Hydrocarbon Conversion over Brønsted and Lewis Acidic Zeolites

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op woensdag 26 september 2007 om 11.00 uur

door

Neelesh Janardan Rane

geboren te Bhusawal, India
Dit proefschrift is goedgekeurd door de promotor:

prof.dr. R.A. van Santen

Copromotor:
dr.ir. E.J.M. Hensen

Neelesh J. Rane

A catalogue record is available from the Eindhoven University of Technology Library

ISBN: 978-90-386-1105-1

Copyright © 2007 by Neelesh J. Rane

The work described in this thesis has been carried out at the Schuit Institute of Catalysis within the Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, The Netherlands. Financial support has been supplied by the Technology Foundation STW.

Cover design: Paul Verspaget (Grafische Vormgeving-Communicatie) and Neelesh J. Rane

Printed at the Universiteitsdrukkerij, Eindhoven University of Technology.
To my dearest parents for their perpetual love and support

"Success is not final, failure is not fatal; it is the courage to continue that counts."
(Winston Churchill)
# Table of Contents

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Introduction and scope</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>Characterization of Ga substituted zeolites prepared by chemical vapor deposition of trimethylgallium</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>Activation of short-chain alkanes over Ga cations in ZSM-5 zeolite</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>Water promoted hydrocarbon activation catalyzed by binuclear Ga sites in ZSM-5 zeolite</td>
<td>49</td>
</tr>
<tr>
<td>5</td>
<td>Olefin cracking over protonic zeolites</td>
<td>63</td>
</tr>
<tr>
<td>6</td>
<td>Difference in mechanism of olefin cracking between Brønsted acidic and Gallium-promoted zeolites</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>Cracking of ( n )-heptane over Brønsted acid sites and Lewis acidic Ga sites in ZSM-5 zeolite</td>
<td>109</td>
</tr>
<tr>
<td>8</td>
<td>Cracking of naphtha-range hydrocarbons over Ga promoted zeolites</td>
<td>141</td>
</tr>
<tr>
<td>Summary</td>
<td></td>
<td>153</td>
</tr>
<tr>
<td>Samenvatting</td>
<td></td>
<td>157</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td></td>
<td>163</td>
</tr>
<tr>
<td>List of Publications</td>
<td></td>
<td>165</td>
</tr>
<tr>
<td>About the author</td>
<td></td>
<td>166</td>
</tr>
</tbody>
</table>
1.1 Introduction to Zeolites

Zeolites are crystalline, porous aluminosilicates made up of a linked framework of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ edge sharing tetrahedra. The metal atoms are surrounded by four oxygen anions at the four corners of a tetrahedron; the tetrahedrally coordinated metals being known as T-sites. The tetrahedra (primary building units) form rings of various sizes which are linked to form complex units (secondary building units, SBU). These secondary building units may be assembled in many ways to give a large number of different zeolite structure types. The network of interconnected tetrahedra constitutes the zeolite framework. Zeolite pore architecture is characterized by the dimensionality and size of the channel system, the latter being determined by the number of oxygen atoms in the ring circumscribing in the opening. The rate of diffusion of a molecule through a zeolite will therefore be determined by a combination of the size of the sorbate and the type of zeolite used. According to the pore size, zeolites are classified into (a) small-pore zeolites with eight member-ring pore apertures having free diameters of 3-4.5 Å. (b) medium-pore zeolites with ten member-ring aperture, 4.5-6 Å in free diameter and (c) large-pore zeolites with twelve member-ring apertures, 6-8 Å.

![Figure 1.1 Schematic representation of a Brønsted acid site](image)

The isomorphous substitution of $\text{Si}^{4+}$ by $\text{Al}^{3+}$ or $\text{Ga}^{3+}$ causes a negative excess charge of the framework. This framework anionic charge is compensated by loosely fixed
cations located in the channels. If cations are exchanged by protons, the zeolite acquires considerable Brønsted acidic properties and can be viewed as a solid acid. Altogether, the structural diversity of zeolites discussed above is responsible for a wide range of interesting zeolite properties such as ion-exchange capacity, specific adsorption behavior, catalytic activity due to acidity, shape selectivity caused by size and polarity of molecules, high thermal stability and resistance against solvents, and wide flexibility for adjustments by isomorphous substitution of framework constituents.

Industrial applications of zeolites are discussed in several reviews [1-6]. Zeolites as catalyst components are no longer confined to production of bulk chemicals [2] and to the petroleum refining industry (cracking, hydrocracking, dewaxing, isomerization, alkylation, disproportionation) [3]. A further field of catalytic application is the isomerization of alkylaromatics [4]. Catalytic processes for fine chemical productions and oxidation reactions are amenable to the employment of tuned and novel zeolites [5]. Another prospective area of zeolite application can be seen in environmental catalysis [6], where hazardous substances in exhaust streams are effectively converted in less noxious or harmless substances by the catalytic action of modified zeolites.

1.2 Changing demand of lower olefins

Ethylene and propylene are the two key building blocks of the petrochemical industry. However, ethylene has always reigned supreme, and consequently the industry evolved around steam cracking technology designed to maximize production of ethylene, with propylene and the other building blocks, butadiene and the aromatics, only coming along as the by-products [7]. Steam cracking is a petrochemical process in which saturated hydrocarbons are broken down into smaller, often unsaturated, hydrocarbons. In steam cracking, a gaseous or liquid hydrocarbon feed like naphtha, LPG or ethane is diluted with steam and then briefly heated in a furnace. Typically, the reaction temperature is around 850°C. The process also results in the slow deposition of coke on the reactor walls. This degrades the effectiveness of the reactor. While the overall demand for ethylene is greater than propylene over this timeframe, the rate of growth for propylene has outpaced ethylene’s growth rate (Figure 1.2).

As demand for key propylene derivatives have grown rapidly over the last 10 years and are likely to continue doing so, industry is facing a dilemma: propylene is booming on the demand side, but on the supply side it is referred to a by-product status with its fortunes linked to the ethylene supply/demand situation. Thus, this raises the question of how industry will address this imbalance and ensure adequate propylene
Introduction and scope

supplies into the future. The growing demand for propylene is driven by the high growth rate of polypropylene, acrylonitrile, propylene oxide, cumene/phenol, oxo alcohols, acrylic acid, isopropyl alcohol, oligomers and other miscellaneous intermediates used, in turn, in a wide range of end-use applications including automotive, construction, consumer durables and non-durables, packaging and electronics. Currently, 70% of the world’s propylene is supplied by co-production from ethylene steam cracking, while 30% is supplied as a byproduct in petroleum refining from fluid catalytic cracking (FCC) [8]. The usual method of propylene production, thermal steam cracking, is limited in the amount of propylene it can produce and is unlikely to sustain this new demand.

Figure 1.2 Regional propylene/ethylene demand ratio growth, 1992–2004 [7].

The impending propylene supply/demand gap has stimulated technology developers to improve or tweak conventional technologies to increase the amount of propylene from them or develop whole new ways to make propylene “on-purpose”[7]. Currently, there are five types of on-purpose propylene production available, including propane dehydrogenation, metathesis, olefins cracking and interconversion, high severity FCC and gas-to-olefins [7,9]

1. Propane dehydrogenation: This technology is most economically viable where there is an inexpensive source of propane, since the price of propane feedstock is overwhelmingly the greatest portion of the propylene production costs by this process. In areas that have stranded supplies of propane, particularly with no local heating market, the value of propane can be low enough to easily justify this technology.

2. Metathesis: Metathesis is a general term for a reversible reaction between two olefins, in which the double bonds are broken and then reformed to form new olefin products. In
order to produce propylene by metathesis, a molecule of 2-butene and a molecule of ethylene are combined to form two molecules of propylene. An option also exists that allows for ethylene-to-propylene metathesis (with butene feedstock), in which an ethylene dimerization unit is added to the front end of the process to make butene as an intermediate step.

3. Olefins cracking and interconversion: The olefins-cracking and interconversion technologies include a broad portfolio of technologies that catalytically convert larger olefin molecules (C₄-C₈) into mostly propylene, but usually with some amounts of ethylene by-product.

4. High severity FCC: High severity FCC refers to a group of technologies that effectively utilize traditional FCC technology and feedstocks, but operate at severe conditions (higher catalyst-to-oil ratios, higher steam injection rates, higher temperatures, riser and bed cracking, optimal feed distribution, hydrotreating of gas oil feedstock, and more ZSM-5 addition) in order to maximize the amount of light-end production including ethylene and propylene. A high severity FCC unit is usually fed with paraffinic gas oils and residues, and makes about 20-25 wt% propylene on feedstock, but with even greater volumes of motor gasoline and distillate by-products.

5. Gas-to-olefins: Gas-to-olefins refers to a group of technologies that convert natural gas to methanol, and then convert the methanol to propylene and/or ethylene.

![Figure 1.3 Projected shortfall of propylene from announced projects [10].](image-url)
New options must be considered to meet the future propylene demands because conventional steam cracking technologies may be unable to close the gap between demand and supply. It is expected that at the end of this decade the amount of propylene produced by the above on-purpose technologies will be close enough to start impacting marginal supplies to the market on a more regular basis. As a result, the economics associated with on-purpose propylene will have a greater impact on propylene pricing.

1.3 Acid catalyzed alkane activation

Thermal (non-catalytic) alkane cracking proceeds via free-radical intermediates, giving product distributions different from those of typical acid-catalyzed cracking [11]. Acid catalyzed reactions of hydrocarbons are now generally accepted to involve carbocations. Two types of carbocations are known, carbenium and carbonium ions. The difference between the two species is that in a carbenium ion the charged carbon atom is three-coordinated and in a carbonium ion five-coordinated. According to the classical alkane catalytic cracking mechanism [12,13], a carbenium ion abstracts a hydride from an alkane, forming another carbenium ion, which can undergo transformations such as cracking, skeletal isomerization and alkylation; carbenium ions are chain carriers, the predominant ones being the most stable that can form, usually tertiary ions such as \( \text{-butyl} \) cations. One of the key issues regarding classical cracking has long been the nature of the initiation [14]. Several possibilities have been recognized [15]: (i) olefins, present as impurities in the feed stream, are protonated by the catalyst (ii) olefins are formed in small amounts by thermal cracking and are protonated by the catalyst (iii) Lewis acid sites on the catalyst abstract hydrides from alkanes, generating carbenium ions and (iv) strong proton-donor sites of the catalyst protonate alkanes to make carbonium ions, which collapse to give carbenium ions. Haag and Dessau’s breakthrough was their demonstration [16] of the importance of the latter of these suggestions, which had only scarcely been mentioned [15,17] before 1984 as a realistic possibility.

The Haag and Dessau mechanism [16] based on Olah’s superacid chemistry [18] is a monomolecular mechanism. According to this mechanism, zeolites protonate alkanes at high temperatures forming a pentacoordinated carbonium ion complex. These carbonium ions can easily collapse to produce \( \text{H}_2 \) or small alkanes: methane, ethane, etc. together with carbenium ions. The elected route, protolytic cracking or dehydrogenation, will depend if the proton attacks a C-C bond or a C-H bond of the reacting alkane. Several authors have presented product distribution data confirming the protolytic cracking mechanism [19-23].
Alternatively, carbenium ions can also be formed from alkanes by hydride transfer towards a carbenium ion

\[
\begin{align*}
R - C - R + H^+ & \rightarrow R - C^+ - R \\
R - C - H + R' & \rightarrow R - C^+ + H - C - R'
\end{align*}
\]

(1.2).

Olefin activation over Brönenst acid sites also leads to a tri-cordinate carbenium ion

\[
\begin{align*}
\text{H}_3C - \text{C} = \text{C} - \text{CH}_3 + H^+ & \rightarrow \text{H}_3C - \text{C} - \text{C}^+ - \text{CH}_3 \\
\text{H}_3C - \text{C} = \text{C} - \text{CH}_3 + H^+ & \rightarrow \text{H}_3C - \text{C} - \text{C} - \text{H} + \text{H}_3C - \text{C} - \text{CH}_3
\end{align*}
\]

(1.3).

1.4 Reactions of carbenium ions

Skeletal isomerization reactions are usually classified into two groups, namely Type A isomerization, which changes the position of a side chain but does not alter the number of primary, secondary, tertiary, and quaternary C atoms in the molecule, or type B isomerization, which changes the degree of branching and consequently the number of primary, secondary, tertiary, and quaternary C atoms in the molecule [24,25].

Type A

\[
\begin{align*}
\text{H}_3C - \text{CH} - \text{CH}^+ - \text{CH}_3 & \rightarrow \text{H}_3C - \text{CH} - \text{CH} - \text{CH}_3 \\
\text{H}_3C - \text{CH} - \text{CH}^+ - \text{CH}_3 & \rightarrow \text{H}_3C - \text{CH} - \text{CH} - \text{CH}_3 \\
\text{ring opening} & \rightarrow \text{CH}_3
\end{align*}
\]

(1.4).
Type A isomerization proceeds through cyclization of the alkylcarbenium ion into an intermediate corner protonated cyclopropane structure (CPCP) followed by reopening of the cyclopropane ring [26].

Type B

\[
\begin{align*}
\text{CH}_3\text{CH}^+\text{CH}_2\text{CH}_2\text{CH}_3 & \rightarrow \text{CH}_3\text{HC}^+\text{CH}\text{CH}_3 \rightarrow \text{CH}_3\text{HC}^+\text{CH}_3 \rightarrow \\
\text{H}_3\text{C} & \text{HC}^+\text{CH}_2\text{H} & \text{H}_3\text{C} & \text{HC}^+\text{CH}_2\text{H} & \\
\text{proton} & \text{ring} & \text{opening} & \\
\text{jump} & & & \\
\text{H}_3\text{C} & \text{HC}^-\text{CH}_2\text{CH}_3 & \rightarrow & \text{H}_3\text{C} & \text{HC}^-\text{CH}_2\text{CH}_3 & \rightarrow
\end{align*}
\]

Type B isomerization typically occurs when prior to the opening of the CPCP intermediate a corner-to-corner proton migration occurs [27,28]. In order for a branching to be generated in a linear carbon chain, the proton jump should involve a displacement of the positive charge toward a corner carbon atom free of alkyl substituents. Since the corner-to-corner proton jump occurs over an important energy barrier, rearrangements of type B are always slower than rearrangements of type A [29].

The stability of the carbenium ions increases with their degree of substitution: tertiary > secondary > primary and the higher the stability of the carbenium ions involved in \( \beta \)-scission, the faster the step. Cracking of alkylcarbenium ions proceeds via \( \beta \)-scission [30]. This reaction involves the migration of two electrons of the C–C bond in the \( \beta \) position of the positively charged C atom towards C–C bond in the \( \alpha \) position. Thus, after the scission, this \( \alpha \) C–C bond becomes unsaturated, while the carbon atom, originally in the \( \gamma \) position, ends up as the electron-deficient carbon atom of a smaller alkylcarbenium ion. Five modes of \( \beta \)-scission of secondary and tertiary alkylcarbenium ions are possible [31]. The distinction between the mechanisms is based on the position of the side chains relative to the charged atom (Figure 1.4). Mechanism A involves tertiary alkylcarbenium ions, type B1 and B2 scissions, involve secondary and tertiary alkylcarbenium ions, while mechanism C involves secondary ions only. Mechanism D is very unlikely because it involves the formation of primary ions. The relative rates of \( \beta \)-scission reactions decrease in the order [30,32]

\[
type A >> type B_1, B_2 > type C >> type D
\]
The susceptibility of an alkylcarbenium ion to $\beta$-scission increases with increasing degree of branching.

\[
\begin{align*}
\text{Type} & \quad \text{Mechanism} \\
A & \quad \text{tertiary} \rightarrow \text{tertiary} + \text{alkene} \\
B_1 & \quad \text{secondary} \rightarrow \text{tertiary} + \text{alkene} \\
B_2 & \quad \text{tertiary} \rightarrow \text{secondary} + \text{alkene} \\
C & \quad \text{secondary} \rightarrow \text{secondary} + \text{alkene} \\
D & \quad \text{secondary} \rightarrow \text{primary} + \text{alkene}
\end{align*}
\]

Figure 1.4 $\beta$-scission mechanisms of secondary and tertiary carbenium ions

1.5 Nature of carbocations

\[
\begin{align*}
\text{Si} & \quad \text{O} \\
\text{Al} & \quad \text{O}
\end{align*}
\]

Figure 1.5 Covalently bound ethoxy group. Adapted from [33].
Although carbocations have never been directly observed on the surface of solid acids, it is thought that they exist as (transient) reaction intermediates. The argument for this assumption is that the observed relative rates of hydrocarbon reactions are in agreement with the behavior predicted on the basis of the relative stabilities of the carbocations that would be involved [34]. Until recently it was believed that adsorbed carbocations are short-lived intermediates with properties similar to those of gaseous or solved carbocations. Kazansky was the first to propose that carbocations are not stable intermediates but transition states [35] and that protonated olefins are converted to alkoxides [36]. Contrarily to carbenium ions, there are little differences in stability between primary, secondary and tertiary alkoxides. The generation of alkoxides has been confirmed experimentally by NMR spectroscopy [37-39] and infrared spectroscopy [40]. Due to the development of quantum chemical calculations it became possible to study the interaction of adsorbed carbocations with the surface of catalysts. These calculations have shown [41-45] that protonation of olefins indeed leads to the formation of alkoxides (Figure 1.5). The hydrocarbon reactions proceed via transition states which are energetically excited ion pairs obtained by elongation of the alkoxide C-O bonds, the alkyl pairs resembling carbenium ions in geometry and charge (highly positive).

1.6 Transformation of alkanes over metal substituted zeolites

The introduction of dehydrogenating species into HZSM-5: Pt, Zn, Ga, etc. increases the rate and selectivity of aromatization [46,47]. Under severe alkane aromatization conditions, Zn$^0$ can be formed by reduction with hydrogen or hydrocarbons and eluted from the catalyst, which constitutes a serious drawback for the industrial use of Zn/ZSM-5 catalysts [48]. Supported Pt has a high activity for the dehydrogenation of alkanes. However, dehydrogenation reactions being highly endothermic are thermodynamically favored only at very high temperatures with as a consequence significant problems of deactivation. Also Pt is an active hydrogenolysis catalyst, while Ga is assumed to exhibit moderate or low activity in hydrogenolysis [20,49,50]. The Cyclar process from UOP and BP using bifunctional Ga/HZSM-5 catalysts [51-53] transforms liquefied petroleum gas (LPG) into BTX hydrocarbons (benzene, toluene, xylenes) with simultaneous formation of a large amount of hydrogen which is also a valuable product. LPG consists mainly of the propane and butane fraction recovered from gas and oil fields and petroleum refining operations. The major reaction steps are paraffin dehydrogenation followed by oligomerization and cyclization. The olefin formation via dehydrogenation and cracking is the rate-controlling step in the aromatization scheme. The relatively low value and abundance of LPG makes it an ideal feedstock for petrochemical applications. This has incited many academic teams to investigate the aromatization of light alkanes especially propane over Ga/HZSM-5 catalysts.
Another reason is the complexity of both the reaction scheme and catalyst system [54]. Despite considerable research efforts in the area of Ga-containing zeolites [55-62], the exact role of gallium in this mechanism has not been totally elucidated yet, with proposals for its role as dehydrogenation function in a pure bifunctional [21,55-57] or concerted mechanism [20] and as a promoter to recombinitive hydrogen removal during alkane dehydrogenation on Brønsted acid sites [58-61] receiving most attention. Determining the precise role of Ga in these reaction steps has proven difficult mainly because the nature of the active Ga species remains unclear. This is essentially due to the large differences in composition of the Ga samples which were used in the investigations: presence of different Ga species with different adsorption and catalytic properties, very low to high concentration of protonic sites, etc., as well as significant modifications of the catalysts which occur frequently under pre-treatment and reaction conditions.

Various preparation methods have been described by which extra-framework gallium can be incorporated into the micropores of HZSM-5: ion-exchange in aqueous solution [62] impregnation [63], chemical vapor deposition (CVD) of GaCl₃ [48] and by physical admixture of Ga₂O₃ [64]. Aqueous ion-exchange mostly results in the presence of gallium oxide particles on the external surface because of the large size of the hydrated Ga³⁺ cation, while washing of gallium-containing zeolites prepared by vapor deposition of GaCl₃ also does not lead to a high Ga dispersion. Reduction in molecular hydrogen at high temperature results in a high mobility of gallium oxide, presumably via Ga₂O₃, leading to a protolysis reaction with the Brønsted acid sites to give reduced cationic species. Such major modifications in the physicochemical properties of the catalyst during the pretreatment and even during the reaction make it difficult to identify the actual active Ga sites.

\[
\text{Ga}_2\text{O}_3 + 2 \text{H}_2 \rightarrow \text{Ga}_2\text{O} + 2 \text{H}_2\text{O} \\
2 \text{ZO}^-\text{H}^+ + \text{Ga}_2\text{O} \rightarrow 2 \text{ZO}^-\text{Ga}^+ + \text{H}_2\text{O}
\]

(1.7)

(1.8)

In this work a systematic approach will be taken for the preparation of Ga/HZSM-5 by chemical vapor deposition of trimethylgallium (TMG) on HZSM-5 with subsequent removal of the methyl groups by treatment with hydrogen or oxygen [65,66]. The reductive route is the preferred one resulting in well-defined gallium dispersion, because oxidation of the methyl groups leads to water formation and hydrolysis of cationic Ga species [67]. The main objective was to improve the understanding of these model Ga/HZSM-5 catalysts with perfectly specified physicochemical characteristics towards hydrocarbon conversions.
1.7 Scope of thesis

Alkane conversion over gallium-containing zeolites proceeds via a complex reaction scheme involving dehydrogenation, cracking, oligomerization and ring-closure steps to arrive at a mixture of olefins and aromatics. Detailed insight into the elementary reaction steps is limited, mainly because of the difficulty in the preparation of well-defined catalytic materials. The complexity of these catalysts is further increased due to changes in the nature of the active Ga species as a function of the reaction conditions.

The main goal of this thesis is to develop a deeper understanding of hydrocarbon activation over Ga-containing zeolites. The approach is to study the various reaction steps over well-defined catalytic reaction sites. For the case of Ga cations in zeolites, such well-defined reaction sites can be prepared by the complete anhydrous chemical vapor deposition of trimethylgallium (TMG) over protonic zeolites. For instance, the complete substitution of Brønsted acid sites by Ga cations in HZSM-5 offers possibilities for direct comparison of Ga species in charge-compensating positions and Brønsted acid sites for the conversion of hydrocarbons.

The preparation of well-defined model HZSM-5 catalysts with charge-compensating \( \text{Ga}^+ \), \( \text{GaH}_2^+ \) and \( \text{GaO}^+ \) species is discussed in chapter 2. To follow the preparation in detail, the evolution of the organometallic precursor is carefully followed by FTIR and XANES at the Ga K-edge. Infrared spectroscopy of adsorbed carbon monoxide was used to probe the various Ga species.

Chapter 3 addresses the role of the various cationic Ga species (\( \text{Ga}^+ \), \( \text{GaH}_2^+ \) and \( \text{GaO}^+ \)) for the dehydrogenation of small-chain alkanes. A large difference exists in the dehydrogenation activity between Brønsted acid sites and Lewis acidic Ga sites. The former mainly catalyze C-C cracking reactions and to a lesser extent dehydrogenation, whereas the latter exhibit a strong preference for C-H activation. The regeneration of Brønsted acid sites during heterolytic dissociative adsorption of alkane over bivalent Zn cations results in high activity but suffers from coking deactivation and secondary aromatization reactions. Chapter 4 reports the stabilization of \( \text{Ga}^{3+} \) ions by \textit{in situ} addition of steam leading to improvement in the rate of propane dehydrogenation over Ga/HZSM-5. This improvement in activity is proposed to be due to the formation of oxygen-bridged Ga dimers.

Chapter 5 and 6 examine the cracking behavior of olefins over protonic and well-defined Ga cations in zeolites. The main reason is the relevance of olefin cracking as an important reaction step in the conversion of alkanes over Ga/HZSM-5 zeolites. The
influence of the acidity, pore size and topology of the zeolite on the nature of cracking are discussed. While olefin cracking over Brønsted acid sites occurs via carbenium ion chemistry, the proposal for activation of olefins on Lewis acidic Ga sites involves carbanion intermediates.

The knowledge from these model systems is utilized to understand in detail the cracking behavior of naphtha-range hydrocarbons in chapters 7 and 8. Chapter 7 discusses the influence of the preparation and pretreatment of Ga/HZSM-5 catalysts on the product selectivity for cracking of \textit{n}-heptane. Cracking of naphtha-range hydrocarbons is further studied over Ga zeolites of variable pore nature and acid site density in chapter 8.

1.8 References

Chapter 2

Characterization of Ga substituted zeolites prepared by chemical vapor deposition of trimethylgallium

The reduction of Ga(CH$_3$)$_3$/HZSM-5 was carefully followed by FTIR and Ga K edge XANES spectroscopic measurements. The chemical vapor deposition of trimethylgallium on HZSM-5 (TMG/HZSM-5) resulted in the replacement of nearly all Brønsted acid sites by dimethylgallium species. Subsequent reduction leads to the removal of the methyl ligands from the cationic Ga clusters giving charge-compensating Ga$^+$ and GaH$_2^+$ species. At high temperatures and in the absence of hydrogen, Ga$^+$ species are most stable although the decomposition of GaH$_2^+$ species is very slow. Direct oxidation of the dimethylgallium/HZSM-5 precursor leads to various forms of gallium oxide species and regeneration of Brønsted acid sites. Oxidation of the reduced Ga$^-$ species yields predominantly GaO$^+$ species.
2.1 Introduction

The structure of the active intrazeolite Ga species and their reactivity under oxidative and reductive conditions has not been fully resolved yet, owing to the wide variety of possible structures. Gallium may be present as gallium oxide, in aggregated form on the external zeolite surface or as small particles in the zeolite micropore space, or in cationic form as oxidic GaO\(^+\) or reduced Ga\(^+\) or GaH\(_2\)\(^+\) species. Most preparation methods (ion-exchange, impregnation, physical admixture and chemical vapor deposition of GaCl\(_3\) \([1-5]\) often lead to the presence of a variety of species. Aqueous ion-exchange mostly results in the presence of gallium oxide particles on the external surface because of the large size of the hydrated Ga\(^3+\) cation, while washing of gallium-containing zeolites prepared by vapor deposition of GaCl\(_3\) also does not lead to a high Ga dispersion. Reduction in molecular hydrogen at high temperature results in a high mobility of gallium oxide, presumably via Ga\(_2\)O, leading to a protolysis reaction with the Brønsted acid sites to give reduced cationic species. The difficulties of characterization of the active species are amplified taking into account the high reactivity of reduced Ga species. For instance, a detailed \textit{in situ} x-ray absorption study of the group of Iglesia \([6]\) revealed the oxidation of reduced Ga species in zeolites (Ga\(^+\)) to Ga\(^3+\) ions, upon cooling in hydrogen. This oxidation was believed to be caused by the enhanced interaction of Ga cations with zeolite framework oxygen atoms.

In order to prepare better-defined Ga species in medium-pore zeolites we address a completely anhydrous route for the preparation of Ga/HZSM-5 consisting of chemical vapor deposition of trimethylgallium (TMG) with subsequent removal of the methyl groups by treatment with hydrogen or oxygen \([7-11]\). The reductive route is the preferred one resulting in better gallium dispersion, because oxidation of the methyl groups leads to water formation and hydrolysis of cationic Ga species. Nevertheless, we also address the oxidation of the zeolite-occluded gallium alkyl species. The chemical nature of reduced and oxidized species was followed by FTIR and XANES spectroscopy at the Ga K edge. Infrared spectroscopy of adsorbed carbon monoxide was employed in an attempt to probe the various Ga species.

2.2 Experimental

Preparation of materials

\(\text{NH}_4\text{ZSM-5}\) (Akzo Nobel, Si/Al \(=20\)) was calcined in a mixture of 20 vol.\% oxygen in nitrogen at a flow rate of 100 Nml/min whilst heating to 823 K at a heating rate
Characterization of Ga substituted zeolites.

of 2 K/min followed by an isothermal period of 4 h to obtain HZSM-5. TMG/HZSM-5 was prepared by chemical vapor deposition of trimethylgallium (TMG, Strem Chemicals, purity > 99%) on dehydrated HZSM-5. To a glass vessel containing dehydrated HZSM-5, 1 ml of TMG was added in an Ar-flushed glove box. After 24 h, the resulting material was evacuated for 2 h in order to remove excess trimethylgallium. The material was kept in argon atmosphere prior to XANES and NMR characterization. The gallium loading was found to be 7.6 wt% by ICP analysis with Ga/Al molar ratio of 1.4. This material when reduced leads to gallium loading of 4.8 wt% with Ga/Al molar ratio of 0.94.

Characterization

Infrared spectra were recorded on a Bruker IFS113v Fourier Transform IR spectrometer with a DTGS detector at a resolution of 2 cm\(^{-1}\). HZSM-5 zeolite was pressed into a self-supporting wafer of about 12 mg and placed in a controlled-environment transmission cell (KRS-5 windows). Prior to recording spectra, the zeolite was dehydrated in a flow of oxygen whilst heating from room temperature to 823 K at a rate of 5 K/min (isothermal period of 15 min at 373 K). After an isothermal period of 1 h at 823 K, the sample was cooled to room temperature in vacuum.

The dehydrated zeolite was exposed to trimethylgallium at a total pressure of 40 mbar for prolonged time. After extensive evacuation, the material was reduced in a mixture of 20 vol.% hydrogen in nitrogen at a flow rate of 5 Nml/min followed by heating to 823 K at a rate of 5 K/min. The resulting material is denoted as TMG/HZSM-5(red). TMG/HZSM-5(red) was further cooled to room temperature either in vacuum or in a mixture of nitrogen and hydrogen. TMG/HZSM-5(red) was also oxidized by exposing the evacuated sample to 50 mbar nitrous oxide at various temperatures. The resulting catalysts are denoted as TMG/HZSM-5(red,ox,T) where T refers to the oxidation temperature. Infrared spectra of adsorbed CO were recorded after cooling the cell with liquid nitrogen. In this way, a constant temperature of 90 K could be maintained. Infrared spectra were measured as a function of CO pressure in a decreasing manner from 40 to 0.05 mbar.

\(^{27}\text{Al}\) MAS NMR measurements were carried out on a Bruker DMX500 spectrometer operating at 130.3 MHz. The sample was rotated in a 4 mm rotor with a spin rate of 12.5 kHz. Single-pulse excitation was used with a 30 degree pulse of 1.5 μs. Thousand scans were accumulated with a time resolution of 5 μs (100 kHz spectral width) and interscan delay of 1 s. A solution of Al(NO\(_3\))\(_3\) was used for shift calibration.
Ga K edge XAS measurements were performed at beamline 17C of the European Synchrotron Radiation facility in Grenoble (ESRF, France). The electron energy and ring current were 2.0 GeV and 200 mA. XANES spectra were recorded with energy steps of 0.5 eV in the XANES region. An amount of catalyst was pressed into a self-supporting wafer calculated to have an absorbance $\mu x$ of 2.5 and placed in a controlled-environment transmission cell. TMG/HZSM-5(red) was obtained by reduction of TMG/HZSM-5 in a flow of 100 Nml/min (20 vol.% hydrogen in nitrogen) at a heating rate of 4 K/min to 793 K. TMG/HZSM-5(red) was further cooled in inert atmosphere in a flow of 100 Nml/min nitrogen at a rate of 4 K/min to 473 K. During these steps, near edge spectra were recorded at regular intervals. Thereafter, TMG/HZSM-5(red,ox) was obtained by exposure of TMG/HZSM-5(red) to a mixture of 30 Nml/min $\text{N}_2\text{O}$ and 10 Nml/min nitrogen for 30 min at 673 K and 473 K.

### 2.3 Results and Discussion

#### Preparation of TMG/HZSM-5

Figure 2.1(a-d) shows the evolution of infrared spectra upon *in situ* exposure of dehydrated HZSM-5 to trimethylgallium vapor. Three bands due to hydroxyl stretching vibrations were identified for the dehydrated parent HZSM-5 zeolite. These bands are assigned to Bronsted acid sites ($3612 \text{ cm}^{-1}$), hydroxyl groups coordinating to extralattice Al ($3664 \text{ cm}^{-1}$) and terminal silanol groups ($3744 \text{ cm}^{-1}$). During exposure to trimethylgallium at room temperature a pronounced decrease of the band belonging to the external silanol groups is observed with time of exposure. On the other hand, the band related to the bridging hydroxyl groups (Bronsted acid sites) decreases considerably slower. The infrared results indicate that the hydroxyl groups of the extra-framework aluminum species also react with trimethylgallium. After prolonged exposure to trimethylgallium, almost all Brønsted acid sites of the zeolite have been replaced. During the vapor deposition, strong bands around 2911 and $3000 \text{ cm}^{-1}$ are observed that mainly arise from the asymmetric C-H stretching vibrations of the methyl groups of gaseous trimethylgallium. The following reactions between trimethylgallium and the hydroxyl groups of the zeolite are proposed [8,10]
Figure 2.1 Room-temperature FTIR spectra of HZSM-5 after (a) calcination in oxygen at 823 K and (b) exposed to 40 mbar Ga(CH$_3$)$_3$ vapor for (b) 1 min, (c) 60 min and (d) 100 min.

\[
\begin{align*}
ZO^-...H^+ + Ga(CH_3)_3 & \rightarrow ZO^-[Ga(CH_3)_2]^+ + CH_4 \\
Si-OH + Ga(CH_3)_3 & \rightarrow Si-O-Ga(CH_3)_2 + CH_4 \\
Al-OH + Ga(CH_3)_3 & \rightarrow Al-O-Ga(CH_3)_2 + CH_4
\end{align*}
\] (2.1)

The relative ease with which the silanol groups react with the trimethylgallium vapor derives from their location at the external zeolite surface. The interaction of the intrazeolite hydroxyl groups requires diffusion of trimethylgallium into the micropore space. Clearly, this diffusion limits the reaction rate of the internal hydroxyl groups with trimethylgallium. However, in contrast to the incomplete exchange in acidic mordenite attributed to blockage of the one-dimensional pores [9], the higher dimensionality of the MFI pore system leads to nearly complete replacement of the Bronsted acid sites. A very small amount of Bronsted acid sites remains, most likely because they are located in sites blocked by surrounding chemisorbed dimethylgallium species. The structural analysis by EXAFS [7] has shown the Ga-C bond distance of $R = 1.95$ Å. It was also suggested that the Ga-alkyl species binds more strongly to one of the oxygen atoms ($R = 1.82$ Å) while a weaker bond with the other surrounding oxygen atoms may not be detected by EXAFS.
Reduction of TMG/HZSM-5

Figure 2.2 Room-temperature FTIR spectra of TMG/HZSM-5 during subsequent reduction at (a) 473 K, (b) 573 K, (c) 673 K and (d) 823 K.

Figure 2.2(a-d) collects the infrared spectra of the temperature-programmed reduction of TMG/HZSM-5. Prior to reduction, excess trimethylgallium was evacuated and the strong stretching vibrations of the methyl groups associated with gas-phase trimethylgallium largely vanished. Instead, weak bands at 2913 and 2970 cm\(^{-1}\) remain which belong to C-H stretching vibrations of the methyl groups of adsorbed dimethyl gallium species [12]. These bands are eliminated during reduction around 673 K. Reduction of TMG/HZSM-5 results in the further disappearance of the small remaining number of Brønsted acid sites. This decrease in Brønsted acidity goes with the reappearance of a significant part of the silanol groups. This points to diffusion of reduced Ga species, initially bonded to silanol groups on the external surface, to the cationic exchange sites located in the micropores. Apparently, reduced Ga species are more stable on the intrazeolite cation-exchange sites than on silanol groups. Indeed, earlier DFT calculations have shown that the cationic exchange site of zeolites is the preferred position of Ga clusters [9].
Figure 2.3 Production of methane (left) and carbon dioxide (right) as a function of temperature in hydrogen (full line) or oxygen (dashed line). The inset shows the hydrogen production during oxidation.

The reduction process is further monitored by a separate temperature programmed reduction experiment. Figure 2.3 shows the evolution of methane as a function of temperature. We observe a small feature around 400 K which we tentatively attribute to some further reaction of physisorbed trimethylgallium with remaining hydroxyl groups. A main production peak of methane with a maximum at 673 K is also observed. Methane production already starts around 600 K. Moreover, we observed the production of very small amounts of ethane, propane and carbon dioxide (alkanes typically two orders of magnitude lower than the amount of methane, carbon dioxide three orders of magnitude lower) during the reductive decomposition of the precursor.

Upon oxidation, mainly carbon dioxide and water is produced around 773 K with small amounts of hydrocarbons, mostly ethane, and hydrogen being released at lower temperatures. This suggests that the alkyl groups eliminate as hydrocarbons and can be dehydrogenated giving hydrogen and coke depositions that are burned at higher temperatures. The coke deposition is confirmed by the observation that the material has turned black below 773 K. The subsequent oxidation of this coke deposit results in the formation of carbon dioxide and water. This also provides an explanation for the higher amount of extraframework Al species derived from the higher intensity of the resonance around 0 ppm for oxidized TMG/HZSM-5 compared to the reduced precursor in the $^{27}$Al NMR spectra (Figure 2.4). We also observe that the vapor deposition of trimethylgallium
only leads to a small degree of dealumination but that subsequent activation and most prominently oxidation increases the amount of octahedral Al species. The reduced catalyst also has some distorted (penta-coordinated) Al species between the sharper resonances at 54 and 0 ppm. This could be due to close interaction with reduced Ga species. One has to be careful with the interpretation of these $^{27}$Al NMR spectra because they were recorded after re-exposure to air. This will particularly affect the as-synthesized and reduced catalysts. This could also explain the larger difference in dealumination degree as derived from infrared spectroscopy compared to $^{27}$Al NMR.

Given the high silica content, we assume that the majority of Ga species are present as mononuclear Ga species and that the following reactions may occur during the reduction with molecular hydrogen.
Characterization of Ga substituted zeolites....

\[
\begin{align*}
ZO^-...[\text{Ga(CH}_3_2]^+ + H_2 & \rightarrow ZO^-...\text{Ga}^+ + 2 \text{CH}_4 \quad (2.4) \\
ZO^-...[\text{Ga(CH}_3_2]^+ + 2 H_2 & \rightarrow ZO^-...[\text{GaH}_2]^+ + 2 \text{CH}_4 \quad (2.5).
\end{align*}
\]

Gallium may thus compensate the framework charge as monovalent Ga\(^+\) ions or as trivalent gallium hydride species. Whereas the compensation of the negative framework charge by monovalent gallium has been proposed earlier [3], only recently evidence for the occurrence of gallium hydrides has been found by a detailed diffuse reflectance infrared spectroscopic study [8]. Accordingly, we recorded infrared spectra during cooling of TMG/HZSM-5(red) from 823 K to room temperature (a) in vacuum and (b) in a mixture of hydrogen and nitrogen. The subsequent spectra from which the spectrum of original dehydrated HZSM-5 (Figure 2.1(a)) has been subtracted are shown in Figure 2.5. We observe two bands at 2046 and 2060 cm\(^{-1}\) upon cooling in reductive atmosphere. These bands are not obtained when the sample is cooled in vacuum. This is in line again with work of Kazansky et al. [8] who found that hydrogen oxidatively adds to monovalent Ga\(^+\) ions in reduced Ga/HZSM-5 prepared by incipient wetness impregnation. Such gallium dihydride species form at temperatures below 723 K in hydrogen atmosphere.

Gallium hydride species are relatively stable and only decompose above 723 K. They are only completely eliminated in vacuum at such temperatures [8]. In agreement with this, quantum-chemical calculations of Bell and co-workers [13] predict a high activation barrier for the desorption of hydrogen from GaH\(_2^+\) \((E_{\text{act}} = 74 \text{ kcal/mol at } 800 \text{ K})\)

\[
ZO^-...[\text{GaH}_2]^+ \quad \Rightarrow \quad ZO^-...\text{Ga}^+ + H_2 \quad (2.6).
\]

It is thus likely that [GaH\(_2\)]\(^+\) species formed via Eq. (2.5) only decompose partially in the reductive hydrogen atmosphere at elevated temperatures.

Further ground for the assignment of these bands to gallium hydrides was provided by exposure to deuterium. To this end, we cooled a TMG/HZSM-5(red) catalyst from 823 K to room temperature in molecular deuterium (Figure 2.5(c)). Two peaks at 1437 and 1480 cm\(^{-1}\) were observed. The ratios of the corresponding Ga-H and Ga-D frequencies were found to be approximately 1.42 and 1.39 for the low and the high frequency peak, thus providing further evidence for the occurrence of gallium-hydrides and gallium-deuterides.
Figure 2.5 Room-temperature FTIR spectra of TMG/HZSM-5 (red) during subsequent cooling in (a) vacuum, (b) \(N_2/H_2\) mixture and (c) \(D_2\) after subtraction of dehydrated HZSM-5 spectra (Figure 2.1 (a))

Figure 2.6 FTIR spectra of calcined HZSM-5 at liquid nitrogen temperature after CO adsorption at pressures of 40, 20, 10, 5, 2, 1, 0.5 and 0.05 mbar. The spectra were recorded from high to low CO pressure. The inset shows the FTIR spectrum of hydroxyl region of dried HZSM-5 at room temperature.
Complementary characterization was carried out by infrared spectroscopy of adsorbed CO. Infrared spectra of CO adsorbed on dehydrated HZSM-5 zeolite as a function of the CO pressure are presented in Figure 2.6. Two prominent bands at 2139 cm\(^{-1}\) and 2173 cm\(^{-1}\) are assigned to physically adsorbed CO in the zeolite micropores [14] and CO adsorbed on Brønsted acid sites [15], respectively. The less pronounced decrease of the latter peak with decreasing CO pressure is in line with the stronger perturbation of the CO stretching vibration due to the stronger interaction with the zeolite protons. In addition to these two main features, two smaller ones are visible around 2090 cm\(^{-1}\) and 2153 cm\(^{-1}\). The band at 2090 cm\(^{-1}\) is from CO in interaction with Brønsted acid sites through the oxygen atom of carbon monoxide. The weak shoulder around 2153 cm\(^{-1}\) has earlier been assigned to CO adsorbed on Si-OH species [16].

Figure 2.7 FTIR spectra of TMG/HZSM-5(red) cooled from 823 K in vacuum at liquid nitrogen temperature after CO adsorption at pressures of 40, 20, 10, 5, 2, 1, 0.5 and 0.05 mbar. The spectra were recorded from high to low CO pressure. The inset shows the FTIR spectrum of hydroxyl region of TMG/HZSM-5(red) at room temperature.

Figure 2.7 shows infrared spectra at various CO pressures on TMG/HZSM-5(red) cooled in vacuum. Compared to the corresponding spectra of the gallium-free parent material, a strong feature is present at 2147 cm\(^{-1}\). The position of this band has been recently assigned to CO coordinating to monovalent Ga\(^+\) species [8]. These species are thought to replace the charge-compensating protons of the original HZSM-5 zeolite. In
accordance with this view, the band due to carbon monoxide coordinating to the bridging hydroxyl groups around 2173 cm$^{-1}$ completely vanished. The assignment of the vibrational band at 2147 cm$^{-1}$ to CO coordinating to low valence Ga species implies that CO is only weakly coordinating to Ga$^+$. The relatively strong decrease of the intensity with CO pressure compared to that of the band assigned to CO on bridging hydroxyl groups is in line with this interpretation. The band at 2167 cm$^{-1}$ most likely relates to CO coordinating to a small fraction of [Ga$^{3+}$(H$^-$)(OH$^-$)]$^+$ species [8]. These species are formed upon hydration of Ga$^+$ species via residual water molecules according to:

\[ \text{ZO}^- \cdot \text{Ga}^+ + \text{H}_2\text{O} \rightarrow \text{ZO}^- \cdot \text{[Ga(H$^-$)(OH$^-$)]}^+ \]

(2.7).

The band around 3680 cm$^{-1}$ in the hydroxyl region relates to Ga-OH species [17]. Its relative weakness suggests that the number of such species is relatively low.

Figure 2.8 Ga K edge XANES spectra of TMG/HZSM-5 during reduction from 373 K to 793 K.

In situ x-ray absorption near-edge spectroscopy (XANES) at the Ga K edge was performed during the reduction of TMG/HZSM-5. To protect the sample from exposure to moisture or oxygen, TMG/HZSM-5 prepared at the home laboratory was transported in a glass ampoule under protective atmosphere to the synchrotron facility. The sample was transferred into a controlled-environment transmission cell in an Ar-flushed glove.
box. Figure 2.8 displays the evolution of the XANES spectra during reduction of TMG/HZSM-5 from room temperature to 793 K in a mixture of nitrogen and hydrogen. At low temperatures, an edge position of about 10373 eV is observed which corresponds to dimethylgallium species [7]. Pronounced changes of the XANES region are observed between 573 and 673 K. The main absorption feature shifts to higher energies, while a shoulder at lower energy becomes visible at 673 K. A further increase in reduction temperature leads to a strong growth of the feature with a maximum at 10371.5 eV. This latter edge is due to monovalent Ga$^+$ species [6,7] that exhibit a somewhat higher absorption maximum than Ga metal [6].

The data suggest that between 573 K and 673 K the methyl ligands of the dimethylgallium species are removed and mainly [GaH$_2$]$^+$ species are formed with a higher absorption maximum. At more elevated temperatures, the spectra contain an increasingly larger contribution of Ga$^+$ species that are most likely formed by partial decomposition of the gallium dihydride species. The removal of hydrogen is indeed a slow process [8] and requires evacuation or purging in He for a prolonged period at high temperature. Hence, we surmise that the XANES spectrum after reduction at 793 K for 1 h points to a mixture of GaH$_2^+$ and Ga$^+$ species. Meitzner et al. [6] argued that the strong interaction of Ga$^+$ with the framework oxygen atoms stabilize these cationic species against further reduction to Ga$^0$.

Figure 2.9 displays the XANES spectra for TMG/HZSM-5(red) cooled from 793 K in reduction atmosphere. Clearly, the maximum belonging to Ga$^+$ species slowly vanishes with decreasing temperature concomitant with an increase of the feature around 10377 eV. The Ga K edge shifts to 10374.5 eV. We attribute these changes to the oxidative addition of H$_2$ to Ga$^+$ to form GaH$_2^+$ (Ga$^{3+}$) species by the reverse reaction of Eq. (2.6). Formerly, this was attributed by Meitzner et al. [6] to an increased interaction of the Ga species with the zeolite framework oxygen atoms.
Oxidation of TMG/HZSM-5(red)

Reduced samples were oxidized by nitrous oxide in order to prevent extensive oxidation, leading to the removal of cationic Ga species from the zeolite exchange sites [10]. Infrared spectra of TMG/HZSM-5(red) oxidized at different temperatures by nitrous oxide are depicted in Figure 2.10. The corresponding CO absorption spectra for TMG/HZSM-5(red,ox,473) and TMG/HZSM-5(red,ox,673) are shown in Figure 2.11. The infrared spectrum of TMG/HZSM-5(red,ox,473) does not show evidence for the regeneration of Brønsted acid sites. Kazansky et al. [10] have shown by volumetric titration that the ratio of converted nitrous oxide and Ga atoms is close to unity. These observations can be explained by the oxidation of univalent Ga$^+$ ions via

$$\text{ZO}^-...\text{Ga}^+ + \text{N}_2\text{O} \rightarrow \text{ZO}^-...[\text{GaO}]^+ + \text{N}_2$$  \hspace{1cm} (2.8).

The above reaction was followed by mass spectrometer wherein TMG/HZSM-5(red) after prolonged treatment in helium for 1 h at 823 K was exposed to nitrous oxide at 473 K. No molecular oxygen was evolved during the decomposition of nitrous oxide. Thus it is inferred that oxidized extraframework Ga species consume one oxygen atom
per Ga ion. Since also no regeneration of Brønsted acid sites is observed, the simplest model for Ga sites is GaO$^+$ ions.

![Figure 2.10 Room-temperature FTIR spectra of (a) HZSM-5 after calcination in oxygen at 823 K and TMG/HZSM-5(red,ox) after N$_2$O exposure at increasing temperature (b) 473 K, (c) 573 K and (d) 673 K.](image)

In the infrared spectrum of adsorbed carbon monoxide on TMG/HZSM-5(red,ox,473) the band due to CO adsorbed on univalent Ga$^+$ species around 2147 cm$^{-1}$ has almost completely disappeared. A small portion of Ga$^+$ species persists after low temperature oxidation. The presence of reduced Ga species is also indicated by the observation of a band at 2167 cm$^{-1}$ related to CO on extra-framework GaOH species [8]. We surmise that these GaOH species derive from oxidation of some remaining GaH$_2^+$ species according to

$$\text{ZO}^...\text{GaH}_2^+ + \text{N}_2\text{O} \rightarrow \text{ZO}^...[\text{Ga}^+\text{(OH)}^\text{–}]^+ + \text{N}_2$$ (2.9).

The low intensity of this band suggests that the extent of Eq. (2.9) is small. When the temperature of oxidation is increased to 573 K (Figure 2.10(c)), regeneration of bridging hydroxyl groups takes place as evidenced by the reappearance of the band around 3612 cm$^{-1}$. Also the band of gallium hydroxide species increases somewhat. The regeneration of Brønsted acid sites is more pronounced in TMG/HZSM-5(red,ox,673). Concomitantly, the band due to Ga-OH species decreases after oxidation at 673 K.
Figure 2.11 FTIR spectra taken at liquid nitrogen temperature after CO adsorption of (a) TMG/HZSM-5(red,ox,473) and (b) TMG/HZSM-5(red,ox,673).

Tentatively, we attribute this regeneration of Brønsted acidity to the following reaction

\[
2 \text{ZO}^-\cdot[\text{Ga(H}^\text{-})(\text{OH}^\text{-})]^+ + 2 \text{N}_2\text{O} \rightarrow 2 \text{ZO}^-\cdot\text{H}^+ + \text{Ga}_2\text{O}_3 + 2 \text{N}_2 + \text{H}_2\text{O} \quad (2.10).
\]
The more heterogeneous Ga speciation after high-temperature oxidation is confirmed by the infrared spectrum of adsorbed CO in Figure 2.11 (b). While the band of CO adsorbed on monovalent Ga$^+$ species has completely vanished, the spectrum contains vibrational bands of CO adsorbed to Bronsted acid sites (2173 cm$^{-1}$) and exposed Ga$^{3+}$ sites in gallium oxide microphases (2235 cm$^{-1}$) [14]. A small amount of the latter species was also present in TMG/HZSM-5(red,ox,473).

![Graph](image.png)

*Figure 2.12 Ga K edge XANES spectra of (a) TMG/HZSM-5(red) at 793 K, (b) TMG/HZSM-5(red,ox,673) and (c) TMG/HZSM-5(red,ox,473).*

No evidence was found for carbon monoxide absorption to charge-compensating GaO$^+$ species. Therefore, it appears that these species are not amenable to experimental observation by infrared spectroscopy of adsorbed CO. This is in line with recent quantum-chemical calculations describing the interaction of CO with various gallium-oxo clusters, which indicate a very weak interaction between CO and GaO$^+$ species [18]. Figure 2.12 shows the XANES spectra upon oxidation of reduced TMG/HZSM-5 by nitrous oxide at 473 K and 673 K. Clearly, there is a pronounced shift of the Ga K edge to higher binding energies. The change is due to oxidation of the Ga$^+$ to Ga$^{3+}$ species.

In contrast, a direct oxidative treatment at 823 K on as-synthesized TMG/HZSM-5 (Figure 2.13(c)) results in considerable regeneration of Bronsted acid sites. The regeneration of about 60% of the original amount of bridging hydroxyl groups
indicates that a considerable amount of the gallium species has been transformed into neutral gallium oxide species occluded in the zeolite micropores as small or on the external surface as larger aggregates.

Moreover, we note that the band related to hydroxyl groups coordinating to extraframework Al species has increased considerably and is higher than in the original material. This points to extensive dealumination during the oxidative treatment deriving from steaming effects by water at elevated temperatures produced by oxidation of hydrocarbons or hydrocarbon residue. The band also appears to be broader which might relate to the occurrence of hydroxyl groups coordinating to extraframework Ga ions that give rise to a vibrational band around 3680 cm$^{-1}$. The IR spectrum of the reduced material shows no regeneration of the acid sites suggesting that all exchange sites are occupied by reduced Ga species (Ga$^+$ or GaH$_2^+$). The middle spectrum (Figure 2.13(b)) is the one of a catalyst that was oxidized at 823 K after reduction of TMG/HZSM-5. The spectrum resembles that of oxidized TMG/HZSM-5 precursor albeit that the extent of regeneration of Brønsted acid sites amounts to about 15% which is considerably lower than after direct oxidation. This indicates that the latter sample predominantly contains [GaO]$^+$ species. One also observes a band due to OH groups on extraframework Ga species which could mean that part of the charge-compensating ions are present in the form of Ga(OH)$_{2}^{2+}$ species.

Figure 2.13 Room-temperature FTIR spectra of TMG/HZSM-5 after (a) reduction at 823 K, (b) reduction at 823 K followed by oxidation at 823 K and (c) oxidation at 823 K.
2.4 Conclusions

Well-defined cationic Ga species can be prepared from a HZSM-5 precursor that was reacted with trimethylgallium. The methyl ligands of the resulting cationic Ga(CH$_3$)$_2^+$ species can be removed by reduction in hydrogen, resulting in Ga$^+$ and GaH$_2^+$ species that compensate the negative zeolite framework charge. At elevated temperatures, Ga$^+$ and GaH$_2^+$ species co-exist in a hydrogen atmosphere, whereas the latter ones are slowly decomposed to Ga$^+$ species only at high temperature in the absence of hydrogen. Oxidation by nitrous oxide at a temperature of 473 K oxidizes Ga$^+$ to GaO$^+$ species. The presence of minor amounts of GaH$_2^+$ species which were not eliminated during pretreatment results in the formation of [Ga$^{3+}$(H$^-$)(OH$^-$)]$. Oxidation of such species at more elevated temperatures leads to clustered gallium-oxide particles and regeneration of Brønsted acid sites.

2.5 References

18. G. M. Zhidomirov, personal communication.
Chapter 3

Activation of short-chain alkanes over Ga cations in ZSM-5 zeolite

A detailed comparison of the reactivity of Brønsted acid sites (HZSM-5) and Ga\(^+\) ions (reduced TMG/HZSM-5) in propane dehydrogenation shows that the former convert propane via protolytic cracking with methane, ethylene and propylene as hydrocarbon products, whereas monovalent Ga\(^+\) ions almost exclusively produce propylene. The reaction data suggest that propane is converted over Ga\(^+\) and not over GaH\(_2\)\(^+\) species. The initial rate of propane dehydrogenation is highest for GaO\(^+\) ions, although rapid deactivation is observed. This is due to the high barrier for the regeneration of the gallyl ion compared to that for the formation of less active Ga\(^+\) ions.

Hydrocarbon activation on HZSM-5 modified by bivalent Zn proceeds via distinctly different mechanism as compared to univalent Ga cations. The stronger molecular adsorption of ethane by the acid-base pairs formed by distantly separated cationic Zn\(^{2+}\) and basic oxygen sites results in strong polarizability of adsorbed ethane already at room temperature and subsequent heterolytic dissociative adsorption at moderate temperatures. In contrast, molecular adsorption of ethane on Ga\(^+\) species is weak. However, at high temperatures dissociative adsorption also takes place via oxidative addition of the hydrocarbon, resulting in the formation of ethyl and hydride fragments coordinating to the gallium species. This distinct difference in alkane activation has direct consequences for hydrocarbon conversions involving dehydrogenation.
3.1 Introduction

Alkanes can be converted to alkenes and aromatics over Ga or Zn promoted medium-pore size zeolites. Gallium has the advantage over zinc of being less volatile under practical reducing conditions at high temperature [1]. The reaction mechanism is thought to consist of a complex scheme involving dehydrogenation, oligomerization and ring-closure steps. Despite considerable research efforts in the area of Ga-containing zeolites [2-10], the exact role of gallium in this mechanism has not been totally elucidated yet, with proposals for its role as dehydrogenation function in a pure bifunctional [2-5] or concerted mechanism [6] and as a promoter to recombinative hydrogen removal during alkane dehydrogenation on Brønsted acid sites [7-10] receiving most attention. Determining the precise role of Ga in these reaction steps has proven difficult [2-13], mainly because the nature of the active Ga species remains unclear.

In order to prepare better-defined Ga species in medium-pore size zeolites we have examined the completely anhydrous route consisting of chemical vapor deposition of trimethylgallium (TMG) with subsequent removal of the methyl groups by treatment with hydrogen or oxygen [14-17]. The reductive route is the preferred one resulting in better gallium dispersion, because oxidation of the methyl groups leads to water formation and hydrolysis of cationic Ga species. It is the purpose of this chapter to compare the catalytic activities of various well-defined charge-compensating Ga species (Ga\(^+\), GaH\(_2\)\(^+\), GaO\(^+\)) encaged in the micropore space of HZSM-5 zeolite. The reactivity of these cationic Ga species in propane dehydrogenation was studied. We will discuss the critical role of the various cationic Ga species for the reaction mechanism of alkane dehydrogenation. We have also found that the activation of alkane over Ga\(^+\) and Zn\(^{2+}\) ions proceeds via two distinctly different mechanisms. The consequences of this different ways of alkane activation are evaluated by studying the catalytic conversion of ethane over zinc- and gallium-modified HZSM-5.

3.2 Experimental

Preparation of materials

NH\(_4\)ZSM-5 (Akzo Nobel, Si/Al =20) was calcined in a mixture of 20 vol.\% oxygen in nitrogen at a flow rate of 100 Nml/min whilst heating to 823 K at a heating rate of 2 K/min followed by an isothermal period of 4 h to obtain HZSM-5. TMG/HZSM-5 was prepared by chemical vapor deposition of trimethylgallium (TMG, Strem Chemicals, purity > 99\%) on dehydrated HZSM-5. To a glass vessel containing dehydrated HZSM-5,
1 ml of TMG was added in an Ar-flushed glove box. After 24 h, the resulting material was evacuated for 2 h in order to remove excess trimethylgallium. On reduction, a Ga/Al molar ratio of 0.94 was obtained. Zn/ZSM-5 was prepared by exposing well-dehydrated HZSM-5 to zinc metal vapor, leading to the replacement of Brønsted acid sites by divalent zinc cations concomitant with evolution of molecular hydrogen. This leads to a final Zn/Al molar ratio of 0.5.

**Catalytic reactivity measurements**

A model catalytic study of ethane and propane conversion was carried out in an atmospheric-pressure single-pass flow reactor equipped with a sixteen-valve sample loop system for chromatographic (GC-17A, FID, KCl/Al₂O₃ plot column) product analysis at short reaction times. The feed consisted of 1 vol% C₂H₆ and 5 vol.% C₃H₈ in He at a total flow rate of 100 Nm/min. After preparation in an Ar-flushed glove-box, catalysts were loaded in the quartz reactor and transferred to the reaction setup under protective atmosphere. The WHSV was kept at 1.6 h⁻¹ and 11.7 h⁻¹ for ethane and propane respectively. The catalyst weight amounted to 50 mg for both Zn/ZSM-5 or TMG/HZSM-5 zeolites. Catalyst pretreatment involved in situ reduction in a flow of hydrogen of 100 Nm/min whilst heating from room temperature to 823 K at a rate of 5 K/min followed by an isothermal period of 2 h (Zn/ZSM-5(red) and TMG/HZSM-5(red)). The reaction temperature was 823 K and the reaction products were followed for 3 h.

One sample was pretreated in the same manner as TMG/HZSM-5(red) and additionally kept in He for 1 h at 823 K. This sample is denoted by TMG/HZSM-5(red,He). Another catalyst was prepared by cooling TMG/HZSM-5(red) to 473 K in He followed by exposure to a flow of 1 vol.% N₂O in He of 100 Nm/min for 1 h. Finally, the catalyst was brought to reaction temperature (823 K) in flowing He. This material is denoted as TMG/HZSM-5(red,ox,473 K). For comparison, the proton form of ZSM-5 was brought to the reaction temperature in a flow of 20 vol.% O₂ in He (HZSM-5).

**3.3 Results and discussion**

The conversion of propane as a function of the reaction time for HZSM-5, TMG/HZSM-5(red), TMG/HZSM-5(red,He) and TMG/HZSM-5(red,ox,473 K) is shown in Figure 3.1. The corresponding selectivities are listed in Table 3.1.
Chapter 3

Figure 3.1 Conversion of propane as a function of reaction time at 823 K (WHSV = 11.7h⁻¹) over (a) HZSM-5, (b) TMG/HZSM-5(red,He), (c) TMG/HZSM-5(red) and (d) TMG/HZSM-5(red,ox,473).

The conversion of propane over the Brønsted acid sites of HZSM-5 at 823 K primarily results in the formation of methane and ethylene in comparable amounts and a small amount of propylene. No higher-boiling hydrocarbons were observed in the effluent gas phase. The conversion remained nearly constant, which indicates that no strong coking
deactivation occurs under the given reaction conditions. Nevertheless, the carbon balance was not totally closed, indicating the formation of some coke products. The composition of the product mixture corresponds to that of protolytic cracking which has been proposed to proceed via a pentacoordinated carbonium ion transition state [18].

Table 3.1 Propane dehydrogenation over HZSM-5, TMG/HZSM-5(red), TMG/HZSM-5(red,He) and TMG/HZSM-5(red,ox,473 K) at 823 K (WHSV = 11.7 h⁻¹, p = 1 atm).

<table>
<thead>
<tr>
<th>TOS(min)</th>
<th>X(%)</th>
<th>CH₄</th>
<th>C₂H₄</th>
<th>C₃H₆</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HZSM-5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>38</td>
<td>37</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>6</td>
<td>39</td>
<td>38</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>7</td>
<td>37</td>
<td>37</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>7</td>
<td>39</td>
<td>38</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMG/HZSM-5(red)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>83</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>76</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>6</td>
<td>3</td>
<td>4</td>
<td>76</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>6</td>
<td>3</td>
<td>5</td>
<td>76</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMG/HZSM-5(red,He)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>5</td>
<td>9</td>
<td>85</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>5</td>
<td>5</td>
<td>8</td>
<td>86</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>6</td>
<td>4</td>
<td>7</td>
<td>88</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>6</td>
<td>4</td>
<td>7</td>
<td>82</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMG/HZSM-5(red,ox,473 K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>24</td>
<td>7</td>
<td>13</td>
<td>63</td>
<td>7</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>5</td>
<td>8</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>7</td>
<td>4</td>
<td>5</td>
<td>84</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>6</td>
<td>4</td>
<td>5</td>
<td>84</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>87</td>
<td>0</td>
</tr>
</tbody>
</table>
TMG/HZSM-5(red) exhibits a very different catalytic behavior. Whereas the initial conversion is relatively low, it increases with reaction time and remains constant at prolonged reaction times. Propylene is the main hydrocarbon product identified in the reactor effluent with selectivity close to 80% with minor amounts of methane and ethylene. Despite the observation that the carbon balance was not totally closed which points to coke formation, catalyst deactivation is limited. Deactivation might be partially masked by the increase in conversion with reaction time. The very different product composition between HZSM-5 and TMG/HZSM-5(red) derives from the difference in charge-compensating species in HZSM-5 (Bronsted acid sites) and TMG/HZSM-5(red) (reduced Ga species).

An important question relates to the nature of the active species for alkane activation. Kazansky et al. [17] have shown that dissociation of ethane may take place over Ga\(^+\) species in reduced Ga/HZSM-5, leading to grafted ethyl and hydride species according to

\[
Z\text{O}^-...\text{Ga}^+ + \text{C}_2\text{H}_6 \rightarrow Z\text{O}^-...[\text{Ga}(\text{H})(\text{C}_2\text{H}_5^-)]^+ \quad (3.1).
\]

The resulting grafted alkyl species were found to decompose to yield ethylene. Quantum-chemical calculations have shown that the activation of paraffins over Ga\(^+\) species proceeds through a transition state involving the basic oxygen groups of the zeolite lattice [19].

The experimental observation of increasing propane conversion with reaction time for TMG/HZSM-5(red) is in favor of Ga\(^+\) as the active species. Prior to reaction, TMG/HZSM-5(red) was kept in molecular hydrogen at 823 K. Under these conditions, a significant part of the charge-compensating species will be gallium-dihydrides [15,20]. These species are relatively stable and only decompose slowly in the absence of hydrogen, even at high temperature [15]. Replacement of the pretreatment hydrogen flow by the reactant mixture (C\(_3\)H\(_8\)/He) will result in a slow increase of the number of Ga\(^+\) species at the expense of the number of GaH\(_2^+\) species. The increase in activity with reaction time corroborates with the assignment of Ga\(^+\) species as the active sites. We propose that the reaction mechanism for propane conversion over TMG/HZSM-5(red) is made up by the following (not necessarily elementary) reaction steps

\[
\begin{align*}
Z\text{O}^-...\text{Ga}^+ + \text{C}_3\text{H}_8 & \rightleftharpoons Z\text{O}^-...[\text{Ga}(\text{H})(\text{C}_3\text{H}_7^-)]^+ \quad (3.2) \\
Z\text{O}^-...[\text{Ga}(\text{H})(\text{C}_3\text{H}_7^-)]^+ & \rightarrow Z\text{O}^-...\text{Ga}^+ + \text{H}_2 + \text{C}_3\text{H}_6 \quad (3.3).
\end{align*}
\]
We thus propose that the increase in conversion with reaction time is due to an increase of the number of Ga$^+$ species at the expense of less active GaH$_2^+$ species. This proposal also implies that the rate of Eqs. (3.2) and (3.3), i.e. the rate of formation of propylene, is lower than the rate of hydrogen removal from GaH$_2^+$ species or that GaH$_2^+$ is not a necessary intermediate, but actually suppresses the reaction. The need for a low H$_2$ partial pressure agrees with the view of Iglesia and co-workers [10] who have proposed that Ga increases the rate of hydrogen desorption in the complex scheme of hydrocarbon conversion. Further reactions may include further dehydrogenation of olefins to coke products, which explains the non-closed carbon balance.

Further support for this hypothesis is provided by an experiment in which TMG/HZSM-5(red) was exposed to inert He atmosphere at 823 K for 1 h. In this case, the propane conversion is nearly constant from the start of the reaction as follows from Figure 3.1. Extensive exposure to a He flow leads to the decomposition of a significant part of GaH$_2^+$ species [15]. A small difference was noted in the product composition of TMG/HZSM-5(red) and TMG/HZSM-5(red,He). Although the propylene selectivity in both cases was close to 90%, the latter material produced a slightly higher amount of ethylene and methane. This may point to a small contribution of protolytic cracking. The required Brønsted acid sites can derive from trace amounts of water in the He flow via [15]

$$\text{ZO}^-...\text{Ga}^+ + 2\text{H}_2\text{O} \rightarrow \text{ZO}^-...[\text{Ga}^{3+}(\text{OH})_2]^+ + \text{H}_2 \quad (3.4)$$

$$\text{ZO}^-[\text{Ga}^{3+}(\text{OH})_2]^+ \rightarrow \text{ZO}^-...\text{H}^+ + \text{GaOOH} \quad (3.5).$$

The catalytic performance of the oxidized gallium-containing zeolites is different from their reduced counterpart. TMG/HZSM-5(red,ox,473) has a higher initial propane conversion compared to TMG/HZSM-5(red). However, the activity decreases strongly during the first 20 min. Initially, the product mixture is mainly made up by propylene with ethylene, methane and aromatics as minor side products (Table 3.1). At prolonged reaction times, the selectivity to propylene increases strongly. The higher conversion on TMG/HZSM-5(red,ox,473) compared to TMG/HZSM-5(red) indicates that propane reacts at a higher rate over GaO$^+$ species than over Ga$^+$ species. Tentatively, we propose that propane is activated over GaO$^+$ species via

$$\text{ZO}^-...\text{GaO}^+ + \text{C}_3\text{H}_8 \quad \Leftrightarrow \quad \text{ZO}^-...[\text{Ga(OH)}(\text{C}_3\text{H}_7)]^+ \quad (3.6).$$

Decomposition of this complex gives propylene via

$$\text{ZO}^-...[\text{Ga(OH)}(\text{C}_3\text{H}_7)]^+ \quad \Leftrightarrow \quad \text{ZO}^-...[\text{Ga(H)}(\text{OH})]^+ + \text{C}_3\text{H}_6 \quad (3.7).$$
Further dehydrogenation of propylene over GaO\(^+\) species might then lead to aromatics. On the other hand, the importance of Brønsted acid sites for dehydrocyclization has been stressed [10]. Although infrared spectroscopic characterization (Chapter 2, Figure 2.10(b)) has clearly shown that in TMG/HZSM-5(red,ox,473) the extent of Bronsted acid site regeneration is negligible, we cannot rule out that upon heating in inert atmosphere to 823 K a small number of such sites is regenerated. The presence of a small amount of such acidic sites can also explain the formation of small amounts of methane and ethylene.

Although deactivation of zeolite-catalyzed hydrocarbon conversion is often attributed to coke formation, we propose an alternative mechanism for the deactivation of TMG/HZSM-5(red,ox,473) during propane conversion. Regeneration of the GaO\(^+\) species requires the reaction of

\[
\text{ZO}^-\cdot\text{[Ga(H)(OH)]}^+ \rightleftharpoons \text{ZO}^-\cdot\text{[GaO]}^+ + \text{H}_2
\]  

(3.8).

An alternative reaction pathway is provided by

\[
\text{ZO}^-\cdot\text{[Ga(H)(OH)]}^+ \rightleftharpoons \text{ZO}^-\cdot\text{Ga}^+ + \text{H}_2\text{O}
\]  

(3.9).

The reactions of GaO\(^+\) and Ga\(^+\) with hydrogen and water, respectively, have recently been experimentally verified [17]. Moreover, Gonzales et al. [20] have shown that the formation of univalent species by desorption of water according to Eq. (3.9) \(E_{\text{act}} = 62\) kcal/mol; \(\Delta G_{800K} = 1.0\) kcal/mol) is more favorable than regeneration of the initial GaO\(^+\) species according to Eq. (3.8) \(E_{\text{act}} = 73\) kcal/mol; \(\Delta G_{800K} = 28.6\) kcal/mol). This is in line with the computed difficult regeneration of the gallyl ion [21]. Another pathway proceeds via reduction of GaO\(^+\) species with hydrogen produced by propane dehydrogenation

\[
\text{ZO}^-\cdot\text{[GaO]}^+ + \text{H}_2 \rightleftharpoons \text{ZO}^-\cdot\text{Ga}^+ + \text{H}_2\text{O}
\]  

(3.10),

for which Bell and co-workers [20] calculated \(\Delta G_{800K} = -28.3\) kcal/mol. It is thus likely that deactivation is largely due to the formation of less active Ga\(^+\) from the initially predominant GaO\(^+\) species. We stress that the difference in total turnover number (mol propane per mol gallium) between TMG/HZSM-5(red,ox,473) and TMG/HZSM-5(red) during the reaction is much larger than unity. We calculate that on average 1000 molecules of propane are converted per GaO\(^+\) species before it is reduced to Ga\(^+\). This implies that GaO\(^+\) regeneration is possible under the reaction conditions, providing a more facile pathway to the olefin than Ga\(^+\). The turn over rates calculated as the molar
rate of propylene formation per mol of the active sites of H\textsuperscript{+}, Ga\textsuperscript{+} and GaO\textsuperscript{+} cationic species are 3.5 h\textsuperscript{-1}, 21 h\textsuperscript{-1} and 57 h\textsuperscript{-1} respectively.

**Figure 3.2** Conversion of propane as a function of reaction time at 823 K (WHSV = 11.7 h\textsuperscript{-1}) over TMG/HZSM-5(red,ox) with intermittent oxidation by nitrous oxide for 1 h at 473 K. Corresponding selectivities are collected in Table 3.2.

In order to validate the hypothesis that deactivation is due to GaO\textsuperscript{+} reduction, spent TMG/HZSM-5(red,ox,473) was cooled from reaction temperature to 473 K in flowing He. Subsequently, the catalyst was exposed to a flow (100 Nml/min) of 1 vol.% N\textsubscript{2}O in He, heated in inert He atmosphere to 823 K and again exposed to the reaction mixture. Figure 3.2 combines the results of these successive catalytic experiments. Clearly, a mild oxidation at low temperature by nitrous oxide results in regeneration of the initial catalytic activity. The relatively low oxidation temperature excludes the possibility of oxidation of coke deposits. The clear inference to be drawn is that the deactivation of TMG/HZSM-5(red,ox,473) in propane dehydrogenation is due to reduction of GaO\textsuperscript{+} to Ga\textsuperscript{+} species with a lower intrinsic activity.
### Table 3.2 Propane dehydrogenation over TMG/HZSM-5(red,ox,473 K) at 823 K
(WHSV = 11.7 h^{-1}, p = 1 atm)

<table>
<thead>
<tr>
<th>TOS(min)</th>
<th>X(%)</th>
<th>( \text{CH}_4 )</th>
<th>( \text{C}_2\text{H}_4 )</th>
<th>( \text{C}_3\text{H}_6 )</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMG/HZSM-5(red,ox,473 K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>24</td>
<td>7</td>
<td>13</td>
<td>63</td>
<td>7</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>5</td>
<td>8</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>7</td>
<td>4</td>
<td>5</td>
<td>84</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>6</td>
<td>4</td>
<td>5</td>
<td>84</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>87</td>
<td>0</td>
</tr>
<tr>
<td>Regenerated TMG/HZSM-5(red,ox,473 K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>24</td>
<td>7</td>
<td>13</td>
<td>65</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>13</td>
<td>5</td>
<td>9</td>
<td>78</td>
<td>3</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>4</td>
<td>7</td>
<td>82</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>9</td>
<td>4</td>
<td>6</td>
<td>82</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>7</td>
<td>4</td>
<td>5</td>
<td>87</td>
<td>0</td>
</tr>
</tbody>
</table>

The active sites for ethane dissociative adsorption and dehydrogenation [22] over zinc-modified HZSM-5 are acid-base pairs involving low-coordinated bivalent zinc cations located at isolated aluminum-occupied oxygen tetrahedra and distantly separated basic oxygen atoms of the zeolite framework. As the positive charge of these \( \text{Zn}^{2+} \) ions is only partially compensated, they show properties similar to Lewis super acids. Molecular adsorption of ethane by such sites is peculiar. At a typical temperature above 450 K heterolytic dissociative adsorption of ethane takes place resulting in the formation of zinc-ethyl fragments and acid sites that compensate the negative framework charge at the basic sites of the zeolite framework. Subsequent decomposition of alkyl species results in formation of ethylene. In summary, the following reaction scheme has been proposed [22]

\[
\text{ZO}^-\ldots\text{Zn}^{2+} + \text{ZO}^- + \text{C}_2\text{H}_6 \rightarrow \text{ZO}^-\ldots\text{Zn}^{2+}\text{C}_2\text{H}_6 + \text{ZO}^- \\
\text{ZO}^-\ldots\text{Zn}^{2+}\text{C}_2\text{H}_6 + \text{ZO}^- \rightarrow \text{ZO}^-\ldots\text{Zn}^{2+}\text{C}_2\text{H}_5^- + \text{ZO}^-\ldots\text{H}^+ \\
\text{ZO}^-\ldots\text{Zn}^{2+}\text{C}_2\text{H}_5^- + \text{ZO}^-\ldots\text{H}^+ \rightarrow \text{ZO}^-\ldots\text{Zn}^{2+}\cdot\text{H} + \text{ZO}^-\ldots\text{H}^+ + \text{C}_2\text{H}_4
\]  (3.11)
The difference in the mechanism of alkane activation should have direct consequences for the product mixture observed during catalytic hydrocarbon conversion. To this end, we also studied the conversion of ethane over Zn/ZSM-5(red) and TMG/HZSM-5(red) at elevated temperatures. The conversion as a function of the reaction time for both zeolites is displayed in Figure 3.3. Zn/ZSM-5(red) displays a much higher conversion than TMG/HZSM-5(red). This corresponds to the finding that ethane is more readily activated over the zinc–oxygen acid–base pairs than over Ga$^+$ species. TMG/HZSM-5(red) almost shows a stable activity as a function of the reaction time. Moreover, the catalyst remains white after reaction, indicative of the absence of large amounts of coke formation.

**Figure 3.3** Conversion of ethane over (a) Zn/ZSM-5(red) and (b) TMG/HZSM-5(red) as a function of the reaction time (50 mg prereduced catalyst, total flow 100 Nml/min, 1 vol.% ethane in He, $T = 823$ K, atmospheric pressure). Corresponding selectivities are collected in Table 3.3.

Table 3.3 collects the selectivity data of both zeolites as a function of the reaction time. The only product observed during ethane conversion over TMG/HZSM-5(red) is ethylene. The further conversion of ethylene to oligomers or aromatics is impeded by the absence of Brønsted acidity in TMG/HZSM-5(red), although one should also take into account the relatively low conversion. Extensive studies in the past have suggested that Brønsted acid sites are required for the aromatization of the oligomeric intermediates. On
the other hand, Zn/ZSM-5(red) exhibits a much higher ethane conversion and the product mixture contains aromatics, mostly benzene. The concomitant formation of aromatic products should be explained by the regeneration of Brønsted acid sites via heterolytic dissociative adsorption of ethane according to reaction (3.11). Moreover, this leads to coke formation as observed by a physical colour change of the catalyst to black and pronounced deactivation. Also, the carbon balance is not closed for Zn/ZSM-5(red) (Table 3.3) due to the deposition of carbonaceous residue in the catalyst bed. This deactivation leads to a lower conversion, a concomitant increase in ethylene selectivity and less pronounced coke formation at higher reaction times. This may be primarily attributed to the deactivation of Brønsted acid sites that play an important role in the formation of aromatics and coke.

Table 3.3 Reaction data for ethane conversion over Zn/ZSM-5(red) and TMG/HZSM-5(red) as a function of the reaction time (TOS)

<table>
<thead>
<tr>
<th>TOS(min)</th>
<th>X(%)</th>
<th>S_{ethylene}(%)</th>
<th>S_{aromatics}(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn/ZSM-5(red)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>34</td>
<td>70</td>
<td>4</td>
</tr>
<tr>
<td>30</td>
<td>24</td>
<td>83</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>22</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>21</td>
<td>87</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>20</td>
<td>93</td>
<td>0</td>
</tr>
<tr>
<td>TMG/HZSM-5(red)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>&gt;95</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>&gt;95</td>
<td>0</td>
</tr>
<tr>
<td>60</td>
<td>5</td>
<td>&gt;95</td>
<td>0</td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>&gt;95</td>
<td>0</td>
</tr>
<tr>
<td>150</td>
<td>4</td>
<td>&gt;95</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^{a}\)Prereduced catalyst (50 mg, feed of 100 Nml/min of 1 vol. % ethane in He, \(T = 823 \text{ K}, \ P = 1 \text{ atm.}\)

\(^{b}\)Ethane conversion (X) and selectivities (S) to ethylene and aromatics. The aromatics slate is mostly benzene with small traces of toluene and xylenes. No other products are observed. Deviation from 100% selectivity implies coke formation.
3.4 Conclusions

A distinct difference in the product distribution during propane dehydrogenation is noted between protons (HZSM-5) and Ga$^+$ ions (reduced Ga/HZSM-5). Whereas HZSM-5 cracks propane via protolytic cracking yielding methane, ethylene and propylene (paraffinic C-C and C-H bond activation), propane is dehydrogenated with high selectivity to propylene (paraffinic C-H bond activation) over monovalent Ga$^+$ ions. The experimental data indicate that the monovalent Ga$^+$ species are more active than GaH$_2^+$ species. Compared to these cations, GaO$^+$ are most active, with propylene being the main product, indicating that paraffinic C-H bond activation is preferred. However, deactivation in this case is pronounced which is due to the high energy barrier associated with regeneration of the gallyl (GaO$^+$) ion compared to the elimination of water to give less active Ga$^+$ species.

Ethane is strongly adsorbed on Zn/ZSM-5 at room temperature, leading to strong polarizability of the hydrocarbon. Upon heating, the complex dissociates readily over the Lewis acid Zn$^{2+}$–basic oxygen pairs, regenerating Brønsted acid sites. Ethane is only weakly adsorbed on reduced Ga/HZSM-5 and hydrocarbon activation is proposed to occur via oxidative addition over univalent Ga$^+$ ions at elevated temperatures. This results in the formation of ethyl and hydride fragments grafted to gallium, which decompose upon further heating into ethylene and gallium dihydrides. The absence of Brønsted acid formation in Ga/HZSM-5 upon hydrocarbon activation results in the stable and selective conversion of ethane into ethylene. On the other hand, Zn/ZSM-5 displays a higher initial activity but suffers from coking deactivation and secondary aromatization reactions due to the generation of Brønsted acidity.

3.5 References

Chapter 4

**Water promoted hydrocarbon activation catalyzed by binuclear Ga sites in ZSM-5 zeolite**

Propane dehydrogenation over Ga/HZSM-5 is substantially improved upon addition of steam to the hydrocarbon feed. This rate enhancement can be understood by an increase of the steady-state concentration of hydroxylated binuclear Ga cationic reaction intermediates. The hydrogen recombination, required to initiate the catalytic cycle, is strongly favored over binuclear Ga$^{3+}$ complexes compared to mononuclear sites due to the increased acidity of the bridging hydroxyl bond in the former complexes.
4.1 Introduction

Catalytic reactivity of hydrocarbons in zeolites can be profoundly affected by extraframework transition metal cationic clusters. MFI zeolites containing dehydrogenating species such as Ga, Zn and Pt form the basis for light alkane aromatization processes [1,2]. Combining partial alkane dehydrogenation with subsequent olefin conversion is another option [3]. Another appealing example is the incorporation of methane into gasoline products in the MTG process over Ga/HZSM-5 [4]. Current catalytic literature on Zn and Ga promoted zeolites mainly refers to systems in which the state of the cationic cluster is not well defined [1,2]. As a starting point for this study a zeolitic material has been chosen in which Ga$^+$ can be considered as a single site catalyst. The enhancement in the rate of alkane activation by Ga/HZSM-5 by water, as discussed here, relates to transformation of these single Ga$^+$ centers to a cationic Ga dimer Ga$_2$O$_2$$^{2+}$ complex.

Recent experimental [5-8] and computational [9-13] studies have contributed to understanding of the mechanism of alkane activation by single site Ga Lewis acid sites. As candidate active sites, various mononuclear Ga cations (Ga$^+$, GaH$_2$$^+$, GaH$^{2+}$, GaO$^+$) have been considered [8-13]. Earlier studies [6,10] have shown that H$_2$O formation is energetically far more favorable than H$_2$ desorption over these mononuclear GaO$^+$ species. Indeed, oxidized Ga/HZSM-5 rapidly looses its high initial activity in propane conversion due to Ga$^{3+}$ reduction to Ga$^+$ [8]. According to this reaction scheme, GaO$^+$ can be stabilized by addition of steam. Herein we report experimental results showing that addition of steam to a hydrocarbon feed substantially improves the rate of alkane dehydrogenation over Ga/HZSM-5 and results in stable operation. A mechanistic model is proposed supported by DFT calculations to compute the thermochemistry of various possible cationic Ga species formed upon hydroxylation. Also, energy barriers are reported associated with H$_2$ recombination.

4.2 Experimental

Preparation of materials

NH$_4$ZSM-5 (Akzo Nobel, Si/Al=20) was calcined in a mixture of 20 vol.% oxygen in nitrogen at a flow rate of 100 Nml/min whilst heating to 823 K at a heating rate of 2 K/min followed by an isothermal period of 4 h to obtain HZSM-5. TMG/HZSM-5 was prepared by chemical vapor deposition of trimethylgallium (TMG, Strem Chemicals, purity > 99%) on dehydrated HZSM-5. To a glass vessel containing dehydrated HZSM-5,
1 ml of TMG was added in an Ar-flushed glove box. After 24 h, the resulting material was evacuated for 2 h in order to remove excess trimethylgallium. This material when reduced had a Ga/Al molar ratio very close to unity.

$^{27}$Al NMR spectroscopy

$^{27}$Al MAS NMR measurements were carried out on a Bruker DMX500 spectrometer operating at 130.3 MHz. The sample was rotated in a 4 mm rotor with a spin rate of 12.5 kHz. Single-pulse excitation was used with a 30 degree pulse of 1.5 µs. A solution of Al(NO$_3$)$_3$ was used for shift calibration.

Temperature-programmed H$_2$ desorption

Temperature-programmed H$_2$ desorption was carried out in a TPD setup coupled to a quadrupole mass spectrometer (Balzers TPG 215). Prior to the thermal desorption, TMG/HZSM-5 was reduced in a flow of hydrogen of 100 Nml.min$^{-1}$ whilst heating to 823 K at a rate of 5 K.min$^{-1}$ followed by an isothermal period of 2 h. The sample was additionally kept in He for 1 h at 823 K. The sample was then cooled to 473 K and exposed to a flow of 50 Nml.min$^{-1}$ of 0.3 vol.% H$_2$O in He for 1 h. Subsequently, the temperature was raised from 473 K to 823 K at a rate of 10 K.min$^{-1}$. For comparison, dehydrated HZSM-5 was brought to 473 K in He and also exposed to 0.3 vol.% H$_2$O in He whilst heating from 473 K to 823 K at a rate of 10 K.min$^{-1}$.

Catalytic activity measurements

Propane conversion was carried out in a single-pass atmospheric quartz reactor by passing a mixture of C$_3$H$_8$ (5 kPa) in He at a WHSV = 11.8 h$^{-1}$ at 823 K. Gas flows were regulated by thermal mass flow controllers (Brooks). Water was added via a well-thermostated saturator. Prior to reaction, TMG/HZSM-5 was reduced in a flow of hydrogen of 100 Nml.min$^{-1}$ whilst heating to 823 K at a rate of 5 K.min$^{-1}$ followed by an isothermal period of 2 h. The sample was additionally kept in He for 1 h at 823 K (Ga/HZSM-5). Experiments were carried out by increasing the steam partial pressure from the lowest value (0 kPa) to the highest (4 kPa) whilst maintaining a certain partial pressure for at least 1h. In a separate experiment, the catalyst was directly exposed to $p_{H_2O}$ of 0.3 kPa and the catalytic performance was followed for 4 h. For comparison, dehydrated HZSM-5 was brought to the reaction temperature in a flow of 20 vol.% O$_2$ in He. Product analysis was carried out by an online three-column gas chromatograph (Compact GC, Interscience) equipped with PLOT Al$_2$O$_3$/KCl (FID), Molsieve-5Å (TCD)
and RTX-1 (TCD) columns. Reaction products include methane, ethylene, propylene and hydrogen as main products and small quantities of benzene, toluene and xylenes (BTX). Minor quantities of C\textsubscript{4} olefins were detected. Typically, >96\% of the carbon was accounted for. Besides molar hydrocarbons selectivities, the number of moles of H\textsubscript{2} produced per mole converted propane was determined.

### 4.2 Results and discussion

Figure 4.1 summarizes the chemistry of Ga species in HZSM-5 zeolite. Trimethylgallium reacts with the Brønsted acid sites to Ga(CH\textsubscript{3})\textsubscript{2}\textsuperscript{+} species and methane. Reduction leads to grafted GaH\textsubscript{2}\textsuperscript{+} ions that are quite stable below 723 K and only decompose above 773 K [6]. Their slow decomposition rate is corroborated by the computed high activation barrier for hydrogen desorption [10]. The Ga-H vibration can be observed by infrared spectroscopy [6]. After hydrogen desorption, univalent Ga ions are obtained that compensate the negative framework of the zeolite lattice. These ions are identified by the characteristic stretching vibration (2147 cm\textsuperscript{-1}) of weakly adsorbed CO [6,8]. We found that oxidation of Ga\textsuperscript{+} ions by nitrous oxide is suitable to transform Ga\textsuperscript{+} ions to GaO\textsuperscript{2+} ions. Thus, it appears possible to prepare ZSM-5 zeolite with the predominant presence of H\textsuperscript{+}, Ga\textsuperscript{+} or GaO\textsuperscript{2+} as charge-compensating ions.

![Figure 4.1 Synthesis of [Ga\textsuperscript{+}]ZSM-5, [GaO\textsuperscript{2+}]ZSM-5 and [GaH\textsubscript{2}\textsuperscript{+}]ZSM-5 from HZSM-5.](image)

Quantum-chemical computations [13] showed that C-H bond activation over reduced Ga/HZSM-5 proceeds over the Lewis acid-base pair formed by Ga\textsuperscript{3+} and a zeolite framework basic oxygen atom (ZO\textsuperscript{2-}...Ga\textsuperscript{3+}). The experimentally observed higher activity of carefully oxidized Ga\textsuperscript{+} species in ZSM-5, proposed to be gallyl (GaO\textsuperscript{2+}) ions [8], derives from more facile C-H bond cleavage over the stronger Lewis acid-base pair formed by Ga\textsuperscript{3+} and the extraframework oxygen atom. One may propose the following elementary reaction steps in alkane (RH) dehydrogenation over the gallyl ion

\[
[\text{Ga}^{3+}\text{O}^{2-}]^+ + \text{R-H} \rightarrow [\text{Ga}^{3+}(\text{R'})(\text{OH}')]^+ 
\] (4.1)
[Ga\(^{3+}\)(R')(OH')]\(^+\) \rightarrow [Ga\(^{3+}\)(H')(OH')]\(^+\) + R\(^-\) \quad (4.2)

[Ga\(^{3+}\)(H')(OH')]\(^+\) \rightleftharpoons [Ga\(^{3+}\)O\(^2-\)]\(^+\) + H\(_2\) \quad (4.3).

While a high energy barrier is associated with the H\(_2\) desorption and regeneration of GaO\(^+\) sites, a more facile pathway leads to the formation of Ga\(^+\) species and most likely water [10]. Indeed, oxidized Ga/HZSM-5 rapidly looses its high initial activity in propane conversion due to Ga\(^{3+}\) reduction to Ga\(^+\) [8].

![Figure 4.2 Reactant conversion (X) and selectivity to dehydrogenated products (S) during reaction of propane over Ga/HZSM-5 as a function of the water partial pressure.](image)

Reaction experiments were carried out over initially reduced Ga\(^+\) ions stabilized in ZSM-5 zeolite. Figure 4.2 clearly shows that co-feeding of water significantly increases the conversion of propane. The conversion passes a maximum at \(p_{H2O}\) of 0.3 kPa. The activities of Ga/HZSM-5 with water co-feeding (0.01 \(\leq p_{H2O} \leq 4\) kPa) are higher than that of Ga/HZSM-5 in the absence of steam as well as that of HZSM-5 (Chapter 3; Figure 3.1(a,b)). Table 4.1 lists the reaction results as a function of water partial pressure. The very different product composition between Ga/HZSM-5 in the absence of steam and HZSM-5 points to a change in the mechanism from protolytic hydrocarbon activation involving C-H and C-C bond cleavage to dominant C-H activation over the Lewis acidic Ga cations. Addition of water to the feed strongly increases activity.
Chapter 4

Table 4.1 Conversion ($X$) and molar hydrocarbon product distribution during reaction of propane over Ga/HZSM-5 as a function of the steam partial pressure and over parent HZSM-5 (50 mg catalyst, atmospheric pressure, $T = 823$ K, WHSV = $11.8$ h$^{-1}$)

<table>
<thead>
<tr>
<th>$p_{\text{H}_2\text{O}}$ (kPa)</th>
<th>$X$ (%)</th>
<th>CH$_4$ (%)</th>
<th>C$_2$H$_6$ (%)</th>
<th>C$<em>4$H$</em>{10}$ (%)</th>
<th>C$_2$H$_4$ (%)</th>
<th>C$_3$H$_6$ (%)</th>
<th>C$_4$H$_8$ (%)</th>
<th>BTX$^a$ (%)</th>
<th>H$_2$$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>7</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>9</td>
<td>80</td>
<td>2</td>
<td>3</td>
<td>1.06</td>
</tr>
<tr>
<td>0.01</td>
<td>14</td>
<td>7</td>
<td>1</td>
<td>0</td>
<td>15</td>
<td>65</td>
<td>4</td>
<td>7</td>
<td>1.1</td>
</tr>
<tr>
<td>0.05</td>
<td>16</td>
<td>8</td>
<td>1</td>
<td>0</td>
<td>16</td>
<td>63</td>
<td>3</td>
<td>7</td>
<td>1.16</td>
</tr>
<tr>
<td>0.3</td>
<td>19</td>
<td>10</td>
<td>1</td>
<td>1</td>
<td>19</td>
<td>58</td>
<td>2</td>
<td>7</td>
<td>1.19</td>
</tr>
<tr>
<td>0.5</td>
<td>16</td>
<td>11</td>
<td>0</td>
<td>1</td>
<td>19</td>
<td>61</td>
<td>2</td>
<td>4</td>
<td>1.11</td>
</tr>
<tr>
<td>1</td>
<td>14</td>
<td>11</td>
<td>0</td>
<td>1</td>
<td>19</td>
<td>62</td>
<td>2</td>
<td>4</td>
<td>1.08</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>21</td>
<td>65</td>
<td>1</td>
<td>2</td>
<td>0.98</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>5</td>
<td>42</td>
<td>0</td>
<td>0</td>
<td>42</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>0.24</td>
</tr>
</tbody>
</table>

[a] benzene, toluene, xylenes; [b] moles of H$_2$ per mole converted C$_3$H$_8$.

The main product remains propylene although with increasing water content somewhat increased amounts of methane and ethylene are formed. The formation of methane and ethylene is due to protolytic propane cracking and points to some regeneration of Brønsted acid sites formed upon hydrolysis of gallium species [6]. More ethylene than methane is formed in this case due to proton-catalyzed oligomerization/cracking reactions. Also the amount of aromatics increases slightly at higher conversion. The carbon selectivity to dehydrogenated products remains well over 85%. The increased dehydrogenation activity of Ga/HZSM-5 over HZSM-5 is obvious from the increased amount of hydrogen formed. No carbon oxides were detected in the reactor effluent. The activity decrease at higher $p_{\text{H}_2\text{O}}$ is likely due to over hydrolysis of the active intrazeolitic Ga-sites.

To determine catalyst stability in the presence of steam, the conversion of propane over Ga/HZSM-5 was followed as a function of the reaction time at a steam partial pressure of 0.3 kPa for 4 h. Catalyst performance was found to be stable over a period of at least 4 h (Figure 4.3). Table 4.2 lists the product distribution as a function of reaction time. Initially, there is a gradual rise in the propane conversion to the formation of hydroxylated Ga species that are the reaction intermediates. After this, a small decrease of the conversion is observed. Concomitant with this decrease the methane selectivity increases slightly suggesting that the small decrease is due to regeneration of protons and loss of a small number of cationic Ga complexes into neutral structures.
Figure 4.3 Propane conversion over Ga/HZSM-5 exposed to a steam partial pressure of 0.3 kPa.

Table 4.2 Conversion ($X$) and molar product distribution during reaction of propane over Ga/HZSM-5 exposed to a steam partial pressure of 0.3 kPa (50 mg catalyst, atmospheric pressure, $T = 823$ K, WHSV = 11.8 $h^{-1}$).

<table>
<thead>
<tr>
<th>TOS (min)</th>
<th>$X$ (%)</th>
<th>CH$_4$ (%)</th>
<th>C$_2$H$_6$ (%)</th>
<th>C$<em>4$H$</em>{10}$ (%)</th>
<th>C$_2$H$_4$ (%)</th>
<th>C$_3$H$_6$ (%)</th>
<th>C$_4$H$_8$ (%)</th>
<th>BTX$^{[a]}$ (%)</th>
<th>H$_2$$^{[b]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>18</td>
<td>11</td>
<td>1</td>
<td>1</td>
<td>17</td>
<td>54</td>
<td>2</td>
<td>8</td>
<td>1.13</td>
</tr>
<tr>
<td>30</td>
<td>21</td>
<td>12</td>
<td>1</td>
<td>1</td>
<td>19</td>
<td>52</td>
<td>2</td>
<td>7</td>
<td>1.11</td>
</tr>
<tr>
<td>60</td>
<td>19</td>
<td>12</td>
<td>1</td>
<td>1</td>
<td>19</td>
<td>53</td>
<td>2</td>
<td>7</td>
<td>1.09</td>
</tr>
<tr>
<td>120</td>
<td>18</td>
<td>13</td>
<td>0</td>
<td>1</td>
<td>19</td>
<td>54</td>
<td>1</td>
<td>5</td>
<td>0.99</td>
</tr>
<tr>
<td>180</td>
<td>18</td>
<td>13</td>
<td>0</td>
<td>1</td>
<td>19</td>
<td>55</td>
<td>1</td>
<td>5</td>
<td>1.00</td>
</tr>
<tr>
<td>240</td>
<td>18</td>
<td>13</td>
<td>0</td>
<td>1</td>
<td>19</td>
<td>55</td>
<td>1</td>
<td>4</td>
<td>0.96</td>
</tr>
</tbody>
</table>

$^{[a]}$ benzene, toluene, xylenes; $^{[b]}$ moles of H$_2$ per mole converted C$_3$H$_8$. 

55
Figure 4.4 $^{27}$Al NMR spectra of (a) as-synthesized TMG/HZSM-5 and (b) Ga/HZSM-5 after prolonged dehydrogenation of a propane feed at a steam partial pressure of 4 kPa.

$^{27}$Al MAS NMR measurements were carried out to determine whether the steam treatment induces structural damage to the zeolite framework. Figure 4.4 compares the normalized $^{27}$Al NMR spectra of fresh TMG/HZSM-5 and Ga/HZSM-5 after exposure to steam (highest steam partial pressure 4 kPa) for prolonged time. The spectra contain a dominant resonance around 54 ppm attributed to tetrahedral Al sites that are present in the MFI framework. There is a small broad signal around 0 ppm indicative of the presence of some extraframework octahedral Al. The main conclusion is that prolonged conversion of a steam-containing propane feed does not lead to noticeable framework damage and massive redistribution of Al species. In contrast, simple oxidation of as-synthesized TMG/HZSM-5 forming carbon dioxide and water results in significant increase in the amount of octahedral Al species (Chapter 2, Figure 2.4(c)) followed by regeneration of a significant amount of Bronsted acid sites (Chapter 2, Figure 2.13(c)). Clearly, the oxidation of methyl groups and removal of Ga species from charge compensating positions of dimethylgallium/HZSM-5 destabilizes the zeolite framework to a certain extent.

Table 4.3 Comparison of reaction energies ($\Delta E$) and activation barrier energies ($\Delta E_{\text{act}}$) for $\text{H}_2$ and $\text{H}_2\text{O}$ desorption over various Ga clusters. Adapted from [10].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E$ [kJ/mol]</th>
<th>$\Delta E_{\text{act}}$ [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\left[\text{Ga}^{3+}(\text{H})\text{(OH)}^-\right]^+ \rightarrow \text{GaO}^+ + \text{H}_2$</td>
<td>242</td>
<td>305</td>
</tr>
<tr>
<td>$\left[\text{Ga}^{3+}(\text{H})\text{(OH)}^-\right]^+ \rightarrow \text{Ga}^+ + \text{H}_2\text{O}$</td>
<td>128</td>
<td>259</td>
</tr>
</tbody>
</table>
The promoting effect of water may be represented by formation of low-coordinated \( \text{Ga}^{3+} \) ions on the cationic positions of the zeolite. The heterolytic dissociative adsorption and dehydrogenation of ethane have been earlier shown over low coordinated \( \text{Ga}^{3+} \) ions on the surface of neutral \( \text{Ga}_2\text{O}_3 \) clusters [14]. Alternatively, the promoting effect may be attributed to the formation of reactive partly hydrolyzed gallium species.

For mononuclear gallium sites, the catalytic cycle is initiated by desorption of \( \text{H}_2 \) from \( [\text{Ga}^{3+}(\text{H}^-)\text{(OH}^-)^+ \) to form the \( \text{GaO}^+ \) ion. However, Table 4.3 shows that the energy barrier for hydrogen recombination is prohibitively high (305 kJ.mol\(^{-1}\)). The reason is the very low acidity of the hydrogen atom attached to the oxygen atom. In agreement with earlier computations [11] water formation is strongly favored. We propose that multinuclear Ga sites are formed. To establish computationally whether such species can be generated upon water adsorption and this facilitates hydrogen desorption, we studied the interaction of two distantly placed \( \text{Ga}^+ \) ions with \( \text{H}_2\text{O} \) by quantum-chemical cluster calculations in the DFT formalism. The Ga ions are stabilized by two negatively charged Al-containing oxygen tetrahedra embedded in a cluster of 14 T atoms representing the elongated eight-membered ring from the wall of the sinusoidal channel of MFI zeolite [15].

![Figure 4.5 Relative stability of binuclear cationic Ga species in eight-membered ring of ZSM-5 zeolite [15].](image)
Water dissociation over cluster I is exothermic ($\Delta E = -102$ kJ.mol$^{-1}$, Figure 4.5) and leads to formation of structure II which is in fact a [Ga$^{3+}$(H$^-$)(OH$^-$)]$^+$ ion of which the hydroxyl group coordinates to the neighbouring Ga$^+$ ion. This structure can rearrange via migration of the hydroxyl H atom to the Ga$^+$ ion to give structure III, an oxygen-bridged binuclear [(Ga$^{3+}$(H$^-$))$_2$O]$^{2+}$ ion. The latter rearrangement allows additional stabilization energy of 44 kJ.mol$^{-1}$. Reaction of a second water molecule with structure III results in further stabilization of the extraframework gallium dimer by 69 kJ.mol$^{-1}$ and gives structure IV (Figure 4.5). Structure IV contains an almost square-planar Ga$_2$O$_2$ core with hydrides and protons bound to the extraframework Ga cations and O anions, respectively. Rearrangement of IV to the conventional situation with two isolated [Ga$^{3+}$(H$^-$)(OH$^-$)]$^+$ ions (structure V) interacting via a hydrogen bond costs 68 kJ.mol$^{-1}$.

Table 4.4 Comparison of reaction energies ($\Delta E$) and activation barrier energies ($\Delta E_{act}$) for H$_2$ and H$_2$O desorption over various Ga clusters. Adapted from [15]. Roman letters refer to structures in Figure 4.5.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta E$</th>
<th>$\Delta E_{act}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[kJ/mol]</td>
<td>[kJ/mol]</td>
</tr>
<tr>
<td>II $\rightarrow$ VI $+ H_2$</td>
<td>147</td>
<td>263</td>
</tr>
<tr>
<td>II $\rightarrow$ I $+ H_2O$</td>
<td>102</td>
<td>230</td>
</tr>
<tr>
<td>IV $\rightarrow$ VII $+ H_2$</td>
<td>127</td>
<td>211</td>
</tr>
<tr>
<td>IV $\rightarrow$ II $+ H_2O$</td>
<td>113</td>
<td>142</td>
</tr>
</tbody>
</table>

Since hydrogen atom recombination over the hydroxylated structures II and IV is required to initiate the reactive site for alkane dehydrogenation, we evaluated the corresponding energetics. Reaction energies and activation barriers are listed in Table 4.4. Coordination of the hydroxyl group of [Ga(H)(OH$^-$)]$^+$ ion to the neighbouring gallium cation results in a significant decrease of the reaction energy for H$_2$ recombination (147 kJ.mol$^{-1}$) as compared to that from isolated [Ga(H)(OH)]$^+$ (242 kJ.mol$^{-1}$, Table 4.3). On the contrary, the effect on H$_2$O desorption is much smaller. Very similar trends are noted for H$_2$ and H$_2$O desorption from structure IV. The strong decrease in the activation energy for H$_2$ recombination on the Ga dimer is due to the increased acidity of the OH group. Compared to the [Ga$^{3+}$(H$^-$)(OH$^-$)]$^+$ ion the OH bond is weaker in the dimer which can be understood from the bond order conservation principle [16]. Moreover, for the dimer complex, H$_2$ recombination does not result in complete
decomposition of the stable tetrahedral arrangement around the Ga ions. Hydrogen recombination from the isolated \([\text{Ga}^{3+}(\text{H}^-)(\text{OH}^-)]^+\) ion results in less stable three-fold coordinated Ga.

![Graph showing hydrogen production vs. temperature](image)

**Figure 4.6** Production of hydrogen as a function of temperature during exposure of (a) HZSM-5 and (b) Ga/HZSM-5 to a gas flow of 0.3 vol.% \(\text{H}_2\text{O}\) in He.

![Cluster model of binuclear Ga ion](image)

**Figure 4.7** Binuclear \(\text{Ga}_2\text{O}_2^{2+}\) ion stabilized in a cluster model representing an elongated 8-membered ring from the wall of the sinusoidal channel of ZSM-5 [17].
These theoretical insights imply that H$_2$ desorption should be rather facile from such hydroxylated Ga clusters in ZSM-5. To verify this, we carried out a temperature-programmed experiment over Ga/HZSM-5 in an atmosphere of 0.3 vol.% H$_2$O in He. Figure 4.6 shows the evolution of hydrogen as a function of temperature. A main hydrogen production peak with a maximum at 600 K is observed. In a similar experiment, no hydrogen was formed over HZSM-5. Furthermore, the presence of oxygen-bridged Ga dimers (Ga$_2$O$_2$ core) was also confirmed by EXAFS analysis of X-ray absorption spectra at the Ga K edge [15,17] for an oxidized model catalyst obtained by oxidation by nitrous oxide of Ga/HZSM-5 at 473 K. Four O atoms are observed at a distance of 1.84 Å. A further Ga-Ga coordination is identified at an interatomic distance of 2.98 Å with a coordination number close to 1. A Ga-Al backscatterer at a distance of 2.72 Å with a coordination number of 1.1 is included. These structural data evidence the presence of a Ga$_2$O$_2$ core structure coordinating to the zeolite oxygen anions with a structure in qualitative agreement with the DFT calculations (Figure 4.7). Whilst EXAFS analysis provides averaged structural data, the computations have been carried out for one specific ring structure [15]. A detailed study of siting of bivalent cations has shown a preference for the occurrence of Al pairs in the ring structures of ZSM-5 zeolite for Si/Al ratios up to 22 [18]. Hydrogen was successfully utilized as an effective probe for the siting of these bivalent cations by Kazansky et al. [19].

![Figure 4.8 Proposed reaction cycle for alkane dehydrogenation over binuclear Ga cations in the presence of water.](image-url)
Figure 4.8 shows the proposed reaction cycle for alkane dehydrogenation. The addition of water to reduced Ga cations stabilizes binuclear hydroxyl-bridged Ga cationic reaction intermediates. The increased acidity of the bridging hydroxyl bond and the stable tetrahedral configuration around Ga$^{3+}$ facilitate H$_2$ desorption. The higher activity of dimeric oxygen-bridged Ga species compared to single site Ga$^+$ species is in line with the lower energy for H$_2$ recombination [13]. Dehydrogenation of an alkane may then proceed via its heterolytic dissociation over the Lewis acid-base pair formed by Ga$^{3+}$ and the basic extraframework oxygen atom, olefin desorption and hydrogen desorption. Similar to earlier findings for the single site Ga$^+$ catalyst [13], the last two steps may take place in a concerted manner. Continuous addition of water is required to maintain a high steady-state concentration of the hydroxylated reaction intermediate.

4.4 Conclusions

Co-feeding of water over monovalent Ga$^+$ ions strongly increases the conversion of alkane. This improvement in activity is proposed to be due to the formation of oxygen-bridged Ga dimers. The product distribution clearly reflects the preference for C-H bond activation. The hydrogen recombination, required to initiate the catalytic cycle, is strongly favored over binuclear Ga$^{3+}$ complexes compared to mononuclear GaO$^+$ sites. This is due to the increased acidity of the bridging hydroxyl bond in the binuclear oxygen-bridged Ga dimers. Alkane dehydrogenation may take place over these Ga dimers heterolytically over the Lewis acid-base pair formed by Ga$^{3+}$ and the basic extraframework oxygen atom.

4.5 References

Chapter 5

Olefin cracking over protonic zeolites

Cracking of olefins in the C₄-C₈ range was studied over HZSM-22, HZSM-5 and HBEA zeolites. Due to the relatively narrow unidirectional pores of HZSM-22 (TON, 4.6 x 5.7 Å), the rate of bimolecular olefin oligomerization is low compared to monomolecular cracking. Conversion of olefins occurs primarily via direct monomolecular cracking of the starting olefin. Hence, the rates of 1-butene and 2-methyl-2-butene cracking are very low, because these reactions proceed via primary carbenium ion intermediates with high transition state barrier energies. The cracking rate of C₆-C₈ olefins is much higher because of the much lower energy barriers associated with secondary and tertiary carbenium ion transition states.

The larger pores of HZSM-5 (MFI, tridirectional pores, 5.3 x 5.6 Å and 5.1 x 5.5 Å) and H-Beta (BEA, tridirectional pores, 6.6 x 6.7 Å and 5.6 x 5.6 Å) result in a higher rate of oligomerization reactions. Dimerization of 1-butene and 2-methyl-2-butene to corresponding higher olefins leads to increased olefin conversion compared to HZSM-22 because subsequent cracking reactions can occur via secondary and tertiary carbenium ions. While the dimerization route is dominant at low temperatures, higher temperatures lead to a decreased contribution of bimolecular reactions caused by decreased pore occupancies and an increased contribution of direct monomolecular cracking.
5.1 Introduction

Light olefins, especially ethylene and propylene, are major industrial chemical intermediates that serve as building blocks for an array of chemical and plastic products. Increasing demand for propylene over that for ethylene has put stress on conventional propylene sources, in particular steam cracking of naphtha-range hydrocarbons. This has spurred the further development and commercialization of on-purpose propylene production technologies for petrochemical plants, refineries and stand-alone units [1]. One such developing technology involves upgrading low value olefin (C₄-C₈ olefins) rich streams by their conversion into light olefins [2-14].

The importance of zeolite solid acids in many hydrocarbon conversion processes has led to a large body of research [15-20]. Briefly, in the classical view about hydrocarbon cracking, carbenium ions can crack via $\beta$-scission to smaller olefinic and carbenium fragments. The chain reaction propagates via abstraction of an hydride from a reacting hydrocarbon by the carbenium ion [21,22]. Cracking of paraffinic feedstocks is thought to be initiated by monomolecular protolytic cracking [23], involving a pentacoordinated carbonium ion complex formed upon direct attack of the Brønsted acid proton on one of the carbon atom in the hydrocarbon. Product distribution data [24-30] are consistent with this view and the decomposition of the carbonium ion into an adsorbed carbenium ion and an alkane or hydrogen. Besides cracking these carbenium ions can also undergo skeletal isomerization, alkylation and aromatization [31-34].

Olefin cracking over zeolites with Brønsted acidity involves the initial activation of the olefin on the acidic site to form a tricoordinate carbenium ion intermediate, with subsequent scission of a carbon-carbon bond at the $\beta$ position relative to the positive charge to form a free olefin and a smaller carbenium ion. The smaller carbenium ion intermediate thereafter undergoes deprotonation to a smaller olefin, the reverse of the protonation reaction. The nature of carbenium ion has been widely debated in the past. Physical characterization of the adsorbed intermediates on solid acid catalysts indicates that no adsorbed carbenium ions exist as stable intermediates. The alternative explanation given by Kazansky and co-workers [35-38] is that the stable intermediate instead consists of covalently bonded alkoxide species. Formation of secondary alkoxy species is preferred over primary alkoxy formation because of a large difference in activation energies [39-41]. This is illustrated in Figures 5.1 and 5.2 for the formation of iso- and normal-propoxy alkoxide species over a zeolitic proton. The transition state formed by partial stretching of C-O bond of covalent alkoxide precursors leads to separation of charges creating a positively charged structure similar to what is conventionally termed the carbenium ion. This carbenium-like transition state is responsible for acid-catalyzed
Olefin cracking over protonic zeolites

reactions of olefins. On the other hand, NMR, UV-visible and IR spectroscopic evidence suggest that only in the absence of steric constraints stable covalent alkoxy intermediates are formed [42,43].

Transition States

Figure 5.1 Reaction mechanisms involved in the chemisorption of propylene catalyzed by an acidic zeolite [39].

Figure 5.2 Reaction energy diagrams of the chemisorption reaction of propylene catalyzed by an acidic chabazite (Si/Al=11) as obtained from the periodic calculations [39]. All energies are in kJ/mol.
Many groups in the past have made an effort to study olefin cracking on protonated zeolites [44-47]. Buchanan et al. [44] estimated relative rates of monomolecular carbenium ion cracking pathways for C_5-C_8 olefins over ZSM-5 of high SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio. Low hydrocarbon partial pressures were employed to minimize bimolecular reactions. Buchanan [45] found that at 538°C, the cracking of hexene was predominantly of monomolecular nature over steamed ZSM-5, while Abbot and Wojciechowski [46] reported a bimolecular cracking route over ZSM-5 at 404°C. An important question which needs to be addressed is which zeolite parameters influence the relative rates of bimolecular or monomolecular pathway of the olefin cracking reaction over zeolites. In this chapter we analyze the effects of parameters such as pore size, Brønsted acid strength of the zeolite and the reaction temperature on the activity and selectivity of olefin cracking.

5.2 Experimental

\(\text{NH}_4\text{ZSM-22 (Shell, Si/Al = 39), NH}_4\text{ZSM-5 (Akzo Nobel, Si/Al = 20), NH}_4\text{ZSM-5 (Akzo Nobel, Si/Al = 40) and NH}_4\text{BEA (PQ Zeolites, Si/Al = 38) were calcined in a mixture of 20 vol \% O}_2 \text{ in N}_2 \text{ at a flow rate of 100 Nml/min whilst heating to 823 K at a rate of 2 K/min followed by an isothermal period of 4 h to obtain the protonated forms of these zeolites. The zeolites are designated as ZEO(x) where ZEO denotes the zeolite and x the Si/Al molar ratio. Table 5.1 shows the characteristics of the zeolites employed.}

\text{Olefin cracking reactions were carried out in a tapered element oscillating mass balance (Rupprecht and Patashnick TEOM 1500 pulse mass analyzer) at atmospheric pressure and a temperature of 773 K. Product analysis was carried out by an online three-column fast gas chromatograph (Compact GC, Interscience) equipped with PLOT Al}_2\text{O}_3/\text{KCl, Molsieve (5 Å) and RTX-1 columns. Prior to the activity measurements, the catalyst were pretreated in O}_2 \text{ whilst heating to 773 K at a rate of 2 K/min followed by an isothermal period of 2 h. The TEOM microreactor was charged with 30 mg of catalyst (sieve fraction 125-250 µm) firmly packed between two plugs of quartz wool. All the mass changes were corrected for the gas density differences. The feed mixture for 1-butene cracking was delivered by thermal mass flow controller and consisted of 0.7 vol. \% 1-butene in He at a total flow rate of 145 Nml/min. The feed mixture for higher olefins was composed by a saturating device using He as the carrier gas. Feed concentrations used were 3.6 vol.% for 2-methyl-2-butene, 3 vol.% for 1-hexene, 2.5 vol.% for 1-heptene and 2.3 vol.% for 1-octene. Weight hourly space velocity (WHSV) is defined as (olefin feed, g/h)/(catalyst loading, g). Space velocity (SV) is defined as (olefin feed, mol/h)/(active sites, mol). Conversion is defined as follows}
$X(\%) = \left( \frac{C_{\text{reactant}} - \Sigma C_{\text{reactant}}}{C_{\text{reactant}}} \right) \times 100$

where $C_{\text{reactant}}$ denotes the concentration of the reactant olefin, and $\Sigma C_{\text{reactant}}$ includes the concentration of reactant olefin as well as its isomers at the exit stream. Hydrocarbon selectivities are reported on a carbon basis as the percentage of the converted moles of reactant that appears as each molar reaction product. Coke formation is obtained from the non-closed mass balance.

5.3 Results and discussion

Monomolecular cracking over HZSM-22(39)

Figure 5.3 Conversion (left) of (a) 1-butene, (b) 2-methyl-2-butene, (c) 1-hexene, (d) 1-heptene and (e) 1-octene and relative mass change (right) over HZSM-22(39) at 773 K.

Figure 5.3 shows the conversion and the relative mass change as a function of the reaction time during cracking of 1-butene, 2-methyl-2-butene, 1-hexene, 1-heptene and 1-octene over HZSM-22(39) at 773 K. The rate of olefin cracking increases strongly with the carbon number. The reason for the increased cracking rate with hydrocarbon chain length is twofold. First of all, 1-butene and 2-methyl-2-butene cracking involves primary carbenium ion transition states, whereas cracking of higher olefins proceeds via energetically less demanding routes involving secondary and tertiary carbenium ions. Moreover, a higher hydrocarbon chain length leads to increased interaction with the zeolite wall and thus a higher surface coverage and olefin cracking rate [44].
Table 5.1 Composition and characteristics of the zeolites

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al</th>
<th>Topology</th>
<th>Pore Diameter (Å)</th>
<th>Member-rings</th>
<th>Dimensionality</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-22</td>
<td>39</td>
<td>TON</td>
<td>4.6 x 5.7 Å</td>
<td>10 6 5</td>
<td>1</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>20</td>
<td>MFI</td>
<td>5.3 x 5.6 Å, 5.1 x 5.5 Å</td>
<td>10 6 5 4</td>
<td>3</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>40</td>
<td>MFI</td>
<td>5.3 x 5.6 Å, 5.1 x 5.5 Å</td>
<td>10 6 5 4</td>
<td>3</td>
</tr>
<tr>
<td>HBEA</td>
<td>38</td>
<td>BEA</td>
<td>6.6 x 6.7 Å, 5.6 x 5.6 Å</td>
<td>12 6 5 4</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 5.2 \(\text{C}_4-\text{C}_8\) olefin cracking over HZSM-22 (39) at 773 K, \(p = 1\) atm

<table>
<thead>
<tr>
<th>Olefin</th>
<th>WHSV X (h(^{-1}))</th>
<th>X (%)</th>
<th>Selectivity (%)</th>
<th>Alkanes</th>
<th>Coke</th>
<th>iC(_4^-)/\Sigma C_4^-)</th>
<th>(R_{\text{Coke}}) *</th>
<th>(H_2) #</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Olefins</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(C_2^-)</td>
<td>(C_3^-)</td>
<td>(C_4^-)</td>
<td>(C_5^-)</td>
<td>(C_6^-)</td>
<td>(C_7^-)</td>
</tr>
<tr>
<td>1-Butene</td>
<td>4</td>
<td>3</td>
<td>52</td>
<td>25</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>2-Methyl-2-Butene</td>
<td>22</td>
<td>47</td>
<td>44</td>
<td>48</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>23</td>
<td>94</td>
<td>4</td>
<td>89</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1-Heptene</td>
<td>21</td>
<td>93</td>
<td>2</td>
<td>47</td>
<td>47</td>
<td>2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1-Octene</td>
<td>22</td>
<td>99</td>
<td>10</td>
<td>37</td>
<td>39</td>
<td>11</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

* No aromatics were obtained

* \(R_{\text{Coke}}\) = Initial rate of coke formation measured by TEOM (10\(^{-4}\) mg/mg-min)

* \(H_2\) = Mol. of \(H_2\) produced/mol. of olefin reactant
HZSM-22 deactivates during olefin conversion. The decrease in conversion is more pronounced for 1-hexene than for the other reactants. This difference is in line with the initial relative mass changes (Table 5.2) that indicate highest coke formation for 1-hexene conversion. The total amount of coke built up on the catalyst increases from 1-butene to 1-hexene in line with the increased cracking rate. Surprisingly, the rate of coke formation for 1-heptene and 1-octene are substantially lower and less coke is built up during the course of the reaction. Tentatively, this is attributed to steric hindrance against formation of oligomers from long-chain olefins (>C₆). On the other hand, it might also be that diffusion of these higher olefins into the micropores is substantially slower than for 1-hexene. Conversion of such higher olefins might take place at the pore mouths of the zeolite crystals [48]. Table 5.2 summarizes the product distribution for the conversion of the C₄-C₈ olefins over HZSM-22. The product selectivities do not change appreciably with conversion. The product distribution can be understood in terms of stability of the intermediate carbenium ions formed as transition states during cracking of the olefin reactants.

The stability and relative concentrations of carbenium ions decrease in the order: tertiary > secondary > primary [49]. Processes which involve the formation of a primary cation are energetically very unfavorable. The nomenclature of Weitkamp et al. [50] will be followed for analysis of the cracking mechanisms. In short, type A denotes the β-scission of tertiary carbenium ion leaving behind a new tertiary carbenium ion (tertiary-tertiary), type B₁ denotes β-scission of secondary forming tertiary (secondary-tertiary), B₂ tertiary-secondary, C secondary-secondary, D₁ primary-secondary and D₂ secondary-primary. The possibility of undergoing a more facile type of scission (D < C < B < A) increases with the degree of branching [49]. This nomenclature was further extended by Buchanan and co-workers introducing types E₁ and E₂ involving primary-tertiary and tertiary-primary carbenium ions, respectively [44]. In order to explain the formation of ethylene from direct monomolecular cracking of butenes, we introduce type F which involves primary-primary carbenium ions.

Thus, Figure 5.4 shows the pathways for direct cracking of C₄ and C₅ olefins. Despite the high energy barrier associated with type F cracking involving primary to primary carbenium ion cracking, this mechanism constitutes the only direct pathway from butenes to ethylene. Indeed, this agrees with the very low conversion of 1-butene over HZSM-22 compared to the other reactants. Besides ethylene, the products also include propylene and pentene. These products must derive from dimerization of the reactant leading to octene followed by its cracking to smaller olefins (butenes or propylene and pentene). We note here that double bond and skeletal isomerization reaction rates of
olefins were significant [51]. However, the fraction of \(i\)-butene from the total of butenes was 0.39 which is very close to the thermodynamic equilibrium [52].

![Figure 5.4 \(\beta\)-scission modes of monomolecular cracking of C\(_4\) and C\(_5\) carbenium ions.](image)

The higher fraction of propylene compared to pentenes is explained by subsequent cracking of pentenes to ethylene and propylene. From a mass balance calculation an estimation can be made of the ratio between direct ‘monomolecular’ cracking of 1-butene and ‘bimolecular’ cracking after bimolecular dimerization of 1-butene. Under these conditions, a value of about 2 is obtained. Thus, the rate of 1-butene cracking to ethylene is about twice that of its dimerization to octenes followed by cracking to ethylene and propylene. The formation of alkanes due to hydrogen transfer reactions is balanced by formation of coke. A small amount of dehydrogenation reactions also produce molecular hydrogen which may be attributed to dehydrogenation of oligomeric species. Under these circumstances, no aromatics were detected.

Direct cracking of 2-methyl-2-butene results in formation of ethylene and propylene. This reaction should proceed via type D\(_1\) cracking involving primary to secondary carbenium ion cracking. This route should exhibit a lower barrier and indeed the conversion of 2-methyl-2-butene is substantially higher than that of 1-butene. The alternative type F mechanism involving primary to primary cracking is energetically unfavorable compared to the type D\(_1\). In this case, we observe small amounts of butenes and hexenes which indicates a minor contribution of intermediate decene formation via pentene oligomerization. This result implies that the ratio of monomolecular cracking over bimolecular cracking should be considerably higher than for the 1-butene case. Again, a rough mass balance calculation shows that about 7\% of 2-methyl-2-butene conversion proceeds via dimerization to decenes followed by cracking to lighter olefins. Thus, the ratio of mono- over bimolecular cracking for 2-methyl-2-butene (~13) is considerably higher than for 1-butene cracking (~ 2). This difference is due to the lower
energy barrier associated with primary-to-secondary carbenium ion cracking of the C₅ olefin.

\[
\begin{align*}
\text{CH}_3\text{CHCHCHCH}_3 & \xrightarrow{\text{H}^+} \text{CH}_3\text{CHCH}_2\text{CH}^+\text{CH}_3 & \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}^+ + \text{CH}_2\text{CHCH}_3 & \rightarrow 2 \text{C}_3=\text{C}^=\text{H}^- & \text{C} \\
\text{CH}_3\text{C}_2\text{CHCHCHCH}_2 & \xrightarrow{\text{H}^+} \text{CH}_3\text{C}_2\text{CHCH}_2\text{CH}^+ & \text{CH}_3\text{C}_2\text{CHCH}^+ + \text{H}_2\text{C}^=\text{H}_2 & \rightarrow \text{C}_4^= + \text{C}_2^- & \text{D}_1 \\
\text{CH}_3\text{CHCH}^+ & \xrightarrow{\text{H}^+} \text{CH}_3\text{C}_2\text{CHCH}_2\text{CH}^+ & \text{CH}_3\text{C}_2\text{CHCH}^+ + \text{H}_2\text{C}^=\text{H}_2 & \rightarrow \text{D}_1 & \text{E}_1
\end{align*}
\]

*Figure 5.5 Favorable β-scission modes of monomolecular cracking of C₆ carbenium ions.*

Figure 5.5 illustrates the possible cracking pathways for cracking of hexenes. Compared to 2-methyl-2-butene, a very high conversion is found for 1-hexene cracking over HZSM-22 at 773 K. The much higher cracking rate of hexenes is due to the possibilities to crack this olefin via secondary and tertiary carbenium ions. Type C cracking leads to the selective formation of propylene and is the preferred cracking mechanism over types D₁ and E₁, which lead to ethylene and butene. Although type E₁ involves formation of tertiary carbenium ion, it cracks via primary carbenium ion and hence is suppressed compared to type C involving secondary carbenium ion cracking. From the product distribution in Table 5.2 the ratio of secondary over primary carbenium cracking rates from C₆ olefin can be roughly estimated to be about 10. The mechanisms occur mainly through isomers of the reactant and indeed it is known that the rate of double bond and skeletal isomerization of hexenes is not limiting cracking reaction of olefins under comparable conditions [44,53]. The occurrence of both n-butene and i-butene in addition to ethylene suggests D₁ and E₁ mechanisms apply leading to secondary and tertiary butyl ions, respectively. On the other hand, the i-butene/total butenes ratio of 0.38 is very close to the ratio obtained during conversion of 1-butene. Under these conditions, the thermodynamic i-butene/total butenes ratio is indeed close to 0.4 [52].

Figure 5.6 illustrates the dominant direct cracking mechanisms of heptenes. Type C, B₁ and B₂ mechanisms should be favored and lead to the formation of propylene and
butenes. Types \text{D}_1 \text{ and } \text{E}_1 \text{ mechanisms lead to minor amounts of ethylene and pentenes from } \text{C}_7 \text{ cracking. The ratio of secondary and tertiary over primary carbenium cracking rates can be estimated from Table 5.2 to be about } 24 \text{ which is approximately twice the value obtained for } \text{C}_6 \text{ olefin cracking. Tentatively, this can be attributed to the occurrence of tertiary to secondary carbenium ion cracking mechanism (B}_2 \text{ which provide the energetically most favorable route in olefin cracking. Finally, 1-octene cracking proceeds at a very high rate and nearly complete conversion is obtained. Some of the possible dominant direct cracking pathways are listed in Figure 5.7.}

\text{Figure 5.6 Favorable } \beta\text{-scission modes of monomolecular cracking of } \text{C}_7 \text{ carbenium ions.}

Summarizing, the narrow pores of HZSM-22 limit bimolecular oligomerization of olefins. Therefore, the cracking reactions proceed mainly through direct cracking of the reactant olefin and selectivity patterns cohere well with the expected distributions based on relative stabilities of carbenium ions that form the transition states for } \beta\text{-scission. Hence, cracking of } \text{C}_6\text{-C}_8 \text{ olefins over HZSM-22(39) is considerably easier than cracking of } \text{C}_4 \text{ and } \text{C}_5 \text{ olefins. Cracking of the former proceeds via energetically more favorable}
pathways involving secondary and tertiary carbenium ions compared to primary carbenium ions that are involved for C₄ and C₅ olefins.

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-\text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{H}^+ \rightarrow \text{C}_6= + \text{C}_2= \quad \text{D}_1 \]

\[ \text{CH}_3\text{CH}_2\text{CH}-\text{H}^+ \rightarrow \text{CH}_3\text{CH}+\text{H}^+ \rightarrow \text{iC}_6= + \text{C}_2= \quad \text{E}_1 \]

\[ \text{CH}_3\text{CH}_2\text{CH}-\text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{H}^+ \rightarrow \text{C}_5= + \text{C}_3= \quad \text{C} \]

\[ \text{CH}_3\text{CH}_2\text{CH}-\text{H}^+ \rightarrow \text{CH}_3\text{CH}+\text{H}^+ \rightarrow \text{iC}_5= + \text{C}_3= \quad \text{B}_1 \]

\[ \text{CH}_3\text{CH}+\text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH}^+= \text{H}^+ \rightarrow \text{2iC}_4= \quad \text{A} \]

\[ \text{CH}_3\text{CH}_2\text{CH}-\text{H}^+ \rightarrow \text{CH}_3\text{CH}+\text{H}^+ \rightarrow \text{iC}_4= + \text{iC}_4= \quad \text{B}_2 \]

*Figure 5.7 Favorable $\beta$-scission modes of monomolecular cracking of C₈ carbenium ions.*

**Rate of cracking of primary carbenium ions**

The formation of ethylene necessarily involves cracking of primary carbenium ions. In the conversion of C₄ and C₅ olefins, this is the only direct cracking mechanism. Hence, one may estimate the ratio of cracking of C₄ and C₅ primary carbenium ions from the ethylene yield on HZSM-22(39). Assuming pseudo-first order kinetics ($k_{\text{cracking}} = -SV \cdot \ln (1-X)$), the ratio of the first-order rate constants is estimated to be

\[
\frac{k_{\text{pentene}}}{k_{\text{butene}}} \approx 130 \quad (5.1).
\]
The reason for this substantial difference lies in the higher energy barrier associated with butene cracking (type F, primary to primary carbenium ion) compared to pentene cracking (type D, primary to secondary carbenium ion). The narrow one-dimensional pores of ZSM-22 limit bimolecular oligomerization reactions. This is most evident from the relevant small influence of cracking routes via dimerization. Indeed, only for 1-butene conversion dimerization reactions contribute substantially to the overall conversion due to the very low rate of type F cracking.

**Monomolecular vs. bimolecular cracking**

**Effect of pore size and acidity**

*Figure 5.8 Conversion (left) of 1-butene and percentage mass change (right) of (a) HZSM-22(39), (b) HZSM-5(20), (c) HZSM-5(40) and (d) HBEA(38) at 773 K, WHSV = 4h⁻¹.*

Figure 5.8 displays the conversion and relative mass change as a function of the reaction time for 1-butene cracking over HZSM-22(39), HZSM-5(20), HZSM-5(40) and HBEA(38) at 773 K. All the catalysts show nearly stable conversion during the course of the reaction, except for HZSM-5(20) which deactivates slowly. HZSM-5(20) exhibits the highest activity in C₄ conversion. The relative mass changes decrease in the order HZSM-22 > HBEA > HZSM-5(20) > HZSM-5(40). Table 5.3 lists the product distribution and initial coke formation rate for C₄ olefin cracking at 773 K for the various zeolites. The product distribution over HZSM-5(20) is indicative of the predominant conversion of 1-butene via oligomerization followed by cracking of the product.
Table 5.3 1-Butene cracking on different zeolites at 773 K, WHSV = 4h⁻¹, p = 1 atm

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>X (%)</th>
<th>Olefins</th>
<th>Selectivity (%)</th>
<th>Aromatics</th>
<th>Coke</th>
<th>iC₄⁻/ΣC₄⁻</th>
<th>R_{Coke} *</th>
<th>H₂⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₂⁻</td>
<td>C₃⁻</td>
<td>C₅⁻</td>
<td>C₁</td>
<td>C₃</td>
<td>C₄</td>
<td>C₆H₆</td>
</tr>
<tr>
<td>HZSM-22(39)</td>
<td>3</td>
<td>52</td>
<td>25</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>HZSM-5(20)</td>
<td>40</td>
<td>30</td>
<td>58</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>HZSM-5(40)</td>
<td>5</td>
<td>17</td>
<td>50</td>
<td>26</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>HBEA(38)</td>
<td>11</td>
<td>18</td>
<td>43</td>
<td>17</td>
<td>1</td>
<td>0</td>
<td>12</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 5.4 1-Butene cracking on HZSM-5 at 773 K, p = 1 atm, feed 0.7 vol. % 1-butene in He

<table>
<thead>
<tr>
<th>Si/Al Wt (mg)</th>
<th>X (%)</th>
<th>Olefins</th>
<th>Selectivity (%)</th>
<th>Aromatics</th>
<th>Coke</th>
<th>iC₄⁻/ΣC₄⁻</th>
<th>H₂⁻²</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₂⁻</td>
<td>C₃⁻</td>
<td>C₅⁻</td>
<td>C₆⁻</td>
<td>C₁</td>
<td>C₃</td>
<td>C₄</td>
</tr>
<tr>
<td>20</td>
<td>15</td>
<td>20</td>
<td>23</td>
<td>59</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>40</td>
<td>30</td>
<td>5</td>
<td>17</td>
<td>50</td>
<td>26</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>120</td>
<td>20</td>
<td>19</td>
<td>57</td>
<td>13</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>115</td>
<td>86.2</td>
<td>7</td>
<td>11</td>
<td>51</td>
<td>28</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* R_{Coke} = Initial rate of coke formation measured by TEOM (10⁻⁴ mg/mg-min)
²H₂ = Mol. of H₂ produced/mol. of olefin reactant
k = first-order rate constant, h⁻¹ (k = SV / ln (1-X)).
higher olefins. The product distribution may be understood considering that 1-butene reacts via an octene intermediate to propylene and ethylene in the ratio of 2:1 that is

$$2 \text{C}_4\rightarrow \text{C}_8 \rightarrow \text{C}_3 \rightarrow \text{C}_5 \rightarrow 2 \text{C}_3 \rightarrow \text{C}_2$$

Clearly, the larger pores of HZSM-5 are more favorable for bimolecular reactions than those of HZSM-22. Thus, the conversion of 1-butene is considerably higher than over HZSM-22. This is also accompanied by the formation of a small but noticeable amount of aromatics.

HZSM-5(40) with half the Brønsted acid site density exhibits a significantly lower activity. Again, the product distribution points to the dominance of dimerization prior to cracking. The higher pentenes selectivity is in line with the lower conversion and can be understood from reaction equation 5.2. The much lower activity for HZSM-5(40) compared to HZSM-5(20) is surprising. Quantum chemical calculations have shown that olefin dimerization reactions of olefins proceed over single Brønsted acid site by a stepwise or concerted mechanism [54]. To understand this in more detail, we compared the first-order rate constants for 1-butene conversion (Table 5.4) as a function of the Si/Al ratio for a set of HZSM-5 zeolites. We observe that this rate constant is highest for HZSM-5(20). Increasing the Si/Al ratio to 40 leads to a substantial decrease of the rate constant and a further decrease of the Al content does not result in substantial changes of this rate constant. For ZSM-5, it has been put forward that Al substitutions (ca. 50-70%) are preferentially located in the deformed six-membered ring at the intersections between the sinusoidal and straight channels by detailed spectroscopy of Co$^{2+}$-exchanged ZSM-5 zeolites with Si/Al ratios between 12 and 22 [55]. The difference between Co$^{2+}$ ions located at Al pairs in the channels and at the intersections has been noted by Kazansky et al. [56]. These intersections offer a larger space (ca. 9 Å) than the channels themselves (5.3 x 5.6 Å and 5.1 x 5.5 Å) and could therefore accommodate bimolecular transition states more easily. Preferential location of Al in the channels at lower Al content is not likely because most of the T atoms in the MFI unit cell are located at the intersections. Tentatively, it is suggested that the occurrence of proximate Al substitutions provide a facile pathway for 1-butene dimerization, possibly via a mechanism involving two nearby alkoxy species. Upon lowering the Al content to Si/Al = 40 and above, the number of Al pairs is expected to decrease strongly and the dimerization reaction may proceed via a less favorable pathway involving a single Brønsted acid site.
Table 5.5 1-Butene cracking at 773 K, p = 1 atm, feed 0.7 vol. % 1-butene in He

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al</th>
<th>WHSV (h⁻¹)</th>
<th>X (%)</th>
<th>Selectivity (%)</th>
<th>C₂⁻</th>
<th>C₃⁻</th>
<th>C₅⁻</th>
<th>C₃⁷/C₂⁻</th>
<th>C₅⁷/C₂⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-22</td>
<td>39</td>
<td>4</td>
<td>3</td>
<td>52</td>
<td>25</td>
<td>12</td>
<td>0.48</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>HZSM-5</td>
<td>40</td>
<td>4</td>
<td>5</td>
<td>17</td>
<td>50</td>
<td>26</td>
<td>2.94</td>
<td>1.77</td>
<td></td>
</tr>
<tr>
<td>HZSM-5</td>
<td>115</td>
<td>0.8</td>
<td>7</td>
<td>11</td>
<td>51</td>
<td>28</td>
<td>4.64</td>
<td>2.03</td>
<td></td>
</tr>
<tr>
<td>HZSM-5</td>
<td>40</td>
<td>0.8</td>
<td>20</td>
<td>19</td>
<td>57</td>
<td>13</td>
<td>3</td>
<td>2.19</td>
<td></td>
</tr>
<tr>
<td>HZSM-5</td>
<td>20</td>
<td>4</td>
<td>40</td>
<td>30</td>
<td>58</td>
<td>3</td>
<td>1.93</td>
<td>1.85</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.5 collects the propylene to ethylene ratio as a function of the conversion for the various experiments. If cracking were to follow predominantly the dimerization pathway, one expects at high conversion a propylene to ethylene ratio of 2. At lower conversion, we observe formation of substantial quantities of pentenes as an intermediate product of cracking of octene intermediates. In principle, this implies that with decreasing conversion the propylene to ethylene ratio should increase strongly. Indeed, this ratio is found to increase from about 2 for HZSM-5(20) at 40% conversion to 4.6 for HZSM-5(115) at 7% conversion. The theoretical propylene to ethylene ratio as derived from a hypothetical full conversion of intermediate pentenes, i.e. giving one ethylene and one propylene, results in ratios close to 2 for these ZSM-5 zeolites. However, for HZSM-22 we find a propylene to ethylene ratio of 0.48 and a theoretical ratio of 0.57. This agrees with our conclusion that there is a substantial contribution of direct monomolecular 1-butene cracking over HZSM-22. Clearly, the data show a small but noticeable contribution of direct monomolecular cracking over HZSM-5(40) at 5% conversion. At higher conversion, consecutive dimerization reactions dominate the overall 1-butene conversion, however.

HBEA(38) is more active than HZSM-5 with a comparable acid site density (Table 5.3). The data here also suggests a small contribution of monomolecular cracking of 1-butene. More importantly, the larger pore diameter of the BEA topology (12-membered rings, pore size 6.6 x 6.7 Å and 5.6 x 5.6 Å) allows hydrogen transfer, as evidenced from the higher butanes selectivity as well as increased aromatics and coke formation compared to the HZSM-5 zeolites. The high initial coke formation rate predicted by TEOM measurements on HZSM-22 compared to HZSM-5 and HBEA zeolites is difficult to understand. This may be attributed to the diffusion hindrance to the long chain molecules out of the one-dimensional pore system [57].
Table 5.6 compares the product distribution of 2-methyl-2-butene and 1-hexene cracking over the various zeolites. Cracking of HZSM-22(39) should proceed via direct monomolecular cracking of C\textsubscript{5} primary carbenium ion cracking pathway (D\textsubscript{1} type, Figure 5.4). Indeed, the main products are equimolar amounts of ethylene and propylene with only very small amounts of butenes and hexenes. As mentioned before, dimerization pathways are less important because of the higher reaction rate of direct cracking of pentenes. The product distribution of 2-methyl-2-butene cracking over HZSM-5(40) is very similar to that on HZSM-5(20). Here, the product distribution indicates that both monomolecular direct cracking and bimolecular cracking compete. On similar lines, cracking via pentene dimer also occurs on HBEA(38) zeolite. High initial coke formation rate is obtained on HZSM-22(39) as was also observed for 1-butene cracking. But the total coke formation (Figure 5.9) is lower than HBEA(38) and HZSM-5(20).

![Graph showing conversion and mass change](image_url)

*Figure 5.9 Conversion (left) of 2-methyl-2-butene and percentage mass change (right) of (a) HZSM-22(39), (b) HZSM-5(20), (c) HZSM-5(40) and (d) HBEA(38) at 773 K, WHSV = 22h\textsuperscript{-1}.*
Table 5.6 2-Methyl-2-butene cracking on different zeolites at 773 K, WHSV = 22 h\(^{-1}\) and p = 1 atm

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>X (%)</th>
<th>Olefins</th>
<th>Alkanes</th>
<th>Aromatics</th>
<th>Coke</th>
<th>iC(_4^-)/ΣC(_4^-)</th>
<th>R(_{Coke})*</th>
<th>H(_2^#)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(_2^-)</td>
<td>C(_3^-)</td>
<td>C(_4^-)</td>
<td>C(_6^-)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HZSM-22(39)</td>
<td>47</td>
<td>44</td>
<td>48</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.33</td>
<td>6.68</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HZSM-5(20)</td>
<td>95</td>
<td>37</td>
<td>38</td>
<td>14</td>
<td>0</td>
<td>5</td>
<td>2</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.4</td>
<td>3.12</td>
<td>0.064</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HZSM-5(40)</td>
<td>45</td>
<td>37</td>
<td>41</td>
<td>15</td>
<td>1</td>
<td>4</td>
<td>0</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.47</td>
<td>1.4</td>
<td>0.026</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HBEA(38)</td>
<td>70</td>
<td>19</td>
<td>38</td>
<td>23</td>
<td>2</td>
<td>11</td>
<td>2</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.44</td>
<td>3.34</td>
<td>0.055</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* R\(_{Coke}\) = Initial rate of coke formation measured by TEOM (10\(^{-4}\) mg/mg-min)

# H\(_2\) = Mol. of H\(_2\) produced/mol. of olefin reactant

1-Hexene cracking on different zeolites at 773 K, WHSV = 23 h\(^{-1}\) and p = 1 atm

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>X (%)</th>
<th>Olefins</th>
<th>Alkanes</th>
<th>Aromatics</th>
<th>Coke</th>
<th>iC(_4^-)/ΣC(_4^-)</th>
<th>R(_{Coke})*</th>
<th>H(_2^#)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(_2^-)</td>
<td>C(_3^-)</td>
<td>C(_4^-)</td>
<td>C(_5^-)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HZSM-22(39)</td>
<td>94</td>
<td>4</td>
<td>89</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.38</td>
<td>39.4</td>
<td>0.036</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HZSM-5(20)</td>
<td>95</td>
<td>25</td>
<td>50</td>
<td>14</td>
<td>1</td>
<td>6</td>
<td>2</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.36</td>
<td>13.95</td>
<td>0.112</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HZSM-5(40)</td>
<td>88</td>
<td>10</td>
<td>74</td>
<td>12</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.0</td>
<td>4.43</td>
<td>0.004</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HBEA(38)</td>
<td>82</td>
<td>7</td>
<td>75</td>
<td>9</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.33</td>
<td>10.51</td>
<td>0.072</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* R\(_{Coke}\) = Initial rate of coke formation measured by TEOM (10\(^{-4}\) mg/mg-min)

# H\(_2\) = Mol. of H\(_2\) produced/mol. of olefin reactant
Table 5.7 1-Hexene cracking on HZSM-5(20) at 773 K, p = 1 atm

<table>
<thead>
<tr>
<th>WHSV (h⁻¹)</th>
<th>Wt. (mg)</th>
<th>X (%)</th>
<th>Selectivity (%)</th>
<th>Olefins</th>
<th>Alkanes</th>
<th>Aromatics</th>
<th>Coke</th>
<th>iC₄⁻/ΣC₄⁻</th>
<th>H₂ #</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C₂ =</td>
<td>C₃ =</td>
<td>C₄ =</td>
<td>C₅ =</td>
<td>C₇ =</td>
<td></td>
<td></td>
</tr>
<tr>
<td>542</td>
<td>1</td>
<td>34</td>
<td>13</td>
<td>70</td>
<td>11</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>271</td>
<td>2</td>
<td>62</td>
<td>13</td>
<td>71</td>
<td>12</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>144</td>
<td>5</td>
<td>90</td>
<td>14</td>
<td>67</td>
<td>13</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>73</td>
<td>10</td>
<td>94</td>
<td>18</td>
<td>61</td>
<td>14</td>
<td>1</td>
<td>0</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>22</td>
<td>30</td>
<td>95</td>
<td>25</td>
<td>50</td>
<td>14</td>
<td>1</td>
<td>0</td>
<td>6</td>
<td>2</td>
</tr>
</tbody>
</table>

# H₂ = Mol. of H₂ produced/mol. of olefin reactant
The results for 1-hexene cracking present a case where direct monomolecular cracking of the starting olefin is the preferred route. Indeed, the product composition over HZSM-22(39) is indicative of predominant secondary carbenium ion cracking with a small contribution of primary carbenium ion intermediates. This result is also found for HZSM-5(40) as well as HBEA(38). Clearly, the rate of cracking reactions of hexenes avoiding primary carbenium ion transition states is so high that dimerization of the starting olefin is not relevant. On the other hand, we observe that the product distribution over HZSM-5(20) is totally different. This may be attributed to the very high conversion which may result in further dimerization and cracking of the product olefins. To further underpin this explanation, the space velocity was varied for 1-hexene conversion over HZSM-5(20) at 773 K. The results in Table 5.7 confirm that at lower conversion the product distribution is comparable to the distributions found for HZSM-5(40) and HBEA(38).

Similar to 1-hexene, the rate of direct C\textsubscript{7} and C\textsubscript{8} olefin cracking via secondary and tertiary carbenium ions is very high. Thus, the product distribution for 1-heptene cracking is dominated by propylene and butenes (Table 5.8). Only for HZSM-5(20) consecutive reactions of olefins lead to a higher selectivity to ethylene. These results underpin once more that dimerization reactions are restricted in zeolites with a low proton density. As observed earlier, the initial coke formation rate for the zeolites increases from C\textsubscript{4}-C\textsubscript{6} olefin reactants after which it decreases with the carbon number of the olefins.

Summarizing, the required monomolecular cracking of 1-butene over HZSM-22 which involves formation of primary carbenium ion results in a very low reactivity. Zeolites with more favorable pore dimensions allow dimerization reactions to proceed 1-butene cracking. The higher olefin product molecules crack at a higher rate because of possibilities to crack via secondary and tertiary carbenium ions. The results indicate that a reasonable proton density is required to catalyze such dimerization reactions, even for a zeolite with the BEA topology. Increasing the olefin chain length results in a decreased importance of bimolecular cracking because of the intrinsic higher reactivity of the starting olefins. Especially, for C\textsubscript{6+} olefins direct monomolecular cracking is dominant. In patent literature describing processes for the conversion of higher olefinic feeds [4-14] to preferably propylene, catalysts are often 10-membered ring zeolites, especially with the MFI topology with rather high Si/Al ratios (>150). Clearly, such catalysts limit bimolecular reactions and decrease the yield of ethylene. Comparing HZSM-5(20) and HZSM-5(40), we generally observe higher ethylene yields for the former when hexenes, heptenes and octenes are dominant in the reaction mixture. Lighter olefins are more difficult to convert and one predicts that HZSM-5 zeolites with a relatively low proton density would leave butenes in the feed mixture largely unconverted.
Table 5.8 1-Heptene cracking on different zeolites at 773 K, WHSV = 21 h⁻¹ and p = 1 atm

| Zeolite     | X        | Selectivity (%) | Olefins | Alkanes | Aromatics | Coke | iC₄⁻/ΣC₄⁻ | R_{Coke} * | H₂  
|-------------|----------|-----------------|---------|---------|-----------|------|------------|----------|-----
|             | (%)      |                 | C₂⁻     | C₃⁻     | C₄⁻      | C₅⁻  | C₆⁻       |          |     |
| HZSM-22(39) | 93       | 2               | 48      | 47      | 2         | 0    | 1         | 0.36     | 5.5 |
| HZSM-5(20)  | 98       | 24              | 49      | 18      | 2         | 5    | 1         | 0.39     | 6.24|
| HZSM-5(40)  | 94       | 3               | 51      | 42      | 1         | 1    | 0         | 0.5      | 2.4 |
| HBEA(38)    | 99       | 3               | 54      | 35      | 2         | 3    | 1         | 0.43     | 6.22|

HZSM-22(39) 93 2 48 47 2 0 0 1 0.36 5.5 0.033  
HZSM-5(20)  98 24 49 18 2 5 1 1 0.39 6.24 0.061  
HZSM-5(40)  94 3 51 42 1 1 0 0 0.5 2.4 0.04  
HBEA(38)    99 3 54 35 2 3 1 2 0.43 6.22 0.046

*: R_{Coke} = Initial rate of coke formation measured by TEOM (10⁻⁴ mg/mg-min)  
# H₂ = Mol. of H₂ produced/mol. of olefin reactant.

1-Octene cracking on different zeolites at 773 K, WHSV = 22 h⁻¹ and p = 1 atm

| Zeolite     | X        | Selectivity (%) | Olefins | Alkanes | Aromatics | Coke | iC₄⁻/ΣC₄⁻ | R_{Coke} * | H₂  
|-------------|----------|-----------------|---------|---------|-----------|------|------------|----------|-----
|             | (%)      |                 | C₂⁻     | C₃⁻     | C₄⁻      | C₅⁻  | C₆⁻       |          |     |
| HZSM-22(39) | 99       | 10              | 37      | 39      | 11        | 0    | 0         | 3        | 0.39|
| HZSM-5(20)  | 99       | 28              | 44      | 16      | 2         | 2    | 5         | 3        | 2.97|
| HZSM-5(40)  | 99       | 10              | 39      | 38      | 10        | 1    | 1         | 0        | 2.19|
| HBEA(38)    | 99       | 4               | 34      | 48      | 9         | 1    | 3         | 0        | 8.9 |

HZSM-22(39) 99 10 37 39 11 0 0 3 0.39 2.97 0.048  
HZSM-5(20)  99 28 44 16 2 2 5 1 0.44 2.19 0.128  
HZSM-5(40)  99 10 39 38 10 1 1 0 0.41 8.9 0.052  
HBEA(38)    99 4 34 48 9 1 3 0 1 0.42 5.41 0.077

* R_{Coke} = Initial rate of coke formation measured by TEOM (10⁻⁴ mg/mg-min)  
# H₂ = Mol. of H₂ produced/mol. of olefin reactant.
Table 5.9 1-Hexene cracking on different zeolites at variable temperatures, p = 1 atm

<table>
<thead>
<tr>
<th>Temp. X</th>
<th>Selectivity (%)</th>
<th>Olefins</th>
<th>Alkanes</th>
<th>Aromatics</th>
<th>Coke</th>
<th>iC₄⁻/ΣC₄⁻</th>
<th>H₂#</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>(%)</td>
<td>C₂⁻</td>
<td>C₃⁻</td>
<td>C₄⁻</td>
<td>C₅⁻</td>
<td>C₇⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>673</td>
<td>22</td>
<td>8</td>
<td>82</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>773</td>
<td>43</td>
<td>6</td>
<td>87</td>
<td>3</td>
<td>0.4</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HZSM-22 (39, 5 mgs, WHSV = 144 h⁻¹)

<table>
<thead>
<tr>
<th>Temp. X</th>
<th>Selectivity (%)</th>
<th>Olefins</th>
<th>Alkanes</th>
<th>Aromatics</th>
<th>Coke</th>
<th>iC₄⁻/ΣC₄⁻</th>
<th>H₂#</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>(%)</td>
<td>C₂⁻</td>
<td>C₃⁻</td>
<td>C₄⁻</td>
<td>C₅⁻</td>
<td>C₇⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>573</td>
<td>48</td>
<td>1</td>
<td>20</td>
<td>34</td>
<td>31</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>673</td>
<td>73</td>
<td>9</td>
<td>44</td>
<td>29</td>
<td>11</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>773</td>
<td>90</td>
<td>14</td>
<td>67</td>
<td>13</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HZSM-5 (20, 5 mgs, WHSV = 144 h⁻¹)

<table>
<thead>
<tr>
<th>Temp. X</th>
<th>Selectivity (%)</th>
<th>Olefins</th>
<th>Alkanes</th>
<th>Aromatics</th>
<th>Coke</th>
<th>iC₄⁻/ΣC₄⁻</th>
<th>H₂#</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>(%)</td>
<td>C₂⁻</td>
<td>C₃⁻</td>
<td>C₄⁻</td>
<td>C₅⁻</td>
<td>C₇⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>673</td>
<td>34</td>
<td>8</td>
<td>58</td>
<td>20</td>
<td>12</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>773</td>
<td>46</td>
<td>10</td>
<td>77</td>
<td>10</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HZSM-5 (40, 5 mgs, WHSV = 144 h⁻¹)

<table>
<thead>
<tr>
<th>Temp. X</th>
<th>Selectivity (%)</th>
<th>Olefins</th>
<th>Alkanes</th>
<th>Aromatics</th>
<th>Coke</th>
<th>iC₄⁻/ΣC₄⁻</th>
<th>H₂#</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K)</td>
<td>(%)</td>
<td>C₂⁻</td>
<td>C₃⁻</td>
<td>C₄⁻</td>
<td>C₅⁻</td>
<td>C₇⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>673</td>
<td>34</td>
<td>8</td>
<td>58</td>
<td>20</td>
<td>12</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>773</td>
<td>46</td>
<td>10</td>
<td>77</td>
<td>10</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^# H_2 = \text{Mol. of } H_2 \text{ produced/mol. of olefin reactant}$
Effect of temperature

The effect of temperature on the cracking behavior was further studied for 1-hexene cracking over HZSM-5 and HZSM-22 zeolites. Table 5.9 lists the product distribution of 1-hexene cracking on HZSM-22(39), HZSM-5(20) and HZSM-5(40) at various temperatures. To decrease the influence of bimolecular cracking, lower amounts of catalysts were used. The product distribution did not vary to a large extent with temperature for HZSM-22(39) which shows that monomolecular cracking remains the dominant mechanism. At lower temperature, we observe a higher amount of pentenes because these are not fully converted at 673 K. However, for HZSM-5, the product distribution changes considerably with temperature. At lower temperatures, higher selectivities to butenes and pentenes are observed along with minor amounts of heptenes. This points to shift from monomolecular cracking of hexenes to dimerization of hexenes prior to cracking. The resulting C_{12} intermediate will crack to lighter olefins and because of the lower temperature the product composition is dominated by propylene, butenes and pentenes. Both butenes and pentenes can only be cracked further via primary carbenium ions which are energetically unfavorable and hence require higher cracking temperatures. On the other hand, the influence of dimerization reactions is minor at the highest temperature (773 K), likely because at this temperature the sorption constant and the pore occupancy decrease strongly.

If we now compare the product distribution on HZSM-5(20) with HZSM-5(40) at the same temperature one observes somewhat higher amounts of propylene in the latter zeolite. Since propylene from C_6 olefin cracking is the result of monomolecular cracking of secondary carbenium ion, one can conclude that the rate of monomolecular cracking on HZSM-5(40) is higher than that on HZSM-5(20). This is in line with our earlier result stressing the significant amount of Brønsted acid sites in the spacious intersections of HZSM-5(20) capable of accommodating C_6 dimer.

5.4 Conclusions

Cracking of olefins over HZSM-22, a medium pore sized zeolite with a one-dimensional-ten-member-ring channel and narrow pores compared to HZSM-5, occurs mainly via direct monomolecular cracking of the long-chain olefin. While the cracking occurs mostly via isomers of the olefins, the isomerization doesn’t limit the cracking rate. The rate of monomolecular cracking of 1-butene and 2-methyl-2-butene is very low, because these reactions proceed via primary carbenium ions with very high transition state barriers. Since ethylene is formed essentially via the primary carbenium ions,
selectivity data towards ethylene formation was used to estimate the rate of direct cracking of \( \text{C}_4 \) and \( \text{C}_5 \) primary carbenium ions. The rate of primary \( \text{C}_4 \) carbenium ion cracking forming another energetically unfavorable primary carbenium ion is approximately 130 times lower than primary-secondary cracking of \( \text{C}_5 \) carbenium ions. Elevated cracking rates are observed for \( \text{C}_6-\text{C}_8 \) olefins as more energetically favorable monomolecular modes involving secondary and tertiary carbenium ions become available for \( \beta \)-scission.

The cracking rate of 1-butene and 2-methyl-2-butene is enhanced over HZSM-5 and HBEA zeolites because cracking now proceeds via subsequent cracking of the olefin dimer involving secondary and tertiary carbenium ions. The larger pores of these zeolites thus allow for dimerization reactions to occur. Although, dimerization is known to occur over a single Brønsted acid site the improved dimerization rate with acidity stresses the importance of close vicinity of another acid site probably playing a role in stabilization of the dimer. The more than proportional decrease in the dimerization rate with decrease in acidity is in line with this notion. Dimerization is further proposed to occur within the rather large pore intersections of these zeolites. This also relates to the importance of preferential location of acid sites in the pore intersections of the zeolites capable of accommodating the olefin dimer.

The monomolecular cracking rates involving secondary and tertiary carbenium ions for \( \text{C}_6-\text{C}_8 \) olefins are so high that dimerization is not relevant over all zeolites. Nevertheless, variable temperature experiments reveal dimerization route as the dominant mechanism at low temperatures while at higher temperatures rates of monomolecular reaction increase due to decreased pore occupancies.

5.5 References

22. F. C. Whitmore, J. M. Church, J. Am. Chem. Soc. 54 (1932) 3710.
Chapter 6

Difference in mechanism of olefin cracking between Brønsted acidic and Gallium-promoted zeolites

Cracking of olefins in the C₄-C₆ range was studied over Brønsted acidic and cationic Ga species at the ion-exchange sites of ZSM-22 and ZSM-5 zeolite. Olefin cracking over Brønsted acidic zeolites occurs via the well-established carbenium-ion mechanism, leading to the preferential formation of the products from secondary and tertiary carbenium ion transition states. In contrast, the selectivity pattern over Lewis acidic Ga sites is distinctly different. Whilst cracking of hexenes over protonic sites leads preferentially to propylene, substantially higher amounts of ethylene are observed over gallium-exchanged zeolites. The results are explained by cracking of olefins over Lewis acid base pairs formed by Ga⁺ coordinating to the basic zeolite oxygen anions. A mechanism is proposed where a proton is abstracted from the carbon in the β-position to the olefin double bond and the univalent Ga⁺ ion stabilizes an allylic carban-ion intermediate. The proton attacks the allylic bond of the intermediate effectively leading to the starting olefin, a product olefin where the double bond has shifted or a cyclopropyl intermediate. Hydride shift in this cyclopropyl intermediate leads to a skeletal isomer of the reactant olefin or two smaller olefins. The increase in the rate of olefin conversions over cationic Ga species from C₄ through C₆ olefins is proposed to be due to the relative ease of removal of allylic proton from the higher olefins.
6.1 Introduction

In recent years, propylene consumption growth rate continues to outpace that of ethylene putting stress on traditional propylene sources, in particular steam crackers. Flexibility in propylene production in steam crackers is very limited and is based mostly on operating severity and the ability to change feeds from gas to liquids that some crackers have. The impending propylene supply/demand gap has stimulated technology developers to improve conventional technologies to increase the amount of propylene or to develop alternative ways to make propylene (‘on purpose’ approaches). One example of the latter approach is the development of cracking processes of low value C\textsubscript{4}-C\textsubscript{8} olefinic streams to ethylene and propylene [1]. Olefin cracking over Brønsted acid zeolites involves the initial adsorption of the olefin on an acidic site to an alkoxy species followed by its cracking via a positively charged carbenium ion transition state species leading to the scission of a carbon-carbon bond at the $\beta$ position relative to the positive charge of the organocation to form a free olefin and a smaller alkoxy species [2-6]. The smaller carbenium ion intermediate thereafter undergoes deprotonation to a smaller olefin, i.e. the reverse of the adsorption reaction. Brønsted acid catalyzed hydrocarbon cracking goes through carbenium-ion transition states formed by partial stretching of the C-O bond of covalent alkoxide precursors.

There is a large difference in the dehydrogenation selectivity of Brønsted acid sites and Lewis Ga sites. The former mainly catalyze C-C cracking reactions and to a lesser extent dehydrogenation, the latter exhibit a preference for C-H activation [7]. In this study, we evaluate the performance of gallium cations stabilized at the cation-exchange sites in microporous zeolites in olefin cracking. The main reason is to understand if and how the mechanism of olefin cracking differs from that over Brønsted acidic sites in view of the above-mentioned difference in alkane activation. A second reason is the relevance of olefin cracking as an important reaction step in the conversion of alkanes over Ga/HZSM-5 zeolites [8]. To this end, we study the conversion of a range of olefins (1-butene, 2-methyl-2-butene and 1-hexene) over HZSM-5 and HZSM-22 and their Ga-exchanged counterparts.

6.2 Experimental

NH\textsubscript{4}ZSM-5 (Akzo Nobel, Si/Al =20) and NH\textsubscript{4}ZSM-22 (Shell, Si/Al =39) were calcined in a mixture of 20 vol.% oxygen in nitrogen at a flow rate of 100 Nml/min whilst heating to 823 K at a heating rate of 2 K/min followed by an isothermal period of 4 h to obtain HZSM-5 and HZSM-22, respectively. Chemical vapor deposition of
trimethylgallium on HZSM-5 and HZSM-22 was carried out using the procedure described in chapter 3. This method leads to TMG/HZSM-5 with Ga/Al atomic ratio of 1.4 and TMG/HZSM-22 with a Ga/Al atomic ratio of 0.7.

An amount of catalyst was loaded into a tapered element oscillating microbalance (Rupprecht and Patashnick TEOM 1500 pulse mass analyzer). Prior to reaction, TMG/HZSM-5 and TMG/HZSM-22 were reduced in a flow of hydrogen of 100 Nm³/min whilst heating to 823 K at a rate of 5 K/min followed by an isothermal period of 1 h. These catalysts were additionally kept in He for 1 h at 823 K. These samples are denoted as Ga⁺/HZSM-5 and Ga⁺/HZSM-22. Other catalysts were prepared by cooling Ga⁺/HZSM-5 and Ga⁺/HZSM-22 to 473 K in He followed by exposure to a flow of 1 vol.% N₂O in He of 100 Nm³/min for 1 h. Finally, the catalyst was brought to reaction temperature in flowing He. These materials are denoted as Ga₂O₂⁡²⁺/HZSM-5 and Ga₂O₂⁡²⁺/HZSM-22, respectively. For comparison, the proton forms of ZSM-5 (HZSM-5) and ZSM-22 (HZSM-22) zeolites were brought to the reaction temperature in a flow of 20 vol.% O₂ in He.

The conversion of 1-butene, 2-methyl-2-butene and 1-hexene was studied at atmospheric pressure and a temperature of 773 K. Typical catalyst amounts for studying 1-hexene and 2-methyl-butene conversion was 10 mg while for 1-butene conversion an amount of 30 mg was used. The conversion of 1-hexene was also studied at a temperature of 673 K. The reaction feed mixture consisted of a mixture of the olefin in He with the following volume fractions, that is 0.7 vol.% 1-butene, 2.8 vol.% 2-methyl-2-butene and 3.2 vol.% 1-hexene. Weight hourly space velocity (WHSV) is defined as (olefin feed, g/h)/(catalyst loading, g) while space velocity (SV) is defined as (olefin feed, mol/h)/(active sites, mol). Conversion is defined as follows

\[
X(\%) = \left( \frac{C_{\text{reactant}} - \sum C_{\text{reactant}}}{C_{\text{reactant}}} \right) \times 100
\]

where \( C_{\text{reactant}} \) denotes the concentration of the reactant olefin, and \( \Sigma C_{\text{reactant}} \) includes the concentration of the reactant olefin as well as its isomers at the exit stream. Hydrocarbon selectivities are reported on a carbon basis as the percentage of the converted moles of reactant that appears as each molar reaction product. Coke formation is obtained from the non-closed mass balance.
6.3 Results and discussion

Carbanion cracking on Ga zeolites

Table 6.1 lists the product distribution of 1-hexene cracking over HZSM-5, HZSM-22, Ga\(^+\)/HZSM-5 and Ga\(^+\)/HZSM-22 at 673 K and 773 K. Cracking of olefins over acidic zeolites occurs via carbenium ion intermediate, followed by scission of C-C bond in \(\beta\)-position, to form a smaller carbenium ion intermediate and a free olefin. Monomolecular cracking is dominant over HZSM-5 at higher temperatures due to the decreased surface coverage (pore occupancy) [Chapter 5]. From the product distribution in Table 6.1 it follows that apart from HZSM-5 the product distribution does not change appreciably with temperature. Figure 6.1 illustrates the elementary monomolecular \(C_6\) carbenium ion conversion reaction steps. Skeletal isomerization of the hexene exceeds the rate of cracking and hence does not limit the cracking rate [2]. The dominant monomolecular cracking route over Brønsted acid sites involves cracking of secondary carbenium ion intermediate from hexene to two molecules of propylene while the primary carbenium ion leads to ethylene and butene. Clearly, the monomolecular route is the dominant mechanism for cracking of 1-hexene over HZSM-22.
## Table 6.1 1-Hexene cracking on different zeolites at 673 K, WHSV = 68 h⁻¹ and p = 1 atm

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>X (%)</th>
<th>Olefins</th>
<th>Selectivity (%)</th>
<th>Alkanes</th>
<th>Aromatics</th>
<th>Coke</th>
<th>iC₄⁻/ΣC₄⁻</th>
<th>H₂&lt;sup&gt;#&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₂⁻</td>
<td>C₃⁻</td>
<td>C₄⁻</td>
<td>C₅⁻</td>
<td>C₁</td>
<td>C₃</td>
<td>C₄</td>
</tr>
<tr>
<td>HZSM-22</td>
<td>35</td>
<td>6</td>
<td>80</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Ga⁺/HZSM-22</td>
<td>12</td>
<td>6</td>
<td>80</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>84</td>
<td>10</td>
<td>43</td>
<td>16</td>
<td>3</td>
<td>1.8</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Ga⁺/HZSM-5</td>
<td>43</td>
<td>26</td>
<td>29</td>
<td>27</td>
<td>6</td>
<td>0.6</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

1-Hexene cracking on different zeolites at 773 K, WHSV = 68 h⁻¹ and p = 1 atm

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>X (%)</th>
<th>Olefins</th>
<th>Selectivity (%)</th>
<th>Alkanes</th>
<th>Aromatics</th>
<th>Coke</th>
<th>iC₄⁻/ΣC₄⁻</th>
<th>H₂&lt;sup&gt;#&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C₂⁻</td>
<td>C₃⁻</td>
<td>C₄⁻</td>
<td>C₅⁻</td>
<td>C₁</td>
<td>C₃</td>
<td>C₄</td>
</tr>
<tr>
<td>HZSM-22</td>
<td>63</td>
<td>5</td>
<td>85</td>
<td>3</td>
<td>0.4</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Ga⁺/HZSM-22</td>
<td>22</td>
<td>22</td>
<td>46</td>
<td>18</td>
<td>2</td>
<td>0.8</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>94</td>
<td>18</td>
<td>61</td>
<td>14</td>
<td>1</td>
<td>0.1</td>
<td>1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Ga⁺/HZSM-5</td>
<td>57</td>
<td>27</td>
<td>31</td>
<td>24</td>
<td>2</td>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<sup>#</sup>H₂ = Mol. of H₂ produced/mol. of olefin reactant
Chapter 6

We calculated a pseudo first-order rate constant for the direct primary cracking of 1-hexene to ethylene and butenes based on the conversion and selectivity to ethylene. We assume here that direct monomolecular cracking dominates over bimolecular cracking pathways. Assuming pseudo-first order kinetics \( k_{primary} = -SV \cdot \ln(1-X) \), the first-order rate constants for monomolecular primary cracking can be estimated at 773 K. \( k_{primary} \) for HZSM-22 is approximately 148 h\(^{-1}\). Bimolecular cracking dominates over HZSM-5 with a Si/Al ratio of 20 at 673 K leading to formation of butenes and pentenes. The formation of these relatively higher olefins from hexene follows from

\[
2 \text{C}_6 = \rightarrow \text{C}_{12} = \rightarrow \text{C}_4 = + \text{C}_8 = \rightarrow \text{C}_4 = + \text{C}_3 = + \text{C}_5 = \rightarrow \text{C}_4 = + 2 \text{C}_3 = + \text{C}_2 = \quad (6.1)
\]

At higher temperature (773 K), monomolecular cracking becomes more important than cracking routes via dimerization. The product distribution shifts to ethylene and propylene at the expense of the higher olefins. The ethylene yield increases because at the higher reaction temperature the rate of primary carbenium cracking increases.

The first order rate constant for primary cracking \( k_{primary} \) for HZSM-5 at 773 K can be estimated to be about 448 h\(^{-1}\). This enhanced primary cracking over HZSM-5 compared to that on HZSM-22 is not well understood. Possibly, it is due to single file diffusion in the unidirectional pores of HZSM-22 that limits the rate considerably. Although, very high conversion of 1-hexene on HZSM-5 is observed under the present reaction conditions, considerable primary cracking is also observed at lower conversions (Chapter 5, Table 5.7). The observed ratio of \( i \)-butenes/total butenes is 0.32 on HZSM-22 and 0.43 on HZSM-5. The lower amounts of \( i \)-butenes on HZSM-22 is possibly due to inability of HZSM-22 to accommodate the bulky tertiary carbenium ion of hexene required for \( \text{E}_1 \) type of cracking mechanism (primary-tertiary carbenium cracking).

1-Hexene cracking was also studied over gallium-promoted zeolites prepared by chemical vapor deposition of trimethylgallium. It has been shown earlier that trimethylgallium can effectively replace all the Brønsted acid sites in HZSM-5, resulting in mononuclear dimethylgallium species and the Ga/Al ratio obtained was close to 1.4 [9]. These species when reduced at a higher temperature of 823 K lead to dominant monovalent \( \text{Ga}^+ \) and minor trivalent \( \text{GaH}_2^+ \) species at cationic exchange positions in the zeolite. To remove the \( \text{GaH}_2^+ \) species, reduced GaZSM-5 was kept in an inert atmosphere leading to \( \text{Ga}^+ \) active species at the exchange sites (\( \text{Ga}^+/\text{HZSM-5} \)). Chemical vapor deposition was also carried out on HZSM-22, leading to Ga/Al atomic ratio of 0.7. Clearly, trimethylgallium cannot access all the acid sites due to the unidirectional pore
system of HZSM-22. The Ga/Al ratio of lower than unity in Ga⁺/HZSM-22 suggests the composition of the active sites being 70% Ga⁺ ions and 30% Brønsted acid sites.

The conversion over the Ga⁺ exchanged zeolites is lower than over the Brønsted acid zeolites (Table 6.1). In all cases, complete (HZSM-5) or partial (HZSM-22) exchange of protons with Ga⁺ species results in substantially higher selectivities to ethylene than observed for the Ga-free zeolites. In order to explain this large difference in product distribution, it would appear useful to explore possibilities of olefin activation over the Lewis acid-base pair formed by Ga⁺ and the zeolite oxygen anion in a similar fashion as proposed for activation of alkanes. Recently, it was shown that a gallium alkyl hydride is an intermediate cation in the dehydrogenation of alkanes [10]. The reaction pathway to this intermediate proceeds via heterolytic C-H dissociation over the above-mentioned Lewis acid-base pair. The resulting Ga-alkyl species is oxidized in a consecutive step by the Brønsted acid site to form a Ga alkyl hydride species, i.e. \([\text{Ga}^+ (\text{R})(\text{H})]^+\). C-H bond activation of an olefin with more than two carbon atoms will preferentially occur at a sp³ carbon atom adjacent to the double bond (C-H bond energy ethyl ~ 423 kJ/mol, C-H bond energy vinyl ~ 465 kJ/mol vs. C-H bond energy allyl ~361 kJ/mol [11]) to form an allylic hydrocarbon. Heterolytic C-H bond cleavage thus leads to a Brønsted acid site and a Ga-allylic hydrocarbon complex. Preliminary quantum-chemical calculations have shown that the activation of an olefin over Ga⁺ species may proceed through an intermediate involving such heterolytic dissociation of olefin over the Lewis acid-base pair formed by the univalent Ga⁺ ion and the zeolite oxygen anion [12]. The calculated reaction energy for the activation of 2-butene involving this step was found to be about +237 kJ/mol, which is of the same order as the activation of ethane over the same site. Thus, the activation of 1-hexene over univalent Ga⁺ species is proposed to involve

\[
\text{C}_6\text{H}_{12} + \text{Ga}^+ \rightarrow \text{C}_6\text{H}_{11}^+ \text{Ga}^+ \text{H}^+ + \text{O} \quad \text{(6.2)}
\]

The formation of an allylic carbanion is beneficial as the allylic bond is more stable. This allylic carbanion has the following mesomeric structures [13]
and will be represented as follows

In principle, such an intermediate structure may rearrange to a Ga$^{3+}$(R$^-$)(H$^+$) cation with R$^-$ being the allylic hydrocarbon. Desorption may proceed again via intermediate (6.4) and subsequent reaction of the Brønsted acid site with the allylic bond. Proton transfer to the original carbon atom ($\gamma$) leads to formation of the starting olefin, whilst transfer to the $\alpha$-carbon atom leads to 2-hexene. This last reaction is then effectively a double bond isomerization of 1-hexene. Transfer to the second carbon ($\beta$) results in an alkylcyclopropane intermediate. The computed reaction energy is -165 kJ/mol [12]. Due to the high strain in the cyclopropane ring, this intermediate should be very reactive and subsequently undergo internal hydride transfers leading to the skeletal isomerized products (2-methyl-1-pentene) or cracked products, i.e., a linear butene and ethylene, respectively.
The cracking step (b) from equation 6.5 proceeds in the following manner

\[
\begin{align*}
\text{H}_3\text{C} \quad \text{CH}_2 \quad \text{H} & \quad \beta \quad \text{H} \\
\text{b} & \\
\text{H} & \\
\text{CH}_2 \quad \text{CH}_2 \quad \text{H} & \quad \text{b} \\
\end{align*}
\]

(6.6).

The cracking of carbanions due to breakage of an ethyl C-H bond has been reported over supported manganese or iron catalysts [14]. Alkali-exchanged zeolites and alkali-impregnated carbon and magnesia, were tested as catalysts for the side-chain alkylation of toluene with methanol [15]. Pajonk and Tanany [16] suggested that the isomerization of 1-butene over the Lewis centers of zirconia proceeds via allylic carbanions. Similar suggestions were put forward by Baba et al. [17] for 1-butene isomerization over low-valent lanthanide exchange Y zeolite. Notably, such reactions were carried out at low temperatures and no cracking of 1-butene was observed. The involvement of carbanions in isomerization was also suggested for double-bond migration in 1-hexene over the basic sites of titania-zirconia [18].

Figure 6.2 summarizes some of the possible types of carbanion cracking mechanisms through various isomers of 1-hexene. It is evident from Figure 6.2 that the
formation of i-butene occurs only from cracking of branched isomers from 1-hexene. The ratio of i-butene/total butenes on Ga⁺/HZSM-22 at 773 K is 0.21 compared to 0.42 on Ga⁺/HZSM-5. This probably evidences that the bulky isomer of 1-hexene (methyl pentene) responsible for formation of i-butene is difficult to accommodate into the narrow micropores of Ga⁺/HZSM-22.

Figure 6.2 Possible monomolecular carbanion cracking mechanisms from C₆ olefin on Ga zeolites.

The overall cracking reactions can be formulated by either of the following reactions
Olefin cracking over Ga zeolites

The product distribution of 2-methyl-2-butene cracking carried out over acidic and Ga exchanged ZSM-5 and ZSM-22 zeolites is shown in Table 6.2. All the zeolites listed except HZSM-5 crack 2-methyl-2-butene with high selectivity to ethylene and propylene. Figure 6.3 illustrates the type D₁ monomolecular cracking occurring on acidic zeolites which involves the cracking of primary carbenium ion via an isomer of 2-methyl-2-butene to a secondary carbenium ion of propylene.

\[
\text{ZO}^--[\text{Ga}^{+3}(\text{C}_6\text{H}_{11})(\text{H})]^{+} \rightarrow \text{ZO}^--\text{Ga}^{+} + \text{C}_2\text{H}_4 + \text{C}_4\text{H}_8 \quad (6.7)
\]

\[
\text{ZO}^--[\text{Ga}^{+3}(\text{C}_6\text{H}_{11})(\text{H})]^{+} \rightarrow \text{ZO}^--\text{Ga}^{+} + 2\text{C}_3\text{H}_6 \quad (6.8)
\]

Over the Ga⁺ exchanged zeolites higher amounts of aromatics and coke are formed compared to their protonated counterparts. This is due to the increased rate of dehydrogenation and subsequent ring closure steps possible on cationic Ga⁺ species. The higher amount of hydrogen produced over Ga zeolites is in agreement with this notion. Benzene is the preferred aromatic product over Ga zeolites. Clearly, this points to the ability of Ga⁺ ions to catalyze successive dehydrogenations of 1-hexene including the final ring-closure step.

Over the Ga⁺ exchanged zeolites higher amounts of aromatics and coke are formed compared to their protonated counterparts. This is due to the increased rate of dehydrogenation and subsequent ring closure steps possible on cationic Ga⁺ species. The higher amount of hydrogen produced over Ga zeolites is in agreement with this notion. Benzene is the preferred aromatic product over Ga zeolites. Clearly, this points to the ability of Ga⁺ ions to catalyze successive dehydrogenations of 1-hexene including the final ring-closure step.

The butenes/ethylene ratio is much higher than unity over HZSM-5 at 673 K which indicates a large contribution of cracking via oligomerized intermediates. On the other hand, the ratio is close to unity over Ga⁺/HZSM-5 at 673 K. This suggests that direct cracking is the predominant route over this catalyst.

Carbanion cracking over Ga₂O₂²⁺ ions

The product distribution of 2-methyl-2-butene cracking carried out over acidic and Ga exchanged ZSM-5 and ZSM-22 zeolites is shown in Table 6.2. All the zeolites listed except HZSM-5 crack 2-methyl-2-butene with high selectivity to ethylene and propylene. Figure 6.3 illustrates the type D₁ monomolecular cracking occurring on acidic zeolites which involves the cracking of primary carbenium ion via an isomer of 2-methyl-2-butene to a secondary carbenium ion of propylene.

\[
\begin{align*}
\text{CHR}^+ & \rightarrow \text{CHR}^+ + \text{H}^+ \\
\text{CHR} & \rightarrow \text{CHR}^+ + \text{H}^+ \\
\text{H}^+ & \rightarrow \text{H}^+ + \text{C}_3^+ + \text{C}_2^= \\
\end{align*}
\]

Figure 6.3 β-scission mode of monomolecular cracking of C₅ carbenium ion.
Table 6.2 2-Methyl-2-butene cracking on different zeolites at 773 K, WHSV = 51 h\(^{-1}\) and p = 1 atm

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>X^a (%)</th>
<th>C(_2^)</th>
<th>C(_3^)</th>
<th>C(_4^)</th>
<th>C(_5^)</th>
<th>C(_6^)</th>
<th>C(_7^)</th>
<th>C(_8^)</th>
<th>Coke</th>
<th>iC(_4^)/ΣC(_4^)</th>
<th>H(_2^)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-22</td>
<td></td>
<td>10</td>
<td>45</td>
<td>45</td>
<td>2</td>
<td>2</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
<td>1</td>
</tr>
<tr>
<td>Ga(^+)/HZSM-22</td>
<td></td>
<td>4</td>
<td>46</td>
<td>46</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>3</td>
</tr>
<tr>
<td>Ga(_2)O(_2^+)/HZSM-22</td>
<td></td>
<td>11</td>
<td>46</td>
<td>45</td>
<td>1</td>
<td>0</td>
<td>1.9</td>
<td>0.2</td>
<td>0</td>
<td>0.3</td>
<td>6</td>
</tr>
<tr>
<td>HZSM-5</td>
<td></td>
<td>74</td>
<td>39</td>
<td>39</td>
<td>15</td>
<td>1</td>
<td>0.4</td>
<td>1</td>
<td>0.8</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>Ga(^+)/HZSM-5</td>
<td></td>
<td>24</td>
<td>41</td>
<td>42</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Ga(_2)O(_2^+)/HZSM-5</td>
<td></td>
<td>44</td>
<td>40</td>
<td>41</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>0.2</td>
<td>0.1</td>
<td>1.7</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^a\) H\(_2^\) = Mol. of H\(_2\) produced/mol. of olefin reactant.
Due to spatial constraints of the ZSM-22 pores, direct cracking of 2-methyl-2-butene is dominant over this zeolite. Cracking via the primary carbenium ion intermediate is energetically unfavorable leading to lower conversions of 2-methyl-2-butene compared to 1-hexene. Over HZSM-5 dimerization occurs enabling a significant contribution of bimolecular cracking (~35%), which present a more favorable reaction path. The reason is that cracking may occur via secondary or tertiary carbenium ions of oligomers of 2-methyl-2-butene. Consequently, hexene intermediates lead to the formation of butenes and ethylene.

\[
\begin{align*}
H_3C-CH_2-CH_2\text{CH}_2\text{CH}_2& \to H_3C-CH_2-CH_2\text{CH}_2\text{CH}_3 & C_3= + C_2= \\
H_3C-CH_2\text{CH}_2\text{CH}_3& \to H_3C-CH_2\text{CH}_2\text{CH}_3 & C_3= + C_2= \\
H_2C=CH-CH_2-CH_3& \to H_2C=CH-CH_2-CH_3 & C_3= + C_2= \\
H_3C-CH_2-CH_2\text{CH}_2\text{CH}_3& \to H_3C-CH_2-CH_2\text{CH}_2\text{CH}_3 & C_3= + C_2= \\
H_3C-C=CH-CH_3& \to H_3C-C=CH-CH_3 & C_3= + C_2= \\
\end{align*}
\]

*Figure 6.4 Possible monomolecular carbanion cracking mechanisms of C₅ olefin on Ga zeolites.*

Over Ga⁺/HZSM-5 and Ga⁺/HZSM-22 lower conversions are obtained. Despite this, higher selectivities to ethylene and propylene evidence a higher contribution of cracking of primary carbanions. A mechanism of 2-methyl-2-butene cracking over Ga⁺ cationic species is similar to the one proposed for 1-hexene via the alkylcyclopropane
Chapter 6

intermediate displayed in equation 6.6. Figure 6.4 shows the possible pathways for the cracking of 2-methyl-2-butene via carbanion mechanism. Bond shift as well as skeletal isomerization will occur over Ga$^{+}$ species to form the various isomers from 2-methyl-2-butene.

In addition to the zeolites containing Ga$^{+}$ active sites, 2-methyl-2-butene cracking was also studied over zeolites containing oxidized Ga cationic clusters to evaluate the activity of such species for olefin conversion (Table 6.2). EXAFS analysis of X-ray absorption spectra at the Ga K edge [19] confirmed the presence of oxygen-bridged Ga dimers (Ga$_2$O$_2^{2+}$) upon oxidation by nitrous oxide of Ga$^{+}$/HZSM-5 at 473 K. Higher 2-methyl-2-butene conversions are obtained over Ga$_2$O$_2^{2+}$/HZSM-5 and Ga$_2$O$_2^{2+}$/HZSM-22 compared to Ga$^{+}$/HZSM-5 and Ga$^{+}$/HZSM-22, respectively. However, the product distribution over reduced and oxidized Ga/HZSM-5 is very similar, suggesting that also over the Ga oxo dimer structures, olefins are cracked via a carbanion-type mechanism. The following reactions illustrate the conversion of pentenes over Ga$_2$O$_2^{2+}$ ions.

\[
\begin{align*}
C_5H_{10} + (ZO')_2 \cdots Ga_2O_2^{2+} & \rightarrow (ZO')_2 \cdots [Ga^{3+}(C_5H_9)(OH)(O^2-)Ga^{3+}]^{2+} \quad (6.9) \\
(ZO')_2 \cdots [Ga^{3+}(C_5H_9)(OH)(O^2-)Ga^{3+}]^{2+} & \rightarrow (ZO')_2 \cdots Ga_2O_2^{2+} + C_3H_6 + C_2H_4 \quad (6.10)
\end{align*}
\]

Figure 6.5 Conversion of 2-methyl-2-butene as a function of reaction time at 773 K (WHSV = 51 h$^{-1}$) over (a) Ga$_2$O$_2^{2+}$/HZSM-5 and (b) Ga$_2$O$_2^{2+}$/HZSM-22.
This reaction scheme implies regeneration of the active Ga oxo dimer structure. Nevertheless, as earlier reported, these species may deactivate to less active Ga\(^{3+}\) ions due to water desorption with concomitant reduction of Ga\(^{3+}\) to Ga\(^{2+}\) [7]. The deactivation of Ga\(_2\)O\(_2^{2+}\)/HZSM-5 and Ga\(_2\)O\(_2^{2+}\)/HZSM-22 is evidenced by Figure 6.5. Likely, deactivation is due to water desorption from [(HGa)\(_2\)(OH)\(_2\)]\(^{2+}\) intermediate structures which may be formed during hydrogen transfer reactions balanced by the formation of aromatics and coke. The final stable activities (after 80 min) of these oxidized Ga zeolites are very close to the activity of their reduced counterparts stressing the formation of Ga\(^{2+}\) species from the [(HGa)\(_2\)(OH)\(_2\)]\(^{2+}\) intermediates.

**Dimerization/Oligomerization over Ga zeolites**

The results for 1-butene cracking (Table 6.3) evidence a higher reactivity of 1-butene over Ga\(^{+}\)/HZSM-22 compared to HZSM-22. The conversion over Ga\(_2\)O\(_2^{2+}\)/HZSM-22 is higher than over its reduced counterpart, although also here deactivation takes place over the first hour of reaction. The activity of HZSM-22 is very low because dimerization is limited in ZSM-22 and direct cracking of 1-butene to ethylene involves energetically unfavorable primary carbenium ion transition states (Figure 6.6). In contrast to the case presented for HZSM-22, HZSM-5 shows a higher activity than its Ga\(^{+}\)-containing counterpart. The reason in this case is the possibility of 1-butene cracking via its oligomers. The higher conversion over HZSM-5 is thus attributed to the cracking of secondary or tertiary carbenium ions from oligomers of 1-butene.

![Figure 6.6 β-scission mode of monomolecular cracking of C\(_4\) carbenium ion.](image)

The product distribution of 1-butene conversion over Ga\(^{+}\)/HZSM-5 suggests that dimerization followed by cracking is one of the routes to the formation of equimolar amounts of propylene and pentenes. Nevertheless, monomolecular cracking is also revealed by the formation of ethylene. Comparatively, higher 1-butene conversions are obtained over Ga\(_2\)O\(_2^{2+}\)/HZSM-5, which includes further conversion of pentenes. Figure 6.7 shows the monomolecular cracking mechanism of 1-butene via carbanion chemistry, which occurs over Ga zeolites. From the product distribution, the ratio of monomolecular carbanion vs. bimolecular cracking of 1-butene over Ga\(^{+}\)/HZSM-5 and Ga\(_2\)O\(_2^{2+}\)/HZSM-5 is estimated to be about 1.7. Clearly, carbanion chemistry occurring on cationic Ga species promotes significant monomolecular (carbanion) cracking, which is not observed over Brønsted acid sites in ZSM-5. Additionally, increased amounts of aromatics and
Coke are observed over the cationic Ga species compared to HZSM-5 due to successive dehydrogenation and ring closure steps. The higher conversion over the Ga$_2$O$_2^{2+}$/HZSM-5 catalyst affords a higher aromatics yield than that over Ga$^+$/HZSM-5. The ratio of i-butene/total butene over HZSM-5 is 0.4 which is very close to the thermodynamic equilibrium [20]. This points to rapid isomerization of 1-butene, likely via dimerization followed by cracking. Nevertheless, the i-butene/total butene ratio of 0.2 over the Ga incorporated ZSM-5 zeolites is well below the thermodynamic ratio. The lower amount of i-butene may be understood in terms of the lower stability of carbanions that lead to the branched intermediates that yield i-butene upon cracking of dimers of 1-butene. This also implies that skeletal isomerization of 1-butene is limited.

![Monomolecular carbanion cracking mechanism of C$_4$ olefin on Ga zeolites.](image)

The product distribution for HZSM-22 can be understood by a combination of direct cracking (66%) and bimolecular cracking (33%). Over Ga$^+$/HZSM-22 a totally different product distribution is observed. Moreover, this product distribution is different from Ga$^+$/HZSM-5. Significantly higher conversions of 1-butene are observed for Ga$^+$/HZSM-22 and Ga$_2$O$_2^{2+}$/HZSM-22 than for HZSM-22. The product distribution shows a high selectivity to pentenes compared to propylene. This could be explained by elevated rate of oligomerization reactions between intermediate and the reactant olefins. Olefins higher than C$_5^-$ are readily cracked further while olefins lower than C$_4^-$ are oligomerized fast to higher olefins. Clearly, this would lead to pentenes as the dominant higher olefin product. The presence of Ga cations will also promote the preferential cracking of oligomers to ethylene.
Table 6.3 1-Butene cracking on different zeolites at 773 K, WHSV = 4h\(^{-1}\), p = 1 atm

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>X (%)</th>
<th>Olefins</th>
<th>Selectivity (%)</th>
<th>Coke</th>
<th>iC(_4^+)/ΣC(_4^+)</th>
<th>H(_2^#)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C(_2^+)</td>
<td>C(_3^-)</td>
<td>C(_5^-)</td>
<td>C(_6^-)</td>
<td>C(_1)</td>
</tr>
<tr>
<td>HZSM-22</td>
<td>3</td>
<td>52</td>
<td>25</td>
<td>12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ga(^+)/HZSM-22</td>
<td>24</td>
<td>42</td>
<td>7</td>
<td>35</td>
<td>0</td>
<td>4.5</td>
</tr>
<tr>
<td>Ga(_2)O(_2^+)/HZSM-22</td>
<td>33</td>
<td>50</td>
<td>6</td>
<td>30</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>HZSM-5</td>
<td>40</td>
<td>30</td>
<td>58</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Ga(^+)/HZSM-5</td>
<td>30</td>
<td>33</td>
<td>20</td>
<td>21</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ga(_2)O(_2^+)/HZSM-5</td>
<td>51</td>
<td>36</td>
<td>24</td>
<td>5</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^\#\)H\(_2\) = Mol. of H\(_2\) produced/mol. of olefin reactant
Over the gallium-containing ZSM-22 catalysts much lower aromatics selectivities are observed than over their ZSM-5 counterparts. This is most likely due to the smaller pore diameter of the ZSM-22 zeolite.

Assuming pseudo first-order kinetics \( k = -SV \cdot \ln (1-X) \) the rate constants for cracking of \( \text{C}_4-\text{C}_6 \) olefins are shown in Table 6.4. Clearly, the rate constant for cracking over protons decreases one order of magnitude going from hexenes to pentenes and again going from pentenes to 1-butene. This is in line with the increasing energy barrier for cracking of carbenium ions: primary-primary > primary-secondary > secondary-secondary. For the rate constants over \( \text{Ga}^+ \) an order of magnitude decrease is found going from 1-hexene to 2-methyl-2-butene. However, the rate constants for 2-methyl-2-butene and 1-butene are almost similar in line with the notion that the most likely intermediate is a primary carbanion.

### Table 6.4 Pseudo first-order reaction constant \( (k, \text{h}^{-1}) \) for cracking of olefins over zeolites, 773 K, 1 atm

<table>
<thead>
<tr>
<th>Reactant Olefin</th>
<th>WHSV (h(^{-1}))</th>
<th>ZSM-22 ( k_H^+ )</th>
<th>ZSM-22 ( k_{Ga}^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Hexene</td>
<td>68</td>
<td>2028</td>
<td>520</td>
</tr>
<tr>
<td>2-Methyl-2-butene</td>
<td>51</td>
<td>193</td>
<td>77</td>
</tr>
<tr>
<td>1-Butene</td>
<td>4</td>
<td>6</td>
<td>51</td>
</tr>
</tbody>
</table>

### 6.4 Conclusions

Conversion of \( \text{C}_4-\text{C}_6 \) olefins was studied over cationic Ga species and Brønsted acid sites in ZSM-5 and ZSM-22 zeolites. Although, Brønsted acid sites show the preference for formation of propylene via secondary carbenium ion cracking with low transition barrier, substantially higher amounts of ethylene are observed over gallium-exchanged zeolites. 1-Hexene reacts with a lower rate on \( \text{Ga}^+ \) ions compared to Brønsted acid sites but the product distribution is essentially derived by monomolecular carbanion cracking chemistry. The carbanion cracking over Ga cations involves abstraction of an allylic hydrogen atom from the olefin followed by subsequent stabilization of the allylic carbanion intermediate by a univalent \( \text{Ga}^+ \) ion. The reprotonation of the allylic bond leads to the starting olefin, a double bond isomer of the olefin or a alkylcyclopropane intermediate. Hydride shifts in this latter intermediate lead to skeletal isomers of the
Olefin cracking over Ga zeolites

reactant olefin or two smaller olefins. The increase in the cracking rate over cationic Ga species from \( \text{C}_4 \) through \( \text{C}_6 \) olefins is proposed to be due to the decreased C-H bond energy of the allylic H atom. The cracking rate of 2-methyl-2-butene and 1-butene via dimerization is high over HZSM-5 because monomolecular cracking involves cracking of energetically unfavorable primary carbenium ion. Nevertheless, the rate of monomolecular cracking of these olefins over cationic Ga species is substantially enhanced leading to increased amounts of ethylene.

6.5 References

Chapter 7

Cracking of *n*-heptane over Brønsted acid sites and Lewis acidic Ga sites in ZSM-5 zeolite

A series of gallium-containing ZSM-5 zeolites prepared by wet impregnation, ion-exchange and chemical vapor deposition (CVD) methods are compared in the cracking of *n*-heptane. Impregnation results in the dispersion of some of the gallium oxide clusters into the zeolite pore network as charge-compensating Ga species after calcination. Reduction of impregnated Ga/HZSM-5 catalysts leads to complete transformation of the oxidic Ga precursors to charge-compensating Ga\(^+\) and GaH\(^{2+}\) species. A small amount of divalent GaH\(^{2+}\) species can be stabilized; however, with increasing Ga/Al ratio monovalent cations dominate. While a model Ga/HZSM-5 catalyst prepared by CVD of Ga(CH\(_3\))\(_3\) containing mainly charge-compensating Ga cations displays high selectivity to dehydrogenated products (olefins, toluene and coke), catalysts with a lower Ga/Al ratio display improved activity with a product mixture resulting from contributions of Ga sites (dehydrogenation, aromatization, olefin cracking) and of Brønsted acid sites (protolytic cracking, olefin cracking). The synergy between Ga dehydrogenation sites and Brønsted acid sites is proposed to improve the dehydrogenation rate: the high acidity of the zeolitic proton facilitates hydrogen recombination and concomitant removal of product olefin from the Ga active sites. Ion-exchanged Ga/HZSM-5 catalyst which combines a difficult to reduce gallium oxide phase and high Brønsted acidity has the highest activity with relatively weak coke formation.
Chapter 7

7.1 Introduction

Light olefins are important building blocks for the chemical industry that are mostly produced by non-catalytic steam cracking of hydrocarbon feedstocks at high temperature. There is a strong desire to replace this process by an alternative that would require less demanding reaction conditions. An additional disadvantage is the limited control over the propylene-to-ethylene ratio in the olefins slate coming from steam crackers, whilst the demand for propylene is growing faster than that for ethylene. Hence, on-purpose processes for propylene production have been receiving more attention recently [1,2]. Catalytic cracking of naphtha-range hydrocarbons over acid zeolite appears attractive [3-7]. Since the transformation of long paraffins to short olefins occurs at least partly via carbenium ion chemistry, such a process should produce more propylene than ethylene.

Acidic microporous zeolites such as HZSM-5 are potential catalysts for the cracking of naphtha-range hydrocarbons. Paraffin conversion over protons in zeolites proceeds via two mechanisms [8-10]. The first one, mostly termed protolytic cracking, involves the formation of a carbonium ion followed by cracking of the C-H or C-C bond resulting in formation of hydrogen or paraffins, respectively, and a carbenium ion. In contrast to this monomolecular mechanism, the second one is bimolecular and involves hydride transfer reactions between an adsorbed carbenium ion and a reactant molecule leading to a chain mechanism in which carbenium ions evolve to smaller ones via β-scission. It is important to note that the current understanding is that carbonium and carbenium ions are the transition states in the transformation of adsorbed alkoxy species [11-14]. Hydrogen transfer is another reaction which catalyzes the redistribution of hydrogen in the final products resulting in the formation of hydrogenated and dehydrogenated products such as paraffins, aromatics and coke. The size of the channels and cavity of HZSM-5 are such that bimolecular hydride and hydrogen transfer reactions and the growth of carbonaceous deposits are more limited than in zeolites with larger pores such as BEA or FAU.

Alternative to the conversion of hydrocarbons over Brønsted acid sites is their activation over Lewis acid sites. Particularly, Ga and Zn cations exchanged in HZSM-5 have received wide attention because these catalysts allow the conversion of light paraffins to aromatics [15-17]. Recent experimental and theoretical work has shown that Ga⁺ species activate paraffins via heterolytic dissociation over the Lewis acid-base pair formed by the univalent Ga⁺ ion and the zeolite oxygen anion [18,19]. Although activation of paraffins over the Lewis acid-base pair formed by Ga³⁺ oxidic cations is
more favorable, these species deactivate to less active Ga\(^+\) ions. Clustered gallium oxides are also expected to be active for paraffins activation as suggested by a recent infrared study of the activation of ethane over Ga\(_2\)O\(_3\) [20]. The mechanism of aromatization is considered to be bifunctional [21-23], proceeding through a series of dehydrogenation, oligomerization and cyclization steps.

With respect to the formation of olefins, there is a large difference in the dehydrogenation activity between Brønsted acid sites and Lewis Ga sites. The former mainly catalyze C-C cracking reactions and to a lesser extent dehydrogenation, while the latter exhibits a strong preference for C-H activation. Without further cracking of the carbenium ion resulting from C-C cleavage such as is the case for propane, the olefins-to-paraffins ratio is much closer to unity for Brønsted acid sites than it is for Lewis Ga sites [19]. Starting from longer hydrocarbons, higher olefins-to-paraffins ratios are obtained because of consecutive cracking of the longer olefins produced in the initial protolytic cracking step. When bimolecular hydride transfer is limited as for HZSM-5, one predicts olefins-to-paraffins ratios of about 2 [24]. Dehydrogenation of paraffins over Lewis Ga sites should lead to higher olefin yields. For the cracking of longer olefins to smaller ones, proton transfer of sufficient strength are desired, although it is also possible to crack olefins over Lewis Ga sites.

The purpose of this study is to further investigate the influence of the Ga content in HZSM-5 on the conversion of \(n\)-heptane which is a suitable model reactant for the linear hydrocarbons in naphtha feedstocks. Our strategy is to combine Lewis Ga sites for the dehydrogenation of the paraffin feedstock (\(n\)-heptane) with Brønsted acid sites for the cracking of higher olefins (\(n\)-heptene) to light olefins. Issues to be addressed are the balance between Lewis Ga sites and Brønsted acid sites, the nature and location of the Ga active sites and the influence of the preparation and pretreatment of Ga/HZSM-5 catalysts on catalyst activity, selectivity and stability. Changes in the nature of Ga species were carefully characterized by TPR, FTIR and X-ray absorption near-edge spectroscopy at the Ga K edge.

### 7.2 Experimental

#### Preparation of materials

\(\text{NH}_4\text{ZSM-5 (Akzo Nobel, Si/Al =20) was calcined in a mixture of 20 vol. } \% \text{ O}_2 \text{ in } \text{N}_2 \text{ at a flow rate of 100 Nmol/min whilst heating to 823 K at a rate of 2 K/min followed by an isothermal period of 4 h to obtain HZSM-5.} \)
Chapter 7

Ga/HZSM-5 catalysts were prepared by the following methods. Wet impregnation of HZSM-5 was carried out using an aqueous solution of Ga(NO$_3$)$_3$ (Aldrich Chemical; 99.9999% purity) of appropriate concentrations to arrive at the desired Ga/Al ratio. The resulting materials were dried and are denoted as Ga(x-IMP)/HZSM-5 where x is the Ga/Al molar ratio. Ion exchange was performed by adding a 0.05 M Ga(NO$_3$)$_3$ (Aldrich Chemical; 99.9999% purity) solution dropwise to a 100 mL aqueous slurry containing 3 g of HZSM-5 whilst maintaining the pH of solution at 2 via simultaneous addition of NH$_4$OH. The mixture was then stirred and refluxed at 373 K for 4 h. Subsequently, the mixture was filtered and the residue was washed several times with distilled water. The catalyst was then dried overnight at 393 K and calcined. This material is denoted as Ga(x-ION)/HZSM-5.

A further material was prepared by chemical vapor deposition of trimethylgallium [19,25]. Trimethylgallium (1 mL) (TMG, Strem Chemicals, purity > 99%) was added to a glass vessel containing well-dried HZSM-5 in an Ar-flushed glove box. After 24 h, the resulting material was evacuated for 2 h to remove unreacted trimethylgallium and gaseous reaction products. The resulting material had a Ga/Al molar ratio close to unity [19,25] and was kept in Ar atmosphere prior to catalytic measurements. This sample is referred to as Ga(CVD)/HZSM-5.

Catalysts subjected to either oxidative or reductive pretreatments are indicated by (ox) and (red) suffices, respectively.

Characterization

Temperature programmed reduction

Temperature programmed reduction (TPR) was carried out in a flow apparatus equipped with a fixed bed reactor, a computer-controlled oven and a thermal conductivity detector. Typically, an amount of catalyst was contained between two quartz wool plugs in a quartz reactor. Prior to TPR, the catalyst was oxidized by exposure to a flowing mixture of 5 vol.% O$_2$ in He whilst heating to 823 K at a rate of 10 K/min. The catalyst was then cooled to room temperature in flowing nitrogen. TPR was performed by heating the catalyst in 4.5 vol.% H$_2$ in He at a flow rate of 8 ml/min, whilst heating from room temperature to 1073 K at a ramp rate of 10 K/min.
Inductively Coupled Plasma- Optical emission spectrometry (ICP-OES)

The gallium content of the catalysts was determined by ICP-OES. To extract gallium, a known amount of catalyst was initially treated in concentrated HF and subsequently dissolved in a 10 M sulfuric acid. The Ga loadings and resulting Ga/Al ratios are tabulated in Table 7.1. The Ga loading of the sample prepared by CVD was determined after in situ reduction before metal extraction.

Table 7.1 Gallium content and Ga/Al molar ratios of Ga/HZSM-5

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Method of incorporation</th>
<th>Loading Ga (wt.%)</th>
<th>Ga/Al (molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(0.13-IMP)/HZSM-5(ox)</td>
<td>Wet impregnation</td>
<td>0.69</td>
<td>0.13</td>
</tr>
<tr>
<td>Ga(0.25-IMP)/HZSM-5(ox)</td>
<td>Wet impregnation</td>
<td>1.32</td>
<td>0.25</td>
</tr>
<tr>
<td>Ga(0.39-IMP)/HZSM-5(ox)</td>
<td>Wet impregnation</td>
<td>1.94</td>
<td>0.39</td>
</tr>
<tr>
<td>Ga(0.62-IMP)/HZSM-5(ox)</td>
<td>Wet impregnation</td>
<td>3.01</td>
<td>0.62</td>
</tr>
<tr>
<td>Ga(0.6-ION)/HZSM-5(ox)</td>
<td>Ion-exchange</td>
<td>3.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Ga(CVD)/HZSM-5(red)</td>
<td>Chemical vapor deposition</td>
<td>4.8</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Nitrogen porosimetry

The pore size, surface area and pore volume of the oxidized Ga/HZSM-5 was obtained by nitrogen adsorption porosimetry (Micromeritics, ASAP 2000). Dubinin-Astakhov [26] and Horvath-Kawazoe [27] methods were employed for characterization of the microporosity.

Infrared spectroscopy

Infrared spectra were recorded on a Bruker IFS113v Fourier Transform IR spectrometer with a DTGS detector at a resolution of 2 cm\(^{-1}\). An in situ transmission IR cell with KRS-5 windows was used. The zeolite samples were pressed into self-supporting wafers with a density of about 9 mg/cm\(^3\). Prior to recording spectra, the sample was dehydrated by treatment in an oxygen flow at 823 K for 30 min. Reduction was achieved by flowing a mixture of 20 vol.% H\(_2\) in N\(_2\) at a flow rate of 5 mL/min followed by heating to 823 K at a rate of 5 K/min with an isothermal period of 1 h.
Finally, the catalyst was cooled to room temperature in vacuum (pressure lower than $10^{-5}$ mbar). All infrared spectra were normalized to the zeolite framework overtones of dehydrated HZSM-5. Infrared spectra of adsorbed CO were recorded after cooling the cell with liquid nitrogen. In this way, a constant temperature of 90 K could be maintained. Infrared spectra were measured at various CO pressures up to the saturation pressure.

**X-ray absorption near-edge spectroscopy**

Ga K edge XAS measurements were performed at the Dutch-Belgian beamline of the European Synchrotron Radiation Facility in Grenoble (France). The electron energy and the ring current were 2.0 GeV and 200 mA, respectively. An amount of zeolite material calculated to have an absorbance $\mu.X$ of 2.5 was pressed into a self-supporting wafer and placed in a controlled atmosphere transmission cell. Spectra were recorded with sampling steps of 0.5 eV in the XANES region.

$^{27}$Al NMR spectroscopy

$^{27}$Al MAS NMR measurements were carried out on a Bruker DMX500 spectrometer operating at 130.3 MHz. The sample was rotated in a 4 mm rotor with a spin rate of 25 kHz. Single-pulse excitation was used with a 30 degree pulse of 1.5 $\mu$s. A solution of Al(NO$_3$)$_3$ was used for shift calibration.

**Catalytic measurements**

Catalytic activity measurements were carried out in a tapered element oscillating microbalance (Rupprecht and Patashnick TEOM 1500 pulse mass analyzer) at atmospheric pressure and a temperature of 823 K. The TEOM system combines a catalytic reactor with a high-resolution microbalance that generates real-time measurements of mass changes during gas-solid reactions. The TEOM measures mass changes based on inertial forces, presenting various advantages over conventional gravimetric microbalances such as (i) a well-defined flow profile, eliminating possible heat and mass diffusion and buoyancy phenomena, (ii) a very fast response time in the order of 0.1 s and (iii) a high mass resolution across the entire range of pressure and temperature. Briefly, a feedback system including a resonator maintains the oscillation of the tapered tube. The natural frequency changes as a function of the mass of the tapered tube. This mass change is thus determined by the change of the oscillating frequency through the following equation.
\[ \Delta m = K_0 \left( \frac{1}{f_1^2} - \frac{1}{f_0^2} \right) \]

where \( \Delta m \) is the weight change, \( K_0 \) the spring constant, \( f_0 \) the oscillation frequency at the start of the experiment and \( f_1 \) the oscillation frequency at a given time during the experiment. \( K_0 \) is relatively constant over a large temperature range and changes slightly with temperature. In a typical experiment, the tapered tube is charged with 30 mg of catalyst (sieve fraction 125-250µ), firmly packed between two plugs of quartz wool. All the mass changes were corrected for the gas density differences. Product analysis was carried out by online gas chromatography (Shimadzu GC-17A, FID). The use of a FID detector does not allow quantification of the produced molecular hydrogen. Selectivities are therefore reported on a molar basis for the product hydrocarbons. The reactant feed consisted of 2.4 vol.% \( n \)-heptane in He at a WHSV of 43 h\(^{-1}\). The total gas flow was 200 Nml/min. Prior to the activity measurements, the catalyst was either treated in a reductive (\( \text{H}_2 \), final reduction temperature 823 K) or oxidative (20 vol.% \( \text{O}_2 \) in He, final oxidation temperature 823 K) atmosphere with a slow ramp rate of 5 K/min and kept at the final temperatures for 2 hrs.

### 7.3 Results and discussion

#### Thermodynamic calculations

Table 7.2 Equilibrium hydrocarbon composition of \( n \)-heptane (2.4 vol.% in He) to olefins and hydrogen excluding paraffins and aromatics at 823 K and 1 atm.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (mol.%)</th>
<th>Yield (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2^= )</td>
<td>71.9</td>
<td>61.7</td>
</tr>
<tr>
<td>( \text{C}_3^= )</td>
<td>23.5</td>
<td>30.3</td>
</tr>
<tr>
<td>( \text{C}_4^= )</td>
<td>4.1</td>
<td>7.1</td>
</tr>
<tr>
<td>( \text{C}_5^= )</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>( \text{C}_6^= )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \text{C}_7^= )</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The thermodynamic equilibrium properties of the reaction mixture for \( n \)-heptane cracking was computed at various temperatures and a constant pressure of 1 atm by the GIBBS routine implemented in the Outokumpu Software [28]. Initial calculations
involved the conversion of \( n \)-heptane to \( C_1-C_4 \) paraffins, \( C_2-C_7 \) olefins, aromatics (benzene, toluene and xylenes) and hydrogen. As expected methane is the most thermodynamically stable product comprising 80 mol.% of the equilibrium mixture. The remainder of the mixture is dominated by aromatics. To obtain a thermodynamic equilibrium distribution for olefins from \( n \)-heptane, paraffins and aromatics were not included in subsequent calculations. The results are listed in Table 7.2. At the reaction temperature applied in this study (823 K), the conversion of \( n \)-heptane is not thermodynamically limited and equilibrium propylene/ethylene and propylene/butenes molar ratios are calculated to be 0.3 and 5.7 respectively.

**Characterization of Ga/HZSM-5**

![Graph showing FTIR spectra]

*Figure 7.1 FTIR spectra at room temperature of the hydroxyl region of dehydrated HZSM-5 in comparison with Ga(0.25-IMP)/HZSM-5, Ga(0.39-IMP)/HZSM-5, Ga(0.62-IMP)/HZSM-5 and Ga(0.6-ION)/HZSM-5 (‘o’ refers to the oxidized sample, ‘r’ to the subsequently reduced sample).*

Figure 7.1 displays the infrared spectra of the hydroxyl region for the impregnated and ion-exchanged Ga/HZSM-5 samples with increasing Ga content after calcination and subsequent reduction. The spectrum of well-dehydrated HZSM-5 is included for comparison. The intensities of the band corresponding to the bridging hydroxyl groups around 3610 cm\(^{-1}\) for the calcined Ga/HZSM-5 zeolites are lower than the corresponding band in HZSM-5. The intensities for the reduced catalysts are lower than for the calcined
ones. From these infrared spectra, the degree of exchange of the Brønsted acid hydroxyl groups by cationic Ga species was calculated as compared to the HZSM-5 precursor. The values are collected in Table 7.3. For the calcined zeolites, the degree of proton exchange increases with Ga content. The hydrated Ga cation is too large to enter the micropores of HZSM-5 and in general gallium oxide particles are found to agglomerate on the external surface [29,30]. Calcination results in partial migration of gallium oxide particles into the micropores and in the replacement of a small portion of protons by cationic gallium species [17,29,31]. The exchange degree of the reduced samples also increases with increasing Ga content. Moreover, compared to the calcined samples the exchange degree increases upon subsequent reduction in line with the notion that neutral gallium oxide particles reduce to mobile Ga$_2$O species that react with the Brønsted acid sites [29,30] according to

$$\text{Ga}_2\text{O} + 2 \text{ZO}^- \cdots \text{H}^+ \rightarrow 2 \text{ZO}^- \cdots \text{Ga}^+ + \text{H}_2\text{O}.$$  

The reduced monovalent Ga species include Ga$^+$ and GaH$_2^+$ species that co-exist in a ratio depending on the reaction conditions [32] via

$$\text{ZO}^- \cdots \text{Ga}^+ + \text{H}_2 \Leftrightarrow \text{ZO}^- \cdots \text{GaH}_2^+.$$  

![Figure 7.2 FTIR spectra of adsorbed carbon monoxide at liquid nitrogen temperature of HZSM-5, Ga(0.62-IMP)/HZSM-5(ox) and Ga(0.62-IMP)/HZSM-5(red) (full line at CO saturation coverage, dashed line at 0.1 mbar CO).](image)
Infrared spectra of adsorbed CO on HZSM-5 and oxidized and reduced Ga(0.62-IMP)/HZSM-5 are shown in Figure 7.2. For HZSM-5, two prominent bands are observed at 2139 cm\(^{-1}\) and 2173 cm\(^{-1}\) corresponding to physically adsorbed CO in the zeolite micropores [33] and CO chemisorbed to the Brønsted acid sites [34]. Calcined Ga(0.62-imp/HZSM-5) exhibits a less pronounced band at 2173 cm\(^{-1}\) in correspondence with the decreased density of protons. After reduction, the band at 2173 cm\(^{-1}\) further decreases due to replacement of Brønsted acid sites by Ga\(^+\) species. This substitution is further underpinned by the appearance of a band related to weak CO chemisorption to Ga\(^+\) ions [32]. At a high partial pressure of CO this band is only visible as a shoulder around 2147 cm\(^{-1}\), but when the band of physisorbed CO is decreased at lower CO pressure the band at 2147 cm\(^{-1}\) is clearly resolved. The absence of bands around 2230 cm\(^{-1}\) indicates that no large agglomerates of gallium oxide were present [35,36]. These results qualitatively agree with the trends observed for this sample in Figure 7.1.

Inspection of Table 7.3 learns that the proton exchange degrees for these reduced catalysts are higher than expected on the basis of the presence of monovalent Ga cations [29-32]. The higher proton exchange degree is related to the presence of reduced cations with a higher charge. GaH\(^{2+}\) species can be stabilized by two proximate negative charges, for instance deriving from the presence of two framework Al ions in a five-membered ring of the zeolite lattice. Quantitative determination of such proximate tetrahedral Al sites has been reported earlier in Co-ZSM-5 catalysts [37]. Reduction in Ga/HZSM-5 may occur according to

\[
\text{Ga}_2\text{O} + (\text{ZO}^-\text{...H}^+)_2 + \text{ZO}^-\text{...H}^+ \rightarrow (\text{ZO}^-)_2\text{GaH}^{2+} + \text{ZO}^-\text{...Ga}^+ + \text{H}_2\text{O}.
\]

Under the assumption that reduced Ga species are present as monovalent (Ga\(^+\) or GaH\(^{2+}\)) or divalent (GaH\(^{2+}\)) species, the fraction of these species is estimated. These results are also listed in Table 7.3. For Ga(0.13-IMP)/HZSM-5, a large fraction of the Ga species (77%) is present as divalent GaH\(^{2+}\) species. With increasing Ga content, this value decreases. Infrared spectra of adsorbed CO for the various reduced catalysts as a function of the Ga loading (not shown here) showed an increasing (decreasing) intensity of the band at 2147 cm\(^{-1}\) (2173 cm\(^{-1}\)) in line with the increasing replacement of Brønsted acid sites by reduced Ga species. No bands distinguishing the various types of reduced Ga cations could be identified. The absolute amount of divalent Ga cations as a function of the Ga content displays a maximum at a Ga/Al ratio of 0.39 with about 40% of the framework Al atoms compensating divalent Ga species. At a higher Ga content this value decreases again. A higher Ga content may thus lead to further reduction of the divalent Ga cations to monovalent Ga cations according to
Table 7.3 Degree of exchange of Brønsted acid sites as compared to HZSM-5 and the contributions of monovalent (Ga\(^+\)) and divalent (GaH\(^{2+}\)) reduced Ga species in impregnated Ga/HZSM-5 zeolites upon reduction.

<table>
<thead>
<tr>
<th>Ga/Al ratio</th>
<th>Fraction of Brønsted acid sites</th>
<th>Fraction of divalent Ga species upon reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ZO(^-))..H(^+)(<em>{Ga/HZSM-5})/(ZO(^-))..H(^+)(</em>{HZSM-5})</td>
<td>Ga(<em>{divalent}/(Ga</em>{divalent}+Ga_{monovalent}))</td>
</tr>
<tr>
<td></td>
<td>Calcined Reduced</td>
<td>(Ga(_{divalent}/Al))</td>
</tr>
<tr>
<td>0.13</td>
<td>0.89 0.77</td>
<td>0.77 0.10</td>
</tr>
<tr>
<td>0.25</td>
<td>0.93 0.63</td>
<td>0.49 0.12</td>
</tr>
<tr>
<td>0.39</td>
<td>0.65 0.41</td>
<td>0.51 0.2</td>
</tr>
<tr>
<td>0.62</td>
<td>0.69 0.29</td>
<td>0.15 0.09</td>
</tr>
</tbody>
</table>
Ga$_2$O + (ZO$^-$)$_2$...GaH$^{2+}$ + ZO$^-$...H$^+$ $\rightarrow$ 3 ZO$^-$...Ga$^+$ + H$_2$O.

The occurrence of GaH$^{2+}$ sites was considered in recent computational studies of paraffin activation over reduced Ga cations [18,38]. Likely, in catalysts with Ga/Al ratios close to or higher than unity the predominant charge-compensating species are monovalent cations [19,25].

The reduction behavior of Ga(0.6-ION)/HZSM-5 presents some differences to that of impregnated Ga/HZSM-5. The replacement of Brønsted acid sites is less pronounced in the calcined catalyst. This indicates that the ion-exchange procedure has not been very effective and a large part of the Ga ions have ended up as gallium oxide on the external zeolite surface. Similarly, upon reduction the intensity of the bridging hydroxyl band only decreases slightly. About 36% of the protons are replaced by reduced Ga cations. Thus, the gallium oxide phase in Ga(0.6-ION)/HZSM-5 appears more difficult to reduce than the gallium oxide phases in the impregnated catalysts.

![Graph](attachment:image.png)

**Figure 7.3** TPR profiles of (a) HZSM-5, (b) Ga(0.39-IMP)/HZSM-5(ox), (c) Ga(0.62-IMP)/HZSM-5(ox), (d) Ga(CVD)/HZSM-5(ox) and (e) Ga(0.6-ION)/HZSM-5(ox).

Temperature programmed (hydrogen) reduction (TPR) profiles for the various Ga-containing ZSM-5 zeolites are shown in Figure 7.3. The gallium-containing samples
show a broad hydrogen consumption feature starting around 700 K. The hydrogen consumption is attributed to reduction of the neutral gallium oxide clusters to the cationic Ga\(^{\text{III}}\) and GaH\(^{2+}\) species. The broadness of the peaks suggests that reduction proceeds slowly. The reduction peak is more pronounced for Ga(0.62-IMP)/HZSM-5(ox) than for Ga(0.39-IMP)/HZSM-5(ox) in line with the higher Ga loading. The reduction extends over a large temperature range and does not appear to be complete at the highest temperature (1073 K). Southward et al. [39] and Brabec et al. [40] have also pointed out the incomplete reduction of Ga\(_2\)O\(_3\) clusters up to 1273 K. However, in the TPR experiments a lower hydrogen partial pressure was applied, while a prolonged isothermal period at 823 K was applied in the spectroscopic and catalytic activity measurements. Reduction of Ga(0.6-ION)/HZSM-5(ox) proceeds in two steps. At relatively low temperatures (820 K) a small part of Ga\(^{3+}\) is reduced, while the remaining part is reduced at approximately 1010 K. The more difficult reducibility of the gallium oxide phase is tentatively explained by the larger gallium oxide particles. The small shoulder at lower temperature (820 K) could indicate the reduction of a small amount of gallium oxide present in the micropore space. The TPR profile for Ga(CVD)/HZSM-5(ox) shows a very broad reduction feature extending from 550 K to 940 K. Clearly, this represents a broad distribution of gallium oxide clusters ranging from very small, likely cationic Ga-oxo dimeric (Ga\(_2\)O\(_2\)\(^{2+}\)) species (low reduction temperature) to large Ga\(_2\)O\(_3\) clusters on the external surface (high reduction temperature). A recent catalytic study [41] has shown that the dispersion in oxidized Ga(CVD)/HZSM-5 is substantially higher than that in an calcined impregnated Ga/HZSM-5. The higher dispersion was argued to be related to the higher dispersion of the precursor of the Ga(CVD)/HZSM-5 catalyst.

\(^{27}\)Al MAS NMR measurements were carried out to determine whether the ion-exchange or impregnation methods induce structural damage to the zeolite framework. Figure 7.4 compares the normalized \(^{27}\)Al NMR spectra of parent HZSM-5 and Ga/HZSM-5 materials. All the spectra contain a dominant resonance around 54 ppm attributed to tetrahedral Al sites that are present in the MFI framework. There is a small broad signal around 0 ppm indicative of the presence of some extraframework octahedral Al. No significant dealumination or redistribution of Al species is observed in Ga/HZSM-5 materials.
The nitrogen sorption isotherms of HZSM-5 and oxidized impregnated Ga/HZSM-5 display typical type I behavior as expected for microporous solids. For analysis of the isotherms, Dubinin-Astakhov and Horvath-Kawazoe methods were employed. The results of the nitrogen adsorption experiments are tabulated in Table 7.4. The decrease in the median pore diameter ($d_{H-K}$) with Ga loading reflects the presence of Ga in the zeolite micropores either in the form of cationic Ga-oxo dimeric species or neutral gallium oxide clusters. This finding is underpinned by lower values for the micropore volume and for the specific surface area of Ga(0.39-IMP)/HZSM-5(ox). The values for Ga(0.62-IMP)/HZSM-5(ox) suggest a smaller contribution of intra-zeolite Ga species, while those for Ga(0.6-ION)/HZSM-5(ox) indicate that only a very small amount of gallium oxide species are present inside the micropores.

Figure 7.4 $^{27}$Al NMR spectra of (a) parent HZSM-5 and oxidized (left) and reduced (right) (b) Ga(0.39-IMP)/HZSM-5(20), (c) Ga(0.62-IMP)/HZSM-5(20) and (d) Ga(0.6-ION)/HZSM-5(20).
Table 7.4 The equivalent surface area ($S_{D,A}$) and limiting micropore volume ($V_{D,A}$) calculated using the Dubinin-Astakhov method and the Horvath-Kawazoe median pore diameter ($d_{H,K}$) by nitrogen adsorption.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{D,A}$ (m$^2$/g)</th>
<th>$V_{D,A}$ (cm$^3$/g)</th>
<th>$d_{H,K}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>467</td>
<td>0.16</td>
<td>5.9</td>
</tr>
<tr>
<td>Ga (0.39-IMP)/HZSM-5(ox)</td>
<td>279</td>
<td>0.1</td>
<td>4.4</td>
</tr>
<tr>
<td>Ga (0.62-IMP)/HZSM-5(ox)</td>
<td>323</td>
<td>0.11</td>
<td>4.5</td>
</tr>
<tr>
<td>Ga (0.6-ION)/HZSM-5(ox)</td>
<td>407</td>
<td>0.15</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table 7.5 Parameters of deconvoluted peaks in XANES spectra of Ga/HZSM-5

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Edge</th>
<th>Ga(t) species (eV)</th>
<th>Ga(o) species (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Position</td>
<td>FWMH</td>
</tr>
<tr>
<td>Ga(CVD)/HZSM-5(ox)</td>
<td>10374.3</td>
<td>10375.6</td>
<td>4.09</td>
</tr>
<tr>
<td>Ga(0.6-ION)/HZSM-5(ox)</td>
<td>10374.5</td>
<td>10375.9</td>
<td>3.86</td>
</tr>
<tr>
<td>Ga(0.39-IMP)/HZSM-5(ox)</td>
<td>10374.9</td>
<td>10376.2</td>
<td>3.83</td>
</tr>
<tr>
<td>Ga(0.62-IMP)/HZSM-5(ox)</td>
<td>10374.5</td>
<td>10376.2</td>
<td>3.83</td>
</tr>
<tr>
<td>$\beta$-Ga$_2$O$_3$</td>
<td>10375.2</td>
<td>3.8</td>
<td>3.7</td>
</tr>
</tbody>
</table>

$^1$ Sample N-3 from Nishi et al. [42] with a particle size of 18 nm.
Insight into differences in the coordination environment of Ga was obtained by analysis of the Ga K edge region of X-ray absorption spectra of the calcined zeolites. The fine structure just above the edge reflects the local symmetry around the X-ray absorbing atom. Figure 7.5 shows the normalized Ga K edge XANES spectra for oxidized Ga(CVD)/HZSM-5 and Ga(0.6-ION)/HZSM-5 and the corresponding deconvolution. The XANES spectra consist of two peaks around 10375 and 10379 eV. These features relate to $1s \rightarrow 4p$ electron transitions of Ga atoms in tetrahedral and octahedral coordination, respectively [42]. The weaker feature at higher energy (10385 eV) is influenced by multiple scattering of photoelectrons by neighboring atoms [43]. To estimate the ratio of tetrahedral Ga(t) and octahedral Ga(o) atoms, the XANES spectra were deconvoluted according to the procedure by Iwasawa [43]. Briefly, the two peaks close to 10375 and 10379 eV were fitted by employing for each component an arctangent curve for continuum absorption and a Gaussian curve for the white line. The energy of the inflection point of the arctangent curve is chosen the same as that of the corresponding Gaussian curve. The feature at 10385 eV was not considered in this deconvolution. The fit parameters (energy of the absorption feature and the corresponding FWHM and peak area) and edge energies are collected in Table 7.5. For comparison, the corresponding data of $\beta$-Ga$_2$O$_3$ particles derived from calcination of gallium nitrate [42] are included. The edge energies of all catalyst are around 10374.5 ± 0.4 eV in line with earlier work [41]. The energies of the tetrahedral and octahedral components are around 10375.5 and 10379.5 eV, respectively. Ideally, the ratio of Ga(t) and Ga(o) atoms in $\beta$-Ga$_2$O$_3$ should be 1.0, but substantially lower values have been reported when the crystallinity is lowered.

Indeed, large particles of commercial $\beta$-Ga$_2$O$_3$ gave a ratio close to unity [42]. The $\beta$-Ga$_2$O$_3$ particles in Table 7.5 have a particle size of 18 nm. A lower ratio can also be caused by the presence of crystal phases with a higher fraction of octahedral Ga atoms. For our purpose, it is sufficient to note that substantial differences occur in the series of Ga-containing zeolites. Ga(CVD)/HZSM-5 contains the highest fraction of tetrahedral Ga ions, while the impregnated and ion-exchanged zeolites display lower ratios. The Ga(t)/Ga(o) ratio of the ion-exchanged zeolite Ga(0.6-ION)/HZSM-5 is closest to that of $\beta$-Ga$_2$O$_3$. This agrees with the surmise that rather large Ga$_2$O$_3$ crystallites that are difficult to reduce are present in this catalyst.
Figure 7.5 Ga K-edge XANES (circles) of (a) Ga(CVD)/HZSM-5(ox) and (b) Ga(0.6-ION)/HZSM-5(ox) and the fitted spectrum (solid line), which is composed of two sets of Gaussian and arctangent functions for octahedral and tetrahedral contributions.

The highest fraction of tetrahedral Ga atoms found in Ga(CVD)/HZSM-5 derives from the high Ga dispersion of the dimethyl gallium precursor. Oxidation of such species leads to a mixture of cationic Ga-oxo dimeric species and small gallium oxide particles, predominantly present in the micropores [41]. The higher dispersion of the gallium oxide phase in Ga(CVD)/HZSM-5(ox) followed from the substantially higher rate of hydrogen-deuterium exchange compared to that of calcined Ga/HZSM-5 zeolite prepared by impregnation. Ga(0.39-IMP)/HZSM-5 and Ga(0.62-IMP)/HZSM-5 exhibit a lower Ga(t)/Ga(o) ratio suggesting a higher fraction of Ga$_2$O$_3$ particles. We expect that the cationic species have a distorted tetrahedral coordination, while aggregated forms of gallium oxide exhibit octahedral and tetrahedral coordination.

**Catalytic activity measurements**

**HZSM-5 and Ga(CVD)/HZSM-5**

Figure 7.6 shows the conversion as a function of the reaction time for \(n\)-heptane cracking over HZSM-5, Ga(CVD)/HZSM-5(red) and Ga(CVD)/HZSM-5(ox) at 823 K. Shown in Figure 7.7 is the relative mass change of the catalyst as a function of the
reaction time as measured in the TEOM balance. The corresponding hydrocarbon selectivities are collected in Table 7.6. There is no thermodynamic limitation to the conversion of $n$-heptane at 823 K (Table 7.2). HZSM-5 exhibits the highest initial conversion. Relatively little deactivation is observed for this catalyst. The initial conversion of Ga(CVD)/HZSM-5(ox) is also relatively high but deactivation is pronounced within the first hour. For longer reaction times, the conversion of Ga(CVD)/HZSM-5(ox) is very similar to the conversion of Ga(CVD)/HZSM-5(red) which was almost constant ($\sim 15\%$) during the course of the reaction.

![Conversion (%) vs. Reaction Time (min) for HZSM-5, Ga(CVD)/HZSM-5(ox), and Ga(CVD)/HZSM-5(red)](image)

*Figure 7.6* $n$-heptane cracking over (☐) HZSM-5, (○) Ga(CVD)/HZSM-5(ox) and (∆) Ga(CVD)/HZSM-5(red) ($T = 823$ K, WHSV = 43 h$^{-1}$).

The hydrocarbon product mixture for HZSM-5 predominantly contains paraffins ranging from methane to butanes and olefins ranging from ethylene to butenes. No aromatics were observed. C-H bond cleavage of $n$-heptane leading to heptene and hydrogen would in principle lead to the exclusive formation of olefins from $n$-heptane. Paraffins lighter than $n$-heptane derive from protolytic cracking which results in the formation of methane and hexene, ethane and pentene and so forth. Hydrogen and methane can only be the products of protolytic cracking. Due to the decreasing C-H bond energy with increasing hydrocarbon carbon number, the rate of protolytic cracking increases with carbon number.
Table 7.6 Molar selectivities for \textit{n}-heptane cracking on HZSM-5 and Ga (CVD)/HZSM-5 catalysts (T = 823 K, WHSV = 43 h$^{-1}$, p = 1 atm)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>X (%)</th>
<th>Paraffins CH$_4$</th>
<th>C$_2$H$_6$</th>
<th>C$_3$H$_8$</th>
<th>C$<em>4$H$</em>{10}$</th>
<th>$\Sigma$C$<em>n$H$</em>{2n+2}$</th>
<th>Olefins$^1$ C$_2$H$_4$</th>
<th>C$_3$H$_6$</th>
<th>C$_4$H$_8$</th>
<th>$\Sigma$C$<em>n$H$</em>{2n}$</th>
<th>Aromatics C$_6$H$_6$</th>
<th>C$_7$H$_8$</th>
<th>C$<em>8$H$</em>{10}$</th>
<th>Coke</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5(20)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>54</td>
<td>5</td>
<td>7</td>
<td>9</td>
<td>7</td>
<td>28</td>
<td>15</td>
<td>34</td>
<td>15</td>
<td>64</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>60</td>
<td>49</td>
<td>5</td>
<td>7</td>
<td>9</td>
<td>8</td>
<td>29</td>
<td>15</td>
<td>35</td>
<td>16</td>
<td>66</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>120</td>
<td>47</td>
<td>5</td>
<td>7</td>
<td>9</td>
<td>8</td>
<td>29</td>
<td>15</td>
<td>35</td>
<td>16</td>
<td>66</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>180</td>
<td>48</td>
<td>5</td>
<td>7</td>
<td>9</td>
<td>8</td>
<td>29</td>
<td>16</td>
<td>35</td>
<td>16</td>
<td>67</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Ga (CVD)/HZSM-5(red)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>0</td>
<td>3</td>
<td>16</td>
<td>26</td>
<td>9</td>
<td>51</td>
<td>0</td>
<td>10</td>
<td>0</td>
<td>36</td>
</tr>
<tr>
<td>60</td>
<td>14</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>5</td>
<td>16</td>
<td>30</td>
<td>11</td>
<td>57</td>
<td>0</td>
<td>9</td>
<td>0</td>
<td>29</td>
</tr>
<tr>
<td>120</td>
<td>15</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>5</td>
<td>17</td>
<td>32</td>
<td>13</td>
<td>62</td>
<td>0</td>
<td>9</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>180</td>
<td>15</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>5</td>
<td>17</td>
<td>34</td>
<td>13</td>
<td>64</td>
<td>0</td>
<td>9</td>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td>Ga (CVD)/HZSM-5(ox)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>45</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>9</td>
<td>18</td>
<td>31</td>
<td>19</td>
<td>68</td>
<td>2</td>
<td>10</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>60</td>
<td>16</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>7</td>
<td>16</td>
<td>29</td>
<td>17</td>
<td>62</td>
<td>0</td>
<td>10</td>
<td>0</td>
<td>21</td>
</tr>
<tr>
<td>120</td>
<td>14</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>4</td>
<td>17</td>
<td>33</td>
<td>10</td>
<td>60</td>
<td>0</td>
<td>10</td>
<td>0</td>
<td>26</td>
</tr>
<tr>
<td>180</td>
<td>15</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>5</td>
<td>16</td>
<td>32</td>
<td>9</td>
<td>57</td>
<td>0</td>
<td>10</td>
<td>0</td>
<td>28</td>
</tr>
</tbody>
</table>

$^1$Equilibrium olefin molar compositions from \textit{n}-heptane at 823 K: C$_3$H$_6$/C$_2$H$_4$ = 0.3, C$_3$H$_6$/C$_4$H$_8$ = 5.7
Thus, the cracking rate of the product paraffins is lower than that of the reactant. The highest hydrocarbons in the product mixture are butanes, likely because formation of pentanes requires the formation of a very unstable C\textsubscript{2} carbenium ion. The product carbenium ions from the initial protolytic cracking step thus range from C\textsubscript{3} to C\textsubscript{7}. These olefins are further converted via cracking (β-scission), oligomerization and isomerization steps to a mixture of ethylene, propylene and butenes. Clearly, the propylene/ethylene ratio (2.2) is very deviant from the thermodynamic ratio. The reason is that formation of ethylene by cracking of a higher olefin involves an unfavorable primary carbenium ion transition state. Thus, the preference for propylene over ethylene derives from the lower activation barriers involved in the conversion of secondary or tertiary carbenium ions. Notably, equal amounts of ethylene and butenes are formed. In essence, the product distribution is kinetically determined. The exact distribution of olefins is difficult to predict because product paraffins higher than methane will also undergo protolytic cracking themselves. Also further hydride reactions are involved but they only lead to hydrogen redistribution and do not change the olefins-to-paraffins ratio. The initial olefins-to-paraffins ratio is close to two in agreement with earlier results [24]. Finally, hydrogen transfer reactions increase the paraffinic content but also lead to hydrogen-

Figure 7.7 Relative catalyst mass change with respect to reaction time for n-heptane cracking over (□) HZSM-5, (○) Ga(CVD)/HZSM-5(ox) and (△) Ga(CVD)/HZSM-5(red) (T = 823 K, WHSV = 43 h\textsuperscript{-1}).

Chapter 7
deficient species that are not observed in the gas-phase. These reactions lead to coke as observed by the increase of the mass of the catalyst as well as the deficiency in the carbon mass balance. Typically, we found that the amount of carbon missing from the gas chromatographic analysis was higher than the carbon probed by the TEOM analytical system. This difference should be due to the deposition of carbonaceous species outside the catalyst. Indeed, we observed black soot deposits on the internal parts of the TEOM system after reaction.

The conversion of the Ga(CVD)/HZSM-5(red) is approximately constant over the reaction time. The product composition, however, is totally different from the one observed for HZSM-5. Notably, the amount of paraffins is very low. The olefins-to-paraffins ratio decreases from about 17 to 12 during the course of the reaction. The lower selectivity to paraffins is compensated by increased amounts of dehydrogenation products. In addition to toluene which is observed as the only aromatic product, extensive amounts of coke are formed. The formation of substantially more carbonaceous deposits over the reduced Ga-containing zeolite is underpinned by the larger catalyst mass changes with reaction time. The initial mass change rate (Table 7.7) for HZSM-5 is about 1.5 times lower than that of Ga(CVD)/HZSM-5(red). The mass change rates of HZSM-5 and Ga(CVD)/HZSM-5(red) decay strongly with reaction time (not shown).

Table 7.7 Initial mass change rates of Ga/HZSM-5 catalysts in comparison with HZSM-5 during n-heptane cracking at 1 atm and 823 K.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Initial Conversion (%)</th>
<th>Initial mass change rate ($10^{-4}$ mg/mg-min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-5</td>
<td>54</td>
<td>3.4</td>
</tr>
<tr>
<td>Ga (CVD)/HZSM-5(red)</td>
<td>14</td>
<td>4.9</td>
</tr>
<tr>
<td>Ga (CVD)/HZSM-5(ox)</td>
<td>45</td>
<td>3</td>
</tr>
<tr>
<td>Ga (0.39-IMP)/HZSM-5(red)</td>
<td>68</td>
<td>8.9</td>
</tr>
<tr>
<td>Ga (0.39-IMP)/HZSM-5(ox)</td>
<td>75</td>
<td>3.1</td>
</tr>
<tr>
<td>Ga (0.62-IMP)/HZSM-5(red)</td>
<td>49</td>
<td>11.2</td>
</tr>
<tr>
<td>Ga (0.62-IMP)/HZSM-5(ox)</td>
<td>76</td>
<td>4.6</td>
</tr>
<tr>
<td>Ga (0.6-ION)/HZSM-5(red)</td>
<td>46</td>
<td>4.1</td>
</tr>
<tr>
<td>Ga (0.6-ION)/HZSM-5(ox)</td>
<td>88</td>
<td>1.2</td>
</tr>
</tbody>
</table>
In Ga(CVD)/HZSM-5(red), virtually all Brønsted acid sites are replaced by monovalent Ga\(^+\) species [19,25]. One should also take into account the possibility of some monovalent GaH\(_2\)\(^+\) species. Recently, we have shown by infrared spectroscopy [44] that paraffins are activated over cationic Ga\(^+\) species via a gallium alkyl intermediate. For \(n\)-heptane, this results in

\[
C_7H_{16} + \text{ZO}^- \cdots \text{Ga}^+ \rightarrow \text{ZO}^- \cdots [\text{Ga}^{+3}(C_7H_{15})(H)]^+.
\]

Quantum-chemical calculations have shown that the activation of paraffins over Ga\(^+\) species proceeds through a transition state involving the basic oxygen groups of the zeolite lattice [18]. The corresponding Ga-H vibration and the vibrations of the grafted alkyl group have been identified by infrared spectroscopy for activation of ethane over Ga\(^+\) sites [44]. The conversion of propane over these latter sites results in the formation of propylene and hydrogen [19]. Dissociation of this complex may lead similarly to heptenes and hydrogen via

\[
\text{ZO}^- \cdots [\text{Ga}^{+3}(C_7H_{15})(H)]^+ \rightarrow \text{ZO}^- \cdots \text{Ga}^+ + C_7H_{14} + \text{H}_2.
\]

The resulting heptenes are rapidly cracked to ethylene, propylene and butenes over Ga\(^+\), most likely via alkyl intermediates. Pentenes were not observed under these reaction conditions. The propylene/ethylene ratio over the Ga zeolites is initially lower than over HZSM-5. Moreover, we observe that the gallium-promoted catalyst produces a higher ethylene/butenes ratio. A tentative explanation is the difference in the mechanism of olefin cracking over Lewis acid Ga and Brønsted acid sites. Interestingly, toluene is the only aromatic product observed for Ga/HZSM-5. This observation points to the ability of Ga\(^+\) species to catalyze successive dehydrogenations of an \(n\)-heptene intermediate including the final ring-closure step. Earlier, the aromatization step in Ga/HZSM-5 catalysts has been linked to the simultaneous presence of Brønsted acid sites in addition to Ga cations [15-17]. Clearly, the present results indicate that Ga\(^+\) species are able to aromatize \(n\)-heptene in the absence of Brønsted acid sites.

The oxidized precursor Ga(CVD)/HZSM-5(ox) has a higher initial activity but deactivation is pronounced (Figure 7.6). After a reaction time of 1 h, the activity has become stable at a value very similar to the constant activity of Ga(CVD)/HZSM-5(red). Close inspection of the selectivity data shows that at the initial stages of the reaction, the product composition is intermediate to that of HZSM-5 and Ga(CVD)/HZSM-5(red). After oxidation, Ga(CVD)/HZSM-5 contains a mixture of Brønsted acid sites (about 60% of the original number in HZSM-5) and oxidic Ga species present in the form of cations.
and in more aggregated form. Protolytic cracking over protons leads to paraffins and olefins as hydrocarbon products, whereas oxidic Ga species catalyze dehydrogenation, cracking and aromatization.

Dehydrogenation over cationic Ga species [19] and over neutral gallium oxide aggregates [20] has been reported. Initially, a small amount of benzene is observed. Benzene derives from oligomerization of propylene followed by successive dehydrogenation and ring-closure steps. The presence of small amounts of benzene points to a higher dimerization activity of olefins in the presence of protons. The main aromatic product is toluene. The higher activity of Ga(CVD)/HZSM-5(ox) stems from the presence of more active Ga dehydrogenation sites [19] and the presence of protons. Two mechanisms contribute to the strong deactivation with reaction time. First, protons are replaced by reduced Ga cations as reduction of aggregated Ga oxide species occurs. The decrease in Bronsted acidity is also evident from the decrease in the paraffins selectivity. Second, highly active and highly dispersed oxidic Ga cations cannot be regenerated easily in the catalytic cycle [19,45]. Instead, water desorption leads to less active reduced Ga species. This deactivation mechanism is underpinned by the resemblance of the product distribution after prolonged reaction times to the one of Ga(CVD)/HZSM-5(red). This reduction of Ga$^{3+}$ to active Ga$^{+}$ sites agrees well with the conclusions of recent studies of n-butane aromatization over Ga-containing TON and MFI zeolites [46,47]. We do not expect that coke deactivation plays a major role because the initial mass change rate of Ga(CVD)/HZSM-5(ox) is almost similar to that of HZSM-5 and substantially lower than that of Ga(CVD)/HZSM-5(red). On the other hand, after about 1 h of reaction the rate of coke formation (Figure 7.7) of Ga(CVD)/HZSM-5(ox) becomes slightly higher than that of HZSM-5. Indeed, after prolonged reaction the selectivity to coke products increases to values also found for the reduced Ga(CVD)/HZSM-5 catalyst. This finding suggests that carbonaceous products are formed more easily over reduced Ga species than over oxidic Ga species, despite our finding that the latter species are more effective in the dehydrogenation of paraffins.

**Ga(IMP)/HZSM-5**

The activities and product distributions of reduced and oxidized Ga(0.39-IMP)/HZSM-5 and Ga(0.62-IMP)/HZSM-5 catalysts differ substantially from those of catalysts containing predominantly protons or reduced Ga species as active sites. The activity parameters as a function of the reaction time are listed in Table 7.8 and 7.9. An important observation is that in general Ga(IMP)/HZSM-5 catalysts exhibit increased initial activities over HZSM-5 and Ga(CVD)HZSM-5(red).
Table 7.8 Molar selectivities for n-heptane cracking on Ga (0.39-IMP)/HZSM-5 catalysts (T = 823 K, WHSV = 43 h⁻¹, p = 1 atm)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>X (%)</th>
<th>Paraffins</th>
<th>Product selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH₄</td>
<td>C₂H₆</td>
</tr>
<tr>
<td>5</td>
<td>68</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>60</td>
<td>60</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>120</td>
<td>51</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>180</td>
<td>41</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

|            |       | Ga (0.39-IMP)/HZSM-5(red) | |
| 5          | 75    | 6   | 2    | 4    | 4     | 16       | 17   | 35   | 15   | 67     | 3    | 6    | 1     | 7    |
| 60         | 60    | 5   | 2    | 3    | 4     | 14       | 15   | 37   | 19   | 70     | 2    | 4    | 0     | 9    |
| 120        | 43    | 4   | 2    | 3    | 4     | 13       | 13   | 40   | 24   | 77     | 1    | 4    | 0     | 5    |
| 180        | 33    | 4   | 2    | 3    | 2     | 11       | 12   | 40   | 26   | 78     | 0    | 4    | 0     | 7    |
Table 7.9 Molar selectivities for n-heptane cracking on Ga (0.62-IMP)/HZSM-5 catalysts (T = 823 K, WHSV = 43 h\(^{-1}\), p = 1 atm)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>X (%)</th>
<th>Paraffins</th>
<th></th>
<th>Olefins</th>
<th></th>
<th>Aromatics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH(_4)</td>
<td>C(_2)H(_6)</td>
<td>C(_3)H(_8)</td>
<td>C(_4)H(_10)</td>
<td>ΣC(<em>n)H(</em>{2n+2})</td>
<td>C(_2)H(_4)</td>
</tr>
<tr>
<td>5</td>
<td>49</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>8</td>
<td>13</td>
</tr>
<tr>
<td>60</td>
<td>27</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>120</td>
<td>25</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>9</td>
<td>15</td>
</tr>
<tr>
<td>180</td>
<td>24</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>8</td>
<td>14</td>
</tr>
</tbody>
</table>

Ga (0.62-IMP)/HZSM-5(red)

| 5         | 76    | 5         | 2         | 3       | 5       | 15        | 16       | 37       | 17       | 70       | 2       | 6       | 1       | 6     |
| 60        | 36    | 4         | 2         | 3       | 2       | 11        | 14       | 39       | 25       | 78       | 1       | 5       | 0       | 5     |
| 120       | 21    | 4         | 2         | 2       | 2       | 10        | 14       | 40       | 28       | 82       | 0       | 6       | 0       | 2     |
| 180       | 17    | 4         | 3         | 2       | 1       | 10        | 13       | 39       | 28       | 80       | 0       | 6       | 0       | 4     |

Ga (0.62-IMP)/HZSM-5(ox)
Oxidized catalysts containing a combination of Brønsted acid sites, extraframework cationic and neutral gallium oxide clusters as active sites are initially more active than their reduced counterparts that contain predominantly protons and mono- (Ga\(^+\)) and divalent (GaH\(^{2+}\)) cationic species.

These findings point to synergy between Brønsted acid sites and the various Ga species. Earlier, it has been proposed [48] that propane activation over Ga-containing zeolites occurs via a pseudo-protonated cyclopropane intermediate involving both protons and Ga\(^+\) species. An alternative explanation is given by recent finding that the largest contribution to the activation barrier in the dehydrogenation of paraffins over reduced Ga sites is the concerted removal of hydrogen and the olefin from the cationic \([\text{Ga}^{3+}(\text{R}^-)(\text{H}^-)]^+\) cation [18]. This step involves recombination of the negatively charged hydride ion with the slightly negatively charged H atom at the \(\beta\)-position of the alkyl group. The involvement of a more acidic zeolitic proton in the proximity of the cation Ga complex may facilitate its dissociation to hydrogen and an olefin. Finally, the hydride ion reduces Ga\(^{3+}\) to Ga\(^+\) and is donated back to the zeolite as a proton. This explanation provides a molecular interpretation for the earlier experimental observations that hydrogen recombination is facilitated in Ga/H-ZSM-5 catalysts [16,49]. Such mechanism may also explain the higher activity of the oxidized catalysts, since here the proton density is higher. On the other hand, earlier work has also provided evidence that Ga\(^{3+}\) oxide cations are more active than reduced Ga species for propane activation [19]. Moreover, neutral gallium oxide clusters are also able to activate paraffins [20]. Thus, the increased activity of the oxidized catalysts over Ga(CVD)/HZSM-5(ox) is likely due to a combination of high dehydrogenation activity of gallium oxide species in combination with relatively larger number of Brønsted acidic sites.

Ga(0.39-IMP)/HZSM-5 and Ga(0.62-IMP)/HZSM-5 catalysts show pronounced deactivation during the reaction. The deactivation in oxidized catalysts is attributed to the gradual reduction of gallium oxide species and to coke formation. From the infrared spectra it follows that a substantial part of Ga must be present in the form of charge-compensating gallium oxide cationic species. Their subsequent reduction is also evident from the observation that the activity of the oxidized catalysts resembles that of the reduced catalysts after prolonged reaction times. The deactivation in reduced catalysts however, is primarily attributed to the formation of carbonaceous material. This surmise is corroborated by the high initial mass change rates of reduced Ga(0.39-IMP)/HZSM-5 and Ga(0.62-IMP)/HZSM-5 (Table 7.7). Clearly, the higher deactivation rate must be due to increased dehydrogenation rates related to the close proximity of the reduced Ga sites and the Brønsted acid sites.
Paraffin cracking on Ga(IMP)/HZSM-5 catalysts results in paraffins, olefins, aromatics and coke. The product distribution is due to contributions of cracking over Brønsted acid sites and over Ga species. Protolytic cracking of paraffins and β-scission of higher olefins over protons leads to a mixture of paraffins and olefins as hydrocarbon products, while Ga species catalyze the dehydrogenation, cracking and aromatization. Likely, the rate of dehydrogenation is increased by synergy between proximate reduced Ga sites and protons. After 5 min of reaction, the ethylene/butenes ratio is close to one suggesting that initially cracking is dominated by Brønsted acid sites. A significant difference in the product distribution to that of HZSM-5 and Ga(CVD)/HZSM-5(red) is the formation of aromatics (benzene and xylenes) in addition to toluene. This should be due to the higher rate of dimerization reactions of light olefins over protonic sites followed by ring-closure over Ga species. In line with this, an increase of the Ga content (Ga(0.39-IMP)/HZSM-5 vs. Ga(0.62-IMP)/HZSM-5) leads to a decrease of the contribution of paraffins, benzene and xylenes in the product mixture.

**Ga(0.6-ION)/HZSM-5**

Table 7.10 summarizes the catalytic performance as a function of the reaction time during $n$-heptane conversion at 823 K over Ga(0.6-ION)/HZSM-5. Ga(0.6-ION)/HZSM-5(ox) has the highest initial activity amongst the present catalysts. The active sites in Ga(0.6-ION)/HZSM-5(ox) include cationic Ga-oxo dimeric species, protons and larger extraframework gallium oxide aggregates. Infrared and X-ray absorption near-edge spectroscopic results suggest that smaller amounts of Ga cationic species are present compared to the Ga/HZSM-5 catalysts prepared by impregnation. Instead, larger agglomerated gallium oxide species are likely present at the external zeolite surface, which have been found more difficult to reduce. The high activity of this catalyst may thus be explained by the high concentration of Brønsted acid sites augmented by dehydrogenation sites largely present on the external surface. The product distribution reflects contribution from these species. Moreover, we note that during reaction the selectivity to dehydrogenated products increases at the expense of the paraffins selectivity. This is taken as an indication that at least part of the gallium oxide phase reduces and part of the Brønsted acid sites are replaced by reduced Ga species. Indeed, the product distribution after a reaction time of 3 h resembles that of the reduced catalyst. Comparing Ga(0.6-ION)/HZSM-5(red) with Ga(0.62-IMP)/HZSM-5(red), we note that the initial conversion is very similar. However, the former catalyst produces more paraffins in line with the higher proton density. The lower dehydrogenation rate is further corroborated by a three times lower rate of coke formation (Table 7.7) compared to its impregnated counterpart. Hence, deactivation of the ion-exchanged catalyst with reaction time is somewhat less pronounced.
Table 7.10 Molar selectivities for \(n\)-heptane cracking on Ga (0.6-ION)/HZSM-5 catalysts (\(T = 823\) K, WHSV = 43 h\(^{-1}\), \(p = 1\) atm)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>X (%)</th>
<th>Paraffins</th>
<th>Product selectivity (%)</th>
<th>Olefins</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH(_4)</td>
<td>C(_2)H(_6)</td>
<td>C(_3)H(_8)</td>
<td>C(<em>4)H(</em>{10})</td>
</tr>
<tr>
<td>5</td>
<td>46</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>60</td>
<td>36</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>120</td>
<td>30</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>180</td>
<td>28</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH(_4)</td>
<td>C(_2)H(_6)</td>
<td>C(_3)H(_8)</td>
<td>C(<em>4)H(</em>{10})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>88</td>
<td>6</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>60</td>
<td>68</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>120</td>
<td>48</td>
<td>5</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>180</td>
<td>39</td>
<td>4</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 7.8 Initial mass change rates over (○) oxidized and (△) reduced Ga/HZSM-5 as a function of their initial n-heptane conversions.

Finally, Figure 7.8 shows the initial mass change rates as a function of initial conversion for the Ga/HZSM-5 catalysts (Table 7.7). Clearly, the coke formation rate increases linearly with conversion for reduced Ga/HZSM-5 catalysts while this rate is lower and almost independent on conversion for oxidized catalysts. This result again stresses that reduced Ga species catalyze the formation of carbonaceous deposits more efficiently than their oxidized counterparts.

7.4 Conclusions

Ga/HZSM-5 zeolites were prepared by wet impregnation, ion-exchange and chemical vapor deposition methods. Already after calcination part of the Bronsted acid sites are replaced by charge-compensating Ga$^{3+}$-oxo cations. Most of the Ga species, however, are retained as neutral gallium oxide clusters on the external zeolite surface. Reduction of impregnated zeolites at 823 K results in the protolysis of mobile Ga-oxide clusters, resulting in the substitution of the Brønsted acid sites by monovalent Ga$^+$ and divalent GaH$^{2+}$ species. With increased Ga loading, monovalent Ga$^+$ species are the dominant charge-compensating species in reduced Ga/HZSM-5. The XANES spectra of oxidized ion-exchanged catalyst shows significant amount of octahedral Ga species in the
form of neutral gallium oxide clusters. FTIR upon reduction and hydrogen TPR point to a
difficult to reduce gallium oxide phase in this material. Chemical vapor deposition results
in better dispersion of Ga species into the zeolite micropores, resulting in well-defined
Ga\(^+\) sites upon reduction.

The product distribution depends critically on the presence of the Brønsted acid
sites and Ga dehydrogenation sites. While protolytic cracking followed by cracking of
long-chain carbenium ions by \(\beta\)-scission leading to light olefins and alkanes is dominant
in HZSM-5, monovalent Ga\(^+\) in reduced Ga(CVD)/HZSM-5 produce mainly toluene,
olefins and coke. This clearly shows that Ga\(^+\) sites catalyze the further dehydrogenation
and ring-closure of \(n\)-heptene. Catalysts containing both Brønsted acid sites and reduced
or oxidized Ga species behave as bifunctional catalysts. The product slate is more
complex and involves products from dehydrogenation, cracking, oligomerization and
aromatization. Clear synergy is observed when protons are combined with proximate Ga
species; likely the high acidity of the zeolitic protons facilitates the hydrogen
recombination step in the dehydrogenation of alkanes. Increase of the Ga/Al ratio leads to
an increase of the selectivity to dehydrogenated products at the expense of the formation
of alkanes. Nevertheless, the total light olefin content of such bifunctional catalysts is
only marginally higher than over pure protonic zeolites. Oxidized catalysts display higher
reactivity than their reduced counterparts because the proton content in the former is
higher. After prolonged reaction time oxidized and reduced catalysts tend to show similar
activity due to gradual formation of reduced Ga species (Ga\(^+\) and GaH\(^2+\)) at the expense
of zeolitic protons. Highest activity is obtained with oxidized Ga(0.6-ION)/HZSM-5
because the gallium oxide phase in this case is difficult to reduce.

7.5 References

   195.
8. W. O. Haag, R. M. Dessau, Proc. 8th Int. Congress on Catalysis, Berlin,
   Dechema, Frankfurt am Main, 2 (1984) 305.
Chapter 8

Cracking of naphtha-range hydrocarbons over Ga promoted zeolites

Gallium-containing ZSM-5 and ZSM-22 zeolites prepared by wet impregnation and chemical vapor deposition methods are compared in the cracking of \textit{n}-heptane and \textit{n}-hexane. Brønsted acid sites catalyze protolytic cracking and olefin cracking leading to a mixture of alkanes and light olefins. The product olefin distribution depends on the acid site density and the topology of the zeolite. Bifunctional catalysts containing both protons and reduced Ga species increase the selectivity to dehydrogenated products at the expense of paraffins formation. Reduced Ga cations catalyze dehydrogenation, olefin cracking and ring-closure steps. Additionally, the selectivity to ethylene increases with increasing Ga content in the cracking catalyst. This can be understood in terms of a preference for cracking of higher olefins to ethylene over Ga\(^+\) ions.
8.1 Introduction

The conversion of paraffins over Ga/HZSM-5 is considered to proceed in a bifunctional manner over Brønsted acid sites as well as Ga sites [1-3]. Activation of the paraffins may proceed via protolytic cracking or via heterolytic dissociation over the Ga sites. In previous chapters various candidate active sites of Ga cations (Ga\(^+\), GaH\(^+\), GaH\(^2+\), Ga\(_2\)O\(_2\)\(^2+\)) have been considered. The activation of paraffins over Brønsted acid sites leads to preferential cracking of C-C bonds while over the Ga cations the C-H bond cleavage is dominant leading selectively to the olefin [4]. The resulting olefins are further converted over the Brønsted acid sites via \(\beta\)-scission reactions and over Ga cations via a mechanism involving Ga-alkyl intermediates. In this chapter, cracking of \(n\)-heptane and \(n\)-hexane was studied with a strategy to combine Lewis Ga sites for the dehydrogenation of the alkane feedstock with Brønsted acid sites (or Lewis Ga sites) for the cracking of intermediate higher olefins to light olefins. It has been shown in earlier chapters that at high temperatures, conversion of olefins in the C\(_6\)-C\(_8\) range over Brønsted acid sites proceeds preferentially via direct monomolecular cracking. This is due to the possibilities to crack these olefins via \(\beta\)-scission of secondary and tertiary carbenium ions. These routes limit the formation of ethylene. On the other hand, our understanding of olefin conversion over Lewis acidic Ga cations predicts increased ethylene selectivities.

8.2 Experimental

Preparation of materials

NH\(_4\)ZSM-5 (Akzo Nobel, Si/Al 20 and 40) and NH\(_4\)ZSM-22 (Shell, Si/Al 39) were calcined in a mixture of 20 vol. \% O\(_2\) in N\(_2\) at a flow rate of 100 Nml/min whilst heating to 823 K at a rate of 2 K/min followed by an isothermal period of 4 h to obtain HZSM-5 and HZSM-22 respectively.

Ga substituted HZSM-5 and HZSM-22 catalysts were prepared by the following methods. Wet impregnation of HZSM-5 was carried out using an aqueous solution of Ga(NO\(_3\))\(_3\) (Aldrich Chemical; 99.9999% purity) of appropriate concentrations to arrive at the desired Ga/Al ratio. The resulting materials were denoted as Ga(x-IMP)/ZEO(y,z) where \(x\) is the Ga/Al molar ratio; \(y\) is the Si/Al ratio and \(z\) the pretreatment on the catalyst. Chemical vapor deposition of trimethylgallium [4,5] was carried out on HZSM-5 (Akzo Nobel, Si/Al 20) and HZSM-22 (Shell, Si/Al 39). Trimethylgallium (1 mL) (TMG, Strem Chemicals, purity > 99%) was added to a glass vessel containing well-dried zeolites in an Ar-flushed glove box. After 24 h, the resulting material was evacuated for 2
Cracking of naphtha-range hydrocarbons…

h to remove unreacted trimethylgallium and gaseous reaction products. The resulting materials were kept in Ar atmosphere prior to catalytic measurements. These samples when reduced are referred to as Ga(1.0-CVD)/HZSM-5(20,red) and Ga(0.7-CVD)/HZSM-22(39,red) and had Ga/Al molar ratios close to unity and 0.7 respectively.

**Catalytic measurements**

Catalytic activity measurements were carried out in a tapered element oscillating microbalance (Rupprecht and Patashnick TEOM 1500 pulse mass analyzer) at atmospheric pressure and a temperature of 823 K. In a typical experiment, the tapered tube is charged with 30 mg of catalyst (sieve fraction 125-250µ), firmly packed between two plugs of quartz wool. Product analysis was carried out by an online three-column fast gas chromatograph (Compact GC, Interscience) equipped with PLOT Al₂O₃/KCl, Molsieve (5 Å) and RTX-1 columns. The reactant feed consisted of 2.4 vol.% \( n \)-heptane or 3.8 vol.% \( n \)-hexane in He at a WHSV of 43h\(^{-1}\) and 30h\(^{-1}\) respectively. Prior to the activity measurements, the Ga substituted zeolites were treated in a reductive (\( \text{H}_2 \), final reduction temperature 823 K) atmosphere with a slow ramp rate of 5°C/min and kept at the final temperatures for 2 hrs. For comparison, HZSM-5 and HZSM-22 zeolites were brought to reaction temperature of 823 K in oxidative (20 vol.% \( \text{O}_2 \) in He) atmosphere.

**8.3 Results and discussion**

**\( n \)-Heptane cracking**

Table 8.1 shows the hydrocarbon selectivities for cracking of \( n \)-heptane over HZSM-22(39), Ga(0.25-IMP)/HZSM-22(39,red) and Ga(0.7-CVD)/HZSM-22(39,red). C-C bond cleavage over Brønsted acid sites in HZSM-22 (protolytic cracking) leads to formation of paraffins in the range from \( \text{C}_1-\text{C}_4 \) and corresponding olefins in the range of \( \text{C}_3-\text{C}_6 \) while C-H bond cleavage leads to heptenes and hydrogen. Hexenes and heptenes are not observed in the product distribution because they are easily converted by cracking reactions to a mixture of lower olefins including ethylene, propylene, butenes and pentenes. The olefin product distribution is dominated by propylene and butenes with ethylene/pentenes and propylene/butenes ratios close to 1. This distribution of lower olefins reflects subsequent cracking of intermediate heptenes. Indeed, it has been shown in chapter 5 that monomolecular cracking of heptene results in equimolar propylene and butene over HZSM-22 and dominates over primary carbenium cracking which gives ethylene and pentenes.
Table 8.1  Molar selectivities for \( n \)-heptane cracking at 823 K on HZSM-22(39), Ga(0.25-IMP)/HZSM-22(39,red) and Ga(0.7-CVD)/HZSM-22(39,red) catalysts (WHSV = 43 h\(^{-1}\), p = 1 atm)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>X (%)</th>
<th>Paraffins</th>
<th>Product selectivity (%)</th>
<th>Olefins</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \text{CH}_4 )</td>
<td>( \text{C}_2\text{H}_6 )</td>
<td>( \text{C}_3\text{H}_8 )</td>
<td>( \text{C}<em>4\text{H}</em>{10} )</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>4</td>
<td>9</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>60</td>
<td>3</td>
<td>4</td>
<td>9</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>4</td>
<td>9</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>150</td>
<td>2</td>
<td>4</td>
<td>9</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>HZSM-22(39)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>6</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>60</td>
<td>7</td>
<td>6</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>150</td>
<td>6</td>
<td>6</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Ga(0.25-IMP)/HZSM-22(39,red)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>9</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>60</td>
<td>6</td>
<td>10</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>150</td>
<td>3</td>
<td>10</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

144
Table 8.2  Molar selectivities for \( n \)-heptane cracking at 823 K on HZSM-5(20), Ga(1.0-CVD)/HZSM-5(20,red) and Ga(0.39-IMP)/HZSM-5(20,red) catalysts (WHSV = 43 h\(^{-1}\), p = 1 atm)

<table>
<thead>
<tr>
<th>Time (min) X (%)</th>
<th>Paraffins</th>
<th>Product selectivity (%)</th>
<th>Olefins</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH(_4)</td>
<td>C(_2)H(_6)</td>
<td>C(_3)H(_8)</td>
<td>C(_4)H(_10)</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------</td>
<td>-------------------------</td>
<td>---------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>54</td>
<td>5</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>60</td>
<td>49</td>
<td>5</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>120</td>
<td>47</td>
<td>5</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>180</td>
<td>48</td>
<td>5</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>60</td>
<td>14</td>
<td>0</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>120</td>
<td>15</td>
<td>0</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>180</td>
<td>15</td>
<td>0</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>68</td>
<td>6</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>60</td>
<td>60</td>
<td>5</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>120</td>
<td>51</td>
<td>5</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>180</td>
<td>41</td>
<td>5</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>
Chapter 8

The rate of C-C bond cleavage during protolytic cracking has been earlier shown to be 2-3 times higher than the rate of dehydrogenation for propane conversion in HZSM-5 [6,7]. Nevertheless, the heptene derived by C-H bond cleavage of the reactant paraffin significantly influences the olefin distribution compared to olefins derived by C-C bond cleavage and subsequent β-scission.

Ga(0.25-IMP/HZSM-22(39,red)) and Ga(0.7-CVD)/HZSM-22(39,red) contain Brønsted acid sites as well as Ga⁺ as active species. The conversions over these Ga-containing ZSM-22 zeolites are higher than over the HZSM-22 parent zeolite. The catalysts produce more aromatics and coke and exhibit an increased olefins-to-paraffins ratio. Clearly, the partial replacement of Brønsted acid sites by Ga⁺ ions leads to a decreased contribution of protolytic cracking compensated by an increase of dehydrogenation over Ga⁺ ions. The decrease in activity is primarily attributed to coking. The Ga⁺ species provide a dehydrogenation function via

$$\text{C}_7\text{H}_{16} + \text{ZO}^\cdash\text{Ga}^+ \rightarrow \text{ZO}^\cdash[\text{Ga}^+(\text{C}_7\text{H}_{15})(\text{H})]^+ \rightarrow \text{ZO}^\cdash\text{Ga}^+ + \text{C}_7\text{H}_{14} + \text{H}_2.$$  

The resulting heptene intermediates are rapidly cracked to ethylene, propylene and butenes over both Ga⁺ and Brønsted acid sites. Nevertheless, the distribution of olefins for Ga(0.25-IMP)/HZSM-22(39,red) is close to that for HZSM-22 showing that the small amounts of Ga⁺ species do not largely influence the distribution of olefins strongly. As discussed in chapters 5 and 6, there is a distinct difference in the cracking mechanism of higher olefin cracking over Ga⁺ ions (carbanion) and Brønsted acid sites (carbenium). Via the proposed carbanion mechanism over Ga⁺ ions increased selectivities to ethylene are obtained compared to carbenium ion cracking routes over Brønsted acid sites. The slightly higher amounts of coke and aromatics in the Ga substituted ZSM-22 zeolites are attributed to oligomerization reactions over protonic sites followed by ring-closure steps over Ga⁺ cationic species.

With the increase of Ga content from Ga(0.25-IMP/HZSM-22(39,red)) to Ga(0.7-CVD)/HZSM-22(39,red), there is a small but distinct increase in aromatics and coke due to the increase in the number of Ga⁺ dehydrogenation sites. Moreover, there is an increased selectivity to ethylene compensated by a decrease of the amount of butenes over Ga(0.7-CVD)/HZSM-22(39,red). This is explained by increased olefin cracking over Ga⁺ ions via the carbanion mechanism. Correspondingly, the amount of pentenes is not higher because they are converted further. However, the exact distribution of olefins is difficult to predict as the protolytic cracking derived paraffins will also undergo dehydrogenation over Ga⁺ ions leading to range of olefins.
The detailed discussion of \textit{n}-heptane cracking over HZSM-5(20), Ga(0.39-IMP)/HZSM-5(20,red) and Ga(1.0-CVD)/HZSM-5(20,red) has been given in chapter 7. Table 8.2 summarizes the results. The formation of olefins via protolytic cracking and \(\beta\)-scission of the intermediate higher olefins in HZSM-5 makes it difficult to predict the exact olefin distribution. Moreover, the higher proton density in HZSM-5 allows for significant consecutive reactions of olefins further enhancing the complications [Chapter 5]. It is observed that equal amounts of ethylene and butenes are formed and propylene/butene ratio obtained is 2.3. This ratio is much higher than reported for HZSM-22 (ratio = 1) because of consecutive oligomerization and cracking reactions of olefins in the large ZSM-5 zeolite micropore space.

The product distribution over Ga(1.0-CVD)/HZSM-5(20,red) show lower selectivity to paraffins compensated by increased amounts of dehydrogenation products. In Ga(1.0-CVD)/HZSM-5(20,red), virtually all Brønsted acid sites are replaced by monovalent Ga\(^+\) species [4,5]. Selective \textit{n}-heptane dehydrogenation over Ga\(^+\) ions results into heptenes which are rapidly cracked to ethylene, propylene and butenes over Ga\(^+\). The difference in the cracking mechanism over Ga\(^+\) sites (carbanion) leads to a higher ethylene/butene ratio (ratio 1.8) as compared to that over Brønsted acid sites (carbonium). This further stresses the preferential formation of ethylene via carbanion mechanism over Ga\(^+\) ions. The formation of the only aromatic product toluene points to the ability of Ga\(^+\) ions to catalyze successive dehydrogenations of an \textit{n}-heptene intermediate including the final ring-closure step.

Ga(0.39-IMP)/HZSM-5(20,red) contains predominantly Brønsted acid sites and mono- (Ga\(^+\)) and divalent (GaH\(^{2+}\)) cationic species. The higher density of tetrahedral Al and low Ga/Al ratio allows for the stabilization of divalent GaH\(^{2+}\) species. The increased conversion over this catalyst points to a synergy between Brønsted acid sites and cationic Ga species. The product distribution shows contribution from both Brønsted acid sites and cationic Ga species. It has been proposed in chapter 7 that the increased activity is due to increase in the dehydrogenation rate during the synergy between proximate reduced Ga sites and Brønsted acid sites.

Similar trends (Table 8.3) are observed for the cracking of \textit{n}-heptane over HZSM-5(40) and Ga(0.25-IMP)/HZSM-5(40,red). The Brønsted acid sites in HZSM-5(40) catalyze protolytic cracking followed by \(\beta\)-scission of resulting olefins. The large deviation from propylene/butene ratio of 1 point to the fact that in addition to the monomolecular cracking of heptene, which is derived from C-H bond cleavage of \textit{n}-heptane the olefin distribution over HZSM-5(40) is significantly influenced by olefins derived by C-C bond cleavage and subsequent \(\beta\)-scission.
Table 8.3 Molar selectivities for \(n\)-heptane cracking at 823 K on HZSM-5(40) and Ga(0.25-IMP)/HZSM-5(40,red) catalysts (WHSV = 43 h\(^{-1}\), p = 1 atm)

<table>
<thead>
<tr>
<th>Time (min) X (%)</th>
<th>Paraffins</th>
<th>Product selectivity (%)</th>
<th>Olefins</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH(_4)</td>
<td>C(_2)H(_6)</td>
<td>C(_3)H(_8)</td>
<td>C(_4)H(_10)</td>
</tr>
<tr>
<td>HZSM-5(40)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 21 4 7 9 9 29</td>
<td>10 33 20</td>
<td>3</td>
<td>66 0 0</td>
<td>0 0 5</td>
</tr>
<tr>
<td>60 18 4 7 9 9 29</td>
<td>11 33 19</td>
<td>3</td>
<td>66 0 0</td>
<td>0 0 5</td>
</tr>
<tr>
<td>120 18 4 8 9 9 30</td>
<td>11 33 19</td>
<td>3</td>
<td>66 0 0</td>
<td>0 0 4</td>
</tr>
<tr>
<td>180 18 4 8 9 9 30</td>
<td>11 32 19</td>
<td>3</td>
<td>65 0 0</td>
<td>0 0 5</td>
</tr>
<tr>
<td>Ga (0.25-IMP)/HZSM-5(40,red)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 36 3 2 2 2 5 12</td>
<td>9 38 24</td>
<td>2</td>
<td>73 1 2</td>
<td>1 11</td>
</tr>
<tr>
<td>60 33 3 2 2 5 12</td>
<td>9 36 24</td>
<td>2</td>
<td>71 1 2</td>
<td>1 13</td>
</tr>
<tr>
<td>120 31 3 2 2 5 12</td>
<td>8 36 23</td>
<td>2</td>
<td>69 1 1</td>
<td>1 16</td>
</tr>
<tr>
<td>180 30 3 3 2 5 13</td>
<td>8 35 24</td>
<td>2</td>
<td>69 1 1</td>
<td>0 16</td>
</tr>
</tbody>
</table>
In addition to the formation of paraffins and olefins over Brønsted acid sites, Ga\(^+\) ions catalyze dehydrogenation, aromatization and olefin cracking. Introduction of Ga\(^+\) significantly improves the olefins-to-paraffin ratio although the propylene/butene is very similar to that over HZSM-5(40). The higher rate of oligomerization reactions of light olefins over protonic sites followed by ring-closure over Ga species leads to increased amounts of aromatics and coke over Ga(0.25-IMP)/HZSM-5(40,red). Nevertheless, the oligomerization rate is considerably lower over Ga(0.25-IMP)/HZSM-5(40,red) compared to Ga(0.39-IMP)/HZSM-5(20,red) stressing the importance of Brønsted acid sites for oligomerization.

**n-Hexane cracking**

The product distribution of \(n\)-hexane conversion over HZSM-5(20) and Ga(0.25-IMP)/HZSM-5(20,red) is given in Table 8.4. The presence of Ga\(^+\) dehydrogenation sites in Ga(0.25-IMP)/HZSM-5(20,red) increase the olefin/paraffin ratio slightly above 3 (ratio for HZSM-5(20) = 2.1). Lower alkanes arising from protolytic cracking over Brønsted acid sites will also dehydrogenate to olefins over Ga\(^+\) in Ga(0.25-IMP)/HZSM-5(20,red), but at a lower rate. Furthermore, formation of coke and aromatics is enhanced over Ga(0.25-IMP)/HZSM-5(20,red) compared to HZSM-5(20). Activation of \(n\)-hexane over Ga\(^+\) will lead to hexene which will further crack via carbanion mechanism to lower olefins or undergo successive dehydrogenation and ring closure steps. The higher amount of benzene is in line with the notion of aromatization of hexene. The presence of toluene and xylenes is attributed to oligomerization of lower olefins over Brønsted acid sites followed by ring closure steps over Ga\(^+\). As proposed earlier, Ga\(^+\) also promotes the ethylene formation compared to that over Brønsted acid sites in HZSM-5(20).

Quantitatively, similar product distribution is obtained for \(n\)-hexane cracking over HZSM-5(40) and Ga(0.25-IMP)/HZSM-5(40,red) except for the olefin distribution (Table 8.5). The olefin distribution over HZSM-5(40) shows significant preference for propylene with ethylene/butene ratio of 0.57. It could be argued that the elusive formation of lower olefins is dominated by cracking of hexene derived from C-H bond cleavage of \(n\)-hexane in addition to olefins from C-C bond cleavage and subsequent \(\beta\)-scission over the Brønsted acid sites. The preference of hexene cracking towards propylene is due to dominant cracking via secondary carbenium ion over cracking of primary carbenium ion forming ethylene and butene.
Table 8.4 Molar selectivities for $n$-hexane cracking at 823 K on HZSM-5(20) and Ga(0.25-IMP)/HZSM-5(20,red) catalysts (WHSV = 32 h$^{-1}$, p = 1 atm)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>X (%)</th>
<th>Product selectivity (%)</th>
<th>Molar selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Paraffins</td>
<td>Olefins</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH$_4$</td>
<td>C$_2$H$_6$</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>57</td>
<td>7</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>51</td>
<td>7</td>
</tr>
<tr>
<td>120</td>
<td></td>
<td>50</td>
<td>7</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td>45</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>88</td>
<td>7</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>77</td>
<td>6</td>
</tr>
<tr>
<td>120</td>
<td></td>
<td>68</td>
<td>6</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td>62</td>
<td>6</td>
</tr>
</tbody>
</table>

HZSM-5(20)

Ga(0.25-IMP)/HZSM-5(20,red)
Table 8.5 Molar selectivities for \( n \)-hexane cracking at 823 K on HZSM-5(40) and Ga(0.25-IMP)/HZSM-5(40,red) catalysts (WHSV = 32 h\(^{-1}\), \( p = 1 \) atm)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>X (%)</th>
<th>Paraffins</th>
<th>Olefins</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH(_4)</td>
<td>C(_2)H(_6)</td>
<td>C(_3)H(_8)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>9</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>8</td>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>120</td>
<td></td>
<td>8</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td>8</td>
<td>5</td>
<td>14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>X (%)</th>
<th>Paraffins</th>
<th>Olefins</th>
<th>Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH(_4)</td>
<td>C(_2)H(_6)</td>
<td>C(_3)H(_8)</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>13</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td>9</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>120</td>
<td></td>
<td>10</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td>8</td>
<td>5</td>
<td>9</td>
</tr>
</tbody>
</table>
With introduction of Ga\textsuperscript{+} dehydrogenation sites, not only the overall olefin/paraffin ratio increases but also the ethylene/butene ratio is improvised to 1.6. The oligomerization of lower olefins followed by dehydrogenation and ring closure steps leads to minor amounts of aromatics over Ga(0.25-IMP)/HZSM-5(40,red). Notably, hexene is not completely converted over both the catalysts due to lower conversions.

### 8.4 Conclusions

The product distribution from cracking of naphtha-range hydrocarbons depends significantly on the presence of the Brønsted acid sites and Ga dehydrogenation sites. The protolytic cracking followed by subsequent cracking of intermediate higher olefins by $\beta$-scission is dominant over Brønsted acid sites leading to a range of alkanes and olefins. The olefin distribution is dominated by cracking of the olefin, derived from C-H bond cleavage of the alkane reactant. Over narrow-pore zeolites (i.e. HZSM-22) and zeolites with low proton density this cracking occurs monomolecularly via facile carbenium ion transition state with low activation barriers. Catalysts containing both Brønsted acid sites and reduced Ga species behave as bifunctional catalysts. The product slate is more complex and involves products from dehydrogenation, cracking, oligomerization and aromatization. Reduced Ga cations catalyze dehydrogenation, olefin cracking and ring-closure steps. The olefin cracking over Ga\textsuperscript{+} ions shows clear preference for ethylene formation via carbanion mechanism. Increase of the Ga/Al ratio leads to an increase of the selectivity to dehydrogenated products at the expense of the formation of alkanes. Nevertheless, the total light olefin content of such bifunctional catalysts is only marginally higher than over pure protonic zeolites.

### 8.5 References

Summary

Hydrocarbon Conversion over Brønsted and Lewis Acidic Zeolites

Gallium-containing zeolites have been intensively studied in the last decade because of their use as catalysts in the aromatization of light paraffins. Contrary to the well-understood mechanism of alkane activation over Brønsted acid sites in zeolites, the structure of Ga cationic complexes and their role in the catalytic cycle of hydrocarbon conversion remains the subject of intense controversy. The current understanding of alkane activation over protonated zeolites involving carbocations is described in chapter 1. The current state-of-affairs about the preparation, characterization and reactivity of Ga/HZSM-5 zeolites is briefly summarized in chapter 1. The precise role of Ga species in the activation of paraffins is not clear yet, mainly because of the challenges associated with the preparation of well-defined Ga reaction sites in the zeolite.

Chapter 2 introduces a preparation method starting from an organometallic Ga(CH$_3$)$_3$ precursor to disperse well-defined Ga species in the zeolite micropores. The main objective was to prepare a model Ga/HZSM-5 catalyst with well-defined single site reduced Ga$^+$ sites. Such a model catalyst allows a detailed comparison of the reaction mechanism of the activation of alkanes and alkenes in comparison to conventional routes over Brønsted acid sites. Chemical vapor deposition with trimethylgallium results in the complete replacement of Brønsted acid sites by dimethylgallium species. This process and subsequent conversion of the dimethylgallium species to reduced and oxidized Ga species was followed in situ by FTIR and XANES spectroscopy at the Ga K edge. The methyl ligands of the resulting Ga(CH$_3$)$_2$$^+$ species can be removed by reduction, resulting in Ga$^+$ and GaH$_2$$^+$ species that compensate the negative zeolite framework charge. At elevated temperatures and in the absence of hydrogen, Ga$^+$ species are most stable. The reductive elimination of dihydrogen from GaH$_2$$^+$ species is very slow. Oxidation by nitrous oxide at a temperature of 473 K oxidizes Ga$^+$ to Ga$^{3+}$. The quantitative reaction of one nitrous oxide molecule per Ga$^+$ suggests the formation of GaO$^+$ ions in line with earlier suggestions from literature. However, EXAFS analysis of X-ray absorption spectra at the Ga K edge confirmed the presence of oxygen-bridged Ga dimers (Ga$_2$O$_2$$^{2+}$) rather than mononuclear GaO$^+$ species. Alternatively, direct oxidation of the
Summary

dimethylgallium/HZSM-5 precursor leads to various forms of gallium oxide species and regeneration of a significant amount of Brønsted acid sites.

The catalytic activities of Ga cations (Ga$^+$, GaH$_2$$^+$, Ga$_2$O$_2$$^{2+}$) for the activation of propane were compared to the performance of the parent acidic zeolite (Chapter 3). Brønsted acid sites convert propane via the well-established protolytic cracking mechanism with methane, ethylene and propylene (paraffinic C-C and C-H bond activation) as hydrocarbon products. Reduced Ga$^+$ ions almost exclusively produce propylene (paraffinic C-H bond activation). The catalytic data and quantum-chemical calculations suggest that propane is converted over Ga$^+$ and not over GaH$_2$$^+$ ions. The initial rate of propane dehydrogenation is highest for the Ga$_2$O$_2$$^{2+}$ ions, although rapid deactivation is observed. This deactivation is due to the high barrier for the regeneration of the Ga$_2$O$_2$$^{2+}$ ion compared to that for the desorption of water to give less active Ga$^+$ species. The activation of alkane over Zn$^{2+}$ ions proceeds via a somewhat different mechanism. The difference in alkane activation is evaluated by studying the catalytic conversion of ethane over Zn$^{2+}$ and Ga$^+$ modified HZSM-5 involving dehydrogenation. Ethane is heterolytically adsorbed over Zn$^{2+}$ and basic oxygen sites, subsequently regenerating Brønsted acid sites. This regeneration results in high initial activity over Zn/ZSM-5 but with reaction time the catalyst suffers from coking deactivation. In contrast, molecular adsorption of ethane on Ga$^+$ ions results in the formation of ethyl and hydride fragments coordinating to the gallium species. The absence of regeneration of Brønsted acid sites in Ga/HZSM-5 upon alkane activation results in the stable and selective conversion of ethane into ethylene.

As hydroxylated Ga species can be considered the product of water dissociation over Ga$^+$ ions, the effect of water addition was studied during propane conversion over Ga/HZSM-5 in chapter 4. Co-feeding of water over monovalent Ga$^+$ ions substantially increases the conversion of propane. This rate improvement is proposed to be due to the stabilization of hydroxylated Ga intermediates. Quantum-chemical calculations suggest that H$_2$ recombination is much easier over hydroxylated Ga dimers than from the mononuclear [Ga$^{3+}$(H)(OH)]$^{+}$ species. This is due to the increased acidity of the bridging hydroxyl bond in the binuclear oxygen-bridged Ga dimers.

Hydrocarbon activation was further investigated for the conversion of olefins over Brønsted acid sites and Lewis acid Ga cations in the zeolites. The main reason was to understand how the pathways of olefin conversion over Lewis Ga cations differ from those over Brønsted acid sites. Monomolecular olefin cracking over Brønsted acid sites (Chapter 5) proceeds via the well-known carbenium ion chemistry. It involves the initial activation of the olefin to form a tricoordinate carbenium ion intermediate, with
subsequent scission of the carbon-carbon bond at the $\beta$ position relative to the positive charge to form a free olefin and a smaller carbenium ion. The smaller carbenium ion intermediate thereafter undergoes deprotonation to a smaller olefin, the reverse of the protonation reaction. The stability and relative concentrations of carbenium ions decrease in the order: tertiary $>$ secondary $>$ primary. Since carbenium ion cracking of C$_4$ and C$_5$ olefins should proceed via primary carbenium ions with high transition state energy barriers, their reactivity is much lower than those of higher olefins. Cracking of C$_6$-C$_8$ olefins involves secondary and tertiary carbenium ion transition states with substantially lower barriers. The nature of olefin cracking over protonated zeolites depends on the acid density and zeolite pore topology in addition to the type of carbenium ion involved for the monomolecular cracking. Due to the relatively narrow unidirectional pores of HZSM-22, the rate of bimolecular olefin oligomerization is low compared to monomolecular cracking. The less restricted pore space of HZSM-5 and HBEA lead to increased rates of bimolecular dimerization reactions. Therefore, compared to HZSM-22, dimerization of 1-butene and 2-methyl-2-butene to higher olefins and subsequent cracking leads to higher overall reaction rates over HZSM-5 zeolite. Monomolecular cracking is dominant in the conversion of higher olefins. The temperature also influences the importance of bimolecular reactions. At low temperatures, bimolecular reactions become increasingly important, likely because of the increased pore occupancies.

Olefin cracking was also undertaken over ZSM-5 and ZSM-22 zeolites with cationic Ga species at the zeolite exchange positions (Chapter 6). The selectivity pattern of olefin cracking over Lewis acidic Ga sites is distinctly different from that over Brønsted acid sites. Brønsted acid sites mainly convert 1-hexene to propylene. Over Ga$^+$ sites substantially higher amounts of ethylene are found. A mechanism of olefin activation over cationic Ga species is proposed which involves removal of an allylic hydrogen atom from the olefin to form a zeolitic proton and an allylic carbanion intermediate. This latter intermediate is stabilized by the Ga$^+$ ion. Reprotonation of allylic bond leads to a double bond isomer of the starting olefin or an alkylcyclopropane intermediate. Hydride shift in this intermediate results in the skeletal isomer of the reactant olefin or two smaller olefins. The increase in the cracking rate over cationic Ga species from C$_4$ through C$_6$ olefins is proposed to be due to the decreased C-H bond energy of the allylic H atom. The increased selectivity to ethylene can be understood by the higher stability of primary carbanions over secondary and tertiary carbanions. Thus, the selectivity pattern for olefin cracking over the Lewis acid-base pairs formed by Ga$^+$ and the zeolite oxygen anions is determined by the stability of the intermediate carbanions.
Ga/HZSM-5 zeolites were also prepared by wet impregnation and ion-exchange methods (Chapter 7) in addition to the methods leading to well-defined Ga reaction sites. Impregnation results in the incorporation of some of the gallium oxide clusters into the zeolite pore network as charge-compensating Ga species after calcination. Reduction of impregnated Ga/HZSM-5 catalysts leads to complete transformation of the oxidic Ga precursors to charge-compensating Ga\(^+\) and GaH\(^{2+}\) species. A small amount of divalent GaH\(^{2+}\) species can be stabilized; however, with increasing Ga/Al ratio monovalent cations dominate. The XANES spectra of oxidized ion-exchanged catalyst shows a significant amount of octahedral Ga species in the form of neutral gallium oxide clusters. FTIR and TPR data reveal difficult to reduce gallium oxide phase in the Ga/HZSM-5 prepared by the ion-exchange method.

Ga/HZSM-5 zeolites may find a possible application in the selective conversion of naphtha-range hydrocarbons to ethylene and propylene as a potential replacement to the energy-intensive thermal cracking process. To this end, cracking of naphtha-range hydrocarbons was studied over Ga/HZSM-5 and Ga/HZSM-22 zeolites (Chapter 7 and 8). While protolytic cracking followed by cracking of intermediate olefins by β-scission leading to light olefins and alkanes is dominant over Brønsted acid sites, Ga species catalyze dehydrogenation, olefin cracking and ring-closure steps. Catalysts containing both Brønsted acid sites and reduced or oxidized Ga species behave as bifunctional catalysts. The product slate is more complex and involves products from dehydrogenation, cracking, oligomerization and aromatization arising from contributions of Ga cationic and Brønsted acid sites. Clear synergy is observed when protons are combined with proximate Ga species leading to improved conversions. Possibly, the high acidity of the zeolitic protons facilitates the hydrogen recombination step in the dehydrogenation of alkanes. Oxidized Ga/HZSM-5 catalysts display higher reactivity than their reduced counterparts because the proton content in the former is higher. Ion-exchanged Ga/HZSM-5 catalyst which combines a difficult to reduce gallium oxide phase and high Brønsted acidity has the highest activity with relatively weak coke formation. After prolonged reaction time oxidized and reduced catalysts tend to show similar activity due to gradual formation of reduced Ga species (Ga\(^+\) and GaH\(^{2+}\)) at the expense of zeolitic protons. Nevertheless, the total light olefin content of such bifunctional catalysts is only marginally higher than over pure protonic zeolites. The olefin distribution strongly depends on the subsequent cracking of the intermediate olefin derived by dehydrogenation of the reactant alkane, acidity and topology of the zeolite. The intermediate olefin cracking over reduced Ga cations occurs via carbanion mechanism leading to substantial promotion of ethylene formation.
Samenvatting

Hydrocarbon Conversion over Brønsted and Lewis Acidic Zeolites

Gallium-houdende zeolieten zijn in het laatste decennium uitgebreid bestudeerd vanwege hun toepassing als katalysatoren in de aromatisering van lichte koolwaterstoffen. In tegenstelling tot het goed begrepen mechanisme van alkaan activering door Brønsted zure protonen in zeolieten is de structuur van de kationische Ga complexen en hun rol in koolwaterstofconversie een onderwerp van discussie in de wetenschappelijke literatuur. Ons begrip van alkaanaktivering door zure zeolieten via carbokationen is beschreven in hoofdstuk 1. Verder wordt hier in het kort een samenvatting gegeven van aspecten aangaande de bereiding, karakterisering en reactiviteit van Ga/HZSM-5 katalysatoren. De exacte rol van Ga in de aktivering van koolwaterstoffen is nog niet helemaal bekend. Dit komt voornamelijk omdat het een uitdaging is om goedgedefinieerde Ga deeltjes te maken in zeolieten.

In hoofdstuk 2 wordt aandacht besteed aan de bereiding van Ga/HZSM-5 via het organometaal Ga(CH₃)₃ (trimethylgallium) complex. Dit leidt tot gedispergeerde en gedefinieerde Ga deeltjes in de microporiën van het zeoliet. Het belangrijkste doel is om een model Ga/HZSM-5 katalysatoren te bereiden met gedefinieerde single site gereduceerde Ga⁺ ionen. Met behulp van een dergelijke modelkatalysator kunnen we gedetailleerd het reactiemechanisme van alkaan en alken conversie vergelijken tussen Ga⁺ ionen en zure protonen. Chemical vapor deposition van trimethylgallium resulteert in vervanging van zure protonen door dimethylgallium ionen. Dit proces alsmede de volgende conversie van deze ionen tot gereduceerde en geoxideerde Ga ionen wordt gevolgd door in situ FTIR (Fourier Transform Infrared Spectroscopy) en XANES (X-ray Absorption Near-Edge Spectroscopy) rond de Ga K absorptie-edge. De methyl liganden van de gevormde kationische Ga(CH₃)₂⁺ deeltjes kunnen worden verwijderd als methaan door reductie. Dit resulteert in Ga⁺ en GaH₂⁺ ionen die de negatieve lading van het zeolietrooster compenseren. Bij hoge temperatuur en in de afwezigheid van waterstof zijn Ga⁺ ionen het meest stabiel. De reductieve eliminatie van waterstof van GaH₂⁺ ionen is langzaam. Oxidatie van zulke deeltjes door lachgas (N₂O) bij een temperatuur van 473 K leidt tot vorming van Ga³⁺ ionen. De kwantitatieve reactie van één lachgas molecul per Ga⁺ ion suggereert de vorming van GaO⁺ ionen in overeenstemming met indicaties uit de
literatuur. Echter, structuuranalyse middels EXAFS (Extended X-ray Absorption Fine Structure) bevestigt de aanwezigheid van Ga dimeren die gebrugd worden door twee zuurstofanionen. Een alternatief voor de verwijdering van de methyl liganden is de directe oxidatie van de dimethylgallium/HZSM-5 precursor. Dit leidt tot een minder gedefinieerde katalysator met verschillende types gallium oxide deeltjes en regeneratie van een aanzienlijke hoeveelheid Brønsted zure protonen.

De katalytische aktiviteit van verschillende Ga kationen (Ga$^+$, GaH$_2^+$, Ga$_2$O$_2^{2+}$) ZSM-5 zeoliet voor de aktivering van propaan wordt vergeleken met de activiteit van de zure uitgangszeoliet in hoofdstuk 3. Zure protonen zetten propaan om via het bekende protolytische kraakmechanisme met methaan, etheen en propeen als koolwaterstofproducten door aktivering van de C-C and C-H bindingen. Het intermediair is hier het vijfgecoordeerde carboniumion. Ga$^+$ ioniën produceren bijna uitsluitend propene en aktiveren dus selectief de C-H binding van propaan. De katalytische data en kwantum-chemische berekeningen suggereren dat propane omgezet wordt over Ga$^+$ ioniën en niet over GaH$_2^+$ ioniën. Echter, de initiële reactiesnelheid is het hoogste voor propaandehydrogenering over Ga$_2$O$_2^{2+}$ ioniën. Een nadeel hierbij is dat snelle deaktivering van deze katalysator optreedt. Deze deaktivering is gerelateerd aan de hoge energiebarriere voor regeneratie van de Ga$_2$O$_2^{2+}$ ioniën vergeleken met desorptie van water. Dit laatste proces leidt tot vorming van de minder actieve Ga$^+$ ioniën. Alkaanaktivering door Zn$^{2+}$ ioniën in HZSM-5 zeoliet verloopt via een ander mechanisme. Dit wordt bestudeerd door het volgen van de omzetting van ethaan over ZSM-5 zeoliet die Zn$^{2+}$ danwel Ga$^+$ ioniën bevatten. Ethaan wordt heterolytisch geadsorbeerd over Zn$^{2+}$ ioniën en de basische oxygen anionen van het zeolietrooster. Desorptie van etheen leidt tot regeneratie van zure protonen die zorgen voor een hoge initiële activiteit. Daarbij worden meer aromaten gevormd. Uiteindelijk leidt dit tot deaktivering door vorming van coke. Moleculaire adsorptie van etaan aan Ga$^+$ ioniën leidt tot vorming van ethyl en hydride liganden. De afwezigheid van regeneratie van zure sites resulteert in een stabiele en selectieve conversie van etaan naar etheen.

Aangezien dehydroxyleerde Ga ioniën beschouwd kunnen worden als het product van de dissociatie van water aan Ga$^+$ ioniën, wordt het effect van toevoeging van water op de omzetting van propaan gekatalyseerd door Ga/HZSM-5 onderzocht (hoofdstuk 4). Toevoegen van water aan de propaanvoeding over een single site Ga$^+/ZSM-5$ katalysator leidt tot een substantiële verbetering van de propaanconversie. Deze verhoging van de reactiesnelheid wordt veroorzaakt door stabilisering van gehydroxyleerde Ga intermediairen. Aanvullende kwantum-chemische berekeningen suggereren dat waterstofrecombinatie over zulke intermediairen veel sneller verloopt dan over mono-nucleaire [Ga$^3+(H^-)(OH^-)]^+$ ioniën. Het verschil kan begrepen worden door de toegenomen
zuurheid van de bruggende hydroxyl groep in de binucleaire Ga deeltjes. Experimenteel wordt gevonden dat H$_2$ desorbeert tijdens een temperatuur geprogrammeerd experiment waarbij Ga$^+/ZSM-5$ wordt blootgesteld aan water. De gevonden desorptie-energie komt overeen met de kwantum-chemisch voorspelde energie.

Koolwaterstofactivering wordt verder onderzocht voor de omzetting van olefines over Bronsted zuure protonen en Lewis zure Ga kationen in zeolieten. De belangrijkste reden is om te begrijpen hoe de reactiepaden van olefines over Ga sites verschillen van die van olefineomzetting over protonen. Daartoe wordt eerst in hoofdstuk 5 het monomoleculaire kraken van olefines over protonen nader onderzocht. Het kraken vindt plaats via het carbeniumion mechanisme. Hierbij wordt initieel het olefine geactiveerd door adsorptie aan het proton tot een drievoudig gecoördineerd carbeniumion intermediair, gevolgd door het verbreken van de koolstof-koolstof binding op de $\beta$ positie van de positieve lading. Dit resulteert in een vrij olefine en een kleiner carbeniumion. Middels deprotonatie van dit carbeniumion ontstaat er dan een olefine. De stabiliteit en relative concentraties van carbeniumionen neemt af in de volgorde: tertiaire > secundaire > primaire carbeniumionen. Omdat het kraken van C$_4$ en C$_5$ olefines verloopt via primaire carbeniumionen en de daarbijhorende hoge energiebarrieres, is hun reaktiviteit veel lager dan die van hogere olefines. Het kraken van C$_6$-C$_8$ olefines verloopt via secundaire en tertiaire carbeniumion overgangstoestanden met een aanzielijke lagere energiebarriere. Het mechanisme van olefine kraken over protonische zeolieten hangt af van de protonendichtheid en de porietopologie van het zeoliet naast het type carbeniumion. Omdat ZSM-22 relatief nauwe, unidirectionele poriën bezit, is de snelheid van bimoleculaire olefine oligomerisatie laag vergeleken met monomoleculair kraken van olefines. De grotere poriën van HZSM-5 en HBETA zeolieten leiden tot verhoogde reactiesnelheden van bimoleculaire dimerisatiereacties. Daarom verloopt de dimerisatie van 1-butene en 2-methyl-2-butene naar hogere olefines en vervolgkrakreacties sneller over HZSM-5 dan over HZSM-22. Voor hogere olefines is monomoleculair kraken dominant. Ook de temperatuur is van invloed. Bij lagere temperaturen wordt kraken voorafgegaan door bimoleculaire dimerisatie belangrijker, waarschijnlijk door toenemende poriebezettings met reactanten.

De volgende stap is onderzoek naar de conversie van olefines over ZSM-5 en ZSM-22 zeolieten waarbij de protonen vervangen zijn door Ga kationen (hoofdstuk 6). De selectiviteitspatronen in olefine kraken over Lewis zure Ga sites verschilt sterk van die over zure protonen. Over zure protonen wordt 1-hexeen voornamelijk omgezet in propeen. Echter, over Ga$^+$ ionen worden substantieel grotere hoeveelheden etheen gevormd. Een mechanisme voor de olefine omzetting door Ga kationen wordt geformuleerd. Hierbij abstraheert een basisch roosterzuurstofanion een allylisch
waterstofatoom van het olefine zodat er een zuur proton wordt gevormd en een allylisch carbanion intermediair. Dit koolwaterstofintermediair coordineert aan het Ga kation. Reprotonatie van de allylische binding leidt tot een isomeer van het uitgangsolefine waarbij de dubbele binding is verschoven of een alkylcyclopropane intermediair. Hydrideverplaatsingen in dit laatste intermediair leiden uiteindelijk tot de vorming een skeletismeer van het uitgangsolefine of twee kleinere olefines. Gaande van C₄ naar C₆ olefines neemt de kraakactiviteit toe, hetgeen gerelateerd is aan de afnemende C-H bindingsenergie van het allylische waterstofatoom in het reactant. De hogere selectiviteit van ethaan kan begrepen worden in termen van een hogere stabiliteit van primaire carbanionen dan van secundaire en tertiaire carbanionen. De productverdeling tijdens het kraken van olefines over Lewis zuur-base paren van Ga kationen en roosterzuurstofanionen wordt dus bepaald door de relatie van de intermediaire carbanionen.

Een serie Ga/HZSM-5 zeolieten worden gemaakt door middel van impregnering- en ionwisselingsmethoden in hoofdstuk 7. Deze worden vergeleken met de eerder ontwikkelde methode die leidt tot goedgedefinieerde Ga ionen. Impregnering leidt tot ionwisseling van een gedeelte van de zeolietprotonen. Reductie van zulke katalysatoren leidt tot verdere ionwisseling van protonen met Ga en GaH²⁺ ionen. Een klein gedeelte van de negatieve roosterlading wordt gecompenseerd door tweewaardige GaH kationen: echter, met toenemende Ga/Al verhouding beginnen de éénwaardige kationen te domineren. XANES spectra van geoxideerde samples laten zien dat in de ionwisselde katalysatoren een grotere hoeveelheid octaedrische Ga ionen aanwezig zijn dan in de katalysatoren bereid via impregneratie. Samen met FTIR en data verkregen middels Temperature Programmed Reduction suggereert dit dat in ionwisselde katalysatoren een gallium oxide fase aanwezig is die moeilijker te reduceren valt dan de gallium oxide fase in geïmpregneerde samples.

protonen zich in de nabijheid vinden van Ga kationen. Een mogelijke verklaring voor deze synergie is dat de sterke zuurheid van de protonen waterstofrecombinatie versnelt tijdens de dehydrogenering van alkanen. Geoxideerde Ga/HZSM-5 katalysatoren laten een hogere activiteit zien dan gereduceerde katalysatoren, vanwege de hogere Brønsted zuurheid van de geoxideerde katalysatoren. De hoogste activiteit wordt verkregen voor een iongewisselde Ga/HZSM-5 katalysatoren die een moeilijk te reduceren gallium oxide fase combineert met een hoge dichtheid aan zure protonen. Echter, de totale yield van lichte olefines over zulke bifunctionele katalysatoren is maar marginaal hoger dan over zure katalysatoren. De olefine productverdeling hangt af van de vervolgkraakreacties van de intermediaire olefines, de zuurheid en de zeoliet topologie. Met toenemende hoeveelheid Ga kationen neemt de hoeveelheid etheen licht toe vanwege reactiepaden van carbanion intermediairen.
Acknowledgements

I wish to express my sincere appreciation to Prof. Rutger van Santen for giving me an opportunity to carry out my Ph.D. work under his supervision. His dedication to science, his knowledge, valuable insights, patience and encouragement have been a strong motivating force. I am grateful for his meticulous guidance throughout the length of the project and for being a tremendous source of inspiration. I would also like to extend my gratitude to my co-promoter Dr. Emiel Hensen; his acute and effective research methodology has been an ideal to exemplify throughout my research work. His eye for fine detail and apt solutions to problems has been a great asset. His contribution towards structuring this thesis and manuscripts of the articles is highly acknowledged.

I am grateful to Prof. Vladimir Kazansky (Moscow), Prof. Rob van Veen (Shell) and Prof. Dieter Vogt for their constructive comments and remarks on my thesis. I appreciate the time they took to review my thesis. Special thanks to Evgeny Pidko for the theoretical contribution he brought to my project. That helping hand was certainly needed to shed light on the enthralling results my experiments (sometimes) produced. Also thanks for the long discussions on Gallium that we have had in the past. I acknowledge Jan Koegler (ABB Lummus), Marcello Rigutto (Shell), Matthijs Ruitenbeek (Sabic), Michiel Schenk (Dow), Nico Boots and Chris Marcelis (STW), for several discussions, in person or via email and for being critical about my results and the interpretation thereof.

I am grateful to Pieter Magusin and Brahim Mezari for helping me with solid-state NMR measurements and interpretation. I am also thankful to Adelheid Elemans-Mehring for her assistance with the ICP measurements. Peter Lipman (Chemical Reactor Engineering) is acknowledged for his help with Nitrogen Adsorption Porosimetry experiments. I am thankful to Prof. Hans Niemantsverdriet for allowing me to attend his group meetings during the initial period of my Ph.D. His tips on how to present my work will certainly place me in good stead for the future. I would also like to thank Technology Foundation STW, the applied science division of NWO, and the technology program of the Ministry of Economic Affairs for their financial support. Shell Research and Technology Centre Amsterdam (SRTCA) is highly acknowledged for providing the TEOM reactor system.

It has been my privilege to work in the SKA group alongside fine researchers and colleagues. I am grateful to all SKA members not only for their cooperation, helpful discussion and assistance but also for their kindness and friendship. I greatly appreciate the timely technical assistance from Tiny Verhoeven, Wout van Herpen and Robert van Teeffelen. Research life was much accelerated when you all were around! I can hardly imagine the completion of this thesis without the skillfully built setup initiated by the late Joop van Grondelle, which was later modified by Robert. Elize, Marion and Therese Anne are all acknowledged for their help in administrative matters.

I have thoroughly enjoyed my last four years in the fun-filled working environment provided at SKA. I did not realize how my name changed from Neelesh (the collector) to Nelly, Neeli or even McNelly. Special thanks to Michel, Pieter vG., Martijn, Annelies,
Acknowledgements

Alessandro, Dilip, Frans, Farid, Gabriela, Yejun, Ying, Vittorio, Arjan, Monique and the guests Keqiang, Artem, Volkan and Pieter (Leuven) for their daily help concerning research and every aspect of life. Thanks to all of you especially for tolerating my pleasant singing in the lab STW 3.79. Mayela and Zhu are also acknowledged for their initial help during my start-up experiments.

Dilip, it was great sharing the office with you. Certainly, I haven’t met an Indian researcher with so much passion for Australian Cricket, the Ferrari F1 Team and Manchester United Football Club. Thanks also for always being “game” when it came to parties, drinking or eating out. Emiel H., Michel, Vittorio, Pieter vG., Alessandro and Daniel C.; thanks for the (most) important discussions during the much-needed coffee breaks.

Special thanks to Happy Ad, Han Wei, Noor, Dilip, Subu, Abdool, Yogesh B., Sharan, Denzil and Prabashini for all the wonderful dinners and get-togethers which we had in the past. I really appreciate the time and effort you guys took to help me through the frustration and giving me a much-needed break from work. I will certainly cherish those memories of night-long discussions. Prabashini, Denzil and Abdool are acknowledged for providing nice and spicy Indian dishes with a South African flavor. However, I still have to try your priceless South African Bunny Chow. Emiel vK. and Davy are acknowledged for translating at-times my complicated Dutch mails! I am also thankful to Peter T., Sander, Eero, Armando, Freek and Maarten who have been helpful to me in one way or the other. Although, I was not a frequent visitor to the SKA Borrel, whenever I attended I always found it to be a great gathering at the end of the week. I have thoroughly enjoyed the time and discussions with Thijs, Jos, Michèle, Barry, Mabel, Nollaig, Jarno, Katharina, Maria, Gijsbert, Evgeny, Bouke, Paul, Laura, Daniel T., Arjan, Tiny, Patrick, Christian and José during the Borrel.

Special thanks to Chaitanya, Vinit, Vinod, Ramesh and Sreejit for helping me out with everyday problems especially during my initial period at Eindhoven. I will always appreciate the friendly night-outs I had with David, Blanca, Luigi, Chiara, José, Daniel T., Barbara, Lorenzo, Ramona and Dilip. I would also like to thank Anish, Nilesh K., Girish, Mano, Sachin, Dilna, Merina, Subi, Vinayak, Keshav, Greg, Ashriti, Sai, Rahul and Riyaz for all the enjoyable times we had together.

I am deeply indebted to my parents and my brother who have always provided me with the moral support and encouragement. I am grateful for their understanding, especially for allowing me to pursue studies in an international environment. Special thanks to my UICT friends-Sanjay, Ritesh, Rahul and Vinit for helping me through the difficult times. I am thankful to Dr. R. V. Chaudhari (currently at University of Kansas) for guiding me through the critical decisions during my career.

I also extend my appreciation to all the people who were not mentioned above but have helped me in one way or other to complete my work successfully.
List of Journal Publications


Neelesh was born on 31st May 1979 in Bhusawal, India. He moved to Mumbai along with his parents in June 1985. He graduated in Chemical Engineering from University Institute of Chemical Technology (UICT, formerly UDCT), Mumbai (June 2000). After receiving University Graduate Scholarship (UGS) and Research Assistantship (RA) for his M.S., he joined the Chemical Engineering department at the University of Cincinnati, Ohio, USA in September 2000. His Master’s dissertation was entitled “Sol-gel synthesis and characterization of mesoporous ceria membranes” (March 2003) under the supervision of Prof. Jerry Y. S. Lin. In September 2003, he joined the Schuit Institute of Catalysis at the Technische Universiteit Eindhoven, The Netherlands. Here he worked towards his Ph.D. in the area of Heterogeneous Catalysis, and more specifically in the field of selective hydrocarbon conversion over zeolites, under the supervision of Dr. Emiel J. M. Hensen and Prof. Dr. Rutger A. van Santen. The Ph.D. project was financially supported by Technology Foundation STW, the applied science division of NWO, and the technology program of the Ministry of Economic Affairs. The most important results of his Ph.D. research are described in this thesis.