Chapter 6

Results on isomerization of *1*-Hexene

The results on the products obtained from the reaction of *1*-Hexene with the various catalysts will be dealt with in the following manner:

- Mass balance and inertness of the reactor system;
- Conversion;
- Selectivity;
- Double bond shift;
- Cracking;
- Coking; and lastly the comparison between the three catalysts.

6.1   Confirmation on the mass balance and inertness of the reactor system

Mass balance

Firstly, a blank run was done in the reactor to verify the mass balance of the system. The same reactor as described in the previous chapter was used.

The reactor was loaded with glass beads and secured on both ends with glass wool. This blank run was done at 400 °C in the exact same way as the experimental runs which contained the catalysts. Three data points were collected over a time span of ±70 hours. These three data points were collected by analyzing both the liquid and off-gas products during the blank run.

When *1*-hexene was introduced into the reactor system, 96% - 98% of the total mass of liquid and gas of *1*-hexene was recovered over the 70 hours. The mass balance during this entire period was 100±4%, as shown in Figure 6.1.
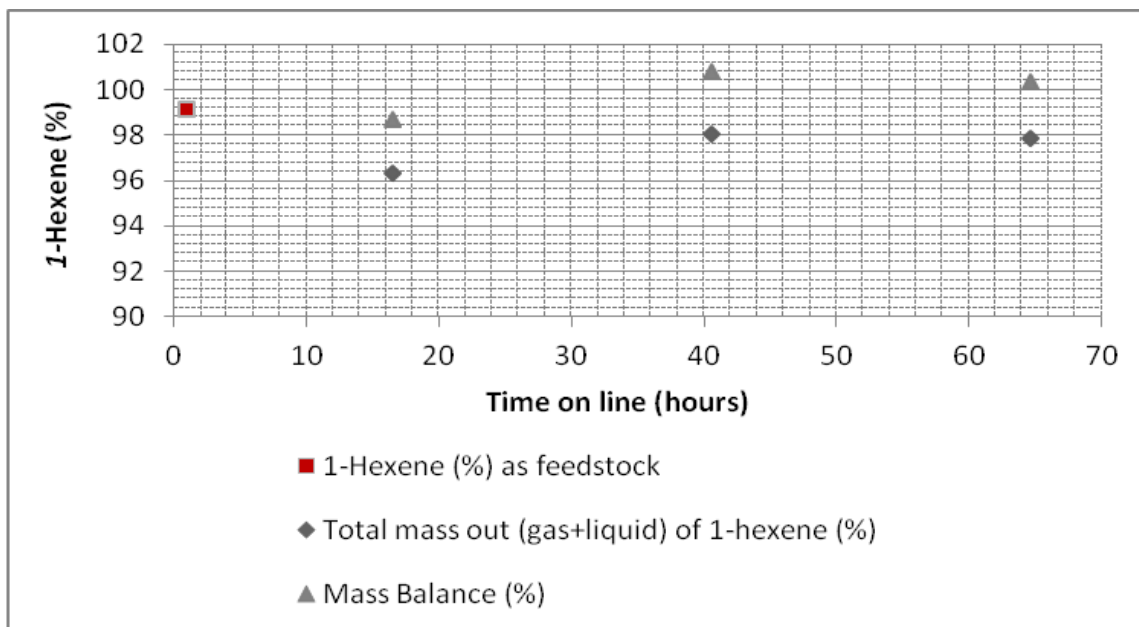
Figure 6.1: Blank run with *1*-hexene (%) as feedstock versus total mass out (gas+liquid) (%) as a function of time on line (hours). The mass balance over the time span is also included

Inert reactor system

For confirmation on the inertness of the reactor system it should be verified whether any other reactions take place within the reactor while at the experimental temperatures. The conversion of *1*-hexene was calculated during the blank run which was described above. From Figure 6.2 it is evident that a very low percentage of the *1*-hexene was converted and that the amount of *1*-hexene introduced is approximately equal to the amount of *1*-hexene recovered. The 0-3% conversion of *1*-hexene may be ascribed to the formation of *2*-hexene and *3*-hexene, which is the double bond shift of *1*-hexene. To conclude, the reactor could be considered inert.
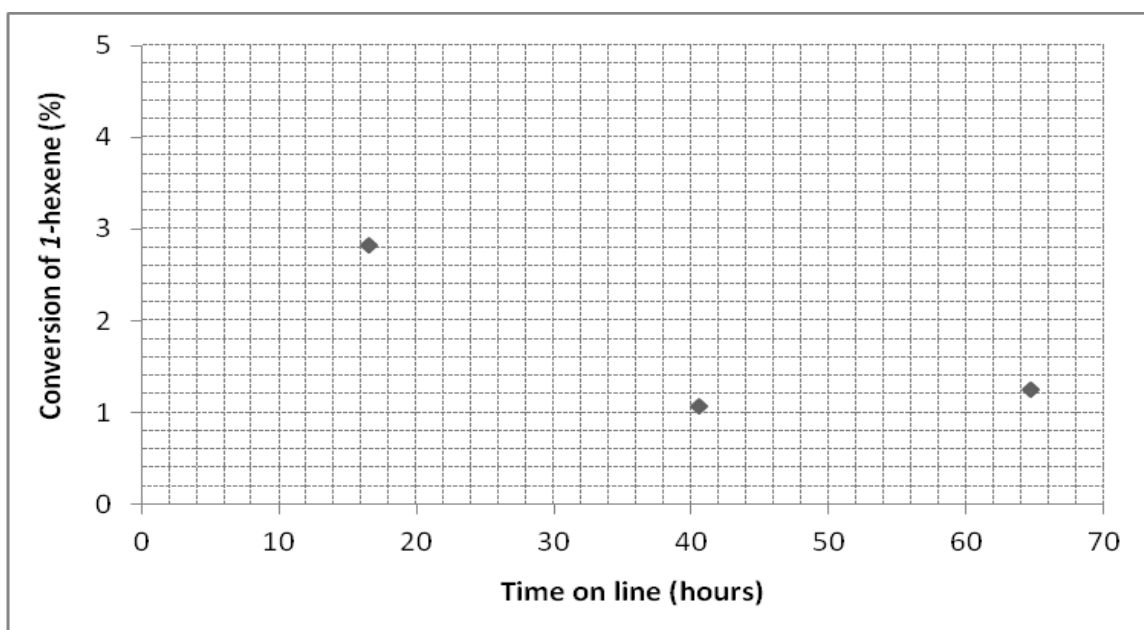
Figure 6.2: Conversion of *1*-hexene (%) versus time on line (hours) during a blank run done at 400 °C

6.2   *n*-Hexene reacted over Eta alumina catalyst

Conversion of hexene

Figure 6.3 shows the conversion of *1*-hexene. The conversion stayed constant as time increased and it is believed that *1*-hexene was in thermodynamic equilibrium with *2*-hexene and *3*-hexene.
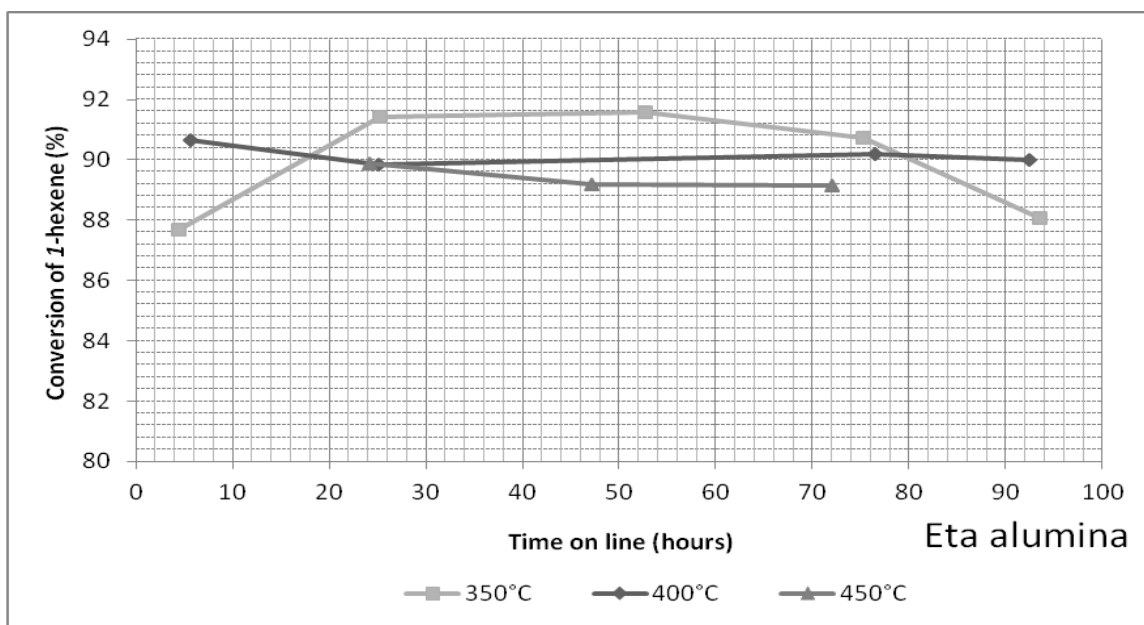

Figure 6.3: Conversion of *1*-hexene (%) after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the Eta alumina catalyst

Because the reaction of interest was skeletal isomerization, rather than double bond shift, conversion and selectivity calculations are based on *n*-hexene (*1,2,3*-hexene) rather than the feed material, *1*-hexene.
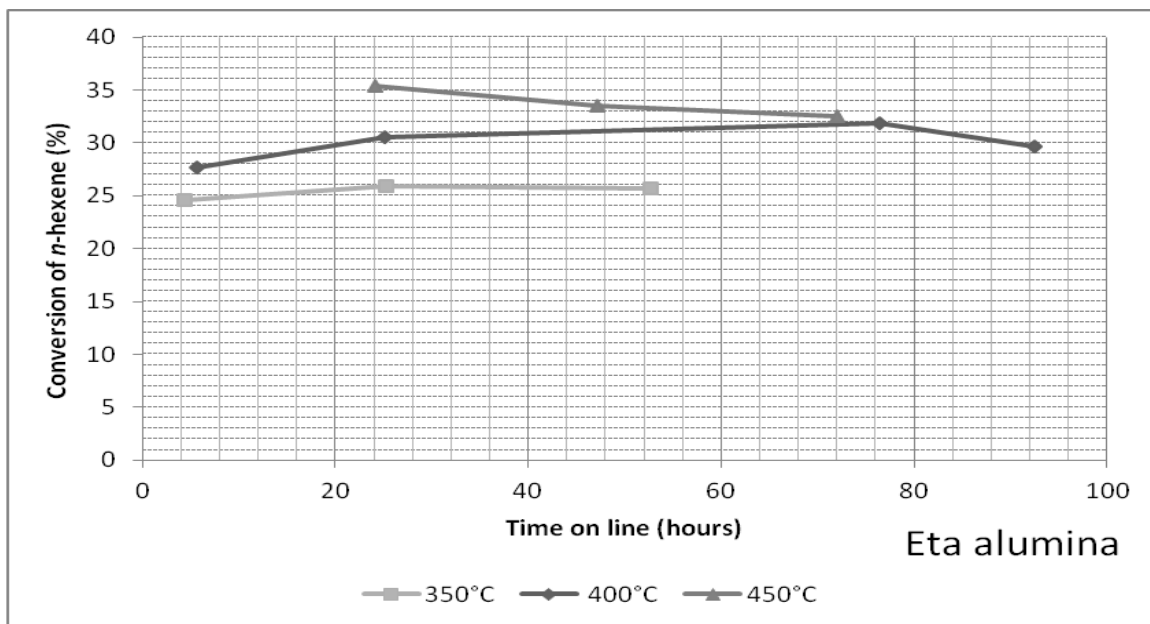
Figure 6.4: Conversion of *n*-hexene (%) after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the Eta alumina catalyst

The conversion of *n*-hexene remained relatively constant at 350 °C, 400 °C and 450 °C (Figure 6.4). This low conversion at all three temperatures can be attributed to weak activity of the Eta alumina catalyst.

Steady state conversion was obtained as the conversion after 52-72 hours on line (Figure 6.5).
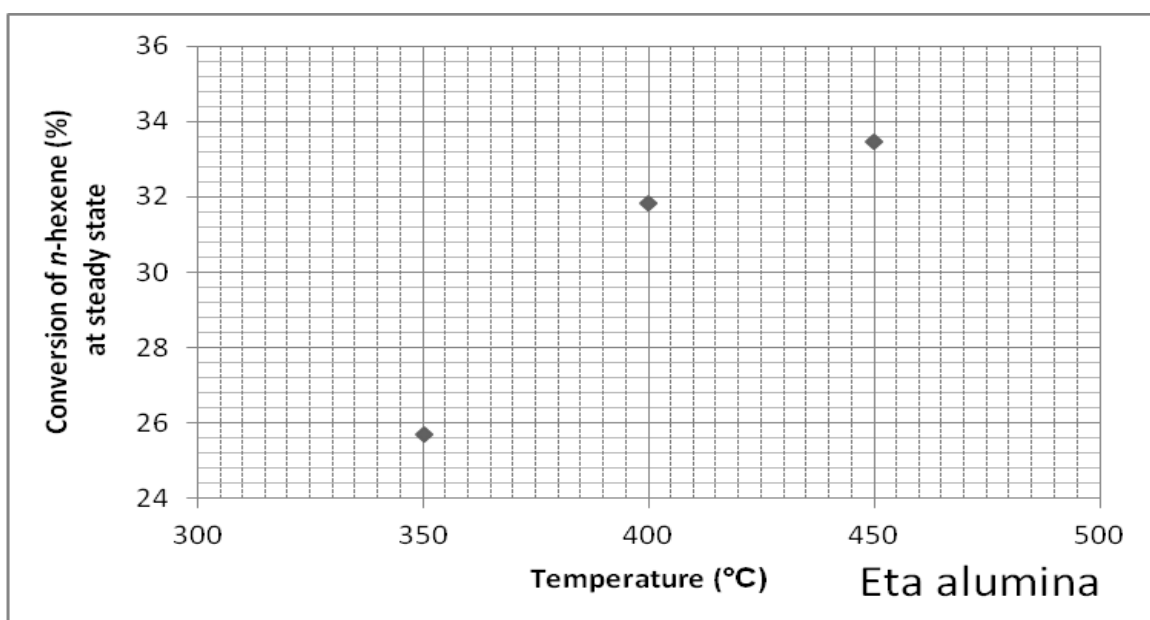

Figure 6.5: Conversion of *n*-hexene (%) at steady state versus temperatures of 350 °C, 400 °C and 450 °C obtained over the Eta alumina catalyst

Selectivity to branched hexene based on n-hexene

Branched C_6 components were used to collectively describe the branched isomers occurring from the reaction of *n*-hexene over the various catalysts. The main branched C_6 components which were identified were the methyl pentenes such as *4*-methyl-*cis*-*2*-pentene, *3*-methyl-*2*-pentene and *3*-methyl-*trans*-*2*-pentene. All the other branched C_6 components were lumped with these and are referred to throughout this Chapter as ''branched C_6 components''.

At all three temperatures; 350 °C, 400 °C and 450 °C, the selectivity to branched C_6 components were as high as 90%. This indicates that skeletal isomerization occurred with *n*-hexene over the Eta alumina catalyst. Very few of the other components formed (<C_6 and C_7-C_{11}).
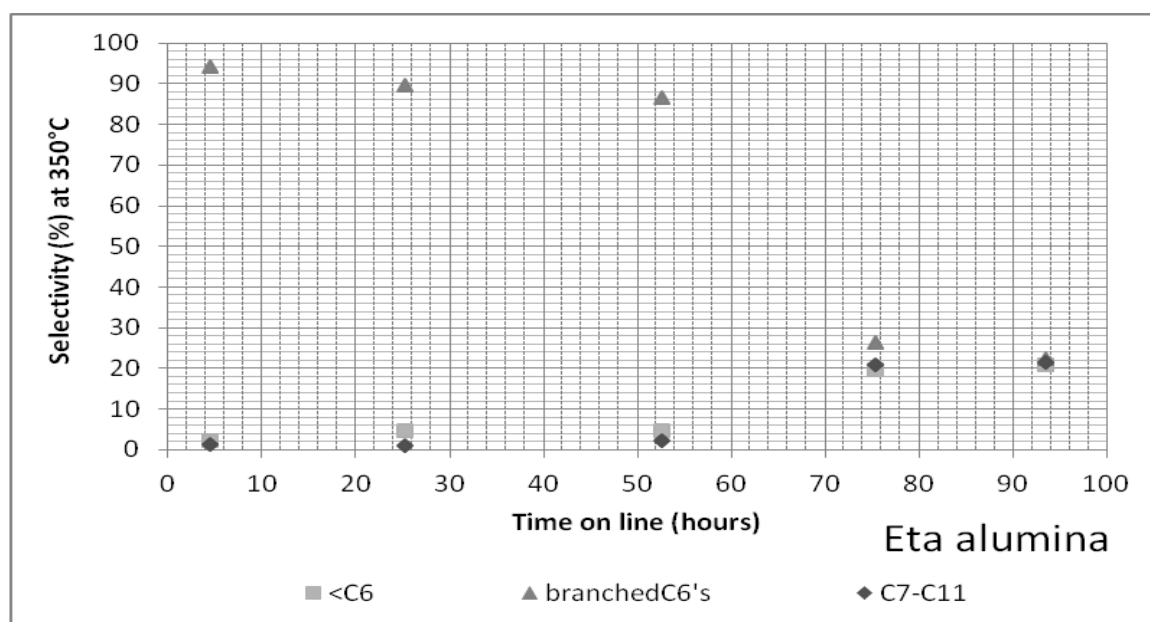

Figure 6.6: Selectivity (%) based on *n*-hexene as feedstock, at 350 °C over the Eta alumina catalyst
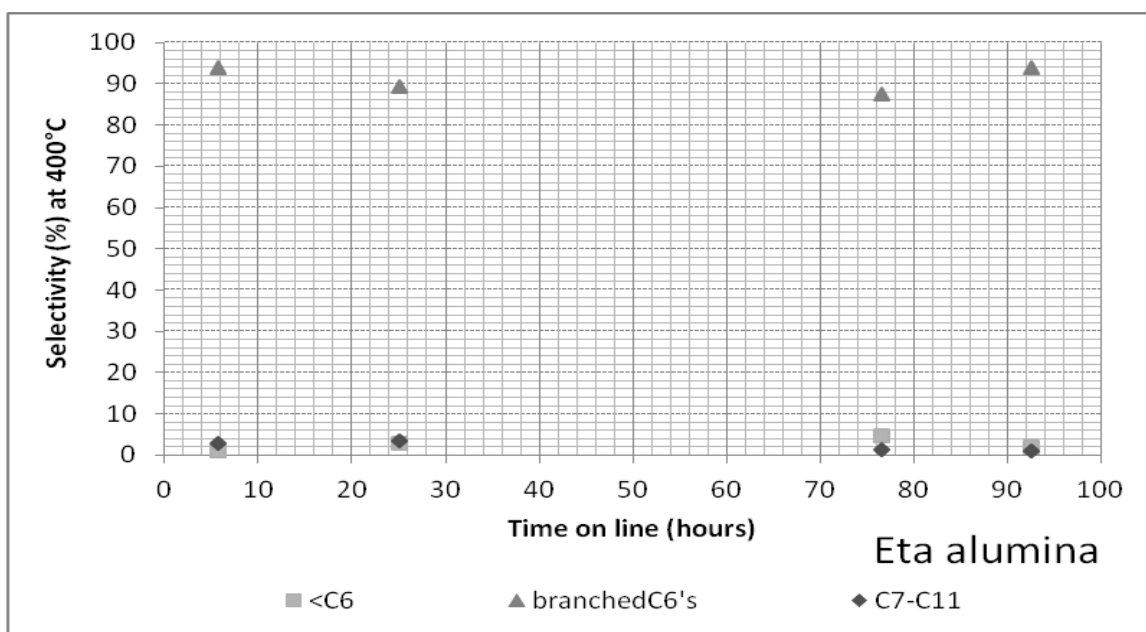
Figure 6.7: Selectivity (%) based on *n*-hexene as feedstock, at 400 °C over the Eta alumina catalyst
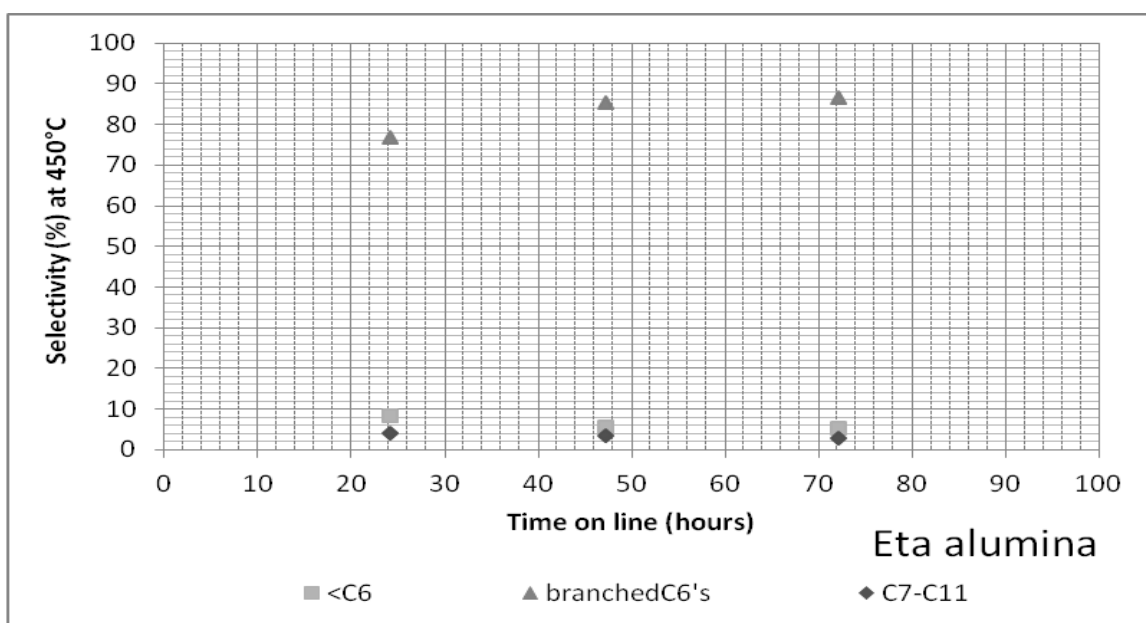

Figure 6.8: Selectivity (%) based on *n*-hexene as feedstocks, at 450 °C over the Eta alumina catalyst

Double bond shift of 1-hexene

From the *1*-hexene that was reacted over the Eta alumina catalyst, *2*-hexene and *3*-hexene formed at all three temperatures according to Scheme 6.1. Double bond shifts from *1*-hexene to *2*-hexene and *3*-hexene appeared to form to the same extent as time went by, although at 350 °C, double bond shifts increased as the time on line increased. This relates well to the high conversion of *1*-hexene, and Figure 6.9 illustrates that most of the *1*-hexene converted to *2*-hexene and *3*-hexene. These are all in thermodynamic equilibrium. All hexene coversion calculations were thus based on *n*-hexene.
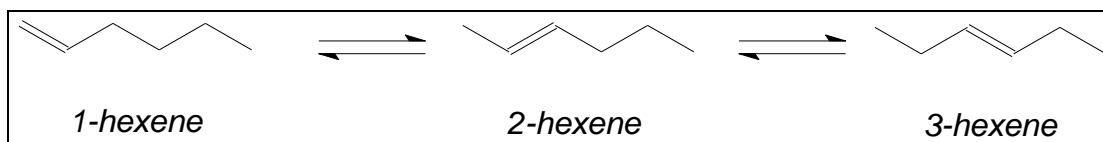
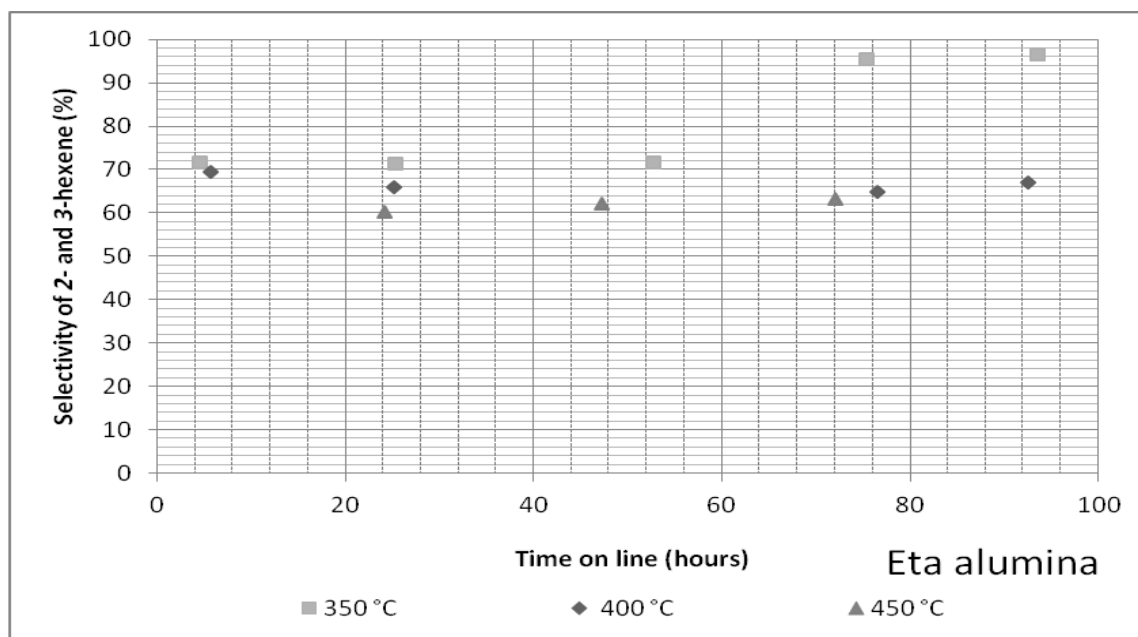Scheme 6.1: Double bond shift from *1*-hexene to *2- and 3*-hexene

Figure 6.9: Selectivity of *2- and 3*-hexene (%) as a function of time on line (hours) at temperatures of 350 °C, 400 °C and 450 °C over the Eta alumina catalyst. *2- and 3*-hexene formation is indicative of double bond shifts

Cracking of n-hexene

Cracking of *n*-hexene occurred and compounds of fewer than C_6 were formed. It was observed that cracking increased over time at 350 °C. At the higher temperatures, 400 °C and 450 °C, less cracking occurred and seemed to decrease with the increase in time (Figure 6.10). For the higher temperatures, cracking was less than 10%.
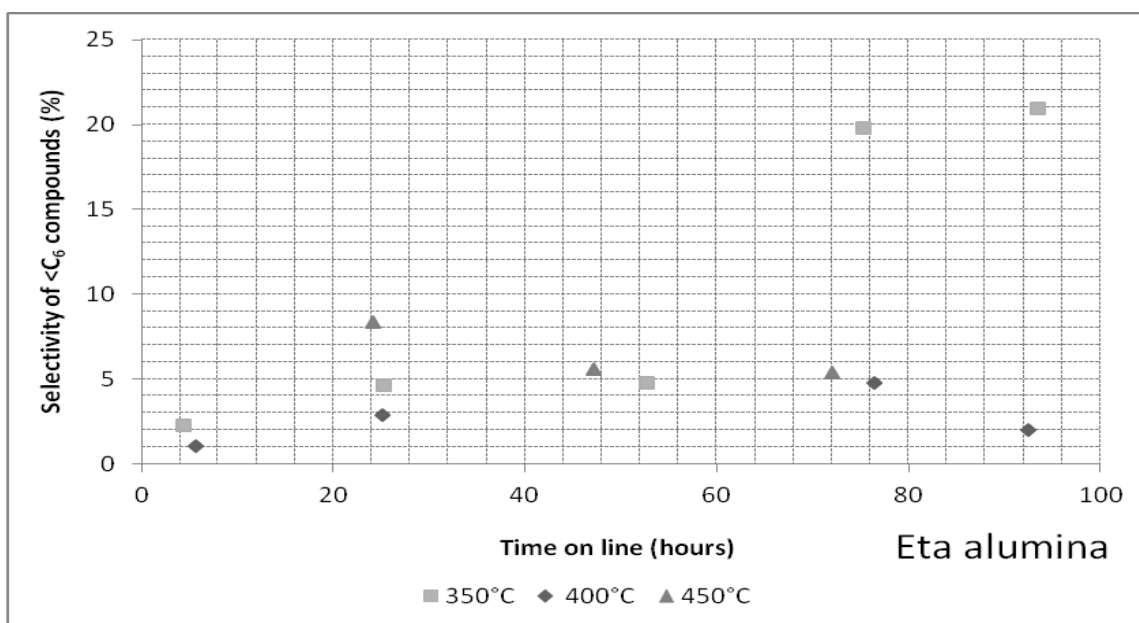
Figure 6.10: Selectivity of compunds <C$_6$ (%) based on *n*-hexene as a function of time on line (hours) at temperatures of 350 °C, 400 °C and 450 °C over the Eta alumina catalyst. The formation of compounds of fewer than C$_6$ is indicative of cracking

Cracking occured on the acid sites of the catalyst as described earlier and the decrease in cracking signifies that the acid sites of the Eta alumina catalyst were blocked and the opportunity for coking to take place as time increases is evident as shown in Figure 6.11.

Coking of the Eta alumina catalyst

Figure 6.11 indicates that the fixed carbon started at an expected 0% for the fresh Eta alumina catalyst and then at 350 °C, the carbon increased to 3.2% and then unpredictably dropped to 1.0% and 1.6%, respectively as temperatures increased to 400 and 450 °C. Referring to Figure 6.4 and Figure 6.5, the same phenomenon occurred at 350 °C, which shows that the catalyst was deactivated and thus an increase in carbon was observed at 350 °C.
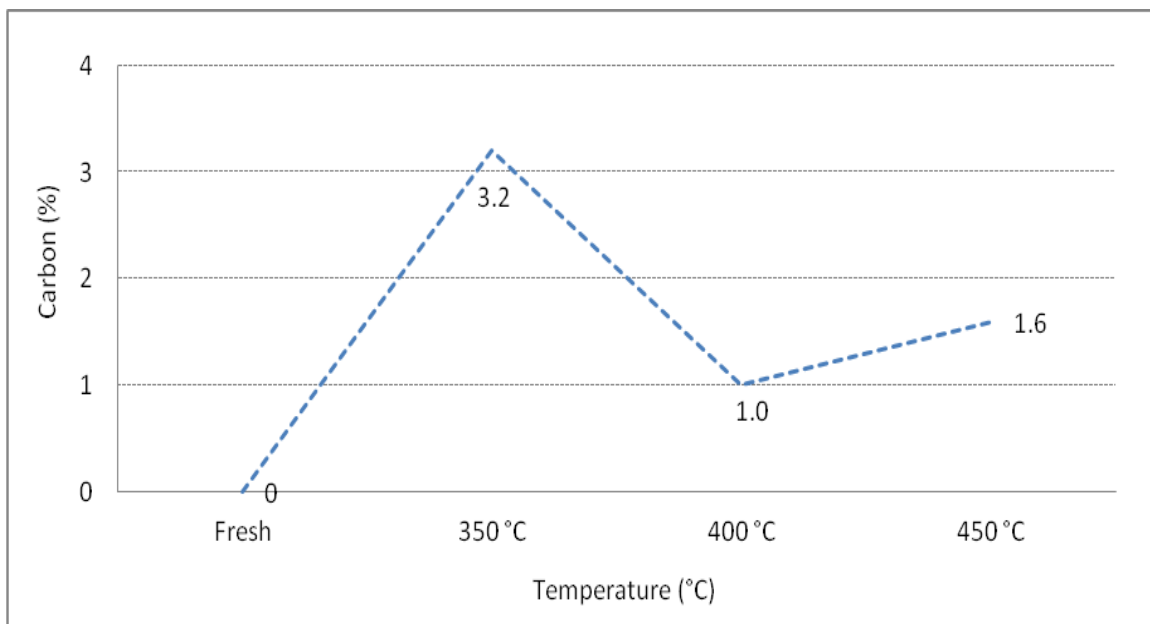
Figure 6.11: Carbon (%) of fresh Eta alumina and spent Eta alumina after reactions at temperatures of 350 °C, 400 °C and 450 °C

The increase in fixed carbon at 350 °C correlates well with the slight decrease in pore volume of the Eta alumina catalyst as shown in Figure 6.12. The decrease in fixed carbon at 400 °C then again relates well to the slight increase in pore volume and at 450 °C the pore volume decreased with the increase in fixed carbon. To summarise, it is evident that an increase in fixed carbon (signifying coke formation) blocked the pores of the catalysts and that resulted in a decrease in pore volume.
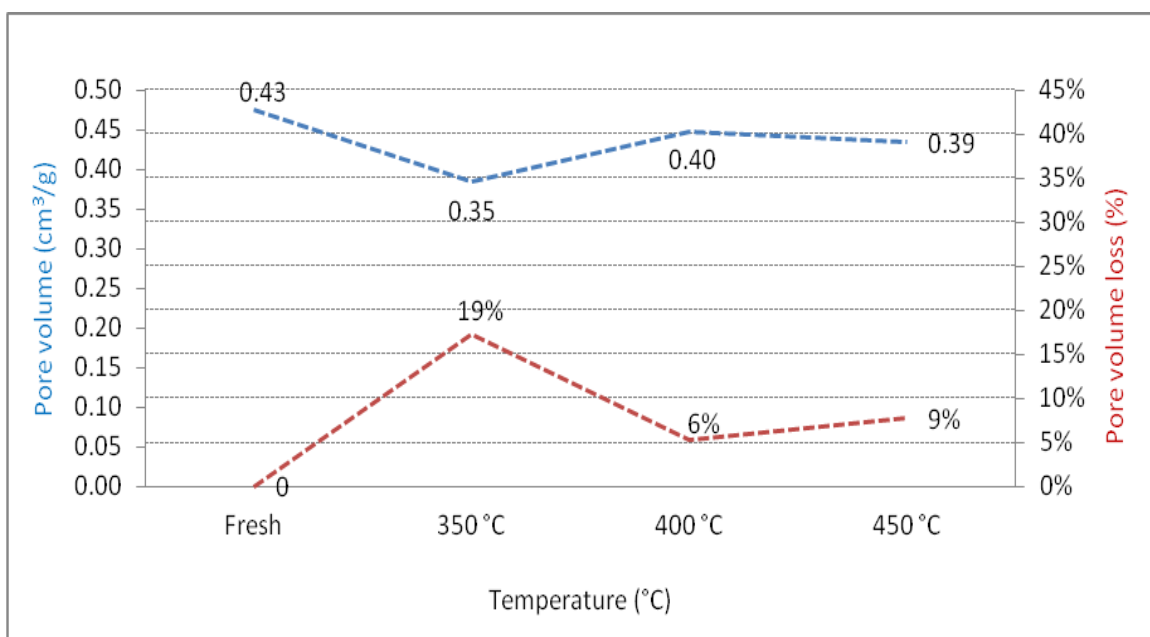

Figure 6.12: Pore volume (cm^3/g) of fresh Eta alumina and spent Eta alumina and pore volume loss (%) of fresh Eta alumina and spent Eta alumina after reactions at temperatures of 350 °C, 400 °C and 450 °C
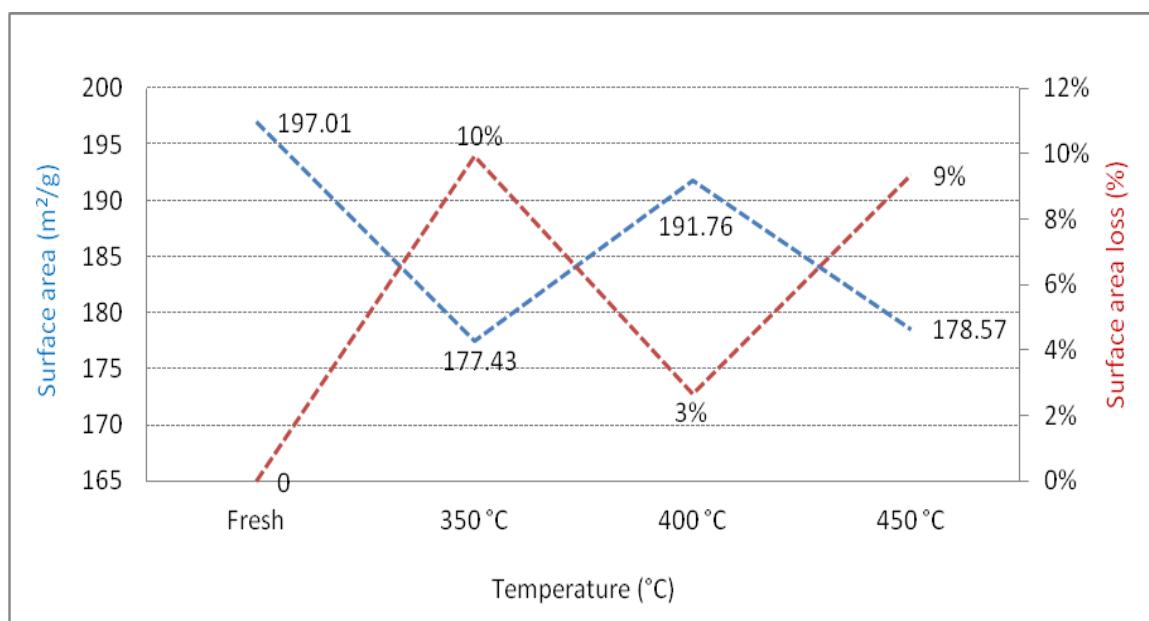
Figure 6.13: Surface area (m²/g) of fresh Eta alumina and spent Eta alumina and surface area loss (%) of fresh Eta alumina and spent Eta alumina after reactions at temperatures of 350 °C, 400 °C and 450 °C

Results of the surface area changes of the Eta alumina catalyst after reaction with *1*-hexene at the various temperatures are given in Figure 6.13. The change in surface area followed the same trend as the change in pore volume as given in Figures 6.12 and 6.13 with respect to carbon. A fascinating observation is that the same amount of surface area and pore volume is lost (9%) of the Eta alumina catalyst as temperature increases to 450 °C.

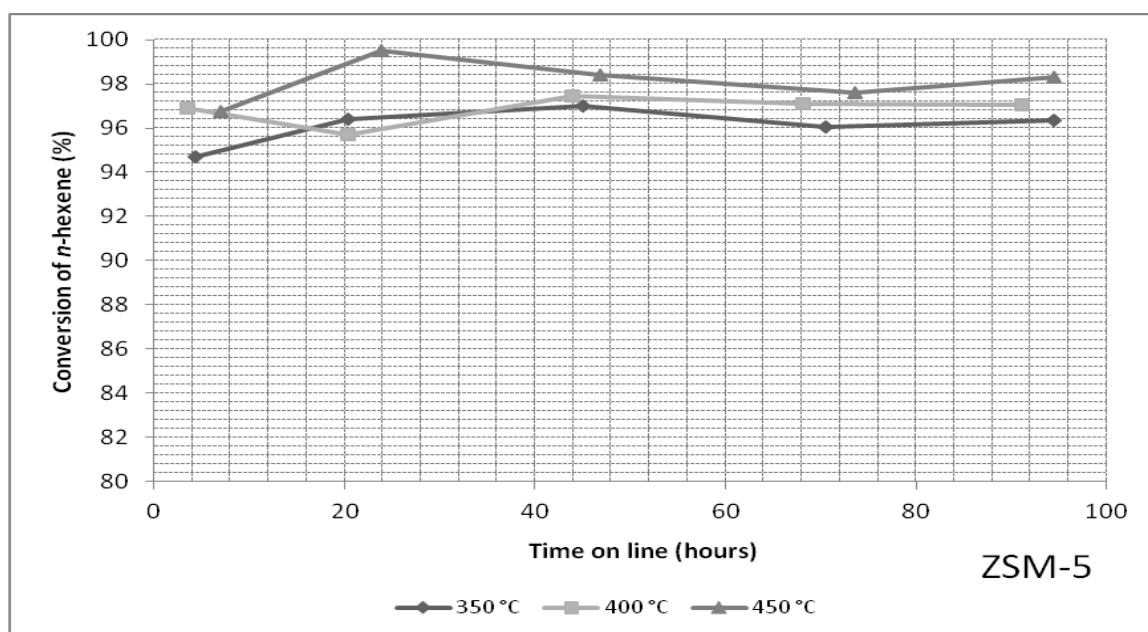## 6.3   *1*-Hexene reacted over ZSM-5 catalyst

Conversion of hexene

Figure 6.14: Conversion of *n*-hexene (%) after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the Eta alumina catalyst

The conversion of *n*-hexene remained relatively constant at 350 °C, 400 °C and 450 °C. The high conversion of *n*-hexene shows that ZSM-5 is a very active catalyst.

For all three temperatures, steady state was obtained between 43 and 46 hours on line. Conversion at steady state is used to compare results obtained at the different temperatures. Figure 6.15 shows that the ZSM-5 catalyst had the lowest activity at 350 °C and that the activity increased with an increase in temperature which relates well to Figure 6.14 (where the highest conversion of *n*-hexene was obtained at 450 °C).
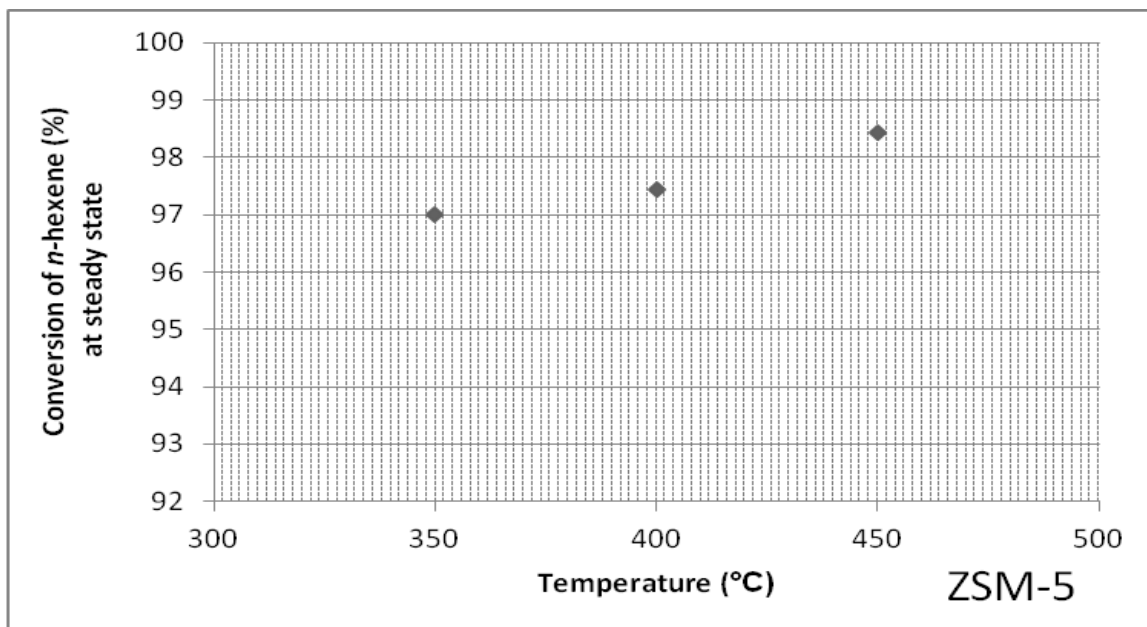
Figure 6.15: Conversion of *n*-hexene (%) at steady state after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the ZSM-5 catalyst

Selectivity of n-hexene

At all three temperatures; 350 °C, 400 °C and 450 °C, the selectivity to components smaller that C_6 were as high as 90%. This is indicative of cracking. Contacting *n*-hexene over the ZSM-5 catalyst produced less than 20% of branched C_6 and C_7-C_{11} components which shows that very little isomerization took place during the reaction (Figure 6.16, 6.17 and 6.18).
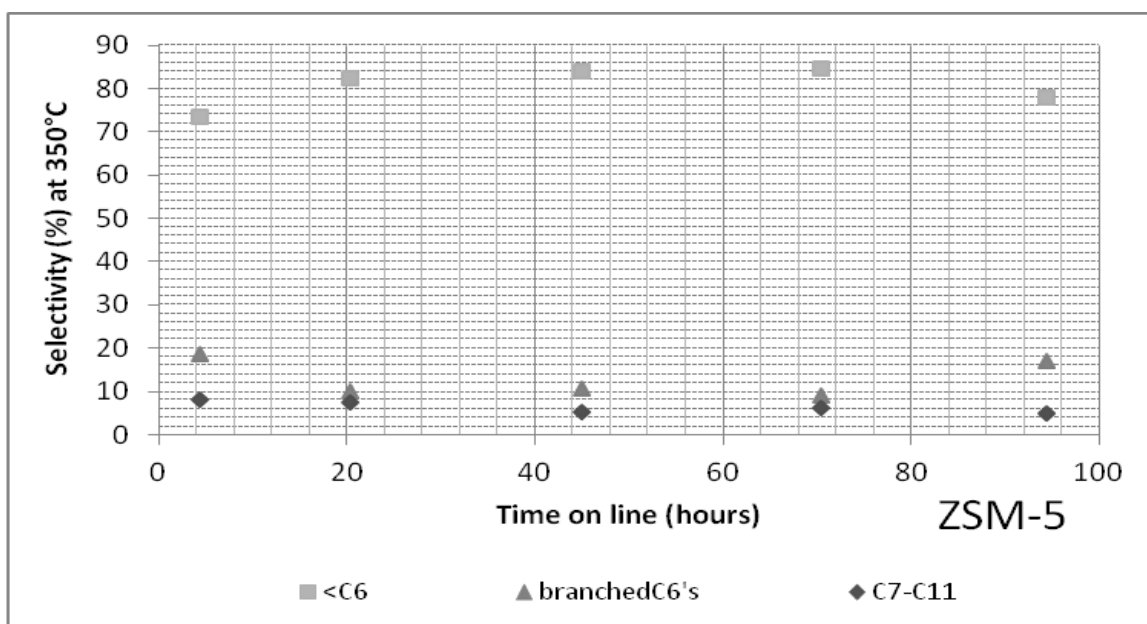

Figure 6.16: Selectivity (%) based on *n*-hexene as feedstock, at 350 °C over the ZSM-5 catalyst
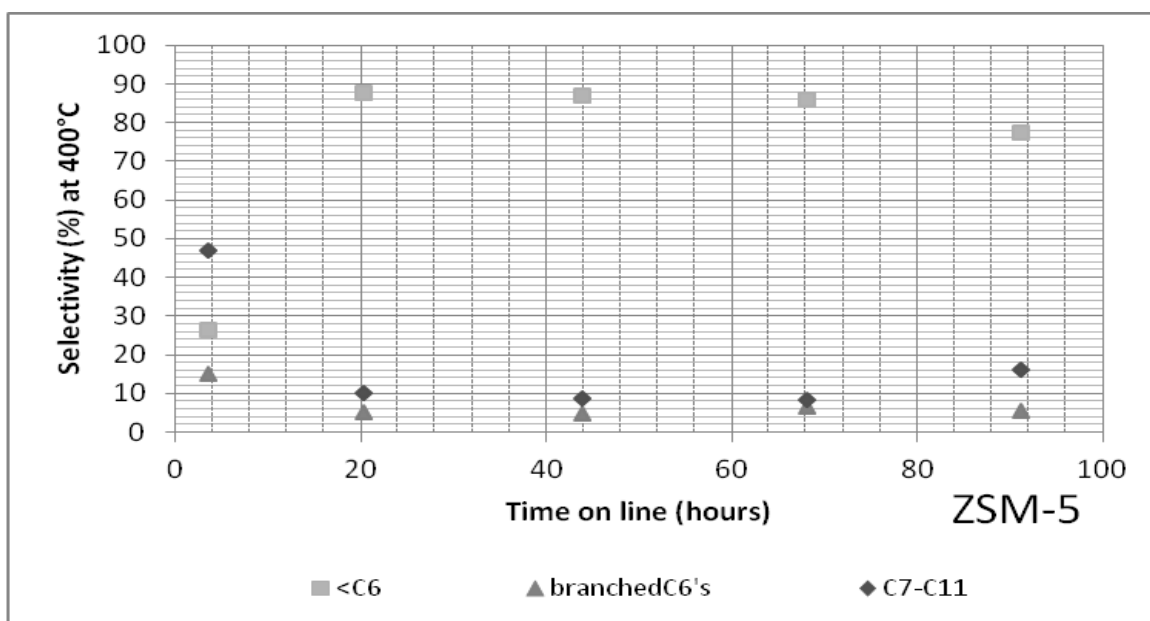
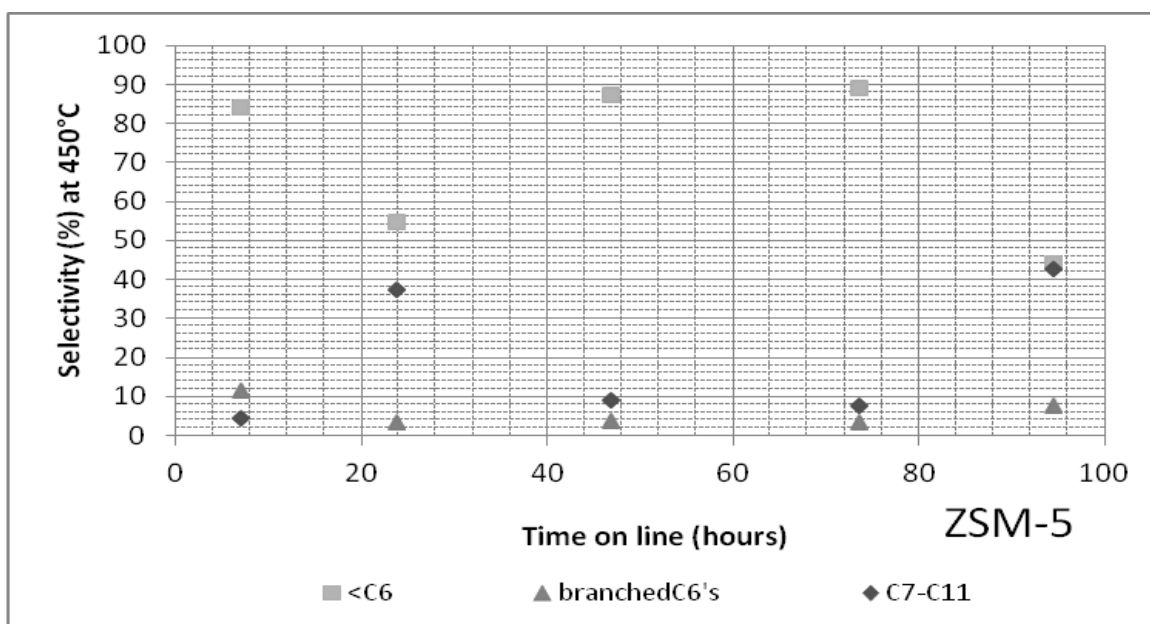**Figure 6.17: Selectivity (%) based on *n*-hexene as feedstock, at 400 °C over the ZSM-5 catalyst**

Figure 6.18: Selectivity (%) based on *n*-hexene as feedstocks, at 450 °C over the ZSM-5 catalyst

Double bond shift of 1-hexene

From the *1*-hexene that was reacted over the ZSM-5 catalyst, a small amount of *2*-hexene and *3*-hexene formed at all three temperatures. This shows that double bond shifts occurred but to a small degree (Figure 6.19).
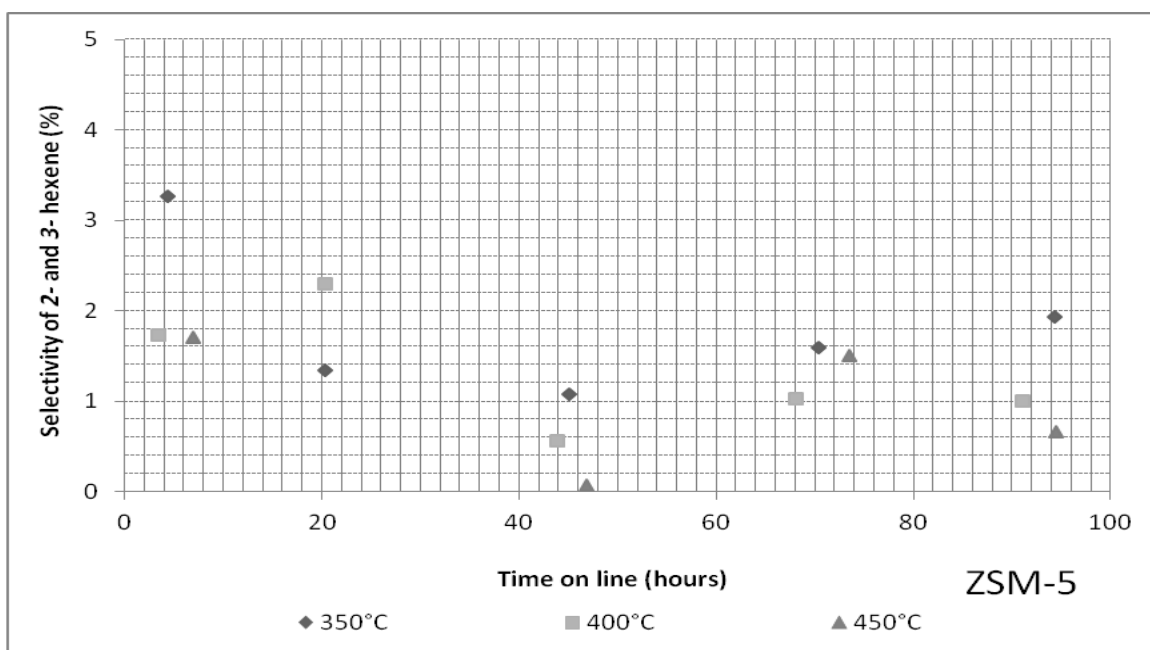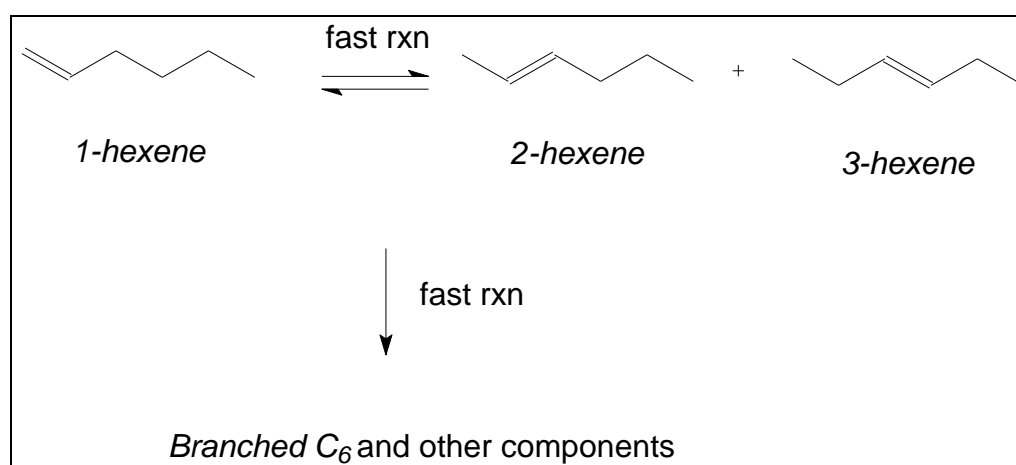
Figure 6.19: Selectivity of *2- and 3-*hexene (%) as a function of time on line (hours) at temperatures of 350 °C, 400 °C and 450 °C over the Eta alumina catalyst. *2- and 3-*hexene formation is indicative of double bond shift

Keeping this in mind and referring to Figure 6.14, the conversion of *n*-hexene was very high at all temperatures indicating that double bond shifts as well as isomerization and even cracking occurred fast on the ZSM-5 catalyst.

Scheme 6.2: Reaction indicating double bond shift, branched C_6 and other components occurring fast on the ZSM-5 catalyst

Cracking of n-hexene

Between 70%-90% of all products formed at all three temperatures were shorter than C_6, showing that cracking was a major reaction over ZSM-5. As a result, only a small amount of branched C_6 compounds was formed.
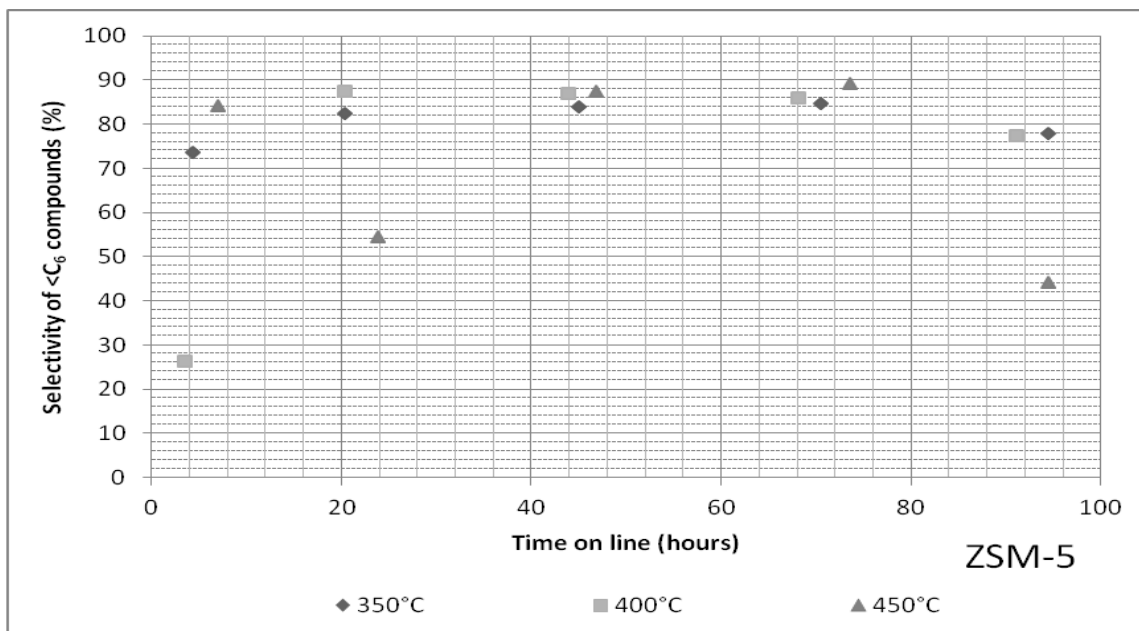
Figure 6.20: Selectivity of compunds <C$_6$ (%) based on *n*-hexene as a function of time on line (hours) at temperatures of 350 °C, 400 °C and 450 °C over the Eta alumina catalyst. The formation of compounds of fewer than C$_6$ is indicative of cracking

Coking of the ZSM-5 catalyst

In Figure 6.21 the results of carbon percentages on the spent catalysts are plotted against temperature. From Figure 6.21 it is evident that coking on the ZSM-5 catalyst increased with an increase in temperature.
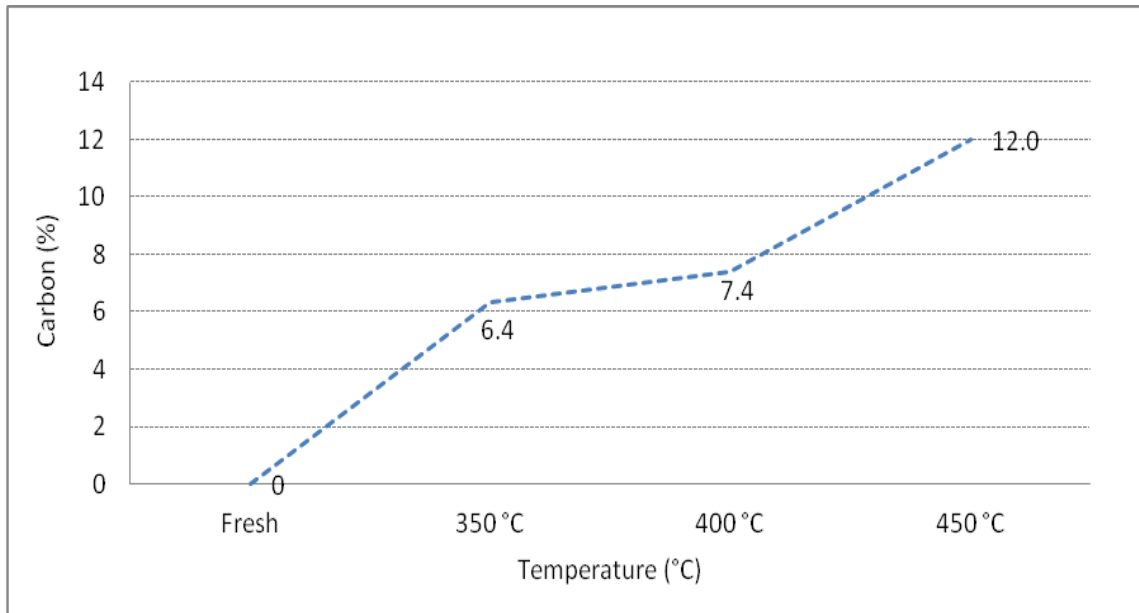

Figure 6.21: Carbon (%) of fresh ZSM-5 and spent ZSM-5 after reactions at temperatures of 350 °C, 400 °C and 450 °C

Likewise, the pore volume seemed to decrease slightly. With an increase in temperature the ZSM-5 catalyst had lost 30% of its pore volume due to the amount of coke formed (Figure 6.22).
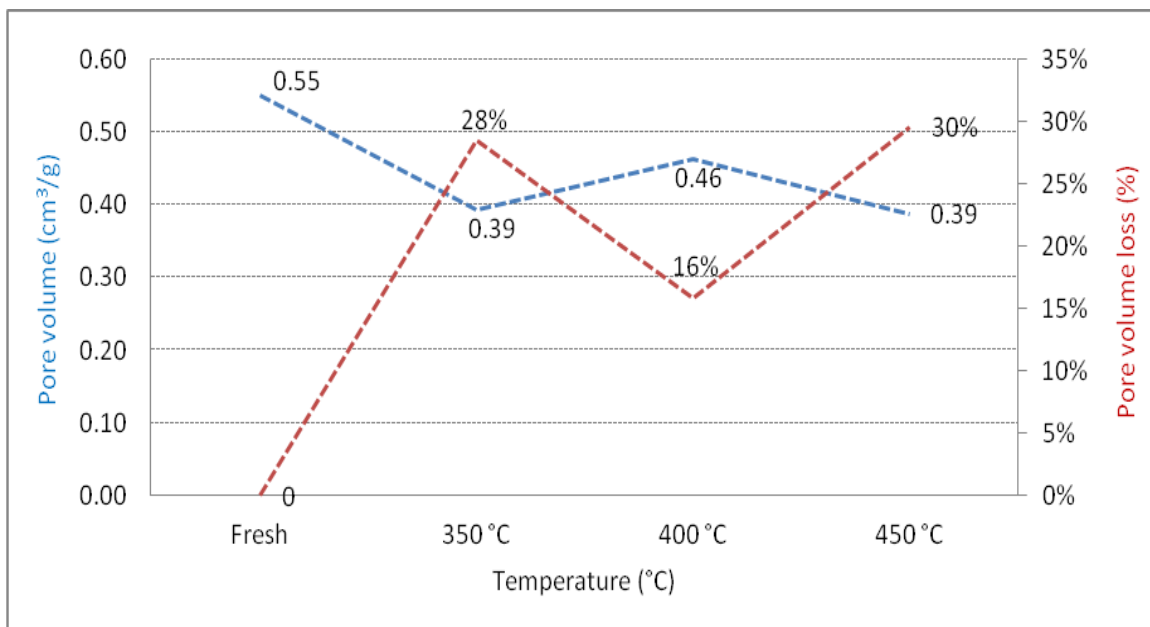
Figure 6.22: Pore volume (cm^3/g) of fresh ZSM-5 and spent ZSM-5 and pore volume loss (%) of fresh ZSM-5 and spent ZSM-5 after reactions at temperatures of 350 °C, 400 °C and 450 °C

Surprisingly, the surface area showed an increase from 350 °C with increase in temperature which indicates that the greatest loss of the surface area is at 350 °C compared to the 31% loss at 450 °C (Figure 6.23).
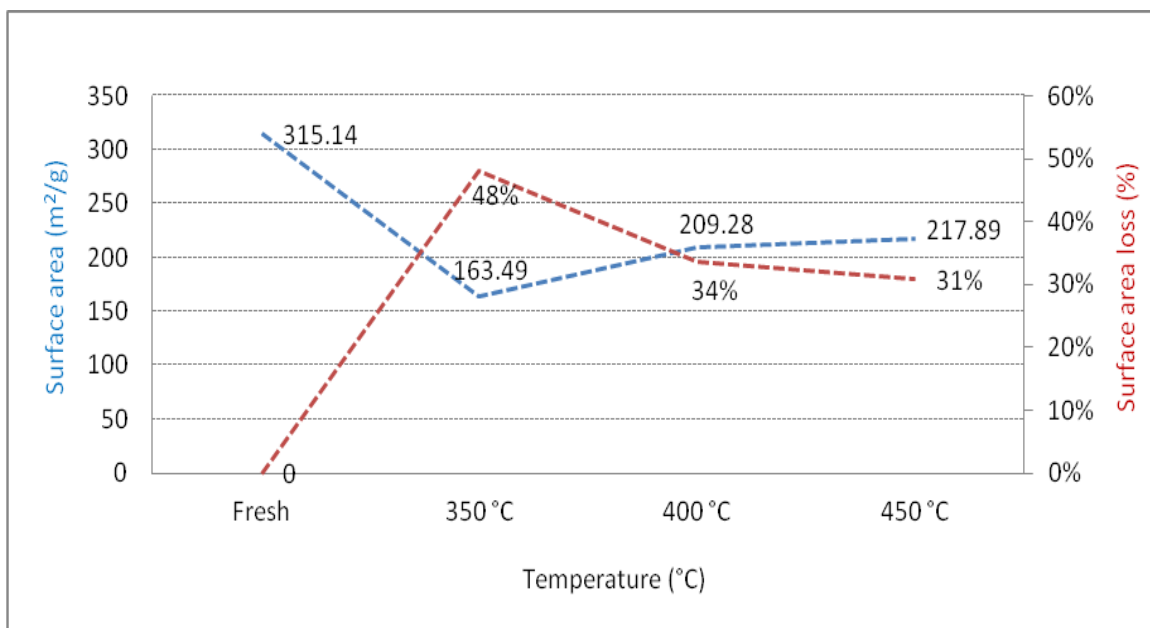

Figure 6.23: Surface area (m^2/g) of fresh ZSM-5 and spent ZSM-5 and surface area loss (%) of fresh ZSM-5 and spent ZSM-5 after reactions at temperatures of 350 °C, 400 °C and 450 °C

6.4 *1*-Hexene reacted with Siralox 40 catalyst

Conversion of n-hexene

The calculated conversion of *n*-hexene using the Siralox 40 catalyst showed a rapid decline with an increase in time, indicating severe deactivation of the catalysts (Figure 6.24). At 450 °C, the catalyst stabilised after 20 hours on line to a conversion of approximately 70%. The conversion of *n*-hexene continuously decreased with time when in contact with the Siralox 40 catalyst at 350 °C.
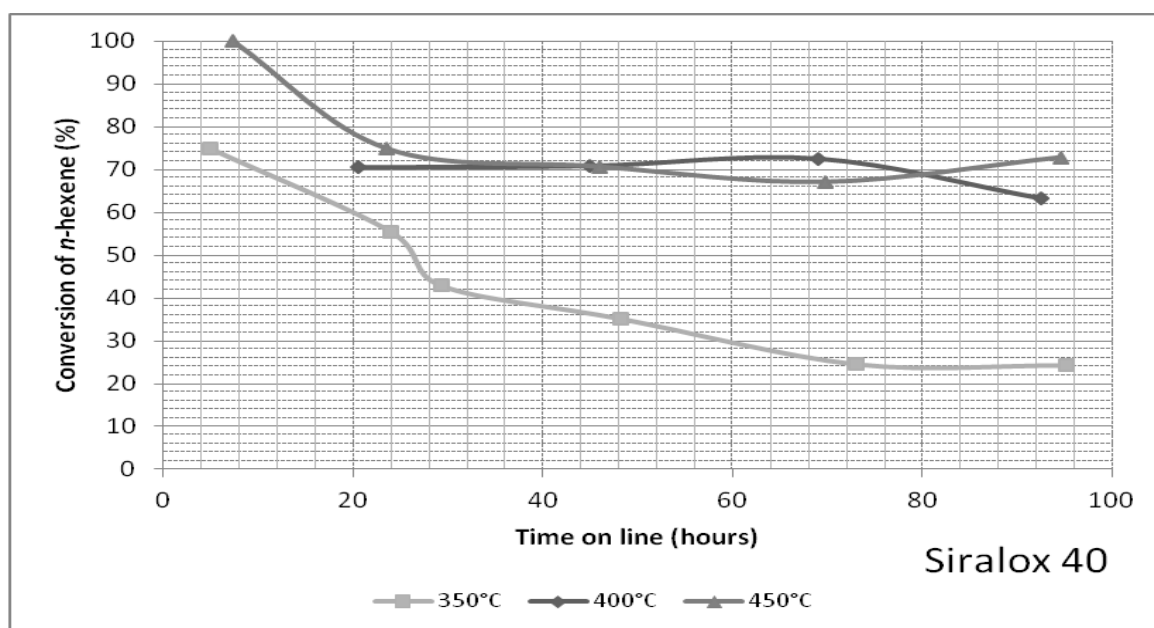

Figure 6.24: Conversion of *n*-hexene (%) after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the Siralox 40 catalyst, indicating that steady state was obtained

Steady state conversion was obtained as the conversion after 44-49 hours on line. The conversion of *n*-hexene as well as the catalyst's activity was lowest at 350 °C. Catalyst deactivation seemed to be a factor contributing to the observed low conversion of *n*-hexene.
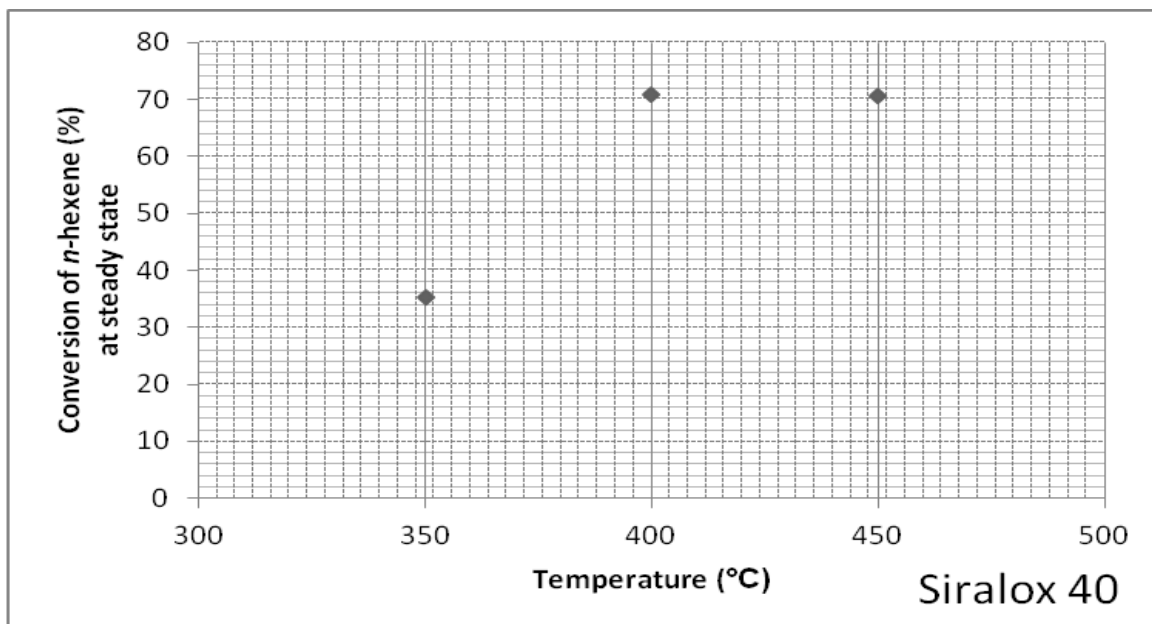
Figure 6.25: Conversion of *n*-hexene (%) at steady state after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the Siralox catalyst

Selectivity of n-hexene

In Figure 6.26, 6.27 and 6.28 the formation of branched C_6 components is shown as a function of time on line. At the end of the period on line it seemed as if the skeletal isomerization reaction continued to increase. The reaction of *n*-hexene with the Siralox 40 catalyst produced high selectivity towards the branched C_6 components.
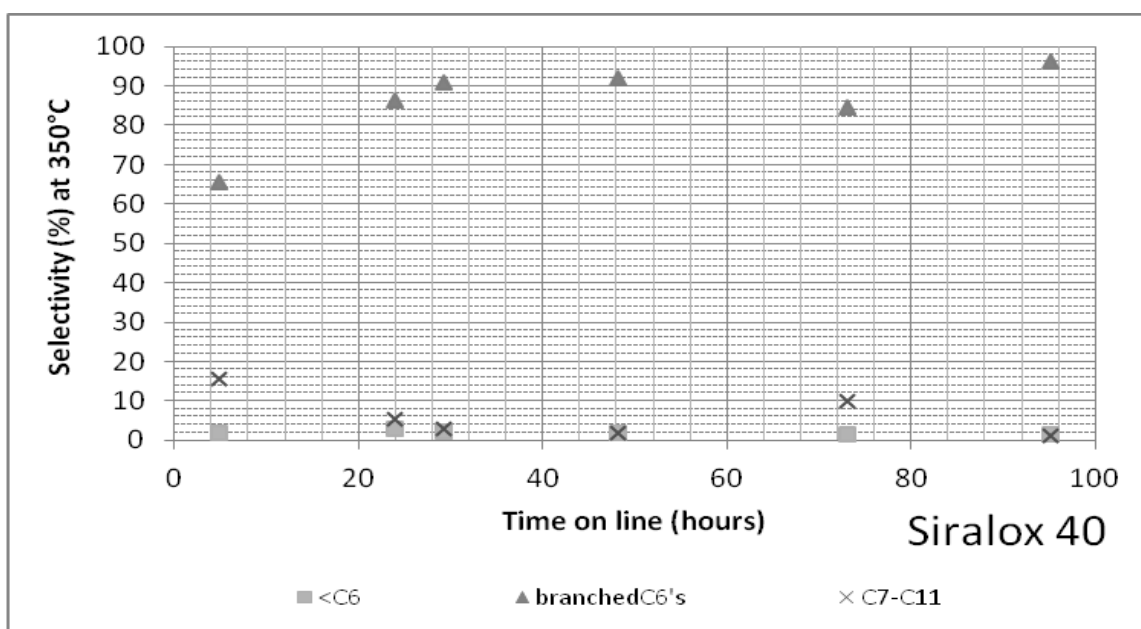

Figure 6.26: Selectivity (%) of desired products based on *n*-hexene obtained at 350 °C over the Siralox 40 catalyst
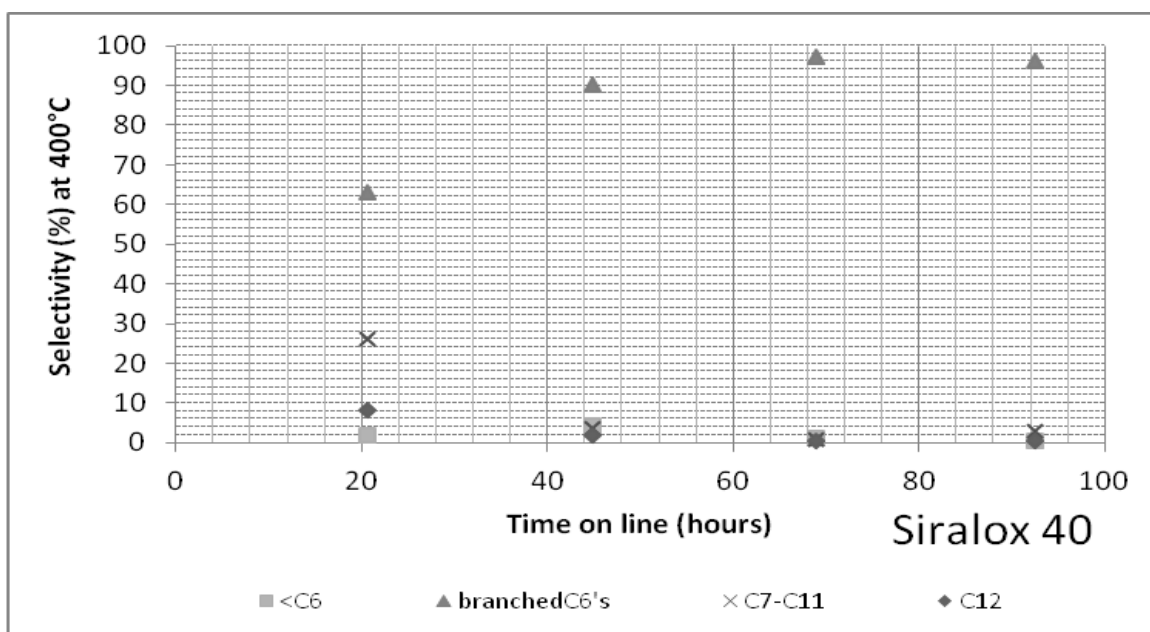
Figure 6.27: Selectivity (%) of desired products based on *n*-hexene obtained at 400 °C over the Siralox 40 catalyst
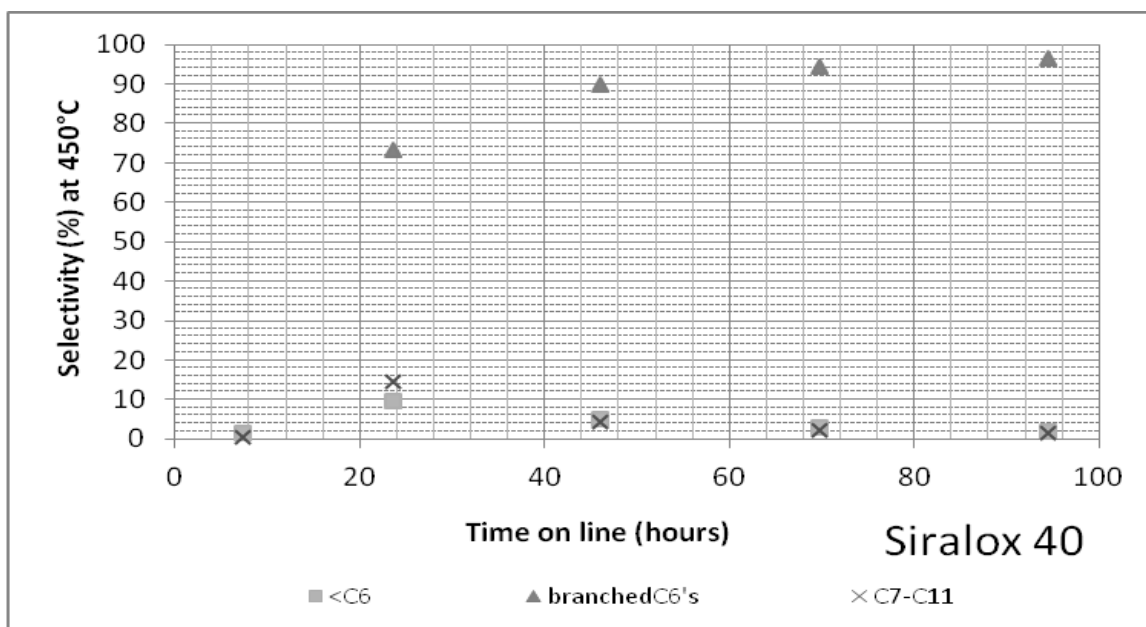

Figure 6.28: Selectivity (%) of desired products based on *n*-hexene obtained at 450 °C over the Siralox 40 catalyst

Double bond shift of 1-hexene

The selectivity towards the formation of *2*-hexene and *3*-hexene from the reaction of *1*-hexene was plotted in Figure 6.29 to indicate the amount of double bond shifts that occurred. The highest selectivity of approximately 70% was at 350 °C. At both 400 °C and 450 °C, much less *2*-hexene and *3*-hexene was formed.
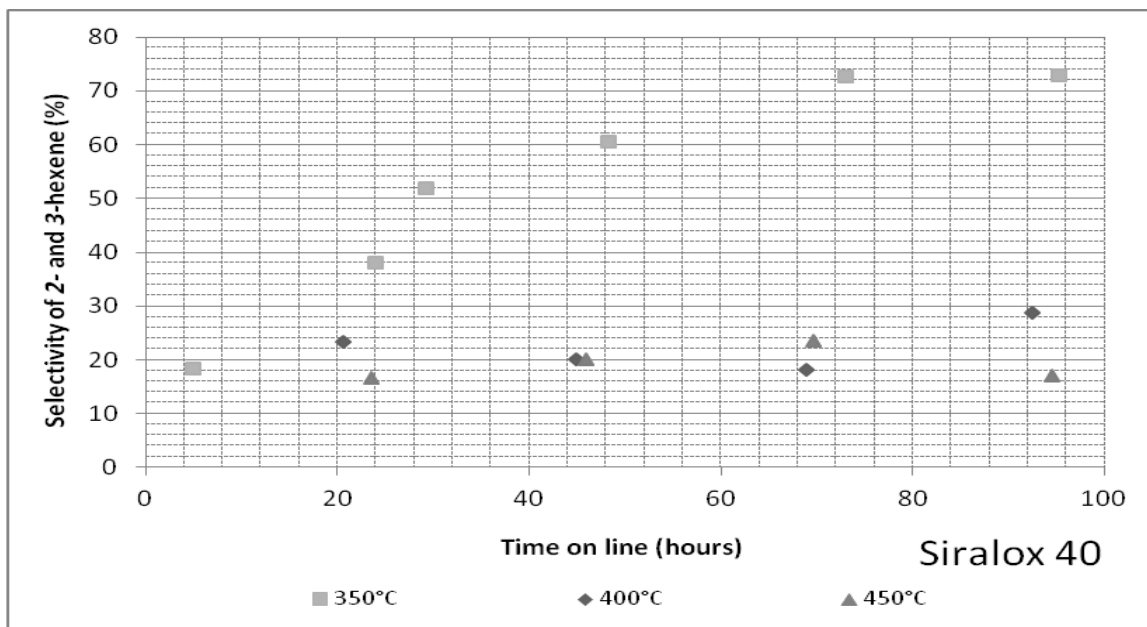
Figure 6.29: Selectivity of *2- and 3*-hexene (%) based on *1*-hexene as a function of time on line (hours) at temperatures of 350 °C, 400 °C and 450 °C over the Siralox 40 catalyst. *2- and 3*-hexene formation is indicative of double bond shifts

Cracking of n-hexene

The results of the investigation into the selectivity of compounds smaller than C_6 with time on line are presented in Figure 6.30. From the figure it follows that little cracking of *n*-hexene to compounds less than C_6 occurred at 350 °C and 400 °C, but at 450 °C, 10% of the *n*-hexene cracked initially and then the amount decreased gradually as time increased.
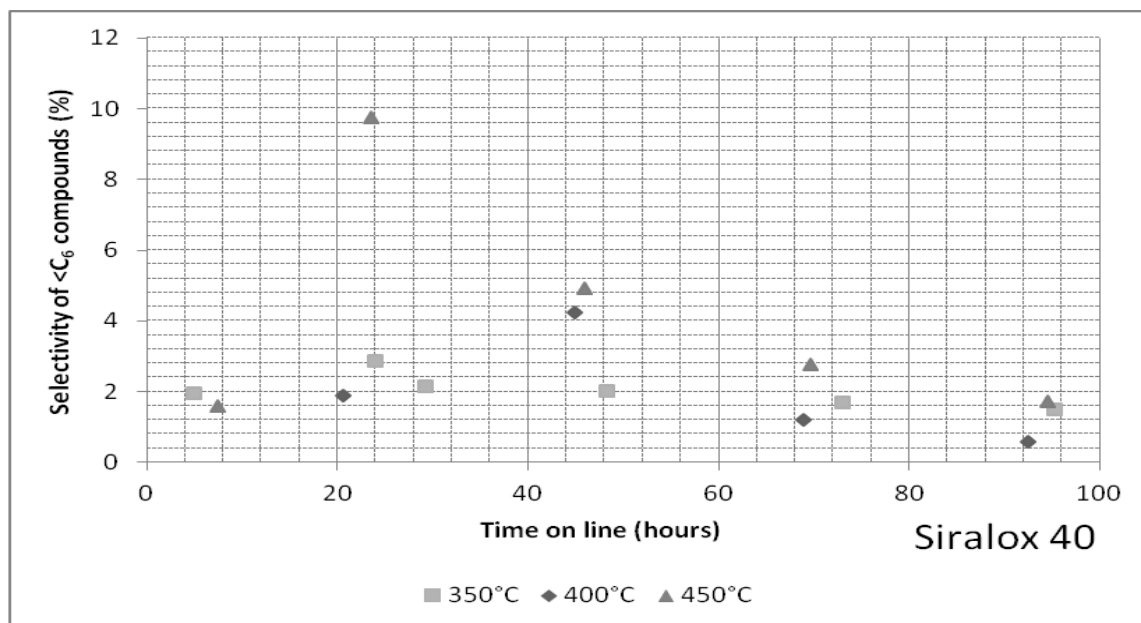

Figure 6.30: Selectivity of compunds <C_6 (%) as a function of time on line (hours) at temperatures of 350 °C, 400 °C and 450 °C over the Siralox 40 catalyst. The formation of compounds less that C_6 is indicative of cracking

Coking of the Siralox 40 catalyst

Figure 6.31 illustrates that the amount of carbon deposited on the fresh catalyst is 0.2% instead of 0%, indicating that the fresh Siralox 40 catalyst contained a certain amount of organic material. The carbon content on the Siralox 40 catalyst increased with an increase in temperature after reaching steady state on line, which relates well to the surface area and pore volume data obtained of the spent Siralox 40 catalyst at all three temperatures.
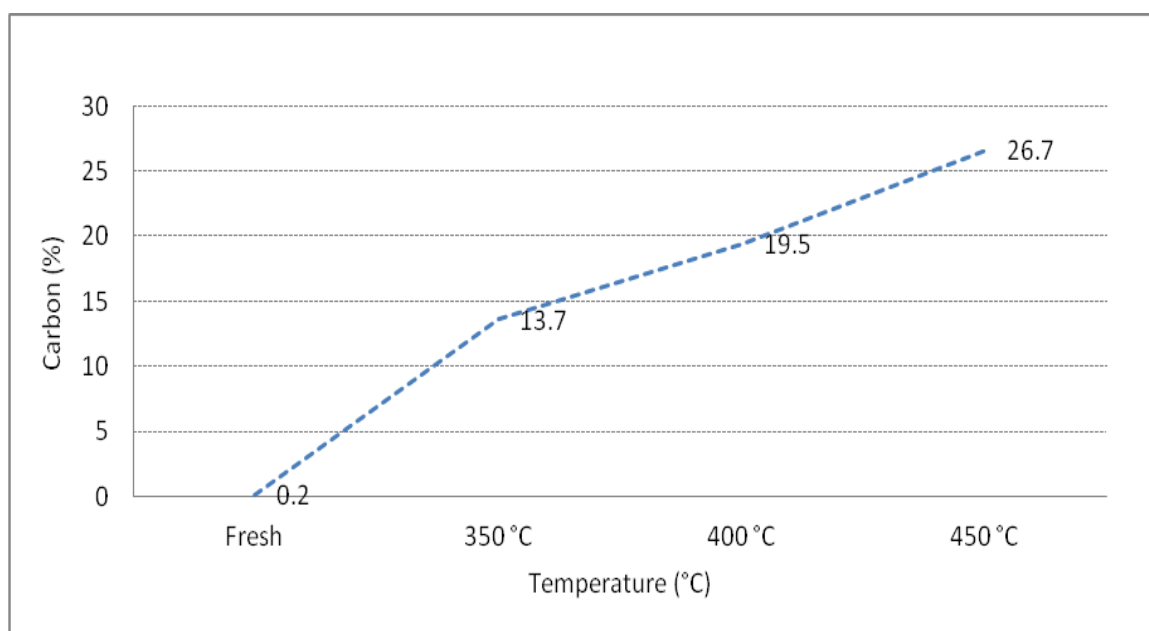

Figure 6.31: Carbon (%) of fresh Siralox 40 and spent Siralox 40 after reactions at temperatures of 350 °C, 400 °C and 450 °C

With an increase in temperature of the Siralox 40 catalyst, the amount of coking on the catalyst increased, which caused the catalyst's pores to be blocked, creating smaller pore volumes. The catalyst lost 58% of its pore volume probably as a result of the indicated coking.
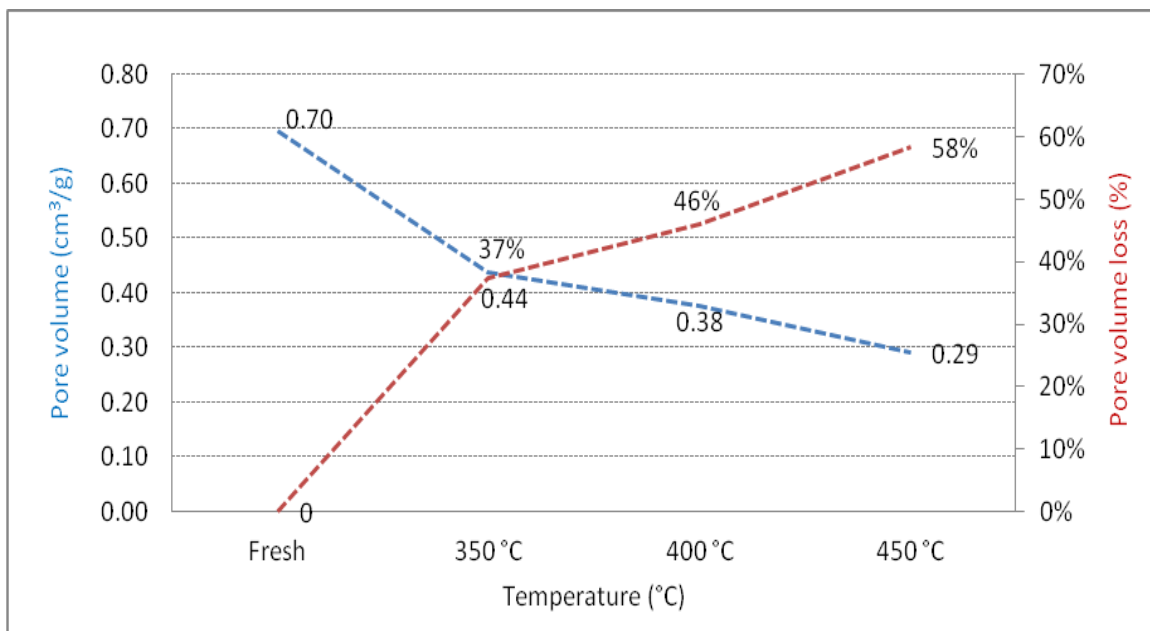
Figure 6.32: Pore volume (cm³/g) of fresh Siralox 40 and spent Siralox 40 and pore volume loss (%) of fresh Siralox 40 and spent Siralox 40 after reactions at temperatures of 350 °C, 400 °C and 450 °C

The increase of coking with temperature also caused the surface area to decrease, as can be seen from Figure 6.33. At 450 °C, 66% of the catalyst surface area was lost probably due to coking which is almost similar to the loss in pore volume (58%).
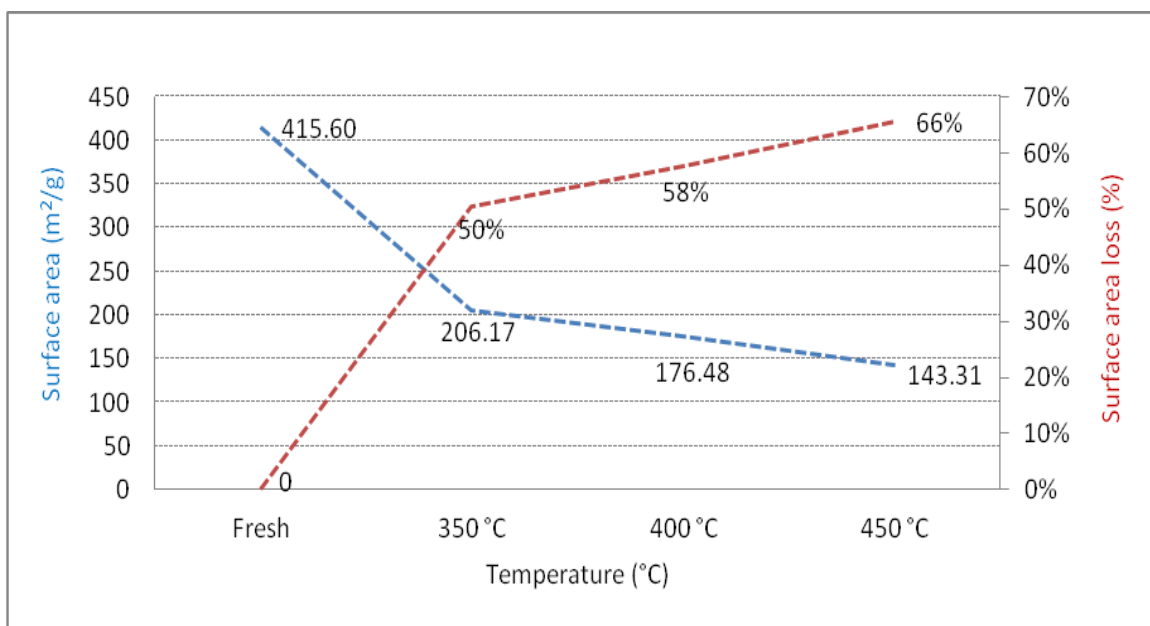

Figure 6.33: Surface Area (m²/g) of fresh Siralox 40 and spent Siralox 40 and surface area loss (%) of fresh Siralox 40 and spent Siralox 40 after reactions at temperatures of 350 °C, 400 °C and 450 °C

6.5   Comparisons of the three catalysts

Conversion of n-hexene

Steady state conversion was obtained as the conversion after 60-80 hours on line. The conversion of *n*-hexene for the different catalysts at the different temperatures (similarly to *1*-butene) showed that ZSM-5 had the highest conversion (between 98% to 100%) as temperature increased. The conversion over Siralox 40 was less than when using ZSM 5. The best performance of Siralox 40 was at 400 °C and 450 °C, compared to the lower conversion observed at 350 °C. Eta alumina had the lowest conversion, which was indicative of Eta alumina's low activity.
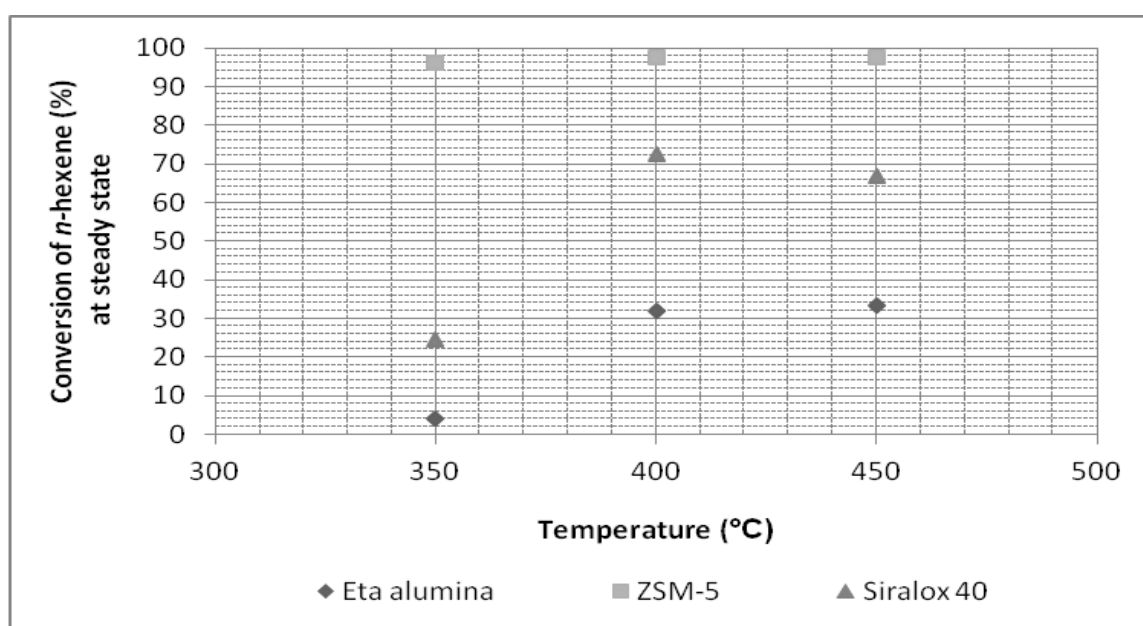

Figure 6.34: Conversion of *n*-hexene (%) at steady state after reactions at temperatures of 350 °C, 400 °C and 450 °C obtained over the three catalysts

Selectivity of n-hexene towards desired products

The main aim of this study was not only to skeletally isomerize *1*-butene to *iso*-butene, but also to do skeletal isomerization of *n*-hexene to its branched isomers. Of the three different catalysts used, Eta alumina, ZSM-5 and Siralox 40, the only two catalysts showing selectivity towards skeletal isomerization in the case of *n*-hexene was Siralox 40 and Eta alumina.

The thermodynamic equilibrium of *n*-hexene and branched C_6 compounds was simulated by Aspen software [Aspen, 2001]. These simulations showed that *n*-hexene could achieve a maximum conversion of approximately 80% at the minimum temperature used in this study (350 °C). The calculated conversion

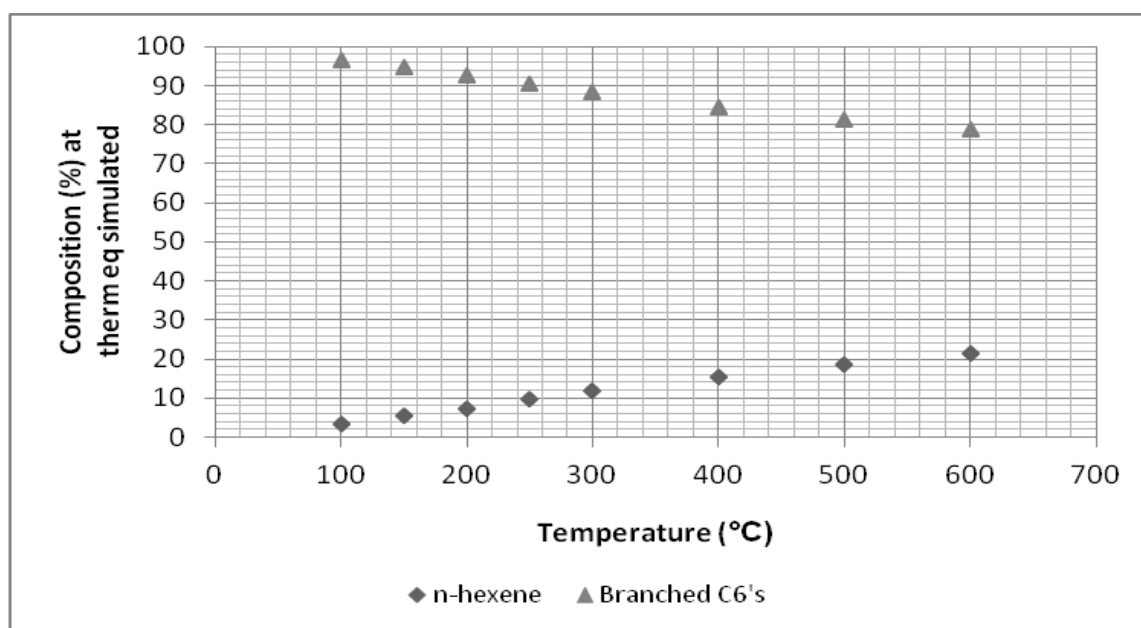decreases slowly as temperature increases as shown in Figure 6.35.

Figure 6.35: Simulation of the composition (%) of *n*-hexene and branched C$_6$ components indicating the maximum conversion that can be reached between temperatures of 100 °C to 600 °C at thermodynamic equilibrium. The maximum amount of branched isomers (%) to be obtained at 350 °C is approximately 80%

Selectivity data of the branched C$_6$ compounds from the experimental runs was taken for each catalyst at steady state (Eta alumina catalyst between 47 and 54 hours on line, ZSM-5 catalyst between 43 and 47 hours on line and Siralox 40 catalyst between 29 and 46 hours on line). Only the three different temperatures at which the experiment was executed were used and compared to the temperatures of the same composition data obtained from simulated thermodynamic equilibrium. This was simulated at temperatures; 300 °C, 400 °C and 500 °C. Comparing this simulated thermodynamic equilibrium data to the runs done in this experiment; it was found that Siralox 40 and Eta alumina catalysts were very active catalysts for skeletal isomerization. Both of these catalysts were also very close to thermodynamic equilibrium. Since Siralox 40 and Eta alumina were the only two catalysts that resulted in amounts of products close to calculated thermodynamic equilibrium conditions, they are the preferred catalysts for skeletal isomerization of *n*-hexene. Should cracking products be the choice, ZSM-5 would be the better of the three catalysts to use. ZSM-5 was the least selective to branched C$_6$ compounds and no skeletal isomerization occurred using ZSM-5 with *n*-hexene.
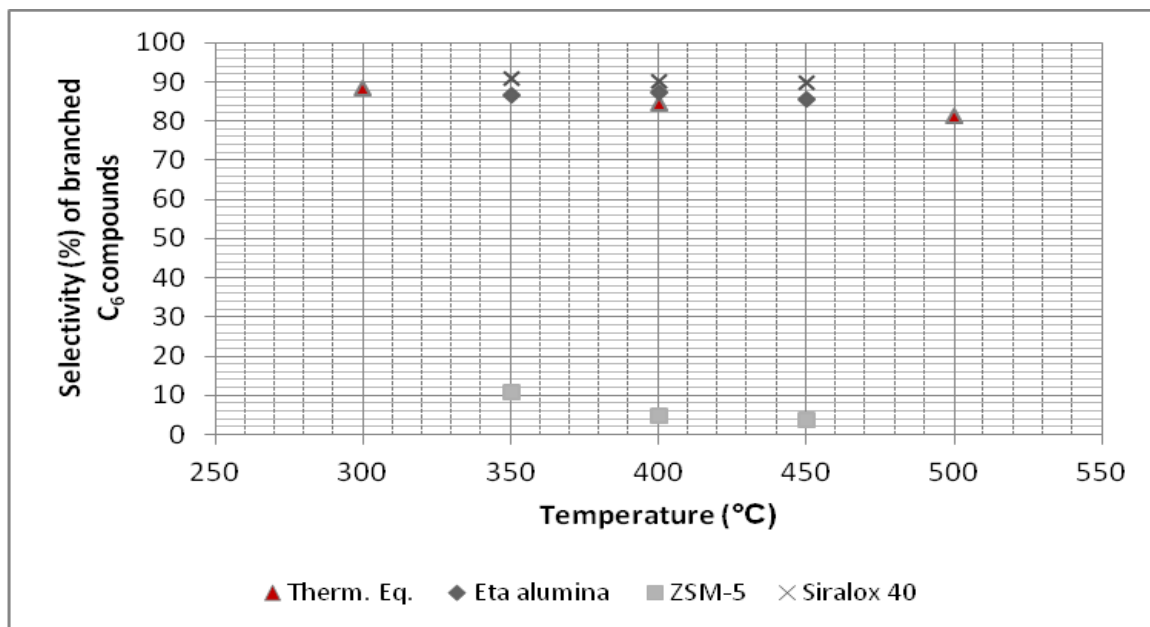
Figure 6.36: Selectivity (%) based on *n*-hexene obtained at steady state for each experimental run over the three catalysts, compared to the simulated thermodynamic composition

Coking of the three catalysts

As presented in Figure 6.37, between the three catalysts tested, Siralox 40 was the catalyst that coked most. This was also the case when *1*-butene was reacted over the Siralox 40 catalyst. The ZSM-5 catalyst also coked as the temperature increased. Eta alumina, however, had a stable coke content between 400 °C and 450 °C (1% and 1.6% respectively), although the coke content at 350 °C was found to be 3.2%.
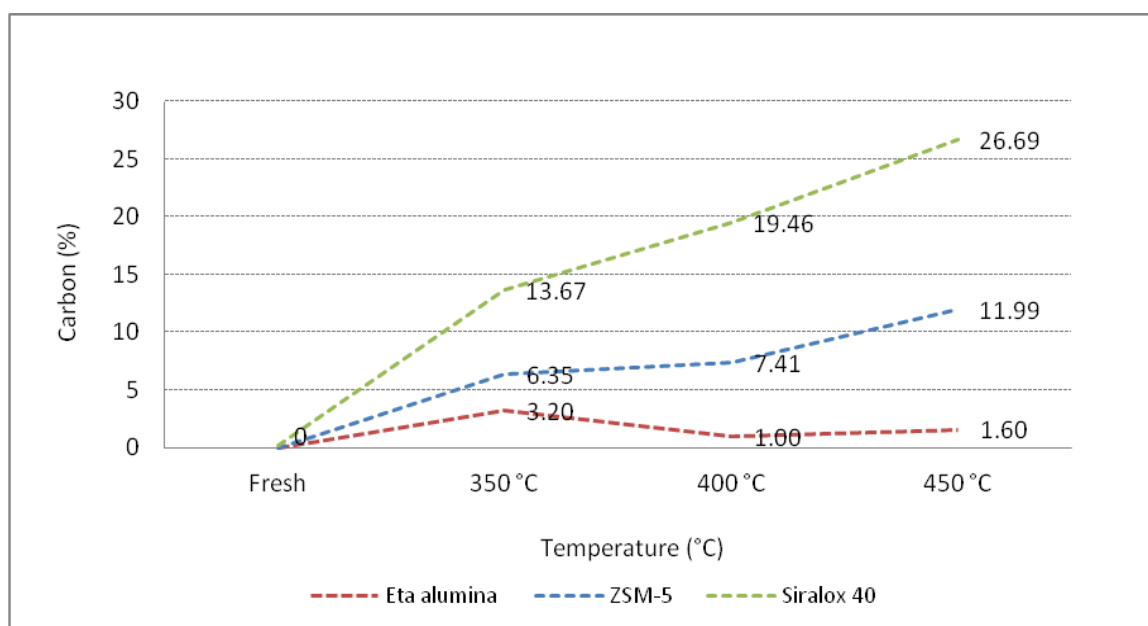

Figure 6.37: Comparison between carbon content (%) of the three fresh and spent catalysts at temperatures of 350 °C, 400 °C and 450 °C

A relation between the formation of coke on the catalyst and the pore volume and surface area of the catalysts can be made. Comparing Figure 6.37 with Figure 6.38 and 6.39, it can be seen that with a small amount of coke formed, no significant difference or change in the surface and pore volume existed. When the amount of coke on the catalyst increased considerably, a decrease in the pore volume and the surface area of the catalysts was observed.
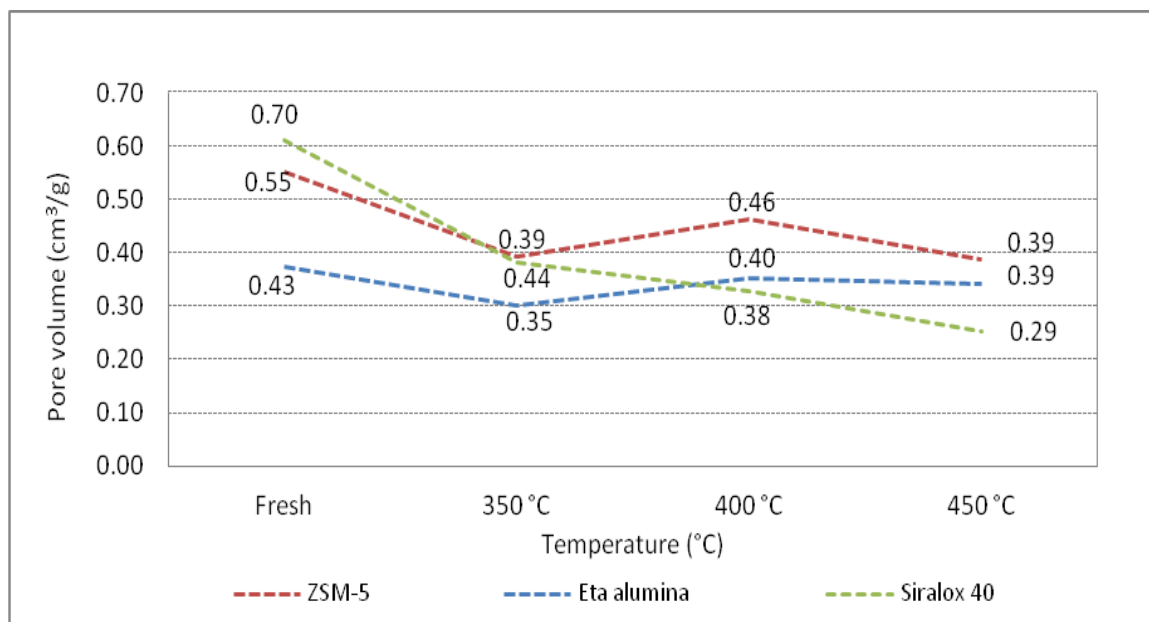

Figure 6.38: Comparison between pore volume (cm^3/g) of three fresh and spent catalysts at temperatures of 350 °C, 400 °C and 450 °C
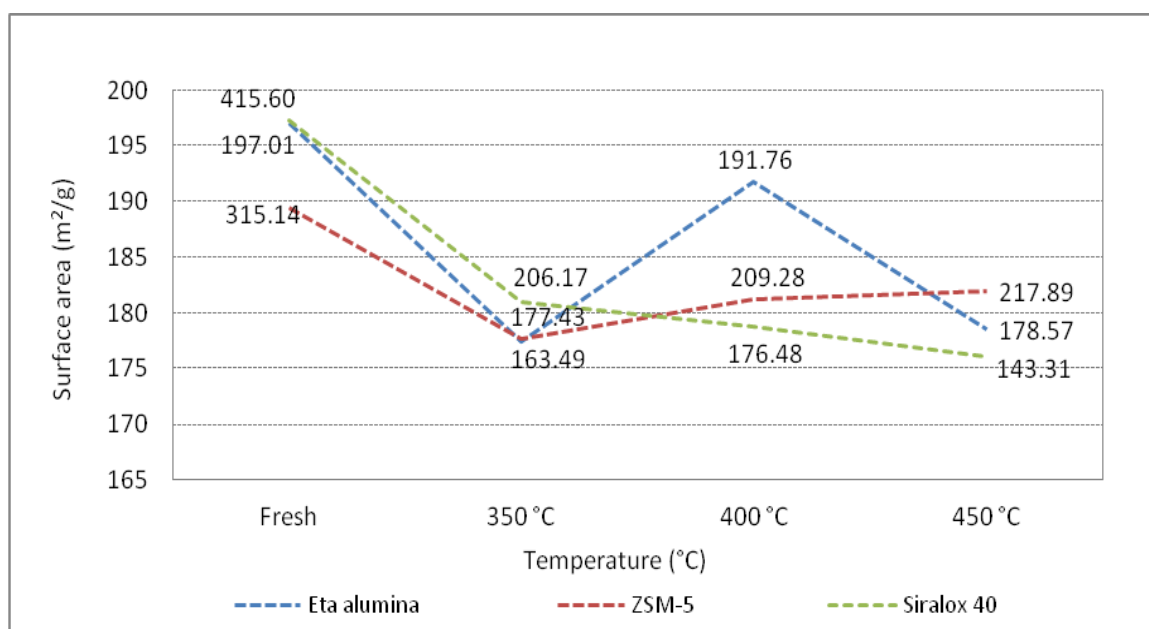

Figure 6.39: Comparison between surface area (m^2/g) of three fresh and spent catalysts at temperatures of 350 °C, 400 °C and 450 °C