

Chapter 5

Results of isomerization of 1-Butene

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

- Explanation of conversion, selectivity, mass balance and steady state;
- Thermodynamic equilibrium;
- Conversion;
- Selectivity;
- Hydrogen transfer;
- Cracking;
- Coking;
- Surface acidity; and lastly the comparison of the three catalysts.

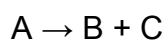
To start with, a short explanation of conversion, selectivity and mass balance calculations is given. The definition of steady state is also given, as these calculations and terms are used throughout the study.

5.1 Conversion, selectivity, mass balances and steady state

Conversion

Conversion means disappearance of the reactants. When a chemical reaction takes place, some portions of the reactants react and get converted to various products [Bartholomew et al., 2006].

Considering the following reaction:



The conversion will then be calculated as follows:

$$\text{Conversion} = \frac{A_{\text{in}} - A_{\text{out}}}{A_{\text{in}}} \times 100$$

with A_{in} the concentration of the feed in, A_{out} the concentration of the feed out and B the concentration of the products that formed.

Selectivity

Multiple reactions take place in the reactor, giving various products. Some products may be desirable while others may be less desirable and some completely undesirable. The selectivity may thus be defined as the conversion of the reactant to the desirable product divided by the overall conversion of the reactant. It may also be stated as the amount of the converted feed that was reacted to the desired product [Bartholomew et al., 2006].

Based on the reaction given, selectivity can be calculated as follows (with similar meaning of the terms):

$$\text{Selectivity} = \frac{B}{A_{in} - A_{out}} \times 100$$

Mass balance

The mass balance concept is set up due to the conservation of mass. Matter can neither be created nor destroyed, but it can be changed in form. The purpose of the mass balance is to show that all mass can be accounted for in the analysis. When liquid and gas phase components can form, the mass balance is given by:

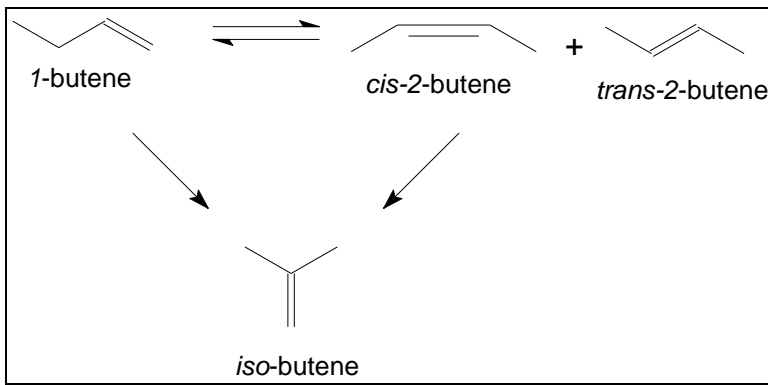
$$\text{Mass balance} = \frac{\text{Liquid product}_{out} + \text{gas}_{out}}{\text{Total feed}_{in}} \times 100$$

Steady state

Steady state is reached in a process when variables such as temperature, concentration and pressure are constant at a defined point in the process [Cornils et al., 2003]

5.2 Thermodynamic equilibrium

The isomerization of *n*-butene involves a simultaneous reversible rearrangement of straight chain butenes to *iso*-butene as well as *cis/trans* rearrangements. This is represented in Scheme 5.1.



Scheme 5.1: Isomerization of butene [Choudhary, 1974]

The thermodynamic equilibrium was simulated between between 1-butene, *cis*-2-butene and *trans*-2-butene (Figure 5.1). 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) property methods [Aspen, 2001].

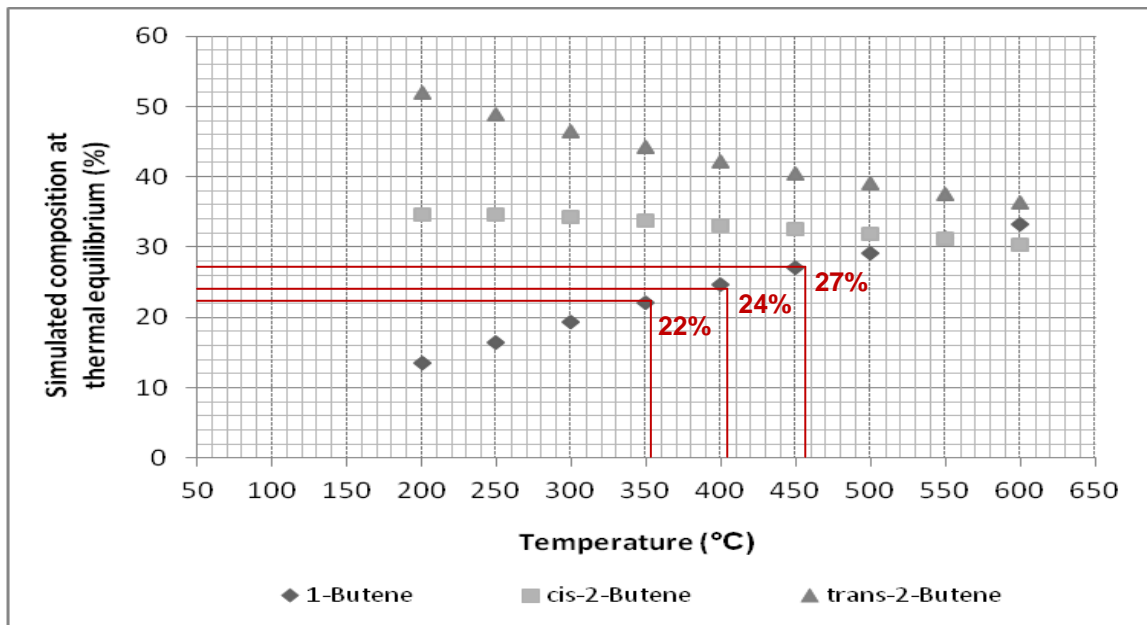


Figure 5.1: Simulation of the composition (%) of 1-butene, *cis*-2-butene and *trans*-2-butene. This indicates the maximum conversion of 1-butene that can be reached at temperatures 350 °C, 400 °C and 450 °C at thermodynamic equilibrium

Figure 5.1, simulating the thermodynamic equilibrium between 1-butene, *cis*-2-butene and *trans*-2-butene, shows that a maximum conversion of 78% at 350 °C, a conversion of 76% at 400 °C and a conversion of 73% at 450 °C can be reached when contacting 1-butene over a catalyst.

5.3 1-Butene reacted with Eta alumina catalyst

Conversion of 1-butene

Comparison of 1-butene conversion over the Eta alumina catalyst indicated that the highest conversion of 1-butene was obtained at the lowest (350 °C) temperature and that the lowest conversion of 1-butene was obtained at the highest temperature of 450 °C (Figure 5.2). Calculations were performed under atmospheric pressure.

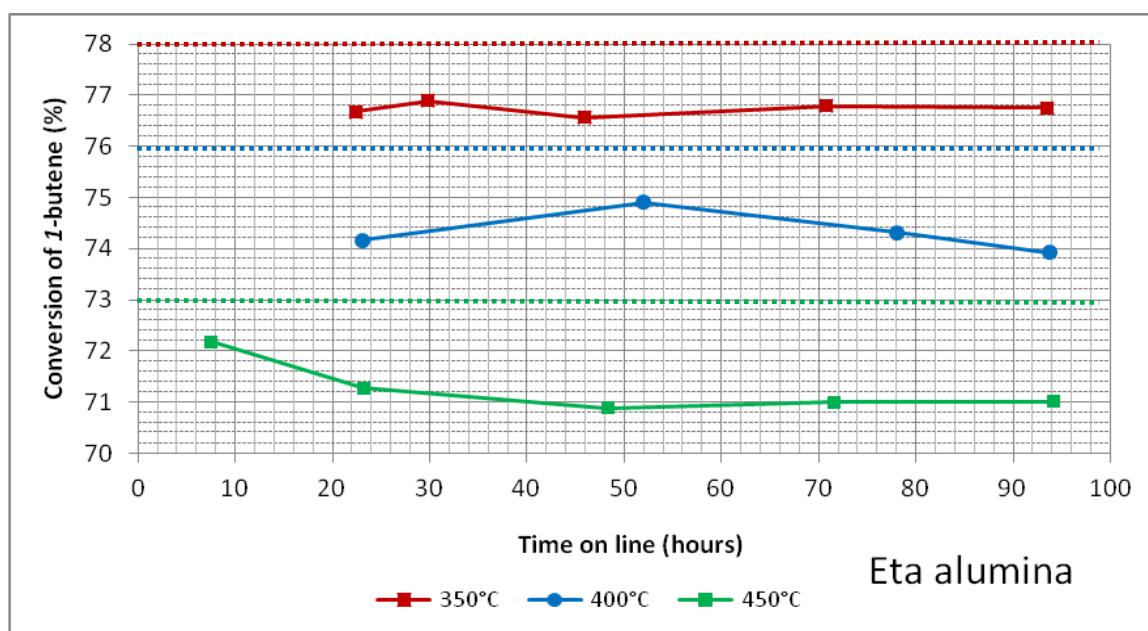


Figure 5.2: Conversion of 1-butene (%) at temperatures of 350 °C, 400 °C and 450 °C using the Eta alumina catalyst, indicating that steady state was obtained. The dotted lines are equilibrium as calculated with PSRK using Aspen software [Section 5.2]

From Figure 5.2, the conversion at all three temperatures reached were $\pm 2\%$ from the maximum thermodynamic conversion values that could be obtained as simulated using Aspen software. From this it was deduced that the reaction of 1-butene over the Eta alumina catalyst had reached thermodynamic equilibrium.

Steady state conversion was obtained as the conversion after 70-78 hours on line (Figure 5.2). Figure 5.3 shows that the 1-butene conversion over Eta alumina declined as the temperature increased which is in correlation with the calculated thermodynamic equilibrium (Figure 5.1) which also decreased as the temperature increased.

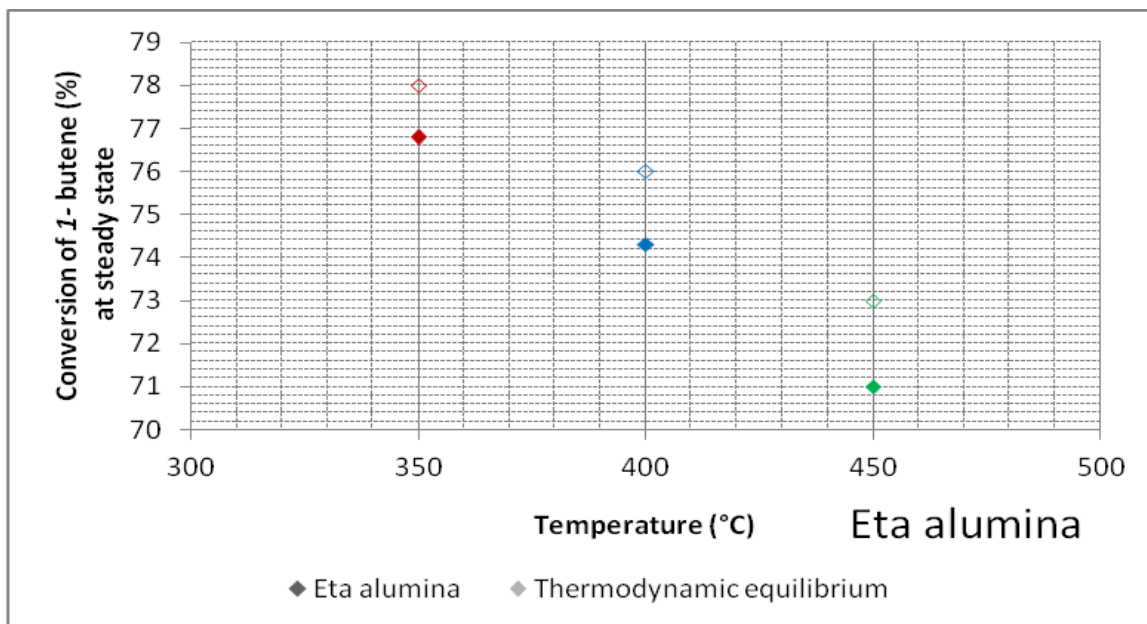


Figure 5.3: Comparison between Eta alumina catalytic conversion of 1-butene (%) at steady state (filled data points) and the calculated thermodynamic equilibrium (open data points) at the temperatures of 350 °C, 400 °C and 450 °C.

Products obtained from conversion of 1-butene over Eta alumina

At temperatures of 350 °C, 400 °C and 450 °C almost no skeletal isomerization of 1-butene to *iso*-butene took place over the Eta alumina catalyst for the whole temperature range evaluated. The highest selectivity was towards *trans*-2-butene, followed by *cis*-2-butene. This indicates a double bond shift, while Eta alumina had very low activity towards skeletal isomerization.

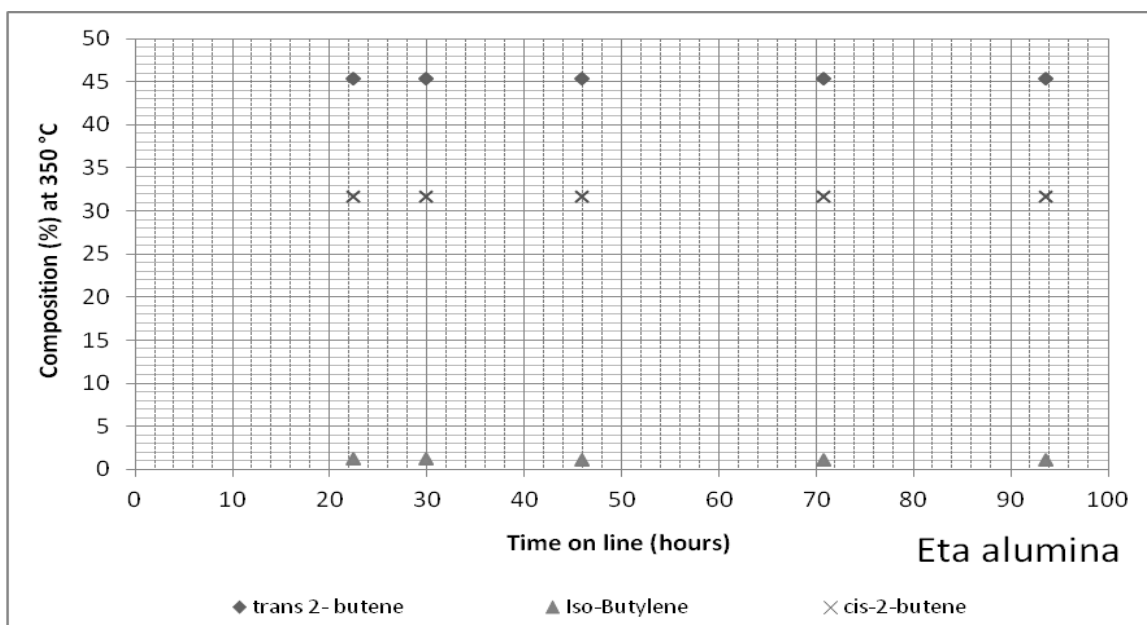


Figure 5.4: Composition (%) of desired products obtained at 350 °C over the Eta alumina catalyst

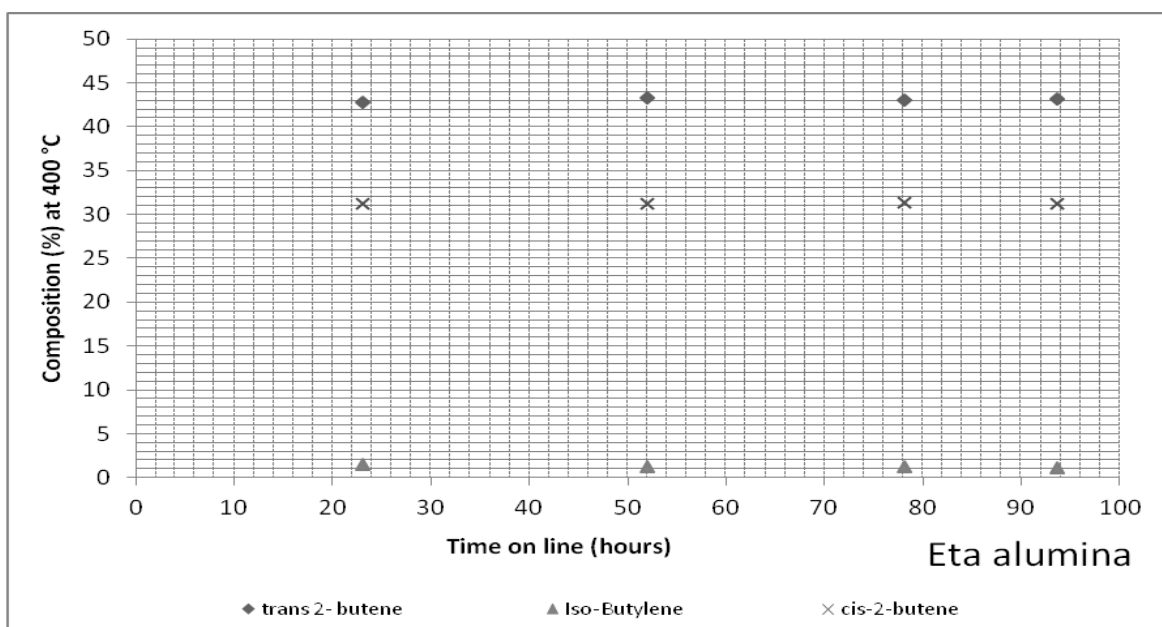


Figure 5.5: Composition (%) of desired products obtained at 400 °C over the Eta alumina catalyst

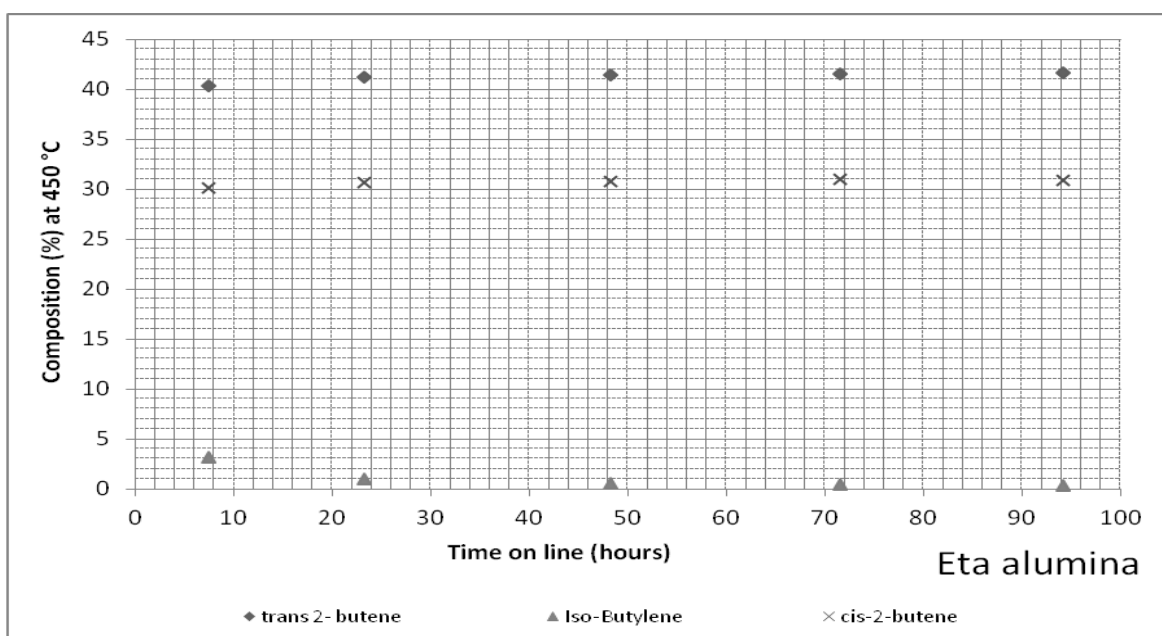


Figure 5.6: Composition (%) of desired products obtained at 450 °C over the Eta alumina catalyst

It seems that the activation energy of the reaction using the Eta alumina catalyst is high in comparison to the activation energy of the compound's double bond shift reaction. Thus, there may be a kinetic advantage for the production of *cis/trans*-2-butene. Since the product of interest is *iso*-butene, it can be concluded that Eta alumina is not a suitable catalyst for the production of *iso*-butene (at very high temperatures, equilibrium is far away from *iso*-butene formation). This is concluded in Section 5.7.

Hydrogen transfer

From the 1-butene that was reacted over the Eta alumina catalyst, butane was obtained which is an indication of hydrogen transfer (Figure 5.7 and Scheme 5.2). Hydrogen transfer from 1-butene to butane occurred to the greatest extent at 400 °C. The least amount of butane was formed at 350 °C.

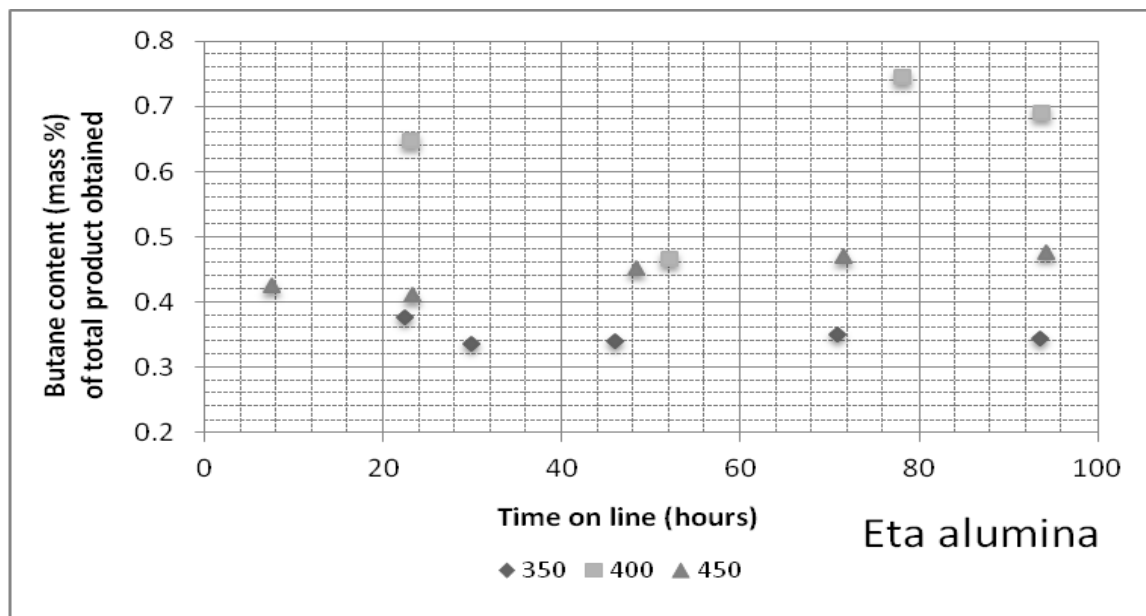
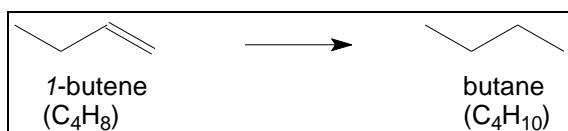


Figure 5.7: Butane content (mass %) of the total product obtained as a function of time on line (hours) at 350 °C, 400 °C and 450 °C over the Eta alumina catalyst. Butane formation is indicative of hydrogen transfer

In view of the reaction of 1-butene to butane as shown in Scheme 5.2, it is clear that two hydrogens are needed to chemically balance the reaction.



Scheme 5.2: Reaction from 1-butene to butane

Three main products that formed which may be responsible for hydrogen transfer are displayed in Figure 5.8. They are propene, butadiene and hydrogen.

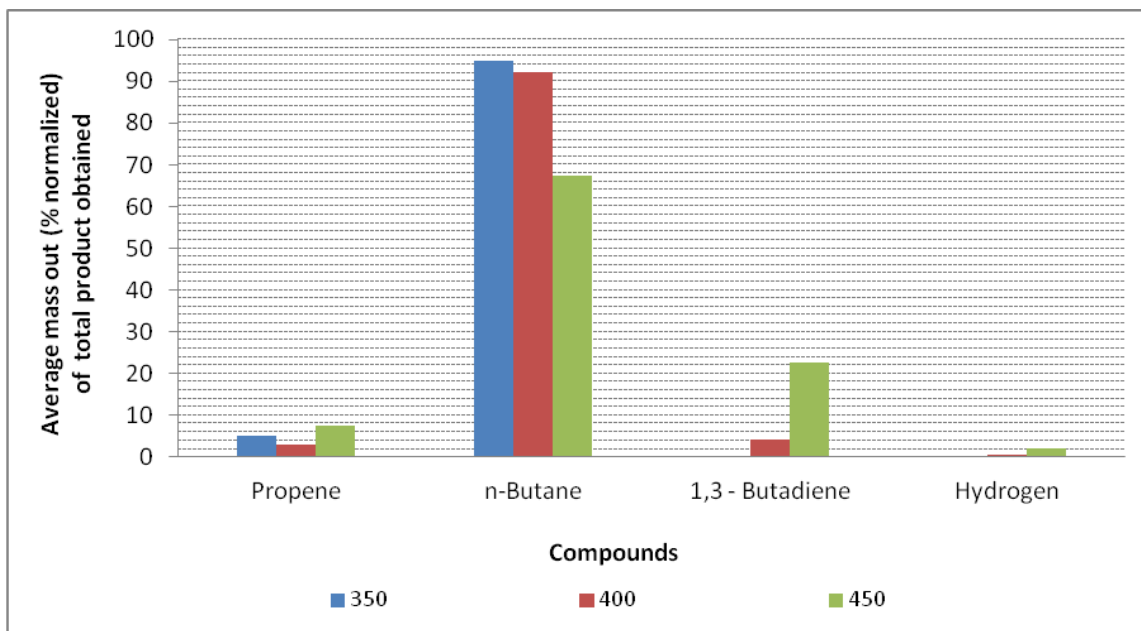
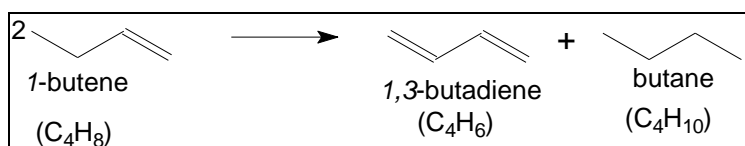
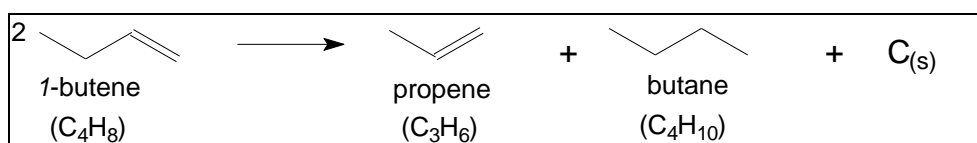


Figure 5.8: Average mass out (% normalized) of total product obtained at 350 °C, 400 °C and 450 °C over the Eta alumina catalyst. Butane formation is indicative of hydrogen transfer

Considering Figure 5.8, it is clear that butane and propene formed at all three temperatures; 300 °C, 400 °C and 450 °C. 1,3-Butadiene formed only at 400 °C and 450 °C. Little hydrogen formed. Taking this into account, the two hydrogens needed may have formed during the next proposed reactions (Schemes 5.3 and 5.4).



Scheme 5.3: Reaction from 1-butene to butane and 1,3-butadiene



Scheme 5.4: Reaction from 1-butene to butane, propene and coke

Scheme 5.3 indicates that for every two 1-butenes that is fed over Eta alumina, one butane molecule and one 1,3-butadiene molecule forms. Considering Figure 5.8 it is possible that this reaction occurs at 400 °C and 450 °C.

Scheme 5.4 illustrates that one propene, one butane and solid carbon is formed when for two 1-butene molecules fed over Eta alumina. The solid carbon that forms is referred to as coke deposited on the Eta alumina catalyst and the largest amount was observed at 450 °C, as can be seen from Figure 5.10.

Cracking

Cracking of 1-butene to propene was also observed. Propene formation is indicative of cracking [Figure 5.9]. Cracking to propene was initially high at 450 °C and then it decreased quickly at 350 °C. The decrease of propene content at 400 °C was similar to the decrease of propene at 450 °C (Figure 5.9).

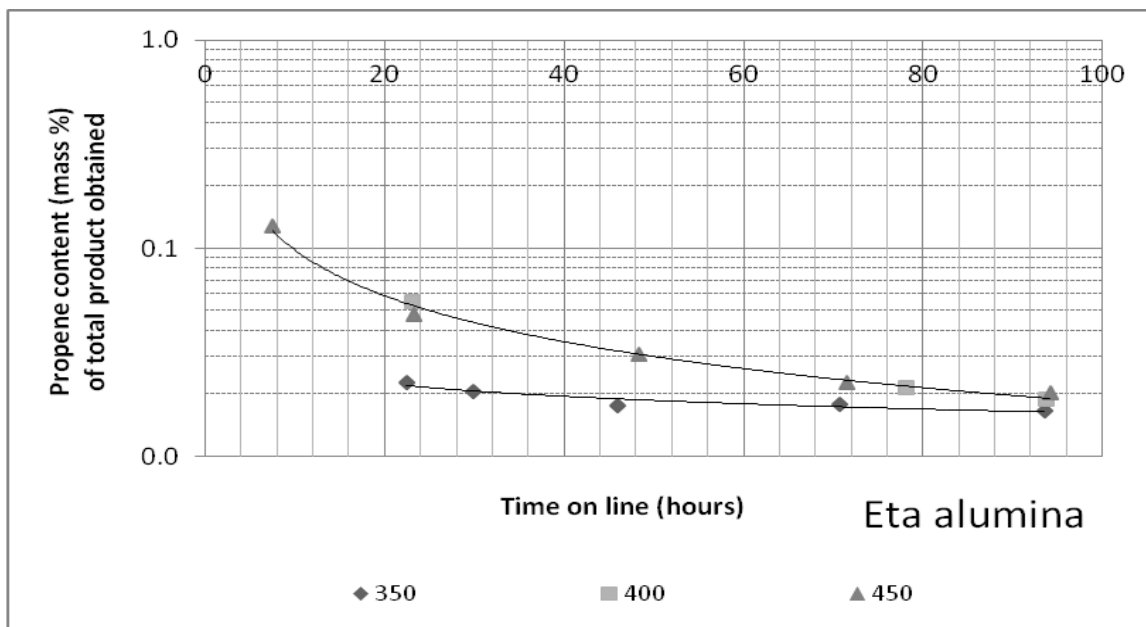
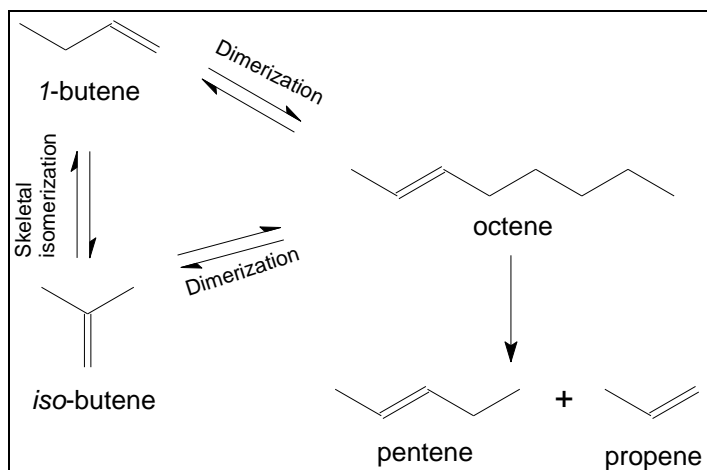


Figure 5.9: Propene content (mass %) as a function of time on line (hours) at 350 °C, 400 °C and 450 °C formed over the Eta alumina catalyst. Propene formation is indicative of cracking

Cracking of 1-butene forms propene and a small amount of methane. However, data shows that more pentene was formed than methane. This suggests that the reaction showed in Scheme 5.5 played a more significant role than direct cracking to propene and methane.



Scheme 5.5: Reaction mechanism for C₄⁻ isomerization

Likewise to what is observed from this study, Ozmen et al. [1993] also stated that two routes are taking place during skeletal isomerization of 1-butene. The one route is known as direct skeletal isomerization where *iso*-butene is formed from 1-butene and the other is the dimerization route, where octene is formed. From this dimerization reaction other olefins may be created in addition to the *iso*-butene. These olefins are pentene and propene which were also observed and correlated to the data obtained when reacting 1-butene over Eta alumina in this study.

Cracking occurs on the acid sites of the catalyst [Bhatia, 1990]. The decrease in cracking rate with time on line signifies that the number of acid sites are decreasing, possibly by coke formation. The most coking took place at 450 °C as shown in Figure 5.10.

Coking of the Eta alumina catalyst

Figure 5.10, 5.11 and 5.12 are comparisons of the results obtained from the fresh catalyst to the spent catalyst which was reacted over 1-butene at different temperatures. At 450 °C, the fixed carbon content was 6.3%, which shows that coking occurred to the greatest extent at the highest temperature, whilst very little coking occurred at the lower temperatures of 350 °C and 400 °C.

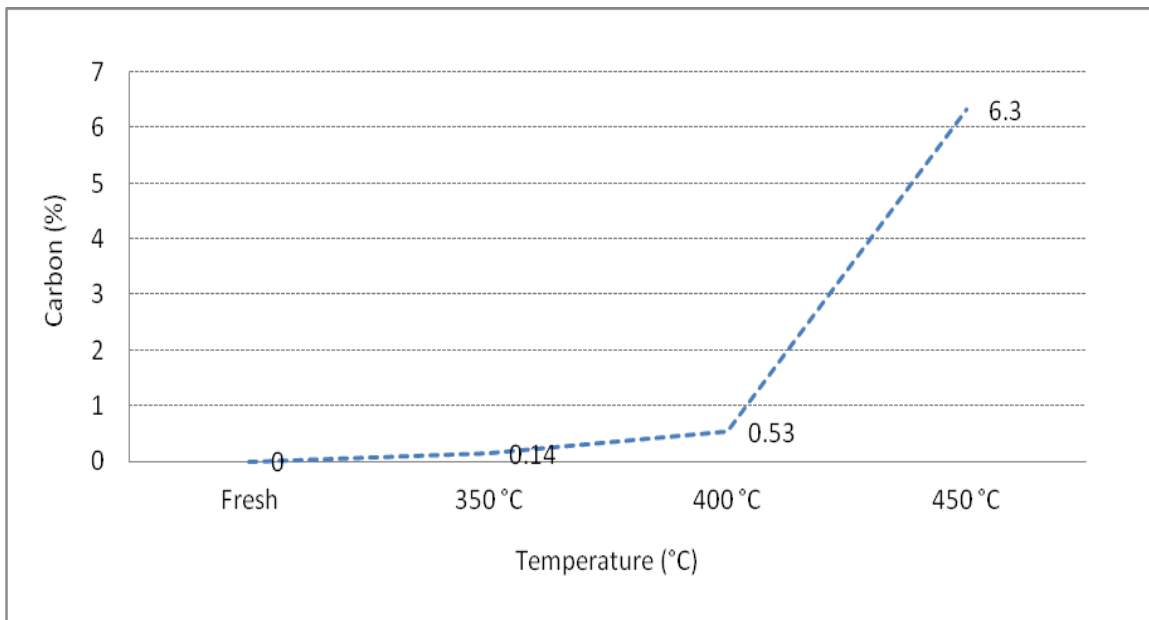


Figure 5.10: Carbon (%) of fresh Eta alumina and spent Eta alumina after reactions at temperatures of 350 °C, 400 °C and 450 °C

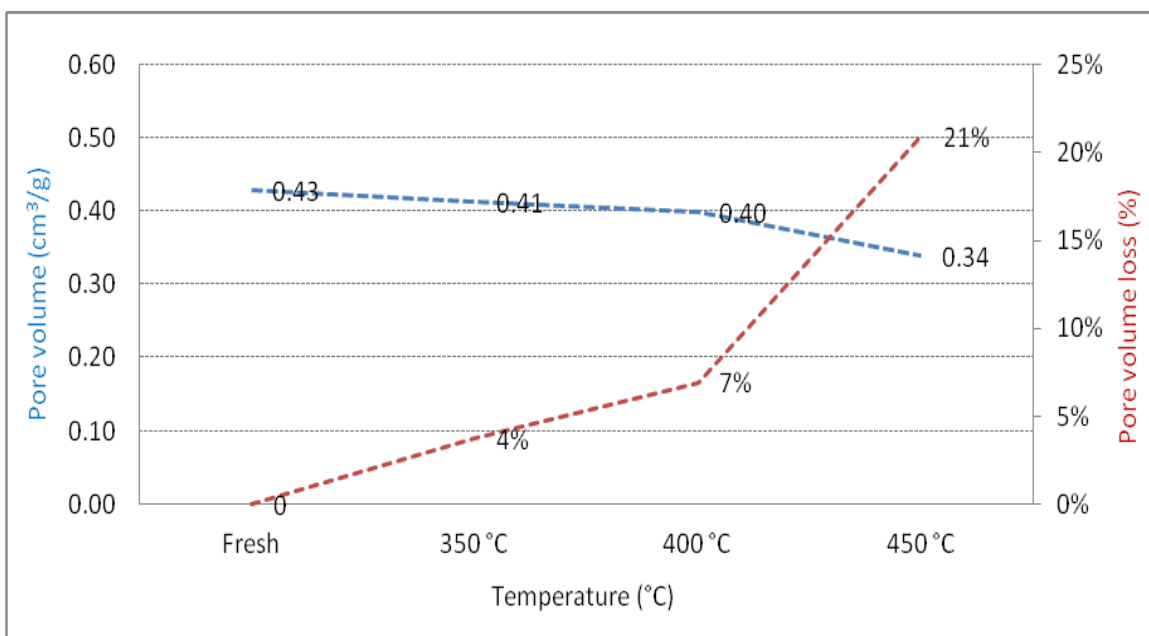


Figure 5.11: Pore volume (cm³/g) of fresh Eta alumina and spent Eta alumina and pore volume loss (%) of fresh Eta alumina and spent Eta alumina after reactions at temperatures of 350 °C, 400 °C and 450 °C

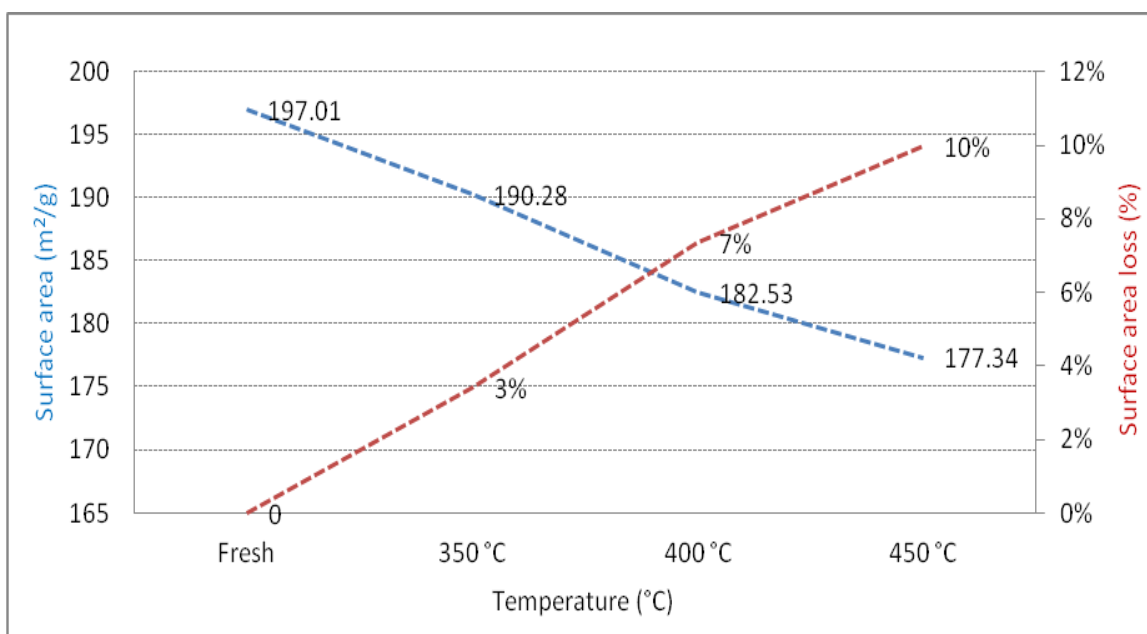


Figure 5.12: Surface area (m²/g) of fresh Eta alumina and spent Eta alumina and surface area loss (%) of fresh Eta alumina and spent Eta alumina after reactions at temperatures of 350 °C, 400 °C and 450 °C

Both Figure 5.11 and 5.12 indicate that with an increase in temperature the pore volume of the catalyst decreased and the surface area of the catalyst decreased. For the reaction performed at 450 °C, the catalyst lost 21% of its pore volume and 10% of its surface area which might be due to the high amount of coke being formed (Figure 5.10).

5.4 1-Butene reacted with ZSM-5 catalyst

Conversion of 1-butene

The conversion versus reaction time on line (Figure 5.13) for the ZSM-5 catalyst reveals that most of the 1-butene was converted at 400 °C. The least amount of 1-butene was converted at the lowest temperature of 350 °C, which is contradictory to the behaviour of 1-butene over the Eta alumina catalyst (Figure 5.2). Conversion of 1-butene was between 97% to 100% at all three temperatures.

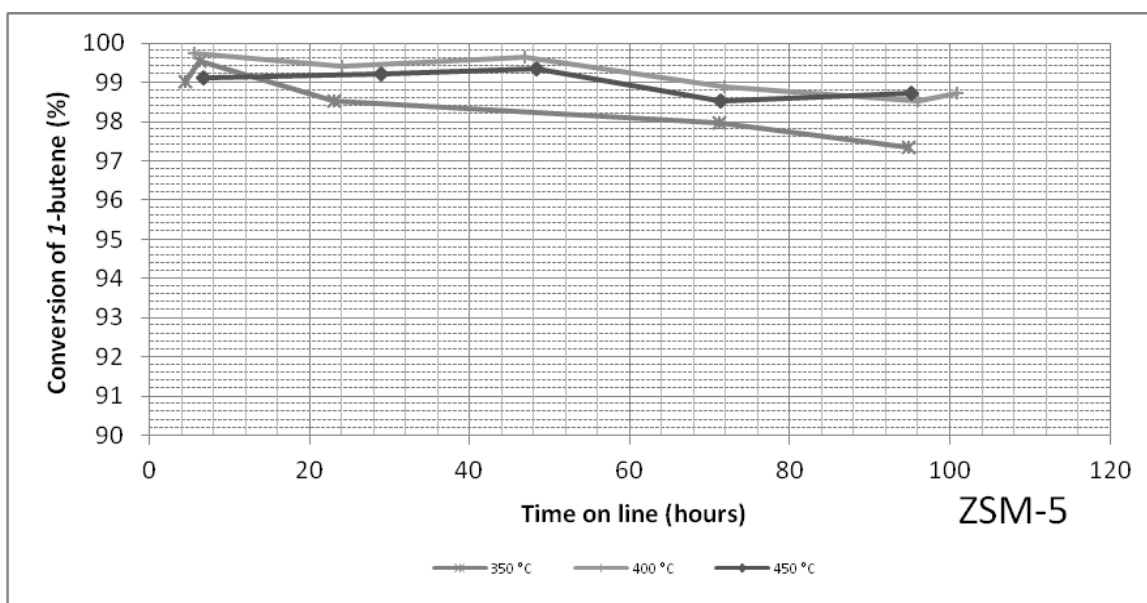
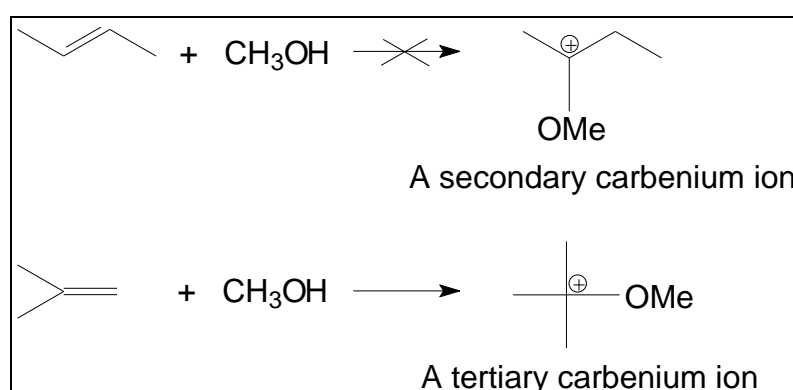


Figure 5.13: Conversion of 1-butene (%) after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the ZSM-5 catalyst

Conversion of *n*-butene

The conversion and selectivity were not only calculated for 1-butene, but also for *n*-butene (sum of 1-, *trans*-2- and *cis*-2-butene). The latter is a more realistic representation of the process.

In Chapter 1 (Section 1.1), the production of ethers by reacting the *iso*-olefin with methanol was discussed. The *iso*-olefins can serve as a feedstock to produce ethers. The formation of *iso*-butene can form via a few proposed mechanisms as discussed in Chapter 2 (Section 2.5.3). However, from Section 2.5.1 (Chapter 2) it is clear that carbocations play an important role in these mechanisms. Carbocations' stabilities increase in such a way that a tertiary carbenium ion is more stable than a secondary or primary carbenium ion [Chapter 2, Section 2.5.1]. Therefore, reacting the secondary butene with methanol will form a less stable ether than the reaction of the *iso*-butene with methanol which results in a carbenium cation, the more stable ether (OMe).



Scheme 5.6: Formation of ether as a secondary and tertiary carbenium ion [de Klerk, 2008]

The conversion versus time on line (Figure 5.14) using the ZSM-5 catalyst reveals that most of the *n*-butene is converted at 400 °C and 450 °C. The least amount of *n*-butene is converted at the lowest temperature (350 °C). Conversion of *n*-butene was between 88% to 98% at all three temperatures and a similar trend to that for 1-butene was observed.

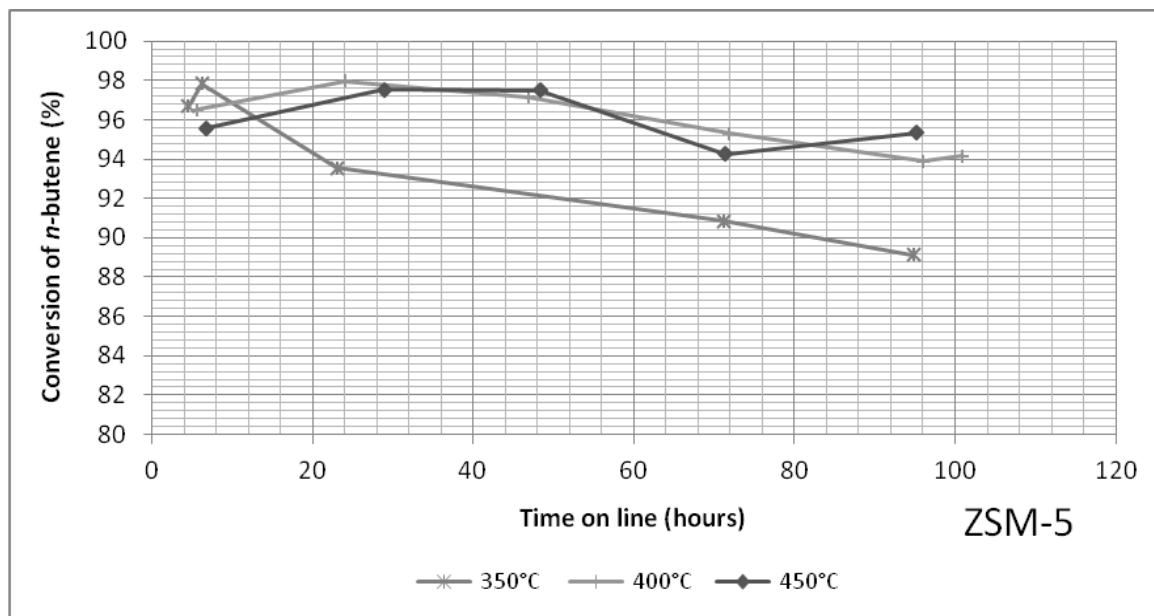


Figure 5.14: Conversion of *n*-butene (%) after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the ZSM-5 catalyst

Steady state conversion of 1-butene and *n*-butene was obtained after 71-72 hours on line (Figure 5.14). Figure 5.15 shows that the 1-butene and *n*-butene conversion at steady state over ZSM-5 first increased and then decreased slightly. The conversion of 1-butene was more or less at 98% for all three temperatures, whereas the conversion of *n*-butene started at 90% and reached 94% with an increase in temperature. This does not correlate with the thermodynamic equilibrium of 1-butene (Figure 5.2), which decreases as the temperature increases (Figure 5.15).

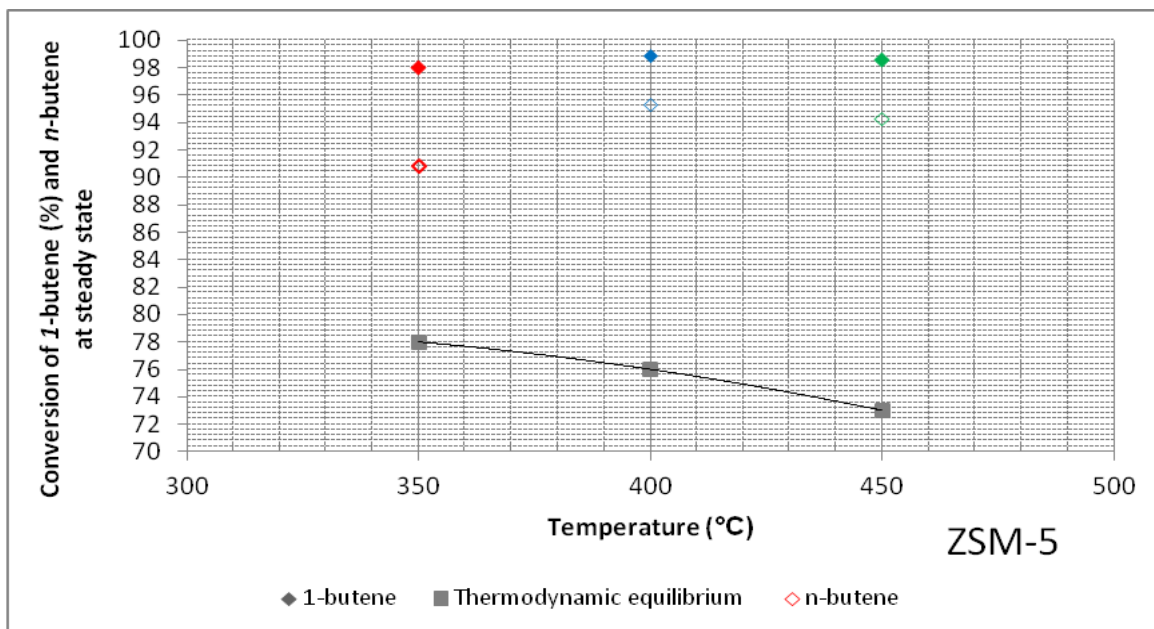


Figure 5.15: Conversion of 1-butene (%) and *n*-butene at steady state after reactions at temperatures of 350 °C, 400 °C and 450 °C obtained over the ZSM-5 catalyst. The conversion is compared to the thermodynamic equilibrium data obtained from Figure 5.1

The conversion of 1-butene is much higher than the thermodynamic equilibrium for a reaction system where only butene isomerization takes place. This shows that side reactions took place. A major side-product that formed was C_5^+ compounds as shown in Figure 5.16.

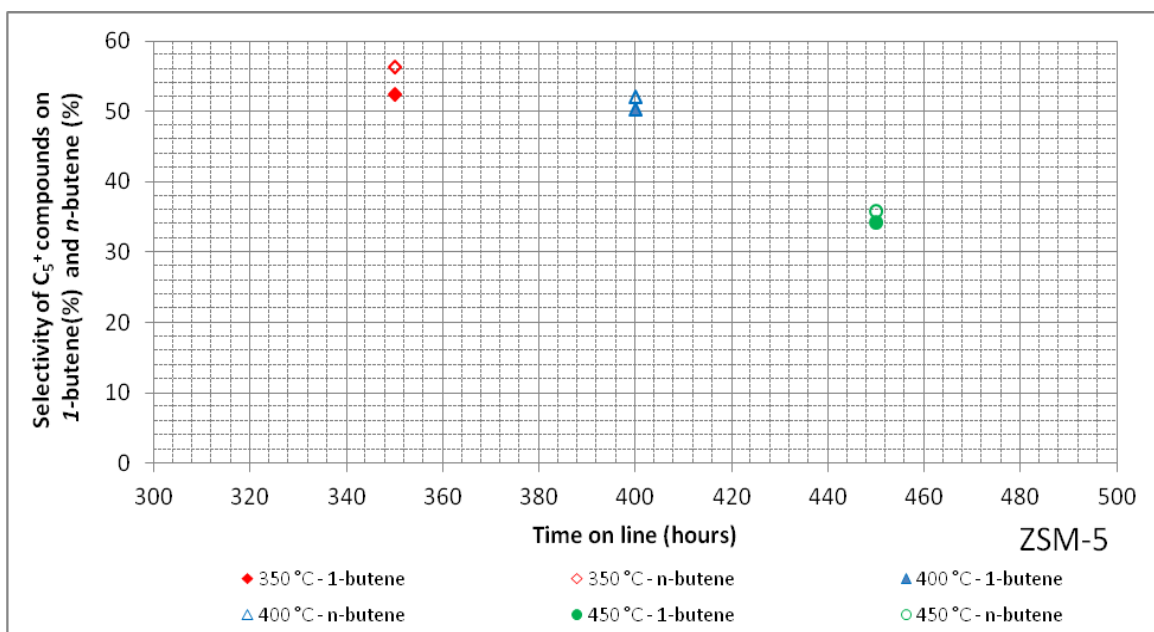
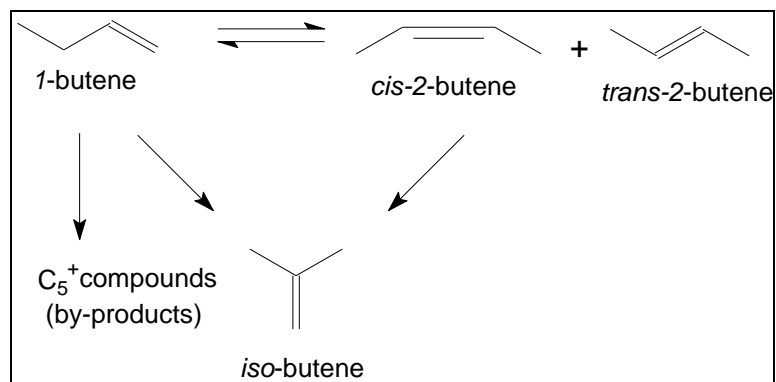


Figure 5.16: Selectivity of C_5^+ compounds on 1-butene (%) and *n*-butene (%) after reactions at temperatures of 350 °C, 400 °C and 450 °C obtained over the ZSM-5 catalyst

From Figure 5.16 it is observed that approximately 35% to 55% of C_5^+ compounds form with the reaction of butene over ZSM-5. It can also be observed that the selectivities of C_5^+ compounds during the reaction of 1-butene and *n*-butene are very similar.

A Scheme is proposed (Scheme 5.7) indicating that, in addition to the formation of the *iso*-olefin (Scheme 5.1), C_5^+ compounds (by-products) formed which is the reason for the conversion of butene being higher than the conversion at the thermodynamic equilibrium (Figure 5.15).



Scheme 5.7: Isomerization of butene and formation of C_5^+ compounds

Selectivity of butene towards desired products

Comparing the reaction of 1-butene and *n*-butene using the ZSM-5 catalyst, no significant difference occurred when considering Figures 5.17 and 5.18. In both cases, 350 °C was the most effective temperature for skeletal isomerization to *iso*-butene of the three temperatures. The selectivity to *iso*-butene increased with time and at approximately 100 hours between 14% and 16% of *iso*-butene was formed based on 1-butene and/or *n*-butene as feedstock. At 400 °C and 450 °C the selectivity towards *iso*-butene was much lower than at 350 °C.

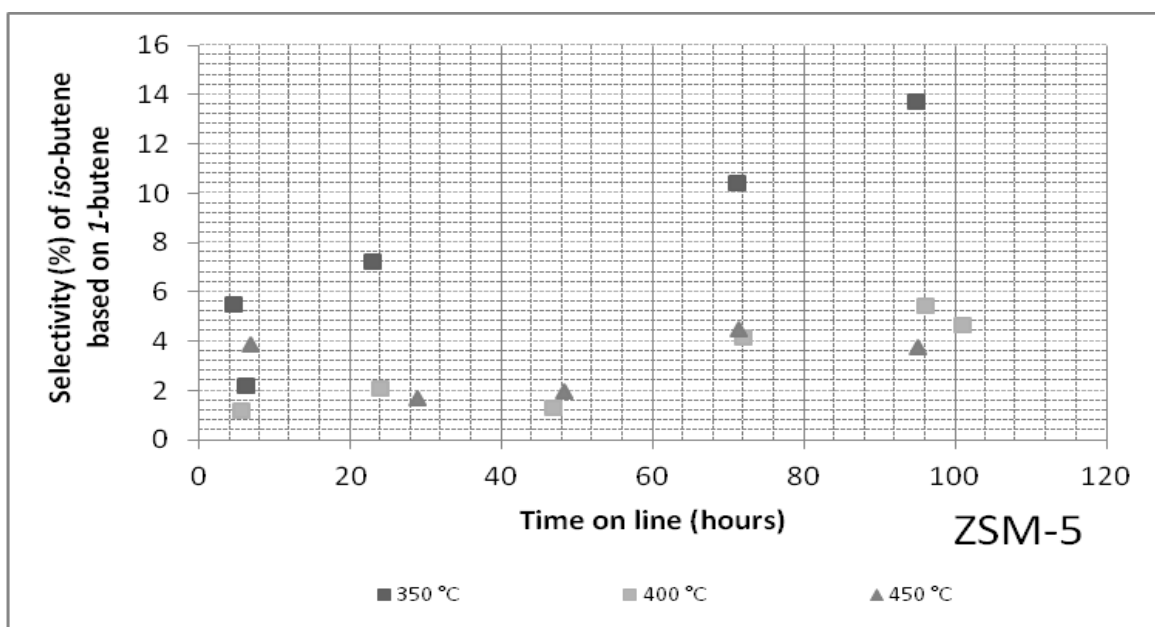


Figure 5.17: Selectivity (%) of *iso*-butene based on *1*-butene at 350 °C, 400 °C and 450 °C over the ZSM-5 catalyst

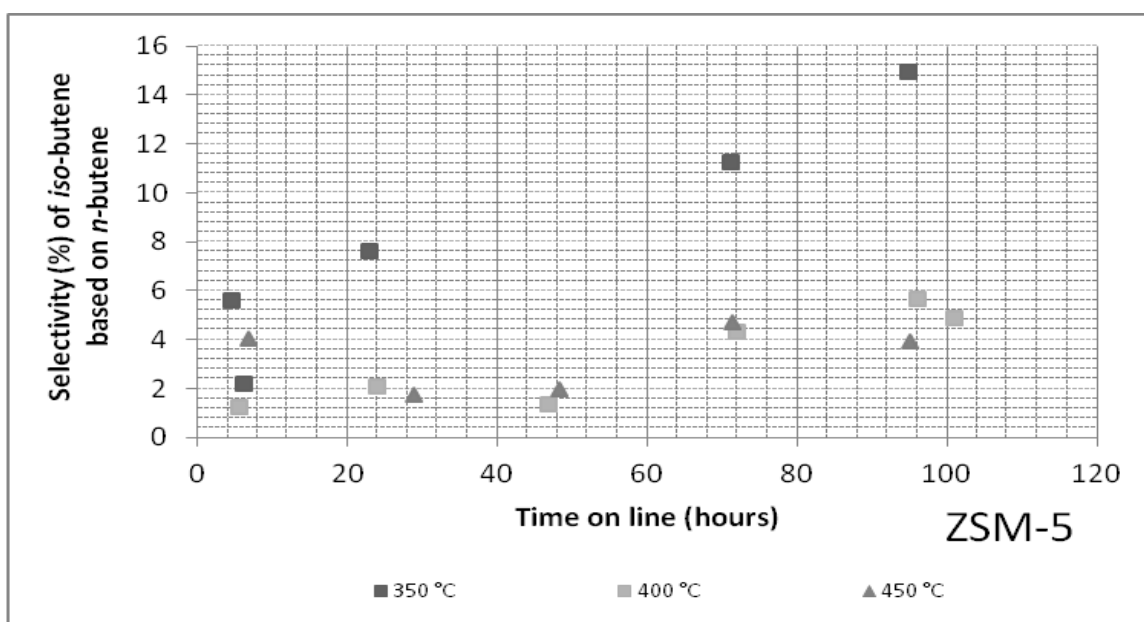


Figure 5.18: Selectivity (%) of *iso*-butene based on *n*-butene at 350 °C, 400 °C and 450 °C over the ZSM-5 catalyst

Figures 5.19, 5.20 and 5.21 summarize the selectivities of *cis*-2-butene, *trans*-2-butene and *iso*-butene when based on *1*-butene at temperatures of 350 °C, 400 °C and 450 °C. At 350 °C and 400 °C the selectivity to *iso*-butene increases and at 450 °C it remains between 2% and 5% for the time on line. *Trans*-2-butene follows the same trend as *iso*-butene whereas *cis*-2-butene shows an increase in selectivity at 350 °C and then no further change occurs at 400 °C and 450 °C. The formation of *cis*-2-butene and *trans*-2-butene is indicative of reactions involving double bond shifts, but in the reaction of *1*-butene over ZSM-5, much less of these products are formed than for Eta alumina.

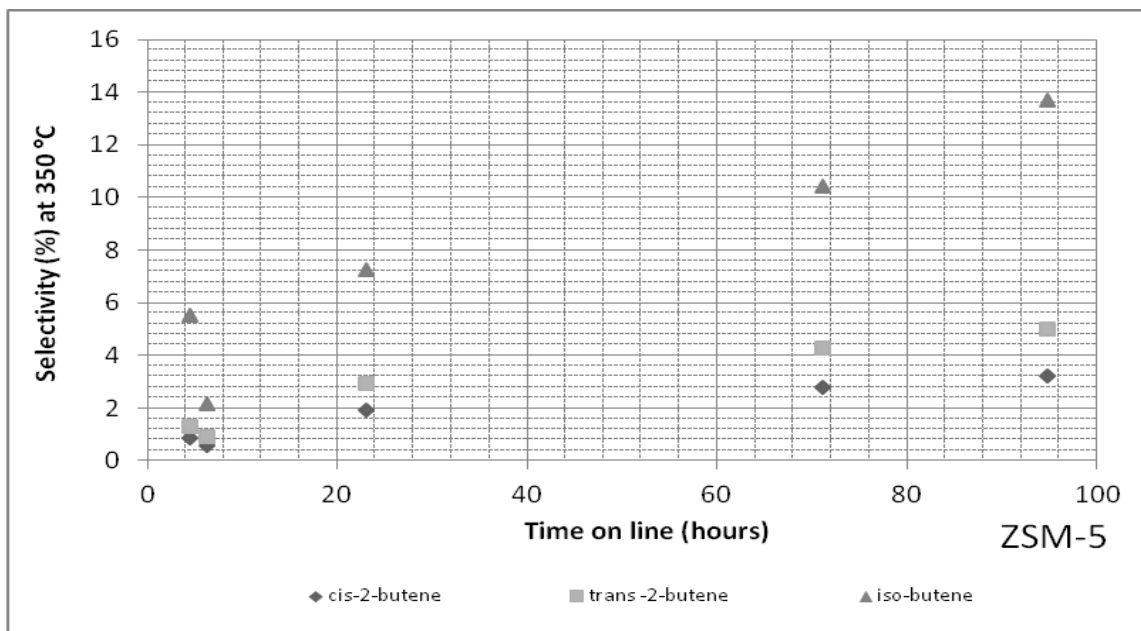


Figure 5.19: Selectivity (%) of *cis*-2-butene, *trans*-2-butene and *iso*-butene based on 1-butene at 350 °C over the ZSM-5 catalyst

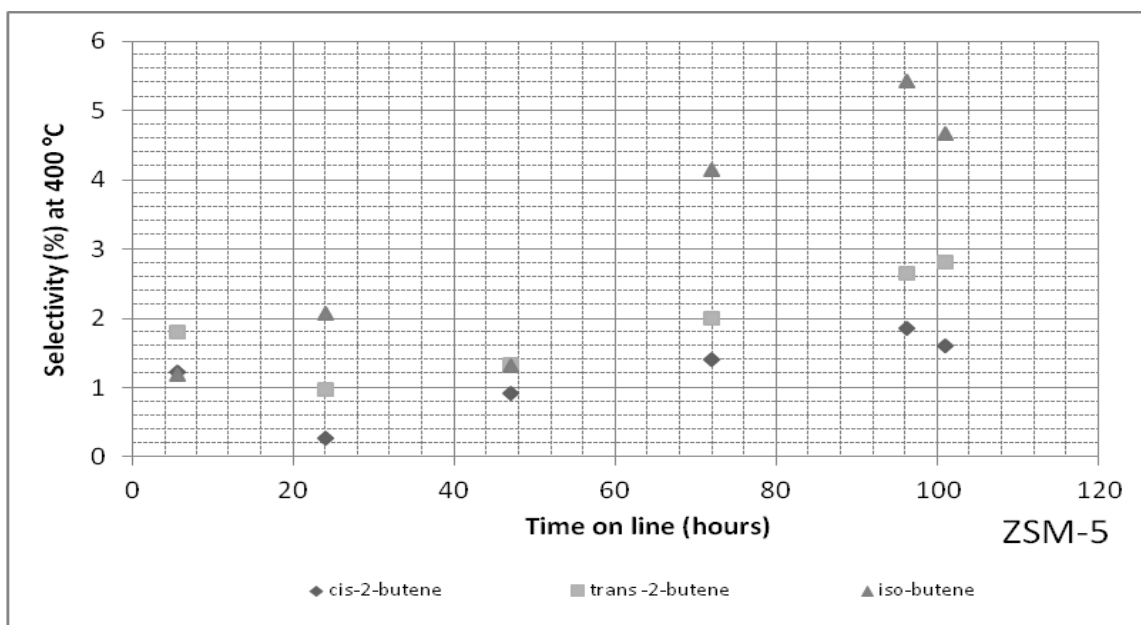


Figure 5.20: Selectivity (%) of *cis*-2-butene, *trans*-2-butene and *iso*-butene based on 1-butene at 400 °C over the ZSM-5 catalyst

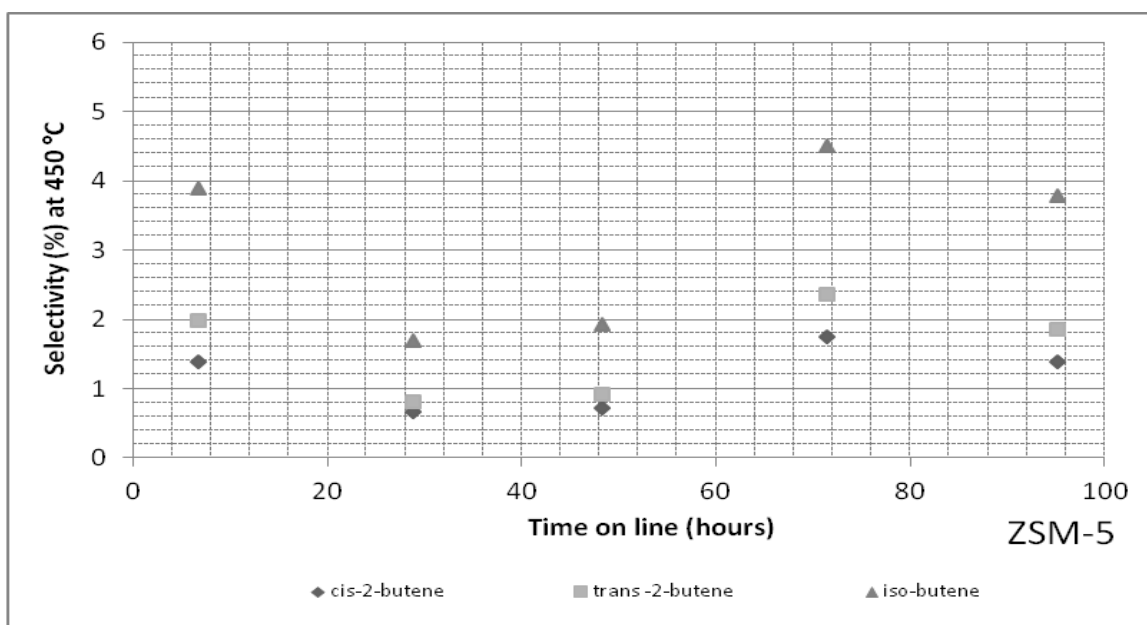


Figure 5.21: Selectivity (%) of *cis*-2-butene, *trans*-2-butene and *iso*-butene based on 1-butene at 450 °C over the ZSM-5 catalyst

Hydrogen transfer

A hydrogen transfer step in the reaction was observed with the conversion of 1-butene. Butane was formed and similar to the Eta alumina catalyst, most butane formed at a temperature of 400 °C. As indicated previously, butane formation is indicative of hydrogen transfer.

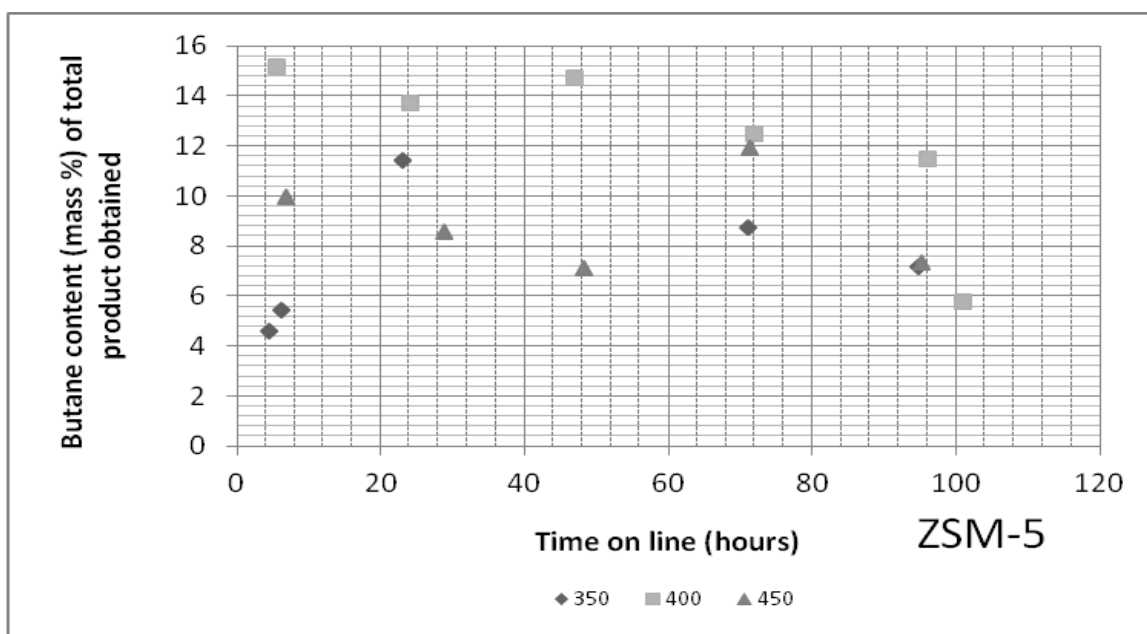


Figure 5.22: Butane content (mass %) as a function of time on line (hours) at temperatures of 350 °C, 400 °C and 450 °C over the ZSM-5 catalyst

The products most probably responsible for hydrogen transfer are displayed in Figure 5.23. From Figure 5.23 it follows that little or no methane, 1,3-butadiene and hydrogen formed during the reaction of 1-butene over ZSM-5.

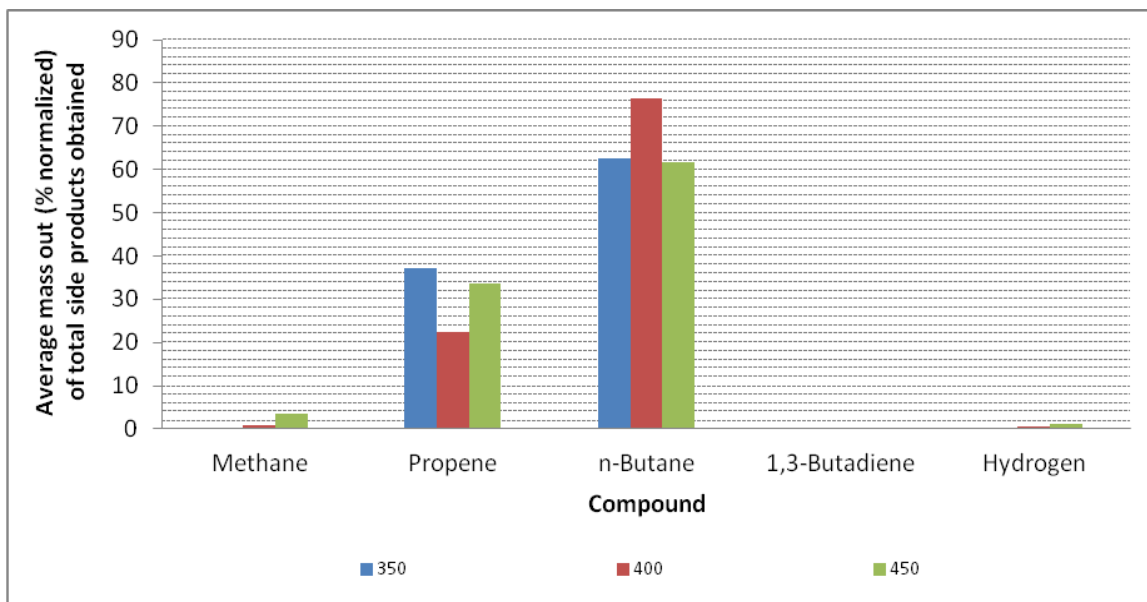
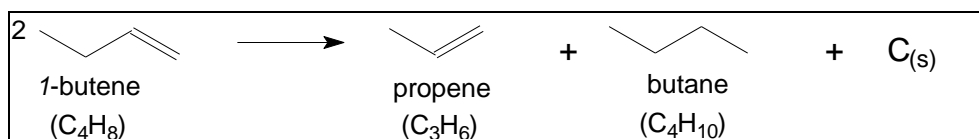


Figure 5.23: Average mass percentage in terms (% normalized) of total side products obtained at temperatures of 350 °C, 400 °C and 450 °C over the ZSM-5 catalyst

Since propene is the most abundant product it again seems that the reaction will follow the following route:



Scheme 5.8: Reaction from 1-butene to butane

Cracking

Cracking of 1-butene to form propene increases with time using the ZSM-5 catalyst. The amount of cracking products was largest at 350 °C, thereafter at 450 °C, while the least cracking products were formed at 400 °C. This is different than was the case with Eta alumina as catalyst.

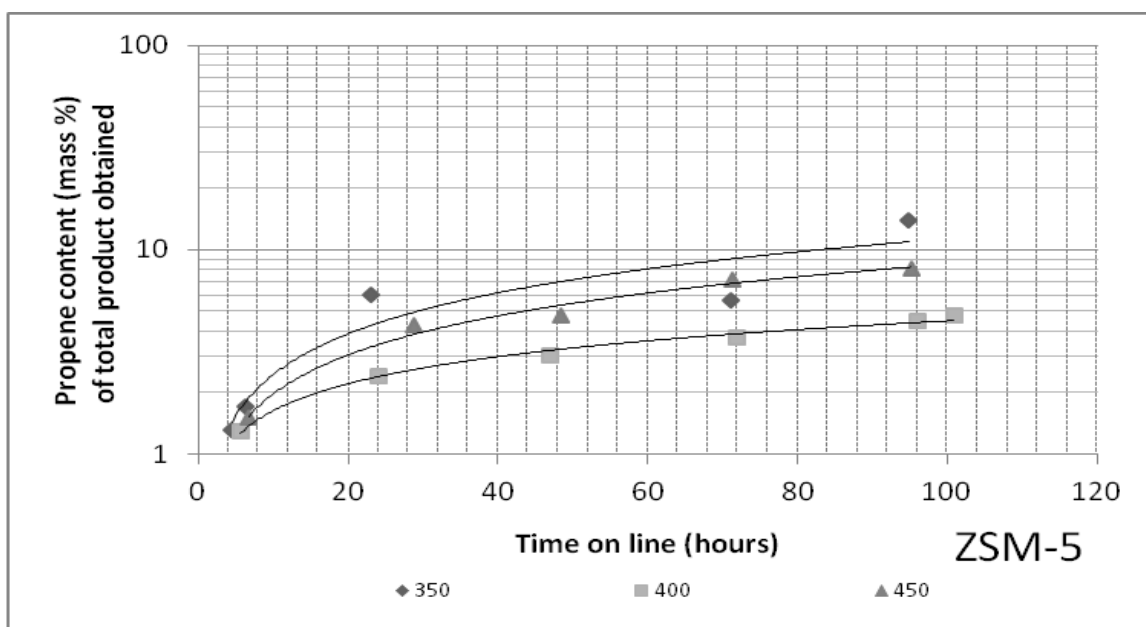


Figure 5.24: Propene content (mass %) of the total product obtained as a function of time on line (hours) at 350 °C, 400 °C and 450 °C over the ZSM-5 catalyst

The increase in percentage cracking to propene at 350 °C (Figure 5.24) indicates that less coke formed at 350 °C (Figure 5.25), allowing more cracking to occur on the unblocked acid sites. This behaviour is different from the results using the Eta alumina catalyst (Figure 5.9).

Coking of the ZSM-5 catalyst

The carbon content on the catalyst indicates that coking of the spent ZSM-5 catalyst started at 350 °C and increased with temperature, as shown in Figure 5.25.

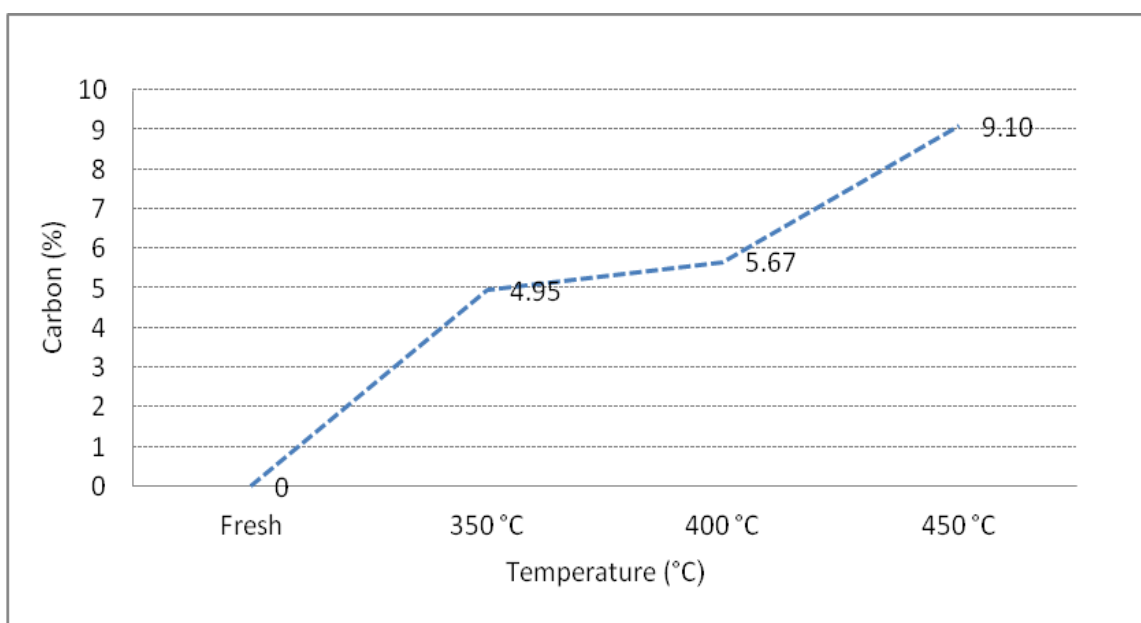


Figure 5.25: Carbon (%) of fresh ZSM-5 and spent ZSM-5 after reactions at temperatures of 350 °C, 400 °C and 450 °C

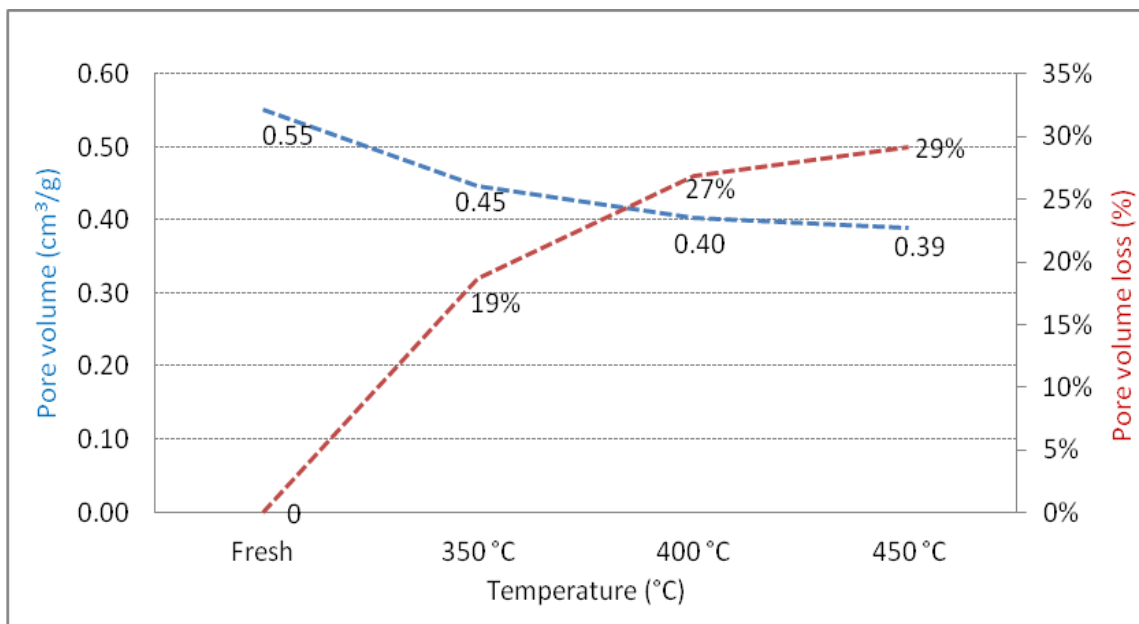


Figure 5.26: Pore volume (cm³/g) of fresh ZSM-5 and spent ZSM-5 and pore volume loss (%) of fresh ZSM-5 and spent ZSM-5 after reactions at temperatures of 350 °C, 400 °C and 450 °C

Although the coke formation increases with an increase in temperature, the pore volume stabilises. This indicates that the pores of the ZSM-5 catalyst seem not to be blocked further. A maximum of 29% loss was observed at 450 °C (Figure 5.26).

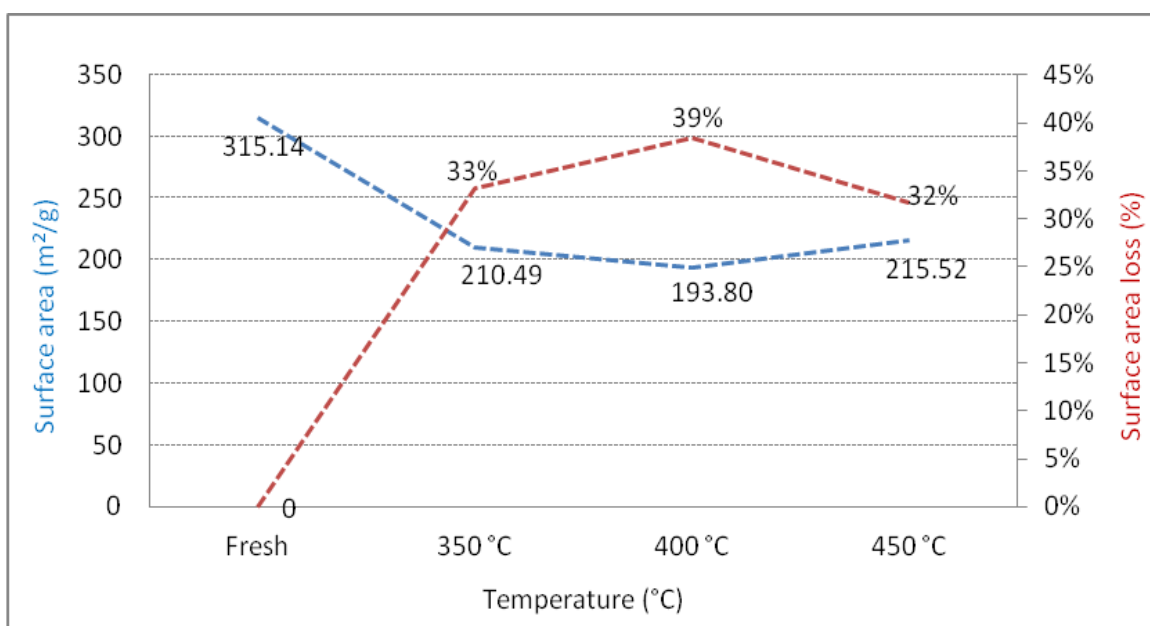


Figure 5.27: Surface area (m²/g) of fresh ZSM-5 and spent ZSM-5 and surface area loss (%) of fresh ZSM-5 and spent ZSM-5 after reactions at temperatures of 350 °C, 400 °C and 450 °C

The surface area also shows small differences between the temperatures and stabilises similarly to the pore volume. Figure 5.27 indicates that, with an increase in temperature, the surface area of the catalyst does not change

significantly and at 450 °C, the catalyst lost 32% of its surface area, possibly due to coking (Figure 5.25).

5.5 1-Butene reacted with Siralox 40 catalyst

Conversion of 1-butene

The conversion of 1-butene was quite stable between 70% and 80% for all three runs. The run performed at 350 °C showed the highest conversion of 1-butene and at a temperature of 450 °C the least amount of 1-butene was converted, although still significantly high.

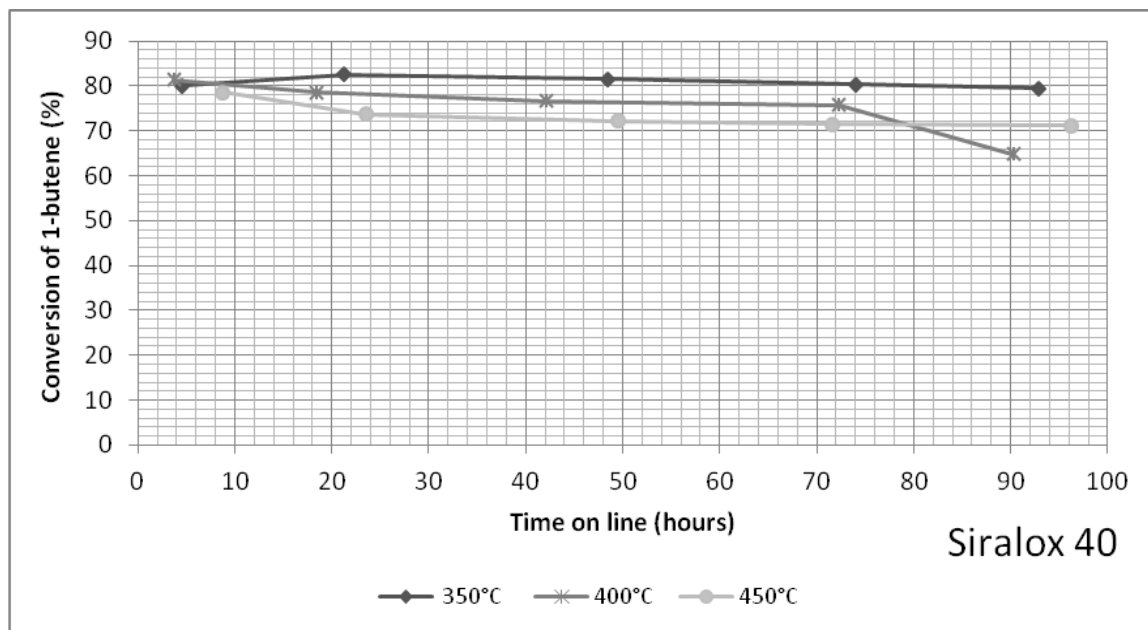


Figure 5.28: Conversion of 1-butene (%) after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the Siralox 40 catalyst

Conversion of *n*-butene

Calculating the conversion of *n*-butene and not 1-butene, Figure 5.29 indicates that a conversion of less than 25% is obtained compared to the 1-butene. The conversion on *n*-butene decreases significantly with time.

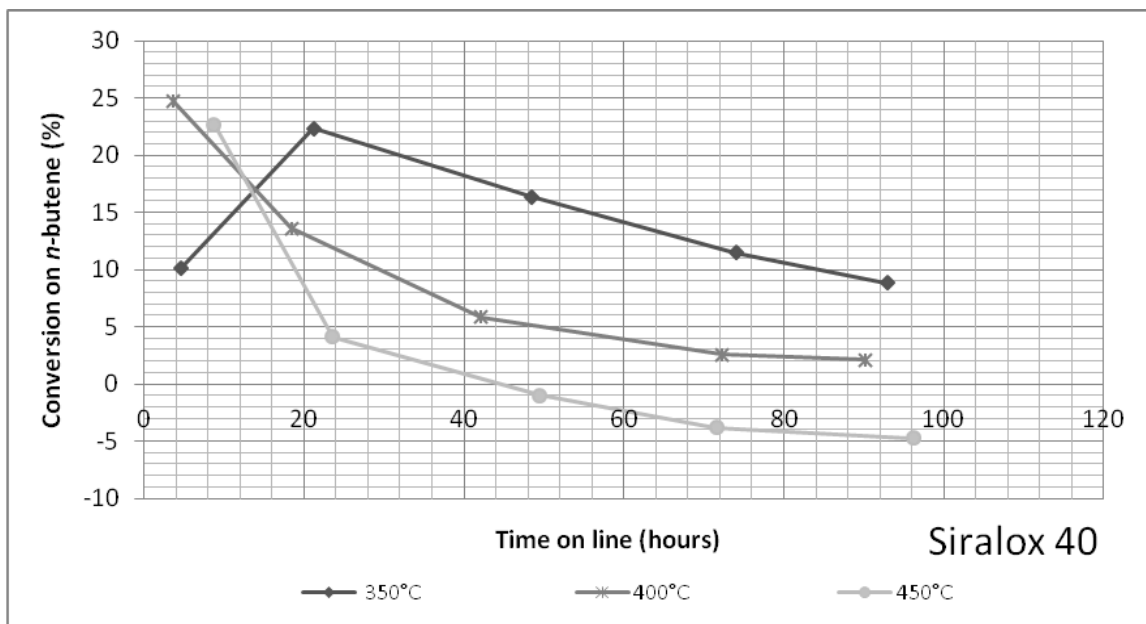


Figure 5.29: Conversion of *n*-butene (%) after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the Siralox 40 catalyst

Steady state conversion was obtained after 71-74 hours on line (Figure 5.29). Figure 5.30 indicates that the conversion of 1-butene at steady state using the Siralox 40 catalyst decreased from ±80% to ±71% with increasing temperature. The thermodynamic conversion at these three temperatures behaved similarly and also decreased with time. At 350 °C the theoretical thermodynamic conversion is lower at 78% than the observed conversion of 81%. This phenomenon may be due to the C₅⁺ compounds that form mostly at 350 °C and not at 400 °C and 450 °C.

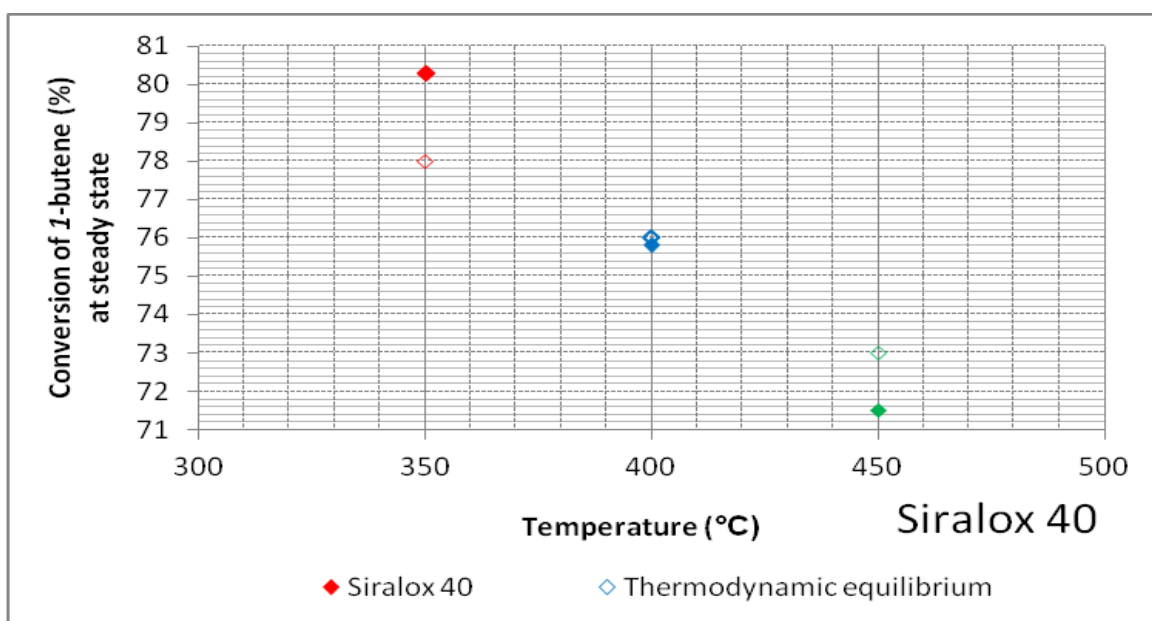


Figure 5.30: Comparison between the conversion of 1-butene (%) at steady state and the thermodynamic equilibrium at temperatures of 350 °C, 400 °C and 450 °C obtained over the Siralox 40 catalyst

Selectivity of 1-butene towards desired products

At all three experimental temperatures (Figure 5.31, 5.32 and 5.33), skeletal isomerization was little, and in all three instances the selectivity to *iso*-butene decreased with time on line. The selectivity towards *cis*-2-butene was less than 50% at all three temperatures and an increase in *cis*-2-butene formation took place with time. The amount of *trans*-2-butene increased with time at all three temperatures and reached a selectivity above 50%. *Cis*-2-butene and *trans*-2-butene indicated double bond shift reaction steps.

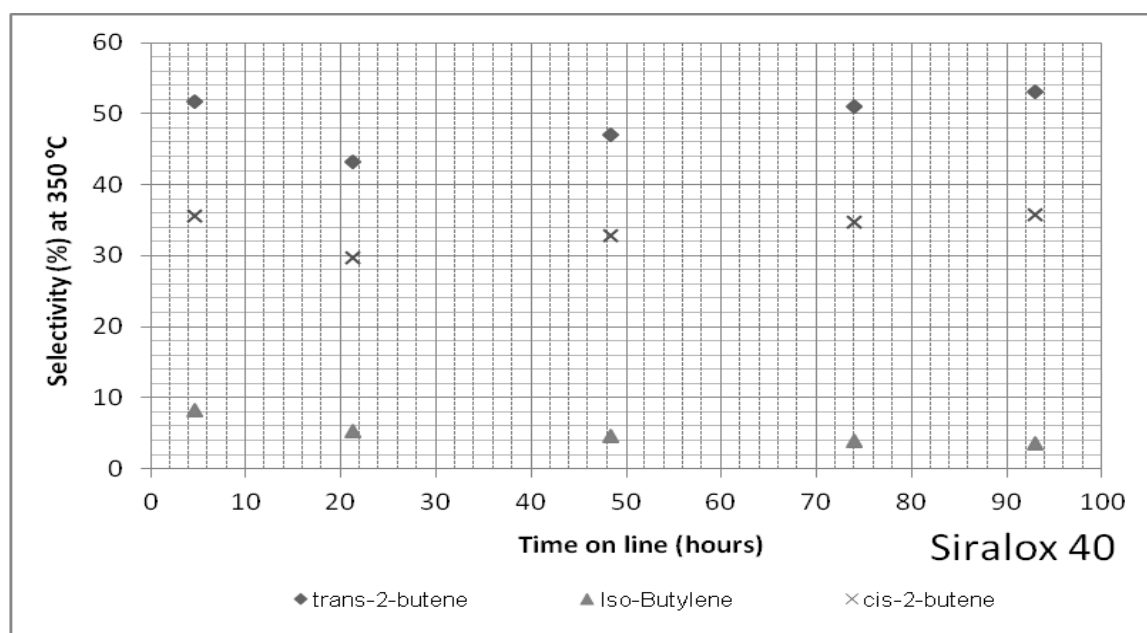


Figure 5.31: Total selectivity (%) of desired products obtained at 350 °C over the Siralox 40 catalyst

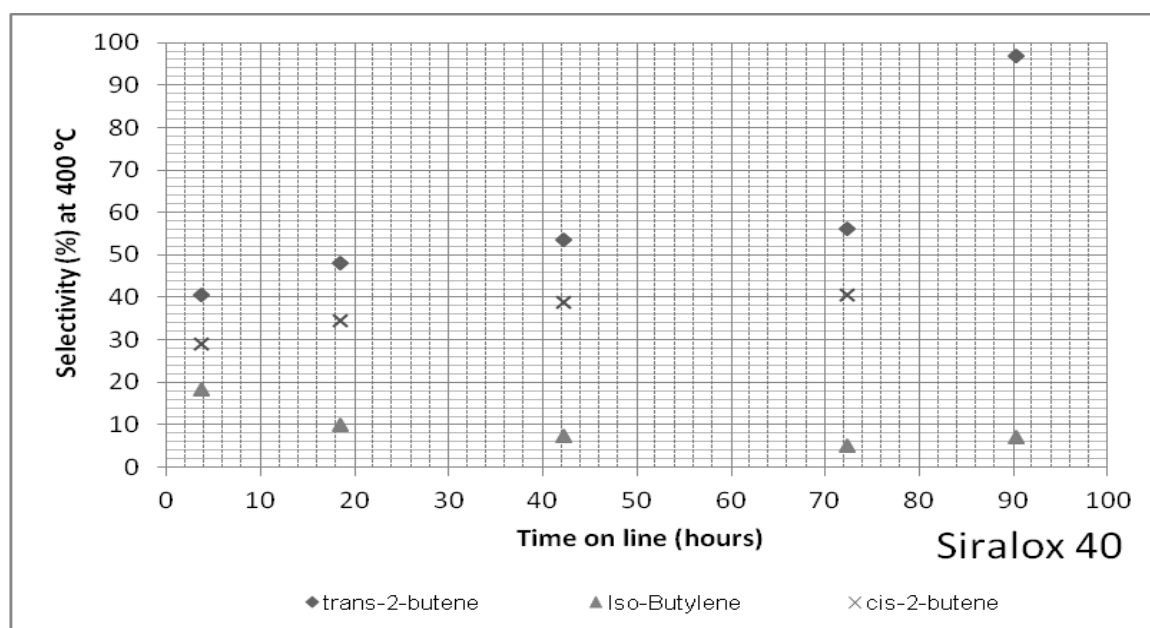


Figure 5.32: Total selectivity (%) of desired products obtained at 400 °C over the Siralox 40 catalyst

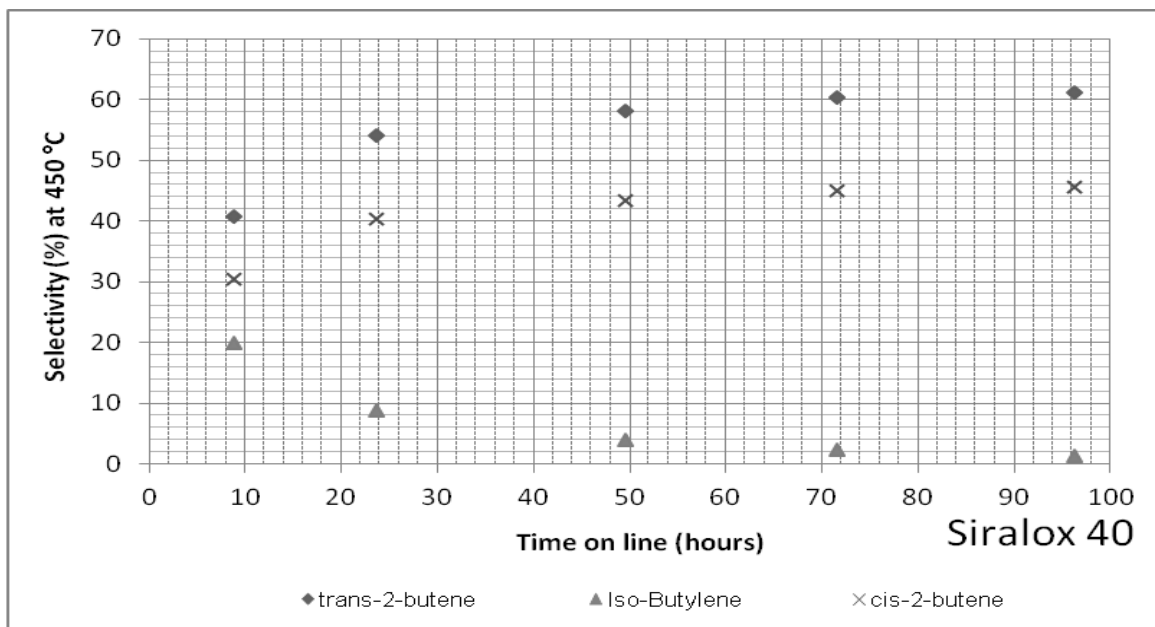


Figure 5.33: Total selectivity (%) of desired products obtained at 450 °C over the Siralox 40 catalyst

As with the Eta alumina catalyst, very little to no isomerization took place during the reaction of 1-butene over the Siralox 40 catalyst at all three temperatures. From Figure 5.34, it is evident that 1-butene contacted over the Siralox 40 catalyst was operating at approximately the maximum conversion achievable, when compared to the thermodynamic equilibrium values calculated with PSRK using Aspen software .

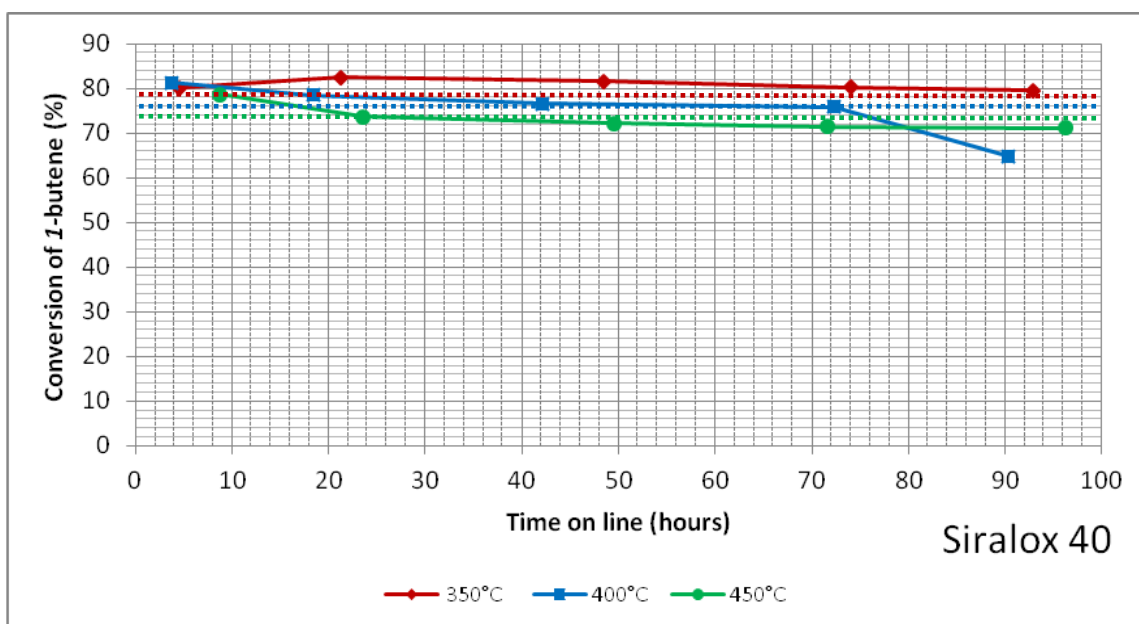


Figure 5.34: Conversion of 1-butene (%) after reaction at temperatures of 350 °C, 400 °C and 450 °C obtained over the Siralox 40 catalyst. The dotted lines are equilibrium data as calculated with PSRK using Aspen software

Hydrogen transfer

Although low, butane formation was observed, showing that hydrogen transfer was catalyzed and an increased amount of butane with time on line at a temperature of 350 °C is evident from results (Figure 5.35). At 400 °C and 450 °C hydrogen transfer appears to decrease with time on line and then stayed approximately constant for the remaining time period.

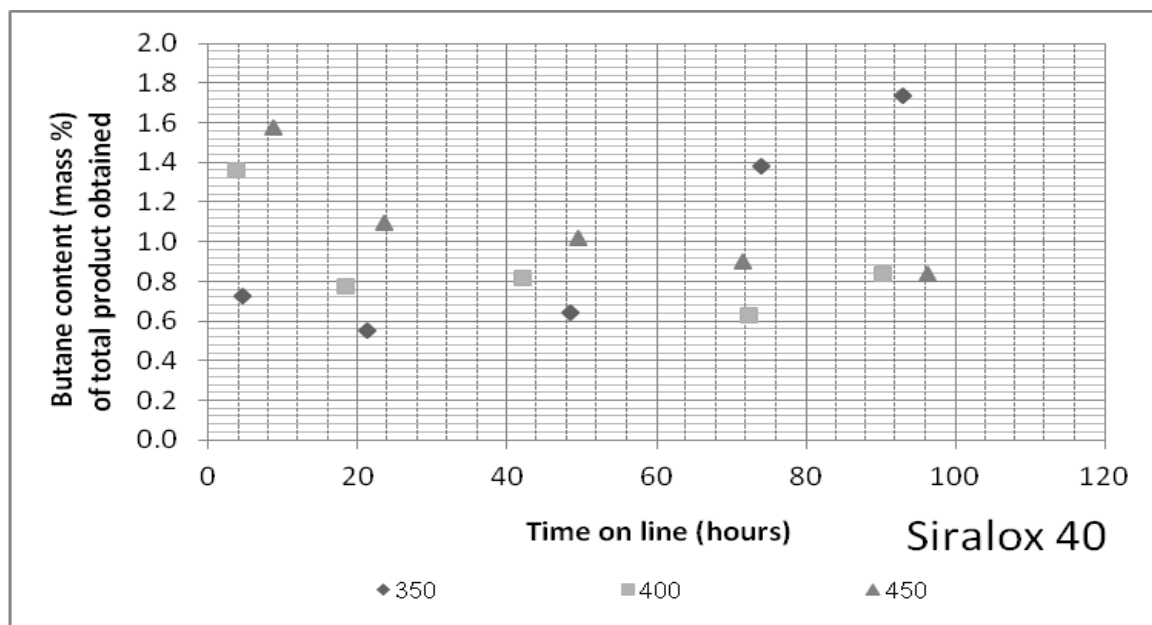


Figure 5.35: Butane content (mass %) as a function of time on line (hours) at temperatures of 350 °C, 400 °C and 450 °C over the Siralox 40 catalyst

As with ZSM-5, the hydrogen transfer that results in the formation of butane (using Siralox 40 as catalyst) is believed to also come from the propene and butane that is produced (Scheme 5.8). Two facts that support the statement is that little 1,3-butadiene and/or hydrogen is formed during the reaction with Siralox 40. The other observation is that the conversion of 1-butene resulted in mostly *n*-butenes and *iso*-butene and very few by-products.

Cracking

A very small amount of cracking of 1-butene to propene occurred at all three temperatures (Figure 5.36). As previously described, propene formation is indicative of cracking. Initially, cracking was the highest at 450 °C followed by 400 °C and 350 °C. For the higher temperatures, however, the amount of cracking decreased rapidly with time.

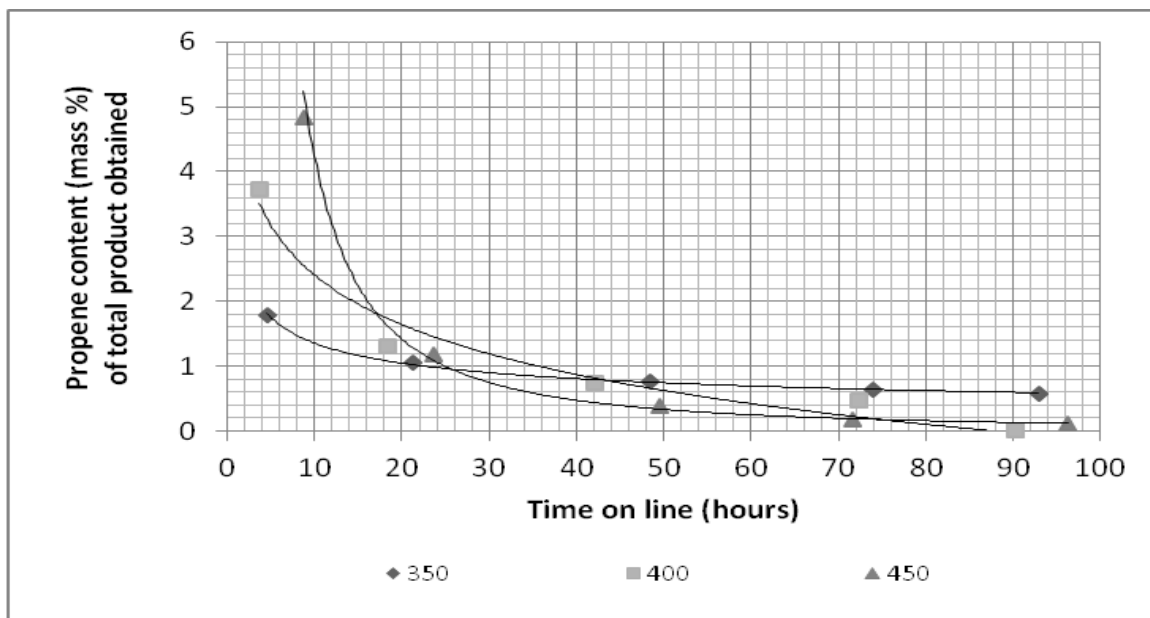


Figure 5.36: Propene content (mass %) as a function of time on line (hours) at temperatures of 350 °C, 400 °C and 450 °C over the Siralox 40 catalyst

Since a decrease in cracking with respect to propene occurs (Figure 5.36), it is expected that coking took place, blocking the acid sites as shown by the increase in coke percentage with time (Figure 5.37).

Coking of the Siralox 40 catalyst

Figure 5.37 indicates that coking increased with temperature on the Siralox 40 catalyst, which relates well to the surface area and pore volume data obtained from the spent Siralox 40 catalyst at all three temperatures (Figures 5.38 and 5.39).

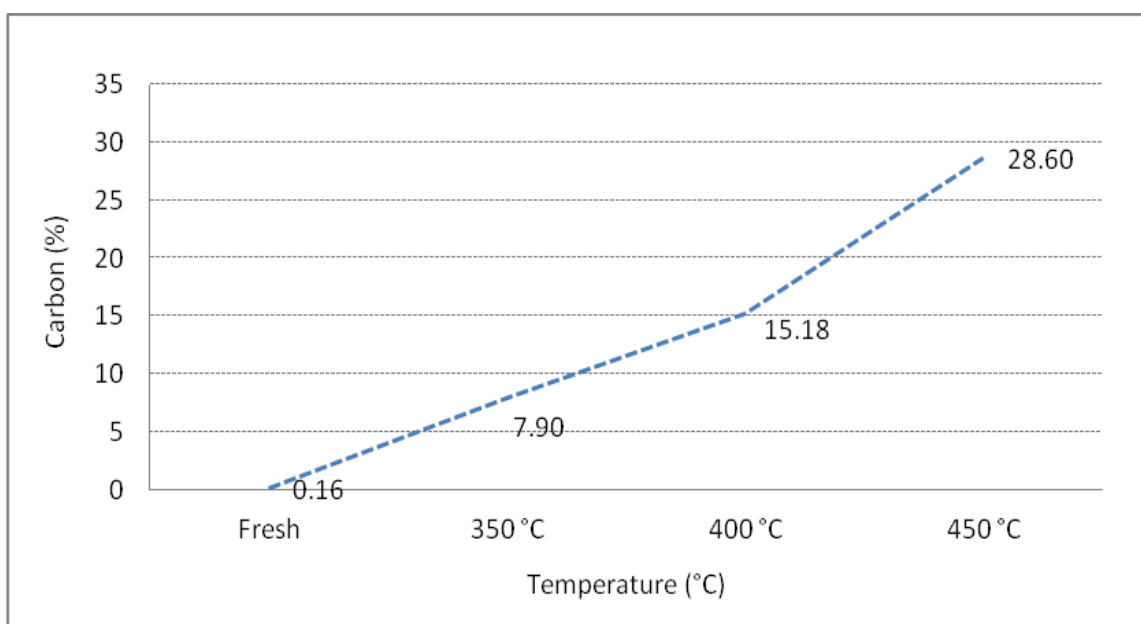


Figure 5.37: Carbon (%) of fresh Siralox 40 and spent Siralox 40 after reactions at temperatures of 350 °C, 400 °C and 450 °C

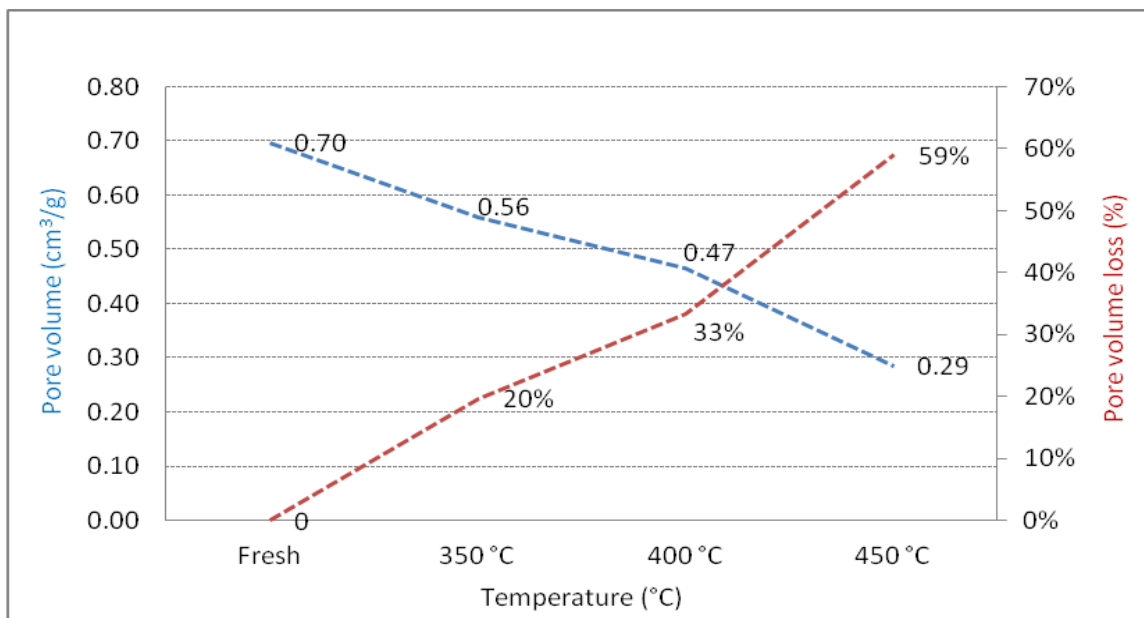


Figure 5.38: Pore Volume (cm³/g) of fresh Siralox 40 and spent Siralox 40 and pore volume loss (%) of fresh Siralox 40 and spent Siralox 40 after reactions at temperatures of 350 °C, 400 °C and 450 °C

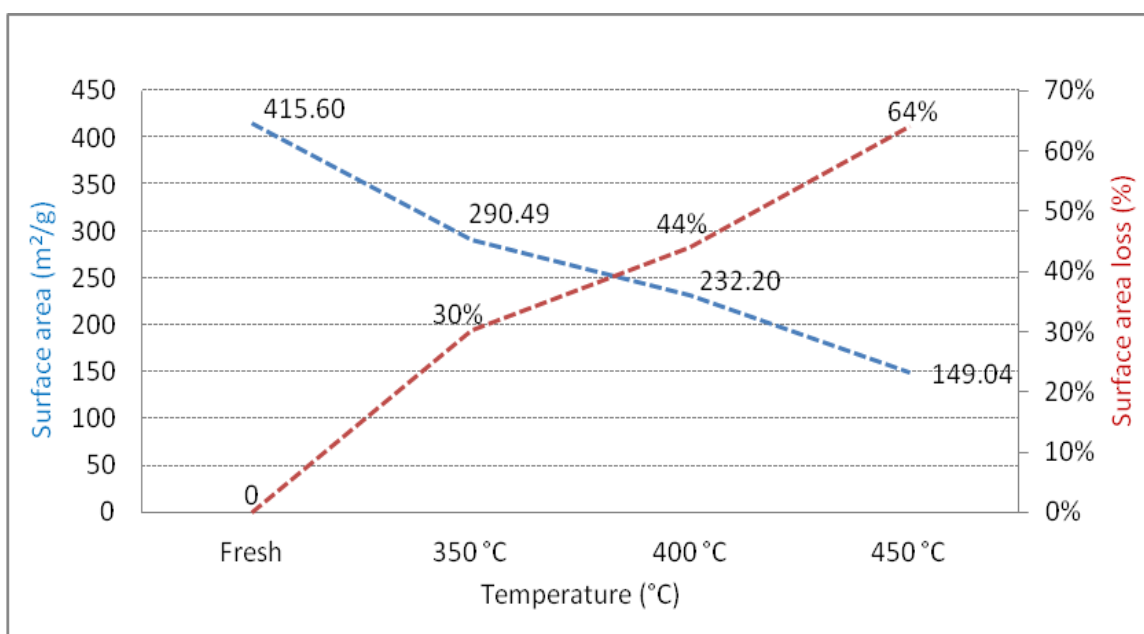


Figure 5.39: Surface Area (m²/g) of fresh Siralox 40 and spent Siralox 40 and surface area loss (%) of fresh Siralox 40 and spent Siralox 40 after reactions at temperatures of 350 °C, 400 °C and 450 °C

With an increase in temperature, when using the Siralox 40 catalyst, the amount of coking on the catalyst increases, which results in the catalyst pores to be blocked, creating smaller pore volumes and less surface area for the reaction of 1-butene to take place (Figures 5.38 and 5.39).

With increased coking, the pore volume and surface area decreased. Figure 5.38 also indicates that with an increase in temperature the pore volume of the catalyst decreased and when reaching 450 °C, the catalyst lost 59% of its pore volume due to coking. The surface area also showed a decrease and Figure

5.39 indicates that at 450 °C, 64% of the catalyst surface area was lost due to coking.

5.6 Surface acidity of the three catalysts

Another aspect that is important for the skeletal isomerization of 1-butene to *iso*-butene is the surface acidity of the catalyst. As stated in Chapters 2 and 4, Brønsted acidity is a very important requirement for a successful catalyst to skeletally isomerize.

CO adsorption

The acid sites on the Eta alumina, ZSM-5 and Siralox 40 catalysts were qualitatively characterized by DRIFT after CO adsorption. These catalysts were evaluated before and after experiments at 400 °C in a fixed bed reactor.

Referring to Chapter 4, Section 4.3, results on the fresh Eta alumina catalyst showed predominantly Lewis acidity with some weakly acidic AlOH species. The fresh ZSM-5 catalysts showed predominantly Brønsted acidity (bridging OH species) with small quantities of Lewis acid sites. The fresh Siralox 40 catalyst had low concentrations of Lewis acid sites and also low concentrations of Brønsted acidity.

The acid sites on the three catalysts after the reaction with 1-butene at 400 °C were also characterised by DRIFT after CO adsorption. The following spectra were obtained (Figure 5.40).

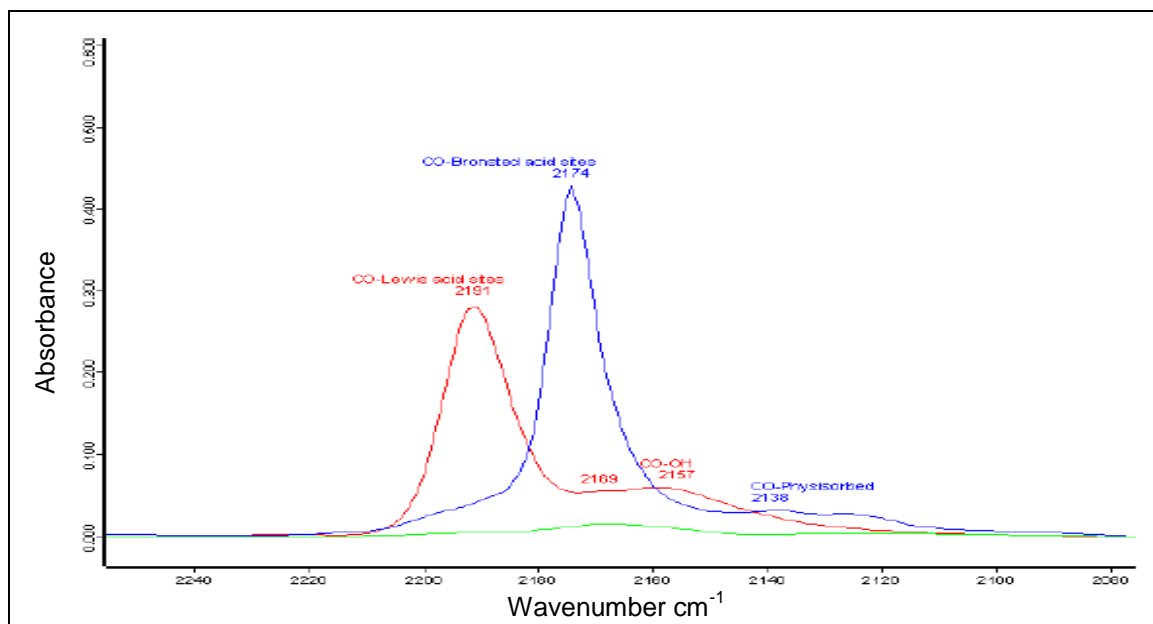


Figure 5.40: The spectrum obtained after the adsorption of CO on Eta alumina (red), ZSM-5 (blue) and Siralox 40 (green)

Figure 5.40 illustrates the OH environments with the stretching vibrations of the interacting CO. The acid sites in the spent catalysts were drastically reduced at 2174 cm⁻¹ (ZSM-5) and 2191 cm⁻¹ (Eta alumina) (Figure 5.40) compared to the fresh analogues (Figure 4.8, 4.9 and 4.10). The spectrum obtained after CO adsorption on the spent Siralox 40 catalyst displayed no bands indicating that no detectable acid sites remain on the Siralox 40 catalyst after it was in contact with the feed.

N-propylamine Pulse chemisorptions – TPD-MS

The Brønsted acid sites accessible on the fresh and spent catalysts were semi-qualitatively characterized by the *n*-propylamine pulse chemisorptions-TPD-MS method and the data of the analyses are presented in Figures 5.41, 5.42 and 5.43.

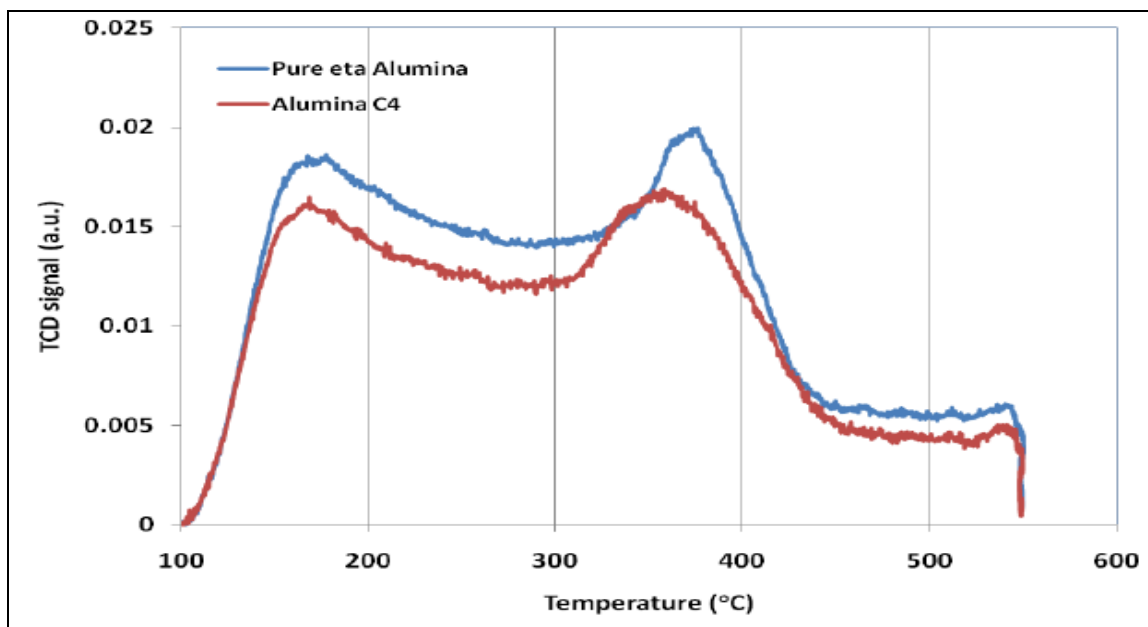
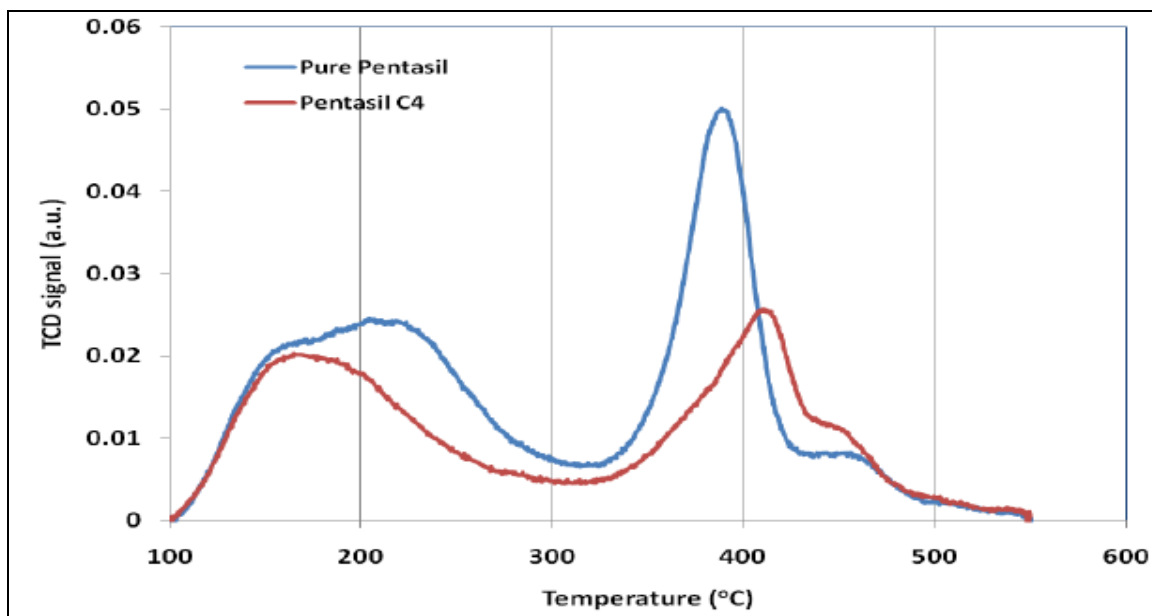


Figure 5.41: TPD of *n*-propylamine on fresh Eta alumina (blue profile) and spent Eta alumina (red profile)



*ZSM-5 also referred to as Pentasil

Figure 5.42: TPD of a *n*-propylamine on fresh ZSM-5 (blue profile) and spent ZSM-5 (red profile)

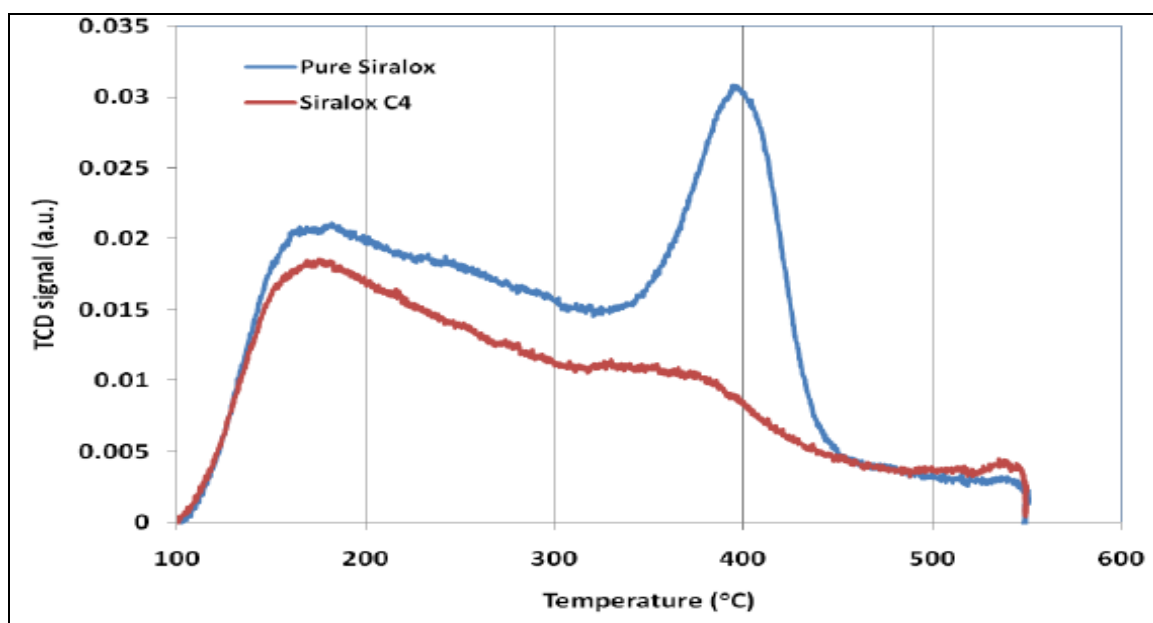


Figure 5.43: TPD of *n*-propylamine on pure Siralox 40 (blue profile) and spent Siralox 40 (red profile)

The formula as discussed in Chapter 4, section 4.3 was used again for the determination of Brønsted acid sites on the spent catalysts and the calculated results are given in Table 5.2.

Table 5.1
Number of Brønsted acid sites on the fresh catalysts [Chapter 4, section 4.3]

Catalyst	Brønsted Acid Sites ($\mu\text{moles/g}$) $A_{\text{cal}}/V_{\text{cal}}$
Fresh Eta alumina	9.86
Fresh ZSM-5	21.79
Fresh Siralox 40	14.85

Table 5.2
Number of Brønsted acid sites on the spent catalysts

Catalyst	Brønsted Acid Sites ($\mu\text{moles/g}$) $A_{\text{cal}}/V_{\text{cal}}$
Spent Eta alumina	10.49
Spent ZSM-5	13.79
Spent Siralox 40	0.00

The desorption spectra (TPD) showed that the highest number of Brønsted acid sites were observed on the fresh ZSM-5 followed by fresh Siralox 40 catalyst and then fresh Eta alumina (Table 5.1 and Figure 5.44).

Except for Eta alumina, the Brønsted acid sites in the spent catalysts were significantly lower than the respective fresh catalysts (Table 5.2 and Figure 5.44). The Brønsted acid sites for Siralox 40 were totally removed after the reaction in the reactor at 400 °C, which was also observed from the CO-DRIFT analysis (Figure 5.40).

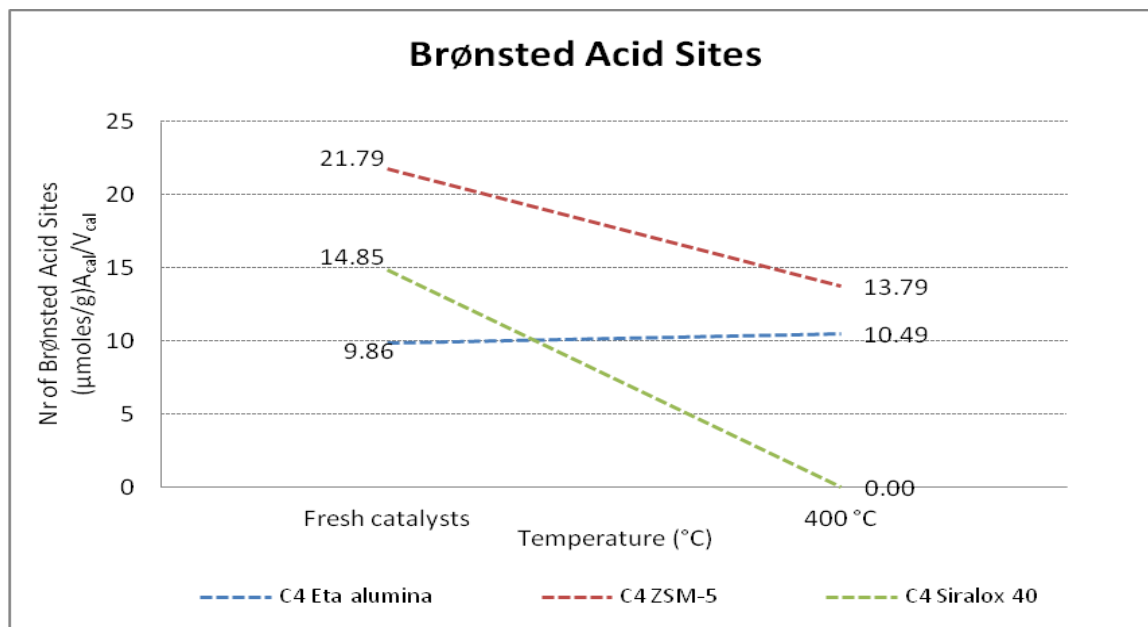


Figure 5.44: Number of Brønsted Acid Sites of fresh Eta alumina, ZSM-5 and Sirolax 40 compared to the spent Eta alumina, ZSM-5 and Sirolax 40 at 400 °C

As stated before, skeletal isomerization prefers Brønsted acid sites [Chapter 2 and 4]. This relates well to the ZSM-5 catalyst which had the highest number of Brønsted acid sites and caused the most skeletal isomerization. More double bond shifts occurred with the other two catalysts, which had Lewis acid sites.

5.7 Comparisons of the three catalysts

Composition of 1-butene towards desired products

The main aim of this study is to do skeletal isomerization of 1-butene to *iso*-butene. Between the three different catalysts used (Eta alumina, ZSM-5 and Siralox 40) the only catalyst showing selectivity towards skeletal isomerization was ZSM-5. Even here selectivity remained below 15%. The thermodynamic equilibrium of 1-butene to the desired products was simulated by Aspen software. It simulated that 1-butene can be converted to *iso*-butene at a maximum conversion of 50% at the minimum temperature used in this study (350 °C) and decreases slowly as temperature increases as shown in Figure 5.45.

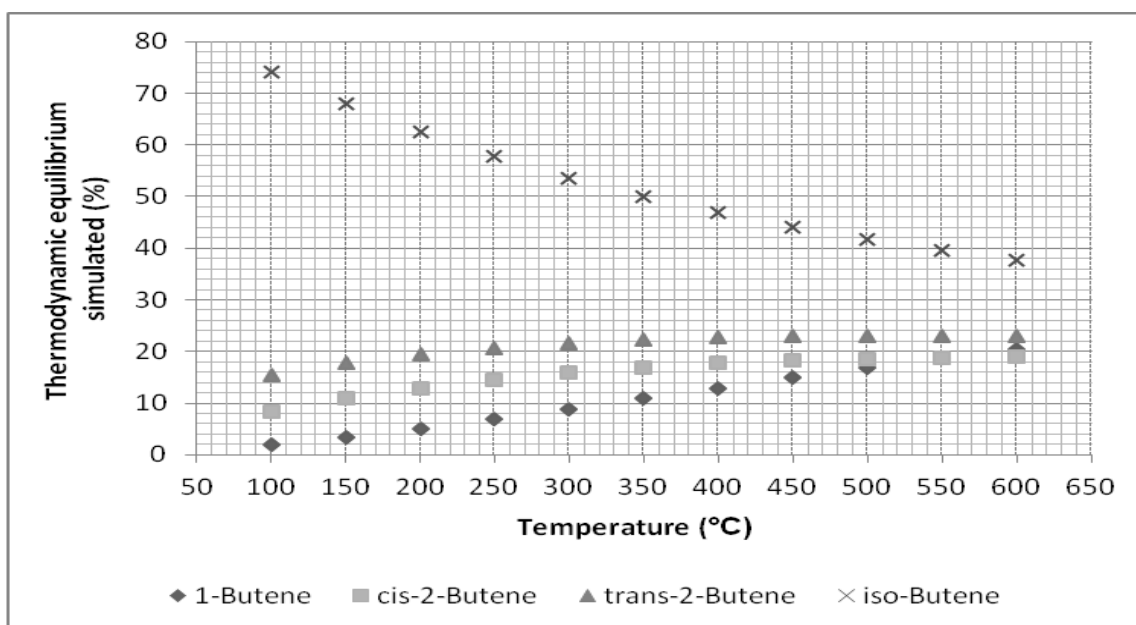


Figure 5.45: Simulation of the thermodynamic equilibrium (%) of desired products that can be reached between temperatures of 100 °C to 600 °C. The calculated maximum amount of *iso*-butene (%) to be obtained at 350 °C is 50%

Figure 5.45 shows that, the lower the temperature, the higher the possible yield of *iso*-butene. In reality, a plant would run at lower temperatures and obtain high selectivities of *iso*-butene. Lower temperatures also lower the operational costs of the company.

Higher temperatures increase the reaction rate, whilst lower temperatures are advantageous for conversion of *1*-butene to *iso*-butene. Therefore, operation should occur at the lowest temperature possible while maintaining a decent reaction rate.

Experimental selectivity data for each catalyst at steady state (Section 5.3, 5.4 and 5.5 - as stipulated in the individual *selectivity* sections), are compared with the selectivity data of thermodynamic equilibrium as simulated by Aspen software. Comparing this simulated thermodynamic equilibrium data to the runs done in this experiment; it was found that none of the three catalysts were very active catalysts for skeletal isomerization of *1*-butene to *iso*-butene. None of the three catalysts gave product concentrations that were close to the calculated equilibrium values (Figure 5.46). ZSM-5 is the catalyst that was most selective towards *iso*-butene formation, especially at 350 °C. It seems that ZSM-5 also lowered the activation energy when in contact with the *1*-butene to form *iso*-butene. The Eta alumina and Siralox 40 catalysts did not lower the activation energy to such an extent when in contact with the *1*-butene feed for the formation of *iso*-butene.

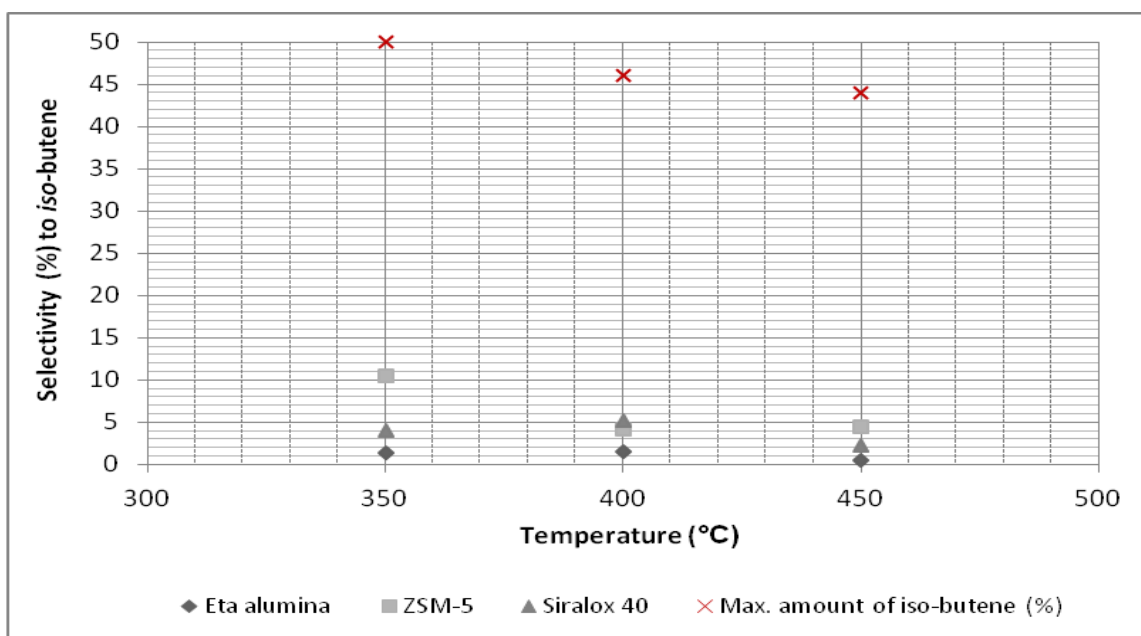


Figure 5.46: Selectivity (%) *iso*-butene obtained at steady state for each experimental run over the three catalysts, compared to theoretical maximum amount of *iso*-butene that can be obtained (50%, 46% and 44%, respectively)

Conversion of 1-butene

The conversion of 1-butene between the three catalysts at three temperatures showed that ZSM-5 caused the highest conversion with time on line at all three temperatures. The conversion using Siralox 40 and Eta alumina was similar and between 60% and 80% conversion (as defined previously) of the 1-butene was obtained.

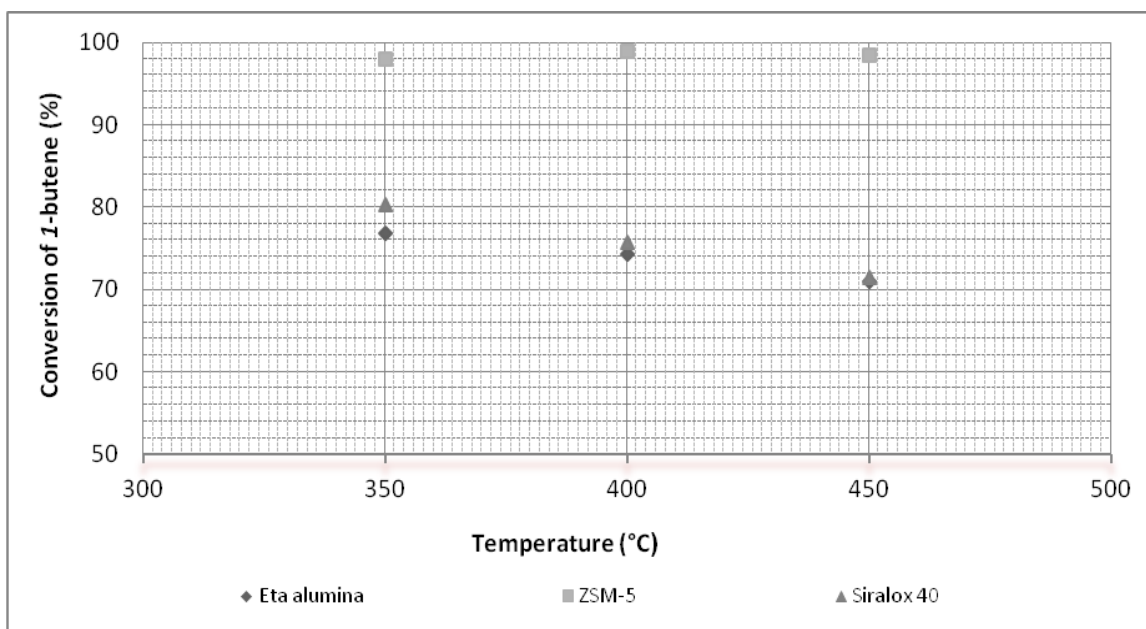


Figure 5.47: Conversion of 1-butene (%) at temperatures of 350 °C, 400 °C and 450 °C using the catalysts Eta alumina, ZSM-5 and Siralox 40 versus time on line

Deactivation of catalysts

Moulijn et al., [2001] described catalyst deactivation as a complex process, which may be caused by a variety of processes. They mentioned three reasons for catalyst deactivation:

- decrease in the number of active sites;
- decrease in the quality of the active sites; and
- decrease in accessibility of the pore space [Beeckman et al., 1991; Guisnet et al., 1997a].

The mentioned authors stated that deactivation can occur due to site coverage, pore blockage and structure alterations depending on pore size dimensions and the presence of cavities. When the active sites in pores and cavities are unavailable for catalysis due to blocking of the active sites by carbonaceous products, it is due to so called "site coverage". When a pore is made inaccessible because it is impossible for reactants to diffuse to the active sites inside the pore, it is because of "pore blockages" and lastly when the strength and number of the active sites are changed it is known as "structure alterations".

Coking of the three catalysts

From Figure 5.48, the Siralox 40 catalyst caused the coke percentage to increase drastically as the temperature increased, whereas the ZSM-5 catalyst showed a slight increase in coke percentage with temperature increase. On Eta alumina coking only started at a temperature of 450 °C.

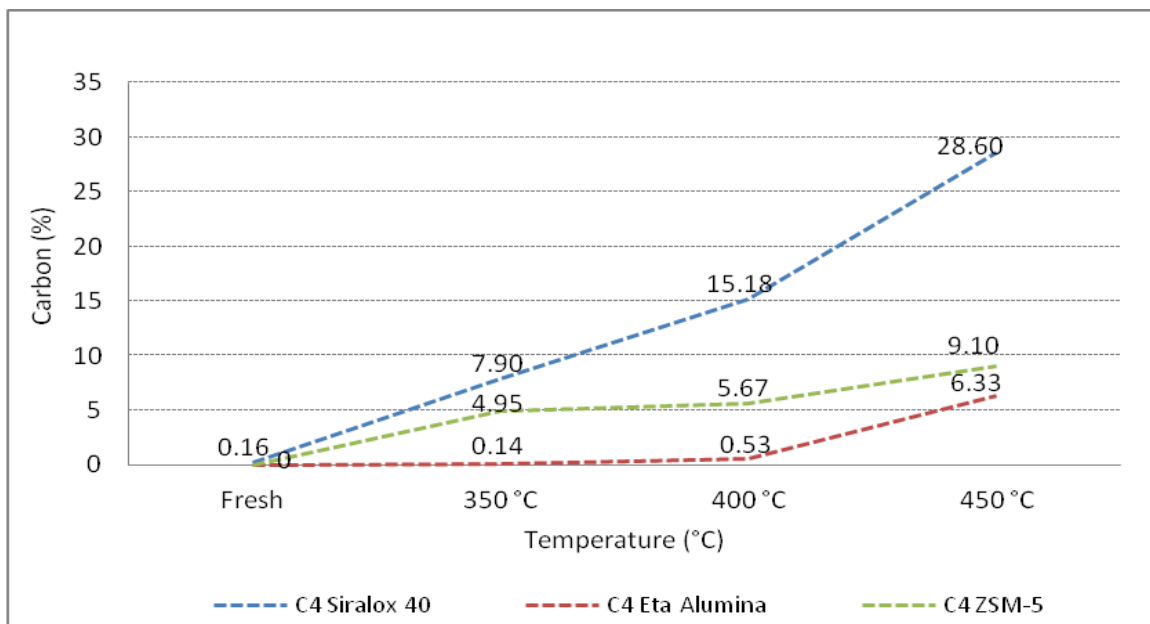


Figure 5.48: Comparison between carbon content (%) of the three fresh and spent catalysts at temperatures of 350 °C, 400 °C and 450 °C

Pore volume and surface area

The pore volume of the Siralox 40 catalyst decreased with an increase in temperature because coking blocked the pores. With the ZSM-5 catalyst the pore volume of the fresh catalyst was big but with an increase in temperature the pores of the catalysts did not seem to decrease considerably. The pore volume and surface area of the Eta alumina catalysts did not change at all with an increase in temperature, revealing the inactivity of this catalyst. The surface area of the Siralox 40 and ZSM-5 catalysts behaved similarly to the pore volume of the two catalysts.

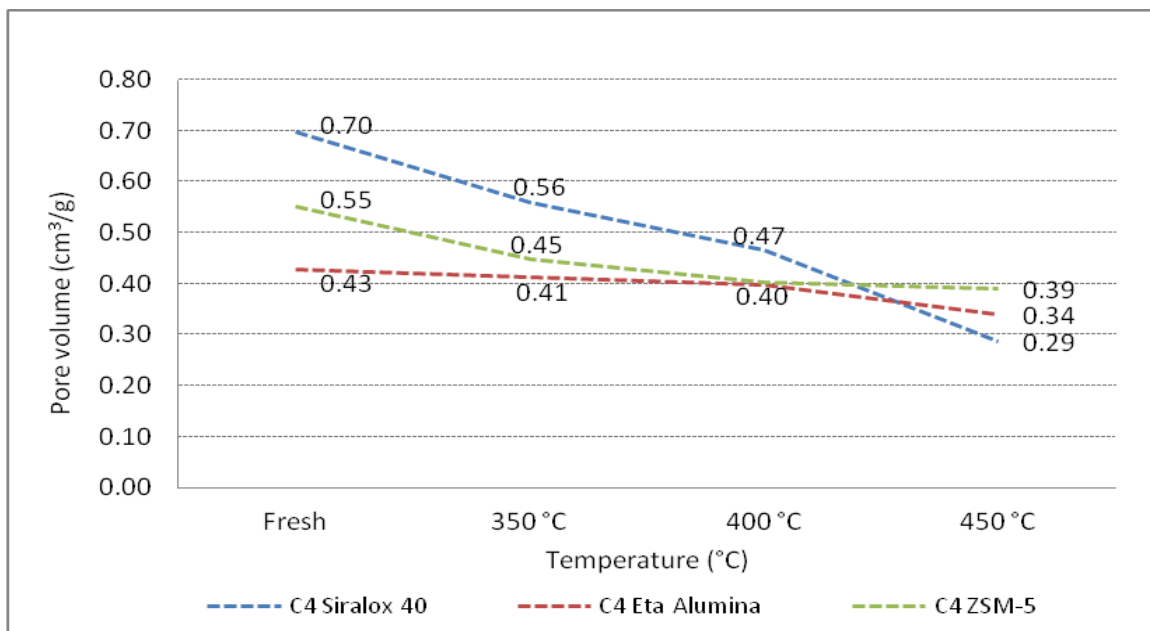


Figure 5.49: Comparison between pore volume (cm³/g) of three fresh and spent catalysts at temperatures of 350 °C, 400 °C and 450 °C

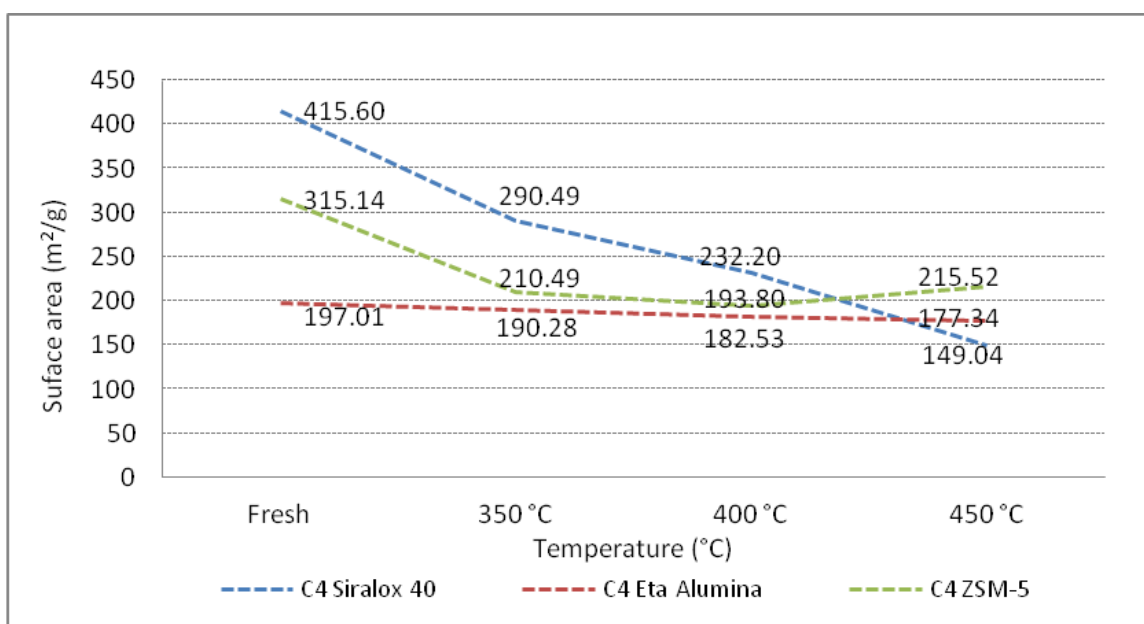


Figure 5.50: Comparison between surface area (m²/g) of three fresh and spent catalysts at temperatures of 350 °C, 400 °C and 450 °C

The spent catalysts and the fresh catalyst were calcined and analysed for surface area and pore volume. This was done to confirm whether the decrease in surface area and pore volume was due to coking (as shown above) or due to change in catalyst structure during the reaction with 1-butene.

After calcination, a visual observation on the catalysts showed that the only catalyst that returned back to its original colour was Eta Alumina, showing that the coke that was formed on this catalyst was burned off with calcination.

The other spent catalysts that were calcined still showed little brown/black particles and did not return back to their fresh original colour.

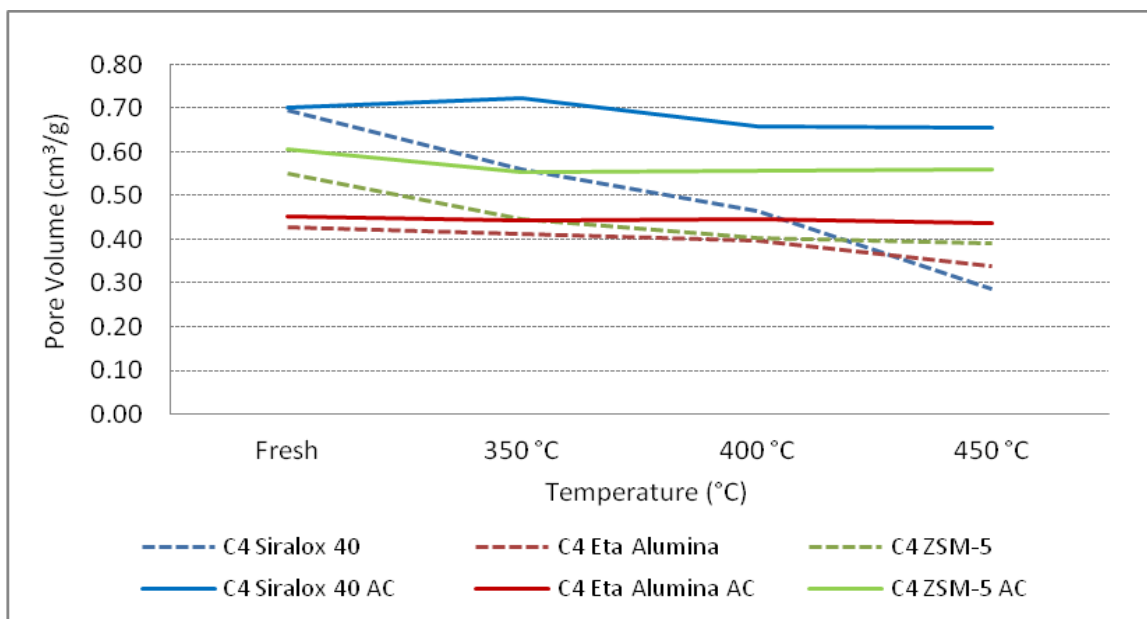


Figure 5.51: Comparison of the pore volume (cm³/g) between three spent catalysts and the spent catalysts after calcination (AC) at temperatures of 350 °C, 400 °C and 450 °C

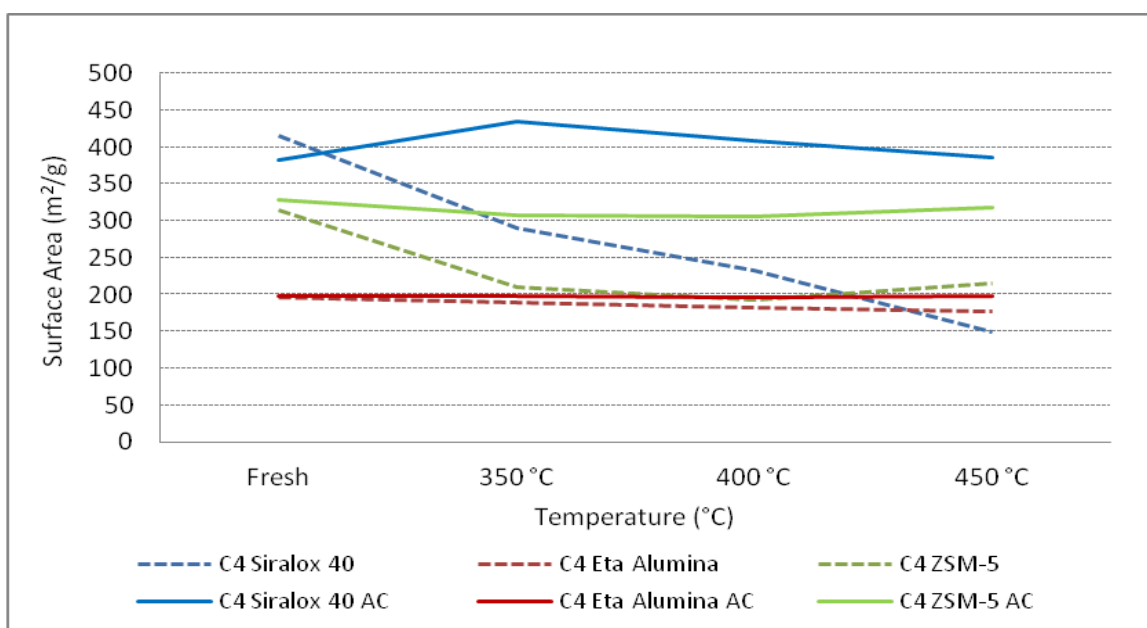


Figure 5.52: Comparison of the surface area (m²/g) between three spent catalysts and the spent catalysts after calcination (AC) at temperatures of 350 °C, 400 °C and 450 °C

The surface areas and pore volumes of the spent catalysts after calcination and the fresh catalysts are similar (Figure 5.51 and Figure 5.52). It can be concluded that the structure of the catalyst did not change during the reaction with 1-butene, because if the structure had changed during the reaction with 1-butene, the pore volume and surface area after calcination would have been much lower than the surface area and pore volume before calcination of the spent catalyst. The catalysts thus seem to undergo only coking.