Chapter 4

Characterization of Reactants

Fresh catalyst characterization

The catalysts, Eta alumina, ZSM-5 and Siralox 40, used in this study were analysed using the following techniques:

1. X-ray diffraction (XRD);
2. Inductively coupled plasma (ICP);
3. Surface acidity;
4. Thermal gravimetric analysis (TGA);
5. Surface area; and
6. Pore volume.

The three feed compounds, *1*-butene, *1*-hexene and *1*-octene were also characterized to verify the composition of each.

4.1 X-Ray Diffraction (XRD) Analysis

XRD analysis was performed only on the fresh catalysts. This analysis was done to qualitatively determine the composition of each of the fresh catalysts. The following results were found for the three different catalysts.

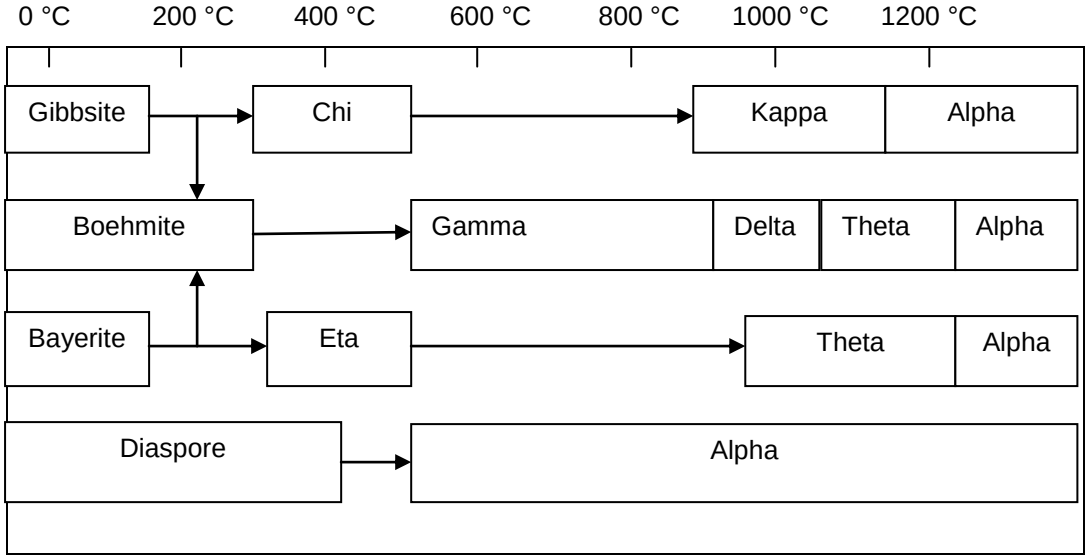
a) Eta alumina

The alumina family consist of more than 12 well-characterized amorphous or crystalline structures. The structure and property of a given alumina depend on its [Bartholomew et al., 2006]:

- Preparation;
- Purity;
- Dehydration; and
- Thermal treatment history.

The Eta alumina used in this study originates from high surface area, hydrated alumina, Bayerite. From Table 4.1 it can be seen that Bayerite converts in the region of 300 °C to Eta alumina which stays in this phase between temperatures of 300 °C and 500 °C before it will change phase to Theta alumina [Bartholomew et al., 2006].

Table 4.1
Alumina phases present at different temperatures [Bartholomew et al., 2006].



The powder diffractogram for Eta alumina is shown in Figure 4.1. The XRD analysis indicated that the Eta alumina catalyst contained either Gamma-Alumina (γ-Al_2O_3) or Eta-alumina (η–Al_2O_3). Laboratory XRD cannot distinguish between γ- and η-alumina as these are well described *iso*-structural phases.

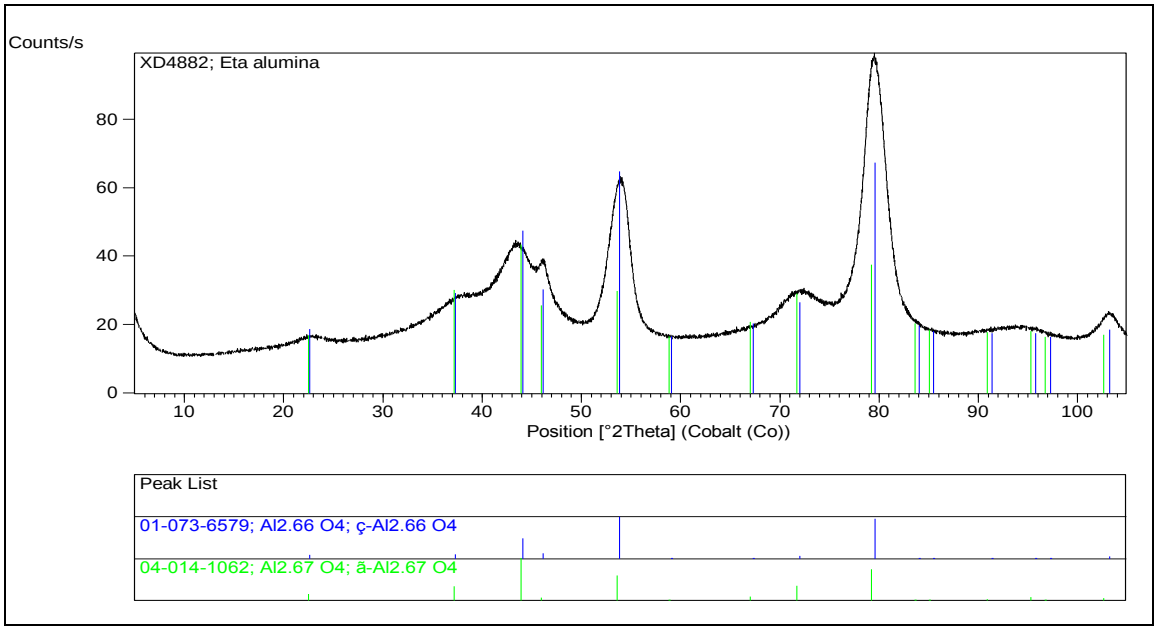
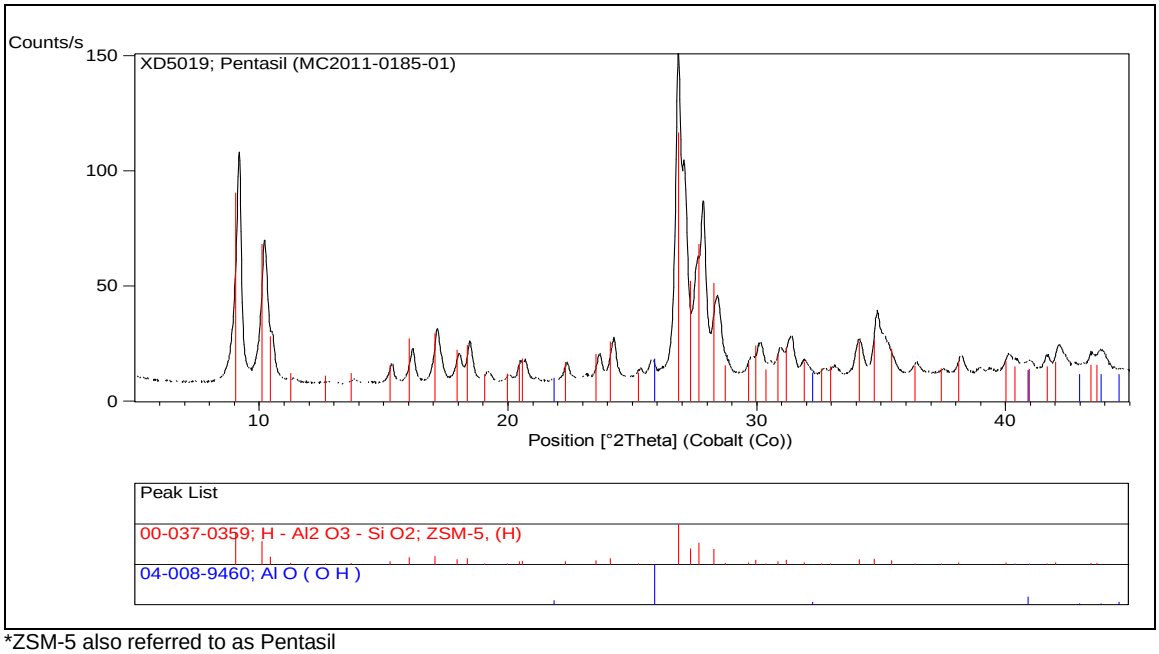


Figure 4.1: X-ray diffractogram of η-alumina

From the XRD analysis the reference phase peak intensities of the η – Al_2O_3 fits the experimental diffractogram better than that of γ-alumina.

b) ZSM-5

The powder diffractogram of the ZSM-5 catalyst is shown in Figure 4.2. The XRD analysis of the ZSM-5 catalyst showed that the catalyst contained mainly ZSM-5 (H-Al_2O_3-SiO_2) and some traces of diaspore (AlO(OH)).



*ZSM-5 also referred to as Pentasil

Figure 4.2: X-ray diffractogram of ZSM-5

In literature, ZSM-5 (Zeolite Socony Mobil – 5), is classified as a zeolite which consists of a microporous, crystalline aluminosilicate which belongs to the pentasil family and has a chemical formula of $Na_nAl_nSi_{96-n}O_{192}\cdot 16H_2O$ ($0<n<27$) (Figure 4.3). It can be found in nature or it can be synthesized. The ZSM-5 zeolite, which is part of the MFI (mordenite framework inverted) framework was used as the catalyst since it is commonly used as an isomerization catalyst. It has an orthorhombic unit cell with a two-dimensional channel structure where large 10-ring channels (5.5 Å x 5.1 Å) are connected via other large 10-ring channels (5.3 Å x 5.6 Å) as shown in Figure 4.4 [Baerlocher et al., 2001]. ZSM-5 was patented by Mobil Oil Company in 1975 and it is widely used in the petroleum industry as a heterogeneous catalyst.

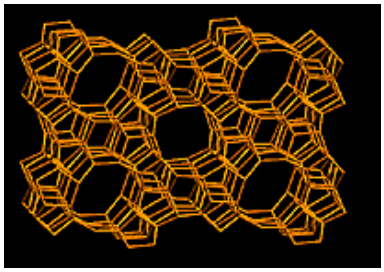


Figure 4.3: The molecular structure of ZSM-5

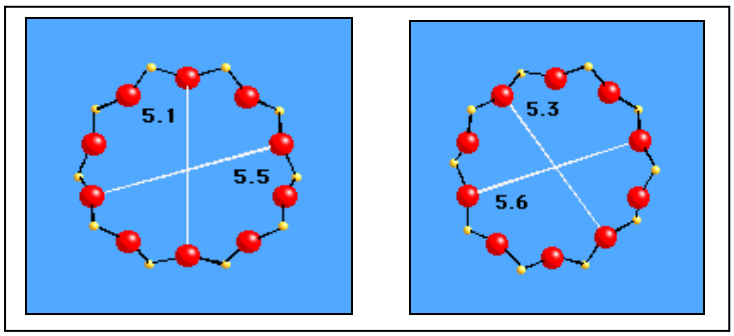


Figure 4.4: The first 10-ring channel of ZSM-5 and the second 10-ring channel of ZSM-5

Zeolite catalysts are favoured in the petroleum and petrochemical industries because of the following attributes [Horsley, 1993]:

1. They are active solid-acidic catalysts;
2. Their unique structure allows shape selectivity, used to direct catalytic reactions toward desired products and to limit undesirable side reactions such as coking;
3. They are resistant to chemical attack;
4. They have high thermal and hydrothermal stability; and
5. They are more environmentally friendly.

c) Siralox 40

The powder X-ray diffractogram of Siralox 40 is shown in Figure 4.5. The XRD analysis indicated that the Siralox 40 catalyst contained γ-Alumina (γ-Al_2O_3), θ–Alumina (θ-Al_2O_3) and amorphous material, possibly quartz-SiO_2.

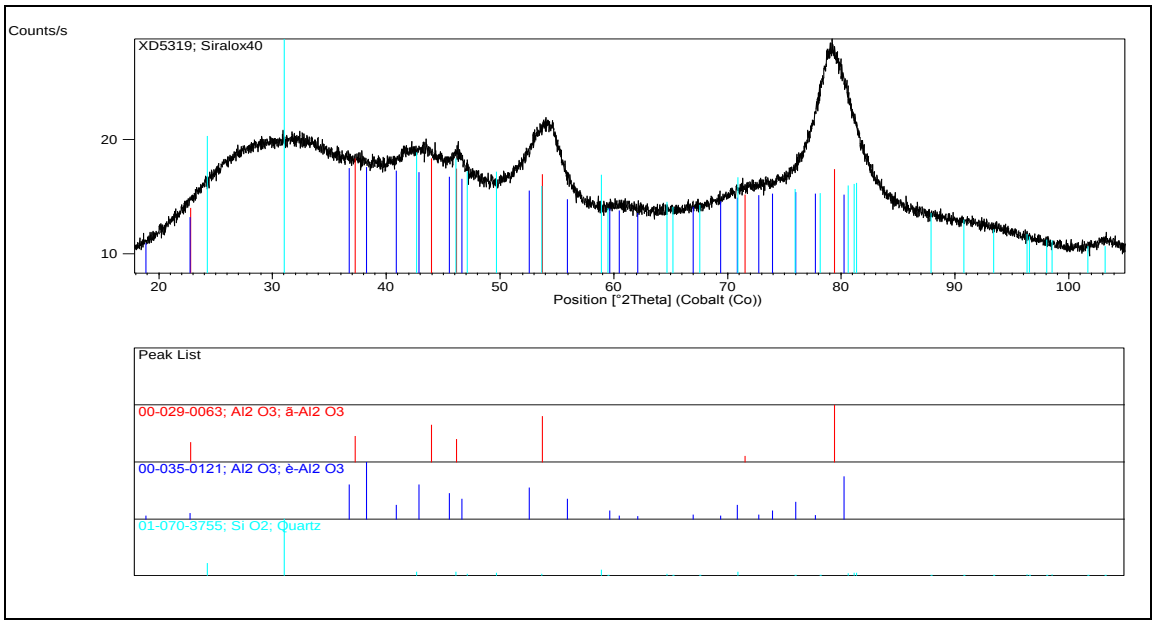


Figure 4.5: X-ray diffractogram of Siralox 40

Siralox 40 is a silica alumina type catalyst. A silica alumina catalyst is an amorphous solid with a high surface area and has the formula $(SiO_2)_m(Al_2O_3)_n$. It is very strongly acidic and is often used as a catalyst support [Bartholomew et al., 2006].

4.2 Inductively Coupled Plasma (ICP) Analysis

The ICP technique was used to determine which elements were present in the three fresh catalysts. This analysis was only done on the fresh catalysts, mainly to obtain the Si/Al ratio present in the fresh catalysts.

Table 4.2
***Elemental analysis for the fresh catalysts**

	Eta alumina	ZSM-5	Siralox 40
Elements	**Results (mass %)**	**Results (mg/kg)**	**Results (mg/kg)**
Ca	<0.010	<0.390	<0.390
K	<0.010	15.780	63
Mg	<0.010	<1.100	<1.100
Mo	0.031	<8.100	513
Na	0.072	200.00	36
Ni	<0.010	324	<8.3

	Eta alumina	ZSM-5	Siralox 40
Elements	**Results (mass %)**	**Results (mass %)**	**Results (mass %)**
Al	50.3	13.18	29.32
Si	0.400	26.500	15.5

*****Accuracy is represented by the last decimal place

From this elemental analysis it is observed that Siralox 40 contains a relatively high concentration of potassium (K), molybdenum (Mo) and sodium (Na). Lesser amounts of the potassium with no molybdenum and very high sodium and nickel were observed for the ZSM-5 catalyst. Eta alumina showed very little to none of these elements. The Si/Al ratio for the three catalysts is summarised in Table 4.3.

Table 4.3
***Si/Al ratio for the fresh catalysts**

	Si : Al
Eta alumina	1:126
ZSM-5	1:0.5
Siralox 40	1:1.9

*****Accuracy is represented by the last decimal place

Pieta et al. [2010] stated that silica alumina is more stable than fresh alumina. Using the silica alumina ratio as an indication, ZSM-5 and Siralox 40 will thus be more stable that Eta alumina (Table 4.3). They also stated that the catalytic properties are generally ascribed to the surface acidity and that the number and strength of these sites depend on the alumina content. Thus, as the alumina content increases, the acid number also increases but a decrease in acidic strength occurs. A comparison between the zeolite and amorphous silica alumina used in this study cannot be done directly as they are from different families of acidic catalysts. However, ZSM-5 is expected to have the highest acid number (to be confirmed with TPD analysis) but a low acidic strength because it has the highest silica to alumina ratio (Table 4.3).

4.3 Surface Acidity

N-propylamine Pulse chemisorptions –TPD-MS

The *n*-proylamine pulse chemisorptions –TPD-MS method was used to semi-quantitatively characterize the Brønsted acid sites accessible on the fresh catalysts. This is necessary for understanding skeletal isomerization. Brønsted acid site density is an essential factor as stated earlier in Chapter 2 [Damon et al., 1977]. Skeletal isomerization is reported to be catalyzed by Brønsted acid sites and therefore it is the most important requirement for the catalyst to have good Brønsted acidity.

Two detectors are used in this method of analysis. The TCD (thermal conductivity detector), which shows the residual amine and ammonia from the chemisorptions (Figure 4.6) and the MSD (mass spectrometer detector), which isolates the propylene signal to allow the calculation of the acid sites concentration as shown in Figure 4.7.

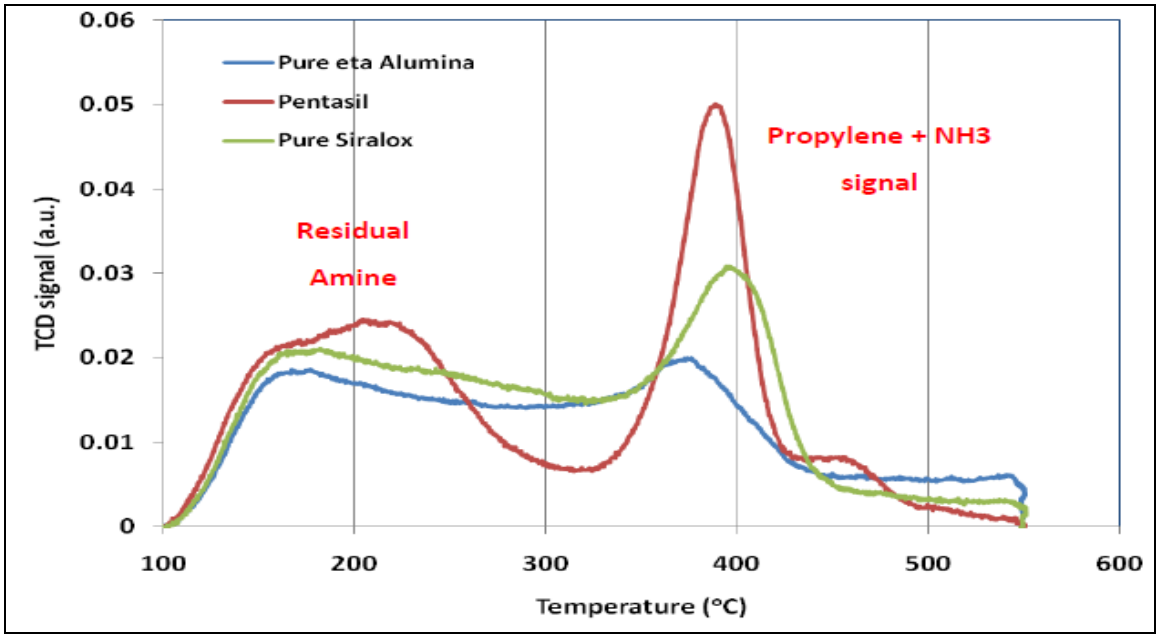


Figure 4.6: TPD spectra of *n*-proylamine on fresh Eta-alumina (blue profile), fresh ZSM-5 (red profile) and fresh Siralox 40 (green profile)

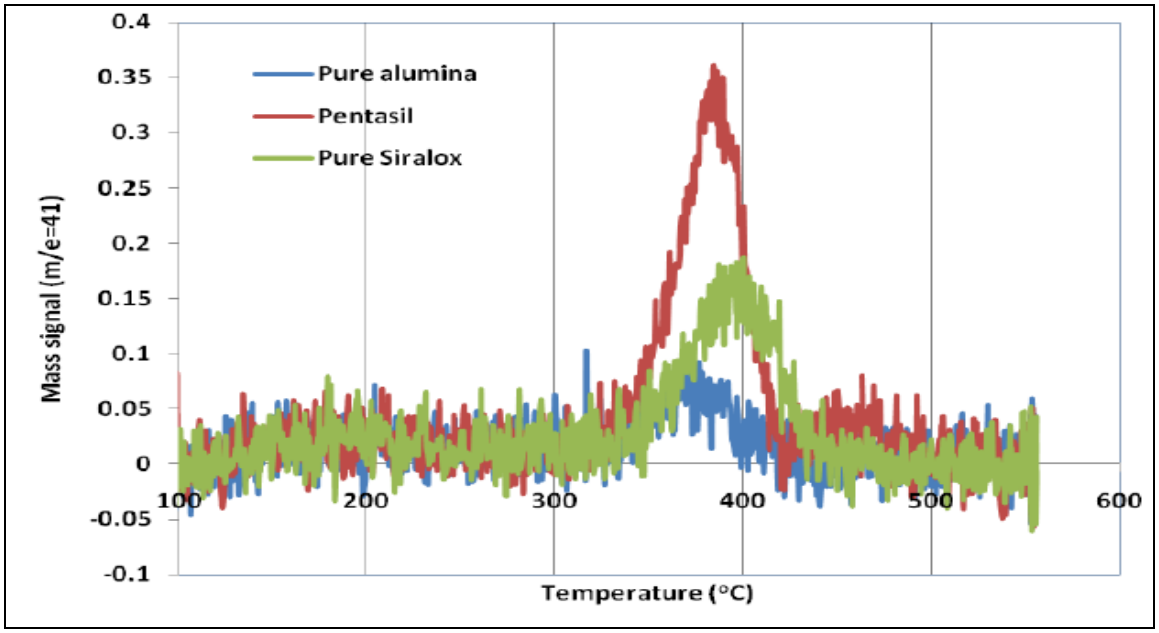


Figure 4.7: MS data of evolved propylene on fresh Eta-alumina (blue profile), fresh ZSM-5 (red profile) and fresh Siralox 40 (green profile)

From Figures 4.6 and 4.7 it is clear that for all the catalysts the temperature at which maximum desorption occurred was between 370 °C – 400 °C. Table 4.4 shows the difference in the calculated number of Brønsted acid sites between the fresh catalysts. The mass spectrometer (MS) must be calibrated in order to obtain quantitative data. This is achieved by injecting a known volume of the gas to be detected (propylene), V_{cal} through the septum. The peak area, A_{cal} of the mass spectrometer signal for propylene can be obtained from the AutoChem peak-editing software [Autochem, 1997 – 2011]. The ratio of (V_{cal}/ A_{cal}) can be used as a calibration factor for the calculations of Brønsted acid sites concentrations, N_{as}, using the formula below:

$$N_{as} = A_{pms}\,(V_{cal}/A_{cal})(L/10^3 cc)(mole/22.414L@STP)(10^6 \mu moles/mole)$$

However, the complete calibration has not yet been performed due to the need for system modifications which are still pending. As the mass spectrometer response calibration factor (V_{cal}/A_{cal}) for the amine is as yet undetermined the number of acid sites per gram sample can only be determined semi-quantitatively. The product (N_{as}/g)(A_{cal}/ V_{cal}) is thus reported in this study.

Table 4.4
***Number of Brønsted acid sites on the fresh catalysts**

Catalyst	Approximated Brønsted Acid Sites (μmoles/g) A_{cal}/V_{cal}
Pure Eta alumina	9.86
Pure ZSM-5	21.79
Pure Siralox 40	14.85

*****Accuracy is represented by the last decimal place

Table 4.4 illustrates that the highest number of Brønsted acid sites were observed on the fresh zeolite (ZSM-5), followed by the fresh amorphous silica alumina (Siralox 40) and the fresh Eta-alumina.

CO adsorption

The DRIFT spectra at increasing CO coverages for ZSM-5, Siralox 40 and Eta alumina are given in Figures 4.8, 4.9 and 4.10, respectively. The spectra obtained after CO adsorption were referenced to spectra before CO adsorption. This is useful to indicate the depletion or formation of species. Negative bands

indicate the depletion of OH species and positive bands indications the formation of new species following the interaction with CO.

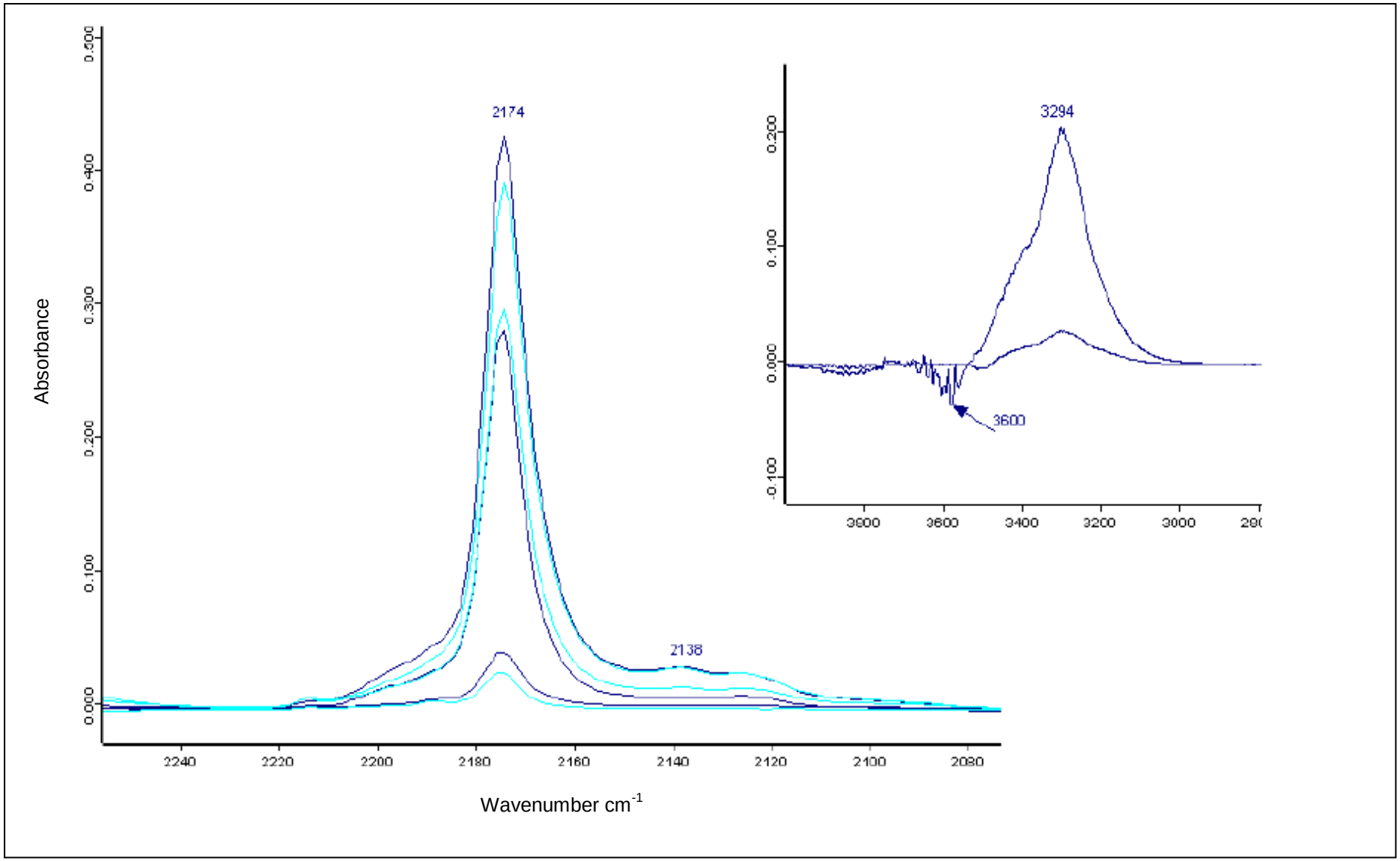


Figure 4.8: DRIFT spectra of fresh ZSM-5 in at different CO coverages. The insert shows changes in the OH region

In the DRIFT spectra of fresh ZSM-5 the following information was obtained. At low CO coverage, when only the strongest acid sites are interacting with CO, a band is observed at 2174 cm^{-1} which can be assigned to CO interacting with Brønsted acid sites of the type Si-OH-Al which are typically found in zeolites [Kustov et al., 1987]. At high CO coverage when all the acid sites are saturated with CO, the band at 2174 cm^{-1} is very strong and another band exists at 2138 cm^{-1} as shown in Figure 4.8. This band at 2138 cm^{-1} is assigned to CO physically adsorbed in the channels of the zeolite and it does not correspond to acid sites. Focussing on the insert, it shows changes in the OH region. The band at 3294 cm^{-1} is a positive band which arises from a hydrogen-bond complex of CO and the Si-OH-Al species whilst the negative band at 3600 cm^{-1} indicates the depletion of the Si-OH-Al species.

Considering the DRIFT spectra of fresh Eta alumina (Figure 4.9), three bands were observed. A strong band at 2191 cm^{-1} was observed at a high CO coverage and a second and third broad band formed when sites were saturated with CO. These bands formed at 2169 cm^{-1} and 2157 cm^{-1}. These bands existed in the region where CO was interacting with weakly acidic AlOH environments in alumina [Gatta et al., 1976].

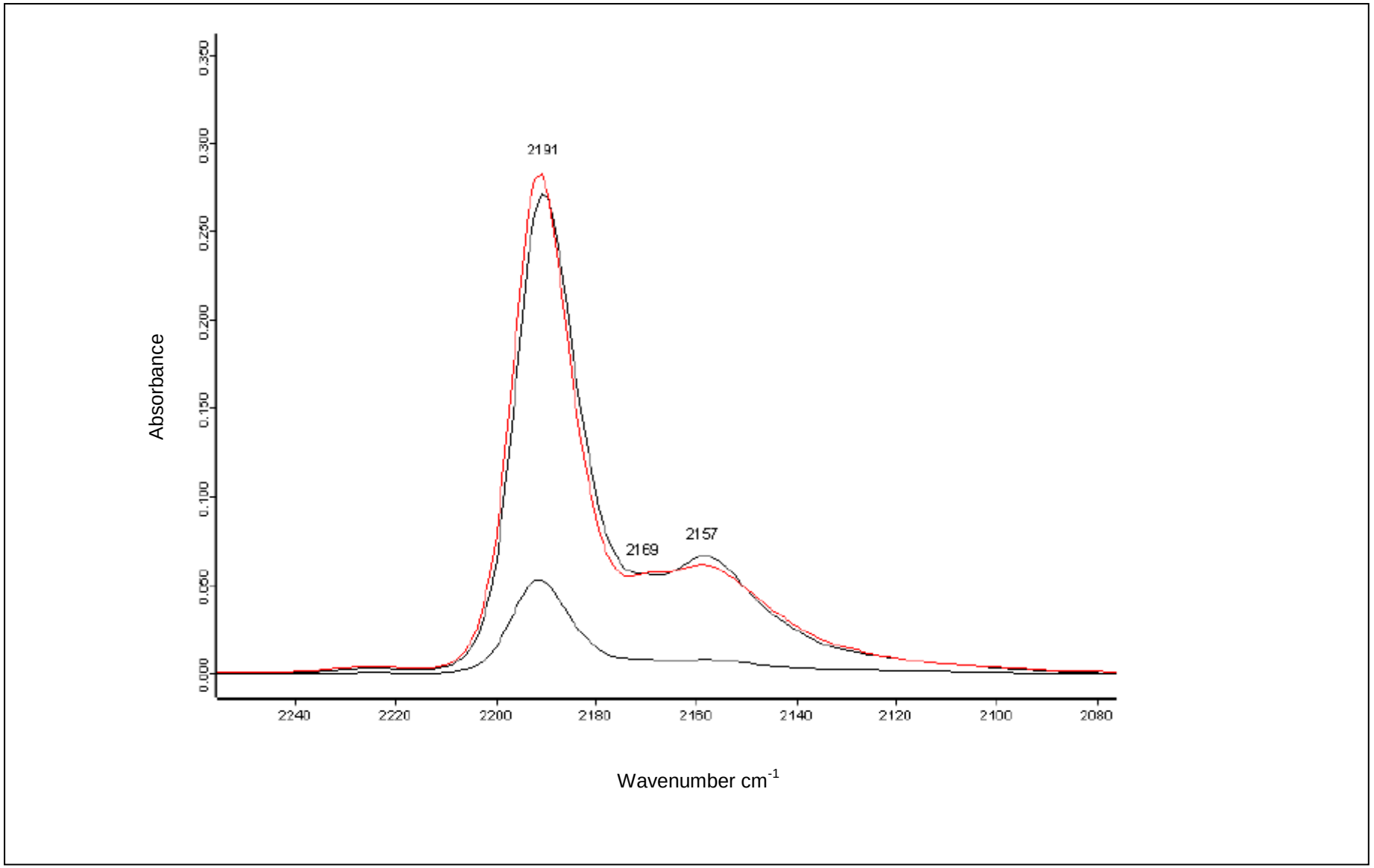


Figure 4.9: DRIFT spectra of fresh Eta alumina at different CO coverages

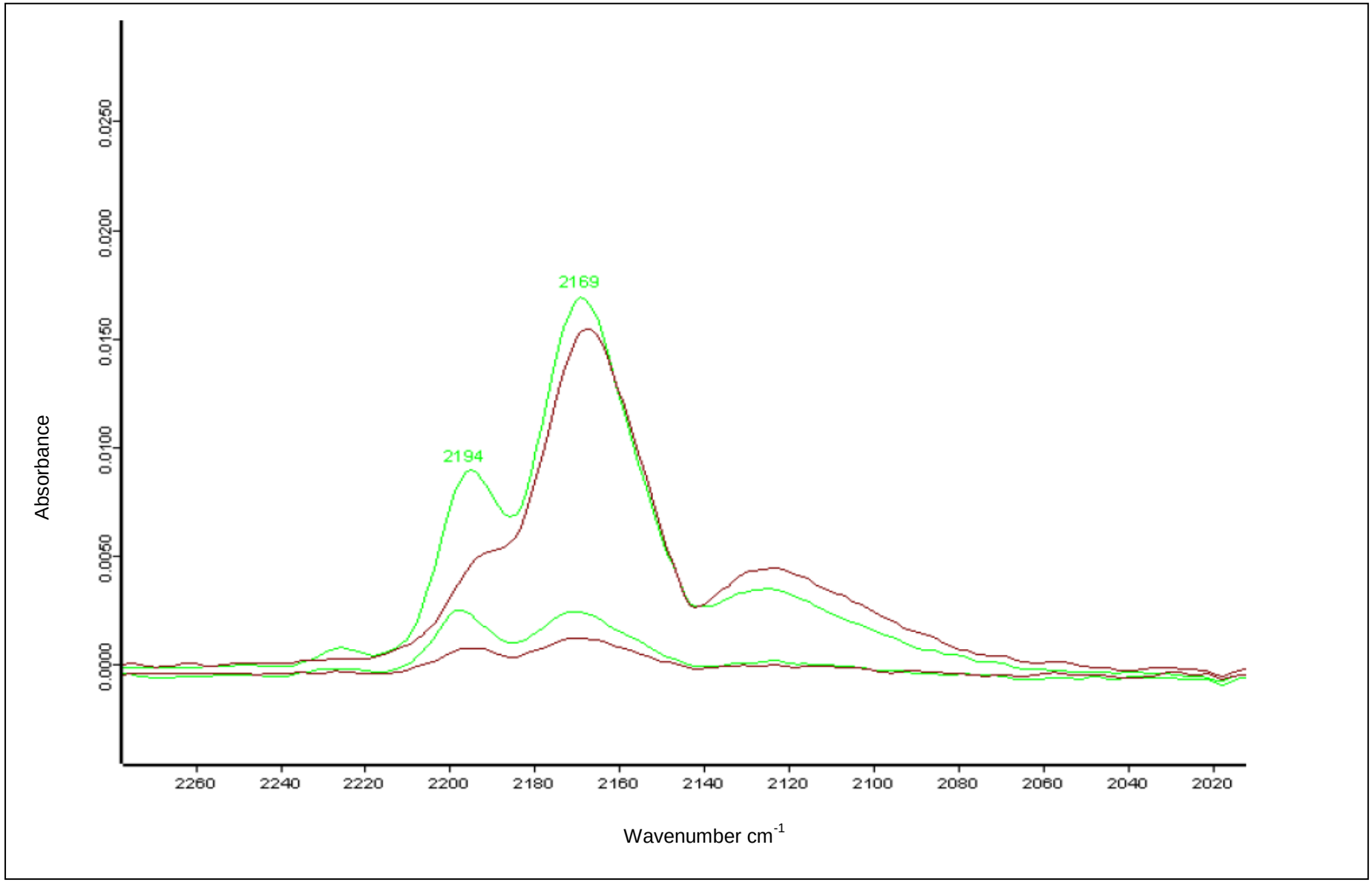


Figure 4.10: DRIFT spectra of fresh Siralox 40 at different CO coverages

The DRIFT spectra for fresh Siralox 40 (Figure 4.10) show the formation of two bands. The band at 2194 cm^{-1} shows the interaction of CO with the medium strong Lewis acid sites on alumina. The broader peak at 2169 cm^{-1} can be the interaction of CO with OH species. It is not possible to say whether strong Brønsted acid sites, as the case with ZSM-5, existed on the surface of Siralox 40.

4.4 Thermal Gravimetric Analysis (TGA)

TGA was done on the fresh catalysts to obtain the amount of fixed carbon present in the fresh catalysts. To explain how the results were calculated, a result sheet is shown in Figure 4.11. The fixed carbon amounts for the three catalysts were calculated and summarized in Table 4.5.

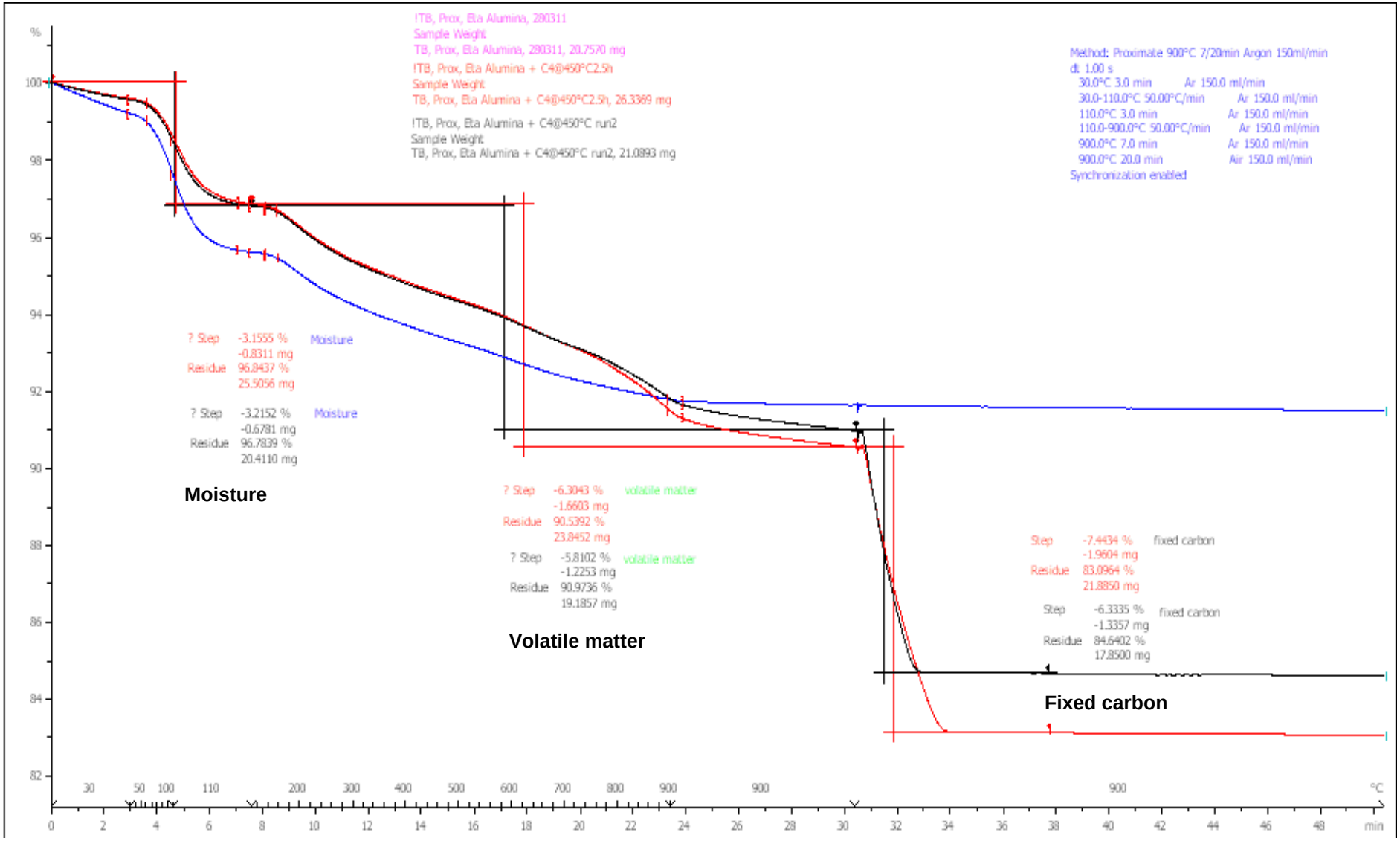


Figure 4.11: Typical TGA results sheet for fresh Eta alumina catalyst

Table 4.5
***Fixed Carbon analysis for the fresh catalysts**

Elements	Eta alumina Results	ZSM-5 Results	Siralox 40 Results
Fixed Carbon (%)	0	0	0.16

*****Accuracy is represented by the last decimal place

Siralox 40 was the only catalyst that showed a small amount of carbon.

4.5 Surface Area (SA) and Pore Volume (PV) Analysis

Surface area and pore volume analyses were performed on the fresh catalysts. The results are summarized in Table 4.6.

Table 4.6
***Surface area and pore volume analysis of the fresh catalysts**

	Eta alumina Results	ZSM-5 Results	Siralox 40 Results
PV (cm^3/g)	0.43	0.55	0.70
SA (m^2/g)	197.01	315.14	415.60

*****Accuracy is represented by the last decimal place

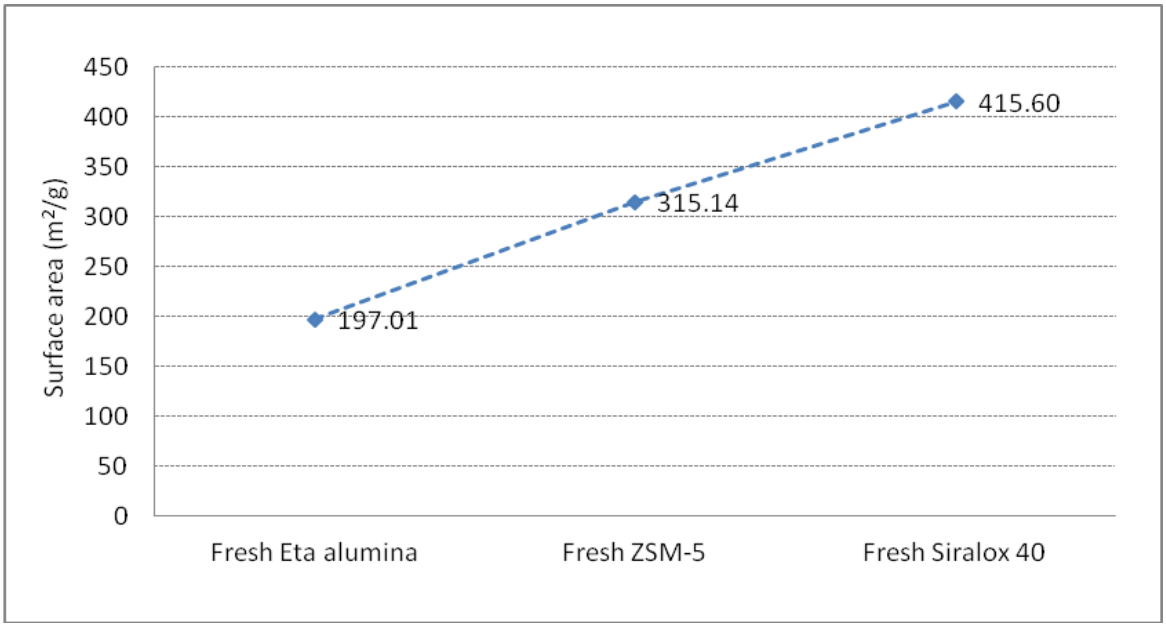


Figure 4.12: Surface Area (m^2/g) results for fresh Eta alumina, fresh ZSM-5 and fresh Siralox 40 catalysts

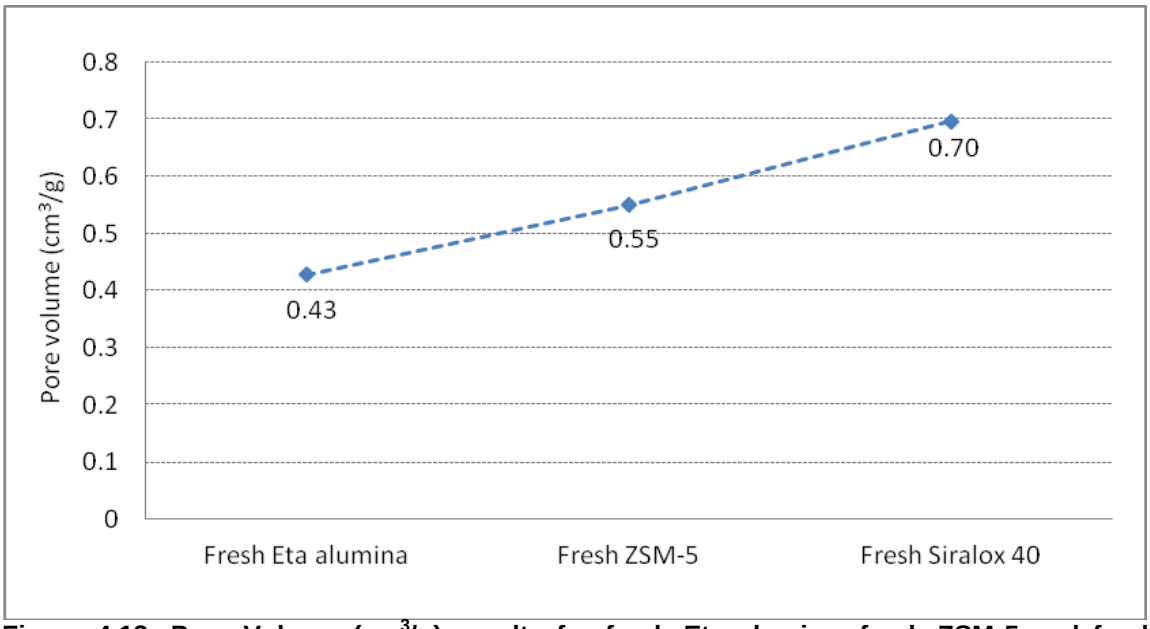


Figure 4.13: Pore Volume (cm^3/g) results for fresh Eta alumina, fresh ZSM-5 and fresh Siralox 40 catalysts

The surface area and pore volume data obtained for the three fresh catalysts indicate that fresh Siralox 40 had the biggest pores and greatest surface area followed by the fresh ZSM-5 and fresh Eta alumina catalyst.

4.6 Feed compositions

1-Butene

The butene used in this study was obtained from the Polyethylene business unit, Poly 2 (Midlands site, Sasolburg). A refinery gas analysis was conducted on the *1*-butene feed to determine the composition, and the results are listed in Table 4.7.

Table 4.7
Feed composition of *1*-butene

Compound	Volume %
C_6^+	6.21
Methane	0
Ethane	0
Ethylene	0
Propane	0.01
Cyclopropane	0
Propylene	0
Iso-butane	0.03
n-Butane	0.36
Propadiene	0
Acetylene	0
trans-2-butene	0.11
1-Butene	93.17
iso-butylene	0.10
cis-2-butene	0.09
iso-Pentane	0
n-Pentane	0
1,3-Butadiene	0.01
trans-2-pentene	0.01
1-pentene	0
2-methyl-*2*-butene	0.04
cis-2-pentene	0
Hydrogen	0

1-Hexene

The feed used for the isomerization of hexene was 97% *1*-hexene. The hexene was obtained from Merck. A GC analysis was done on the *1*-hexene. A summary of the results is given in Table 4.8. The percentages were calculated according to areas under the GC peaks.

Table 4.8
Feed composition of *1*-hexene

Compounds	%
1-hexene	99.12
2+*3*-Hexene	0.79
$<C_6$	0.01
branchedC_6's	0.08
C_7-C_{11}	0.01
C_{12}	0.00
$>C_{12}$	0.00

1-Octene

The feed used for the isomerization of octene was 98% *1*-octene. The octene was obtained from Merck. As for *1*- hexene, a summary of the results is given in Table 4.9.

Table 4.9
Feed composition of *1*-octene

Compounds	%
1-octene	99.13
2,3,4-octene	0.39
branched C_8's	0.16
lighter than C_8	0.06
C_9-C_{15}	0.26
C_{16}	0
$>C_{16}$	0

In Chapter 5, Chapter 6 and Chapter 7 the characterization of the products obtained using these catalysts and feed compounds will be discussed in detail.