charge is created in the zeolite lattice. This charge must be compensated. In natural and as-synthesized zeolites this is usually done by a sodium or potassium ion. By exchanging these metal ions by other (metal) ions the properties of the zeolite can be changed. By introducing a proton a solid acid catalyst can be obtained.

Zeolites in any form are also very useful catalyst supports. By combining deposited small metal particles on an acid zeolite, a bifunctional catalyst can be prepared.

1.4. Zeolite pore size and shape effects

The influence of pore size and shape on a reaction can be understood in terms of shape selectivity and confinement.

Shape selectivity can be divided into three, well-accepted types:

1. Reactant shape selectivity: some reactants of the feed will fit into the zeolite pores and will react; others, which are too large, will not.
2. Transition state shape selectivity: when a transition state between a certain reactant and product is too large to be formed inside the pores, the corresponding product will not be detected.
3. Product shape selectivity: when a product is too large to exit the pores once it is formed, this product will also not be found.

Some other, less common, types of molecular selectivity are:
1. Concentration effect\textsuperscript{11}. This effect describes the increased concentration of hydrocarbons in zeolites, thus favoring bimolecular reactions. The 'cage effect' is a special case: molecules with the size of heptane and octane perfectly fit into the erionite cages, thus reducing their mobility and enhancing their residence times and reactivity.
2. Molecular traffic control\textsuperscript{12}. This effect describes qualitatively the transport of molecules with different shape and/or size in the intracrystalline volume of zeolites having two distinct types of pores as in the case of MFI-type zeolites.
3. Molecular circulation\textsuperscript{13}. This effect determines the way in which a reactant molecule approaches the pore mouth.
4. Energy gradient selectivity\textsuperscript{14}. This effect applies to the tortuosity of the zeolite channels and the differences in the field gradient caused by isomorphic substitution.
5. Inverse shape selectivity\textsuperscript{15}. Zeolites, whose pore size range from 7 to 7.4 Å, show a preferred adsorption and hydrocracking activity of dimethylbutanes versus n-hexane. This effect is explained by attractive forces, as opposed to repulsive forces as is the case in most examples of shape selectivity.

The basis of the confinement theory was established by De Boer and Custers in 1934\textsuperscript{16}. These authors correlated adsorption effects to the Van-der-Waals interaction between sorbate and oxygen atoms. A larger number of coordinating surface atoms led to an enhanced attractive force between sorbate and sorbent. This is illustrated in Figure 1.3. The grey circles depict an adsorbed molecule. The larger shapes represent the ring of oxygen atoms of a zeolite pore.

![Large round pore, little interaction](image1.png)
![Large ellipsoid pore, more interaction](image2.png)
![Small round pore, lots of interaction](image3.png)

**Figure 1.3. Zeolite sorbate interaction**

The definition of the confinement or surface curvature effect as defined by Derouane is: “A surface curvature effect exists when the size of the host structure and the guest molecule becomes comparable”\textsuperscript{17}. According to this definition such an effect should exist in reactions of organic molecules in zeolites. This effect can also be noticed in diffusion. If a pore is larger than the diffusing molecule, the molecule will be ‘creeping’ along the pore wall. When both diameters become comparable, the molecule will “float” on the oxygen electron clouds and its diffusion constant will be much larger than expected.
A very nice example of the influence of adsorption effects is given by experiments by Kapteijn et al. using silicalite-1 (the all-silica ZSM-5) membranes\(^\text{18}\). This membrane is used to separate n-butane and helium. At lower temperatures the outlet stream is n-butane enriched. The zeolite is filled with n-butane since its adsorption enthalpy is higher than that of helium. The n-butane will therefore diffuse faster through the membrane than the helium. At higher temperatures the situation is reversed and the outlet stream is enriched in helium. Now the higher diffusivity of helium has become the determining factor since the membrane is no longer filled with n-butane.

Confinement can also explain the ‘kink’ in the adsorption isotherm of n-hexane on silicalite\(^\text{19}\). At low coverages, the hexane will adsorb randomly in the zeolite pores. At a coverage of approximately 50 %, the molecules will order by preferential siting in the zigzag channels, because of the higher interaction. At higher coverages, the straight channels will also be filled and the adsorption isotherm will show a discontinuity.

A special type of diffusion is single-file diffusion. This phenomenon can occur in one-dimensional pore systems such as zeolite L, Mordenite, ZSM-22 and ALPO-5. Since the molecular diameter of a linear hydrocarbon is similar to the diameter of a zeolite pore, the diffusing molecules cannot pass each other\(^\text{20}\). The rate of diffusion is then suppressed by the fact that a molecule cannot proceed until space has been freed by other molecules\(^\text{21}\).

1.5. Goal of this research

The influence of pore-size and shape on the hydro-isomerization will be determined by testing different zeolites, showing different adsorption enthalpies for the reactant n-hexane. Kinetic data will be determined. The results will be compared to those obtained by computer modelling.

Chapter 2 gives a review about the present issues in the literature concerning hydro-isomerization. General, mechanistic issues and kinetics of this reaction as well as current theories concerning the acidity of zeolites and its influence on catalysis are discussed.

In Chapter 3 an introduction to kinetic modelling is given. Special attention is paid to microkinetic modeling. It also describes the numerical method used for the simulations. In Chapter 4 the elementary steps chosen to represent the hydro-isomerization in the modelling are highlighted. The data that describe these steps (pre-exponential factors and activation energies) were either taken from literature, calculated from zeolite characterization or are estimated. A detailed discussion about the parameters of each step is given.

Chapter 5 is dedicated to the experiments that were performed. The first part focuses on characterization of the catalysts used as well as determining the best set of conditions at which to measure kinetic parameters such as orders of reaction and activation energies. The
second part describes these measurements at atmospheric pressure and correlates them to intrinsic catalyst characteristics. In Chapter 6, the results of the simulations are described. They are correlated to the experimental kinetics and a fundamental discussion is given about the most important features.

Two appendices are included at the end of this thesis. Appendix 1 describes the details of the programs used as well as the component coding. Appendix 2 lists the values of the parameters used in the simulations.

Literature cited.

[14] Mirodatos, C.; Barthomeuf, D. J. Cat. 1985, 93, 246
In this chapter a review of literature dealing with hydro-isomerization will be given. The attention will be focused on the reaction of n-hexane. Different results and ideas will be compared and discussed. A separate paragraph is dedicated to the acidity of zeolites and its role in catalysis.

2.1. Hydro-isomerization in general

In the late 1950's and early 1960's the first articles about 'hydro-isomerization' appeared. One of the first articles in the field of bifunctional catalysis speaks of 'Houdriforming': the reforming of the Houdry Laboratories\textsuperscript{1}. It was found that in the presence of a noble metal the stability of acid catalysts was greatly improved. This was attributed to rapid hydrogenation of coke precursor molecules\textsuperscript{2}. Weisz, one of the first who tried to explain the enhanced activity of these catalysts at lower temperatures, compared their behavior to that of the normal cracking catalysts. He proposed a bifunctional mechanism in which the metal performs dehydrogenation of the feed alkane and a hydrogenation of isomer alkenes. The acid sites catalyze the actual isomerization (see Figure 2.1.).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.1.png}
\caption{Schematic representation of Weisz' bifunctional mechanism}
\end{figure}
Weisz performed two sets of experiments to help prove this mechanism.

1. A platinum loaded silica showed a low activity in producing iso-hexanes from hexane. Pure silica/alumina was not very active either in this reaction. A mechanical mixture of the two showed high isomerization activity.

2. A conversion of 43% to skeletal isomers was achieved by contacting 1-hexene with a 11% Al₂O₃ containing silica-alumina cracking catalyst at 300 °C. Paál et al. repeated the first of these 'Weisz' experiments with a mixture of EUROPT-1, a standard 6.3% Pt/Silica, and HY (catalyst 1). The n-hexane was also exposed to a two-stage set-up consisting of a bed of EUROPT-1 followed by a bed of HY (catalyst 2). Another experiment involved the catalysts placed in the opposite order (catalyst 3). In all cases the hexane was recycled (see Figure 2.2.). Differences in activities and selectivities between the three types of beds were only found at the initial stage of the experiment. When the reactant was exposed to catalyst 2, the product composition was similar to the one obtained from catalyst 1. When the reactant was led over catalyst 3, the initial composition resembled that of pure EUROPT-1. These experiments proved that the primary activation of an alkane was much faster on metallic sites than acidic sites.

Hydro-cracking is related to hydro-isomerization and is in fact a consecutive reaction to the isomerization. Data obtained from this reaction are therefore also applicable to hydro-isomerization. The four types of β-scission that play a role in hydro-cracking are listed in Table 2.1.

### Table 2.1. Possible β-scission mechanisms

<table>
<thead>
<tr>
<th>Type</th>
<th>Ions involved</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>tert → tert</td>
<td><img src="image" alt="Example A" /></td>
</tr>
<tr>
<td>B1</td>
<td>sec → tert</td>
<td><img src="image" alt="Example B1" /></td>
</tr>
<tr>
<td>B2</td>
<td>tert → sec</td>
<td><img src="image" alt="Example B2" /></td>
</tr>
<tr>
<td>C</td>
<td>sec → sec</td>
<td><img src="image" alt="Example C" /></td>
</tr>
</tbody>
</table>

| tert   | tertiary       |
| sec    | secondary      |

Figure 2.2. Catalyst types from the experiments of Paál et al.
In the next paragraphs parameters, influencing hydro-isomerization or hydro-cracking activity and selectivity, will be discussed.

2.1.1. Metal deposition procedure

Review articles about this subject are published by Sachtler and Zhang\textsuperscript{7} and Gates\textsuperscript{8}. Here a short conclusion of their study is given. The two most frequently used methods to deposit a noble metal on a support are ion exchange and ‘incipient wetness’ impregnation using metal (complex) cations. Since the latter method also introduces a stoichiometric amount of anions, the former is preferred. Moreover, Jao \textit{et al.} found lower dispersions for impregnated Mordenite\textsuperscript{9}. Probably part of the metal was deposited outside the zeolite pores and the neutral platinum precursors agglomerated to larger platinum particles.

Ion exchange can be performed competitively or non-competitively. Ribeiro reported a dependence of the metal dispersion on the relative amount of metal salt and ammonia in the exchange solution\textsuperscript{10}. It was concluded that competitive exchange yields a more disperse and active catalyst. A drawback of this method is, however, that the calcination step must be carried out with extra care since large particles may result from the reduction of the metal by the ammonium ions. Larger particles expose less metal surface and are therefore less active per gram deposited.

The anion in the metal complex is usually chloride or hydroxide. Since chloride has a strong interaction with the aluminium in the zeolite framework, it is not easily removed. This may alter the apparent acidity relative to the true acidity of the zeolite protons. An extra advantage of the hydroxide ion is that the exchange of a proton will lead to formation of water. In all other cases the exchange solution will be acidified. This may lead to zeolite destruction.

2.1.2. Noble metal to acid sites ratio

Both palladium and platinum are used in the hydro-isomerization. Palladium is more sulfur resistant than platinum and has a low hydrogenolysis activity but may form hydrides\textsuperscript{12}. Moreover, the hydrogenation-dehydrogenation activity of platinum is much higher\textsuperscript{13}. Most of the recent research is performed on platinum-loaded zeolites.

Gianetto \textit{et al.} found that at atmospheric pressure a ratio of acid to platinum sites (H\textsuperscript{+}/Pt) of less than 10 was necessary to obtain an ideal, ‘Weisz’, bifunctional catalyst\textsuperscript{14}. This ratio was close to the one reported by Degnan \textit{et al.}, who found that one exposed platinum atom per six framework aluminium atoms (acid sites) was needed\textsuperscript{15}. The latter authors used a simple dual-site model to show how an imbalance in hydrogenation and acid function can even alter the apparent reaction network of the observable chemical species in the system. This was also recognized by Alvarez \textit{et al.}\textsuperscript{11a}. They found that when there was not enough platinum present both mono- and di-branched products were formed as primary products. At
higher platinum loadings sufficient platinum was available to hydrogenate mono-branched isomers before they underwent a second isomerization.

In their study of the activity and selectivity of β-zeolite, Yashima et al. found that a H⁺/Pt of 13, on more acidic sample a ratio of 7, was needed for an optimum conversion and yield of 2,2-dimethylbutane\textsuperscript{16}.

At higher pressures (for example 30 bar) only 0.01 platinum sites per acid site are needed\textsuperscript{17} (H⁺/Pt = 100). Grau and Parera, however, found that the activity for n-octane reaction increased continuously as a function of the platinum loading of a Mordenite catalyst\textsuperscript{18}. This was probably due to suppression of coke formation. Blomsma et al. found that on noble metal loaded β-zeolite both mono-molecular and bimolecular mechanisms are responsible for the isomerization and cracking of heptane\textsuperscript{19}. The bimolecular mechanism was found to be suppressed by increasing the metal function. The highest platinum dispersions were achieved by competitive exchange with a NH₄⁺/Pt\textsuperscript{2} ratio in the solution of 25.

Most authors have found an optimum in the hydro-isomerization activity as a function of metal loading. At lower loadings the rate of hydrogenation-dehydrogenation is too low, while at higher loadings the metal may become too active and cracking (hydrogenolysis) will take place\textsuperscript{20}.

2.1.3. Pretreatment temperature
It is generally accepted that calcination of the platinum tetra-ammonium complex before reduction is necessary in order to obtain a homogeneous metal distribution\textsuperscript{10,21}. When the complex is immediately reduced after the deposition, neutral, mobile metal hydrides will be formed. These hydrides may cluster or diffuse out of the zeolite. All authors report that a low heating rate and a high flow rate when calcining the complex is necessary to obtain high dispersions. In between calcination and reduction the sample should be cooled to room temperature in an inert atmosphere.

Leglise et al. investigated the influence of the reduction temperature on the activity and selectivity of a Pd/HY catalyst under atmospheric pressure\textsuperscript{22}. They found that a reduction temperature of 573 K yielded a stable, highly active and selective catalyst. Samples reduced above 773 K initially favored cracking. During a deactivation period this was changed into a high isomerization selectivity. TEM measurements showed that this effect was due to a lowered dispersion of the metal. Since the acid sites coke more rapidly than the hydrogenation sites, the isomerization yield increases after deactivation of the acidic sites that are responsible for cracking. (See also 2.1.7., Ribeiro et al.)

Carvill et al. calcined all samples at 783 K and investigated the influence of the reduction temperature on metal dispersion and activity\textsuperscript{23}. In the case of a 3-dimensional pore system (ZSM-5), a reduction at 573 K yielded a less disperse, but more active catalyst than did samples reduced at 723 K. In the case of a 1-dimensional system (MOR), it may be
beneficial to create large metal particles\textsuperscript{21}. These particles may locally destroy the zeolite, thus creating a 3-dimensional pore system allowing diffusing molecules to pass each other. If the zeolite structure stays intact, single file diffusion conditions are fulfilled and the products formed deep inside the pores are unable to escape.

Jao \textit{et al.} found that a sample reduced at 803 K had a lower hydro-isomerization activity than a sample reduced at 723 K\textsuperscript{9}. However, the former sample was more stable in a feed containing 500 ppm sulfur.

Gianetto \textit{et al.} did not find any significant influence of the reduction temperature on the metal dispersion of a Pt/HZSM-5 zeolite\textsuperscript{24}. The best metal dispersion was achieved by calcination of the ammonia from the platinum tetra-amine complex at 573 K. Other authors obtained similar results for Pt/X and Pt/Y zeolites\textsuperscript{25,26}.

2.1.4. Hydrogen and hexane partial pressure.

According to the classical bifunctional mechanism, depicted in Figure 2.1., assuming that the isomerization is rate determining and the reverse reaction can be neglected (differential conditions), the following rate equation is obtained\textsuperscript{27}:

\[
R = \frac{K_{\text{dehydr}} \cdot K_{\text{prot}} \cdot k_{\text{isom}} \left( \frac{P_{\text{nC6}}}{P_{\text{H2}}} \right) \cdot C_{\text{H+}}}{1 + K_{\text{dehydr}} \cdot K_{\text{prot}} \cdot \left( \frac{P_{\text{nC6}}}{P_{\text{H2}}} \right)} = k_{\text{overall}} \cdot P_{\text{nC6}}^n \cdot P_{\text{H2}}^m
\]

$K_{\text{dehydr}}$ = equilibrium constant of dehydrogenation
$K_{\text{prot}}$ = equilibrium constant of protonation
$k_{\text{isom}}$ = rate constant of isomerization
$P_{\text{nC6}}$ = partial pressure of n-hexane
$C_{\text{H+}}$ = concentration of active acid sites
$P_{\text{H2}}$ = partial pressure of hydrogen
$k_{\text{overall}}$ = overall rate constant
$n$ = overall order of the reaction in n-hexane
$m$ = overall order of the reaction in hydrogen

When equation (2.1) applies, an order in hexane between 0 and 1 and an order in hydrogen between -1 and 0 is expected. The true value depends on the relative values of the reaction constants. The order in hydrogen will have the same absolute magnitude as the order in hexane but with an opposite sign.

Most hydro-isomerization experiments are performed at pressures above 10 bar. Some values are given in Table 2.2. A pseudo zero-order dependence in hexane can be found when the zeolite is completely filled with hexane\textsuperscript{28}. An order of 1 means that under these conditions the zeolite is almost empty. In general large negative orders in hydrogen are found, except on an aged catalyst. This is due to deactivation of the platinum on the catalyst. Since
most authors do not find that $m = -n$, equation (2.1) is not entirely valid. In most cases reactions or phenomena other than the isomerization also play a role in the catalyst activity.

**Table 2.2. Orders of reaction at high pressure**

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>$P$ [bar]</th>
<th>order in hydrogen</th>
<th>order in hexane</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOR</td>
<td>30</td>
<td>-0.75</td>
<td>0.7</td>
<td>Guisnet *et al.*³¹</td>
</tr>
<tr>
<td>MOR</td>
<td>20</td>
<td>?</td>
<td>1</td>
<td>Li *et al.*²⁹</td>
</tr>
<tr>
<td>MOR</td>
<td>14</td>
<td>?</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>MOR (nC₅)</td>
<td>11</td>
<td>-0.89</td>
<td>0.53</td>
<td>Liu *et al.*³⁰</td>
</tr>
<tr>
<td>BEA (nC₅)</td>
<td>3</td>
<td>-0.5</td>
<td>?</td>
<td>Blomsma *et al.*¹⁹</td>
</tr>
<tr>
<td>FAU</td>
<td>40</td>
<td>-0.85</td>
<td>0.6-0.8</td>
<td>Guisnet *et al.*³¹</td>
</tr>
<tr>
<td>FAU (fresh)</td>
<td>40</td>
<td>-0.85</td>
<td>0.5</td>
<td>Guisnet *et al.*³¹</td>
</tr>
<tr>
<td>FAU (fresh)</td>
<td>40</td>
<td>-0.45</td>
<td>0.6</td>
<td>Guisnet *et al.*³¹</td>
</tr>
<tr>
<td>FAU (aged)</td>
<td>40</td>
<td>-0.6</td>
<td>0.6</td>
<td>Guisnet *et al.*³¹</td>
</tr>
<tr>
<td>FAU (aged)</td>
<td>40</td>
<td>-0.15</td>
<td>1</td>
<td>Guisnet *et al.*³¹</td>
</tr>
</tbody>
</table>

Guisnet *et al.* measured the order in hydrogen under atmospheric pressure on a dealuminated Mordenite sample with a Si/Al ratio of 68³¹. They found a positive instead of negative order. This unexpected feature was attributed to deactivation effects. This conclusion is supported by work of Yori *et al.* on isomerization of n-butane over HMOR and Pt/HMOR³². They found a beneficial influence of the hydrogen partial pressure at atmospheric pressure on the catalyst stability due to hydrogenation of coke intermediates from the acid sites. However, the initial activity at higher hydrogen partial pressures was lower due to coverage of strong acid sites by hydrogen. This resulted in a positive order in hydrogen at steady state conditions and a negative order when the initial activity is considered. Meusinger and Corma performed n-heptane cracking experiments at elevated pressure (4.7-24 bar hydrogen, total pressure 24 bar, diluting gas nitrogen) on HZSM-5³³. They also found a positive order in hydrogen due to hydrogenation of the products from the acid sites since the desorption of products was the rate determining step.

### 2.1.5. Absolute pressure

It is generally found that the stability of the catalyst is beneficially influenced by higher absolute hydrogen pressure. Guisnet *et al.* found that under atmospheric pressure the initial activity of a 0.3 wt.% Pt/HMOR decreased with an increase in Si/Al ratio (obtained by dealumination)¹¹b. At high pressure (30 bar), however, the activity went through a maximum at the lowest Si/Al ratio where there are no aluminium atoms left in the next nearest neighborhood of an acid site. This means that the reaction is controlled by the acidity of the
acid sites (see paragraph 2.2.1.). Froment found that the rate of hydro-isomerization of n-decane decreased with increasing total pressure in a pressure range of 7 - 100 bar\textsuperscript{28}.

\subsection*{2.1.6. Zeolite}
Most of the literature about hydro-isomerization deals with experiments performed on Mordenite or zeolite Y. Ribeiro \textit{et al.} concluded from their work that, in the case of a metal surface area of 0.5 m\textsuperscript{2}/g, the selectivities observed with HY could be explained by a bifunctional mechanism\textsuperscript{10,27}. Using Pt/HMOR, the selectivities were similar to those on a normal acid catalyst. They concluded that in this case the platinum was responsible for hydrogenation of coke precursors thus limiting both the rate and level of coking and the deactivation. In another study, using more types of zeolites, the influence of pore structure on selectivity in hydro-cracking and hydro-isomerization of n-heptane was investigated\textsuperscript{34}. It was concluded that both the characteristics of the active sites and the pore structure determine the distribution of monobranched isomers and cracking products as well as activity and stability of the catalyst. It was suggested that this reaction could be used for determining the pore structure of zeolites, replacing n-decane hydro-conversion.

Some work has been reported on β-zeolite\textsuperscript{15,19}, ZSM-5\textsuperscript{24}, ZSM-22 and SAPO's\textsuperscript{35} (Silico-Alumino-Phosphates). Pt/β-zeolite is an extremely promising new catalyst for hydro-isomerization because of its tunable Si/Al ratio and its 3-dimensional, 12-ring pore system\textsuperscript{36}. ZSM-5 exhibits restricted transition state shape selectivity resulting in monomethyl isomer products only\textsuperscript{37,38}.

Martens \textit{et al.} concluded from their experimental and Molecular Graphics study that ZSM-22 exhibits zeolite pore-mouth catalysis for hydro-isomerization of n-decane\textsuperscript{39}. Type C hydrocracking (see Table 2.1) is not possible on this zeolite, resulting in a low cracking rate. Both effects combined, result in a very selective isomerization catalyst which is active under very mild conditions. In a consecutive publication, they studied heptadecane isomerization, also on ZSM-22\textsuperscript{40}. The pattern of branching was explained by a lock-and-key principle based on the crystallographic planes of the zeolite crystals and the zeolite chain.

Parlitz \textit{et al.} studied different palladium loaded SAPO's and the corresponding non-acidic ALPO's to investigate the influence of acidity and pore apertures on the hydro-isomerization of n-heptane\textsuperscript{35}. One of their main conclusions concerned the high cracking selectivity of SAPO-5, a 1-dimensional, 12 ring system. This effect was attributed to the reduced accessibility of part of the bridged hydroxyl groups within the molecular sieve framework. Those different locations were confirmed by infrared OH vibration spectra recorded after adsorption of the reactant molecule. Campelo \textit{et al.}, however, concluded that SAPO-5 cracks less than SAPO-11 from their experiments with hexane\textsuperscript{41}.
2.1.7. Acidity and Si/Al ratio

Koradia et al. performed experiments at high pressure. They reported a maximum in activity at a maximum number of strong acid sites\(^{42}\). This is in accordance with work of Guisnet et al. (see paragraph 2.1.3.).

Ribeiro et al. found that strong Bronsted acid sites disappeared almost completely after coking\(^{43}\). Strong sites were defined as those sites on which pyridine remained adsorbed up to 573 K. This implies that under aged conditions less strong acid sites perform the reaction. In a more recent paper, however, Ribeiro et al. conclude on the basis of a selectivity and activity change that coke preferentially poisons the platinum hydrogenation sites\(^{44}\).

In research performed by Zhan et al., platinum loaded NaX, NaY, HY and HX zeolites were tested\(^{45}\). NaX showed typical non-acidic behavior. NaY, on the contrary, turned out to be an outstanding aromatization catalyst. This was probably due to the interaction between basic and platinum sites.

2.1.8. Reaction temperature

The isomerization selectivity of a catalyst is generally found to pass through a maximum as a function of temperature. At higher temperatures the isomers produced are consumed in consecutive reactions such as cracking\(^{46}\). Moreover, thermodynamic restrictions on the reaction mixture exist.

Most activation energies reported are between 140 and 230 kJ/mol for n-hexane on HY and between 110 and 150 kJ/mol for n-hexane on Mordenite. The range given on HY zeolite is very large, the higher values might be a result of hydro-cracking as a side reaction or different orders of reaction (see equation (2.2)\(^{47}\)). On both zeolites there seems to be no trend in activation energy as a function of Si/Al ratio nor as a function of absolute pressure or metal function.

\[
E_{\text{act,app}} = E_{\text{act,true}} - n \cdot [\Delta H_{\text{prot,ads}} + \Delta H_{\text{ads,n=C6}} + \Delta H_{\text{dehyd}}]
\]

\(E_{\text{act,app}}\) = apparent activation energy
\(E_{\text{act,true}}\) = activation energy of the surface reaction
\(n\) = order of the reaction in n-hexane
\(\Delta H_{\text{prot,ads}}\) = enthalpy of protonation of an adsorbed n-hexene
\(\Delta H_{\text{ads,n=C6}}\) = adsorption enthalpy of n-hexene
\(\Delta H_{\text{dehyd}}\) = enthalpy of dehydrogenation of n-hexane

Otten et al. found unusually low activation energies (59-67 kJ/mol) in their study of n-hexane isomerization on a Pt/HMOR zeolite\(^{48}\). The values are approximately one-half of the apparent activation energy measured by others on similar catalysts. This usually indicates that diffusion limitations play a role. Corma\(^{49}\), however, stated that it is not uncommon to find that, in processes in which intra-zeolitic pore diffusion is the rate determining step, the experimental activation energy exceeds values of 15 kcal/mol (62 kJ/mol).
In their paper, Roberts and Lamb explained that pore diffusion resistance does not always lead to activation energy falsification. Their point was illustrated by a slow, irreversible reaction (for example cracking) reacting in parallel with a fast, reversible reaction (for example isomerization). The difference in the apparent and true activation energy of the slow reaction depends on the equilibrium constant ($K_{fast}$) and the enthalpy change of the fast, reversible reaction ($\Delta H_{fast}$). If $K_{fast}$ is small compared to unity, or if $\Delta H_{fast}$ is close to zero, a diffusion resistance will not cause a falsification of the activation energy of the slow reaction. However, if $K_{fast}$ is large compared to unity and if $\Delta H_{fast}$ is large, this may result in observation of a negative activation energy for the slow, reversible reaction (for an endothermic reaction). For an exothermic reaction one obtains an activation energy that is much higher than the true apparent activation energy. This is summarized in the table below.

**Table 2.3. Summary of falsification of activation energies by pore diffusion limitations**

<table>
<thead>
<tr>
<th>Case 1</th>
<th>$K_{fast}$</th>
<th>$\Delta H_{fast}$</th>
<th>slow: $E_{act,observed}$</th>
<th>$E_{act,true}$</th>
<th>apparent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>&lt;&lt; 1</td>
<td>small</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 2</td>
<td>&lt;&lt; 1</td>
<td>large</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 3</td>
<td>&gt;&gt; 1</td>
<td>small</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 4a</td>
<td>&gt;&gt; 1</td>
<td>large, endothermic</td>
<td>&lt; 0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case 4b</td>
<td>&gt;&gt; 1</td>
<td>large, exothermic</td>
<td>&gt; 2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In all other cases, the observed activation energy of the fast reaction is indeed one-half of the true apparent activation energy. Since (hydro-)isomerization is a process with a small reaction enthalpy and an equilibrium constant close to one, the activation energy of cracking will be one half of the true apparent activation energy under diffusion limited conditions.

Rödenbeck et al. used Monte Carlo simulations to examine the influence of single-file diffusion on activation energies. Their purpose was to explain data by Karpinski et al. who found that the activation energy of the palladium-catalyzed conversion of neopentane measured on a L zeolite was higher than on a Y zeolite. The former zeolite has a 1-dimensional pore system while the latter has a 3-dimensional system of cages. It was shown that the apparent activation energy under single-file conditions may exceed that of a non-diffusion-limited situation. Whether this is the case depends on the reactant residence time on a site (depends on surface coverage), the adsorption/desorption activation energy and the real activation energy of conversion.

Liu et al. found a bend in the Arrhenius plot of the isomerization of n-pentane over a Pt/HMOR catalyst. In the lower temperature range they measured a higher activation energy (145 kJ/mol) than at higher temperature (112 kJ/mol) and even higher temperature (55 kJ/mol). They attributed this effect to single-file diffusion. At lower temperatures the zeolite...
is filled with n-pentane, resulting in reaction only at the sites close to the pore mouth. When
the temperature is increased, the number of available sites is increased which leads to a higher
apparent activation energy. When all sites are available the true apparent activation energy is
obtained. There are, however, some remarks to be made against their interpretation. Firstly,
closer observation of their Arrhenius plot leads to the conclusion that the full line is curved.
Secondly, they do not take into account a possible change in orders of reaction since they use
a rate of reaction (mol/gcat s).

2.1.9. Number of carbon atoms in the n-paraffin
Weitkamp et al. performed a series of measurements using C$_9$ through C$_{16}$ n-alkanes and a
Pt/HZSM-5 catalyst$^{38}$. They showed the existence of a minimum in the carbon number
distribution of hydro-cracking. Products containing half the number of carbon atoms of the
reactant were hardly found, meaning a low probability of center cracking. Haag showed the
existence of a compensation or isokinetic effect as a function of chain length in a range of
butane to decane$^{53}$.

One might expect that when the reacting alkane is very large and has a high
adsorption enthalpy on a zeolite, the isomerization will become inhibited by product
desorption. This is, however, very difficult to verify experimentally because the cracking rate
increases enormously in reaction of n-C$_7$ and longer n-alkanes. This effect can be explained
by PCP isomerization (see paragraph 2.3.) and leads to products having a lower adsorption
enthalpy.

2.1.10. Co-reactant in the feed
Martin et al. used a co-reactant (20%) in a feed of normal paraffins as a means to study
changes in zeolite shape and size selectivities$^{54}$. They concluded that the apparent activation
energy is not changed by introduction of an aromatic co-feed. An effect that could be
observed is a change in the overall rates of isomerization due to site suppression and/or pore
blockage. Even a non-shape selective zeolite could be made shape selective by co-feeding
aromatics. Guisnet et al. came to the same conclusion on the basis of their experiments using
lower co-feed contents$^{55}$. When aromatics, napthenes and higher alkanes were used, the
deactivation rate increased. This was due to the fact that these reactants produced cracking
products such as olefins and aromatics leading to extra coke formation.
2.2. Acidity

An excellent introduction in this field is given by Jacobs and Martens in 1991. In the next paragraphs ideas developed by different authors about acidity and protonation of reactant molecules will be discussed.

2.2.1. Influence of Si/Al ratio

Most authors, especially those from industry, report intrinsically different acidity for different zeolites. For instance ZSM-5 is considered to be a more acidic zeolite than zeolite Y. A difference is even thought to be present on zeolites containing the same relative amount of aluminium atoms per unit cell.

The Next Nearest Neighbor (NNN) theory predicts that the intrinsic acid strength of an acid site is dependent on the number of aluminium atoms in the next nearest neighborhood. The O-H bond strength is thought to decrease (meaning an increase in the acid strength) until all NNN-atoms are silicon. Barthomeuf calculated this critical Si/Al ratio for different zeolites. She found a value of 9.5 for MFI, 9.4 for MOR, 8.3 for OFF and 6.8 for FAU structures. Since ZSM-5 (MFI) can only be synthesized with Si/Al ratios higher than 16, the calculated value can never be checked experimentally. The value for Mordenite has been experimentally confirmed by Stach and Jänchen in their study of the acidity of dealuminated Mordenites.

The number of acid sites decreases with the Si/Al ratio, since every Brønsted acid site is associated with an aluminium atom in the framework. The overall acidity is therefore strongest at that Si/Al ratio resulting in a maximum amount of aluminium atoms without one being in the Next Nearest Neighborhood of the other. Wachtler published a review article about 'The Role of Next Nearest Neighbors in Zeolite Acidity and Activity'.

The picture sketched in Figure 2.3. is only valid when one compares different samples of the same zeolite. Another important point to consider is the stability of the reactant base when it has accepted the proton. The more stable the carbenium ion created, the more acidic
the zeolite will seem. This stability will vary for different zeolites and it can be understood in terms of the ‘confinement effect’ or ‘solvated molecules’. The more a carbenium ion interacts with the oxygen atoms of the zeolite lattice, the more it will be stabilized. Therefore zeolites with small pores will *seem* more acidic than those with larger pores because of this enhanced stabilization \(^{62,63}\).

Polarizability is also an important feature of zeolites because of electronic effects described with the HSAB-principle (Hard and Soft Acid and Base)\(^{64}\). This principle says that a soft acid will preferably interact with a soft base and visa versa. Soft species are relatively large and are highly polarizable. In zeolite terms: if both sodium ions (soft acids) and protons (hard acids) are present, olefins (soft bases) will preferentially adsorb on the Na\(^+\) ions\(^{65}\).

### 2.2.2. Acidity theories

Olah (Nobel prize in chemistry winner 1994) has developed a theory to explain the acidity of superacids\(^{66}\). He proposed a superelectrophiles as being the reactive intermediate in many electrophilic reactions. Unlike the stable intermediates, superelectrophiles cannot be isolated. Electrophiles are compounds that are electron deficient. Superelectrophiles are doubly electron deficient (dipositive) electrophiles whose reactivity greatly exceeds that of their parents in aprotic or conventional acidic media. Examples of some superelectrophiles and their parents are given in Figure 2.5\(^{67}\).

![Figure 2.4. A superelectrophile as reactive intermediate](image)

This superelectrophile theory has been very valuable in explaining the superacidity of solid acids like Naftion-H and its activity in Fluid Catalyzed Cracking (FCC). It is however doubtful whether this theory can be extended to explain the acidity of zeolites towards reactants in the gas phase. Some others have used Quantum Chemistry to try to understand (zeolite) acidity from basic principles\(^{68}\). One main disadvantage of this method is that applicability is restricted to isolated systems containing a finite number of atoms.
Nevertheless, it can be used to describe acid-sorbate interaction processes, which are a very important feature in (zeolite) acidity.

Most of the work in this field deals with simple molecules like NH3 or H2O. One tries to calculate the degree of interaction of such a molecule with a zeolite cluster containing a proton while optimizing the geometry. Although there is disagreement about details, it is generally accepted that the lattice oxygen atoms play a decisive role in the bond formation between reactant base and zeolite cluster.

Kazansky defined an alkoxy species to be the species that emerged from the adsorption of an alkene on an acid site. This species is characterized by a covalent bond between an oxygen atom from the zeolite lattice and a carbon atom of the alkene. The neighboring carbon atom is coordinated to another lattice oxygen atom (see Figure 2.6b: \( \sigma \)-complex).

![Figure 2.6. \( \pi \)- and \( \sigma \)-complex](image)

Other authors have also recognized the existence of an alkoxy species. Datka described it in a more qualitative way than Kazansky. He stated that the stabilizing effect of the negative charge of the oxygen atoms on cations is more important than the destabilizing influence. NMR data of 1-octene adsorbed on HZSM-5, as presented by Stepanov et al., can also be explained by formation of an alkoxy species. In that paper this species is referred to as a silyl octyl ether.

In Table 2.4, it is shown that the differences in stability of alkoxy species are not as large as in case of free cations. According to Kazansky's theory, carbenium ions in zeolites are transition states rather than stable intermediates.

### Table 2.4. Differences in carbenium ion stability

<table>
<thead>
<tr>
<th></th>
<th>Enthalpy differences [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>primary vs. secondary</td>
</tr>
<tr>
<td>alkoxy species</td>
<td>10</td>
</tr>
<tr>
<td>free gas-phase ion</td>
<td>( \pm 70 )</td>
</tr>
</tbody>
</table>
2.2.3. Carbonium versus carbenium ions

Although alkoxy species are the intermediates in acid catalysis by zeolites, the hydroisomerization of an alkane will still take place via a carbenium ion. There are in principle three mechanisms for the generation of carbenium ions\(^{76}\).

I. protonation of the alkane forming a non-classical, penta-coordinated, carbonium ion, followed by removal of hydrogen resulting in a tri-coordinated carbenium ion.

\[
\begin{align*}
\text{R-CH-CH}_2\text{-R'} + \text{H}^+ & \rightarrow \text{R-CH}\text{-CH}_2\text{-CH}_2\text{-R'} + \text{H}_2 \\
\text{R-CH}_2\text{-CH}_2\text{-R}' & \rightarrow \text{R-CH}_2\text{-CH}_3 + \text{HR}'
\end{align*}
\]

Figure 2.7. Carbenium and carbenium ion

II. hydride transfer from a carbenium ion to an alkane.

\[
\begin{align*}
\text{R-CH-R''} & \rightarrow \text{R-CH-CH}_2\text{-R'} \\
\text{R-CH}_2\text{-CH}_2\text{-R'} & \rightarrow \text{R-CH}_2\text{-CH}_3 + \text{HR}'
\end{align*}
\]

Figure 2.8. Hydride transfer

III. dehydrogenation of the alkane by a noble metal to form alkenes that are in turn protonated into carbenium ions.

\[
\begin{align*}
\text{R-CH}_2\text{-CH}_2\text{-R'} & \rightarrow \text{R-CH-CH}_2\text{-R'} \\
\text{R-CH}_2\text{-CH}_3 + \text{HR}' & \rightarrow \text{R-CH-CH}_2\text{-R'}
\end{align*}
\]

Figure 2.9. Carbenium ion from olefin

A combination of these three mechanisms is also possible.

When platinum is present in the zeolite it will dehydrogenate the reactant alkane. This makes mechanism III more important than mechanism I to initiate the formation of carbenium ions since the activation energy for mechanism I is much higher than for III\(^{3,5}\).
Moreover, several authors have found that zeolites have lower acidity towards σ-bonds compared to superacids\(^{77}\). In those acidity terms they are comparable to sulfuric acid\(^{78}\).

In zeolite chemistry, mechanism II probably involves an alkoxy species and an alkane. It is thought to be unimportant at higher platinum loadings since bimolecular reactions are sterically suppressed in small pores, even though a high reactant concentration (as found in zeolites) favors hydride transfer\(^{79}\). Blomsma et al. found that in the hydro-isomerization and cracking of n-heptane the dimerization cracking is much less important than classical isomerization, but this mechanism is always active\(^{19}\). It might be argued that when not many cracking products are found, dimerization cracking isomerization can almost completely be ruled out. Liu et al. compared pentane and butane isomerization over a platinum loaded sulfated zirconia and a platinum-loaded Mordenite\(^{30}\). They concluded that bimolecular reactions are all but impossible on this zeolite. Research by Baltanas et al. showed that hydride donation of an alkane to a carbenium ion is $10^7$-$10^8$ times slower than the protonation of an alkene\(^{80}\). Even the deprotonation rate of a tertiary carbenium ion is approximately $10^4$ times faster than hydride transfer.

In addition to the ‘initiation’ of carbenium ions, the ‘termination’ of product carbenium ions must also be considered. Meusinger and Corma have suggested a direct hydrogenation of the alkoxy species with molecular hydrogen into a zeolite proton and an alkane\(^{33}\).
2.3. Protonated Cyclopropane isomerization

Once the alkoxy species have been formed, isomerization can take place. This is assumed to involve the Protonated Cyclopropane mechanism (PCP) when n and m are equal to, or larger than 1 (Figure 2.10).\textsuperscript{81,82} This mechanism operates via a carbenium ion transition state.

\begin{equation}
\text{H-(CH}_2\text{)}_n\text{-CH-CH}_2\text{-CH-CH}_2\text{-(CH}_2\text{)}_m\text{-H}
\end{equation}

\begin{equation}
\text{H-(CH}_2\text{)}_n\text{-CH-CH-CH-(CH}_2\text{)}_m\text{-H}
\end{equation}

\text{\(\delta^+\text{CH}_2\text{-CH}\text{-CH}_2\text{-(CH}_2\text{)}_m\text{-H}\)}

\text{\(\delta^-\text{Si}\text{-Al}\)}

\text{\(\sigma\text{-complex of n-alkoxy}\)}

\text{\(\sigma\text{-complex of iso-alkoxy}\)}

\text{Figure 2.10. Mechanism of PCP isomerization}

Weitkamp was one of the first to apply the PCP mechanism to hydro-isomerization and hydro-cracking\textsuperscript{83}. In two articles by Sie the PCP mechanism was used to explain many characteristics of hydro-isomerization and hydro-cracking\textsuperscript{84}. While classical theory has failed to explain the following features, PCP clarifies their origin.

* A steep increase in cracking activity of an acid catalyst exists as a function of chain length of the molecule. Chains longer than 6 carbon atoms are very difficult to isomerize selectively without significant cracking. Martens and Jacobs stated that also protonated cycloalkanes larger than cyclopropane can be involved in reaction of these n-alkanes\textsuperscript{85}.

* Methane and ethane are virtually absent as cracking products.

* The production of propane is relatively low compared to the production of longer alkanes.

* Existence of a characteristic pattern of branching of the cracked products.

Therefore the PCP mechanism was assumed to be the appropriate mechanism for the isomerization step in the simulation model.
2.4. Conclusions

It was shown that many different parameters influence the activity of zeolites in hydro-isomerization of n-hexane. Not only reaction conditions but also catalyst characteristics play a decisive role. It is therefore very important to characterize the catalyst acid sites and platinum function using different techniques. When the activity and selectivity of different zeolites must be evaluated, it is useful to choose samples which have the same acid strength. This simplifies direct comparison of the measured activities per acid site. The procedure for depositing platinum on the zeolite and the pre-treatment thereafter must also be optimized beforehand to obtain an ideal bifunctional catalyst.
Chapter 2

Literature cited.


[74] Kazansky, V.B.; Frash, M.B.; Van Santen, R.A. unpublished results


Issues in hydro-isomerization


In this chapter an introduction to the methods previously used to model kinetics will be given. Since we used microkinetics, special attention will be paid to this method. Finally, the numerical method for solving the problem will be discussed.

3.1. Methods of kinetic modelling

Modelling of catalytic reaction kinetics usually focuses on deriving information about rate parameters. This is done by evaluating conversions and selectivities and thus rates of reaction as a function of temperature (activation energies) and pressure (order of reaction). Depending on the method used, a description of the apparent kinetics or insight in molecular processes is obtained. Methods leading to the former will be described in sub-paragraph 3.1.1. The microkinetics method and other methods leading to insight are respectively dealt with in sub-paragraphs 3.1.2. and 3.1.3.

3.1.1. Methods describing apparent kinetics

Guisnet uses this approach based on the rate equation derived from a simple bifunctional mechanism. Since the main goal is to establish ideal bifunctional behavior, the experimental data are plotted according to the linearized rate equation. When the data points form a straight line they are used to quantify the applicability of the rate equation. There are two major disadvantages to this method:

1. fitting experimental data to a linearized equation only proves that the equation is not wrong; it does not prove that it is right.
2. when there is a poor fit one cannot easily see the reason. This requires a more elaborate reaction mechanism, without all the assumptions necessary to derive the ideal bifunctional
rate equation. A set of data that does not fit the linear equation is therefore not taken in consideration. Spivey and Bryant derived 12 possible rate equations using different assumptions for the hydro-isomerization of n-hexane and n-pentane on Mordenite and zeolite Y. The kinetic measurements at high pressure performed on both zeolites and using both reactants were fitted to these equations. Two different kinetic expressions were selected. In the case of Mordenite it was found that the isomerization was rate controlling. The equilibrium constant of adsorption of n-hexane was much larger than that for hydrogen and n-pentane. A dual-site mechanism was operable. The same was true for a Y zeolite except that the adsorption constants for both n-pentane and n-hexane were larger than that for hydrogen. The selected equations were then used to extract kinetic constants.

Li and Zhu developed a method which they called a 'two point method'. This method was based on another method, developed in 1962, by Wei and Prater. It uses a matrix of rate constants of inter-conversion of isomer hexanes. The matrix is then fitted to different 'composition vectors' to obtain values for rate constants. Chen et al. used the same method under the name 'combined Wei-Prater-Li method' to perform a kinetic analysis of their competitive reaction experiments (see also Chapter 2).

3.1.2. Microkinetics

In this method elementary steps are used. These steps describe the processes involved on a molecular scale. In heterogeneous catalysis this means adsorption and desorption steps and reactions in the adsorbed state. These reactions are represented by a forward and a reverse step. No forward step is a priori assumed to be rate determining or at equilibrium with its reverse step.

Each step is described by a pre-exponential factor and an activation energy. Collision and transition-state theory are used to estimate the pre-exponential factors. Activation energies are more difficult to estimate. Arrhenius plots of experiments performed separately from the reaction that is modeled, may be a source of activation energies. Also catalyst characteristics such as adsorption isotherms can be used. Thermodynamic data are used to constrain the activation energies. The difference between the activation energy of the forward and reverse reaction must be equal to the reaction enthalpy.

In this way a complete set of parameters describing the reaction is build. These are then fed into conventional catalytic engineering equations. Thus generating a set of differential equations that must be solved to obtain the outlet concentrations as a function of inlet concentrations and reaction conditions. The validity of the over-all kinetics can be checked experimentally. There are three types of ideal reactors possible: the batch, the plug flow and the continuously stirred tank reactor. In case of a plug flow reactor intermediate gas phase and surface concentrations are obtained. Thus information as a function of length along
the reactor bed is gained. It may be possible that only part of the bed participates in the actual reaction. In the final stage the model can be adjusted to experiments to obtain final values for the activation energies and pre-exponential factors. Constraints have to be used. From the calculations information is gained about which steps are reversible, at equilibrium, kinetically significant and which is the rate determining step.

Dumesic et al. applied this microkinetics method to isobutane cracking catalyzed by acid zeolites. It was shown that hydride transfer and oligomerization reactions are negligible at the reactor inlet. These have become dominant pathways at the reactor outlet. It was also found that olefin desorption and carbenium ion isomerization are equilibrated processes.

We also used this method, but without a final fitting procedure. In Chapter 4, a discussion is presented on the elementary steps used in the modelling of the hydroisomerization of n-hexane.

3.1.3. Other methods giving insight
A group in Gent is one which also uses elementary steps in their modelling. Since they normally work with large molecules like octane or decane, extensive lumping must be used in order to obtain a system of equations which can be reliably fitted to the experimental data. It is also necessary to exclude some smaller molecules from the model. When lumping is applied, different but similar species are treated the same to reduce the complexity of the problem. Froment's group used single-event kinetics as a basis of lumping. This means that for every elementary step the change in molecular configuration is determined. A similarity decision is then made on the basis of these configurations. In earlier work (for example in the work of Ramage et al.) lumping was based on compound classes or boiling point range. The main disadvantage of this method is that the derived rate coefficients depend on feed composition and reactor configuration.

Model discrimination is always performed by comparing the fit of the different models to the experimental data. The set of experiments is designed to allow maximum model discrimination. In this way pre-exponential factors and activation energies can be obtained. One can, however, make some critical remarks against this method. Firstly, it makes assumptions about which steps are at equilibrium and which step is rate determining (usually an acid function such as isomerization). Secondly, it uses data obtained in superacid solution and true carbenium ions instead of alkoxy-type species when modelling the reaction on zeolites.

Watson et al. also use lumping in their modelling of n-heptane cracking. The use of linear free energy relationships (LFERs) generates a tool to derive a small number of matrices of compound classes and reaction families to describe the complete reaction network. Pre-exponential factors obtained by Dumesic are used to fit their data.

Based on this method, the following conclusions were reached:
* the majority of the available acid sites is empty
* protonation of olefins is characterized by a low activation energy
* alkyl and hydride shifts are much faster than PCP isomerization
* parameter estimation by fitting gives excellent correspondence between calculation and observation

3.2 Description of the numerical method used

The programs used were developed here in Eindhoven by the catalytic engineering group of professor Marin to model the oxidative coupling of methane. A detailed description of these programs can be found in an undergraduate report by Van der Leek\(^6\). In the next subparagraphs the program and the expansions made to the simulation program to model the hydroisomerization reaction will be discussed.

3.2.1 The problem to be solved

The gas phase concentrations and surface coverages are simulated as a function of position along the reactor bed. The changes in concentrations in a differential volume element of a plug flow reactor are given by the input via convection minus the output via convection added to the production by the reaction:

\[
\frac{dC_i}{dt} = \frac{V}{dz} \cdot F_{v,i} - F_{v,i} \cdot dz \cdot C_i + R_{v,i}A_s dz
\]

- \( V \): volume of volume element [m\(^3\)]
- \( C_i \): concentration of component i [mol/m\(^3\)]
- \( F_v \): feed volumetric flow [m\(^3\)/s]
- \( z \): axial co-ordinate [m]
- \( A_s \): reactor cross-sectional surface area [m\(^2\)]
- \( R_{v,i} \): rate of formation of component i [mol/m\(^3\)/s]

At steady state conditions the \( dC_i/dt = 0 \). Surface species enter nor leave a volume element so their rate of formation is also equal to 0. When equation (3.1) is rewritten and weight fractions are used, one obtains for gas phase species:

\[
\frac{dw_i}{dz} = \frac{M_iR_{v,i}}{\phi_m}
\]

- \( w_i \): weight fraction of component i [-]
- \( M_i \): molecular weight of component i [g/mol]
- \( \phi_m \): feed mass flux [g/m\(^2\)/s]

Weight fractions were used instead of linear gas velocity (u) times the molar concentration (C\(_i\)). It was shown previously\(^7\) that a big error can be introduced when using u(dC\(_i\)) as an estimation
Kinetic modelling

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of d(uC₄). The effect of the change in volume flux due to reaction must be accounted for. Although this is not the case in hydro-isomerization we still used this approach. The exact solution is obtained by using weight fractions. The net rate of formation of a component i is given by:

\[
R_{v,i} = \sum_{k=1}^{N} \nu_{k,i} r_k a_{v,cat}
\]

- \( N \) = number of reactions involved [-]
- \( \nu \) = stoichiometric factor [-]
- \( r_k \) = rate of a single reaction [mol/m² cat s]
- \( a_{v,cat} \) = volumetric catalyst surface area [m² cat/m³ bed]

The net volumetric rates of formation can be calculated by substituting equation (3.4) into equation (3.3). These rates can then be included in equation (3.2). In this way a set of non-linear differential equations is obtained, which cannot be solved analytically. The numerical method used for the gas phase concentrations is given in sub-paragraph 3.2.2. The surface coverages needed another approach and this is discussed in sub-paragraph 3.2.3.

\[
(3.4) \quad r_k = A \exp \left( \frac{-E_{act,k}}{RT} \right) \prod_{i=1}^{N_{comp}} c_i^{u_i} \prod_{h=1}^{N_{surf}} c_h^{u_h}
\]

- \( A \) = pre-exponential factor [depends on order of reaction]
- \( E_{act,k} \) = activation energy of reaction k [kJ/mol]
- \( N_{comp} \) = number of gas components involved [-]
- \( N_{surf} \) = number of surface species involved [-]

The method used to calculate the gas phase concentrations is the routine of Dente. The change in weight fraction as a function of the position along the length of the reactor is divided in a production and a disappearance term.

\[
\left(3.5\right) \quad \frac{dw_i}{dz} = \frac{M_i A_s}{\phi_m} \left( \sum_j \nu_{i,j}^f r_j^f + \sum_j \nu_{i,j}^d r_j^d \right)
\]

- \( w_i \) = weight fraction of component i [-]
- \( z \) = axial co-ordinate [m]
- \( M_i \) = molecular weight of component i [g/mol]
- \( A_s \) = reactor cross-sectional surface area [m²]
- \( \phi_m \) = feed mass flow [g/m² s]
- \( \nu_{i,j}^f \) = stoichiometry of component i in formation reaction j [-]
- \( \nu_{i,j}^d \) = stoichiometry of component i in disappearance reaction j [-]
- \( r_j^f \) = rate of formation reaction j [mol/m³ s]
- \( r_j^d \) = rate of disappearance reaction j [mol/m³ s]
A $F_{1,i}$ and $F_{2,i}$ are defined as shown in equations (3.6a) and (3.6b):

\[
(3.6a) \quad F_{1,i} = \frac{M_i \, A_s \sum_j v_{i,j} \, r_j}{\phi_m}
\]

\[
(3.6b) \quad F_{2,i} = \frac{M_i \, A_s \sum_j v_{i,j} \, r_j^d}{w_i \, \phi_m}
\]

Equation (3.5) can then be rewritten into:

\[
(3.7) \quad \frac{dw_i}{dz} = F_{1,i} - w_i \, F_{2,i}
\]

By integration of equation (3.7) over an interval $[z, z+\Delta z]$ equation (3.8) is obtained. It is assumed that $F_1$ and $F_2$ are just a function of $z$.

\[
(3.8) \quad w_i(z+\Delta z) = w_i(z) \exp\left(-\int_0^{\Delta z} F_{1,i}(\xi) \, d\xi\right) + \int_0^{\Delta z} F_{1,i}(\xi) \exp\left(-\int_0^{\Delta z} F_{2,i}(\tau) \, d\tau\right) \, d\xi
\]

In equation (3.8) $\xi$ and $\tau$ are dummy variables. In the case of molecules, Dente proposed to choose the iteration step $\Delta z$ in such a way that it makes $(F_{2,i} \Delta z)_{\text{max}}$ smaller than 0.3–0.5. The relative change in $F_{2,i}$ and $F_{1,i}$ in the interval $[z, z+\Delta z]$ is in that case very small, so the average values can be taken. According to Dente, this gives:

\[
(3.9) \quad w_i^{\text{hl}}(z+\Delta z) = w_i(z) \exp(-F_{1,i}^{(0)} \Delta z) + \frac{F_{1,i}^{(0)}}{F_{2,i}^{(0)}} \left[1 - \exp(-F_{2,i}^{(0)} \Delta z)\right]
\]

The letter $h$ stands for the $h^\text{th}$ iteration step. After normalization to square the mass balance one obtains:

\[
(3.10) \quad w_i^{(h+1)}(z+\Delta z) = \frac{w_i^{(h+1)}(z+\Delta z)}{\sum_{i=1}^n w_i^{(h+1)}(z+\Delta z)}
\]

The stop criterion of the iteration has been reached when the correction factor minus 1 is within the chosen accuracy. In our program equation (3.10) is applied to slow reacting molecules. In case of fast reacting gas phase species, another calculation method should be used. They are then treated as radicals in Dente's definition. If the chosen $\Delta z$ leads to a $(F_{2,i} \Delta z)$ larger than 20, equation (3.8) can be rewritten. Clymans suggested to use equation (3.11) because it lead to fast convergence to the analytically calculated stationary state.

\[
(3.11) \quad w_i^{(h+1)}(z+\Delta z) = \left(w_i^{(h)}(z+\Delta z) \frac{F_{1,i}}{F_{2,i}}\right)^{\frac{1}{2}}
\]
3.2.3. Surface concentrations

In contrast to the oxidative coupling of methane, in our case the reactions involving gas phase species are solely adsorption steps. The rate of adsorption was found to be very high (hexane in the gas phase turned out to be at equilibrium with the adsorbed state). Since the real reaction rate is much lower, the new weight fractions should be calculated using equation (3.9).

In cases where $F_2$ is so large that $\Delta z$ must be very small to fulfill the criterion mentioned above, another approach is used. In this approach, $\Delta z$ is made small enough to make the change in gas phase concentration of a species smaller than 0.5. A differential volume element of a plug flow reactor (PFR) can then be redefined as a mini-CSTR (Continuously ideally Stirred Tank Reactor). The full PFR is then a cascade of CSTRs. This results in:

$$w_{i+1}^z(z + \Delta z) = \frac{w_i(z) + F_{1,i}^h \Delta z}{1 + F_{2,i}^h \Delta z}$$

$F_1$ and $F_2$ are in this case calculated from the gas phase concentration values at $[z + \Delta z]$.

Another expansion made concerns the calculation of surface concentrations. The original simulation program could only take into account one type of surface sites. It was already shown in Chapter 2 that at least two types of sites are needed in the hydro-isomerization over a bifunctional catalyst: platinum and acid sites. A third type of site was added to account for the physisorption of the different molecules on the zeolite. A consequence of this expansion was that transport steps to and from the adsorption sites and the other two types of sites had to be added to the reaction mechanism. This was done by defining a transport reaction (see Figure 3.1. and paragraph 4.4.).

\[ n-C_6(\text{adsorbed}) + \text{empty acid site} \rightarrow n-C_6(\text{physisorbed on acid site}) + \text{empty adsorption site} \]

**Figure 3.1. Example of transport reaction**

The individual surface concentrations can be calculated using equation (3.13) for each group.

$$\frac{d\theta_i}{dt} = \sum_j v_{ij} r_j = 0$$
In this way a dependent system of differential equations is obtained. In order to make it possible to solve the problem the three mass balances are needed, making the system independent:

(3.14a) \( L_{\text{tot,Pt}} = \sum_i C_{i,\text{Pt}} \)

(3.14b) \( L_{\text{tot,H+}} = \sum_i C_{i,H+} \)

(3.14c) \( L_{\text{tot,zeo}} = \sum_i C_{i,\text{zeo}} \)

- \( L_{\text{tot,Pt}} \) = total concentration of platinum sites [mol/m\(^2\)_cat]
- \( L_{\text{tot,H+}} \) = total concentration of acid sites [mol/m\(^2\)_cat]
- \( L_{\text{tot,zeo}} \) = total concentration of zeolite adsorption sites [mol/m\(^2\)_cat]
- \( C_{i,\text{Pt}} \) = concentration of \( i \)-covered or empty platinum site [mol/m\(^2\)_cat]
- \( C_{i,H+} \) = concentration of \( i \)-covered or empty acid site [mol/m\(^2\)_cat]
- \( C_{i,\text{zeo}} \) = concentration of \( i \)-covered or empty adsorption site [mol/m\(^2\)_cat]

The thus obtained independent system of equations can be solved numerically by the NAG library routine C05NBF. This routine solves a system of \( N \) non-linear equations containing \( N \) unknowns. It uses surface coverages for stability. In every iteration step this routine is called. If C05NBF generates negative surface coverages or coverages larger than 1, these values are reset and C05NBF is called again. When the routine does not converge, it is possible to change the initial guesses for the surface coverages relative to a deviation from the true solution, as given by C05NBF, and call it again. After a user supplied maximum number of times recalling without success, the routine is stopped.
3.2.4. What changes if what experimental parameter changes

When one simulates another zeolite the following parameters must be changed in the input files.

1. The change in adsorption enthalpy and entropy respectively affect the activation energy and pre-exponential factor of desorption for all alkanes and alkenes. In the case of small pores the activation energy of adsorption of the dimethylbutanes may also be affected.

2. The new intracrystalline diffusion coefficient and corresponding activation energies might effect the rate of transport of the surface species from one site to another.

3. The number of acid sites changes only with a change in Si/Al ratio. The number of platinum sites and atoms per cluster will change with dispersion and loading. The number of adsorption sites will change with the n-hexane adsorption capacity of the zeolite. From the resulting number of adsorption sites the number of acid and platinum sites must be subtracted to account for the space occupied by these sites.

4. The specific surface area of the zeolite affects the concentration of all types of sites. The BET surface area must be corrected for the size of the reactant (nitrogen versus n-hexane). This correction is based on the BET pore volume relative to the n-hexane adsorption capacity in ml/g.

When the order of the reaction in hexane or hydrogen must be determined, nitrogen must be added to allow a change in partial pressure of respectively hexane and hydrogen without changing the total flow:

1. Nitrogen must be added as a ‘reactant’

2. The volume percentage of the appropriate reactant must be changed. This will also affect the total molar flow (mol/s) of reactants.

When the apparent activation energy of the reaction must be calculated, the reaction temperature must be varied. When the influence of the total pressure is investigated, both the overall pressure and the total molar flow (mol/s) will be changed.
Literature cited.


4

Discussion of elementary steps

In this chapter, the parameters describing the elementary steps used to simulate the hydroisomerization will be discussed. The estimation of the values or the choice of literature values for the pre-exponential factors and activation energies will be described. A summary of the parameters found is given in Appendix 2.

4.1 The steps

Since the mechanism has already been dealt with in chapter 2, this paragraph will only give a summary of the results.

The hydro-isomerization was divided into the following reaction steps:

1. adsorption of the reactant on the zeolite
2. dehydrogenation of the reactant on the platinum clusters
3. isomerization on the acid sites
4. hydrogenation of the products on the platinum clusters
5. desorption of the products from the zeolite

Between these steps transport takes place between the different sites. A schematic representation of the mechanism can be found on the next page. The three columns represent the three types of sites, being platinum, adsorption and acid sites. Transport of species takes place to and from adsorption sites.
Figure 4.1. Scheme of elementary steps in hydro-isomerization
4.2 Adsorption and desorption on the zeolite

4.2.1. Activation energies

The activation energy of adsorption of n-hexane was estimated to be 10 kJ/mol, taking into account the reaction temperature and the pore rim surface diffusion barrier as described by Derouane et al.\textsuperscript{1}. In the case of somewhat more difficult adsorption (for example dimethylbutanes on ZSM-5) the activation energy was estimated to be 15 kJ/mol. The adsorption enthalpies of the different alkanes on the different zeolites were either measured\textsuperscript{2} or averaged from different literature sources and references cited therein\textsuperscript{1,3}.

The adsorption enthalpy of 1-hexene on an all-silica zeolite was assumed to be equal to that of n-hexane\textsuperscript{3c}. This assumption agrees with data of Lechert et al. for butane/butene\textsuperscript{4}. When the alkene adsorbs on the acid sites as a π-complex, approximately 20 kJ/mol should be added to account for the extra interaction. Hufton et al. found up to 15 kJ/mol difference in adsorption enthalpy of butenes and the corresponding butanes on a silicalite (all silica ZSM-5) sample\textsuperscript{5}. This was, however, ascribed to structure defects exhibiting strong interactions with alkenes and aromatics. This is therefore only apparent at very low concentrations. It might be important when considering zeolite β since this zeolite exhibits more structural defects than other zeolites due to stacking faults\textsuperscript{6}. Adsorption enthalpies of other olefins were extrapolated from an article of Harlfinger et al., also on butane/butene\textsuperscript{7}. The assumption is made that 3-hexene behaves like 2-hexene, and 2-hexene in turn is comparable to 2-butene.

4.2.2. Pre-exponential factor

The values for the pre-exponential factors of desorption from a ZSM-5 catalyst of the alkanes and alkenes were estimated from an article of Zhdanov et al.\textsuperscript{8}. These values were chosen to be close to the lower limit of the range given, that is $10^{15}$ s\textsuperscript{-1} for paraffins, and $10^{14}$ s\textsuperscript{-1} for olefins due to the more restrained transition state of the latter. The values for the pre-exponential factors of adsorption were calculated from the desorption pre-exponent using the equilibrium constants for adsorption and the activation energies for adsorption and desorption. The equilibrium constants for adsorption were calculated from equilibrium adsorption data\textsuperscript{9,10}. Due to the commensurate freezing of n-hexane in MFI-type zeolites\textsuperscript{11}, high temperature data are the most reliable source for calculating the pre-exponential factors of adsorption.

The pre-exponential factors obtained for adsorption were then assumed to be the same for all other zeolites. This seems acceptable since the transition-state partition functions will not change much from zeolite to zeolite. Since the enthalpy of adsorption will affect the activation energy of desorption, the pre-exponential factor of desorption is also changed due to a change in entropy of adsorption. This is an example of the compensation effect\textsuperscript{12}. 
4.3 Adsorption and desorption on platinum

The values of the data needed for the elementary steps of dissociative adsorption and associative desorption of hydrogen on platinum were taken from an article of Norton et al.\textsuperscript{13}. They found the adsorption to be slightly activated and the corresponding sticking probability to be approximately 0.2\textsuperscript{14}. The dissociative adsorption enthalpy of hydrogen on platinum sites, resulting in strongly adsorbed hydrogen atoms, was deduced from data given by Dumesic\textsuperscript{15} and Campbell\textsuperscript{16}. This enthalpy has a value of 125 kJ/mol.

4.4 Transport from one site to another

The rate of transport of a species was deduced from intracrystalline diffusion data. The activation energy of transport from an adsorption site to a platinum or an acid site was put equal to the activation energy of diffusion. When there are no steric constraints on a diffusing molecule the activation energy for surface diffusion is about 20 \% of the adsorption enthalpy\textsuperscript{8}. In the case of zeolites there is no real surface diffusion, so the activation energies for transport were deduced from different sources and literature cited therein: ZSM-5\textsuperscript{17}; \beta\textsuperscript{18} and ZSM-22\textsuperscript{19}. When an activation energy of diffusion could not be found this value was estimated on basis of molecule\textsuperscript{20} and zeolite dimensions and structure\textsuperscript{21}.

In the next sub-paragraphs the calculation of the activation energies of transport from acid and platinum sites is described. The pre-exponential factors of transport reactions were calculated by ‘fitting’ on diffusion data in zeolites. These data were obtained from the same sources as used for the estimation of activation energies. The activation energies and the surface coverages were then used to calculate a ‘rate’ of diffusion. In case of hexene transport to and from an acid site the situation was different while the molecule was protonated. These parameters will be dealt with in paragraph 4.6.

4.4.1. Adsorption and desorption on acid sites

The physisorption enthalpies of alkanes on acid sites were calculated from the difference in their adsorption enthalpy on all-silica and acidic zeolites. Typically, a value of 2 to 3 kJ/mol was used.

4.4.2. Adsorption and desorption on platinum particles

The relative adsorption coefficients of olefins and paraffins on platinum were calculated from an equation given in an article by Cervený \textit{et al.}\textsuperscript{22}, using values for $E_s$ and $\sigma^*$ as given by Taft\textsuperscript{23}. The parameter $E_s$ accounts for the steric effects of a substituent on a base molecule, relative to a methyl group. The parameter $\sigma^*$ accounts for the polarity of a substituent.
The adsorption enthalpy of 1-hexene on platinum was calculated from the equilibrium constant for adsorption as given by Brehm et al.\textsuperscript{24}. The adsorption enthalpy of n-hexane was deduced from the article of Campbell et al.\textsuperscript{16}. The values for the other molecules could be calculated from these two data by drawing parallels with 1-hexene and butenes\textsuperscript{25}.

4.5 Hydrogenation and dehydrogenation

The hydrogenation and dehydrogenation can be described with a two-step reaction: the hydrogen atoms are added or abstracted one by one\textsuperscript{26}. This classical Horiuti-Polanyi mechanism was adapted using new evidence\textsuperscript{16,24}. This results in:

\begin{align*}
(1) & \quad \text{Pt} + \text{PtC}_6\text{H}_{14} \quad \longrightarrow \quad \text{PtC}_6\text{H}_{15} + \text{PtH} \\
(2) & \quad \text{PtC}_6\text{H}_{13} + 2 \text{Pt} \quad \longrightarrow \quad \text{Pt}_2\text{C}_6\text{H}_{12} + \text{PtH}
\end{align*}

The rates and activation energies of hydrogenation of cis- and trans-alkenes are nearly the same but their adsorption characteristics on platinum are not. According to Taylor the rate-determining step must be the hydrogen addition to the half-hydrogenated species\textsuperscript{27}. Hydrogenation of both cis- and trans-alkenes involves that same species. The same reasoning holds for the dehydrogenation. To simplify the simulation, a one-step mechanism was assumed:

\begin{align*}
(1) & \quad \text{Pt} + \text{PtC}_6\text{H}_{14} \quad \longrightarrow \quad \text{Pt}_2\text{C}_6\text{H}_{12} + \text{H}_2
\end{align*}

An article by Campbell et al. was used as a basis to calculate the different pre-exponential factors and activation energies for dehydrogenation\textsuperscript{16}. The energies involved in hydrogenation were made consistent using the dehydrogenation data and thermodynamics and closing the energy scheme as shown in Figure 4.2. This scheme contains the values for the difference in formation enthalpy of the gas phase species involved, adsorption and activation energies. The thermodynamic data were taken from the literature\textsuperscript{28}.
The activation energies of step 1 and 2 for cis-2-hexene were obtained from the article of Campbell et al.\textsuperscript{16}. An estimation of this energy for the backward step 1 was taken from an article of Brehm et al.\textsuperscript{24}. This resulted in Figure 4.2. for cis-2-hexene.

\[
\begin{align*}
C_6H_{14} + 4 \text{Pt} & \quad \Delta H_{\text{ads}} = 87.8 \\
C_6H_{14}\text{Pt} + 3 \text{Pt} & \quad \Delta H_{\text{ads}} = 16.32 \\
C_6H_{12}\text{Pt}_2 + \text{PtH} + 2\text{Pt} & \quad \Delta H_{\text{formation}} = 114.76
\end{align*}
\]

**Figure 4.2.** Energy diagram (kJ/mol) of the hydrogenation of cis-2-hexene at 500 K

The resulting activation energies for the (de)hydrogenation of cis-2-hexene are shown schematically in Figure 4.3.

\[
\begin{align*}
C_6H_{12}\text{Pt}_2 + 2\text{PtH} & \quad 50 \\
C_6H_{13}\text{Pt} + \text{PtH} + 2\text{Pt} & \quad 92 \\
C_6H_{12}\text{Pt} + 3\text{Pt} & \quad 55.2
\end{align*}
\]

**Figure 4.3.** Energy diagram (kJ/mol) of surface hydrogenation of cis-2-hexene.

The relative dehydrogenation rates of the different paraffins to the corresponding olefins were calculated from two articles of Cerveny et al.\textsuperscript{29,30}. Since the activation energies were given for the gas phase, the adsorption enthalpies of the alkanes were used to correct these data towards surface-reaction activation energies. In order to obtain the correct surface species equilibrium it was taken into account that alkenes are adsorbed on two platinum sites, as opposed to one in case of paraffins. The reaction rates given were corrected in a similar way using the adsorption equilibria. The pre-exponential factor and activation energy for 2-hexene
Discussion of elementary steps 45

were known so the surface-reaction rate for this compound could be calculated. The other pre-exponential factors were obtained from the relative surface-reaction rates and the known activation energies. The pre-exponential factors of hydrogenation could then be calculated from the equilibrium dehydrogenation constants (as deduced from thermodynamics) and from the rate constants. In this calculation it was assumed that the adsorbed alkane is in 'gas phase equilibrium' with its adsorbed alkenes. The probability that a particular compound is formed was also taken into account. The pre-exponential factor for dehydrogenation of n-hexane to form 1-hexene was therefore twice as large as that for formation of 3-hexene.

4.6 Protonation and deprotonation

It is generally known that primary carbenium ions in the gas and liquid phase are far less stable than secondary or tertiary ions. However, according to Kazansky, carbenium ions in zeolites are adsorbed as an alkoxy species (see also Chapter 2)\textsuperscript{31}. Therefore, primary species may exist in the adsorbed state. Since the isomerization takes place in the 'desorbed' state, in a carbenium ion-like transition state, only secondary and tertiary carbenium ions were accounted for in the simulation model\textsuperscript{32}.

In Figure 4.4, and Figure 4.5., energy schemes for the formation of a secondary and a tertiary carbenium ion are given. These data were calculated from quantum chemical calculations by Kazansky \textit{et al.}, by subtracting approximately 20-30 kJ/mol from their calculated values to account for the overestimation of the energies by these calculations\textsuperscript{33}. An important feature to notice is that here the activation energies for a tertiary alkoxy species are lower than for a secondary species. This is contrary to the order used by Baltanas \textit{et al.}\textsuperscript{34}. The values obtained were the same for each zeolite, the adsorption enthalpy ($\Delta H_{\text{ads}}$) does vary as a function of pore structure.

![Figure 4.4. Energy (kJ/mol) scheme of a secondary carbenium ion](image-url)
Chapter 4

4.7 Isomerization on acid sites

The isomerization was assumed to take place according to the protonated cyclopropane (PCP) mechanism\(^{32}\). Only conversions between secondary and tertiary carbonium ions were taken into account, including both branching and non-branching isomerization steps. The data found by Brouwer on superacids were used as a basis\(^{35}\). In zeolites, however, the carbenium ions are activated complexes rather than existing adsorbed species\(^{36}\). The adsorbed intermediate on these materials is an alkoxy species\(^{37-38}\). Transition state theory can be used to derive an equation for the rate constant of isomerization\(^{15}\). Activation of the alkoxy species into a carbenium ion-like species involves σ-bond lengthening between the carbon atom of the molecule and the oxygen atom of the zeolite. This gives the equation below:

\[
(4.1) \quad k_{\text{isomerization}} = A_{\text{Brouwer}} \cdot A_{\text{lengthening}} \exp\left(\frac{-\left(E_{\text{act,Brouwer}} + E_{\text{act,lengthening}}\right)}{RT}\right)
\]

where:
- \(A_{\text{Brouwer}}\) = pre-exponential factor of mono-molecular reaction
- \(A_{\text{lengthening}}\) = pre-exponential factor of bond lengthening

Table 4.1. Protonation and deprotonation data

<table>
<thead>
<tr>
<th>Type of ion</th>
<th>(A_{\text{protonation}}) [mol/m(^2)s]</th>
<th>(E_{\text{act,protonation}}) [kJ/mol]</th>
<th>(A_{\text{deprotonation}}) [mol/m(^2)s]</th>
<th>(E_{\text{act,deprotonation}}) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>secondary</td>
<td>(2.8 \times 10^5)</td>
<td>50</td>
<td>(2.1 \times 10^{11})</td>
<td>130</td>
</tr>
<tr>
<td>tertiary</td>
<td>(2.8 \times 10^5)</td>
<td>37</td>
<td>(9.7 \times 10^{11})</td>
<td>120</td>
</tr>
</tbody>
</table>

**Figure 4.5.** Energy (kJ/mol) scheme of a tertiary carbenium ion

The pre-exponential factors of protonation and deprotonation were calculated from Dumesic\(^{15}\). His data on the protonation from the gas phase were recalculated by taking into account the number of acid sites, Kazansky's activation energies and the adsorption equilibrium constants for the alkenes on the zeolite. This resulted in the data listed in Table 4.1.
The activation energy of bond lengthening was estimated to be 20 kJ/mol lower than the deprotonation enthalpy. An estimation of $A_{\text{Brouwer}}$ for lengthening was derived from an article of Guisnet et al.\textsuperscript{39}. Assuming that isomerization is the rate determining step, the rate of branching must be approximately $1 \cdot 10^3$ kmol/m$^3$s. To account for the chance of making a certain 'carbenium ion' some of the pre-exponential factors were multiplied by a factor of 2 or 4. The activation energies are calculated in Table 4.2. Note that these values are much higher than those that have been used earlier.\textsuperscript{15,24,40} These authors used liquid phase, carbenium ion isomerization values that were below 50 kJ/mol instead of isomerization from alkoxy species. Their values for the pre-exponential factor of PCP isomerization can therefore not be used in our simulation. Since a better estimation could not be found, the final pre-exponential factor of isomerization was obtained from fitting it in factors of 10. A plausible conversion on a Mordenite catalyst at standard conditions was used as the fitting criterion. This is therefore the only parameter that has been fitted on experiments. The value obtained was now set and was used for all other simulations.

### Table 4.2. Activation energies of isomerization

<table>
<thead>
<tr>
<th>Type of isomerization</th>
<th>Branching</th>
<th>Brouwer</th>
<th>Lengthening</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[y/n]</td>
<td>[kJ/mol]</td>
<td>[kJ/mol]</td>
<td>[kJ/mol]</td>
</tr>
<tr>
<td>secondary to secondary</td>
<td>y</td>
<td>22.0</td>
<td>110.0</td>
<td>132.0</td>
</tr>
<tr>
<td>secondary to tertiary</td>
<td>y</td>
<td>30.4</td>
<td>110.0</td>
<td>140.4</td>
</tr>
<tr>
<td>tertiary to secondary</td>
<td>y</td>
<td>76.5</td>
<td>100.0</td>
<td>176.5</td>
</tr>
<tr>
<td>tertiary to tertiary</td>
<td>y</td>
<td>71.0</td>
<td>100.0</td>
<td>171.0</td>
</tr>
<tr>
<td>secondary to tertiary</td>
<td>n</td>
<td>2.0</td>
<td>110.0</td>
<td>112.0</td>
</tr>
<tr>
<td>secondary to secondary</td>
<td>n</td>
<td>8.4</td>
<td>110.0</td>
<td>118.4</td>
</tr>
<tr>
<td>tertiary to secondary</td>
<td>n</td>
<td>56.5</td>
<td>100.0</td>
<td>156.5</td>
</tr>
</tbody>
</table>

The equilibrium gas phase ratios of the isomers and their temperature dependence were used as constraints. In this way the set of kinetic parameters was made consistent with thermodynamics.
Literature cited.

Discussion of elementary steps


[32] Chapter 2 of this thesis


In this chapter the catalysts used, their preparation, characterization and behavior in the hydro-isomerization reaction will be discussed. An interpretation of the kinetic data as a function of catalyst characteristics is the main feature of this chapter. Mechanistic aspects will also be addressed.

5.1. Catalyst characterization methods

In the next sub-paragraphs different types of techniques used to determine the amount, strength and character of the zeolite acidic sites are discussed. Reviews about this subject can be found in articles by Farneth and Gorte, Rabo and Gajda, Van Hooff and Roelofsen and Barthomeuf. The latter also correlates acidity and catalysis.

5.1.1. Indicators

The most commonly used method for characterization of acidity in the liquid phase is less suitable for zeolites. Most indicators are too large to enter the zeolite pores so the measured acidity can never be the real acidity of the acid sites inside the pores. A better way to use indicators is in an acid-base titration or, when they are small enough to enter the pores, as a probe in spectroscopy.

Superacids have been characterized for many years by measuring their Hamett acidity function, $H_0$. The protonation of the indicator, a weak base, is the reverse of dissociation of the conjugate acid. Hamett defined an $h_0$ and $H_0$ as a measure of proton donating ability of an acidic solvent to a base B. These definitions are given in equations (5.1) and (5.2). Superacids are defined as acids having an $H_0$ value which is lower than -12. For HMordenite, values between -13.7 and -12.4 have been measured. Using
solid state NMR less negative numbers are obtained, from which HY and HZSM-5 cannot be classified as superacids.

\[
(5.1) \quad h_0 = K_a \frac{C_{BH+}}{C_B} = a_{H^+} \frac{\gamma_B}{\gamma_{BH^+}}
\]

(5.2) \[ H_0 = -\log (h_0) \]

\begin{align*}
K_a & = \text{equilibrium constant of deprotonation} \\
C_x & = \text{concentration of } x \\
a_x & = \text{activity of } x \\
\gamma_x & = \text{activity coefficient of } x
\end{align*}

5.1.2. TPD of bases

The bases that are most widely used are ammonia, pyridine and a series of amines. The Temperature Programmed Desorption is based on heating a sample after adsorption of a base. The stronger the acid site in the zeolite, the higher the temperature at which the base will desorb. This technique can also be used quantitatively when it is combined with a gravimetric method.

TPD gives good results when comparing different samples of one zeolite structure with different acidities. Comparison between samples with different structure, may give false information. This is then due to diffusion problems, influencing the desorption peak maximum. Especially TPD of larger bases such as pyridine may have this problem. Kapustin et al. came to the same conclusion on the basis of their comparison of ammonia TPD and calorimetry. They found that the temperature of desorption of ammonia is not only influenced by the acid strength but also by the number of sites and the zeolite structure. TPD can, however, provide an estimation of the adsorption enthalpy of ammonia on acid sites. The temperature shift of the desorption peak(s) by variation of both the carrier gas flow-rate and the amount of zeolite sample is then monitored.

Another issue is raised when the probe base reacts, for instance, when ammonia dissociates into \( NH_2^\cdot \) and \( H^+ \) that can adsorb on both acidic and basic sites. This will make the interpretation of the obtained data very complicated. A desorption peak in the TPD might originate from different species. This problem can be anticipated by using a mass-spectrometer. Parillo and Gorte used the reactivity of iso-propylamine to characterize acidity. They attributed desorption of this base to physisorption, chemisorption on acid sites will at higher temperatures lead to decomposition to propene and ammonia.
5.1.3. Infra-red spectroscopy

A review about (IR) spectra of adsorbed alkenes and alkanes is given by Dimitrov and Bezouhanova\textsuperscript{13}. An older, but more extensive review is given by Ward\textsuperscript{14}. Recently, Lercher\textit{ et al.} published a review of infrared studies of the surface acidity of zeolites using a probe molecule\textsuperscript{15}. Infra-red can be used on zeolites to give information about the OH-bond strength. Moreover, if one uses a (weak) base as a sorbate, it can give information about sites with different strength or type of interaction with the sorbate. Kazansky stated: "The only proper way to proceed is to follow the response of hydroxyl groups to their interaction with adsorbed bases"\textsuperscript{16}.

The most widely used probes are: CO, ammonia, pyridine, and more recently acetonitrile\textsuperscript{17}, tetrachloroethylene\textsuperscript{18} and hydrogen cyanide\textsuperscript{19}. IR can also be used to determine site accessibility by measuring the empty zeolite and one filled with the appropriate (bulky) probe base\textsuperscript{20}. IR spectra of a zeolite containing a probe base, recorded at different temperatures, can be used as a means to follow a 'TPD' of that base\textsuperscript{21}. In this way differences in acid site strength can be obtained.

5.1.4. UV-Visible spectroscopy

There are not many authors who use ultraviolet-visible spectroscopy. One example is an article by Kiricsi\textit{ et al.} on the interaction and reaction of neopentane\textsuperscript{22}. Neopentane is used since it contains only quaternary and primary carbon atoms and thus only generates primary carbocation ions upon protonation.

5.1.5. Calorimetry

Calorimetry can be used to measure the number of acid sites by titration as well as the heat of adsorption of a base on these acid sites. The most commonly used bases are ammonia and pyridine. Parillo and Gorte stated that ammonia adsorbs on Lewis acid sites with a heat of adsorption above 300 kJ/mol, while Brønsted sites give a heat of adsorption of approximately 145 kJ/mol\textsuperscript{23}. Kapustin\textit{ et al.} used a combination of IR and calorimetry to assign heats of adsorption of ammonia on acid zeolites to Brønsted or Lewis sites\textsuperscript{24}. They found that values of 120-150 kJ/mol could be assigned to Brønsted sites. Physisorption of ammonia on Lewis acid sites yielded 100 kJ/mol and dissociative adsorption on these sites yielded 170 kJ/mol.

Calorimetry can also be used with other sorbates as long as they do not react with the acid sites, in that case the measured heat is a sum of the heat of reaction and of adsorption. For this reason alkenes cannot be used on acid zeolites, although it would be interesting considering the relevance towards catalysis.
5.1.6. MAS NMR spectroscopy
A review about application of NMR methods to catalysis has recently been published by Fraissard et al.\textsuperscript{25}.

Using solid-state \textsuperscript{1}H NMR one can quantify the concentration, strength of acidity and the accessibility of the sites\textsuperscript{26}. However, until now this method can only be used for Brønsted acid sites, preferentially combined with an adsorbed species. The NMR spectrum will show a shift in the chemical shift upon adsorption of a base which is a measure of acid strength.

Measurement of \textsuperscript{13}C, \textsuperscript{1}H and \textsuperscript{15}N MAS NMR on an adsorbed weak base in combination with \textit{ab initio} calculations yields valuable information about the interaction of a zeolite and the adsorbed base\textsuperscript{27}. Acetonitrile adsorbed on a zeolite is a good candidate for this method.

The number of silicon atoms having 0, 1, 2, 3 or 4 aluminium neighbors can be measured by \textsuperscript{29}Si MAS NMR. Each will give a signal at a different chemical shift. This information can then be used to determine the Si/Al ratio in the zeolite framework and thus the maximum amount of Brønsted acid sites. Using \textsuperscript{27}Al MAS NMR one can estimate the relative importance of extra-framework aluminum species.

Magnetic resonance on electrons (EPR or ESR) can also be used to characterize acidity. Gutsze \textit{et al.} used NO as a probe to look at Lewis acidity in ZSM-5\textsuperscript{28}.

5.1.7. X-ray photoelectron spectroscopy
Although XPS is a surface technique, the penetration depth of 50 Å could be sufficient to be used in zeolite characterization. It has been used for characterization of the aluminium atoms in the zeolite framework and the nitrogen atom of adsorbed pyridine\textsuperscript{29}.

5.1.8. Atomic adsorption spectrometry
With AAS of both silicon and aluminium one can determine the total Si/Al ratio. This is however a destructive technique. The sum of Brønsted and Lewis acid sites can thus be obtained.

5.1.9. Acid cracking
Acid cracking of n-hexane is also used to compare acidity of different samples\textsuperscript{30}. One big advantage of this method is that it characterizes the level of acid activity in reactions. A disadvantage of acid cracking is that it cannot distinguish between intrinsic proton acidity and pore size and shape effects.
5.2. Catalyst preparation

The β-zeolite, ZSM-5 and ZSM-22 samples were obtained in the sodium form from Exxon Chemicals in Machelen, Belgium. The Mordenite was obtained from Shell Research and Technology Centre in Amsterdam, The Netherlands.

Conversion to the protonated form was carried out via the following procedure. The sodium atoms in the zeolites were exchanged with ammonium by stirring in an aqueous 1 M ammonium nitrate solution overnight at room temperature. This was repeated three times with a fresh solution. The samples were then filtered, washed, dried at 60 °C and calcined. The calcination procedure consisted of drying periods in nitrogen at 100 °C (45 min) and 120 °C (60 min). The temperature was then increased at a rate of 5 °C/min to 510 °C. This temperature was held for 1 hour. The sample was subsequently cooled to 250 °C and oxygen (20 volume %) was added to the nitrogen flow. After stabilization of the temperature, the calcination was completed by reheating at 5 °C/min to 500 °C.

Platinum loading of the zeolites was performed by an overnight ion exchange at room temperature with a highly diluted platinum tetra-ammonium hydroxide solution. The zeolite was filtered and subsequently dried. The filtrate was checked for platinum by UV-VIS to establish the true loading of the zeolite. The dried sample was then treated in one of the following ways:

a1) Calcination by heating at a rate of 0.5 °C/min in a 50 Nml/min 80/20 nitrogen/oxygen flow to 450 °C. Followed by a 2 hour dwell period and subsequent cooling in nitrogen to room temperature. The reduction of the platinum particles was immediately thereafter performed by heating at a rate of 5 °C/min in a 50 Nml/min hydrogen flow to 400 °C. This was followed by a 2 hour dwell period and subsequent cooling in nitrogen to room temperature. Such a sample is referred to as a pure sample that has been pretreated ex situ.

a2) The pure ex situ pretreated sample was embedded in a silica matrix (Aerosil Degussa 380) by making a gel in which the zeolite particles were dispersed in an ultrasonic bath. The gel consisted of 9 ml water per gram of silica. The water was carefully evaporated overnight at 60 °C. Such a sample is referred to as an embedded sample.

a3) The pure ex situ pretreated sample was physically mixed with the double weight of silica of the same sieve fraction. Such a sample is referred to as a mixed sample.

a4) One Shell zeolite sample was already loaded with 0.5 wt.% platinum and calcined at 500 °C (CLA 80842). After embedding and before reaction the sample was reduced inside the reactor. This sample is referred to as the Shell pretreated sample.

b) In case of a pure sample that was pretreated in situ, calcination and reduction were performed inside the reactor. In this way the sample was not exposed to water and air between pretreatment and use in the catalytic reaction.
All samples were pressed for 1 minute at 5 tons in a hydraulic press. After crushing and sieving, a sieve fraction of 125-500 µm was used in the reactor. Further treatment of these samples will be discussed in paragraph 5.4.

5.3. Results of catalyst characterization

In Table 5.1., general characteristics of the different zeolites are given.

Table 5.1. General characteristics of the four zeolites used

<table>
<thead>
<tr>
<th>Other names</th>
<th>MOR</th>
<th>BEA</th>
<th>TON</th>
<th>MFI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generalized formula</td>
<td>$H_n[Al_{n}Si_{48-n}O_{96}]$</td>
<td>$H_n[Al_{n}Si_{64-n}O_{128}]$</td>
<td>$H_n[Al_{n}Si_{24-n}O_{48}]$</td>
<td>$H_n[Al_{n}Si_{26-n}O_{192}]$</td>
</tr>
<tr>
<td>Si/Al ratio</td>
<td>10</td>
<td>12.5</td>
<td>35</td>
<td>28</td>
</tr>
<tr>
<td>n in formula</td>
<td>4.4</td>
<td>4.7</td>
<td>0.67</td>
<td>3.3</td>
</tr>
<tr>
<td>$M'$ of unit cell</td>
<td>2884 [g/mol]</td>
<td>3845 [g/mol]</td>
<td>1442 [g/mol]</td>
<td>5768 [g/mol]</td>
</tr>
<tr>
<td>Spatial structure</td>
<td>1-Dimensional</td>
<td>3-Dimensional</td>
<td>1-Dimensional</td>
<td>3-Dimensional</td>
</tr>
<tr>
<td>Number oxygen atoms in ring</td>
<td>12</td>
<td>12 X 12</td>
<td>10</td>
<td>10 X 10</td>
</tr>
<tr>
<td>Ring sizes (Å)</td>
<td>(6.5 x 7.0)</td>
<td>(6.4 x 7.6)</td>
<td>(4.4 x 5.5)</td>
<td>(5.3 x 5.6)</td>
</tr>
<tr>
<td>Lattice density</td>
<td>17.2 T/nm$^3$</td>
<td>15 T/nm$^3$</td>
<td>19.7 T/nm$^3$</td>
<td>17.9 T/nm$^3$</td>
</tr>
</tbody>
</table>

* Molecular weight

The size of the zeolite pores is given in two ways. Both the number of oxygen atoms in the ring that forms the cross-section of the pore and its diameter in Ångström are listed. The lattice density is given in $T$-atoms per nm$^3$. $T$-atoms are aluminium and silicon atoms in the zeolite framework. The larger pores of β-zeolite may be referred to as ‘MOR pores’, the smaller pores as ‘MFI pores’. 
Table 5.2. Results of characterization of the zeolites used

<table>
<thead>
<tr>
<th>Analysis</th>
<th>MOR (2.0 wt.% Pt)</th>
<th>BEA (1.6 wt.% Pt)</th>
<th>TON (0.7 wt.% Pt)</th>
<th>MFI (0.5 wt.% Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JP number</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IR: v(OH) [cm⁻¹]</td>
<td>3608</td>
<td>3609</td>
<td>3600</td>
<td>3611</td>
</tr>
<tr>
<td>Δ v CD₃CN [cm⁻¹]</td>
<td>1069</td>
<td>1078</td>
<td>1072</td>
<td>1073</td>
</tr>
<tr>
<td>ⁱH NMR δ [ppm]</td>
<td>4.1</td>
<td>4.3, 5.1</td>
<td>4.4</td>
<td>4.2</td>
</tr>
<tr>
<td>²⁷Al NMR δ [ppm]</td>
<td>-1.0, 54.5</td>
<td>-0.9, 53.4</td>
<td>53.4</td>
<td>-1.0, 55.2</td>
</tr>
<tr>
<td>Si/Al ratio framework</td>
<td>12.5</td>
<td>17.0</td>
<td>44.7</td>
<td>40.7</td>
</tr>
<tr>
<td>H/Pt framework</td>
<td>2.0</td>
<td>1.6</td>
<td>2.0</td>
<td>1.6</td>
</tr>
<tr>
<td>SEM crystal size [µm]</td>
<td>~ 5</td>
<td>~ 1</td>
<td>≤ 1</td>
<td>4</td>
</tr>
<tr>
<td>Ambient water 12.6 wt.%</td>
<td>12.6</td>
<td>9.6 wt.%</td>
<td>4.4 wt.%</td>
<td>5.6 wt.%</td>
</tr>
<tr>
<td>BET (nC₆) pore volume [cm³/g]</td>
<td>0.20</td>
<td>0.30</td>
<td>0.05</td>
<td>0.17</td>
</tr>
<tr>
<td>(0.07)</td>
<td>(0.26)</td>
<td>(0.055)</td>
<td>(0.164)</td>
<td></td>
</tr>
<tr>
<td>BET surface area [m²/g]</td>
<td>585.8</td>
<td>763.5</td>
<td>144.3</td>
<td>477.5</td>
</tr>
<tr>
<td>ΔH_ads [kJ/mol]</td>
<td>71.9</td>
<td>70</td>
<td>81.5</td>
<td>82</td>
</tr>
</tbody>
</table>

Since the ZSM-22 and ZSM-5 samples had different crystal sizes, each was given a JP number. Within one zeolite type the samples came from the same synthesis batch and therefore had similar characteristics.

5.3.1. IR spectroscopy

The methodology of the recording of the IR-spectra on the empty zeolite and the one on which acetonitrile was adsorbed is given in an article by Jänchen et al. In Table 5.2, the peak position of the OH stretch vibration of the Brønsted acid site is given. This peak shifts upon acetonitrile adsorption and gives two broad bands. The shift (in cm⁻¹), based on the weighted average of these new bands, is also given. Both numbers are a measure of Brønsted acidity. The higher the position of the OH-peak and the smaller the shift upon acetonitrile adsorption the lower the acidity.
The Mordenite sample contained some Lewis acidity. The CN stretch vibrations gave two bands in the difference spectrum at approximately 2313 and 2330 cm\(^{-1}\). The former was due to weak Lewis acidity from penta-coordinated aluminium, the latter stemmed from tri-coordinated aluminium giving stronger sites.

Zeolite \(\beta\) is an intergrowth hybrid of two related but distinctive structures: polymorph A (tetragonal) and polymorph B (monoclinic)\(^{33}\). Since there are many stacking faults in the resulting structure, zeolite \(\beta\) contains much more silanol groups than the other zeolites. This was confirmed by the IR spectrum. It showed peaks at 3609 (bridging hydroxyls) and 3784 cm\(^{-1}\) (slightly acidic hydroxyls associated with aluminium that is leaving the framework) and a silanol peak at 3738 cm\(^{-1}\) (terminal hydroxyls and hydroxyls at lattice defects)\(^{34}\). All peaks are shifted upon deuterated acetonitrile adsorption to a broad peak at 3500 cm\(^{-1}\). This zeolite also contained some Lewis acidity. The CN stretch vibration gave a band indicating strong Lewis acidity at approximately 2328 cm\(^{-1}\).

The ZSM-22 sample contained a few strong (2330 cm\(^{-1}\)) and weak (2303 cm\(^{-1}\)) Lewis acid sites. ZSM-5 had only strong Lewis sites (2325 cm\(^{-1}\)). Since the OH-stretch vibrations and the shift upon acetonitrile adsorption were the same for all zeolites used, it may be concluded that they all had the same acid strength.

5.3.2. \(^{27}\)Al NMR spectroscopy

The \(^{27}\)Al NMR spectroscopy showed Lewis acidity for Mordenite, \(\beta\) and ZSM-5. The IR spectroscopy, however, did also show Lewis acidity for ZSM-22. The fact that aluminium is a quadrupole center means that peaks may be become too broad to see when the environment is asymmetrical. This would explain the absence of a peak in the \(^{27}\)Al NMR spectrum of ZSM-22.

The \(^{29}\)Si NMR of all-silica \(\beta\) has three sets of lines around -111, -113 and -115 ppm which are due to silicon atoms whose neighbors are all also silicon. The framework Si/Al ratio of this zeolite was however obtained by fitting the signals representing silicon without aluminum neighbors with only two peaks. The equation used for all zeolites is\(^{5}\):

\[
\text{Si/Al} = \sum \frac{I_0}{\sum 0.25 \cdot n \cdot I_n}
\]

\(I_0\) = Intensity of peak representing Si without Al neighbors
\(I_n\) = Intensity of peak representing Si with \(n\) Al neighbors
\(n\) = Number of Al neighbors

The \(^1\)H NMR spectrum of zeolite \(\beta\) sample showed many silanol groups, which was already found by IR. Both the ZSM-5 and the ZSM-22 spectra contained silanol peaks as large as the peaks from the acid sites. The latter are relatively small because they both had a high Si/Al
ratio. Since the $^1$H chemical shift for the acid sites are in the same range for all zeolites used, it supports the conclusion from the IR that they all had the same acid strength.

5.3.3. Hydrogen chemisorption
Hydrogen chemisorption gives a measure of platinum dispersion. A H/Pt value larger than approximately 1.4 represents a highly dispersed catalyst. The values given in Table 5.2. are typical for the range of catalysts used. The hydrogen was adsorbed on the metal at 250 °C. The chemisorption isotherms were then measured at room temperature using a conventional glass apparatus. The H/Pt was determined by extrapolation of the high pressure part of the desorption isotherm to zero pressure. The intercept gave the amount of chemisorbed hydrogen. Details about the method used to measure the H/Pt are described elsewhere 35. A way to check the dispersion before reduction was to look at the color of the sample after calcination. When the sample was slightly green, the platinum(II) atoms are coordinated to the zeolite oxygen atoms and no auto-reduction leading to larger particles had taken place. This meant that the calcination had been successful.

5.3.4. SEM crystal size
The crystal size was determined by SEM. The Mordenite and β-zeolite samples consisted of agglomerated crystals. The diameters given in Table 5.2. are of the crystals themselves. The Mordenite agglomerates were up to 20 μm in size. Zeolite β-agglomerates of up to 200μm were observed.

5.3.5. Pore volume and surface area
The BET pore volume and surface area in Table 5.2. were obtained by adsorbing nitrogen at liquid nitrogen temperature. The pore volumes for n-hexane at 25 °C are given in parentheses. BET can also be used to look for the existence of meso-pores in the zeolite samples. When a step is observed in the BET-isotherm at a relative pressure of 0.4, meso-pores are present in the sample. Mordenite and β-zeolite showed almost no nitrogen adsorbed volume in meso-pores. ZSM-22 had very little micro-pore volume, and no step was observed in the isotherm. The ZSM-5 sample on the contrary may have contained some meso-pores.

5.3.6. Adsorption enthalpy
The ΔH$_{ads}$ values given are the calorimetrically measured heats of adsorption of n-hexane. The accuracy of these measurements gives an error of less than 1 kJ/mol. Generally, a smaller pore size led to higher adsorption enthalpy. β-Zeolite seemed to be an exception to this rule because its heat of adsorption is relatively low. Its low density (Table 5.1.) might be causing this 36. Huddersman and Klimeczyk also found that Mordenite and zeolite β have similar heats of adsorption 37. An extrapolation of Configurational Bias Monte Carlo calculations on all-
silica β-zeolite confirmed the value of approximately 70 kJ/mol\(^3\). The value of ZSM-22 was not measured here but was taken from results of Eder\(^3\).

5.3.6. Liquid phase hydrogenation
Besides hydrogen chemisorption, we used another method to characterize the platinum particles. Liquid phase hydrogenation experiments of 1-hexene in n-heptane were performed. The rate of hexene conversion was determined by measuring the decrease in pressure of the hydrogen atmosphere above the liquid phase as a function of time. In the beginning of the experiment reactant is readily available and the reaction will be zero-order in n-hexene. At low conversions a straight line was obtained as a function of time (see Figure 5.2.)\(^4\). The slope of this line was a measure of the reaction rate. At a conversion of approximately 80% the experimental points will deviate from the straight line due to a shift towards a first-order reaction. Mass-transfer limitations of 1-hexene played an increasing role when the points deviated at decreasing conversion. The exact point of deviation was also dependent on the reaction rate. The higher the reaction rate, the earlier mass transfer problems will occur.

5.4. Equipment
Hexane (Janssen Chimica 99+% purity), delivered by a HP1050 HPLC pump, was evaporated into flowing hydrogen or a hydrogen/nitrogen mixture. The gas flows were controlled by thermal mass-flow controllers. The full mixture was then flowed through a fixed-bed, continuous flow reactor at atmospheric pressure. Quartz reactors with an internal diameter of 4 and 8 mm were used, typically filled with 50 to 200 mg of catalyst. Details will be given where appropriate. Reaction products were analyzed on-line using a HP5890 Series II gas chromatograph equipped with a FID detector and a Chrompack fused silica column with a Al\(_2\)O\(_3\)/KCl coating.

The temperature range employed was 220-260 °C. The WHSV was tuned by using an amount of catalyst which yielded a conversion below 10% at standard conditions. These
conditions were: atmospheric pressure, 0.03 ml/min liquid flow of n-hexane, 145 Nml/min flow of hydrogen (H₂/nC₆ molar ratio 28) and a temperature of 240 °C. When necessary, nitrogen was used as diluting gas. A hydrogen/n-hexane molar ratio of above 20 was used to minimize deactivation by coking. The order of reaction in n-hexane was determined in a partial pressure range of 19.2 to 42.3 mbar at a fixed hydrogen pressure of 846 mbar. The order of reaction in hydrogen was determined in a partial pressure range of 677 to 966 mbar at a fixed n-hexane pressure of 33.8 mbar.

Following an aging period (see next paragraph), the activity reached a stable plateau. The catalysts could then be used for up to 1000 hours on stream without further loss of activity. On average, the experimental error amounts to 10 %. We defined a Turn Over Frequency as the number of moles reactant converted per mole of acid site per time unit (second or hour). All Bronsted acid sites were taken into account since they were all strongly acidic and these were assumed to be active in the reaction. In case of the Mordenite, however, only approximately one-third of the acid sites can be reached by n-hexane⁴¹. It might therefore be argued whether in this case the TOF must be calculated using only one-third of the sites. The thus calculated values are given in parentheses where needed.

5.5. Diffusion limitation experiments

5.5.1. External diffusion limitations

The presence of external diffusion limitations was tested in two ways. The first test consisted of a variation of the flow rate at a constant space time. When the conversion remains constant, the reaction is not diffusion limited⁴². This means that the conversion has to be constant over experiments with proportionally different total flow, reactant flow and amount of catalyst. The conversion (X) of experiment A and B must satisfy equation (5.4).

\[
\frac{X(A)}{X(B)} = a = 1
\]

Two experiments were performed where in experiment B the total flow was doubled relative to experiment A. Using an embedded 0.5 wt.% Pt/HMOR sample and a reactor with an internal diameter of 8 mm, a value of \( a = 0.93 \) was obtained. Since the average error in all measurements is approximately 10 %, this value does point to absence of diffusion limitations. The result using a pure in situ pretreated 2.0 wt.% Pt/HMOR catalyst in a 4 mm reactor was more conclusive. In this case a value for \( a = 1.0 \) was obtained.

The second test was performed using a constant amount of catalyst, performing an experiment at an \( x \) times higher WHSV, caused by an \( x \) times lower space time. This should, when there are no diffusion limitations, result in an \( x \) times lower conversion. In mathematical terms:
Equation (5.5) was tested in an 8 mm quartz reactor using an embedded 0.5 wt.% Pt/HMOR sample and in a 4 mm tube using a pure in situ pretreated 2.0 wt.% Pt/HMOR catalyst. A flow in the range from 100 to 300 Nml/min was used. It was found that the product of conversion and WHSV reached a constant value at flows above 125 Nml/min. These results showed that external diffusion limitations could be excluded when a total flow of 150 Nml/min was used in all future experiments.

5.5.2. Internal diffusion limitations

The occurrence of internal diffusion limitations was tested using a 8 mm quartz tube and a set of three embedded ZSM-5 samples with different crystal sizes: < 1 \( \mu \)m (JP1502), ± 4 \( \mu \)m (JP1503) and ± 12 \( \mu \)m (JP1504). When the relative catalyst efficiency (\( \eta' \)) is independent of the relative Weisz modulus (\( \Phi' \)), the real efficiency is 1.

\[
\Phi' = \frac{p^2}{6} \cdot \frac{R_0}{D_{\text{eff}} \cdot C_0} \quad \text{and} \quad \eta'(2) = \frac{\Phi'(2)}{\Phi'(1)} = \frac{p^2(2) \cdot R(2)_{\text{o}}}{p^2(1) \cdot R(1)_{\text{o}}}
\]

Table 5.3. Relative Weisz modulus and efficiency versus crystal size

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal size</th>
<th>( \Phi' )</th>
<th>( \eta' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>JP1502</td>
<td>0.6</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>JP1503</td>
<td>3.5</td>
<td>41.2</td>
<td>1.2</td>
</tr>
<tr>
<td>JP1504</td>
<td>12</td>
<td>432.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Using \( p = \frac{1}{2}d \), where \( d \) = particle diameter, one obtains the results listed in Table 5.3. The relative efficiency and Weisz modulus are normalized relative to the JP1502 sample. Since the reaction rate and thus the relative efficiency are independent of the relative Weisz modulus, the real efficiency must be 1 and the real Weisz modulus must be lower than 0.1.

Using \( p = \frac{1}{2}d \), where \( d \) = particle diameter, one obtains the results listed in Table 5.3. The relative efficiency and Weisz modulus are normalized relative to the JP1502 sample. Since the reaction rate and thus the relative efficiency are independent of the relative Weisz modulus, the real efficiency must be 1 and the real Weisz modulus must be lower than 0.1.

The Weisz modulus of sample JP1502 is therefore smaller than 2.3 \( \times \) 10\(^{-4}\). The \( D_{\text{eff}} \) calculated from this value is 8 \( \times \) 10\(^{14}\) m\(^2\)/s at 513 K. This is approximately the same value as obtained by Haag et al. for n-hexane on a ZSM-5 catalyst at 538 K. They also calculated their value from a Weisz modulus.
From Table 5.3, it can be concluded that internal diffusion limitations do not play an important role in these experiments. A trend that can be observed as a function of crystal size is the 2-MP/3-MP ratio. This ratio increases from 3.4 through 3.6 to 3.8 with increasing crystal diameter. This issue will be discussed in paragraph 5.8.

The same type of experiment was performed on two TON samples. Here a \( \eta' \) of 0.28 was found for the 4 \( \mu \text{m} \) crystal sample relative to the sample containing crystals smaller than 1 \( \mu \text{m} \). This means that, at least on 4 \( \mu \text{m} \) ZSM-22 crystals, internal diffusion limitations do play a role. This change in activity as a function of crystal size can also be explained by pore-mouth catalysis. When the crystals are 4 times smaller, 4 times more pore openings are available for reaction which leads to an almost 4 times higher activity. This special feature of ZSM-22 will be also be discussed in more detail in paragraph 5.8.

5.6. Pretreatment

Each catalyst was subjected to an aging period. After a pretreatment at 450 °C in flowing hydrogen (50 Nml/min) the catalyst was submitted to 20 hours of standard reaction conditions (see paragraph 5.4.). Since the amount of material differed from catalyst to catalyst, the WHSV also differed. During this treatment, after an initial deactivation period, a stable level of activity was reached.

The Shell pretreated catalyst was shown to be 50% more active than an embedded 0.5 wt.% Pt/HMordenite. However, the H/Pt of the former catalyst was lower (~1) than the latter catalyst (~1.5). Exposure to moist air between calcination and reduction apparently results in less disperse platinum\(^{45} \). Liquid phase hydrogenation also showed a higher activity per platinum atom for the Shell pretreated catalyst (a factor of 2). The selectivity of the Shell pretreated catalyst towards the bulkiest isomer 2,2-dimethylbutane was a factor of 1.5 higher than the embedded sample. This suggested a partly destroyed pore system which creates more space inside the Mordenite pores. This destruction would also lead to a pseudo 3-dimensional pore system which enhances molecular diffusion what would result in the higher activity observed experimentally.
In Figure 5.3, it is shown that a pretreatment temperature of 450 °C was needed to obtain the most active catalyst at steady state level. This effect was attributed to drying of the catalyst when treating the catalyst for the first time. Between measurements the catalyst was re-activated by an in situ hydrogen pretreatment. This resulted temporarily in a higher activity, which was leveled out, depending on the zeolite type, in a 4 to 10 hour period. A partial cleaning of the platinum and acid sites was assumed to be responsible for the high initial activity.

Pretreatment of the embedded catalyst at high temperature in flowing nitrogen resulted in a non-active catalyst. This feature can be explained in two ways. Firstly, it can be attributed to a re-oxidation of the highly dispersed platinum particles by the acid sites under an inert atmosphere (Figure 5.4a.)\(^{46}\). This oxidation is facilitated by water desorbing from the silica matrix\(^{45}\). In this way less metal is available for the hydrogenation/dehydrogenation function which leads to a less active catalyst. The catalyst activity can be restored by a high-temperature re-hydrogenation under flowing hydrogen (Figure 5.4b.).

\[
\begin{align*}
(a) \quad \text{Pt}^0 + 2 \text{H}^+ & \xrightarrow{\text{N}_2} \text{Pt}^{2+} + \text{H}_2 \\
(b) \quad \text{Pt}^{2+} + \text{H}_2 & \xrightarrow{\text{H}_2} \text{Pt}^0 + 2 \text{H}^+
\end{align*}
\]

Figure 5.4. Re-oxidation and re-hydrogenation of platinum

A second explanation could be that the platinum particles are covered by hydroxyl groups that make them inaccessible for n-hexane to undergo reaction. Infra-red spectroscopy may provide the evidence for this explanation. In the IR spectrum of a pure, high temperature (450 °C, 1.10\(^{-6}\) bar) pretreated 2 wt.% Pt/HMOR two new peaks appeared in comparison to a HMOR and a pure, low temperature pretreated (350 °C, 1.10\(^{-6}\) bar) 1 wt.% Pt/HMOR\(^{47}\). One peak at \(\pm 2060\text{ cm}^{-1}\) and another at 3270 cm\(^{-1}\) were observed. Both peaks became smaller after recording the spectrum at 340 °C and reappeared after reduction at 250 °C for 1 hour, recording the spectrum at 250 °C.

The 2060 cm\(^{-1}\) peak was assigned to a PtH species\(^{48}\). The wavenumber of 3270 cm\(^{-1}\) resembles that of strongly perturbed Bronsted acid sites. Taking into account the absence of this band in HMOR, this suggested a hydrogen bridge connected to a platinum site. This can be either a PtOH species, formed by splitting of water into PtOH and PtH-species and bridged...
to a framework oxygen\textsuperscript{49}, or a Brønsted acid site bridged to a platinum site. Such a hydrogen bridge breaks down at higher temperatures or if the platinum is covered with hydrogen after high temperature reduction, the applied 250 °C is apparently not high enough.

In case of 0.5 wt.% Pt/HZSM-5 and pure 0.7 wt.% Pt/HZSM-22 catalysts it was shown that a pretreatment at 450 °C in flowing hydrogen did not improve the steady state activity, but decreased the stability. Therefore, a pretreatment temperature of 250 °C was chosen in these cases.

A pure \textit{ex situ} pretreated 1.6 wt.% Pt/β catalyst showed an increase in cracking products after high pretreatment temperature (450 °C) relative to a pretreatment at 250 °C. The stability was the same in both cases. A pretreatment temperature of 250 °C was chosen between measurements after the initial activation stage at 450 °C.

5.7. Kinetics theory

5.7.1. Orders of reaction

We performed our kinetic measurements under differential conditions (conversion below 10 %). Therefore reverse reactions could be neglected. When the catalyst acts as an ideal bifunctional catalyst, such as depicted in Figure 2.1., the rate of reaction can then be expressed by equation (5.8).

\[ R = \frac{K_{\text{dehyd}} \cdot K_{\text{prot}} \cdot k_{\text{isom}} \cdot \left( \frac{P_{\text{nC6}}}{P_{\text{H2}}} \right)}{1 + K_{\text{dehyd}} \cdot K_{\text{prot}} \cdot \left( \frac{P_{\text{nC6}}}{P_{\text{H2}}} \right)} \]  

\text{(5.8)}

\[ R \] = rate of reaction  
\[ K_{\text{dehyd}} \] = equilibrium constant of dehydrogenation  
\[ K_{\text{prot}} \] = equilibrium constant of protonation  
\[ k_{\text{isom}} \] = rate constant of isomerization  
\[ P_{\text{nC6}} \] = partial pressure of n-hexane  
\[ P_{\text{H2}} \] = partial pressure of hydrogen

From this equation one expects an order in n-hexane between 0 and 1 and a negative order in hydrogen (between 0 and -1). The hydrogen order will have the same absolute value as the n-hexane order but will be opposite in sign.

Our first experiments on both pure and embedded Mordenite catalysts with a low platinum loading showed positive orders in hydrogen. This was attributed to a shift in rate determining step. When, for example, the hydrogenation of the product alkenes becomes rate determining a positive influence of the hydrogen partial pressure will arise. Another explanation might be that deactivation effects play a role. Deactivation effects can be
excluded when the activity is checked at high hydrogen partial pressure after experiments at low partial pressure. When the activities before and after the low partial pressure experiments are the same, no deactivation has occurred. Only experiments where this activity was constant were used. The possibility of falsification of orders of reaction due to deactivation could thus be excluded.

When the zeolite and platinum are almost completely covered with reactant, for example decane, equation (5.8) is no longer valid\textsuperscript{50}. The order in the reactant now becomes 0. A change in reactant partial pressure no longer influences the coverage and, therefore, the activity. The order of the reaction in hydrogen will be -1. An increase in hydrogen partial pressure will shift the dehydrogenation equilibrium maximally to the left. There are some assumptions that will lead to a rate equation that quantifies these orders. When it is for instance assumed that the transfer of the product hexenes towards the platinum for hydrogenation is the rate determining step one obtains equation (5.9).

\begin{equation}
R = k_{\text{transfer}} \frac{K_{\text{prot}}K_{\text{dehydr}}}{K_{\text{prot}}K_{\text{dehydr}} \frac{P_{n\text{C6}}}{P_{\text{H2}}} - 1} \left(1 - \left(1 + \frac{K_{\text{dehydr}}}{P_{\text{H2}}} \cdot \frac{K_{\text{prot}}^\text{Pt,}\text{dec},\text{C6}P_{n\text{C6}}}{1 + K_{\text{prot}}^\text{Pt,}\text{dec},\text{C6}P_{n\text{C6}}} \right) \right)
\end{equation}

\[K_{\text{prot}}^\text{Pt,}\text{nC6} = \text{equilibrium constant of n-hexane adsorption on platinum}\]

When the hydrogen (partial) pressure is high, the order in hydrogen will be 0 and the order in n-hexane will be between 0 and 1. Alternatively, when the n-hexane (partial) pressure is high the order in n-hexane becomes 0 and the hydrogen order -1.

It is also possible that the hexanes/hexenes are only at equilibrium inside the zeolite pores. When it is assumed that the hexane adsorbed on platinum may be neglected, one obtains equation (5.10).

\begin{equation}
R = \frac{k_{\text{prot}}K_{\text{prot}}K_{\text{dehydr}}}{K_{\text{prot}}K_{\text{dehydr}} \frac{K_{\text{prot}}^\text{Pt,}\text{dec},\text{C6}P_{n\text{C6}}}{1 + K_{\text{prot}}^\text{Pt,}\text{dec},\text{C6}P_{n\text{C6}}} \left(1 + \frac{K_{\text{prot}}^\text{Pt,}\text{dec},\text{C6}P_{n\text{C6}}}{1 + K_{\text{prot}}^\text{Pt,}\text{dec},\text{C6}P_{n\text{C6}}} \left(1 - \frac{K_{\text{dehydr}}}{P_{\text{H2}}} \right) \right) \right)
\end{equation}

\[K_{\text{prot}}^\text{Pt,}\text{dec},\text{C6} = \text{equilibrium constant of hydrogen dissociation}\]

From this equation orders in hexane and hydrogen of 0 are calculated at high hexane pressures. In case of high hydrogen pressures, an order in hydrogen of -1 will be found. The order in hexane will be between 1 (low hexane pressure) and 0 (high hexane pressure). The latter case is exactly what was found in the reaction of n-decane over a Pt/USY catalyst\textsuperscript{50}. In case of octane the order in the hydrocarbon was no longer 0. It is therefore to be expected that in case of n-hexane this extreme will not be measured.
5.7.2. Activation energy

From the measured data we wanted to extract intrinsic activation energies (the activation energy of isomerization on a zeolite). If the n-alkoxy isomerization is the rate determining step the reaction rate can be expressed as:

\begin{equation}
(5.11) \quad R = k_{\text{Ison}} \cdot \theta_{\text{alkoxy}} = k_{\text{app}} \cdot P_{C6}^n \cdot P_{H2}^m
\end{equation}

$R$ = rate of reaction
$k_{\text{Ison}}$ = rate constant of isomerization
$k_{\text{app}}$ = apparent rate constant
$\theta_{\text{alkoxy}}$ = coverage of n-alkoxy species
$n$ = order of reaction in n-hexane
$m$ = order of reaction in hydrogen
$P_{C6}$ = partial pressure of n-hexane
$P_{H2}$ = partial pressure of hydrogen

The coverage of n-alkoxy species can be expressed in the protonation equilibrium of the hexenes, using the mass balance over the acid sites. The partial pressure of hexene can be calculated from the hexane/hexene equilibrium. This results in:

\begin{equation}
(5.8) \quad R = k_{\text{iso}} \frac{K_{\text{prot}} \cdot K_{\text{dehydr}} \cdot \left( \frac{P_{C6}}{P_{H2}} \right)}{1 + K_{\text{prot}} \cdot K_{\text{dehydr}} \cdot \left( \frac{P_{C6}}{P_{H2}} \right)}
\end{equation}

$K_{\text{prot}}$ = equilibrium constant of protonation
$K_{\text{dehydr}}$ = dehydrogenation equilibrium constant

When one takes the derivative of the natural logarithm of the reaction rate towards the reciprocal of the temperature using equation (5.8), one obtains:

\begin{equation}
(5.12) \quad R_g T^2 \frac{\partial}{\partial T} \ln \left[ k_{\text{iso}} \cdot \frac{K_{\text{prot}} \cdot K_{\text{dehydr}} \cdot \left( \frac{P_{C6}}{P_{H2}} \right)}{1 + K_{\text{prot}} \cdot K_{\text{dehydr}} \cdot \left( \frac{P_{C6}}{P_{H2}} \right)} \right] = RT^2 \frac{\partial}{\partial T} \ln \left[ k_{\text{iso}} \cdot \frac{K_{\text{all}} P_{all}}{1 + K_{\text{all}} P_{all}} \right]
\end{equation}

$R_g$ = gas constant
$K_{\text{all}} = K_{\text{prot}} \cdot K_{\text{dehydr}}$
$P_{all} = \frac{P_{C6}}{P_{H2}}$

Or:

\begin{equation}
(5.13) \quad = R_g T^2 \frac{1}{k_{\text{iso}}} \frac{\partial k_{\text{iso}}}{\partial T} + R_g T^2 \frac{1}{K_{\text{all}}} \frac{\partial K_{\text{all}}}{\partial T} \frac{1}{1 + K_{\text{all}} P_{all}}
\end{equation}
In the ideal case that the surface reaction of a reactant is rate determining, the correlation between order of reaction and surface coverage is given by equation (5.14)\(^51\).

\[
(5.14) \quad n = 1 - \theta_{\text{reactive intermediate}}
\]

One can verify that this equation is exact and valid when \(\theta_{\text{reactive intermediate}}\) is approximately zero or approaches unity. A linear interpolation between the two extremes gives the equation above. When this equation is used, one obtains:

\[
(5.15) \quad -E_{\text{act,app}} = -E_{\text{act,iso}} + n \cdot \left[ \Delta H_{\text{prot,g}} + \Delta H_{\text{dehyd}} \right]
\]

- \(E_{\text{act,app}}\) = apparent activation energy
- \(E_{\text{act,iso}}\) = activation energy of isomerization from the adsorbed state
- \(\Delta H_{\text{prot,g}}\) = protonation enthalpy of hexene from the gas phase
- \(\Delta H_{\text{dehyd}}\) = enthalpy of dehydrogenation

The protonation enthalpy of hexene from the gas phase can be expressed as the sum of the protonation enthalpy from the adsorbed state and the adsorption enthalpy on the zeolite.

\[
(5.16) \quad E_{\text{act,iso}} = E_{\text{act,app}} + n \cdot \left[ \Delta H_{\text{prot,ads}} + \Delta H_{\text{ads-C6}} + \Delta H_{\text{dehyd}} \right]
\]

- \(\Delta H_{\text{prot,ads}}\) = protonation enthalpy of n-hexene from the adsorbed state
- \(\Delta H_{\text{ads-C6}}\) = adsorption enthalpy of n-hexene

It is assumed that the adsorption enthalpy of hexene is equal to that of hexane (see arguments in paragraph 4.2.).

A feature that is related to the one just described is the compensation effect. This effect means that a linear increase in the logarithm of the pre-exponential factor of reaction will occur with increasing apparent activation energy\(^52\). Thus a decrease in reaction rate due to the increase in activation energy is (partially) compensated by an increase in pre-exponential factor. This compensation effect is often found for a series of similar reactants reacted over one catalyst or one reactant reacted over similar catalysts\(^53\). It can be understood in terms of entropy and enthalpy of reaction. The natural logarithm of the pre-exponential factor represents the entropy, the activation energy the enthalpy. When it is assumed that the reaction can be written as an adsorption and a reaction term, one obtains:

\[
(5.17) \quad R = k_{\text{RDS}} \frac{K_{\text{ads}} \cdot P_{\text{reactant}}}{1 + K_{\text{ads}} \cdot P_{\text{reactant}}}
\]

- \(k_{\text{RDS}}\) = rate constant of the Rate Determining Step
- \(K_{\text{ads}}\) = equilibrium constant of adsorption
- \(P_{\text{reactant}}\) = partial pressure of reactant

Or in our case:
In these equations, the reaction term is the same for a series of catalysts or reactants. The adsorption equilibrium constant is a function of adsorption enthalpy and entropy. Indeed linear relationships between enthalpies and entropies of reaction were found\textsuperscript{54}. We already used the compensation effect in Chapter 3 to calculate activation energies and pre-exponential factors for the (de)hydrogenation of the different alkanes.

5.8. Activity and selectivity

The activities of the pure \textit{ex situ} pretreated samples and those embedded were comparable. The \textit{in situ} pretreated samples were less active which is probably due to the lower dispersion of platinum. Since in the latter case the zeolites were pressed into agglomerates before pretreatment, the mass transport of the desorbing ammonia will be hindered. It was previously found that only when this ammonia is removed quickly by a low heating rate and high oxygen/nitrogen flow rate a high dispersion is obtained\textsuperscript{45}. Mobility of partially calcined platinum atoms and auto-reduction by the ammonia will otherwise result in large metal particles.

We were especially interested in studying the acid catalyzed part of the reaction. The platinum function was, therefore, made non-rate determining. This was tested using both pure \textit{ex situ} pretreated and embedded Mordenites (pretreated at 250 °C) samples as well as two \textit{β} samples. The activities of these catalysts as a function of acid to platinum site ratio are given in Figure 5.5. All acid sites and platinum atoms were taken into account. Since the platinum was homogeneously distributed in the zeolite, the platinum in the side pockets of the Mordenite will be as inaccessible for n-hexane as those acid sites. The activities were normalized to the activity of the 0.5 wt.% Pt/zeolite sample.

An extra increase in activity was
observed for the 3 wt.% Pt sample when pure ex situ pretreated catalysts were used for this test. This was probably due to local destruction of the Mordenite framework which facilitates molecular diffusion. This destruction was caused by large platinum particles. This was confirmed by a relatively low H/Pt of this catalyst. Also liquid phase hydrogenation of 1-hexene over this catalyst showed a very low activity per platinum atom. This indicated that some atoms are not available to the reaction because they were inside a metal particle. Moreover, the experimental points deviated from linearity going from 0.5 to 2.0 wt.% loaded Mordenites at increasingly low conversion. The 3 wt.% Pt/HMOR samples deviated at a much higher conversion level. This again indicated a 3-dimensional pore system of the catalyst.

Selectivities of the product isomers also indicated that at least 2.0 wt.% platinum was needed on the Mordenite to establish equilibrium. In Figure 5.6, the 2-methylpentane/3-methylpentane (2-MP/3-MP) ratio and the cracking selectivity are plotted versus the platinum content. The amount of 2,2-dimethylbutane (22-DMB) was very low and difficult to detect (its retention time was almost equal to methylcyclopentane, which was a contaminant in the feed n-hexane). Therefore, the dimethylbutanes ratio could not always be used as a means to characterize the platinum function. The sum of these products was a more reliable source of information and is also plotted.

![Figure 5.6. Selectivities and 2-MP/3-MP ratio versus platinum content](image)

On Mordenite the 2-MP/3-MP ratio decreased with increasing metal loading. At a Pt/H⁺ ratio of over 0.067 the equilibrium value was reached. Since the hydrogenation function was increased at higher loading, secondary acid-catalyzed reaction was suppressed. The amount of cracking and dimethylbutanes was thus decreased, showing more bifunctional behavior of the catalyst.

In Table 5.4., a trend towards lower orders in n-hexane on Mordenite catalysts at higher loading can be observed. Note that the orders listed on the 0.5 and 1.0 wt.% samples were measured on pure in situ pretreated catalysts. They could, however, still be compared to
the other two while it was found that the orders of reaction for Mordenites hardly change as a function of pretreatment. The decrease in the n-hexane order implied that the zeolite got more and more covered and the usage of the available acid sites increased. At a loading of 3.0 wt.% the hydrogen order was suddenly very negative and the n-hexane order had increased again. The n-hexane and hydrogen order of reaction were now almost equal, except for the sign. This is a feature of the ideal bifunctional mechanism according to Weisz under differential conditions (equation (5.8)). A change in mechanism or rate determining step must have taken place.

<table>
<thead>
<tr>
<th>metal loading [wt.%]</th>
<th>MOR, embedded pretreated at 250°C</th>
<th>MOR, pure pretreated at 450°C</th>
<th>BEA, pure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-C₆</td>
<td>H₂</td>
<td>n-C₆</td>
</tr>
<tr>
<td>0.5</td>
<td>0.42</td>
<td>-0.18</td>
<td>0.34</td>
</tr>
<tr>
<td>1.0</td>
<td>0.32</td>
<td>-0.02</td>
<td>0.24</td>
</tr>
<tr>
<td>1.6</td>
<td>0.24</td>
<td>-0.08</td>
<td>0.13</td>
</tr>
<tr>
<td>2.0</td>
<td>0.31</td>
<td>-0.23</td>
<td>0.19</td>
</tr>
<tr>
<td>3.0</td>
<td>0.24</td>
<td>-0.08</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The decrease in the order of reaction in n-hexane is explained by a mechanism in which the transport of iso-hexenes to the platinum sites for hydrogenation is rate determining. The larger the amount of platinum available the easier the platinum is reached by the iso-hexenes and the more zeolite will be used in the reaction. This results in a higher coverage and thus a lower order. The same change in mechanism can explain the increase in the apparent activation energy (see Table 5.10.).

A check for the optimum platinum loading was also performed using β-zeolite. The TOF of a 0.5 wt.% Pt/Hβ was found to be 1.5 times lower than a 1.6 wt.% Pt/Hβ (Pt/H⁺ ratio of 0.067). This effect was less pronounced than on the Mordenite catalyst, which would confirm the change in rate determining step on the latter zeolite. The dimethylbutanes selectivity and order of reaction in n-hexane also increased. It was found by means of the Arrhenius activation energy that the reaction on the higher loaded sample was diffusion limited in the temperature range above 245 °C. The falsification of the reactant order is then given by57:
\[ (5.18) \quad n_{\text{obs}} = n + \frac{n-1}{2} \frac{d \ln \eta}{d \ln \Phi} \]

In which \( \frac{d \ln \eta}{d \ln \Phi} \) varies from 0 to -1, resulting in an observed order which is higher than the true order.

On the \( \beta \)-zeolite the 2-MP/3-MP ratio also decreased at increasing platinum loading. An opposite trend was observed for the sum of the dimethylbutanes. This sum increased with platinum content which was mainly due to an increase in 2,2-dimethylbutanes. This would confirm an increase in mono-molecular activity versus bi-molecular activity. The cracking activity increased from a 0.5 wt.% platinum to a 1.6 wt.% platinum sample. This was mainly due to an increase in acid cracking. This could be explained by high residence times due to some diffusion limitations.

An optimized \( \text{Pt/H}^+ \) ratio of 0.067 was used. This ratio was also used for the other two zeolites. Unless stated otherwise, the platinum loading used and three-letter codes of the zeolites are:

- TON(1): 0.7 wt.% Pt/HZSM-22, crystal size \( \leq 1 \mu m \)
- TON(4): 0.7 wt.% Pt/HZSM-22, crystal size 4 \( \mu m \)
- MOR: 2.0 wt.% Pt/HMordenite
- MFI: 0.5 wt.% Pt/HZSM-5
- BEA: 1.6 wt.% Pt/H\( \beta \)

In Table 5.5., a summary of the activities of the pure \textit{ex-situ} pretreated zeolites at 240 °C is given. The corresponding adsorption enthalpies for n-hexane are also listed.

### Table 5.5. Activities at 240 °C of the zeolites used

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>( \Delta H_{\text{ads}} ) [kJ/mol]</th>
<th>WHSV [g/gh]</th>
<th>TOF [mol/mol h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFI</td>
<td>82</td>
<td>12.6</td>
<td>54</td>
</tr>
<tr>
<td>TON(1)</td>
<td>81.5</td>
<td>13.5</td>
<td>7.9</td>
</tr>
<tr>
<td>TON(4)</td>
<td>81.5</td>
<td>10.0</td>
<td>2.2</td>
</tr>
<tr>
<td>MOR</td>
<td>71.9</td>
<td>8.1</td>
<td>9.7 (29.1)</td>
</tr>
<tr>
<td>BEA</td>
<td>70</td>
<td>25.9</td>
<td>27.8</td>
</tr>
</tbody>
</table>

The TOF is a factor of 5 (1\( \frac{1}{2} \)) higher for a ZSM-5 than for a Mordenite catalyst. The \( \beta \)-zeolite is 1\( \frac{1}{2} \) times less active than the ZSM-5 catalyst. When indeed only one-third of the acid sites in Mordenite are available for the reaction of n-hexane, the \( \beta \)-zeolite and Mordenite are equally active. However, it was shown that the reaction on \( \beta \)-zeolite might be diffusion limited at 240 °C. Since Mordenite and \( \beta \) have similar adsorption enthalpies, this would confirm an adsorption effect as well as (single-file) diffusion problems in the Mordenite.
Otherwise, the low conversion indicates that the reaction in the Mordenite catalysts is even more diffusion limited than $\beta$. The *ex situ* pretreated Mordenite containing 3 wt.% platinum is approximately $1\frac{1}{2}$ times more active than the Mordenite in Table 5.5. This could confirm diffusion problems in the 2.0 wt.% catalyst. Another possibility is that the $\beta$-zeolite is relatively too active due to a bi-molecular mechanism, despite the diffusion limitations.

The ZSM-22 catalyst with 4 $\mu$m crystals is very inactive compared to ZSM-5 which has the same adsorption enthalpy. This means that only a part of the sites is taking part in the reaction. This indicates pore-mouth catalysis, which was already noted in paragraph 5.5.2. Another explanation would be similar to the Mordenite case: (single-file) diffusion. These hypotheses were tested using 4 times smaller TON crystals and, therefore, 4 times more pore-mouths. Indeed the smaller ZSM-22 crystals are almost 4 times more active, which would be consistent with pore-mouth catalysis. The activity is, however, still not as high as would be expected from its adsorption enthalpy. Since the pore volume for n-hexane is equal to the BET pore volume, all sites are in principle available for reaction. Assuming that the activity per active site of the ZSM-22 is equal to that of ZSM-5, the sites that contribute to the activity can be estimated. Only 4% of the acid sites is then active on the 4 $\mu$m crystals, for the 1 $\mu$m crystals this is 15%.

In Table 5.6, the selectivities to the four hexane isomers as a function of zeolite are given at standard conditions. The ratios of 2-methylpentane/3-methylpentane (2-MP/3-MP) and 2,2-dimethylbutane/2,3-dimethylbutane (22-DMB/23-DMB) are also listed. These ratios are 1.5 and 2.5 at equilibrium respectively.

### Table 5.6. Product selectivities (mol%) for different zeolites at 240 °C

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>2-MP</th>
<th>3-MP</th>
<th>2-MP/3-MP</th>
<th>23-DMB</th>
<th>22-DMB</th>
<th>22-DMB/23-DMB</th>
</tr>
</thead>
<tbody>
<tr>
<td>TON(1)</td>
<td>55.6</td>
<td>19.5</td>
<td>2.9</td>
<td>0</td>
<td>0</td>
<td>not applicable</td>
</tr>
<tr>
<td>TON(4)</td>
<td>45.4</td>
<td>32.6</td>
<td>2.7</td>
<td>0</td>
<td>0</td>
<td>not applicable</td>
</tr>
<tr>
<td>MFI</td>
<td>73.9</td>
<td>22.2</td>
<td>3.3</td>
<td>0.3</td>
<td>0</td>
<td>not applicable</td>
</tr>
<tr>
<td>MOR</td>
<td>50.5</td>
<td>33.3</td>
<td>1.5</td>
<td>10.5</td>
<td>1.7</td>
<td>0.2</td>
</tr>
<tr>
<td>BEA</td>
<td>53.4</td>
<td>34.2</td>
<td>1.6</td>
<td>3.7</td>
<td>2.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The overall selectivities towards isomerization were usually very high. Only up to 6 mole percent cracking products were found at conversions below 10%. ZSM-5 and the 0.5 wt.% $\beta$ even showed an isomerization selectivity of over 99 percent. The ZSM-22 catalysts were exceptions to this rule. The isomerization selectivity was only 80%. This might have been due to a reaction only at the pore-mouth of the zeolite crystals or high residence times. When the platinum is highly dispersed inside the crystals these cannot be reached by the reactant and an acid (cracking) mechanism is obtained. Indeed, the cracking product pattern was that of acid cracking: mostly propane. The low activity in the liquid phase due to
diffusion problems and the high H/Pt also indicated that the platinum is situated inside the zeolite pores. In contrast, when the platinum is poorly dispersed very high isomerization selectivities can be obtained\(^6^0\). The cracking selectivity was lowered on the smaller crystals.

Mordenite and zeolite β converted n-hexane to the methylpentanes in their equilibrium ratio. Due to the low conversion the di-branched products were formed to a lesser extent. The selectivity towards 2,2-dimethylbutane was especially low since the formation of this isomer involves a secondary carbenium ion or a methyl shift of 2,3-dimethylbutane\(^6^1\). This molecule cannot be formed by a dimerization and cracking mechanism\(^6^8\). In this mechanism the isomers are formed by dimerization of n-hexane, followed by isomerization of n-dodecane and cracking to the hexane products. The formation of 2,3-dimethylbutane involves a tertiary ion. The 2,3-dimethylbutane can even be formed by direct transformation of n-hexane when the reactant is isomerized twice before it is hydrogenated on the platinum. This may be the case at low platinum loading or zeolites with a 1-dimensional pore system, such as Mordenite\(^6^2\). At higher conversions the selectivity towards 2-methylpentane decreased while the dimethylbutanes selectivities increased. Apparently, the latter isomers were formed from 2-methylpentane.

The ZSM-5 and ZSM-22 catalysts showed product shape selectivity since the dimethylbutanes were formed in very low quantities (if any). Also the 2-MP/3-MP ratio was far from equilibrium on both catalysts. An explanation could be that 3-methylpentane is just a little bit bulkier than 2-methylpentane. The effective size of 3-methylpentane (4.4 X 5.8 Å) is very close to that of a ZSM-5 pore (5.3 X 5.6 Å or 5.1 X 5.5 Å)\(^4^4\). From the structure of 2-methylpentane it can be expected that the effective size of this molecule is less (see Figure 5.7.). Another explanation is that the mono-branched products can only adsorb with the linear part of the chain into the ZSM-22 catalyst. This results in a higher adsorption energy for 2-methylpentane than for 3-methylpentane\(^6^0,6^3\).

The 2-MP/3-MP ratio increases with increasing crystal size on the ZSM-5, on the ZSM-22 the opposite trend is observed. This means that two different mechanisms are operable to establish the enhanced selectivity for 2-methylpentane over 3-methylpentane. A size effect is more probable on ZSM-5 since it is increasingly difficult for the more bulky product to diffuse out of a crystal at increasing crystal size. Larger ZSM-22 crystals means less pore-mouths to react in. The adsorption effect will, therefore, be less pronounced.

From Table 5.5. it may be concluded that a higher adsorption enthalpy leads to a higher activity. The enhanced adsorption enthalpy of n-hexane of a catalyst will lead to an
increased amount of adsorbed n-hexane. The reactive compound is, however, the n-alkoxy species. Such a species is formed when n-hexene adsorbs on an acid site. The main feature of this species is a covalent bond between a carbon atom of the hydrocarbon and the oxygen atom of the zeolite. This n-alkoxy coverage should also be higher to be able to explain the enhanced activity.

Another possible explanation is schematically shown in Figure 5.8, for an almost empty zeolite. It is assumed that the true activation energy of isomerization (True $E_{\text{act}}$) is the same for all zeolites. Whether this assumption is valid will be discussed in paragraph 5.10. The net activation energy (Net $E_{\text{act}}$) for isomerization is then lowered on a ZSM-5 catalyst because of its higher adsorption enthalpy ($\Delta H_{\text{ads}}$). The simulations, discussed in Chapter 6, will also give evidence which of the two hypotheses is correct.

### 5.9 Orders of the reaction in n-hexane and hydrogen

The most important orders of the reaction in n-hexane measured on both embedded and pure catalysts are listed in Table 5.7. All orders are in the range expected. The orders that were measured as a function of temperature (not all are shown here) are found to be relatively independent of that temperature.

**Table 5.7. Order of the reaction in n-hexane as a function of temperature**

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>MFI embedded</th>
<th>MFI pure</th>
<th>TON, pure</th>
<th>MOR embedded</th>
<th>MOR pure</th>
<th>BEA pure</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>0.46</td>
<td></td>
<td>1</td>
<td>0.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>0.54</td>
<td>0.51 (ex situ)</td>
<td>0.7</td>
<td>1.0</td>
<td>0.24</td>
<td>0.14</td>
</tr>
</tbody>
</table>

* pretreated at 250 °C
The orders in n-hexane measured on pure Mordenites are lower than those measured on embedded catalysts. This same effect was also noticed in earlier experiments, using a lower WHSV, where the embedded system was compared to the mixed system. These values are given in parentheses in Table 5.8. Apparently, an embedded Mordenite catalyst is covered less than a pure one. The order plots were curved on the mixed system; higher hexane partial pressures led to lower order. This might indicate that the rate determining step was changing. Another possibility is that the surface coverage was changing towards full coverage at higher n-hexane partial pressures.

Equation (5.14) can be used to explain trends observed in the order of reaction in n-hexane. An increase in order means a decrease in coverage. The two zeolites with a three-dimensional pore system, \(\beta\)-zeolite and ZSM-5, showed similar orders when considering that the value of 0.69 might be obtained under diffusion limited conditions. The ZSM-22(4) zeolite appeared to be almost empty, since the order of reaction in n-hexane in that case was 1. This supports the conclusion of pore-mouth catalysis (paragraphs 5.5.2. and 5.8.). The coverage of the ZSM-22 sample with smaller crystals was higher, which indicates that more sites were used in the reaction. This enhanced usage of acid sites was already calculated from the activity data. Using equation (5.14), coverages of 0 and 30 percent are obtained. From the activity data values of respectively 4 and 15 percent were calculated. This is a reasonable agreement considering the crudeness of estimation.

The measured orders of reaction in hydrogen as a function of temperature are given in Table 5.9. The orders on Mordenite and ZSM-22 catalysts are very close to 0. Apparently here a situation is obtained were a delicate balance exists between the rate of the isomerization, the rate of transport of the product hexenes to platinum and deactivation effects. Whether the order in hydrogen is positive or negative depends on details of catalyst preparation and pretreatment.

### Table 5.8. Orders of reaction in n-hexane at 240 °C

<table>
<thead>
<tr>
<th>Platinum loading [wt.%]</th>
<th>Mordenite</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pure</td>
<td>embedded*</td>
</tr>
<tr>
<td>0.5</td>
<td>0.34 (0.24)</td>
<td>0.42 (0.50)</td>
</tr>
<tr>
<td>1</td>
<td>0.24</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>0.14</td>
<td>0.24</td>
</tr>
<tr>
<td>3</td>
<td>0.19</td>
<td>0.31</td>
</tr>
</tbody>
</table>

* pretreated at 250 °C

### Table 5.9. Order of the reaction in hydrogen as a function of temperature

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>MFI embedded</th>
<th>MFI pure</th>
<th>TON, pure</th>
<th>MOR embedded</th>
<th>MOR pure</th>
<th>BEA pure</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>-0.41</td>
<td>0</td>
<td>0</td>
<td>-0.08</td>
<td>0.04</td>
<td>-0.29</td>
</tr>
<tr>
<td>240</td>
<td>-0.24</td>
<td>-0.25 (ex situ)</td>
<td>0</td>
<td>-0.03</td>
<td>-0.08</td>
<td>0.04</td>
</tr>
</tbody>
</table>
The orders of reaction in hydrogen on ZSM-5 and β-zeolite at 240 °C are all similar; approximately -0.25. The order in hydrogen measured on a 3 wt.% Pt/HMOR catalyst has approximately the same value. This indicates that here the same, bifunctional mechanism is operating.

5.10. Activation energies

A wide variety of catalysts and their kinetic data are listed in Table 5.10. The sixth column contains the calculated activation energies of isomerization of n-alkoxy species. For the $\Delta H_{\text{prot,ads}}$ a value of 80 kJ/mol and for the $\Delta H_{\text{dehyd}}$ a value of -114.8 kJ/mol was used.

Table 5.10. Apparent and true activation energies

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>n</th>
<th>m</th>
<th>$E_{\text{act,app}}$ [kJ/mol]</th>
<th>$\Delta H_{\text{ads,iso6}}$ [kJ/mol]</th>
<th>$E_{\text{act,iso}}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFI, embedded</td>
<td>0.54</td>
<td>-0.24</td>
<td>104</td>
<td>82</td>
<td>129.5</td>
</tr>
<tr>
<td>MFI, pure (ex situ)</td>
<td>0.51</td>
<td>-0.25</td>
<td>103</td>
<td>82</td>
<td>127.1</td>
</tr>
<tr>
<td>TON(1), pure (ex situ)</td>
<td>0.7</td>
<td>~0</td>
<td>103</td>
<td>81.5</td>
<td>135.7</td>
</tr>
<tr>
<td>TON(4), pure (ex situ)</td>
<td>1.0</td>
<td>~0</td>
<td>86</td>
<td>81.5</td>
<td>132.7</td>
</tr>
<tr>
<td>½%MOR, embedded</td>
<td>0.42</td>
<td>-0.2</td>
<td>106</td>
<td>71.9</td>
<td>121.6</td>
</tr>
<tr>
<td>1%MOR, embedded*</td>
<td>0.32</td>
<td>~0</td>
<td>101</td>
<td>71.9</td>
<td>112.9</td>
</tr>
<tr>
<td>2%MOR, embedded</td>
<td>0.24</td>
<td>~0</td>
<td>111</td>
<td>71.9</td>
<td>119.9</td>
</tr>
<tr>
<td>3%MOR, embedded*</td>
<td>0.31</td>
<td>-0.23</td>
<td>114</td>
<td>71.9</td>
<td>125.5</td>
</tr>
<tr>
<td>½%MOR, pure (in situ)</td>
<td>0.34</td>
<td>~0</td>
<td>96.2</td>
<td>71.9</td>
<td>108.8</td>
</tr>
<tr>
<td>1%MOR, pure (in situ)</td>
<td>0.24</td>
<td>0.12</td>
<td>94.8</td>
<td>71.9</td>
<td>103.7</td>
</tr>
<tr>
<td>2%MOR, pure (in situ)</td>
<td>0.14</td>
<td>~0</td>
<td>107</td>
<td>71.9</td>
<td>112.2</td>
</tr>
<tr>
<td>2%MOR, pure (ex situ)</td>
<td>0.13</td>
<td>~0</td>
<td>106</td>
<td>71.9</td>
<td>110.8</td>
</tr>
<tr>
<td>3%MOR, pure (ex situ)</td>
<td>0.19</td>
<td>-0.25</td>
<td>115.2</td>
<td>71.9</td>
<td>122.2</td>
</tr>
<tr>
<td>½%BEA, pure (ex situ)</td>
<td>0.53</td>
<td>-0.24</td>
<td>115.9</td>
<td>70</td>
<td>134.7</td>
</tr>
<tr>
<td>1.6%BEA, pure (ex situ)</td>
<td>0.5 (0.69)</td>
<td>-0.29</td>
<td>113 (98.8)</td>
<td>70</td>
<td>131 (123.1)</td>
</tr>
</tbody>
</table>

* pretreated at 250 °C

The resulting activation energies range from 100 to 130 kJ/mol. The assumption that the isomerization is the rate determining step is questionable in some cases. The 1 wt.% pure in situ pretreated Pt/HMordenite catalyst can be discarded because of its positive order in
hydrogen. In all other cases there seems to be a trend that a low apparent activation energy is 'compensated' by a high order in n-hexane. This in agreement with equation (5.16). Still, a range of 110-130 kJ/mol is obtained for the true activation energy.

The Arrhenius plot measured on the 1.6 wt.% Pt/Hβ is curved. The activation energy is lower at higher temperatures. In the lower temperature range (220 to 233°C) the activation energy is 113.3 kJ/mol. In the higher temperature range (248 to 260°C) it is 67.3 kJ/mol. This strongly points to the conclusion that the reaction is diffusion limited in the higher temperature range. Since this catalyst is the most active of all (in mol/g-h), this is a very real possibility. Work of Philippou et al. confirm that isomerization over zeolite β proceeds quickly via a mono-molecular PCP mechanism. Another explanation is that the coverage of reactive intermediates and thus the order of reaction in n-hexane have changed significantly. The assumption of Arrhenius behavior is then no longer valid. However, the 0.5 wt.% Pt/Hβ shows a straight Arrhenius plot. The apparent activation energy is similar to the value obtained on the sample with the higher loading in the lower temperature range. This strongly supports the conclusion that the reaction on the latter catalyst is diffusion limited at higher temperatures.

When a catalyst does not conform to the ideal bifunctional behavior (equation (5.8)) the isomerization may not be the (only) rate determining step. Therefore, equation (5.16) cannot be used. The data on the Mordenite catalysts with lower loading suggest (co)rate determining steps. One possibility is the transport to platinum for hydrogenation of the product alkenes. In that case equation (5.9) must be differentiated with respect to the reciprocal of the temperature in order to obtain the correct equation. This cannot be done in a straightforward manner. Instinctively one would expect that the sum of the apparent activation energy and the appropriate reaction enthalpies would yield a value for the activation energy of deprotonation.

From the discussion in paragraph 4.6. and 4.7. in Chapter 4 of this thesis a value for the deprotonation activation energy is obtained which is approximately 10 kJ/mol lower than the true activation energy of isomerization. Indeed two groups of true activation energies can be distinguished in Table 5.10. One contains values of around 111 kJ/mol and the other of around 125 kJ/mol. The former would then represent the value for the activation energy of deprotonation. The latter is the true intrinsic activation energy of isomerization on a zeolite. The catalysts that were the most active in a range of catalysts or showed the most negative order in hydrogen (the ones indicated with X) indeed rendered values for the highest true activation energies.

The calculated isomerization activation energy of approximately 125-130 kJ/mol is much higher than the one in the liquid phase (approximately 30 kJ/mol). This is due to the fact that in catalysis by acid zeolites alkoxy species are the reactive intermediates. The covalent C-O bond between carbon chain and zeolite lattice has to be (partially) dissociated
before isomerization. The carbenium ion is in this case a transition state. The measurements showed that increasing adsorption enthalpy of a zeolite leads to lower apparent activation energy and higher activity.

Campelo et al. studied the hydro-isomerization and hydrocracking of n-hexane over SAPO-5 and SAPO-11 under a hydrogen pressure of 5 bar. From the data given in this article apparent and true activation energies were calculated. The following assumptions were made:

1. the heats of adsorption are the same as on the corresponding ALPO
2. the enthalpy of protonation in SAPO’s is also 80 kJ/mol
3. the order of reaction in hexane is 1

The results, given in Table 5.11., show that here also a higher adsorption enthalpy leads to a lower activation energy. Secondly, the calculated true activation energies are close to each other and to the true activation energy from Table 5.10. This last feature may be pure coincidence since assumptions 2 and 3 are both questionable.

<table>
<thead>
<tr>
<th>Molecular sieve</th>
<th>$E_{\text{act,app}}$</th>
<th>$\Delta H_{\text{ads,nC6}}$</th>
<th>$E_{\text{act,iso}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAPO-5</td>
<td>104</td>
<td>59</td>
<td>128</td>
</tr>
<tr>
<td>SAPO-11</td>
<td>94</td>
<td>74.5</td>
<td>134</td>
</tr>
</tbody>
</table>

Data of Liu et al. on hydro-isomerization of n-pentane over Mordenite were also used a basis for comparison. The reported order in n-pentane was used to calculate surface coverages via equation (5.14). When a linear dependence on the temperature was assumed, true activities could be calculated and a true activation energy of 135 kJ/mol was obtained. This was slightly higher than the value from Table 5.10 due to the lower adsorption enthalpy of n-pentane on Mordenite. It could thus also be shown that the claim of the authors that the reaction is single-file diffusion limited in the lower temperature range is not necessarily true.

Larsson published a similar approach to explain the stepwise change of activation energies and the isokinetic or compensation effect. He assumed a mechanism in which 'transient' species are involved in the rate determining step. These transient species are molecules which adsorb weakly on the catalyst. The apparent activation energy now becomes identical to the true activation energy and the rate of reaction is still governed by the gas phase concentration of the reactant.
In Figure 5.9., the apparent activation energies for the different catalysts used in this study are plotted versus the logarithm of the pre-exponential factor of the rate of reaction. Since this plot is a straight line the compensation effect is valid for our series of catalysts (see paragraph 5.6.). The line drawn is represented by: \( \ln(A_{\text{app}}) = 0.37 \cdot E_{\text{act,app}} \text{[kJ/mol]} - 12.8. \) Despite the relatively low activity of the ZSM-22 (4) catalyst, the point representing this catalyst does not lie far from the straight line. This means that the data set of activity, activation energy and orders of reaction still represent the same reaction (isomerization) as was the case for all other catalysts.
5.11. Conclusions

The catalyst pretreatment and reaction conditions were optimized. In this way the isomerization on the acid sites was made rate determining. An optimum platinum to acid site ratio of 0.067 was found. A total flow exceeding 125 ml/min assured the absence of internal and external diffusion limitations.

ZSM-22 showed pore-mouth catalysis due to its 1-dimensional pore system with relatively small pores. This zeolite was therefore relatively unreactive. Both ZSM-5 and ZSM-22 showed shape selectivity while no dimethylbutanes were formed and the monomethylpentanes ratio was not at equilibrium. The latter was at equilibrium on both large-pore zeolites, Mordenite and β. The reaction on β-zeolite may have become diffusion limited at higher temperatures due to its high activity per gram. The Mordenite may have showed some single-file diffusion problems.

Since all four zeolites were equally acidic their activities per acid site could be directly compared. It was shown that a higher adsorption enthalpy led to a lower apparent activation energy and, thus, a higher activity per acid site. On the high-silica zeolites under investigation the activation energy of isomerization with respect to a n-alkoxy intermediate was the same for all structures and amounted to approximately 125 kJ/mol. This value is much higher than in the liquid phase because of the energy needed to break or lengthen the bond between the alkoxy carbon and zeolite lattice oxygen. In acid catalysis by zeolites the carbenium ion is a transition state rather than an intermediate. The adsorption effects could also be illustrated by the existence of a compensation effect between the apparent pre-exponential factor and apparent activation energy of reaction for all catalysts.
Literature cited.

[34] Bates, S.P.; Van Santen, R.A. unpublished results
[71] Larsson, R. Cat. Lett. 1996, 36, 171-173
Chapters 3 and 4 respectively discussed the details regarding the simulation method and the parameters used. Two appendices at the end of this thesis give more details. In this chapter, the results of the simulations will be presented and discussed. A comparison between these results and those obtained experimentally will be made. Paragraph 6.1. contains some general remarks and paragraph 6.2 describes the conditions applied. The next two sections investigate the influence of integration step size and adsorption enthalpy and entropy on the simulations. Finally, the results at atmospheric (6.5) and elevated (6.6) pressure will be presented and discussed.

6.1. General remarks

The simulations were performed using data that described the experimental conditions and catalysts as accurately as possible. In this way a direct comparison between computer generated kinetic data and those obtained experimentally could be made. The simulated surface coverages cannot be determined in steady-state experiments. Such measurements require in situ techniques such as NMR or Positron Emission Profiling (PEP)\(^1\).

6.1.1. Conversion

At low conversions (< 20 %) a linear dependence of the simulated conversions on the axial position in the reactor (z) was observed. In this conversion range the reaction could be assumed to occur under differential conditions, at higher conversions (for example in case of reaction on ZSM-5 at 260 °C) non-linear behavior was observed. In that case the TOF and surface coverages decreased linearly with position z. This decrease in coverages and activity as a function of z was observed for all simulations and can be attributed to an increase in reverse reactions or a decrease in n-hexane partial pressure due to conversion. The total
decrease was a few percent in case of the surface coverages but could amount up to 12% for the TOF.

The adsorption enthalpies of the alkenes had little influence on the simulation as long as the resulting equilibrium constant was large enough to keep them from desorption. No gas phase alkenes were found at the outlet of the reactor in either the simulations or in the experiments. This means that hexane/hexene equilibrium may only exist inside the zeolite pores. The simulations showed that this was the case anywhere in the catalyst bed.

6.1.2. Selectivities
The simulated 2MP/3MP (2-methylpentane/3-methylpentane) ratios were lower than those obtained experimentally. Chapter 5 showed that on a Mordenite catalyst this ratio was at its equilibrium value.

The simulated selectivities for the dimethylbutanes, 2,2-dimethylbutane (2,2-DMB) and 2,3-dimethylbutane (2,3-DMB), are very low, usually almost zero. This might indicate that the resulting mono-branched product coverages are too low for consecutive reactions to occur. These consecutive reactions consist of branching as well as non-branching isomerization.

In Chapter 5 it was shown that on a ZSM-22 catalyst high selectivities for 2-methylpentane were obtained. This was also observed by Martens et al. for 2-methylalkanes in general. This was attributed to adsorption effects in combination with pore mouth catalysis. It is assumed that only the straight part of a paraffin chain can penetrate the zeolite pores. This leads to an adsorption enthalpy of 2-methylpentane that is 4/6th of the one for n-hexane. The 3-methylpentane can only interact with the zeolite pore wall using 3 of its 6 carbon atoms (see Figure 6.2.).

**Figure 6.2.** Adsorption of methylpentanes in 'ZSM-22'
This hypothesis was checked by applying different adsorption and protonation enthalpies for 2- and 3-methylpentane. The pre-exponential factors of desorption and thus the adsorption entropies were also changed. These data can be found in Appendix 2.3. The parameter set of ZSM-5 was used as a basis to build the ‘ZSM-22’ parameter set. When the pre-exponential factors were not changed together with the adsorption enthalpies, desorption of product alkenes was observed. These alkenes formed 45% of the product mixture in the first part of the reactor, decreasing to 9% at the end of the reactor.

The activity of the ‘ZSM-22’ was the same as the ZSM-5 catalyst. It was found experimentally that ZSM-22 is not nearly as active as ZSM-5, which led to the conclusion that the reaction is only taking place at the pore-mouths. This is not confirmed by the simulations using the ‘ZSM-22’ model where the catalyst characteristics were not that of a real ZSM-22 but of a ZSM-5 catalyst. The 2-MP/3-MP ratio on ZSM-5 is 1.08 at 240 °C. On the ‘ZSM-22’ catalyst, this ratio is 1.08 at the end of the reactor when entropy effects were taken into account and 1.3 when they were not changed. When only the adsorption parameters were changed a value of 1.13 was found. In the last two cases also a decrease in the ratio was observed. Without entropy effects this was a much larger effect than when only adsorption parameters were taken into account.

It may be concluded from the results mentioned above that the selectivity ratio is shifted in the right direction when performing these test simulations. However, it is clear that a more thorough study including both adsorption enthalpy and entropy effects is needed to solve the problem of the non-equilibrium ratio in ZSM-22.

6.2. Range of conditions

6.2.1. Atmospheric pressure
Standard conditions at atmospheric pressure were the same as used in the experiments. This means a temperature of 513 K, a hydrogen partial pressure of 966 mbar and a n-hexane partial pressure of 33.8 mbar (H_2/nC_6 = 28). The catalyst loading was 200 mg for 0.5 wt.% Pt/HZSM-5 and 2.0 wt.% Pt/HMordenite, in case of 1.6 wt.% Pt/HB-zeolite only 100 mg was used. The total molar flow (including hydrogen, excluding nitrogen) was 1.12 x 10^4 mol/s.

The apparent activation energy was simulated in the same temperature range as employed experimentally. Two extra points at 553 and 573 K were also calculated to investigate the linearity of the Arrhenius activation energy.

The order of the reaction in hydrogen at a given temperature was calculated by simulating the reaction at different hydrogen partial pressures. The applied partial pressure range was 677 - 966 mbar at a fixed n-hexane partial pressure of 33.8 mbar. The order of the reaction in n-hexane at a given temperature was calculated by simulating the reaction at
different n-hexane partial pressures. The applied partial pressure range is 19.18 - 42.30 mbar at a fixed hydrogen partial pressure of 846 mbar.

6.2.2. Elevated pressure
Since no experiments were performed at elevated pressure, these simulations were compared to literature data reported by Guisnet et al. Standard conditions were: 30 bar total pressure, \( \text{H}_2/n\text{C}_6 \) ratio 9, a temperature of 513 K and a WHSV of 3 h\(^{-1}\). Platinum loadings of 0.5 wt.\% were used. The activation energies were calculated in the same temperature range as was used at atmospheric pressure.

The orders of reaction in hydrogen and n-hexane were simulated at a total pressure of 33 bar and at a temperature of 240 °C. A n-hexane pressure of 3 bar and a hydrogen pressure between 10 and 30 bar was used for the determination of the order in hydrogen. The n-hexane order was simulated by keeping the hydrogen pressure constant at 27 bar whilst varying the n-hexane pressure between 1.3 and 6 bar.

6.3. Influence of integration step size

The influence of integration step size was investigated by calculating orders of reaction using different numbers of steps through the catalyst bed. When the reaction exhibits ideal bifunctional behavior and equation (6.1) applies, the order in hydrogen must have the same value but an opposite sign compared to the hexane order.

\[
\begin{align*}
R &= k_{\text{iso}} \frac{K_{\text{dehyd}} \cdot K_{\text{prot}} \left( \frac{P_{n\text{C}_6}}{P_{\text{H}_2}} \right)}{1 + K_{\text{dehyd}} \cdot K_{\text{prot}} \left( \frac{P_{n\text{C}_6}}{P_{\text{H}_2}} \right)} \\
K_{\text{dehyd}} &= \text{equilibrium constant of dehydrogenation} \\
K_{\text{prot}} &= \text{equilibrium constant of protonation} \\
P_{n\text{C}_6} &= \text{n-hexane partial pressure} \\
P_{\text{H}_2} &= \text{hydrogen partial pressure}
\end{align*}
\]

In Table 6.1., the simulated orders of reaction at atmospheric pressure for ZSM-5 and Mordenite are listed as a function of number of steps. The parameter set used for Mordenite is an old description of this zeolite containing different parameters than used in later simulations. The data by this set can therefore not be compared to the real Mordenite data given elsewhere in this chapter. However, the trends observed will give valuable information about factors influencing the simulations. Since the bed length in all simulations is the same,
the number of steps through the bed can directly be correlated to the step size. The validity of the CSTR approximation increases as the step size decreases.

**Table 6.1.** Orders of reaction on Pt/HMordenite and Pt/HZSM-5 as a function of number of steps used in the simulation

<table>
<thead>
<tr>
<th>Number of steps</th>
<th>Step size [10^{-7} m]</th>
<th>Mordenite</th>
<th>ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^4</td>
<td></td>
<td>nC$_6$ order</td>
<td>H$_2$ order</td>
</tr>
<tr>
<td>1</td>
<td>19</td>
<td>-0.16</td>
<td>0.223</td>
</tr>
<tr>
<td>10</td>
<td>1.9</td>
<td>0.135</td>
<td>-0.11</td>
</tr>
<tr>
<td>&gt;10</td>
<td>&lt;1.9</td>
<td>0.132</td>
<td></td>
</tr>
</tbody>
</table>

An order closer to zero can be observed when smaller steps are used. This effect is probably due to an enhanced validity of the assumption that the change in concentration from one step to the other must be small (equations (3.9) and (3.12) in paragraph 3.2.). Since there are relatively slight changes in TOF as a function of hydrogen or n-hexane partial pressure, the validity of the assumption may play a role in the accuracy of the simulated conversions. The order in hydrogen seems to be the most sensitive for the number of steps. This sensitivity of the hydrogen order towards conversion might also be the reason for the large scattering in the experimental data. The hydrogen order might be too close to zero to be determined accurately.

Another explanation for the zero order in hydrogen on the Mordenite catalyst found experimentally is that transport problems are playing an important role (see paragraph 5.8.). This hypothesis was checked by using the same parameter set but lowering the pre-exponential factors of all transport steps to and from platinum by a factor of $10^5$. The resulting order in hydrogen was indeed approximately zero, while the TOF at standard conditions stayed almost constant. Nevertheless, to avoid any influence of step size, in all future simulations a minimum of 100000 steps was used.

6.4. Influence of adsorption enthalpy and entropy

In order to investigate the sensitivity of simulations for the adsorption enthalpy a series of calculations was performed at atmospheric pressure. The same MFI parameter set was used each time. Only the activation energy of desorption was changed since the difference between the activation energy of adsorption and desorption gives the adsorption enthalpy. The main results are given in Table 6.2.
Table 6.2. MFI data as a function of adsorption enthalpy

<table>
<thead>
<tr>
<th>ΔH_{ads} [kJ/mol]</th>
<th>θ_{n-hexane} (at 240 °C)</th>
<th>θ_{n-alkoxy} (at 240 °C)</th>
<th>E_{act,app} [kJ/mol] (at 240 °C)</th>
<th>TOF [h⁻¹] (at 240 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>68</td>
<td>0.088</td>
<td>0.36</td>
<td>60.2 ± 8.5</td>
<td>9.9</td>
</tr>
<tr>
<td>78</td>
<td>0.50</td>
<td>0.78</td>
<td>106.0 ± 5.2</td>
<td>20.7</td>
</tr>
<tr>
<td>82</td>
<td>0.72</td>
<td>0.90</td>
<td>111.3 ± 4.0</td>
<td>23.6</td>
</tr>
<tr>
<td>88</td>
<td>0.91</td>
<td>0.98</td>
<td>127.2 ± 2.6</td>
<td>25.7</td>
</tr>
<tr>
<td>110°</td>
<td>0.97</td>
<td>0.98</td>
<td>129.0 ± 1.6</td>
<td>25.8</td>
</tr>
</tbody>
</table>

* ΔH_{ads} of the products were changed accordingly

When the n-alkoxy surface coverage is almost one (ΔH_{ads} ≥ 85 kJ/mol), and therefore the order in n-hexane zero, the activation energy becomes very close to the activation energy of isomerization on a zeolite obtained experimentally (127 kJ/mol). This was also predicted by equation (5.15). Figure 6.3 gives the plot for calculating a normalized activation energy making use of normalized TOFs. These TOFs were calculated by only taking into account the sites covered by a reactive intermediate; the n-alkoxy sites.

In Figure 6.4, the n-alkoxy and hexane coverage as well as the TOF are plotted versus the adsorption enthalpy used. A higher adsorption enthalpy leads to a higher TOF, higher coverages and higher activation energy. However, the normalized TOFs are approximately the same (27 h⁻¹) for all adsorption enthalpies in Table 6.2. The n-alkoxy coverage and TOF reach a maximum at an adsorption enthalpy of approximately 85 kJ/mol. The n-hexane coverage keeps increasing slowly towards full coverage.
This is in contradiction with the effect we will see in paragraph 6.5, comparing ZSM-5, zeolite β and Mordenite. In that case the n-alkoxy coverages are very similar and the activation energy decreases with increasing adsorption enthalpy. Also the normalized TOFs are not equal. It may therefore be concluded that the enthalpy of adsorption plays an important role in determining surface coverages of zeolites but that another factor is also relevant. Since the adsorption entropy is a likely candidate, calculations were performed to investigate its influence. These simulations were performed using in all simulations the same Mordenite-like parameter set except for the pre-exponential factor of n-hexane desorption.

When the pre-exponential factor of n-hexane desorption is too low, the coverage becomes almost 1 and an activation energy of 126 kJ/mol is calculated (see Table 6.3.). This is very close to the activation energy of n-alkoxy isomerization on a zeolite obtained experimentally. The TOF is practically unaffected by the pre-exponential factor when the alkoxy coverage has become practically one.

Again it is shown that the activation energy based on the normalized TOFs is the same for all parameter sets. In contrast with the case of the MFI adsorption enthalpies, the normalized TOF now changes as a function of parameter set. This means that the adsorption entropy can play a decisive role in the simulated activity. The same effect of adsorption entropy was also noticed in calculations on the β-zeolite.

Table 6.3. Activities, activation energy and coverages as a function of pre-exponential factor of desorption of n-hexane for a 0.5 wt.% Pt/HMOR catalyst*

<table>
<thead>
<tr>
<th>Pre-exponential factor [mol/m² catalyst·s]</th>
<th>TOF [h⁻¹] at 240 °C</th>
<th>normalized TOF [h⁻¹] at 240 °C</th>
<th>θ_{n-hexane} at 240 °C</th>
<th>θ_{n-alkoxy} at 240 °C</th>
<th>E_{act,app} kJ/mol</th>
<th>E_{act,norm} kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.91·10⁶</td>
<td>4.98</td>
<td>5.0</td>
<td>0.70</td>
<td>0.99</td>
<td>126</td>
<td>128</td>
</tr>
<tr>
<td>4.91·10⁸</td>
<td>4.62</td>
<td>5.1</td>
<td>0.32</td>
<td>0.91</td>
<td>117</td>
<td>130</td>
</tr>
<tr>
<td>1.0·10⁹</td>
<td>6</td>
<td>7</td>
<td>0.18</td>
<td>0.85</td>
<td>105</td>
<td>128</td>
</tr>
</tbody>
</table>

* Old Mordenite parameter set
6.5. Atmospheric pressure results

6.5.1. Standard conditions

Table 6.4. contains the simulation data for Mordenite, ZSM-5 and zeolite β at standard conditions. Values at the reactor outlet are given. The activities measured on the pure ex situ pretreated catalysts are given in parentheses. The simulated activities were approximately one-half of the values obtained experimentally. In Chapter 4 it was stated that the pre-exponential factor of the isomerization steps was adjusted to obtain a reasonable conversion at standard conditions. The values for these pre-exponential factors may have been a factor of two too low. The ZSM-5 catalyst was the most active by a factor of 5 relative to Mordenite catalyst and a factor of 1½ relative to zeolite β. This was true both experimentally and in the simulations. The activity of β-zeolite was simulated relatively accurately without using the bimolecular mechanism. The activities calculated by only taking into account those acid sites that are covered by n-alkoxy species, showed the same trend, even when all Mordenite sites (in stead of only one-third) were assumed to take part in the reaction. This resulted in a TOF of 13.6 h⁻¹ which made the Mordenite nearly as active as the β-zeolite. Since the adsorption enthalpies of both zeolites are similar, this confirms an adsorption effect.

Table 6.4. Simulation data at standard conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>2.0 wt.% Pt/HMOR</th>
<th>0.5 wt.% Pt/HZSM-5</th>
<th>1.6 wt.% Pt/Hβ</th>
</tr>
</thead>
<tbody>
<tr>
<td>θₙ-hexane</td>
<td>0.62</td>
<td>0.72</td>
<td>0.69</td>
</tr>
<tr>
<td>θₙ-alkoxy</td>
<td>0.91</td>
<td>0.90</td>
<td>0.92</td>
</tr>
<tr>
<td>TOF [h⁻¹]</td>
<td>4.54 (9.7)</td>
<td>23.83 (54.0)</td>
<td>16.26 (27.8)</td>
</tr>
<tr>
<td>Normalized TOF [h⁻¹]</td>
<td>5.0 (15.0)</td>
<td>26.0</td>
<td>17.7</td>
</tr>
<tr>
<td>θₙ-hexane,Pt</td>
<td>0.055</td>
<td>0.084</td>
<td>0.075</td>
</tr>
<tr>
<td>θₙ-hexane,Pt</td>
<td>2.9·10⁻⁶</td>
<td>3.5·10⁻⁶</td>
<td>3.8·10⁻⁶</td>
</tr>
<tr>
<td>θₙ-Pt</td>
<td>0.82</td>
<td>0.79</td>
<td>0.80</td>
</tr>
<tr>
<td>θ_empty,Pt</td>
<td>0.13</td>
<td>0.12</td>
<td>0.12</td>
</tr>
</tbody>
</table>

A higher adsorption enthalpy for n-hexane led to an increased n-hexane coverage of the catalyst but not necessarily to an increased n-alkoxy coverage. This means that, although the adsorption was strongest on ZSM-5, the proton coverage was hardly affected. The hypothesis in paragraph 5.6, proposing that the higher activity of ZSM-5 compared to
Mordenite was due to an enhanced coverage of reactive species, is therefore not true under these conditions. The second hypothesis, proposing that the higher activity was due to a lower apparent activation energy was already confirmed by the experiments.

Despite the similar adsorption enthalpy, Mordenite and β-zeolite coverages were not equal. The n-hexane coverage of β is relatively high, leading to other coverages also being higher than expected. A higher coverage of a zeolite with adsorbed n-hexane also led to a higher n-hexane coverage of platinum. The dependence of the n-hexane coverage of the platinum (θ<sub>n-hexane,Pt</sub>) on the type of zeolite was the same as the n-hexane coverage of the adsorption sites. An increase was observed from MOR through β to ZSM-5. Since the amount of empty platinum sites are very similar, the dissociated hydrogen coverage decreased in the same order.

6.5.2. Influence of hexane and hydrogen partial pressures

The orders of reaction in n-hexane and hydrogen were only simulated for ZSM-5 and Mordenite. The approximate equation (5.14), discussed in Chapter 5, is now also used. It predicts that the sum of reactant coverage and order is one. It is exact at coverages close to one or zero.

\[
(6.2) \quad n = (1 - \theta_{\text{reactant}}) \text{ or } \theta_{\text{reactant}} = (1 - n) \text{ or } (\theta_{\text{reactant}} + n) = 1
\]

\[n = \text{order in the reactant}\]

\[\theta_{\text{reactant}} = \text{surface coverage of reactive intermediate}\]

The order in n-hexane was estimated from the conversions at two hexane partial pressures. In Figure 6.5., this estimated n-hexane order (n) and the simulated n-alkoxy coverages at 240 °C are plotted versus the n-hexane partial pressure. The order in n-hexane decreased as a function of partial pressure. Since the coverage of active (n-alkoxy) species approached unity, the rate could not be increased more by a higher coverage. The order in hexane therefore decreased to zero. The sums in Figure 6.5. are all larger than one. It was therefore concluded that equation (6.2) is moderately valid in our case. The validity is slightly higher for Mordenite than for ZSM-5, especially in the high hexane partial pressure regime.

In Table 6.5., the n-alkoxy, adsorbed n-hexane and n-hexenes coverages of platinum are listed as a function of hydrogen partial pressure. The platinum coverage of dissociated
hydrogen increased slightly as a function of hydrogen pressure, mainly covering empty sites. Although the amount of adsorbed n-hexanes stayed almost constant, the amount of n-hexenes decreased. This was due to a shift in the equilibrium. The higher the hydrogen partial pressure, the more the equilibrium was shifted towards n-hexane. The decrease in n-hexenes resulted in a decrease in n-alkoxy coverage and therefore also in a decrease in activity. This resulted in a negative order in hydrogen for both zeolites.

Table 6.5. Coverages as a function of hydrogen partial pressure at 240 °C and a n-hexane pressure of 33.8 mbar

<table>
<thead>
<tr>
<th>PH₂ [mbar]</th>
<th>Mordenite</th>
<th>ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>θₙ-alkoxy</td>
<td>θₙ-hexane</td>
</tr>
<tr>
<td>682</td>
<td>0.95</td>
<td>0.53</td>
</tr>
<tr>
<td>867</td>
<td>0.93</td>
<td>0.59</td>
</tr>
<tr>
<td>966</td>
<td>0.91</td>
<td>0.62</td>
</tr>
</tbody>
</table>

In Table 6.6., the values of the orders of reaction simulated at atmospheric pressure are summarized. Both experimentally and in the simulations a higher n-hexane order is obtained on a ZSM-5 catalyst than on a Mordenite catalyst. According to equation (6.2) this would mean a lower reactive intermediate coverage of ZSM-5. However, it was already shown that these coverages are approximately equal. This supports the conclusion that this equation is less valid for ZSM-5 than for Mordenite. The discrepancy between the absolute values for the hexane and hydrogen order already could be explained by equation (5.10) where it was assumed that hexane/hexene equilibrium existed only inside the zeolite pores. Another possibility is that the isomerization and the hydrogenation of products are co-rate determining steps.

Table 6.6. Summary of orders of reaction

<table>
<thead>
<tr>
<th>Hydrogen order</th>
<th>Hexane order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation</td>
<td>Experiment</td>
</tr>
<tr>
<td>Mordenite</td>
<td>-0.12</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>-0.13</td>
</tr>
</tbody>
</table>
6.5.3. Temperature effects

The relative rates of the different elementary steps between 220 °C and 260 °C on both a ZSM-5 and a Mordenite catalyst were investigated. The rates of the isomerization on the acid sites and the hydrogenation of the methylpentenes were both slow and of the same order of magnitude. Apparently here a situation was obtained where two groups of steps are co-rate determining. This was especially possible since two types of sites were involved. It was also found that the hydrogenation of isomers became more rate determining at higher temperatures. This is not surprising since the activation energy for isomerization (± 135 kJ/mol) is much higher than that for hydrogenation (± 40 kJ/mol).

Table 6.7. Simulated surface coverages and TOF as a function of temperature and zeolite

<table>
<thead>
<tr>
<th>T [K]</th>
<th>2.0 wt.% Pt/HMordenite</th>
<th>0.5 wt.% Pt/HZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_{n\text{-hexane}}$</td>
<td>$\theta_{n\text{-alkoxy}}$</td>
</tr>
<tr>
<td>493</td>
<td>0.77</td>
<td>0.98</td>
</tr>
<tr>
<td>513</td>
<td>0.62</td>
<td>0.91</td>
</tr>
<tr>
<td>533</td>
<td>0.44</td>
<td>0.73</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T [K]</th>
<th>1.6 wt. % Pt/Hβ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_{n\text{-hexane}}$</td>
</tr>
<tr>
<td>493</td>
<td>0.82</td>
</tr>
<tr>
<td>513</td>
<td>0.69</td>
</tr>
<tr>
<td>533</td>
<td>0.51</td>
</tr>
</tbody>
</table>

In Table 6.7, the simulated activities of Mordenite, ZSM-5 and zeolite β are given as a function of temperature. The experimental values are shown in parentheses. The surface coverages of n-alkoxy species and n-hexane are also included in the table. The simulations showed that higher temperatures led to higher TOFs, but lower surface coverages. Especially the decrease in n-alkoxy coverage is important since these are the reactive intermediates. This means that the increase in rate constant, due to
the increase in temperature, more than compensated the decrease in the surface coverage of
the active species. Figure 6.6. shows that for ZSM-5 and Mordenite the temperature
dependence was slightly overestimated while in case of β the temperature dependence was
rather good.

Table 6.8. contains the platinum surface coverages of a Mordenite, a ZSM-5 and a β
catalyst. A decrease with temperature of the n-hexane coverage of platinum also led to a
decrease in n-hexene coverage.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>2.0 wt.% Pt/HMordenite</th>
<th>0.5 wt.% Pt/HZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-atom</td>
<td>n-hexane</td>
</tr>
<tr>
<td>493</td>
<td>0.86</td>
<td>0.066</td>
</tr>
<tr>
<td>513</td>
<td>0.82</td>
<td>0.055</td>
</tr>
<tr>
<td>533</td>
<td>0.75</td>
<td>0.043</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T [K]</th>
<th>1.6 wt.% Pt/Hβ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-atom</td>
</tr>
<tr>
<td>493</td>
<td>0.84</td>
</tr>
<tr>
<td>513</td>
<td>0.80</td>
</tr>
<tr>
<td>533</td>
<td>0.74</td>
</tr>
</tbody>
</table>

In Table 6.9., the simulated activation energies as a function of zeolite (and therefore
adsorption enthalpy) are summarized. The values on the ZSM-5 and Mordenite catalysts were
approximately 10 percent higher than those obtained experimentally. Both simulations and
experiments, however, showed that a higher adsorption enthalpy leads to a higher activity due
to a lower apparent activation energy. The simulations on the β-zeolite rendered relatively too
low activation energies, the entropy of adsorption has probably been too high in the
calculations.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Adsorption enthalpy [kJ/mol]</th>
<th>Activation energy [kJ/mol]</th>
<th>experimental</th>
<th>simulated</th>
<th>normalized</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>apparent true</td>
<td></td>
<td>apparent true</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MFI</td>
<td>82</td>
<td>103</td>
<td>127.1</td>
<td>111.0</td>
<td>120.4</td>
</tr>
<tr>
<td>MOR</td>
<td>71.9</td>
<td>107</td>
<td>119.9</td>
<td>114.0</td>
<td>121.0</td>
</tr>
<tr>
<td>BEA</td>
<td>70</td>
<td>113</td>
<td>131</td>
<td>111.4</td>
<td>116*</td>
</tr>
</tbody>
</table>

MOR: 2.0 wt.% Pt/HMOR (Si/Al = 10)
MFI: 0.5 wt.% Pt/HZSM-5 (Si/Al = 28)
BEA: 1.6 wt.% Pt/Hβ (Si/Al = 12.5)

* n-hexane order estimated by using equation (6.2)
At elevated temperatures the competition between a lower surface coverage, leading to lower activities, and higher rate constants eventually caused a decrease of the slope in the Arrhenius plot. This led to lower apparent activation energies at higher temperatures and a curved Arrhenius plot. This effect was the most profound when the coverage is relatively low. The latter effect was represented by the large error in the 95% confidence interval. The Arrhenius plot using normalized TOFs stayed linear (see Figure 6.9.). The normalized activation energy was not a function of temperature or zeolite. The values obtained for Mordenite and ZSM-5 were approximately equal. Contrary to what is expected, the normalized and true activation energies had not the same value. In case of β-zeolite the same trend is observed. This indicates that equation (5.15) is not valid since the isomerization is not the only rate determining step.

6.5.4. Platinum loading
The activity of a 0.5 wt.% Pt/HMOR was also simulated as a function of temperature to allow a check of the influence of the metal loading found experimentally. The results are shown in Table 6.10. Only those parameters that were different as a function of loading are listed. The simulated activation energy was 109 kJ/mol. A slight change in activity was found. At 240 °C an increase of a factor of 1.1 was observed while the amount of platinum was increased by a factor of 4. In the experiments the activity was increased by a factor of 3. The simulated increase is due to a equally large increase in n-alkoxy coverage caused by an increase in n-hexene coverage of the platinum. The latter effect was probably due to n-hexene being adsorbed on two platinum sites thus doubling the influence of platinum loading. The observed increase at 240 °C (our standard temperature) was the root of the increase in loading.

Table 6.10. Influence of platinum loading

<table>
<thead>
<tr>
<th>T [K]</th>
<th>0.5 wt.% Pt/HMOR</th>
<th>2.0 wt.% Pt/HMOR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-hexene,Pt</td>
<td>n-alkoxy</td>
</tr>
<tr>
<td>493</td>
<td>1.1·10⁻⁶</td>
<td>0.93</td>
</tr>
<tr>
<td>513</td>
<td>1.5·10⁻⁶</td>
<td>0.82</td>
</tr>
<tr>
<td>533</td>
<td>2.0·10⁻⁶</td>
<td>0.64</td>
</tr>
</tbody>
</table>

The large increase as a function of platinum loading found experimentally and the small change found in the simulations indicated that in the experiments another factor was present. In case of the experiments it was proposed that the 0.5 wt.% sample could not use all available sites due to diffusion problems. The simulations do not take this effect into account. It would decrease the coverage of the adsorbed n-hexane. The decrease in adsorbed n-hexane also decreases the amount of hexenes produced and therefore the n-alkoxy coverage and the
activity. In fact, the increase in activity is very close to the one found experimentally for the β catalysts. This zeolite is not as strongly influenced by diffusion limitations at 240 °C.

Another feature that could be observed is that the n-hexene coverage of the platinum increased with temperature on a 0.5 wt.% sample and decreased on the higher loaded sample. At low loadings the desorption due to higher temperature was more than compensated by an increase in platinum activity. Thus the temperature dependence of the n-alkoxy coverage was suppressed. This led to a lower apparent activation energy. Since the surface activation energy of isomerization does not change, the order in n-hexane must increase. This is evidenced by a decrease in n-alkoxy coverage. These same trends, lower activation energy and higher order of reaction in n-hexane, were also observed experimentally.

6.6. Elevated pressure results

6.6.1. Temperature effects

The results of high pressure simulations for a 0.5 wt.% Pt/HZSM-5 catalyst are given in Table 6.11., for a 0.5 wt.% Pt/HMordenite catalyst this is done in Table 6.12. The data in parentheses are percentages of the value obtained at atmospheric pressure. The n-hexane coverages of adsorption sites (θ_{n-hexane}) and platinum (θ_{n-C6,Pt}) were higher under high pressure. This was not surprising since the n-hexane pressure was about 3000 mbar instead of 34 mbar and the hydrogen to n-hexane ratio had decreased by a factor of 3. However, the n-alkoxy coverage and therefore the activity were lower under 30 bar. Guisnet et al. also reported lower activities at high pressure (a factor of 5, using a Mordenite catalyst with a Si/Al ratio of 8)\textsuperscript{3}. Froment found the same phenomenon on a Pt/H-USY catalyst using n-decane as a reactant\textsuperscript{6}. The lower n-alkoxy coverage is due to a competition between n-hexane and n-hexenes for the available acid sites.

Table 6.11. Comparison of activity and coverages at high and low pressure of a ZSM-5 catalyst

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Pressure: 1 bar</th>
<th>Pressure: 30 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>θ_{n-hexane}</td>
<td>θ_{n-alkoxy}</td>
</tr>
<tr>
<td>493</td>
<td>0.86</td>
<td>0.98</td>
</tr>
<tr>
<td>513</td>
<td>0.72</td>
<td>0.90</td>
</tr>
<tr>
<td>533</td>
<td>0.53</td>
<td>0.72</td>
</tr>
</tbody>
</table>

For a ZSM-5 catalyst both the n-alkoxy coverage and the TOF were under high pressure approximately 80% of those under atmospheric pressure. The rate constant had, therefore, not changed. This means that the same reactions were rate determining in both cases. At higher temperatures, the activity was decreased slightly more than to 80% of the
value at atmospheric pressure. At the same time the n-hexane coverage of the adsorption sites was relatively more increased. The rate of desorption was thus increasingly decreased relative to the rate of isomerization. The simulated apparent activation energy at high pressure \((107 \pm 2.9)\) was slightly lower than at atmospheric pressure \((111 \pm 4.0)\).

### Table 6.12. Comparison of activity and coverages at high and low pressure of a 0.5 wt.% Pt/Mordenite catalyst

<table>
<thead>
<tr>
<th>T [K]</th>
<th>(\theta_{\text{n-hexane}})</th>
<th>(\theta_{\text{n-alkoxy}})</th>
<th>(\theta_{\text{n-C6,pt}})</th>
<th>TOF ([\text{h}^{-1}])</th>
<th>(\theta_{\text{n-hexane}})</th>
<th>(\theta_{\text{n-alkoxy}})</th>
<th>(\theta_{\text{n-C6,pt}})</th>
<th>TOF ([\text{h}^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>493</td>
<td>0.77</td>
<td>0.93</td>
<td>0.066</td>
<td>1.35</td>
<td>0.997</td>
<td>0.78 (84%)</td>
<td>0.56</td>
<td>1.12 (83%)</td>
</tr>
<tr>
<td>513</td>
<td>0.62</td>
<td>0.82</td>
<td>0.055</td>
<td>4.11</td>
<td>0.992</td>
<td>0.67 (82%)</td>
<td>0.52</td>
<td>3.29 (80%)</td>
</tr>
<tr>
<td>533</td>
<td>0.44</td>
<td>0.64</td>
<td>0.043</td>
<td>9.86</td>
<td>0.985</td>
<td>0.54 (84%)</td>
<td>0.47</td>
<td>8.16 (83%)</td>
</tr>
</tbody>
</table>

Table 6.12. shows similar trends for the Mordenite catalyst as observed for ZSM-5. The simulated activation energy at high pressure \((109 \pm 1.9 \text{ kJ/mol})\) was also slightly lower than at atmospheric pressure \((114 \pm 3.2 \text{ kJ/mol} \text{ for the 2.0 wt.% loaded catalyst})\). Guisnet et al. also found lower activation energies at high pressure\(^3\). They measured a much stronger influence of pressure on a Mordenite with a Si/Al ratio of 8. Under high pressure an activation energy of 29 kcal/mol \((121 \text{ kJ/mol})\) was found, under atmospheric pressure a value of 32-36 kcal/mol \((134-151)\). They attributed this large difference to acid cracking as a side reaction under atmospheric pressure, which has a much higher activation energy than hydro-isomerization and hydro-cracking. Despite the fact that the simulations showed a lowered apparent activation energy at high pressure on the Mordenite, its value stayed lower than on the ZSM-5. The activity of the latter stays therefore also higher at 30 bar. The Arrhenius plots representing all simulated apparent activation energies are given in Figure 6.7.

![Figure 6.7. Arrhenius plots of ZSM-5 and Mordenite at low and elevated pressure](image-url)
In Figure 6.8., the n-alkoxy coverages are given for both zeolites as a function of temperature at both pressures. The higher catalyst stability that is observed under high pressure\textsuperscript{7} might be due to the lower n-alkoxy coverage calculated. A lower concentration of reactive species will also affect the probability of side reactions such as polymerization. The formation of coke will therefore be suppressed at high pressure and low n-alkoxy coverage.

In Figure 6.9., the full simulated Arrhenius plots are given. The two points at higher temperatures (280 °C and 300 °C) clearly deviate from the straight line obtained between 220 and 240 °C. The total plot is curved. Since only acid sites occupied by a n-alkoxy species are responsible for reaction these must be used for the normalized activation energy. In that case straight lines are obtained.

The value for 0.5 wt.% Pt/HMOR at high pressure was lower than all other normalized activation energies (see Table 6.13.). The normalized TOFs are also listed in Table 6.13. On one type of zeolite these TOFs did not change much as a function of pressure. This means that in these cases the rate determining step had been not changed. The decrease in normalized TOF at elevated pressure and temperatures above 533 K on Mordenite was, however, significant since the normalized activation energy ($E_{act,\text{norm}}$) was lowered. The plot was also not

\[ \ln(\text{TOF}) = E_{act} \left( \frac{1}{1000} \right) ] \]

Figure 6.8. N-alkoxy coverages as a function of temperature

Figure 6.9. Expanded Arrhenius plots, the influence of n-alkoxy coverage
Simulated kinetics

completely straight anymore, the high temperature points deviated from the extrapolation of the low temperature line. The value for the low temperature range was the same as the other values (128.9 kJ/mol). The value of the normalized activation energy determined from the full temperature range suggested that deprotonation had become the rate determining step\(^8\). Indeed a shift was observed in the slowest step, but towards hydrogenation of the product alkene.

Table 6.13. Normalized TOFs [h\(^{-1}\)] as a function of pressure and temperature

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Mordenite</th>
<th>ZSM-5</th>
<th>ß-zeolite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5 wt.% Pt</td>
<td>2.0 wt.% Pt</td>
<td>1 bar</td>
</tr>
<tr>
<td>493</td>
<td>1.5</td>
<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>513</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>533</td>
<td>15.3</td>
<td>15.4</td>
<td>15.0</td>
</tr>
<tr>
<td>553</td>
<td>44.4</td>
<td></td>
<td>40.1</td>
</tr>
<tr>
<td>573</td>
<td></td>
<td>117.7</td>
<td>78.4</td>
</tr>
</tbody>
</table>

\(E_{act,\text{norm}}[\text{kJ/mol}]\): 129.1 129.2 119.4 128.0 126.4 125.4

In Table 6.14., atomic hydrogen coverages of the platinum sites are listed. In Figure 6.10., some other platinum coverages are plotted as a function of temperature. The dashed lines represent ZSM-5 data while the drawn lines represent Mordenite. As could be expected, the number of empty sites decreased under high pressure. The n-hexane that was desorbed from the platinum as a function of temperature at higher pressure was mostly replaced by hydrogen. The atomic hydrogen coverages in Table 6.14., therefore, increased with temperature. At atmospheric pressure, both the n-hexane and hydrogen coverage of platinum decreased as a function of temperature.

Table 6.14. Comparison of atomic hydrogen coverages of platinum at high and low pressure

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Pressure: 1 bar</th>
<th>Pressure: 30 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZSM-5 MOR</td>
<td>ZSM-5 MOR</td>
</tr>
<tr>
<td>493</td>
<td>0.82 0.86</td>
<td>0.31 0.43</td>
</tr>
<tr>
<td>513</td>
<td>0.79 0.82</td>
<td>0.36 0.47</td>
</tr>
<tr>
<td>533</td>
<td>0.74 0.75</td>
<td>0.42 0.51</td>
</tr>
</tbody>
</table>
6.6.2. Orders of the reaction in n-hexane and hydrogen

In Table 6.15., the platinum coverages as a function of hydrogen pressure, at 240 °C and a n-hexane pressure of 3 bar, are given for both ZSM-5 and Mordenite. Obviously, the amount of dissociated hydrogen will increase with increasing hydrogen pressure. The space on the platinum needed was only partially obtained by replacing the n-hexane. Above a hydrogen pressure of 20 bar both the n-hexane and the dissociated hydrogen coverages were almost constant. The n-hexene coverage decreased continuously with the hydrogen pressure. Apparently, the dehydrogenation equilibrium was shifted towards n-hexane, which could be expected at high pressure and high hydrogen to n-hexane ratio. The rate of reaction was thus suppressed by adding hydrogen. Negative orders are obtained, which are listed in Table 6.19.

Table 6.15. Platinum coverages as a function of hydrogen pressure at 240 °C and a n-hexane pressure of 3 bar

<table>
<thead>
<tr>
<th>PH2 [bar]</th>
<th>0.5 wt.% Pt/Mordenite</th>
<th>0.5 wt.% Pt/HZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>empty</td>
<td>n-hexane</td>
</tr>
<tr>
<td>1*</td>
<td>0.127</td>
<td>0.055</td>
</tr>
<tr>
<td>10</td>
<td>0.035</td>
<td>0.510</td>
</tr>
<tr>
<td>20</td>
<td>0.020</td>
<td>0.503</td>
</tr>
<tr>
<td>30</td>
<td>0.013</td>
<td>0.506</td>
</tr>
</tbody>
</table>

*p_{HC} = 0.034 bar

The order of the reaction in hydrogen on both Mordenite and ZSM-5 became increasingly negative at higher hydrogen pressures (from -0.2 at 10-15 bar to -0.6 at 25-30 bar). The inhibiting effect of the hydrogen on the hydrogenation equilibrium became more pronounced at higher hydrogen pressures. The calculated order of reaction seemed to be a logarithmic function of the n-alkoxy coverage. In Table 6.16., the simulated n-alkoxy and
adsorbed n-hexane coverages as well as the activities are given. The decrease in TOF as a function of hydrogen pressure could completely be explained by the decrease in the n-alkoxy coverage for both catalysts. The lowering of this coverage was due to the lower supply of n-hexenes as evidenced by Table 6.15.

**Table 6.16.** Activities and surface coverages as a function of hydrogen pressure at 240 °C and a n-hexane pressure of 3 bar.

<table>
<thead>
<tr>
<th>Pm [bar]</th>
<th>θ_{n-hexane}</th>
<th>θ_{n-alkoxy}</th>
<th>TOF [h⁻¹]</th>
<th>θ_{n-hexane}</th>
<th>θ_{n-alkoxy}</th>
<th>TOF [h⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.62</td>
<td>0.82</td>
<td>4.11</td>
<td></td>
<td>0.72</td>
<td>0.90</td>
<td>23.83</td>
</tr>
<tr>
<td>0.981</td>
<td>0.93</td>
<td>4.61</td>
<td></td>
<td>0.988</td>
<td>0.94</td>
<td>24.33</td>
</tr>
<tr>
<td>0.990</td>
<td>0.80</td>
<td>3.92</td>
<td></td>
<td>0.993</td>
<td>0.80</td>
<td>20.70</td>
</tr>
<tr>
<td>0.993</td>
<td>0.65</td>
<td>3.16</td>
<td></td>
<td>0.995</td>
<td>0.65</td>
<td>16.83</td>
</tr>
</tbody>
</table>

*p_{AC6} = 0.034 bar

In Table 6.17., the simulated platinum coverages are given as a function of n-hexane pressure. On the Mordenite catalyst the n-hexane coverage increased with increasing n-hexane pressure. The n-hexene coverage went through a maximum at approximately 2.5 bar. The initial increase due to a shift in the equilibrium is reversed due to competitive adsorption. This last effect is probably also the reason for the relatively high n-hexene coverage at atmospheric total pressure and therefore lowest n-hexane pressure.

**Table 6.17.** Platinum coverages as a function of n-hexane pressure at 240 °C and a hydrogen pressure of 27 bar

<table>
<thead>
<tr>
<th>P_{nC6} [bar]</th>
<th>empty n-hexane</th>
<th>empty n-hexene</th>
<th>n-hexene</th>
<th>n-hexene</th>
<th>H-atom</th>
<th>n-hexene</th>
<th>n-hexene</th>
<th>H-atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.034</td>
<td>0.127</td>
<td>0.055</td>
<td>1.5·10⁻⁶</td>
<td>0.82</td>
<td>0.12</td>
<td>0.084</td>
<td>3.5·10⁻⁶</td>
<td>0.79</td>
</tr>
<tr>
<td>1.3</td>
<td>0.022</td>
<td>0.30</td>
<td>3.2·10⁻⁷</td>
<td>0.68</td>
<td>0.019</td>
<td>0.39</td>
<td>4.0·10⁻⁷</td>
<td>0.59</td>
</tr>
<tr>
<td>3.7</td>
<td>0.013</td>
<td>0.56</td>
<td>3.8·10⁻⁷</td>
<td>0.43</td>
<td>0.0098</td>
<td>0.67</td>
<td>3.5·10⁻⁷</td>
<td>0.32</td>
</tr>
<tr>
<td>6.0</td>
<td>0.0090</td>
<td>0.69</td>
<td>3.0·10⁻⁷</td>
<td>0.31</td>
<td>0.0069</td>
<td>0.77</td>
<td>2.5·10⁻⁷</td>
<td>0.22</td>
</tr>
</tbody>
</table>

*p_{H2} = 1 bar

The n-hexane coverage on the adsorption sites increased with increasing n-hexane pressure (see Table 6.18.). Since the coverage was already very high at pressures above 1 bar, the increase was not as pronounced as the matching platinum coverage. The decrease in n-alkoxy coverage as a function of n-hexene platinum coverage at n-hexane partial pressures above 2.5 bar on a Mordenite catalyst was less pronounced, the initial increase was suppressed by the competition with n-hexane for available acid sites. This led to a curved plot of ln(TOF) versus ln(p_{nC6}), the order plot. The order in n-hexane decreased at increasing n-hexane pressure and was a logarithmic function of the n-alkoxy coverage. On a ZSM-5
catalyst there was even a slight decrease in n-alkoxy coverage although the TOF kept increasing. The iso-alkoxy coverage did increase with n-hexane pressure. The deprotonation of products from the acid sites had become the rate determining step.

Table 6.18. Activities and surface coverages as a function of n-hexane pressure at 240 °C and a hydrogen pressure of 27 bar.

<table>
<thead>
<tr>
<th>PnC6 [bar]</th>
<th>θ_n-hexane</th>
<th>θ_n-alkoxy</th>
<th>TOF [h⁻¹]</th>
<th>θ_n-hexane</th>
<th>θ_n-alkoxy</th>
<th>TOF [h⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.034</td>
<td>0.62</td>
<td>0.82</td>
<td>4.11</td>
<td>0.72</td>
<td>0.90</td>
<td>23.83</td>
</tr>
<tr>
<td>1.3</td>
<td>0.981</td>
<td>0.68</td>
<td>3.01</td>
<td>0.987</td>
<td>0.70</td>
<td>16.00</td>
</tr>
<tr>
<td>3.7</td>
<td>0.994</td>
<td>0.69</td>
<td>3.40</td>
<td>0.996</td>
<td>0.69</td>
<td>18.11</td>
</tr>
<tr>
<td>6.0</td>
<td>0.996</td>
<td>0.68</td>
<td>3.40</td>
<td>0.998</td>
<td>0.69</td>
<td>18.16</td>
</tr>
</tbody>
</table>

Table 6.19. summarizes the simulated n-hexane and hydrogen orders. The values at atmospheric pressure are included. The values obtained experimentally are given in parentheses.

Table 6.19. Summary of simulated orders of reaction at high and low pressure and 240 °C

| Order in | Mordenite | ZSM-5 | |
|----------|-----------|-------| |
| n-hexane | 0.19 (0.13) | 0.08 | 0.203 (0.54) | 0.08 |
| hydrogen | -0.14 (~0) | -0.34 | -0.13 (-0.24) | -0.33 |

The simulated high pressure orders of reaction in n-hexane were closer to zero than those obtained under atmospheric pressure, the hydrogen orders were further from zero. When these values are compared to the values measured by Guisnet et al. the hexane orders are too low and the hydrogen orders not negative enough. The plots of the orders were curved. The logarithm of the active species coverage cannot increase proportionally to the logarithm of the pressure since it is already at its maximum value. Froment also found an independence of the rate of reaction of the n-alkane partial pressure. He used, however, n-decane on Pt/H-USY that has a higher adsorption enthalpy than n-hexane. This might indicate a too high adsorption equilibrium in the simulation model.

The high pressure experiments by Guisnet et al. were performed at 300 °C. A quick check of the orders on a Mordenite catalyst was performed. These calculations learned that the order in n-hexane was approximately 1 under these conditions (0.7 experimental). The n-alkoxy coverages were very low in this case. The hydrogen order was more negative, approximately -0.4 to -0.5 over the full hydrogen pressure range (-0.78 experimental). Both orders were now much closer to the experimental values, confirming the influence of temperature on the orders of reaction.
To make the values for the high pressure hydrogen and n-hexane orders easier to compare, Table 6.20. gives values for these orders at approximately 3 bar n-hexane and 27 bar hydrogen. The values for both orders of a Mordenite catalyst have not the same value except for the sign. It may therefore be concluded that also in this case equation (6.1) is not valid. One observes that at the same conditions the n-alkoxy coverages of both ZSM-5 and Mordenite are similar. The orders of reaction are also similar and in case of hydrogen largely negative.

The sum of order of reaction in n-hexane and n-alkoxy coverage is now much lower than 1. In equation (6.2) it is assumed that the acid sites that are not covered with a reactive intermediate are empty. This assumption is not valid under elevated pressure while n-hexane also covers a significant amount of acid sites thus decreasing the n-alkoxy coverage.

### Table 6.20. Simulated orders of reaction at a hydrogen pressure of 27 bar and a n-hexane pressure of 3 bar and a temperature of 240 °C

<table>
<thead>
<tr>
<th></th>
<th>Mordenite</th>
<th>ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Order in n-hexane</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>Order in hydrogen</td>
<td>-0.63</td>
<td>-0.59</td>
</tr>
<tr>
<td>n-alkoxy coverage</td>
<td>0.69</td>
<td>0.69</td>
</tr>
</tbody>
</table>

6.7. Conclusions

It was shown that the simulations accurately describe trends found in the atmospheric pressure experiments. The simulated TOFs are a factor of two lower than the experimental values for all zeolites due to the ‘tuning’ of the pre-exponential factor of isomerization in factors of ten only. Activation energies are reproduced within ten percent. The selectivities for the dimethylbutanes are, however, almost zero while the mono-methylpentanes ratio is also too low.

In order to understand catalytic activity changes as a function of zeolite it is very important to consider not only the adsorption enthalpy. The pre-exponential factor of adsorption and, therefore, the entropy of adsorption plays a decisive role in the simulations. Since a compensation effect is observed for these two parameters, both will be changed simultaneously from one zeolite to another. There may exist a zeolite with an optimum combination of these two factors leading to an optimum coverage.

High adsorption enthalpy and entropy for a particular zeolite will give a low apparent activation energy which leads to high activities. At the same time the coverage of the zeolite is increased. The rate determining step will change from the isomerization step, which is enhanced by higher coverages, to desorption processes, which are inhibited by higher adsorption enthalpies.
Another important feature is the influence of the change in surface coverage as a function of temperature. The points in the Arrhenius plot at higher temperatures deviate from the extrapolation of the activation energy at lower temperatures in both simulations and measurements. The curved plot is not due to a change in rate determining step or diffusion limitations but to a change in coverage of the reactive intermediate, the n-alkoxy species. When the change in n-alkoxy coverage is taken into account and, therefore normalized TOFs are used, a straight line is obtained. The thus calculated activation energy is a normalized activation energy and is the same for all zeolites simulated.

When the pressure is increased, the n-hexane coverage is increased. Due to competitive adsorption between n-hexane and n-hexene for the available acid sites, the n-alkoxy coverage is decreased. The activity of a catalyst is therefore lower under elevated pressure. The rate determining step is not changed since the normalized activation energies at atmospheric and high pressure are equal. The Mordenite catalyst is an exception since at temperatures above 260 °C the normalized TOFs are not constant as function of pressure. A change towards hydrogenation as the slowest step is observed. This leads to a lower normalized activation energy. The order of reaction in n-hexane is practically zero under 3 bar of n-hexane and a hydrogen pressure of 27 bar, the order of reaction in hydrogen is more negative than at atmospheric pressure and has a value of -0.6.

Literature cited.

[4] Chapter 5 of this thesis
[7] Paragraph 2.1.5. of this thesis
[8] Paragraph 5.10. of this thesis
In this appendix the programs used, Rosc8 and Convert2, are described. The number and codes used in their input files are also explained in terms of the components they represent. In paragraph AI.3. Reacth.dat and examples of Kinhl.dat and Mechhl.dat are given.

### A1.1 Description of Convert2

Convert2 converts an user-supplied mechanism with kinetic parameters (input file Reacth.dat) to two other files: Kinhl.dat and Mechhl.dat. The first kinetic parameter of each reaction in Reacth.dat is A, the second is b and the last is \( E_{\text{act}} \), so the rate constant of each reaction becomes:

\[
\begin{align*}
    k &= A \ T^b \ \exp \left( \frac{-E_{\text{act}}}{R \ T} \right) \\
    k &= \text{rate constant} \\
    A &= \text{pre-exponential factor} \\
    b &= \text{non linearity factor} \\
    T &= \text{temperature} \\
    E_{\text{act}} &= \text{activation energy} \\
    R &= \text{gas constant}
\end{align*}
\]

The reaction rate of an elementary step is given by:

\[
\begin{align*}
    r &= k \ C_{\text{molec}}^n \ 0^3_{\text{surf}} \\
    r &= \text{reaction rate} \\
    C_{\text{molec}} &= \text{concentration of a molecule} \\
    n &= \text{stoichiometric coefficient} \\
    0_{\text{surf}} &= \text{surface coverage of a surface specie}
\end{align*}
\]

All odd reaction numbers are forward reactions, all even numbers are reverse reactions. Convert2 also reads Bankh.dat. This file contains two times seven parameters to calculate the thermodynamics of the used molecules via a polynomial function. The first seven parameters are used for temperatures higher than 1000 K, the second seven for temperatures between 300 and 1000 K.
After conversion, Kinhl.dat contains the kinetic parameters and Mechhl.dat the mechanism consisting of the numbers of 3 reactants and 3 products. These numbers are user supplied and when there are less than 3 reactants and/or products, the remaining places are filled with a dummy number. All maximum array dimensions can be found in Maxdims.cmn. Below, all subroutines are described. The flow scheme of Convert2 is given in Figure A1.1.

**Ab:** Reads for each component the data from Bankh.dat. When necessary, it can also calculate its enthalpy and entropy of formation and output them in Hs.dat.

**Bet:** Calculates Beta1 and Beta2 from the A's and b's from Bankh.dat.

**Beta:** This routine converts a set of gas phase and wall reactions to one datafile: Mechhl.dat, which is used to calculate Beta1 and Beta2.

**Convert2:** Main program, it converts a set of reactions to two data inputfiles for Rose8.

**Matrix:** Reads the data from Meche2.dat into a matrix of 3 (reactants) + 3 (products) for every gas phase or wall reaction.

**Ontraf:** Recognizes a reaction and divides it into its reactant and product components.

**Prepmh:** Writes the mechanism in code to Mechhl.dat.

**Prepmhb:** Writes Meche2.dat containing the data from the gas phase and wall reactions.

**Read:** Reads Reacth.dat and Beta12.dat.

**Readb:** Reads the forward gas phase and wall reactions from Reacth.dat.

**Prepkt:** Writes the data from the beta's and reaction constants to Kinhl.dat.

**Ratecoef:** Calculates the free energy and the rate constant of the reverse gas phase and wall reactions. This routine writes it's results to Ratec.dat.

---

**Figure A1.1.** Flow scheme of Convert2

### 4.2 Description of Rose8

Rose8 is a program to simulate concentrations of products and surface species of a steady state driven tube reactor. The tree of the program is shown in Figure A1.2.

**Anasur:** Contains the analytical solution of the differential equations, if there is one.

**C05NBF:** This NAG library routine is used to calculate the surface coverages. It finds a zero of a system of N non-linear functions by a modification of the Powell hybrid method.

**Conan:** May be used to perform a contribution analysis. Outputs its results in Conan.dat.

**Consel:** Calculates conversion and selectivities from the calculated mole fractions and the feed composition.

**Fosub1:** Reads Falloff.dat, which contains the molecules' falloff data.

**Fosub2:** Calculates relative rates as a function of pressure and temperature.

**Init:** Reads the data file Starth.dat, which contains information about species used, the dimension of the problem and some printing and simulation options.
Initi: Calculates the number of one and two radical initiations and terminations.
Kindat: Reads the file Kinhl.dat.
Kinout: Makes Network.dat and Reacout.dat from Reacth.dat.
Matrix: Puts the data from Mechhl.dat in a matrix.
Modeling: Main program. When the option simulation is used, it calls Simall.
Numsur: Calculates the surface species concentrations by using C05NBF.
Output: Outputs results.
Read: Reads Mechhl.dat.
Reactor: Calculates reactor correction factors such as catalyst surface per bed volume.
RS: Calculates the rate of the reactions from the rate constants and concentrations.
Rsc: Calculates the rate constants from A, b and E_a, at a given temperature.
Simall: Calls Reactor and Simone for every experiment.
Simone: Calls Twdente and outputs the results via Output.
Start: Reads the data file Input.dat. Via this file one can also steer the simulation.
Surfcn: Is used by C05NBF to calculate the value of the change in concentrations of the surface species as calculated by the rate expressions.
Twdente: The initial radical and surface species concentrations can be estimated or supplied in data files. In case of an analytical solution, the equations are included in Anasur. When a numerical solution is needed, Numsur is used. The method and the algorithm of Dente, used in this routine, were explained in Chapter 3.
Wtmol: Calculates mole fractions from weight fractions.

MODELING

Figure A1.2. Flowscheme of Rose8
A1.3. Component coding

The components used in the simulations are divided into four groups: molecules, surface species on platinum sites, surface species on acid sites; and surface species on adsorption sites. The first group contains all possible gas phase hexanes, hexenes and hydrogen. An inert, "third body" is also included.

A1.3.1. Molecules

<table>
<thead>
<tr>
<th>Nr</th>
<th>Code</th>
<th>Component name</th>
<th>Nr</th>
<th>Code</th>
<th>Component name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M</td>
<td>third body</td>
<td>13</td>
<td>MP24</td>
<td>4-methyl-1-pentene</td>
</tr>
<tr>
<td>2</td>
<td>C61=</td>
<td>1-hexene</td>
<td>14</td>
<td>MP31</td>
<td>3-methyl-1-pentene</td>
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<tr>
<td>3</td>
<td>C2=C6</td>
<td>cis-2-hexene</td>
<td>15</td>
<td>MP3C2</td>
<td>3-methyl-cis-2-pentene</td>
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<tr>
<td>4</td>
<td>T2=C6</td>
<td>trans-2-hexene</td>
<td>16</td>
<td>MP3T2</td>
<td>3-methyl-trans-2-pentene</td>
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<tr>
<td>5</td>
<td>H2</td>
<td>hydrogen</td>
<td>17</td>
<td>[=3MP</td>
<td>2-ethyl-1-butene</td>
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<tr>
<td>6</td>
<td>NC6</td>
<td>n-hexane</td>
<td>18</td>
<td>MP2</td>
<td>2-methylpentane</td>
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<tr>
<td>7</td>
<td>C3=C6</td>
<td>cis-3-hexene</td>
<td>19</td>
<td>MP3</td>
<td>3-methylpentane</td>
</tr>
<tr>
<td>8</td>
<td>T3=C6</td>
<td>trans-3-hexene</td>
<td>20</td>
<td>DM22=</td>
<td>3,3-dimethyl-1-butene</td>
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<tr>
<td>9</td>
<td>MP21=</td>
<td>2-methyl-1-pentene</td>
<td>21</td>
<td>DM231=B</td>
<td>2,3-dimethyl-1-butene</td>
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<tr>
<td>10</td>
<td>MP22=</td>
<td>2-methyl-2-pentene</td>
<td>22</td>
<td>DM232=B</td>
<td>2,3-dimethyl-2-butene</td>
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<tr>
<td>11</td>
<td>MP2C3=</td>
<td>4-methyl-cis-2-pentene</td>
<td>23</td>
<td>DM22</td>
<td>2,2-dimethylbutane</td>
</tr>
<tr>
<td>12</td>
<td>MP2T3=</td>
<td>4-methyl-trans-2-pentene</td>
<td>24</td>
<td>DM23</td>
<td>2,3-dimethylbutane</td>
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A1.3.2. Platinum sites

<table>
<thead>
<tr>
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<th>Component name</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>PT</td>
<td>empty platinum site</td>
</tr>
<tr>
<td>52</td>
<td>NC6PT</td>
<td>adsorbed n-hexane</td>
</tr>
<tr>
<td>53</td>
<td>H2PT</td>
<td>adsorbed molecular hydrogen molecule</td>
</tr>
<tr>
<td>54</td>
<td>PTH</td>
<td>adsorbed hydrogen atom</td>
</tr>
<tr>
<td>55</td>
<td>PTH1=C6</td>
<td>adsorbed 1-hexene with still one H attached</td>
</tr>
<tr>
<td>56</td>
<td>PTH1=C6</td>
<td>adsorbed 1-hexene</td>
</tr>
<tr>
<td>57</td>
<td>PTH2=</td>
<td>adsorbed 2-hexene with still one H attached</td>
</tr>
<tr>
<td>58</td>
<td>C2=C6PT</td>
<td>adsorbed cis-2-hexene</td>
</tr>
<tr>
<td>59</td>
<td>T2=C6PT</td>
<td>adsorbed trans-2-hexene</td>
</tr>
<tr>
<td>60</td>
<td>PTH3=C6</td>
<td>adsorbed 3-hexene with still one H attached</td>
</tr>
<tr>
<td>61</td>
<td>C3=C6PT</td>
<td>adsorbed cis-3-hexene</td>
</tr>
<tr>
<td>62</td>
<td>T3=C6PT</td>
<td>adsorbed trans-3-hexene</td>
</tr>
<tr>
<td>63</td>
<td>PT1=2MP</td>
<td>adsorbed 2-methyl-1-pentene</td>
</tr>
<tr>
<td>64</td>
<td>PT2=2MP</td>
<td>adsorbed 2-methyl-2-pentene</td>
</tr>
<tr>
<td>65</td>
<td>PT3=2CMP</td>
<td>adsorbed 4-methyl-cis-2-pentene</td>
</tr>
<tr>
<td>66</td>
<td>PT3=2TMP</td>
<td>adsorbed 4-methyl-trans-2-pentene</td>
</tr>
<tr>
<td>67</td>
<td>PT4=2MP</td>
<td>adsorbed 4-methyl-1-pentene</td>
</tr>
<tr>
<td>68</td>
<td>PT1=3MP</td>
<td>adsorbed 3-methyl-1-pentene</td>
</tr>
<tr>
<td>69</td>
<td>PT2=3CMP</td>
<td>adsorbed 3-methyl-cis-2-pentene</td>
</tr>
<tr>
<td>70</td>
<td>PT2=3TMP</td>
<td>adsorbed 3-methyl-trans-2-pentene</td>
</tr>
<tr>
<td>71</td>
<td>[=3MPPT</td>
<td>adsorbed 2-ethyl-1-butene</td>
</tr>
<tr>
<td>72</td>
<td>PTH1=2MP</td>
<td>adsorbed 2-methyl-1-pentene with still one H attached</td>
</tr>
<tr>
<td>73</td>
<td>PTH2=2MP</td>
<td>adsorbed 2-methyl-2-pentene with still one H attached</td>
</tr>
<tr>
<td>74</td>
<td>PTH3=2MP</td>
<td>adsorbed 4-methyl-2-pentene with still one H attached</td>
</tr>
<tr>
<td>Nr</td>
<td>Code</td>
<td>Component name</td>
</tr>
<tr>
<td>----</td>
<td>----------</td>
<td>-----------------------------------------------------</td>
</tr>
<tr>
<td>75</td>
<td>PTH4=2MP</td>
<td>adsorbed 4-methyl-1-pentene with still one H attached</td>
</tr>
<tr>
<td>76</td>
<td>PTH1=3MP</td>
<td>adsorbed 3-methyl-1-pentene with still one H attached</td>
</tr>
<tr>
<td>77</td>
<td>PTH2=3MP</td>
<td>adsorbed 3-methyl-2-pentene with still one H attached</td>
</tr>
<tr>
<td>78</td>
<td>PTH[=3MP</td>
<td>adsorbed 2-ethyl-1-butene with still one H attached</td>
</tr>
<tr>
<td>79</td>
<td>PT2MP</td>
<td>adsorbed 2-methyl-pentane</td>
</tr>
<tr>
<td>80</td>
<td>PT3MP</td>
<td>adsorbed 3-methyl-pentane</td>
</tr>
<tr>
<td>81</td>
<td>PT22=DBM</td>
<td>adsorbed 3,3-dimethyl-butene</td>
</tr>
<tr>
<td>82</td>
<td>PT23=DBM</td>
<td>adsorbed 2,3-dimethyl-1-butene with still one H attached</td>
</tr>
<tr>
<td>83</td>
<td>PT23=DBM</td>
<td>adsorbed 2,3-dimethyl-2-butene with still one H attached</td>
</tr>
<tr>
<td>84</td>
<td>PT22=DBM</td>
<td>adsorbed 3,3-dimethyl-butene with still one H attached</td>
</tr>
<tr>
<td>85</td>
<td>PT1H3=DM</td>
<td>adsorbed 2,3-dimethyl-1-butene with still one H attached</td>
</tr>
<tr>
<td>86</td>
<td>PT2H3=DM</td>
<td>adsorbed 2,3-dimethyl-2-butene with still one H attached</td>
</tr>
<tr>
<td>87</td>
<td>PT222DMP</td>
<td>adsorbed 2,2-dimethyl-butane</td>
</tr>
<tr>
<td>88</td>
<td>PT232DMP</td>
<td>adsorbed 2,3-dimethyl-butane</td>
</tr>
</tbody>
</table>

Note: All alkenes are adsorbed on two platinum sites.

### A1.3.3. Acid sites

<table>
<thead>
<tr>
<th>Nr</th>
<th>Code</th>
<th>Component name</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>HZ</td>
<td>empty acid site</td>
</tr>
<tr>
<td>102</td>
<td>NC6HZ</td>
<td>n-hexane adsorbed on an acid site</td>
</tr>
<tr>
<td>103</td>
<td>H2HZ</td>
<td>adsorbed molecular hydrogen molecule</td>
</tr>
<tr>
<td>104</td>
<td>HZ2POC6</td>
<td>n-hexane cation with a positive charge on the 2nd carbon atom</td>
</tr>
<tr>
<td>105</td>
<td>HZ3POC6</td>
<td>n-hexane cation with a positive charge on the 3rd carbon atom</td>
</tr>
<tr>
<td>106</td>
<td>HZ2PO3MP</td>
<td>3-methyl-pentane cation with a positive charge on the 2nd C atom</td>
</tr>
<tr>
<td>107</td>
<td>HZ3PO3MP</td>
<td>3-methyl-pentane cation with a positive charge on the 3rd C atom</td>
</tr>
<tr>
<td>108</td>
<td>HZ2PO2MP</td>
<td>2-methyl-pentane cation with a positive charge on the 2nd C</td>
</tr>
<tr>
<td>109</td>
<td>HZ3PO2MP</td>
<td>2-methyl-pentane cation with a positive charge on the 3rd C</td>
</tr>
<tr>
<td>110</td>
<td>HZ4PO2MP</td>
<td>2-methyl-pentane cation with a positive charge on the 4th C</td>
</tr>
<tr>
<td>111</td>
<td>HZ2MP</td>
<td>adsorbed 2-methyl-pentane</td>
</tr>
<tr>
<td>112</td>
<td>HZ3MP</td>
<td>adsorbed 3-methyl-pentane</td>
</tr>
<tr>
<td>113</td>
<td>HZ2PO23D</td>
<td>2,3-dimethylbutane cation with a positive charge on the 2nd C</td>
</tr>
<tr>
<td>114</td>
<td>HZ3PO22D</td>
<td>2,2-dimethylbutane cation with a positive charge on the 3rd C</td>
</tr>
<tr>
<td>115</td>
<td>HZ22DMB</td>
<td>adsorbed 2,2-dimethyl-butane</td>
</tr>
<tr>
<td>116</td>
<td>HZ23DMB</td>
<td>adsorbed 2,3-dimethyl-butane</td>
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</table>

### A1.3.4. Adsorption sites

<table>
<thead>
<tr>
<th>Nr</th>
<th>Code</th>
<th>Component name</th>
</tr>
</thead>
<tbody>
<tr>
<td>126</td>
<td>ZEO</td>
<td>non reactive adsorption site in the zeolite</td>
</tr>
<tr>
<td>127</td>
<td>NC6ZEO</td>
<td>adsorbed n-hexane</td>
</tr>
<tr>
<td>128</td>
<td>H2ZEO</td>
<td>hydrogen</td>
</tr>
<tr>
<td>129</td>
<td>ZEO1=C6</td>
<td>adsorbed 1-hexene</td>
</tr>
<tr>
<td>130</td>
<td>C2=C6ZEO</td>
<td>adsorbed cis-2-hexene</td>
</tr>
<tr>
<td>131</td>
<td>T2=C6ZEO</td>
<td>adsorbed trans-2-hexene</td>
</tr>
<tr>
<td>132</td>
<td>C3=C6ZEO</td>
<td>adsorbed cis-3-hexene</td>
</tr>
<tr>
<td>133</td>
<td>T3=C6ZEO</td>
<td>adsorbed trans-3-hexene</td>
</tr>
<tr>
<td>134</td>
<td>ZEO1=2MP</td>
<td>adsorbed 2-methyl-1-pentene</td>
</tr>
</tbody>
</table>
Details of programs used

<table>
<thead>
<tr>
<th>Nr</th>
<th>Code</th>
<th>Component name</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>ZE02=2MP</td>
<td>adsorbed 2-methyl-2-pentene</td>
</tr>
<tr>
<td>136</td>
<td>ZE3=2CMP</td>
<td>adsorbed 4-methyl-cis-2-pentene</td>
</tr>
<tr>
<td>137</td>
<td>ZE3=2TMP</td>
<td>adsorbed 4-methyl-trans-2-pentene</td>
</tr>
<tr>
<td>138</td>
<td>ZEO4=2MP</td>
<td>adsorbed 4-methyl-1-pentene</td>
</tr>
<tr>
<td>139</td>
<td>ZEO1=3MP</td>
<td>adsorbed 3-methyl-1-pentene</td>
</tr>
<tr>
<td>140</td>
<td>ZE2=3CMP</td>
<td>adsorbed 3-methyl-cis-2-pentene</td>
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<tr>
<td>141</td>
<td>ZE2=3TMP</td>
<td>adsorbed 3-methyl-trans-2-pentene</td>
</tr>
<tr>
<td>142</td>
<td>[=3MPZE0</td>
<td>adsorbed 2-ethyl-1-butene</td>
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<tr>
<td>143</td>
<td>ZEO2MP</td>
<td>adsorbed 2-methyl-pentane</td>
</tr>
<tr>
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<td>ZEO3MP</td>
<td>adsorbed 3-methyl-pentane</td>
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<tr>
<td>145</td>
<td>ZE22=DMB</td>
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</tr>
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<td>146</td>
<td>ZE23=DM1</td>
<td>adsorbed 2,3-dimethyl-1-butene</td>
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<tr>
<td>147</td>
<td>ZE23=DM2</td>
<td>adsorbed 2,3-dimethyl-2-butene</td>
</tr>
<tr>
<td>148</td>
<td>ZE022DMB</td>
<td>adsorbed 2,2-dimethyl-butane</td>
</tr>
<tr>
<td>149</td>
<td>ZE023DMB</td>
<td>adsorbed 2,3-dimethyl-butane</td>
</tr>
</tbody>
</table>

A1.4. Examples of Convert2 input/output files

A1.4.1. Example of React.dat

513.,
0.0, 4,
1,'A + B > C', 1.10000000E+03, 0.000, 10.00
2,'C > A + B', 1.00000000E+13, 0.000, 78.00
3,'C + D > E + F', 1.79000000E+17, 0.000, 25.53
4,'E + F > C + D', 4.87943000E+10, 0.000, 45.54

The first number indicates the standard temperature at which the data are given. On the next line the amount of gas phase, wall and surface reactions are given respectively. On the third line the first reaction is given. First its number then the reaction followed by the pre-exponential factor, temperature dependence factor and activation energy in kJ/mol.

A1.4.2. Example of Kin.dat

1,0.110000000E+04,0.0000000000E+00,0.10000000E+02,
2,0.100000000E+14,0.0000000000E+00,0.78000000E+02,
3,0.179000000E+18,0.0000000000E+00,0.25530000E+02,
4,0.487943000E+11,0.0000000000E+00,0.45540000E+02,

This file contains the reaction number, the pre-exponential factor, the temperature dependence factor and activation energy in kJ/mol for each reaction.

A1.4.3. Example of Mech.dat

1, 1, 2, 128, 3, 128, 128,
2, 3, 128, 128, 1, 2, 128,
3, 3, 4, 128, 5, 6, 128,
4, 5, 6, 128, 3, 4, 128,

In this file the reactions are given in component numbers. Each reaction has three reactants and three products. Empty spaces are filled with the dummy number (in the example 128).
A1.5. Examples of Rose8 input/output files

A1.5.1. Example of Starthdat

- **Part A**
  - NUMBER OF MOLECULES, NMOL: 23
  - NUMBER OF RADICALS, NRAD: 0
  - NUMBER OF SURFACE SPECIES, PT, NPSURF: 24
  - NUMBER OF SURFACE SPECIES, ACID, NHSURF: 15
  - NUMBER OF SURFACE SPECIES, ZEOLITE, NZSURF: 23
  - NUMBER OF GASPHASE REACTIONS, NGAS: 0
  - NUMBER OF SURFACE REACTIONS, NCAT: 0
  - NUMBER OF WALL REACTIONS, NWALL: 0
  - NUMBER OF EXPERIMENTS, NEXP: 1
  - NUMBER OF A-FACTORS FOR REGRESSION, NPA: 0
  - NUMBER OF B-FACTORS FOR REGRESSION, NPB: 0
  - NUMBER OF E-FACTORS FOR REGRESSION, NPE: 0
  - NUMBER OF STEPS THROUGH BED, NUMSTEP: 900
  - NEW (0) OR CONTINUATION (1), IDISK: 0
  - SIMUL(1), ROSENBR(2), MARQUARDT(3), IOPT: 1
  - MAXIMUM NUMBER OF ITERATIONS, MAXFROS: 100
  - PRINT CONTROL IN REGRESSION, IPRIN: 1
  - PRINT Rs? 1=Y, 0=N, number: IPRIN, NRK: 0, 210
  - PRINT ks and STOP? 1=Y, 0=N, IPRIN: 0
  - LOOP C05NF? Times, 1=N, 0=Y, IPRINF: 0, 10

- **Part B**

- **Part C**

- **Part D**

Part A In this part one can give the size of the problem in terms of number of species, reactions and experiments. Moreover, the number of steps through the catalyst bed (and thus the step size), the type of modelling (Simulation, Rosenbrock or Marquardt) and the maximum number of iterations can be controlled.

Part B Here one can control what must be printed during the modelling. The calculated rates (R) and rate constants (k) can be printed to file (rrate.dat) and screen respectively. When C05NF crashes, it is possible to let the program calculate its own, new initial values for the surface coverage after which the routine is called again. When the program has still not found a zero after 10 loops, the program is stopped.

Part C These are the numbers of the components involved in the mechanism.

Part D These are parameters to control the Marquardt type modelling.

A1.5.2. Example of Input.dat

- **1**: iso, 2: T-profile, 3: heat transfer, TYPSIM: 1
- **1**: mol-%, 2: conc, 3: wt%, 4: X and S, TYPOUT: 4
- **0**: N, 1: Y sensitivity analysis, ISEN: 0
- **0**: N, 1: Y contribution analysis, ICA, FRACON: 0, 4
Part A
In this part of *Input.dat* questions are asked about the type of modelling that must be done and what catalyst and what diluting material must be used.

Part B
Here one can give for each 'experiment' a number and a title of 40 characters maximum. The next 5 lines give the volume percentages of the different components in the input gas stream.

Part C
These 5 lines give the volume percentages of the different components in the gas stream after the reactor bed.

Part D
First the number of places where the temperature of the catalyst bed was measured can be given (minimum 2). In the next line one can give the distance (m) from the beginning of the bed of these places, followed by the measured temperatures (K). The numbers in the line below that line represent the total pressure (Pa), the total molar flow (mol/s) of reactants, the weight (kg) of the catalyst and the weight (kg) of the diluting material respectively. The last line contains the inner diameter (m) of the reactor, the outer diameter (m) of the thermocouple inside the reactor bed, the bed length and the type of feed (in our case always 7).
In this appendix the parameters used to simulate the results in Chapter 6 are given. In the first paragraph the elementary steps of the mechanism are given. Paragraph A2.2. lists the physical characteristics of the three zeolites simulated. Paragraph A2.3. lists the activation energies and pre-exponential factors of the elementary steps. Usually, identical values are used for all zeolites. For brevity only the values that are different for different zeolites are listed.

A2.1. The zeolites

A2.1.1 General
Density of bed diluent 2200 kg/m³
Specific surface area of bed diluent 4.29·10⁵ m²/kg

A2.1.2 2.0 wt.% Pt/HMordenite
Density of porous catalyst 1368 kg/m³
Specific surface area of catalyst 1.95·10³ m²/kg
Porosity of the catalyst 0.26 m³/m³
Concentration of surface platinum 1.75·10⁷ mol/m²
Number of atoms in a Pt cluster 5
Concentration of active acid sites 1.88·10⁻⁶ mol/m²
Concentration of zeolite sites 2.79·10⁻⁶ mol/m²

A2.1.3 0.5 wt.% Pt/HZSM-5
Density of porous catalyst 1368 kg/m³
Specific surface area of catalyst 6.55·10³ m²/kg
Porosity of the catalyst 0.26 m³/m³
Concentration of surface platinum 3.91·10⁻⁸ mol/m²
Number of atoms in a Pt cluster 5
Concentration of active acid sites 4.38·10⁻⁷ mol/m²
Concentration of zeolite sites 2.11·10⁻⁶ mol/m²

A2.1.4 1.6 wt.% Pt/Hβ
Density of porous catalyst 1368 kg/m³
Specific surface area of catalyst 6.62·10³ m²/kg
Values of parameters used

Porosity of the catalyst 0.33 m³/m³
Concentration of surface platinum 1.23·10⁻⁷ mol/m²
Number of atoms in a Pt cluster 5
Concentration of active acid sites 1.60·10⁻⁶ mol/m²
Concentration of zeolite sites 3.04·10⁻⁶ mol/m²

A2.2. Activation energies and pre-exponential factors of elementary steps

A2.2.1. Values

Since the rate of reaction is always given in mol/m²s, the dimension of the pre-exponential factor changes according to the stoichiometry of the reaction involved. This means that for adsorption the dimensions are m³/m²s. All other surface reactions have mol/m²s dimensions. Adsorption sites are abbreviated as Zeo. Unless stated otherwise, the parameters for zeolite β are the same as for Mordenite and all other data are equal for all zeolites. In a separate table the dehydrogenation/hydrogenation data are given.

Table A2.1. Simulation data

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Pre-exponential factor [mol/m²s]</th>
<th>Activation energy [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>forward</td>
<td>reverse</td>
</tr>
<tr>
<td>Adsorption n-hexane, MOR *[m³/m²s]</td>
<td>14.6³</td>
<td>1.5·10⁸</td>
</tr>
<tr>
<td>Adsorption n-hexane, MFI *[m³/m²s]</td>
<td>14.6³</td>
<td>1.0·10⁹</td>
</tr>
<tr>
<td>Adsorption n-hexane, BEA *[m³/m²s]</td>
<td>14.6³</td>
<td>6.8·10⁷</td>
</tr>
<tr>
<td>Transport n-hexane from Zeo to H⁺ or Pt site</td>
<td>2.9·10⁸</td>
<td>2.3/10⁸</td>
</tr>
<tr>
<td>Transport n-hexenes from Zeo to Pt site</td>
<td>1.2·10¹²</td>
<td>2.9·10⁸</td>
</tr>
<tr>
<td>Adsorption n-hexenes, MOR *[m³/m²s]</td>
<td>14.6³</td>
<td>1.5·10⁷</td>
</tr>
<tr>
<td>Adsorption n-hexenes, MFI *[m³/m²s]</td>
<td>14.6³</td>
<td>1.0·10⁸</td>
</tr>
<tr>
<td>Protonation to secondary ion</td>
<td>1.5·10⁸</td>
<td>2.1·10¹¹</td>
</tr>
<tr>
<td>2-methylpentenes, ZSM-22</td>
<td>1.5·10⁸</td>
<td>2.1·10¹¹</td>
</tr>
<tr>
<td>3-methylpentenes, ZSM-22</td>
<td>1.5·10⁸</td>
<td>2.1·10¹¹</td>
</tr>
<tr>
<td>Branching isomerization alkoxy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary to secondary from 2-methylpentenes, ZSM-22</td>
<td>4.1·10³</td>
<td>4.1·10³</td>
</tr>
<tr>
<td>from 3-methylpentenes, ZSM-22</td>
<td>4.1·10³</td>
<td>4.1·10³</td>
</tr>
<tr>
<td>Secondary to tertiary from 2-methylpentenes, ZSM-22</td>
<td>4.1·10³</td>
<td>4.1·10³</td>
</tr>
<tr>
<td>from 3-methylpentenes, ZSM-22</td>
<td>4.1·10³</td>
<td>4.1·10³</td>
</tr>
<tr>
<td>Tertiary to tertiary from 2-methylpentenes, ZSM-22</td>
<td>4.1·10³</td>
<td>4.1·10³</td>
</tr>
<tr>
<td>from 3-methylpentenes, ZSM-22</td>
<td>4.1·10³</td>
<td>4.1·10³</td>
</tr>
<tr>
<td>Reaction</td>
<td>Pre-exponential factor [mol/m^2s]</td>
<td>Activation energy [kJ/mol]</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td></td>
<td>forward</td>
<td>reverse</td>
</tr>
<tr>
<td>Non-branching isomerization alkoxy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary to secondary</td>
<td>4.1·10^3</td>
<td>4.1·10^3</td>
</tr>
<tr>
<td>from 2-methylpentenes, ZSM-22</td>
<td>4.1·10^3</td>
<td>4.1·10^3</td>
</tr>
<tr>
<td>from 3-methylpentenes, ZSM-22</td>
<td>4.1·10^3</td>
<td>4.1·10^3</td>
</tr>
<tr>
<td>Non-branching isomerization alkoxy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary to tertiary</td>
<td>4.1·10^3</td>
<td>4.1·10^3</td>
</tr>
<tr>
<td>from 2-methylpentenes, ZSM-22</td>
<td>4.1·10^3</td>
<td>4.1·10^3</td>
</tr>
<tr>
<td>from 3-methylpentenes, ZSM-22</td>
<td>4.1·10^3</td>
<td>4.1·10^3</td>
</tr>
<tr>
<td>To dimethylbutenes, ZSM-22</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Protonation to tertiary ion</td>
<td>3.4·10^8</td>
<td>9.7·10^11</td>
</tr>
<tr>
<td>2-methylpentenes, ZSM-22</td>
<td>3.4·10^8</td>
<td>9.7·10^11</td>
</tr>
<tr>
<td>3-methylpentenes, ZSM-22</td>
<td>3.4·10^8</td>
<td>9.7·10^11</td>
</tr>
<tr>
<td>Transport iso-hexenes from Zeo to Pt</td>
<td>5.7·10^15</td>
<td>5.7·10^15</td>
</tr>
<tr>
<td>Adsorption iso-hexenes, MOR [^{[m^3/m^2s]}]</td>
<td>5.25·10^-4</td>
<td>1.0·10^-8</td>
</tr>
<tr>
<td>Adsorption iso-hexenes, MFI [^{[m^3/m^2s]}]</td>
<td>5.25·10^-4</td>
<td>1.0·10^-8</td>
</tr>
<tr>
<td>Adsorption 2-methyl-pentenes, ZSM-22 [^{[m^3/m^2s]}]</td>
<td>5.25·10^-4</td>
<td>3.16·10^-2</td>
</tr>
<tr>
<td>Adsorption 3-methyl-pentenes, ZSM-22</td>
<td>5.25·10^-4</td>
<td>1.0·10^-7</td>
</tr>
<tr>
<td>Transport 2-methyl-pentane from Zeo to H^+ or Pt site</td>
<td>1.4·10^-11</td>
<td>1.4·10^-11</td>
</tr>
<tr>
<td>Transport 3-methyl-pentane from Zeo to H^+ or Pt site</td>
<td>1.4·10^-11</td>
<td>1.4·10^-11</td>
</tr>
<tr>
<td>Adsorption methyl-pentanes, MOR [^{[m^3/m^2s]}]</td>
<td>5.25·10^-4</td>
<td>1.0·10^-9</td>
</tr>
<tr>
<td>Adsorption methyl-pentanes, MFI [^{[m^3/m^2s]}]</td>
<td>5.25·10^-4</td>
<td>1.0·10^-9</td>
</tr>
<tr>
<td>Adsorption 2-MP, ZSM-22 [^{[m^3/m^2s]}]</td>
<td>5.25·10^-4</td>
<td>3.16·10^-2</td>
</tr>
<tr>
<td>Adsorption 3-MP, ZSM-22 [^{[m^3/m^2s]}]</td>
<td>5.25·10^-4</td>
<td>1.0·10^-8</td>
</tr>
<tr>
<td>Transport di-methylbutenes from Zeo to Pt site, MOR</td>
<td>5.5·10^-17</td>
<td>5.5·10^-17</td>
</tr>
<tr>
<td>Transport di-methylbutenes from Zeo to Pt site, MFI</td>
<td>5.5·10^-16</td>
<td>5.5·10^-16</td>
</tr>
<tr>
<td>Adsorption di-methylbutanes, MOR [^{[m^3/m^2s]}]</td>
<td>3.25·10^-3</td>
<td>1.0·10^-9</td>
</tr>
<tr>
<td>Adsorption di-methylbutanes, MFI [^{[m^3/m^2s]}]</td>
<td>3.25·10^-3</td>
<td>1.0·10^-9</td>
</tr>
<tr>
<td>Transport di-methylbutanes from Zeo to H^+ or Pt site, MOR</td>
<td>1.2·10^-14</td>
<td>1.2·10^-14</td>
</tr>
<tr>
<td>Transport di-methylbutanes from Zeo to H^+ or Pt site, MFI</td>
<td>1.2·10^-12</td>
<td>1.2·10^-12</td>
</tr>
<tr>
<td>Dissociative adsorption H(_2) on Pt [^{[m^3/m^2s]}]</td>
<td>1.0·10^-3</td>
<td>1.7·10^-9</td>
</tr>
</tbody>
</table>
The dehydrogenation on the Pt sites is listed as the forward reaction for each reaction.

**Table A2.2. Hydrogenation/dehydrogenation simulation data**

<table>
<thead>
<tr>
<th>Alkane</th>
<th>Reaction</th>
<th>Pre-exponential factor [mol/m²s]</th>
<th>Activation energy [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>forward</td>
<td>reverse</td>
</tr>
<tr>
<td>n-hexane</td>
<td></td>
<td>3.7·10⁴</td>
<td>2.7·10⁹</td>
</tr>
<tr>
<td></td>
<td>1-hexene</td>
<td>1.2·10⁸</td>
<td>9.69·10⁷</td>
</tr>
<tr>
<td></td>
<td>cis-2-hexene</td>
<td>1.2·10⁷</td>
<td>1.63·10⁸</td>
</tr>
<tr>
<td></td>
<td>trans-2-hexene</td>
<td>5.32·10⁷</td>
<td>6.50·10⁹</td>
</tr>
<tr>
<td></td>
<td>cis-3-hexene</td>
<td>5.32·10⁷</td>
<td>5.1·10⁹</td>
</tr>
<tr>
<td></td>
<td>trans-3-hexene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-methylpenta-</td>
<td>2-methyl-1-pentene</td>
<td>2.5·10⁶</td>
<td>3.06·10⁸</td>
</tr>
<tr>
<td>2-methyl-2-pentene</td>
<td>3.7·10⁷</td>
<td>1.87·10⁹</td>
<td>55.27</td>
</tr>
<tr>
<td>4-methyl-cis-2-pentene</td>
<td>6.91·10⁷</td>
<td>5.95·10⁹</td>
<td>55.24</td>
</tr>
<tr>
<td>4-methyl-trans-2-pentene</td>
<td>6.91·10⁷</td>
<td>6.72·10⁹</td>
<td>55.22</td>
</tr>
<tr>
<td></td>
<td>4-methyl-1-pentene</td>
<td>1.18·10⁵</td>
<td>1.98·10⁹</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>3-methyl-1-pentene</td>
<td>3.2·10⁵</td>
<td>5.31·10⁸</td>
</tr>
<tr>
<td>3-methyl-cis-2-pentene</td>
<td>7.0·10⁷</td>
<td>3.77·10⁹</td>
<td>55.28</td>
</tr>
<tr>
<td>3-methyl-trans-2-pentene</td>
<td>7.0·10⁷</td>
<td>2.75·10⁹</td>
<td>55.25</td>
</tr>
<tr>
<td></td>
<td>2-ethyl-1-butene</td>
<td>1.24·10⁵</td>
<td>1.99·10⁸</td>
</tr>
<tr>
<td>3,3-dimethyl-1-butene</td>
<td>1.73·10⁵</td>
<td>4.68·10⁹</td>
<td>40.29</td>
</tr>
<tr>
<td>2,3-dimethyl-1-butene</td>
<td>5.5·10⁵</td>
<td>1.70·10⁹</td>
<td>55.29</td>
</tr>
<tr>
<td>2,3-dimethyl-2-butene</td>
<td>2.7·10⁷</td>
<td>7.45·10⁹</td>
<td>55.22</td>
</tr>
</tbody>
</table>
A2.2.2. Correction factors

The values for the pre-exponential factors and activation energies of the elementary reaction steps in Reacth.dat were collected from different sources (see Chapter 4). Surface coverages are used for reacting surface species and the rate of reaction is defined as a change of surface concentration (mol/m² s) per second. The pre-exponential factors in Reacth.dat therefore contain a fixed number of sites. All rate constants, calculated from these data, are corrected by a factor accounting for the real amount of sites involved in that particular step. In case of Pt the concentration of sites present on a Pt metal surface \((1.7 \cdot 10^5 \text{ mol/m}^2)\) is used for the fixed number. For both other types of sites a round number in the proximity of the real maximum surface concentration is taken \((1.10^6 \text{ mol/m}^2)\). In this way the site balance could still be accounted for. The factors that are used are:

\[
\begin{align*}
\text{Acfpt} &= \frac{Ltp}{1.7 \cdot 10^5} \\
\text{Acfptdif} &= \frac{Ltp}{1.0 \cdot 10^5} \\
\text{Acfhz} &= \frac{Lth}{1.0 \cdot 10^5} \\
\text{Acfzo} &= \frac{Ltz}{1.0 \cdot 10^5}
\end{align*}
\]

- \(Ltp\) = total concentration of reachable Pt sites, based on metal loading and dispersion
- \(Lth\) = total concentration of acid sites, based on base titration or Si/Al ratio
- \(Ltz\) = total concentration of adsorption (zeo) sites, based on the adsorption capacity for \(n\)-hexane minus \(Lth\), to obtain net available space

The next table lists which factor is used for which reaction:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>factor used</th>
</tr>
</thead>
<tbody>
<tr>
<td>de- or adsorption (zeo site)</td>
<td>Acfzo</td>
</tr>
<tr>
<td>transport from zeo to Pt site</td>
<td>Acfzo, Acfptdif, reciprocal of amount of atoms in one cluster</td>
</tr>
<tr>
<td>de- or adsorption Pt site</td>
<td>Acfpt</td>
</tr>
<tr>
<td>de- or hydrogenation</td>
<td>Acfpt</td>
</tr>
<tr>
<td>transport from zeo to acid site</td>
<td>Acfzo, Acfhz</td>
</tr>
<tr>
<td>protonation</td>
<td>Acfzo, Acfhz</td>
</tr>
<tr>
<td>deprotonation</td>
<td>Acfzo, Acfhz</td>
</tr>
<tr>
<td>isomerization on acid site</td>
<td>Acfhz</td>
</tr>
<tr>
<td>transport from acid to zeo site</td>
<td>Acfzo, Acfhz</td>
</tr>
<tr>
<td>transport from Pt to zeo site</td>
<td>Acfzo, Acfptdif</td>
</tr>
</tbody>
</table>
Hydro-isomerization is a process that is used worldwide to convert low octane n-alkanes into high octane iso-alkanes. This process is catalyzed by noble metal loaded acidic zeolites. In this project, the parameters that determine the activity and selectivity of platinum loaded catalysts were investigated. The attention was focused on the effects caused by the adsorption enthalpy and entropy of the substrate molecule on the zeolite.

Four high-silica zeolites that had different pore systems and pore sizes were used. They showed, therefore, different adsorption characteristics for the substrate, n-hexane. These zeolites were tested in the hydro-isomerization reaction in a fixed bed, plug flow reactor operating at atmospheric pressure. Kinetic data such as orders of the reaction in hydrogen and hexane as well as activation energies were determined. The activities of the different zeolites were compared in terms of TOFs (Turn Over Frequencies). TOF was defined as mole of substrate converted per mole of active site per time unit. Since all tested zeolites had the same intrinsic acidity, TOFs gave the opportunity to directly correlate activity to adsorption effects.

Complementary to the experiments, computer simulations were performed. In these simulations elementary reaction steps were used to describe the hydro-isomerization. The activation energies and pre-exponential factors needed to calculate reaction rate constants were estimated from quantum chemistry, transition state theory, separate experiments and catalyst characteristics. The method used for simulating gas phase concentration as well as surface species coverages along the length of the catalyst bed was based on the microkinetics method as developed by Dumesic. This means that no forward step was a priori assumed rate determining or equilibrated with its reverse step.

At low platinum loadings and atmospheric pressure, the platinum function was (co)-rate determining. This resulted initially in a positive order of the reaction in hydrogen measured experimentally. This order is negative, between 0 and -1, for an ideal bifunctional catalyst. The hydrogenation of the product isomers was the (co)-rate determining step as evidenced by the simulations.
Catalysts based on ZSM-5 were found to be the most active per acid site. This zeolite exhibits the highest adsorption enthalpy for n-hexane of the zeolites tested. ZSM-22, with the same adsorption enthalpy, showed pore-mouth catalysis and therefore a very low activity. It was estimated that on 1 μm crystals only 10 to 20 per cent of the sites were used in the reaction. Mordenite also showed relatively low apparent activity. In this case probably only one-third of the sites were available for reaction. When this zeolite was compared to β-zeolite on basis of this assumption, their activities were the same. Since their adsorption enthalpies for n-hexane were also the same this meant adsorption controls the reactivity.

It was shown by both the experiments and the simulations that the differences in activity of the different zeolites are due to the different adsorption enthalpies for the substrate. It was found that a higher adsorption enthalpy leads to higher activity and lower apparent activation energy. However, the intrinsic activation energy of isomerization from the adsorbed state was the same for all zeolites tested. The value of this activation energy of isomerization catalyzed by the proton of the zeolite is high: ± 125-130 kJ/mol. The carbenium ion activation energy in the liquid phase is approximately 30 kJ/mol.

The simulated surface coverages at atmospheric pressure were very high, even at a temperature of 513 K. Zeolite coverages of n-hexane of over 50 per cent and almost full acid sites coverages by n-alkoxy species were simulated. These n-alkoxy species are the reactive intermediates and arise when n-hexene molecules are adsorbed on zeolite protons. Carbenium ions are transition states relative to these stable n-alkoxy intermediates. The simulations showed that higher adsorption enthalpy led to higher hexane coverages of the zeolites but not to enhanced coverages of n-alkoxy species. The lowered apparent activation energy was therefore the reason for the higher activity of these zeolites. It was also shown that the adsorption entropy plays an important role. When only the adsorption enthalpy was changed in stead of the free energy of adsorption (which includes the adsorption entropy) the n-alkoxy coverages were changed. Moreover, the trend towards lower apparent activation energy at higher adsorption enthalpy was reversed.

At higher total pressure and lower hydrogen to hexane molar ratio, the activity of a catalyst was lower. This was due to a lowered n-alkoxy coverage caused by competition of the n-hexene and n-hexane for the available acid sites. A pressure of 30 bar led to more negative orders of reaction in hydrogen and hexane orders closer to zero.
Samenvatting

Hydro-isomerisatie wordt wereldwijd gebruikt om n-alkanen met een laag oktaangetal om te zetten naar iso-alkanen met een hoger oktaangetal. Dit proces wordt gekatalyseerd door edelmetaal-beladen zure zeolieten. Dit projekt richtte zich op de parameters die de activiteit en selectiviteit van platina beladen katalysatoren bepalen. De aandacht werd geconcentreerd op de effecten van adsorptie-enthalpie en -entropie van het substraat molecuul op het zeoliet op de reactie.

Vier zeolieten met een hoog gehalte aan silicium werden gebruikt. Ze bezaten elk een ander porie-systeem en/of een andere diameter van de porie. Deze monsters vertoonden verschillende adsorptie-karakteristieken voor het substraat n-hexaan. De zeolieten werden getest in de hydro-isomerisatie reactie onder atmosferische druk, gebruik makend van een vast-bed propstroom reactor. Kinetische data zoals orden van reactie in waterstof en n-hexaan, evenals activeringsenergiën werden bepaald. De activiteiten van de verschillende monsters werd vergeleken in termen van TOFs (Turn Over Frequencies). TOF werd gedefinieerd als molen n-hexaan geconverteerd per mol actieve plaats per tijdeenheid. Omdat alle geteste zeolieten een gelijke intrinsieke zuursterkte bezaten, konden de TOFs gebruikt worden om activiteit aan adsorptie effecten direct aan elkaar te corrélérer.

Complementair aan de experimenten werden computer simulaties uitgevoerd. In deze simulaties werden elementaire reactie stappen gebruikt om de hydro-isomerisatie te beschrijven. De activeringsenergiën en pre-exponentiële factoren die nodig waren om reactie-snelheidsconstanten te berekenen, werden geschat met behulp van quantum chemie, overgangscomplex-theorie, aparte experimenten en katalysator-karakteristieken. De microkinetiek methode van Dumesic was de basis voor de methode die gebruikt werd. Deze houdt in dat, a priori, geen enkele voorwaartse stap snelheidsbepalend werd verondersteld dan wel geëquilibréerd met zijn teruggaande stap. Gasfase concentraties alsmede oppervlaktebezettingsgraden als functie van plaats in het katalysatorbed werden hiermee gesimuleerd.

Bij lage platina belading en atmosferische druk, was de platina functie (mede)snelheidsbepalend. Dit resulteerde in een positieve orde van de reactie in waterstof in de eerste metingen. Een negatieve orde, tussen 0 en -1, kan verwacht worden wanneer de
katalysator ideaal bifunctioneel gedrag vertoond. De simulaties toonden aan dat de hydrogenering van product-isomeren de mede-snelheidsbepalend stap was.

ZSM-5 gebaseerde katalysatoren waren het actiefst per zure plaats. Dit zeoliet heeft van de geteste zeolieten de hoogste adsorptie-enthalpie voor n-hexaan. ZSM-22, met dezelfde adsorptie-enthalpie, vertoonde poriemond katalyse en daardoor een erg lage activiteit. Geschat werd dat op 1 μm kristallen maar 10 tot 20 procent van de protonen deelde in de reactie. Op Mordeniet werden ook relatief lage schijnbare activiteiten gemeten. In dit geval werd waarschijnlijk maar één-derde van de plaatsen gebruikt in de reactie. Wanneer dit zeoliet op basis van deze aannemer werd vergeleken met zeoliet β, waren de activiteiten gelijk. Aangezien hun adsorptie-enthalpiën ook gelijk waren, betekende dit dat adsorptie de activiteit bepaald.

Zowel de experimenten als de simulaties lieten zien dat de verschillen in activiteit van de verschillende zeolieten werd veroorzaakt door de verschillen in adsorptie-enthalpie voor n-hexaan. Een hogere adsorptie-enthalpie leidde tot een lagere schijnbare activeringsenergie. De intrinsieke activeringsenergie van isomerisatie vanuit de geadsorbeerde toestand was echter hetzelfde voor alle geteste zeolieten. De waarde voor deze activeringsenergie van isomerisatie gekatalyseerd door een proton in een zeoliet is hoog: ± 125-130 kJ/mol. De carbenium ion activeringsenergie in de vloeistoffase bedraagt ongeveer 30 kJ/mol.

De gesimuleerde oppervlakte-bezettingsgraden zijn erg hoog, zelfs bij een temperatuur van 513 K. Waarden voor de bezettingsgraad van het zeoliet van boven de 50 procent alsmede een bijna volledige bezetting van de zure plaatsen door lineaire alkoxy-adsorbaten werden gesimuleerd. Deze adsorbaten zijn de actieve intermediairen in de reactie en ontstaan wanneer een n-hexeen molecule op een proton van het zeoliet adsorbeert. Carbenium ionen zijn in dit geval de overgangscomplexen ten opzichte van het stabiele alkoxy-adsorbat. De simulaties toonden ook aan dat een hogere adsorptie-enthalpie leidde tot hogere hexaan bezettingsgraden maar niet tot een hogere bezettingen van de zure plaatsen. De verlaagde activeringsenergie was daarom verantwoordelijk voor de verhoogde activiteit van deze zeolieten. De adsorptie-entropie is een andere belangrijke factor. Wanneer alleen de adsorptie-enthalpie werd verandert in plaats van de vrije energie van adsorptie (met daarin verdwenen de adsorptie-entropie), veranderden de n-alkoxyadsorbaat-bezettingsgraden wel. Ook de trend naar lagere activeringsenergie bij hoger adsorptie-enthalpie werd omgedraaid.

De activiteit van een katalysator werd onderdrukt onder hogere druk en lagere waterstof/koolwaterstof verhouding. Dit werd veroorzaakt door een lagere n-alkoxy bezettingsgraad doordat n-hexeen moest wedijveren met de n-hexaan voor de beschikbare zure plaatsen. Een druk van 30 bar leidde ook tot meer negatieve orden van reactie in waterstof en hexaan orden dichter bij nul.
Dankwoord

Om maar eens met een cliché te beginnen: 'mijn naam mag dan op de voorkant staan, dit boekje is geenszinds het werk van één persoon'. Vele mensen binnen en buiten TAK hebben er op de een of andere manier aan bijgedragen, al was het maar in de vorm van een prettige werksfeer. Natuurlijk zijn er mensen die ik met name wil noemen. Ten eerste mijn promotor Rutger van Santen. Ik kon altijd bij je binnen vallen om dingen te bespreken en je had nieuwe ideeën leveren als ik valse slagsel. Jouw deur stond altijd open voor als ik weer een technisch of ander probleem had. En in je rol als 'advocaat van de duivel' dwong je me nog eens goed na te denken of dat wat ik dacht te weten wel waar was.

Professor Lercher wil ik bedanken voor het feit dat hij mijn tweede promotor wilde zijn en de beide andere leden van de kernecommissie, professors Van Hooff en Marin, voor het mede corrigeren van het manuscript. Jochem, bedankt voor het meedenken op adsorptie-gebied, ook toen je weer terug was naar Duitsland. Ook al die andere e-mails, faxen en gewone post die heen en weer vlogen, hebben mij altijd veel plezierige momenten bezorgd. Dankzij Leon van den Oetelaar kan Rob van Veen een moeilijke vraag bedenken voor de 29e. Rob, ook je koeriersdiensten heb ik zeer op prijs gesteld.


In de afgelopen 4 jaar heb ik het voorrecht gehad om 3 afstudeerders en een researchstagiare te begeleiden. Simon, het heeft je veel geploeter gekost, maar zonder jou zou de 'reformer' na een jaar nog geen zinnige metingen hebben opgeleverd. Eric, je hebt in maar drie maanden toch veel bij elkaar gemeten. Pieter, je hebt tijdens jouw jaar het project echt op gang geholpen. En Johan heeft als laatste het meetwerk, beschreven in hoofdstuk 5, zo goed als afgerond.

Noud, ik heb de afgelopen jaren prettig met je samen kunnen werken, vooral op het gebied van platina. Maar ook over mechanismen, kinetiek en zo hebben we regelmatig zitten discussiëren. Hoofdstuk 6 zou heel wat magerder zijn geworden zonder de hulp van Pieter Couwenberg, Harold van Garderen, Rob Berger en Eric Meijer. Alle zwavelvazen wil ik bedanken dat ik regelmatig mocht binnen vallen om van alles en nog wat te lezen of praktische dingen te vragen.

Een hele serie analyses en karakteriseringen van katalysatoren betekent dat er een hele serie mensen voor mij bezig zijn geweest om die metingen uit te voeren en te helpen met interpreteren. Adelheid (AAS), Eugene (BET), Jos (IR), Leo van de Ven en Jan de Haan (NMR), Martien en Simon (SEM), en Willy (adsorptie-metingen), bedankt! Wout, jij bedankt voor alle reparaties.

De vrijdagmiddag- en avondborrels waren altijd een aangename afsluiting van de werkweek. De (on)zinnige discussies met mijn (ex-)kameraden en andere metalen Imre, Robert, Pieter, Marius, Noud, Bruce, Frank, Piet en Marnix waren ook zeer verhelderend.

Pap en mam, jullie hebben mij de mogelijkheid gegeven te studeren, en later ook te promoveren. Aan jullie en ook mijn schoonouders ben ik dank verschuldigd voor alle steun, in welke vorm dan ook. En dan rest mij nog één persoon te noemen, waarmee ik de laatste jaren liep en leed heb gedeeld. Bedankt, Wim, voor alles!

En nu maar hopen dat ik niemand vergeten ben.

Annemieke
Curriculum Vitae

Annemieke van de Runstraat werd geboren op 28 februari 1969 te Velsen. Na 6 jaar in Broek in Waterland te hebben gewoond, verhuisde ze naar Holten (Overijssel) en doorliep daar het ongedeelde VWO aan de Scholengemeenschap Holten en deed examen in 8 vakken. In 1987 begon ze haar studie Chemische Technologie aan de Universiteit Twente. De keuze van organische chemie als afstudeerrichting resulteerde in een onderzoek getiteld 'Terfenyl gebaseerde liganden voor de herkenning van zware metaalionen; synthese en toepassing in een chemisch gemodificeerde veld effect transistor' onder leiding van Prof. Dr. Ir. D.N. Reinhoudt.

In 1992 kwam ze in dienst van SON/NWO als OIO. Het promotie-onderzoek werd verricht in de vakgroep Anorganische Chemie en Katalyse van de Technische Universiteit Eindhoven. De resultaten van die 4 jaar rondneuzen in de wereld van zeoliet adsorptie-effecten op de zuurgekatalyseerde hydro-isomerisatie van n-hexaan onder begeleiding van Prof. Dr. R.A. van Santen, staan beschreven in dit proefschrift.
Stellingen

1. Het is voor auteurs van een congresbijdrage geen goede stimulans om hun papers op tijd in te sturen als de organisatoren van het congres zich tot 3 maal toe niet aan hun eigen deadline houden.

2. De fit in een artikel van Svoboda et al. is inderdaad uitstekend: de gefitte lijn in figuur 3a steekt consequent boven de experimentele punten uit.


3. Ondanks wat vaak gedacht wordt, zijn de rechten en plichten van AIOs en OIOs niet gelijk. De eerste kan bijvoorbeeld tot 25% van zijn/haar tijd ingezet worden voor onderwijs, de tweede tot 10%. Een OIO daarentegen moet voor elke congresbezoek, groot of klein, binnen- of buitenland een beurs aanvragen en daarna een verslag schrijven van 2 tot 4 pagina’s.

4. Liu et al. hebben niet persé gelijk als ze zeggen dat de kromme Arrheniusplot veroorzaakt wordt door single-file diffusie.


5. Als men op zoek is naar het schaap met vijfpoten is het waarschijnlijk verstandiger om zich te richten op twee schapen.

6. Het is zeer gevaarlijk conclusies te trekken naar aanleiding van de lineariteit of kromming van een lijn door vier (inclusief de oorsprong) punten.


8. Een reactiesnelheidsvergelijking afleiden naar aanleiding van een versimpeld en gedefalanceerd mechanisme om daarna experimentele data uit te zetten volgens de gelineariseerde versie ervan kan, indien de lijn inderdaad recht is, slechts bewijzen dat het model niet fout is; nooit dat het waar is.


10. Het OBP\(^1\) is voor de meeste AIOs/OIOs een wassen neus, het OBP\(^2\) daartegen is onmisbaar.

11. Er zijn onderzoekers die niet alles uit hun data halen wat erin zit. Bijvoorbeeld activiteit en selectiviteit meten als functie van temperatuur en dan geen activeringsenergie afschatten.


13. Soms is het makkelijker vergiffenis te krijgen dan toestemming.

A. van de Runstraat
13-11-1996

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\(^1\) Opleidings en Begeleidings Plan
\(^2\) Ondersteunend en Begeleidend Personeel