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The Effect of CO₂ on the Activation of a Precipitated Iron Fischer-Tropsch Catalyst

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To Ken, with all my love.

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Abstract

The effect of CO₂ on the activation of a precipitated iron catalyst by hydrogen and carbon monoxide was investigated. The iron-based catalyst was precipitated from a mixture of iron nitrate and copper nitrate then bound by the addition of potassium waterglass to achieve a final catalyst precursor composition of 3.8K₂O/4.8Cu/26.9SiO₂/100Fe. The activation procedures used four different gas compositions: 5%H₂/Ar, 0.15%CO₂/4.7%H₂/Ar, 4.8%CO/He and 0.15%CO₂/4.8%CO/He.

The catalyst was characterised by temperature-programmed reduction (TPR) of the catalyst precursor and BET surface area, transmission electron spectroscopy (TEM), Mössbauer spectroscopy (MS) and Fischer-Tropsch synthesis after isothermal reduction (16 hours at 220°C for H₂ reductions and 300°C for CO activations).

The greatest influence was seen in the temperature-programmed reduction. The addition of CO₂ to the reduction gas had a negative influence on the H₂ reductions and surprisingly, a positive influence on the CO activation. It is postulated that the latter could be due to the retarding of carbon formation thereby allowing further reduction of iron species.

The conditions chosen for the isothermal reductions viz. 16 hours at 220°C for H₂ reduction and 16 hours at 300°C for CO activation did not show any differences with respect to the catalyst characteristics when CO₂ was present during reduction. There were however, major differences in the catalyst characteristics after the H₂ reduction and CO activation. The CO-activated catalyst sintered more and had a high degree of reduction with the major phase being χ -carbide. The H₂-reductions would appear not to have reduced the catalyst at all, although some sintering did occur.

The reductions prior to synthesis were performed in a higher flow rate than those before catalyst characterisation. The H₂-reduced catalyst initially had a lower activity when CO₂ had been present in the synthesis gas. When CO₂ was not present, the catalyst behaviour was stable. With CO₂ in the reduction gas, the activity of the catalyst increased with time on stream. There was little difference in the performance during the Fischer-Tropsch

synthesis of the catalyst activated in CO and that of the catalyst activated in CO₂-containing CO.

Trends seen between the catalysts activated in H₂ and CO were a lower activity for the latter with a higher methane selectivity, higher water gas shift activity (based on CO₂ selectivity) and a higher acid value.

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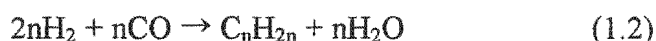
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Chapter 1 - Introduction

Fischer-Tropsch (F-T) synthesis is the hydrogenation of carbon monoxide to form longer chain hydrocarbons such as paraffins and olefins (Storch *et al.* 1951). The Fischer-Tropsch reaction can be utilised to transform difficult-to-transform feedstocks (for example, coal, natural gas and biomass) into liquid hydrocarbons. The reaction can be written as follows:

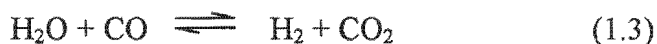


The reaction is highly exothermic with $\Delta H_{R(227^\circ\text{C})} = -167.4 \text{ kJ/mol}$ per unit carbon formation (Jager 1998, Frohning 1980).

The most commonly used catalysts for the Fischer-Tropsch synthesis are based on cobalt and iron (Schulz *et al.*, 1994). Nickel and ruthenium do show Fischer-Tropsch activity but the former tends to produce only methane and the latter is expensive and not readily available (Dry 1990).

The Fischer-Tropsch synthesis can be viewed as a polymerisation reaction, which takes place at the surface of the catalyst. The monomers for this polymerisation reaction are made in-situ from the reagents, carbon monoxide and hydrogen. Therefore this reaction has been named a non-trivial surface polymerisation (Schulz *et al.* 1988).

For the formation of the monomers in this reaction the C-O bond in carbon monoxide must be cleaved. This leads to surface oxygen species, which can be removed with H_2 yielding water as a side product or with CO , yielding carbon dioxide as a side-product. Carbon dioxide can also be formed in a side reaction under Fischer-Tropsch conditions via the water gas shift reaction:



This reaction is also exothermic with $\Delta H_{R(227^\circ\text{C})} = -39.8 \text{ kJ/mol}$ (Frohning 1980).

1.1. Historical Perspective

The main development of Fischer-Tropsch process occurred in the first half of the century. The thrust of the development took place in Germany where it was first commercialised. Due to the oil shortage during the 2nd World War, the production of synthetic oil was very important to Germany's war effort. Two routes were followed to produce this synthetic oil: Fischer-Tropsch synthesis and coal hydrogenation. The latter contributed significantly more to the war effort.

The hydrogenation of carbon monoxide was first observed by Sabatier and Senderens in 1902 when they noted that a reduced nickel catalyst produced methane from a mixture of carbon monoxide and hydrogen (Storch *et al.* 1951). The first mention of longer chain hydrocarbons was in a patent filed by BASF in 1913 that claimed the conversion of CO and H₂ to liquid products at high temperature and pressure. The catalyst used was cobalt-based.

In 1923, Frans Fischer and Hans Tropsch synthesised mainly oxygenates over alkalised iron turnings at temperatures between 400 and 450°C and pressures of 101 – 152 bar (Storch *et al.* 1951). They found that the product spectrum could be shifted to olefins and paraffins with very few oxygenates by lowering the pressure to 7.1 bar. Unfortunately, the activity of the catalyst decreased sharply at the lower pressures. An iron and zinc oxide catalyst, reported in 1925, was the first catalyst to produce Fischer-Tropsch products at atmospheric pressure and a temperature of 370°C. Mixtures of cobalt and chrome oxides were however found to be more active. Finely divided cobalt was also found to be more effective than iron, producing liquid products at temperatures 20°C lower than the iron.

A breakthrough in the preparation of Fischer-Tropsch catalyst came in 1931, when a nickel/thoria catalyst was made using kieselguhr as a support (Storch *et al.* 1951). The catalyst had a higher activity and was also stable. By 1934, a pilot scale plant had been commissioned and when nickel was found to not be commercially viable, the nickel catalyst was replaced with cobalt/thoria on kieselguhr. The standard commercial catalyst between 1937 and 1944 was 100Co/15ThO₂/8MgO/200 Kieselguhr S120. There were three

manufacturing plants i.e. Ruhr, Brabag and Wintershall and they were an important part of the German war effort until extensive bombing in 1944 (Storch *et al.* 1951).

The development of the iron catalyst was continued although it was not ready for commercialisation when the war broke out. The advantage of the iron catalyst would have been availability of the metal and a greater flexibility in the product spectrum. Research into the iron catalyst intensified as the cobalt shortage became more critical. It was found in 1937 that by increasing the pressure, the activity and lifetime of the iron catalyst increased significantly. The development of the catalyst pre-treatment also played an important role in making the catalyst economically viable (Storch *et al.* 1951).

The U.S. Bureau of Mines and American oil industry also started a programme on iron-based Fischer-Tropsch catalysts in 1943. This led to the establishment of a fluidised -bed operation in Brownsville, Texas in 1948 based on natural gas. It was eventually closed down in 1953 due to economic reasons (Sie *et al.* 1991).

The major post-war developer of Fischer-Tropsch synthesis has been South Africa. The commercial operation in Sasolburg, South Africa was based on two types of iron catalyst. The lower temperature fixed bed operation on a potassium and copper promoted precipitated iron catalyst and the higher temperature fluidised bed operation on a fused iron catalyst (Dry 1981). These plants came on line in 1955 and the higher temperature operation expanded to Secunda (Sasol 2 and 3) in the early 1980s (Dry 1990). A more recent commercial application is the high temperature Mossgas operation, also in South Africa, which came on line in 1991 (van Rensburg 1990).

The most recent commercial operation based on cobalt is Shell's fixed bed operation in Malaysia, which came on line in 1993 (Sie *et al.* 1991, Adesina 1996).

Both the Mossgas process and Shell's Malaysian process are based on natural gas and the current Sasol operations are based on coal as feedstock. All other Fischer-Tropsch processes start from coal as their feedstock.

1.2. Economic Significance

The discovery of huge oil deposits in the Middle East in the early sixties moved the focus away from coal based processes to crude oil. There was very little further development in the Fischer - Tropsch technology until the oil crises, the first in the early 1970s and the second in the early 1980s. This was when Sasol 2 and 3 were erected and Mobil's methanol-to-gasoline (MTG) came on line in New Zealand (Adesina 1996).

Although there is no longer a crisis in oil supply, considerable focus has recently been given to the Fischer-Tropsch process. Advances in process technology for both syngas production and utilisation have made the "gas-to-liquids" (GTL) technology more feasible. Capital costs of F-T projects have been halved through factors such as lower cost synthesis gas production and improved reactor technologies.

The most expensive part of the process is the production of synthesis gas, with coal as a feedstock being more expensive than natural gas. Even with natural gas, a recent study has shown the process to be feasible only if the natural gas has a price of 0.5\$/Mscf and the oil price is between \$14 and \$16/barrel (Gradassi 1998). Natural gas also has a demand as a fuel, particularly in developed countries. This makes it too expensive as a feedstock. However, in remote areas, where natural gas has a low value due to the high transportation costs or even a negative cost, liquid fuels from natural gas has become an interesting option. Another reason why there is renewed interest in Fischer-Tropsch technology is that there is also a greater environmental pressure to utilise the natural gas currently being flared. These gas reserves are often associated with oil fields where they are flaring the gas.

The advantage of Fischer-Tropsch will therefore have to lie in areas where the natural gas has a negative value, where there are environmental considerations or where the natural gas is situated in remote areas where there is no demand or where piping it does not make economic sense. The gas therefore has a negative value and a negative impact on the environment.

Not only can Fischer-Tropsch (F-T) synthesis be a more environmentally positive process, the F-T products can even be used to upgrade fuels produced from crude oil as they are of a better quality with respect to aromatic content, sulphur and nitrogen compounds. The product can achieve a premium due to these environmental advantages.

Two major improvements in reactor technology, which attribute to the reduction in the process costs, have been the movement from a fixed bed reactor to a slurry bed reactor and, in Sasol's Secunda operation, the shift from the circulating fluidised bed to the fixed fluidised bed (Jager 1998). Both the fixed fluidised bed and the slurry reactor are a more simple design and are therefore cheaper to construct. They also have a higher production capacity per reactor.

The advantage of the slurry bed over the fixed bed is that it facilitates easier heat removal as the liquid medium acts as a heat sink for the reaction. The catalyst particles are smaller which improves the effectiveness of the catalyst as there are no diffusion limitations. The slurry reactor also allows for catalyst addition on-line. There are advantages to the fixed bed such as ease of separation of the product from the catalyst but if this can be overcome, then the slurry bed is a better option.

Comparing the circulating fluidised bed with the fixed fluidised bed, the hydrodynamics are less severe, it is easier to operate and the cost of maintenance is lower. One of the reasons for this is the catalyst is not being circulated and therefore you have no abrasion of the standpipe.

1.3. Fischer -Tropsch Catalysts

Most transition metals have some degree of hydrogenating capability and of these metals, ruthenium, iron, cobalt and nickel are generally regarded as having Fischer-Tropsch activity (Adesina 1996). The order of hydrogenating capability decreases as you move left across the periodic table, that is nickel is more hydrogenating than cobalt and cobalt is more hydrogenating than iron (Dry 1981). In fact, nickel is so hydrogenating that it is not really suitable as a FT catalyst. It tends to form too much methane. Ruthenium is too expensive and the supply is very limited. The two most commonly used catalysts are therefore based on iron and cobalt (Dry 1981).

Cobalt as a catalyst has the advantage of being very resistant to reoxidation. Although Vannice (Vannice 1975) states that the intrinsic activity of Fe is greater than that of Co, the catalyst will not deactivate as fast as the Fe catalyst. It also has no water gas shift activity, which means that the usage ratio of the catalyst (the ratio of H_2 converted to CO converted) will be a lot closer to the ratio of the feed composition. There will not be any conversion of CO to CO_2 (greenhouse effect). Unfortunately, the catalyst is not very sensitive to promoters and the product spectrum is therefore not very flexible. The metal itself is very expensive.

By comparison, iron is cheap, readily available and allows for more flexibility as it can be promoted to change product selectivity and to shift the Schultz-Flory distribution (Dry 1981). It can also be operated over a broader temperature range. The disadvantage of the iron catalyst is that it deactivates more quickly but because of the cost, this can be addressed by frequent catalyst replacement. Iron catalysts do catalyse the water gas shift reaction (WGS). This may be of aid to the catalyst as it lowers the partial pressure of water and decreases the rate of reoxidation. The water gas shift reaction allows the catalyst to adjust the H_2/CO ratio. Iron can therefore be more readily used with lower H_2/CO ratios. Dry (Dry 1981) states WGS "is important since it means that the CO_2 can also be

hydrogenated to oils (reverse shift followed by F-T) and that feed gases with H₂/CO ratios below 2 can be utilised".

1.4. Activation of Iron Catalysts

1.4.1. Thermodynamics

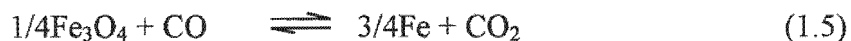
The most common methods for preparing iron Fischer-Tropsch catalysts are precipitation, impregnation onto a support and fusion. The catalyst must then be activated i.e. reduced to the zero valence state by a suitable reducing agent. Two common reducing agents are hydrogen and carbon monoxide. Two stages can be seen in the reduction of iron - a fast reduction from Fe₂O₃ to Fe₃O₄ followed by a slow reduction of the latter to metallic iron, or in the case where CO is present, to iron carbide (Bukur *et al.* 1995(a)).

Thermodynamically, the reduction of iron by CO is more favourable (Storch *et al.* 1951). For the reduction of magnetite with hydrogen:



The equilibrium concentration of $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ is 0.014 at 227°C (calculated with data from Chase 1985, Barin 1989 and Knacke *et al.* 1991). This means that if the molar ratio of water to hydrogen is larger than 0.014, iron oxide (Fe₃O₄) cannot be reduced to metallic iron. Furthermore, if under reaction conditions the molar ratio of water to hydrogen is larger than 0.014, metallic iron will reoxidise.

For the reduction of magnetite with carbon monoxide:



The equilibrium concentration of $p_{\text{CO}_2}/p_{\text{CO}}$ is 1.92 at 227°C (calculated with data from Barin 1989, 1993 and Knacke *et al.* 1991). This means that if the molar ratio of carbon dioxide to carbon monoxide is larger than 1.92, iron oxide (Fe₃O₄) cannot be reduced to

metallic iron. Comparing the values for the reduction of magnetite with hydrogen and with carbon monoxide, it can be seen that the reduction with carbon monoxide yields a higher utilisation of the reducing agent in a single-pass reduction step.

1.4.2. Kinetics

Thermodynamic data indicates that iron will be more easily reoxidised by H_2O than by CO_2 . It is generally seen that the formation of a new solid phase at the expense of another solid phase proceeds only at the interface between both phases (Boudart 1968). As such an interface must exist, the first step in the reaction is the formation of this interface. Once these reaction centres are formed, they tend to act as a “catalyst” to spread the reaction.

The shrinking core model is a general mechanism proposed for describing the reduction of metal oxide particles where the reaction proceeds at the solid reactant/solid product interface. This model, therefore, visualises a shrinking core of unconverted oxide surrounded by a growing shell of solid reaction product (see Figure 1-1). The rate of reaction can be determined by the rate of chemical reaction at the interface or it can be controlled by the rate the diffusion of the reducing gas to the phase boundary.

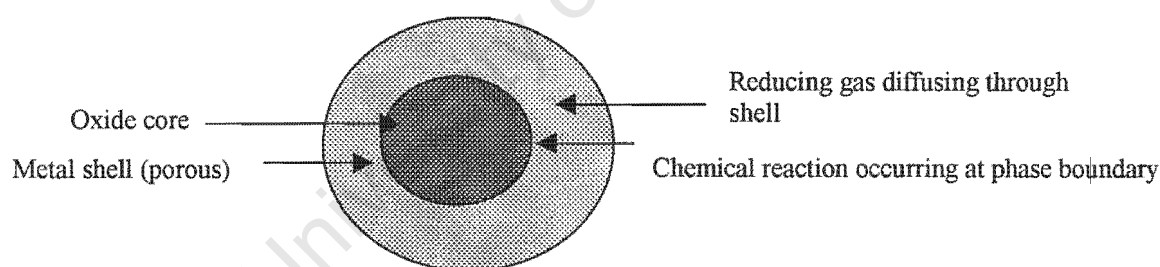


Figure 1-1: Schematic representation of the shrinking core model

In order to describe the kinetics of a reaction involving a solid, we need to first determine the rate at which the original reaction centres are formed. This is known as the rate of nucleation. The second aspect would be determining the rate at which the interface advances through the unconverted solid i.e. the growth of the new phase. The overall rate is

often seen to be an S-shaped curve where the interface is created, it grows and then shrinks as the reaction proceeds (Boudart 1968).

Generally, the rate of reduction of a solid by a gas to form another solid can be seen as a function of temperature and two concentration dependent terms (Wimmers *et al.* 1986) i.e.:

$$r = d\alpha/dt = k_1(T)f(\alpha)f'(p_{(\text{reactant gas})};p_{(\text{product gas})}) \quad (1.6)$$

where α is the degree of reduction.

A number of such rate equations representing various models proposed in literature (Harrison 1969, Šesták *et al.* 1971, Šesták *et al.* 1973) can be seen in Table 1-1.

Table 1-1: Functions of Different Reduction Models

Reduction Model	$f(\alpha)$
Three-dimensional nucleation according to Avrami-Erofeev	$(1-\alpha)(-\ln(1-\alpha))^{2/3}$
Two-dimensional nucleation according to Avrami-Erofeev	$(1-\alpha)(-2\ln(1-\alpha))^{1/2}$
Two-dimensional phase boundary ^{a,b.}	$2(1-\alpha)^{1/2}$
Three-dimensional phase boundary ^{a,b.}	$3(1-\alpha)^{1/3}$
Three-dimensional diffusion according to Jander ^{a,b.}	$3/2(1-\alpha)^{1/3}((1-\alpha)^{-1/3}-1)^{-1}$
Unimolecular decay	$1-\alpha$

^{a.} Shrinking core model

^{b.} Chemical reaction rate determining

^{c.} Diffusion rate determining

Wimmers (Wimmers *et al.* 1986) showed that the best model to fit the reduction of small Fe_2O_3 particles (diameter: $0.3\mu\text{m}$) was the three-dimensional nucleation model of Avrami-Erofeev. They did this by calculating theoretical TPR curves from the various proposed models and then finding the best fit to experimental data.

It has been found, however, that with increasing particle size or reduction temperature, the rate determining step changes. The rate determining step in small particles tends to be either the diffusion of the gas molecule generated over the surface (due to high curvature and therefore surface energy) (Themelis and Gauvin 1962) or nucleation. As the particle size increases, this shifts to topochemical effects i.e. the reaction at the phase boundary or the rate diffusion through the product layer (Themelis and Gauvin 1963, Turkogdan and Vinters 1972). A good correlation with kinetics based on a mixed-control mechanism

where both the reaction rate at the phase boundary and the rate of diffusion of the gaseous reactants and products through the metal shell are taken into account, has been described (Barański *et al.* 1972).

Another model proposed to explain deviations from the simple shrinking core mechanism, is that of a crackling core. Park and Levenspiel (Park and Levenspiel 1975) initially view the particle as non-porous. This non-porous solid then begins to fissure and crackle as it begins to react with the gaseous component. This fissuring and crackling moves progressively inwards to form a grainy material as the reaction proceeds further. This allows the gaseous reactant to move inward without any diffusional constraint. It is then able to react with the grainy material according to the shrinking core model.

1.4.3. Parameters affecting the Activation

The earlier development of Fischer-Tropsch was reviewed by Storch, Golumbic and Anderson in 1951 (Storch *et al.* 1951). As early as 1937, The Kaiser Willhelm Institut für Kohlenforschung reported that reduction of the precipitated iron catalyst using hydrogen at 360°C was unsuccessful in activating the catalyst for medium pressure synthesis. They then concentrated their efforts on the pretreatment of iron catalysts, focussing on CO and CO/H₂ mixtures. The aim of the pretreatment was to achieve the best balance between the highest possible activity while maintaining the desired selectivity and stability during the Fischer-Tropsch synthesis.

1.4.3.1 Effect of Promoters

Copper is well known as a promoter for the reduction of iron catalysts. Wielers (Wielers *et al.* 1990) showed that copper facilitates the reduction of ferric ions to zero-valent iron. They suggested that hydrogen migration from the reduced copper atoms to the ferric ions could be responsible for the reducibility of these ferric ions. O'Brien (O'Brien *et al.* 1997) has shown that promotion with copper lowered the reduction temperature and increased the Fischer-Tropsch activity regardless of whether the catalyst was pretreated in hydrogen,

syngas or carbon monoxide. The evidence was thought to support the fact that the reduction of iron proceeds via a nucleation mechanism. Copper (II) oxide reduces at ~150 -200°C lower than iron oxide (O' Brien *et al.* 1997) and can therefore act as a nucleation site to accelerate the reduction of the iron oxide. The reduction was also accelerated with increasing levels of copper. It would seem that a reduction promoter such as copper creates the small islands, which catalyse the reduction process. In the case of hydrogen this may be aided by spillover effects of atomic hydrogen onto the metal oxide. Carbon monoxide is however not able to spill over, but the metallic centres can be an aid in creating the starting point of reduction.

1.4.3.2 Effect of Pressure

In 1940, Pichler (Pichler and Merkel, 1949) reported the results of such pretreatment studies using CO or CO/H₂ mixtures. He concluded that activation at elevated pressures was undesirable. Catalyst pretreated at atmospheric or even sub-atmospheric pressures yielded a catalyst with a high activity. He ascribed this to the fact that lower pressures favour carbide formation over free carbon deposition (Table 1-2). With increasing pressure the amount of free carbon increases dramatically, whereas the amount of carbon incorporated as carbide actually decreases.

Table 1-2: Effect of pressure on carbide and free carbon formation for an alkalized iron catalyst after 25 hour pretreatment at 325°C (Storch *et al.* 1951)

Pressure (bar)	Grams carbon per 10g Fe	
	Free Carbon	Carbide
0.1	2.21	0.45
1.0	4.23	0.34
15.2	Not determined	0.10

1.4.3.3 Effect of Temperature

The study by Pichler (Pichler and Merckel 1949) also looked at the effect of activation temperature on the activity of the catalyst. The catalyst became more active with increasing activation temperature with a maximum activity and stability being reached at 315 - 325°C. Catalysts activated at temperatures lower than 300°C showed more pronounced deactivation with time on stream. Free carbon showed a sharp increase above 325°C. Bukur (Bukur *et al.* 1989) obtained similar trends with respect to temperature and pressure as those observed by Pichler, although not all his results could be explained. The study by Bukur also included reducing the precipitated iron catalyst at various temperatures using H₂. In contrast to the CO and syngas activations, the higher temperature reduction produced a less active catalyst. This can be attributed to the higher partial pressure of water at higher temperatures, which not only inhibits the reduction of the iron catalyst, but also enhances sintering. This will lead to a loss of active metal surface area. Dry (Dry, 1981) states that low temperature (180 - 220°C) and high space velocities are required to avoid this loss of surface area after reduction.

1.4.3.4 Effect of gas composition

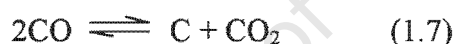
1.4.3.4.1 Stability

Catalysts activated in H₂ tended to show a higher stability than those activated in CO or syngas but this at the expense of activity. A possible explanation for this was put forward by Bukur (Bukur *et al.* 1995(b)). He suggested that the concentration of hydrogen on the surface of the catalyst during F-T synthesis plays an important role in stabilising the catalyst. If the rate of hydrogenation of the surface carbon species is equal to the rate of dissociation of the CO on the surface, then there will be very little chance of carbon deposition on the surface.

This may agree with the competition model proposed by Niemantsvedriet (Niemantsvedriet and van der Kraan 1980, 1981) which states that the carbon species found

on the surface of the catalyst as a result of CO dissociation can be consumed via three competing reactions viz. migration into the metal to form carbides, reaction with hydrogen to form hydrocarbons or conversion to graphitic carbon which will poison the catalyst. If a catalyst is pretreated in CO or syngas and, if carbides are the active phase, then you would expect a more active catalyst with such pretreatment. However, the catalyst would also deactivate more strongly as there is less carbon reacting to form carbides and therefore more carbon available for conversion to graphitic carbon. According to this model, catalysts reduced in hydrogen should show an initial increase in activity as iron is converted to iron carbide, followed by a decline in activity once carbiding of the catalyst is complete (Bukur *et al.* 1995(b)). The CO-activated catalyst was more stable and active than the catalyst activated in CO-rich syngas.

The same research group (Bukur *et al.* 1995(a)) analysed the activation of a standard Ruhrchemie catalyst by CO at 280°C and found that more CO₂ was produced than could be accounted for by both reduction of the iron oxide and the formation of carbides. They concluded that the excess CO₂ was probably due to the formation of carbonaceous deposits on the catalyst via the Boudouard reaction viz.



1.4.3.4.2 Selectivity

Apart from the effect of gas composition on activity and stability as discussed above, it has been found that activation using the different gas compositions also led to differences in selectivity. In ongoing studies by Bukur (Bukur *et al.* 1989, 1995(b)), reduction in H₂ leads to higher methane selectivity and therefore lower C₅₊ selectivity. The catalysts activated in H₂ also tended to have a higher water gas shift selectivity. Later work done by the same group (Bukur *et al.* 1997) shows apparently conflicting results where the methane selectivity of the CO and syngas activated catalysts is initially higher than that of the H₂-activated catalyst. Although no explanation is given for the differences, the earlier work was performed in a fixed bed reactor and the later work in a slurry reactor.

1.4.3.4.3 Phase Composition

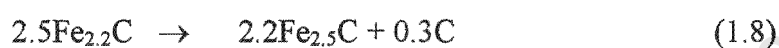
The following phases have been noted in an activated, precipitated iron catalyst:

- a. Metallic iron is often not present in the carbided catalyst i.e. one that has been activated in CO or H₂/CO. This indicates that, if carbides are formed from the zero-valent state of iron, it must be a very fast reaction (the thermodynamics would appear to be the driving force for this). Metallic iron is believed to be active for Fischer-Tropsch as evidenced by the fact that there is an initial activity for H₂-reduced catalysts.
- b. Iron carbide, viz. ϵ' -carbide (Fe_{2.2}C) and χ -carbide (Hägg – Fe_{2.5}C). ϵ' -carbide has a hexagonal structure and is metastable at FT conditions. There is speculation that ϵ' -carbide may be a more active phase than the monoclinic χ -carbide. One of the articles referring to this is a study published in 1998 by Jin and Datye (Jin and Datye 1998) on an active and deactivated catalyst. It was found that the deactivated catalyst contained only χ -carbide, whereas the active catalyst contained both ϵ' -carbide and χ -carbide.
- c. Magnetite is either due to the partial reduction of hematite or the reoxidation of the iron. This was seen in by Bukur (Bukur *et al.* 1995(a)). Samples of catalyst withdrawn from the inlet of a fixed bed reactor consisted only of ϵ' -carbide whereas samples taken further down the reactor (where the gas composition is more oxidising due to reaction products) contained both ϵ' -carbide and magnetite.
Reymond (Reymond *et al.* 1982) among others have speculated that magnetite may be the active phase.
- d. Hematite that has not undergone reduction.

There is, up to now, no general agreement on which phase is the most active phase for the Fischer-Tropsch synthesis. Metallic iron and iron carbide both seem to be active as a catalyst for this reaction.

It would appear that the gas composition during reduction has a large effect on the phases present in the iron catalyst.

Tau (Tau *et al.* 1984) has shown that the addition of a small quantity of H₂ during activation in CO aids the formation of carbides. Bukur (Bukur *et al.* 1995(a), 1995(b)) found that catalysts reduced in hydrogen formed ϵ' -carbide during Fischer-Tropsch synthesis whereas those activated in syngas formed χ -carbide. Similar conclusions can be drawn from in-situ X-ray diffraction (XRD) studies by Jung (Jung and Thomson 1992, 1993). They did, however, show some correlation between particle size and carbide phase formed, with smaller iron particles (16nm) forming ϵ' -carbide and larger particles (30nm) forming χ -carbide at 523K when activated in CO. Higher carburisation temperatures tended to favour χ -carbide, even for prereduced catalysts but this is expected as the ϵ' -carbide is metastable. Deactivation of the catalyst was also related to this conversion viz.:



The resultant formation of this free carbon on the surface not only blocks active sites but is thought to act as nucleation sites for further buildup of inactive carbon.

1.4.3.4.4 Reaction Products

The concentration of the reaction products of a reversible reaction will have an effect on the rate of reaction (le Chatelier's principle). From the thermodynamic data (Section 1.4.1), we would expect very low partial pressures of H₂O to inhibit the rate of reduction of Fe₃O₄ by H₂. This is indeed the case. Wimmers (Wimmers *et al.* 1986) found that the addition of 3% H₂O increased the required reduction temperature of Fe₃O₄ to iron by 75-95°C (depending on heating rate). They also found a shift to greater reduction temperatures with increasing sample sizes in their "dry" runs. They ascribed this to the effect of the product H₂O.

Even more importantly, the reoxidation of the surface of an iron ammonia synthesis catalyst was found to occur at ratios of pH₂O/pH₂ 1000 times smaller than that required to form bulk-phase oxides (Almquist and Black, 1926). This is thought to occur because of the difference in free energy between the crystalline iron and the surface iron atoms.

Very little work has been done on the effect of CO_2 on the rate of reduction or activation of the iron catalyst. One study described in Storch (Storch *et al.* 1951) showed the addition of H_2O effected the rate of reduction of a fused iron catalyst reduced at 550°C . This effect was even more pronounced when CO_2 and CH_4 were also present in the feed gas (Figure 1-2). It seems unlikely that CH_4 would have an effect on the rate of reduction. Figure 1-2 also shows that small impurities of CO can also effect the rate of reduction slightly at 550°C .

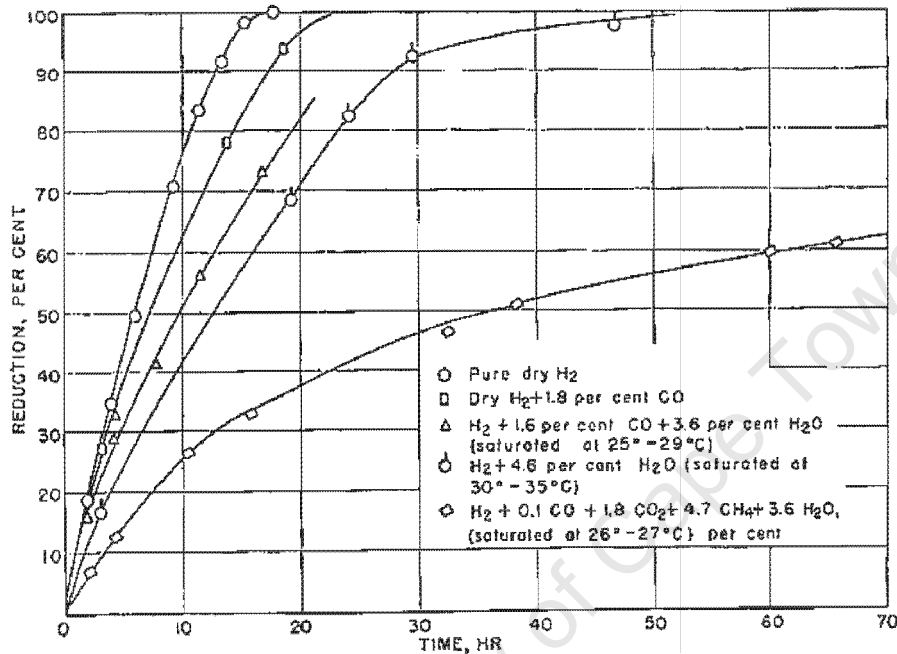


Figure 1-2: Rate of reduction of fused iron catalyst at 550°C (Unpublished work of U.S. Bureau of Mines as published in Storch *et al.* 1951 - p299)

CO_2 is a reaction product in both CO -activated catalysts and those activated in syngas. For those iron Fischer-Tropsch catalysts activated in syngas, the water gas shift reaction viz.



may also play a role in the formation of CO_2 . CO_2 may also be found as an impurity in the H_2 used to reduce commercial catalysts. This seemed to be the reason for studies done by Ruhrchemie on the effect of CO_2 and H_2O on the reduction of an alkali promoted cobalt catalyst in H_2 . Their results are shown in Figure 1-3.

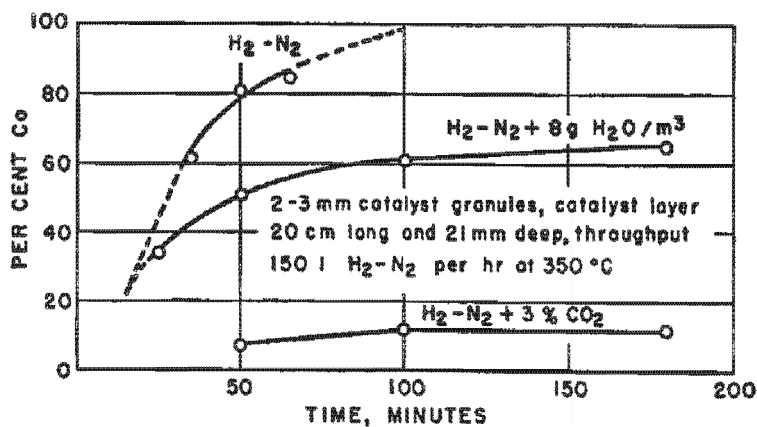


Figure 1-3: Rate of reduction of cobalt catalysts: Effect of CO₂ and H₂O (Storch *et al.* 1951 - p205)

The reoxidation of cobalt by CO₂ is even less thermodynamically likely than the reoxidation of iron. The equilibrium ratio of $p_{\text{CO}_2}/p_{\text{CO}}$ for the Co/CoO system is 1.75×10^4 at 227°C (as compared to 1.92 for the Fe/Fe₃O₄ system). Methane was noted in the product stream during the reduction with 3% CO₂. There was also less CO₂ and it was thought that the CO₂ was probably hydrogenated according to the following reaction:



The product of the reaction is two moles of water per mole of CO₂ reacted.

The Ruhrchemie commercial, cobalt-based operation included a synthesis reactor, which converted the CO₂ in the effluent from the reduction reactor (2g/m³) to methane. The gas was then dried and recycled to the reduction unit. This gives an indication of how important the removal of CO₂ was to the commercial reduction of the cobalt catalyst.

From the work of Almquist (Almquist and Black 1926), it has been shown that the ratio of $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ required to oxidise the surface of an iron catalyst is a lot lower than that

calculated thermodynamically. Although CO_2 is thermodynamically less likely to reoxidise metallic iron, it has also been shown that CO_2 has an effect on the reduction of both iron and cobalt by H_2 (Storch *et al.* 1951).

The most probable mechanism for the lowering of the reduction rate in the above studies is the reoxidation of the newly created Fischer-Tropsch sites by the product water formed through the hydrogenation of the CO_2 or the effect of this H_2O on the kinetics of the reduction. If this were the case, then one would not expect to see a large negative effect of small quantities of CO_2 on the CO activation. The surface of the iron catalyst is very different to the bulk composition, so reoxidation may occur when it was not thermodynamically expected. The aim of this study is to see what the effect of CO_2 will be on the reduction of a precipitated iron catalyst by both CO and H_2 .

Chapter 2 - Experimental

2.1 Catalyst Precursor Preparation

The catalysts prepared were based on the Ruhrchemie catalyst viz.

100Fe/5Cu/5K₂O/25SiO₂. The preparation procedure is described in Frohning (Frohning *et al.* 1977).

An attempt was made to dissolve the iron in concentrated nitric acid (55% by volume) as described in the above reference but the reaction proved difficult to control due to the exothermic nature of the dissolution. For this reason, a solution of iron (III) nitrate and copper (II) nitrate was prepared by weighing out 578g of Fe(NO₃)₃·9H₂O (AR grade - Merck) and 15g of Cu(NO₃)₂·3H₂O (AR grade - Merck) and dissolving the iron in sufficient distilled water to make a two-litre solution. This gave a final solution of 40g Fe/l and 2g Cu/l. The sodium carbonate (Na₂CO₃) solution was made such as to allow a stoichiometric precipitation with the Fe/Cu solution. This was achieved by dissolving 235g of Na₂CO₃ (99.5% - Promark Chemicals) in enough distilled water to make two litres of solution. The final solution was therefore 117.5g Na₂CO₃/l (as opposed to the 100g/l required by Frohning).

Both solutions were heated to 85°C and then the Fe/Cu nitrate solution was added to the Na₂CO₃ solution as rapidly as possible. Constant stirring was maintained throughout the precipitation. The final pH requirement was between 7 and 8. After completing the precipitation, the solution was allowed to age for 15 minutes. The slurry was then filtered and the remaining solids were washed with heated, distilled water in order to remove the remaining sodium nitrate (NaNO₃). Washing was continued until the conductivity of the filtrate was less than 120μS. The precipitate was dried for 20 minutes by passing high-pressure air (3 bar) through the filter.

A sample of the precipitate was analysed for Fe content (see 2.2.1). This allowed for accurate addition of the potassium waterglass.

The potassium waterglass used was Silchem K2250 (Silicate and Chemical Industries). This solution contained 20.9% SiO_2 by mass and the $\text{SiO}_2:\text{K}_2\text{O}$ ratio was 2.5:1. This meant that in order to achieve the correct ratio of $\text{SiO}_2:\text{Fe}$, an excess of K_2O is added. Concentrated nitric acid was added to the solution to form potassium nitrate (KNO_3) and this facilitated the removal of the excess potassium.

The Fe/Cu precipitate was reslurried in distilled water. This was done at room temperature. The calculated amount of potassium waterglass silica was then added to the slurry. A stoichiometric amount of nitric acid (calculated on the amount of excess potassium) was added and the slurry filtered to remove the filtrate.

The resulting catalyst precursor was dried in an oven at 120°C and atmospheric pressure. The dried precursor was crushed and sieved into two fractions viz. 38 - $250\mu\text{m}$ and 250 - $500\mu\text{m}$.

2.2 Catalyst Characterisation

2.2.1 Iron content determination

The sample (precipitate or catalyst sample) was dissolved in concentrated hydrochloric acid (HCl) after which a slight excess of stannous chloride (SnCl_2) was added to reduce the Fe^{3+} to Fe^{2+} . Excess stannous chloride was removed as a precipitate by the addition of mercury chloride (HgCl_2). The ferrous ion was then titrated against potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) using sodium diphenylamine sulphonate as indicator.

Approximately 5.0g of catalyst sample (accurately weighed out) was dissolved in 40 ml of a 6.5N HCl solution (prepared from GR Grade for Analysis - Merck). The solution was boiled under reflux for one hour to dissolve the sample. This solution was made up to 500ml in a volumetric flask and filtered. 25ml of this solution was pipetted into a 500ml Erlenmeyer flask. 25ml of a HCl (10N) (CP - CJ Chemicals): deionised water (1:1) solution

was added to the flask and the solution was brought to the boil. Stannous chloride (AR min 98% - Glassworld) was added dropwise until the solution just went clear. A further two drops were then added. The solution was cooled under CO₂. A 10ml volume of HgCl₂ (AR min 99.9% - Glassworld) was added to the solution and the solution was allowed to stand for a further three minutes. 50ml of a phosphoric acid-sulphuric acid mixture (prepared by mixing 500ml of 98% H₂SO₄ (AR min 98% - Merck) and 400ml of 85% H₃PO₄ (A.C.S. Grade - Aldrich) and made up to 5000ml) was then added and the solution was made up to approximately 300ml. Two drops of diphenylamine sulphonate indicator (prepared from sodium diphenylamine sulphonate (CP - Unilab)) was added and the solution titrated against a 0.05N K₂Cr₂O₇ solution ((prepared from K₂Cr₂O₇ (AR min 99.5% - Glassworld))) until a light red colour.

2.2.2 Atomic Absorption Spectrophotometry

In flame atomic absorption (AA) spectrophotometry, atomisation of the sample is carried out in the flame. The vapour from the sample is then interposed into the light path of a spectrophotometer. The location of the absorption lines can identify the elemental components in a sample and the absorbance of a line is generally proportional to the concentration of the absorbing species. The instrument is usually calibrated with a series of known concentrations of the element of interest. For a further description of atomic absorption spectrophotometry, *Fundamentals of Analytical Chemistry* (Skoog and West 1982) discusses the subject in more detail.

Atomic absorption spectrophotometry was used to quantify the Na, K and Cu in the catalyst samples. The instrument used was a Varian SpectraAA-10. For the sodium analysis a wavelength of 589nm was used and a slit width of 0.5nm. The potassium analysis used a wavelength of 766.5nm and a slit width of 1.0nm. The copper analysis was performed using a wavelength of 324.8nm and a slit width of 0.5nm.

The analyses were performed on the solution prepared in the first step of Chapter 2.2.1. The solution was filtered to remove the SiO₂ which could cause blockages within the

instrument. The sample is then diluted to contain 0.18g Fe and 45cm³ of 0.5N HCl (based on the known concentration of iron in the sample).

The absorption is measured with the AA by using a standard solution containing the same concentration of Fe and HCl and a known amount of the element to be analysed. The blank also contained these concentrations of Fe and HCl.

The potassium analyses used a blank and standard that also contained CsCl (AR min 99.5% - SAARChem). This was to improve the sensitivity of the reading. This was prepared by diluting 10 cm³ of a 1000mg/dm³ CsCl solution to 500 cm³. The preparation of the standard solution (4.5mg K/dm³) involved first dissolving 5.1g of Fe₂O₃ in 72.0cm³ of 6.5N HCl. The blank solution for the sodium analyses was prepared by dissolving approximately 3.6g of iron wire in 72.0ml 6.5N HCl and 30ml of deionised water. Water was used as the blank for copper.

2.2.3 Determination of silica

The silica in the catalyst samples was determined by a gravimetric method. The sample was dissolved in HCl, the bulk of the water carefully evaporated and the sample dried at 110°C for one hour at atmospheric pressure. The soluble salts are further dissolved in dilute HCl and the insoluble fraction filtered off using ashless filter paper. The insoluble fraction is then recovered by heating the sample to 940°C. This fraction is weighed and wet with concentrated sulphuric acid (H₂SO₄). Concentrated hydrofluoric acid (HF) is then added to the wet sample to form SiF₄. This is volatile and will vaporise as the solution is heated. The remaining insoluble fraction is heated to 940°C and then weighed. The difference in mass between the insoluble fraction before the addition of HF and after the addition of HF is the mass of the silica in the sample.

The initial dissolution was performed using approximately 1.0g of catalyst precursor, accurately weighed and wet with 20ml of deionised water. A 50ml volume of HCl (10N) was added to the sample and the sample was heated until the soluble fraction was dissolved. The filtration used a Whatman 42 filter paper due to the fineness of the silica.

The fraction remaining on the filter paper was initially washed using a 5% HCl solution and then was washed using deionised water. The sample was ashed at 940°C for approximately 90 minutes. The sample obtained after after ashing was wet with a 1:1 H₂SO₄:deionised water (by volume) solution and then 15ml of 48% HF (GR - Merck) was added. The volatile fraction was vaporised by heating and the remaining fraction was again placed in an oven for 90 minutes at 940°C at atmospheric pressure.

2.2.4 Surface area determination

The surface area (SA) and total pore volume (TPV) are important physical properties of the catalyst. This property is measured by using the physical adsorption of gases on solid surfaces due to van der Waals-London forces. For multilayer adsorption, the BET equation developed by Brunauer, Emmet and Teller is used to calculate the surface area of the solid and the pore volume is calculated from the total adsorption. Scholten (Scholten, 1993) describes the derivation of the BET equation.

The surface area was measured using a Micromeritics Tristar. The adsorbing gas was N₂ and the adsorption took place at -195.8°C. The sample was prepared by degassing the catalyst at 240°C for 16 hours. Atmospheric pressure was 0.88 bar and the adsorption points (relative pressures) can be seen in Table 2-1.

Table 2-1: Relative pressures of adsorption points

Point Number	Relative pressure
1	0.080
2	0.100
3	0.120
4	0.160
5	0.180
6	0.200
7	0.250
8	0.550
9	0.995

Where the relative pressure is P/P_0 and P_0 is atmospheric pressure.

The BET equation is relevant until $P/P_0 = 0.3$ where it is linear. Points 8 and 9 are included for the calculation of the pore volume.

2.3 Effect of gas composition on the activation of the precipitated iron catalyst

The objective of this study was to determine the effect, if any, of a CO_2 impurity in the reducing gas stream on the extent and rate of reduction of the precipitated iron catalyst. This would be further extended to the Fischer-Tropsch performance of the catalyst.

An impurity of 3% CO_2 was added to each of the reducing gases viz. hydrogen and carbon monoxide. The gases were supplied by Fedgas. Four gas compositions were used (see Table 2-2).

Table 2-2: Composition of reducing gases

	Gas composition (vol %)
1.	5% H_2 /Ar
2.	0.15% CO_2 /4.7% H_2 /Ar
3.	4.8% CO/He
4.	0.15% CO_2 /4.7% CO/He

As previously commented on, Wimmers (Wimmers *et al.* 1986) showed that the addition of 3% H_2O affected the temperature required to reduce small Fe_2O_3 particles. Storch (Storch *et al.* 1951) reported that a 3% impurity of CO_2 severely affected the reduction of a cobalt Fischer-Tropsch catalyst in a mixture of 75% H_2 and 25% N_2 (see Figure 1-3).

2.3.1 Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) is a thermal technique that is used to measure the reducibility of a metal oxide. The basic principle is that a reducing gas is passed over a metal oxide while the temperature is increased according to a linear programme. The quantity of the reducing gas consumed is measured by the difference between the inlet gas

and the outlet gas concentrations. The most common method of analysing this difference is by the change in thermal conductivity (Kaptein, *et al.* 1993). TPR can provide both qualitative and quantitative data.

The inert gases that formed the balance of the gas compositions were chosen based on their thermal conductivities relative to N₂ (see Table 2-3). The thermal conductivity of the inert gas should not be close to that of the reactant gas as the change in thermal conductivity of the overall gas composition with the consumption of reactant would not be great enough to be measurable if it were.

Table 2-3: Thermal conductivities of common gases (relative to N₂) (Lide 1998)

Gas	Thermal conductivity
Ar	0.68
N ₂	1.00
He	5.84
H ₂	7.07
CO	0.97
CO ₂	0.62
CH ₄	1.29

The reaction products will interfere with the thermal conductivity detector due to either the thermal conductivity e.g. CO₂ (see Table 2-3) or due to the sensitivity of the detector to the gas e.g. H₂O. Therefore, they need to be removed from the gas stream before analysis. An explanation of how these products were removed is contained in Appendix 1.

The temperature-programmed reductions were performed on a Micromeritics Autochem 2910. The instrument was first calibrated for each gas type. Details of the calibration are contained in Appendix 2.

In our experiments, approximately 0.050g of sample (MSC3) was accurately weighed into a sample tube (see Table 2-4). The gas flow rate was 50 ml(STP)/min and the temperature was ramped from 50°C to between either 800 or 900°C. The heating rate was 10°C/min.

Table 2-4: Details of TPR experiments

TPR	Gas Composition	Mass catalyst (g)
MSC3 - T1	5% H_2 /Ar	0.0493
MSC3 - T2	0.15% CO_2 /4.7% H_2 /Ar	0.0495
MSC3 - T2R	0.15% CO_2 /4.7% H_2 /Ar	0.0510
MSC3 - T3	4.8%CO/He	0.0497
MSC3 - T4	0.15% CO_2 /4.7%CO/He	0.0494
MSC3 - T4R	0.15% CO_2 /4.7%CO/He	0.0496

2.3.2 Isothermal Reduction

The catalyst (MSC3) was reduced isothermally to determine the effect of different gas compositions on the surface area, phase composition and morphology of the catalyst. The reductions using the gases containing H_2 and CO respectively were not done at the same temperature, but rather at a temperature that is more optimal for each gas type. Dry (Dry 1981), in his review of the Fischer-Tropsch synthesis, points out that reduction in H_2 at temperatures between 180°C and 220°C produced active catalysts. Reduction at 300°C gave poor results. High linear space velocities are also required to give high surface areas after reduction. Anderson (Anderson, 1956) describes the optimum conditions for CO activation as 0.1 bar and 325 - 345°C. Free carbon formation, however, has been noted as showing a sharp increase above 325°C (Storch, 1951).

Catalyst (2g, 38 μm - 250 μm fraction) was reduced according to the following temperature programme:

1. 1°C/min until 220°C (H_2 reductions) or 300°C (CO reductions)
2. 16 hrs at 220°C (H_2 reductions) or 16 hrs at 300°C (CO reductions)
3. Cooling sample to room temperature.

The flow of the gas was set at 78ml/min which corresponds to 39ml(STP)/(g.min) catalyst.

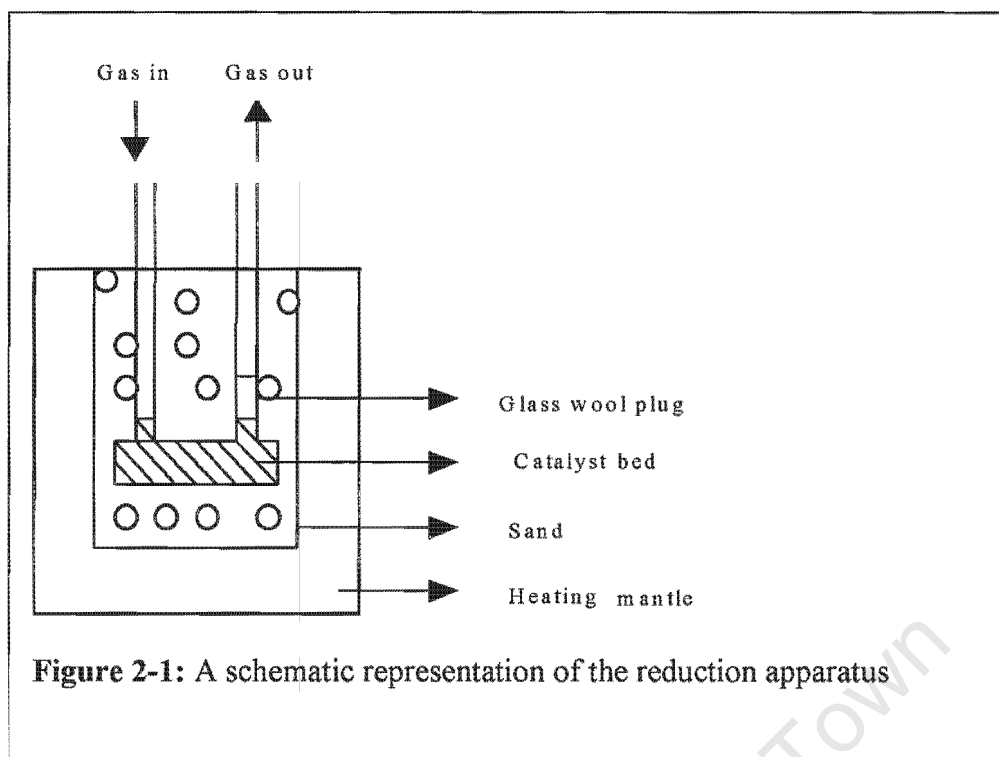


Figure 2-1 is a schematic representation of the reduction apparatus. Sufficient catalyst was loaded to completely fill the base of the glass reactor. This ensured there was no preferential flow over the catalyst bed. A glass wool plug prevented catalyst loss. The heating mantle was filled with sand to ensure proper distribution of the heat. Flow was set using a bubble flow controller.

Four reductions were performed. Table2-5 summarises the reduction conditions.

Table2-5: Reduction conditions for the isothermal reduction ($t_{\text{Reduction}}=16$ hrs; WHSV =39ml(STP)/(g.min))

Reduction Run Reference	Gas Composition	Temp (°C)
MSC3 – R0	None	
MSC3 - R1	5% H_2 /Ar	220
MSC3 - R2	0.15% CO_2 /4.7% H_2 /Ar	220
MSC3 - R3	4.8%CO/He	300
MSC3 - R4	0.15% CO_2 /4.7%CO/He	300

The catalyst sample was then unloaded under argon (Ar). Roughly half of the sample was unloaded into molten wax, the remaining catalyst was unloaded onto a dry ice (CO₂) bed and then covered with dry ice in order to passivate the catalyst. The samples were submitted for Mössbauer and TEM analysis respectively.

2.3.3 Transmission Electron Spectroscopy

Transmission electron microscopy (TEM) is used to determine catalyst morphology with a resolution tunable in the range of 10^{-4} - 10^{-10} m and to obtain structural information by lattice imaging and microdiffraction techniques. This gives valuable information as to the microstructure of the catalyst that cannot be obtained from a bulk technique such as Mössbauer spectroscopy. A more detailed description of TEM is given by Gallezot (Gallezot and Leclercq 1994).

The images were taken using a Philips CM200 Transmission Electron Microscope. The microscope was fitted with a lanthanum hexaboride (LaB₆) filament and operated at 200kV. The condenser aperture used was a 50 micron platinum aperture and the objective aperture was a 40 micron platinum aperture. The sample was mounted on a copper grid with a holey carbon mesh (lacey formvar) by dipping the grid into the catalyst powder. The bright field images were taken on a charge collecting device (CCD) camera.

The following techniques were applied to aid in the identification of the phases:

- a. lattice imaging (physical measurement of the lattice fringes)
- b. fast Fourier transformation (FFT) plot
- c. X-ray diffractogram

In all three techniques, the results are related to the d-spacings of the observed crystal phase. Energy dispersive X-ray spectroscopy analysis (EDS) was also used to help characterise the catalyst.

2.3.4 Mössbauer Spectroscopy (MS)

Mössbauer spectroscopy (MS) is a bulk technique that provides information on the oxidation states, the magnetic field and the lattice symmetry of a number of elements including iron. Bussière (Bussière 1994) gives a more detailed description of Mössbauer spectroscopy.

The Mössbauer experiments were performed with a 50 mCi Co^{57} source in a rhodium matrix. The spectrometer was operated in a symmetric constant acceleration mode with 100 μs dwell time per channel. The spectra were collected over 1024 channels in a mirror image format.

Approximately 80mg of the sample was ground to a fine powder and thereafter mixed with a Mössbauer inert material. This amount of sample gave a mass to area of ca. 30mg/cm² when loaded into the sample holder. This allowed for a Mössbauer signal with minimal distortion due to secondary effects. The experiments were performed at either 25°C or -196°C (i.e. using liquid nitrogen) and the data collected over 36 hours to obtain a minimum of 500 000 counts per channel.

The data was analysed using a least-square fitting routine that models spectra as a combination of quadrupole doublets and sextuplets based on a Lorentzian line-shape profile. The spectral components were identified based on their isomeric shift (δ), quadrupole splitting (Δ) and hyperfine magnetic field (H). The isomeric shift values are reported relative to metallic iron ($\alpha\text{-Fe}$) and the iron content of each phase is determined from their relative peak areas.

Both a fresh sample (MSC3-R0) and MSC3-R1 to R4 (see Table2-5) were submitted for analysis. For MSC3-R1, both the sample unloaded in wax and the sample passivated in CO_2 were submitted (called MSC3-R1(a) and -R1(b) respectively). This was to ascertain whether the method of passivation played a role in the results obtained.

2.3.5 Fischer-Tropsch Synthesis

The fact that different reducing gases and conditions lead to different activities, selectivities and stabilities of a particular catalyst during Fischer-Tropsch synthesis is well documented in the literature. Fischer-Tropsch synthesis runs were therefore included determine what the effect of CO_2 in the reducing gas had on the performance of the reduced catalyst. The Fischer-Tropsch runs were performed in a fixed bed reactor.

2.3.5.1 Reactor operation

A flow diagram of the experimental set up for Fischer Tropsch reaction is shown in Figure 2-2.

From Figure 2-2 it can be seen that three mass flow controllers supplied the various gases to the reactor. These were Brooks mass flow controllers. MFC1 was attached to the reducing gas and had a 120nl/hr capacity. MFC2 was attached to the argon that was used as an internal standard and had a 30nl/hr capacity. MFC 3 controlled the flow of the synthesis gas and had a capacity of 18nl/hr. The mass flow controllers were calibrated using a bubble flow controller and a stopwatch accurate to a hundredth of a second. The temperature and atmospheric pressure were noted and the flows normalised to standard temperature and pressure. All the flow controllers were calibrated at atmospheric pressure. The calibrations are contained in Appendix 3.

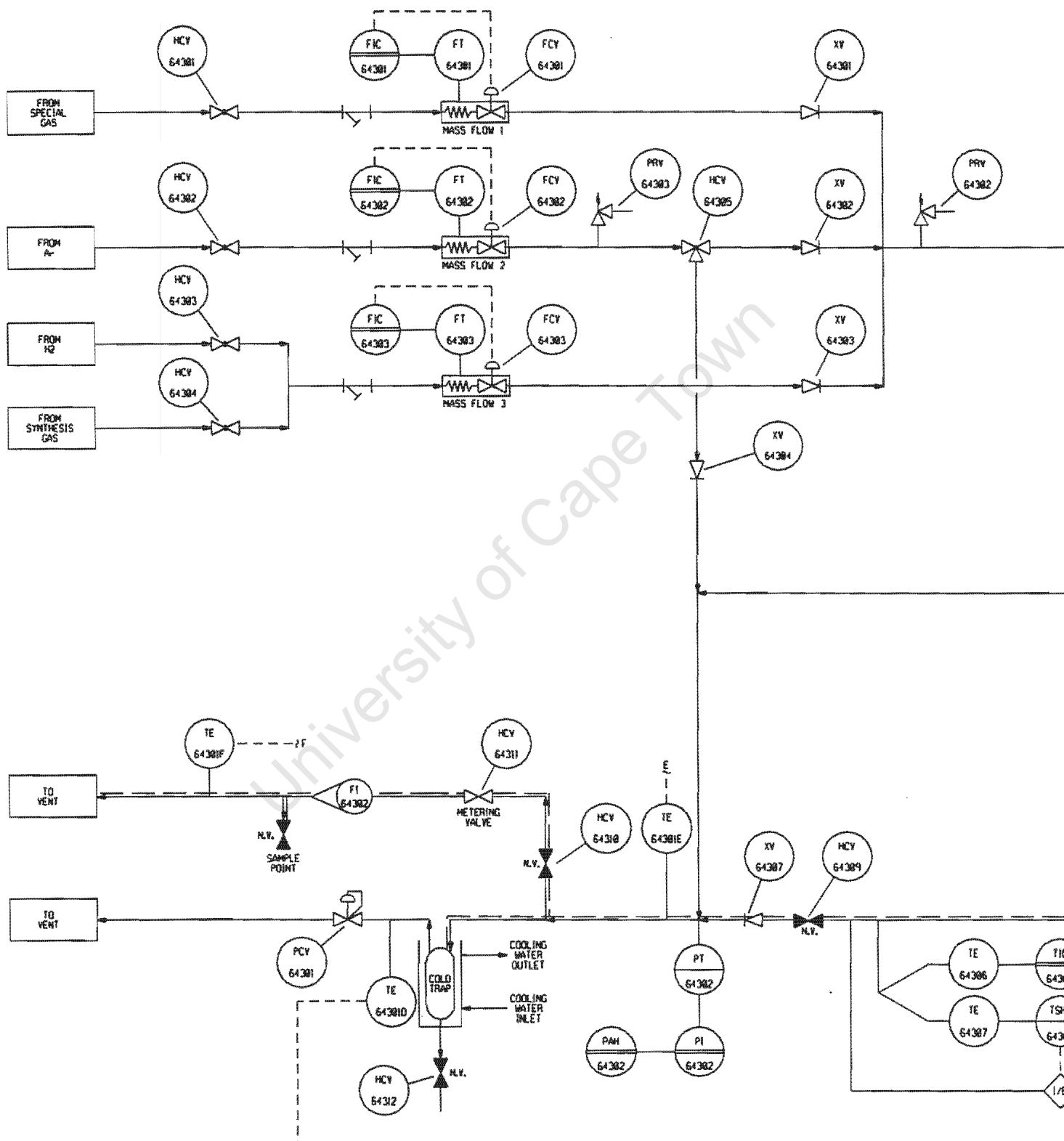


Figure 2-2: Flow diagram of the experimental set-up for Fischer-Tropsch synthesis

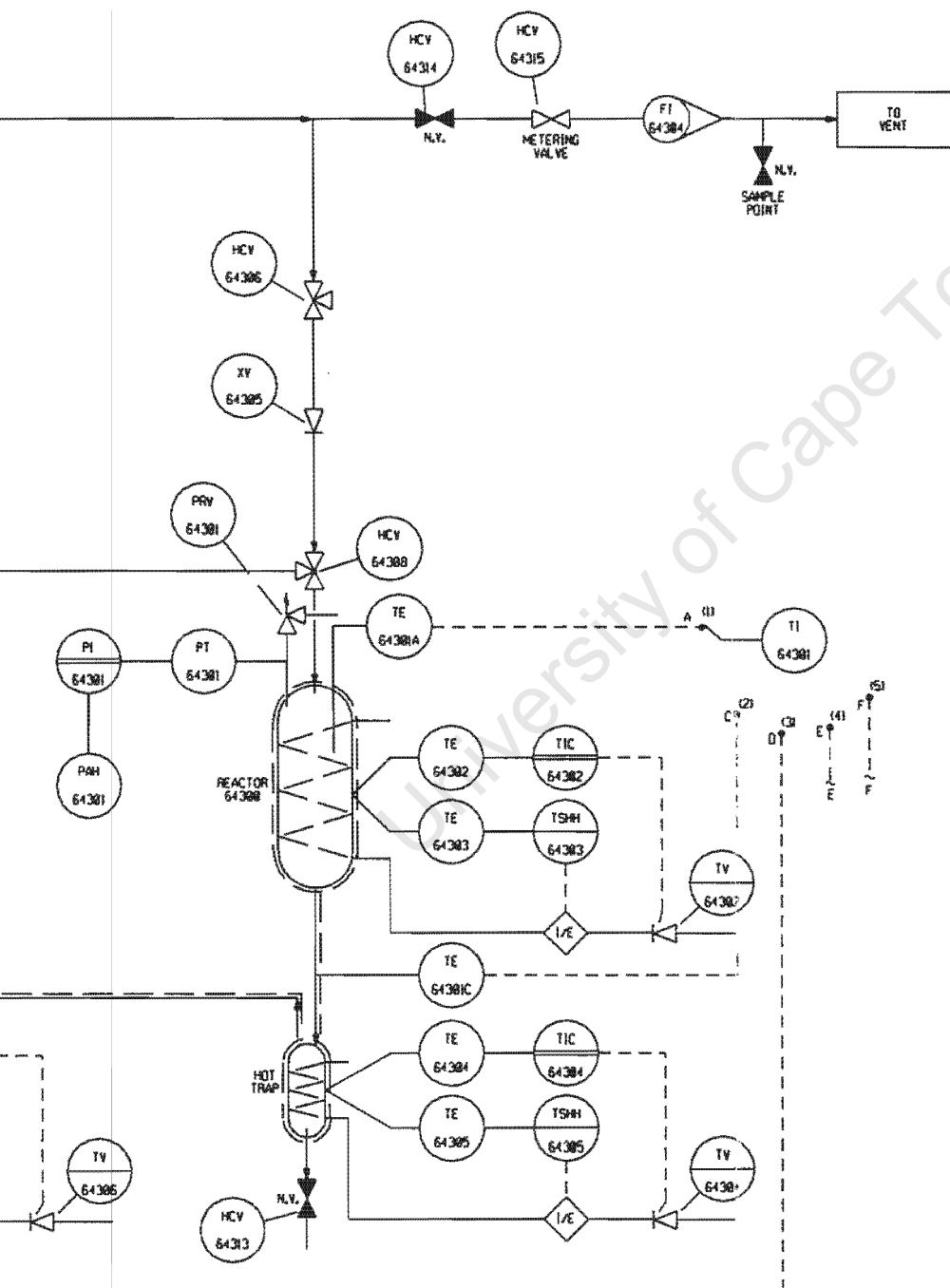
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REFERENCE DRAWINGS

REFERENCE DRAWINGS

CHANGE CONTROL REGISTER

REV BY DATE DESCRIPTION



LEGEND

LAST NUMBERS USED

CHECK VALVE	XV	6430
FLOW	F	6430
HAND CONTROL VALVE	HCV	6431
PRESSURE	PT	6430
TEMPERATURE	TE	6430
PRESSURE RELIEF VALVE	PRV	6430
PRESSURE CONTROL VALVE	PCV	6430

All Property Rights Reserved.

		DISCIPLINE CIRCULATION			APPROVAL		
SOL	MOD. NO.	DISCIPLINE	DATE	SIGN	TASK	DATE	SIGN
		PROCESS			DESIGNED	25.01.96	T.C.
		MECHANICAL			DRAWN	25.01.96	MEK
		CIVIL			CAD MOD	22/01/98	L.L.
		STRUCTURAL			CHECKED	22/01/98	T.C.
		ELECTRICAL			ENGINEER APPR		
		C & I	22/01/98	T.C.	CLIENT'S APPR		

Dimensions in mm unless otherwise stated

Dimensions in mm unless otherwise stated



SASTECH R&D

SUBJECT:

BASIC CATALYST RESEARCH
LABORATORY 2
REACTOR 64300

TITLE: P & I D

Dwg No. 6400-A1-000-0769

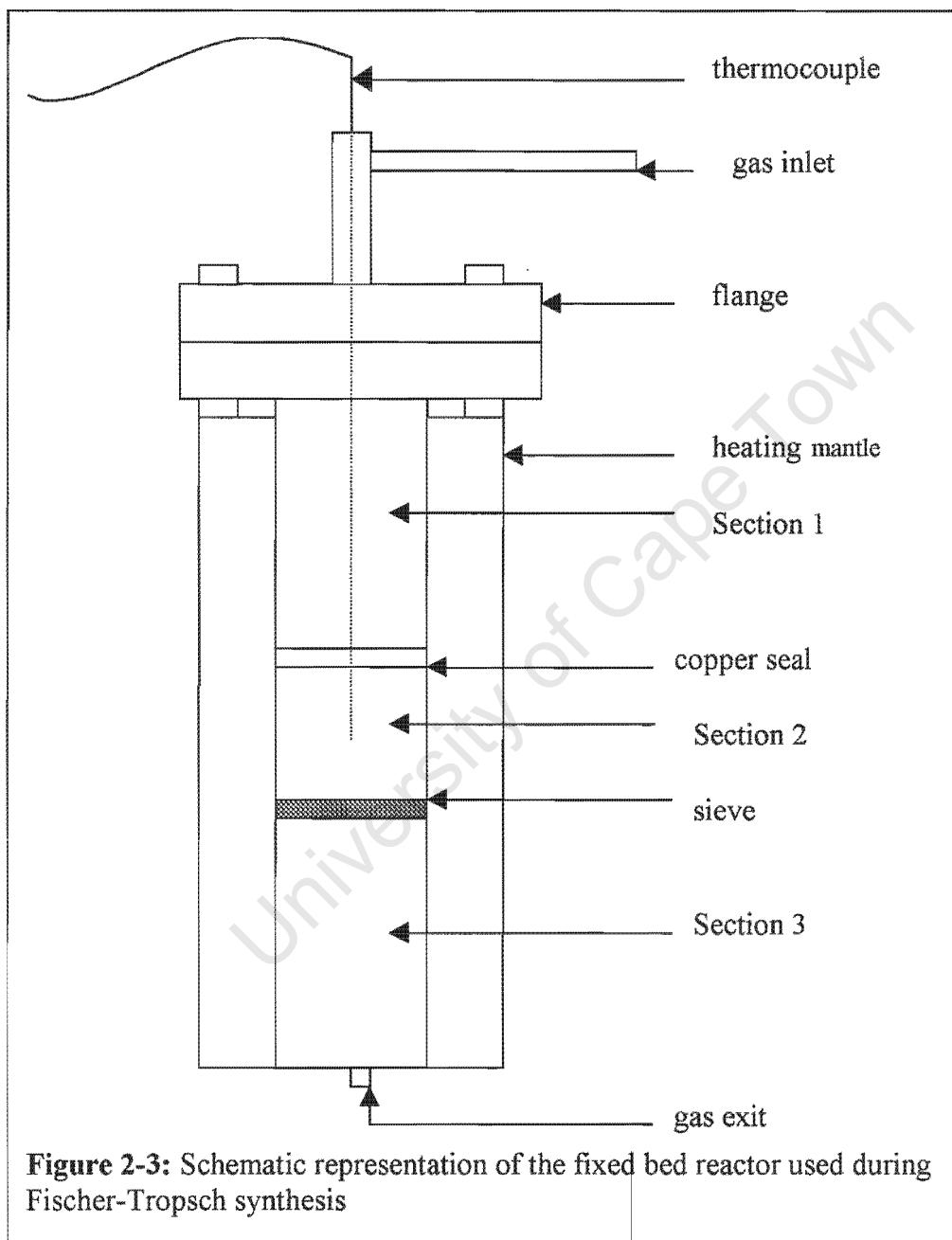
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The schematic diagram of the reactor is shown in Figure 2-3. Section 1 was filled with carborundum to act as a preheating zone. Section 2 was the catalyst bed. The temperature was controlled by the heating mantle while a thermocouple monitored the internal temperature of the catalyst bed.



Fischer-Tropsch synthesis runs were performed on the catalyst reduced under different conditions. Table 2-6 is a summary of these conditions. The reductions were carried out

using the same temperature programmes as the isothermal reductions for each respective gas composition. The flow rates were higher due to limitations of the mass flow controller (i.e. 100ml/g/min versus 39ml/g/min at STP for the isothermal runs).

Table 2-6: Reduction conditions for the in-situ reduction prior to Fischer-Tropsch synthesis ($t_{\text{Reduction}} = 16$ hrs; WHSV = 100ml (STP)/(g.min))

Synthesis Run Reference	Gas Composition	ReductionTemp (°C)
MSC3 - S1	5%H ₂ /Ar	220
MSC3 - S2	0.15%CO ₂ /4.7%H ₂ /Ar	220
MSC3 - S3	4.8%CO/He	300
MSC3 - S4	0.15%CO ₂ /4.7%CO/He	300

The reductions were carried out in situ i.e. in the Fischer-Tropsch reactor.

The catalyst bed (Section 2 – see Figure 2-3) was loaded with 2ml of MSC3 (250µm - 500µm fraction) and diluted with 2ml of quartz (149µm - 420µm fraction). After reduction (as described above), the pressure was slowly increased to 20 bar under argon. Once this pressure had been obtained, the gas flow was switched over to synthesis gas (in the case of CO reductions, the reactor was first cooled to 220°C). The Fischer-Tropsch reaction was carried out at 220°C.

The synthesis gas was obtained from the commercial Fischer-Tropsch synthesis plant and the H₂/CO ratio fluctuated. For this reason daily inlet samples were analysed when calculating the conversions. The space velocity of synthesis gas was 2.5l(STP)/g/hr. A low flow of argon (approximately 10%, accurately measured) was maintained as an internal standard. The hot trap, outlet sample point and the connecting lines were maintained at a temperature of 200°C. The cold trap was at room temperature. Sampling of the outlet stream included a gas sample just after the hot trap and drainings from the hot trap and cold trap.

Gas samples were taken using a glass ampoule system where the glass ampoule is prepared under vacuum.

2.3.5.2 Data evaluation

2.3.5.2.1 Conversions, yields and selectivities

The gas samples were analysed by gas chromatography (GC) using both a TCD (thermal conductivity detector) to measure the permanent gases and a FID (flame ionisation detector) to detect the hydrocarbons.

The TCD measurements were performed using two different gas chromatograms (Gow-Mac GC Series 580). Both systems used two columns in series. The first was a Porapak Q followed by a Molecular Sieve 13X. The flow in both systems was reversed before the CO₂ reached the second column. This allowed for separation of the gas without the CO₂ sticking to the molecular sieve.

The difference between the two GC systems was in the carrier gas used. First the sample was analysed using argon as the carrier gas. This allowed for a more accurate measurement of the H₂ and then there was a switch by the detector to the second system where helium was used as the carrier gas in order that the other gases could be measured (see Table 2-3 for the relative thermal conductivities). The flow of the carrier gases was 20ml/min and the temperature was maintained at 50°C.

The system was calibrated by analysing a gas mixture of known concentrations. The internal standard, argon was included in this gas mixture. The flow of a particular gas in a sample was then calculated using the following formula:

$$(\text{Molar flow})_i = (\text{Molar flow})_{\text{Ar}} \cdot \left(\frac{\%i}{\%\text{Ar}} \right)_{\text{in calibration mix}} \cdot \left(\frac{\text{peak area Ar}}{\text{peak area } i} \right)_{\text{calibration}} \cdot \left(\frac{\text{peak area } i}{\text{peak area Ar}} \right)_{\text{sample}}$$

(Equation 2.1)

The H₂ and CO conversion were then calculated using these flows:

$$X_i = \frac{(\text{Molar flow})_{i, \text{inlet}} - (\text{Molar flow})_{i, \text{outlet}}}{(\text{Molar flow})_{i, \text{inlet}}} \cdot 100\% \quad (\text{Equation 2.2})$$

Both the methane and CO₂ yields (Y_{CO₂} and Y_{CH₄}) and selectivities (S_{CO₂} and S_{CH₄}) were also calculated from the TCD data:

$$Y_i = \frac{(\text{Molar flow})_{i, \text{inlet}} - (\text{Molar flow})_{i, \text{outlet}}}{(\text{Molar flow})_{\text{CO, inlet}}} \cdot 100\% \quad \text{in mol-\%} \quad (\text{Equation 2.3})$$

$$S_i = \frac{(\text{Molar flow})_{i, \text{inlet}} - (\text{Molar flow})_{i, \text{outlet}}}{(\text{Molar flow})_{\text{CO, inlet}} - (\text{Molar flow})_{\text{CO, outlet}}} \cdot 100\% \quad \text{in mol-\%} \quad (\text{Equation 2.4})$$

The FID analyses were performed on a Perkin Elmer Autosystem XL. The column used was a Petrocol DH150 and the carrier gas was hydrogen. The velocity of the hydrogen was 27cm/s. The temperature was started at -60°C, where it was held before being ramped at 45°C/min to -20°C. From -20°C to 220°C, the temperature was ramped at 2°C/min. The lower temperature allowed for better separation of the C₂ hydrocarbons.

An internal hydrocarbon standard was not included in or added to the synthesis gas. Instead the known flow of methane from the TCD results was used to calculate the flows of the higher hydrocarbons. This was done using the following equation:

$$(\text{Molar flow})_{\text{HC}} = (\text{Molar flow})_{\text{CH}_4} \cdot \frac{RF_{\text{CH}_4}}{RF_{\text{HC}}} \cdot \frac{(\text{Peak area HC}) / N_c}{\text{Peak area CH}_4} \quad (\text{Equation 2.5})$$

where N_c is the number of carbons in the hydrocarbon molecule.

The hydrocarbon selectivity was calculated relative to the CO that was converted to hydrocarbons (i.e. excluding the CO converted to CO₂):

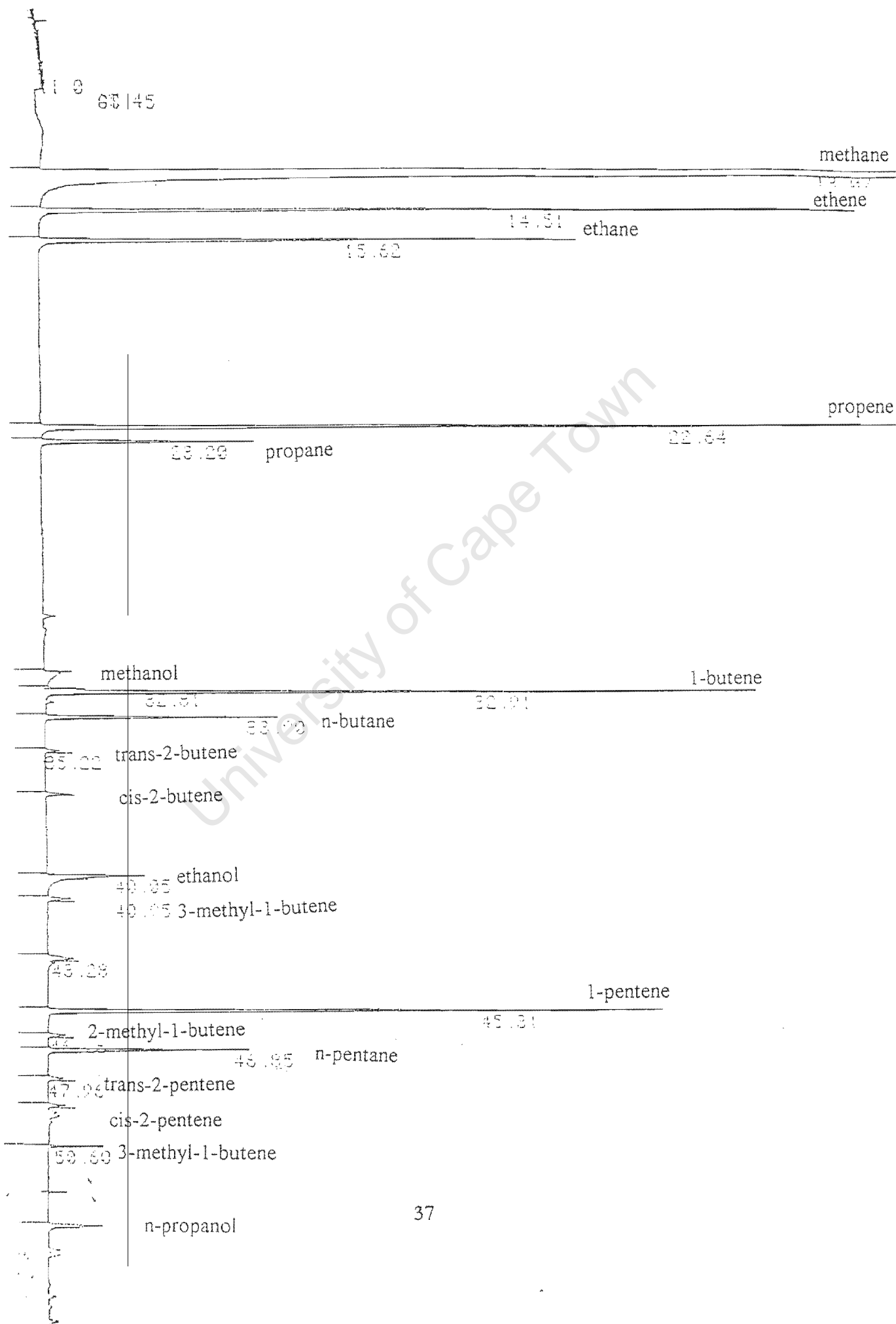
$$S_i = \frac{\left((\text{Molar flow})_{\text{HC,outlet}} - (\text{Molar flow})_{\text{HC,inlet}} \right) \cdot N_C}{\left((\text{Molar flow})_{\text{CO,inlet}} - (\text{Molar flow})_{\text{CO,outlet}} \right) - \left((\text{Molar flow})_{\text{CO}_2,\text{outlet}} - (\text{Molar flow})_{\text{CO}_2,\text{inlet}} \right)} \cdot 100\% \quad \text{in C-}$$

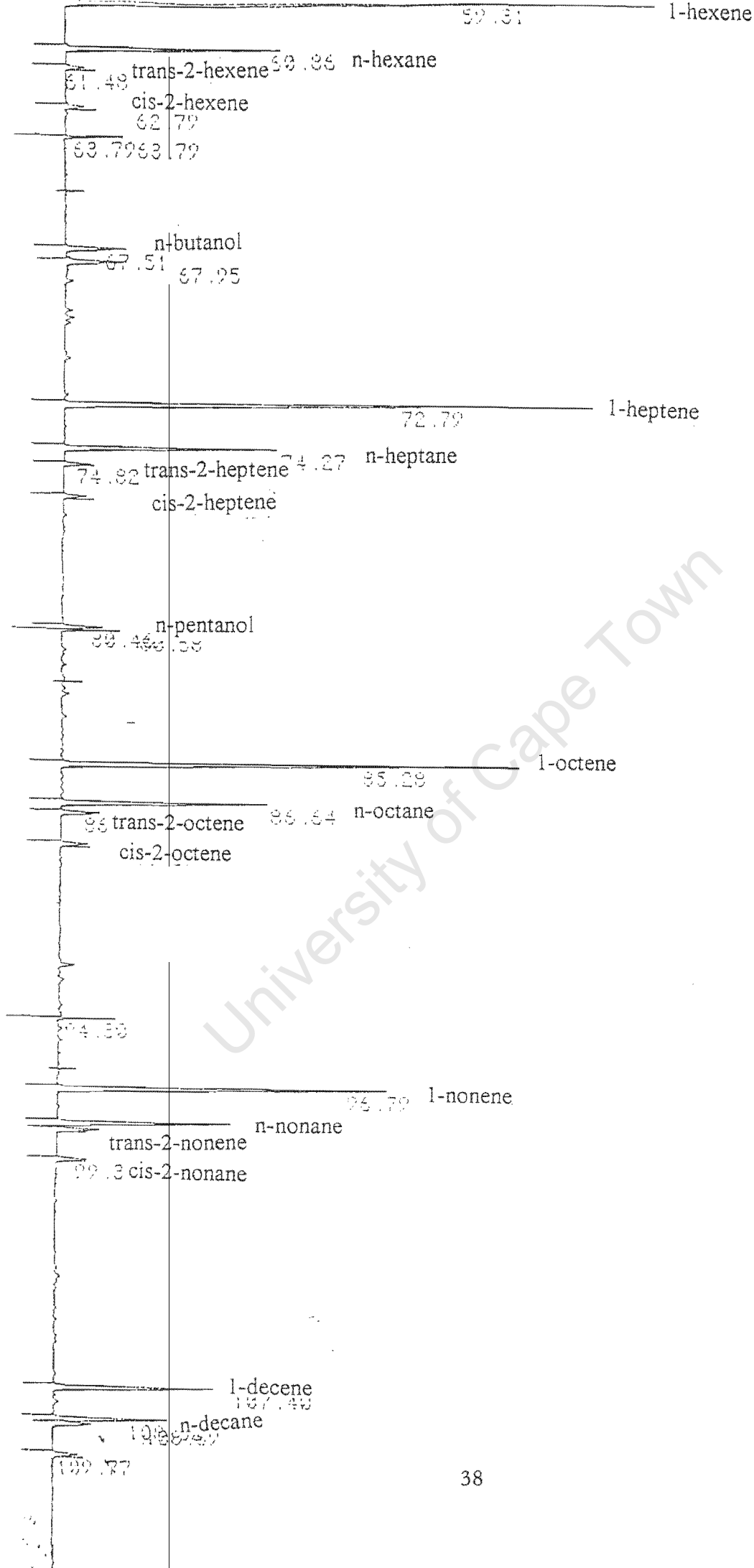
(Equation 2.6)

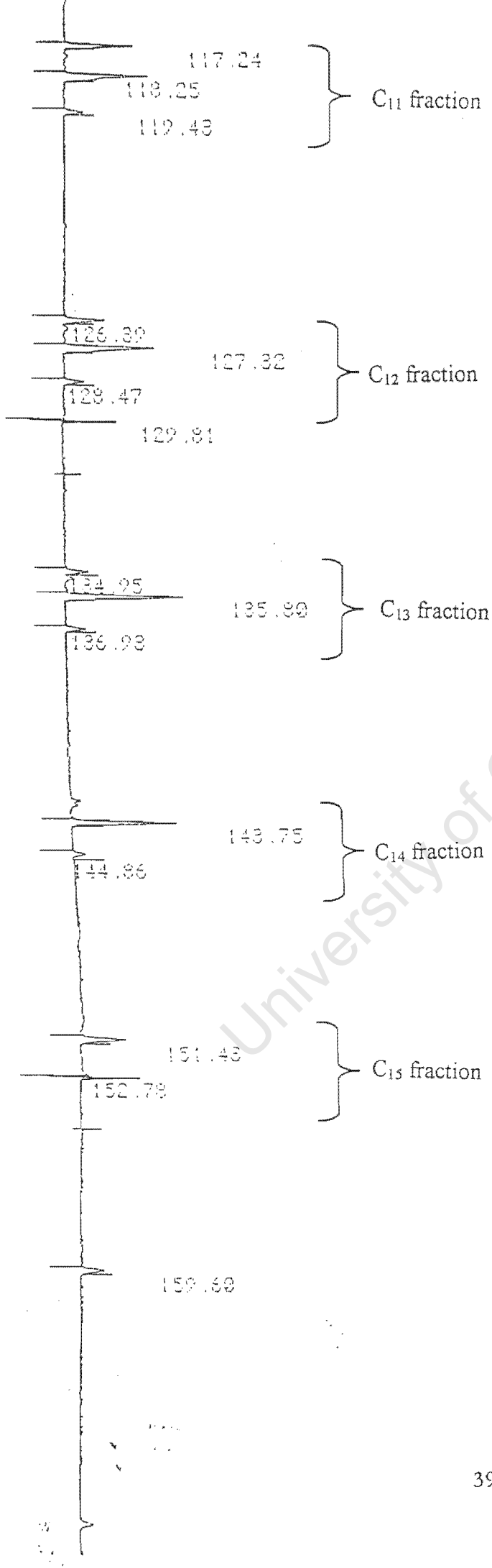
The C% yield of the hydrocarbons was calculated relative to the total CO flow into the reactor system using an equation similar to 2.4. The mol-% yield could be calculated by converting the flow to moles.

A typical FID GC chromatogram is shown in Figure 2-4.

Figure 2-4: Typical GC chromatogram obtained from the FID analyses (MSC3 reduced in 0.15%CO₂/4.7%H₂/Ar for 16 hours at 220°C – after 24 hours of Fischer-Tropsch synthesis)







2.3.5.2.2 Carbon balance

The total carbon balance of the system was calculated from the above data:

$$\text{Carbon balance} = 100 - (X_{\text{CO}} - Y_{\text{CO}_2} - Y_{\text{CH}_4} - Y_{\text{C}_{2+}}) \quad (\text{Equation 2.7})$$

The C_{2+} yield included the wax produced. The C% yield was calculated by converting the mass wax to an equivalent "carbon flow" and then using equation 2.4.

2.3.5.2.3 Chain growth probability (α)

The chain growth probability (α) of the products is based on the fact that the Fischer-Tropsch catalyst is a polymerisation reaction and is calculated by an application of the Schultz-Flory equation (Dry 1981):

$$\log \left(\frac{n_i}{\sum_{i=1}^{\infty} n_i} \right) = N_c \cdot \log \alpha + \log \left(\frac{(1-\alpha)^2}{\alpha} \right) \quad (\text{Equation 2.8})$$

where n_i is the mole fraction and N_c is the number of carbons.

This is known as the Anderson-Schultz-Flory equation. By plotting the log of the mole fraction versus the carbon number, we get a linear plot with the slope equal to $\log \alpha$. From this we can calculate the chain growth probability.

2.3.5.2.4 Acid value

The acid value was measured by titrating the reaction water against a 0.05 N KOH solution. The solution was prepared from AR Grade KOH pellets (85% min - Merck).

The acid value was calculated as mg KOH/(g reaction water).

Chapter 3 - Results

3.1 Catalyst preparation

Three catalyst precursors (MSC1, MSC2 and MSC3) were prepared in order to try and achieve the required K_2O level. The catalysts were prepared by adding an iron and copper nitrate solution to a sodium carbonate solution. The initial pH of the Na_2CO_3 solution was 11.04. The metal nitrate solution was added over a period of approximately 30 minutes. The long addition times were due to foaming. Addition of the metal nitrate solution was discontinued once the pH of the slurry reached 7.0. In each of these preparations, the reaction was not stoichiometric. 270, 500 and 420 ml of the Fe/Cu nitrate solution remained for MSC1, MSC2 and MSC3 respectively. The pH of the slurry increased by $\sim 0.10 - 0.15$ units on ageing.

In Table 3-1, the obtained elemental compositions of the catalyst precursors are given. The oxygen content is based on the difference in sample mass and the mass calculated from the elemental compositions. Any hydrogen still in the precursor as a hydroxide group is neglected. From molar content (Table 3-1B), it is clear that in the catalyst precursor the molar ratio $O/Fe = 2.06 \pm 0.09$, assuming that Cu is present as CuO, Si as SiO_2 , K as KOH and Na as NaOH. This indicates that iron is present as $Fe(OOH)$ in the catalyst precursor.

During filtration, MSC1 did not form an even layer on the filter cloth. Although the precipitate was washed until the conductivity of the filtrate was less than $120\mu S$, the sodium content of the catalyst (measured in the final catalyst) was still high (see Table 3-1). The mass of washed precipitate recovered was 647g of which 57g was calculated to be iron. The catalyst was reslurried with 450ml of distilled water and to this was added 70g of K-waterglass and 5ml of HNO_3 (55% by volume). An additional 200ml of water was added to rinse out the flask due to bitterness (i.e. precipitate that had not reslurried). The results in Table 3-1 show that the K_2O level was lower than expected.

Table 3-1: Chemical compositions of the precipitated catalyst precursors**A:** Composition on mass basis

Catalyst	Fe (wt.-%)	Cu (wt.-%)	Si (wt.-%)	K (wt.-%)	Na (wt.-%)	O ¹ (wt.-%)
MSC1	51.9	2.8	5.3	1.4	0.7	37.8
MSC2	50.6	2.8	6.0	2.8	<0.1	37.8
MSC3 (Catalyst)	50.1	2.4	6.3	1.6	<0.1	39.6

¹Calculated value based on difference**B:** Composition on molar basis

Catalyst	Fe (mol-%)	Cu (mol-%)	Si (mol-%)	K (mol-%)	Na (mol-%)	O ¹ (mol-%)
MSC1	25.9	1.2	5.3	1.0	0.8	65.8
MSC2	25.2	1.2	6.0	2.0	<0.1	65.7
MSC3 (Catalyst)	24.4	1.0	6.1	1.1	<0.1	67.4

¹Calculated value based on difference**C:** Composition of the catalyst precursors on mass basis relative to iron

Catalyst	Cu g/100g Fe	SiO ₂ g/100g Fe	K ₂ O g/100g Fe	Na g/100g Fe
MSC1	5.4	22.0	3.3	1.3
MSC2	5.5	25.4	6.7	<0.1
MSC3 (Precipitate)		29.0	8.4	
MSC3 (Catalyst)	4.8	26.9	3.8	<0.1

The slurry for MSC2 and MSC3 was filtered through a 250µm mesh after the addition of the K-waterglass and nitric acid. This not only prevented bittiness but also ensured a more homogeneous catalyst.

Only 285g of washed precipitate was recovered during the preparation of MSC2 due to a leaking filter unit. The iron was calculated to be 31g and 250ml of distilled water was used to reslurry the precipitate. A mass of 37g of K-waterglass and 3ml of HNO₃ (55% by volume) was added to the slurry. Thus, MSC2 also had a stoichiometric quantity of HNO₃ added to the slurry but no further water was added once the precipitate had been reslurried. In this case, the K₂O level was too high (6.7 K₂O/100 Fe).

For MSC3, 458g of precipitate was recovered, of which 55g was iron. 430ml of distilled water was used to reslurry the precipitate. The calculated mass of 68g of K-waterglass was added to the slurry but 10ml of HNO₃ (55% by volume; ca. 25% more nitric acid than stoichiometrically required) was added. The objective was to try and lower the K₂O even further. The precipitate obtained from this second step was sent in for K₂O analysis prior to the catalyst precursor being dried. The K₂O level was even higher than MSC2, at 8.4 K₂O/100 Fe. This is probably due to the fact that the amount of precipitate recovered from the first step was greater than for MSC2. The removal of the K₂O by filtration was therefore more difficult. This precipitate was then reslurried in distilled water and filtered. The final K₂O level was 3.8 K₂O/100 Fe.

3.2 Surface area of catalyst precursor

The surface area of the catalyst precursors was determined. Results are shown in Table 3-2. Despite the differences experienced during the catalyst preparation, the surface area, pore volume and thus the average pore size are comparable. This can be attributed to the fact that the catalyst is mainly made up of porous iron oxyhydrate prepared under comparable conditions. The slightly different K and SiO₂-levels do not seem to significantly affect the surface area and pore properties of the catalyst precursor.

Table 3-2: BET results of the precipitated catalysts

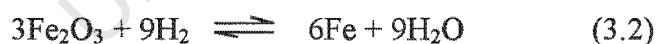
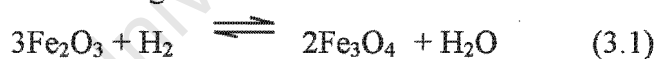
Catalyst	Surface Area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (Å)
MSC1	344	0.54	63
MSC2	327	0.53	64
MSC3	329	0.51	61

3.3 Temperature-Programmed Reduction

Although the catalyst MSC3 had a slightly lower potassium content than the Ruhrchemie catalyst, it was decided to investigate the influence of the reduction atmosphere with this catalyst.

Figure 3-1 shows the temperature-programmed reduction profiles of the reduction in 5% H_2 /Ar and 0.15% CO_2 /4.7% H_2 /Ar mixture. The quantitative evaluation of these TPR-experiments are given Table 3-3. The TPR of MSC3 reduced in H_2 shows three peaks. The first peak contains a shoulder on the low temperature side, which may be due to the reduction of the copper oxide. The first peak is usually associated with the reduction of Fe_2O_3 to Fe_3O_4 (Bukur *et al.* 1995(a)). This is highly favoured thermodynamically and the rate of reduction is fast, as can be seen from the sharpness of the peak. The second peak is normally associated with the reduction of Fe_3O_4 to Fe (Bukur *et al.* 1995(a)). This rate of reaction is much slower as indicated by the peak shape corresponding to a much lower thermodynamic driving. The third peak could be due to reduction of an iron silicate species (Dry 1981).

For the first peak to be associated with the reduction of Fe_2O_3 to Fe_3O_4 , one would expect the H_2 consumed to be 11.1% of the total H_2 consumed by complete reduction. This is derived from the following two reactions:



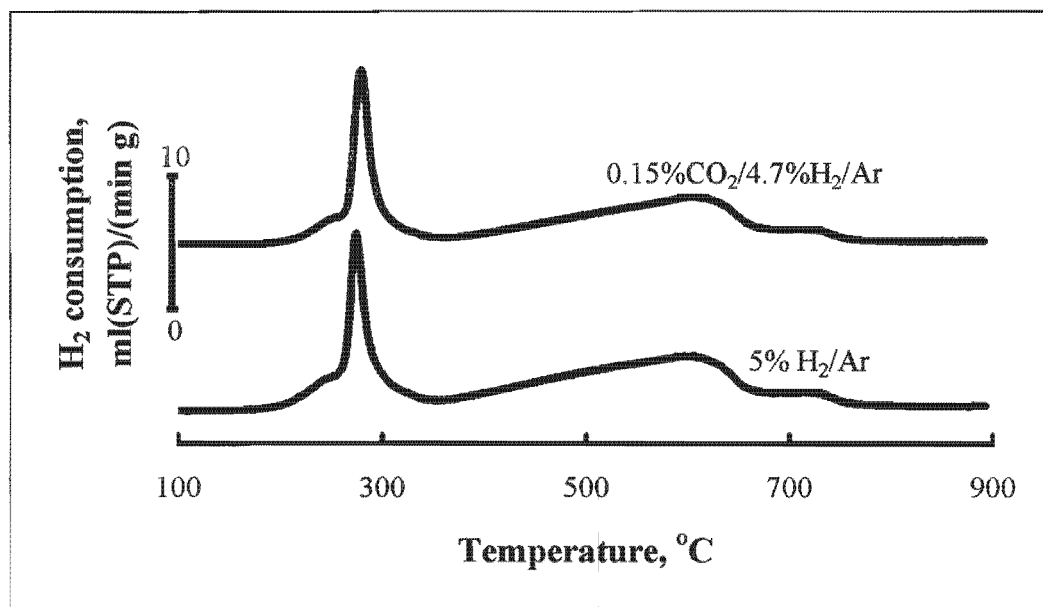


Figure 3-1: Temperature-programmed reduction of catalyst MSC3 in hydrogen-containing atmospheres (5% H_2 /Ar and 0.15% CO_2 /4.7% H_2 /Ar; reduction conditions see Chapter 2.3.1)

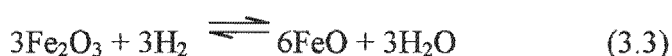
Table 3-3: Quantitative evaluation of temperature programmed reduction of catalyst MSC3 in H_2 -containing atmospheres

Gas composition	5% H_2 /Ar	0.15% CO_2 /4.7% H_2 /Ar	0.15% CO_2 /4.7% H_2 /Ar (repeat)
$T_{\text{reduction start}}$, $^{\circ}\text{C}$	170	180	180
$T_{\text{max 1st maximum}}$, $^{\circ}\text{C}$	274	279	284
$T_{\text{max 2nd maximum}}$, $^{\circ}\text{C}$	606	608	621
$T_{\text{max 3rd maximum}}$, $^{\circ}\text{C}$	733	752	730
H_2 , consumed total, mmol/g	12.62	10.35	9.95
H_2 consumed 1st peak, mmol/g	4.10	3.43	3.63
H_2 , consumed /Fe, mol/mol	1.41	1.15	1.11
% reduction ¹	97	74 ²	71 ²

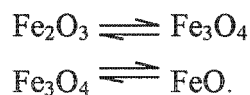
¹ The amount of hydrogen used for the reduction of copper has been subtracted

² Assumed that all H_2 is used for catalyst reduction and not CO_2 hydrogenation

For catalyst MSC3 the reduction of Fe_2O_3 to Fe_3O_4 would correspond to a hydrogen consumption of 1.87 mmol/g (including the reduction of CuO to Cu). In fact, the approximately 33% of total hydrogen consumed agrees more with the following reaction:



If one looks at the phase diagram of iron/oxygen, FeO is not considered a stable phase at the temperatures at which the first reduction peak occurs and it is not seen as a separate phase in a reduced catalyst. It may be possible that the first peak, while corresponding to the reduction (3.3) is in fact a summation of two reduction steps (3.1) and (3.3) i.e.



This would be supported by the shoulder on the left hand side of the peak which cannot correspond only to the reduction of copper oxide i.e.



The hydrogen consumed due only to the shoulder (~7%) is already too much.

The addition of CO₂ to the reduction gas does not seem to alter the reduction behaviour. Although the TPR profiles look very similar, the quantitative evaluation of the TPR experiment shows some differences. The observed degree of reduction when CO₂ is present in the reduction gas mixture is significantly different, although the maximums observed in the TPR-spectra are not shifted much. It was speculated that CO₂ would have no or a negative effect on the reduction in a H₂ atmosphere, therefore the negative effect of the CO₂ on the H₂ reduction is not unexpected. The difference between the reduction in H₂/Ar atmosphere and in an atmosphere containing CO₂ is depicted in Figure 3-2. For comparison the TPR-profile of MSC3 is depicted in a 0.1x magnification as well. At the start of the reduction, more hydrogen is consumed in a reducing atmosphere without carbon dioxide. At ca. 275°C the hydrogen consumption in the atmosphere containing carbon dioxide is higher. The first reduction step(s) are shifted towards a higher temperature. At higher temperatures the difference spectrum follows the TPR-profile of the catalyst indicating a lower rate of reduction. This might be ascribed to reoxidation of the newly created Fischer-Tropsch sites by CO₂. This is thermodynamically not likely for bulk oxidation but could be possible on the surface. The product of such a reaction would have been CO and this would not really have been picked up by the TCD analysis (due to the similarity of the thermal conductivity of Ar and CO).

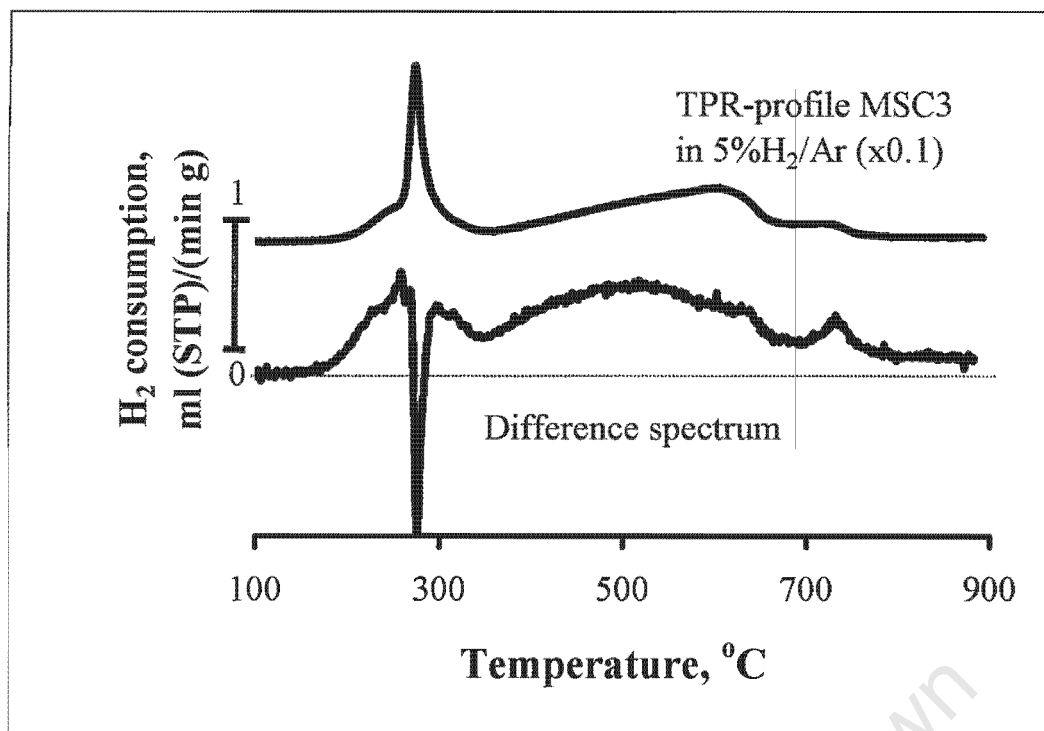


Figure 3-2: Difference of the TPR-profile of MSC3 reduced in 5% H_2 /Ar and the TPR-profile of MSC3 reduced in 0.15% CO_2 /4.7% H_2 /Ar (reduction conditions see Chapter 2.3.1). For comparison the TPR-profile of MSC3 in 5% H_2 /Ar is depicted in a 0.1 x magnification as well.

Under the reduction conditions applied, it is principally possible that CO_2 is hydrogenated. This would result in hydrogen consumption, but not in reduction of the catalyst. Furthermore, this would have increased the partial pressure of the H_2O , which would retard the reduction (Storch *et al.* 1951). Unfortunately, the exit gases from the TPR were not analysed so it was not possible to tell if there was hydrogenation of the CO_2 .

One other possibility that needs to be considered is the fact that CO_2 might adsorb on metallic copper. This might lower the amount of H_2 available for the reduction reaction due to the lower surface area now available for H_2 dissociation and spillover. It would be interesting to see if CO_2 would have a similar effect on the TPR of a catalyst not promoted with copper.

Figure 3-3 shows the temperature-programmed reduction profile of the catalyst precursor MSC3 reduced in carbon monoxide-containing atmospheres. The addition of carbon dioxide to the reducing gas mixture does not seem to change the TPR-profile. The magnitude of CO-consumption is, however, in the presence of CO₂ larger than that without CO₂. A quantitative evaluation of the TPR-experiments is given in Table 3-4.

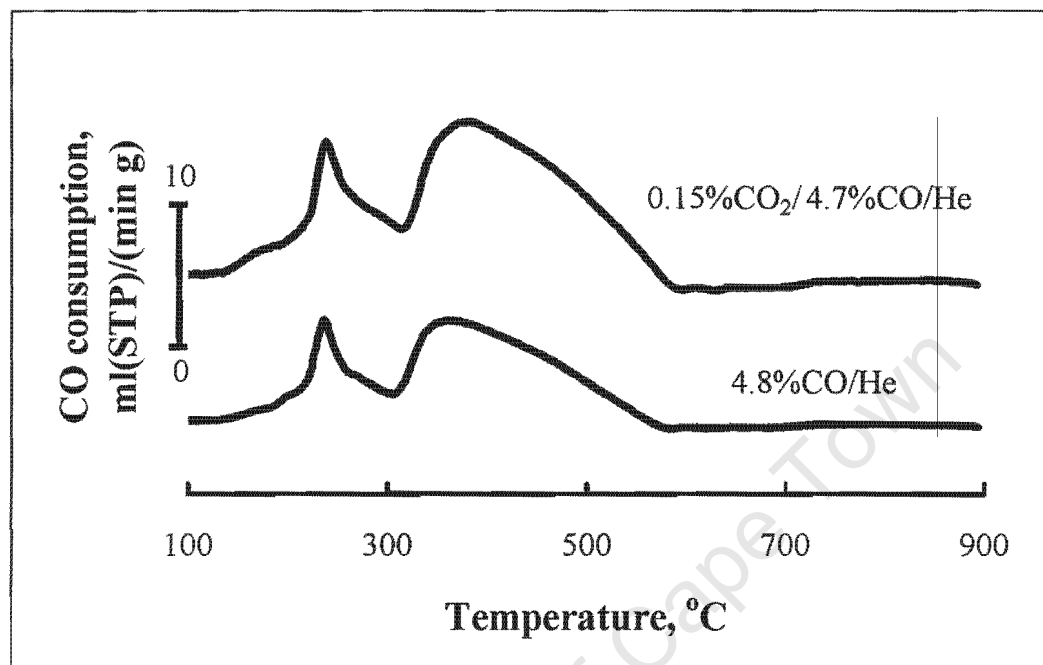


Figure 3-3: Temperature programmed reduction of catalyst MSC3 in carbon monoxide containing atmospheres (5%CO/He and 0.15%CO₂/4.7%CO/He; reduction conditions see Chapter 2.3.1)

The TPR of MSC3 reduced in CO shows only two peaks. These peaks are not as clearly defined as in the H₂ reductions. This could be an indication that there are diffusion limitations associated with the reduction of the precipitated catalyst precursor in CO or could be due to carbide formation.

Again, the first peak is associated with the reduction of Fe₂O₃ to Fe₃O₄ and the second with the reduction of Fe₃O₄ to Fe. Above ca. 565°C, the TPR profile of MSC3 in a CO/CO₂ atmosphere indicates a negative consumption of CO (i.e. CO is being produced). A possible explanation is the reverse carbidisation of iron carbide (Fe_xC + CO₂ → Fe + 2 CO) or, but due to thermodynamic constraints less likely, due to the reverse Boudouard reaction i.e.



The reaction of iron carbide with carbon dioxide might be feasible at higher temperatures for small carbide particles. The reaction of free carbon with carbon dioxide is thermodynamically highly unfavoured.

Table 3-4: Quantitative evaluation of temperature-programmed reduction of catalyst MSC3 in CO-containing atmospheres

Gas composition	5%CO/He	4.7%CO/0.15%CO ₂ /He	0.15%CO ₂ /4.7%CO/He (repeat)
T _{reduction start} , °C	100	86	86
T _{max 1st maximum} , °C	236	237	236
T _{max 2nd maximum} , °C	365	379	377
CO _{consumed total} , mmol/g	6.78	11.56	11.69
CO _{consumed 1st peak} , mmol/g	1.91	3.21	3.43
CO _{consumed} /Fe, mol/mol	0.76	1.29	1.30
% reduction ¹	48	83 ²	83 ²

¹ The amount of CO used for the reduction of copper has been subtracted

² Assumed that all CO is used for catalyst reduction and CO₂ was not transformed into CO

It can be seen from the quantitative evaluation that CO₂ enhances the consumption of CO dramatically. It was speculated that CO₂ would have no or a negative effect on both the H₂ and CO reductions. The positive effect of CO₂ on the TPR of the catalyst reduced in CO was completely unexpected. The reduction of the catalyst precursor MSC3 in the presence of CO does not go to completion. The observed degree of reduction is less than 50%. This indicates that there are severe diffusion constraints or unavailability of iron for reduction, since the reduction with CO is even more favoured than the reduction with H₂.

As was expected from thermodynamics, the reduction in CO started at a lower temperature than the reduction in H₂. The overall degree of reduction, however, was lower for the CO reduced catalyst. There could be a number of mechanisms to explain this. Copper is known to be a reduction promoter in hydrogen atmospheres. Hydrogen may dissociate on copper and spill over to the iron particles, which then reduce. A spill-over effect with carbon

monoxide is not likely to occur. Furthermore, CO is also a larger molecule than H_2 and therefore the lower total degree of reduction could be due to kinetic constraints, if the reaction is kinetically controlled due to diffusion constraints. It may also be possible that the deposition of free carbon could limit the diffusion of CO through the metallic outer core towards the solid/solid interface where the reaction takes place. The positive effect of CO_2 in the reduction in CO-containing atmospheres can then be explained by the inhibition of the formation of free carbon, which may block reaction sites or pores through which the gases may diffuse more easily.

It is possible that the degree of reduction for the CO-activated catalysts may be even lower still if one considers the fact that not all the CO is consumed by the reduction of the iron oxide. A percentage may be consumed by the formation of iron carbides and carbon.

3.4 Isothermal Reduction

It was noted that after the reduction of the catalyst in CO, there was a marked decrease in volume after the reduction of the catalyst. This could not be quantified as a portion of the catalyst was unloaded into wax, but it is probably due to sintering of the catalyst and the difference in density between the iron oxide and metallic iron or iron carbides (5.27, 7.87 and 7.60 respectively). The catalyst samples reduced in H_2 did not show this decrease in volume, but the reduction was specifically carried out at a low temperature to prevent sintering and loss of surface area. The results obtained from the characterisation of the catalyst after various reductions are presented below.

3.4.1 BET Surface areas

Table 3-5 summarises the results obtained from the BET-surface area measurement. The catalysts reduced in CO-containing atmospheres (and at higher temperatures viz. $300^\circ C$) lost more surface area and pore volume than the catalysts which were reduced in H_2 -containing atmospheres at lower temperatures. All the reduced catalysts showed a lower

surface area and pore volume than the catalyst precursor. This is in agreement with previous work done by Bukur (Bukur *et al.* 1995(b)). He also noted that a catalyst reduced in H₂ at 280°C, lost less surface area than during the activation in CO. He speculated that this might be due to carbonaceous products blocking the pores of the catalyst. The overall decrease in surface area can be attributed to a partial collapse of the porous iron oxide matrix (Bukur *et al.* 1995(b)). This is supported by the pore size distributions of the catalyst before and after reduction. One can see that there is an increase in the larger pores at the expense of the smaller or micropores.

Table 3-5: BET results of the reduced catalyst MSC3 in different reduction atmospheres

Reduction atmosphere	T _{reduction} (°C)	Surface Area (m ² /g)	V _{pore} (cm ³ /g)	d _{pore} (Å)
Unreduced catalyst	-	329	0.51	61
5%H ₂ /Ar	220	159	0.44	111
0.15%CO ₂ /5%H ₂ /Ar	220	162	0.43	106
4.8%CO/He	300	97	0.21	87
4.7%H ₂ /0.15%CO ₂ /He	300	94	0.21	91

3.4.2 Transmission Electron Spectroscopy

3.4.2.1 Catalysts reduced in H₂

The morphology of the catalyst MSC3 after reduction in hydrogen-containing atmospheres (with and without carbon dioxide) is shown in Figures 3-4 and 3-5. The catalyst consists of a collection of small crystallites. The crystallites that can be measured would appear to be approximately 6nm or smaller in diameter. There also seems to be very little difference in the morphology of the catalyst when reduced in 5%H₂/Ar and when reduced in 0.15%CO₂/4.7%H₂/Ar . Higher magnification does not further elucidate the morphology.

There are a number of different possibilities for the iron phase in the precipitated MSC3 catalyst. Appendix 4 contains the d-spacings of both the possible phases of the unreduced catalyst as well as of the reduced catalyst (both in H₂ and CO). It can be seen from these spacings that it is very difficult to differentiate between similar phases based purely on the

lattice fringes. It is also possible to get distortion of the measured lattice fringe if the image is exactly in focus.

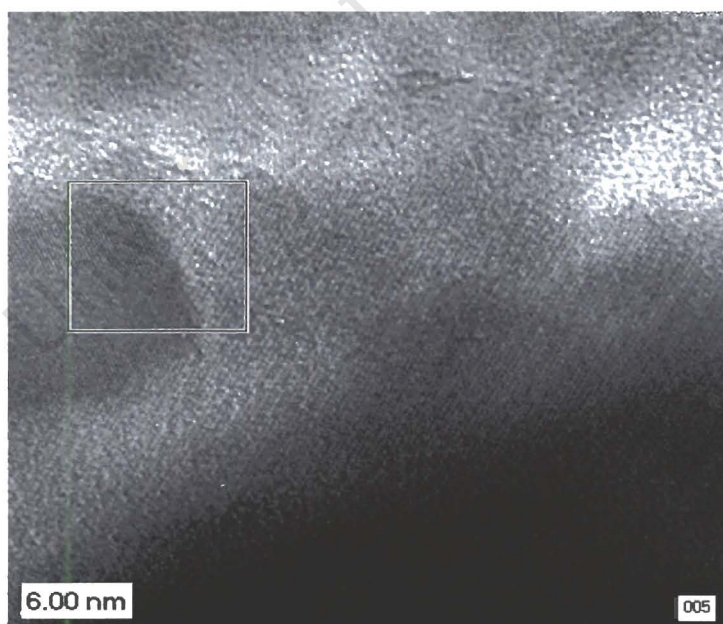
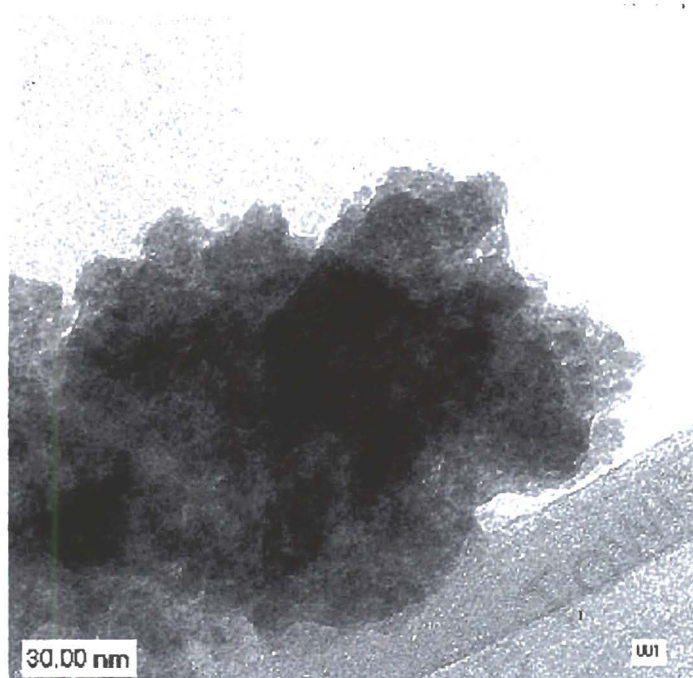


Figure 3-4: TEM micrograph of catalyst MSC3 reduced in 5.0% H_2 /Ar at 220°C for 16hrs (reduction conditions see Chapter 2.3.2)

Looking at the lattice fringes of the crystallites, measurements in the region of 2.2 Å, 3.0 Å, 3.6 Å, 4.2 Å, 4.5 Å and 5.6 Å were seen. A fast Fourier-transformation in the squared off region of Figure 3.4 gave 2.20 Å, 3.00 Å and 3.54 Å. It could be possible that one of

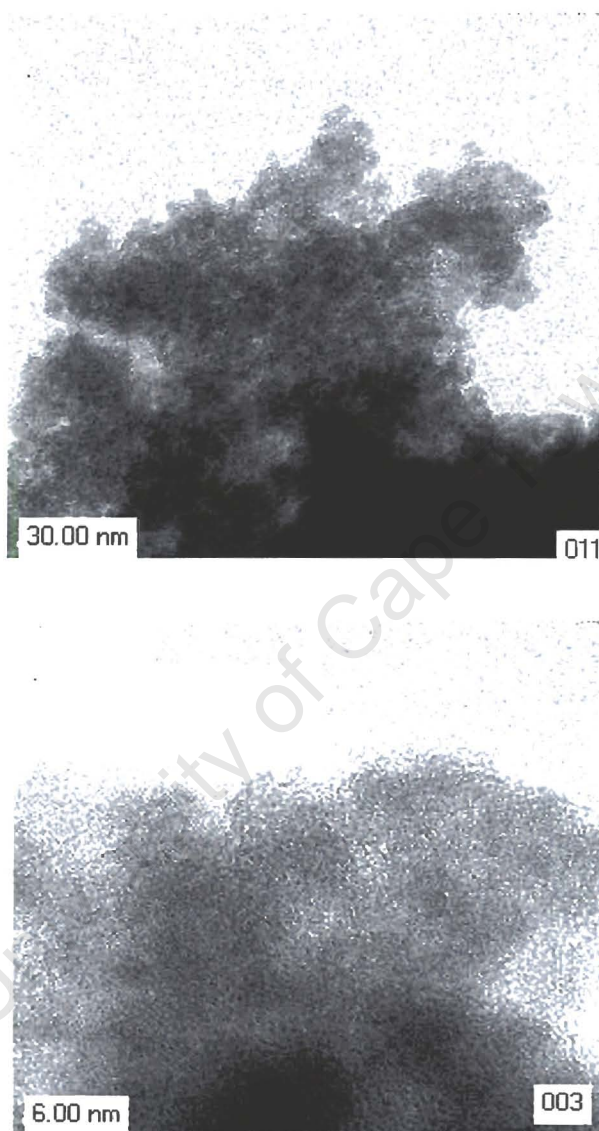


Figure 3-5: TEM micrograph of catalyst MSC3 reduced in 0.15%CO₂/4.7%H₂/Ar at 220°C for 16hrs (reduction conditions see Chapter 2.3.2)

the iron phases may be maghemite. There was no direct evidence for any reduced phases of iron oxide such as magnetite, wüstite or alpha-iron.

Unfortunately, confirmation could not be obtained from X-ray diffraction measurements. The images were too indistinct to measure the spacing accurately. Bulk XRD measurements of the catalyst would also have added to this part of the study as it could have limited the number of possible phases. There was insufficient sample to perform these measurements.

3.4.2.2 Catalysts reduced in CO

The image of the catalyst reduced in 4.8%CO/He and that of the catalyst reduced in 0.15%CO₂/4.7%CO/He can be seen in Figure 3-6 and 3-7 respectively. Again, the slight CO₂ impurity seems to have little effect on the final morphology of the catalyst when the catalyst was reduced in CO. The crystallite sizes were measured between 10 and 60nm. Higher magnification of these crystallites shows a "cherry-like" nodule in an amorphous-like matrix and surrounded on the surface by layered structures.

The main lattice fringe found in the nodule was in approximately 4.9Å. This can only be ascribed to magnetite. The layered structure would appear to be a "graphitic" carbon that has been deposited on the surface (lattice fringe measured in the vicinity of 3.3 Å). No evidence for carbides was seen as we were unable to measure the lattice fringes in the region required (i.e. 2 Å) due to the low resolution of the microscope. Fast Fourier transformations of the area within the nodule confirmed that the lattice fringes matched those of an iron oxide phase and not of a carbide (4.68Å, 4.03 Å, 3.24 Å and 2.01 Å).

EDS analyses were performed on each of the areas represented in Figures 3-6 and 3-7.

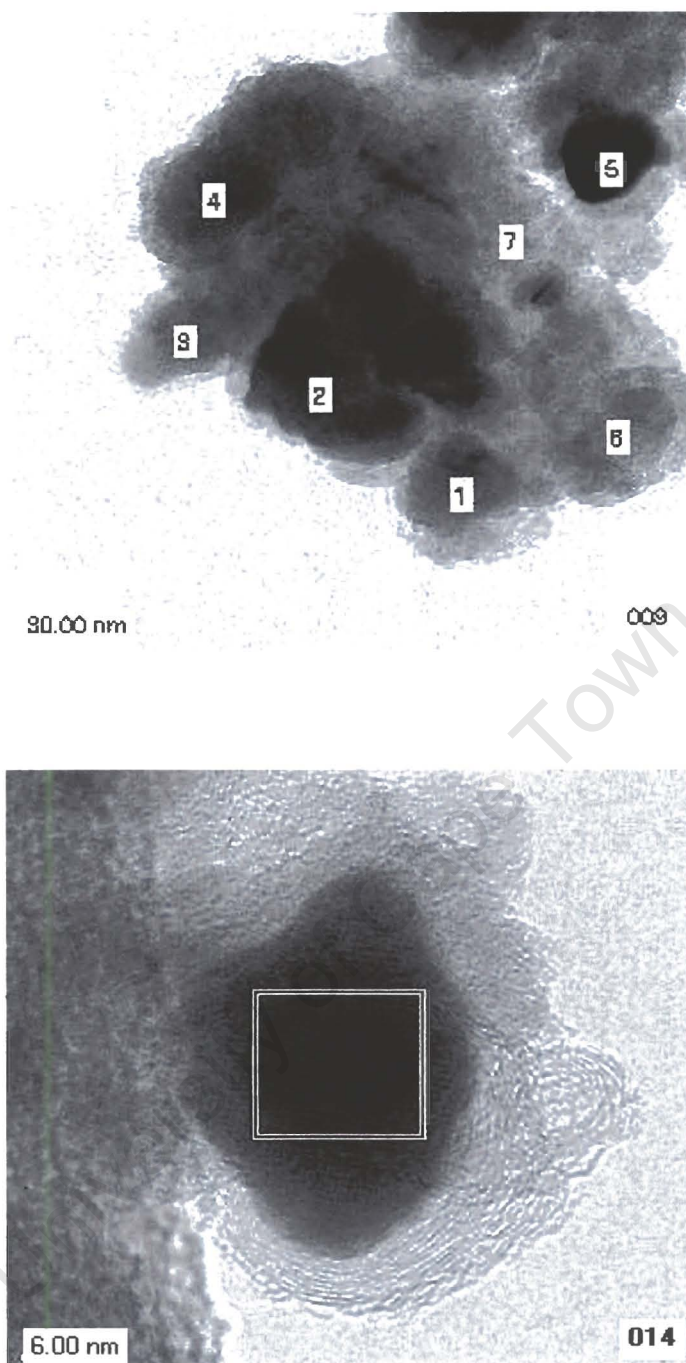


Figure 3-6: TEM micrograph of catalyst MSC3 reduced in 4.8%CO/He at 300°C for 16hrs (reduction conditions see Chapter 2.3.2)

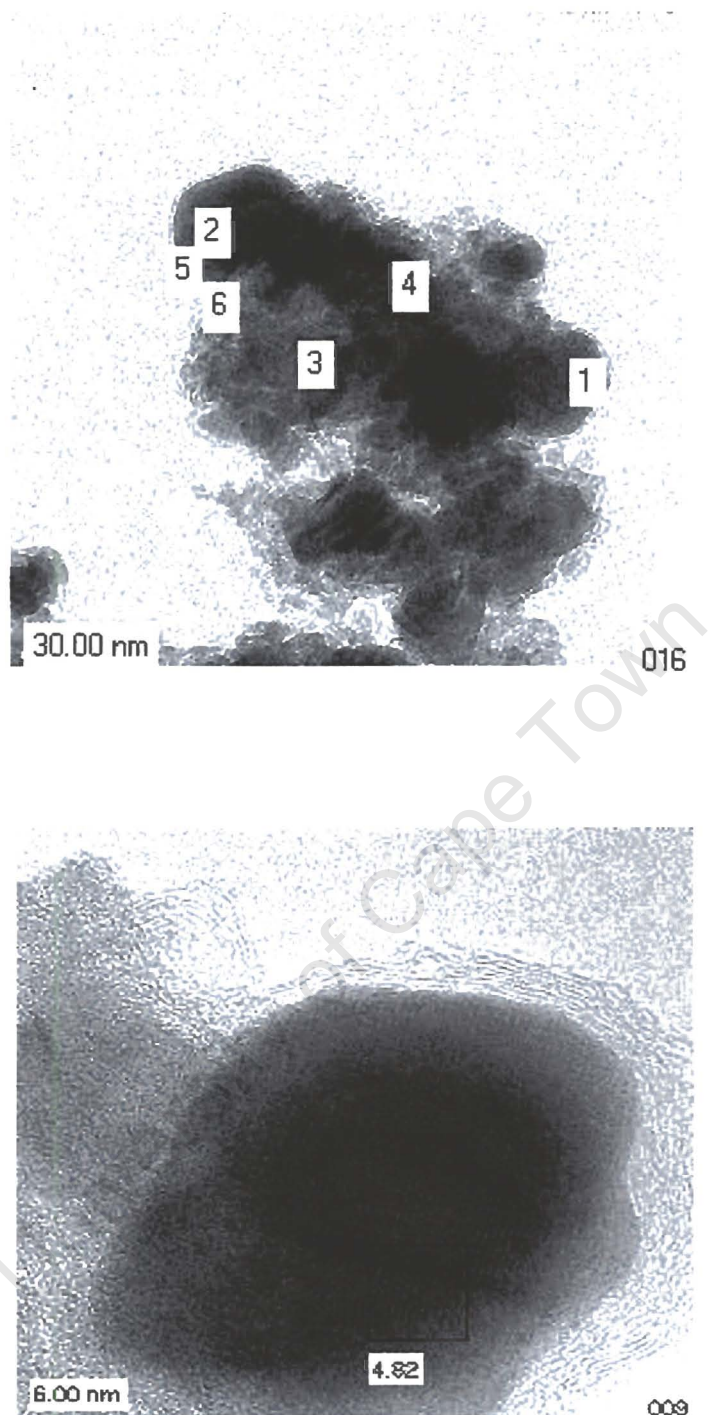


Figure 3-7: TEM micrograph of catalyst MSC3 reduced in 0.15%CO₂/4.8%CO/He at 300°C for 16hrs (reduction conditions see Chapter 2.3.2)

Carbon was found in all the areas, although in varying quantities. In Figure 3-6, area 6 appeared the most oxidic and area 3, the most carbonaceous. The most silica was seen in area 6 and the least in area 3. Areas 4, 6 and 7 contained potassium. The potassium peak

was relatively small. In Figure 3-7, areas 3 and 4 appeared more oxidic while areas 1 and 2 had higher carbon content. Again, the areas higher in oxygen also appeared to be higher in silica. Potassium was seen in all the areas measured. Areas 5 and 6 gave a very high copper content. Area 6 in particular showed a high relative copper, silica and oxygen content. A possible explanation for this is that the segregation of copper to the catalyst surface can occur during CO activation. This could be due to the low solubility of copper in the iron carbide phase as has been noted before (Sault and Datye 1993). It must also be noted, however, that the grid used was a copper grid and these were the areas measured on the periphery of the catalyst sample.

Figure 3-8 shows some examples of the more unusual structures seen on the catalyst MSC3 reduced in carbon monoxide-containing atmospheres. The structures are probably due to outward growth due to carbon incorporation (as carbides) or deposition (as graphitic carbon).

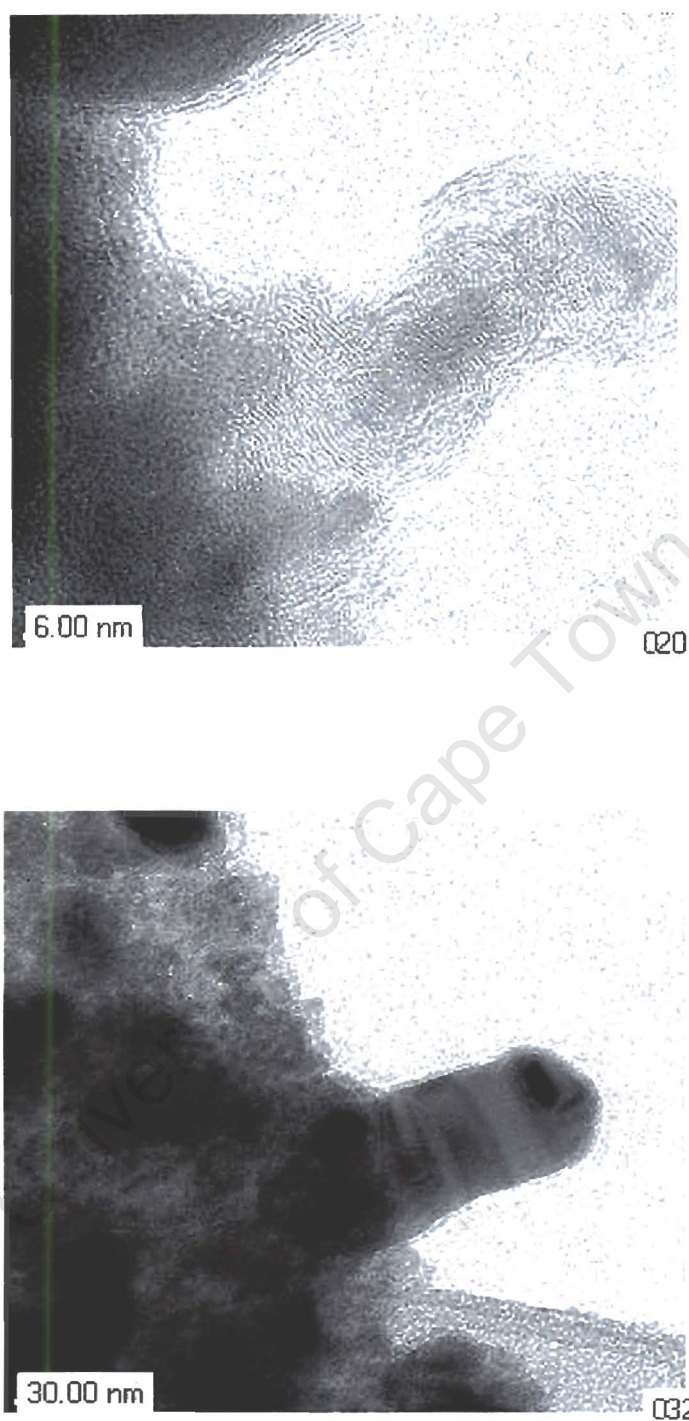
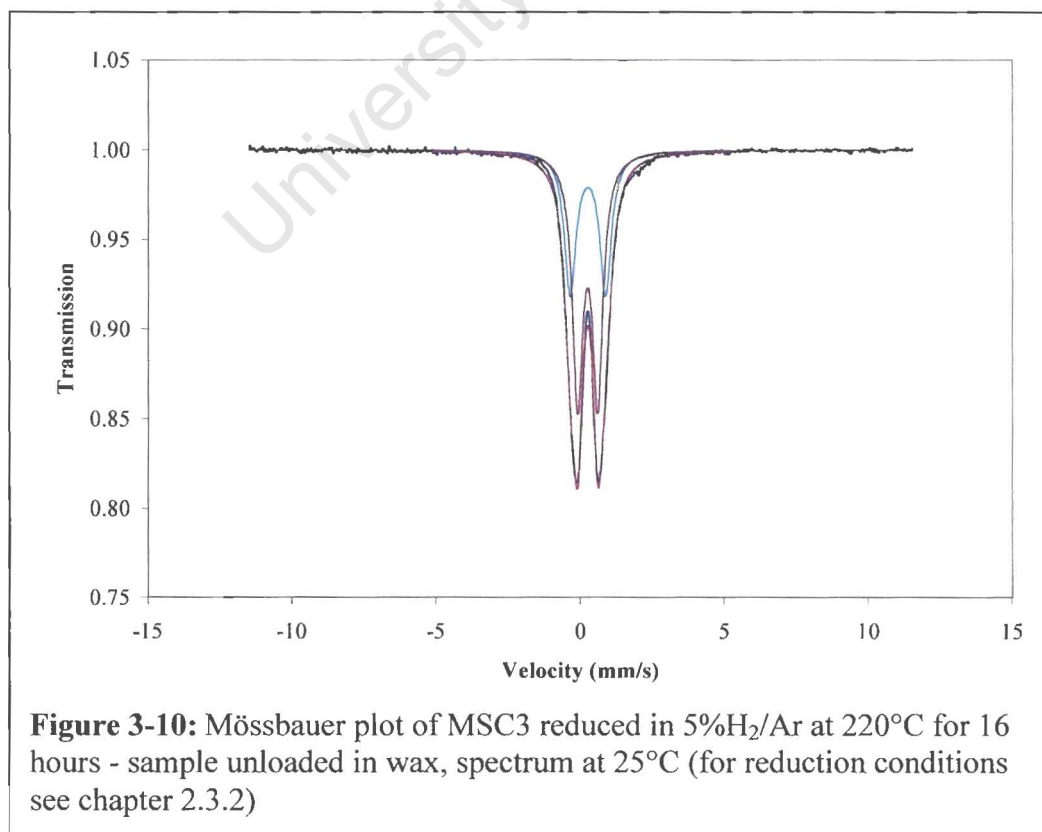
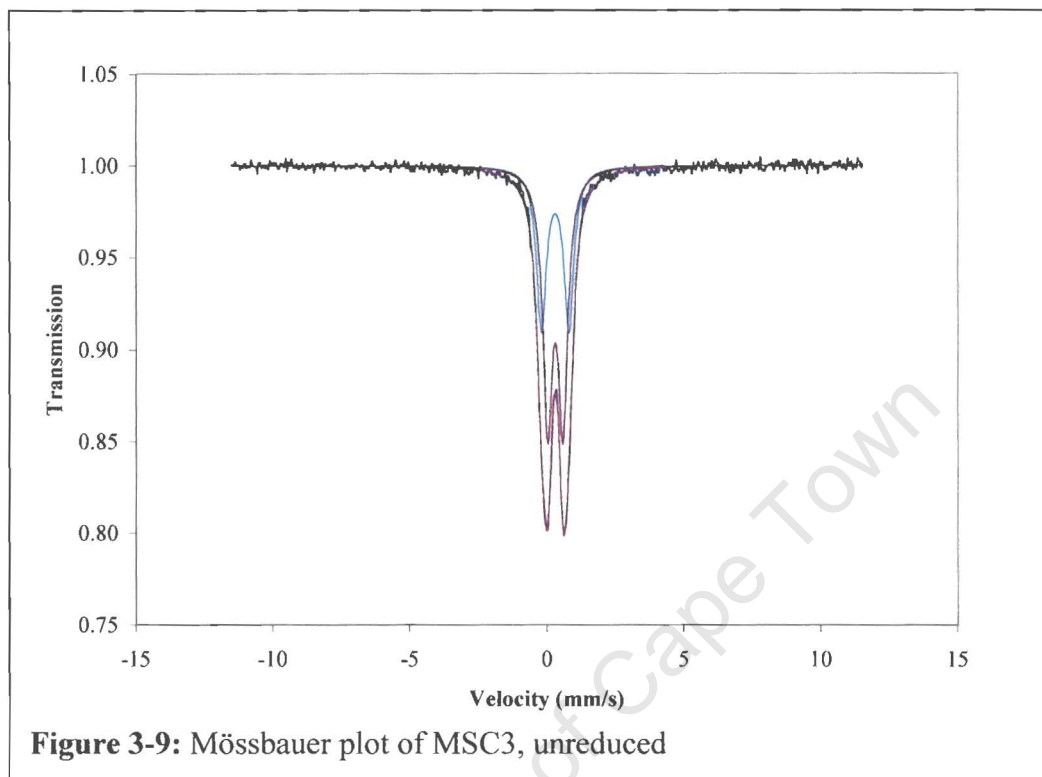


Figure 3-8: TEM micrograph of catalyst MSC3 reduced in 4.8%CO/He at 300°C for 16hrs showing carbonaceous filaments (reduction conditions see Chapter 2.3.2)

3.4.3 Mössbauer Spectroscopy

Mössbauer spectra of the reduced catalyst MSC3 (reduced in various atmospheres) were collected. The spectra of the reduced catalyst are given in Figures 3-9 -3-14.



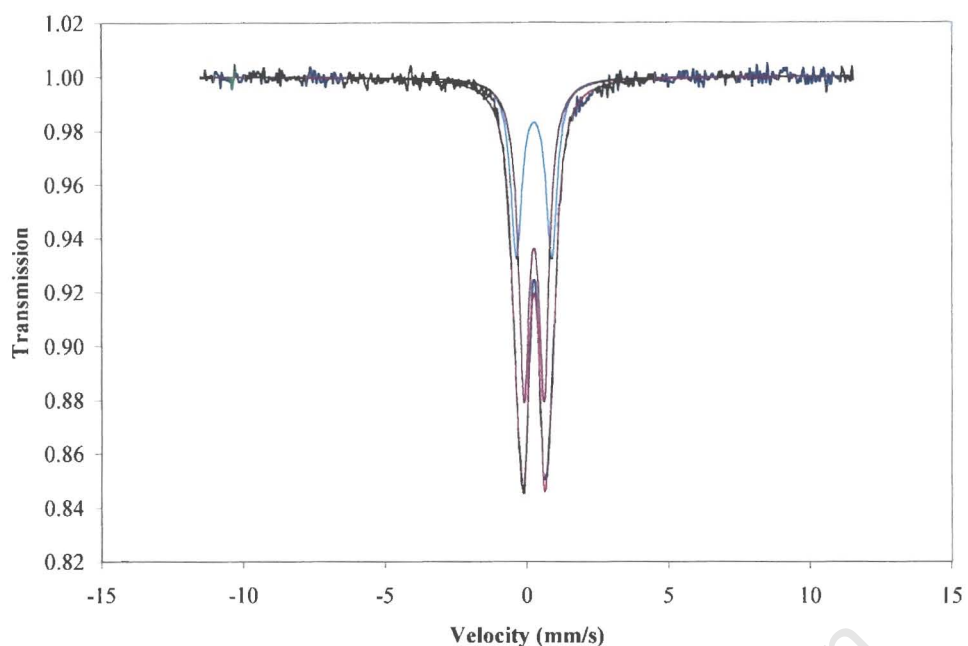


Figure 3-11: Mössbauer plot of MSC3 reduced in 5% H_2 /Ar at 220°C for 16 hours - Sample unloaded in CO_2 , spectrum at 25°C (for reduction conditions see chapter 2.3.2)

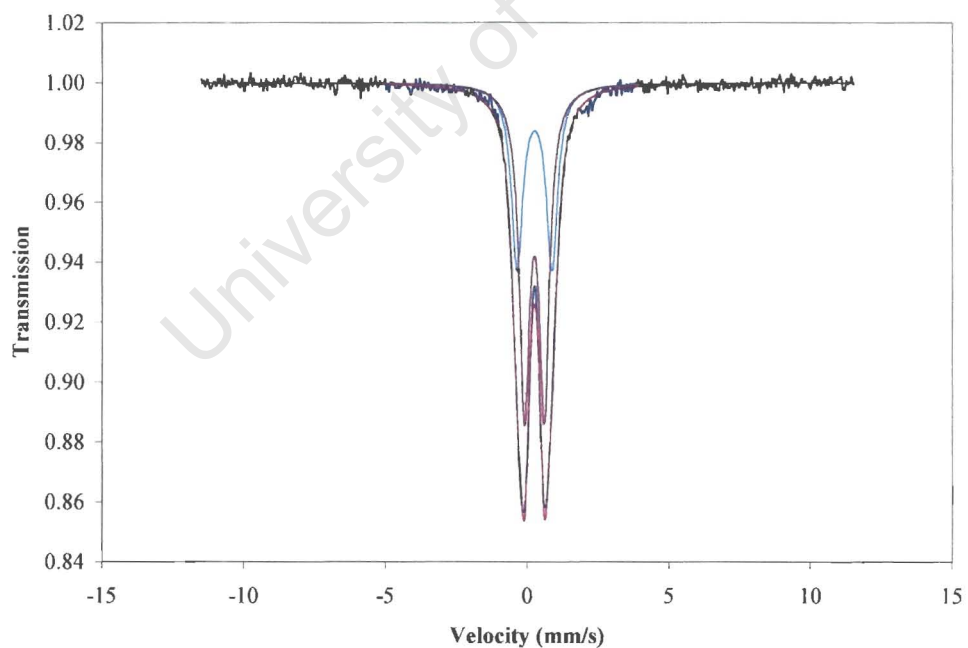
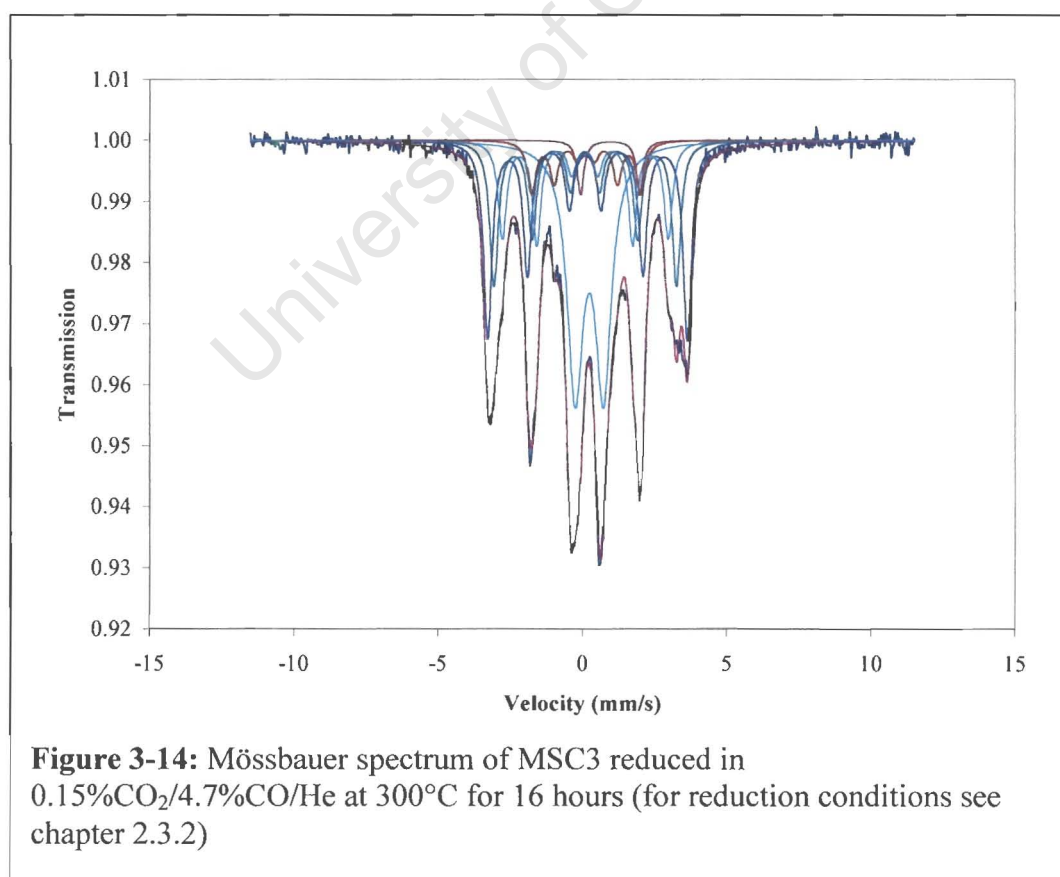
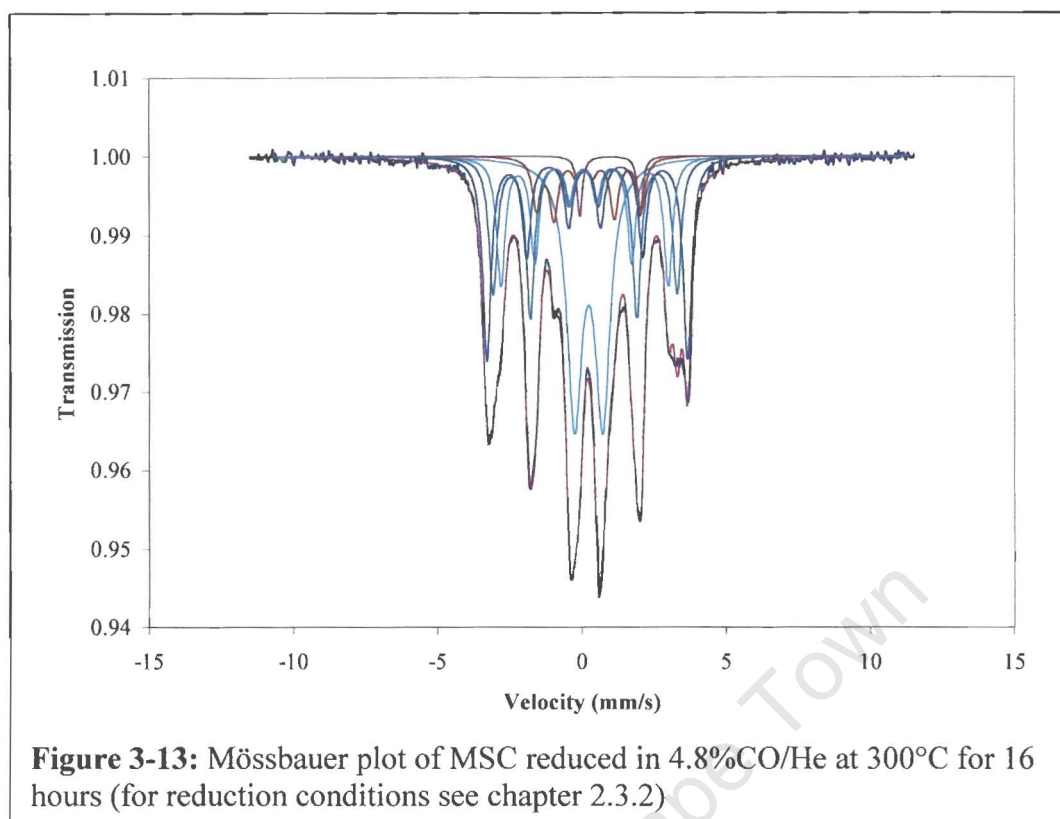


Figure 3-12: Mössbauer plot of MSC3 reduced in 0.15% CO_2 / 4.7% H_2 /Ar for 220°C for 16 hours (for reduction conditions see chapter 2.3.2)



The quantitative evaluation of the Mössbauer experiments are given in Table 3-6.

Table 3-6: Mössbauer results of MSC3 reduced under different conditions

Sample	^a IS (mms ⁻¹)Fe	^a QS (mms ⁻¹)	^b BHF (T)	RA* (Intensity)	Phase
MSC3-R0 (-196°C)	0.40	1.01	-	39.7	Fe ³⁺
	0.40	0.56	-	60.3	Fe ³⁺
MSC3-R1(a) (25°C)	0.36	1.23	-	39.1	Fe ³⁺
	0.35	0.69	-	60.9	Fe ³⁺
MSC3-R1(a) (-196°C)	0.38	1.24	-	35.4	Fe ³⁺
	0.38	0.71	-	64.6	Fe ³⁺
MSC3-R1(b) (25°C)	0.36	1.25	-	38.8	Fe ³⁺
	0.36	0.70	-	61.2	Fe ³⁺
MSC3-R2 (25°C)	0.35	1.23	-	39.2	Fe ³⁺
	0.35	0.70	-	60.7	Fe ³⁺
MSC3-R3 (25°C)	0.24	0.09	21.6	52.2 17.1 2.3 28.4	χ' -Fe _{2.5} C ϵ' -Fe _{2.5} C Fe ²⁺ Fe ³⁺
	0.20	0.05	19.6		
	0.26	0.16	11.2		
	0.18	0.05	18.0		
	1.08	2.09	-		
	0.33	0.98	-		
MSC3-R4 (25°C)	0.24	0.08	21.4	52.0 17.1 2.8 30.1	χ' -Fe _{2.5} C ϵ' -Fe _{2.5} C Fe ²⁺ Fe ³⁺
	0.19	0.06	19.6		
	0.24	0.13	11.7		
	0.18	0.05	17.8		
	1.06	2.05	-		
	0.34	0.98	-		

a±0.02mms⁻¹, b±0.1T, *abundance in % of Fe

The above results show that both the catalyst reduced in 5%H₂/Ar at 220°C and that reduced in 0.15%CO₂/4.8%H₂/Ar in fact, did not reduce. If the catalyst reoxidised, there should have been some Fe²⁺ present as the oxidation of magnetite to hematite is not very favourable. Two passivation methods were used viz. MSC3-R1(a) unloaded into wax and MSC3-R1(b) passivated in CO₂ and both these samples showed no reduction. Reduction in H₂ at 220°C is well known in the literature (Dry 1981 and Bukur 1995(b)). A possible explanation is that the partial pressure of hydrogen was too low due to the fact that a 5%H₂/Ar gas mixture was used (see Table 2-2).

The reduction of the precipitated iron catalyst in 4.8%CO/He and in 0.15%CO₂/4.7%CO/He at 300°C resulted in the formation of Fe²⁺, a mixture of carbides viz. ε'-Fe_{2.2}C and χ-Fe_{2.5}C and some unreduced Fe³⁺. The overall percentage of reduction was very similar for both gas mixtures, being in the order of 70%, of which 52% was as carbides. There was no metallic iron present.

3.5 Fischer-Tropsch synthesis

The Fischer-Tropsch synthesis over catalyst MSC3 was evaluated in various ways. The conversion of CO and H₂ and the yield of the various products were monitored over a period of four days. At low conversion (ca. 20%) the determination of the yield of methane and carbon dioxide could be inaccurate due to the fact that both these compounds are present in the feedgas. The yield of these compounds had to be determined using the difference between the content in the product gas stream and the feed gas stream. The volatile products were analysed (up to C₁₅) using a GC fitted with an FID.

3.5.1 Fischer-Tropsch synthesis using catalyst MSC3 reduced in 5% H₂/Ar

The results of the FT-synthesis using catalyst MSC3 reduced in 5%H₂/Ar at 200°C for 16hrs are shown in Table 3-7. The yield of the organic product compounds after 24 and 96hrs on stream could not be obtained, due to problems with the GC analysis. A carbon balance could thus not be obtained at these times on stream. The carbon balance after 48 and 72hrs on stream was closed to within 8%. The difference might be ascribed to error in the analyses.

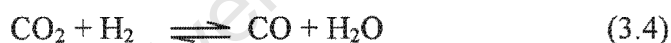
Table 3-7: Results of the Fischer-Tropsch synthesis using catalyst MSC3 reduced in 5% H_2 /Ar at 220°C for 16hrs

Time on stream (hrs)	24	48	72	96
$(H_2/CO)_{inlet}$, mol/mol	2.19	2.15	1.91	2.24
$(H_2/CO)_{usage}$, mol/mol	1.67	2.11	2.10	3.55
X_{CO} , mol-%	32.3	24.6	25.3	22.3
X_{H_2} , mol-%	27.0	25.9	26.5	39.6
Y_{CO_2} , mol-%	2.9	3.9	4.1	-6.8
Y_{CH_4} , mol-%	-0.8	4.4	3.9	-31.5
Y_{C_2+} , mol-%	-	7.9	13.7	-
Wax (mg/h)	2.0	18.3	9.1	4.3
C-balance (%)	-	92	96	-
H_2O acids (mg KOH/g)	-	3.00	2.90	3.08
Chain growth probability, α^1)	-	0.72	0.80	-

¹ Chain growth probability determined from the ASF-plot of the hydrocarbons in the range of C_7 - C_9 hydrocarbons and assuming α_1

The CO-conversion showed a significant drop between the samples after 24 and 48hrs on stream. In the period between 48 and 96hrs the activity remained almost constant.

The H_2 -conversion follows the same trend as the CO-conversion. The determination of the H_2 -conversion after 96hrs on stream seems to be flawed. The usage ratio is 3.98 (based on an inlet H_2/CO of 2.24). The negative CO_2 yield would be an indication of reverse water gas shift. Reverse water gas shift would lead to a higher usage ratio as H_2 is consumed and CO produced via the following reaction:



The inlet flows did indicate a higher CO_2/CO ratio.

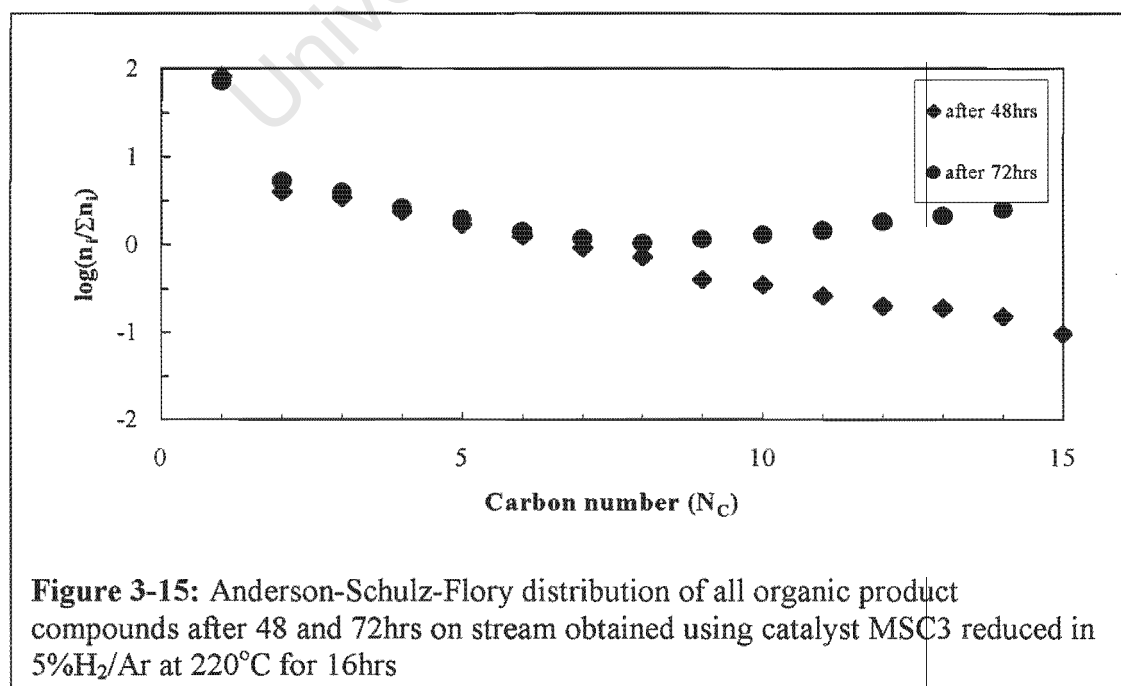
The theoretical usage ratio (assuming reverse water gas shift) was calculated as follows:

$$\text{theoretical usage ratio} = \frac{(2 \cdot \text{CO-consumption} + 3 \cdot \text{CO}_2\text{-consumption})}{\text{CO-consumption}} \quad (\text{Equation 3.1})$$

The second part of the numerator accounts for the H_2 consumed in forming CO from CO_2 then that CO reacting with H_2 to form Fischer-Tropsch products. The theoretical usage ratio was determined to be 2.92. The experimentally determined usage ratio was much higher. Thus, the reverse water gas shift alone cannot account for the results obtained after 96hrs on stream. The carbon balance for this sample is quite good. The error might therefore lie in the determination of the hydrogen content in the feed and/or product gas stream.

The carbon dioxide yield increased steadily over the duration of the Fischer-Tropsch synthesis. The negative value obtained after 96hrs might indicate CO_2 -conversion. However, CO_2 -conversion in the presence of CO on iron-based catalysts is generally low (Riedel *et al.* 1999). A more plausible explanation might be an error in the analysis, since CO_2 -yield was determined by the difference in the content in the inlet and outlet flows. Only the product analysis after 48hrs and 72hrs on stream yielded positive methane yields. Based on these two values the methane yield did not change much.

The chain growth probability (α) was calculated from the Anderson-Schulz-Flory plot (see Figure 3-15). The ASF plot of the sample after 72hrs on stream deviates from the normal ASF plot. Repeating the analysis gave the same result. It is possible that product that had “knocked out” in the bubbler of the ampoule system could have vaporised during sampling (the ampoule is under vacuum) and it would have been included in the product spectrum thus causing a deviation in the heavier fraction. Subsequently, the water in the bubbler was replaced regularly.



Methane does not follow the Schultz-Flory distribution. This is usually seen in Fischer-Tropsch synthesis and might indicate additional reaction pathways for methane formation. The chain growth probability (α) of the hydrocarbons increased between 48hrs and 72hrs on stream from 0.72 to 0.80 (see Table 3-7). This may not be significant as the ASF plot for the sample taken after 72 hours showed an anomalous product spectrum. Although not included in the table, the alpha value for the oxygenates after 48 hours on stream was 0.61. A lower chain growth probability for the oxygenates is usual in Fischer-Tropsch (Erich 1990).

Figure 3-16 shows the olefin content in the fraction of hydrocarbons as a function of carbon number for the products obtained after 48hrs on stream. The total olefin content is high for all the carbon numbers except C₂. This is due to the reactivity of the ethane, which thus may undergo secondary reactions (e.g. hydrogenations) fast (Schulz and Claeys 1999). At higher carbon numbers, the olefin content decreases slightly with increasing carbon number. The high value at C₉ must be ascribed to an error in the analysis.

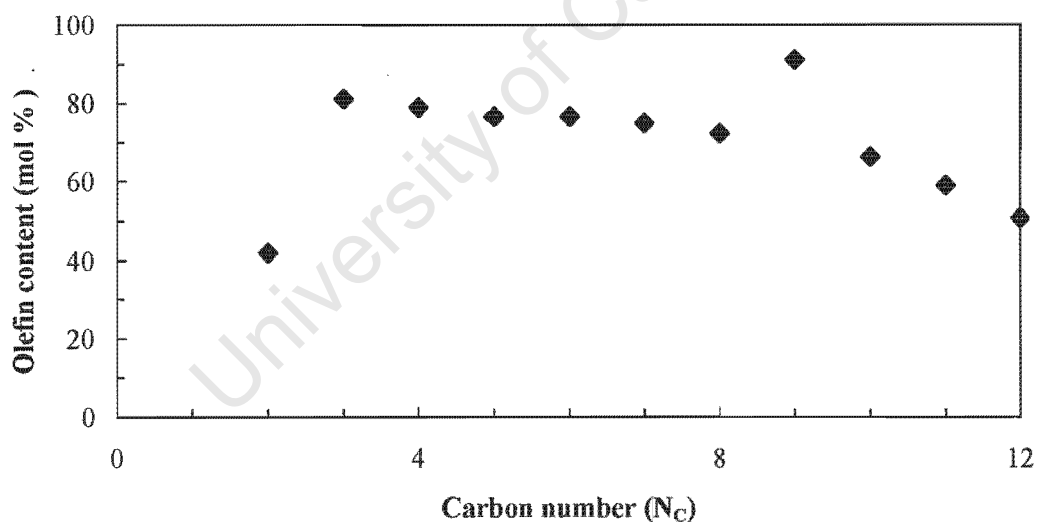


Figure 3-16: Olefin content in the fraction of hydrocarbons after 48hrs on stream obtained using catalyst MSC3 reduced in 5%H₂/Ar at 220°C for 16hrs

Figure 3-17 shows the 1-olefin content in the fraction of linear olefins as a function of carbon number for the products obtained after 48hrs on stream. The 1-olefin content in the range of C₄-C₉ is high (ca. 93 mol-%). At carbon numbers larger than 9 the 1-olefin content decreases rapidly. This could be due to the higher probability for re-adsorption of the longer chains, which will lead to secondary reactions such as double bond isomerisation (Schulz and Claeys 1999).

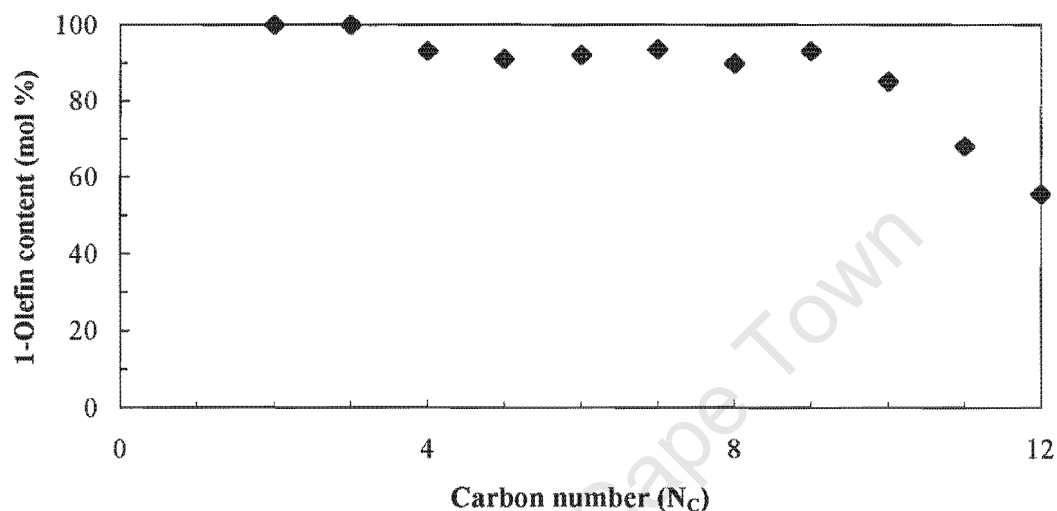


Figure 3-17: 1-olefin content in the fraction of linear olefins after 48hrs on stream obtained using catalyst MSC3 reduced in 5%H₂/Ar at 220°C for 16hrs

The oxygenate content in the product as a function of carbon number is depicted in Figure 3-18. Oxygenates are alcohols, aldehydes and ketones. Acids are not included in the oxygenates, since these figures are solely based on the GC-FID results. The oxygenate content is low and shows a sharp maximum at C₂. Above C₆, any oxygenates present were below the detection limit of the GC.

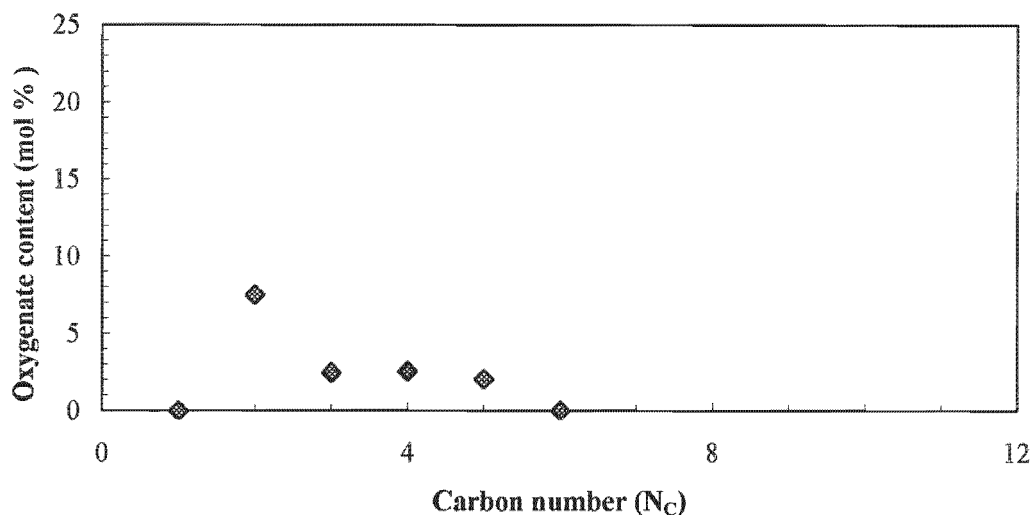


Figure 3-18: Oxygenate content in the Fischer-Tropsch product after 48hrs on stream obtained using catalyst MSC3 reduced in 5% H_2 /Ar at 220°C for 16hrs

3.5.2 Fischer-Tropsch synthesis using catalyst MSC3 reduced in 0.15% CO_2 /4.7% H_2 /Ar

The results of the synthesis run are summarised in Table 3-8.

Table 3-8: Results of the Fischer-Tropsch synthesis using catalyst MSC3 reduced in 0.15% CO_2 /4.7% H_2 /Ar at 220°C for 16hrs

Time on stream (hrs)	24	48	72	96
(H_2/CO) _{inlet} , mol/mol	1.94	1.94	1.96	1.90
(H_2/CO) _{usage} , mol/mol	0.83	0.92	1.50	1.55
X_{CO} , mol-%	11.3	6.4	12.0	19.2
X_{H_2} , mol-%	4.8	3.0	9.2	15.6
Y_{CO_2} , mol-%	3.9	3.7	3.2	2.7
Y_{CH_4} , mol-%	8.3	10.4	7.1	3.5
$Y_{\text{C}_{2+}}$, mol-%	4.0	8.8	9.6	5.2
Wax (mg/h)	-	14.7	28.7	31.6
C-balance (%)	105	116	108	92
H_2O acids (mg KOH/g)	-	2.70	2.71	2.53
Chain growth probability, α^1	0.77	0.77	0.79	0.80

¹ Chain growth probability determined from the ASF-plot of the hydrocarbons in the range of C₃-C₉ hydrocarbons and assuming α_1

The experimentally measured activity of the catalyst after 48hrs on stream (as measured by the CO conversion) does not fit the overall trend of an increasing activity with time on stream. The carbon balance of this sample is much too high (116 C-%). This might be due to a problem during sampling or the GC analysis. In general, the CO conversion increases from 11.2% to 19.2% between 24hrs and 96hrs on stream. This would indicate that the catalyst is still in its induction phase. Over the same four periods, the methane yield decreased from 8.3% to 2.7% and the chain growth probability increases from 0.77 to 0.80. This can be seen in the wax yield. The increase in the chain growth probability may cause a maximum in the yield of volatile C₂₊ - product compounds.

The CO₂ yield decreases with time on line. This indicates a decrease in the water gas shift reaction. As increasing water gas shift reaction is often associated with a deactivating catalyst, this supports the conclusion that the catalyst is still in the induction phase.

Figure 3-19 shows the Anderson-Schulz-Flory distribution of all organic product compounds. With increasing time on stream an increase in the chain growth probability was observed.

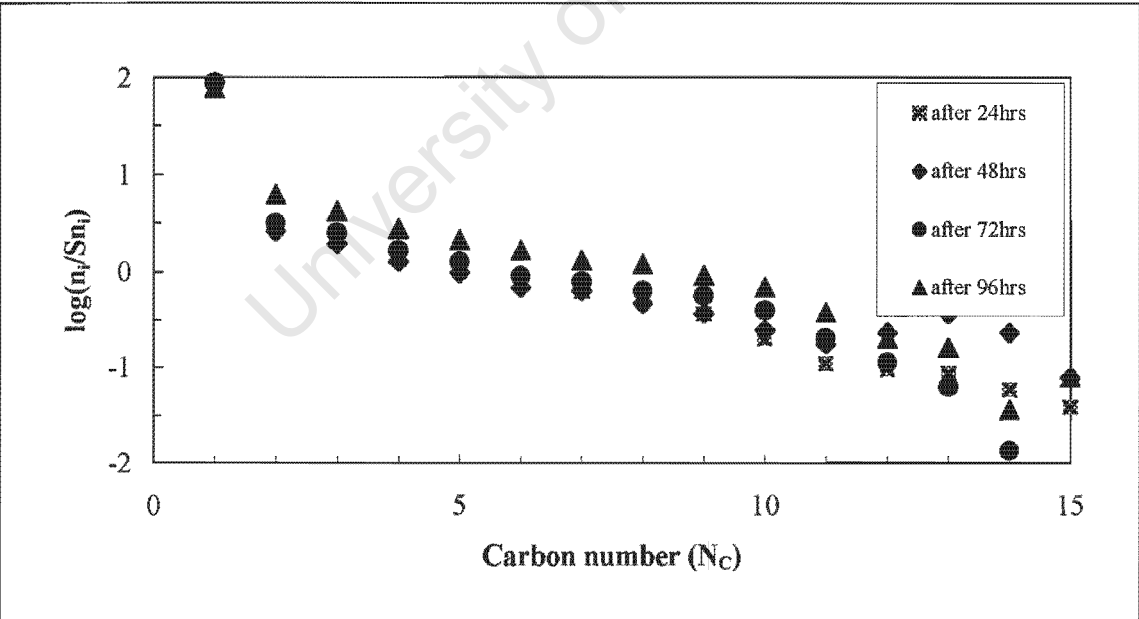


Figure 3-19: Anderson-Schulz-Flory distribution of all organic product compounds at various times on stream obtained using catalyst MSC3 reduced in 0.15%CO₂/4.7%H₂/Ar at 220°C for 16hrs

Figure 3-20 shows the olefin content in the fraction of hydrocarbons after 24hrs on stream. The olefin content did not change significantly with time on stream (see Appendix 5). The olefin content shows the usual behaviour, low at C₂, passing a maximum at C₃ and decreasing with increasing carbon number. The olefin content in the fraction of C₂-hydrocarbons is surprisingly high (70 mol%). This might indicate a low extent of secondary reactions in this system.

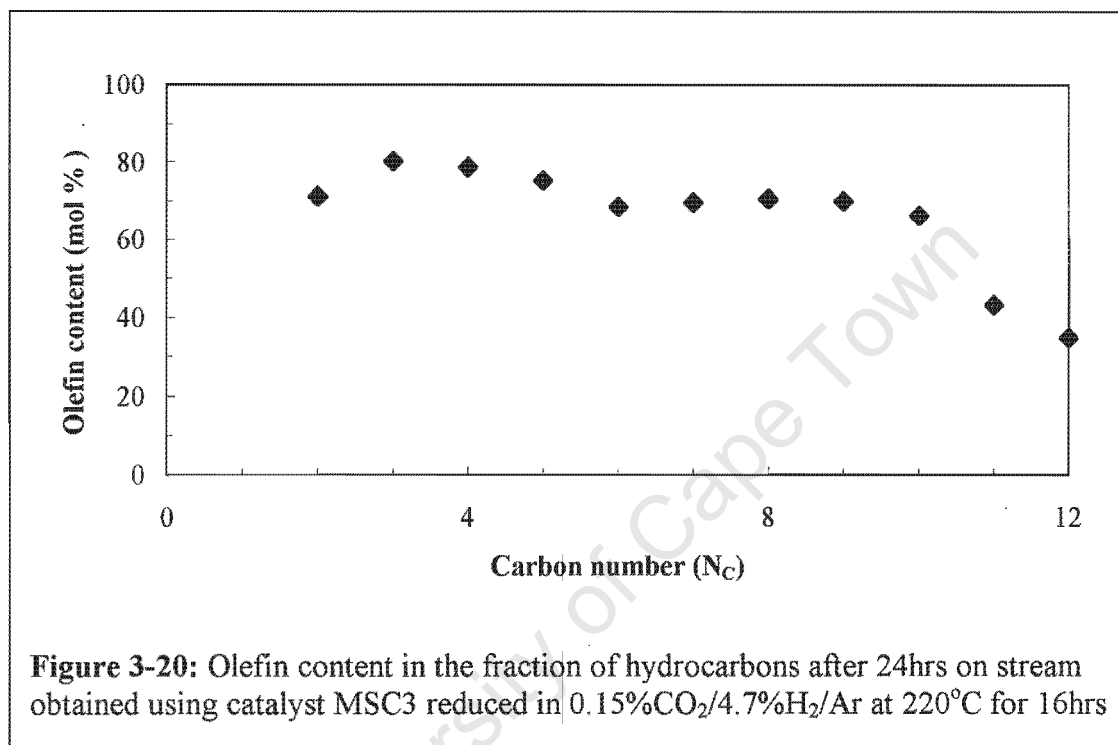
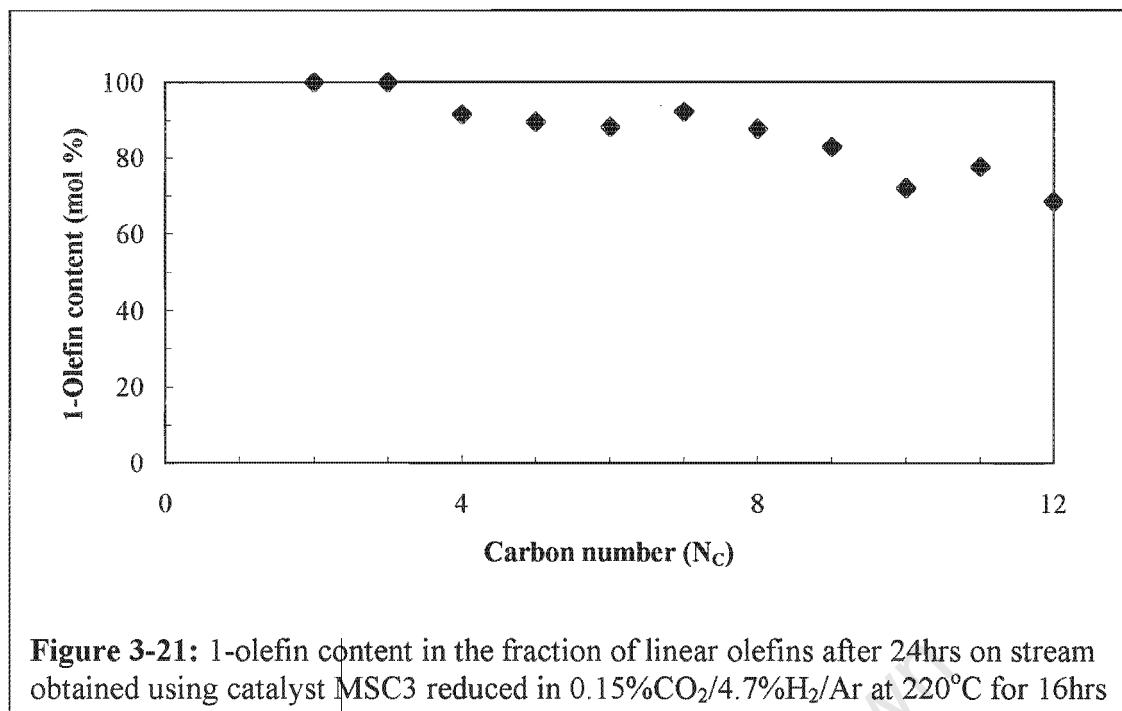
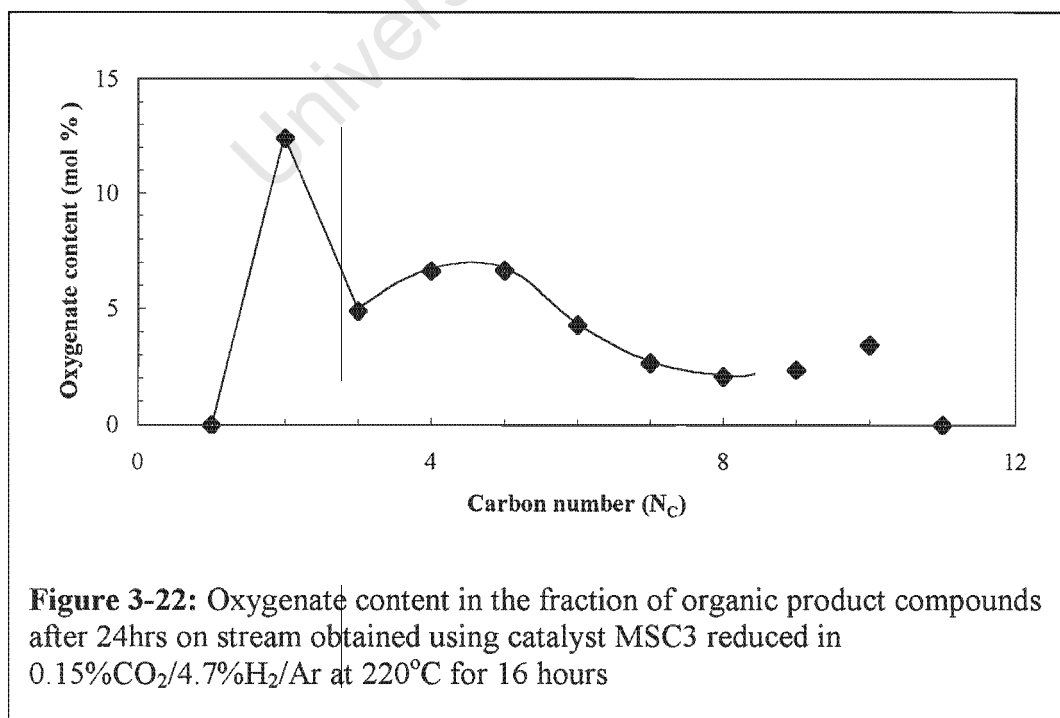


Figure 3-21 shows the 1-olefin content in the fraction of linear olefins as a function of carbon number after 24hrs on stream for catalyst MSC3 reduced in 0.15%CO₂/5%H₂/Ar at 220°C for 16hrs. The 1-olefin content did not change much with time on stream (see Appendix 5). The 1-olefin content is constant between C₄ and C₇ (ca. 90 mol-%). The 1-olefin content decreases for larger carbon numbers, due to the higher probability for re-adsorption leading amongst others, to double bond isomerisation.



The oxygenate content in the product after 24hrs on stream as a function of carbon number is shown in Figure 3-22. The oxygenate shows a typical behaviour (van Steen 1993), low at C₁, high at C₂, passing a minimum at C₃, followed by a maximum at C_{5/6}. The C_(n+1) aldehyde is formed by the addition of CO (Dictor and Bell 1986) to the adsorbed C_n alkyl species and is in equilibrium with the C_(n+1) alcohol (Dry 1981). We therefore have a direct relationship between the C_n hydrocarbon and the C_{n+1} oxygenates selectivity.



3.5.3 Fischer-Tropsch synthesis using catalyst MSC3 reduced in 4.8%CO/He

The results of the Fischer-Tropsch synthesis using catalyst MSC3 reduced in 4.8%CO/He at 300°C for 16 hours are shown in Table 3-9.

Table 3-9: Results of the Fischer-Tropsch synthesis using catalyst MSC3 reduced in 4.8%CO/He at 300°C for 16hrs

Time on stream (hrs)	24	48	72	96
(H ₂ /CO) _{inlet} , mol/mol	2.12	2.14	2.27	2.22
(H ₂ /CO) _{usage} , mol/mol	1.59	1.20	4.20	2.33
X _{CO} , mol-%	23.1	21.0	6.0	16.7
X _{H₂} , mol-%	17.4	11.8	11.1	17.6
Y _{CO₂} , mol-%	6.6	6.5	-6.7	4.8
Y _{CH₄} , mol-%	7.6	8.0	-18.5	8.0
Y _{C₂+} , mol-%	12.7	15.2	3.3	6.1
Wax (mg/h)	0.0	0.4	0.0	5.5
C-balance (%)	104	109	72	97
H ₂ O acids (mg KOH/g)	4.08	4.51	3.68	3.58
Chain growth probability, α_1^1	0.64	0.67	0.79	0.80

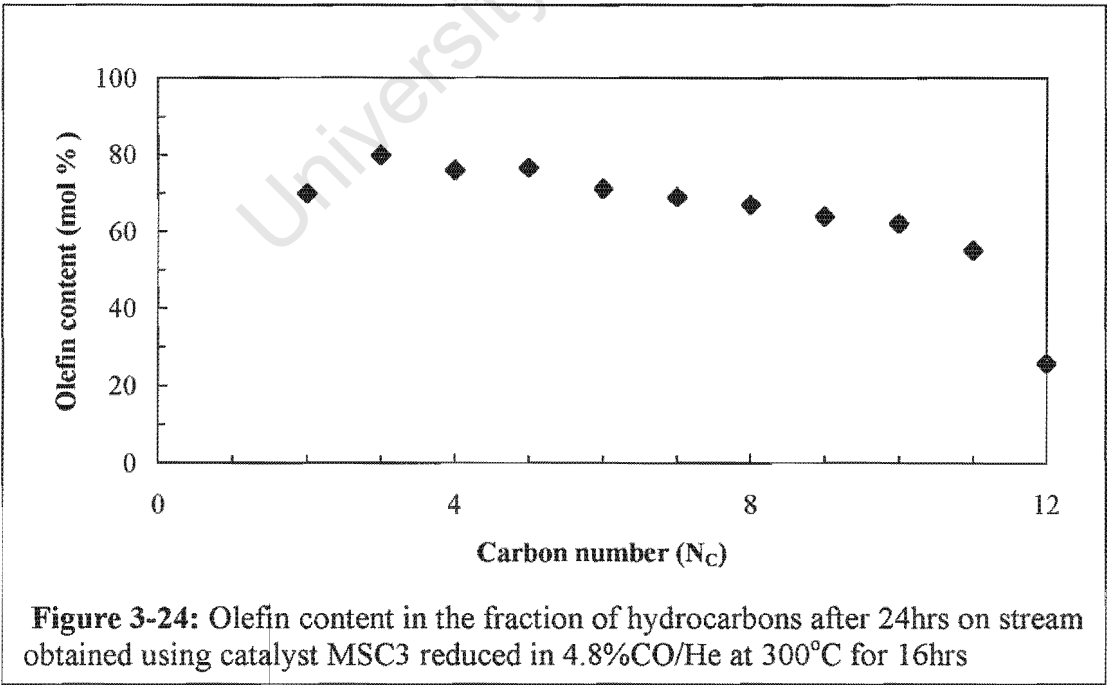
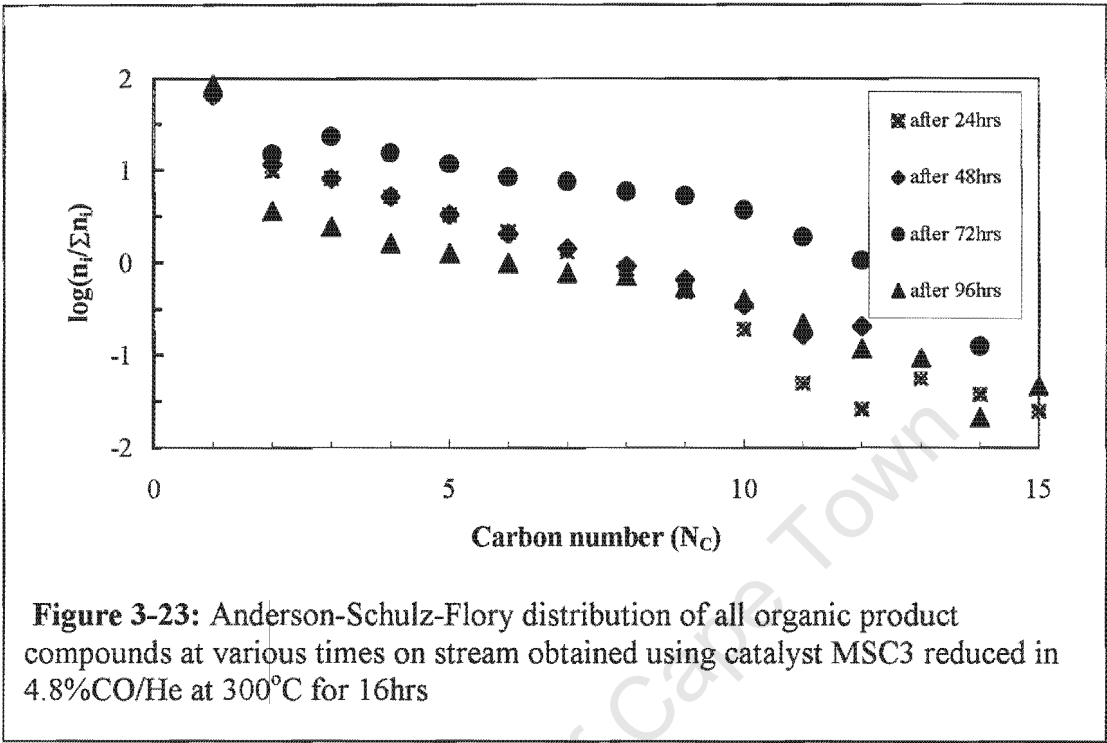
¹ Chain growth probability determined from the ASF-plot of the hydrocarbons in the range of C₃-C₉ hydrocarbons and assuming α_1

The results of after 72hrs on stream do not fit the overall trend of the run. A negative CO₂ and methane yield was obtained, due to the low conversion. The mass balance is also very poor. If we do not include this analysis in our run then the trend is a slight decrease in CO conversion with time. The catalyst is deactivating. The usage ratio after 96hrs on stream is 2.33 compared to 1.59 after 48hrs on stream (based on gas flows). A usage ratio of higher than two would imply that we should have reverse water gas shift. This is not the case, as the CO₂ yield is positive. The methane yield remains constant throughout the run while the chain growth probability (α) increases substantially with time. This is not reflected in the C₂+ yield due to the decreasing CO conversion of the catalyst.

No to very little wax was collected in the hot trap during the run. It has also been noted in the previous runs that very little wax is collected during the first 48hrs. This does not necessarily mean that less wax is being produced during this time than later in the run, but is more likely due to the fact that the wax is filling the pores of the catalyst and the catalyst bed. It is just more clearly seen in this run as the wax yield is lower due to lower chain

growth probability. The wax colour in this run was visually very poor (darkish brown) and the acid values were higher than in the previous two runs.

The hydrocarbon analyses are shown in Figures 3-23 – 3-29.



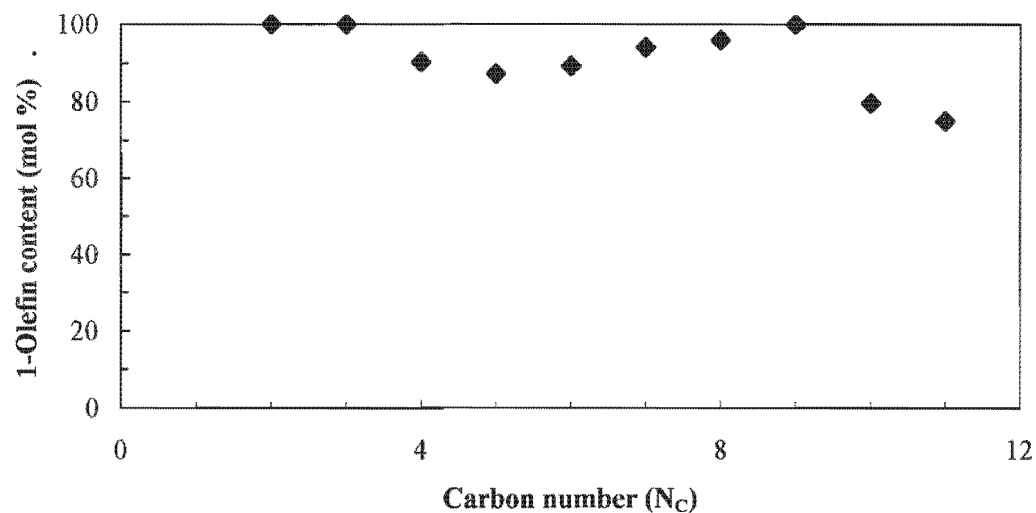


Figure 3-25: 1-olefin content in the fraction of linear olefins after 24hrs on stream obtained using catalyst MSC3 reduced in 4.8%CO/He at 300°C for 16hrs

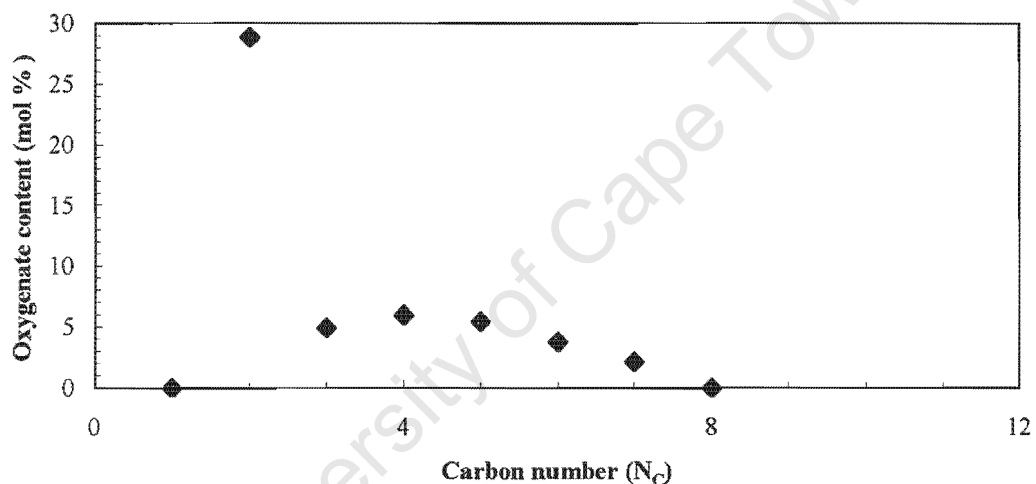


Figure 3-26: Oxygenate content in the fraction of organic product compounds after 24hrs on stream obtained using catalyst MSC3 reduced in 4.8%CO/He at 300°C for 16hrs

Both the olefin content and the 1-olefin content are high. There is a decrease in olefin content with increasing carbon number but this is not as evident in the 1-olefin content. The oxygenate content is low with the exception of C₂ which is extremely high relative to the other carbon numbers. This trend was particularly obvious in the last 48 hours. Again, there is an increase then decrease in oxygenate content with increasing carbon number.

3.5.4 Fischer-Tropsch synthesis using catalyst MSC3 reduced in 0.15%CO₂/4.7%CO/He

The results of the Fischer-Tropsch synthesis using catalyst MSC3 reduced in 0.15%CO₂/4.7%CO/He at 300°C for 16 hours are shown in Table 3-10.

Table 3-10: Results of the Fischer-Tropsch synthesis using catalyst MSC3 reduced in 0.15%CO₂/4.7%CO/He at 300°C for 16hrs

Time on stream (hrs)	24	48	72	96
(H ₂ /CO) _{inlet} , mol/mol	2.38	1.98	2.01	2.09
(H ₂ /CO) _{usage} , mol/mol	10.85	0.75	1.76	1.58
X _{CO} , mol-%	2.4	31.1	50.7	30.1
X _{H₂} , mol-%	11.1	11.8	44.4	22.9
Y _{CO₂} , mol-%	-7.9	10.8	4.9	9.6
Y _{CH₄} , mol-%	-24.9	13.2	-5.0	12.2
Y _{C₂+} , mol-%	19.0	18.0	13.9	6.3
Wax (mg/h)	-	5.4	24.7	34.2
C-balance (%)	84	111	63	98
H ₂ O acids (mg KOH/g)	-	4.31	4.51	4.34
Chain growth probability, α_1	0.63	0.64	0.66	0.67

¹ Chain growth probability determined from the ASF-plot of the hydrocarbons in the range of C₃-C₉ hydrocarbons and assuming α_1

The mass balances of this synthesis run are very poor with only the result after 96 hours being within 90 – 110%. The analysis after 24 hours gave a negative CO₂ yield and both the analyses after 24 hours and 48 hours gave negative methane yields. The mass balances for these two analyses were particularly bad (84 and 63% respectively). If one were to accept the result after 96 hours, then the conversion at this point is higher than the previous run (catalyst reduced at 300°C in 4.8%CO/He for 16 hours). The methane yield is higher than in the previous run and the chain growth probability (α) starts low as in the previous run but does not increase substantially with time on stream.

The initial TCD analysis of this run did not give good results. The problem was traced to an incorrect composition given for the calibration gas.

Again, the wax colour in this run was visually very poor (darkish brown) and the acid values were even higher than in the previous run.

Figure 3-27 shows the Anderson-Schulz-Flory distributions of the organic compounds with time on stream.

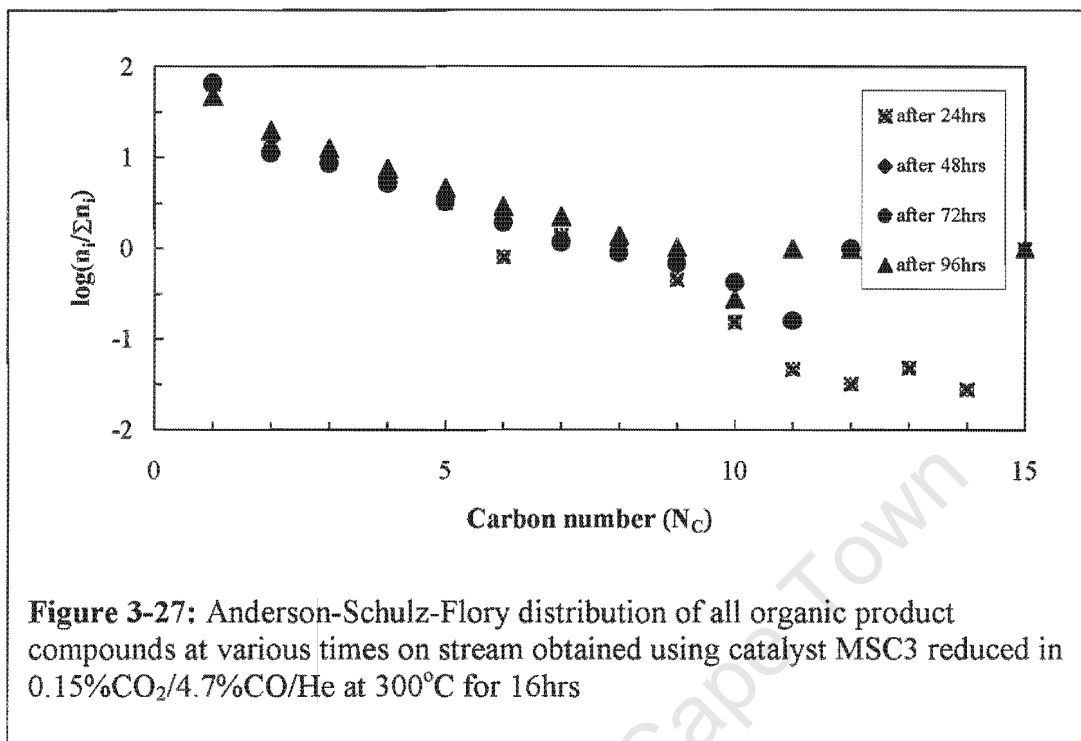
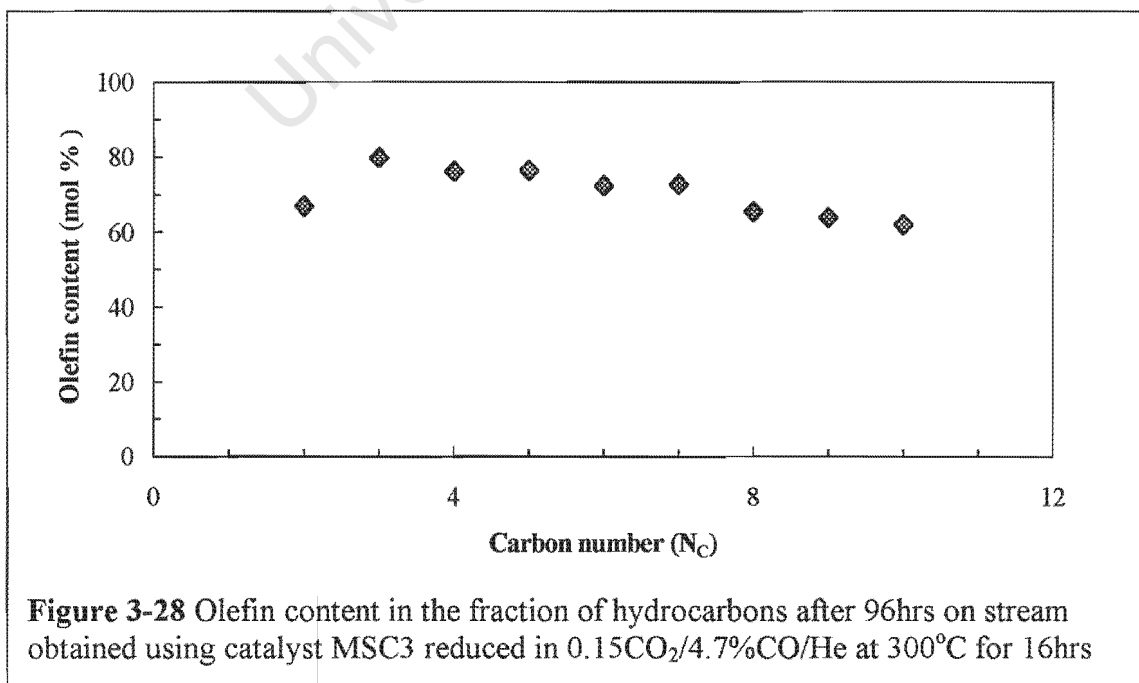
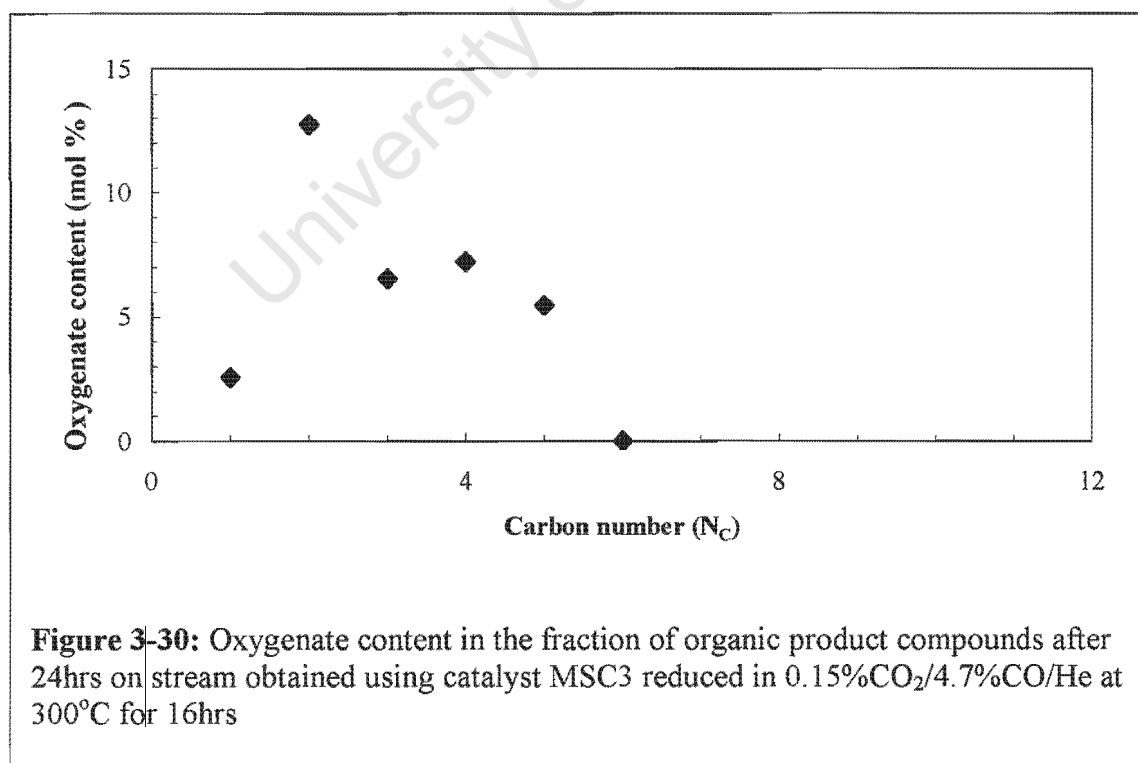
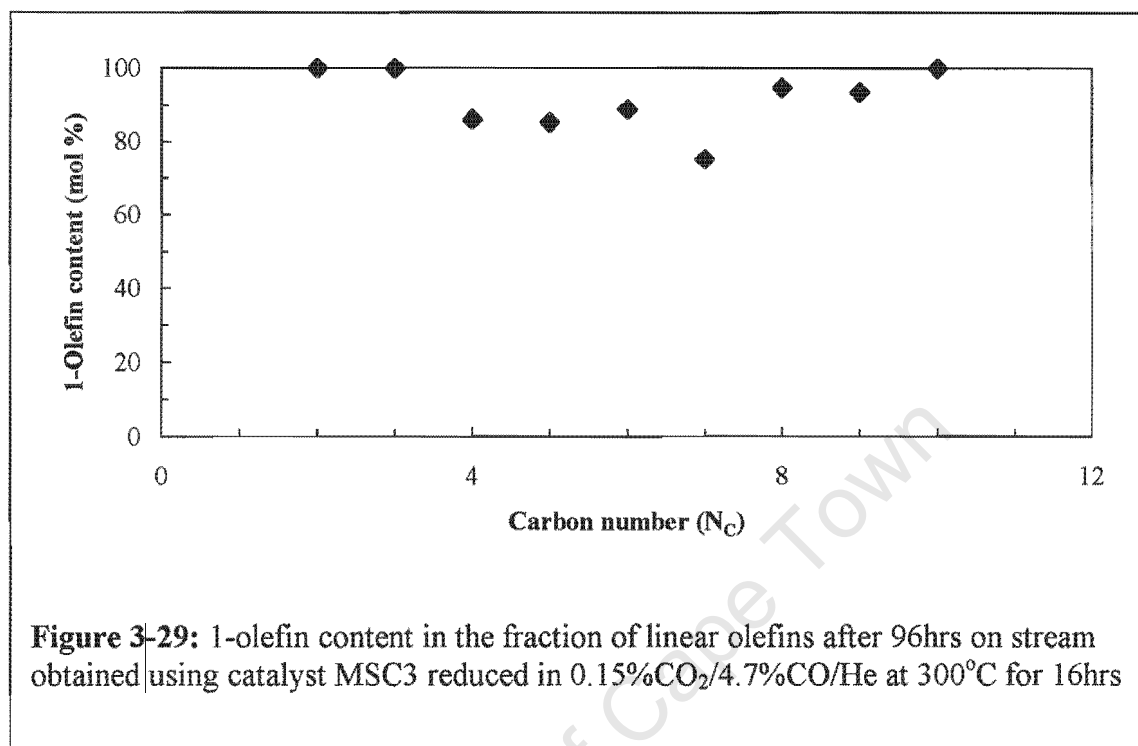


Figure 3-28 shows the olefin content in the fraction of hydrocarbons after 48hrs on stream. The olefin content did not change significantly with time on stream (see Appendix 5). The olefin content shows the usual behaviour, low at C₂, passing a maximum at C₃ and decreasing with increasing carbon number.



The 1-olefin content in the total linear alpha olefins is again very high (see Figure 3-29). There is some scatter in the data but there would appear to be no definite decrease in 1-olefins with increasing carbon number.



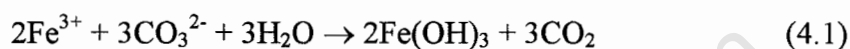
The oxygenate content is low (see Figure 3-30) with the same trend seen as in the previous runs.

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Chapter 4 - Discussion

4.1 Preparation of a precipitated iron catalyst (Ruhchemie)

The results indicate that the preparation of a precipitated Ruhchemie catalyst precursor is not straight forward (see Chapters 3.1 and 3.2). The addition time was difficult to control in the laboratory due to the foaming of the slurry. It would appear that CO₂ is evolved during the precipitation. This could be due to the following reaction:



This may also explain the non-stoichiometry of the reaction. If the CO₂ dissolves in the solution, it could react with the Na₂CO₃ in the following reaction:



This could decrease the effective alkalinity of the solution.

The filtration of the slurries also needs to be carefully controlled, particularly during the second filtration where it is very difficult to control the amount of K₂O removed. It may be an option to consider using a different source of silica as binder and adding the potassium as a salt such as KNO₃. This would allow for much better repeatability of the catalyst precursor preparation as it can be seen that even the amount of precipitate to be filtered or the volume of water added has an effect on the final K₂O levels. What is interesting to note is that even if a stoichiometric amount of HNO₃ is added, too low levels of K₂O can be obtained. This would indicate that the potassium is not only being removed as KNO₃ but possibly also as K-waterglass. This is supported by the fact that the SiO₂ levels of MSC1 are slightly low. The silica level of MSC3 also decreased after it was reslurried and filtered the second time to lower the K₂O level.

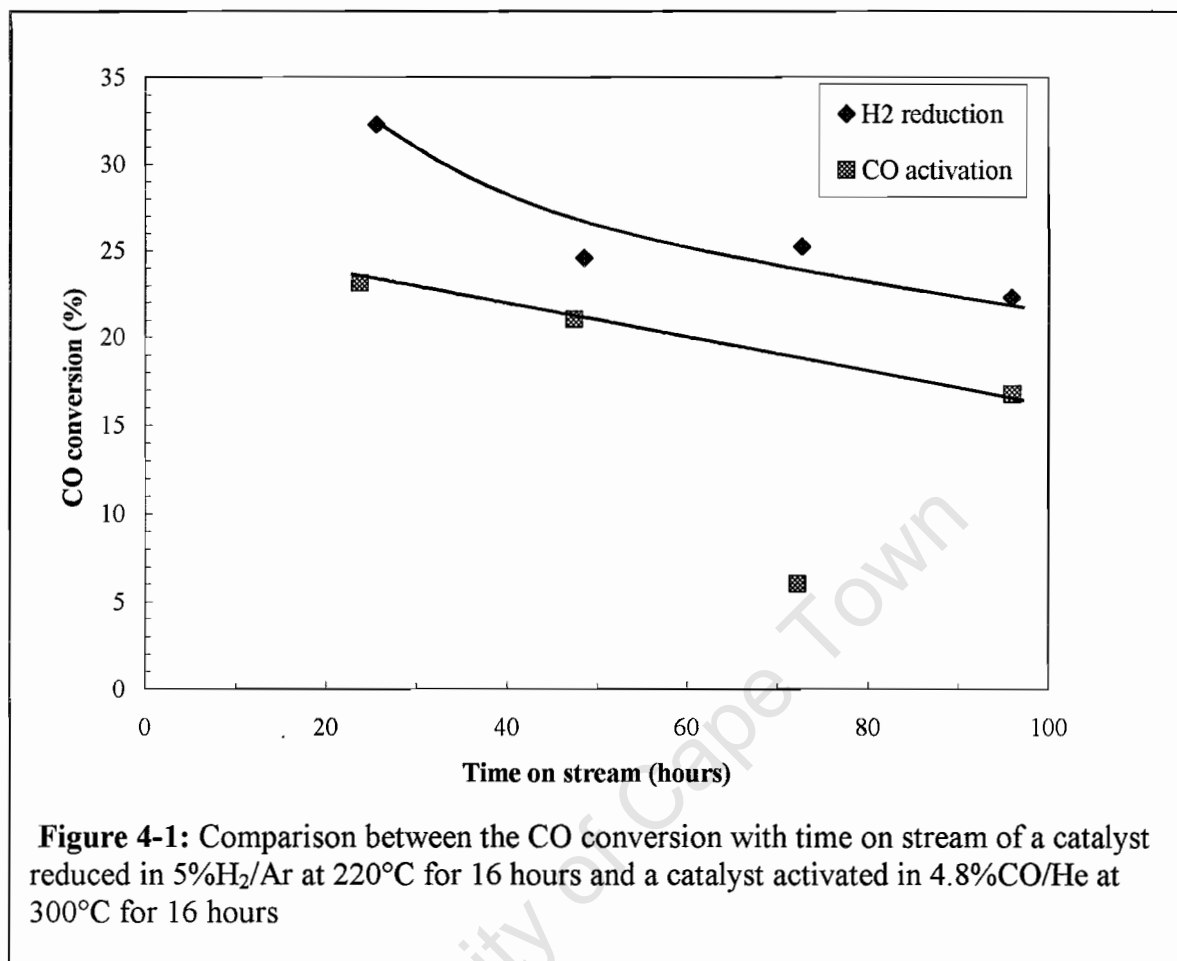
4.2 The effect of gas composition on reduction of a precipitated iron catalyst - CO versus H₂

The TPR profiles of the catalyst reduced in H₂ and CO show that the reduction of the catalyst precursor proceeds differently. These reductions are discussed in Chapter 3.3. Suffice to say that the overall reduction of the catalyst was greater with H₂ activation than when CO was used. Although it could be said that this was due to the reverse Boudouard reaction above approximately 550°C, limiting reduction to the lower temperatures, we were still able to achieve 86% reduction when CO₂ was present. It is therefore principally possible to get a higher degree of reduction with carbon monoxide as a reducing agent.

From the isothermal reductions, a different picture is drawn. Here the degree of reduction is higher for the CO-activated catalyst relative to the catalyst reduced in hydrogen. This trend is not surprising as we chose what has been considered optimum conditions in the literature for each gas type. Therefore, the CO activation was performed at a much higher temperature than the H₂ reduction. What was surprising from the Mössbauer results, however, was the complete lack of reduction at 220°C when the catalyst was reduced in H₂. There was a definite change in colour of the catalyst from reddish-brown to nearly black and the surface area decreased from 346m²/g to 159m²/g. There must have been some sintering of the catalyst. The TEM micrographs do show a lattice fringe in the 4.8Å region. Both magnetite and maghemite have a d-spacing in this region (4.87Å and 4.82Å respectively – see Appendix 4) but the colour of magnetite is known to be black and that of maghemite to be light brown (Schwertmann and Cornell 1991). It is possible that there may have been some reduction but the sample reoxidised during the sample preparation for Mössbauer analysis. The samples were crushed in air during this preparation and not crushed for the TEM analyses. The CO-activated sample showed a high degree of reduction i.e. ~70% of which 52% was in the form of carbides. The TEM micrographs of the catalyst reduced in CO showed a high surface carbon formation.

There are also differences in behaviour when comparing the behaviour of the two catalysts during Fischer-Tropsch synthesis (see Chapters 3.5.1 and 3.5.3). The activity of the catalyst reduced in H₂ is slightly higher than that of the catalyst activated in CO (based on the CO

conversion and omitting 72 hours on stream for the CO-activated catalyst – see Figure 4 - 1). The activity of both catalysts, however, would appear to be deactivating slightly.



The methane yield and selectivity is also higher (almost double) for the CO activated catalyst when compared to the H₂ reduced catalyst and in the CO-activated catalyst, this yield and selectivity increases with time on stream.

The chain growth probability (α) is also lower in the CO-activated catalyst but it does, however, increase with time. We are unable to compare this to the H₂-reduced catalyst due to incomplete hydrocarbon analyses.

The water gas shift activity (based on the CO₂ yield and selectivity) of the catalyst activated in CO is higher than that of the catalyst reduced in H₂ and the acid formation is higher. It would appear that acid formation is may be linked with the water gas shift activity. The

water gas shift reaction is known to occur on the oxidised sites of a catalyst. If the link is due to the active site on the catalyst (i.e. both WGS and acid formation occurring on oxidised sites), then we can speculate that the CO-activated catalyst is more oxidised than the H₂-reduced catalyst or that more oxidised sites are available for reaction on the CO-activated catalyst than on the H₂-reduced catalyst. A possible explanation could be that, while the H₂-reduced catalyst is further reduced in synthesis gas during the first 24 hours of synthesis, the CO catalyst is not (possibly due to diffusion constraints and blockage of the oxidised sites by carbon formation).

The trends above i.e. lower activity (based on CO conversion), higher methane selectivity, water gas shift activity and acid formation are not in general agreement with literature when H₂-reduction and CO-activation are compared (Bukur *et al.* 1989, 1995(b)).

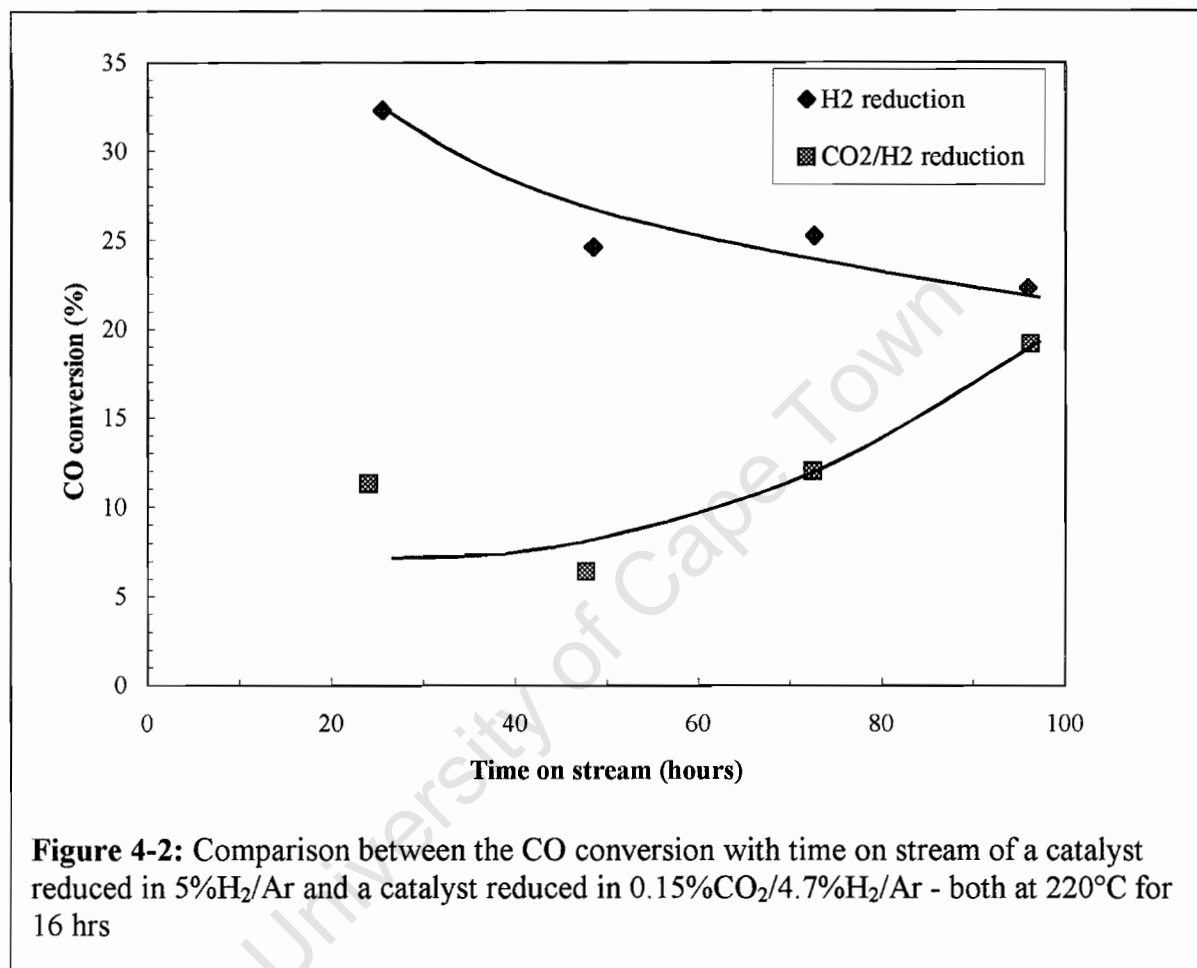
4.3 Effect of CO₂ as an impurity on the reduction of a precipitated iron catalyst

4.3.1 Effect of CO₂ as an impurity on the reduction in H₂

The temperature programmed reduction experiments reducing the catalyst in 5%H₂/Ar and 0.15%CO₂/4.7%H₂/Ar respectively, show that while the CO₂ did not affect the profile of the TPR, it did have a negative effect on the overall degree of reduction. Again, these reductions are discussed in Chapter 3.3.

CO₂ had no effect on the measured characteristics of the catalyst after reduction in H₂. There was no difference in the BET surface area, the transmission electron microscope images or in the degree of reduction (as measured by Mössbauer electron spectroscopy) after reduction. This may be attributable to the fact that no reduction was seen and would imply that even if there were to be a difference, we would not have seen it with the reduction conditions we used viz. 220°C for 16 hours. The difference in the degree of reduction that we saw in TPR was over a much shorter time span and over a temperature range.

Although no differences were seen in the characteristics of the catalyst after the isothermal reduction, there was still a noted difference in the behaviour of the catalyst during Fischer-Tropsch synthesis (see Sections 3.5.1 and 3.5.2). The first is in the activity of the catalyst (see Figure 4-2). The activity of the catalyst reduced in the 0.15%CO₂/4.7%H₂/Ar initially had a much lower activity (based on CO-conversion) than the catalyst reduced when there was no CO₂ impurity present.



While the methane selectivity was higher for the catalyst reduced in the presence of CO₂, it decreased with time on stream. The chain growth probability (α) was stable.

Similarly, the water gas shift reaction (based on CO₂ selectivity and not yield), decreased with time on stream. This is not significantly reflected in the acid value. Again, the final CO₂ selectivity is similar to that of the catalyst reduced in 5%H₂/Ar.

The behaviour of the catalyst reduced in 0.15%CO₂/4.7%H₂/Ar would appear to be that of a catalyst less reduced than that of the catalyst reduced when no CO₂ was present. This is concluded from the fact that the synthesis performance, while poorer initially, is very similar after 96 hours on stream. Synthesis runs of longer duration would be required to confirm this.

A possible explanation could be that flow of both reducing gas mixtures was higher during the reduction before synthesis than the reduction before characterisation due to limitations of the equipment (see Chapter 2.3.5). It may be possible that the effect seen during the TPRs manifested itself during the reductions before synthesis.

4.3.2 Effect of CO₂ as an impurity on the activation in CO

The temperature programmed reduction experiments reducing the catalyst in 4.8%CO/He and 0.15%CO₂/4.7%CO/He respectively, again showed that the CO₂ did not affect the profile of the TPR. Surprisingly, it did however have a positive effect on the overall degree of reduction. This result is discussed in Chapter 3.3.

The characteristics of the catalyst after isothermal activation (16 hours at 300°C) were also very similar regardless of whether CO₂ was present in the activating gas or not. In this case it may be that the activating conditions were too severe or of too long a duration to reflect the advantage that was seen in the temperature-programmed reductions when CO₂ was present. One parameter that was not measured was that of carbon formation. There was no obvious difference in carbon formation when looking at the TEM micrographs, but transmission electron microscopy is more qualitative than quantitative.

Major differences in Fischer-Tropsch synthesis performance when CO₂ is absent and present during activation is not evident (see Chapters 3.5.3 and 3.5.4). This is in contrast to the reductions in H₂ when CO₂ is absent and present. The activity of the catalyst activated in 0.15%CO₂/4.7%CO/He is slightly higher than the catalyst activated in 4.8%CO/He (based on CO conversion - see Figure 4-3). The analyses after 24 and 72 hours on stream are not included in this discussion due to the poor mass balances.

Although the methane yield is higher when the CO₂ was present in the activating gas, there is very little difference in the methane selectivity. Similarly, there is little difference in the water gas shift activity (based on CO₂ selectivity). The acid values are marginally higher.

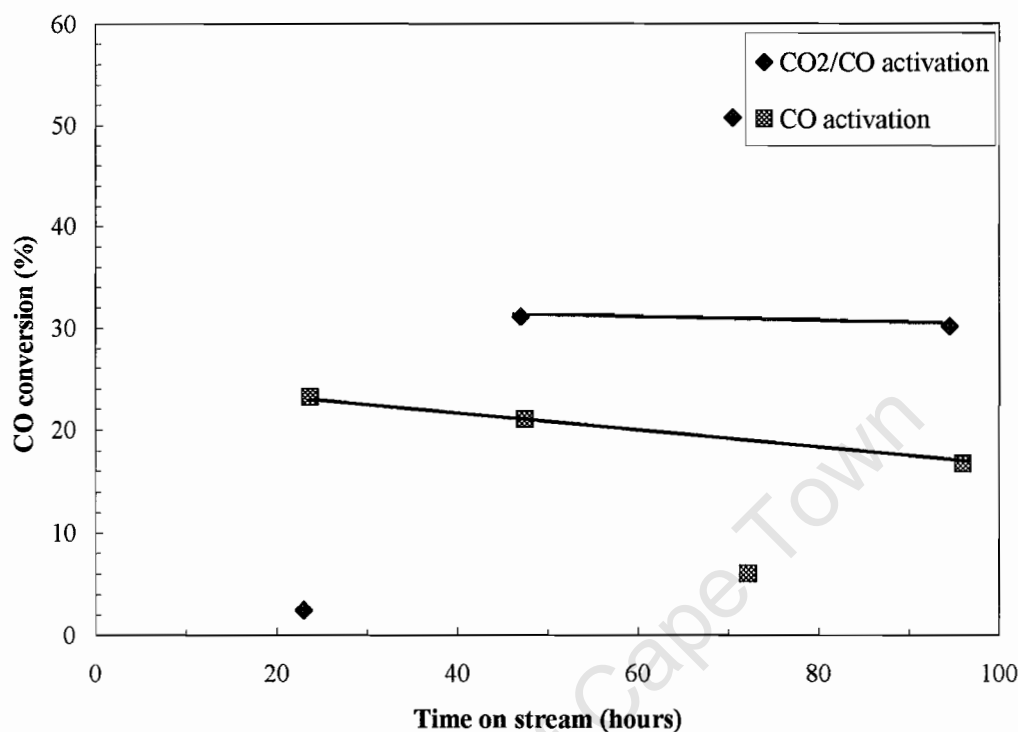


Figure 4-3: Comparison between the CO conversion with time on stream of a catalyst reduced in 4.8%CO/He and a catalyst reduced in 0.15%CO₂/4.7%CO/He - both at 300°C for 16 hrs

The only difference that may have some significance is the fact that the chain growth probability (α) does not increase when CO₂ has been present as an impurity in the activating gas. It might be speculated that the catalyst reduced in carbon monoxide/carbon dioxide mixture will result in a final catalyst structure, which is physically identical with a working Fischer-Tropsch catalyst.

Chapter 5 - Conclusions

CO₂ as an impurity in the activating gas was found to have an influence on the activation of precipitated iron catalysts.

The greatest influence was seen in the temperature-programmed reduction where it had a negative influence on the H₂ reductions and surprisingly, a positive influence on the CO activation. It is postulated that the latter could be due to the retarding of carbon formation thereby allowing further reduction of iron species.

The conditions chosen for the isothermal reductions viz. 16 hours at 220°C for H₂ reduction and 16 hours at 300°C for CO activation did not show any differences with respect to the catalyst characteristics when CO₂ was present. In the case of the H₂ reduction, this probably due to the fact the conditions were too mild. The converse i.e. too severe conditions is probably true for the CO-activation. There were however, major differences in the catalyst characteristics after the H₂ reduction and CO activation. The CO-activated catalyst sintered more and had a high degree of reduction with the major phase being χ -carbide. The H₂-reductions would appear not to have reduced the catalyst at all, although some sintering did occur.

The reductions prior to synthesis were performed in a higher flow than those before catalyst characterisation. The H₂-reduced catalyst initially had a lower activity when CO₂ had been present in the synthesis gas, but this increased with time on stream while the methane and CO₂ selectivity decreased. When no CO₂ was present, the catalyst behaviour was stable. There was little difference in the synthesis performance of the catalyst activated in CO and that of the catalyst activated in CO₂-containing CO.

The fact that there is so little difference between the synthesis performance when CO₂ is present during the CO activation and yet there is quite a significant difference in synthesis performance when CO₂ is present during the H₂ reduction is probably due to the fact that

with the H_2 reduction, the conditions were not reducing enough. This allowed for further reduction to occur. With the CO activations, the conditions were too severe.

Trends seen between the catalysts activated in H_2 and CO were a lower activity for the latter with a higher methane selectivity, higher water gas shift activity (based on CO_2 selectivity) and a higher acid value. This could be due to the fact that the H_2 -reduction was performed at a low temperature viz. 220°C .

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Appendix 1:

The reaction products will interfere with the thermal conductivity detector due to either the thermal conductivity e.g. CO₂ (see Table 2-3) or due to the sensitivity of the detector to the gas e.g. H₂O. Therefore, they need to be removed from the gas stream before analysis.

Table A1 gives the boiling points of the gases that are found or could be found as part of our TPR analyses.

Table A1: Boiling points of common gases (Lide 1998)

Gas	Boiling point (°C)
Ar	-185.9
N ₂	-195.8
He	-268.9
H ₂	-252.9
CO	-191.5
H ₂ O	100.0
CO ₂	-78.4*
CH ₄	-161.4

*sublimation point

In the case of H₂/Ar, a dry ice/acetone bath was used as a trap for the product H₂O. Based on boiling points of the gases, a liquid nitrogen trap would also knock out the CO₂ and possibly any CH₄ that may be formed. This was desired but argon's boiling point is 10°C higher than that of N₂. There was a strong possibility that the Ar would be knocked out. This was proved true by running the gas through an empty cell at room temperature until a stable baseline was obtained. First an acetone/dry ice bath was placed on line. Despite an initial jump (probably due to the initial change in temperature affecting the flow), the baseline stabilised at the same point. The dry ice acetone bath was then replaced with a liquid nitrogen trap. There was a definite shift upwards in the baseline and the run had to eventually be discontinued due to an unacceptable pressure build up in the cold trap. The results are shown in Figure A1(a).

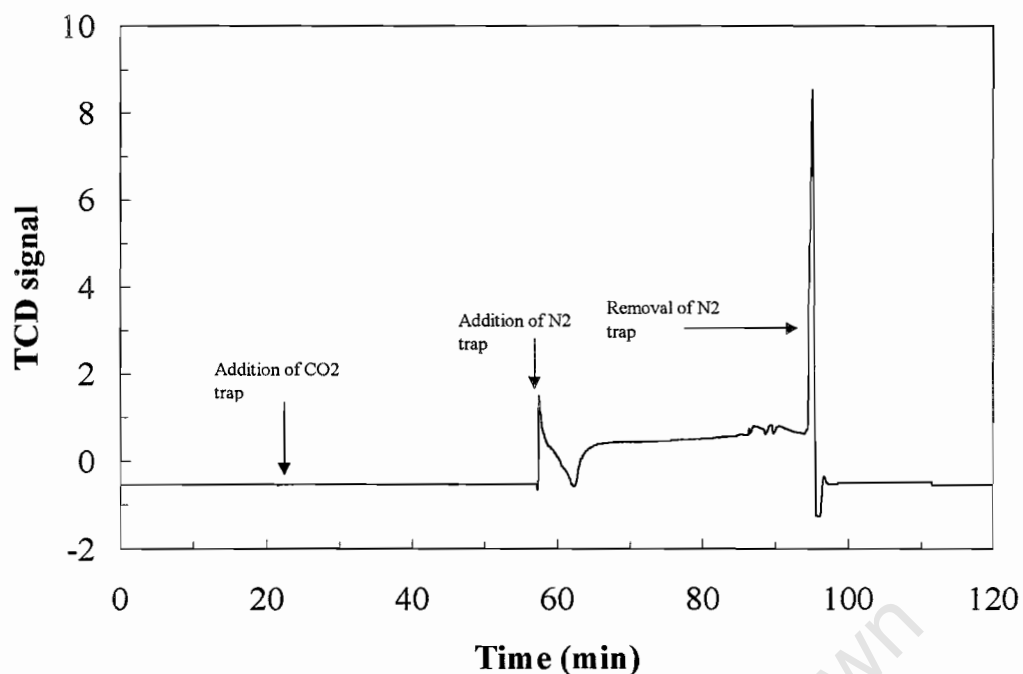


Figure A1(a): Baseline check for H_2/Ar gas mixtures

The conclusion was that while the acetone/dry ice bath was not expected to knock out CO_2 , the liquid nitrogen trap knocked out the Ar. The acetone/dry ice bath was used for the H_2 reductions.

One would expect that liquid nitrogen could also knock out CO which has a boiling point 5°C greater than N_2 . A similar baseline experiment was done on the CO/He mix as Bukur (Bukur 1995(a)) has reported using a liquid nitrogen trap for CO/He TPRs. There was no shift in the baseline on the addition of a liquid nitrogen trap to the experiment (see Figure A1(b)). A liquid nitrogen trap was therefore used in the CO TPRs. In this way, the product CO_2 was knocked out.

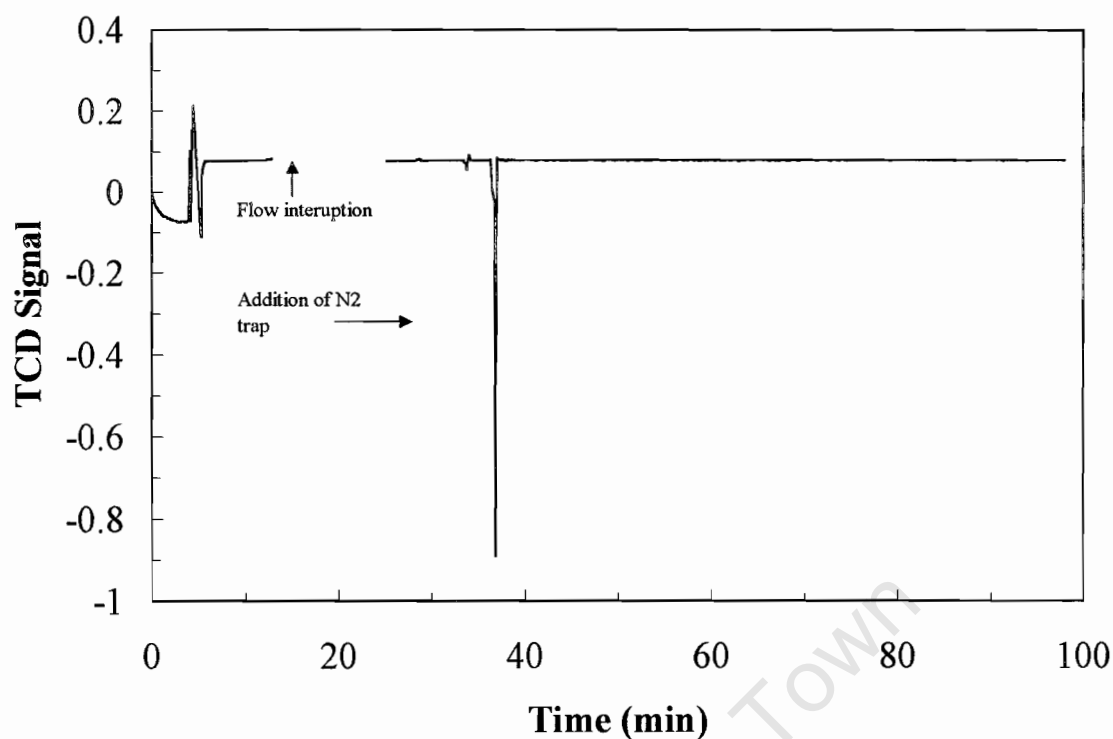


Figure A1(b): Baseline check for CO/He gas mixtures

This is due to the difference in partial pressure of the two gases, where Ar is 95% of the gas mixture and CO only 4.8%, that allows us to use a liquid nitrogen for the CO TPRs but not for the H₂ TPRs. The boiling point of CO at 0.052 bar (i.e. equivalent to a 5.2%CO/He mixture) would be -210.0°C, which is below the temperature of liquid nitrogen (Perry 1984). It is only likely to be trapped from levels of 52% in the gas mixture. Ar, on the other hand, could already be knocked out from levels of 26%.

Appendix 2:

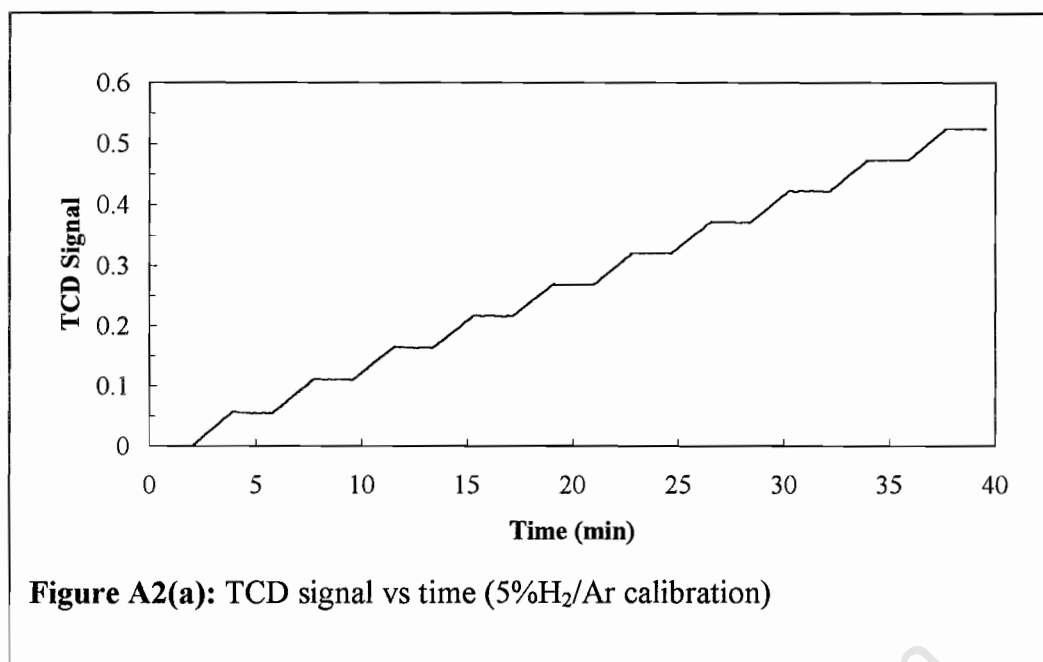
The Autochem 2910 was calibrated for each individual gas mix. The calibration was performed using an empty sample cell. The calibration programme can be seen in Table A2.

Table A2: Calibration programme

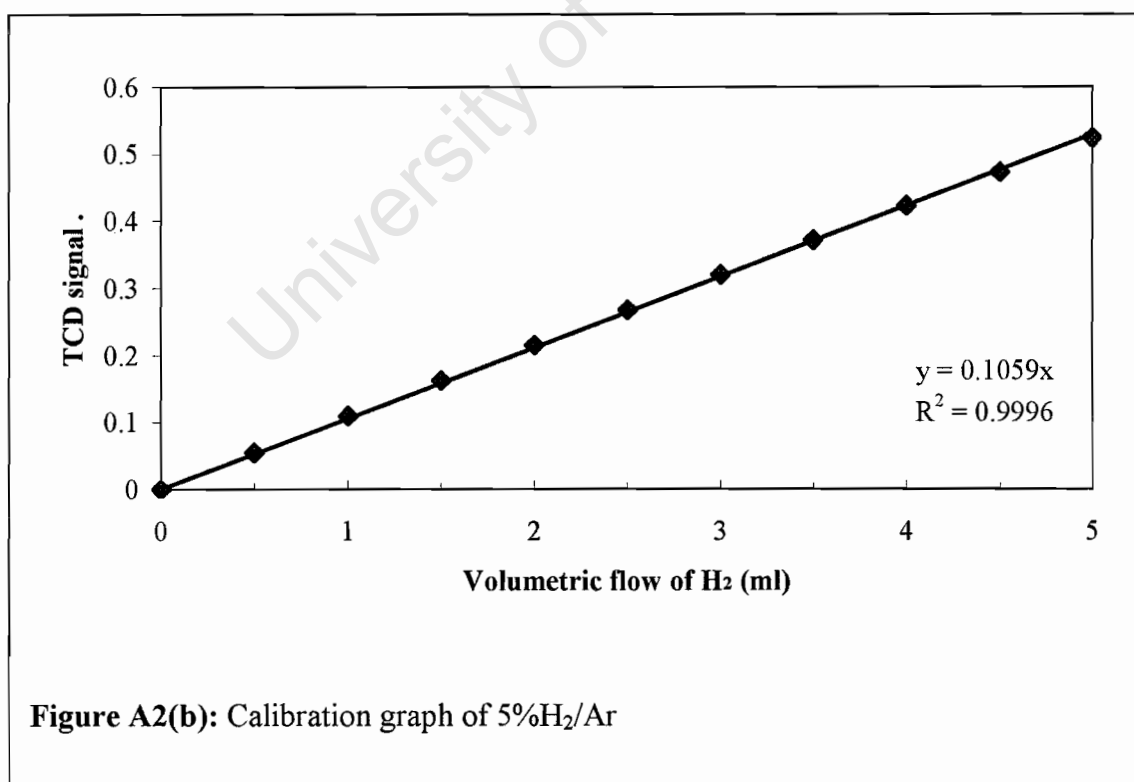
Step	Inert gas flow (nml/min) (1. Ar or 2. He)	Gas mixture flow (nml/min) (1. H ₂ /Ar or 2. CO/He)
1.	50	0
2.	45	5
3.	40	10
4.	35	15
5.	30	20
6.	25	25
7.	20	30
8.	15	35
9.	10	40
10.	5	45
11.	0	50

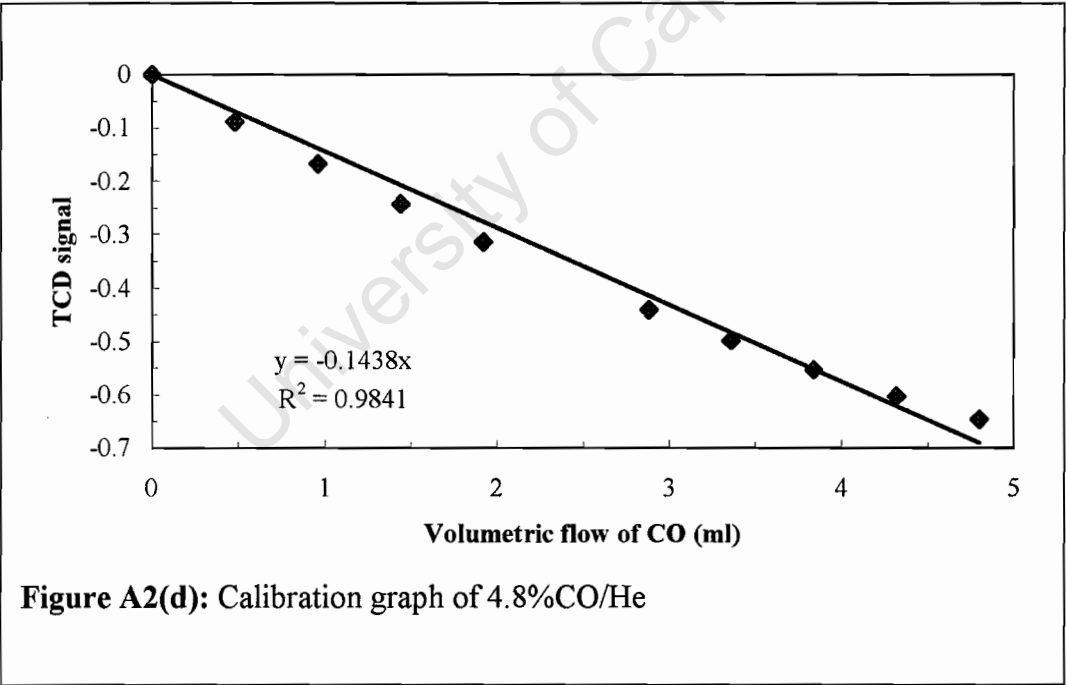
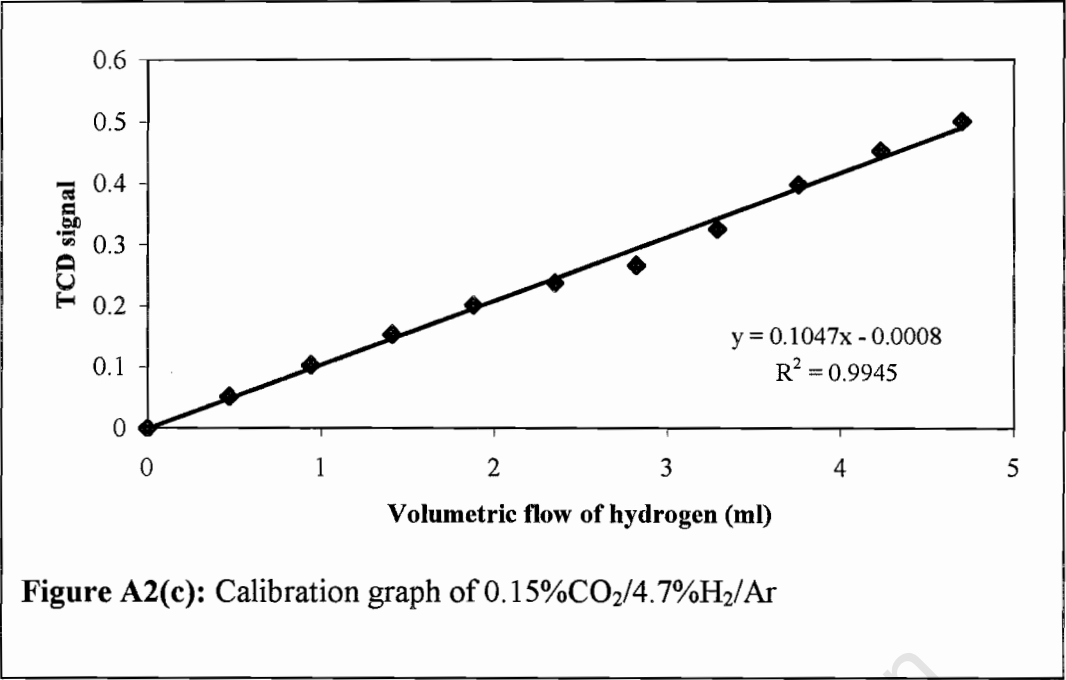
A dry ice/acetone cold trap was used during the H₂/Ar calibrations and a liquid nitrogen cold trap during the CO/He calibrations. This was to ensure the same conditions as during the TPR analyses.

Figure A2(a) is an example of such a calibration where the TCD signal is shown with time. This was for the 5%H₂/Ar gas mixture.



The final calibration graphs obtained were plotted as the flow of the gas mixture versus time. Thus the TCD signal could be related to the flow of the reducing gas in the total gas flow. The calibration graphs can be seen in Figures A2(b) – A2(e).





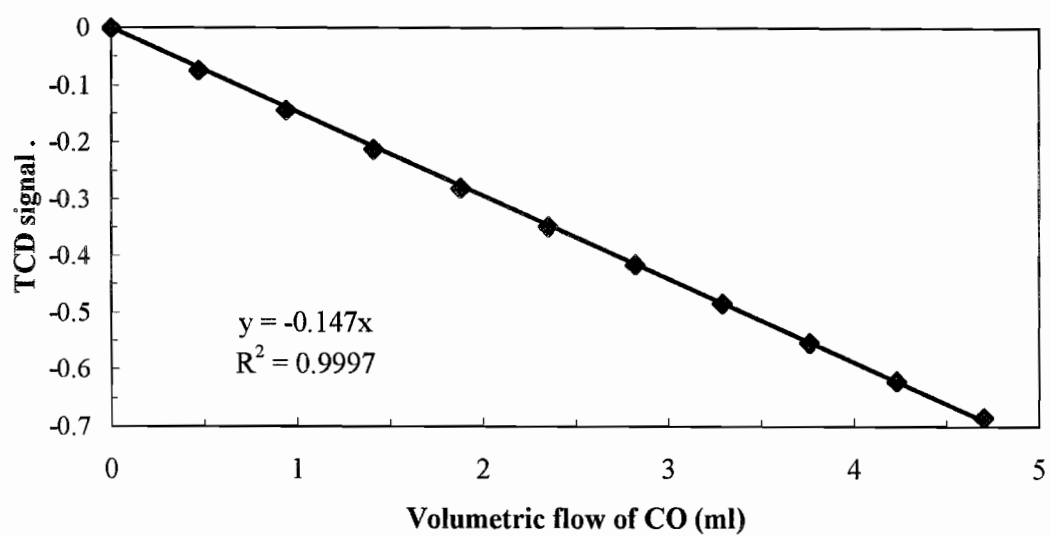
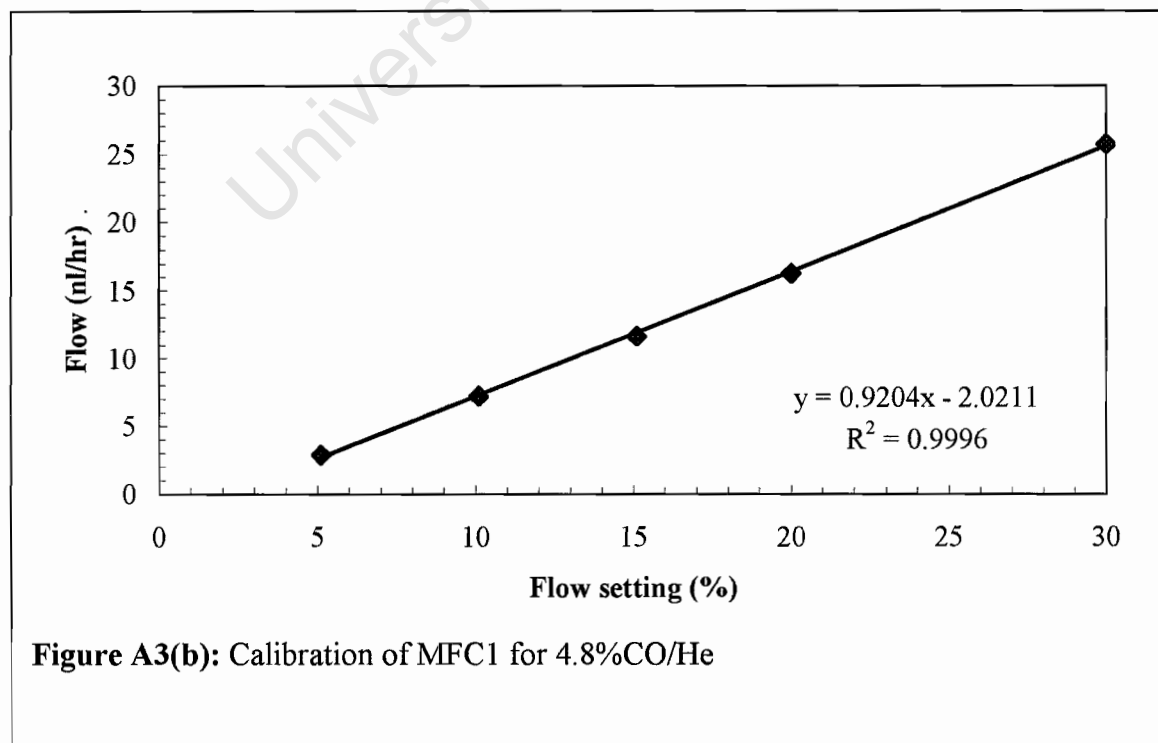
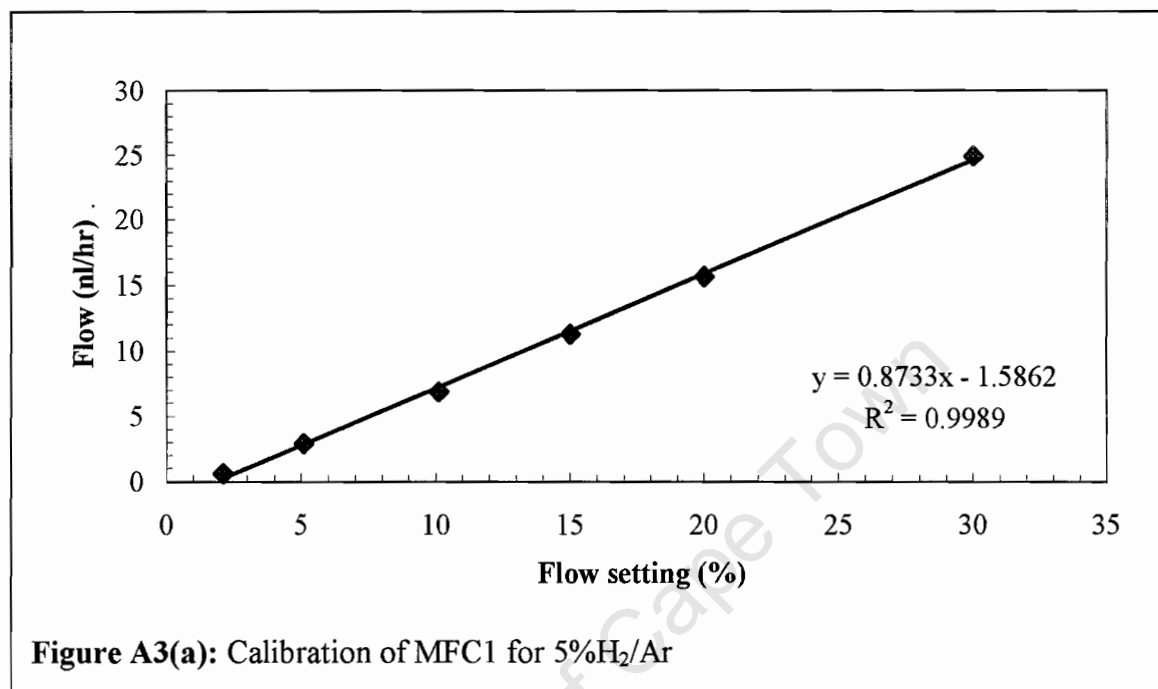


Figure A2(e): Calibration graph of 0.15%CO₂/4.7%CO/He

Appendix 3:

The mass flow controllers were calibrated at atmospheric pressure. Figures A3(a) –A3(d) are the calibrations. The flows were converted are expressed at standard temperature (0°C) and pressure (1 bar).



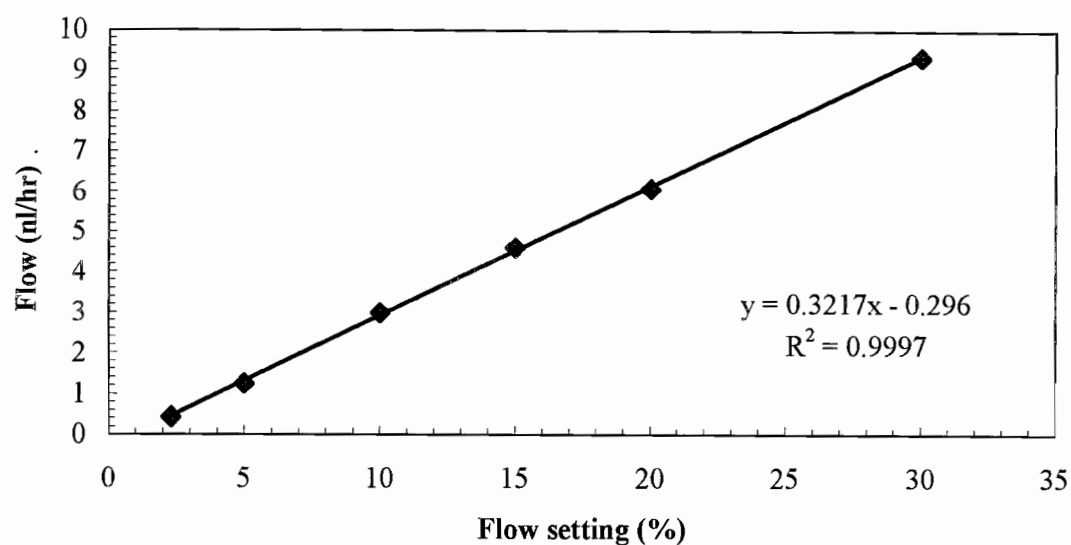


Figure A3(c): Calibration of MFC2 for argon

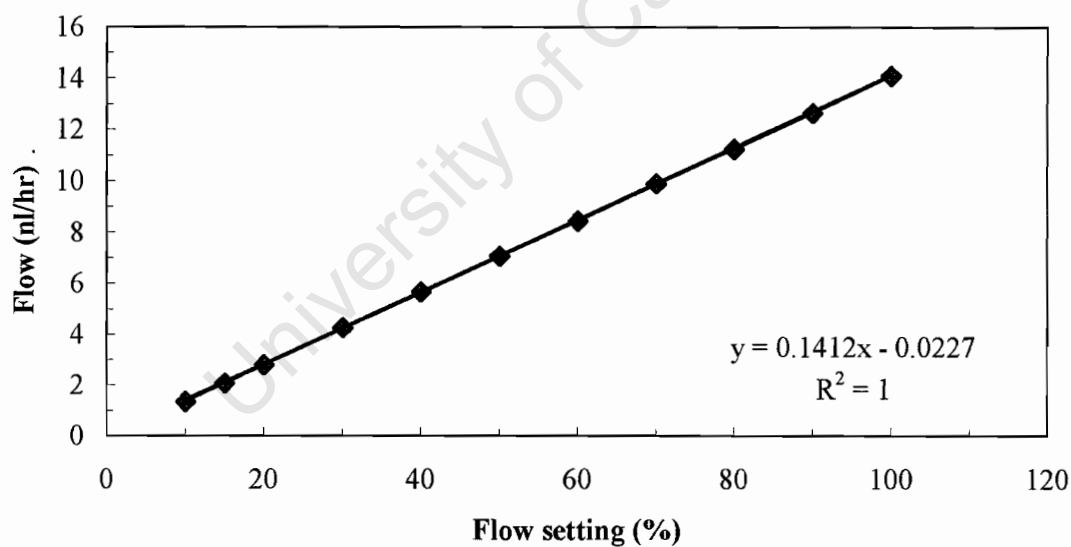


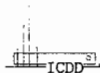
Figure A3(d): Calibration of MFC3 for synthesis gas

The mass flow controller regulating the flow of the reducing gas i.e. MFC1 was only calibrated for 5% H_2 /Ar and 4.8%CO/He. It was assumed that the gas mixtures containing the 0.15% CO_2 would have the same flows as those without CO_2 .

Appendix 4:

University of Cape Town

Fe ₂ O ₃	d(A)	Int	h	k	l	d(A)	Int	h	k	l
Iron Oxide	3.684	30	0	1	2	.8392	3	3	3	0
	2.70	100	1	0	4	.8089	4	3	2	10
	2.519	70	1	1	0	.8014	4	2	4	4
Hematite, syn	2.292	3	0	0	6					
Rad.: CuKα1λ: 1.540598 Filter: Mono	2.207	20	1	1	3					
d-sp: Diff.	2.0779	3	2	0	2					
Cut off: Int.: Diffract. I/Icor.: 2.4	1.8406	40	0	2	4					
Ref: Natl. Bur. Stand. (U.S.) Monogr. 25, 18, 37 (1981)	1.6941	45	1	1	6					
	1.6367	1	2	1	1					
	1.6033	5	1	2	2					
	1.5992	10	0	1	8					
Sys.: Rhombohedral S.G.: R $\bar{3}c$ (167)	1.4859	30	2	1	4					
a: 5.0356(1) b: c: 13.7489(7) A: C: 2.7303	1.4538	30	3	0	0					
α: β: γ: Z: 6 mp: 1350-1360	1.4138	<1	1	2	5					
Ref: Ibid.	1.3497	3	2	0	8					
	1.3115	10	1	0	10					
	1.3064	6	1	1	9					
	1.2592	8	2	2	0					
Dx: 5.270 Dm: 5.260 SS/FOM: F ₃₀ = 69(l.(l.0111, 39)	1.2276	4	3	0	6					
	1.2141	2	2	2	3					
εα: 2.94 ηωβ: 3.22 εγ: Sign:- 2V:	1.1896	5	1	2	8					
Ref: Dana's System of Mineralogy, 7th Ed., I, 529 (1944)	1.1632	5	0	2	10					
	1.1411	7	1	3	4					
	1.1035	7	2	2	6					
	1.0768	2	0	4	2					
Color: Dark reddish brown	1.0557	7	2	1	10					
Pattern taken at 25 C. Sample from Pfizer, Inc., NY, USA,	1.0428	<1	1	1	12					
heated at 800 C for 3 days. CAS #: 1309-37-1. Opaque	1.0393	3	4	0	4					
mineral optical data on specimen from Elba, R1R0=30.2,	.9892	4	3	1	8					
RR2Re=26.1, Disp.=16, VHN=1038 (mean at 100, 200,	.9715	<1	2	2	9					
300), Color values=1 .299, .309, 29.8, 2 .299, .309, 25.7,	.9606	5	3	2	4					
Ref.: IMA Commission on Ore Microscopy QDF. Pattern	.9581	4	0	1	14					
reviewed by Syvinski, W., McCarthy, G., North Dakota State	.9516	5	4	1	0					
Univ., Fargo, ND, USA, ICDD Grant-in-Aid (1990). Agress	.9318	2	4	1	3					
well with experimental and calculated patterns. Additional weak	.9206	2	0	4	8					
reflection [indicated by brackets] was observed. Also called:	.9081	5	1	3	10					
crocus mantis. Also called: venetian red. Also called: ferrite.	.8998	1	3	0	12					
Also called: indian red. Also called: crocus. Al ₂ O ₃ type.	.8954	3	2	0	14					
Corundum group, corundum subgroup. Also called: burnt ochre.	.8789	6	4	1	6					
Also called: rouge. Silver used as an internal stand. PSC:	.8648	1	2	3	8					
hR10. To replace 13-534 and validated by calculated pattern	.8543	3	4	0	10					
24-72. Mwt: 159.69. Volume[CD]: 301.93.	.8436	5	1	2	14					



Fe ₂ O ₃	d(A)	Int	h	k	l	d(A)	Int	h	k	l
Iron Oxide	5.918	5	1	1	0	1.0966	<1	[7	3	0]
	4.822	4	1	1	1	1.0872	7	7	3	1
	3.74	5	2	1	0	1.0439	3	[8	0	0]
Maghemite-C, syn	3.411	5	2	1	1					
Rad.: CuKα λ: 1.54178 Filter: Graph Mono d-sp: Diff.	2.953	35	2	2	0					
Cut off: 15.0 Int.: Diffract. I/lor.: 1.4	2.784	2	2	2	1					
Ref: Schulz, D., McCarthy, G., North Dakota State University, Fargo, North Dakota, USA, ICDD Grant-in-Aid, (1987)	2.6435	2	3	1	0					
	2.5177	100	3	1	1					
	2.4119	3	2	2	2					
	2.3163	1	[3	2	0]					
	2.2320	1	[3	2	1]					
Sys.: Cubic S.G.: P4 ₁ 32 (213)	2.0886	16	4	0	0					
a: 8.3515(22) b: c: A: C:	2.0255	1	4	1	0					
α: β: γ: Z: 10.667mp:	1.9685	<1	[3	3	0]					
Ref: Lindsley, D., Min. Soc. of America, Short Course Notes (Wash., D.C.), 3, L-18 (1976)	1.8224	2	4	2	1					
	1.7045	10	4	2	2					
	1.6703	1	4	3	0					
	1.6379	1	[5	1	0]					
Dx: 4.856 Dm: 4.900 SS/FOM: F ₃₀ = 95(l.0090, 35)	1.6073	24	5	1	1					
σα: ηωβ: 2.74 εγ: Sign: 2V:	1.5507	1	5	2	0					
Ref: Deer, W., Howie, R., Zussman, J., Rock Forming Minerals, 5, 73 (1961)	1.5248	2	5	2	1					
	1.4758	34	4	4	0					
	1.4537	1	4	4	1					
	1.4322	1	5	3	0					
	1.3919	<1	[4	4	2]					
Color: Light brown	1.3730	1	[6	1	0]					
Peak height intensity. Sample from Control Data as used in hard disks. Space group dependent upon preparation (Bernal et al.). Optical data on specimen from Iron Mountain, Shasta County, California, USA. Pattern reviewed by Syvinski, W., McCarthy, G., North Dakota State University, Fargo, North Dakota, USA, ICDD Grant-in-Aid (1990). Agrees well with experimental pattern. Additional weak reflections [indicated by brackets] were observed. σ(I _{obs}) = ±0.067. Spinel group, related structures subgroup. Silicon used as an internal stand. Single-crystal data used. PSC: cP53.33. To replace 4-755 and 24-81. Mwt: 159.69. Volume[CD]: 582.50.	1.3547	1	6	1	1					
	1.3204	3	6	2	0					
	1.3042	1	5	4	0					
	1.273	5	5	3	3					
	1.259	2	6	2	2					
	1.245	<1	[6	3	0]					
	1.2314	<1	[6	3	1]					
	1.2053	1	4	4	4					
	1.1931	<1	[6	3	2]					
	1.1810	1	7	1	0					
	1.1365	<1	[7	2	1]					
	1.1159	2	6	4	2					



Fe5O7(OH)·4H2O	d(A)	Int	h	k	l
Iron Oxide Hydroxide Hydrate	2.50	100	1	1	0
	2.21	80	2	0	0
	1.96	80	1	1	3
Ferrihydrite, syn	1.72	50	1	1	4
	1.51	70	1	1	5
Rad.: MoKα λ: 0.7107 Filter: Beta d-sp:	1.48	80	1	0	6
Cut off: Int.: Estimation I/Icor.:					
Ref: Chukhrov, F. et al., Izv. Akad. Nauk SSSR, 23 (1973)					

Sys.: Hexagonal S.G.: P

a: 5.08 b: c: 9.4 A: C: 1.8504

α: β: γ: Z: 1 mp:

Ref: Van der Giessen, J. Inorg. Nucl. Chem., 28, 2155 (1966)

Dx: 3.796 Dm: 3.800 SS/FOM: F₆ = 2[(0.109, 27)

Color: Yellow, dark brown

Prepared by slow hydrolysis of ferric salts at pH>3, and below 9.5. Measured density and color from Am. Mineral., 60 485 (1975). PSC: hP26. To replace 22-1117. Mwt: 480.30. Volume[CD]: 210.08.

FeO(OH)	d(A)	Int	h	k	l
Iron Oxide Hydroxide	4.70	54	0	0	2
	3.13	89	0	0	3
	2.52	14	1	1	0
Ferrihydrite, syn	2.23	2	1	1	2
	1.98	1	1	1	3
Rad.: CoKa λ: 1.7902	Filter: Graph Mono	d-sp: Diff.			
	1.88	100	0	0	5
Cut off:	Int.: Diffract.	I/Icor.:			
	1.72	1	1	1	4
Ref: Eggleton, R., Fitzpatrick, R., Clays Clay Miner., 36, 111 (1988)	1.51	2	1	1	5
	1.46	40	3	0	0
	1.33	1	1	1	6
	1.27	5	2	2	0
Sys.: Hexagonal	S.G.:				
	1.18	3	[3	1	2]
a: 5.08	b:	c: 9.4	A:	C: 1.8504	1.07
					5 [3 0 6]
α:	β:	γ:	Z:	mp:	
Ref: Ibid.					
Dx: Dm: SS/FOM: F ₁₃ = 2[(0.140, 60)					

Prepared by slow hydrolysis of Fe (N O3)3 ·9 H2 O in deionized water at 75 C. Mwt: 88.85. Volume[CD]: 210.08.

FeO(OH)	d(A)	Int	h	k	l
Iron Oxide Hydroxide	4.98	12	0	2	0
	4.183	100	1	1	0
	3.383	10	1	2	0
Goethite	2.693	35	1	3	0
Rad.: CoKa λ : 1.7902 Filter:	2.583	12	0	2	1
	2.527	4	1	0	1
Cut off: Int.: Diffract. I/Icor.:	2.489	10	0	4	0
	2.450	50	1	1	1
Ref: Harrison, R. et al., Bull. Geol. Surv. G.B., 52, 51 (1975)	2.303	1	2	0	0
	2.253	14	1	2	1
	2.190	18	1	4	0
Sys.: Orthorhombic S.G.: Pbnm (62)	2.089	1	2	2	0
	2.011	2	1	3	1
a: 4.608 b: 9.956 c: 3.0215 A: 0.4628 C: 0.3035	1.920	5	0	4	1
α :	1.802	6	2	1	1
β :	1.7728	1	1	4	1
γ :	1.7192	20	2	2	1
Z: 4 mp:	1.6906	6	2	4	0
Ref: Ibid.	1.6593	3	0	6	0
	1.6037	4	2	3	1
Dx: 4.258 Dm: 4.000 SS/FOM: $F_{30} = 47[(1.0155, 41)]$	1.5637	10	1	5	1
$\epsilon\alpha$: 2.260 $\eta\omega\beta$: 2.393 $\epsilon\gamma$: 2.398 Sign:- 2V: 15(15°)	1.5614	8	1	6	0
Ref: Dana's System of Mineralogy, 7th Ed., I, 680	1.5091	8	0	0	2
	1.4675	2	3	2	0
	1.4541	5	0	6	1
Color: Dark brown	1.4207	2	1	1	2
Specimen from Hindlow quarry, Derbyshire, England, UK	1.3936	3	3	3	0
(E35891). Chemical analysis (wt.%): Si O2 1.84, Fe2 O3	1.3694	2	3	0	1
86.30, H2 O (<105C) 10.79, H2 O (<105C) 0.86, and minor	1.3590	3	1	7	0
MgO, CaO, C O2 and organic C. Lead nitrate used as	1.3459	1	2	6	0
internal standard ($a=7.8568$). Dx for Fe3.88 Six (O H)4.31	1.3173	3	1	3	2
O3.69 ($x \leq 0.012$), formula from chemical analysis	1.2921	<1	0	4	2
with impurities deducted. Opaque mineral optical data on	1.2654	1	3	3	1
specimen from Restonnel, Cornwall, England, UK:	1.2437	1	1	4	2
R1Ro=17.5, RR2Re=15.6, Disp.=16, VHN=667 (mean at	1.1994	1	3	4	1
100, 200, 300), Color values=1 .291, .296, 17.5, 2 .294,	1.1506	1	0	8	1
.299, 15.5, Ref.: IMA Commission on Ore Microscopy QDF.	1.1445	1	4	1	0
Diaspore group. PSC: oP16. To replace 17-536. Mwt: 88.85.	1.1263	1	2	4	2
Volume[CD]: 138.62.					

					d(A)	Int	h	k	l
FeFe₂O₄									
Iron Oxide									
					4.852	8	1	1	1
					2.967	30	2	2	0
					2.532	100	3	1	1
Magnetite, syn									
					2.4243	8	2	2	2
					2.0993	20	4	0	0
Rad.: CuKα1λ: 1.54056 Filter: Ni Beta d-sp:					1.7146	10	4	2	2
Cut off: Int.: Diffract. I/ cor.: 4.90					1.6158	30	5	1	1
Ref: Natl. Bur. Stand. (U.S.) Monogr. 25, 5, 31 (1967)					1.4845	40	4	4	0
					1.4192	2	5	3	1
					1.3277	4	6	2	0
					1.2807	10	5	3	3
Sys.: Cubic S.G.: Fd3m (227)					1.2659	4	6	2	2
a: 8.396 b: c: A: C:					1.2119	2	4	4	4
α: β: γ: Z: 8 mp:					1.1221	4	6	4	2
Ref: Ibid.					1.0930	12	7	3	1
					1.0496	6	8	0	0
					.9896	2	6	6	0
					.9695	6	7	5	1
Dx: 5.197 Dm: 5.176 SS/FOM: F ₂₆ = 58(l.0132, 34)					.9632	4	6	6	2
					.9388	4	8	4	0
εα: ηωβ: 2.42 εγ: Sign: 2V:					.8952	2	6	6	4
Ref: Dana's System of Mineralogy, 7th Ed., I, 698					.8802	6	9	3	1
					.8569	8	8	4	4
					.8233	4	10	2	0
					.8117	6	9	5	1
Color: Black					.80	4	10	2	2

Pattern taken at 25 C. Sample obtained from the Columbian Carbon Co., New York, NY, USA. Spectrographic analysis showed the following major impurities: 0.01 to 0.1% Co, 0.001 to 0.01% Ag, Al, Mg, Mn, Mo, Ni, Si, Ti and Zn. Other data 25-1376. Opaque mineral optical data on specimen from Braastad, Norway: RR2Re=20.1, Disp.=16, VHN100=592, Color values=.311, .314, 20.1, Ref.: IMA Commission on Ore Microscopy QDF. See also 26-1136. a=8.3967 refined in 1975. Al₂ Mg O₄ type. Spinel group, spinel subgroup. Tungsten used as an internal stand. PSC: cF56. To replace 11-614. Mwt: 231.54. Volume[CD]: 591.86.

Fe	d(A)	Int	h	k	l
Iron	2.0268	100	1	1	0
	1.4332	20	2	0	0
	1.1702	30	2	1	1
Iron, syn	1.0134	10	2	2	0
	.9064	12	3	1	0
	.8275	6	2	2	2

Rad.: CuKα1λ: 1.5405 Filter: Ni Beta d-sp:

Cut off: Int.: Diffract. I/Icor.:

Ref: Swanson et al., Natl. Bur. Stand. (U.S.), Circ. 539, IV, 3 (1955)

Sys.: Cubic		S.G.: Im3m (229)		
a: 2.8664	b:	c:	A:	C:
α:	β:	γ:	Z: 2	mp:
Ref: Ibid.				
Dx: 7.875	Dm:	SS/FOM: F ₆ = 225(.0044, 6)		

Color: Gray, light gray metallic

Pattern taken at 25 C. CAS #: 7439-89-6. The iron used was an exceptionally pure rolled sheet prepared at the NBS, Gaithersburg, MD, USA., [Moore, G., J. Met., 5 1443 (1953)]. It was annealed in an H2 atmosphere for 3 days at 1100 C and slowly cooled in a He atmosphere. Total impurities of sample <0.0013% each metals and non-metals. γ-Fe (fcc)=(1390 C) δ-Fe (bcc). Opaque mineral optical data on specimen from Meteorite: RR2Re= 57.7, Disp.=16, VHN=158 (mean at 100, 200, 300), Color values=.311, .316, 57.9, Ref.: IMA Commission on Ore Microscopy QDF. W type. Iron group, iron subgroup. Also called: ferrite.PSC: cl2. Mwt: 55.85. Volume[CD]: 23.55.

36-1248						Wavelength= 1.78897						C			
χ -CFe _{2.5}						d(A)	Int	h	k	l	d(A)	Int	h	k	l
Iron Carbide						3.3221	<1	1	1	$\bar{1}$	1.6894	3	0	2	$\bar{2}$
						2.9309	<1	3	1	0	1.6884	8	5	1	$\bar{2}$
						2.8654	2	4	0	0	1.6616	3	2	2	$\bar{2}$
						2.6522	10	3	1	$\bar{1}$	1.6406	1	4	2	$\bar{1}$
						2.5063	10	0	0	2	1.6279	8	6	0	$\bar{2}$
Rad.: CoK α 1 λ : 1.7890 Filter: d-sp: Calculated						2.4245	10	3	1	$\bar{1}$	1.5820	21	2	2	$\bar{2}$
Cut off: Int.: Calculated I/Icor.:						2.4181	6	2	0	$\bar{2}$	1.5820	21	1	1	$\bar{3}$
Ref: Dirand, M., Afqir, Acta Metall., 31, 1089 (1983)						2.2864	22	0	2	0	1.5291	1	1	1	$\bar{3}$
Sys.: Monoclinic S.G.: C2/c (15)						2.2070	34	1	1	$\bar{2}$	1.5291	1	7	1	$\bar{1}$
						2.1906	27	2	0	2	1.5203	2	3	1	$\bar{3}$
						2.1134	19	1	1	2	1.5163	4	4	2	$\bar{2}$
						2.0800	66	0	2	1	1.5006	2	5	1	$\bar{2}$
						2.0493	100	5	1	0	1.4477	<1	6	2	$\bar{1}$
a: 11.563 b: 4.573 c: 5.058 A: 2.5285 C: 1.1061						2.0253	26	4	0	$\bar{2}$	1.4397	2	1	3	1
α : β : 97.7 γ : Z: 4 mp:						2.0096	35	3	1	$\bar{2}$	1.4325	1	8	0	0
Ref: Senateur, J. et al., C. R. Seances Acad. Sci. (Paris), 255, 1615 (1962)						1.9914	13	2	2	$\bar{1}$	1.4297	<1	6	0	2
Dx: 7.600 Dm: SS/FOM: F ₃₀ = 138 (..0062, 35)						1.9818	18	5	1	$\bar{1}$	1.4235	1	7	1	1
						1.9217	25	2	2	1	1.4009	3	4	2	2
						1.9097	5	6	0	0	1.3807	9	$\bar{3}$	3	1
						1.8215	17	5	1	1					
						1.8148	21	3	1	2					
Peak height intensity. B2 Pd5 type. Also called: Hagg carbide.PSC: mC28. To replace 20-509. Mwt: 303.26. Volume[CD]: 265.04.						1.7873	2	4	2	0					
						1.7724	15	4	0	$\bar{2}$					
						1.7297	12	4	2	$\bar{1}$					

Fe2C	d(A)	Int	h	k	l
Iron Carbide	2.431	16	$\bar{1}$	1	0
	2.402	16	0	1	0
	2.184	40	0	0	2
	2.125	100	$\bar{1}$	1	1
	2.103	100	$\bar{1}$	0	1
Rad.: CoKa λ : 1.7902 Filter:	d-sp: Debye-S. 114.6	1.622	16	$\bar{1}$	1 2
Cut off:	Int.: Estimation I/Icor.:	1.614	16	$\bar{1}$	0 2
Ref: Barton, Gale, Acta Crystallogr., 17, 1460 (1964)		1.397	16	$\bar{1}$	2 0
		1.378	16	$\bar{1}$	1 0
		1.247	16	$\bar{1}$	1 3
		1.243	16	$\bar{1}$	0 3
Sys.: Monoclinic S.G.:		1.176	20	$\bar{2}$	1 2
a: 2.794 b: 2.794 c: 4.360 A: 1.0000 C: 1.5605		1.171	20	$\bar{2}$	2 1
α :	β :	γ : 120.92 Z: 1 mp:	1.165	20	1 1 2
Ref: Ibid.			1.156	20	2 0 1
			1.088	6	0 0 4
			1.061	4	$\bar{2}$ 2 2
			1.049	4	$\bar{2}$ 0 2
Dx: 7.035 Dm:	SS/FOM: $F_{20} = 10[(0.072, 28)$	.99	2	$\bar{1}$	1 4
		.99	2	1	0 4

CAS #: 12011-66-4. Pattern used chromium and cobalt radiation. Crystal system pseudo-hexagonal with Fe in approx. h.c.p. array. Iron catalyst extracted after use in the Fischer-Tropsch process for the synthesis of hydrocarbons from CO and H2. May contain some oxygen. C.D. Cell: a=2.794, b=4.360, c=2.755, β =119.54, a/b=0.6408, c/b=0.6319, S.G.=. Mwt: 123.71. Volume[CD]: 29.20.

C	d(A)	Int	h	k	l
Carbon	3.348	100	0	0	3
	2.081	11	1	0	1
	1.958	9	0	1	2
Graphite-3R, syn [NR]	1.674	6	0	0	6
	1.623	4	1	0	4
	1.460	2	0	1	5
Rad.: CuKα λ: 1.54178 Filter:	d-sp: Calculated				
Cut off:	Int.: Calculated	I/Icor.:			
Ref: Holcombe, Private Communication, (1974)	1.228	4	1	1	0
	1.190	1	1	0	7
	1.153	6	1	1	3
	1.116	1	0	0	9
	1.081	1	0	1	8
	.9902	4	1	1	6
Sys.: Rhombohedral	S.G.: R3 (146)				
a: 2.456	b:	c: 10.044	A:	C: 4.0896	.83
α:	β:	γ:	Z: 6	mp:	.8259
Ref: Holcombe, U.S. AEC Oak Ridge Y-12 Plant, Report Y1887, (1973)					.8014
					.7938
Dx: 2.281	Dm:	SS/FOM: F ₁₆ = 72[(1.0093, 24)			

Peak height intensity, CAS #: 7440-44-0. C type. PSC: hR2.
Mwt: 12.01. Volume[CD]: 52.47.

Appendix 5:

Tables A5(a) –A5(d) contain a summary of the product distribution in the C₁ – C₁₅ fraction of the hydrocarbon products with time on stream.

Table A5(a): Product distributions of the Fischer-Tropsch synthesis using catalyst MSC3 reduced in 5%H₂/Ar at 220°C for 16hrs

Time on Stream (hrs)	24	48	72	96
Olefin content (mol% hydrocarbons)	-	70.8	65.3	-
1-olefin content (mol% olefins)	-	94.8	98.1	-
Oxygenate content (mol % hydrocarbons)	-	2.5	9.9	-

Table A5(b): Product distributions of the Fischer-Tropsch synthesis using catalyst MSC3 reduced in 0.15%CO₂/4.7%H₂/Ar at 220°C for 16hrs

Time on Stream (hrs)	24	48	72	96
Olefin content (mol% hydrocarbons)	69.5	69.9	71.0	65.8
1-olefin content (mol% olefins)	93.9	93.2	93.5	93.7
Oxygenate content (mol % hydrocarbons)	6.4	6.1	6.0	10.5

Table A5(c): Product distributions of the Fischer-Tropsch synthesis using catalyst MSC3 reduced in 4.8%CO/He at 300°C for 16hrs

Time on Stream (hrs)	24	48	72	96
Olefin content (mol% hydrocarbons)	70.7	69.9	76.2	65.8
1-olefin content (mol% olefins)	94.1	94.1	93.3	93.7
Oxygenate content (mol % hydrocarbons)	5.5	5.2	6.5	10.5

Table A5(d): Product distributions of the Fischer-Tropsch synthesis using catalyst MSC3 reduced in 0.15%CO₂/4.7%CO/He at 300°C for 16hrs

Time on Stream (hrs)	24	48	72	96
Olefin content (mol% hydrocarbons)	69.1	73.9	69.7	69.4
1-olefin content (mol% olefins)	91.0	93.9	94.7	91.4
Oxygenate content (mol % hydrocarbons)	4.5	3.3	6.0	6.5