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Microwave induced solid-state interactions for the synthesis of Fischer-Tropsch catalysts

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CHAPTER SIX

RESULTS AND DISCUSSION

6.1 INTRODUCTION

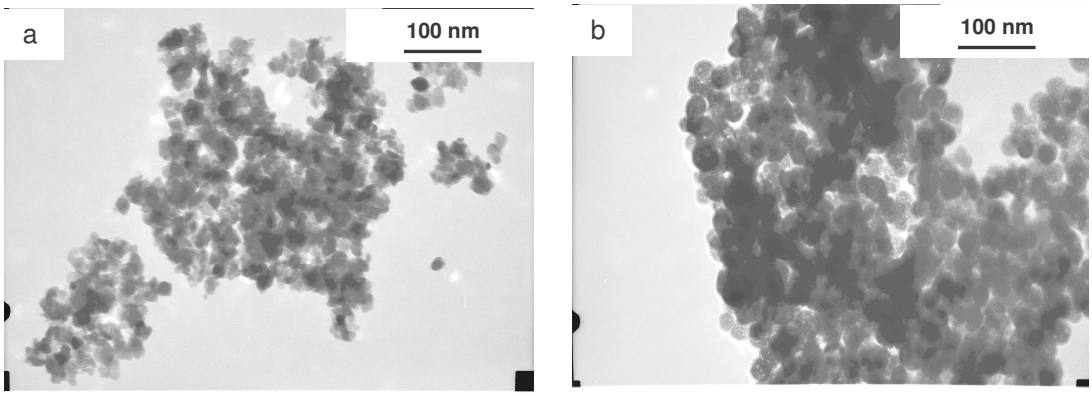
Both conventional and microwave pre-treated catalysts were used to examine a better catalyst for Fischer-Tropsch synthesis (FTS). The results obtained from catalyst characterization and Fischer-Tropsch reactions are reported and discussed in this chapter. Also reported are the results obtained from unsupported catalysts: unpromoted, promoted and partially reduced catalysts. The results are based on the effect of microwave pre-treatment on catalytic activity and selectivity in Fischer-Tropsch synthesis (FTS). The effect of duration (the time the catalyst spends in the microwave for the pre-treatment), the effect of the power level, and the effect of bed size and shape are shown and discussed. A number of characterization techniques i.e. Powder X-ray diffraction (PXRD), temperature programmed reduction (TPR), thermogravimetric analysis (TGA), Mössbauer spectroscopy, transmission electron microscopy (TEM) and scanning electron microscopy (SEM) techniques were used to examine the microwave effect on iron Fischer-Tropsch catalyst precursors. In addition, surface sensitive techniques were also employed to further examine the microwave effect i.e. temperature programmed surface reaction (TPSR) and secondary ion mass spectrometry (SIMS) studies.

6.2 CHARACTERIZATION OF UNSUPPORTED CATALYSTS

6.2.1 MICROWAVE EFFECT

Unsupported catalysts were prepared following the precipitation method. It is important to notice that the predominant iron-containing phase after catalyst preparation is hematite (α-Fe_2O_3). Characterization techniques were used to examine the microwave effect on these catalysts (hematite containing catalysts). The results obtained are displayed below:

6.2.1.1 TEM ANALYSIS



a = Iron catalyst before microwave pre-treatment, b = Iron catalyst after microwave pre-treatment.

Figure 6.1: TEM images of the unsupported catalysts before and after microwave pre-treatment. Iron catalyst was microwave pre-treated at 540 W for 8 s.

The iron oxide samples obtained after drying (110 ^{o}C) and calcination (350 ^{o}C) in air were analyzed using TEM to determine crystallite size distribution. **Figure 6.1** shows TEM images of the obtained unsupported crystallites after calcination at 350 ^{o}C in air.

TEM results were quantified using imageJ programme to determine the distribution of crystallite size (nm). The corresponding histograms demonstrate the distribution of iron crystallites which were measured directly from the TEM images. The distribution of crystallite size is represented in **figure 6.2**. It is clear that the microwave pre-treatment of the iron oxide samples resulted in crystallite growth. The mean and standard deviation for both iron oxide samples is given in **figure 6.2** respectively.

Iron particles agglomerate due to microwave heating resulting to an increase in the particle size.

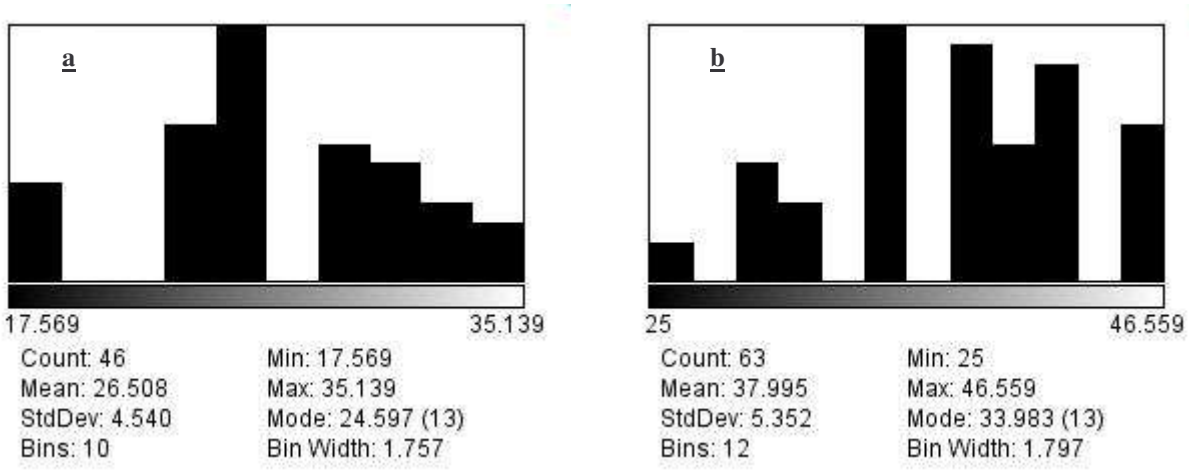


Figure 6.2: Crystallite size distribution (nm) of unsupported iron oxide samples before and after microwave pre-treatment. a = before microwave pre-treatment, b = after microwave pre-treatment.

6.2.1.2 PXRD ANALYSIS

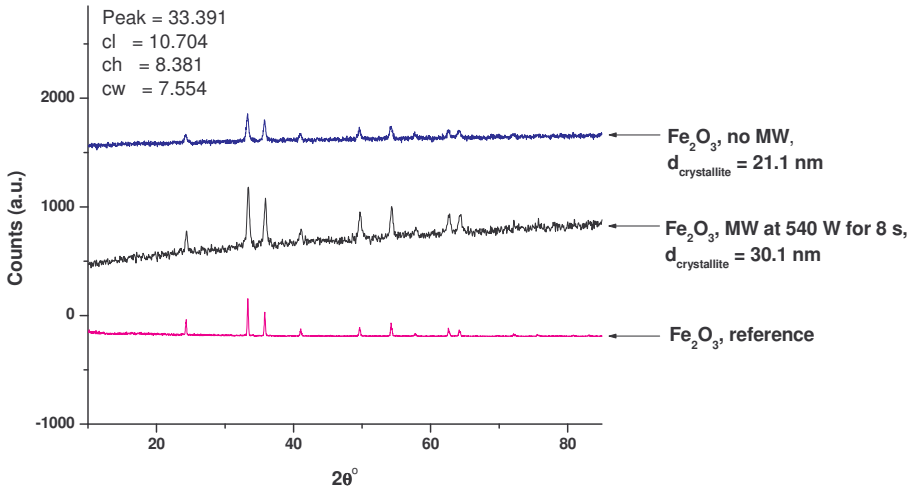


Figure 6.3: Powder X-Ray diffraction patterns of the unpromoted Fe catalysts before and after microwave pre-treatment. Fe_2O_3 containing catalyst was microwave pre-treated at 540 W for 8 s.

The crystallite size of the iron oxide samples were also determined using PXRD analysis. PXRD results were analyzed quantitatively following the PJF XRD analyzer. **Figure 6.3** shows PXRD patterns of the unsupported catalysts before and after microwave pre-treatment. It indicates the diffraction lines due to the hematite phase of the iron catalysts for both samples. The implication from the figure (powder diffraction) is that microwave pre-treatment results in agglomeration of the iron particles thereby intensifying the diffraction peaks.

6.2.1.3 SURFACE AREA

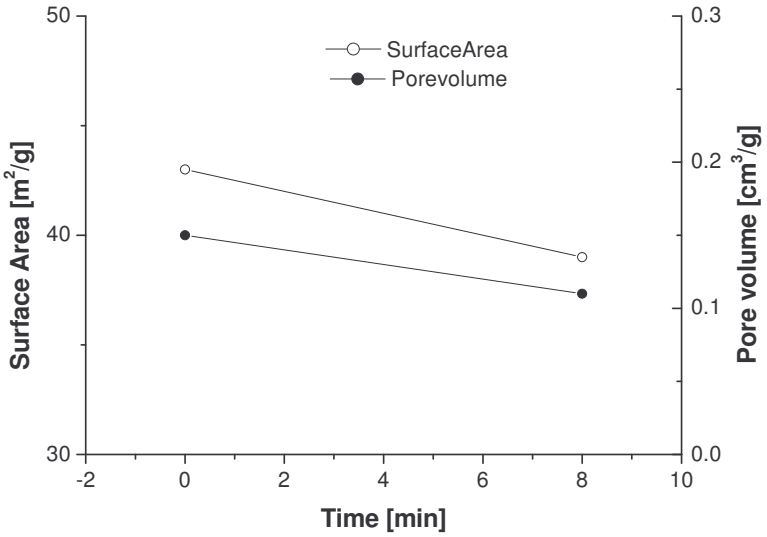


Figure 6.4: Surface area and pore volume obtained from unsupported iron oxide samples before and after microwave pre-treatment. Microwave pre-treatment was done at 540 W for 8 s.

The BET surface area results of the unsupported iron oxide samples before and after microwave pre-treatment are reported in **figure 6.4**. The specific surface area of the unmicrowave pre-treated catalyst was found to be 43 m^2/g; however that of the microwave pre-treated iron catalyst is 37 m^2/g. The surface area was found to decrease slightly with the microwave pre-treatment. This may be due to the increase in crystallite size of the metal oxide particle during the microwave heating. The pore volume was found to follow the same trend as the surface area of these iron composite materials.

The analysis of BET surface area can be linked to the average crystallite size for unsupported iron catalyst, since:

$$S_{BET} = \text{area/mass} = \text{area}/\rho \,.\, \text{volume} = \pi d^2_{crystallite}/\rho.\pi/6.d^3_{crystallite} = 6/\rho.d_{crystallite} \qquad 6.1$$

Knowing the density of α-Fe_2O_3 (5.12g/cm^3), the average crystallite size can be estimated (assuming spherical crystallites).

S_{BET},m^2/g	$d_{crystallite}$, nm
43	27
37	32

In addition, the average pore diameter can be estimated from the analysis of the pore volume. Assuming all pores are cylindrical pores with average length (L_{pore}) and average diameter (d_{pore}):

$$V_{pore}/S_{BET} = \frac{n_{pore} \cdot \pi/4.d^2_{pore} \cdot L_{pore}}{n_{pore} \cdot \pi \cdot d_{pore} \cdot L_{pore}} = d_{pore}/4 \qquad 6.2$$

S_{BET}, m^2/g	V_{pore}, cm^3/g	d_{pore}, nm
43	0.14	13
37	0.12	13

The results from the pore volume analysis investigate that the average diameter of the pore does not change upon microwave pre-treatment. This means that upon microwave heating, the pores of iron catalyst do not change.

TEM, PXRD and BET analysis revealed the increase in particle size of iron oxide samples upon microwave heating (**figure 6.5**).

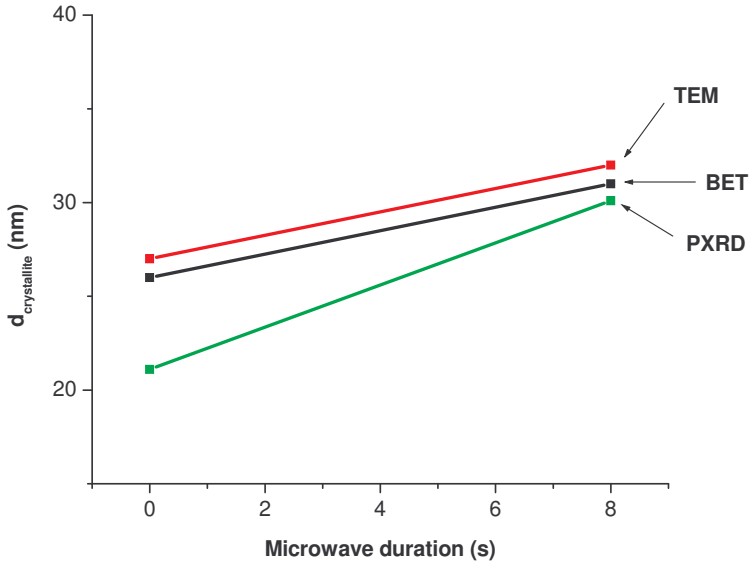


Figure 6.5: Crystallite size (nm) obtained from TEM, PXRD and BET showing the increase in particle size with the microwave heating (540 W for 8 s).

Figure 6.5 shows some discrepancy because the PXRD results showed the lowest crystallite size values. This explains that further work needs to be done in order to explain it, but that as revealed in **figure 6.5**. There is a good agreement in the trend and reasonable good agreement for the microwave samples.

6.2.1.4 H_2-TPR ANALYSIS

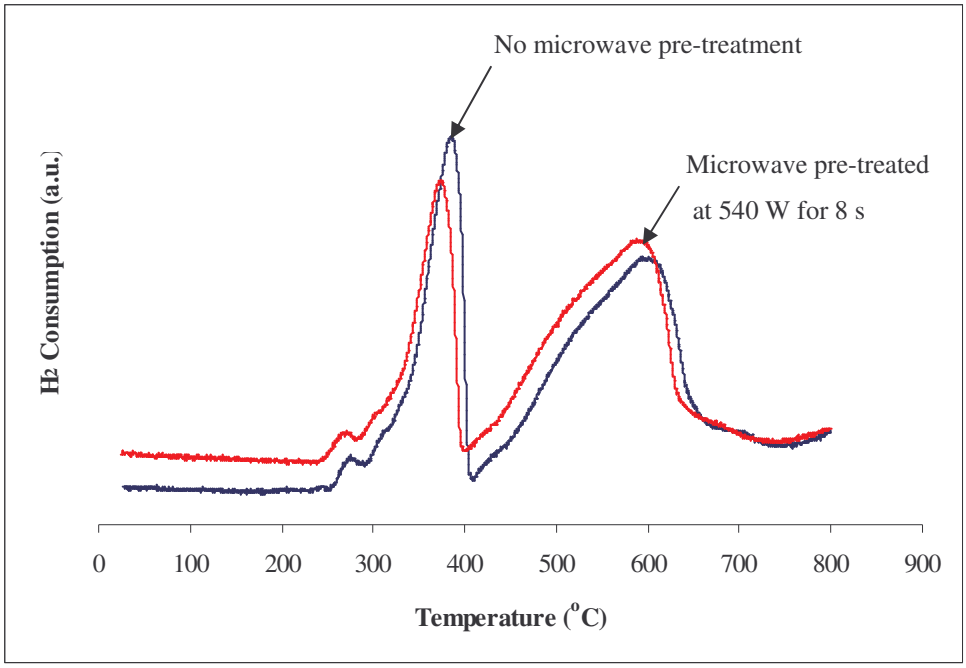
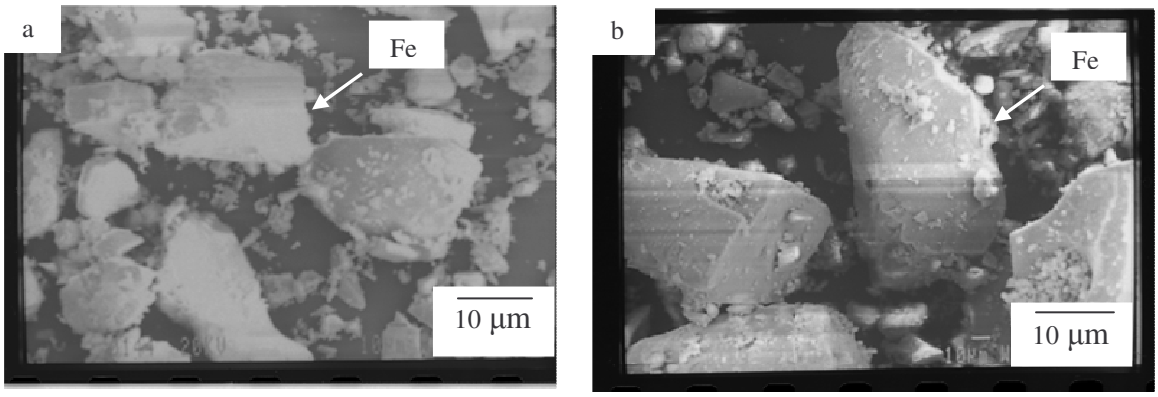


Figure 6.6: TPR profiles of the unsupported catalysts before and after microwave pre-treatment. Both samples were degassed at 5 °C/ min. in helium for 45 min. and reduced in hydrogen at 10 °C/ min.

The unsupported catalysts were further analysed by means of temperature programmed reduction (TPR). The hydrogen consumed by these solids before and after microwave pre-treatment is shown **figure 6.6**. Both TPR profiles show two distinct peaks which investigate a two step reduction of Fe_2O_3 to Fe_3O_4 and Fe_3O_4 to Fe (Iglesia et al., 1993). However, the TPR results showed no significant change brought in by the microwave pre-treatment in the reducibility of the iron catalysts as displayed in **figure 6.6.** Quantitative TPR analysis was not done. TPR was used as an indicative method to examine the microwave effect.

6.2.1.5 SEM ANALYSIS



a = unsupported catalyst before microwave pre-treatment, b = unsupported catalyst after microwave pre-treatment.

Figure 6.7: SEM images of the unsupported catalysts before and after microwave pre-treatment. Microwave pre-treatment was done at 540 W for 8 s.

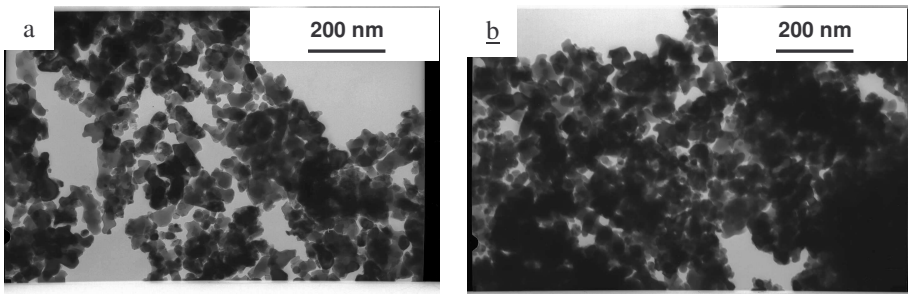
In heterogeneous catalysis, the structure of the catalyst affects its behaviour in chemical reactions. Characterization techniques are therefore used to investigate changes in the morphology of these solids. Scanning electron microscopy (SEM) was used to investigate any structural changes taking place due to microwave pre-treatment. The results showed no significant change in the morphology of these solids after microwave pre-treatment as investigated in **figure 6.7**.

6.3 CHARACTERIZATION OF PARTIALLY REDUCED IRON CATALYSTS

6.3.1 MICROWAVE EFFECT

The unsupported iron catalysts were partially reduced in hydrogen at 300 ^{o}C for 16 h in order to enrich the catalyst with magnetite. Magnetite is a good microwave absorbing medium whereas hematite is not. This work was carried out in order to investigate the microwave effect on a magnetite containing catalyst to examine its effect on catalytic activity and selectivity in Fischer-Tropsch synthesis. The results obtained are displayed below:

6.3.1.1 TEM ANALYSIS



a = unsupported catalyst before microwave pre-treatment, b = unsupported catalyst after microwave pre-treatment.

Figure 6.8: TEM micrographs of partially reduced iron catalysts before and after microwave pre-treatment. The microwave pre-treatment was carried out at 540 W for 8 s.

TEM results of the partially reduced iron FT catalysts showed a slight increase in the particle size after microwave pre-treatment. The distribution of crystallite size is given in **figure 6.9**.

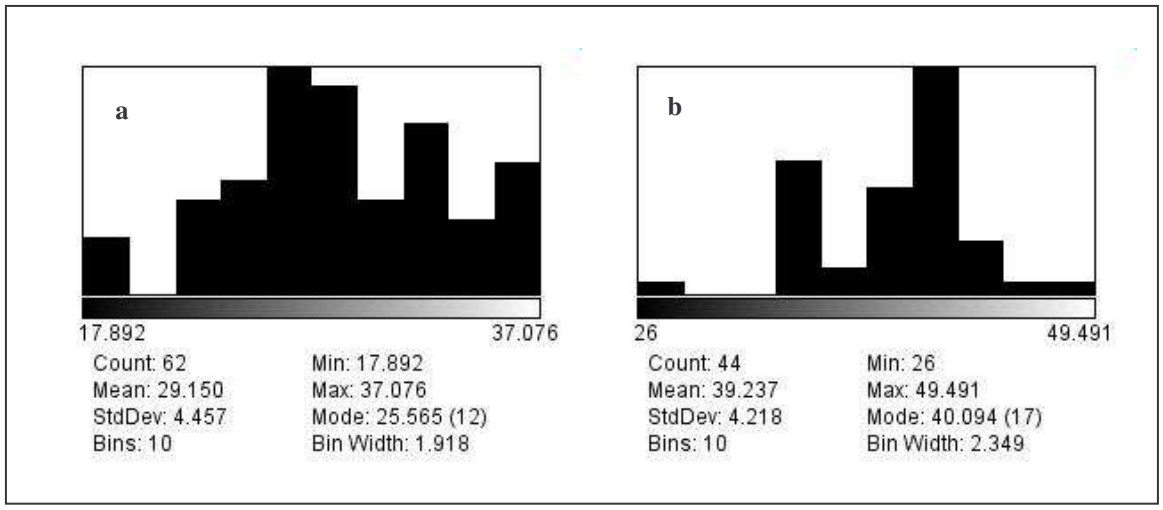


Figure 6.9: Crystalline size distribution (nm) of unsupported iron oxide samples before and after microwave pre-treatment. a = before microwave pre-treatment, b = after microwave pre-treatment.

6.3.1.2 PXRD ANALYSIS

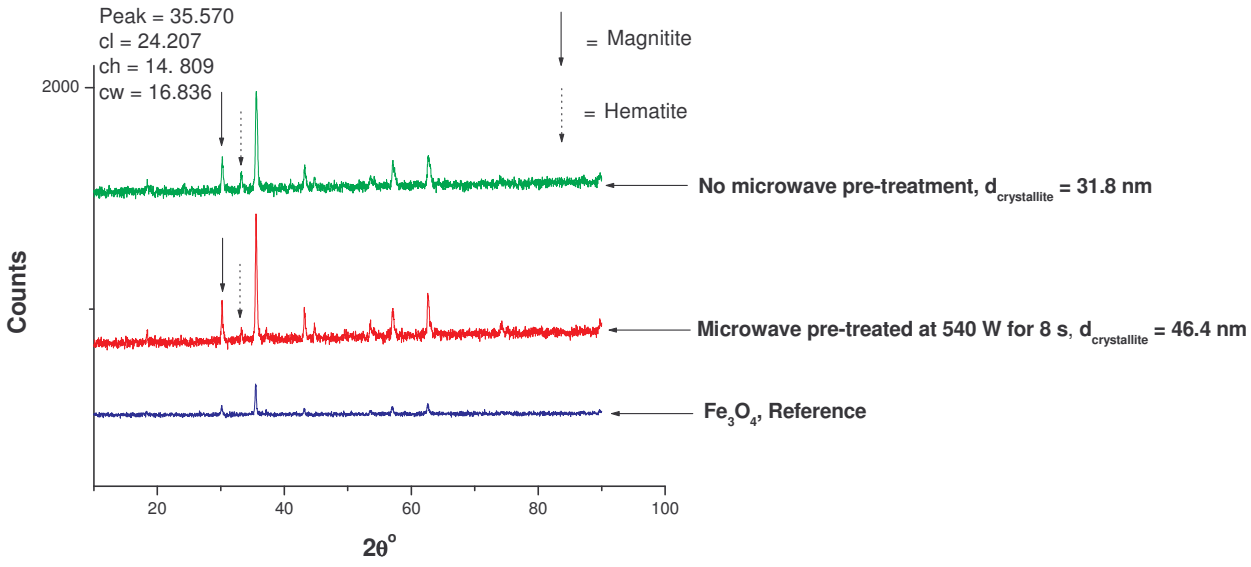


Figure 6.10: PXRD patterns of magnetite containing iron catalysts showing the microwave effect. Both catalysts were partially reduced at 300 ^{o}C in hydrogen.

Powder X-ray diffraction results for partially reduced iron catalysts showed magnetite and hematite present in the catalyst. The analysis of the experimental data revealed that no changes take place in the crystal structure of partially reduced iron catalysts but after microwave pre-treatment the particle size of iron increases. The PXRD results confirm the TEM results obtained in **figure 6.8**.

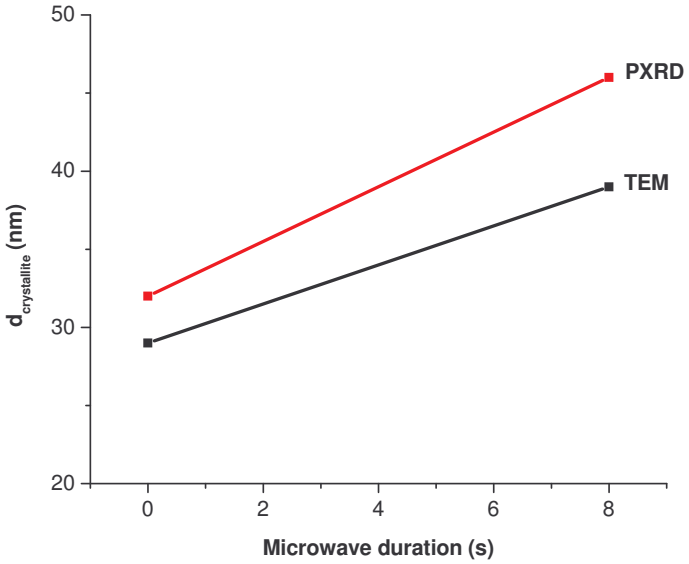


Figure 6.11: Crystallite size (nm) obtained from TEM and PXRD for a partially reduced iron catalyst showing the increase in particle size with the microwave heating (540 W for 8 s).

6.3.1.3 H_2 TPR ANALYSIS

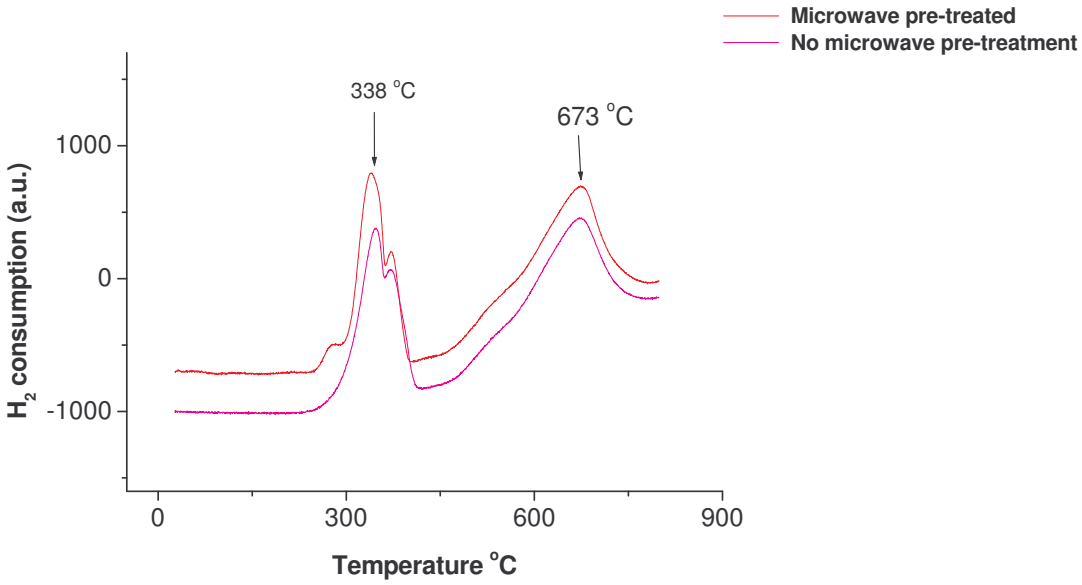


Figure 6.12: TPR profiles of the partially reduced iron catalysts before and after microwave pre-treatment. Microwave pre-treatment was carried out at 540 W for 8 s.

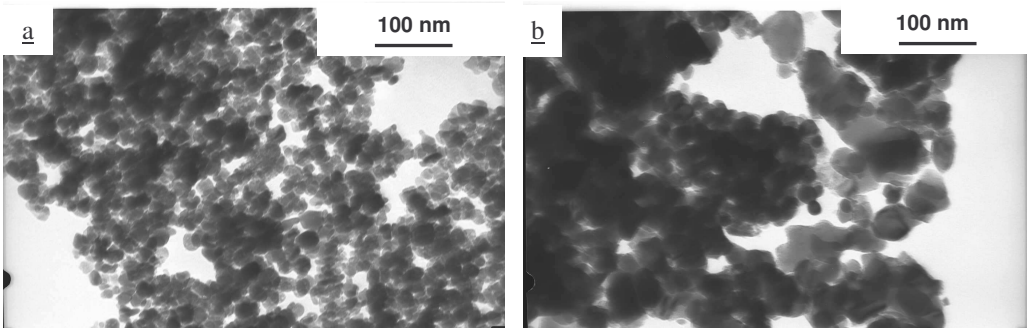
Hydrogen TPR analysis revealed no significant changes in the reduction of iron FT catalyst after microwave heating. Both curves show three reduction peaks. The first two peaks correspond to the reduction of Fe_2O_3 to Fe_3O_4. The reduction of Fe_2O_3 occurs in two steps in this case. The third peak corresponds to the reduction of Fe_3O_4 to metallic iron. TPR peaks due to the reduction of Fe_2O_3 to Fe_3O_4 are relatively narrow due to fast reduction of Fe_2O_3 to Fe_3O_4 whereas a TPR curve due to the reduction of Fe_3O_4 to metallic iron is broad corresponding to the slow transformation process of Fe_3O_4 to metallic iron.

6.4 CHARACTERIZATION OF THE Fe/K CATALYSTS

Potassium containing catalysts were prepared following the precipitation method of catalyst preparation. Characterization techniques were used to investigate the effect of microwave on the promoted iron catalysts. The effect of the power level, effect of duration, effect of bed size and shape were investigated using different analysis techniques. The results obtained are displayed below:

6.4.1 MICROWAVE EFFECT

6.4.1.1 TEM ANALYSIS



a = unsupported catalyst before microwave pre-treatment, b = unsupported catalyst after microwave pre-treatment.

Figure 6.13: TEM images of the Fe/K catalysts before and after microwave pre-treatment. Microwave pre-treatment was carried out at 540 W for 8 s.

TEM micrographs of the obtained Fe/K catalysts are investigated in **figure 6.13**, illustrating the distribution of iron particles. Based on the results, it can be seen that the particle size growth occurs with the microwave pre-treatment as observed from the unpromoted Fe_xO_y catalysts (**figure 6.1**). The crystalline growth occurs due to heating as

the iron particle agglomerates with the microwave heating. The distribution of crystallite size is displayed in **figure 6.14** respectively.

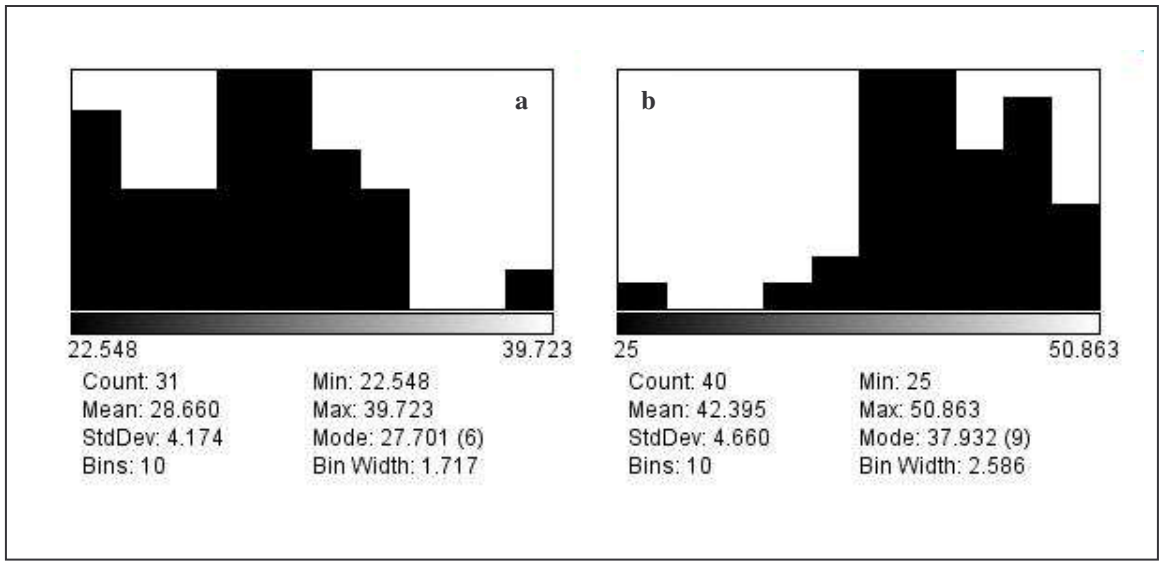


Figure 6.14: Crystallite size distribution (nm) of Fe/K samples before and after microwave pre-treatment. a = before microwave pre-treatment, b = after microwave pre-treatment.

6.4.1.2 PXRD ANALYSIS

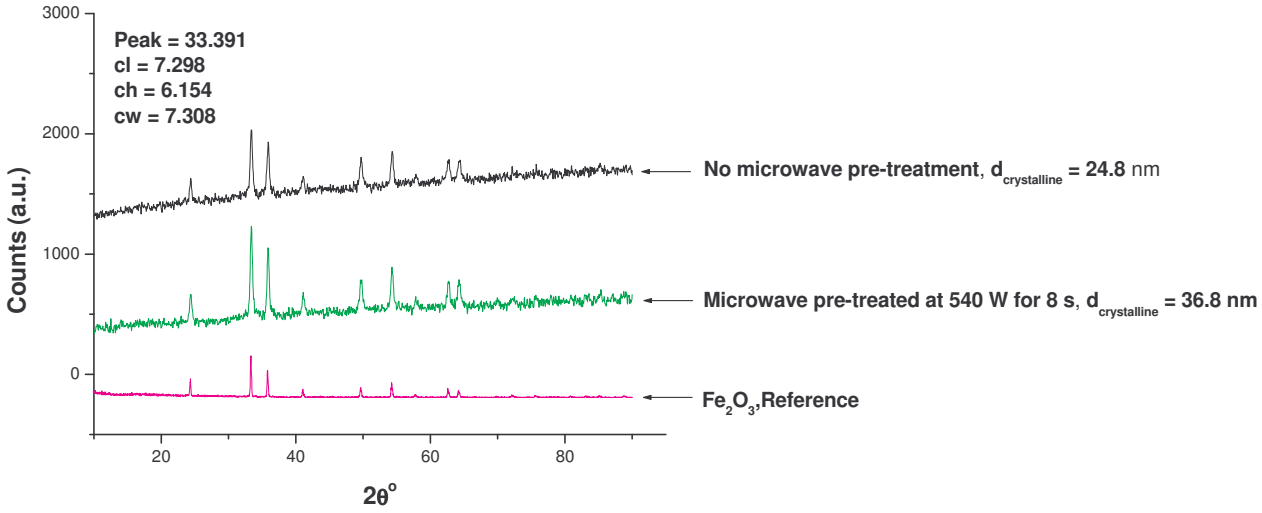


Figure 6.15: PXRD patterns of the Fe/K catalysts before and after microwave pre-treatment showing the effect of microwave pre-treatment on iron catalysts.

The increase in particle size growth of the promoted iron catalysts was further illustrated by powder X- ray diffraction. The results confirm the changes brought in by the microwave pre-treatment on the crystallinity of these composite materials. Based on the results obtained it can be seen that the microwave pre-treatment changes the crystallinity of the promoted Fe catalysts.

6.4.1.3 BET ANALYSIS

Table 6.1: Surface area determination investigating the effect microwave pre-treatment on Fe/K catalysts.

Power level	Surface area (m^2/g)	Pore volume (cm^3/g)
0	38	0.1
540 W	28	0.07

The BET analysis showed that after potassium promotion, the specific surface area pore volume become lower. The decrease in specific surface area was found to be attributed to the fact that potassium enhances the agglomeration of the FeOOH precursor and enlarges the crystallite size of α-Fe_2O_3 after being calcined at 350 ^oC (Yang et al., 2004, Dry 1968).

Following equation 6.1,

S_{BET},m^2/g	$d_{crystallite}$, nm
38	30
28	42

Particle size distribution obtained from TEM, PXRD and BET is listed in **figure 6:16**

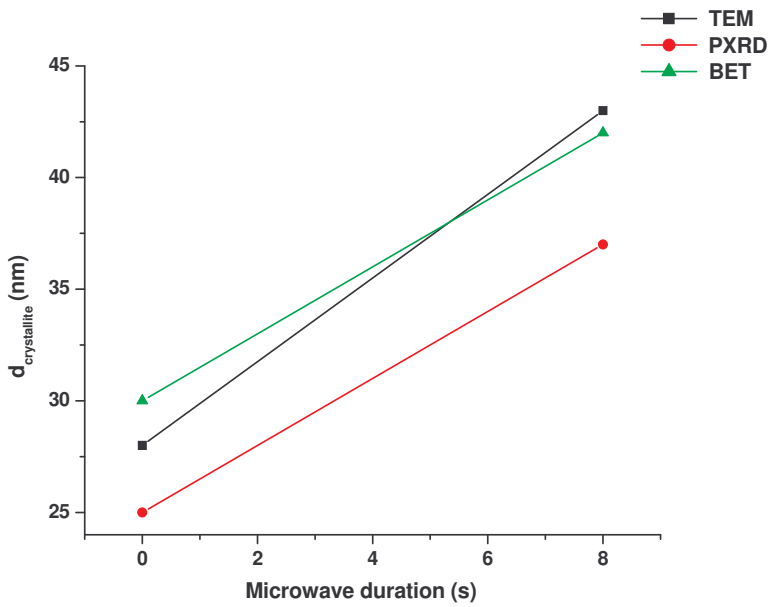


Figure 6.16: Crystallite size (nm) for Fe/K catalysts obtained from TEM and PXRD showing the increase in particle size with the microwave heating (540 W for 8 s).

6.4.2 EFFECT OF THE POWER LEVEL

During the microwave pre-treatment, the power level used was varied with the idea of knowing the optimum level to be used in the pre-treatment of the iron FT catalysts. We examined the optimum level which brings effective changes on catalytic activity and selectivity in Fischer-Tropsch synthesis.

6.4.2.1 TEM ANALYSIS

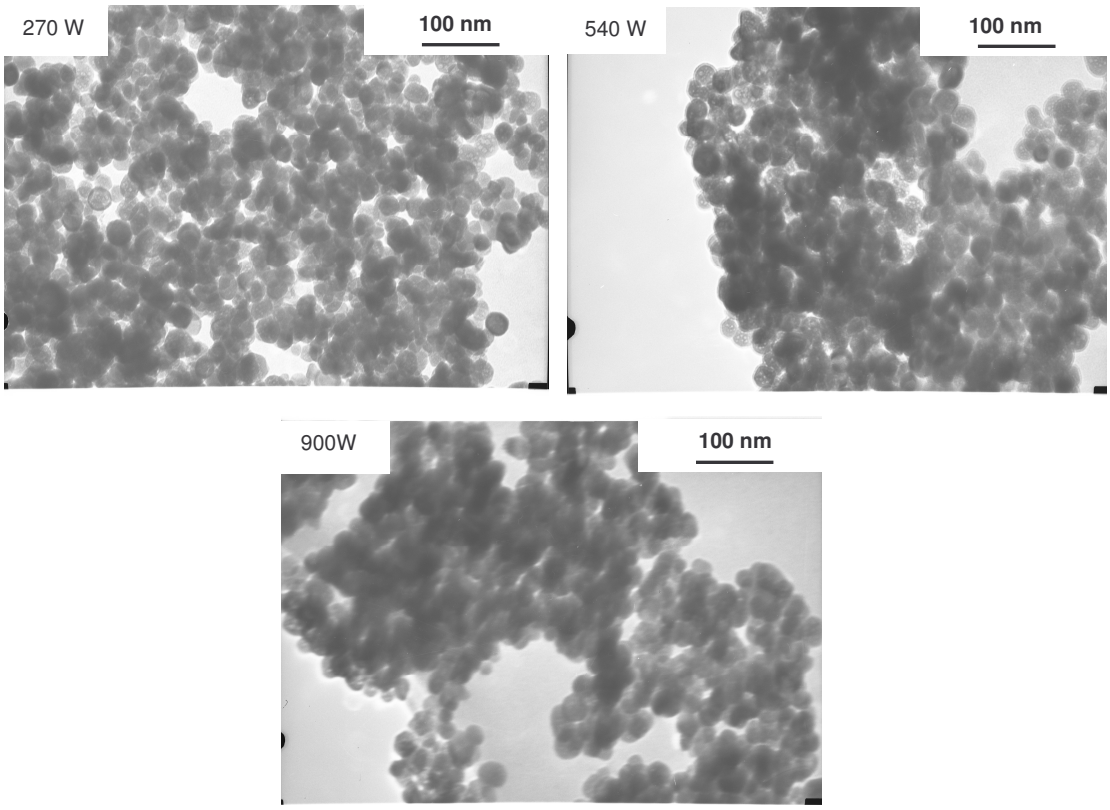


Figure 6.17: TEM micrographs of the microwave pre-treated unsupported iron catalysts investigating the effect of the power level. Microwave pre-treatment was carried out for 8 s at 270 W, 540 W and 900 W respectively.

TEM micrographs of the iron catalysts microwave pre-treated at different power levels are investigated (**figure 6.17**). It can be seen that the particles are spherical in

morphology. It can also be examined from **figure 6.17** that with increasing the power level, the particle size of iron increases. The increase in particle size is probably due to agglomeration as the results of microwave heating. Crystallite size distribution is displayed in **figure 6.18**.

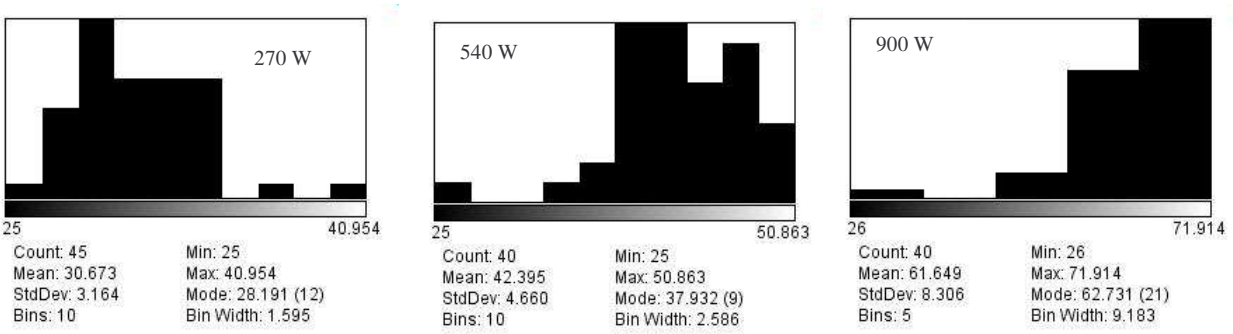


Figure 6.18: Crystallite size distribution (nm) of iron oxide samples microwave pre-treated at different power levels (270, 540 and 900 W) for 8 s.

6.4.2.2 PXRD ANALYSIS

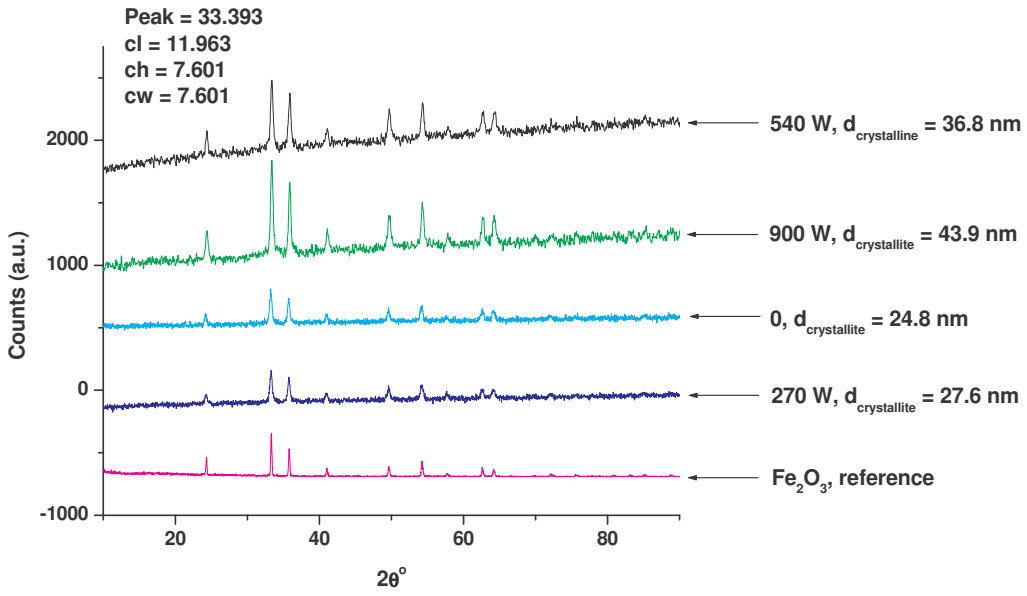


Figure 6.19: PXRD patterns of the Fe/K catalysts microwave pre-treated at different power levels for 8 s.

The effect of the power level on the particle size of the iron particles was also examined by PXRD characterization, the PXRD patterns are investigated in **figure 6.18**. In the figure, it can be seen that the particle size of iron increases with the microwave pre-treatment. The increase in particle size was found to increase with the power level from 270 W to 900 W.

6.4.2.3 SURFACE AREA

Table 6.2: Surface area determination investigating the effect of the power level on Fe/K catalysts. Duration for the microwave pre-treatment was kept constant, 8 s for all the experiments.

Power level	Surface area (m^2/g)	Pore volume (cm^3/g)
0 W	38	0.1
270 W	33	0.09
540W	28	0.07
900 W	21	0.05

BET results are in agreement with both TEM and PXRD results as the particle sizes of the nano-crystallites increases, the specific surface area decreases as investigated in **table 6.1**.

The average crystallite size was calculated from BET results for unsupported iron catalyst, since:

$$S_{BET} = \text{area/mass} = \text{area}/\rho \,.\, \text{volume} = \pi d^2_{crystallite}/\rho.\pi/6.d^3_{crystallite} = 6/\rho.d_{crystallite} \qquad 6.1$$

Knowing the density of α-Fe_2O_3 ($5.12 g/cm^3$), the average crystallite size can be estimated (assuming spherical crystallites).

$S_{BET}, m^2/g$	$d_{crystallite}$, nm
38	30
33	36
28	42
21	56

In addition, the average pore diameter can be estimated from the analysis of the pore volume. Assuming all pores are cylindrical pores with average length (L_{pore}) and average diameter (d_{pore}):

$$V_{pore}/S_{BET} = \frac{n_{pore} \cdot \pi/4.d^2_{pore} \cdot L_{pore}}{n_{pore} \cdot \pi \cdot d_{pore} \cdot L_{pore}} = d_{pore} / 4 \qquad 6.2$$

S_{BET}, m^2/g	V_{pore}, cm^3/g	d_{pore}, nm
43	0.14	13
37	0.12	13
21	0.05	10

The crystallite size obtained from BET, TEM and PRXD is investigated in **figure 6.20**.

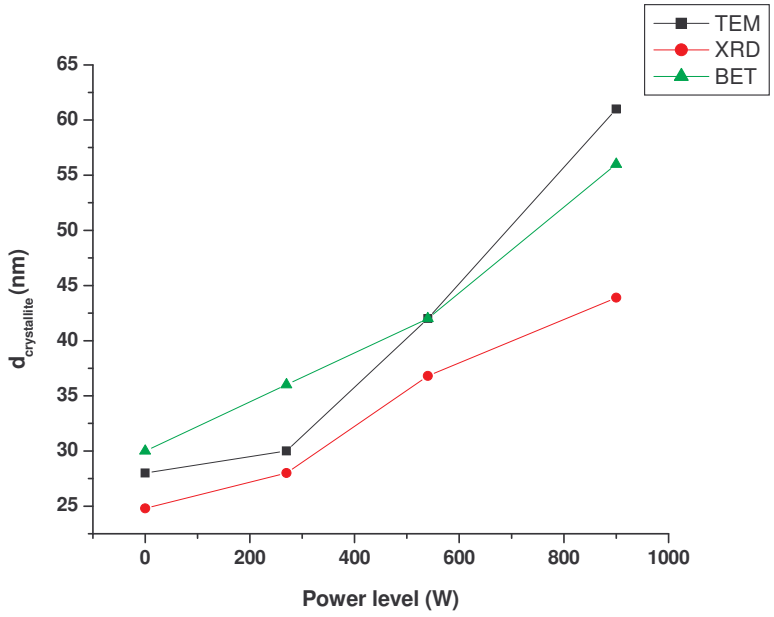


Figure 6.20: Crystallite size (nm) obtained from TEM and PXRD showing the increase in particle size with the microwave heating at different power level (270, 540 and 900W).

6.4.3 EFFECT OF DURATION

When pre-treating the iron catalyst, the time the catalyst spends in the microwave was varied in order to investigate the effect of time. Temperature measurements were taken before and after microwave pre-treatment. The temperature difference was found to increase with increasing microwave pre-treatment time i.e. for 8 s, $\Delta T = 5\ ^{o}C$; 15 s, $\Delta T = 11\ ^{o}C$; 60 s, $\Delta T = 42\ ^{o}C$ respectively. The power level was kept constant (540W) for all the experiments. The temperature difference is calculated from final temperature (after microwave pre-treatment and initial temperature (before microwave pre-treatment). Temperature was measured using a non-contact thermometer and of course represents only a gross mean temperature of the entire sample. Local heating effects are not monitored.

6.4.3.1 PXRD ANALYSIS

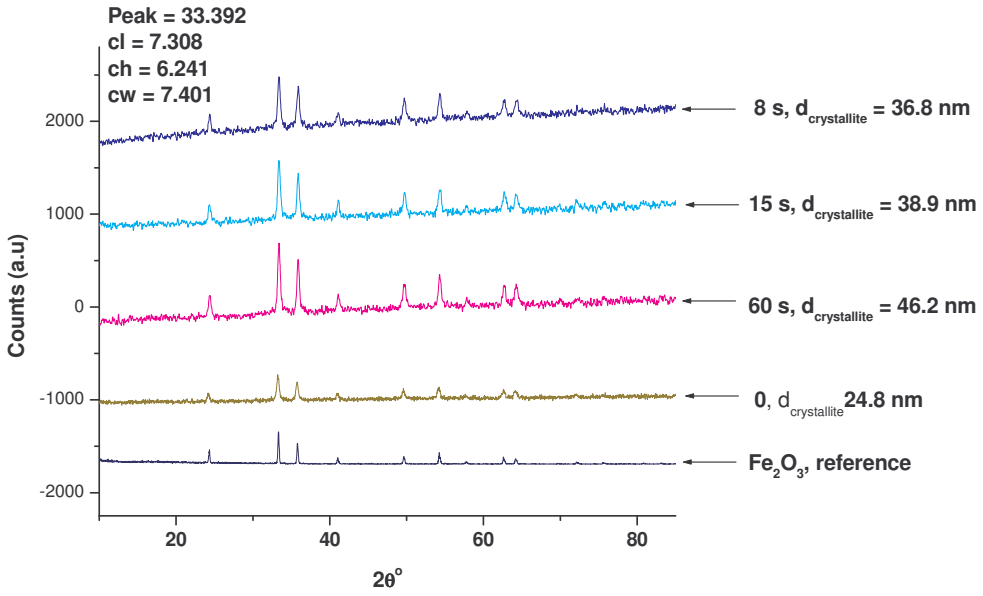


Figure 6.21: PXRD patterns for Fe/K catalysts microwave pre-treated at different times. Microwave pre-treated was carried out at 540 W.

Figure 6.21 shows PXRD patterns of Fe/K catalysts microwave pre-treated at different duration. It indicates the diffraction lines pertaining to the hematite phase of Fe for all samples. The suggestion from the figure is that the time taken by the catalyst in the microwave for pre-treatment does not alter the crystal structure of hematite. The increase in duration of the microwave resulted to the increase in particle size of the unsupported iron oxide samples.

6.4.3.2 BET ANALYSIS

Table 6.3: Surface area determination investigating the effect of duration on Fe/K catalysts.

Duration	Surface area (m^2/g)	Pore volume (cm^3/g)
0	38	0.1
8 s	28	0.07
15 s	25	0.06
60 s	19	0.05

The BET surface areas of Fe/K catalyst microwave pre-treated at different duration are reported in **Table 6.2**. The specific surface area of Fe/K catalyst microwave pre-treated for 8 s was found to be 37 m^2/g, however, that of the Fe/K catalyst microwave pre-treated for 60 s was 18 m^2/g. The decrease in the BET surface area upon microwave pre-treatment was presumably as a result of a re-distribution of the particle size. The particle size of iron increases with increasing duration of the microwave pre-treatment.

Using **equation 6.1**, the average crystallite size can be estimated (assuming spherical crystallites).

$S_{BET}, m^2/g$	$d_{crystallite}$, nm
38	30
28	42

25	47
18	65

The crystallite size distribution obtained for promoted iron oxide samples is displayed in **figure 6.22** (PXRD and BET).

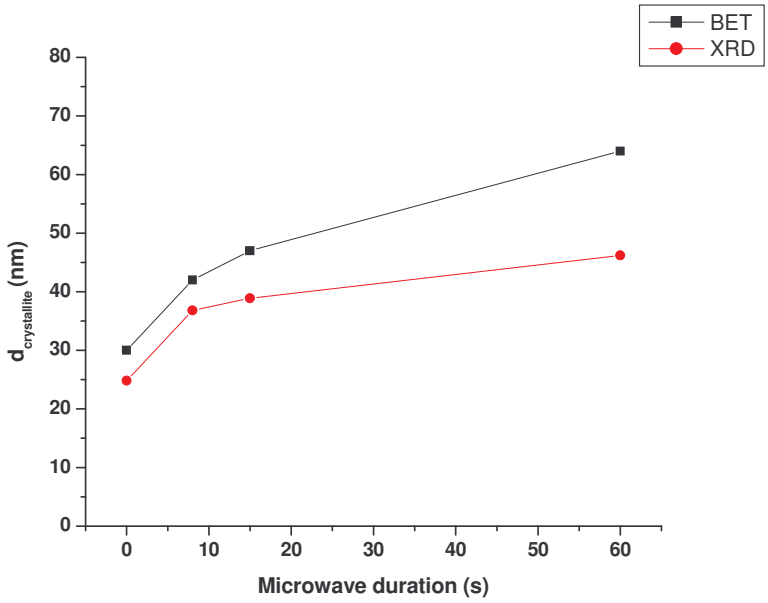


Figure 6.22: Crystallite size (nm) obtained from PXRD and BET for Fe/K catalysts showing the increase in particle size with the microwave heating at different times (0, 8,15, and 60 s).

6.4.4 EFFECT OF BED SIZE AND SHAPE

Iron catalysts were either placed uniformly or unevenly on a Petri dish before being introduced in the microwave for the pre-treatment. This study was carried out to examine the microwave effect.

6.4.4.1 PXRD ANALYSIS

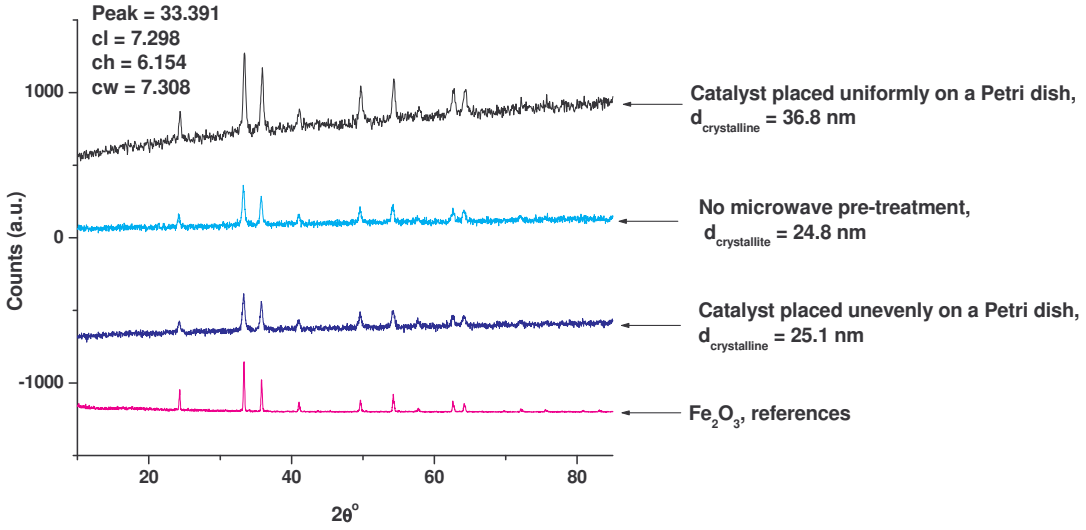


Figure 6.23: PXRD patterns of the Fe/K catalysts both microwave pre-treated at 540 W for 8 s. Bed size and shape was varied to understand the microwave effect.

Experimental analysis revealed that effective absorption of the microwave was obtained at uniform arrangement of the catalyst bed. When the catalyst bed was unevenly arranged, the analysis of the data investigated insignificant changes taking place as compared with before microwave heating.

6.4.4.2 BET ANALYSIS

Table 6.4: Surface area determination investigating the effect of the bed size and shape on promoted iron oxide catalysts.

Condition	Surface area (m^2/g)	Pore volume (cm^3/g)
No MW	38	0.1
Uniform distribution	28	0.07
Uneven distribution	35	0.09

Using **equation 6.1**, the average crystallite size can be estimated (assuming spherical crystallites).

$S_{BET}, m^2/g$	$d_{crystallite}$, nm
38	30
28	42
35	33

6.5 CHARACTERIZATION OF SUPPORTED CATALYST

The microwave effect in Fischer-Tropsch synthesis was also studied using supported iron catalysts. After catalyst preparation, the catalyst precursor was characterized using thermogravimetric analysis (TGA) to investigate the temperature at which the catalyst loses nitrates, temperature programmed reduction (TPR) to investigate the reduction temperature of the iron Fischer-Tropsch catalysts and powder X-Ray diffraction (PXRD) to look into the predominant iron phase and to estimate the particle size of the active metal. X-ray florescence was also used to determine the composition of the catalysts. The prepared catalysts were analyzed for iron and potassium content by means of X-Ray florescence (XRF). **Table 6.4** summarizes the elemental composition of the catalyst calcined, supported Fischer-Tropsch catalysts employed in this work. After that the microwave effect was studied. The results obtained are as follows:

Table 6.5: Elemental composition of the calcined, supported Fischer-Tropsch catalysts.

Nominal metal content (wt %)	Actual Fe content (wt %)	Actual K content (wt %)
$10Fe/2K/SiO_2$	10	2
$10Co/SiO_2$	9.8	------

6.5.1 THERMOGRAVIMETRIC (TGA) ANALYSIS

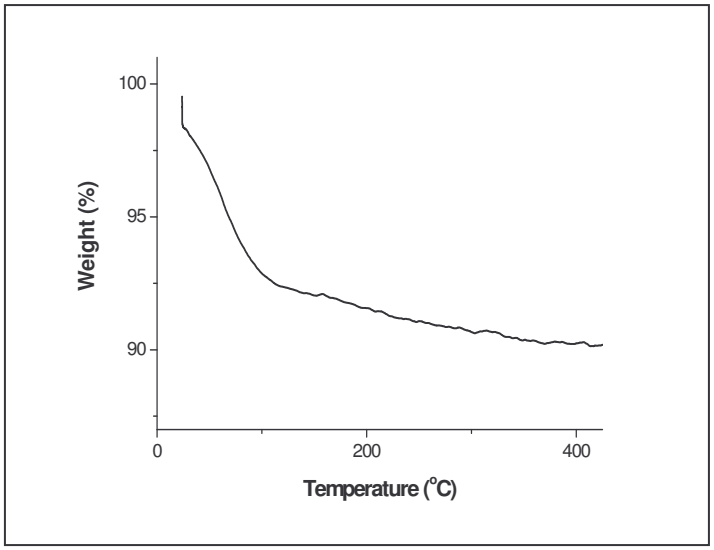


Figure 6.24: A TGA profile of the uncalcined Fe/SiO_2 catalyst.

A TGA under nitrogen atmosphere was obtained in order to check the temperature at which the nitrates were decomposed. The results (**Figure 6.24**) showed that the catalyst was loosing about 3 % (nitrates) at about 250 ^{o}C. 8 % loss below 100 ^{o}C is probably due to moisture. The catalyst was calcined at 350 ^{o}C for 6.5 hrs under air. At this stage the catalyst was almost ready to be reduced. The TPR profile that would give an indication at what temperature the catalyst would be reduced was needed.

6.5.2 TEMPERATURE PROGRAMMED REDUCTION (TPR)

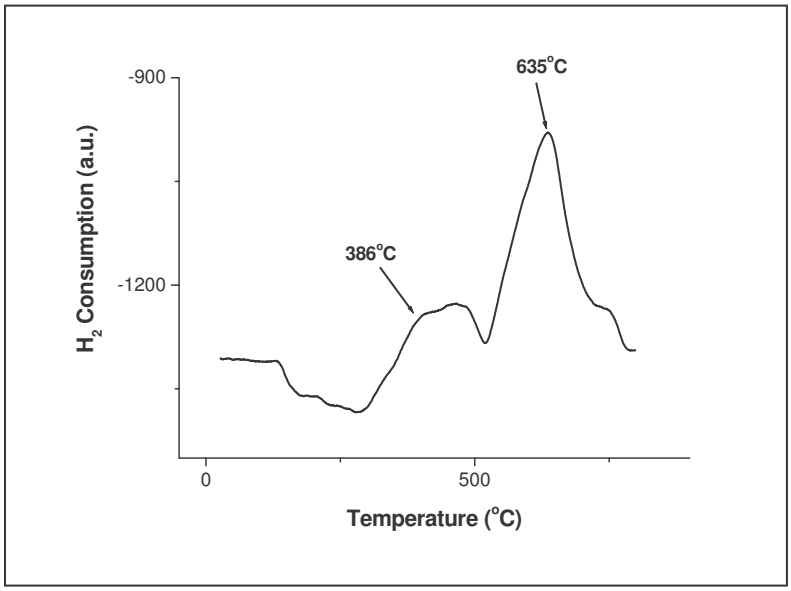


Figure 6.25: A TPR profile of Fe/SiO_2 catalyst calcined at 350 ^oC for 6, 5 h in air.

Temperature programmed reduction (TPR) method has been widely used in the characterizations of solid materials. Much work has been done on the reducibility of bulk iron oxide by temperature programmed reduction. The TPR curve shows a two step reduction process, the first step in the reduction of Fe_2O_3 is its reduction to Fe_3O_4, which is followed by the reduction of Fe_3O_4 to the metallic iron (Fe) (Lin et al., 2003):

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \quad (6.1)$$

$$2Fe_3O_4 + 8H_2 \rightarrow 6Fe + 8\ H_2O \quad (6.2)$$

The TPR results (**figure 6.25**) showed that the catalyst would best be reduced at temperature around 350 ^oC or just above that temperature. TGA results showed that nitrates were removed completely from the catalyst. Fischer-Tropsch reactions were

ready to be carried out. Iron catalysts were reduced at 350 °C, having seen the reduction temperature from the TPR results. The degree of reduction was calculated from the TPR results and found to be 0.68.

6.5.3 PXRD ANALYSIS

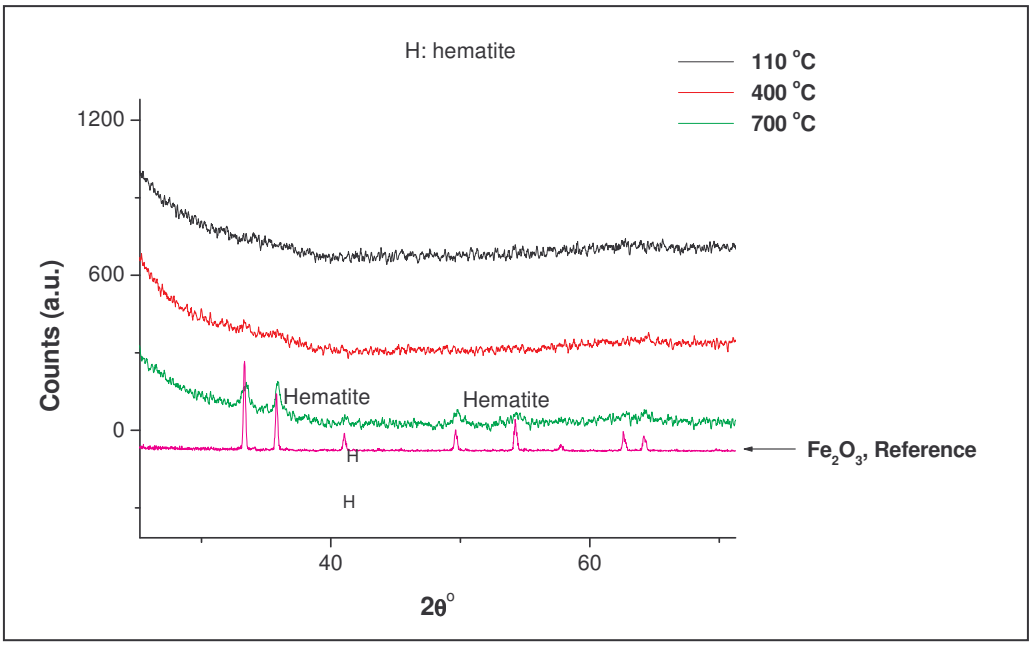


Figure 6.26: PXRD profiles of Fe/SiO_2 catalyst calcined at different temperatures for 6.5 h in air.

Figure 6.26 PXRD results showed that the predominant iron phase after calcination is hematite (α-Fe_2O_3). In addition, iron catalysts when calcined at lower temperatures are amorphous, the crystallinity of these materials showed at 700 °C. The active iron phase in Fischer-Tropsch synthesis is a mixture of the Fe_xC and Fe_3O_4. Therefore (α-Fe_2O_3) requires to be reduced to a mixture of the Fe_xC phase and magnetite or just magnetite prior to Fischer-Tropsch synthesis. The formation of the iron phases during catalyst activation depends on reaction conditions. Anderson reported that the formation of Fe_3C

is thermodynamically favoured over the formation of Fe_3O_4 since the formation of magnetite requires water for re-oxidation of the metallic iron (Anderson, 1984).

6.5.4 SURFACE AREA DETERMINATION

Table 6.6: BET surface areas of the calcined Fe/SiO_2 catalysts with and without potassium promotion.

Catalyst	Surface Area (m^2/g)	Pore volume (ml/g)
Fe/SiO_2	401	0.7
$Fe/K/SiO_2$, K = 2%	285	0.5

Table 6.6 shows the surface area obtained for Fe/SiO_2 catalyst with or without potassium promotion. The BET surface areas of iron catalysts are reported in **Table 6.6**. The specific surface area of the unpromoted Fe/SiO_2 catalyst was found to be 401 m^2/g, however, that of a promoted (2% K) Fe/SiO_2 catalyst was 285 m^2/g. The decrease in the BET surface area upon potassium promotion was presumably as a result of the improvement in agglomeration of the FeOOH precursor; this resulted in further enlargement of the crystallite size of iron (Li et al., 2001).

6.5.5 MöSSBAUER SPECTROSCOPY ANALSIS

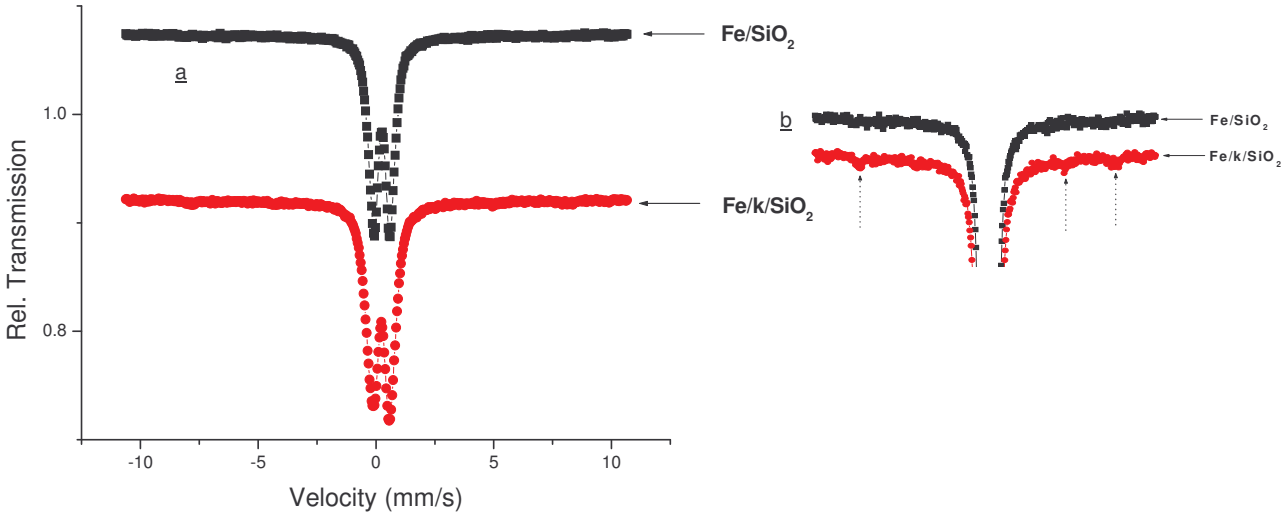
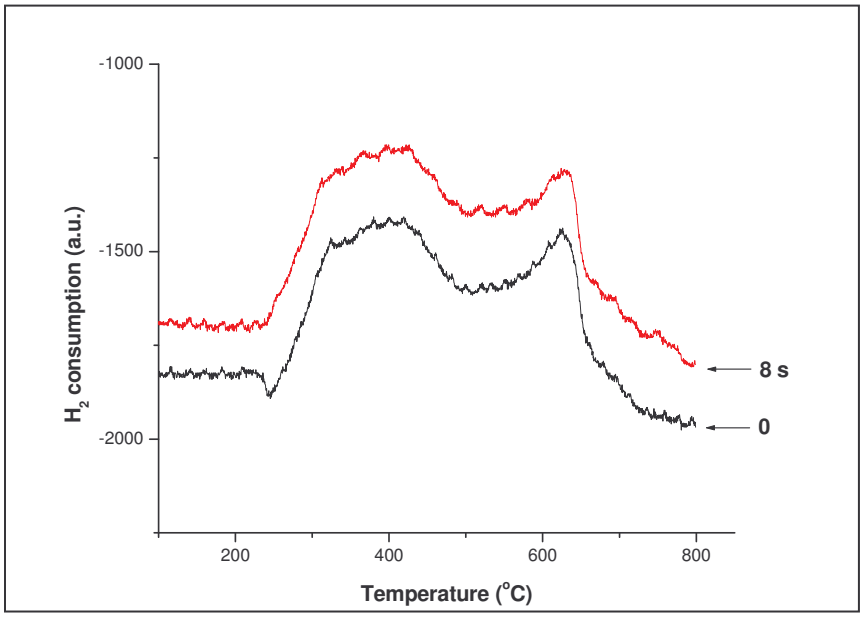


Figure 6.27: Transmission Mössbauer spectra of Fe/SiO_2 samples with or without potassium promotion taken at room temperature. Enlarged image of the same profiles is displayed in b.

Transmission Mössbauer spectroscopy (TMS) results showed a doublet which is symmetric for Fe/SiO_2 catalyst and asymmetric for $Fe/K/SiO_2$ catalyst as investigated in the figure above. TMS spectrum for the Fe/SiO_2 catalyst does not show anything lurking in the wings whereas something in the wings is observed for the $Fe/K/SiO_2$ catalyst. The new curves displayed by the promoted iron catalyst are due to new nanophases formed and the distribution of the particle size. The curves are due to the presence of crystallites greater than 10 nm in diameter. BET results investigated that the surface area is decreasing with the potassium loading. The decrease in surface area may probably be due to increase in particle size seen by Mössbauer spectroscopy.

6.5.6 MICROWAVE EFFECT

6.5.6.1 H_2-TPR ANALYSIS of Fe/SiO_2 CATALYSTS



8 s: microwave pre-treated at 540 W for 8 s, 0: no microwave pre-treatment

Figure 6.28: Hydrogen temperature-programmed reduction (H_2-TPR) profiles of Fe/SiO_2 catalysts before and after microwave pre-treatment. Microwave pre-treatment was done at 540 W.

The reducibility of iron species in the iron-oxide catalyst before and after microwave pre-treatment was investigated by H_2-TPR experiments, and the profiles are shown in **figure 6.28**. In both samples, reduction profiles investigate a two step process, suggesting a reduction of hematite to magnetite and transformation of magnetite to the metallic Fe respectively. The amount of hydrogen consumed by all samples before and after microwave pre-treatment is approximately the same. The TPR profiles showed no significant change in the reducibility of these catalysts before and after microwave pre-treatment.

6.5.6.2 SURFACE AREA

Table 6.7: BET surface areas for the Fe/SiO_2 catalyst before and after microwave pre-treatment.

Duration	Surface Area (m^2/g)	Pore volume (ml/g)
0	401	0.7
8 s	365	0.53

The BET surface areas of Fe/SiO_2 catalysts are reported in **Table 6.7**. The specific surface area of the iron catalyst before microwave pre-treatment was found to be 401 m^2/g, on the other hand, that of the iron catalyst after microwave pre-treatment for 8 s was 365 m^2/g. A slight decrease in the surface area was observed after microwave pre-treatment of the Fe/SiO_2 catalyst.

The surface area of the support (SiO_2) was determined before and after microwave pre-treatment. The results obtained investigate a decrease in the surface area of the support after microwave pre-treatment.

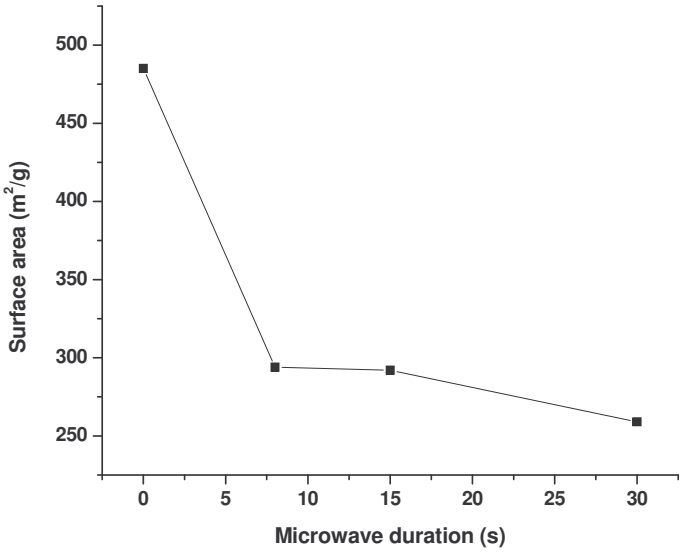


Figure 6.29: BET surface area for SiO_2 support microwave pre-treated at different power levels.

The surface area of the support (SiO_2) was found to decrease dramatically with the microwave pre-treatment. The results are investigated in **figure 6.29**. The decrease in surface area of the support is probably due to changes which occur in the structure of SiO_2 due to microwave heating. Related changes are seen in **figure 6.30** (PXRD results for a Fe/K/SiO_2).

6.5.6.3 PXRD ANALYSIS

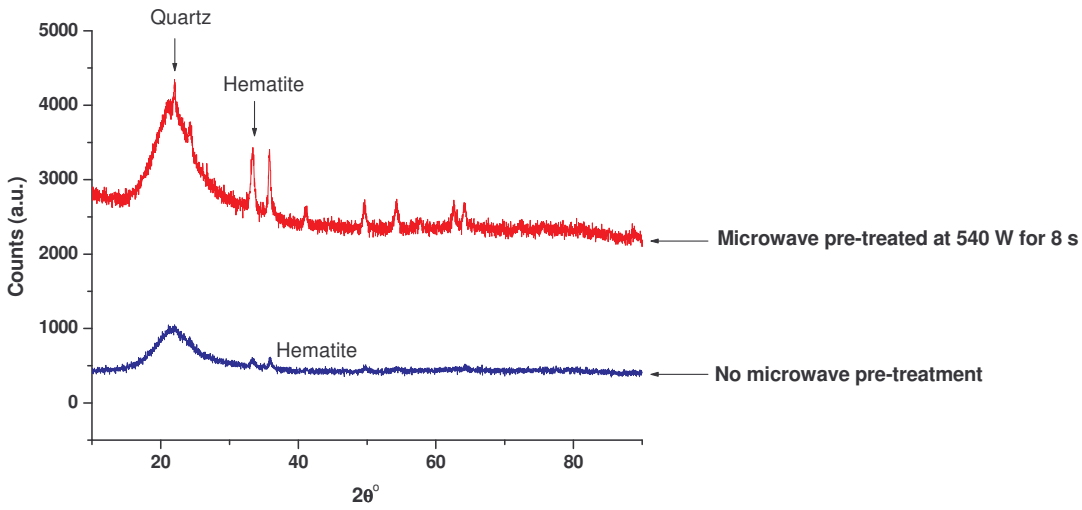


Figure 6.30: PXRD profiles for Fe/K/SiO_2 before and after microwave pre-treatment.

The PXRD results investigated that the microwave pre-treatment alters the crystal structure of SiO_2 while affecting the crystallinity of the supported iron catalysts. One SiO_2 component (quartz) appears after microwave pre-treatment.

6.5.6.4 TEMPERATURE PROGRAMMED SURFACE REACTIONS (TPSR)

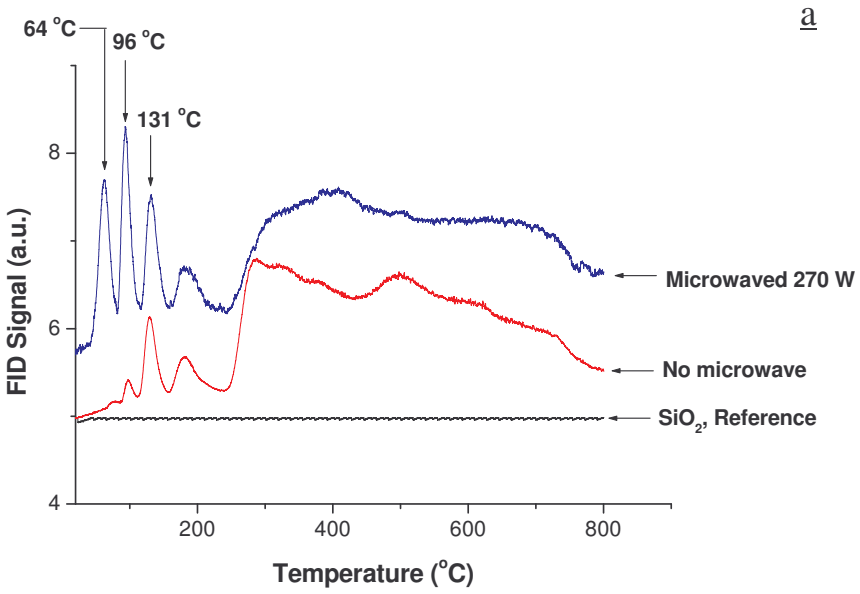


Figure 6.31: TPSR profiles investigating the microwave effect on $Fe/K/SiO_2$ catalysts.

Figure 6.31: shows the microwave effect on $Fe/K/SiO_2$ catalysts. Before the microwave pre-treatment the catalyst exhibits three desorption peaks due to desorbing hydrocarbon products at temperatures lower than 200 ^{o}C. After microwave pre-treatment at 270 W for 8 s, there is an additional desorption peak at 64 ^{o}C. In addition, the amount of the desorbing component increases with the microwave pre-treatment (peaks: 64 ^{o}C, 96 ^{o}C and 131 ^{o}C).

Effect of the power level on $Fe/K/SiO_2$ catalysts was studied afterwards to investigate its effect on the surface properties of $Fe/K/SiO_2$ catalysts. The results are depicted in **figure 6.32**.

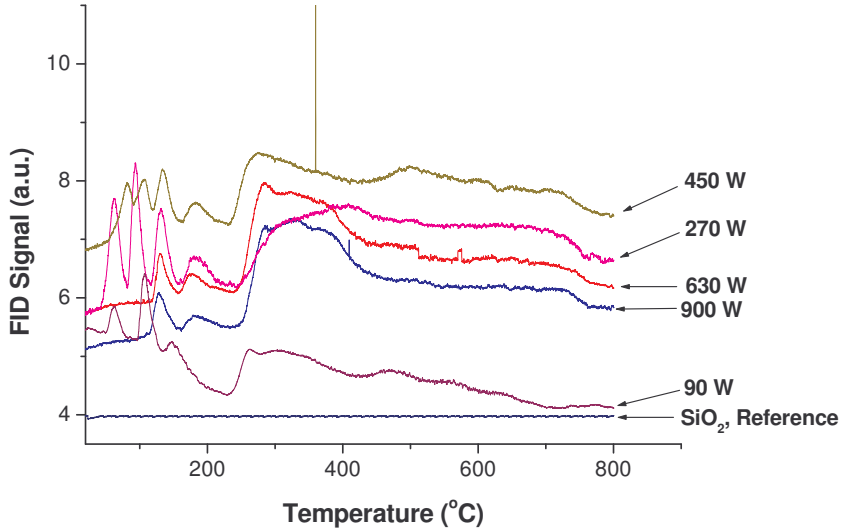


Figure 6.32: TPSR profiles investigating the effect of the power level on Fe/K/SiO_2 catalyst.

Temperature programmed surface reactions (TPSR) have investigated that the microwave pre-treatment alters the surface of these iron-based catalysts. This is displayed in **figure 6.32**, we observe that after microwave pre-treatment, the number of active sites on the surface and the amount of the desorbing hydrocarbon products were altered significantly. The number of active sites increased with the microwave and the volume of the desorbing hydrocarbon product increases as well. We then observed which power level is the optimum. 270 W was found to be the optimum (**figure 6.32**). Furthermore, at power level higher than 360 W i.e. 450 W, TPSR curve display the same chemical properties as the unmicrowave treated samples, the number of active sites decreased and the amount of the desorbing hydrocarbon product. This may be due to the fact that at higher power levels more local heating effects are felt at the surface of the Fe/SiO_2 catalysts resulting in a decrease in catalytic activity.

6.5.6.5 SECONDARY ION MASS SPECTROMETRY (SIMS) ANALYSIS

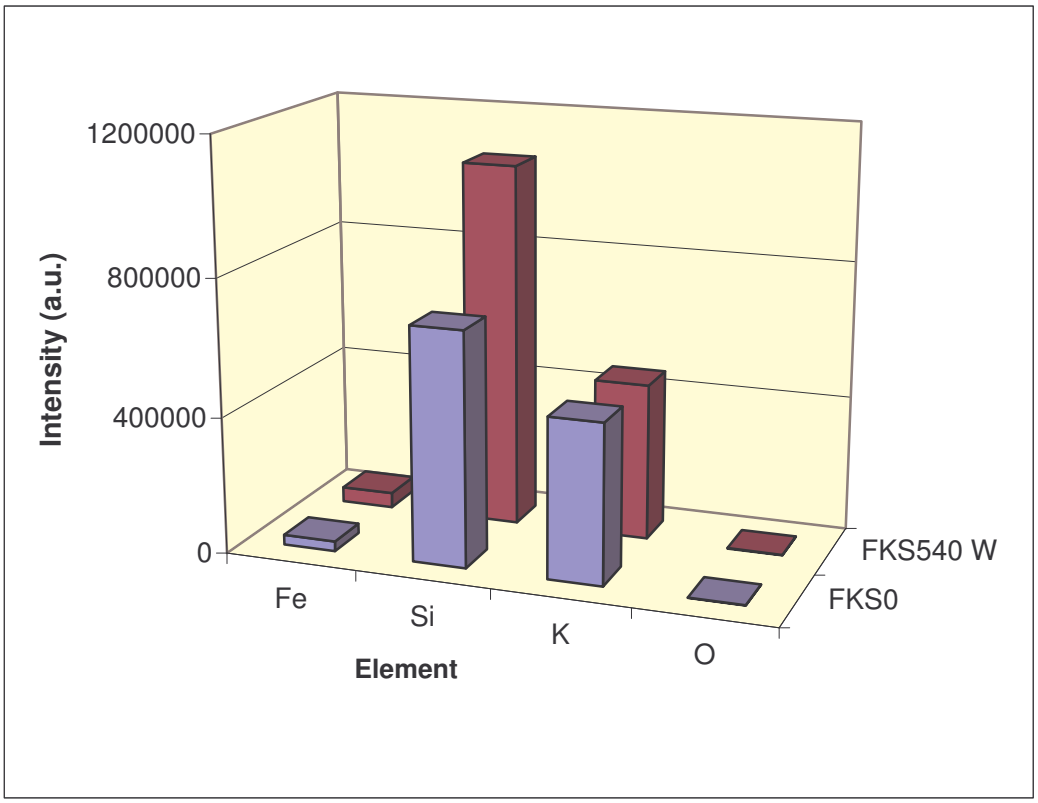


Figure 6.33: SIMS secondary ion intensities against ions present in calcined Fe/K/SiO_2 catalysts obtained before and after microwave pre-treatment. For the microwave pre-treatment, Fe/K/SiO_2 catalyst was heated for 8 s at 540 W.

The ratio of Fe:K before microwave pre-treatment was found to be 0.055, however after microwave heating, this figure increased significantly to 0.095. A slight change in the concentration of iron was observed after microwave pre-treatment of Fe/K/SiO_2 catalyst. These results investigate that microwave pre-treatment alters the surface of the Fe/K/SiO_2 catalysts. There is an effect of microwave radiation on potassium distribution hence the Fe:K ratio changes with the microwave.

6.6 SUMMARY OF THE CHARACTERIZATION RESULTS OF IRON CATALYST AND CONCLUSIONS

The microwave effect has been examined using a variety of bulk characterization techniques; however, the use of bulk techniques did not show any significant changes due to the microwave pre-treatment. On the other hand, when surface sensitive techniques i.e. temperature programmed surface reaction and SIMS measurements were employed on these solid materials, changes were observed to occur on the catalytic surface after microwave pre-treatment.

This was confirmed by an increase in the number of active sites present on the surface brought in by the microwave pre-treatment as compared to the catalyst without the pre-treatment. The amount of the desorbing hydrocarbon product appeared to increase after microwave heating as well.

The microwave effect was observed to depend on the power level used during the pre-treatment. The maximum amount of the desorbing species and the optimum number of active sites present on the catalytic surface were obtained at 270 W. At power levels greater or less than that the microwave effect was observed to be less significant.

The microwave pre-treatment alters the surface properties of the $Fe/K/SiO_2$ catalysts. However, there is no evidence of the microwave effect on the catalyst bulk structure other than the particle size growth noted above.

6.7 FISCHER-TROPSCH SYNTHESIS

6.7.1 EFFECT OF POTASSIUM PROMOTION ON Fe/SiO_2 CATALYSTS

6.7.1.1 ACTIVITY MEASUREMENTS

The catalytic performance of Fe/SiO_2 catalysts before and after microwave pre-treatment was tested using a fixed bed reactor (in all cases). 1.0 g catalyst was loaded. Before Fischer-Tropsch reactions, the catalyst was activated/reduced in hydrogen at 350 ^oC for 16 h at 45 ml/min./g catalyst. The gas mixtures consisted of 30 % CO and 60 % H_2 balanced in N_2 and the total flow was generally 60 ml/min. The course of the reaction was monitored quantitatively by use of a gas chromatograph equipped with a thermal conductivity detector.

All experiments were done at a reaction temperature of 250 ^oC using the total pressure of 20 bar and a H_2: CO ratio of 2:1.

The catalytic activity was expressed as carbon monoxide conversion with respect to time on stream (TOS). The catalytic activity of Fe/SiO_2 catalysts can be affected by alkali promotion depending on the loading of the promoter used. In this work equivalent amount (2%) of potassium was added to Fe/SiO_2 catalysts. The addition of potassium on iron Fischer-Tropsch catalysts resulted to an increase in FTS activity at low potassium concentrations. This is followed by decrease at higher levels of promoter (Bukur et al., 1990).

Carbon monoxide conversion as a function of time on stream for the $Fe/K/SiO_2$ catalysts before and after potassium promotion is shown in **figure 6.34**.

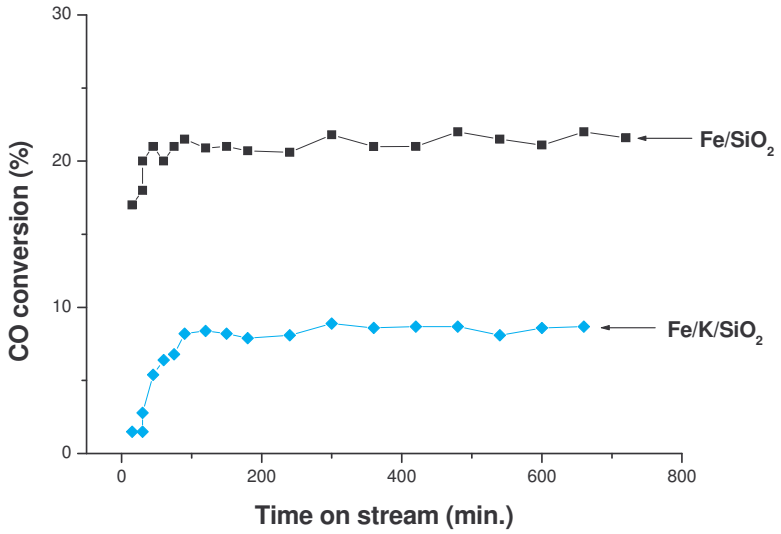


Figure 6.34: CO conversion (%) with time on stream (min.) for the Fe/K/SiO_2 catalysts with or without microwave pre-treatment. Microwave pre-treatment was carried out at 540 W for 8 s.

Carbon monoxide conversion is a rough measure of the overall Fischer-Tropsch activity and stability of an iron catalyst. **Figure 6.34** shows a plot of CO conversion as a function of reaction time on stream for Fe/K/SiO_2 catalysts with or without potassium promotion. In this study potassium promotion of the iron catalysts resulted in decrease in catalytic activity as displayed in the above figure. However, many researchers' reports on the effect of potassium on iron FT catalysts revealed an increase in catalytic activity (Dry et al., 1981; Dry, 2004).

Pichler (1952) reported that K_2CO_3 in low potassium loading (0-0.25wt %) has no effect on the catalytic activity (Pichler, 1952). This may be due to low level of potassium loading. Arakawa and the co-workers discovered that the activity of promoted iron FT catalyst was lower than the unpromoted catalyst (Arakawa, 1983). A decrease in CO conversion was attributed to the fact that, at high potassium loading, potassium covers the iron particles and that the iron particles are not readily available for Fischer-Tropsch reactions. This explains the decrease in catalytic activity with potassium loading as

investigated in **figure 6.34**. Bukur et al., (1990) also reported that at higher levels of promotion, the effect of potassium promotion on iron catalysts results in decrease in FT activity (Bukur et al., 1990).

In the first 100 min., changes in catalytic activity can be seen, these changes are probably due to changes in the iron phase and the formation of the working catalyst (Schulz et al., 1990). Steady state CO conversion was 21% for the unpromoted iron catalyst whereas a lower conversion level of ~9 % was observed after potassium promotion. Although, potassium is known to improve the FTS activity and heavy product fraction, high potassium loading covers the surface of the iron catalyst, resulting in limited promotion effect and a decrease in FTS conversions (Davis et al., 2003).

6.7.1.2 FORMATION OF CARBON DIOXIDE

One way to measure the water gas shift activity of the catalyst is its selectivity towards carbon dioxide. Carbon dioxide selectivity is given as a function of time on stream (min.). In each experiment CO_2 selectivity was analyzed using the on-line gas chromatograph. There are many factors that affect carbon dioxide selectivity such as: carbon monoxide conversion and catalyst promotion with potassium.

The Fischer-Tropsch reaction on iron catalysts is always accompanied by the water gas shift reaction. Carbon dioxide in FT reaction is mainly produced by the water gas shift reaction (**equation 2.2**) in minor quantities. It can also be produced in small amounts by disproportionation of CO (**equation 2.3**). The latter causes catalyst deactivation due to carbon deposition on the active sites present on the catalyst surface (Bartholomew, 1991).

Carbon dioxide selectivity for Fe/SiO_2 and $Fe/K/SiO_2$ catalysts is investigated in **figure 6.35**.

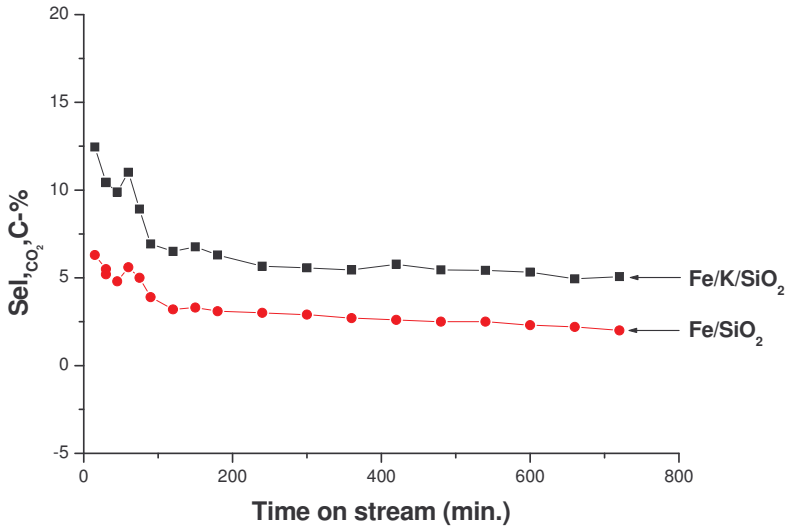


Figure 6.35: Carbon dioxide selectivity as a function of time on stream for Fe/SiO_2 and $Fe/K/SiO_2$ catalysts. The microwave pre-treatment was carried out at 540 W for 8 s.

The low carbon dioxide selectivity was found in the experiment without potassium and is believed to be due to the absence of potassium promotion as potassium enhances activity for the water gas shift. The addition of potassium on iron catalysts has been known to enhance the water gas shift activity (Arakawa et al., 1983; Dictor et al., 1986). High level of CO_2 selectivity in **figure 6.35** is due to the effect of potassium.

6.7.1.3 FORMATION OF ORGANIC PRODUCTS

In all cases, selectivities of hydrocarbon products formed is presented in C-% as a function of the carbon number, N. The hydrocarbon products were analyzed using the on-line GC. Potassium promotion is one of the factors which affect product selectivity.

When the Fe/SiO_2 catalyst was potassium promoted, there was a noticeable change in the selectivity of methane observed as investigated in **figure 6.36**, however, a remarkable change in olefin content was also observed.

6.7.1.3.1 METHANE FORMATION

Generally, methane selectivity must be kept as low as possible in Fischer-Tropsch synthesis, though it is the thermodynamically most favoured hydrocarbon product in Fischer-Tropsch process. There are many ways to subordinate the selectivity of methane:

- Increasing the crystalline size of the metal catalyst (Ojeda et al., 2004).
- Using an optimal promotion i.e. potassium (Bukur et al., 1990).

The methane selectivities obtained in this work are as expected, relatively low because of the promoting effect. Methane selectivity for Fe/SiO_2 catalyst before and after microwave pre-treatment is shown in **figure 6.36**.

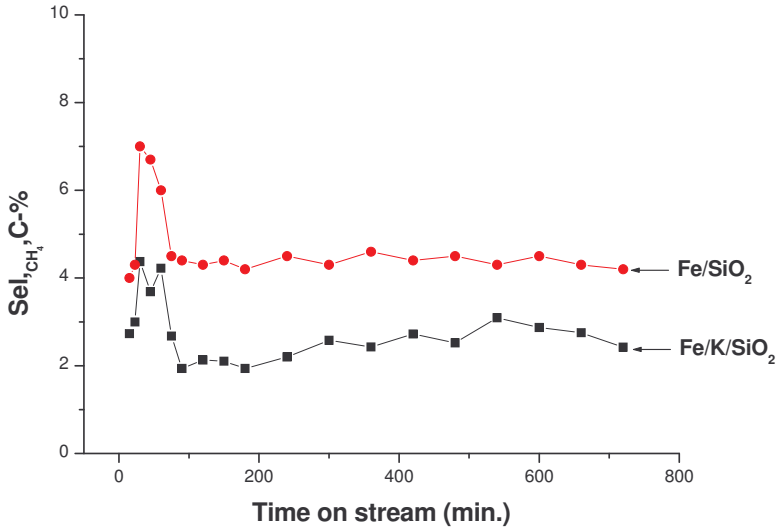


Figure 6.36: Methane selectivity in FTS for Fe/SiO_2 and $Fe/K/SiO_2$ catalysts.

The methane selectivities obtained in the runs with Fe/SiO_2 with or without potassium promotion are shown in **Figure 6.36**. Work of other researchers revealed that potassium promotion decreases methane selectivity and that an increase in potassium loading decreases methane selectivity (Arakawa et al., 1983; Dry, 2004; Dictor et al., 1986).
The results obtained are in agreement with other researchers in that methane selectivity decreased significantly after potassium promotion. The decrease in methane selectivity is attributed to the fact that there is very low concentration of hydrogen species on the surface of the catalyst to further hydrogenate the surface methyl species as methane forms via associative desorption of a methyl species and surface hydrogen. Adding potassium titrates acid sites and introduces base sites on the catalysts thereby inhibiting hydrogen chemisorption and allowing carbon monoxide chemisorption (Dry et al., 1968). Methane selectivity decreases with an increase in the surface basicity of the catalyst. Dry and co-workers explained that the basicity of the catalyst does not only depend on potassium loading but on how well it is distributed on the catalyst surface. Potassium has been known to decrease methane selectivity (Bukur et al., 1990). This means that potassium promotion produces a better catalyst for Fischer-Tropsch synthesis, in FTS one needs to minimize the methane selectivity because converting methane to useful products requires expensive plant construction and formation of high levels of methane also depletes synthesis gas.

6.7.1.3.2 AVERAGE MOLECULER WEIGHT

An increase in average molecular weight or chain growth is normally allowed by the inhibition of the hydrocarbon products desorption (Schulz, 2003). Anderson, Schultz and Flory (ASF) proposed a kinetic model that is most frequently used to describe the product distribution obtained from Fischer-Tropsch synthesis. The ASF kinetic model is shown in **equation 2.4** of section 2. Chain growth probability depends on the rate at which the hydrocarbon products are desorbed. The kinetic model proposed is as follows:

$$W_n / N = (1-\alpha^2)* \alpha^{(n-1)} \quad (2.4)$$

Where n is the carbon number, W_n is the weight fraction of product containing n carbon atoms and α is the chain growth probability. Higher values of alpha correspond to higher molecular weight products whereas lower values correspond to the formation of gaseous products.

Most of FT product distributions do not obey the ASF kinetic model (Iglesia et al., 1993), i.e. they possess relatively high methane selectivity and low yield of ethene relative to the predicted ASF distribution, and a chain length dependent chain growth probability resulting in higher than expected selectivity towards heavy products.

ASF is a plot of log mole fraction of each linear hydrocarbon as a function of carbon number, N. The graph gives a straight line and the slope of the line is the alpha. The value of alpha depends on how long the hydrocarbon product spends time in the active sites of the catalyst surface.

Chain growth probabilities were derived via linear regression from the linear part of the distribution in the carbon number range C_3-C_7 and C_{10}-C_{14}.

The obtained chain growth probabilities for Fe/SiO_2 and $Fe/K/SiO_2$ catalysts are shown in **table 6.8**.

Table 6.8: Chain growth probabilities obtained from Fe/SiO_2 and $Fe/K/SiO_2$ catalysts

Catalyst	α (C3-C7) (%)	α (C10-C14) (%)
$Fe/K/SiO_2$	55	69
Fe/SiO_2	49	59

The obtained chain growth probabilities for the unpromoted catalyst were relatively lower than the promoted catalysts. Potassium is known to inhibit product desorption from the catalyst surface.

6.7.1.3.3 OLEFIN FORMATION

Olefins are considered the main products in Fischer-Tropsch synthesis. Olefins can re-adsorb on the catalyst surface and undergo secondary reactions to form the corresponding secondary olefins or undergo hydrogenation to form paraffins. According to the ASF plot, the olefin to linear hydrocarbons, curve is displayed by relatively low C_2 values and the olefin content decreases with increasing carbon number, N. This echoes the secondary conversion of ethene and long chain olefins. There are many factors which affect the olefin selectivity, including:

- Promoter effect (i.e. potassium addition), secondary reactions i.e. (isomerization and olefin hydrogenation to paraffins) (Bukur et al., 1990).
- Microwave pre-treatment of a potassium containing catalyst (present work).

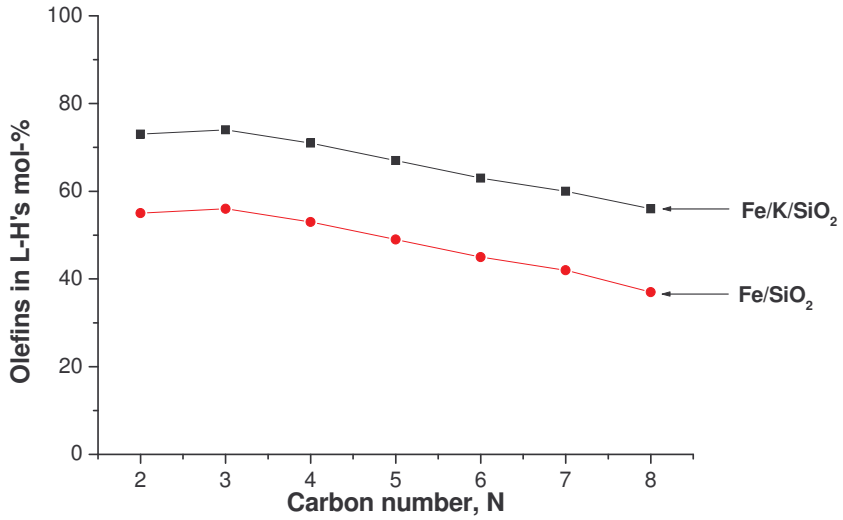


Figure 6.37: Molar content of olefins in corresponding fraction of linear hydrocarbons as a function of carbon number in Fischer-Tropsch after 5h time on stream for Fe/SiO_2 and $Fe/K/SiO_2$.

Both curves show a pattern with relatively low values at C_2 and decreasing olefin content with increasing carbon number. Because ethylene is the most reactive low molecular weight hydrocarbon, it undergoes secondary reactions i.e. re-adsorption on the catalyst surface (Iglesia et al., 1993).

Potassium promotion increases the selectivity towards primary olefins meaning that secondary reactions such as re-adsorption (hydrogenation) or isomerization to cis- and trans- olefins are inhibited (Dry, 2004; Dry, 1981).

Potassium promotion gives rise to low concentration of hydrogen surface species and high CO species on the catalyst surface. This occurs as potassium favours CO chemisorption over hydrogen chemisorption. In conclusion, potassium promotion suppresses secondary reactions because the concentration of hydrogen species on the surface of the catalyst is very low.

6.8 EFFECT OF MICROWAVE PRE-TREATMENT ON Fe/SiO_2 CATALYSTS

6.8.1 ACTIVITY MEASUREMEMNTS OF A CALCINED Fe/SiO_2 CATALYST

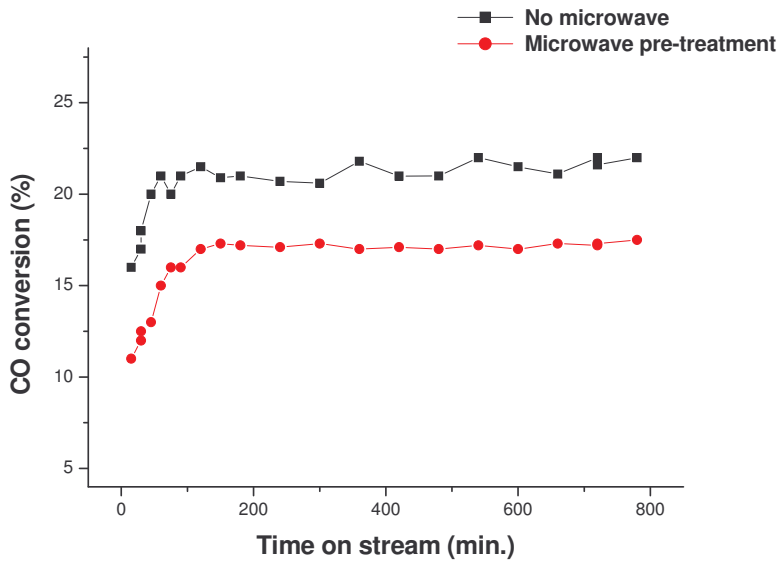


Figure 6.38: CO conversion with time on stream (min.) in the Fischer-Tropsch synthesis for Fe/SiO_2 catalysts before and after microwave pre-treatment. The microwave pre-treatment was carried out at 540 W for 8 s.

The activity of the Fe/SiO_2 catalysts before and after microwave pre-treatment is investigated in **figure 6.38**. High conversion levels (22%) were obtained before the microwave heating. However, the catalytic activity dropped to 16.6 % after samples were exposed to the microwaves. The decrease in catalytic activity is due to crystal growth which occurs due to microwave heating (**figure 6.30**). The surface area decreases with the microwave pre-treatment and the decrease in surface area is due to increasing particle size of iron and the catalytic activity drops.

6.8.2 CARBON DIOXIDE SELECTIVITY

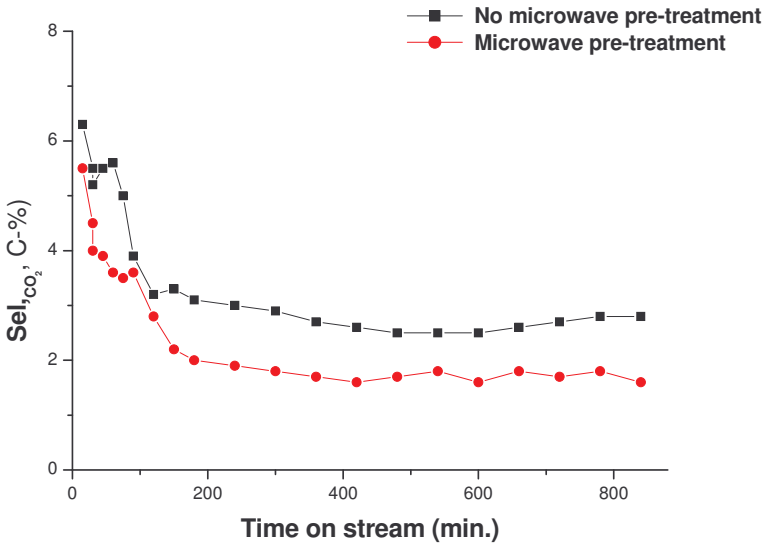


Figure 6.39: Carbon dioxide selectivity as a function of time on stream (min.) for the Fe/SiO_2 catalysts before and after microwave pre-treatment.

Carbon dioxide is known as a product of the water gas shift reaction. Analysis of data investigates that after microwave pre-treatment carbon dioxide formation decreased. The decline in CO_2 selectivity is attributed to lower carbon monoxide conversion obtained after the pre-treatment (**figure 6.38**).

6.8.3 METHANE SELECTIVITY

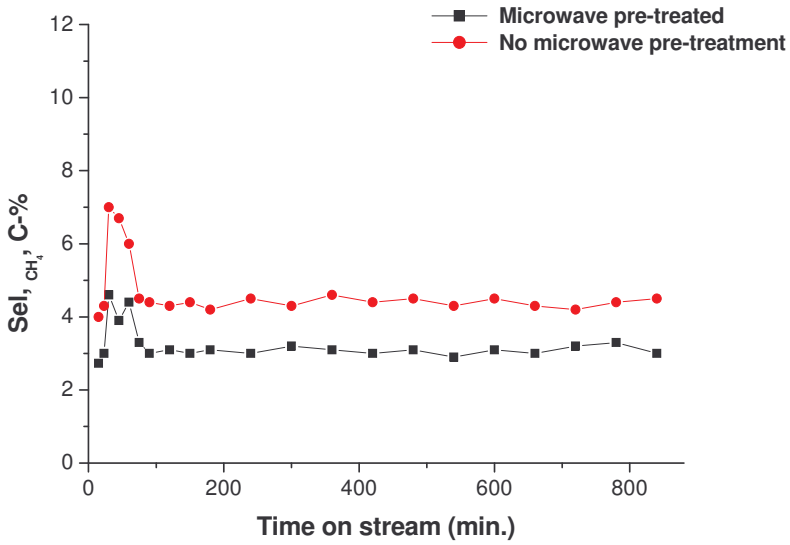


Figure 6.40: Methane selectivity as a function of reaction time on stream (min.) for Fe/SiO_2 catalysts before and after microwave pre-treatment. The microwave pre-treatment was carried out at 540 W for 8 s.

Methane as a thermodynamically most favoured hydrocarbon is to be minimized in the Fischer-Tropsch synthesis. **Figure 6.40** reveals that the microwave pre-treatment suppresses the formation of methane. The decline in methane selectivity is attributed to the increase in particle size of iron catalyst. It has been reported that when the particle size of the active metal increases, methane selectivity drops (Mabaso, 2005).

6.8.4 OLEFIN SELECTIVITY

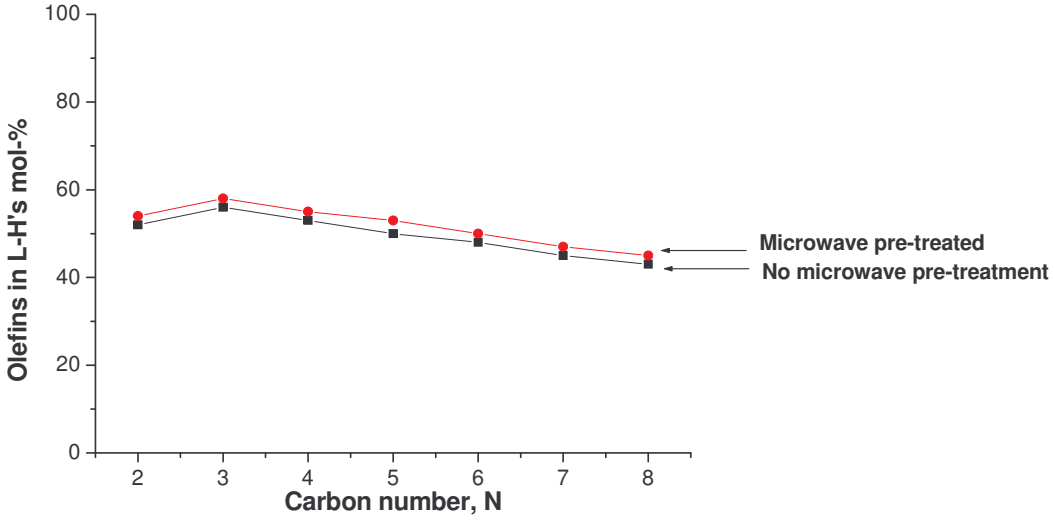


Figure 6.41: Molar content of olefins in corresponding fraction of linear hydrocarbons as a function of carbon number in Fischer-Tropsch synthesis after 5h time on stream for Fe/SiO_2 catalyst before and after microwave pre-treatment. The microwave pre-treatment was carried out at 540 W for 8 s.

Experimental data revealed that there is no significant effect of microwave in the selectivity towards olefins. This shows that the increase in particle size does not necessarily affect the way in which olefins are produced but does suppress the methane formation.

The microwave pre-treatment of Fe/SiO_2 catalyst does not affect the way in which olefins are formed.

6.8.5 MICROWAVE EFFECT ON CATALYTIC ACTIVITY AND SELECTIVITY OF Fe/SiO_2 CATALYST PRECURSORS (DRIED AT 110°C)

6.8.5.1 CARBON MONOXIDE CONVERSION

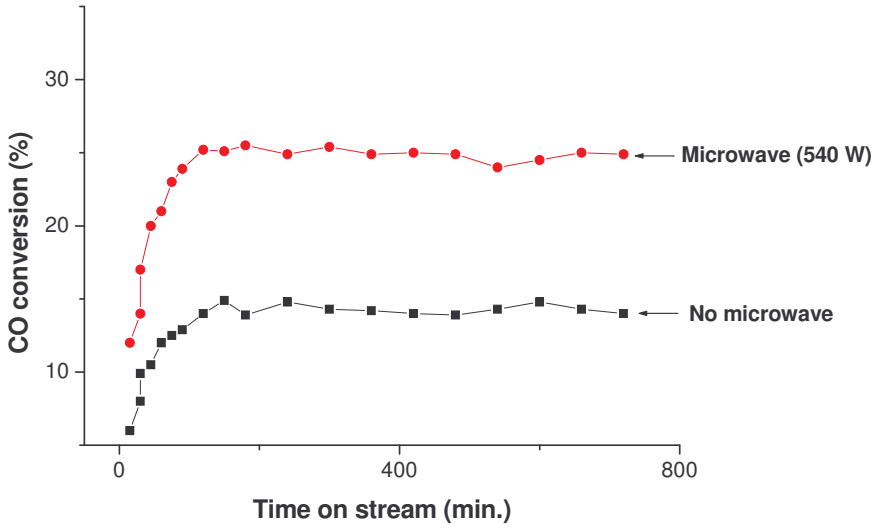


Figure 6.42: Changes in carbon monoxide conversion as a function of time on stream (min.) for the Fe/SiO_2 catalyst precursors before and after microwave pre-treatment. Fe/SiO_2 catalyst was dried at 110 ^{o}C overnight.

When Fe/SiO_2 catalyst precursor dried at 110 ^{o}C overnight was microwave pre-treated at 540 W for 8 s, a significant change was observed in the catalytic activity. **Figure 6.39** displays dramatic changes in catalytic activity of Fe/SiO_2 after microwave pre-treatment from 12% to 25%. The change in catalytic activity was found to be due to the presence of hydroxyl species on the catalytic surface due to water present in the catalyst because Fe/SiO_2 catalyst precursor was not calcined therefore is enriched with water. In addition water is a good microwave absorber. We expect the microwave pre-treated (uncalcined) Fe/SiO_2 catalyst to have more surface hydrogens than the unmicrowaved catalyst.

Because water is a good microwave absorber, the uncalcined catalyst is rich in moisture. After microwave pre-treatment, the OH groups from water result in high concentration of hydrogens on the surface of the catalyst.

6.8.5.2 CARBON DIOXIDE SELECTIVITY

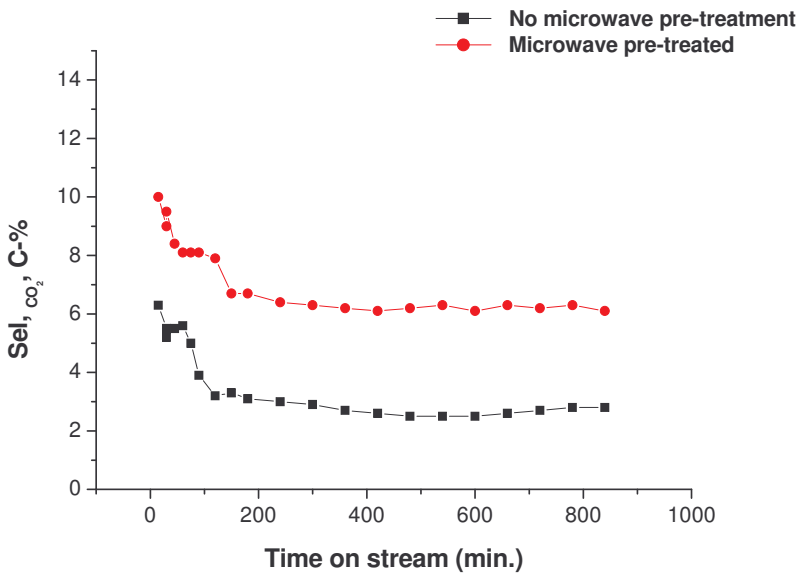


Figure 6.43: Carbon dioxide selectivity (%) as a function of time on stream (min.) for the Fe/SiO_2 catalysts precursors before and after microwave pre-treatment.

Analysis of data investigates that after microwave pre-treatment carbon dioxide formation increased. The increase in CO_2 selectivity is attributed to high carbon monoxide conversion obtained after the pre-treatment (**figure 6.42**).

6.8.5.3 METHANE SELECTIVITY

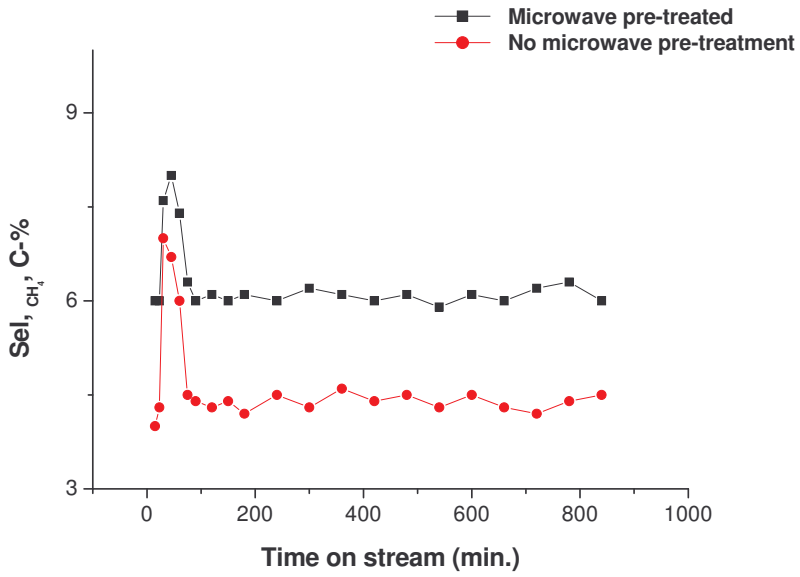


Figure 6.44: Methane selectivity as a function of reaction time on stream (min.) for Fe/SiO_2 catalyst precursors before and after microwave pre-treatment.

Figure 6.44 reveals that the microwave pre-treatment enhances the formation of methane. The increase in methane selectivity is attributed to high concentration of hydrogen species on the surface of the catalyst resulted from the hydroxyl groups present on the catalyst surface.

6.8.5.4 OLEFIN SELECTIVITY

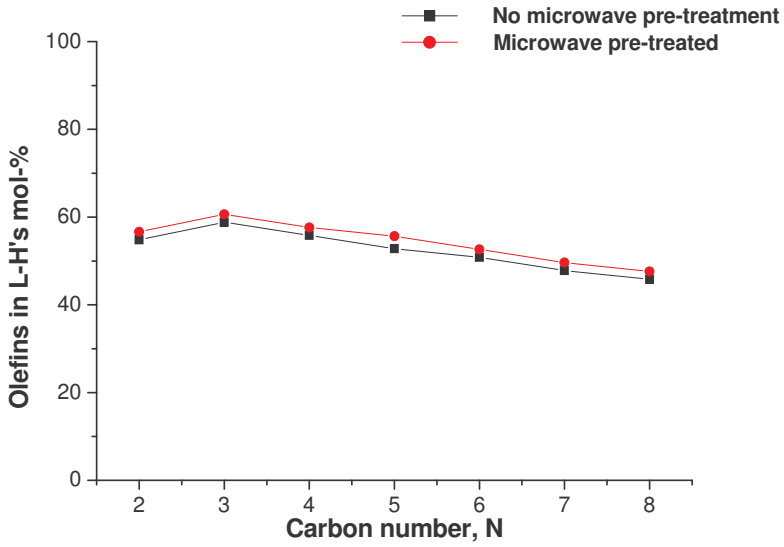


Figure 6.45: Molar content of olefins in corresponding fraction of linear hydrocarbons as a function of carbon number in Fischer-Tropsch after 5h time on stream for Fe/SiO_2 catalyst precursors before and after microwave pre-treatment.

Experimental data revealed that there is no significant effect of microwave in the selectivity towards olefins. This shows that the increase the methane formation is not due to the increase in particle size but due to high concentration of hydrogen species present on the catalyst surface.

The microwave pre-treatment of Fe/SiO_2 catalyst precursor does not affect the way in which olefins are formed.

Figure 6.44 demonstrated that the methane selectivity increased after the pre-treatment. This shows that the Fe/SiO_2 catalyst precursor after microwave pre-treatment is a good hydrogenation catalyst.

Hydrogenation of ethylene for the Fe/SiO_2 catalyst precursor was carried out to examine the effect of microwave. The results obtained are as follows:

6.8.6 HYDROGENATION OF ETHYLENE: ACTIVITY MEASUREMENTS

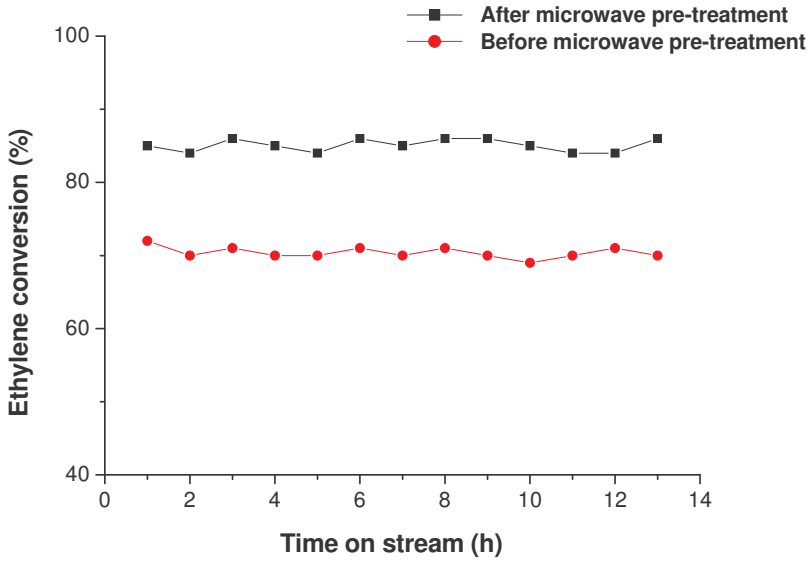


Figure 6.46: Ethylene conversion (%) as a function of reaction time on stream (h) for the Fe/SiO_2 catalyst precursors before and after microwave pre-treatment.

Based on the results obtained from **figure 6.44** (methane selectivity), one would expect the Fe/SiO_2 catalyst precursor to be more hydrogenating as compared to the same catalyst before microwave pre-treatment. Approximately 85 % ethylene was converted to ethane

with respect to the Fe/SiO_2 catalyst precursor after microwave pre-treatment. However, only 70 % ethylene conversion was obtained for the Fe/SiO_2 catalysts before the microwave pre-treatment.

6.9 MICROWAVE EFFECT ON POTASSIUM PROMOTED Fe/SiO_2 CATALYST

6.9.1 CATALYTIC ACTIVITY

Catalytic activity was expressed as carbon monoxide conversion (%) with time on stream (min.). **Figure 6.47** shows the carbon monoxide conversion for the $Fe/K/SiO_2$ catalysts before and after microwave pre-treatment.

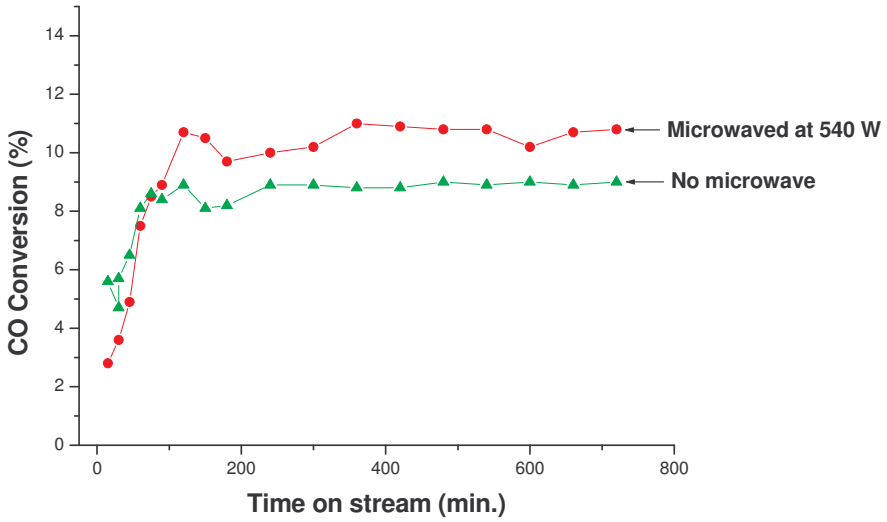


Figure 6.47: Changes in CO conversion in the Fischer-Tropsch synthesis as a function of time on stream for $Fe/K/SiO_2$ catalysts before and after microwave pre-treatment.

The catalytic activity after microwave pre-treatment at 540 W for 8 s increased slightly. The increase in catalytic activity is attributed to the presence of potassium in the Fe/SiO_2 catalyst. The effect of the microwave is promotional in nature. Low conversion levels were found after the microwave pre-treatment of the Fe/SiO_2 catalysts, and the decline in catalytic activity was attributed to the increase in crystal size. After potassium promotion, we observe the enhancement in CO conversion after microwave pre-treatment. However, an increase in particle size was also observed after microwave heating of the potassium containing Fe/SiO_2 catalyst (**figure 6.13** and **6.15**). This did not result in decline in activity like it did to the unpromoted catalyst.

In conclusion, the microwave pre-treatment of the $Fe/K/SiO_2$ catalyst resulted in the enhancement in activity attributed to the effect of the presence of potassium on these solid materials. Therefore the microwave pre-treatment affects the way in which potassium and iron interact.

6.9.2 CARBON DIOXIDE SELECTIVITY

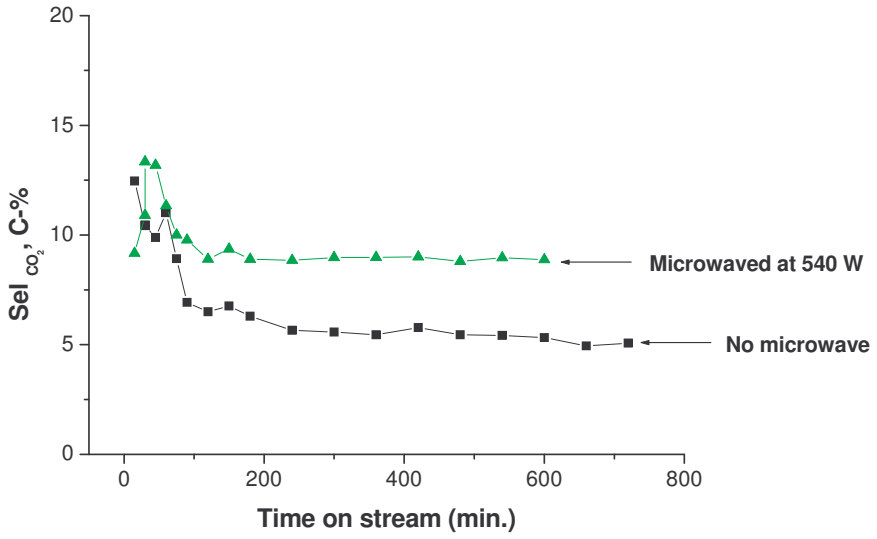


Figure 6.48: CO_2 selectivity as a function of time on stream in the Fischer-Tropsch synthesis for $Fe/K/SiO_2$ catalysts before and after microwave pre-treatment.

Because carbon dioxide is always found in iron Fischer-Tropsch synthesis, for iron is active for the water gas shift reaction. **Figure 6.48** investigates that the microwave pre-treatment enhances the formation of carbon dioxide. High carbon dioxide selectivity may be due to high conversion levels obtained after microwave pre-treatment (**figure 6.47**). There is no evidence that the microwave pre-treatment improves the water gas shift reaction but the enhancement in CO_2 formation is attributed to high carbon monoxide conversions (**figure 6.47**).

6.9.3 METHANE SELECTIVITY

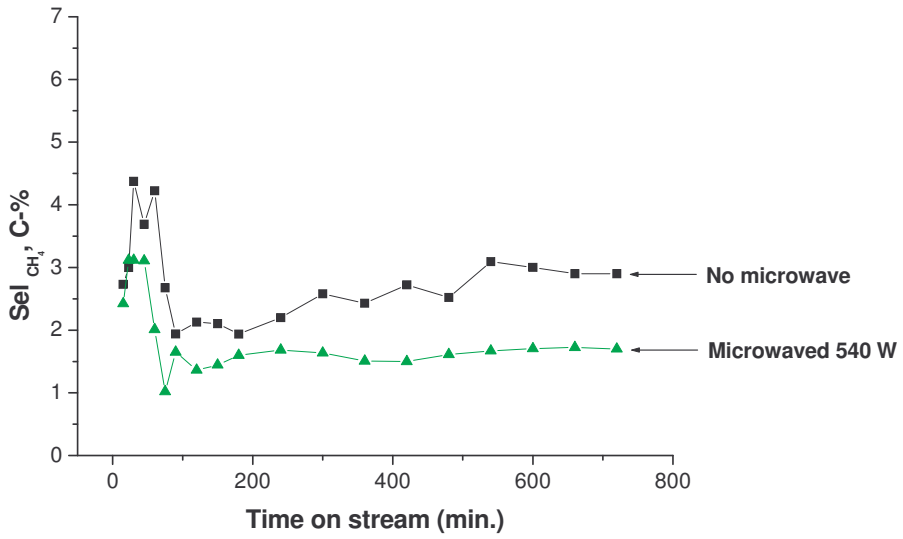


Figure 6.49: Methane selectivity in Fischer-Tropsch synthesis for $Fe/K/SiO_2$ catalysts before and after microwave pre-treatment.

Methane forms via associative desorption of the methyl surface species and surface hydrogen. If the concentration of surface hydrogen is very low, the $-CH_x-$ species on the surface do not undergo hydrogenation to form a saturated hydrocarbon (CH_4). Microwave pre-treatment suppresses methane formation by suppressing secondary reactions such as re-hydrogenation of 1-olefins. Methane is known to be the

thermodynamically favoured hydrocarbon in Fischer-Tropsch synthesis and one should try to minimize its formation.

In this case, the decline in methane formation is attributed to the larger crystal size obtained due to the microwave pre-treatment (**figure 6.13**).

6.9.4 OLEFIN SELECTIVITY

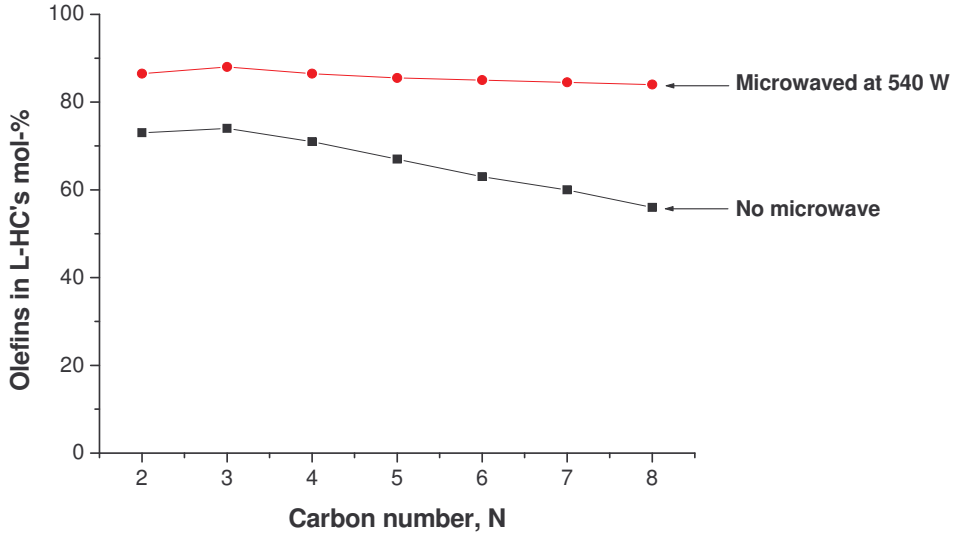


Figure 6.50: Molar content of olefins in corresponding fraction of linear hydrocarbons as a function of carbon number for Fe/K/SiO_2 catalysts before and after microwave pre-treatment.

Fe/K/SiO_2 catalyst before microwave pre-treatment displayed a curve with a relatively low C_2 value followed by a decrease in olefin content as the carbon number increases. After microwave pre-treatment, the curve shows a pattern with slightly higher value of C_2 olefin content, followed by a slight decrease in olefin content as the carbon number increases. This shows that the microwave pre-treatment suppresses the secondary reactions. The olefin selectivity improves with the microwave pre-treatment.

Therefore the increase in olefin content is probably due to the way in which potassium interacts with the active metal (iron).

Chain growth probability obtained from $Fe/K/SiO_2$ catalyst before and after microwave pre-treatment is shown in **table 6.9**.

Table 6.9: Chain growth probabilities obtained from $Fe/K/SiO_2$ catalysts before and after microwave pre-treatment.

Microwave pre-treatment	α (C3-C7) (%)	α (C10-C14) (%)
Before	55	69
After	59	74

6.10 EFFECT OF DURATION ON $Fe/K/SiO_2$ CATALYSTS

Effect of duration (the time the catalyst spends in the microwave for pre-treatment) on microwave pre-treatment was studied and the results obtained are as follows:

6.10.1 CATALYTIC ACTIVITY

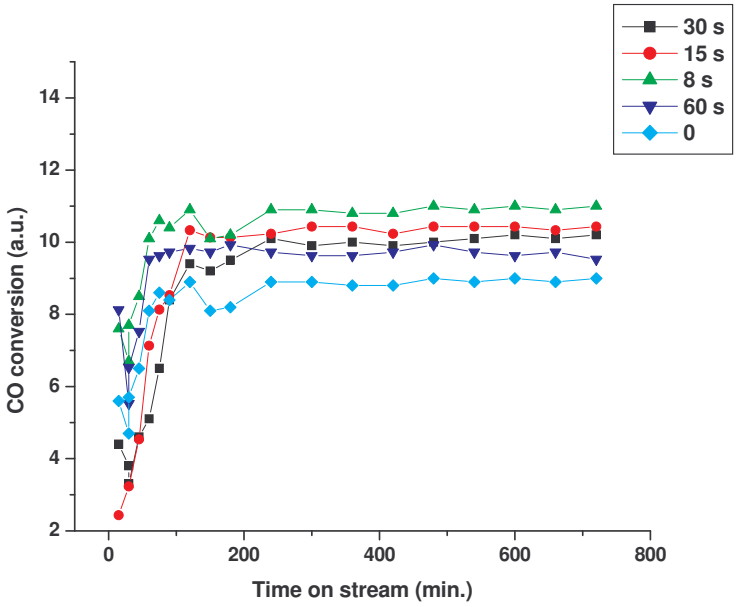


Figure 6.51: Changes in CO conversion (%) in the Fischer-Tropsch synthesis as a function of time on stream (min.) for Fe/K/SiO_2 catalysts microwave pre-treated at different times (s).

The patterns observed in **figure 6.51** exhibit similar features. Steady state conversion was calculated as approximately ~ 10 % for all Fe/K/SiO_2 catalysts microwave pre-treated at different duration. However, before microwave pre-treatment, the experimental analysis investigated that there is a decrease in catalytic activity from 8% to 10% due to potassium promotion (**figure 6.34**). Experimental data suggested that the effect of duration has a minimal effect on catalytic activity but the decrease in catalytic activity at 60 s may be due to strong metal-promoter effect due to high heating for a longer time. Because the active metal sinters at higher temperature. This can affect its behaviour in Fischer-Tropsch reaction. A plot of the activity as a function of the time of microwave pre-treatment:

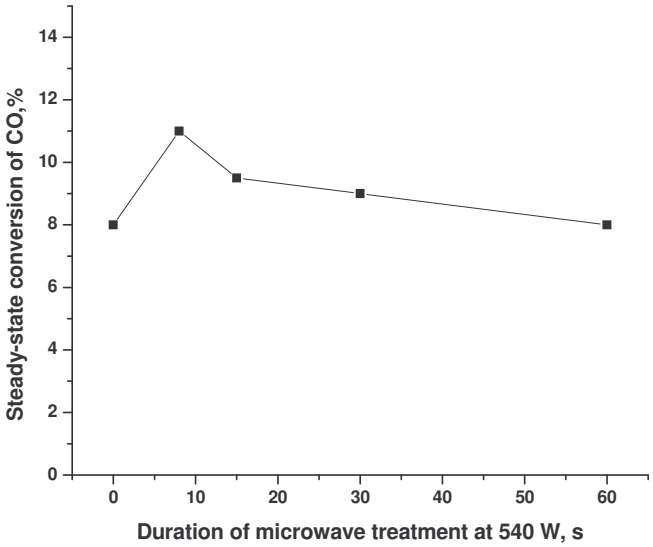


Figure 6.52: Catalytic activity for $Fe/K/SiO_2$ as a function of the time of microwave pre-treatment (s).

6.10.2 CARBON DIOXIDE SELECTIVITY

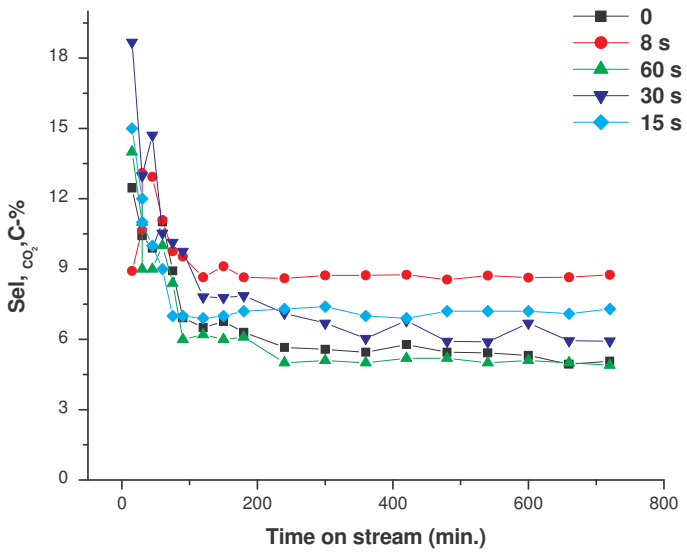


Figure 6.53: Carbon dioxide selectivity as a function of time on stream in the Fischer-Tropsch synthesis for the Fe/K/SiO_2 catalysts microwave pre-treated at different times at 540 W.

Selectivity of carbon dioxide, a product of the water gas shift reaction was investigated looking at the effect of duration and the results are shown in **figure 6.53**. Analysis of the data reveals that the carbon dioxide selectivity changes with respect to increase in duration from 8 s to 60 s. However, at 60 s a drop in carbon dioxide selectivity was observed due to low conversion levels illustrated in **figure 6.51**. The experimental data shows no evidence of the microwave pre-treatment (effect of duration) on the water gas shift activity. High carbon dioxide selectivity shows high CO conversion. The results show that the time taken by the catalyst in the microwave for the pre-treatment is crucial in the Fischer-Tropsch synthesis as it affects the product selectivity and catalytic activity in the process.

6.10.3 METHANE SELECTIVITY

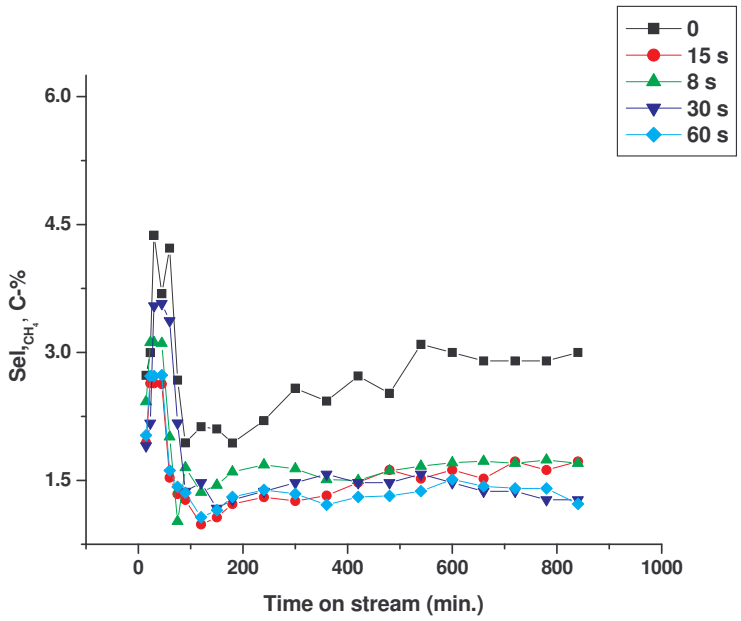


Figure 6.54: Methane selectivity in the Fischer-Tropsch synthesis as a function of time on stream for Fe/K/SiO_2 catalysts microwave pre-treatment for 540 W at different times.

Methane is an undesirable hydrocarbon product in the Fischer-Tropsch synthesis. Methane formation is highly favoured at high hydrogen concentration on the surface of the catalyst. A good hydrogenation catalyst is normally rich in surface hydrogen.

Analysis of the data reveals that the effect of microwave pre-treatment time plays a crucial role in the selectivity of the hydrocarbon products in Fischer-Tropsch process. **Figure 6.54** shows that as the duration increases slightly from 8 to 30 s, the methane formation decreased substantially. This can be explained by the increase in particle size as duration increases from 8 to 30 s.

6.10.4 OLEFIN SELECTIVITY

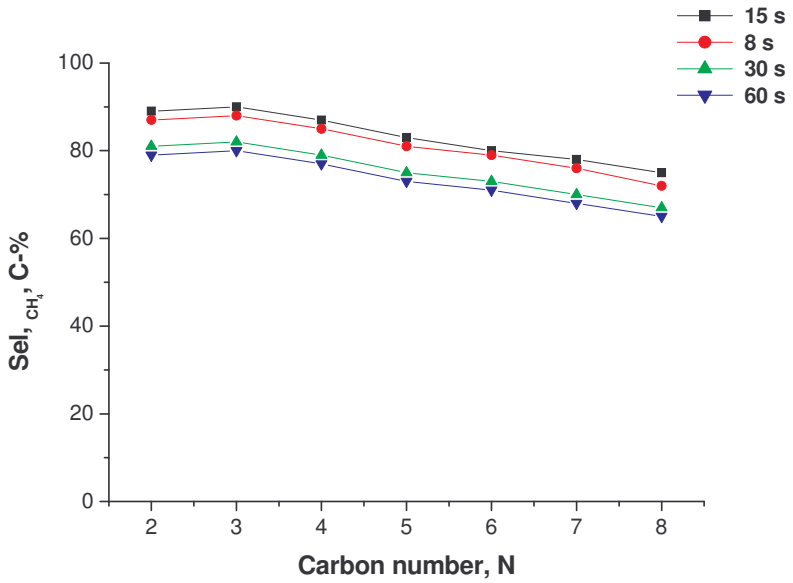


Figure 6.55: Molar content of olefins in corresponding fraction of linear hydrocarbons as a function of carbon number in Fischer-Tropsch synthesis for $Fe/K/SiO_2$ catalysts microwave pre-treatment at 540 W for different times.

Olefin formation is known to be favoured by catalysts with very low hydrogen concentration on the surface. A poor hydrogenation catalyst is normally a good catalyst for producing olefins. Olefins as the main products of Fischer-Tropsch synthesis are produced in large quantities after microwave pre-treatment. The experimental data investigated that the amount of olefins produced in the Fischer-Tropsch reaction does depend on the duration used on microwave pre-treatment. There is a relationship between interaction of potassium with the active metal and the time for microwave pre-treatment, when the catalyst in kept in the microwave for a long time (60), some of the iron particles come together to form a bigger units resulting in an inactive catalyst. This affects the behaviour of the iron catalyst in selectivity and activity in the FTS.

6.11 EFFECT OF THE POWER LEVEL ON Fe/K/SiO_2 CATALYSTS

Effect of the power level was investigated on Fe/K/SiO_2 catalysts with the idea of gaining an understanding of its effect on selectivity and activity in the Fischer-Tropsch synthesis. The results obtained are as follows:

6.11.1 CATALYTIC ACTIVITY

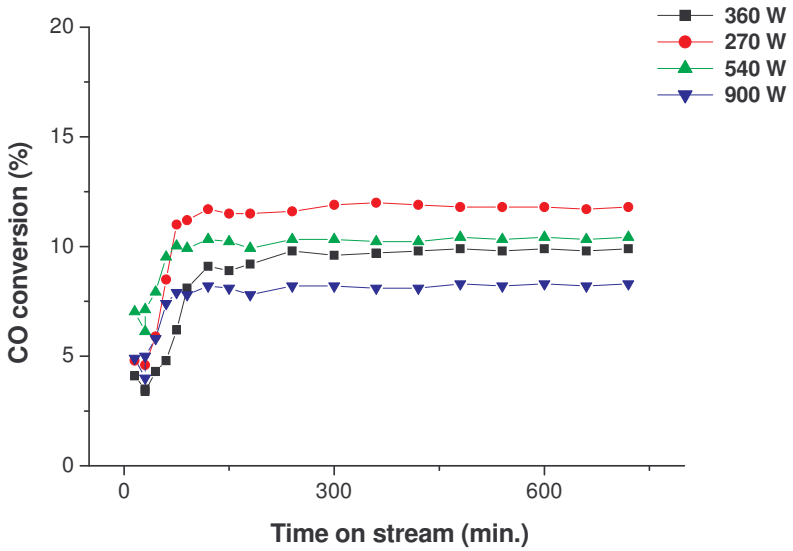


Figure 6.56: Carbon monoxide conversion with time on stream in Fischer-Tropsch synthesis for Fe/K/SiO_2 catalysts microwave pre-treatment at different power levels for 8 s.

The CO conversion remains relatively constant with varying power level. However, at steady state conditions, CO conversion is slightly higher at 270 W as compared to the catalysts microwave pre-treated at other power levels. The average CO conversion was determined by calculation as approximately 10 % for iron catalysts. The experimental

data suggests that microwave pre-treatment has a minimum effect on CO conversion. High conversion levels at 270 W correspond to small particle size obtained at 270 W. Large particle size results in a decline in CO conversion. When the catalyst was microwave pre-treatment at 90 and 180 W, there was no microwave effect observed at these low power levels.

6.11.2 CARBON DIOXIDE SELECTIVITY

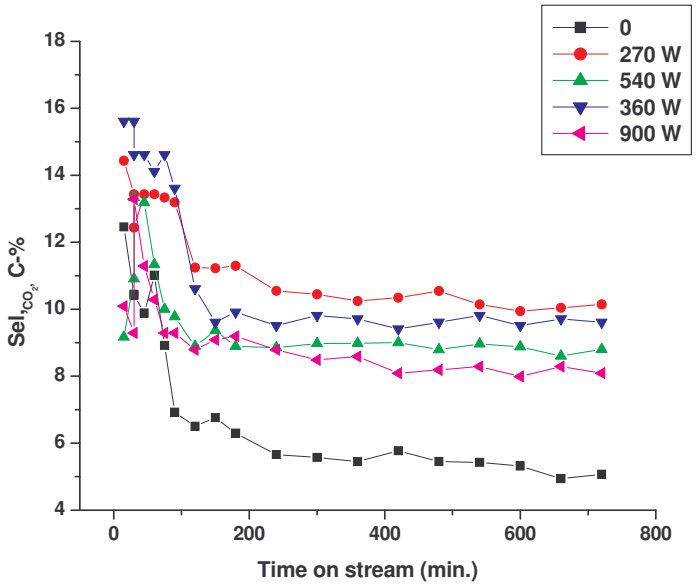


Figure 6.57: Carbon dioxide selectivity as a function of time on stream in the Fischer-Tropsch synthesis for Fe/K/SiO_2 catalysts microwave pre-treated at different power levels for 8 s.

Data analysis revealed that an increase in carbon dioxide also depends on the power level used. 270 W was found to be an optimum power level where a maximum enhanced potassium effect due to microwave effect was observed. The increase in carbon dioxide selectivity can be explained by the increase in catalytic activity.

6.11.3 METHANE SELECTIVITY

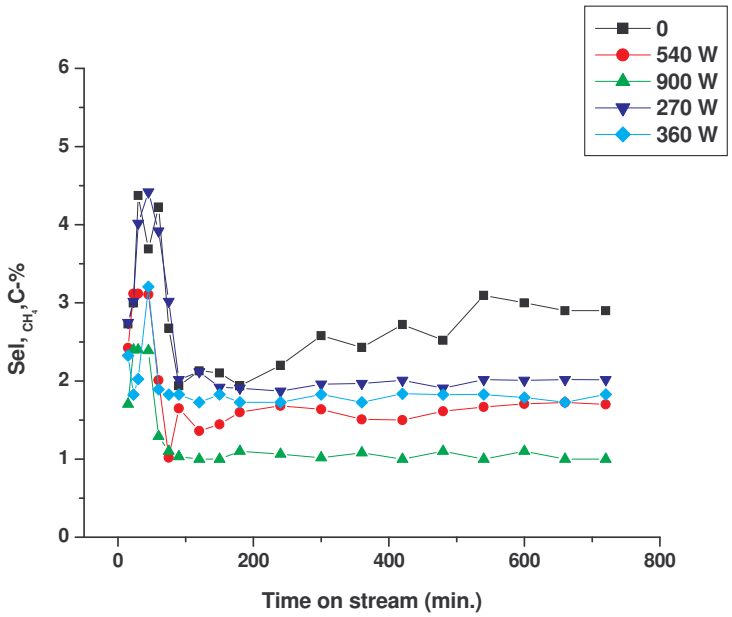


Figure 6.58: Methane selectivity in the Fischer-Tropsch synthesis as a function of time on stream for Fe/K/SiO_2 catalysts microwave pre-treatment at different power level for 8 s.

Selectivity towards methane was found to be affected by the power level. However, there is no significant change observed in methane selectivity between 270 and 360 W. When the catalyst was microwave pre-treated for 8 s at 540 W, the methane formation dropped significantly.

6.11.4 OLEFIN SELECTIVITY

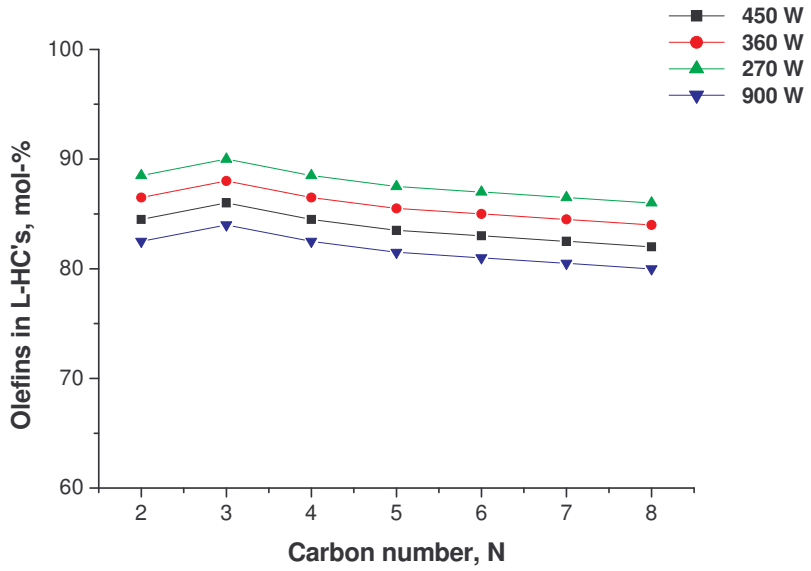


Figure 6.59: Olefins in linear hydrocarbons as a function of carbon number in Fischer-Tropsch synthesis for Fe/K/SiO_2 catalysts microwave pre-treated for 8 s at different power levels.

A poor hydrogenation catalyst consists of a high adsorption of CO species on the surface. This leads to enhanced probability for the formation of primary olefins and reduces readsorption of the 1-olefins to corresponding paraffins.

The olefin content increases with the microwave pre-treatment (**figure 6.59**). It is however important to note that the olefin content obtained in the series with different power levels employed in the catalyst microwave pre-treatment is higher at 270 W. This suggests that there is an optimum power level to be used in order to enhance the probability of 1-olefin formation. This is explained by the temperature-programmed surface reaction studies. At 270 W, the number of adsorption sites increased and the amount of the desorbing component from the catalyst surface increased as compared with the case when using power levels that are higher or lower.

6.12 EFFECT OF BED SIZE AND SHAPE ON Fe/K/SiO_2 CATALYSTS

The catalysts were uniformly placed in a Petri dish for all the experiments except for one set of experiments where the effect of bed size and shape was investigated. This was done in order to examine the microwave effect. The results obtained are as follows:

6.12.1 CATALYTIC ACTIVITY

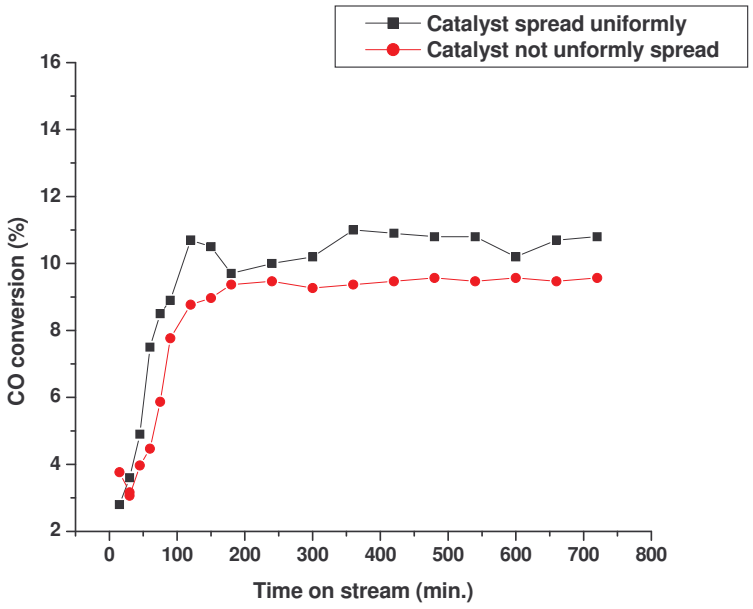


Figure 6.60: CO conversion against time on stream for Fe/K/SiO_2 catalysts in the Fischer-Tropsch synthesis. To investigate the microwave effect: in one case the catalyst was placed uniformly in a Petri dish, on the other hand, the catalyst was not spread uniformly.

The experimental data revealed that the catalytic activity improved after the catalyst was uniformly placed on a Petri dish. This signifies effective absorption of the microwaves after the catalyst is uniformly spread. However, low conversion levels were obtained with an uneven arrangement of the $Fe/K/SiO_2$ catalyst. The analysis shows that, in this case there was not enough absorption of the microwaves due to the order of arrangement of the sample before microwave pre-treatment.

6.12.2 CARBON DIOXIDE SELECTIVITY

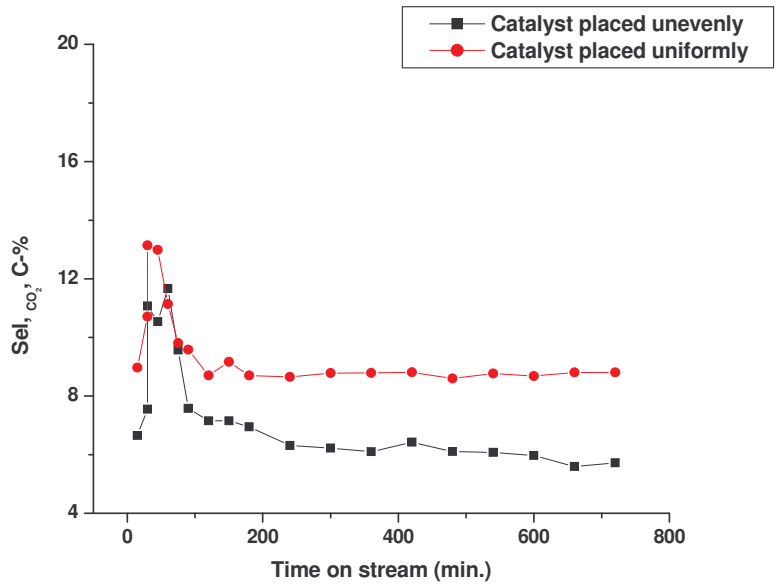


Figure 6.61: Carbon dioxide selectivity as a function of time on stream in the Fischer-Tropsch synthesis for $Fe/K/SiO_2$ catalysts microwave pre-treated.

Effective absorption of the microwaves on an evenly distributed catalyst resulted in high formation of carbon dioxide. High carbon dioxide selectivity was obtained to be due to high carbon monoxide conversion obtained in **figure 6.60**.

6.12.3 METHANE SELECTIVITY

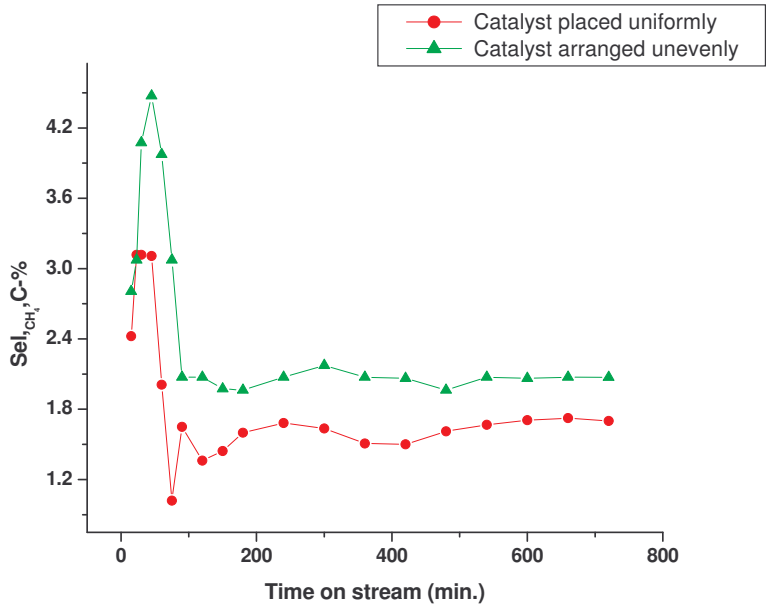


Figure 6.62: Methane selectivity in the Fischer-Tropsch synthesis against time on stream after both samples were microwave pre-treated with varying bed size and shape.

The best Fe/K/SiO_2 catalyst with low methane selectivity was obtained after microwave pre-treatment with the catalyst placed uniformly in a Petri dish. In Fischer-Tropsch synthesis, methane is usually minimized as its formation consumes a lot of synthesis gas.

The decrease in methane formation was due to effective absorption of the microwaves by the iron catalyst. Effective absorption resulted into a significant increase in the particle size of the iron particles. The bigger the particle size of the active metal, the lower the methane formation.

6.12.4 OLEFIN SELECTIVITY

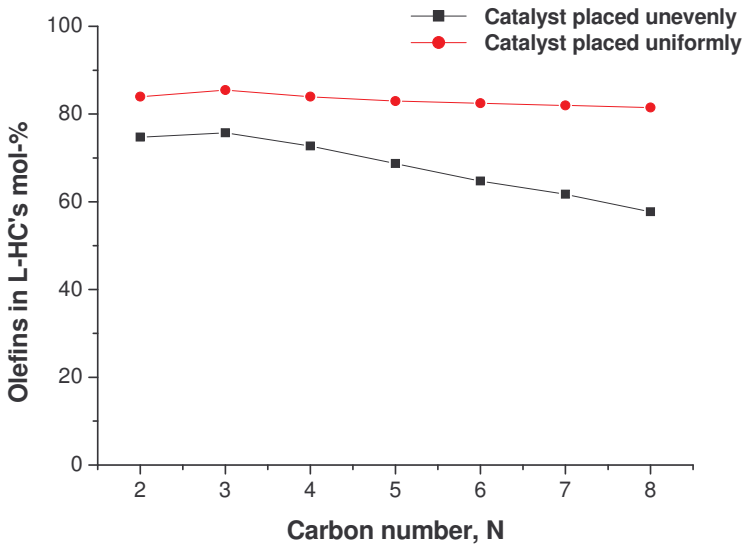


Figure 6.63: Olefins in linear hydrocarbons as a function of carbon number in the Fischer-Tropsch synthesis for the $Fe/K/SiO_2$ catalysts microwave pre-treated with varying bed size and shape.

The content of 1-olefins formed was found to depend on the way in which the catalyst is placed before the microwave pre-treatment. When the catalyst was placed uniformly, maximum absorption of the microwaves seems to take place.

6.13 MICROWAVE EFFECT ON CATALYTIC ACTIVITY AND SELECTIVITY OF A PARTIALLY REDUCED Fe/SiO_2 CATALYST

A Fe/SiO_2 catalyst was prepared by incipient wetness method, dried, calcined and partially reduced at 300 ^oC for 16 h in hydrogen. The purpose of this experiment was to study the microwave effect on a magnetite-containing catalyst because magnetite is a good microwave absorber. Changes in catalytic activity and selectivity were then studied after the microwave pre-treatment. Catalytic activity of the Fe/SiO_2 catalysts before and after microwave pre-treatment is displayed in **figure 6.64**.

6.13.1 ACTIVITY MEASUREMENT

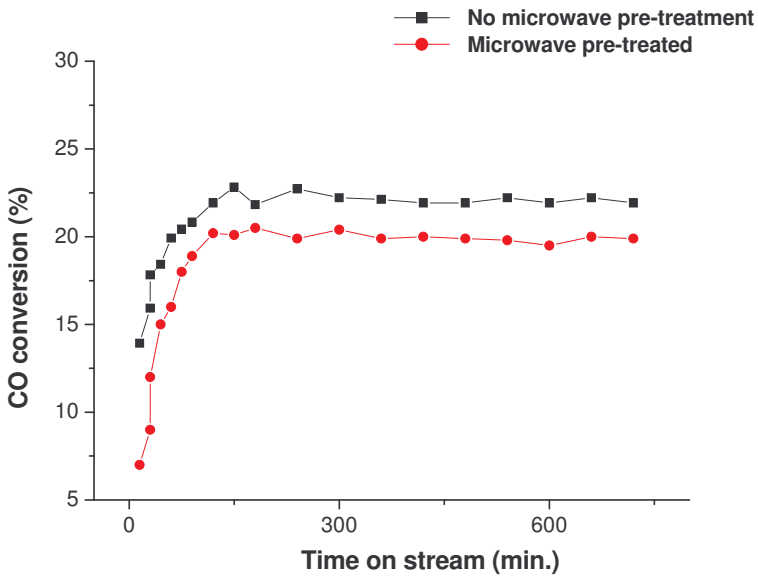


Figure 6.64: Changes in carbon monoxide conversion in the Fischer-Tropsch synthesis as a function of time on stream for Fe/SiO_2 catalysts partially reduced at 300 ^{o}C. FTS experiments were done before and after microwave pre-treatment.

CO conversion for both catalysts is displayed in **figure 6.53**. The catalytic activity is slightly higher for the unmicrowave pre-treated catalyst. Experimental data revealed that the microwave pre-treatment of a partially reduced catalyst resulted to a decline in catalytic activity. The decrease in catalytic activity is probably due to increasing particle growth after microwave heating. Selectivity measurements were carried out to examine the microwave effect. The results are as follows:

6.13.2 CARBON DIOXIDE SELECTIVITY

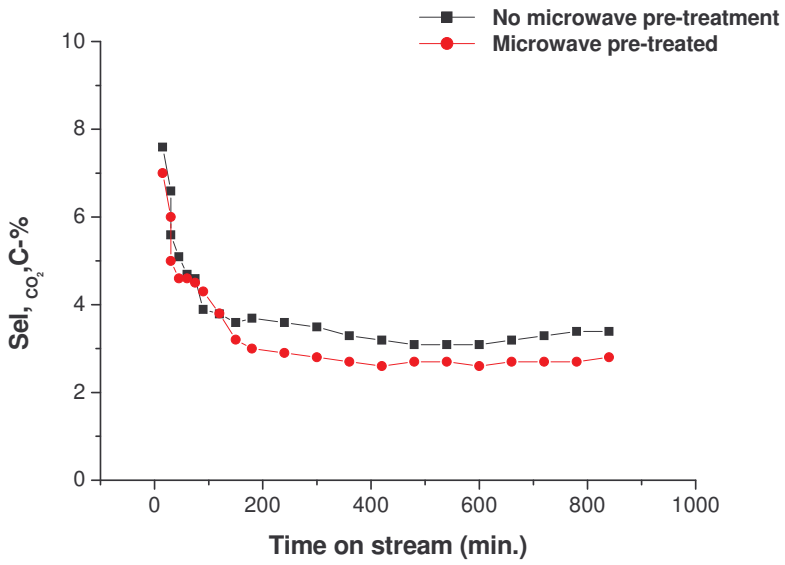


Figure 6.65: Carbon dioxide selectivity as a function of time on stream for the Fe/SiO_2 catalysts partially reduced at 300 ^{o}C for 16 h in flowing hydrogen. FTS experiments were done before and after microwave pre-treatment.

Carbon dioxide selectivity remains constant at the beginning of the reaction. On the other hand, as reaction time proceeds, CO_2 formation decreases for the microwave pre-treated partially reduced iron catalysts.

6.13.3 METHANE SELECTIVITY

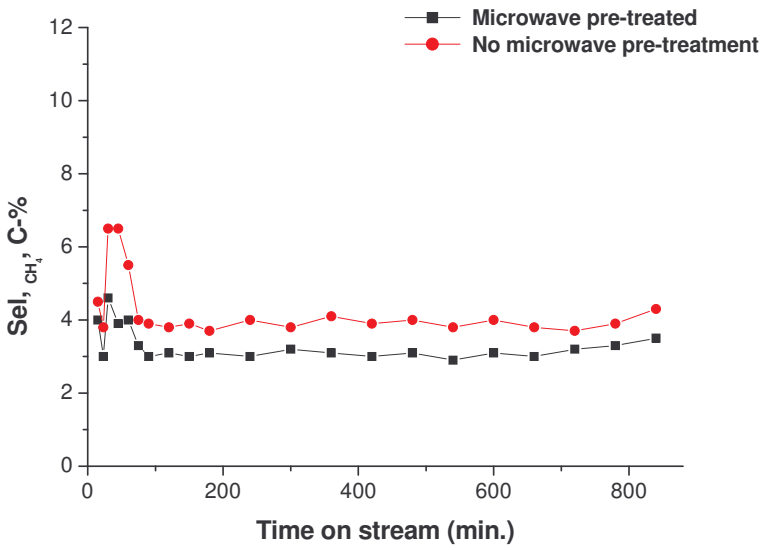


Figure 6.66: Methane selectivity in the FTS as a function of reaction time on stream for the Fe/SiO_2 catalysts before and after microwave pre-treatment. Fe/SiO_2 catalyst was first partially reduced in hydrogen at 300 ^{o}C for 16 h. This was followed by the microwave pre-treatment.

The methane formation was observed to be decreasing with the microwave pre-treatment for the partially reduced Fe/SiO_2 catalyst. Again the decrease in methane formation is probably attributed to the growth of the active metal particles due to microwave heating. The particle size growth resulted in drop in the formation of methane. The experimental results are investigated in **figure 6.66**.

6.13.4 OLEFIN FORMATION

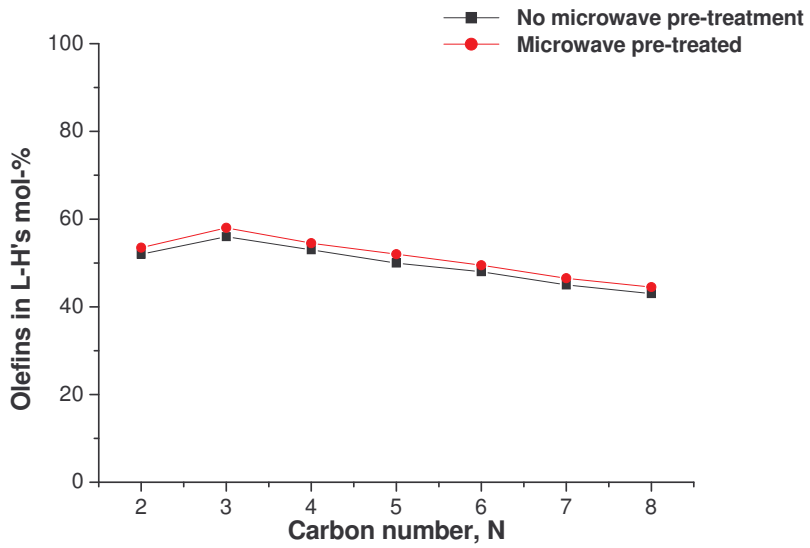


Figure 6.67: Olefins in linear hydrocarbons obtained from Fe/SiO_2 catalysts before and after microwave pre-treatment.

The amount of olefins formed as obtained from FTS experiments did not change with the microwave pre-treatment. There was no potassium promotion in this case suggesting that the microwave effect on olefin formation depends on potassium promotion.

6.14 EFFECT OF CALCINATION TEMPERATURE ON CATALYTIC ACTIVITY AND SELECTIVITY FOR THE Fe/SiO_2 CATALYST IN FTS

Effect of calcination temperature on catalytic activity and selectivity in FTS was examined using unpromoted Fe/SiO_2 catalysts calcined at different temperatures (350, 500 and 700 ^oC).

6.14.1 ACTIVITY MEASUREMENTS

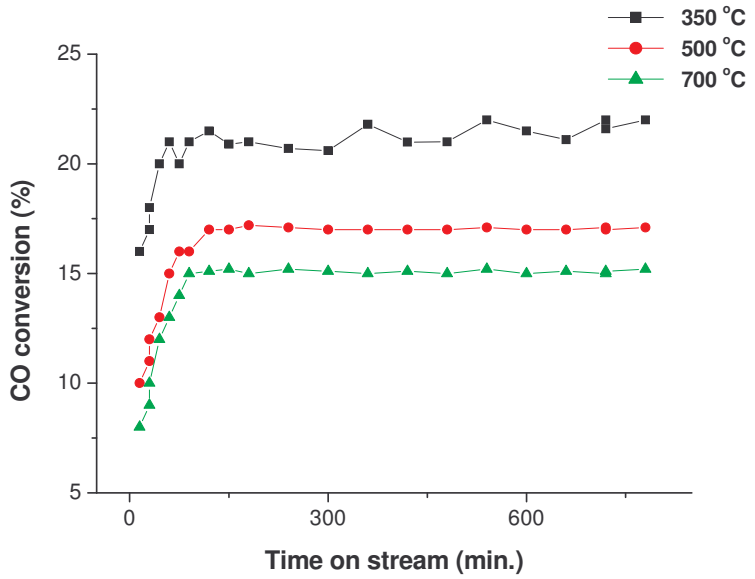


Figure 6.68: CO conversion as a function of time on stream for the Fe/SiO_2 catalysts calcined at different temperatures.

Analysis of data revealed a significant decrease in catalytic activity as the calcination temperature increases. The decline in CO conversion with the calcination temperature is due to the decrease in the surface area resulting from the particle growth due to conventional heating. The results obtained from BET are shown below:

Table 6.10: Surface area determination for Fe/SiO_2 catalysts calcined at different temperatures

Temperature (^oC)	Surface Area (m^2/g)	Pore volume (ml/g)
350	401	0.7
500	312	0.6
700	210	0.4

6.14.2 CARBON DIOXIDE SELECTIVITY

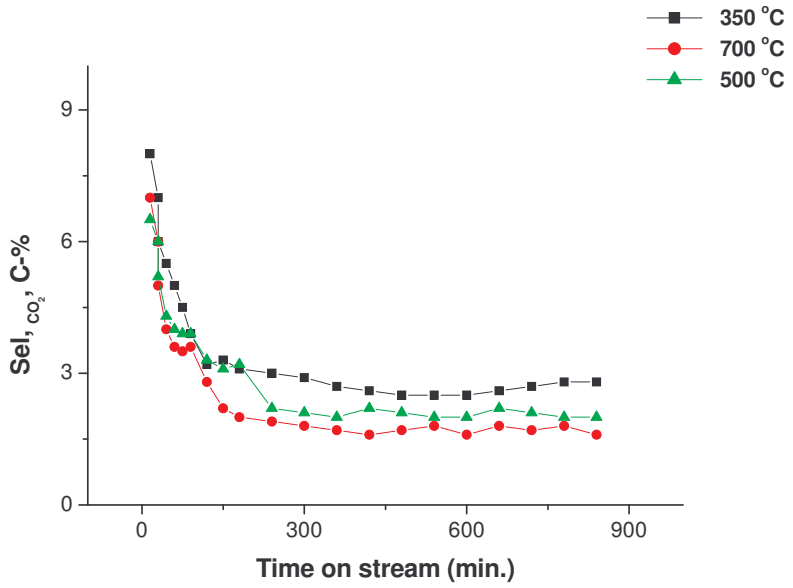


Figure 6.69: Carbon dioxide selectivity as a function of time on stream (min.) for the Fe/SiO_2 catalysts showing the effect of calcination temperature.

The results obtained revealed that as the calcination temperature decreases, the formation of carbon dioxide is favoured. The increase in carbon dioxide formation is due to high conversion level obtained after catalyst calcination at lower temperatures (350 ^{o}C). High CO conversion promotes the formation of carbon dioxide.

6.14.3 METHANE SELECTIVITY

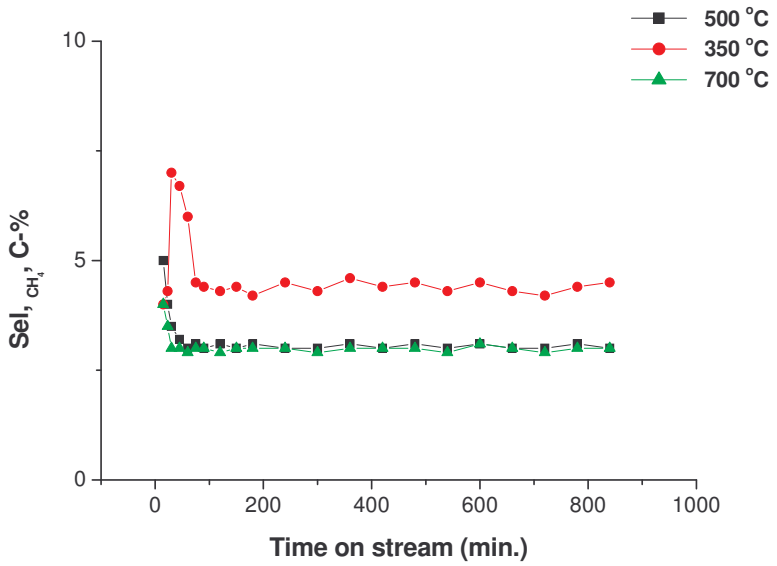


Figure 6.70: Methane selectivity (C-%) with time on stream (min.) for Fe/SiO_2 catalysts calcined at different temperatures.

In principle, methane selectivity should be kept as low as possible, as it requires more demanding and expensive set-up and construction for its conversion to useful products. The methane selectivity obtained for the Fe/SiO_2 catalysts calcined at different temperatures is shown in **figure 6.70.** The results showed a decline in methane selectivity due to increasing calcination temperature. The decline in methane selectivity is probably due to an increase in particle size as the calcination temperature increases.

6.14.4 OLEFIN SELECTIVITY

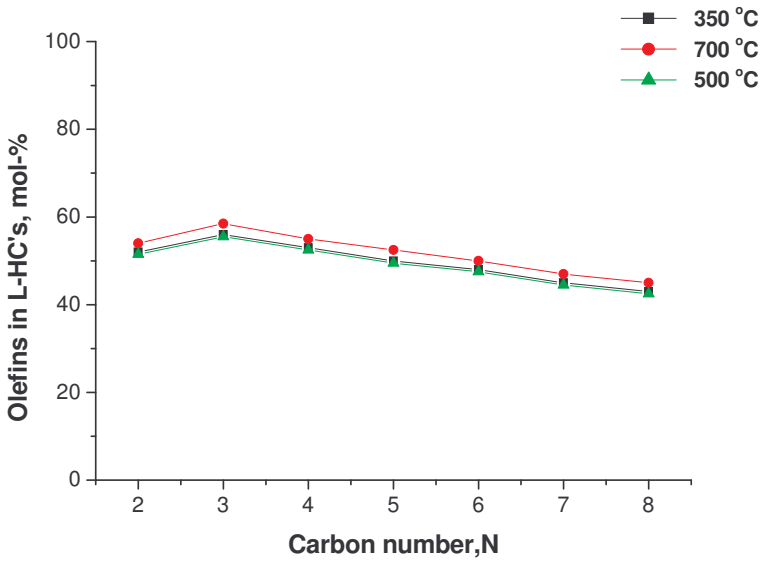


Figure 6.71: Olefins in linear hydrocarbons (C_2 – C_8) obtained from Fe/SiO_2 catalysts calcined at different temperatures.

The olefin formation was not affected by the calcination temperature as shown in **figure 6.71**. All curves follow the same pattern with relatively low values of ethylene followed by a decrease in olefin content as the carbon number increases.

6.15 MICROWAVE EFFECT ON Fe/SiO_2 CATALYSTS CALCINED AT 700 ^oC

6.15.1 CATALYTIC ACTIVITY

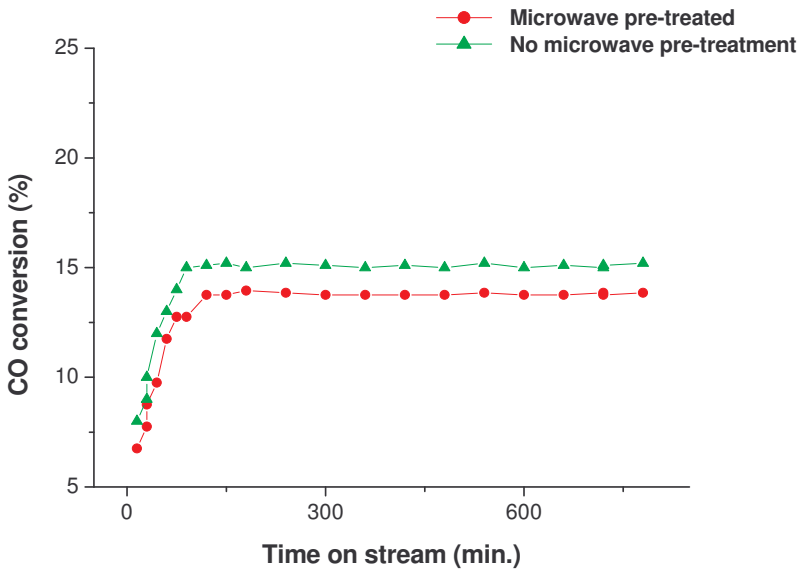


Figure 6.72: CO conversion as a function of time on stream for Fe/SiO_2 catalyst calcined at 700 ^oC. FTS experiments were done before and after microwave pre-treatment.

Microwave pre-treatment resulted in increase in the particle size of the active metal. This is found on promoted and unpromoted Fe/SiO_2 catalysts. When the Fe/SiO_2 catalyst was calcined at 700 ^oC for 6.5 h in air, microwave pre-treatment resulted in the decrease in catalytic activity. The decrease in catalytic activity followed a decrease in particle size of the active metal due to microwave heating. The results are investigated in **figure 6.72**.

6.15.2 CARBON DIOXIDE SELECTIVITY

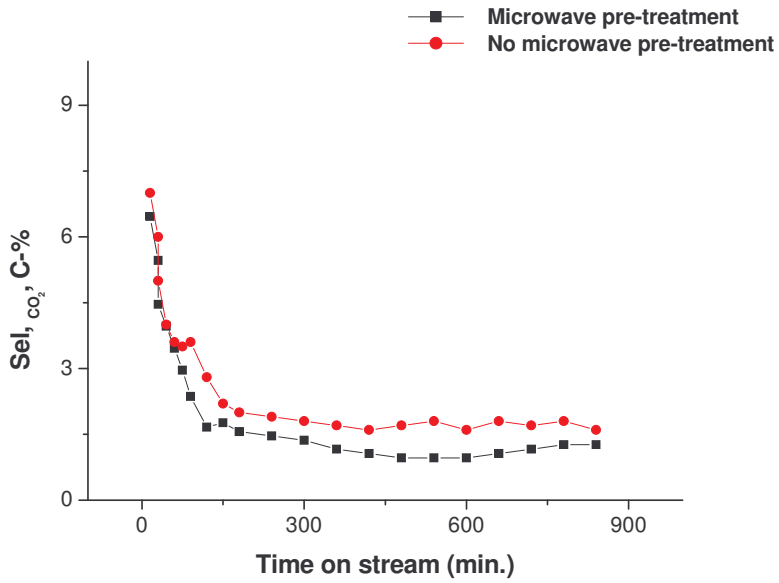


Figure 6.73: Carbon dioxide selectivity as a function of time on stream (min.) for the Fe/SiO_2 catalysts calcined at 700 ^oC. FTS experiments were carried out before and after microwave pre-treatment.

The CO_2 selectivity remains relatively constant at the beginning of the reaction. As the time proceeds, the formation of carbon dioxide for the microwave pre-treated catalyst dropped slightly. The decrease in the formation of carbon dioxide is probably due to the slight decrease in catalytic activity shown in **figure 6.72**.

6.15.3 METHANE SELECTIVITY

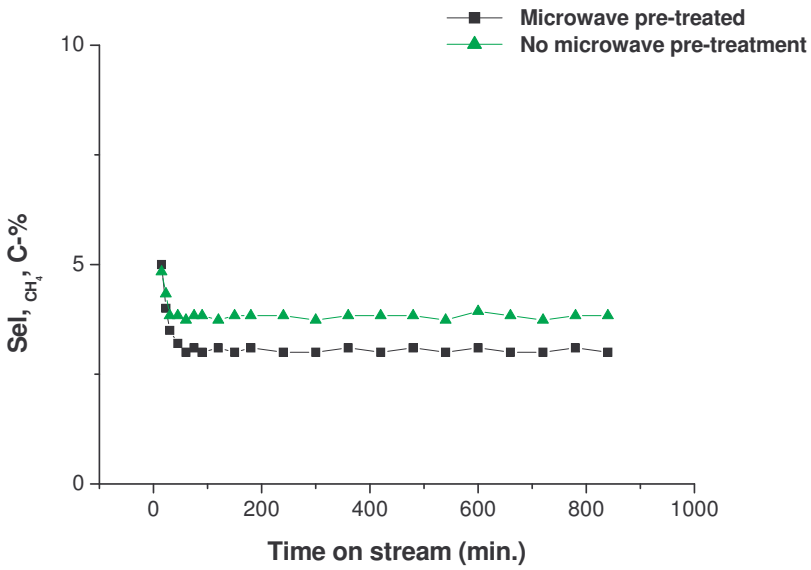


Figure 6.74: Methane selectivity (C-%) with time on stream (min.) for Fe/SiO_2 catalysts calcined at 700 ^{o}C. FTS experiments were carried out before and after microwave pre-treatment.

A drop in methane selectivity was observed after microwave pre-treatment. A decrease in methane selectivity after microwave pre-treatment is due to particle size growth. PXRD results (**figure 6.75**) explain the increase in the particle size of Fe/SiO_2 catalyst after microwave pre-treatment. In addition, the microwave pre-treatment results in broader diffraction peaks. The results are summarized below:

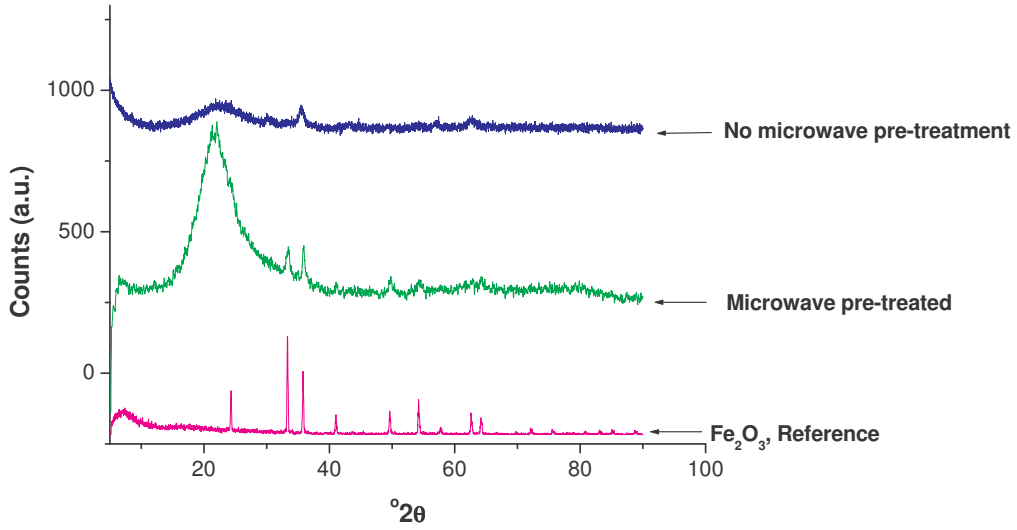


Figure 6.75: PXRD patterns of the Fe/SiO_2 catalysts calcined at 700 ^{o}C for 6.5 h in air. PXRD experiments were taken before and after microwave pre-treatment.

6.16 EFFECT OF MICROWAVE ON UNSUPPORTED IRON CATALYSTS (Fe/K)

6.16.1 FISCHER-TROPSCH SYNTHESIS

6.16.1.1 ACTIVITY MEASUREMENTS

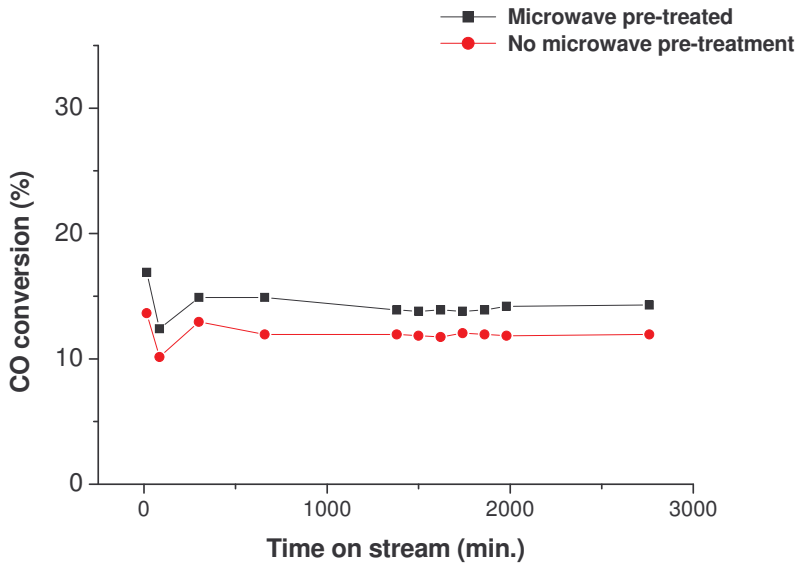


Figure 6.76: CO conversion as a function of time on stream in the FTS for Fe/K catalysts before and after microwave pre-treatment. Microwave pre-treatment was carried out at 540 W for 8 s.

The catalytic activity of the unsupported iron catalyst also improved after microwave pre-treatment. The improvement in catalytic activity is due to the presence of potassium on iron catalyst.

6.16.1.2 CARBON DIOXIDE SELECTIVITY

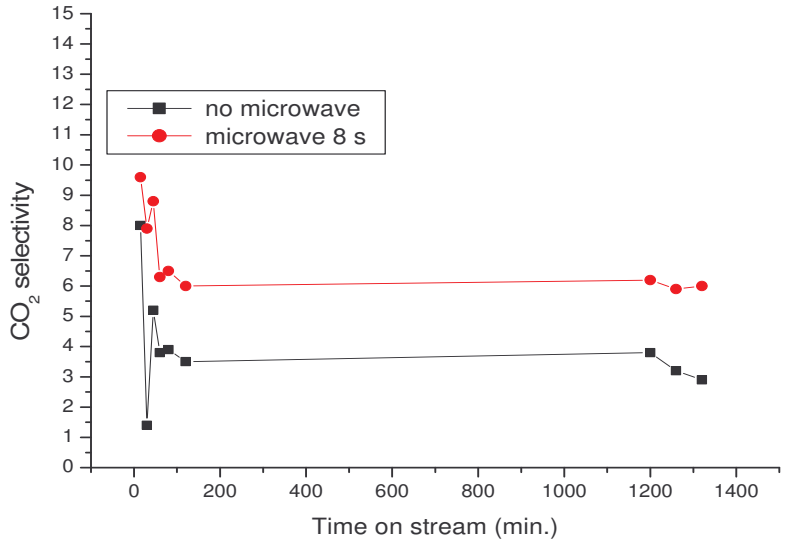


Figure 6.77: CO_2 selectivity as a function of time on stream in the FTS for Fe/K catalysts before and after microwave pre-treatment.

After the pre-treatment of the Fe/K catalyst, carbon dioxide formation was favoured. The increase in CO_2 selectivity is due to high CO conversion level obtained (**figure 6.76**).

6.16.1.3 METHANE SELECTIVITY

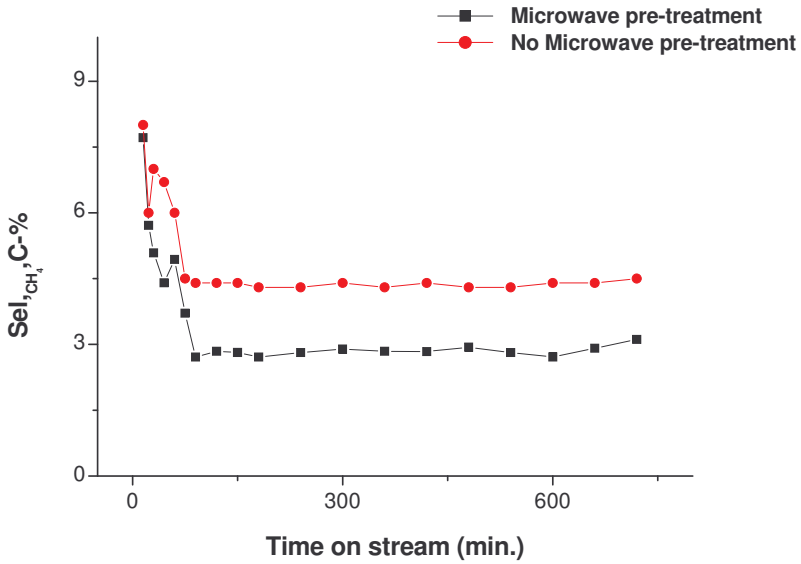


Figure 6.78: Methane selectivity against reaction time on stream for Fe/K before and after microwave pre-treated.

The microwave pre-treatment of the Fe/K catalysts resulted in the decline of methane selectivity due to particle growth which occurs due to microwave heating.

6.16.1.4 OLEFIN SELECTIVITY

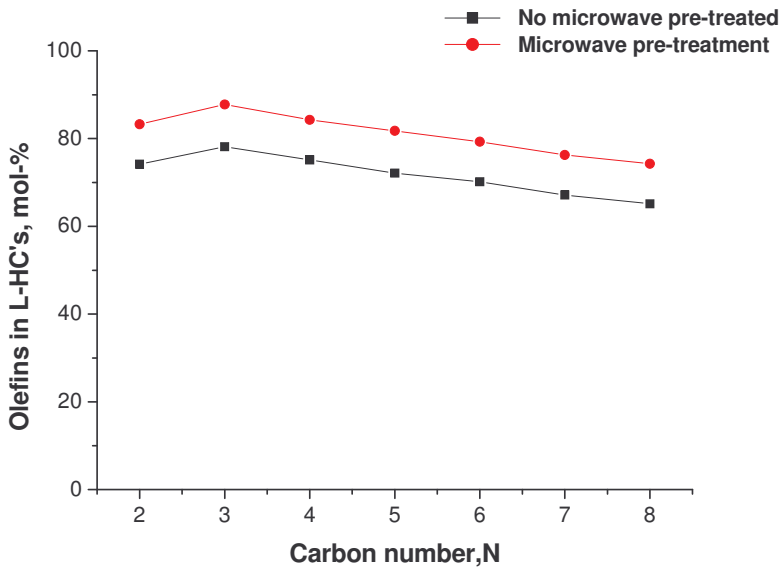


Figure 6.79: Olefins in linear hydrocarbons as a function of time on stream for Fe/K catalysts before and after microwave pre-treatment. Microwave pre-treatment was carried out at 540 W for 8 s for the microwave pre-treated catalyst.

Similar to the supported potassium containing iron catalyst, the microwave pre-treatment enhances the olefin formation. The amount of olefins increases significantly due to the way in which potassium and iron are interacting.

The microwave pre-treatment of both supported and unsupported potassium containing iron catalysts resulted in increase in selectivity towards olefins.

6.17 FISCHER-TROPSCH SYNTHESIS: Co/SiO_2 CATALYSTS

6.17.1 ACTIVITY MEASUREMENTS

The catalytic activity was measured based on carbon monoxide conversion with respect to time on stream. Steady state carbon monoxide conversion was found to be 56 %, higher than CO conversion for the Fe/SiO_2 catalysts. However, high conversion levels of 56 % were obtained for both microwave pre-treated and unmicrowave pre-treated Co/SiO_2 catalysts. The experimental data suggested that the microwave pre-treatment has a minimum effect on catalytic activity.

6.17.2 PRODUCT DICTRIBUTION AND SELECTIVITY

The distribution of products was explained by means of Anderson-Schulz-Flory kinetic model, a logarithmic plot of the mole fraction of each linear hydrocarbon with respect to the carbon number. The graph displayed a straight line and the slope of the line is defined as chain growth probability (allowing the chain to grow). The ASF plots results are investigated below:

Table 6.11: Chain growth probability, α (%) for Co/SiO_2 catalysts before and after microwave pre-treated at 900 W for 15 s.

Carbon number	No microwave pre-treatment	Microwave pre-treatment
C_{10}-C_{14} (α)	69 %	65 %

During Fischer-Tropsch synthesis, chain growth occurs via the addition of surface methylene groups to the adsorbed alkyl groups. Allowing the chain to grow is necessary for Fischer-Tropsch synthesis.

However, analysis of the ASF data showed no significant change in the α-value for the cobalt catalyst before and after microwave pre-treatment at 900 W for 15 s. The results are shown in **table 6.11**. Olefins are considered the main products of Fischer-Tropsch synthesis. The selectivity towards olefins was obtained and the results are displayed below in **table 6.12**.

The C_5 reaction products were analyzed. The results obtained are shown below:

Table 6.12: Information taken from C_5 for the Co/SiO_2 catalysts before and after microwave pre-treatment at 900 W for 15 s.

	MT 0	**MT 15 s**
[a]Degree of branching (%)	0.36	0.28
[b]Degree of 2° hydrogenation (%)	39	30
[c]Degree of double bond shift (%)	43	41

[a] Methyl branching over linear hydrocarbons

[b] Olefins in linear hydrocarbons

[c] Alpha olefins in linear olefins

The results for olefin selectivity showed that the degree of secondary hydrogenation is lower for the microwave pre-treated cobalt catalyst as compared to the unmicrowaved pre-treated one. This shows that with the microwave pre-treatment, the olefin content increases as the microwave pre-treatment holds back secondary reactions such as re-hydrogenation of 1-olefins to corresponding paraffins. These results suggest that a better Co catalyst with higher olefin formation was obtained after microwave pre-treatment at 900 W for 15 s.

6.18 SUMMARY OF CATALYTIC ACTIVITY, PRODUCT DISTRIBUTION AND SELECTIVITY

6.18.1 CARBON MONOXIDE CONVERSION

Positive effects on catalytic activity were established on Fe/SiO_2 catalyst precursors after microwave pre-treatment at 540 W for 8 s. This discovery was due to the presence of -OH- groups on the catalyst surface. Because water is a good microwave absorbing medium, Fe/SiO_2 catalyst precursors after microwave heating displayed enhanced catalytic activity.

The influence of potassium promotion resulted to a decline in catalytic activity. This finding was due to the addition of relatively high potassium loading to the Fe/SiO_2 catalyst precursors. On high level of potassium promotion, iron particles tend to be covered by potassium thereby hiding them from interacting with CO and H_2.

Microwave pre-treatment of potassium promoted Fe/SiO_2 catalyst precursors resulted to a decline in catalytic activity. The decline in carbon monoxide conversion was due to the increase in particle size of the active metal after microwave pre-treatment. However, on microwave pre-treatment of promoted iron catalysts, the catalytic activity was observed to improve. The enhancement in catalytic activity was due to the presence of potassium promotion. The microwave affects the way in which potassium interacts with the active metal (iron).

6.18.2 CARBON DIOXIDE SELECTIVITY

The formation of carbon dioxide was found to increase with potassium promotion. Potassium has been known to enhance the water gas shift activity. However, there is no evidence that the microwave pre-treatment has an effect on the water gas shift reaction. The enhancement in carbon dioxide selectivity was found to be due to high conversion levels. At low carbon monoxide activity, carbon dioxide formation decreased.

6.18.3 METHANE SELECTIVITY

High methane selectivity was only found on Fe/SiO_2 catalysts which were not potassium promoted. On the other hand, the microwave pre-treatment of Fe/SiO_2 catalyst pre-cursors resulted to an increase in the formation of methane. High methane selectivity was found to be due to high concentration of hydrogen species on the catalyst surface resulting from the - OH- groups present in the catalyst surface.

In general, a decline in methane selectivity was observed to be due to the increase in the particle size of iron. The increase in particle size resulted from the microwave heating.

6.18.4 OLEFIN SELECTIVITY

The influence of potassium resulted to an increase in the formation of olefins. Potassium has been known to favour olefin formation over paraffin. The microwave pre-treatment of potassium promoted Fe/SiO_2 catalysts resulted in enhanced potassium effect. The amount of olefins formed after microwave pre-treatment improved significantly. This discovery was found to be due to the interaction between iron and potassium due to microwave pre-treatment.

6.18.5 CHAIN GROWTH

High alpha values were obtained with the potassium promoted iron catalysts, since potassium inhibits desorption of products, allowing the chain to grow. Microwave pre-treatment brings about an increase in chain growth probability. Low alpha values were obtained with the unpromoted iron catalyst.

6.18.6 SUGGESTED FUTURE WORK

- Examine microwave effects at different (various) K levels for Fe or Fe/SiO_2 catalysts.
- Focus on temperature programmed surface reactions (TPSR) and SIMS measurements, since these seem to be the most revealing methods of microwave induced changes in the surface chemistry.