Chapter 3

Experimental methods

3.1 Catalyst preparation

Unsupported and silica supported iron catalysts were prepared in this study. The methodology used for each type of catalyst preparation is discussed below.

3.1.1 Unsupported catalysts

The K/Fe catalysts used in this study were prepared using the pH-controlled continuous precipitation procedure as described by Kölbel and Raleek.[1] A 4 M solution of $Fe(NO_3)_3{\cdot}9H_2O$ was precipitated by the drop-wise addition of 12 M NH_4OH to a pH of 7.2 with continuous stirring. The resultant slurry was stirred for an additional 15 minutes and the final pH was recorded. A centrifuge was used to separate the precipitate from the liquid. The centrifuge speed used was 5000 RPM and this was done for 15 minutes. The precipitate was then dried at room temperature for 12 hours. Subsequently, the precipitate was kept at 120 ^oC for 12 hours to remove water that was incorporated within the precipitate. Calcination was performed at 350 ^oC for 6.5 hours using a heating rate of 10 ^oC/minute.

For the promoted catalysts, appropriate amounts of K_2CO_3 solutions were added to the calcined precursor *via* the incipient wetness pore-filling procedure. The mixture was then re-dried at 120 ^oC for 12 hours and calcined at 350 ^oC for 6.5 hours. The prepared samples had potassium loadings of 0.2, 0.5, 0.7, 1.0 and 1.5 weight percent. For brevity, these catalysts were referred to as *x*K/Fe, where *x* is the weight percent of the K loading.

3.1.2 Silica supported catalysts

Synthesis of $K/Fe/SiO_2$ catalysts was achieved *via* the incipient wetness impregnation technique. A ferric nitrate solution obtained by dissolving $Fe(NO_3)_3{\cdot}9H_2O$ in de-ionized water was added drop-wise to the silica support, ensuring that the pores in the support are filled. The obtained slurry was then dried at 120 ^{o}C for 12 hours to remove moisture. Calcination was performed at 350 ^{o}C for 6.5 hours using a heating rate of 10 ^{o}C/minute. For this study, the loading of iron was maintained at 10 wt. %.

The 10Fe/SiO_2 catalyst base powder was then impregnated with appropriate amounts of K_2CO_3 solutions to produce the desired catalyst compositions. For this study, potassium loadings of 0.2, 0.5, 0.7, 1.0 and 1.5 weight percent were desired. The catalyst was then dried at 120 ^{o}C for 12 hours followed by calcination at 350 ^{o}C for 6.5 hours. For brevity, these catalysts are referred to as xK/10Fe/SiO_2, where x is the potassium loading (wt. %).

The effect of crystallite size was investigated by comparing the bigger crystallites synthesized using the incipient wetness technique against the smaller particles prepared using the deposition precipitation (DP) procedure. Using the DP method, ferric nitrate, potassium carbonate and urea were dissolved in de-ionized water prior to being added drop-wise on to the silica support. Hydrolysis of urea was used to release ammonia *in situ* at a temperature of 100 ^{o}C for 3 hours. The slurry was then dried at 90 ^{o}C under vacuum for 40 minutes followed by another drying period of 12 hours at 120 ^{o}C. Calcination of samples synthesized using the DP technique was also done at 350 ^{o}C for 6.5 hours using a heating rate of 10 ^{o}C/minute. A 1.0 wt. % potassium loading was maintained for the DP prepared catalysts, while the iron loading was kept at 10 wt. %. For brevity, these catalysts are denoted as 1.0K/10Fe/SiO_2-DP.

3.1.3 Microwave pre-treatment of catalysts

About 0.5 g catalyst mass was evenly distributed in a microwave-transparent Pyrex watch glass. A DEFY (900 W, 2.45 GHz) domestic microwave was used to pre-treat the already prepared catalysts. All microwave pre-treatment experiments were done in the solid state. Microwave pre-treatment was done for 10 seconds at a power level of 450 W. The effect of the microwave irradiation time has also been studied. The pre-treatment time was increased from 10 seconds to 20, 30, 40, 60, 300 and 600 seconds. The power level was maintained at 450 W for all experiments.

3.2 Catalyst characterization

3.2.1 BET analysis by N_2 physisorption

Nitrogen adsorption studies were done using the BET method which was derived by Stephen Brunauer, Paul Emmett and Edward Teller. This is a non-destructive method used to determine the surface area, pore volume and pore size distribution of a sample. This method analyses the physical adsorption (physisorption) of gas molecules on solid surfaces.

N_2 physisorption measurements were conducted using a Micromeritics TRISTAR 3000 analyser. Prior to analysis, about 0.2 g of each sample was outgassed for 6 hours at 150 ^{o}C in an atmosphere of nitrogen. The total specific surface areas were determined by the single or multi-point BET methods and pore size distributions were evaluated using the standard Barrett-Joyner-Halenda (BJH) treatment.[2]

3.2.2 X-ray fluorescence (XRF)

Elemental composition of the samples was confirmed using XRF. The XRF data was recorded using a Panalytical PW12404 wavelength dispersive XRF spectrometer. X-rays were generated using a Rh tube with $K\alpha = 24.9$ and $K\beta = 22$. The samples were first mixed with 2% Mowiol binder (polyvinyl glue) before being pressed to pellets using 10 MPa pressure.

3.2.3 Transmission electron microscopy (TEM)

Thin samples for TEM analysis were prepared by crushing the K/Fe and K/Fe/SiO_2 catalysts with a mortar and pestle followed by dispersion in methanol using an ultra-sound bath. An appropriate amount of the sample was then placed onto a carbon coated copper grid, dried and then introduced to the microscope. The samples were studied using a TECHNAI G2 SPIRIT transmission electron microscope operating at an accelerating voltage of 120 keV.

3.2.4 Energy dispersive X-ray spectroscopy (EDS)

EDS is an x-ray technique that was used to identify the elemental composition of the catalysts. When a conducting sample is bombarded with a beam of electrons, x-rays are emitted. The emitted x-rays are unique for a given element and can therefore be used to identify elements present in a given sample. The EDS system used in this study was integrated to the TECHNAI G2 SPIRIT transmission electron microscopy instrument.

3.2.5 Temperature programmed reduction (TPR)

Thermo-analytical techniques are amongst the most important and widely used methods for the characterization of solid materials. Temperature programmed reduction (TPR) is a convenient technique for the characterization of both unsupported and supported metal oxide catalysts. Generally, TPR is used to provide information on the influence of the support material, preparation and pre-treatment procedures, and metal additives on catalyst reducibility.[3] The consumption of the reducing agent (H_2 or CO) is usually followed with a thermal conductivity detector (TCD) as a function of temperature and time.

TPR experiments were performed using a Micromeritics AutoChem II 2920 unit fitted with a TCD detector (Figure 3.1). The calcined catalysts were first weighed before being loaded into a U-shaped quartz tube reactor; *ca* 100 and 200 mg were used for the supported and the unsupported samples, respectively. The samples were then dried at 150 ^oC in a flow of argon gas for an hour to remove adsorbed water. Subsequently the reactor was cooled to 50 ^oC. After that, the catalyst was reduced using a linear temperature program (10 $^oC/min$ to 800 ^oC) in 5% H_2/N_2.

Figure 3.1 The Micromeritics AutoChem II 2920 chemisorption analyzer.

3.2.6 Powder X-ray diffraction (PXRD)

X-rays have wavelengths in the angstrom range and they have enough energy to penetrate and probe the internal structure of solids. The distance between atoms in a crystal is also of this magnitude and so x-rays can be diffracted by crystals. X-ray diffraction is the elastic scattering of x-ray photons by atoms in a periodic lattice. The scattered monochromatic x-rays that are in phase give constructive interference. The lattice spacings, which are characteristic of each compound, are calculated using the Bragg relation from the angle at which the constructive interference leaves the crystal.[4] In this work, PXRD was used to identify bulk crystallographic phases in the catalysts and for estimation of crystallite sizes.

PXRD measurements in this work were performed using a D8 Bruker X-ray diffractometer which utilizes Ni filtered copper Kα radiation at 40 kV and 40 mA. The diffraction patterns were recorded in the scan range of $10^{o} < 2\theta < 90^{o}$. From the recorded patterns, the phases present were identified by comparing the patterns with those reported in the Diffrac^{plus} evaluation package using EVA (V11.0) software package.

3.2.7 Temperature Programmed Surface Reaction-mass spectrometry (TPSR-MS)

The FTS reaction produces a wide spectrum of hydrocarbon chains, and this process starts from the dissociation of CO and H_2 on transient metal surfaces and follows with the hydrogenation and polymerization of surface carbon species. Since the dissociation of CO is one of the key steps in FTS, it is important to investigate the kinetics and the thermodynamics of CO adsorption and its subsequent dissociation on iron catalysts. Using temperature-programmed techniques surface active carbons have been found to be key intermediates in CO hydrogenation, and they have important influences on the activity, selectivity and stability of a catalyst. TPSR is a surface sensitive technique that was used to assess the effect of potassium on the catalytic sites of microwaved samples.

The home-assembled TPSR set-up that was used in this study is illustrated in Figure 3.2. It consists of a gas manifold, a reactor heating unit, a gas chromatography instrument and a mass spectrometer. This set-up is the same as that used by Linganiso.[5] In this technique, the catalyst sample was first weighed before being loaded into a U-shaped quartz reactor. A catalyst mass of 70 mg was maintained for all the unsupported samples, while a mass of 200 mg was used for the silica supported samples. A plug of quartz wool was used to suspend the catalyst. This was done to prevent any of the catalyst material being carried to the reactor outlet. The ends of the reactor were then attached to the gas inlet and outlet points of the apparatus. A thermocouple was placed adjacent to the quartz reactor to monitor the temperature of the catalyst bed.

Reduction of the catalyst was done for 6 hours with pure H_2 at 350°C and 0.2 MPa. The flow rate of H_2 was kept at 45 ml/min. Once reduction was complete, the reactor was cooled down to 25 °C in Ar and then held at 25 °C for 30 minutes to ensure the removal of gaseous H_2. The adsorption of CO was then done at this temperature and 0.3 MPa for 1 hour using 5% CO balanced in Ar. The gas flow rate was maintained at 30 ml/min during CO adsorption.

Physisorbed CO was subsequently flushed out of the reactor using Ar for 30 minutes, ensuring that the TCD baseline levelled off. H_2 was then re-introduced into the reactor to couple with the adsorbed carbon species, the H_2 flow rate used was 20 ml/min. This was done while ramping the temperature of the reactor from 25 ^{o}C to 800 ^{o}C, using a heating rate of 10 ^{o}C/min. Desorbed hydrocarbons and other gases were monitored using a gas chromatography instrument equipped with a flame ionization detector (FID) and a methanator. The FID was kept at 220 ^{o}C and the GC oven temperature was maintained at 250 ^{o}C. The methanator used consisted of a nickel catalyst, and it was kept at 300 ^{o}C. The methanator was normally bypassed during analysis, unless where stated. A Baltzers Prisma quadrupole mass spectrometer (QMS) was also connected to the system to confirm the identity of the products obtained. Profiles of the effluent mole fractions for the components CH_4, H_2O, CO_2 and CO were recorded independently on the QMS when performing these experiments. Preliminary data recorded during the TPSR-MS experiments suggested that higher hydrocarbons (C_2, C_3, etc.) were not detected during the TPSR-MS experiments.

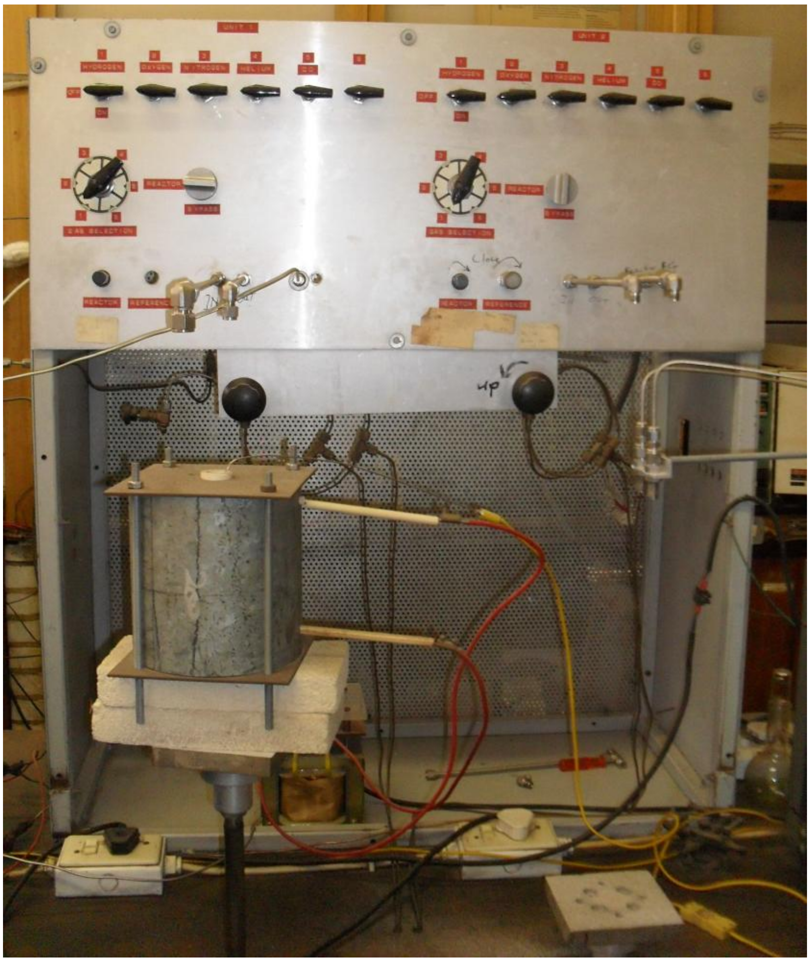

Figure 3.2 The experimental setup used for TPSR experiments.

Deconvolution of the TPSR profiles was achieved by using the Origin 8 software. The deconvoluted data was used to provide information on the contributions of various forms carbon to the total methane produced. Deconvolution of the profiles was done by fitting multiple Gaussian peaks to the profiles. Correlation co-efficient values (R^2) between the actual data and the fitted data that were greater than 0.95 were taken to be adequate. Silica supported catalysts were used to determine the reproducibility of the TPSR-MS technique. Further details on the reproducibility of TPSR-MS are given in to section 5.35.2.

3.2.7.1 Calibration of the flame ionization detector using methane

Methane calibration was carried out to quantify the hydrocarbons that were produced during TPSR experiments. The calibration curve attained is displayed in Figure 3.3. To obtain each calibration point seen in this figure, a minimum of 5 peak areas achieved by injecting the same volume of methane were averaged. A correlation co-efficient (R^2) of 0.997 was accomplished when this method was used for the various volumes of CH_4. Using this calibration, the molecules of methane produced for each gram of catalyst during a TPSR experiment were then determined.

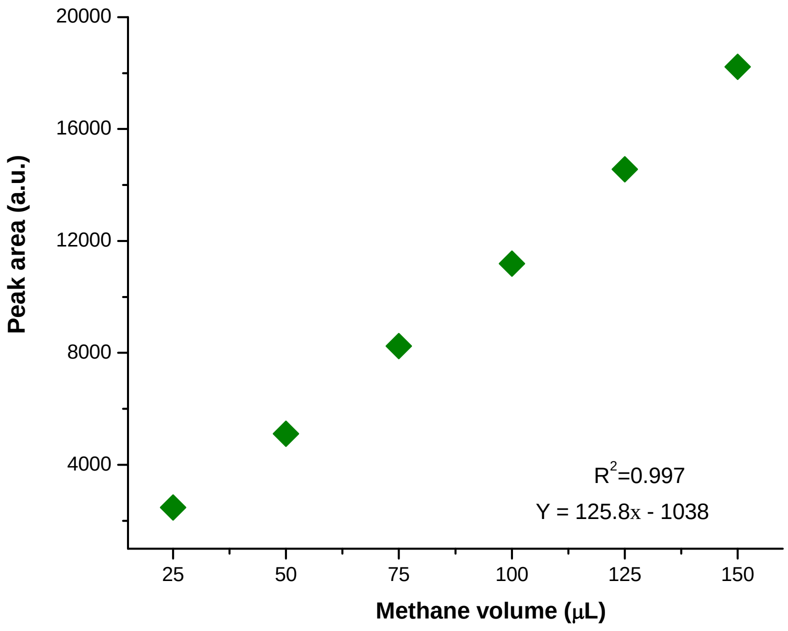

Figure 3.3 A methane calibration curve achieved by injecting volumes between 25 and 150 μL of 100% CH_4. Injections were done using a Hamiltonian-type gas syringe.

3.3 Catalyst evaluation

The effect of microwave pre-treatment on the catalytic properties of the various samples was evaluated using Fischer-Tropsch synthesis.

3.3.1 Fischer-Tropsch reactor studies

3.3.1.1 Gases

All the gases used in this study were supplied by AFROX (African Oxygen) Ltd. The gases used for catalyst characterization and catalyst reduction were Ultra High Purity (UHP) grade gases (99.997% purity). Synthesis gas mixture containing $H_2/CO/N_2$ (0.6/0.3/0.1) was used to supply the reactant gas stream to the catalyst. Argon was used as the carrier gas for both the flame ionization detector (FID) and the thermal conductivity detector (TCD). N_2 was used as an internal standard in order to ensure accurate mass balances.

3.3.1.2 FT reactor setup

The physical setup for the equipment for FT synthesis experiments is shown in Figure 3.4 and it is represented schematically in Figure 3.5. It consisted of a Swagelok stainless steel pipe with a frit, which operated as a fixed bed micro-reactor. A thermocouple was inserted in the reactor to determine the catalyst temperature. The reactor temperature and line temperatures were controlled electronically by using electronic temperature controllers. All lines after the reactor were kept at 150 ^{o}C, and a hot trap was placed immediately after the reactor in order to collect wax. The hot trap was maintained at a temperature of 150 ^{o}C. A second trap kept at ambient temperature was used for the collection of the oil and water mixture. The gas flow rate was controlled using a needle valve and measured by means of a soap flow meter.

Figure 3.4 The two online GCs that were used for the analysis of gaseous products. The GC on the left is fitted with an FID detector and the one on the right is fitted with a TCD detector.

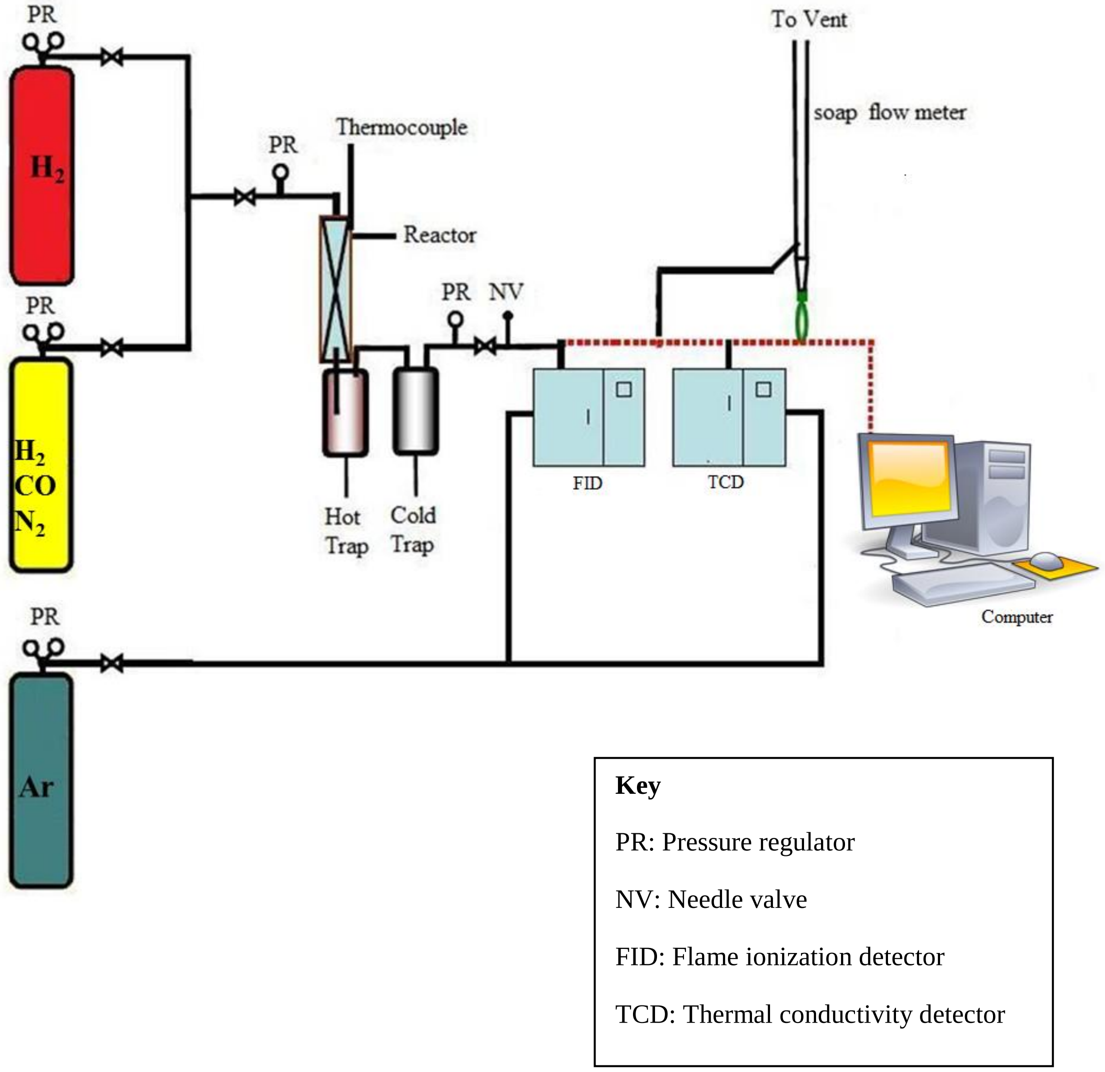

Figure 3.5 A schematic representation of the FT reactor setup.

3.3.1.3 Activity measurements

A catalyst mass of 0.5 g was loaded to a stainless steel fixed bed reactor, and a thermocouple was inserted into the catalyst bed to monitor the temperature. Quartz wool was used to suspend the catalyst bed inside the reactor. Activation of all the catalysts was done *in situ* using hydrogen gas. The catalyst was reduced at 350 ^{o}C using a heating rate of 10 ^{o}C/min. Catalyst activation was done at 0.2 MPa pressure for 16 hours, and the flow rate of hydrogen was maintained at 45 ml/min. Upon completion of the activation process, the reactor was cooled down to 275 ^{o}C. Once the reaction temperature of 275 ^{o}C was attained, synthesis gas was introduced at a flow rate of 20 ml/min and the reactor pressure was raised to 1.0 MPa. The flow rate of the reactor outlet was controlled using a needle valve. A soap bubble flow meter was used to monitor the gas flow rates (see the scheme shown in Figure 3.5).

3.3.1.4 Product analysis

Analysis of the product spectrum was done online using two GCs equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The TCD was used to analyse H_2, N_2, CO, CH_4 and CO_2 while the FID was used to monitor the hydrocarbons in the range C_1-C_8.

Calibration of the detectors was done using a six gas mixture consisting of CH_4 (2.5%), C_2H_4 (0.2%), C_2H_6 (0.5%), CO (10%), CO_2 (5%) balanced with Ar. Syngas (10% N_2, 30% CO, 60% H_2) was also used for calibration. This was done by bypassing the reactor to give H_2, CO and N_2 signals that were not influenced by the catalyst. These peaks were used to calculate the amount of reactants that were fed to the reactor for the duration of the reaction. Typical GC traces recorded during calibration and FTS runs are displayed Figure 3.6, 3.7, 3.8 and 3.9.

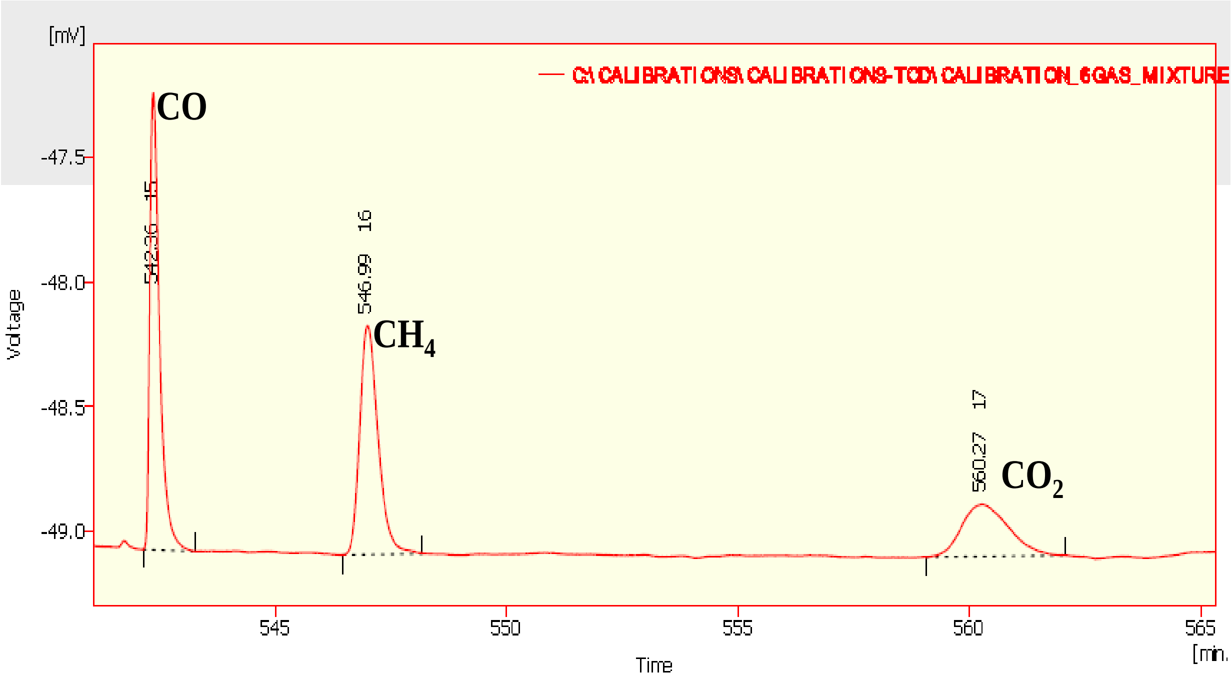

Figure 3.6 A trace for the calibration gas as recorded by the TCD GC.

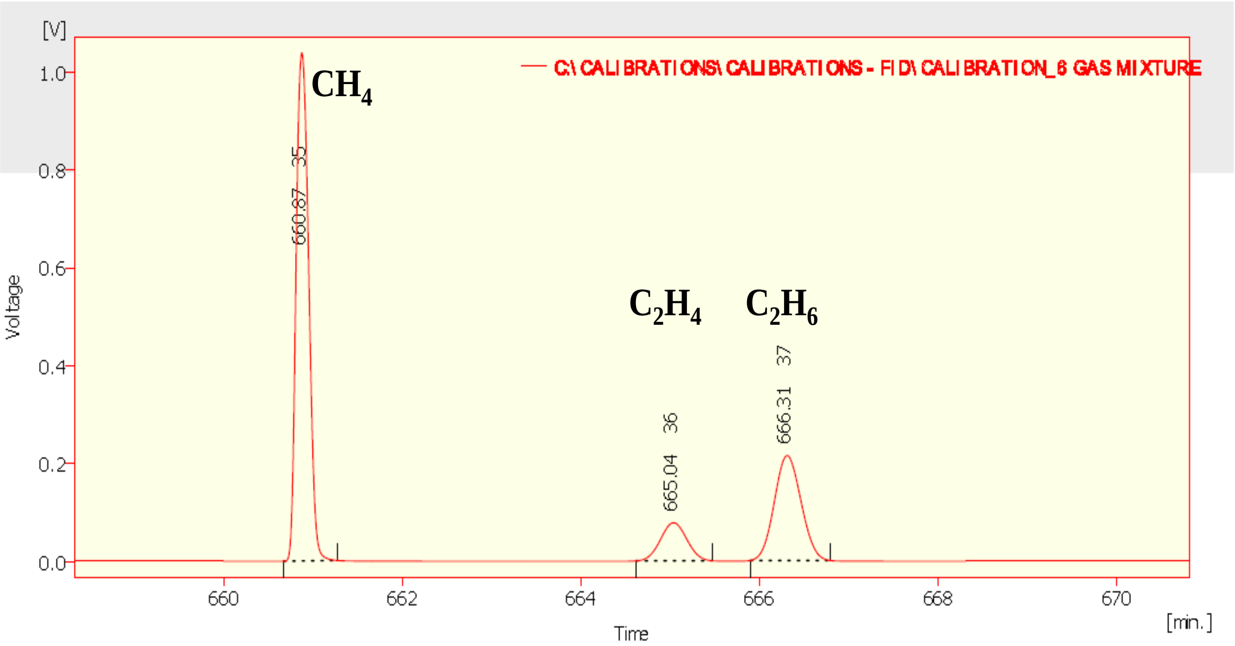

Figure 3.7 A trace for the calibration gas as recorded by the FID GC.

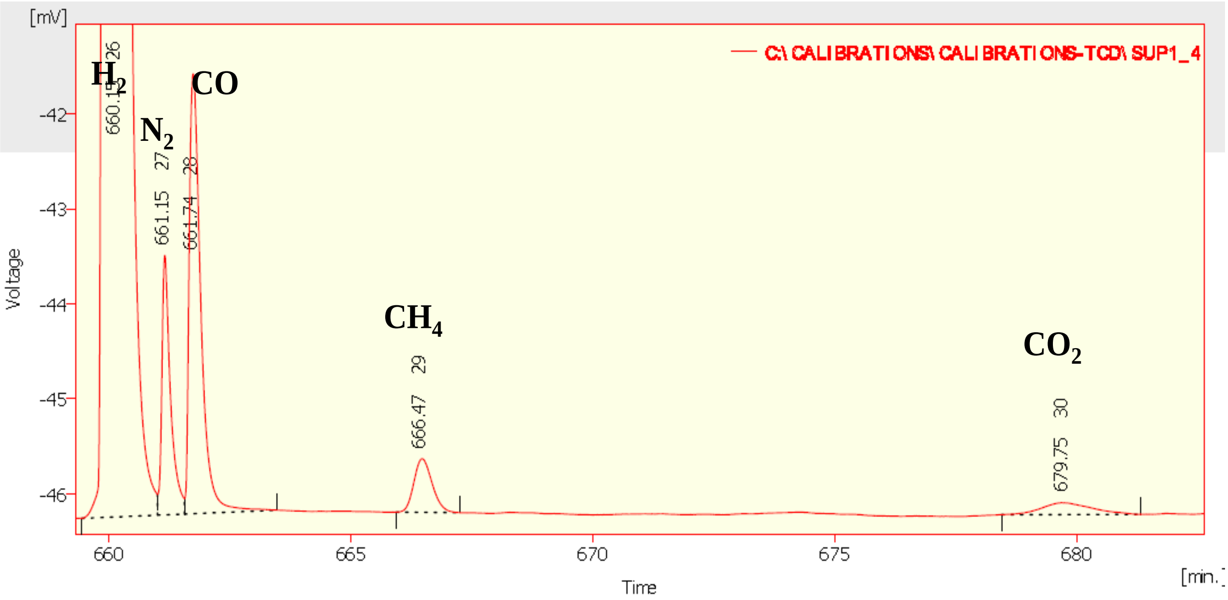

Figure 3.8 A trace for the FTS products as recorded by the TCD GC.

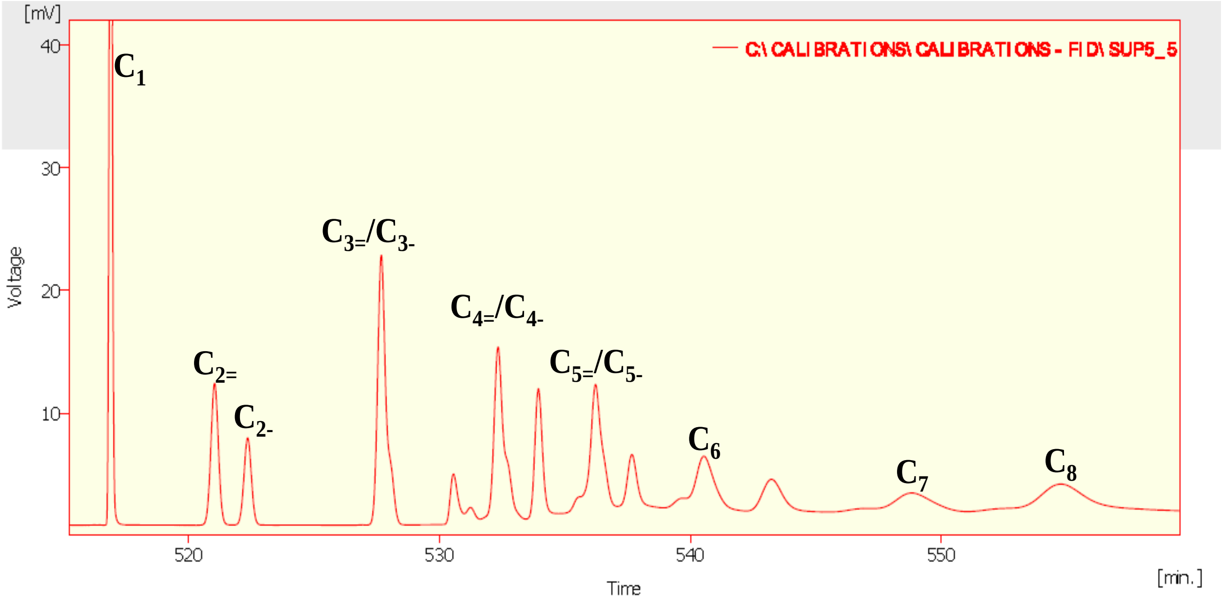

Figure 3.9 A trace for the FTS products as recorded by the FID GC.

3.3.1.5 Mass balance calculations

The calculations used in this work are similar to those reported by Mokoena,[6] Phadi,[7] Price[8] and Hexana.[9] The mass balance was performed on carbon and oxygen. Mass balance results that were in the range 100 ± 5% were accepted as adequate. The time recorded at the end of the mass balance period was used to calculate the rates of the reaction (i.e. FTS, WGS, CO conversion, CO_2 formation)

The outlet flow rate was measured daily using a soap flow meter at ambient pressure and temperature. The reactor feed inlet flow rate was monitored using N_2 gas contained in the syngas cylinder. The equation used to calculate the feed flow rate is given by:

$$F_{in} = \left(\frac{X_{N2,in}}{X_{N2,out}} \right) x\ F_{out} \qquad (3.1)$$

where F_{in} is the total flow rate in mols/s, $X_{N2,in}$ and $X_{N2,out}$ are mole fractions of nitrogen in the synthesis gas and the reactor exit streams in that order. F_{out} is the total reactor exit stream in mol/s.

The percentage of CO conversion was determined as follows:

$$\text{CO conversion (\%)} = \left\{ \frac{CO_{in} - CO_{out} X \left[\frac{N_{2out}}{N_{2in}} \right]}{CO_{in}} \right\} x\ 100\% \qquad (3.2)$$

where CO_{in} and N_{2in} are the peak areas for CO and N_2, respectively, obtained from the calibration done using syn gas. CO_{out} and N_{2out} are the CO and N_2 peak areas obtained from the TCD during the FT reaction.

The product selectivity for hydrocarbons, S_i, was calculated for component x_i as follows:

$$S_i = \left[\frac{\text{mass of component } x_i}{\sum x_i} \right] x\ 100\% \qquad (3.3)$$

The olefin to paraffin ratio (x_2) was calculated using C_2H_4 and C_2H_6 peak areas as shown:

$$\text{Olefin to paraffin ratio } x_2 = \frac{\text{mass of olefin } x_2}{\text{mass of total hydrocarbon } x_2} \qquad (3.4)$$

The rate of CO consumption was determined from the formula:

$$r_{\mathrm{CO}} = \frac{n_{in}}{M} \times f \qquad (3.5)$$

where n_{in} is the molar flow rate of CO entering the reactor, *f* is the CO fractional conversion, and M is the mass of Fe in the catalyst.

The rate of the water gas shift reaction (CO_2 formation) was calculated as follows:

$$r_{\mathrm{CO2}} = \frac{n_{\mathrm{CO}_2}}{M} \qquad (3.6)$$

where n_{CO2} is the molar flow rate of the CO_2 produced, and M is the mass of Fe in the catalyst.

The overall CO consumption rate (r_{CO}), FTS reaction rate (r_{FTS}), CO_2 formation rate (r_{CO2}), and the water gas shift reaction rate (r_{WGS}) in the FTS system can be correlated as follows:

$$r_{\mathrm{WGS}} = r_{CO_2} \qquad (3.7)$$

$$r_{\mathrm{FTS}} = r_{\mathrm{CO}} - r_{CO_2} \qquad (3.8)$$

3.4 References

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