Chapter 8

Impact of catalyst selection with respect to reaction observed

In the first section of this Chapter (Section 8.1), the data obtained from Chapter 5, 6 and 7 were summarized. A comparison is given between isomerization, cracking, formation of heavier products and double bond shift reactions that took place when the three feeds were contacted over the three catalysts. A Speculative interpretation on what was observed follows in section 8.2.

8.1 Isomerization, cracking, formation of heavier products and double bond shift reactions

8.1.1 Isomerization

It should be kept in mind that isomerization of C_6 compounds were based on n-hexene (as with the results in Chapter 6) and not on 1-hexene.

Figure 8.1 shows that isomerization over the Eta alumina catalyst at the three temperatures occurred to the highest extent using the longer chain feedstocks; *n-h*exene and *1*-octene. Little to no branched isomers formed when *1*-butene was contacted over the Eta alumina catalyst.

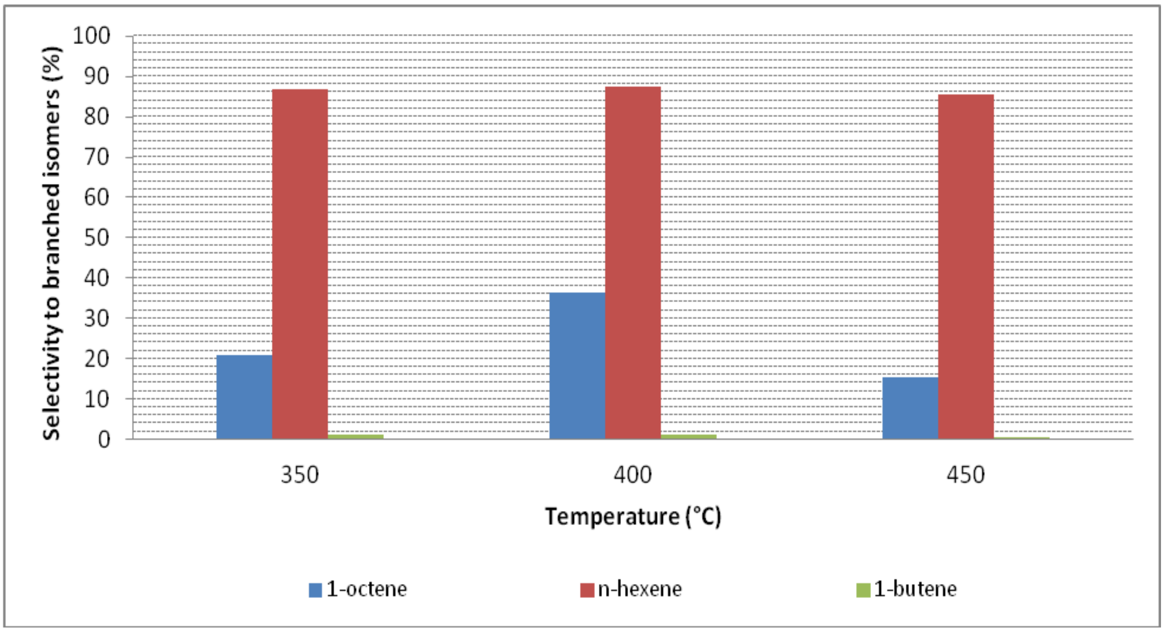

Figure 8.1: Isomerization (%) obtained between the three feeds using the Eta alumina catalyst at temperatures of 350 °C, 400 °C and 450 °C

Figure 8.2 shows that isomerization of less than 14% occurred at all three temperatures using the ZSM-5 catalyst. For the ZSM-5 catalyst, the highest amount of isomerization (9–14%) occurred at 350 °C.

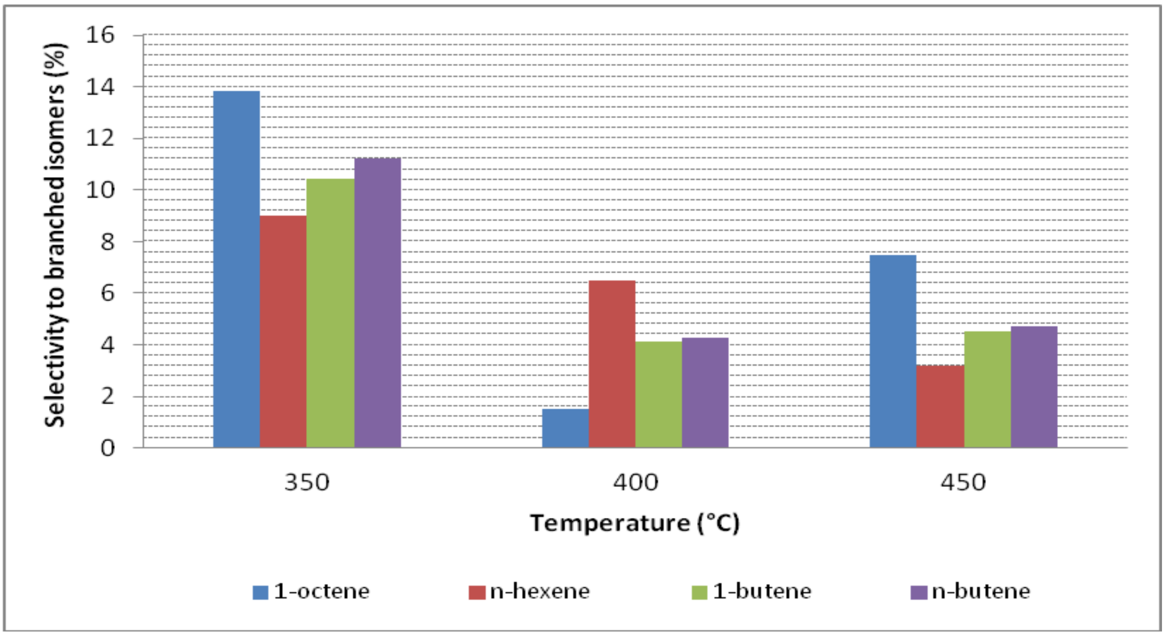

Figure 8.2: Isomerization (%) obtained between the three feeds using the ZSM-5 catalyst at temperatures of 350 °C, 400 °C and 450 °C

Figure 8.3 showed that the longer carbon chains were more subject to skeletal isomerization than the shorter carbon chains. The least amount of isomerization (<10%) occurred with *1*-butene as feedstock. When contacting *n*-hexene over the Siralox 40 catalyst, an increase in the selectivity to branched isomers was observed with an increase in temperature. The *n*-hexene skeletally isomerized (between 30% and 40%) more than the *1*-octene over the Siralox 40 catalyst at temperatures of 350 °C, 400 °C and 450 °C.

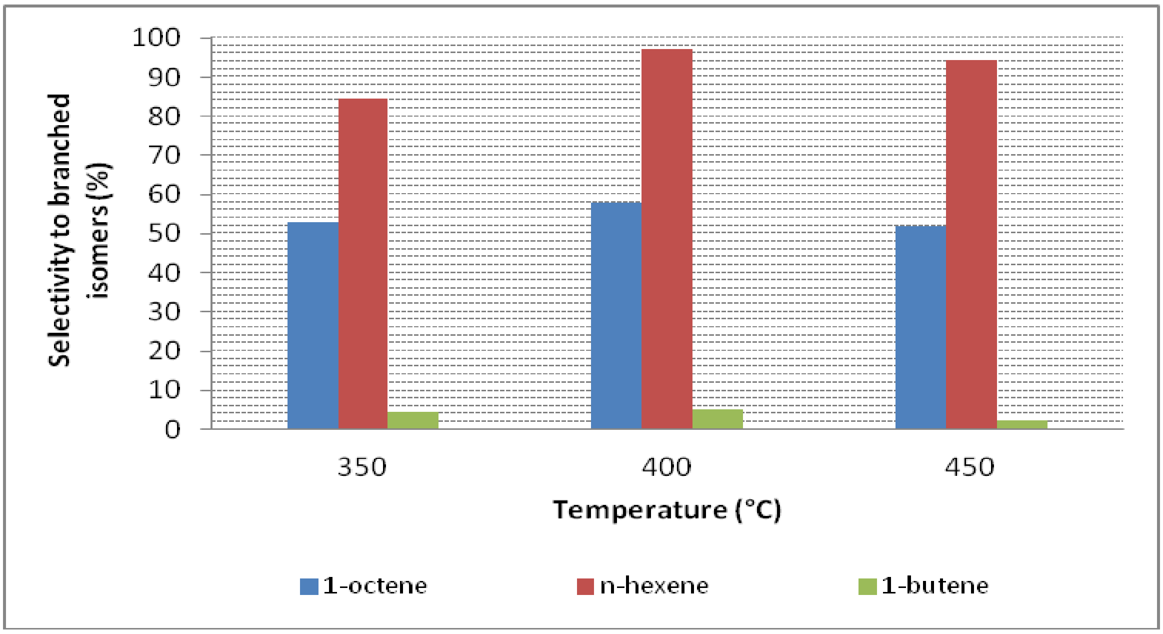

Figure 8.3: Isomerization (%) obtained between the three feeds using the Siralox 40 catalyst at temperatures of 350 °C, 400 °C and 450 °C

8.1.2 Cracking

During the heat treatment of the feeds over the catalysts, cracking was also observed in some reactions. Buchanan et al. [1996] conducted a study on the carbenium ion mechanisms that C_5-C_8 olefins over ZSM-5 catalyst undergo. From this study it was found that hexene has six modes of *β*-scission involving mostly primary (1°) and secondary (2°) cations. In the case of octene, a large number of isomers exist in the isomerization reaction with thirteen predominant *β*-scission structures and cracking types available. Since more energetically favourable (1° < 2° < 3°) modes become available for *β*-scission of the carbenium ions, they stated that cracking rates increase with carbon number for olefins. The results reported in this investigation confirm the conclusions of their study and will be discussed in the next paragraphs.

Figure 8.4 shows that cracking only occurred using *1*-octene and also only at 450 °C. The other two feeds over the Eta alumina catalyst did not indicate a significant degree of the formation of cracking products.

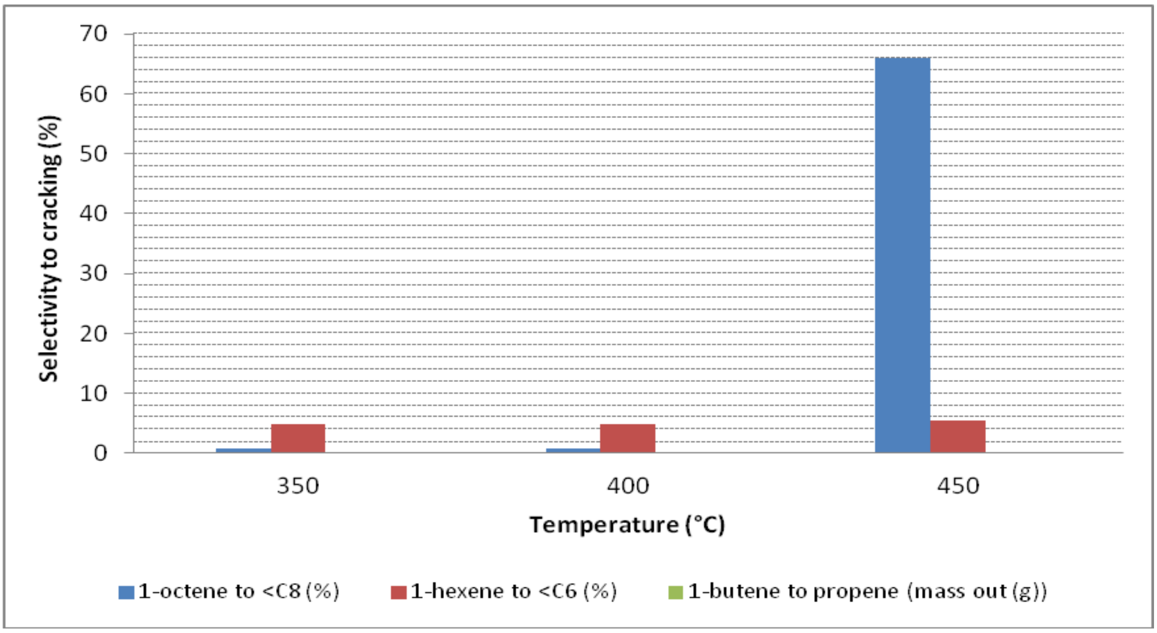

Figure 8.4: Cracking (%) between the feeds using the Eta alumina catalyst at temperatures of 350 °C, 400 °C and 450 °C

Contrary to the Eta alumina catalyst, when contacting the *1*-hexene and *1*-octene over the ZSM-5 catalyst more cracking (between 56% and 94%) was observed at all three temperatures. Between 0% and 10% of cracking was observed when contacting *1*-butene over the ZSM-5 catalyst.

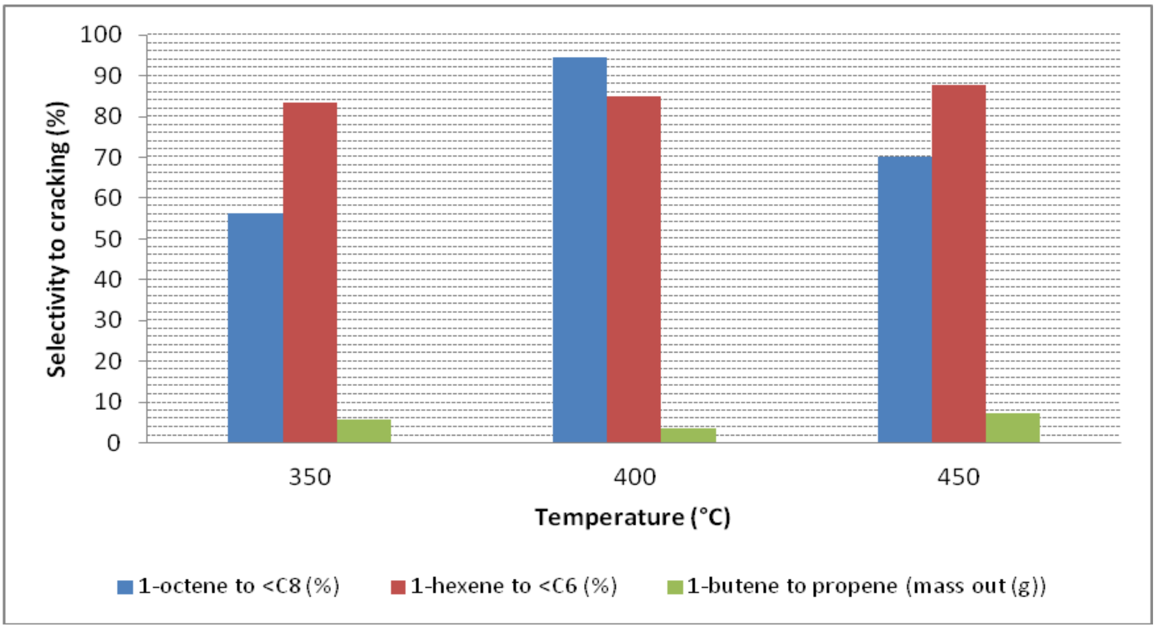

Figure 8.5: Cracking (%) between the feeds using the ZSM-5 catalyst at temperatures of 350 °C, 400 °C and 450 °C

Cracking below 35% was observed when contacting the feedstocks over the Siralox 40 catalyst. The formation of compounds with carbon lengths of less than C_8 occurred most at 450 °C when *1*-octene was contacted over the Siralox 40 catalyst. In the case of *1*-hexene and *1*-butene, cracking was less than 5% at all three temperatures.

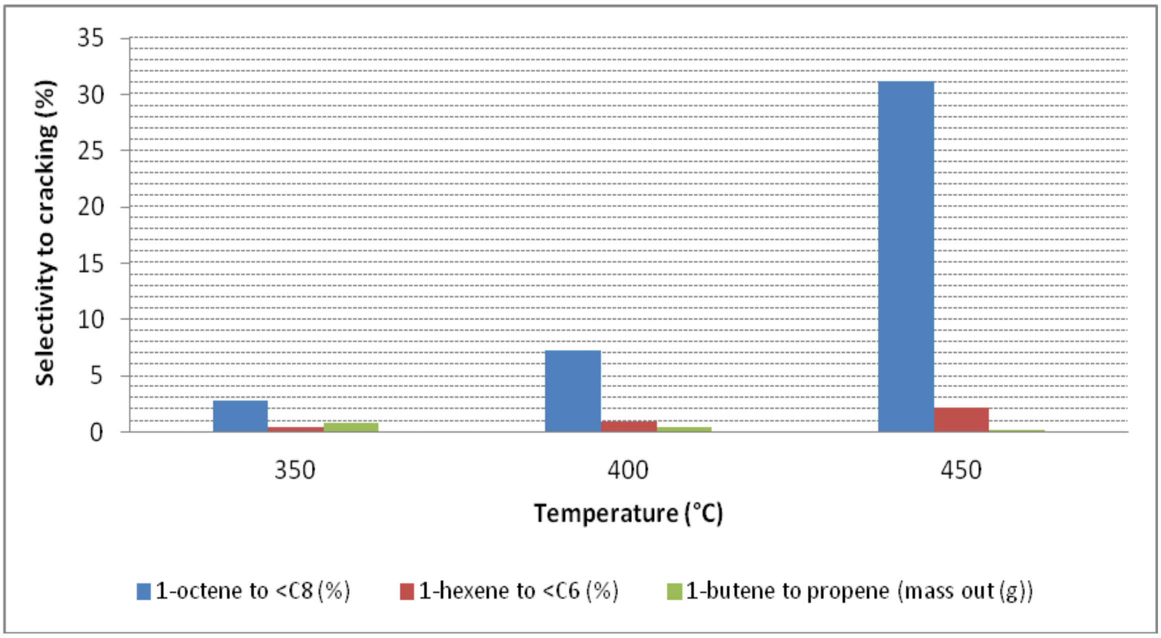

Figure 8.6: Cracking (%) between the feeds using the Siralox 40 catalyst at temperatures of 350 °C, 400 °C and 450 °C

Therefore, the findings of Buchanan et al. [1996] relate well to what was observed in this study. No cracking was observed with the shorter carbon chain (butene) since no energetically favourable modes for *β*-scission are available. More cracking was observed with the longer carbon chains due to the availability of the energetically favourable secondary and tertiary carbenium ions which makes *β*-scission possible.

8.1.3 Formation of heavier products

The percentage heavier products formed were very low. Between 0% and 3.5% products heavier than the feedstocks used, were observed when *1*-hexene and *1*-octene were contacted over Eta alumina. No heavier products formed when *1*-butene was contacted over the Eta alumina catalyst (Figure 8.7).

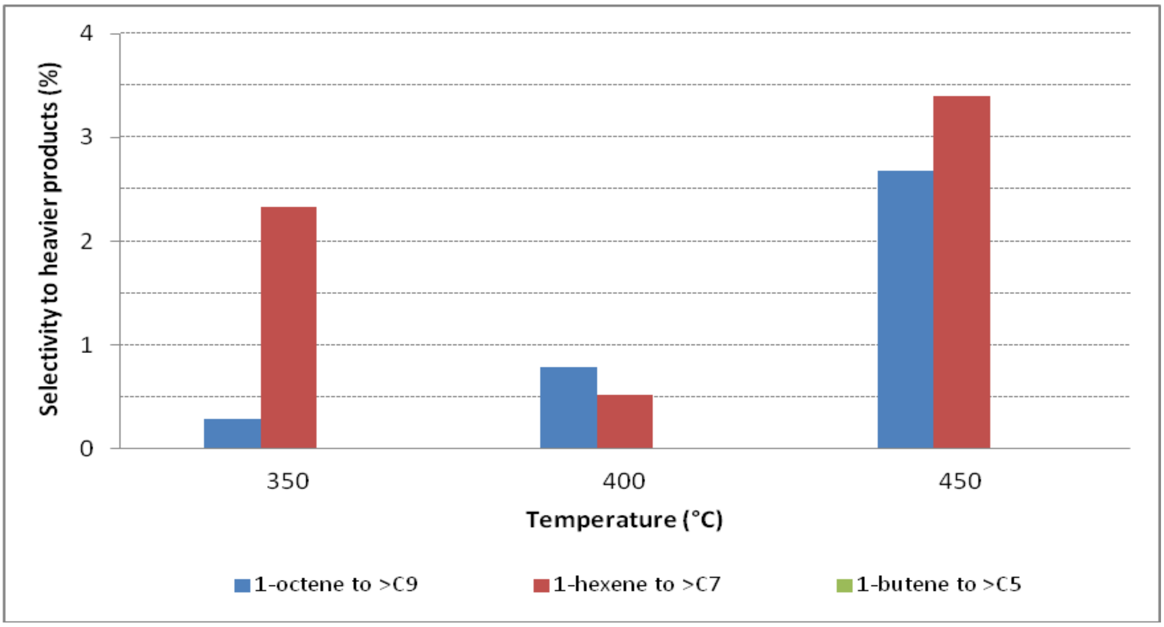

Figure 8.7: Heavier products (%) between the feeds using the Eta alumina catalyst at temperatures of 350 °C, 400 °C and 450 °C

Using ZSM-5 in contact with *1*-butene lead to the formation of products heavier than the reagent used. A decrease in the amount of heavier products formed with an increase in temperature was observed contacting *1*-butene over ZSM-5. Products with carbon lengths longer than C_5 was formed at all three temperatures with the most (52%) at the lowest temperature of 350 °C. The other two feeds had less heavier products formed. For all three the feeds, the formation of products heavier than the feed itself was less than 55%.

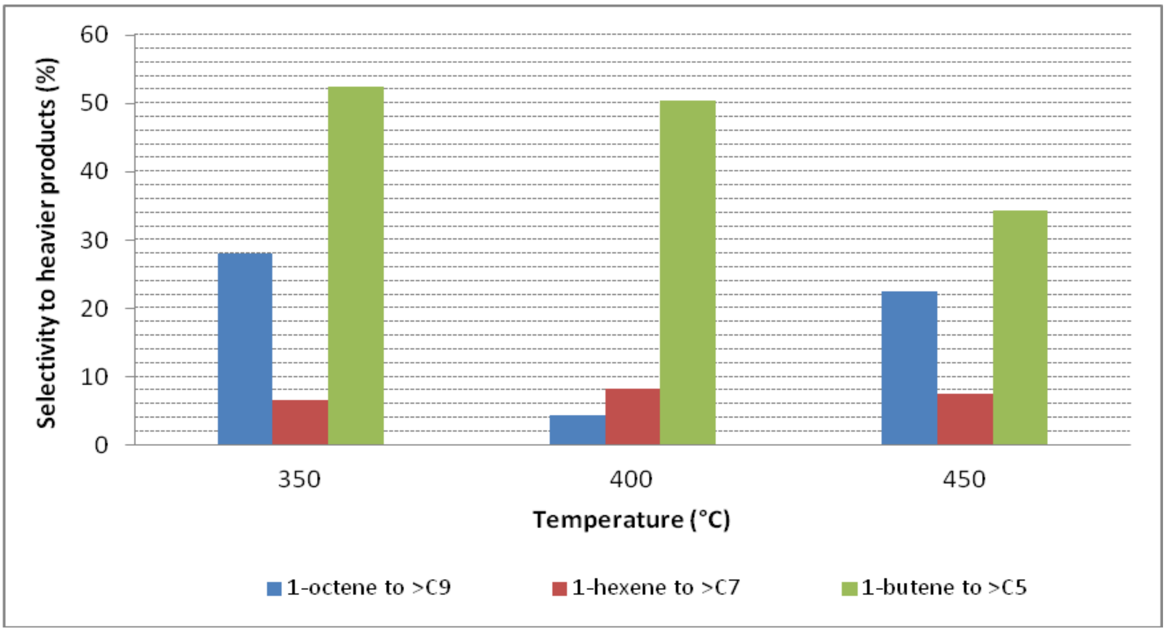

Figure 8.8: Heavier products (%) between the feeds using the ZSM-5 catalyst at temperatures of 350 °C, 400 °C and 450 °C

Figure 8.9 shows that contact of all three the feeds over the Siralox 40 catalyst formed small amounts (less than 4.6%) of heavier products than the specific feed compound.

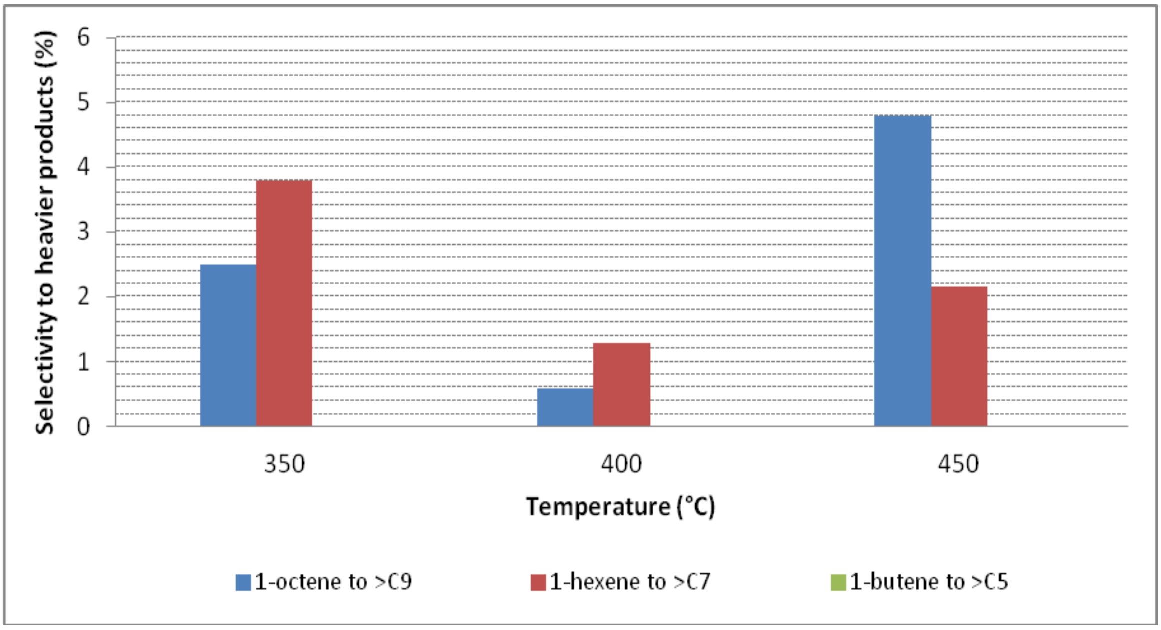

Figure 8.9: Heavier products (%) between the feeds using the Siralox 40 catalyst at temperatures of 350 °C, 400 °C and 450 °C

The selectivity to heavier products using the Eta alumina and Siralox 40 catalysts showed the same trend, that is that *1*-butene over these two catalysts did not form significant amounts of the heavier products. Another observation was that the least amount of products heavier than the respective feeds formed at 400 °C when contacting *1*-hexene and *1*-octene over both these catalysts.

8.1.4 Double bond shift reactions

Reactions resulting in double bond shifts were also observed throughout the study and discussed in Chapters 5, 6 and 7. A comparison between the results obtained using the three different feedstocks and the three catalysts are given below.

Figure 8.10 shows that a high amount of double bond shift reactions (between 60% and 78%) occurred with the Eta alumina catalyst for all three the feedstocks, except when *1*-octene was contacted over the Eta alumina catalyst at 450 °C (±10%).

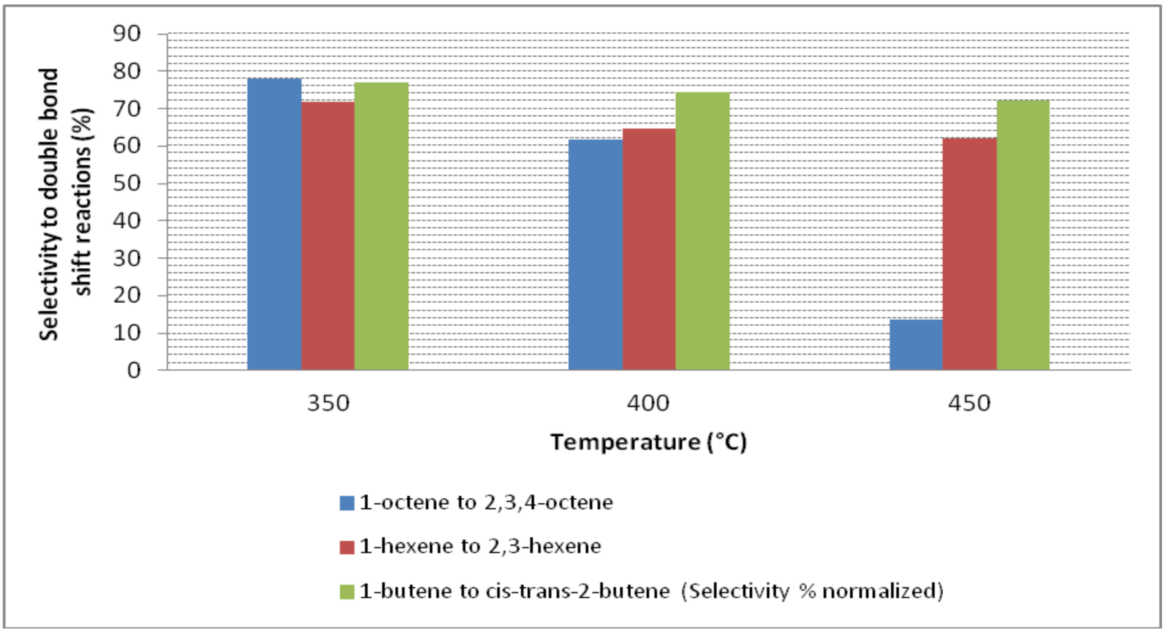

Figure 8.10: Comparison of double bond shift (%) between the feeds using the Eta alumina catalyst at temperatures of 350 °C, 400 °C and 450 °C

Figure 8.11 indicates that the double bond shift reaction of *1*-butene to *cis/trans-2*-butene was the highest at 350 °C (7%) and then it decreased. In the case of *1*-octene, the double bond shift from *1*-octene to *2,3,4*-octene only occurred at 350 °C and not at 400 °C and 450 °C. Contacting ZSM-5 over *1*-hexene formed *2,3*-hexene consistenly at all temperatures. It should also be noted that the reactions of double bond shifts when contacting *1*-butene, *1*-hexene and *1*-octene over the ZSM-5 catalyst were less than 10%.

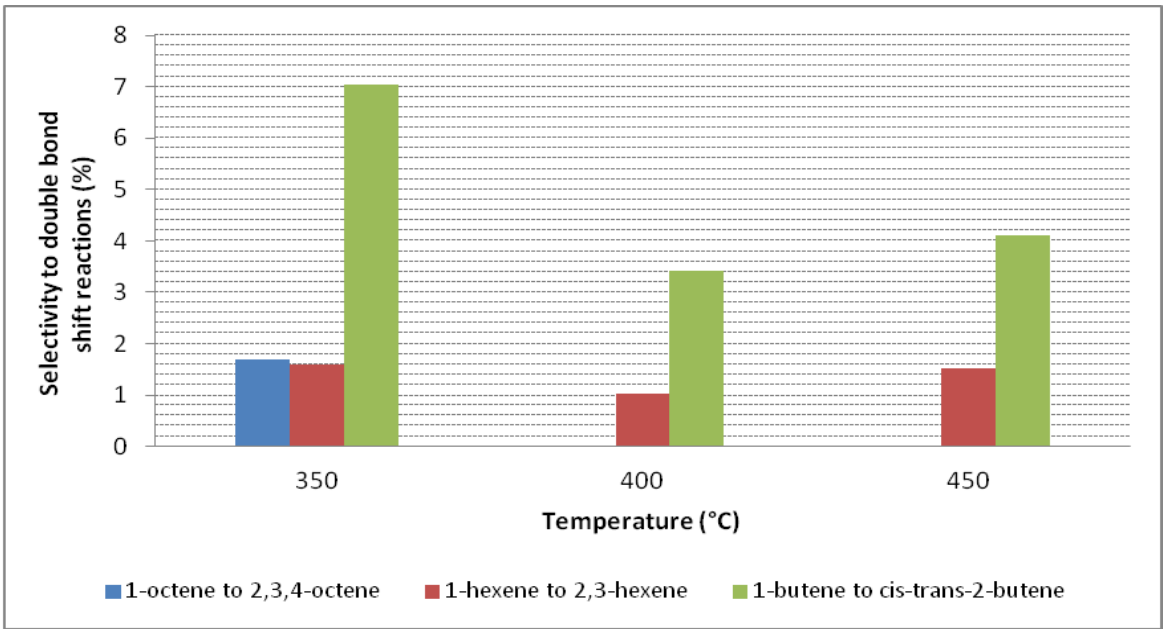

Figure 8.11: Comparison of double bond shift (%) between the feeds using the ZSM-5 catalyst at temperatures of 350 °C, 400 °C and 450 °C

As with Eta alumina, the double bond shift reactions taking place within the Siralox 40 catalyst when contacting it with *1*-butene was high (between 80% and 100%). The double bond shift reactions of *1*-octene over the Siralox 40 catalyst decreased as the temperature increased and in the case of *1*-hexene, the double bond shift reactions were highest at 350 °C and lowest at 400 °C.

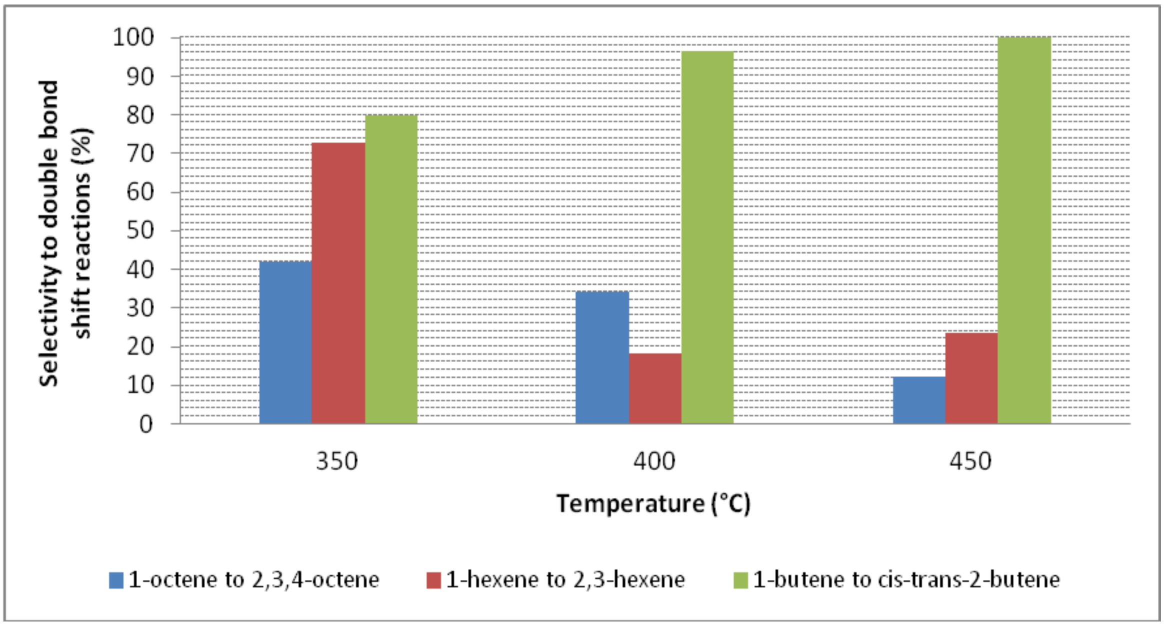

Figure 8.12: Comparison of double bond shift (%) between the feeds using the Siralox 40 catalyst at temperatures of 350 °C, 400 °C and 450 °C

8.2 Discussion

Since isomerization was the main aim of this study and considering Figures 8.1, 8.2 and 8.3 the question arises: "Why does skeletal isomerization occur between a certain feed and catalyst and why does skeletal isomerization not occur with the same catalysts if different feeds are used?"

Although the answer to the question may be complex, the contribution of diffusion of the reagents and products, and acidity of the catalysts on reactions will be speculated about.

8.2.1 Diffusion

When a reactant (liquid or gas) enters the pore system of a catalyst, a few steps are required to convert the reactants into the required products [Schuring D., 2002]. Adsorption of this reactant takes place on the surface of the catalyst or inside the pores of the catalysts. This reactant then needs to move to the reactive sites inside the catalyst pores for conversion to take place, and this movement of reactant inside these pores is known as diffusion. When this reactant reaches the reactive sites, reactions can take place, converting the reactants into various products. Diffusion and desorption of the formed products have to take place for these reactive sites to be freed in order for the next reaction to take place. The products are transported out of the pores of the catalyst. This catalytic cycle is shown in Figure 8.13.

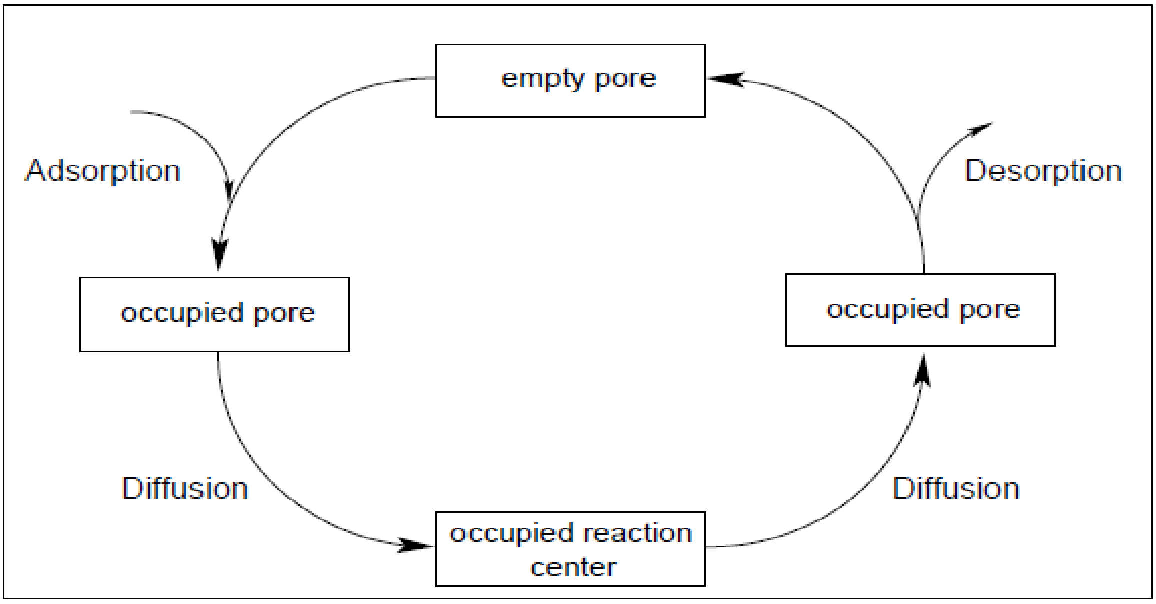

Figure 8.13: The catalytic cycle in zeolite catalysis: The zeolite pores are occupied by adsorption from the gas phase, after which the adsorbed species diffuse to the reactive centres [Schuring D., 2002]

Diffusion has been studied extensively in the past and a vast amount of literature is available [Bhatia, 1990 and van Donk, 2002].

For a reactant to enter the pore mouth of a catalyst, the reactant should obviously have a smaller diameter than that of the catalyst. The sizes of the reactants and the size of the isomers were calculated using the Density Functional Theory with Material Studio as the software program [Accelrys]. The Connolly Surface method [Connolly, 1983] was used to determine the estimated volume of the molecules since the exact volume of a molecule cannot be definitely determined. The structures reported here were calculated and optimized with the Dmol^3 code using the GGA-BLYP functional [Delly, 1990; 1996 and 2000]. The estimated molecular volumes, lengths and diameters of the feedstocks and isomers were measured between the edges of the constructed Connolly surfaces as tabulated in Table 8.1 and 8.2. The molecules of the feedstocks are displayed in Figures 8.14, 8.15 and 8.16 and the isomers are displayed in Figures 8.16, 8.17 and 8.18. It should be kept in mind that these values are estimates that give an indication of the size of the molecule.

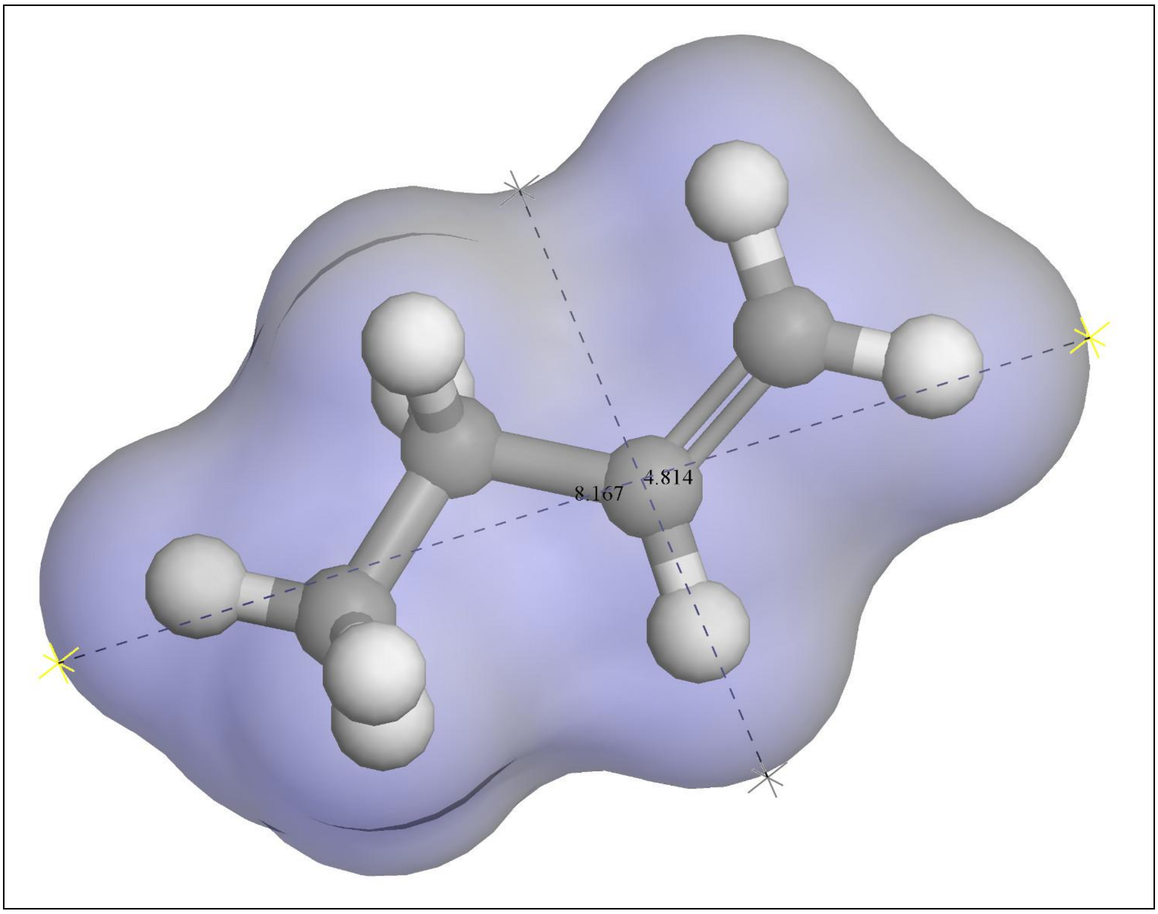

Figure 8.14: Structure of *1*-butene (indicated lengths are in Å)

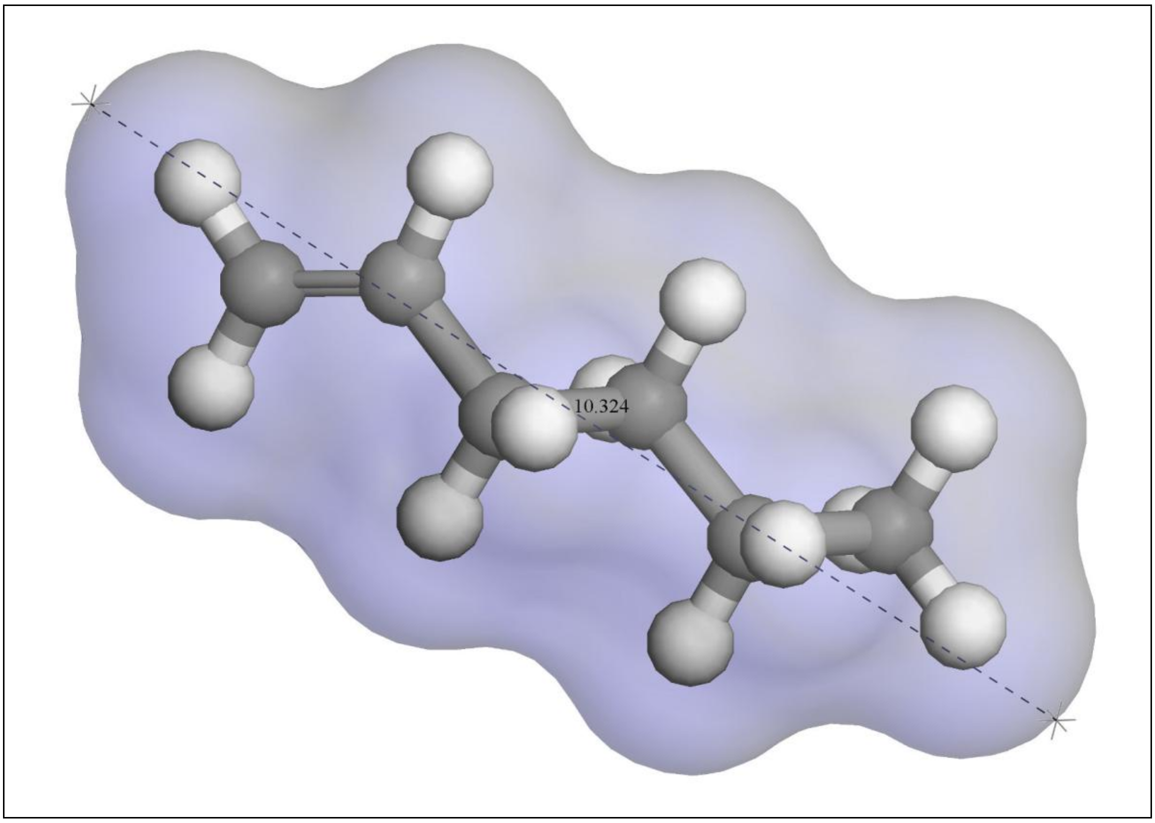

Figure 8.15: Structure of *1*-hexene (indicated lengths are in Å)

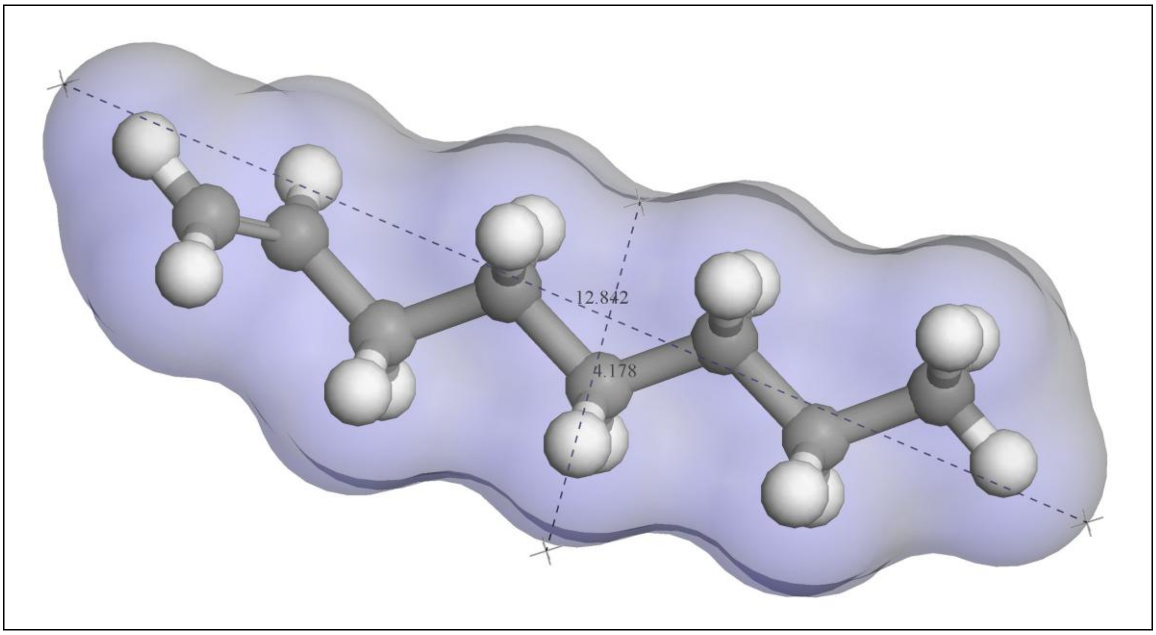

Figure 8.16: Structure of *1*-octene (indicated lengths are in Å)

Table 8.1
The estimated molecular volumes, lengths and diameters of feedstock (carbon numbers) used in this study

	Molecule	Connolly Vol. ($Å^3$)	Length A (nm)	Length B (nm)	Length C (nm)
C_4	*1*-butene	79.42	0.82	0.48	0.43
C_6	*1*-hexene	112.5	1.03	0.48	0.41
C_8	*1*-octene	148.5	1.28	0.42	0.42

Length A is the longest length in the molecule

Length B and C gives an estimate of the remaining ellipsoidal diameters of the molecule

The structures of the isomers of C_4, C_6 and C_8 were also calculated and results for the most bulky isomers are displayed in Figures 8.17 to Figure 8.21 and tabulated in Table 8.2.

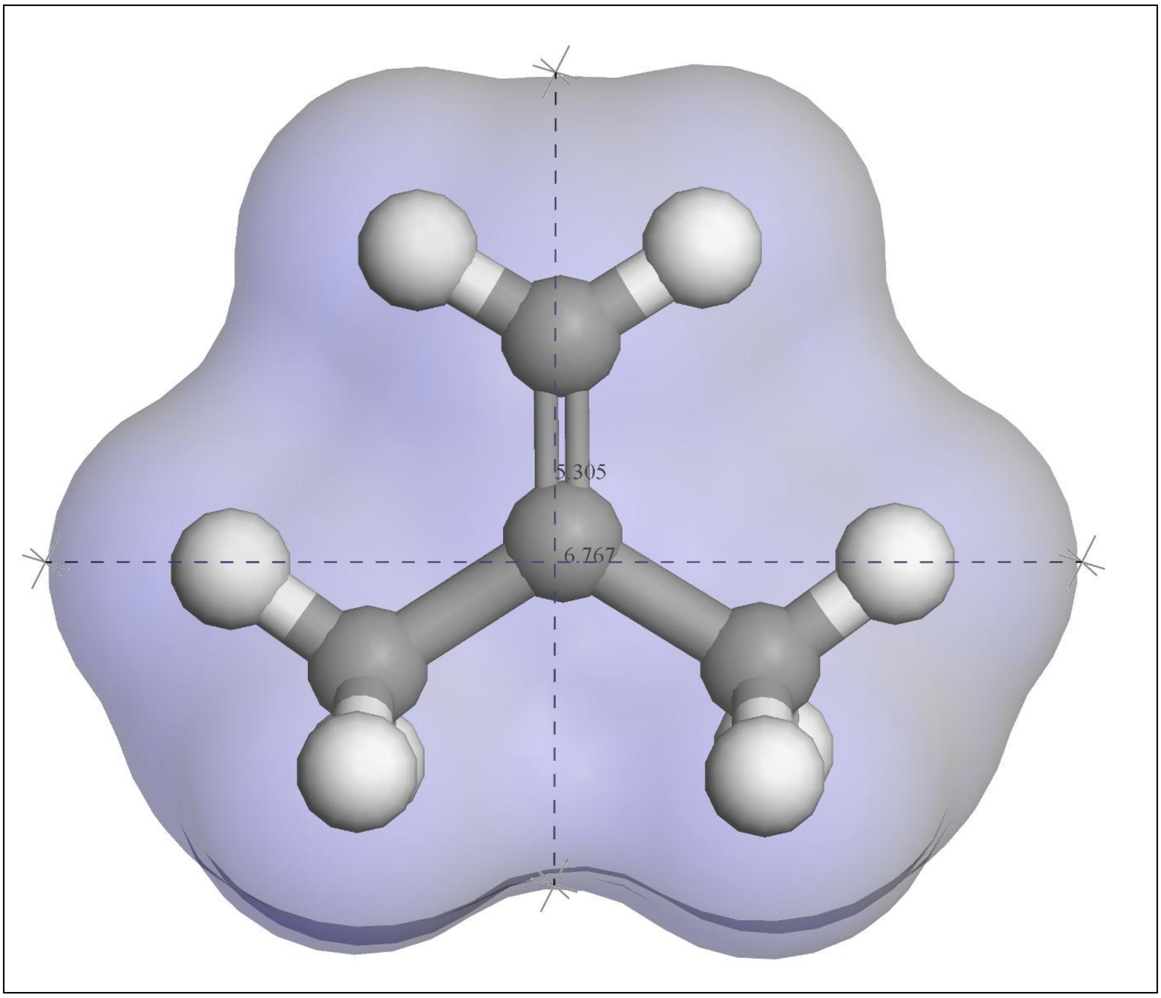

Figure 8.17: Structure of *iso*-butene (indicated lengths are in Å)

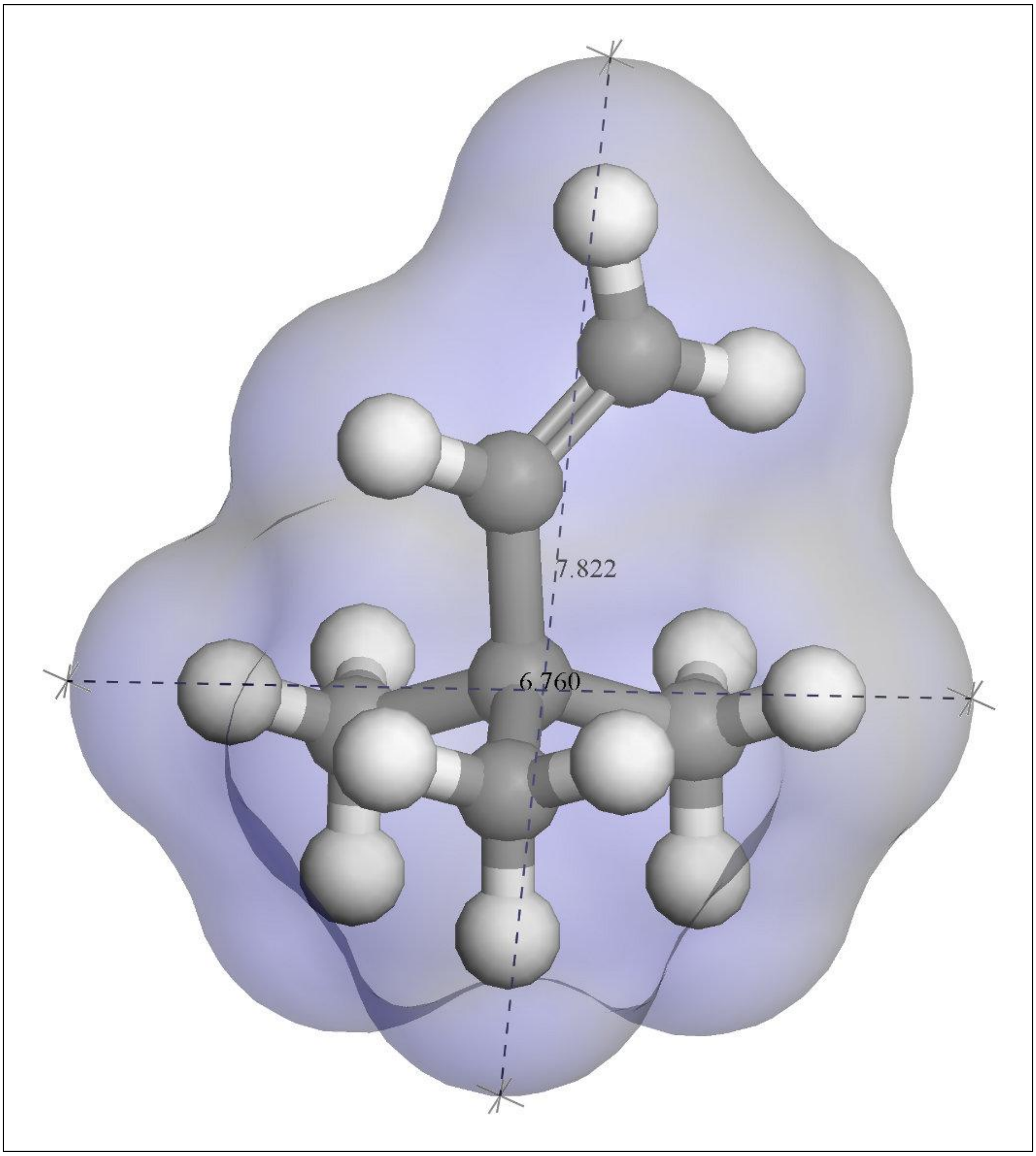

Figure 8.18: Structure of *3,3*-dimethyl-*1*-butene (indicated lengths are in Å)

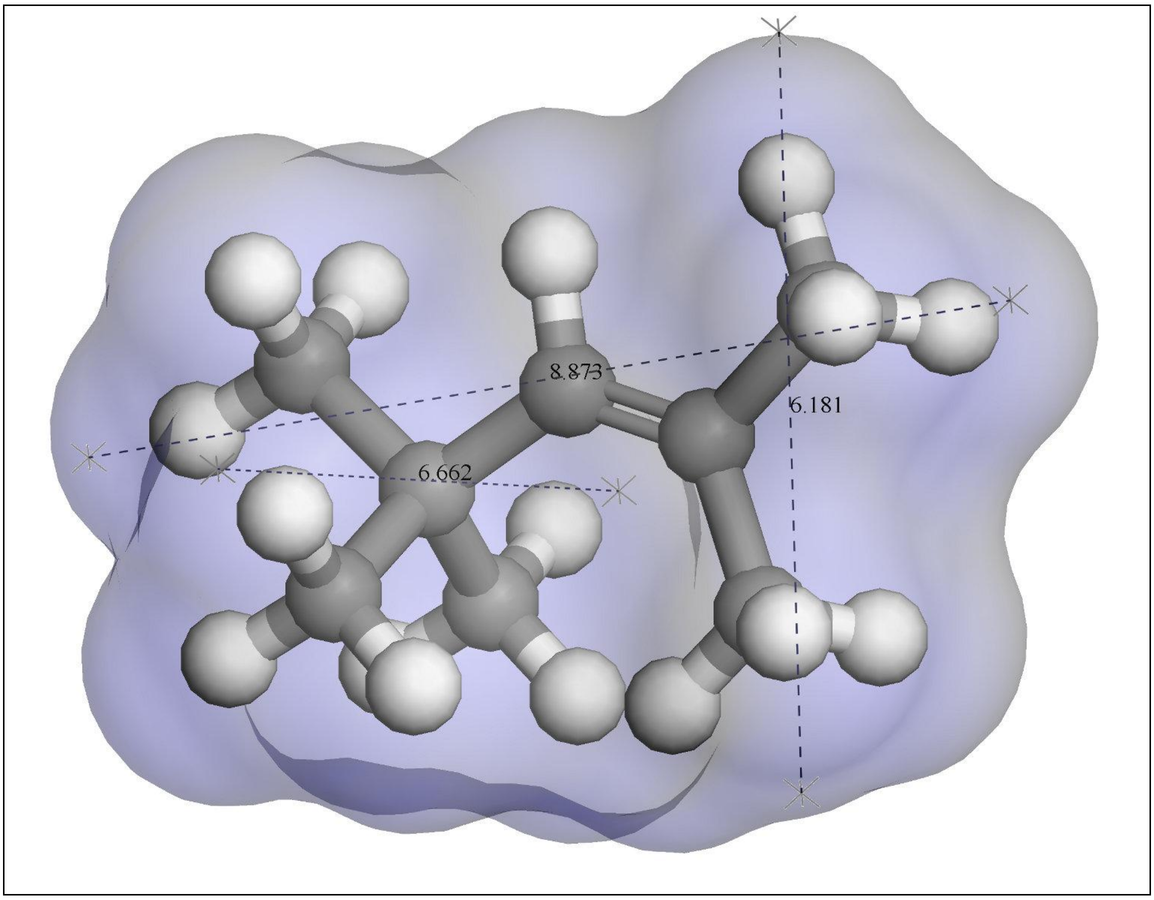

Figure 8.19: Structure of *2,4,4*-trimethyl-*2*-pentene (indicated lengths are in Å)

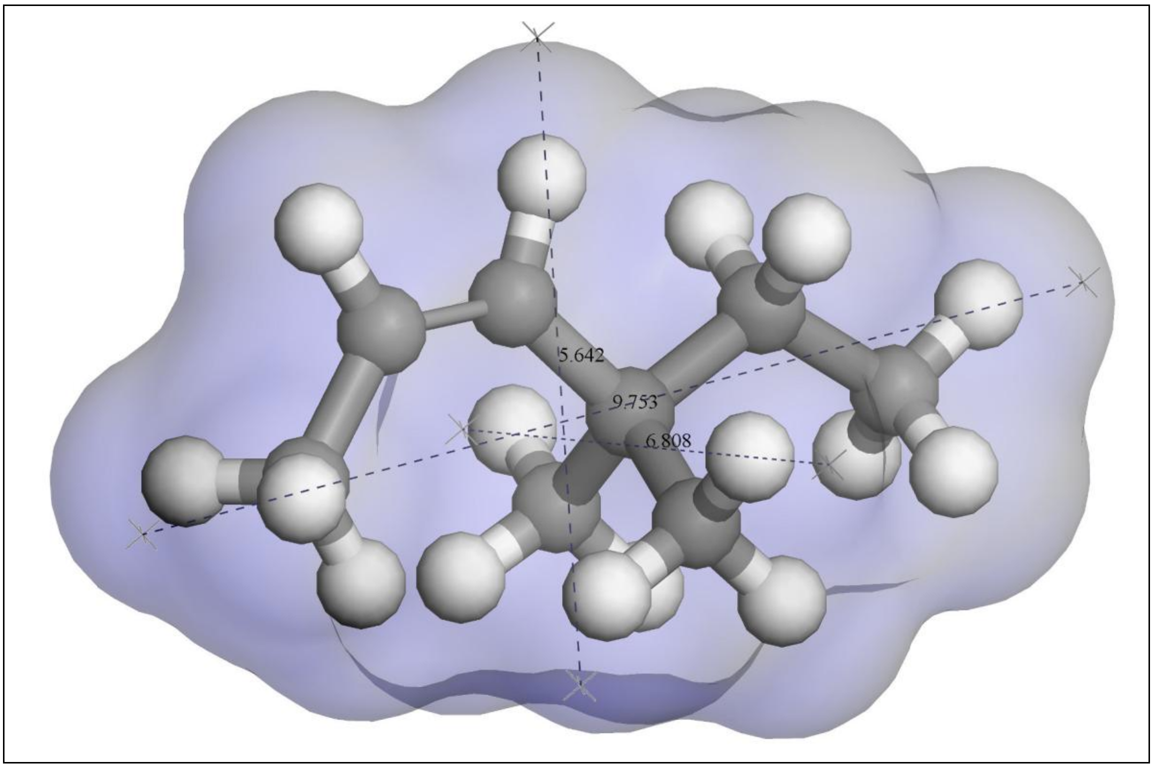

Figure 8.20: Structure of *4,4*-dimethyl-*2*-hexene (indicated lengths are in Å)

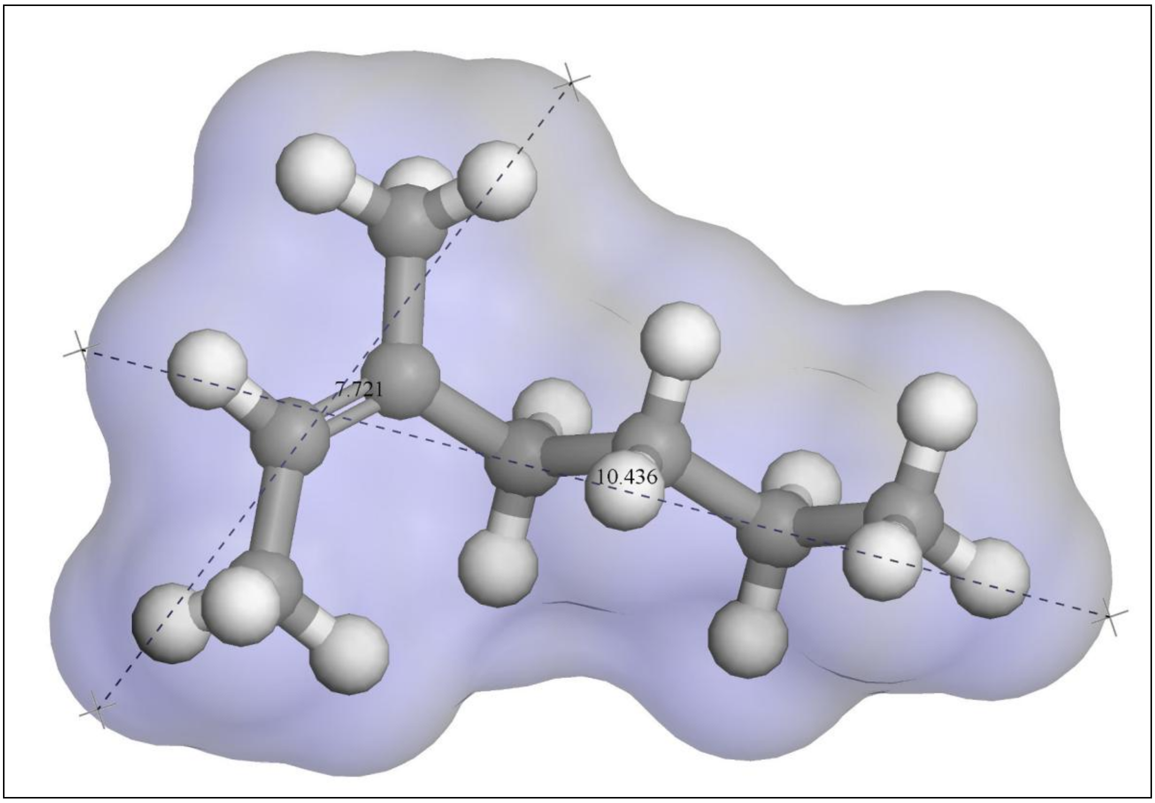

Figure 8.21: Structure of *3*-methyl-*2*-heptene *(cis)* (indicated lengths are in Å)

Table 8.2
The estimated molecular volumes, lengths and diameters of the largest isomers formed in this study

	Molecule	**Connolly Vol. (Å^3)**	**Length A (nm)**	**Length B (nm)**	**Length C (nm)**
C_4	*Iso*-butene	75.84	0.68	0.53	0.42
C_6	*3,3*-dimethyl-*1*-butene	112.8	0.78	0.68	0.68
C_8	*3*-methyl-*2*-heptene (*cis*)	147.8	1.04	0.77	0.42
	4,4-dimethyl-*2*-hexene (*cis*)	147.9	0.98	0.68	0.56
	2,4,4-trimethyl-*2*-pentene	148.1	0.89	0.67	0.62

Length A is the longest length in the molecule

Length B and C gives an estimate of the remaining ellipsoidal diameters of the molecule

The pore size distributions (diameters) of the fresh catalysts were measured. Baerlocher et al. [2001] stated that ZSM-5 has 10-ring channels with pore diameters of approximately 5.4 Å to 6.6 Å. A pore diameter distribution of, in this case, 0.54 nm-0.56 nm was measured for the ZSM-5 catalyst as already reported in Chapter 5. It should be noted that the catalysts used in this study are commercial catalysts which contains fillers, binders etc., therefore the pore size that is measured will differ from literature values. The results are displayed in Table 8.3:

Table 8.3
Diameter of the pores of the fresh catalysts used in this study

Fresh Catalyst	PSD* (nm)
Eta alumina	8.5
ZSM-5	4.6
Siralox 40	7.2

PSD – Pore size distribution

The conclusion made from this data is that all the olefinic feeds; C_4, C_6 and C_8 (Table 8.1) and all the isomeric molecules of C_4, C_6 and C_8 (Table 8.2) used in this study could diffuse through the pores of the three catalysts (Table 8.3). This also indicates that diffusion is unlikely to have the main effect on the selectivities observed for the studied feedstocks and catalysts, assuming that the molecules diffuse with ease to and from the catalytic surface.

8.2.2 Acidity

Since Eta alumina was shown to be the less active catalyst and ZSM-5 the most active catalyst of the three studied, the Brønsted acidity was taken into account.

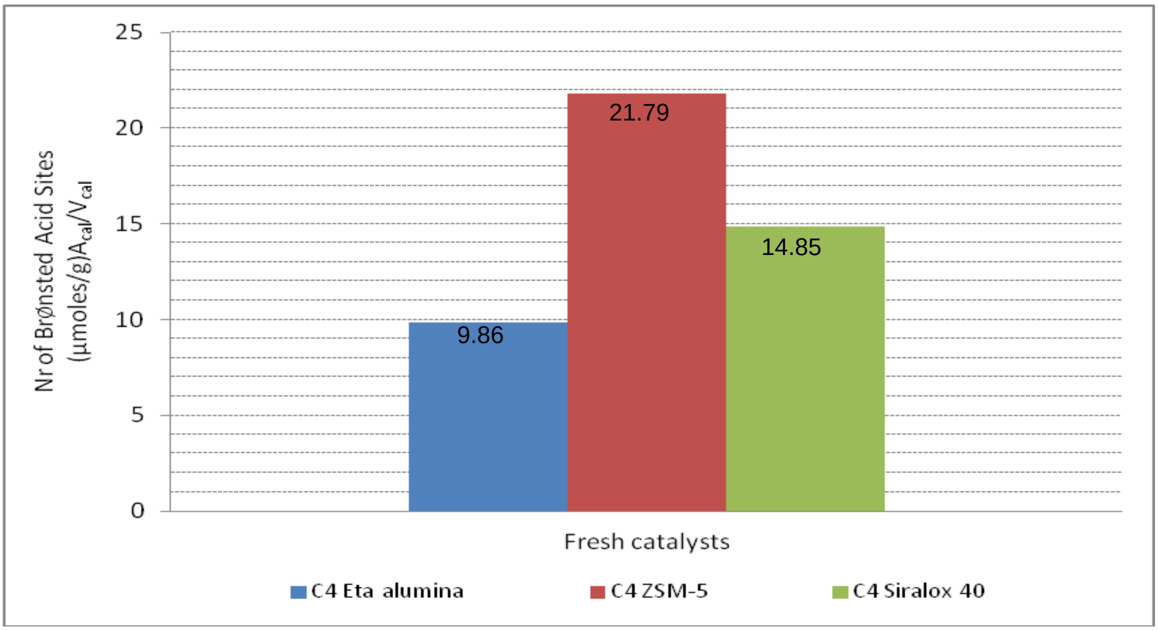

Figure 8.22: Number of Brønsted Acid Sites of fresh Eta alumina, ZSM-5 and Siralox 40 catalysts

Results (Figure 8.22) showed that ZSM-5 has the highest Brønsted acidity, as well as the highest activity. Also evident from Figure 8.22 is that Siralox 40 has a relatively high number of Brønsted acidic sites although fewer than ZSM-5. Eta alumina shows the lowest number of Brønsted acidic sites and it also proved to be the most inactive catalyst for the feedstocks and reactions studied.

Considering the fact that no skeletal isomerization occurred when using the ZSM-5 catalyst (Figure 8.2), it can be speculated that the larger number of Brønsted acidic sites makes ZSM-5 more prone to react longer with the feed. More side reactions may occur within the catalyst and therefore no isomerization is taking place. The side reactions that occur with the ZSM-5 catalyst were cracking (Figure 8.5), the formation of heavier products (Figure 8.8) and double bond shift reactions (Figure 8.11).

Eta alumina and Siralox 40 were more likely to skeletally isomerize C_6 and C_8 olefins to their branched isomers as shown in Figure 8.1 and 8.3. Siralox 40 and Eta alumina also have other reactions taking place simultaneously with skeletal isomerization such as double bond shifts (Figure 8.10 and 8.12), cracking (Figure 8.4 and 8.6) and the formation of heavier products (Figure 8.7 and 8.9).

Chapter 9

Conclusions and Future work

9.1 Conclusion

The main aim of this study was to investigate the degree of skeletal isomerization when contacting short and long carbon chains over three commercial alumina based catalysts (Eta alumina, ZSM-5 and Siralox 40). To reach this goal, butene, hexene and octene were chosen as feedstocks. As stated in Chapter 2, with the restriction of butane's high vapour pressure specification, some of the butane can be marketed as liquefied petroleum gas whereas the bulk of the C_4 material must be refined. Since hexene and octene FT products are high in olefinic nature, and both of these products have poor octane values, it is more valuable to refine those [Dancuart et al., 2004]. From this observation the basis of this study was determined and it was well thought to investigate skeletal isomerization of 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.

The research objectives were achieved as follows:

Objective 1: *Setting up of a suitable reactor system and determination of the loading zone and the length of the catalyst bed within the reactor*

For this study to commence a few aspects needed to be considered and finalized for successful data to be generated. Firstly, a reactor was set up and temperature profiles were measured inside the reactor using the different catalysts to determine the respective loading zones and catalyst beds for each catalyst. It was found that the catalyst beds for each catalysts differed slightly because of the different densities of each catalyst. The catalyst bed length for Eta alumina was 28 mm, for ZSM-5 it was 32 mm and for Siralox 40 the catalyst bed length was 44 mm. All three catalysts were loaded using the same reactor with a total length of 265 mm. The experimental runs were performed at atmospheric pressure and a constant weight hourly space velocity of 5 h^{-1}, with temperature as the only variable (350 °C; 400 °C and 450 °C). These conditions were chosen since it covered the temperature range for isomerization to occur using the three feedstocks as found in the literature study that was done in Chapter 2.

Objective2: *Catalyst characterization using techniques such as thermogravimetric analysis, metal analysis, surface area analysis, pore volume analysis and surface acidity analysis*

The chosen catalysts were characterized using various techniques including thermogravimetric analysis, metal analysis, surface area analysis, pore volume analysis and surface acidity analysis. Thermogravimetric analyses were used to determine the amount of carbon which was deposited on the catalyst after each run.

Metal analyses were done to determine the purity of the catalysts. The characterization confirmed that Siralox 40 contained a relatively high concentration of K, Mo and Na. ZSM-5 contained lesser amounts of K, with no Mo and high Na and Ni. Eta alumina contained small amounts of these elements. From the determination of the Si/Al ratio it was observed that ZSM-5 had the highest Si/Al ratio of the three catalysts.

Surface area and pore volume analyses were also performed on the catalysts to investigate the effect on the various catalysts pore sizes and surface areas when in contact with the different feeds. It was observed that Eta alumina had the smallest pore volume (0.43 cm^3/g) and surface area (197.01 m^2/g) whilst Siralox 40 had the largest pore volume (0.70 cm^3/g) and surface area (415.60 m^2/g). A pore size distribution was also done on the diameter of each fresh catalyst used in this study. It was observed that ZSM-5 was the catalyst with the smallest pore diameter (4.6 nm) followed by Siralox 40 (7.2 nm), which was the catalyst on which the most coke deposited during contact with short and long chain feeds.

Brønsted surface acidity measurements indicated that ZSM-5 has the highest acidity, followed by Siralox 40 and lastly Eta alumina.

Objective 3: *Product characterization using gas chromatographic analyses*

An off-gas sample and a liquid product sample were taken every 24 hours during the experimental procedure. Products of these two streams (the off-gas and liquid) were collected simultaneously and analyzed separately. The products were accurately identified using the different GC systems as discussed in Chapter 3. The retention index system (Kováts indices) was used specifically for octene because of the difficulty in identifying these compounds as discussed in Chapter 7.

Objective 4: *Determination of the effectiveness of various alumina-based catalysts on the conversion and selectivity of olefin skeletal isomerization reactions of the selected compounds*

The outcome of the experimental runs between the reactions of shorter and longer chain feeds over the various catalysts as obtained from Chapter 5, 6 and 7 were discussed in detail in Chapter 8. The Brønsted acidity of the catalysts was measured and these values showed that ZSM-5 was the catalyst having the highest Brønsted acidity, making it a very active catalyst. This correlates well to the fact ZSM-5 is not active during the skeletal isomerization processes and with its high activity it rather undergoes side reactions instead of the preferred skeletal isomerization reactions. Siralox 40 and Eta alumina were the two catalysts that skeletally isomerizes longer carbon chains. The influence of diffusion on the activity of the catalysts was modelled through calculating the molecular sizes and determining the pore diameters. Indication is that diffusion is not the main characteristic that influences the activity of the three catalysts, but rather the Brønsted acidity of the catalytic surfaces.

Objective 5: *Reporting the influence of variation of temperature (350 °C; 400 °C and 450 °C) on the performance of the different catalysts (eta (η)-alumina, H-ZSM-5 and silicated alumina).*

It was observed that none of the three catalysts were active catalysts for the skeletal isomerization of *1*-butene to *iso*-butene at all three temperatures. ZSM-5 was the only catalyst that was selective towards *iso*-butene formation, particularly at 350 °C. The selectivity data obtained from the reaction of *n*-hexene with the three catalysts showed that Siralox 40 and Eta alumina were selective towards skeletal isomerization. Both these catalysts were close to thermodynamic equilibrium at all three temperatures of 350 °C; 400 °C and 450 °C, making them the most preferred catalysts for skeletal isomerization of *n*-hexene. Isomerization of *1*-octene to its branched isomers showed that Siralox 40 was the only catalyst which produced branched C_8 compounds (between 50% and 60%) at all three experimental temperatures. The selectivity of branched C_8 compounds when using Eta alumina is below 50% at all three temperatures and ZSM-5 was the least selective producing the least amount of branched C_8 compounds at the three temperatures.

9.2 Future work

Catalysts

Three catalysts, ranging from weakly to strongly acidic in nature, were chosen for the study and contacted over shorter (C_4) and longer (C_6-C_8) carbon chain olefins as feedstocks. ZSM-5 (the most acidic catalyst, which is from the zeolite family) did not perform well during the isomerization of olefins, but the Eta alumina and the Siralox 40 catalysts showed isomerization above 80% for one of the longer chains. The higher acidity of the ZSM-5 catalyst lead to a higher activity and thus a broader spectrum of products being formed (which resulted in less isomerization). The catalysts (Eta alumina en Siralox 40) with lower acidity performed better as isomerization catalysts. There thus seems to be an optimum acidity for maximum isomerization to occur. It is therefore suggested that more studies be done on the silica alumina family type catalysts for the isomerization of long carbon chains.

Selectivity

The relationship between optimum Brønsted acidity of alumina-based catalysts and optimum isomerization may be investigated to obtain better insight into obtaining the highest selectivity.

In order to successfully compare selectivities of various catalysts it would be preferred that the conversion values of the catalysts should be similar or at least at the optimum (or maximum) conversion possible for the specific catalyst.

Upscale

Olefin skeletal isomerization is of utmost importance and investigated for the improvement of the RON in the refinery fuel pool. It was concluded that high values on the isomerization to branched products were observed when contacting especially *n*-hexene over Eta alumina (selectivity ±90%) and also *n*-hexene over Siralox 40 (selectivity between 90% and 100%). Therefore, a suggestion would be to upscale the experimental runs from the bench scale fixed bed reactor to pilot plant scale reactors. By executing the runs on the pilot plant scale reactors, a lifetime study could be done on the catalyst and more volume of product could be generated which will be advantageous for a RON and MON analysis which requires a minimum of 2 litre liquid product for the analysis.

Regeneration test

A study that needs to be undertaken before industrial use of the catalysts is the verification of the catalysts' regenerability by regenerating the catalyst in situ or the proposal of other ways in which the catalyst life time may be expanded.

Annexures

Annexure A: Safety information on the different feedstocks used in this study

	Butene	**Hexene**	**Octene**
Synonyms	but-*1*-ene, n-butene, butene-1, ethyl ethylene, alpha-butylene, alpha-butene, n-butylene,	butyl ethylene, hex-*1*-ene	octene, oct-*1*-ene
Molecular formula	$C_2H_5CH{=}CH_2$	$C_6 H_{12}$	C_8H_{16}
Appearance	colourless gas	colourless liquid	colourless liquid
Melting point	-185 °C	-141°C to -139 °C	-101 °C
Boiling point	-6.3 °C	62° C to 63 °C	122 °C
Vapour density	2 (air = 1)	2.9 (air = 1)	3.9
Vapour pressure	1970 mm Hg at 21 °C	412 mbar at 38 °C	36 mm Hg at 38 °C
Density (g cm^{-3})	2.37 g/l at 25 °C	0.673	0.715
Flash point	not available	-25 °C (closed cup)	21 °C
Explosion limits	1.6% - 10%	1.2% - 6.9% by volume	0.7% - 3.9%
Autoignition temperature	385 °C	272 °C	230 °C
Water solubility	insoluble	54 mg/l	insoluble
Stability	Stable, but polymerizes exothermically. Highly flammable - readily forms explosive mixtures with air. Incompatible with strong oxidizing agents, halogens, halogen acids, metal salts, boron trifluoride, fluorine, nitrogen oxides.	Stable. Highly flammable - note low flash point. Incompatible with strong oxidizing agents, strong acids, combustible material.	Stable. Highly flammable. Incompatible with strong oxidizing agents, acids.
Toxicology	Asphyxiant. Irritant at low to moderate concentrations. High concentrations may lead to vomiting, convulsions or suffocation.	May cause lung damage if swallowed or inhaled. Skin, eye and respiratory irritant.	Harmful by inhalation and if swallowed. Skin, eye and respiratory irritant.

Annexure B: GC method used in product off-gas analysis

(7890A RGA Series Agilent GC System, STC 1, ETONLY method)

7890A RGA Series Agilent GC System

Inlets

SSL - Front:	EPC Split-Splitless Inlet
Mode:	Split
On	
Heater, °C	200
Pressure, Kpa	205
Total flow, ml/min	867.94 ml/min
Septum Purge Flow	3 ml/min
Split Ratio	150:1
Split Flow	859.22 ml/min
Gas Saver	20ml/min after 2 min

Columns

Description	1: AC 21.073.048: 200°C:35m x 320µm x 8µm		
-	In: Front SS Inlet He		
-	Out: Front Detector FID		
Control Mode:	Flow	5.7281 ml/min	(Initial):0 min He at 80°C Oven Out:Ambient Pressure 35m x 320µm x 8µm

Oven

Oven Temp On

Equilibration Time	0.2 min			
	Rate	Value	Hold Time	Runtime
Ramp	°C/min	°C	min	min
Initial		80	2	2
Ramp 1	35	185	2	7

Detectors

Front Detector FID

Heater	On	190°C
H2 Flow	On	35 ml/min
Air Flow	On	350 ml/min
Makeup Flow	Off	
Const Col + Makeup	Off	
Flame	On	
Electrometer	On	

Back Detector TCD

Heater	On	150°C
Reference Flow	On	18 ml/min
Makeup Flow	Off	
Const Col + Makeup	Off	
Negative Polarity	On	
Filament	On	

Aux Detector TCD

Heater	On	150°C
Reference Flow	On	18 ml/min
Makeup Flow	Off	
Const Col + Makeup	Off	
Negative Polarity	Off	
Filament	On	

Auxilliaries

Thermal Aux#1	On
Thermal Aux#2	On

Runtime

Time (min)	Time (min)	Event Type	Position	Setpoint
1	0.01	Valve	Valve 1	On
2	0.1	Valve	Valve 2	On
3	0.11	Valve	Valve 3	On
4	0.12	Valve	Valve 4	On
5	0.2	Valve	Valve 1	Off
6	0.33	Valve	Valve 6	On
7	0.6	Valve	Valve 2	Off
8	0.9	Valve	Valve 5	On
9	1	Valve	Valve 3	Off
10	1	Valve	Valve 4	Off
11	5	Valve	Valve 5	Off
12	6.99	Valve	Valve 6	Off

Signals

Front Signal	Save On 20 Hz
Back Signal	Save On 20 Hz
Aux Signal	Save On 20 Hz

Annexure C: GC method used in liquid product analysis

(6890 Series Agilent GC System, STC 1, C4 ISOM method)

6890 Series Agilent GC System

Injector

Use back injector

Injection volume	1.0 µl

Washes

	PreInjection	PostInjection
Sample	3	
Solvent A	3	3
Solvent B	3	3
Pumps	3	

Valves

Configure

Valve#:1

Not Configured

Inlets

Front:	EPC Split-Splitless Inlet
Mode:	Split
Gas:	He

On	Actual	Setpoint
Heater, °C	250	250
Pressure, Kpa	62.6	62.6
Total flow, ml/min	24.3	54.4

Split Ratio	50:1
Split Flow	50 ml/min
Gas Saver	20ml/min at 2min

Columns

Column	1
Mode:	Constant Flow
Inlet:	Back
Detector:	MSD
Outlet:	Vacuum

Installed Column

Inventory#: CPSil PONA

Manufacturer's Specifications

Model No: Varian CP 7531 275°C Max

CP-Sil PONA CB

Capillary 50.0mx210µmx0.5µm nominal

He Flow

	Setpoint	Actual	
Pressure	157.4		kPa
Flow	0.9		ml/min
Average Velocity	27		cm/sec

Oven

Oven

Setpoint:	35°C

Ramp	°C/min	Next °C	Hold	Runtime
Initial		35	5	5
Ramp 1	6	300	5	

Oven configuration

Maximum °C:	330
Equilibrium	0.5

min:

Detectors
Front: NO DET Detector

Signals

Signal1
Det
Source: test plot

Data Rate	Minimum Peak Width
20Hz	0.01min

Signal2
Det
Source: test plot

Data Rate	Minimum Peak Width
20Hz	0.01min

Aux
Aux Channel
Thermal Aux#2
Heater
On Setpoint 280°C
Type
MSD

Runtime

Time (min)	Specifier	Parameter	Setpoint
0	Signal 1	Source	Col Comp 1

Options
Pressure Units
kPa

Annexure D: GC method used in liquid product analysis

(6890 Series Agilent GC System, STC 1, TTTC4.M method)

6890 Series Agilent GC System

Injector

Use both injectors

Front Injector

Injection volume	1.0 µl

Back Injector

Injection volume	1.0 µl

Washes for both

	PreInjection	PostInjection
Sample	5	
Solvent A	5	5
Solvent B	5	5
Pumps	5	

Inlets

Front
Mode: Split
Gas: H2

On	Actual
Heater, °C	250
Pressure, Kpa	170.9
Total flow, ml/min	332

Split Ratio	100:1
Split Flow	322 ml/min
Gas Saver	20ml/min at 2.00 min

Columns

Column 1
Mode: Constant Flow
Inlet: Front
Detector: Front
Outlet: Ambient

Manufacturer's Specifications
Model No: Varian CP 8917 325°C Max
VF1MS
Capillary 60.0mx250µmx1.00µm nominal

H2 Flow

	Setpoint	Actual	
Pressure	171		kPa
Flow	3.2		ml/min
Average Velocity	57		cm/sec

Oven

Oven

Setpoint: 30°C

Ramp	°C/min	Next °C	Hold	Runtime
Initial		30	5	5
Ramp 1	6	300	5	55

Oven configuration

Maximum °C: 325

Equilibrium min: 0.25

Detectors

Front: FID Detector	Actual	Setpoint
Heater, °C		250
H2 Flow, ml/min		40
Air Flow, ml/min		450
Makeup Flow		N2
Const Col + Makeup, ml/min		25
Flame	Off	
Electrometer		
Lit Offset		2

Signals

Signal1		Signal2	
Det		Det	
Source:	front detector	Source:	back detector
Data Rate	Minimum Peak Width	DataRate	Minimum Peak Width
10Hz	0.02min	10Hz	0.02min

Annexure E: Selectivity, conversion and mass balance calculations

Selectivity

iso-Butene on *n*-Butenes (%) =

$$\frac{\textit{iso}\text{-Butylene}_{out} - \%\ \textit{Iso}\text{-Butylene}_{in}}{\%(\textit{trans-2}\text{-butene}+\textit{1}\text{-Butene}+\textit{cis-2}\text{-butene})_{in} - \%(\textit{trans-2}\text{-butene}+\textit{1}\text{-Butene}+\textit{cis-2}\text{-butene})_{out}} * 100$$

iso-Hexene on *n*-Hexenes (%) =

$$\frac{\textit{iso}\text{-Hexene}_{out} - \%\ \textit{Iso}\text{-Hexene}_{in}}{\%(\text{Hexene})_{in} - \%(\text{Hexene})_{out}} * 100$$

iso-Octenes on *n*-Octenes (%) =

$$\frac{\textit{iso}\text{-Octene}_{out} - \%\ \textit{Iso}\text{-Octene}_{in}}{\%(\text{Octene})_{in} - \%(\text{Octene})_{out}} * 100$$

Conversion

Conv *n*-butene (%) =

$$\frac{(\textit{trans -2}\text{-butene} + \textit{cis-2}\text{-butene}+\textit{1}\text{-butene})_{in} - (\textit{trans -2}\text{-butene} + \textit{cis-2}\text{-butene}+\textit{1}\text{-butene})_{out}}{(\textit{trans -2}\text{-butene} + \textit{cis-2}\text{-butene}+\textit{1}\text{-butene})_{in}} * 100$$

Conv *n*-hexene (%) =

$$\frac{(\text{hexene})_{in} - (\text{hexene})_{out}}{(\text{hexene})_{in}} * 100$$

Conv *n*-octene (%) =

$$\frac{(\text{octene})_{in} - (\text{octene})_{out}}{(\text{octene})_{in}} * 100$$

Mass balance

$$\frac{\text{Liquid prod out(g)+gas out (g)}}{\text{Total Gas in (g)}} * 100$$