Chapter 2

Literature Review

2.1   Introduction

The first part of this literature review is aimed at describing the fuel specifications for petrol and to obtain an understanding of their purpose as well as why they need to be controlled or monitored. Emphasis will be on the measurement of octane numbers (RON and MON), which is of significant importance to the refiner because it increases refinery profitability [Lugo, 1999], and in this study is the main driver towards the study of skeletal isomerization of olefins. A brief overview of olefin isomerization and the catalysts used is given. To conclude the literature review, olefin skeletal isomerization of the feedstocks used in this study (butene, hexene and octene), catalysts used in previous studies, as well as the mechanisms associated with skeletal isomerization will be discussed in more detail.

2.2   Fuel specifications for petrol

The European motor vehicle emission requirements and EN 228 fuel specifications for petrol is used as a benchmark for fuel quality in South Africa [IFQC, 2012]. The fuel specifications for South Africa based on current European 5 emission requirements are given in Table 2.1.

Table 2.1
Gasoline Fuel specifications for South Africa [IFQC, 2012]

Petrol	Current National Specification	Future National Specification (Euro 5)
Sulphur, max. (ppm m/m)	500	10
Research Octane Number (RON),min.	95; 93; 91	95; 93
Benzene, max. (vol%)	5	1
Aromatic content, max. (vol%)	50	35
Olefins, max. (vol%)		21 / 18
RVP (summer), max.* (kPa)	75	65 (+5 ethanol)

*Reid vapour pressure

2.2.1 Sulphur

The purpose for testing and regulating the sulphur content in petrol is because it negatively affects the performance of catalytic converters by inhibiting the vehicle's catalytic converter from effectively cleaning up the exhaust gases.

Therefore, reducing the sulphur content of gasoline will reduce pollution of gases such as carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NOx) from petrol driven automobiles and ensure that vehicle emission control devices are more effective. Cleaner vehicle technologies will be enhanced by meeting the 50 ppm (m/m) and 10 ppm (m/m) limit concentrations of sulphur content in gasoline [SAPIA, 2008].

2.2.2 Research Octane Number (RON)

The research octane number is a measure of a fuel's resistance to auto-ignition and will be discussed in more detail in Section 2.3.

2.2.3 Benzene

Benzene is a known carcinogen [Bayliss et al., 1998]. Levels of benzene are therefore regulated to control its concentrations in both the evaporative and exhaust emissions. Motor vehicles are the main route of exposure to benzene for most of the human population [SAPIA, 2008].

2.2.4 Aromatics

The aromatic content in fuel released during combustion processes in the vehicle is believed to contribute to air toxins such as hydrocarbons and carbon monoxide [SAPIA, 2008]. Thus, reducing the aromatic content reduces the emission of these gasses from the vehicle, although some of these changes may lower the density of the fuel and in doing so, increase fuel consumption.

2.2.5 Olefins

Although olefins are excellent octane components, they have negative impacts on the environment. Some of the negative effects are listed below:

- Evaporation of olefins into the atmosphere leads to ozone formation [SAPIA, 2008], and in turn has undesirable public health impacts [HEI, 2010].

- Olefins tend to be thermally unstable, reducing the storage stability of fuel and this instability can lead to gum formation or deposits in engine intake systems. Storage stability can be improved by suitable additives, such as antioxidants [Rogers and Voorhees, 1933].

- Combustion of olefins may also lead to the formation of toxic dienes such as *1,3*-butadiene [HEI, 2010].

2.2.6 Reid Vapour Pressure (RVP)

The primary reason for regulating the Reid vapour pressure is to maintain gasoline engine reliability. The vapour pressure is another measure of the volatility of the fuel and has significance mainly to the lighter components, such as butane, in the fuel [SAPIA, 2008].

During summer, when the RVP is high and when midday temperatures can reach 35 °C (±5 °C), the volatility of a petrol fuel increases [SAPIA, 2008]. More components are converted to gaseous vapours (liquid to gas) forming pockets of vapour in the fuel pipelines. This is known as vapour lock [Gary et al., 2004]. Since vehicle petrol pumps can only pump liquids and not vapours, vehicle start-up is made impossible as fuel is not delivered to the fuel injection system.

In contrast, during winter, when the night and early morning temperatures can decrease to -5 °C (±5 °C), fuel with sufficient vapour pressure is essential since a percentage of light hydrocarbons is of utmost importance to enable cold start-up. This volatile percentage of hydrocarbons in the fuel is basically in the vapour phase as it enters the "cold" combustion chamber. During the ignition stroke, the volatile hydrocarbon portion of the gasoline will combust with ease, providing the initial flame front, causing enough heat for complete combustion of the higher boiling point components. If the volatile percentage of light hydrocarbons in the fuel is too low, the formation of the initial flame front will not occur during the ignition stroke and the vehicle engine will not start due to a lack of combustion in the combustion chamber.

Analytical measurement of true vapour pressure poses several difficulties; hence a simpler parameter known as the Reid Vapour Pressure was developed [da Silva et al., 2005]. RVP is used to measure vapour pressure defined as the

absolute vapor pressure and is referenced to a standard temperature of 37.8°C [SAPIA, 2008].

2.3 Relationship between the compression ratio of an internal combustion engine and octane number

The compression ratio of an engine describes the amount of power the engine can deliver.
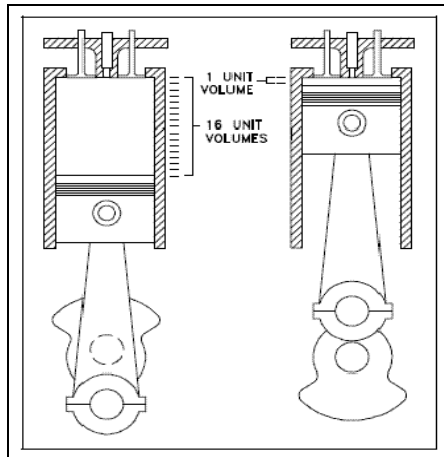
Figure 2.1: Illustration of the compression ratio [DE, 1993]

The compression ratio as shown in Figure 2.1 is the ratio of the cylinder volume at the bottom of the stroke to the volume at the top of the stroke. This means that the higher the compression ratio, the longer the power stroke and the more powerful the engine. In effect, with a higher octane number, the fuel can withstand more compression before detonating [Leffler, 1985].

Evaluating the engine cycle of a four stroke engine as depicted in Figure 2.2, the 'intake" image imitates the first stroke where the air and the fuel is injected into the cylinder as the piston moves down. The "compression" image is the second stroke where the piston moves up and compresses the fuel and air mix. In the "power" and "exhaust" image it is shown that the fuel and air mix ignites with the help of a spark plug. The undesirable opposite of this scenario is, as the air and fuel mix is compressed, it heats up and if it is compressed enough it will auto-ignite without the help of a spark plug. When auto-ignition takes place (fuel ignites before the piston reaches the top of the stroke) the piston will be pushing back against the turning motion of the crank shaft and not pushing with it, causing the phenomenon known as "knocking". Gasoline should not explode, but rather it should burn as quickly as possible. Upgrading to a higher octane will allow the

fuel to withstand the change in physical conditions (increase in temperature and pressure) and not auto-ignite (explode) up to a point where the designed compression ratio of the internal combustion engine has been reached. Since knocking is tough on the mechanical parts of the engine and it works against the engine's power, it needs to be avoided [Leffler, 1985].
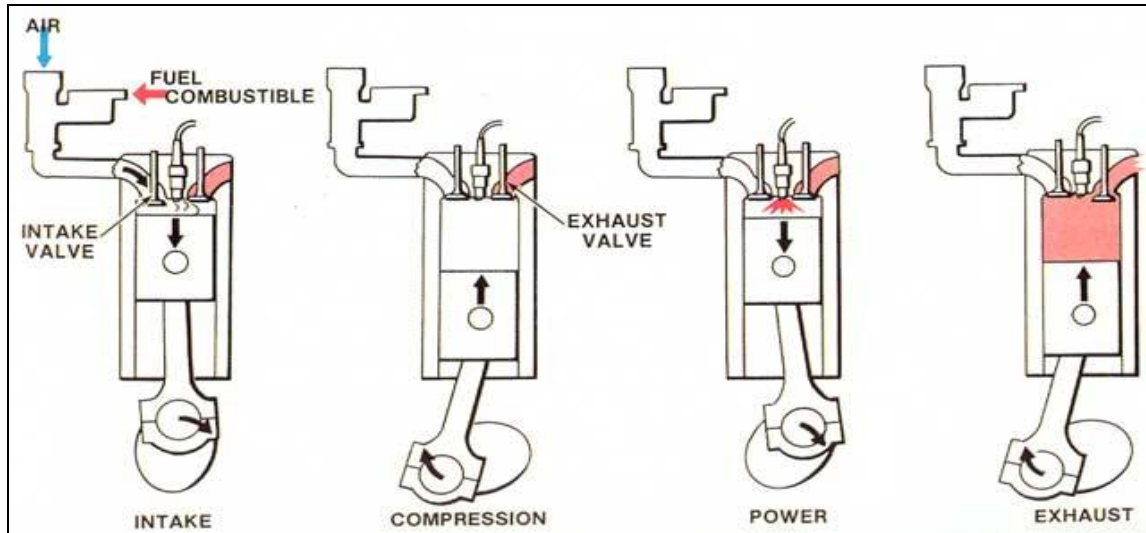

Figure 2.2: Illustration of the engine cycle [Amsoil, 2001]

The relationship between the compression ratio of an internal combustion engine and octane number is one of the reasons why octane numbers are measured. Octane number is the measure of a fuel's resistance to auto-ignition [Favennec, 2001] and auto-ignition is detected by knocking. Knocking is therefore measured with the use of a reference motor called Cooperative Fuel Research (CFR) [Wauquier, 1995]. There are two ways to measure octane numbers, namely Research Octane Number (RON) and Motor Octane Number (MON) [Gary et al., 2004].

RON is determined by running the fuel in a test engine (CFR) with a variable compression ratio under controlled conditions, and comparing the results with those for mixtures of *iso*-octane (*2,2,4*-trimethyl pentane) and *n*-heptane. Unlike other combinations of carbon and hydrogen (such as butane, pentane, hexane and heptane - 4, 5, 6 and 7 carbon atoms respectively), *iso*-octane handles compression very well. When the arbitrary scale was developed, pure *iso*-octane C_8H_{18}, was defined as 100 octane gasoline whilst *n*-heptane, C_7H_{16}, which knocks at a much lower compression ratio, was defined as 0 octane gasoline [Gary et al., 2004].

The RON of hydrocarbons depends closely on their chemical structure. Figure 2.3 shows that the RON varies with the boiling point of each family of hydrocarbons and from all theses hydrocarbons (aromatics, *n*-paraffins, *iso*-paraffins and naphthenes); aromatics followed by *iso*-paraffins have the highest octane number [Albahri et al., 2002].
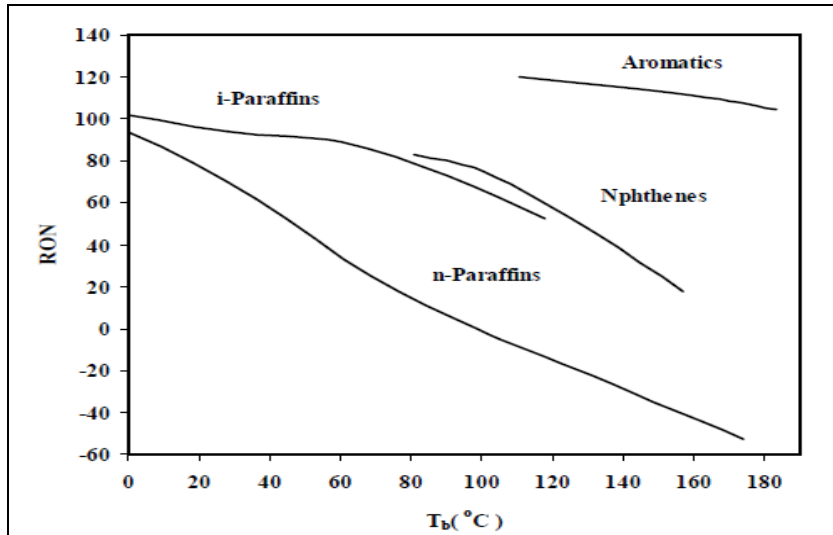

Figure 2.3: Octane numbers versus boiling point for hydrocarbon families [Albahri et al., 2002]

MON is determined in a similar test engine (CFR) to that used for RON testing, but with a preheated fuel mixture and a higher engine speed of 900 rpm instead of 600 rpm as for RON. For both RON and MON, the engine is operated at a constant speed (rpm's) and the compression ratio is increased until knocking occurs [Gary et al., 2004]. The RON test imitates driving under mild conditions such as in towns or cities where acceleration is relatively frequently, whereas the MON test imitates driving under severe conditions such as highways [Gary et al., 2004].

Putting octane numbers and compression ratios in a nutshell: a commercially available petrol fuel which has the same resistance to auto-ignition as the primary reference fuel (a mixture of 95% *iso*-octane and 5% normal heptanes) has an octane number of 95.

An engine that uses a fuel with a higher octane number means that the engine can be designed with a higher compression ratio which in turn has higher engine efficiency [Favennec, 2001].

The MON of a gasoline is always lower than the RON [Wauquier, 1995]. The difference between them (*i.e.* RON–MON) reflects the sensitivity of the performance of the fuel to the two types of driving conditions and is called the *sensitivity* of the fuel. The sensitivity for a final petrol blend should be 10 (±1) [Leffler, 1985].

2.4 The Fischer-Tropsch Refinery and the use of butene, hexene and octene as feedstocks

Fischer–Tropsch (FT) is a technology that has been commercialized in the early 1930s [Leckel, 2009]. It is an established technology that provides gasoline for the South African market [Kamara et al., 2009]. Iron catalyst based FT is divided into two categories, the high temperature Fischer-Tropsch (HTFT) and the low temperature Fischer-Tropsch (LTFT) processes [Leckel, 2009]. Vast amounts of literature is available on the Fischer–Tropsch technology.

The refining pathways for butene, hexene and octene are described based on the original HTFT refinery flow diagram (Figure 2.4).
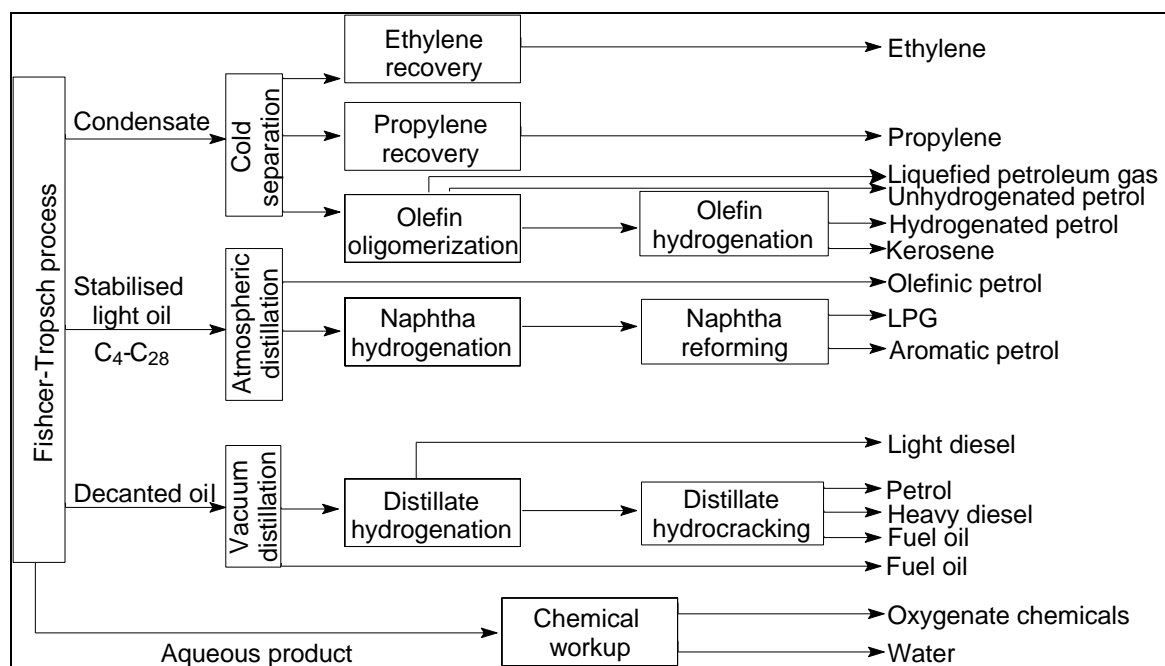
Figure 2.4: High Temperature Fischer-Tropsch (FT) refinery design originally used at Secunda [Kamara et al., 2009]

2.4.1 Butene

The condensate stream from the cold separation unit is fractionated into overheads (C_3 – C_4) and bottoms (C_5 - C_6). These overheads (C_3 – C_4) are used

as the feed in the olefin oligomerization process and thereafter the olefins may be hydrogenated. Unhydrogenated petrol, hydrogenated petrol and kerosene are produced and sent to the petrol pool.

2.4.2 Hexene

The stabilised light oil (SLO) is fractionated under atmospheric distillation and the C_6 product is directly sent to the petrol pool as olefinic petrol.

2.4.3 Octene

In this case the SLO is fractionated under atmospheric distillation whereafter the naphtha fraction which includes C_8, is hydrogenated and reformed to produce high-octane aromatic motor gasoline.

Although butane has a high octane value (RON=111 and MON=98) and can be blended directly into the fuel, it is restricted by its high vapour pressure specification of the final fuel blend. Thus, some of the butane can be marketed as liquefied petroleum gas whereas the bulk of the C_4 material must be refined. The hexene and octene FT products are high in olefinic nature. Both of these products have poor octane values, making it more valuable to refine them [Dancuart et al., 2004]. From this observation the basis of this study was determined and it was well thought to do skeletal isomerization on olefins (butene, hexene and octene) to produce their branched *iso*-olefins which have a high degree of branching and in turn produce a high octane fuel.
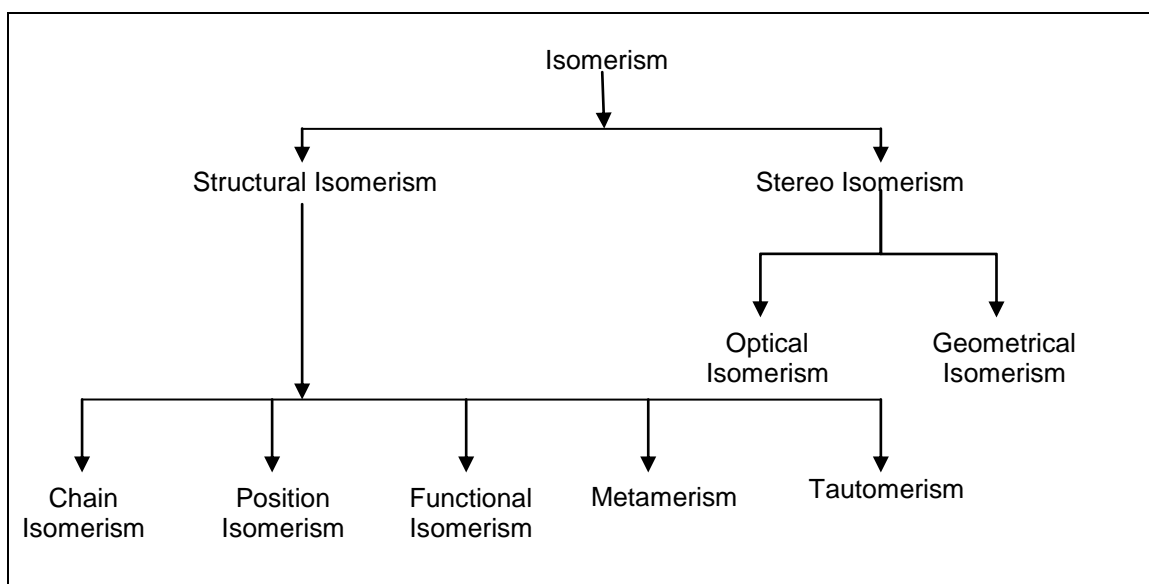
2.5 Isomerization

Isomerization is the chemical process by which a compound is transformed into any of its isomeric forms [Bartholomew et al., 2006]. The isomers of a compound have the same chemical composition but differ in structure; therefore they can be identified and distinguished from each other. Isomerization is possible only in hydrocarbons containing four or more carbon atoms, for example from *n*-butane to *iso*-butane.

Isomerization is classified into two types namely [Petrucci et al., 1993]
- Structural isomerization
- Stereo isomerization

Figure 2.5: Classification of different types of isomerization processes

Paraffin isomerization and olefin isomerization will be discussed in this section as these are of importance to the study. Both are classified under structural isomerization (which arises due to the difference in the arrangement of atoms in the molecule). Furthermore, paraffin and olefin skeletal isomerization are classified as chain isomerization and double bond isomerization. Chain isomerization arises from the difference in the nature and structure of the carbon chain, for example butane to *iso*-butane or butene to *iso*-butene. Double bond isomerization is classified as position isomerization which arises due to the difference in the position of the same functional group or the same substituent while the arrangement of carbon atoms remains unchanged, for example butene which can have two positional isomers; *1*-butene and *2*-butene [Burrows et al., 2009].

### 2.5.1 Paraffin isomerization via carbocation intermediates

Paraffin isomerization is the process in which a linear paraffin (alkane) is converted into its branched isomers. It is commercially refined from C_6 and lighter molecules and used in the production of clean burning and high performance fuels [Kuchar et al., 1999].

The isomerization of paraffins occurs via carbocation intermediates. Carbocations may be subdivided into carbenium ions and carbonium ions. A carbenium ion is a *tri*-coordinated and positively charged carbon ion (Figure 2.6A) and a carbonium ion is a *penta*-coordinated and also positively charged carbon ion (Figure 2.6B) [Bartholomew et al., 2006]).

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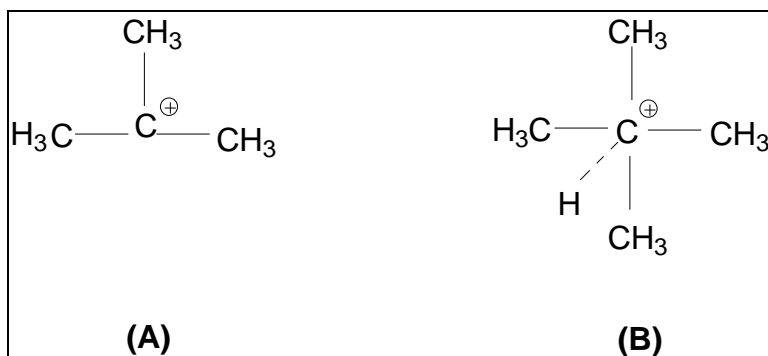
Figure 2.6: Carbocations of which (A) is the carbenium ion of methane and (B) is the carbonium ion of methane

Carbocations' relative stabilities are important since more stable ions require less energy to form. This means that more energy is needed to produce a primary carbocation than a secondary one, and more energy to make a secondary one than a tertiary one. Carbocations' stabilities (Figure 2.7) increase from primary<secondary<tertiary carbenium ions [Weitkamp and Hunger, 2007].
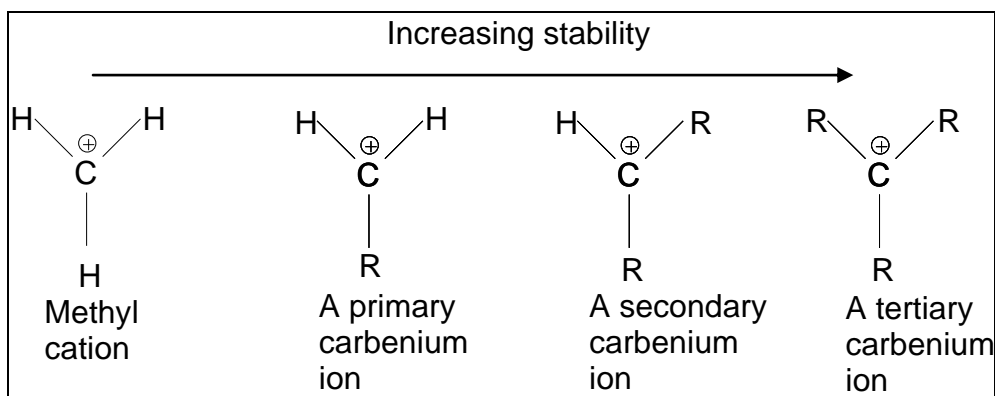

Figure 2.7: Increasing stability of carbenium ions (R is an alkyl group)

Two types of catalysts are available for skeletal isomerization of paraffins. They are monofunctional acidic catalysts such as silica-alumina based materials (very acidic catalysts) and bifunctional catalysts (less acidic zeolite catalysts) [Sie, 1998]. The reaction mechanisms differ depending on the catalyst used [Leprince, 2001].
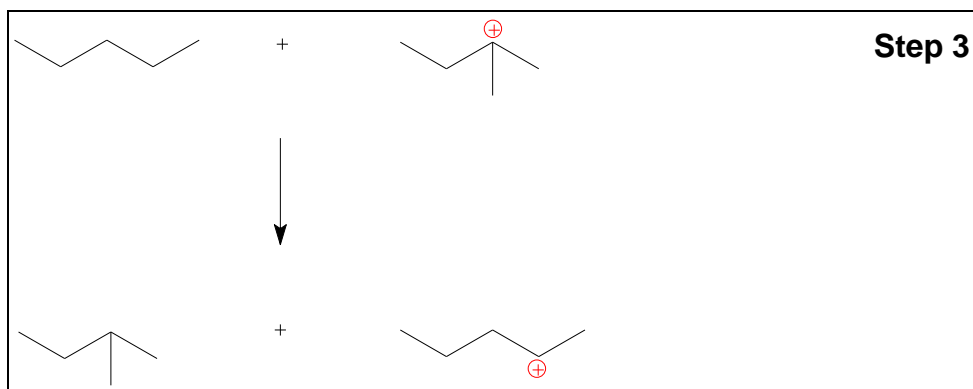
In the case of very *acidic catalyst*, a monofunctional mechanism is implicated and the carbocation is produced by removal of a hydride from the paraffin:
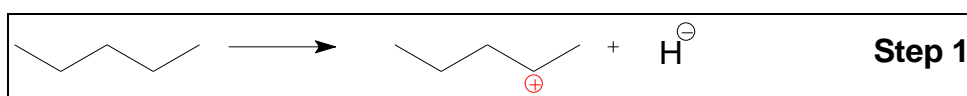
Rearrangement of the secondary carbocation to a more stable tertiary carbocation takes place:
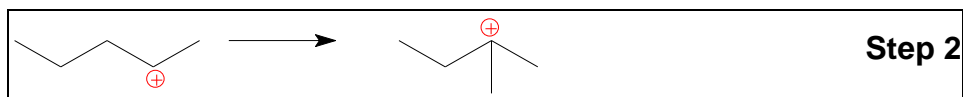

Step 2

The formation of an *iso*-paraffin by hydride (H⁻) transfer between the carbocation formed in Step 2 and another *n*-paraffin molecule:

Step 3

In the case of a *less acidic zeolitic catalyst*, a metal and acid bifunctional mechanism is implicated. An olefin is formed through dehydrogenation of the paraffin on the metal, normally platinum (Pt). Olefin protonation on the acid sites is then responsible for the carbocation formation:

Firstly the *n*-olefin is formed:

Step 4
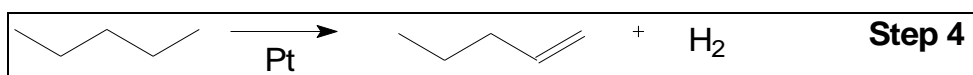
Secondly the carbocation is formed:
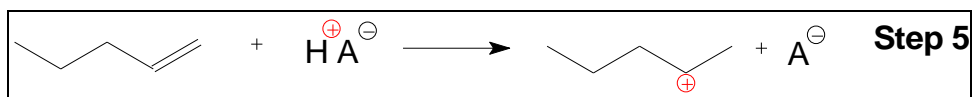
Step 5

Rearrangement of the secondary carbocation to a more stable tertiary carbocation takes place:

Step 6

The formation of the *iso*-olefin:

Step 7

Lastly the formation of the *iso*-paraffin:

Step 8

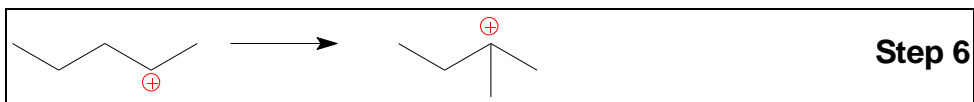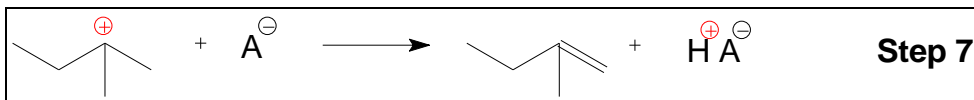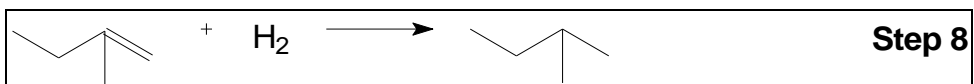### 2.5.2 Olefin isomerization via carbocation intermediates

Isomerization of normal olefins to *iso*-olefins is not a new idea and dates back to the 1850s [Meyers, 1997]. In an article by Dunning [1953], aliphatic olefin isomerization is classified as follows:

- Double bond isomerization
- Skeletal isomerization

Double bond isomerization is for instance the conversion between *1*-butene and *2*-butene. It can be seen as the movement of the double bond and/or *cis-trans* isomerization (Scheme 2.1a). The double bond isomerization mechanism is acid catalyzed and can also take place via a carbocation (step 9), carbanion or radical intermediate in different environments [de Klerk, 2008].

Step 9
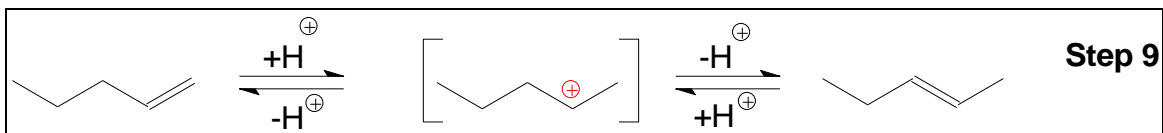
In the case of chain isomerization; with which olefin skeletal isomerization is associated (Figure 2.5), the *n*–olefin is converted to its branched isomer and a change in the structure of the molecule (Scheme 2.1b) occurs [Eleazar, 1984].
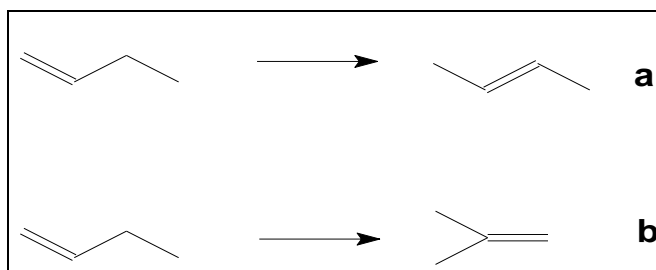
Scheme 2.1: Olefin isomerization showing double bond movement (a) and chain isomerization (b)

2.5.3 Proposed reaction mechanisms for olefin skeletal isomerization

Three main reaction mechanisms for skeletal isomerization of linear butenes into *iso*-butene have been proposed in the literature. They are [van Donk, 2002];

- Monomolecular
- Bimolecular
- Pseudo-monomolecular

In the monomolecular mechanism (Scheme 2.2) it can be seen that the controlling step in the isomerization of *n*-butene to *iso*-butene in the forward direction is the rearrangement of the *sec*-butyl carbonium ion to the less stable primary butyl carbonium ion. The primary butyl carbonium ion contains the branched carbon chain. In the reverse reaction, the formation of the thermodynamically unstable primary carbonium ion from *iso*-butene appears to be the controlling step. The skeletal isomerization of *n*-butene to *iso*-butene requires more severe conditions than for *cis* and *trans* isomerization to occur. This is due to the fact the primary butyl carbonium ion is not thermodynamically favoured [van Donk, 2002] and isomerization to *iso*-butene will occur with difficulty.
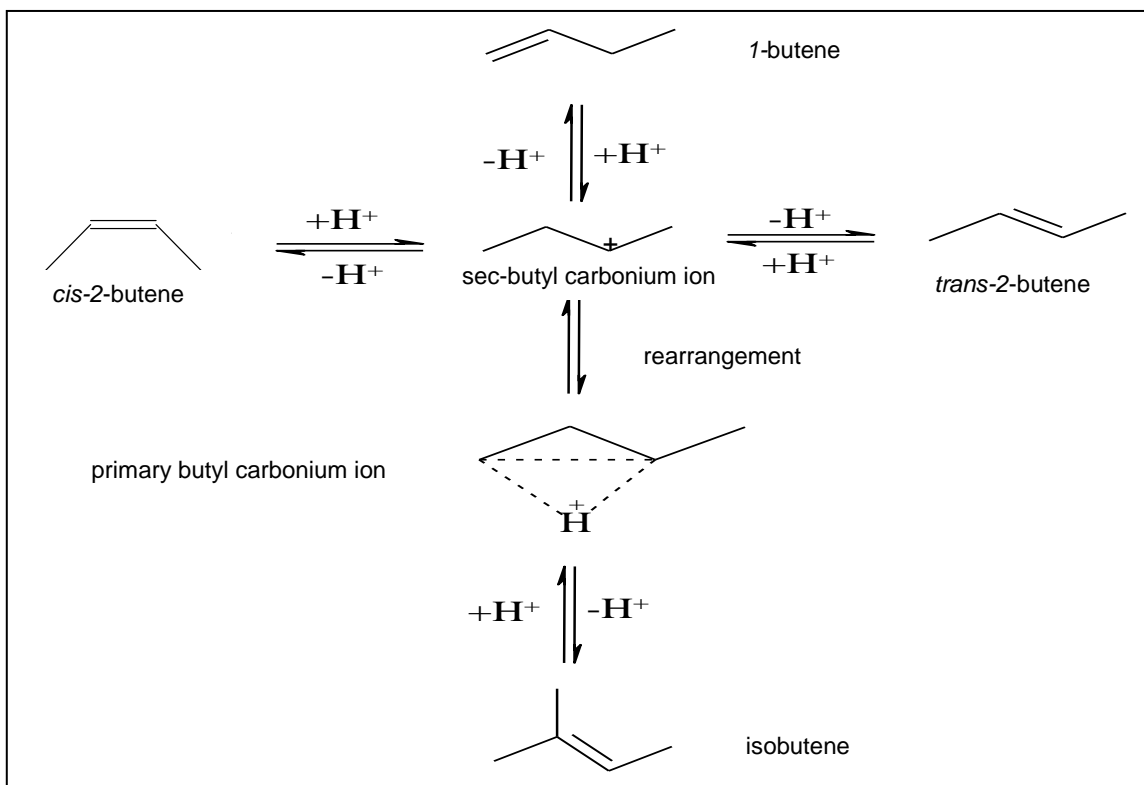
Scheme 2.2: A monomolecular rearrangement of butenes through a protonated cyclopropane intermediate [Domokos, 2002 and De Klerk, 2008]

The bimolecular mechanism proposals can be further subdivided into two separate routes:

- classical bimolecular and the
- co-dimerization paths

In the classical bimolecular proposal, two linear *n*-butenes dimerize (D) into dimethylhexene that undergoes further isomerization (I) and finally cracks (C) into one *iso*-butene and one *n*-butene (Scheme 2.3) [van Donk, 2002].
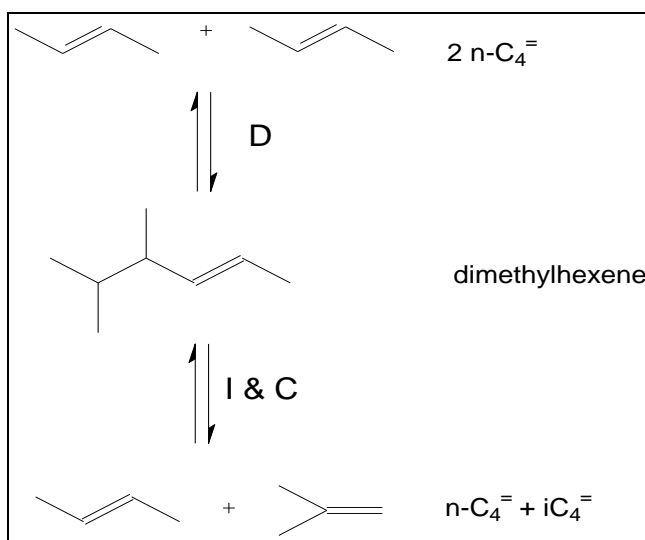
Scheme 2.3: Classical bimolecular mechanism involving dimerization, isomerization and cracking [van Donk, 2002]

In the co-dimerization scheme, one linear and one branched butene combine to form a trimethylpentene, which cracks (C) into two *iso*-butene molecules. The co-dimerization route, also known as the autocatalytic route, is potentially the more selective of the two bimolecular pathways and an easier way to produce *iso*-butene (Scheme 2.4) [van Donk, 2002].
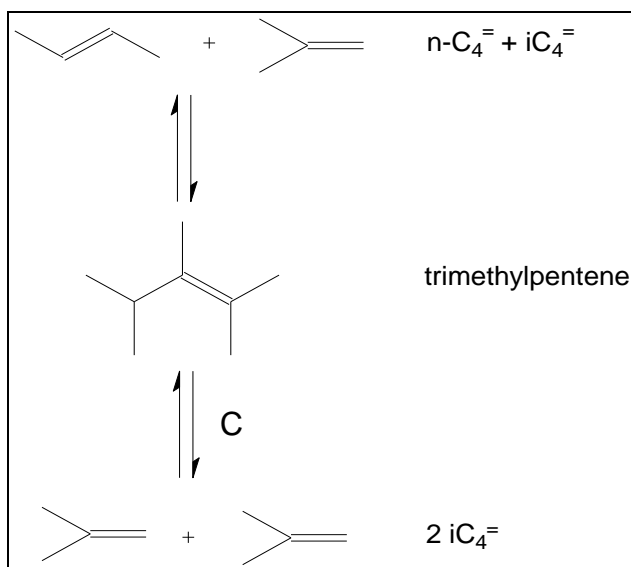
Scheme 2.4: Co-dimerization mechanism involving cracking [van Donk, 2002].

Guisnet et al. [1995, 1997b and 1998] stated that the involvement of a highly unfavourable primary carbenium ion is avoided in the mechanism of the pseudo-monomolecular pathway. The active site (Scheme 2.5) is formed by a carbenium ion that is fixed in the coke that is deposited on the catalyst with time. The butene reacts with this carbenium ion to give a secondary carbenium ion and after a methyl hydride shift, a tertiary carbenium ion is obtained. A methyl shift is

when the carbocation is substituted with the methyl and a hydride shift is when the carbocation is substituted with the hydrogen. This rearrangement of carbocations occurs to form more stable carbocations. *Iso*-butene is finally produced by β-scission of this intermediate and in so doing the active site is also regenerated.
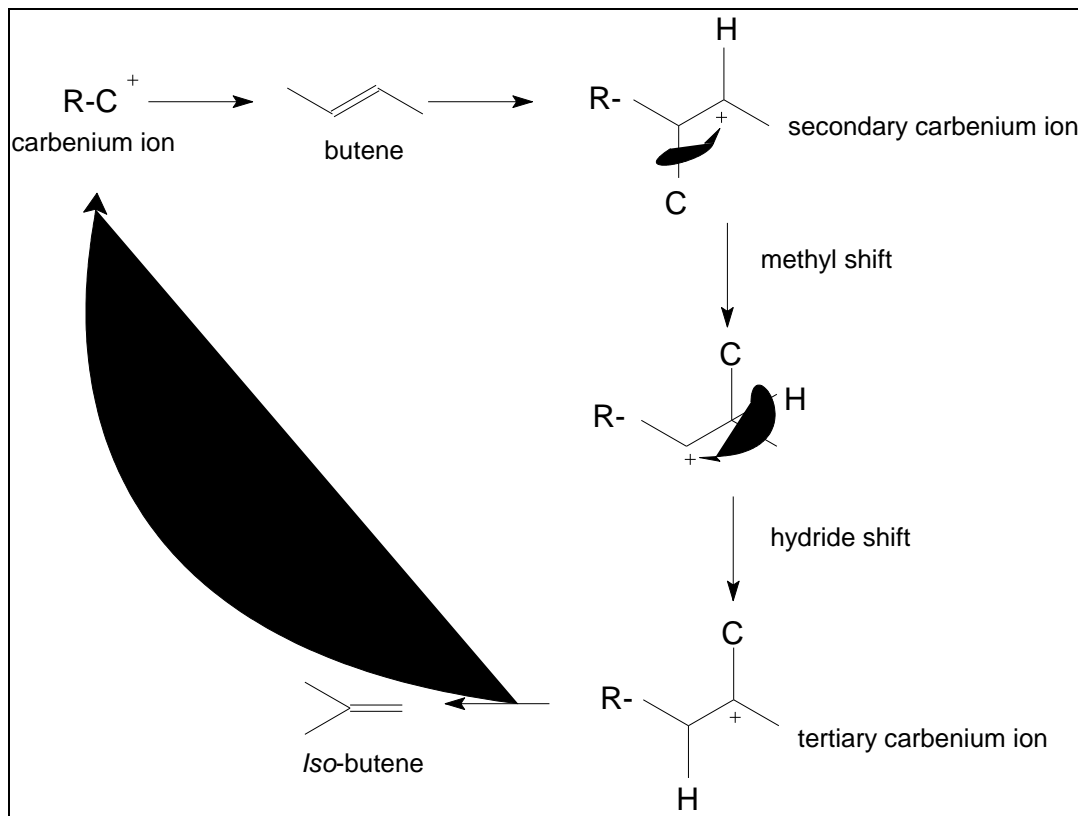
Scheme 2.5: Catalytic cycle in pseudo-monomolecular pathway [Domokos, 2002 and de Klerk, 2008]

β-scission is an important reaction of carbenium ions. This involves the breaking of a carbon-carbon bond located β to the charged carbon atom producing an olefin and another carbenium ion [Ertl et al., 1997].

In the case of octenes, de Klerk [2006] stated that 4 main reactions occur over acid catalysts (Scheme 2.6):

- double bond isomerization
- skeletal isomerization
- oligomerization and cracking.
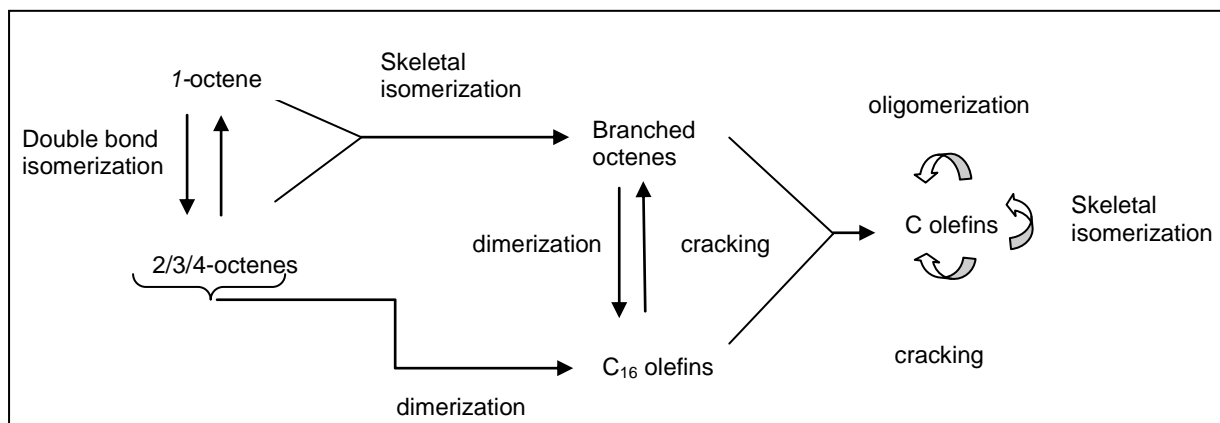
Scheme 2.6: Reaction network of olefin reaction over acid catalyst [de Klerk, 2006]

2.6   Feedstock for olefin isomerization

The following thermodynamic properties set a limit to the octane number that can be obtained by the fullest extent of isomerization of olefins present in the feedstock [Dunning, 1953]:

- heat content;
- heat of formation;
- heat capacities,
- free energies;
- entropies;
- equilibrium constant;
- free energies of isomerization; and
- equilibrium concentration in isomerization reactions.

Thus, taking the isomerization process into account, an unbranched olefin with a low octane value should be selected as a feedstock [Dunning, 1953]. This will result in a greater possibility for octane improvement by means of isomerization [Berg et al., 1946]. For that reason, butene, hexene and octene will be used as feedstocks in this study.

2.7   Thermodynamic equilibrium and operating conditions

A study done by Berg et al. [1946] "Octane Rating Improvement of Olefinic Gasolines by Isomerization" gave more insight regarding the thermodynamics of olefins in the isomerization process. They stated that thermodynamic equilibrium is established when specific reaction conditions (temperature, pressure and composition) are maintained at all times during the isomerization process. To put this into perspective, taking *n*-butene as an example, if the catalyst has channels

with lots of protonic sites, the *n*-butene molecule will undergo a significant amount of successive reactions (from *n*-butene to *iso*-butene and *by*-products) until no change in composition is observed and at a specific temperature and pressure the rate of the forward and backward reaction is the same. The reactants and the products are thus at this stage in thermodynamic equilibrium.

Domokos [2002] used a larger temperature range to investigate and obtain the maximum yield of *n*-butene to *iso*-butene as shown in Figure 2.8. The conversion of *n*-butene to *iso*-butene is shown to be thermodynamically limited. Figure 2.8 shows that the maximum conversion to *iso*-butene is limited to 50% at 350 °C.
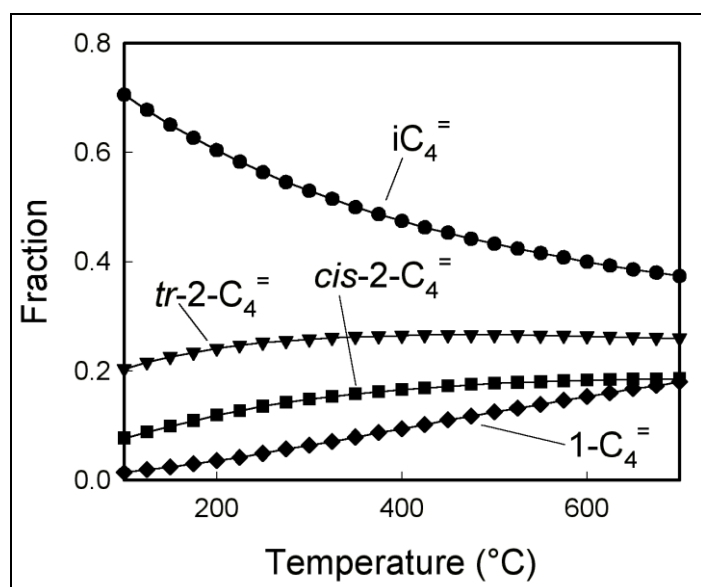
Figure 2.8: Thermodynamic distribution of *n*-butene and *1*-butene isomers versus temperature [Domokos, 2002].

The thermodynamic equilibrium is specific for every set of conditions, and at any equilibrium a set amount of each isomer exists. The possible number of isomers will increase as the number of carbon atoms increase. Pentenes have six isomeric pentenes and hexenes have a number of seventeen possible known isomers. As stated earlier, the octane ratings of the isomers differ significantly with structure. Straight chain compounds will have lower values and highly branched compounds have the highest values. As shown in Table 2.2, the shift of the double bond toward the middle of the olefin molecule usually gives an isomer with a higher octane rating [Berg et al., 1946].

Table 2.2

Octane numbers of Octene [Berg et al., 1946]

Some octane numbers of octene and its isomers

Compound	Octane rating
1-Octene	35
2-Octene	37
3-Octene	68
4-Octene	74
3-Methyl-*1*-heptene	66
6-Methyl-*1*-heptene	63
2-Methyl-2-heptene	71
3-Methyl-2-heptene	74
6-Methyl-2-heptene	66

For the purpose of this study the thermodynamic equilibrium from the reactions of *1*-butene and *1*-hexene towards the desired products was determined to get insight into the optimum selectivity over a wide temperature range for these feedstocks. The thermodynamic equilibrium was determined using Aspen Plus Software in a RGibbs reactor with the use of the NRTL (Non Random To Liquid) and PSRK (Predictive Redich-Kwong-Soave) state of equation [Aspen, 2001].

2.8   Catalysts for olefin isomerization

A long list of catalysts used in previous olefin isomerization studies was compiled by Dunning [1953]. Among these catalysts were a wide variety of catalysts used to catalyze olefin isomerization of feedstocks such as butene, hexene and octene. The temperatures at which these catalysts performed ranged from ±20 °C to ± 600 °C. The outcomes of these reactions were cracking, polymerization and isomerization to different extents.

2.9   Catalysts used for olefin skeletal isomerization based on feedstocks used in this study

2.9.1 Butene

Skeletal isomerization of *n*-butene to *iso*-butene depends on the following characteristics of a catalyst [van Donk, 2002]:

- pore topology,
- acid strength,
- acid site density, and

- location of the acid sites.

The pore structure of the catalyst is the most important feature with regard to selectivity and stability.

Pore topology

Gregg and Sing [1982] explained that pores are classified into three regions according to their size: (1) macropores, (2) mesopores, and (3) micropores. A macropore has a diameter of more than 50 nanometer (nm), a mesopore has a diameter of 2 nm - 50 nm; and a micropore has a diameter of less than 2 nm.
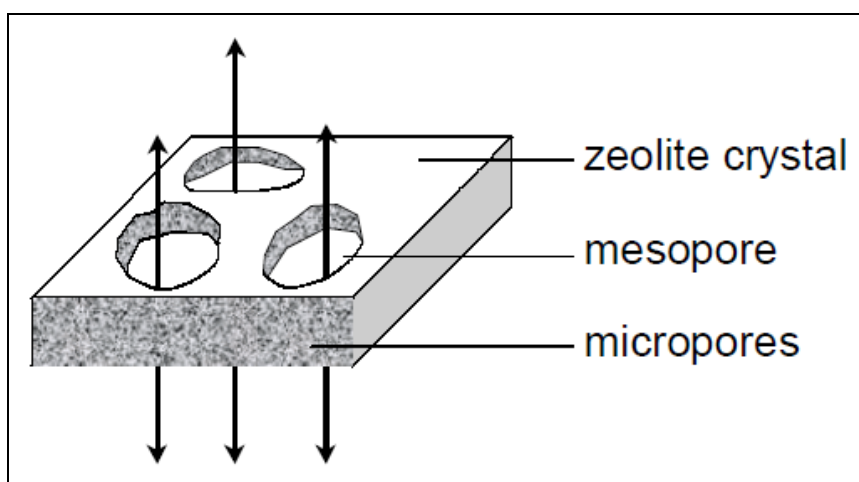
Figure 2.9: Micropores and mesopores of a zeolite crystal [Corma, 1997]

Microporous materials were studied by Houzvicka et al. [1997a], to identify the most suitable structures for skeletal isomerization of butene to *iso*-butene and it was found that the 10-membered molecular sieves with pore diameters between 4 Å and 5.5 Å were the most suitable. The 12-membered ring zeolites do not suppress the formation of carbonaceous deposits and in turn their pores are blocked very quickly. The 8-membered ring zeolites are also not suitable for skeletal isomerization of *n*-butene to *iso*-butene since their pore diameter does not allow the diffusion of *iso*-butene. The *iso*-butene that forms in the pore must escape out of the pore into the bulk phase. Because of their channel dimensions and structure, microporous materials have lead to a breakthrough in the skeletal isomerization of *n*-butene [Houzvicka et al., 1997a] as summarized in Table 2.3.

Table 2.3
Materials tested for Skeletal Isomerization of *n*–Butene [Houzvicka et al., 1997a]

Catalyst	Types	Structure	Isobutene (%)	Stability
ZK-5	KFI	3 dim. ø 3.9Å	1.5	Very Low
SAPO-34	CHA	2 dim. ø 3.8Å	8.3	Low
ZSM-22	TON	5.5 x 4.4Å	23.7	High
Ferrierite	FER	5.4 x 4.2Å and 4.8 x 3.7 Å	33.1	Very High

Houzvicka et al. [1997a] confirmed the above and stated that:"Side reactions can be suppressed and the catalyst's stability largely enhanced when the active sites are placed in noncrossing, 10-memberered ring channels."

Contrary to this, in a different study in the same year, a publication from Houzvicka et al. [1997b] stated that not all 10-membered ring sieves are good catalysts and used the heulandite catalyst as an example. Heulandite has 10-membered ring channels, but performs poorly as a catalyst, because the channels' oval shapes are too narrow for *iso*-butene diffusion. ZSM-5 in turn, has too large cavities which offer enough space for dimerization and by-product formation, resulting in lower selectivity. ZSM-5 was chosen for their study because it is known for its lack of selectivity and to see whether the authors could increase the selectivity of the catalyst whilst preserving its high stability; meaning to keep it at a steady conversion. Conditions that were investigated were the reaction temperature, acidity of the catalyst, crystal size of the catalyst and partial pressure of *n*-butene. A summary of different conditions studied by Houzvicka et al. [1997b] is given in Table 2.4.

Table 2.4
Reaction and catalyst conditions used [Houzvicka et al., 1997b]

Catalyst	Substitute	Temp. (°C)	Crystals size (μm)	Butene pressure (kPa)	Conversion (%)	*Iso*-butene (%)
1	Al	350	*1*-15	5	80.8	13.3
2	Al	500	≈1	5	45.5	22.0
3	Al	500	10-15	5	49.8	25.0
4	Al+TMP	500	1	5	40.7	24.7
5	Fe	500	10-20	5	46.2	28.7
6	Fe	500	10-20	1	51	29.8
7	Fe	500	10-20	1	64.9	24.6
8	Fe	500	10-20	1	48.5	32.3
9	Fe	500	10-20	1	40.1	29.8

[*] The meaning of 1, 2, 3, etc. is the nine different modified ZSM-5 catalyst sample numbers.

With the above changes in reaction conditions and composition of the ZSM-5 catalyst, the yield of *iso*-butene increased from 13 to 30% (Table 2.4) and the conversion stabilizes at 40% between modified catalyst 2 to 5 and again from 8 to 9.

Houzvicka et al. [1999], found that the highest selectivity in *1*-butene isomerization was obtained with ZSM-22 and CoAPO-11 catalysts which are 10-membered ring molecular sieves with a one-dimensional pore system of channels.

ZSM-22 and ZSM-35 were both studied by Byggningsbacka et al. [1998]. They have done various experimental tests on the fresh and deactivated catalysts and did various comparisons between ZSM-22 and ZSM-35. In their study, ZSM-22 demonstrated a much higher selectivity to *iso*-butene than ZSM-35 during the first hours due to the internal pore diffusion limitations. This pore diffusion limitation may be due to the crystal size as summarized in Table 2.5. The crystal size of ZSM-22 was smaller compared to ZSM-35 and Byggningsbacka et al. [1998] described that the activity would improve with decreasing crystal size if internal pore diffusion is the rate limiting step.

Table 2.5
**Effect of crystal size on activity**

Catalyst	Crystal Size	Selectivity to iso-butene (mol%)
ZSM-22 fresh	0.4 µm x 2.9 µm	79
ZSM-35 fresh	1.6 µm x 5.2 µm	53

There was a substantial decrease in the surface area between the fresh and deactivated catalysts. Due to higher coke formation inside the spherical cavities of ZSM-35, it also showed a larger decrease in surface area than ZSM-22. After 1200 minutes reaction time, the deactivated catalyst showed no activity at all (Table 2.6) [Byggningsbacka et al., 1998].

Table 2.6
Differences in fresh and deactivated ZSM type catalysts [Byggningsbacka et al., 1998]

Catalyst	TOS (min)	Surface area (m^2/g)	Selectivity to iso-butene (mol%)
ZSM-22 fresh	1	255.7	74.7
ZSM-22 deactivated	1200	92.2	87.3
ZSM-35 fresh	1	400.6	52.6
ZSM-35 deactivated	1200	39.6	-

Similarly to how Krishna et al. [1994] used Figure 2.10 to explain the relation of surface area over volume ratio to liquid processes for catalysts (not specifically zeolites), the relationship in the figure will be used in this study to indicate the surface area over volume ratio of different catalyst morphologies.
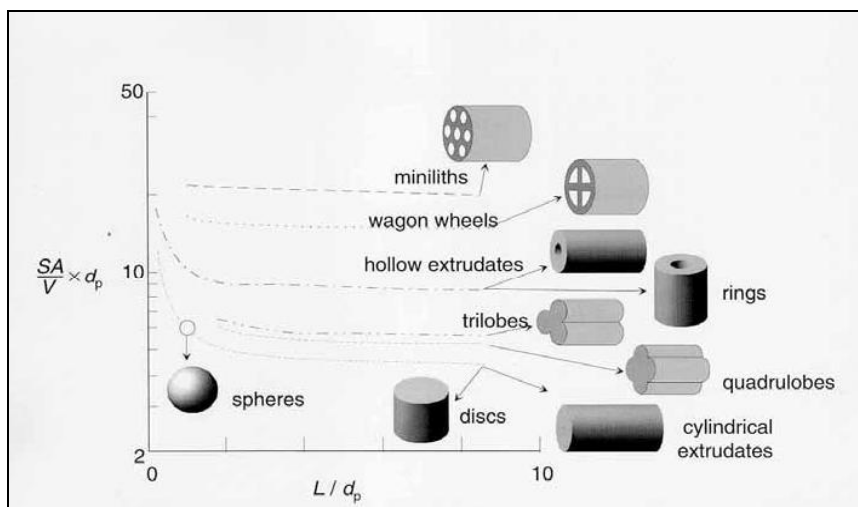
Figure 2.10: Surface area over volume ratio of shaped catalyst particles [Krishna et al., 1994]

An attempt will be made to explain the higher coke formation inside the spherical cavities as described above, with regard to the selectivity in Table 2.6. The surface area to volume ratio (*SA/V*) of rings, hollow extrudates and more difficult shapes such as "wagon wheels" and "miniliths" are greater than the more common cylindrical tablets and cylindrical extrudates of the same outside diameter and length. The extrudates with a clover leaf cross section, namely trilobe or quadrulobe extrudates, have a greater surface-to-volume ratio than cylindrical extrudates of the same maximal outside diameter. It can be seen that round, disk-shaped tablets of a length-to-diameter ratio below 1 (also known as spherical shape) have greater surface areas than cylindrical extrudates of the same diameter with a ratio above 1. Therefore, due to this spherical shape which has a higher surface area than the one-dimensional cylindrical extrudate, and since it was not stated that the spherical cavities of the ZSM-35 is also one-dimensional it is believed that more activity can take place in this spherical cavites and in turn more coking can occur in relation to the one-dimensional channel system of ZSM-22.

Acid sites and acid strength

Besides the pore topology of the catalysts, the acidic sites and strengths are also important factors influencing the *iso*-olefin activity. Olefin skeletal isomerization requires acid sites of intermediate strength and not very strong or very mild acid sites as for acid-catalyzed reactions. Adjustments of the catalyst acidity are required to obtain high catalyst selectivity and stability [Ozmen et al., 1993].

Brønsted and Lewis acid sites are described in literature by Pieta et al. [2010]. They stated that Lewis sites are formed from Brønsted acid sites. Figure 2.11 explains the formation of Lewis acid sites with regards to the fundamental building block of zeolites [Bhatia, 1990]. A tetrahedron of four oxygen anions is surrounding a silicon or aluminium ion, which is arranged so that the oxygen atoms are shared with a silica or alumina tetrahedron. The oxygen anion has an oxidation state of -2 and balances the +4 charge of each silicon ion, making the silica tetrahedra electrically neutral. Since the oxidation state of the aluminium ion is +3 and that of the oxygen anion -2, it results in the aluminium tetrahedron to have a residual charge of -1 (the trivalent aluminium is bonded to four oxygen anions). Thus, each alumina tetrahedron requires a +1 charge from a cation in the structure to maintain electrical neutrality (Figure 2.11A). When this Brønsted

acid site is partially dehydroxylated, Lewis acidity which is an electron acceptor is formed by the removal of the OH groups (Figure 2.11B) [Pieta et al., 2010].
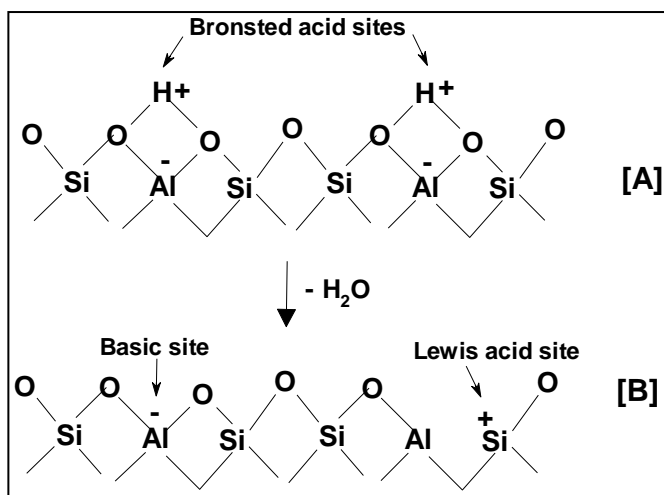

Figure 2.11: In zeolites and silica-alumina, Brønsted acid sites transform into Lewis acid sites [Waghmode et al., 2003]

Ozmen et al. [1993], however proposed that strong Brønsted acid sites lead to catalysts that are efficient and stable for the skeletal isomerization of *n*-butene. Catalysts that also showed good stability and activity other than ferrierite were SAPO 11, MnAPO11, ZSM -22, theta 1 and ZSM-23 [Houzvicka et al., 1996].

Houzvicka et al. [1998] proposed that the acid strength of the catalyst plays an important role in the skeletal isomerization of *n*-butene. The role of acidity was tested on open surface catalysts, namely chlorinated and fluorinated alumina, phosphoric acid on silica, zirconium-oxide treated with sulphuric acid and also on molecular sieves of MFI type, namely [Al]ZSM-5; [Ga]ZSM-5; [Fe]ZSM-5; [B]ZSM-5 and [Al]ZSM-5, all treated with trimethylphoshite. From this data it was observed that the activity of the catalyst is not sufficient when the acidity is too low. However, *iso*-butene selectivity decreases and when the acidity is too high; oligomerization and by-product formation are induced.

An ideal skeletal isomerization catalyst should have a strong enough acidity for skeletal isomerization to occur and not too strong for oligomerization and cracking to occur. It is accepted that the acid strength required for these reactions increases in the order [Canizares et al., 2000]: double bond isomerization << skeletal isomerization < oligomerization ~ cracking.

This shows that strong acid sites favour the undesired oligomerization-cracking reactions and the weaker acid sites favour the skeletal isomerization reactions.

A Zn-silicoaluminophosphate molecular sieve (ZnAPSO-11), a Zn-supported SAPO-11 molecular sieve (Zn/SAPO-11) and an unpromoted SAPO-11 sample were reported to have been used in the catalytic transformation of *1*-butene [Escalante et al., 1997]. The ZnAPSO-11 solid had the highest selectivity towards skeletal isomerization. This catalyst also showed the highest number of acid sites and acid strength. Considering the Zn-supported SAPO-11, a decrease in acidity led to a decrease in skeletal isomerization. Table 2.7 presents this data [Escalante et al., 1997].

Table 2.7
Total acidity, expressed as mmol of ammonia per gram of catalyst desorbed within the 403 - 818K temperature range [Escalante et al., 1997].

Catalyst	Total acidity (mmol of NH_3/g_{cat})	mmoles NH_3/g_{cat}		Molar compostion formula	Selectivity (%)
		130-220°C	220-540°C		
SAPO-11	0.64	0.40	0.24	$(Al_{0.48}P_{0.47}Si_{0.05})O_2$	22.8
ZnAPSO-11	1.3	0.40	0.90	$(Al_{0.44}P_{0.46}Zn_{0.052}Si_{0.051})O_2$	32.4
Zn/SAPO-11	0.40	0.23	0.17	-	4.1

It is understood that skeletal isomerization is catalyzed by Brønsted acid sites [Damon et al., 1977] and therefore the most important requirement for the catalyst is to have good Brønsted acidity, which is the reason for high selectivity of the ZnAPSO-11 catalyst. Alumina is Lewis acidic [Morterra et al., 1979] which means that the lower the alumina content, the lower the Lewis acidity and the higher the Brønsted acidity. Considering the molar compositions of SAPO-11 and ZnAPSO-11, it is evident that the Al^{3+} is lower (mole fraction of 0.44) in ZnAPSO-11 than in SAPO-11 (mole fraction of 0.48) therefore the higher acidity of ZnAPSO-11. Unfortunately these two catalysts cannot be compared to Zn/SAPO-11 with respect to its molar composition since the data was not made available in the referenced study.

Gaffney et al. [1992] described the skeletal isomerization of *1*-butene in a patent. *1*-Butene was reacted with a MgAPSO-31 catalyst at space velocities of 12-139 h^{-1}, temperatures of 299 °C – 839 °C and atmospheric pressure. It was found that the conversion of *1*-butene to *iso*-butene was improved by carrying out the

isomerization at temperatures in excess of 482 °C. Runs at lower temperatures reduced the conversion and selectivity. From this patent it is understood that the desired temperature for skeletal isomerization of olefins using molecular sieve catalysts are at temperatures in excess of 482 °C.

An invention of Myers [1979] provides insight in the regeneration of an alumina isomerization catalyst especially eta and gamma alumina. Reaction temperatures from 370 °C to 430 °C were used and regeneration was initiated at approximately 480 °C. The temperature was slowly increased during regeneration because of the high heat of combustion. From these runs it was understood that the RON increased with wet regenerated catalyst, due to more isomerization taking place and less coke being produced compared to the catalyst regenerated under dry gas conditions. Wet regeneration contained water vapour and the dry gas regeneration was water free. Results are summarized in Table 2.8 [Myers, 1979].

Table 2.8
Typical results of the effect of regeneration of eta and gamma alumina with wet or dry gas [Myers, 1979].

Catalyst	Isomerization Temp (°C)	Regeneration Gas	Coke (%)	Unleaded RON
A	402	Dry	3.15	89.3
A	402	Wet	2.31	89.5
B	398	Dry	3.54	-
B	399	Wet	2.42	88.7
C	400	Dry	2.26	88.1
C	399	Wet	2.59	88.3

In a US patent, Lin et al. [1994] describe isomerization of normal C_4 and C_5 olefins into *iso*-olefins in the presence of the SKISO-11 catalyst under temperature conditions of 200 °C to 650 °C and a pressure of 0.3 to 10 atmospheres. The support used in the catalyst was any crystalline type of Al, preferably eta or gamma alumina. In one of the cases in this patent, Lin et al. [1994] used 99.5% *n*-butene as feed to convert into its isomers over an alumina catalyst. The operating conditions were 1 atm, WHSV of 1 h^{-1} and 250 °C - 450 °C as shown in Table 2.9 with percentages of products formed.

Table 2.9
The product composition of C₄ skeletal isomerization for different operating temperature
[Lin et al., 1994]

Component	Composition (%) at reaction temperature (°C)				
	250	**300**	**350**	**400**	**450**
Butane + C$_3$	0.2	0.3	0.9	4.9	5.0
1-**Butene**	21.7	20.0	19.2	17.1	14.9
Trans-*2*-**butene**	41.5	47.8	46.5	33.2	24.7
Cis-*2*-**butene**	36.6	31.6	30.8	23.1	17.9
Iso-**butene**	-	0.3	2.2	17.3	31.9
C$_5$+	-	-	0.4	4.4	5.6

From Table 2.9 it is evident that the yield of *iso*-butene increases with increasing temperature.

Adams et al. [1983] described the use of a chlorine/fluorine containing compound which activated the alumina catalyst for skeletal isomerization of straight chain olefins in a temperature range of 350 °C to about 550 °C. The catalyst had particle sizes from 0.5 x 10^{-3} cm to about 160 x 10^{-3} cm. 3 to 9% of the pore volume was attributed to pores that had radii of 100 to 1000 Angstroms. High conversion and selectivity were obtained.

2.9.2 Hexene

In the literature review done by Brooks [1955], information was given regarding different catalysts used for the isomerization of *1*-hexene. *1*-Hexene converts to its branched hexenes and a double bond shift also occurs.

- *1*- hexene was contacted with U.O.P. phosphoric acid on infusorial earth catalysts at 335 °C and from this reaction 67% branched hexenes were obtained.

- *1*-hexene was also reacted with anhydrous aluminium sulphate at 250 °C - 275 °C and mixtures of *1*-,*2*-, and *3*-hexenes were yielded. Furthermore, 64% tetramethylethylene was obtained with the conversion of *2,3*-dimethylbutene.

  In this same study, contact was made between *2,3*-dimethyl-*1*-butene and aqueous ammonium chloride at 230 °C and 90 atm pressure which yielded 67% *2,3*-dimethyl-*2*-butene. This phenomenon is known as double bond shift.

- When reacting *1*-hexene over phosphoric acid on pumice at 325 °C to 360 °C for four hours, 32% *2*-methyl-*2*-pentene was obtained.

- Contacting *1*-hexene over pumice impregnated with zinc chloride and hydrogen chloride at 375 °C gave a low yield of 7-12% tetramethylethylene.

From the above information it seems as if the isomerization of *1*-hexene to its branched isomers and double bond shift occurs at relatively low temperatures, *i.e.* between 230 °C and 375 °C.

2.9.3 Octene

Literature studies [Brooks, 1955] reported that *1*-octene and *2*-octene over phosphoric acid on pumice at 350 °C gave partial conversion to $Me_2C=CHC_4H_9$. The authors also found that *1*- and *2*-octenes were isomerized to banched-chain octenes during thermal polymerization using sealed glass at 345 °C – 380 °C. Contacting *1*-octene over beryllium oxide at 450 °C yielded *2*-, *3*-, and *4*-methyl heptenes. Contacting a mixture of *1*- and *3*-octene over pumice impregnated with phosphoric acid or zinc chloride at 250 °C - 325 °C yielded 47% branched-chain octenes and 15%-20% polymers.

The catalytic activities of the two catalysts Al-ZSM-5 and B-MCM-41 were compared in the isomerization of 97.7% pure *1*-octene [Sundaramurthy et al., 2003]. These two catalysts were synthesized using gels with different molar compositions by varying the SiO_2/B_2O_3 ratio in the initial gel to 20, 50, 100 and 200, representing samples A-1, A-2, A-3, A-4, B-1, B-2, B-3 and B-4, respectively (Table 2.10). A fixed bed reactor was used to carry out these catalytic reactions in the temperature range of 200 °C – 350 °C and a space velocity of 3 h^{-1}. Conversion of *1*-octene with respect to temperature and SiO_2/B_2O_3 ratio is given in Table 2.10 [Sundaramurthy et al., 2003].

Table 2.10
Conversion of *1*-octene on A-1 to A-4, B-1 to B-4, AI-ZSM-5 and B-MCM-41 catalysts at different temperatures [Sundaramurthy et al., 2003]

Catalyst	SiO_2/B_2O_3 ratio	Conversion (%) at different temperature (°C)			
		200	250	300	350
A-1	20	21.5	55	83.6	91.3
A-2	50	16	50	80.0	91.1
A-3	100	14.5	45.6	73.4	91.5
A-4	200	11	43	64.3	86.5
AI-ZSM-5	-	29	60	91.0	92.5
B-1	20	15	53.8	69.7	74.4
B-2	50	11.5	47.0	60.0	63.0
B-3	100	8.0	39.4	51.4	57.3
B-4	200	6.5	24.1	40.3	54.1
B-MCM-41	-	26	58.0	86.0	90.0

Table 2.10 indicates how the conversion of *1*-octene increased as the temperature increased in all the catalysts. Higher conversion of *1*-octene was obtained with aluminium substituted catalysts than with boron substituted catalysts due to the presence of strong Brønsted acid sites associated with Al^{3+}. However, with an increase in the SiO_2/B_2O_3 ratio, the conversion of *1*-octene decreased, which is ascribed to the decrease in the number of acid sites present in the catalyst.

In de Klerk's [2006] study the reactivity of *1*-octene at 75-125 °C and atmospheric pressure was pursued. At first *1*-octene in a paraffin matrix was contacted over an Amberlyst 15 catalyst at 75 °C and atmospheric pressure to evaluate the reactivity. From this experiment it was found that Amberlyst 15 catalyzed only the double-bond isomerization of *1*-octene at 75 °C. Between 100 and 125 °C, skeletal isomerization and dimerization were observed and the *1*-octene conversion was 95-100%. Dimerization took place in parallel with skeletal isomerization, and dimerization was not preceded by skeletal isomerization. Thereafter, the *1*-octene was contacted over solid phosphoric acid (SPA) as catalyst. In contrast to the Amberlyst 15 catalyst, de Klerk [2006] observed that no reaction took place using the SPA catalyst at 75 °C and double-bond isomerization occurred only at 100 °C. The conversion was 40% although it was a slow reaction. Double bond isomerization was the main reason for conversion with only a few skeletal isomers and dimers formed. From this it was concluded

that *1*-octene was unreactive over solid phosphoric acid in relation to the Amberlyst 15 catalyst.

In a US patent from Murray [1949], it was stated that isomerization of *1*-octene occurred to a greater extent over alumina impregnated with calcium chloride than over alumina alone. In addition to this the impregnated alumina induced skeletal isomerization whereas alumina alone did not.

In the same US patent from Murray [1949], *1*-octene was passed over granular calcium chloride at atmospheric pressure, a temperature of 400 °C, and a LHSV of 1.0 h^{-1}. This experiment showed that no isomerization took place under these conditions.

A Chinese study by Long et al. [2008a] was executed because 80% of their gasoline comes from the fluid catalytic cracker (FCC) process which contains an olefin content as high as 50-65 volume %. This high olefin content should rather be converted into aromatics or *iso*-paraffins to compensate for the loss of octane number in the gasoline and therefore, Long et al. [2008a] investigated the isomerization of *n*-octene over HZSM-5 catalysts. The outcome of their study was that isomerization and hydrogen transfer of *n*-octene occurred at 200 °C using these catalysts. The products were alkanes and cyclo-olefins instead of aromatics. Cracking also occurred and produced propene, butene and pentene as products [Long et al., 2008a].

The effect of acidity on *n*-octene over potassium modified nanoscale HZSM-5 catalysts was investigated in another study by Long et al. [2008b]. This study mainly focused on the relation of acidic sites with different acid strengths to aromatization activity, but results on olefin isomerization were also noted. Experimentally, the catalyst was impregnated with seven different concentrations of aqueous potassium nitrate, dried and calcined. The potassium (K) contents for the modified zeolites are given in Table 2.11. Along with the potassium contents in Table 2.11, the acid strength distribution is also shown [Long et al., 2008b].

Table 2.11
Acid strength distribution of the potassium modified nanoscale HZSM-5 catalysts [Long et al., 2008b]

Catalyst	K loading (%)	Acid amount (mmol/g)		
		$H_0 \leq -3.0$	$H_0 \leq +2.27$	$H_0 \leq +4.8$
CAT -1	0	0.20	0.30	1.10
CAT -2	1.2	0.10	0.15	0.90
CAT -3	1.9	0.08	0.10	0.80
CAT -4	3.0	0.04	0.08	0.70
CAT -5	3.9	0.006	0.03	0.50
CAT -6	7.8	0	0	0.25
CAT -7	9.3	0	0	0.15

* $H_0 \leq -3.0$, $H_0 \leq +2.27$, $H_0 \leq +4.8$ indicates acid strengths

Table 2.11 indicates that with an increase in the potassium loading, the amount of sites with acid strength decreased. When the potassium reached 7.8%, the amount of acidic sites with acid strengths $H_0 \leq -3.0$ and $-3.0 < H_0 \leq +2.27$ over CAT – 6 and CAT – 7 reduced to zero. This shows that CAT-6 and CAT – 7 with potassium loadings of 7.8% and 9.3% respectively were the only two catalysts that had acid sites with acid strength $+2.27 < H_0 \leq +4.8$.

The reaction of *n*-octene over the nanoscale HZSM-5 catalyst was performed in a fixed bed reactor at 350 °C, 1.5 MPa pressure and 2.0 h^{-1} space velocity. Hydrogen was also introduced as the carrier gas for *n*-octene. Liquid products were analyzed and the outcome of these with respect to acidic sites with acid strength of $H_0 \leq +2.27$ is shown in Figure 2.12 [Long et al., 2008b].
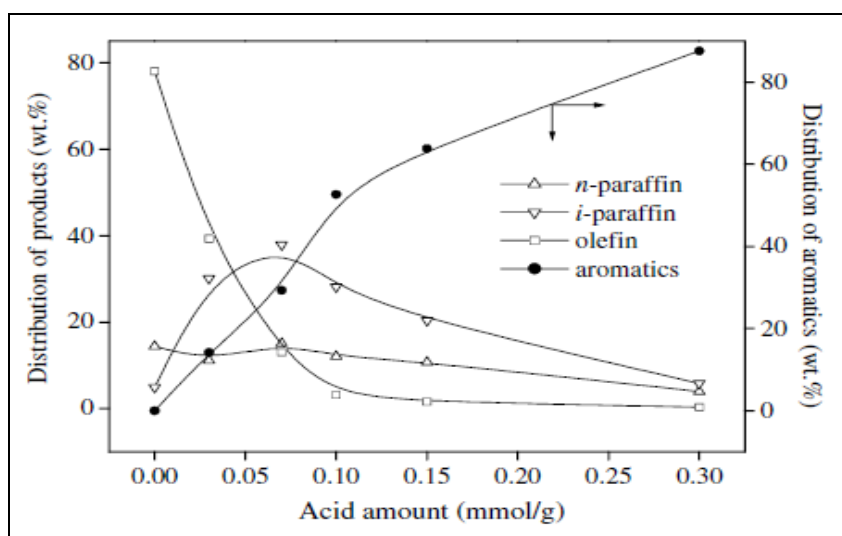
Figure 2.12: Relation between catalytic activity and strong acid sites with acid strength $H_0 \leq +2.27$ [Long et al., 2008b]

Figure 2.12 indicates that strong acidic sites with acid strengths of $H_0 \leq +2.27$ are necessary for the transformation of *n*-octene into aromatics, whilst the weaker acidic sites lead to an increase in the selectivity to olefins. It can also be seen that the *iso*-paraffin selectivity in the liquid products increases and then decreases. A detailed product distribution on the transformation of *n*-octene over these potassium modified catalysts was done and it was found that isomerization of *n*-octene over the HZSM-5 catalyst rather took place on the weak acid sites with acid strength $+2.27 < H_0 \leq +4.8$ [Long et al., 2008b].

2.10 Catalysts for olefin skeletal isomerization used in this study

Considering the preliminary study of the literature done above, it is apparent that information regarding isomerization of C_4 is widespread and easily obtainable whilst information regarding isomerization of C_6 and higher olefins are extremely limited.

Three alumina based catalysts were chosen for this study namely; Eta alumina (pure), ZSM-5 (zeolite) and Siralox (amorphous silica alumina).

Between the three catalysts, Eta alumina is the most inactive catalyst and is very Lewis acidic [Morterra et al., 1979]. ZSM-5 is a zeolite wich has a 10-membered ring structure [Baerlocher et al., 2001] and is very Brønsted acidic. Siralox 40 is a silica alumina catalyst that is an amorphous solid with a high surface area and has the formula $(SiO_2)_m(Al_2O_3)_n$. It has a very strong acidity and is used as a catalyst support [Bartholomew et al., 2006].

The reason for choosing these three catalysts was based on the curiosity of the extent to which isomerization will occur. Therefore, the study used low carbon chain (C_4) to higher carbon chain (C_6 and C_8) olefins as feedstocks and reacted them with very weak non-acidic to a very strong acidic catalyst to investigate the degree of isomerization.