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RHODIUM AS A PROMOTER FOR AN IRON
FISCHER-TROPSCH CATALYST

by

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A thesis submitted for the partial fulfilment of the requirements for the degree of
Masters of Science
in the Department of Chemical Engineering,
University of Cape Town

Promoter: Prof. E. van Steen

2001
DECLARATION

I declare that Rh AS PROMOTER FOR AN FISCHER-TROPSCH CATALYST is my own work and that all the sources I have used or quoted have been indicated and acknowledged by means of complete references.

[Signature]

Genevieve Joost
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My parents for their love, support and understanding.

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ABSTRACT

Rhodium was added as a promoter to an iron based catalyst with, the view to enhance the formation of oxygenates. The base catalyst 100 Fe / 8.7 Cu / 5.6 K₂O / 372 Al₂O₃ was prepared by impregnation. Three catalysts with varying mass ratios of rhodium to iron (1.3 Rh/100 Fe; 2.4 Rh/100 Fe; 3.9 Rh/100 Fe) were prepared by incipient wetness impregnation of the base catalyst using rhodium chloride solution.

Ex-situ reduction studies were performed and Mössbauer spectra were obtained at 298 K. The Fischer-Tropsch activity as well as the water gas shift reaction was influenced by the addition of rhodium. The olefin and 1-olefin content however remained unchanged at similar level of conversion. The catalyst with lowest activity showed the highest olefin and 1-olefin content. Hence the change in the selectivity was related to the change in conversion.

Rhodium enhanced the formation of oxygenates, the alcohol content in the oxygenates in the fraction of higher carbon number organic compounds, and the chain growth probability of the higher carbon numbered oxygenates. This trend was related to a decrease in secondary reactions of the oxygenates. The rhodium level did not seem to influence the oxygenate content. A decrease in temperature and increase in space velocity increased the oxygenate content at the higher carbon numbered oxygenates. The trends observed with rhodium content, change in space velocity and change in temperature were less obvious for the lower oxygenates. The C₂ oxygenate fraction was always high while the C₁ and higher oxygenates were less.
LIST OF ABBREVIATIONS

AA        Atomic adsorption spectroscopy
EDS       Energy dispersive X-ray spectroscopy
FID       Flame ionisation detector
FT        Fischer-Tropsch synthesis
GC        Gas chromatography
ICP       Inductively coupled plasma spectroscopy
MES       Mössbauer emission spectroscopy
r         rate
red       reduction
rxn       reaction
S         selectivity
SV        space velocity
T         temperature
TCD       Thermal conductivity detector
WGS       Water gas shift reaction
X         conversion
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1: INTRODUCTION

The Fischer-Tropsch (FT) process converts CO and H₂ over Fe, Co and Ru based catalysts (Dry, 1990-a) to a variety of products such as olefins, paraffins and oxygenates (Dry, 1990-b).

\[
\text{CO} + \text{H}_2 \xrightarrow{450-700 \text{ K}} \text{C}_n\text{H}_{2n}, \text{C}_n\text{H}_{2n+2}, \text{C}_n\text{H}_m\text{O}
\]

1.1

The FT process was initially developed for the production of fuel. The profitability of making synthetic fuel from synthesis gas has however decreased while there is an increased interest in the production of higher valued chemicals via CO hydrogenation. Oxygenates are considered as high commodity chemicals. There is an especial global demand for alcohols (Harvilicz, 2000).

Methanol is one of the largest volume organic chemicals produced in the world. It is used as solvent and raw material for the production of a number of high valued chemicals. For example methyl-t-butyl ether (MTBE) is produced in the reaction between methanol and isobutanol (Pierantozzi, 1995). Ethanol is produced in a homologation reaction where methanol reacts with CO and H₂. Another important industrial process in which methanol is used as reactant, is the homogeneous Monsanto acetic acid process (Worsham, 1995).

Currently the formation of higher alcohols (C₂-C₆OH), are of great interest. This interest has been sparked by clean fuel regulations. Oxygenates have a high octane number and can fill the gap left by legal restrictions on lead and the aromatic content in fuel (Xiaoding et al., 1987). Oxygenates blended with fuel are expected to change emissions, resulting in the reduction of volatile and toxic compounds from motor exhausts (Verkerk et al., 1999).

Global demand for higher alcohols C₆+ are increasing. C₆-C₁₁ and C₁₂+ alcohols are used as feedstock in the plasticiser and detergent industries respectively and are known as such due to their end uses. The derivatives of the C₆-C₁₈ alcohols are widely used in consumer and industrial products. The demand for higher alcohols stems from trends in the end-use
markets. Increase in plastic production has lead to an increase in the demand of plasticisers. Plasticisers are mainly used in the production of polyvinyl chloride (PVC). The plasticiser loadings in PVC ranges from 20-80 %.

Consumers are demanding multifunctional detergents. The trends are towards concentrated detergents with the capability to disinfect, enhance colour, reduce wrinkles and to be environmentally friendly. Although the demand for the higher alcohols are high the availability of some alcohols are limited (Harvilicz, 2000).

One of the major contributors to the world production of higher alcohols is the hydroformylation process. It is a homogeneous process and converts linear olefins in the presence of CO and H₂ to linear alcohols. Co and Rh based catalysts are used. These catalysts are expensive and in homogeneous catalysis problems are often experienced in separation procedures to prevent catalyst and activity losses. Furthermore the hydroformylation process utilises propene and ethene based olefins making the process strongly dependent on the cost of crude oil and natural gas (Pennington, 1996).

Economics dictates that the limited availability of higher alcohols should be investigated.

The FT process produces oxygenates, unfortunately the alcohols are not produced with high selectivity and are often considered as by-products (Schulz et al., 1999 b). Improving the oxygenate selectivity posses an opportunity to add value to the FT process.

1.1 FT oxygenates
1.1.1 Introduction

The FT synthesis is operated on a large industrial scale. The FT operation is of particular interest to South Africa. In 1955 the first plant, Sasol One, commenced operations and produced hydrocarbon fuel and a variety of chemicals. The FT process in South Africa is based on the gasification of coal to synthesis gas, which is converted into organic products. Interest in the FT process decreased with discovery of big oil fields in Saudi Arabia and Alaska. It became less economically viable to produce synthetic gas from coal. South Africa
was the exception, there was no access to the world oil markets and cheap coal was available. In 1980 and 1982 larger plants, based in Secunda, were established (Dry, 1990-a).

Sasol utilises low temperature FT (LTFT) and high temperature FT (HTFT) which are operated in fixed bed and slurry phase reactors respectively (Espinoza et al, 1999). Iron based catalysts are used in both systems. The price of iron, relative to the other active FT metals govern Sasol’s choice of catalyst. The relative prices of the metals are given below (Dry, 1990-b).

<table>
<thead>
<tr>
<th>Metals</th>
<th>Cost per unit mass (relative to Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1</td>
</tr>
<tr>
<td>Co</td>
<td>230</td>
</tr>
<tr>
<td>Ni</td>
<td>250</td>
</tr>
<tr>
<td>Ru</td>
<td>31,000</td>
</tr>
<tr>
<td>Rh</td>
<td>570,000</td>
</tr>
</tbody>
</table>

Sasol uses iron oxide ores as starting material for the synthesis of the fused catalyst used in the slurry reactors while scrap iron metal is used in the preparation of the precipitated catalyst used in the fixed bed reactors. Iron has high selectivity for olefins, which are important in the Sasol process (Dry, 1990-a). Co and Ru have the advantage over Fe based catalysts in that no oxidation or carbon deposition occurs. The oxidation of the active phase i.e. iron carbides are commonly considered as the active phase (Raupp and Delgass, 1979), leads to loss in active surface area. The deposition of carbon results in catalyst swelling leading to plugging of the fixed bed reactors (Dry, 1990-a). Of interest to our investigation is that Co and Ru are more hydrogenating than Fe thus the yields for oxygenated compounds are higher for Fe based catalysts (Dry, 1990-b). In the commercial Sasol operations the lower molecular weight oxygenates are predominantly present in the water phase of the condensed tail gas leaving the reactor. Oxygenate work-up is complex. The aldehydes, ketones and alcohols are removed as overheads while the bottoms retain the carboxylic acids in the primary distillation tower. The acids are not recovered but are biologically
destroyed. The composition of the chemicals isolated in the water phase, is indicated in Table 1.2 (Dry, 1987).

**Table 1.2** Composition of chemicals in the FT water (mass %) isolated in the Sasol processes.

<table>
<thead>
<tr>
<th>Category</th>
<th>Compound</th>
<th>Synthol</th>
<th>Arge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non acids</td>
<td>Aldehydes</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>CH₃OH</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>C₂H₅OH</td>
<td>55</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>C₃H₇OH</td>
<td>16</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>C₄H₈OH</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>C₅+ OH</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>MEK</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Higher ketones</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Acids</td>
<td>Acetic</td>
<td></td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>Propionic</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>Butyric</td>
<td></td>
<td>9</td>
</tr>
</tbody>
</table>

Below some investigations on oxygenated hydrocarbons, over Fe based catalysts, are discussed.

**1.1.2 Precipitated iron catalysts**

In the early stages of the FT development Storch (1950) reported a special iron catalyst for the production of alcohols. This Ruhrchemie catalyst was prepared using sodium carbonate as precipitating agent. The catalyst composition was 100 Fe : 5 Cu : 10 CaO : 5 Kieselguhr. Alcohols were distilled at different temperature fractions. The volume percent alcohols obtained were high. They were however not sure about the structure of the alcohols produced. Esters and aldehydes were also isolated while smaller quantities of acids were produced.

More recently Schulz et al. (1999-b) investigated a precipitated iron catalyst in a fixed bed
reactor. The catalyst under investigation had the composition 100 Fe: 13 Al₂O₃: 10 Cu: 25 K (weight ratio). The catalyst was prepared by precipitation using NH₃ solution as precipitation agent. The study was based on the concept that the iron catalyst undergoes steady state transformations with time. Up to six episodes of catalyst transformations were characterised. The transformations were associated with change in the catalyst composition in different forms as iron oxides, iron carbides and metallic iron under the influence of CO, H₂, CO₂ and H₂O. These transformations produced changes in rates and product selectivity of the iron catalyst. The alcohols and aldehydes were reported to exhibit the following characteristics. The C₁ (methanol) fraction was low. This was attributed to thermodynamically unfavourable conditions for methanol synthesis. The C₂ was high while the higher carbon number fractions were much less. Initially the selectivity for oxygenates were high at 25 mol-% of which 90 mol-% was aldehydes. Only ethanol's selectivity remained high, at 25 mol-% of the C₂ fraction.

1.1.3 Fused iron catalysts

Satterfield and Huff (1982) investigated the carbon number distribution of FT products over a fused catalyst in a slurry reactor. The fused catalyst contained 2-3 % Al₂O₃, 0.5-0.8 % K₂O, 0.7-1.2 % CaO and < 0.4 SiO₂. The total product composition amounted to about 45 mol % α- and β-olefins, 35 mol-% normal paraffins and 15 mol-% oxygenated hydrocarbons. For the C₁-C₁₀ fraction normal alcohols and aldehydes predominated. Table 1.3 indicates the ratios α- and β-olefins to n-paraffins as well as oxygenates in the total organic products obtained.

<table>
<thead>
<tr>
<th>Carbon number</th>
<th>α and β-olefins/ n-paraffins, mol-%</th>
<th>Oxygenates / total organic, mol-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.2-4.3</td>
<td>0.26-0.37</td>
</tr>
<tr>
<td>3</td>
<td>6.1-8.2</td>
<td>0.16-0.2</td>
</tr>
<tr>
<td>10</td>
<td>3.4-5.1</td>
<td>0.05-0.12</td>
</tr>
</tbody>
</table>

Satterfield and Huff indicated that the Anderson-Schulz-Flory distribution is often applied to
only hydrocarbons at each carbon number. Often oxygenates are neglected which leads to misleading conclusions at lower carbon numbers where significant amounts of oxygenates are formed. In the absence of oxygenates, the Anderson-Schulz-Flory distribution of \( C_1 \) may be too high while the \( C_2 \) appear too low.

Dictor and Bell (1986) reported a fused iron catalyst with composition 2-3 \% \( \text{Al}_2\text{O}_3 \), 0.7-1.2 \% \( \text{CaO} \), 0.5-0.8 \% \( \text{K}_2\text{O} \) and < 0.4 \% \( \text{SiO}_2 \) and also observed that mainly linear aldehydes and alcohols are formed at low conversions (below 5 \%). The Anderson-Schulz-Flory distribution of the \( C_2-C_{11} \) aldehydes were nearly parallel to that of the \( C_{1-10} \) hydrocarbons. This indicated that the hydrocarbons and aldehydes have the same of chain growth probability.

1.1.4 Supported iron catalysts

Highly dispersed metal particles on supports have been widely applied to a number of significant processes. Metal catalysts are usually dispersed on suitable supports to increase the fraction of exposed metal atoms to the reactants. Commercial iron based Fischer-Tropsch (FT) catalysts have usually been fused or precipitated due to the abundance and cheapness of iron.

Some researchers have indicated that supported Fe based catalysts that been developed thus far lack sufficient activity for commercial operations (Xiaoding et al., 1987). Bond (1982) has related FT Fe supported catalysts low activity to strong metal support interactions as the iron may become immersed into the support. Dry (1996) reported that \( \text{Al}_2\text{O}_3 \) and zeolites are not suitable supports for Fe based catalysts due to their acidic nature. He indicated that the higher the “basicity” of the catalyst the higher the average molecular weight of the products while more olefins and alcohols are formed.

Irrespective of some negative reports the catalytic behaviour of FT iron based supported catalysts have received much attention (Lee and Lee, 1989). Small particles are often obtained by dispersing the metals onto porous supports. The correlation between activity and selectivity of catalysts with varying particle size has attracted interest (Boudart et al., 1975). It has also been proposed that supported iron catalysts may be used in the FT
synthesis to improve the physical robustness and thermal stability of the catalyst. A problem normally associated with unsupported catalysts is the production of fines which, plug the fixed bed reactor or cannot be separated at a reasonable rate from the catalyst-containing slurry. O’ Brien et al. (2000) investigated the catalytic behaviour of Fe on a number of different supports and compared the productivity of these supported catalysts to an unsupported precipitated iron catalyst, at 523 K, at 13 bar and a total flow of 3.1 l(n)h⁻¹g⁻¹Fe (H₂/CO = 0.7). The alumina and magnesium aluminate exhibited the highest productivity (0.35 gh⁻¹g⁻¹Fe) while the productivity of the silica and magnesium silicate supported catalysts were lower at 0.2 and 0.05 gh⁻¹g⁻¹Fe respectively. The precipitated catalyst with the same Fe / K and Fe / Cu ratios as the supported catalyst (100 Fe / 6 Cu / 8 K) had a productivity of 0.5 gh⁻¹g⁻¹Fe. The supported alumina catalyst productivity was about 75% of the productivity of the un-supported catalyst. The un-supported catalyst produced less methane and had a higher olefin selectivity, which increased with higher carbon numbers. While the supported catalysts were more robust compared to the un-supported catalyst. Initially the alumina supported catalyst had particles ranging from 60 to 250 µm and after 312 hours of synthesis in a slurry reactor, the particles decreased to a range 30-100 µm. After spray drying and calcination the un-supported catalyst had particles in the range 30-50 µm. 24 Hours of synthesis conditions in a slurry reactor led to the disintegration of the particles to 1-3 µm. It may seem that the attrition resistance as well as the productivity comparisons merits consideration of the supported Fe catalysts for FT synthesis.

Pijolat and Perrichon (1985) reported the synthesis of alcohols from CO and H₂ over a Fe / Al₂O₃ catalyst. A 10-wt % Fe / Al₂O₃ was investigated, which was prepared by deposition precipitation of Fe onto γ-Al₂O₃. The catalyst activity was investigated as a function of total pressure of the H₂/CO mixture between 8 and 30 bars in the temperature range of 473-548 K. Methanol was the major product upon reaction at 473 K and 8 bars. Total alcohol selectivity however decreased with an increase in temperature and pressure. The alcohol and hydrocarbon analysis were interpreted and compared using the Anderson-Schulz-Flory distribution. Results obtained from CO conversions and the Anderson-Schulz-Flory distribution lead to the conclusion that there may be similarities between the formation of the hydrocarbons and alcohols. It was suggested that higher alcohols and hydrocarbons might
have common precursors. CO insertion into a metal-hydrocarbon bond followed by hydrogenation leading to an alcohol with an additional carbon atom was proposed as a possible mechanism for higher alcohol formation.

### 1.2 Thermodynamic considerations

The standard heats of enthalpy and free energy of alcohol formation were calculated for the stoichiometry according to equation 1.2 (Xiaoding et al., 1987) at atmospheric pressure.

\[ n\text{CO} + 2n\text{H}_2 \leftrightarrow C_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Temperature (K)</th>
<th>( \Delta H_R ) (kJ/mol)</th>
<th>( \Delta G_R ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)OH</td>
<td>300</td>
<td>-90.71</td>
<td>-24.86</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>-94.69</td>
<td>-2.30</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>-97.93</td>
<td>21.19</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>-100.46</td>
<td>45.26</td>
</tr>
<tr>
<td>C(_2)H(_5)OH</td>
<td>300</td>
<td>-205.07</td>
<td>-66.25</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>-211.88</td>
<td>-18.91</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>-217.34</td>
<td>29.991</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>-221.57</td>
<td>79.873</td>
</tr>
<tr>
<td>C(_3)H(_7)OH</td>
<td>300</td>
<td>-424.83</td>
<td>-217.69</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>-434.13</td>
<td>-147.19</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>-441.44</td>
<td>-74.57</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>-446.84</td>
<td>-0.66</td>
</tr>
<tr>
<td>C(_4)H(_9)OH</td>
<td>300</td>
<td>-558.58</td>
<td>-286.40</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>-571.00</td>
<td>-193.73</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>-580.79</td>
<td>-98.23</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>-588.24</td>
<td>-0.98</td>
</tr>
<tr>
<td>C(_5)H(_11)OH</td>
<td>300</td>
<td>-707.98</td>
<td>-351.51</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>-721.64</td>
<td>-230.54</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>-732.04</td>
<td>-106.50</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>-739.59</td>
<td>19.36</td>
</tr>
</tbody>
</table>

Upon inspection of the enthalpy values the formation of higher alcohols becomes more exothermic with an increase in carbon number. The free energy decreases with an increase in n, which indicates favourable formation of higher alcohols. An increase in reaction temperature leads to an increase in the \( \Delta G \) thus the system becomes thermodynamically unfavourable for a certain alcohols.

The maximum obtainable conversion for alcohols can be calculated. Stiles et al. (1991)
reported the maximum obtainable conversions of CO hydrogenation to methanol, ethanol, propanol and isobutanol. Methanol is thermodynamically limited at substantial low temperatures. Verkerk et al. (1999) explained the observation by comparing the free energy of methanol with higher alcohols. Methanol formation is less exothermic thus the equilibrium is shifted towards the reverse reaction at lower temperatures compared to the higher homologues. The temperature dependence was more pronounced for the higher alcohols with higher free energy. Temperature was indicated to influence the maximum conversions to higher alcohols (Stiles et al. 1991). For example the calculated maximum conversion to ethanol at 100 bar and 673 K was found to be ~ 95 % while conversion to isobutanol at 100 bar and 673 K was calculated at ~85 %.

The maximum obtainable conversion to alcohols was indicated to be pressure dependent Stiles et al. (1991). The observation was explained with the principle of Le Chatelier. The system will shift its equilibrium in the direction of volume contraction upon pressure increase. The sum of the stoichiometric coefficients for alcohol formation from CO and H$_2$ as indicated by equation 1.2 amounts to –2 for methanol and –6 for propanol. Thus the maximum obtainable conversion to higher alcohols are more pronounced by pressure increase.

In the FT process alcohols are also associated with paraffin, olefin and water formation. The water formed is coupled to carbon dioxide by the water gas shift reaction.

Equation 1.2 can be subsequently rewritten.

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad 1.3
\]

\[
(2n - 1)\text{CO} + (n + 1)\text{H}_2 \leftrightarrow \text{C}_n\text{H}_{2n} + \text{1OH} + (n - 1)\text{CO}_2 \quad 1.4
\]

\[
n\text{CO}_2 + 3n\text{H}_2 \leftrightarrow n\text{C}_n\text{H}_{2n+1}\text{OH} + (2n - 1)\text{H}_2\text{O} \quad 1.5
\]

FT process becomes more favourable in the following order for the same value of n (Xiaoding et al., 1987).

\[
\text{C}_n\text{H}_{2n} > \text{C}_n\text{H}_{2n+1}\text{OH} > \text{C}_n\text{H}_{2n+2}
\]

Besides the formation of paraffins, olefins and oxygenated hydrocarbons other reactions such as hydrogenation, dehydration and dehydrogenation may also occur during the FT
reaction. In actual fact FT catalysts may catalyse the decomposition of alcohols (Murchison et al., 1988).

1.3 FT mechanism

The mechanism of heterogeneous catalytic reactions involve the transport of reactants to the catalyst surface, adsorption of the reactants on the surface, desorption of the products and transport of the products from the surface. The FT synthesis is a slow catalytic process. It may indicate that the catalytic reactions are slow or that a small fraction of the catalyst surface partakes in the catalytic process. Mechanisms proposed for the FT process mostly evaluated reactions of the reactants on the catalyst surface.

1.3.1 Carbide mechanism

Fischer and Tropsch proposed the carbide mechanism in 1926. They suggested that carbides are formed from the reaction of synthesis gas over the catalyst surface followed by hydrogenation, which leads to methylene groups. The methylene groups are subsequently involved in polymerisation reactions to form saturated and unsaturated hydrocarbons. The hypothesis was however criticised because the model could not explain the formation of oxygenates especially methanol and ethanol.

Alternative mechanisms have since been proposed. In 1980 Brady and Petit revisited the carbide theory and asked the question how would methylene groups behave on a metal surface. They examined the products of the reaction of diazomethane (CH$_2$N$_2$) with and without H$_2$ over various transition metal (Ni, Pd, Fe, Co, Ru) surfaces. The expectation was that CH$_2$N$_2$ would dissociate to adsorbed methylene groups. It was found that CH$_2$N$_2$ in the absence of H$_2$ resulted in ethene being the major product formed. It was concluded that CH$_2$ fragments alone on a metal surface is not polymerisable. The CH$_2$N$_2$ / H$_2$ mixture over the metal surfaces produced a mixture of hydrocarbons characteristic of the FT process. It was proposed that during the initiation the methylene group was reduced to a methyl group followed by the insertion of the methylene group into the metal alkyl bonds.
II. 

Scheme 1.1 Polymerisation Mechanism

The polymerisation reaction is currently considered to entail an initiation, propagation and termination step. Initiation involves the formation of a monomer (methylene group) form the CO/H₂, followed by the propagation where monomer units are incorporated into the growing chain. In the termination step, the polymerisation stops and hydrocarbons are desorped (van Steen and Shulz, 1999).

Scheme 1.2 Simplified scheme of the hydrogenation of surface carbon.

McCandlish (1983) indicated that the carbide theory does not adequately explain branching exhibited in the FT process. He proposed that vinylidene surface complexes act as chain initiators. Chain growth was proposed to occur by the insertion of methylene into the carbon-carbon double bond of vinylidene complexes to form a cyclopropyldiene transition state. Rearrangement of the cyclic complex may produce linear (cycle A) or branched (cycle B) products.
Scheme 1.3 Methylene insertion into vinylidene complexes.

The inability of the carbide theory to explain oxygen containing organic compounds inspired Storch and Golumbic (1951) to propose the enol mechanism.

1.3.2 Enol mechanism

The mechanism proposes that oxymethylene species is formed when hydrogen is added to adsorbed CO. The oxymethylene species condenses in a chain growth process.

\[
(CO)\alpha + 2H \rightarrow H_{\cdot}C\cdot\cdot\cdot\cdot\cdotOH
\]

\[
H_{\cdot}C\cdot\cdot\cdot\cdot\cdotOH + R\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·
\]

Scheme 1.4 The proposed enol mechanism

The mechanism has however been discarded. No support for the existence of oxymethylene species or for the condensation reactions has been produced.
1.3.3 CO insertion

An alternative mechanism was proposed one in which “CO insertion” or “alkyl migration” facilitates C-C bond formation. The mechanism postulated that CO insertion into the metal alkyl groups followed by the reduction of the acyl group and the repetition of the CO insertion process leads to chain growth.

\[
\begin{align*}
R & \quad CO \\
\rightarrow & \quad CO \\
& \quad H_2 \\
& \quad CH_2 \\
& \quad \text{etc}
\end{align*}
\]

Scheme 1.5. Proposed CO insertion mechanism

The CO insertion mechanism received credibility from analogous homogeneous organometallic systems, which have been investigated extensively (Anderson and Moss, 1994).

Schulz et al. (1999) introduced the principal of selective inhibition, in which he indicated that the selectivity of the FT process is influenced by changes in the catalyst surface. He proposed that it might seem probable for CO, CH₂ or ethene to be involved in chain growth. This may explain the number of mechanisms proposed for the FT process in an attempt to explain product formation.

1.3.4 Formation of oxygenates in the FT process

Researchers are actively debating the mechanism of syngas conversion to higher alcohols. A commonly proposed mechanism for oxygenate formation in the FT process is associated with CO insertion (Shulz et al., 1999, Xiaoding et al., 1987).

Pijolat and Perricon (1985) investigated a Fe based catalyst for alcohols formation. He proposed that oxygenates might be formed with a hydrocarbon based mechanism and CO insertion into the growing hydrocarbon chain. There may be a close relationship between oxygenate formation, in the FT synthesis and the homogeneous hydroformylation process.
They found that the curves of CO conversions as a function of reaction temperature and the Anderson-Schulz-Flory distribution indicated that the hydrocarbons and the alcohols might have common precursors. In order to investigate CO insertion n-butene was added to the CO/H₂ feed. A five-fold increase in the formation of n-propanol was observed. These results indicated that CO insertion into a metal alkyl bond occurs during the synthesis of higher alcohols.

Schematic model for the synthesis of oxygenates during CO hydrogenation and the role CO insertion plays is depicted in Scheme 1.6 (Xiaoding et al., 1987).

\[
\begin{align*}
\text{CH}_3\text{OH} & \xleftrightarrow{H^*} \text{CO} \xleftrightarrow{*} \text{CO} \\
& \downarrow \text{C}^* + \text{O}^* \xrightarrow{H^*} \text{HO} + \star \\
\text{C}_2\text{H}_5\text{OH} & \xleftrightarrow{H^*} \text{C}_x\text{H}_y\text{CO}^* \xrightarrow{H^*} \text{C}_x\text{H}_y \xrightarrow{H^*} \text{C}_2\text{H}_4 \\
& \downarrow \text{CH}_x^* \\
\text{C}_3\text{H}_7\text{OH} & \xleftrightarrow{H^*} \text{C}_x\text{H}_y\text{CO}^* \xrightarrow{H^*} \text{C}_x\text{H}_y \xrightarrow{H^*} \text{C}_2\text{H}_4 \\
& \downarrow \text{CH}_x^* \\
\text{C}_{n+1}\text{H}_{2n+3}\text{OH} & \xleftrightarrow{H^*} \text{C}_x\text{H}_y\text{CO}^* \xrightarrow{H^*} \text{C}_x\text{H}_y \xrightarrow{H^*} \text{C}_n\text{H}_{2n} \\
& \downarrow \text{CH}_x^*
\end{align*}
\]

**Scheme 1.6** Model for CO hydrogenation for the synthesis oxygenates and hydrocarbons.

The mechanism involves dissociative CO bonding followed by the hydrogenation of the surface carbon to CHₓ (x = 1-3). The CH₂ species are incorporated in the chain growth process while CO insertion terminates chain growth. H addition or β-H of the adsorbed alkyl species may lead to paraffins and olefin respectively.
1.4 Catalyst systems used in oxygenate formation and their associated mechanisms

A number of catalysts have been developed for the conversion of synthesis gas into higher alcohols. Some of these catalysts with possible industrial applications have been focused on below.

1.4.1 Modified methanol catalysts

Alkali promoted methanol catalysts has been reported to convert synthesis gas to higher alcohols. The addition of alkali metals such as K, Rb and Cs to a Cu / Zn / Al₂O₃ methanol catalyst have shown to modify the catalyst (Stiles et al., 1991). The catalyst activity sharply decreased compared to the un-promoted methanol catalyst, in fact the reaction temperature was increased for the reaction to take place. The addition of the alkali metals to the catalyst resulted in an increase of ~ 8 % of the total higher alcohols. The selectivity for the higher alcohols was however low while too much methanol was formed. High methanol selectivity was also reported by Smith et al., (1983) over a Cu / Zn / Al₂O₃ catalyst, promoted with K₂CO₃. Smith investigated the alcohol selectivity as a function of temperature. The methanol selectivity decreased while the higher alcohol selectivity increased with an increase in temperature. The minimum operating temperature was limited by the low higher alcohol productivity while the maximum operating temperature was limited by the catalyst stability.

1.4.1.1 Mechanism associated with the modified methanol catalysts

Smith (1983) attempted to explain the formation of alcohol formation over the Cu / Zn / Al₂O₃ catalyst modified by the addition of K₂CO₃. He proposed that chain growth occurred by one carbon addition to a growing chain as indicated in Scheme 1.7.
\[
\begin{align*}
\text{CO} + \text{H}_2 & \xrightarrow{k} *\text{COH} \quad \text{a} \rightarrow *\text{CCOH} \quad \text{b} \rightarrow *\text{CCCOH} \\
\text{CH}_3\text{OH} & \quad \text{C}_2\text{H}_5\text{OH} \quad \text{n-C}_3\text{H}_7\text{OH} \quad \text{i-C}_4\text{H}_9\text{OH} \\
\end{align*}
\]

- carbon addition to the \( \alpha \) position
- carbon addition to the \( \beta \) position
- desorption
- adsorbed surface species

**Scheme 1.7** A simplified chain growth scheme in the formation of oxygenates.

High methanol selectivity was attributed to a slow first step in the growing chain since \( \alpha \)-addition is much slower compared to \( \beta \)-addition. It was assumed that addition does not occur on an OH group while two carbon addition does not occur at a \( \alpha \)-carbon. Large amounts of 2-methyl-1-propanol (i-C\(_4\)H\(_9\)OH) were obtained. The scheme predicts high amounts of (i-C\(_4\)H\(_9\)OH) as the intermediates cannot grow further. The proposed scheme does not however explain the formation of higher alcohols, \( C \geq 5 \), over modified methanol catalysts (Fattore et al., 1985).

Lietti et al. (1990) performed temperature programmed reactions of C\(_4\) oxygenates on un-promoted and K promoted ZnCr oxide catalysts. He proposed that higher oxygenates are formed by the condensation of shorter chained aldehydes in an aldol like condensation reaction (Scheme 1.8).

\[
\begin{align*}
\text{R}_1\text{CH}_2\text{CHO} + \text{R}_2\text{CHCHO} & \rightarrow \text{R}_1\text{CH}_2\text{CHCHCHO} + \text{H}_2\text{O} \\
\text{R}_1\text{CH}_2\text{CHCHCH}_3 & \end{align*}
\]

**Scheme 1.8** Mechanism for an aldol like condensation.

1.4.2 Co / Cu catalysts

The French Petroleum Institute (IFP) patented several catalysts for the production of higher alcohols from synthesis gas. The catalysts were Cu based to which, substantial amount of
Co was added. Examples of some of the catalysts reported are indicated in Table 1.5.

**Table 1.5** Some reported IFP catalysts.

<table>
<thead>
<tr>
<th>Catalyst composition</th>
<th>Reaction conditions</th>
<th>Alcohol selectivity, C- %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCoKM M = Mn, Cr, Zn, Fe</td>
<td>~60 bars, 523 K, H₂ / CO = 66/19</td>
<td>84-97</td>
<td>Sugier et al., 1978</td>
</tr>
<tr>
<td>CuCoAlZnNa</td>
<td>~60 bars, 543-593 K,</td>
<td>65-70</td>
<td>Courty et al., 1985</td>
</tr>
<tr>
<td>CuCoAlZnCaMgLi</td>
<td>3000 VVh,</td>
<td></td>
<td>1985</td>
</tr>
<tr>
<td>CuCoAlZnNaLi</td>
<td>H₂/CO + CO₂ = 2</td>
<td></td>
<td>1985</td>
</tr>
<tr>
<td>CuCoAlZnNa</td>
<td>~60 bars, 543-593 K,</td>
<td>50-76</td>
<td>Chaumette et al., 1985</td>
</tr>
<tr>
<td>CuCoAlMnZnNa</td>
<td>3000 VVh,</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuCoAlZnPdNa</td>
<td>H₂/2CO + 3CO₂ = 1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Courty et al. (1982) attempted to explain the behaviour of an IFP type catalyst, CuCoCr alkali catalyst. The alcohol selectivity was found to be highly dependent on the preparation and activation procedures. The main preparation method used was co-precipitation of the metal nitrates. Inappropriate co-precipitation and alkaliing procedures led to FT catalysts with low yields of oxygenated compounds. Another method used in the preparation of the catalysts entailed the complexation of the metal nitrates with an α-alcohol poly-acid followed by the decomposition of the homogeneous precursor. This method had a high tendency to uncontrolled decomposition thus it was evaluated as unfavourable for industrial applications. The alcohol selectivity as a function of precursor composition was investigated. It was found that a Cu rich catalyst produced methanol while a Cr rich catalyst showed very little activity. A Co rich catalyst resembled a FT catalyst with methane as the predominant hydrocarbon formed. It was found that in the activated catalyst metallic Co must be present in pure form or alloyed with Cu. The presence of Co as cobalt aluminate or chromite, rendered the catalyst inactive for higher alcohol synthesis. Cu was actively involved in the synthesis of methanol but it also activated the reduction of Co to metallic cobalt. The alkali suppressed the catalyst acidity thus prevented alcohol dehydration.
Stiles et al. (1991) also investigated the IFP patented catalysts. He encountered run-away reactions fusing the catalyst to the reactor. The IFP patents indicated preferred 5-50% cobalt content, but Stiles found that even the lower range cobalt with larger quantities of alkali resulted in uncontrolled reactions. The catalyst Stiles eventually investigated with sufficient stability had a much lower cobalt content, 0.01-2%. It was indicated that there might be substantial risks involved in the commercialisation of the Cu/Co catalysts patented by IFP.

1.4.2.1 Mechanism associated with the Co / Cu catalysts

Courty et al. (1982) evaluated the products obtained over the alkali metal promoted CuCoCr catalyst. They found that the main products (normal primary alcohols) and the secondary products (paraffins, α-olefins and secondary alcohols) followed an Anderson-Schulz-Flory distribution. The Anderson-Schulz-Flory distribution of the hydrocarbons and the alcohols appeared in parallel with similar α-values. This supported a FT mechanism. Stiles et al. (1991) also attempted to investigate the mechanism of the IFP patented catalysts. The catalysts were adapted to contain such less Co, 0.01-2% instead of 5-50%. The products were evaluated over a Cu / Mn / Zn / Co / Cr / K / Cs catalyst. The catalyst produced substantial amounts of aldehydes. Methane was the only detected hydrocarbon formed while high concentrations of i-butanol and n-propanol were observed. The liquid products did not obey the Anderson-Schulz-Flory distribution.

1.4.3 Rh based catalysts

Rh containing catalysts in the conversion of synthesis gas to oxygenates are of great interest from a practical and theoretical point of view (Xiaoding et al., 1987). Rh is however expensive and the possibility that it may be applied on an industrial scale for oxygenate synthesis is minimal. A mechanistic understanding of oxygenate formation from syngas over Rh may be helpful in the design of new catalysts.

Bowker (1992) has indicated that Rh is one of the most interesting elements in the transition metal series in terms of catalytic properties. These properties may be attributed to its position in the periodic table. In the periodic table it borders elements (Fe and Co) which
have the ability to dissociate CO. Rh has the ability to dissociate molecules and is applied to
de-pollute the motor exhausts of NOx. Rh is known to catalyse the dissociation of NOx into
N₂. Rh also borders metals such as Pd, which does not have the ability to dissociate CO.
Rh has been investigated for its CO insertion function in industrially applied homogeneous
processes such as the acetic acid process and the hydroformylation process. Thus CO can
adsorb dissociatively or non-dissociatively on Rh surfaces.

Rh catalysts have been reported to convert synthesis gas with high selectivity to C₂-
oxigenates. A number of factors influence the selectivity and activity of Rh based catalysts.
For example promoters added, different supports used and the reaction conditions to mention
but a few. Therefore the conversion of syngas over a Rh based catalyst can result into a
wide range of products (Burch and Petch, 1992).

One of the first elements investigated as promoter for an Rh based catalyst was Fe. Bhasin
et al. (1978) demonstrated that the addition of Fe influenced the selectivity of a supported Rh
/ SiO₂ catalyst. The addition of Fe enhanced the conversion of synthesis gas to oxygenates,
while increased Fe content increased the alcohol production.

Since Bhasin et al. (1978) report numerous researchers have investigated factors influencing
syngas conversion over Rh based catalysts. Burch (1992) reported the effect reducible oxide
promoters (Fe, Mn and Ce) have on Rh / SiO₂. Low selectivities to hydrocarbons and high
selectivities to ethanol and methanol were observed. Bastein et al. (1987) reported the
preparation and reduction of Rh / V₂O₃ and Rh / SiO₂ promoted with vanadium. It was
concluded that for high oxygenate selectivity the type of support used is important but it is
essential that the support material appear on the surface of the metal surface. Two methods
were proposed to transport support species to the metal surface. One method was partial
dissolution of the support to facilitate precipitation of the support species on or near the metal
surface. The other method mentioned was high temperature reduction causing metal support
interaction resulting in partially covered metal.

Rh is a very versatile catalyst for CO hydrogenation. The selectivity of the various products
over Rh based catalysts is strongly dependent on a number of factors. The effect different
promoters have on Rh based catalysts have been investigated extensively. Understanding the mechanistic implication promoters have on catalysts has been a challenge. Rh's versatility to catalyse syngas can provide probe reactions in which hypothesis can be investigated.

1.4.3.1 Mechanism associated with Rh based catalysts

Some investigators have aimed to understand oxygenate formation especially over Rh to give in-site into the various mechanistic steps involved in alcohol formation.

Ichikawa et al. (1988) predicted that large ensembles of Rh atoms are needed to dissociate CO. While CO insertion requires isolated Rh ions or atoms. He performed hydroformylation reactions over RhFe carbonyl clusters derived catalysts supported on SiO2. The rates of propene hydroformylation increased by 300 times over the RhFe carbonyl clusters compared to that of the Rh4(CO)12 cluster. The selectivities toward iso and n-butanol were substantially improved over the Fe rich bi-metallic clusters. It was concluded that the RhFe clusters provided a discrete intact ensemble of RhFe atoms active for olefin hydroformylation and hydrogenation to give higher alcohols. The electropositive Fe(Fe3+) in the RhFe ensemble may enhance CO migratory insertion and stabilise the formyl and acetyl intermediates (Scheme 1.11), which are subsequently hydrogenated to alcohols.

\[
\begin{align*}
\text{R} & \quad \text{C} \quad \text{O} \\
\text{Rh} & \quad \text{Fe}^\circledast \\
\rightarrow & \quad \text{H}_2 \\
\text{R} & \quad \text{C} \quad \text{H} \quad \text{O} \\
\text{Rh} & \quad \text{Fe} \\
\rightarrow & \quad \text{H}_2 \\
\text{RCH}_2\text{OH} \\
\end{align*}
\]

Scheme 1.11 Two site interaction of C and O with Rh and Fe.

1.4.4 Mo based catalysts

Mo catalysts have been known to be effective in FT synthesis for the production of light hydrocarbons. It has however been found that Mo based catalysts are active for mixed alcohol formation from synthesis gas (Muaramatuy et al., 1987, Youchang et al., 1986)
Dow chemicals have reported a catalyst process for the production of methanol and higher alcohols. The catalysts were agglomerated molybdenum sulfides made by the thermal decomposition of thiomolybdate. These catalysts were reported to be highly sulfur resistant. Furthermore Dow has developed a method in drying the alcohols. Most of the water is removed by the incorporation of zeolites units in the system (Haggin, 1984).

The promotional effect of alkali on MoS$_2$ catalysts has extensively been investigated. Youchang (1986) found that the addition of K$_2$CO$_3$ greatly increased alcohol selectivity. The addition of K$_2$CO$_3$ (30 % by weight) to MoS$_2$ produced a total alcohol yield of 90 %, of which methanol was the major alcohol.

Union Carbide Corporation (Kinkade, 1985) has disclosed an alkali promoted MoS$_2$ catalyst for selectively producing C$_1$-C$_5$ linear primary alcohols from synthesis gas. The MoS$_2$ was prepared by the thermal decomposition of thiomolybdate followed by the introduction of an alkali metal using incipient wetness impregnation. It was claimed that high space velocities, preferably 12,00(l/ldcat/h), resulted in high selectivities to the desired alcohols. Low space velocities promoted hydrocarbon formation at the expense of the alcohol selectivity. The preferred reaction temperature was in the range 548 to 623 K. The higher temperatures favoured the higher alcohol formation but more hydrocarbons were also formed.

Alkali promoted Mo supported catalysts have, also been reported to convert syngas to higher mixed alcohols. Dow patented Mo supported catalysts for CO hydrogenation to alcohols. Their catalysts consisted of elements from the group Mo, W and Re. The catalysts were promoted with alkali or alkaline earth elements. High pressures were utilised with minimum pressures of 52.7 bar and 70 bar (Quarderer and Cochran, 1989).

Many reports have been published on the influence different preparation methods would have on alkali promoted Mo supported catalysts. For example Tatsumi et al. (1986) investigated the effect the sequence of impregnation would have on a Mo / K$_2$CO$_3$ / SiO$_2$ catalyst. Co-impregnation of the salts onto the support favoured hydrocarbon formation while pre-treating SiO$_2$ with K$_2$CO$_3$ improved the alcohol selectivity.
1.4.4.1 Mechanism associated with Mo based catalysts

Tatsumi et al. (1989) investigated the elementary reaction steps for higher alcohols synthesis from \( \text{H}_2/\text{CO} \) over KCl promoted and un-promoted Mo / SiO\(_2\), by the addition of probe molecules.

Addition of ethene resulted in a marked increase in n-propanol. The un-promoted catalyst exhibited higher activity for the hydrogenation of ethene to ethane. This was expected, since alkali promotion suppresses the hydrogenation activity of transition metals known to catalyse CO hydrogenation. Similarly the addition of propene yielded an increase in butanol. The propene hardly changed the isomer distribution of the butanols. The butanol isomer distribution of propene hydroformylation was similar compared to that of CO hydrogenation over the Mo / supported catalysts. These findings suggested that alcohols may be formed via CO insertion into a metal alkyl bond to form acyl species which are subsequently hydrogenated.

The addition of methanol to the \( \text{H}_2/\text{CO} \) feed had a very slight increase in the ethanol formation. It was concluded that the homologation reaction of alcohols might not play a significant role in the formation of alcohols.

Significant amount of C\(_4\) oxygenates (butanol, crotonaldehyde and butyaldehyde) were formed over the K promoted and un-promoted catalyst upon the addition of acetaldehyde. The formation of the C\(_4\) oxygenates were attributed to aldol condensation of acetaldehyde. K promoted catalyst exhibited less C\(_4\) oxygenates and hydrocarbons derived from acetaldehyde compared to the un-promted catalyst. It appeared that aldol condensation might be catalysed by the acid sites on the catalyst. The KCl on the promoted catalyst surface may be poisoning the acid sites. It was concluded that aldol condensation might not be very important in the chain growth process to form higher alcohols.
1.5 Project proposal

Substantial numbers of studies have been devoted for the production of mixed alcohols form syngas. Subsequently a number of mechanisms have been proposed for higher alcohol formation. The Fischer-Tropsch process has been known to produce alcohols but in low yields and selectivity. CO insertion into a metal alkyl bond is a commonly proposed mechanism for alcohol formation during the FT process. Literature indicates that oxygenates formed over Rh using synthesis gas, and oxygenates formed during the FT process may be similar.

Rh is known to catalyse industrially important processes, which are associated with CO insertion, such as the hydroformylation process and the acetic acid process. Rh based catalysts are very versatile during CO hydrogenation. Hydrocarbons may be formed via dissociative CO bonding but Rh may also catalyse C₂ oxygenates, which have been attributed to its ability for CO insertion into metal alkyl bonds.

The hypothesis we are investigating is that Rh as promoter to a Fe based catalyst will lead to enhanced oxygenate formation. Open literature indicated that Fe addition to a Rh supported catalyst enhanced oxygenate formation. We propose that the addition of Rh as promoter to a Fe supported catalyst will lead to enhanced oxygenate formation.

A Fe base case catalyst, containing promoters Cu and K, will be prepared, characterised and tested. The catalyst will be investigated to identify the oxygenate formation during CO hydrogenation. Various amounts of Rh will be added to the Fe based catalyst. These catalysts will be characterised and tested. We want to establish if Rh addition enhances oxygenate formation and what correlation exists between the quantity of Rh added and the oxygenates formed.
2: EXPERIMENTAL

2.1 Catalyst preparation

The salts Fe(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O and K₂CO₃ were purchased from Sigma Aldrich and used as received. RhCl₃·15H₂O was purchased from Next Chimica and was used without purification. The Al₂O₃ (Puralox) was obtained from Condea.

The base catalyst, JG 9, was prepared by dissolving Fe(NO₃)₃·9H₂O (90.4 g, 0.2 mol), Cu(NO₃)₂·3H₂O (4.8 g, 0.02 mol) and K₂CO₃ (1.1 g, 0.01 mol) in de-ionised H₂O (~132 ml) in a round bottom flask. γ-Al₂O₃ (75 g) was added to the brown salt solution. The slurry was mixed and dried on a rotary evaporator until a dry brown free flowing powder was obtained. The drying procedure used on the rotary evaporator is summarised in Table 2.1. During the drying procedure the catalyst stuck to the walls of the round bottom flask and formed lumps. The lumps were broken continuously to ensure even drying. The catalyst was calcined at 523 K for 4 hours.

**Table 2.1** The drying procedure used on the rotary evaporator.

<table>
<thead>
<tr>
<th>Oil Bath Temperature, K</th>
<th>Vacuum, mbar</th>
<th>Rotational Speed, rpm</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>333-343</td>
<td></td>
<td>86</td>
<td>10 min</td>
</tr>
<tr>
<td>333-343</td>
<td>240</td>
<td>86</td>
<td>1 hr</td>
</tr>
<tr>
<td>333-343</td>
<td>50</td>
<td>86</td>
<td>1 hr</td>
</tr>
<tr>
<td>343-353</td>
<td>50</td>
<td>86</td>
<td>~ 3 hours</td>
</tr>
</tbody>
</table>

The recovered catalyst was sieved to obtain particles in the range 38-150 µm. Approximately 100 g sieved catalyst was transferred to a round bottom flask containing a solution of Fe(NO₃)₃·9H₂O (90.4 g, 0.2 mol), Cu(NO₃)₂·3H₂O (4.8 g, 0.02 mol) and K₂CO₃ (1.1 g, 0.01 mol) in de-ionised H₂O (~132 ml). The mixture was mixed and dried on a rotary evaporator, as indicated in Table 2.1, until the catalyst was free flowing. The catalyst was calcined at 523 K for 4 hours and sieved in the fraction 38-150 µm.
Onto three portions of the base catalyst (16 g) different amounts of Rh were loaded. The Rh loadings were determined relative to the Fe mass % obtained for JG 9 (base catalyst). The Rh salt was dissolved in a minimum amount of de-ionised water (~ 7 ml), as determined by the average pore volume of JG 9 (Table 3.3). The Rh solution was added drop-wise with 10 ml syringe to JG 9, which was spread out evenly over a watch glass with a 30 cm diameter. The syringe was rinsed with ~1 ml de-ionised water, which was also added drop-wise to JG 9. The Rh salt added to the different portions of JG 9 are indicated below.

\[ \text{Table 2.2} \quad \text{The RhCl}_3.15\text{H}_2\text{O added to the base catalyst JG 9.} \]

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( \text{RhCl}_3.15\text{H}_2\text{O} )</th>
<th>Rh per 100 mass % Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>JG 9a</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>JG 9A</td>
<td>0.05 g, 0.109 mmoles</td>
<td>0.5</td>
</tr>
<tr>
<td>JG 9B</td>
<td>0.1 g, 0.218 mmoles</td>
<td>0.9</td>
</tr>
<tr>
<td>JG 9C</td>
<td>0.16 g, 0.334 mmoles</td>
<td>1.4</td>
</tr>
</tbody>
</table>

\( ^{a} \) 15 mass % Fe

JG 9A, JG 9B and JG 9C were oven dried at 393 K for 4 hours and calcined 523 K for 4 hours. The catalysts were characterised and tested as indicated in the following sections.

2.2 **Ex-situ reduction of the catalysts**

Ex-situ reduction investigations were performed on the catalysts. The catalysts (3 g) were loaded in a quartz tube. The tube contained a glass wool plug at the bottom, a thermocouple to control the catalyst bed temperature and a second wool plug was placed on the catalyst bed to prevent any catalyst loss during the reduction process. The quart tube was placed in a heating mantel, which contained a thermocouple to control the heating mantle temperature.
The reduction unit. ($T_{\text{red}} = 533$ K, $P_{\text{red}} = 1$ bar, $SV_{\text{red}} = H_2 (1l(n)/gcat/h)$).

The catalysts were reduced in a flow of high purity $H_2$ (purity of 99.9 %, supplied by Fedgas). The $H_2$ flow was controlled with a Brooks mass flow controller. The mass flow controller was calibrated at atmospheric pressure. The flows were normalised to standard pressure (1.013 bar) and temperature conditions (273.15 K) (Appendix A). Reduction was performed at 533 K for 16 hours at 1 bar and a SV of 1 l(n)/gcat/h. After the reduction period the catalyst was cooled down under Ar flow. Transferring the catalyst under Ar, into melted wax covered under a blanket of Ar, passivated the reduced catalyst. These samples were submitted for Mössbauer emission spectroscopy.

JG 9, JG 9A, JG 9B and JG 9C were characterised using elemental analysis, Energy Dispersive X-ray spectroscopy analysis, surface area analysis and Mössbauer emission spectroscopy.
2.3 Catalyst characterisation

2.3.1 Elemental analysis

2.3.1.1 Iron content

The iron content was determined by titration with \( \text{K}_2\text{Cr}_2\text{O}_7 \). It is a well-known method for the determination of iron in ore (Skoog and West, 1982).

The catalysts were prepared by the addition of HCl (~40 ml, 6.5 N) to 5 g sample. The mixture was refluxed for one hour to dissolve the sample. The resulting mixture was diluted to 500 ml. The mixture was filtered and 25 ml of the filtrate was added to a HCl (10 N) : de-ionised water (1 : 1) solution. The solution was heated and brought to boil. To the iron solution SnCl\(_4\) was added drop-wise to reduce the iron (III) to iron (II) species. SnCl\(_4\) was added until the solution become clear. Further two drops were added. Excess reducing agent was removed by the addition of HgCl\(_2\). If upon addition of HgCl\(_2\) a white precipitate formed, the experiment was continued but if a grey precipitate formed the experiment was stopped. A phosphoric-sulphuric acid mixture was prepared by adding H\(_2\)SO\(_4\) (500 ml, 98 % solution) to H\(_3\)PO\(_4\) (400 ml, 85 % solution) and diluting it to 5000 ml. The acid solution (50 ml) was added to the iron sample solution. Two drops of indicator (diphenylamine sulphonate) were added to the iron sample solution. The solution was titrated with \( \text{K}_2\text{Cr}_2\text{O}_7 \) (0.05 N) until a light red colour appeared.

2.3.1.2 Atomic adsorption spectroscopy

Atomic adsorption spectroscopy (AA) was used to quantify K and Cu in the catalyst samples. AA is a well-known analytical technique and has been documented extensively (Christain and Feldman, 1970).

The AA experiments were performed on a Varian SpectrAA-10. The Cu and K analysis were performed at wavelength of 324.8 nm and 589 nm respectively with a slid with of 0.5 nm. Analyses were performed on iron solutions prepared, as described in section 2.3.1.1. The iron solution was diluted to contain iron (0.18 g) and HCl (45 ml, 0.5 N) in 100 ml solution based on the known concentration of the iron in the sample (determined in section 2.3.1.1).
Standard solutions were prepared containing known amounts of the element to be determined. The standard and the blank solutions were prepared to contain the same Fe and HCl content as the iron sample. The analysis for K, CsCl was added to the blank and standard solutions to improve the sensitivity.

2.3.1.3 Inductively coupled plasma spectroscopy

Inductively Coupled Plasma Spectroscopy (ICP) was applied to determine the Rh and Al₂O₃ content in the catalyst samples. ICP became commercially available in the 1970’s and has since grown in popularity. ICP is an atomic emission technique employing plasma atomisation. Argon ions and electrons are the principle conducting species in the argon plasma used for emission analysis. Argon ions forced in a plasma is capable of adsorbing power from external sources to maintain temperatures up to 10 000 K, where further ionisation sustains the plasma further (Skoog and Leary, 1992-b). More detailed discussion on ICP are presented by Montaser (1992).

The ICP analyses were performed on a Vista AX, CCD Simultaneous AGS. The catalyst samples were prepared as indicated in section 2.3.1.1. Standard solutions were prepared containing known amounts of the elements under investigation. The emission spectra of Rh and Al₂O₃ were recorded at 363.5 nm and 396.15 nm respectively.

2.3.2 Energy dispersive X-ray spectroscopy

Energy Dispersive X-ray Spectroscopy (EDS) was used to obtain quantitative information on the distribution of Fe, Cu, K, Al and Rh atoms. EDS X-ray emission is generated by a narrow focused beam electrons. A heated tungsten cathode and accelerating anode produced the electron beam. An optical microscope was used to locate the area to be bombarded. The X-rays emitted are dispersed by a single crystal and detected and analysed with an energy dispersive spectrometer (Skoog and Leary, 1992 b). Reimer (1985) reported a more in-depth description of the technique.
EDS measurements were performed on a Scanning electron microscope, model 1430 LEO SEM. Integrated iXRF energy dispersive X-ray spectrometer was employed fitted with a tungsten filament and operated at 25 kV. The samples were prepared by setting the catalysts in an EPOFIX resin. Samples were then polished to obtain a smooth surface. The smooth surfaces were sputter coated with gold to obtain conductive surfaces.

2.3.3 Surface area determination

The surface area of the catalysts were determined using the BET adsorption theory. The theory incorporates the concept of multi-layer adsorption. Webb (1997) reported a detailed derivation of the BET equation.

The total surface area data were obtained on a Micromeritics Gemini surface area analyser. The measurements were performed at liquid nitrogen temperature using N₂ as adsorbing gas. Catalyst samples (~50 mg, sieved in the range 38-150 μm) were weighed into a sample tube and degassed at 513 K for 16 hours prior to analyses.

2.3.4 Mössbauer Emission Spectroscopy

Mössbauer emission spectroscopy (MES) has extensively been used to extrapolate information on a number of important catalyst systems. MES is a bulk technique that can be provide information about the oxidation state, magnetic field and the lattice symmetry of a number of elements based on the hyperfine interactions between the nucleus and its local environment. Motjope (2000) gives a more detailed description of the Mössbauer effect.

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

The catalyst sample (100 mg) was grounded into a fine powder and mixed with a Mössbauer inert material. The mixture was loaded into a sample holder giving a sample mass area ratio
of 30 mg/cm². This amount of sample was sufficient to give a decent Mössbauer signal with minimal distortion due to secondary effects. Experiments were performed at 298 K and the data were collected over 36 hours to obtain at least 500 000 counts per channel.

Data were analysed using a least-square fitting routine that models the 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), quadruple (Δ) and hyperfine magnetic field (H). The isomeric shift values are reported relative to metallic iron (α-Fe) and the iron content of each phase is determined from their relative peak areas.

2.4 Fischer-Tropsch synthesis

The Fischer-Tropsch investigations of the catalysts were performed in a fixed bed reactor. Atomic adsorption spectroscopy analysis (Table 3.1b) indicated that the final catalyst compositions were i.e. JG 9 ( 0 Rh / 100 g Fe), JG 9 A (1.3 Rh / 100 g Fe), JG 9B (2.4 Rh / 100 g Fe) and JG 9C (3.9 Rh / 100 g Fe).

2.4.1 Reactor operation

The fixed bed reactor was designed to operate from atmospheric pressure to ~ 100 bar and a maximum temperature of 673 K. Reactions were performed at 20 bar and the reaction temperature ranged from 513 to 553 K. All operations were set manually. A flow diagram representing the reactor set-up is indicated in Figure 2.2.
Figure 2.2 Diagram of the reactor set-up.

The unit had three gas lines providing the reactor with H₂, Ar and APG. Bottled Ar and H₂, supplied by Fedgas, were connected to the lines. Sasol Plant APG was fed to the reactor. Daily inlet samples were used to determine the composition of the APG, as it varied. Each gas was controlled independently using Brooks mass flow controllers. The mass flow controllers were calibrated at atmospheric pressure. The flows were normalised to standard pressure (1.013 K) and temperature conditions (273.15 K) (Appendix A). Downstream, the lines were heated to 473 K to prevent product condensation. The set-up also included a hot pot at 473 K for wax collection and a cold pot at 293 K for oil and water collection.

Gas samples of the inlet gas were obtained at the inlet gas sampling point. Gas samples of the outlet were obtained downstream of the reactor after the wax knock out pot. The lines to the outlet sampling points were heated to 473 K. Gas samples were taken using an ampoule
technique. This technique has been well described by Caricato et al. (1993) and Claeys (1997).

The reactor consisted of a stainless steel tube placed in a furnace (Figure 2.3).

![Fixed bed reactor configuration](image)

**Figure 2.3 Fixed bed reactor configuration.**

The reactor bed contained a sieve, which prevented any catalyst loss during the reactor run. Typically 1.5 g catalyst sieved in the range 38 –150 μm diluted with carborandum (38 –150 μm) in a ratio 1:4 were loaded into the catalyst bed. Upstream, glass wool was placed which acted as a pre-heating zone. A thermocouple was placed in the centre of the reactor bed to monitor the bed temperature. Another thermocouple was placed outside of the reactor bed, to monitor the furnace temperature near centre of the catalyst bed. A temperature difference of 293 K was observed between the centre of the reactor bed and the furnace. The entire reactor was covered with copper wire to assist with heat transfer.

The catalysts were reduced in-situ at 533 K using H₂ at a SV of 6.36 (l(l)/gcat/h) at atmospheric pressure. After reduction the catalyst was cooled down to 473 K under Ar. The
pressure was slowly increased under Ar to 20 bar. At 20 bar the APG was introduced into the system. The catalyst bed was increased to 533 K, at which temperature the FT reaction was monitored. Ar setting was reduced to 20% of the APG setting, and used as an internal standard for the gas analyses. The base catalyst JG 9 (no Rh) was tested first to obtain a base line to which the other catalysts, containing Rh, were compared to.

The promoted catalysts were tested randomly. During testing the Rh promoted catalysts the gas chromatographs experienced mechanical problems. A delay in the gas analysis, which enables determination of the APG composition and CO + CO₂ conversions, were experienced. It was assumed that the activity of the catalysts would be very similar as very little Rh was added to each catalyst. The catalysts were tested at very similar APG brooks settings, which were adjusted very slightly according the products, drained. JG 9 was tested at an average syngas space velocity of 15.3 (l/(n)/gcat/h), JG 9A at 13.5 (l/(n)/gcat/h), JG 9 B at 14.9 (l/(n)/gcat/h) and JG 9C 14.2 (l/(n)/gcat/h). The average syngas velocity is given as the APG composition varied during the reactor runs. JG 9A, JG 9B and JG 9C were tested over a period of ~130 hours while JG 9 (0 Rh / 100 g Fe) was tested over a period of ~150 hours. Samples were taken at very similar time intervals for all the catalysts. During the testing of JG 9 (0 Rh / 100 g Fe), after ~122 hours on line problems were experienced with the ampoules. It was decided to take an additional sample at ~144 hours. After the reaction period the APG flow was stopped and the catalyst cooled down under Ar. It was kept under Ar until it was unloaded and submitted for MES.

JG 9C, the catalyst with the highest Rh loading, was investigated under varying space velocity and temperature conditions. The reactor runs investigating temperature and space velocity the pre-treatment conditions were similar to the previous run with JG 9C. During the temperature investigations JG 9C was tested at 513, 533 and 553 K while the average syngas space velocity was 14 (l/(n)/gcat/h). The catalyst was investigated at 5.7, 14.1 and 26.2 (l/(n)/gcat/h) at 533 K and 20 bar. Reaction changes were made randomly and samples were obtained approximately 24 hours after changes in reaction conditions were made.
3: RESULTS

3.1 Catalyst preparation

The base catalyst, JG 9, was prepared by impregnating $\text{Al}_2\text{O}_3$ with aqueous solutions containing $\text{Fe(NO}_3\text{)_3} \cdot 9\text{H}_2\text{O}$, $\text{Cu(NO}_3\text{)_2} \cdot 3\text{H}_2\text{O}$ and $\text{K}_2\text{CO}_3$. The alumina was impregnated in two stages with equal portions of salt in each impregnation. Salts were dissolved in an amount of water that exceeded the pore volume of the support. The alumina was added to the solution, which resulted in a slurry. The slurry was dried on a rotary evaporator. During the drying process the catalyst stuck to the walls of the round bottom flask and formed lumps. The catalyst was scraped from the walls and the lumps were broken continuously to effect even drying until a free flowing catalyst was obtained.

The high level of Cu per 100 g Fe was used to assist with the reduction of the catalyst, since Cu is known as a reduction promoter (Bukur et al., 1989). Dry (1996) indicated that the higher the basicity of the Fe based catalyst, the higher the probability for chain growth, thus elevated levels of $\text{K}_2\text{O}$ was added. The catalysts JG 9A, JG9B and JG 9C were prepared using incipient wetness impregnation method. Different amounts of Rh were added to various portions of JG 9. During each impregnation $\text{RhCl}_3 \cdot 15\text{H}_2\text{O}$ salt was dissolved in sufficient amount of water, which equalled the pore volume of the base catalyst. The chemical compositions of the different catalysts are shown below and are expressed as mass %.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fe (mass %)</th>
<th>Cu (mass %)</th>
<th>K (mass %)</th>
<th>Al (mass %)</th>
<th>Rh (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JG 9</td>
<td>15.0</td>
<td>1.3</td>
<td>0.7</td>
<td>29.4</td>
<td>-</td>
</tr>
<tr>
<td>JG 9A</td>
<td>12.8</td>
<td>1.3</td>
<td>0.9</td>
<td>29.3</td>
<td>0.2</td>
</tr>
<tr>
<td>JG 9B</td>
<td>15.1</td>
<td>1.6</td>
<td>1.0</td>
<td>31.1</td>
<td>0.4</td>
</tr>
<tr>
<td>JG 9C</td>
<td>12.5</td>
<td>1.3</td>
<td>0.8</td>
<td>30.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Table 3.1b  The relative chemical composition of JG 9, JG 9A, JG 9B and JG 9C per 100 g Fe.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu (mass %)</th>
<th>K₂O (mass %)</th>
<th>Al₂O₃ (mass %)</th>
<th>Rh (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JG 9</td>
<td>8.7</td>
<td>5.3</td>
<td>370.7</td>
<td>-</td>
</tr>
<tr>
<td>JG 9A</td>
<td>10.2</td>
<td>8.4</td>
<td>418.0</td>
<td>1.3</td>
</tr>
<tr>
<td>JG 9B</td>
<td>10.6</td>
<td>7.9</td>
<td>388.7</td>
<td>2.4</td>
</tr>
<tr>
<td>JG 9C</td>
<td>10.4</td>
<td>8.0</td>
<td>460.8</td>
<td>3.9</td>
</tr>
</tbody>
</table>

The desired catalyst composition for the base catalyst, JG 9 (100 Fe / 10 Cu / 6 K₂O / 300 Al₂O₃) was not attained. Instead, a catalyst with composition (100 Fe / 8.7 Cu / 5.6 K₂O / 372 Al₂O₃) was isolated. This might be attributed to the preparation method. Al₂O₃ was impregnated twice to obtain a highly dispersed catalyst. The assumption was made that no loss would occur. This assumption was however erroneous. During the drying procedure lumps formed and were broken continuously to ensure even drying. After the first impregnation the catalyst contained a particle size distribution. The catalyst was sieved in the range 38-150 μm resulting in the loss of some fines, which may explain the loss in metal oxides.

It would be expected that increased addition of Rh would lead to a slight decrease in the metal content of the other components (Table 3.1b). The Cu and K₂O levels per 100 g Fe remained almost constant, although higher than that of the base catalyst. The deviation may be related to the loss of iron during the incipient wetness impregnation of Rh. Some iron may have been re-dissolved and deposited onto the glass plates on which the Rh promoted catalysts were prepared.

The EDS photo’s of the catalysts JG 9, JG 9A, JG 9B and JG 9C indicated large spherical particles covered with smaller particles and some irregular shaped particles (Figure 3.1a, b, c and d). The drying procedure was not optimised thus some of the metal particles may have been deposited on the surface of the support and not in the pores of the alumina. Iron nitrate solutions have low pH. This may have influenced the alumina and driven it towards a positively charged surface (Richardson, 1982). The positively charged alumina surface and positive metal ions would repel each other, resulting in metal oxide being deposited on the surface of the alumina.
Figure 3.1a  EDS photo of JG 9 (0 Rh / 100 g Fe) after drying and calcination.

Figure 3.1b  EDS photo of JG 9A (1.3 Rh / 100 g Fe) after drying and calcination.
Figure 3.1c  EDS photo of JG 9B (2.4 Rh / 100 g Fe) after drying and calcination.

Figure 3.1d  EDS photo of JG 9C (3.9 Rh / 100 g Fe) after drying and calcination.
EDS analysis were obtained to indicate differences between the bulk composition and the near surface of the catalyst. The EDS areas were taken randomly of the different catalyst regions. The analyses indicated variations in the Cu / Fe, K / Fe, Fe / Al and Rh / Fe ratios in the different regions for all the catalysts, indicating that the catalysts consist of areas with different metal ratios.

The average metal ratios obtained from the EDS and that of the bulk metal ratios, obtained from AA, were compared. This comparison data are indicated in Table 3.2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cu / Fe</th>
<th>K / Fe</th>
<th>Fe / Al</th>
<th>Rh / Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EDS&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Bulk&lt;sup&gt;b&lt;/sup&gt;</td>
<td>EDS&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Bulk&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>JG 9</td>
<td>0.07</td>
<td>0.09</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>JG 9A</td>
<td>0.09</td>
<td>0.10</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>JG 9B</td>
<td>0.08</td>
<td>0.11</td>
<td>0.03</td>
<td>0.07</td>
</tr>
<tr>
<td>JG 9C</td>
<td>0.09</td>
<td>0.10</td>
<td>0.03</td>
<td>0.07</td>
</tr>
</tbody>
</table>

<sup>a</sup>Average ratios, <sup>b</sup>Obtained from AA

The Cu / Fe bulk ratio in all the catalysts seem to be comparable to that at the surface, indicating that the catalysts consist of an almost even Cu / Fe distribution. Bigger differences between the K / Fe ratio in the bulk and that on the surface were observed for all the catalysts. The K / Fe on the surface is lower, indicating that there is less K on the surface of the catalysts compared to the bulk. The K may be associated with the Al<sub>2</sub>O<sub>3</sub>.

Although the absolute content of the catalyst varied, the Cu / Fe and K / Fe were similar for all the Rh promoted catalyst.

### 3.2 Catalyst characterisation

#### 3.2.1 Surface area of the catalyst

The surface areas of the catalysts were determined (Table 3.3). The pore volume, as well as the average pore diameter decreased upon loading the metal oxides onto the support, indicating that some of the metal oxide deposited inside the alumina pores.
Table 3.3 Surface areas of JG 9, JG 9A, JG9B and JG 9C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Support</td>
<td>156.9</td>
<td>0.47</td>
<td>11</td>
</tr>
<tr>
<td>JG 9</td>
<td>173.2</td>
<td>0.32</td>
<td>7</td>
</tr>
<tr>
<td>JG 9A</td>
<td>183.6</td>
<td>0.33</td>
<td>7</td>
</tr>
<tr>
<td>JG 9B</td>
<td>176.3</td>
<td>0.34</td>
<td>7</td>
</tr>
<tr>
<td>JG 9C</td>
<td>167.9</td>
<td>0.33</td>
<td>7</td>
</tr>
</tbody>
</table>

Upon impregnating the alumina with metal oxides the surface areas increased. The catalysts predominantly consist of Fe³⁺ (MES results, Table 3.5) supported on Al₂O₃. The Fe particles may be contributing to the surface area of the catalysts. Equation 3.1 was used to roughly estimate the surface area of the Fe particles. The following assumptions were however made. The alumina surface area remained constant and the promoters Cu, K₂O and Rh did not contribute significantly to the catalysts surface area.

\[
S_{A(catalyst)} = S_{A(Fe\text{particle})} \times m_{(Fe\text{particle})} + S_{A(Al₂O₃)} \times m_{(Al₂O₃)}
\]

\[m = \text{mass fraction of the catalyst}\]

Equation 3.1

Table 3.4 Estimated Surface area determination of the Fe particles of JG 9, JG 9A, JG9B and JG 9C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Al₂O₃(^a) (mass %)</th>
<th>Fe(^a) (mass %)</th>
<th>Surface area (m²/g)</th>
<th>Surface area of Fe (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JG 9</td>
<td>55.6</td>
<td>15.0</td>
<td>173.2</td>
<td>573.1</td>
</tr>
<tr>
<td>JG 9A</td>
<td>53.5</td>
<td>12.8</td>
<td>183.6</td>
<td>778.6</td>
</tr>
<tr>
<td>JG 9B</td>
<td>58.7</td>
<td>15.1</td>
<td>176.3</td>
<td>598.8</td>
</tr>
<tr>
<td>JG 9C</td>
<td>57.6</td>
<td>12.5</td>
<td>167.9</td>
<td>620.2</td>
</tr>
</tbody>
</table>

\(^a\) Determined by AA

The results indicate that catalysts consist of high surface area Fe particles supported on Al₂O₃.
3.2.2 Mössbauer emission spectroscopy

3.2.2.1 Fresh catalyst

After the catalysts were prepared the fresh catalysts were sieved in the range 38-150 μm. The sieved catalysts were submitted for MES. The MES spectra are shown in Figure 3.2.

![Mössbauer spectra of the fresh catalysts with various Rh loading.](image)

**Figure 3.2** The Mössbauer spectra of the fresh catalysts with various Rh loading.

The hyperfine interaction parameters of the fresh catalysts are shown in Table 3.5.
Table 3.5 The hyperfine interaction parameter data of JG 9, JG 9A, JG9B and JG 9C determined by MES.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>IS (mms⁻¹)Fe</th>
<th>QS (mms⁻¹)</th>
<th>BHF (T)</th>
<th>RA intensity*</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>JG 9 (0 Rh / 100 g Fe)</td>
<td>0.39</td>
<td>-0.16</td>
<td>47.1</td>
<td>20.2</td>
<td>α-Fe₂O₃</td>
</tr>
<tr>
<td>JG 9A (1.3 Rh / 100 g Fe)</td>
<td>0.39</td>
<td>-0.22</td>
<td>47.1</td>
<td>21.3</td>
<td>α-Fe₂O₃</td>
</tr>
<tr>
<td>JG 9B (2.4 Rh / 100 g Fe)</td>
<td>0.4</td>
<td>-0.22</td>
<td>48.2</td>
<td>28.8</td>
<td>α-Fe₂O₃</td>
</tr>
<tr>
<td>JG 9C (3.9 Rh / 100 g Fe)</td>
<td>0.39</td>
<td>-0.16</td>
<td>47.1</td>
<td>29.5</td>
<td>α-Fe₂O₃</td>
</tr>
</tbody>
</table>

*Error ± 2 %

MES spectra of the fresh catalysts revealed the presence of α-Fe₂O₃ (Table 3.5). A reduced hyperfine field for hematite was observed (47.1) relative to previously reported data (51.7) (Motjope, 2000). This may be due to a distorted environment or small particles with average particle size to small to posses bulk properties (Lee and Lee, 1989).

Two paramagnetic doublets with hyperfine parameters, indicative of Fe³⁺ with small particles of approximately 4 nm, were observed. The large quadrupole splitting indicated a distorted non-cubic environment around the Fe³⁺ ion located at the surface of the catalyst. The smaller quadrupole splitting was associated with a less distorted Fe³⁺ ion located in the bulk of the catalyst.

The results indicate that a large portion of the catalysts consist of small Fe³⁺ species in distorted environment.
3.2.2.2 Ex-situ reduced catalysts

The catalysts were reduced ex-situ under H₂ (1 l(n)/gcat/h) for 16 hours at 533 K at atmospheric pressure. Catalysts were transferred into melted wax, under Ar, to passivate the catalyst surface. The wax covered catalysts were analysed with Mössbauer spectroscopy. Spectra obtained for the reduced catalysts are shown in Figure 3.3.

\[ \text{Reduced } JG \text{ samples} \]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{mosssbauer_spectra.png}
\caption{The Mössbauer spectra of the reduced catalysts with various Rh loading. (T_{\text{red}} = 533 K, P_{\text{red}} = \text{atmospheric}, S_{\text{V,red}} = 1 (l(n)/gcat/h)).}
\end{figure}

The hyperfine interaction parameters of the reduced catalysts are shown in Table 3.6.
Table 3.6 Hyperfine interaction parameters of the reduced JG 9, JG9A, JG 9B and JG9C determined by MES (\(T^{\text{red}} = 533\) K, \(P^{\text{red}} = \text{atmospheric}\), \(SV^{\text{red}} = 1\) (l(n)/gcat/n))

<table>
<thead>
<tr>
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<th>BHF</th>
<th>RA</th>
<th>Phase</th>
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<td>(mms(^{-1}))</td>
<td>(T)</td>
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<td>32.8</td>
<td>Fe(^{3+})</td>
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<tr>
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<td>43.8</td>
<td>28.3</td>
<td>Fe(^{2+})</td>
</tr>
<tr>
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<td>35.9</td>
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<td>29.7</td>
<td>Fe(^{3+})</td>
</tr>
<tr>
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<td></td>
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</tr>
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<tr>
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<td>Fe(^{3+})</td>
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<td>0.31</td>
<td>-0.02</td>
<td>48.1</td>
<td></td>
<td>Fe(^{2+})</td>
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<tr>
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<td>1.03</td>
<td></td>
<td>29.8</td>
<td>Fe(^{3+})</td>
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</tbody>
</table>

\(^a\) Error ± 2 %

The trends observed for the different Fe phases as a function of Rh loading is indicated in Figure 3.4.
Figure 3.4 % Fe of the reduced catalyst with different Rh loading. \( T_{\text{red}} = 533 \text{ K}, P_{\text{red}} = \) atmospheric, \( SV_{\text{red}} = 1 \text{ (l/(n)/gcat/h)} \).

The data indicate that the catalysts were not fully reduced under the reaction conditions used. The reduced catalysts consisted of different iron species such as \( \alpha\)-Fe, Fe\(_3\)O\(_4\), Fe\(^{2+}\) and Fe\(^{3+}\). Rh addition enhanced the reduction of Fe\(^{3+}\) to \( \alpha\)-Fe with JG 9 B, while JG 9A and JG 9C were influenced marginally.

3.2.2.3 Spent catalyst

The catalysts were investigated under FT reaction conditions. The catalysts were reduced with \( H_2 \) (6.36 \( (l/(n)/gcat/h) \) at 533 K for 16 hours at atmospheric pressure. The FT reactions were performed at 533 K and 20 bar. JG 9 (0 Rh / 100 g Fe) was tested at an average syngas space velocity of 15.3 \( (l/(n)/gcat/h) \) for \( \sim \) 150 hours. The promoted catalysts were tested at average space velocities of JG 9A (1.3 Rh / 100 g Fe) 13.5 \( (l/(n)/gcat/h) \), JG 9B (2.4 Rh / 100 g Fe) 14.9 \( (l/(n)/gcat/h) \) and JG 9C (3.9 Rh / 100 g Fe) 14.2 \( (l/(n)/gcat/h) \) for \( \sim \)130 hours.

The difference in space velocity and the time on line (Motjope, 2000) may have an influence on the Fe phases. After the reactor run the catalysts were unloaded and submitted for MES. The spectra are shown in Figure 3.5.
Figure 3.5 The Mössbauer spectra of the spent catalysts with various Rh loading. \( T^{\text{red}} = 533 \text{ K}, P^{\text{red}} = \text{atmospheric}, SV^{\text{red}} = H_2 (6.36 \text{ (l(n)/gcat/h)}), T^{\text{xn}} = 533 \text{ K}, P^{\text{xn}} = 20 \text{ bar}, SV^{\text{xn}} = (JG 9 = 15.3 \text{ (l(n)/gcat/h)}), JG 9A = 13.5 \text{ (l(n)/gcat/h)}, JG 9B = 14.9 \text{ (l(n)/gcat/h)}, JG 9C = 14.2 \text{ (l(n)/gcat/h)}).

The hyperfine interaction parameters of the spent catalysts are shown in Table 3.7.
Table 3.7 Hyperfine interaction parameters of spent JG 9, JG9A, JG 9B and JG9C determined by MES. ($T_{\text{red}} = 533 \text{ K}, P_{\text{red}} = \text{atmospheric}, SV_{\text{red}} = H_2 (6.36 (l(n)/gcat/h), T_{\text{oxn}} = 533 \text{ K}, P_{\text{oxn}} = 20 \text{ bar}, SV_{\text{oxn}} = (JG 9 = 15.3 (l(n)/gcat/h), JG 9A = 13.5 (l(n)/gcat/h), JG 9B = 14.9 (l(n)/gcat/h), JG 9C = 14.2 (l(n)/gcat/h))$)

<table>
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<tr>
<th>Catalyst</th>
<th>IS (mms$^{-1}$)</th>
<th>QS (mms$^{-1}$)</th>
<th>BHF (T)</th>
<th>RA intensity$^a$</th>
<th>Phase</th>
</tr>
</thead>
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<td>JG 9</td>
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<tr>
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<td>Fe$_3$O$_4$</td>
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<tr>
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<td>-0.01</td>
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<tr>
<td></td>
<td>0.18</td>
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<td></td>
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<td>-</td>
<td>41.8</td>
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<td>0.09</td>
<td>17.0</td>
<td>40.8</td>
<td>$\varepsilon'$-Fe$_{2.2}$C</td>
</tr>
<tr>
<td>(1.3 Rh / 100 g Fe)</td>
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<td>42</td>
<td>12.1</td>
<td>Fe$_3$O$_4$</td>
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<tr>
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<td>0.98</td>
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<td>0.13</td>
<td>43.9</td>
<td>14.4</td>
<td>Fe$_3$O$_4$</td>
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<tr>
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<td>-</td>
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<tr>
<td>JG 9C</td>
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<td>0.06</td>
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<td>39.4</td>
<td>$\varepsilon'$-Fe$_{2.2}$C</td>
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<tr>
<td>(3.9 Rh / 100 g Fe)</td>
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<td>0.06</td>
<td>44.3</td>
<td>12.9</td>
<td>Fe$_3$O$_4$</td>
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<td>0.96</td>
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<td>42.6</td>
<td>Fe$^{3+}$</td>
</tr>
</tbody>
</table>

$^a$ Error ± 2%

The trends observed in the Fe phases are shown in Figure 3.6.
Figure 3.6 % Fe phases of the spent catalysts with Rh loading. \((T_{\text{red}} = 533 \text{ K}, P_{\text{red}} = \text{atmospheric}, SV_{\text{red}} = H_2 (6.36 \text{ l/(n)/gcat/h}), T_{\text{xn}} = 533 \text{ K}, P_{\text{xn}} = 20 \text{ bar}, SV_{\text{xn}} = (JG 9 = 15.3 \text{ l/(n)/gcat/h}), JG 9A = 13.5 \text{ l/(n)/gcat/h}), JG 9B = 14.9 \text{ l/(n)/gcat/h}), JG 9C = 14.2 \text{ l/(n)/gcat/h})\).

No \(\alpha\)-Fe was observed indicating that the \(\alpha\)-Fe formed during reduction was converted. \(\varepsilon'\)-Fe\(_{2.2}\)C was the only carbide detected. \(\varepsilon'\)-Fe\(_{2.2}\)C and Fe\(^{3+}\) appear to be the dominant phases present. The relative amounts of the Fe phases did not vary significantly in the spent catalysts. It may seem that the transformations for the promoted and un-promoted catalysts, were similar with the exception of JG 9B (2.4 Rh / 100 g Fe), which exhibited more Fe\(^{2+}\) and less \(\varepsilon'\)-Fe\(_{2.2}\)C species.

3.3 Fischer-Tropsch Synthesis

The Fischer-Tropsch synthesis behaviour of the catalysts JG 9, JG 9A, JG 9B and JG 9C were evaluated. Plant APG was used as source of the syngas. APG contains impurities such as light hydrocarbons and CO\(_2\). The yields of these compounds were determined by analysing the feed gas and product stream and obtaining the differences in these gasses. The product streams were analysed using GC with a FID or TCD detector. Examples of the chromatograms can be seen in Appendix B. Peaks corresponding to oxygenates in the gas phase showed a tail, which may cause error in the determination of the amounts of oxygenated compounds formed. The ampoule samples was used to detect oxygenates up to C\(_6\), while oil samples were analysed to determine the higher oxygenates. n-Decane in the oil fraction was used as internal standard to quantify the products in the gas phase.
3.3.1 Fischer-Tropsch synthesis over JG 9 (0 Rh / 100 g Fe)

The base catalyst, JG 9 (0 Rh / 100 g Fe) was tested at 533 K, 20 bar and an average syngas space velocity of 15.3 (l/(n)/gcat/h). At these conditions CO + CO₂ conversions to organic compounds of between 20-30 mol-% were obtained. The catalyst activity for FT synthesis did not seem to change with time on line.

![Graph showing CO + CO₂ conversions over time](image)

**Figure 3.7** The CO + CO₂ conversions at various times on line over JG 9 (0 Rh / 100 g Fe). (Tₚ = 533 K, Pₚ = atmospheric, SVₚ = H₂ (6.36 (l/(n)/gcat/h), Tₓₚ = 533 K, Pₓₚ = 20 bar, SVₓ = 15.3 (l/(n)/gcat/h)). At these conversions the CO₂ selectivities were high and varied between 30-45 mol-% with time on line (Figure 3.8). The CO₂ selectivity seems to increase with time on line.

![Graph showing CO₂ selectivity over time](image)

**Figure 3.8** The CO₂ selectivities at various time on line over JG 9 (0 Rh / 100 g Fe). (Tₚ = 533 K, Pₚ = atmospheric, SVₚ = H₂ (6.36 (l/(n)/gcat/h), Tₓₚ = 533 K, Pₓₚ = 20 bar, SVₓ = 15.3 (l/(n)/gcat/h)).
A reaction in which CO$_2$ can be formed over an iron catalyst is the water gas shift reaction (WGS), CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$ (Felmer et al., 1981). A measure of the extent of the WGS reaction can be obtained by following the WGS coefficient.

\[
RQ_{WGS} = \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}}
\]

3.2

Figure 3.9 The Water gas shift coefficient at various times on line over JG 9 (0 Rh / 100 g Fe). (T$^{red}$ = 533 K, P$^{red}$ = atmospheric, SV$^{red}$ = H$_2$ (6.36 l/(l(h/gcat))), T$^{ox}$ = 533 K, P$^{ox}$ = 20 bar, SV$^{ox}$ = 15.3 (l/(l(h/gcat))).

The RQ$_{WGS}$ with time on line was below equilibrium indicating that the WGS reaction took place. The trends observed in the RQ$_{WGS}$ with time on line were similar to that observed with the CO$_2$ selectivity.

The FT reaction produces water and the WGS requires water to proceed. Thus the WGS reaction is limited by the water formed in the FT reaction, $r_{WGS} \leq r_{FT}$. Initially the RQ$_{WGS}$ was low indicating a low rate in the WGS reaction. With time on line the RQ$_{WGS}$ increased, resulting in high CO$_2$ selectivity and decrease in H$_2$ conversion. This may have led to higher CH$_4$ formation since the H$_2$ concentration is proportional to CH$_4$ formation (Felmer J., et al., 1981).
The methane selectivities show a large amount of scatter as a function of time on line (Table 3.8). The variations in the methane seem to influence the mass balance obtained. At high methane selectivity higher mass balances were obtained while at low methane selectivities lower mass balances were obtained. The outlet and inlet gas ampoules were not collected simultaneously. Obtaining the difference between the inlet and outlet may not be a good indication of the methane formation since the APG composition fluctuates during the run.

Table 3.8 Methane selectivity, C-balance and chain growth probability at various times on line over JG 9 (0 Rh / 100 g Fe). $T^{\text{red}} = 533 \, \text{K}, \, P^{\text{red}} = \text{atmospheric}, \, SV^{\text{red}} = \text{H}_2 \, (6.36 \, \text{l(n)/gcat/h}), \, T^{\text{rxn}} = 533 \, \text{K}, \, P^{\text{rxn}} = 20 \, \text{bar}, \, SV^{\text{rxn}} = 15.3 \, (\text{l(n)/gcat/h}).$

<table>
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<th>Time on line, hrs</th>
<th>26</th>
<th>49</th>
<th>73</th>
<th>97</th>
<th>144</th>
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</thead>
<tbody>
<tr>
<td>$S_{\text{CH}_4}, , (\text{C-%})$</td>
<td>1.53</td>
<td>45.90</td>
<td>4.80</td>
<td>23.98</td>
<td>39.38</td>
</tr>
<tr>
<td>C-balance (C-%)</td>
<td>84.6</td>
<td>105</td>
<td>89</td>
<td>97</td>
<td>101</td>
</tr>
<tr>
<td>$\alpha$-value, $C_6-C_{10}$</td>
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<td>0.59</td>
<td>0.63</td>
<td>0.61</td>
<td>0.62</td>
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</table>

The chain growth probability of JG 9 was determined from the Anderson-Schulz-Flory distribution. The sum of the rates of organic product formation in a certain carbon number fraction were plotted versus carbon number. Typical Anderson-Schulz-Flory distributions were obtained. The $C_1$ fraction at 26 and 73 hours were however situated below the linear curve. This can be attributed to the low methane levels at these points (Table 3.8). Rather low chain growth probabilities were obtained for iron based catalysts. Chang et al. (1989) investigated CO hydrogenation over iron based catalysts supported on TiO$_2$, Al$_2$O$_3$, TiO$_2$ and NaZSM-5. Chain growth probabilities of 0.73±0.04 were obtained, carbon number range was however not indicated.
Figure 3.10 Anderson-Schulz-Flory distribution of all organic products at the various times on line over JG 9 (0 Rh / 100 g Fe). ($T^\text{red} = 533$ K, $P^\text{red} = \text{atmospheric}, SV^\text{red} = H_2$ (6.36 l(n)/gcat/h), $T^\text{xn} = 533$ K, $P^\text{xn} = 20$ bar, $SV^\text{xn} = 15.3$ l(n)/gcat/h)).

Figure 3.11 shows the olefin content in the fraction linear hydrocarbons with time on line. The olefin content did not change significantly with time on line. The olefin content was low at $C_2$, reached a maximum at $C_3$ and decreased sharply with carbon number. The strong decline at high carbon numbers and the low olefin content in the $C_2$ fraction indicates that the olefins are far from primary selectivity and secondary reactions may be taking place (Bukur et al., 1989).

Figure 3.11 The olefin content in linear hydrocarbons with time on line over JG 9 (0 Rh / 100 g Fe). ($T^\text{red} = 533$ K, $P^\text{red} = \text{atmospheric}, SV^\text{red} = H_2$ (6.36 l(n)/gcat/h), $T^\text{xn} = 533$ K, $P^\text{xn} = 20$ bar, $SV^\text{xn} = 15.3$ l(n)/gcat/h)).
Figure 3.12 shows the 1-olefin content in the fraction linear olefins as a function of carbon number. The 1-olefin content at C₄ and C₅ were constant at ~80 mol-%. The 1-olefin content then sharply decreased with carbon number. This trend indicates that the 1-olefins are far from primary selectivity and that double bond isomerisation occurred (Bukur et al., 1989).

![Graph showing 1-Olefin content as a function of carbon number.]

**Figure 3.12** 1-Olefin content in the fraction linear olefins at various times on line over JG 9 (0 Rh / 100 g Fe). \( T_{\text{red}} = 533 \text{ K}, P_{\text{red}} = \text{atmospheric}, SV_{\text{red}} = H_2 (6.36 \left( l/(n)/gcat/h \right)), T_{\text{rxn}} = 533 \text{ K}, P_{\text{rxn}} = 20 \text{ bar}, SV_{\text{rxn}} = 15.3 \left( l/(n)/gcat/h \right) \).  

The oxygenate content in the hydrocarbons, in the gas phase, as a function of carbon number is shown in Figure 3.13.

![Graph showing Oxygenate content as a function of carbon number.]

**Figure 3.13** Oxygenate content in the hydrocarbons at various times on line over JG 9 (0 Rh / 100 g Fe). \( T_{\text{red}} = 533 \text{ K}, P_{\text{red}} = \text{atmospheric}, SV_{\text{red}} = H_2 (6.36 \left( l/(n)/gcat/h \right)), T_{\text{rxn}} = 533 \text{ K}, P_{\text{rxn}} = 20 \text{ bar}, SV_{\text{rxn}} = 15.3 \left( l/(n)/gcat/h \right) \).
The oxygenates isolated, consisted predominantly of alcohols. The trends observed are similar to that observed with previous reports (Schulz et al., 1999). The \( \text{C}_1 \) fraction was low, with the exception of \( \sim 26 \) and 73 hours on line. This may be attributed the low methane levels at these time intervals (Table 3.8). The \( \text{C}_2 \) levels are high while the higher carbon number oxygenates are less. The oxygenate content for the higher oxygenates seem to be independent of carbon number as the curve appears almost horizontal. Oxygenate content in the gas phase seems not to be influenced by time on line. It is however scattered which may be related to error in the determination of the amounts of alcohols formed, since oxygenates show tails.

Oxygenates from \( \text{C}_9 \) were investigated in the oil fraction. The lower carbon number oxygenates are less volatile than there olefin and paraffin carbon number counterparts, therefore the lower carbon numbered oxygenate content in the oil fraction always appear high. Oxygenate content in the \( \text{C}_9-\text{C}_{15} \) hydrocarbon fraction over JG 9 (0 Rh / 100 g Fe) is shown in Figure 3.14. The oxygenate content shows a sharp decline with increased carbon number, this may be attributed to secondary reactions. It also appears that the oxygenate content decreased with time on stream.

![Graph](image)

**Figure 3.14** Oxygenate content in the hydrocarbons, in the oil phase, at various times on line over JG 9 (0 Rh / 100 g Fe). (\( T^{\text{red}} = 533 \text{ K} \), \( P^{\text{red}} = \text{atmospheric} \), \( SV^{\text{red}} = H_2 \) (6.36 (l(n)/gcat/h)), \( T^{\text{rxn}} = 533 \text{ K} \), \( P^{\text{rxn}} = 20 \text{ bar} \), \( SV^{\text{rxn}} = 15.3 \) (l(n)/gcat/h)).

Figure 3.15 shows the alcohol content in the oxygenates in the oil. The alcohol content is high, \( \sim 70-90 \) mol-\%. This indicates that the oxygenates consist predominantly of alcohols. The graph shows a gradual increase in alcohol content with increase in carbon number, which may be related to the conversion of some oxygenates to alcohols. It has
been suggested that the hydrogenation of aldehydes lead to the formation of alcohols (Dictor and Bell, 1986). The alcohol content in the fraction oxygenates may also increase due to an increase in the equilibrium distribution of the alcohols with an increase in carbon number. At C₁₂ the alcohol content decreased, which may be related to secondary reactions of the alcohols.

![Graph showing alcohol content in oxygenates versus carbon number](image)

**Figure 3.15** Alcohol content in the fraction oxygenates, in the oil phase, at various times on line over JG 9 (0 Rh / 100 g Fe). (Tₚ = 533 K, Pₚ = atmospheric, SVₚ = H₂ (6.36 (l(n)/gcat/h), Tₓn = 533 K, Pₓn = 20 bar, SVₓn = 15.3 (l(n)/gcat/h)).

The Anderson-Schulz-Flory distribution of the oxygenates and the hydrocarbons in the oil fraction were obtained by plotting the sum of the rates in a certain carbon number versus the carbon number. The oxygenate distribution is shown in Figure 3.16.

![Graph showing Anderson-Schulz-Flory distribution](image)

**Figure 3.16** The Anderson-Schulz-Flory distribution of the oxygenates in the oil fraction at various times on line over JG 9 (0 Rh / 100 g Fe). (Tₚ = 533 K, Pₚ = atmospheric, SVₚ = H₂ (6.36 (l(n)/gcat/h), Tₓn = 533 K, Pₓn = 20 bar, SVₓn = 15.3 (l(n)/gcat/h)).
The curve shows a slight deviation at C_{12}-C_{13} where it appears less steep indicating a change in chain growth probability. The \( \alpha \)-values of the oxygenates and hydrocarbons were determined in the C_{10}-C_{12} range. The chain growth probabilities are shown in Table 3.9. The chain growth probability of the oxygenates are lower compared to that of the hydrocarbons. This trend has been reported previously (Dictor and Bell, 1986). The \( \alpha \)-value of the oxygenates after \( \sim \)144 hours on line are slightly lower than at the beginning of the run while the hydrocarbons chain growth probability remained almost constant.

<table>
<thead>
<tr>
<th>Time on line, hrs</th>
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<th>49</th>
<th>73</th>
<th>97</th>
<th>144</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygenates, C_{10}-C_{12}</td>
<td>0.53</td>
<td>0.52</td>
<td>0.51</td>
<td>0.51</td>
<td>0.49</td>
</tr>
<tr>
<td>Hydrocarbons, C_{10}-C_{12}</td>
<td>0.76</td>
<td>0.73</td>
<td>0.74</td>
<td>0.74</td>
<td>0.77</td>
</tr>
</tbody>
</table>

### Table 3.9
The chain growth probabilities of the oxygenates and hydrocarbons in the oil fraction over JG 9 (0 Rh / 100 g Fe). (\( T^{\text{red}} \) = 533 K, \( P^{\text{red}} \) = atmospheric, \( SV^{\text{red}} \) = H_{2} (6.36 l(n)/gcat/h), \( T^{\text{rxn}} \) = 533 K, \( P^{\text{rxn}} \) = 20 bar, \( SV^{\text{rxn}} \) = 15.3 (l(n)/gcat/h)).

#### 3.3.2 Fischer-Tropsch synthesis over JG 9A (1.3 Rh / 100 g Fe)

JG 9A was tested at an average space velocity of 13.5 (l(n)/gcat/h), 20 bar and 533 K. Under these conditions the CO + CO_{2} conversion to organic products were between 15-20 %.

![Figure 3.17](image) CO + CO_{2} conversions at various times on line over JG 9A (1.3 Rh / 100 g Fe). (\( T^{\text{red}} \) = 533 K, \( P^{\text{red}} \) = atmospheric, \( SV^{\text{red}} \) = H_{2} (6.36 l(n)/gcat/h), \( T^{\text{rxn}} \) = 533 K, \( P^{\text{rxn}} \) = 20 bar, \( SV^{\text{rxn}} \) = 13.5 (l(n)/gcat/h)).

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At these conversions the CO$_2$ selectivities were high, between 25-35 mol-%. The CO$_2$ selectivity was low but increased with time on line, see Figure 3.18.

![Graph](image)

**Figure 3.18** CO$_2$ selectivity at various time on line over JG 9A (1.3 Rh / 100 g Fe). (T$_{red}^{\text{red}}$ = 533 K, P$_{red}^{\text{red}}$ = atmospheric, SV$_{red}^{\text{red}}$ = H$_2$ (6.36 l/(n)/gcat/h), T$_{\text{Rxn}}^{\text{Rxn}}$ = 533 K, P$_{\text{Rxn}}^{\text{Rxn}}$ = 20 bar, SV$_{\text{Rxn}}^{\text{Rxn}}$ = 13.5 (l/(n)/gcat/h)).

Looking at the WGS coefficient (Figure 3.19) which followed the extent of the WGS reaction. The RQ$_{\text{WGS}}$ was below equilibrium indicating that CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$ was favoured. The trends observed in the RQ$_{\text{WGS}}$ were similar to that of the CO$_2$ selectivities. It was initially low then increased slightly with time on line. The RQ$_{\text{WGS}}$ was lower than that of JG 9 (0 Rh / 100 g Fe).

![Graph](image)

**Figure 3.19** The RQ$_{\text{WGS}}$ at various times on line over JG 9A (1.3 Rh / 100 g Fe). (T$_{red}^{\text{red}}$ = 533 K, P$_{red}^{\text{red}}$ = atmospheric, SV$_{red}^{\text{red}}$ = H$_2$ (6.36 l/(n)/gcat/h), T$_{\text{Rxn}}^{\text{Rxn}}$ = 533 K, P$_{\text{Rxn}}^{\text{Rxn}}$ = 20 bar, SV$_{\text{Rxn}}^{\text{Rxn}}$ = 13.5 (l/(n)/gcat/h)).
The methane selectivity was initially low but increased with time on line. It did however not exhibit the same fluctuation observed in JG 9 (0 Rh / 100 g Fe).

**Table 3.10** Methane selectivity, C-balance and α-values at various times on line over JG 9A (1.3 Rh / 100 g Fe). \((T^\text{red} = 533 \text{ K}, P^\text{red} = \text{atmospheric}, SV^\text{red} = \text{H}_2 (6.36 \text{ (l(n)/gcat/h)}, T^\text{rxn} = 533 \text{ K}, P^\text{rxn} = 20 \text{ bar}, SV^\text{rxn} = 13.5 \text{ (l(n)/gcat/h)})).

<table>
<thead>
<tr>
<th>Time on line, hrs</th>
<th>26</th>
<th>72</th>
<th>97</th>
<th>122</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S_{\text{CH}_4}), (C-%)</td>
<td>13</td>
<td>16.8</td>
<td>26.3</td>
<td>32.1</td>
</tr>
<tr>
<td>C-balance (C-%)</td>
<td>94.5</td>
<td>96.6</td>
<td>100.7</td>
<td>99.4</td>
</tr>
</tbody>
</table>

The Anderson-Schulz-Flory distribution was obtained by plotting the sum of the rates of all organic products in a certain carbon number fraction against the carbon number. Typical Anderson-Schulz-Flory distributions were obtained (Figure 3.20). The curve shows a slight change in the slope near \(C_6\). Dictor (1986) reported similar trends near \(C_8\) and related it to the inherent property of the catalyst. Chain growth probability in the range \(C_6\)-\(C_{10}\) were obtained at the various times on line, see Table 3.10. It appears that the chain growth probability decreased slightly with time on line.

![Figure 3.20](image)

**Figure 3.20** The Anderson-Schulz-Flory distribution at various times on line over JG 9A (1.3 Rh / 100 g Fe). \((T^\text{red} = 533 \text{ K}, P^\text{red} = \text{atmospheric}, SV^\text{red} = \text{H}_2 (6.36 \text{ (l(n)/gcat/h)}, T^\text{rxn} = 533 \text{ K}, P^\text{rxn} = 20 \text{ bar}, SV^\text{rxn} = 13.5 \text{ (l(n)/gcat/h)})).

The linear olefin content in the linear hydrocarbon fraction is shown in Figure 3.21. The \(C_2\) fraction is low and reached a maximum at \(C_3\). The olefin content then decreased sharply with increased carbon number. This indicates secondary reactions on primary formed olefins.
Figure 3.21 Olefin content in the linear hydrocarbons at various times on line over JG 9A (1.3 Rh / 100 g Fe). ($T_{\text{red}}$ = 533 K, $P_{\text{red}}$ = atmospheric, $SV_{\text{red}}$ = H$_2$ (6.36 (l(l(n)/gcat/h)), $T_{\text{rxn}}$ = 533 K, $P_{\text{rxn}}$ = 20 bar, $SV_{\text{rxn}}$ = 13.5 (l(l(n)/gcat/h)).

Initially the 1-olefin content in the linear olefins were high at ~ 85 mol-% (Figure 3.22). It then gradually decreased with carbon number. The decrease in the 1-olefin content was not as strong as that observed for JG 9 (0 Rh / 100 g Fe), indicating that secondary reactions occurred to a lesser extent.

Figure 3.22 1-Olefin content in the fraction linear olefins at various times on line over JG 9A (1.3 Rh / 100 g Fe). ($T_{\text{red}}$ = 533 K, $P_{\text{red}}$ = atmospheric, $SV_{\text{red}}$ = H$_2$ (6.36 (l(l(n)/gcat/h)), $T_{\text{rxn}}$ = 533 K, $P_{\text{rxn}}$ = 20 bar, $SV_{\text{rxn}}$ = 13.5 (l(l(n)/gcat/h)).

Figure 3.23 shows the oxygenate content in the hydrocarbons in the gas phase over JG 9A (1.3 Rh / 100 g Fe). Similar trends as that over JG 9 (0 Rh / 100 g Fe) were observed.
The C₁ fraction was low, the C₂ levels were high while the higher carbon numbered oxygenate fractions were low.

![Graph](image1)

**Figure 3.23** Oxygenate content in the hydrocarbons at various times on line over JG 9A (1.3 Rh / 100 g Fe). (T^{red} = 533 K, P^{red} = atmospheric, SV^{red} = H₂ (6.36 (l(n)/gccat/h), T^{xon} = 533 K, P^{xon} = 20 bar, SV^{xon} = 13.5 (l(n)/gccat/h)).

The oxygenate content in the hydrocarbon fraction, in the oil, is shown in Figure 3.24. The oxygenate content shows a sharp decline with an increase in carbon number, which may be attributed to secondary reactions.

![Graph](image2)

**Figure 3.24** Oxygenate content in the hydrocarbons, in the oil phase, at various times on line over JG 9A (1.3 Rh / 100 g Fe). (T^{red} = 533 K, P^{red} = atmospheric, SV^{red} = H₂ (6.36 (l(n)/gccat/h), T^{xon} = 533 K, P^{xon} = 20 bar, SV^{xon} = 13.5 (l(n)/gccat/h)).

The alcohols in the oxygenate fraction in the oil phase is shown in Figure 3.25. The alcohol content in the range C₉-C₁₅ is high, ~70-90 mol-%. The alcohol content increased with increased carbon number. This may be related to the conversion of some oxygenates.
to alcohols or due to some experimental artifacts. Near C₁₃ the alcohol content decreased. The decrease may be related to secondary reactions of the alcohols.

**Figure 3.25** Alcohol content in the oxygenate fraction, in the oil phase, at various times on line over JG 9A (0 Rh / 100 g Fe). (T<sup>red</sup> = 533 K, P<sup>red</sup> = atmospheric, SV<sup>red</sup> = H₂ (6.36 l(n)/gcat/h), T<sup>rxn</sup> = 533 K, P<sup>rxn</sup> = 20 bar, SV<sup>rxn</sup> = 13.5 (l(n)/gcat/h)).

The Anderson-Schulz-Flory distribution of the oxygenates and the hydrocarbons in the oil fraction were obtained by plotting the sum of the rates in a certain carbon number versus the carbon number (Figure 3.26).

**Figure 3.26** The Anderson-Schulz-Flory distribution of the oxygenates in the oil fraction at various times on line over JG 9A (1.3 Rh / 100 g Fe). (T<sup>red</sup> = 533 K, P<sup>red</sup> = atmospheric, SV<sup>red</sup> = H₂ (6.36 l(n)/gcat/h), T<sup>rxn</sup> = 533 K, P<sup>rxn</sup> = 20 bar, SV<sup>rxn</sup> = 13.5 (l(n)/gcat/h)).

Linear plots were obtained for the oxygenates at the different time intervals, with a slight change in the slope near C₁₂. This may indicate a change in chain growth probability. The α-values of the oxygenates and hydrocarbons were determined in the C₁₀-C₁₂ range. The chain growth probabilities of the hydrocarbons and oxygenates in the range C₁₀-C₁₂ are
shown in Table 3.11. The chain growth probability of the oxygenates are lower compared to that of the hydrocarbons, but higher compared to that obtained over JG 9 (0 Rh / 100 g Fe) (Table 3.10).

**Table 3.11** The chain growth probabilities of the oxygenates and hydrocarbons in the oil fraction over JG 9A (1.3 Rh / 100 g Fe). (T<sup>red</sup> = 533 K, P<sup>red</sup> = atmospheric, SV<sup>red</sup> = H<sub>2</sub> (6.36 (l(ln)/gcat/h), T<sup>xn</sup> = 533 K, P<sup>xn</sup> = 20 bar, SV<sup>xn</sup> = 13.5 (l(ln)/gcat/h)).

<table>
<thead>
<tr>
<th>Time on line, hrs</th>
<th>26</th>
<th>73</th>
<th>97</th>
<th>122</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygenates, C&lt;sub&gt;10&lt;/sub&gt;-C&lt;sub&gt;12&lt;/sub&gt;</td>
<td>0.67</td>
<td>0.64</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>Hydrocarbons, C&lt;sub&gt;10&lt;/sub&gt;-C&lt;sub&gt;12&lt;/sub&gt;</td>
<td>0.84</td>
<td>0.83</td>
<td>0.83</td>
<td>0.83</td>
</tr>
</tbody>
</table>

### 3.3.3 Fischer-Tropsch synthesis over JG 9B (2.4 Rh / 100 g Fe)

JG 9B was tested at an average syngas space velocity of ~ 14.9 (l(ln)/gcat/h), 20 bar and 533 K. Under these conditions CO + CO<sub>2</sub> conversions to organic products of between 20-30 mol-% were obtained.

![Figure 3.27](image.png)

**Figure 3.27** The CO + CO<sub>2</sub> conversions at various times on line over JG 9B (2.4 Rh / 100 g Fe). (T<sup>red</sup> = 533 K, P<sup>red</sup> = atmospheric, SV<sup>red</sup> = H<sub>2</sub> (6.36 (l(ln)/gcat/h), T<sup>xn</sup> = 533 K, P<sup>xn</sup> = 20 bar, SV<sup>xn</sup> = 14.9 (l(ln)/gcat/h)).

JG 9B exhibited lower CO<sub>2</sub> selectivities compared to JG 9. The CO<sub>2</sub> selectivities obtained were ~30-40 mol-% and did not vary significantly with time on line.
Figure 3.28 The CO₂ selectivity at various times on line over JG 9B (2.4 Rh / 100 g Fe). 
($T^{\text{red}} = 533$ K, $P^{\text{red}} = \text{atmospheric}$, $SV^{\text{red}} = H_2 (6.36 \text{ l(n)/gcat/h})$, $T^{\text{xn}} = 533$ K, $P^{\text{xn}} = 20$ bar, $SV^{\text{xn}} = 14.9 \text{ l(n)/gcat/h}$).

Plotting the RQ$_{\text{WGS}}$ at various times on line (Figure 3.29) followed the extent of the WGS reaction. The RQ$_{\text{WGS}}$ were below the equilibrium curve indicating that the forward reaction $\text{CO} + H_2 \rightarrow \text{CO}_2 + H_2$ was favoured during the reaction run. The trend in the curve was similar to that observed with CO₂ selectivities.

Figure 3.29 The WGS coefficient at various times on line, over JG 9B (2.4 Rh / 100 g Fe). 
($T^{\text{red}} = 533$ K, $P^{\text{red}} = \text{atmospheric}$, $SV^{\text{red}} = H_2 (6.36 \text{ l(n)/gcat/h})$, $T^{\text{xn}} = 533$ K, $P^{\text{xn}} = 20$ bar, $SV^{\text{xn}} = 14 \text{ l(n)/gcat/h}$).

The methane selectivities were lower compared to that of JG 9. The methane increased with time on line.

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Table 3.12  Methane selectivity, C-balance and $\alpha$-values obtained over JG 9B (2.4 Rh / 100 g Fe). ($T_{\text{red}} = 533 \text{ K}, P_{\text{red}} = \text{atmospheric}, SV_{\text{red}} = \text{H}_2 (6.36 \text{ (l(n))/gcat/h}), T^{\text{xn}} = 533 \text{ K}, P^{\text{xn}} = 20 \text{ bar}, SV^{\text{xn}} = 14.9 \text{ (l(n))/gcat/h})$.

<table>
<thead>
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<th>Time on line, hours</th>
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<th>73</th>
<th>97</th>
<th>122</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{\text{CH}_4}$ (C-%)</td>
<td>15.3</td>
<td>18.9</td>
<td>17.2</td>
<td>21.8</td>
</tr>
<tr>
<td>C-balance (C-%)</td>
<td>91.54</td>
<td>90.01</td>
<td>93.28</td>
<td>92.78</td>
</tr>
<tr>
<td>$\alpha$-values, C$<em>6$-C$</em>{12}$</td>
<td>0.63</td>
<td>0.63</td>
<td>0.66</td>
<td>0.64</td>
</tr>
</tbody>
</table>

The chain growth probability of JG 9B was obtained by plotting the sum of the rates of formation of organic products in a certain carbon number. Typical Anderson-Schulz-Flory distributions were obtained. The C$_2$ fraction was however lower, which may be ascribed to the higher ethene activity. A slight change in the slope was observed near C$_6$. Previous reports have indicated similar results and was ascribed to the inherent properties of the catalyst (Dictor, 1986). The chain probabilities in the range C$_6$-C$_{10}$ were obtained and are shown in Table 3.12. The chain growth probability did not seem to change with time on line.

![Figure 3.30](image)

**Figure 3.30** The Anderson-Schulz-Flory distribution at various times on line over JG 9B(2.4 Rh / 100 g Fe). ($T_{\text{red}} = 533 \text{ K}, P_{\text{red}} = \text{atmospheric}, SV_{\text{red}} = \text{H}_2 (6.36 \text{ (l(n))/gcat/h}), T^{\text{xn}} = 533 \text{ K}, P^{\text{xn}} = 20 \text{ bar}, SV^{\text{xn}} = 14.9 \text{ (l(n))/gcat/h})$.

The olefin content in the linear hydrocarbon fraction is shown in Figure 3.31. Bell shaped curves were obtained. The C$_2$ fraction was low, a maximum was observed at C$_3$ followed by a strong decrease in the olefin content with carbon number. The sharp decline at the higher carbon numbers is an indication that the olefins are far form primary selectivities. Secondary reactions may be the cause of the sharp decrease in olefin content.
Figure 3.31 Olefin content in linear hydrocarbons at various times on line over JG 9B (2.4 Rh / 100 g Fe). \( (T^\text{red} = 533 \text{ K}, P^\text{red} = \text{atmospheric}, SV^\text{red} = \text{H}_2 (6.36 \text{ l(n)/gcat/h}), T^\text{rxn} = 533 \text{ K}, P^\text{rxn} = 20 \text{ bar}, SV^\text{rxn} = 14.9 \text{ l(n)/gcat/h}) \).

The graph obtained, of the 1-olefin content in the linear hydrocarbons against carbon number (Figure 3.32) reiterated the concept that the higher carbon number olefins undergo secondary reactions. If primary selectivity was observed, a horizontal line would have been expected. The C₄ and C₅ were high at ~ 85 mol-% and sharply decreased with carbon number.

Figure 3.32 1-Olefin content in the linear olefin fraction at various times over JG 9B (2.4 Rh / 100 g Fe). \( (T^\text{red} = 533 \text{ K}, P^\text{red} = \text{atmospheric}, SV^\text{red} = \text{H}_2 (6.36 \text{ l(n)/gcat/h}), T^\text{rxn} = 533 \text{ K}, P^\text{rxn} = 20 \text{ bar}, SV^\text{rxn} = 14.9 \text{ l(n)/gcat/h}) \).

Figure 3.33 shows the oxygenate content in the hydrocarbons formed over JG 9B (2.4 Rh / 100 g Fe), in the gas phase. Similar trends were observed over JG 9 (0 Rh / 100 g Fe) and JG 9A (1.3 Rh / 100 g Fe). The C₁ fraction was low, the C₂ levels higher and the
higher carbon numbered oxygenate fractions were low. The oxygenate content did not seem to show a trend with time on line.

Figure 3.33 Oxygenate content in the hydrocarbons at various times on line over JG 9B (2.4 Rh / 100 g Fe). ($T_{\text{red}}^* = 533$ K, $P_{\text{red}}^* = \text{atmospheric}$, $SV_{\text{red}}^* = H_2$ (6.36 l(n)/gcat/h), $T_{\text{xn}}^* = 533$ K, $P_{\text{xn}}^* = 20$ bar, $SV_{\text{xn}}^* = 14.9$ l(n)/gcat/h)).

The oxygenate content in the fraction hydrocarbons, in the oil, over JG 9B (2.4 Rh / 100 g Fe) is shown in Figure 3.34. The oxygenate content shows a decline with increased carbon number, which may be ascribed to secondary reactions. The oxygenate content seem to decrease with time on line.

Figure 3.34 Oxygenate content in the hydrocarbons, in the oil phase, at various times on line over JG 9B (2.4 Rh / 100 g Fe). ($T_{\text{red}}^* = 533$ K, $P_{\text{red}}^* = \text{atmospheric}$, $SV_{\text{red}}^* = H_2$ (6.36 l(n)/gcat/h), $T_{\text{xn}}^* = 533$ K, $P_{\text{xn}}^* = 20$ bar, $SV_{\text{xn}}^* = 14.9$ l(n)/gcat/h)).

Figure 3.35 shows that in the oil the alcohol content in the oxygenate fraction was (~80-90 mol-%). The alcohol content increased with carbon number. This increase may be
ascribed to the conversion of some of the oxygenates to alcohols. At C13 the alcohol content gradually decreased, which may be related to secondary reactions of the alcohols or experimental artifacts.

![Graph showing the alcohol content in the oxygenate fraction over time.](image)

**Figure 3.35** Alcohol content in the oxygenate fraction, in the oil phase, at various times on line over JG 9B (2.4 Rh / 100 g Fe). (T^\text{red} = 533 K, P^\text{red} = \text{atmospheric}, SV^\text{red} = H_2 (6.36 (l(n)/gcat/h)), T^\text{xn} = 533 K, P^\text{xn} = 20 \text{ bar}, SV^\text{xn} = 14.9 (l(n)/gcat/h)).

Figure 3.36 shows the Anderson-Schulz-Flory distribution of the oxygenates in the oil fraction. The Anderson-Schulz-Flory distribution of the hydrocarbons in the oil fraction was obtained in a similar fashion. The $\alpha$-values of the oxygenates and hydrocarbons were determined in the C10-C12 range and are shown Table 3.13.

![Graph showing the log of the formation rate over time.](image)

**Figure 3.36** The Anderson-Schulz-Flory distribution of the oxygenates in the oil fraction at various times on line over JG 9B (2.4 Rh / 100 g Fe). (T^\text{red} = 533 K, P^\text{red} = \text{atmospheric}, SV^\text{red} = H_2 (6.36 (l(n)/gcat/h)), T^\text{xn} = 533 K, P^\text{xn} = 20 \text{ bar}, SV^\text{xn} = 14.9 (l(n)/gcat/h)).
The chain growth probabilities of the oxygenates are lower compared to that of the hydrocarbons.

Table 3.13  The chain growth probabilities of the oxygenates and hydrocarbons in the oil fraction over JG 9B (2.4 Rh / 100 g Fe). ($T_{\text{red}}^\text{rad} = 533$ K, $P_{\text{red}}^\text{rad} = \text{atmospheric}$, $SV_{\text{red}}^\text{rad} = H_2$ (6.36 (l(n)/gcat/h)), $T_{\text{rxn}}^\text{rad} = 533$ K, $P_{\text{rxn}}^\text{rad} = 20$ bar, $SV_{\text{rxn}}^\text{rad} = 14.9$ (l(n)/gcat/h)).

<table>
<thead>
<tr>
<th>Time on line, hrs</th>
<th>49</th>
<th>73</th>
<th>97</th>
<th>122</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygenates, $C_{10-12}$</td>
<td>0.64</td>
<td>0.64</td>
<td>0.63</td>
<td>0.62</td>
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<tr>
<td>Hydrocarbons, $C_{10-12}$</td>
<td>0.77</td>
<td>0.77</td>
<td>0.77</td>
<td>0.77</td>
</tr>
</tbody>
</table>

3.3.4 Fischer-Tropsch synthesis over JG 9C (3.9 Rh / 100 g Fe)

At an average space velocity of 14.2 (l(n)/gcat/h), 20 bar and 534 K, CO + CO$_2$ conversions to organic products of ~20 mol-% were obtained.

![Graph](image)

**Figure 3.37** CO + CO$_2$ conversions at various times on line over JG 9C (3.9 Rh / 100 g Fe). ($T_{\text{rad}}^\text{red} = 533$ K, $P_{\text{rad}}^\text{red} = \text{atmospheric}$, $SV_{\text{rad}}^\text{red} = H_2$ (6.36 (l(n)/gcat/h)), $T_{\text{rxn}}^\text{rad} = 533$ K, $P_{\text{rxn}}^\text{rad} = 20$ bar, $SV_{\text{rxn}}^\text{rad} = 14.2$ (l(n)/gcat/h)).

CO$_2$ formation during the reaction was high at ~40 mol-%. The CO$_2$ selectivity appeared almost constant with time on line.
**Figure 3.38** CO₂ selectivity at various times on line over JG 9C (3.9 Rh / 100 g Fe). ($T_{\text{red}} = 533$ K, $P_{\text{red}} = \text{atmospheric}$, $SV_{\text{red}} = H_2 (6.36 \text{ l/(n)/gcat/h})$, $T_{\text{on}} = 533$ K, $P_{\text{on}} = 20$ bar, $SV_{\text{on}} = 14.2 \text{ l/(n)/gcat/h}$).

Figure 3.39 shows the $RQ_{\text{WGS}}$ of JG 9C as a function of time on line. The WGS reaction approached equilibrium to a greater extent, than that of JG 9A and JG 9B. Thus indicating that WGS activity over JG 9C was higher.

**Figure 3.39** Water Gas coefficient at various times on line over JG 9C (3.9 Rh / 100 g Fe). ($T_{\text{red}} = 533$ K, $P_{\text{red}} = \text{atmospheric}$, $SV_{\text{red}} = H_2 (6.36 \text{ l/(n)/gcat/h})$, $T_{\text{on}} = 533$ K, $P_{\text{on}} = 20$ bar, $SV_{\text{on}} = 14.2 \text{ l/(n)/gcat/h}$).

The methane formation over JG 9C (Table 3.14) was higher compared to that of JG 9A (1.3 Rh / 100 g Fe) and JG 9B (2.4 Rh / 100 g Fe). In addition the WGS coefficient was higher indicating higher CO₂ and H₂ concentrations, which may explain the high methane formation since methane formation is proportional to the H₂ concentration (Felmer et al., 1981).
Table 3.14 Methane selectivity, C-balance and $\alpha$-value at various times on line over JG 9C (3.9 Rh / 100 g Fe). \((T^{\text{red}} = 533 \, \text{K}, \quad P^{\text{red}} = \text{atmospheric}, \quad SV^{\text{red}} = H_2 (6.36 \, (l/(n))/gcat/h), \quad T^{\text{xn}} = 533 \, \text{K}, \quad P^{\text{xn}} = 20 \, \text{bar}, \quad SV^{\text{xn}} = 14.2 \, (l/(n))/gcat/h)).

<table>
<thead>
<tr>
<th>Time on line, hrs</th>
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<th>48</th>
<th>72</th>
<th>97</th>
<th>119</th>
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<td>$S_{CH_4}$ (C-%)</td>
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<td>23.6</td>
<td>32.9</td>
<td>27.8</td>
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<tr>
<td>C-balance (C-%)</td>
<td>98.7</td>
<td>94.3</td>
<td>96.9</td>
<td>95.6</td>
<td>99.6</td>
</tr>
<tr>
<td>$\alpha$-values, C$<em>6$-C$</em>{10}$</td>
<td>0.60</td>
<td>0.62</td>
<td>0.62</td>
<td>0.61</td>
<td>0.61</td>
</tr>
</tbody>
</table>

The chain growth probability of JG 9C is shown in Figure 3.40. Typical Anderson-Schulz-Flory distributions were obtained. The C$_2$ was lower which may be attributed to the high reactivity of ethene. The chain growth probabilities, at the various time intervals, were determined and are shown in Table 3.14.

![Graph showing Anderson-Schulz-Flory distribution over JG 9C with carbon number (N$_c$) on the x-axis and log(f$_{formation}$) on the y-axis.](image)

**Figure 3.40** Anderson-Schulz-Flory distribution over JG 9C (3.9 Rh / 100 g Fe). \((T^{\text{red}} = 533 \, \text{K}, \quad P^{\text{red}} = 1 \, \text{bar}, \quad SV^{\text{red}} = H_2 (6.36 \, (l/(n))/gcat/h), \quad T^{\text{xn}} = 533 \, \text{K}, \quad P^{\text{xn}} = 20 \, \text{bar}, \quad SV^{\text{xn}} = 14.2 \, (l/(n))/gcat/h)).

The linear olefins in the linear hydrocarbons (Figure 3.41) exhibited similar trends compared to JG 9, JG 9A and JG 9B. The C$_2$ fraction was low, the olefin content then maximised at C$_3$ followed by a steep decline with carbon number.
Figure 3.41 The olefin content in linear hydrocarbons over JG 9C (3.9 Rh / 100 g Fe). ($T_{\text{red}} = 533 \text{ K, } P_{\text{red}} = 1 \text{ bar, } SV_{\text{red}} = H_2 (6.36 (l(n)/gcat/h)), T_{\text{rxn}} = 533 \text{ K, } P_{\text{rxn}} = 20 \text{ bar, } SV_{\text{rxn}} = 14.2 (l(n)/gcat/h))$.

The 1-olefin content in the linear olefins is indicated in Figure 3.42. The C4 fraction was high followed by a decrease in the 1-olefin content decreased with carbon number. Similar trends were observed with JG 9, JG 9A and JG 9B and may be ascribed to secondary reactions of the olefins.

Figure 3.42 1-Olefin content in the linear olefins over JG 9C (3.9 Rh / 100 g Fe). ($T_{\text{red}} = 533 \text{ K, } P_{\text{red}} = 1 \text{ bar, } SV_{\text{red}} = H_2 (6.36 (l(n)/gcat/h)), T_{\text{rxn}} = 533 \text{ K, } P_{\text{rxn}} = 20 \text{ bar, } SV_{\text{rxn}} = 14.2 (l(n)/gcat/h))$.

The oxygenate content in the hydrocarbons in the gas phase is shown in Figure 3.43.
Figure 3.43 Oxygenate content in the hydrocarbons at various times on line over JG 9C (3.9 Rh / 100 g Fe). \((T^{\text{red}} = 533 \text{ K}, P^{\text{red}} = \text{atmospheric}, SV^{\text{red}} = H_2 (6.36 \text{ (l(n)/gcat/h)}, T^{\text{rxn}} = 533 \text{ K}, P^{\text{rxn}} = 20 \text{ bar}, SV^{\text{rxn}} = 14.2 \text{ (l(n)/gcat/h)})).\)

Similar trends were observed with JG 9 (0 Rh / 100 g Fe), JG 9A (1.3 Rh / 100 g Fe) and JG 9B (2.4 Rh / 100 g Fe). The \(C_2\) levels were high while the \(C_1\) and the higher carbon numbered oxygenate fractions were low. The curve at the higher carbon number oxygenates appear almost horizontal indicating that the termination step of the oxygenates may not be dependent on the chain length (Schulz et al., 1999).

The oxygenate content, in the oil, in the fraction \(C_9-C_{15}\) hydrocarbons over JG 9C (3.9 Rh / 100 g Fe) is shown in Figure 3.44.

Figure 3.44 Oxygenate content in the hydrocarbons, in the oil phase, at various times on line over JG 9C (3.9 Rh / 100 g Fe). \((T^{\text{red}} = 533 \text{ K}, P^{\text{red}} = \text{atmospheric}, SV^{\text{red}} = H_2 (6.36 \text{ (l(n)/gcat/h)}, T^{\text{rxn}} = 533 \text{ K}, P^{\text{rxn}} = 20 \text{ bar}, SV^{\text{rxn}} = 14.2 \text{ (l(n)/gcat/h)})).\)
The curve showed a sharp decrease with increase in carbon number indicating secondary reactions of the oxygenates.

Figure 3.45 shows the alcohol content in the oxygenate fractions. The alcohol content was high in the oil phase, ~80-90 mol-%. The alcohol content gradually increased with carbon number, while it showed a decrease near $C_{13}$. Changes in the curve may be related to the conversion of some of the oxygenates to alcohols and the secondary reaction of the alcohols respectively.

![Graph showing alcohol content in oxygenate fractions over time.](image)

**Figure 3.45** Alcohol content in the oxygenate fraction, at various times on line over JG 9C (3.9 Rh / 100 g Fe). ($T^{\text{red}} = 533$ K, $P^{\text{red}} = \text{atmospheric}$, $SV^{\text{red}} = H_2$ (6.36 l(l)/gcat/h), $T^{\text{xn}} = 533$ K, $P^{\text{xn}} = 20$ bar, $SV^{\text{xn}} = 14.2$ l(l)/gcat/h)).

Figure 3.46 shows the Anderson-Schulz-Flory distribution of the oxygenates.

![Graph showing Anderson-Schulz-Flory distribution.](image)

**Figure 3.46** The Anderson-Schulz-Flory distribution of the oxygenates in the oil fraction at various times on line over JG 9C (3.9 Rh / 100 g Fe). ($T^{\text{red}} = 533$ K, $P^{\text{red}} = 1$ bar, $SV^{\text{red}} = H_2$ (6.36 l(l)/gcat/h), $T^{\text{xn}} = 533$ K, $P^{\text{xn}} = 20$ bar, $SV^{\text{xn}} = 14.2$ l(l)/gcat/h)).
The Anderson-Schulz-Flory distribution of the oxygenates was obtained by plotting the sum of the rates of the oxygenate products in a particular carbon number against carbon number. Linear plots were obtained at the various time intervals. The chain growth probability of the oxygenates and the hydrocarbons were determined and are shown in the Table 3.15. The chain growth probabilities of the oxygenates were lower compared to that of the hydrocarbons.

**Table 3.15** The chain growth probabilities of the oxygenates and hydrocarbons in the oil fraction over JG 9C (3.9 Rh / 100 g Fe). ($T_{\text{red}} = 533 \text{ K}$, $P_{\text{red}} = \text{atmospheric}$, $SV_{\text{red}} = H_2$ (6.36 (l(n)/gcat/h)), $T_{\text{rxn}} = 533 \text{ K}$, $P_{\text{rxn}} = 20 \text{ bar}$, $SV_{\text{rxn}} = 14.2$ (l(n)/gcat/h)).

<table>
<thead>
<tr>
<th>Time on line, hrs</th>
<th>49</th>
<th>73</th>
<th>97</th>
<th>122</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygenates, C_{10-12}</td>
<td>0.63</td>
<td>0.65</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td>Hydrocarbons, C_{10-12}</td>
<td>0.77</td>
<td>0.86</td>
<td>0.72</td>
<td>0.77</td>
</tr>
</tbody>
</table>

3.3.5 Temperature Investigations over JG 9C (3.9 Rh / 100 g Fe)

The behaviour of JG 9C (3.9 Rh / 100 g Fe) was investigated at an average space velocity of 14 (l(n)/gcat/h), 20 bar and various temperatures (513, 533 and 553 K). Under these conditions the CO + CO₂ conversions to hydrocarbons increased with an increase in temperature. A minimum of ~ 11 mol-% at 513 K while a maximum of ~31 mol-% was obtained at 553 K.

**Figure 3.47** CO + CO₂ conversions at various temperatures over JG 9C (3.9 Rh / 100 g Fe). ($T_{\text{red}} = 533 \text{ K}$, $P_{\text{red}} = 1 \text{ bar}$, $SV_{\text{red}} = H_2$ (6.36 (l(n)/gcat/h)), $P_{\text{rxn}} = 20 \text{ bar}$, $SV_{\text{rxn}} = 14$ (l(n)/gcat/h)).
The integral rate data on the CO + CO₂ conversions to organic products enabled the determination of the apparent activation energy for the formation of the organic products over the fixed bed. Activation energy of 61 kJ/mol for hydrocarbon formation was observed.

![Graph showing the Arrhenius plot](image)

**Figure 3.48** The Arrhenius plot between 513 and 553 K over JG 9C (3.9 Rh / 100 g Fe). (T⁰ = 533 K, Pₐ = 1 bar, SVᵢ = H₂ (6.36 (l/(n/gcat/h)), Pᵢ = 20 bar, SVᵢ = 14 (l/(n/gcat/h))).

The apparent activation energy was lower but of the same magnitude than that reported by (Felmer et al., 1981). They indicated an activation energy of 78 kJ/mol for the formation of C₂-C₅ hydrocarbons in a fixed bed reactor over a precipitated catalyst consisting of Fe:Cu:K₂O in a ratio 100:20:1. Low activation energy for CO hydrogenation over Rh / Al₂O₃ and Rh / TiO₂ was ascribed to lower activation barriers for CO dissociation. The activation of C=O bonds was proposed to occur via interaction of the oxygenate end of the carbonyl group and the exposed cation at the edge of the metal/support interface (Ioannides and Verykios, 1993).

The temperature changes seem to influence the CO₂ selectivity over JG 9C (3.9 Rh / 100 g Fe). The CO₂ selectivity increased from ~22 to ~ 40 mol-%, with the temperature increase from 533 K to 553 K. A further increase in temperature had no significant influence on the CO₂ selectivity.
Figure 3.49 The CO$_2$ selectivity at various temperatures over JG 9C (3.9 Rh / 100 g Fe). ($T^{\text{red}} = 533$ K, $P^{\text{red}} = 1$ bar, $SV^{\text{red}} = H_2$ (6.36 (l(n)/gcat/h)), $P^{\text{rxn}} = 20$ bar, $SV^{\text{rxn}} = 14$ (l(n)/gcat/h)).

The RQ$_{\text{WGS}}$ was below the equilibrium curve indicating that the reaction CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$ was favoured. The increase in temperature from 513 K to 534 K resulted in a closer approach to equilibrium leading to an increase in CO$_2$. Further increase in temperature from 533 K to 553 K did not lead to an increase in the CO$_2$ levels. This may be attributed to an increase in the reverse WGS reaction CO$_2$ + H$_2$ $\rightarrow$ CO + H$_2$O since there is a closer approach to equilibrium.

Figure 3.50 Water gas coefficient at various temperatures over JG 9C (3.9 Rh / 100 g Fe). ($T^{\text{red}} = 533$ K, $P^{\text{red}} = 1$ bar, $SV^{\text{red}} = H_2$ (6.36 (l(n)/gcat/h)), $P^{\text{rxn}} = 20$ bar, $SV^{\text{rxn}} = 14$ (l(n)/gcat/h)).
The methane selectivity increased with temperature from 513 to 533 K. Further increase in temperature lead to a decrease in methane formation. This may be explained by the reverse WGS reaction since H₂ are consumed and the methane formation is proportional to the H₂ concentration. The methane selectivity at the various temperatures are shown in Table 3.16.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>513</th>
<th>533</th>
<th>553</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_{\text{CH}_4} ), (C-%)</td>
<td>10.4</td>
<td>49.5</td>
<td>27.4</td>
</tr>
<tr>
<td>C-balance, (C-%)</td>
<td>92.3</td>
<td>99.1</td>
<td>93.3</td>
</tr>
<tr>
<td>( \alpha )-value, ( \text{C}<em>6-\text{C}</em>{10} )</td>
<td>0.62</td>
<td>0.61</td>
<td>0.62</td>
</tr>
</tbody>
</table>

The chain growth probability at the various temperatures was obtained from the Anderson-Schulz-Flory distribution. At the lower temperatures, 513 and 534 K deviations in the \( \text{C}_1 \) and \( \text{C}_2 \) fractions were observed. The \( \text{C}_1 \) fraction was above while the \( \text{C}_2 \) plot was below the linear plot.

![Figure 3.51 Anderson-Schulz-Flory distribution at the various temperatures over JG 9C (3.9 Rh / 100 g Fe). (\( T^{\text{red}} = 533 \) K, \( P^{\text{red}} = 1 \) bar, \( SV^{\text{red}} = H_2 \) (6.36 (l/(n)/gcat/h)), \( P^{\text{xn}} = 20 \) bar, \( SV^{\text{xn}} = 14 \) (l/(n)/gcat/h)).](image)

The increase in temperature resulted in an increase in the rate of organic product formation. The curves at the different temperatures were nearly parallel indicating similar chain growth probabilities. The \( \alpha \)-values at the various temperatures in the \( \text{C}_6-\text{C}_{10} \) fraction were obtained, these are indicated in Table 3.16.
The chain growth probability did not change significantly with an increase in temperature. It would be expected that an increase in temperature would lead to a further decrease in the $\alpha$-value. However secondary re-incorporation of the primary formed olefins or change in the reactors partial pressures caused by change in conversions may have an influence on the chain growth probability.

The olefin content in the fraction linear hydrocarbons is shown in Figure 3.52. An increase in temperature led to a decrease in the olefin content. The trends observed in the olefin content at the different temperatures appear similar. The $C_2$ is low with a maximum at $C_3$ followed by a sharp decline in olefin content with carbon number.

![Figure 3.52](image)

**Figure 3.52** The olefin content in the linear hydrocarbon fraction at various temperatures over JG 9C (3.9 Rh / 100 g Fe). ($T^{\text{red}} = 533$ K, $P^{\text{red}} = 1$ bar, $SV^{\text{red}} = H_2$ (6.36 (l(n)/gcat/h), $P^{\text{rxn}} = 20$ bar, $SV^{\text{rxn}} = 14$ (l(n)/gcat/h)).

Increase in temperature also led to a decrease in the 1-olefin content (Figure 3.53). A higher 1-olefin content was observed at the lower temperature, 513 K. The shape of the curve, at 513 K, appeared more horizontal compared to that at 533 and 553 K. The curves at the higher temperatures sharply decreased with an increase in carbon number indicating a higher degree of secondary reactions.
Figure 3.53 1-Olefin content in the fraction linear olefins at various temperatures over JG 9C (3.9 Rh / 100 g Fe). (T$_\text{red}^{\infty}$ = 533 K, P$_\text{red}^{\infty}$ = 1 bar, SV$_\text{red}^{\infty}$ = H$_2$ (6.36 (l(n)/gcat/h), P$_\text{xn}^{\infty}$ = 20 bar, SV$_\text{xn}^{\infty}$ = 14 (l(n)/gcat/h)).

The trends observed for oxygenate content in the hydrocarbons in the gas phase seem not to be influenced significantly by the change in temperature. The C$_1$ and the higher carbon numbered oxygenate fractions were low while the C$_2$ fraction was high.

Figure 3.54 Oxygenate content in the hydrocarbons at various temperature over JG 9C (3.9 Rh / 100 g Fe). (T$_\text{red}^{\infty}$ = 533 K, P$_\text{red}^{\infty}$ = 1 bar, SV$_\text{red}^{\infty}$ = H$_2$ (6.36 (l(n)/gcat/h), P$_\text{xn}^{\infty}$ = 20 bar, SV$_\text{xn}^{\infty}$ = 14 (l(n)/gcat/h)).

The oxygenate content in the hydrocarbons, in the oil, at the various temperatures shows a strong decline with increased carbon number (Figure 3.54). A slight decrease in oxygenate content was observed with an increase in temperature. This may be ascribed to secondary reactions since it is more prone to occur at higher temperatures.
Figure 3.55 Oxygenate content in the hydrocarbons, in the oil phase, at various temperatures over JG 9C (3.9 Rh / 100 g Fe). ($T_{\text{red}} = 533$ K, $P_{\text{red}} = $ atmospheric, $SV_{\text{red}} = H_2$ (6.36 (l(n)/gcat/h)), $P_{\text{ixn}} = 20$ bar, $SV_{\text{ixn}} = 14$ (l(n)/gcat/h)).

Figure 3.56 shows the alcohol content in the oxygenate fractions in the oil phase. The alcohol content was high, 65-95 mol-%. Trends observed at the various temperatures appear similar. The temperature changes seem to influence the alcohol content very slightly. Change in reaction conditions may lead to change in the partial pressures of the gasses over the reactor, which may influence the alcohol content. For example, variation in the $H_2$ partial pressure may influence the hydrogenation of aldehydes to alcohols.

Figure 3.56 Alcohol content in the oxygenate fraction over JG 9C (3.9 Rh / 100 g Fe). ($T_{\text{red}} = 533$ K, $P_{\text{red}} = $ atmospheric, $SV_{\text{red}} = H_2$ (6.36 (l(n)/gcat/h)), $P_{\text{ixn}} = 20$ bar, $SV_{\text{ixn}} = 14$ (l(n)/gcat/h)).

Anderson-Schulz-Flory distributions of the oxygenates and hydrocarbons in the oil fraction were obtained at various temperatures. Linear plots were obtained at the various temperatures for oxygenate formation.
Figure 3.57 The Anderson-Schulz-Flory distribution of the oxygenates in the oil fraction at various temperatures over JG 9C (3.9 Rh / 100 g Fe). \( (T_{\text{red}} = 533 \text{ K}, P_{\text{red}} = 1 \text{ bar}, SV_{\text{red}} = H_2 \ (6.36 \ \text{l(n)/gcat/h}), T_{\text{non}} = 533 \text{ K}, P_{\text{non}} = 20 \text{ bar}, SV_{\text{non}} = 14 \ (\text{l(n)/gcat/h})). \)

The chain growth probability of the hydrocarbons and the oxygenates were determined in the \( C_{10}-C_{12} \) fraction and are shown in Table 3.17. The chain growth probabilities of the oxygenates are lower compared to that of the hydrocarbons. The chain growth probability of the hydrocarbons and oxygenates decreased with an increase in temperature from 513 to 533 K. Further increase in temperature seems not to influence the chain growth probability.

Table 3.17 The chain growth probabilities of the oxygenates and hydrocarbons in the oil fraction over JG 9C (3.9 Rh / 100 g Fe). \( (T_{\text{red}} = 533 \text{ K}, P_{\text{red}} = \text{atmospheric}, SV_{\text{red}} = H_2 \ (6.36 \ \text{l(n)/gcat/h}), P_{\text{non}} = 20 \text{ bar}, SV_{\text{non}} = 14 \ (\text{l(n)/gcat/h})). \)

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>513</th>
<th>533</th>
<th>553</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygenates, ( C_{10}-C_{12} )</td>
<td>0.75</td>
<td>0.63</td>
<td>0.63</td>
</tr>
<tr>
<td>Hydrocarbons, ( C_{10}-C_{12} )</td>
<td>0.90</td>
<td>0.77</td>
<td>0.77</td>
</tr>
</tbody>
</table>

3.3.6 Change in Space velocity over JG 9C (3.9 Rh / 100 g Fe)

JG 9C was investigated under varying space velocities. Samples were taken \(~24\) hours after a change in the syngas space velocity was made. Figure 3.58 shows the \( \text{CO} + \text{CO}_2 \) conversions to organic products with change in space velocity.
Figure 3.58 CO + CO₂ conversions over JG 9C (3.9 Rh / 100 g Fe). \((T^{\text{red}} = 533 \, \text{K}, \, P^{\text{red}} = 1 \, \text{bar}, \, SV^{\text{red}} = H₂ (6.36 \, (l(n)/gcat/h), \, T^{\text{xn}} = 533 \, \text{K}, \, P^{\text{xn}} = 20 \, \text{bar}).\)

The increase in space velocity lead to a decrease in CO + CO₂ conversions to organic products. The decrease in conversion may be ascribed to a decrease in contact time between the catalyst and the synthesis gas.

The CO₂ selectivities were high at ~ 40 mol-%. The CO₂ selectivity decreased slightly with an increase in space velocity.

Figure 3.59 CO₂ selectivity at various space velocities over JG 9C (3.9 Rh / 100 g Fe). \((T^{\text{red}} = 533 \, \text{K}, \, P^{\text{red}} = 1 \, \text{bar}, \, SV^{\text{red}} = H₂ (6.36 \, (l(n)/gcat/h), \, T^{\text{xn}} = 533 \, \text{K}, \, P^{\text{xn}} = 20 \, \text{bar}).\)

Plotting the WGS (Figure 3.60) coefficient monitored the WGS reaction as a function of varying space velocity. The coefficients were below the equilibrium line indicating that the WGS reaction was favoured. Increase in space velocity led to a slight decrease in the WGS coefficient, a similar trend as that observed for the CO₂ selectivity.
Figure 3.60 WGS coefficient at varying space velocity over JG 9C (3.9 Rh / 100 g Fe). (T_{red} = 533 K, P_{red} = 1 bar, S\!V_{red} = H_2 (6.36 (l(n)/gcat/h), T^{xn} = 533 K, P^{xn} = 20 bar).

The methane selectivity decreased with an increase in space velocity. This may be attributed to decrease in CO + CO2 conversion as well as a decrease in secondary reactions leading to the formation of methane, such as cracking of the longer chained hydrocarbons.

Table 3.18 Methane selectivity, C-balance and α-values at various space velocities over JG 9C (3.9 Rh / 100 g Fe). (T_{red} = 533 K, P_{red} = 1 bar, S\!V_{red} = H_2 (6.36 (l(n)/gcat/h), P^{xn} = 20 bar, T^{xn} = 533 K)

<table>
<thead>
<tr>
<th>Space velocity, (l(n)/gcat/h)</th>
<th>5.7</th>
<th>14.1</th>
<th>26.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_{CH4}, (C-%)</td>
<td>35.70</td>
<td>20.62</td>
<td>28</td>
</tr>
<tr>
<td>C-balance, (C-%)</td>
<td>106.91</td>
<td>87.46</td>
<td>99.24</td>
</tr>
<tr>
<td>α-value, C_6-C_10</td>
<td>0.62</td>
<td>0.64</td>
<td>0.61</td>
</tr>
</tbody>
</table>

A mass balance of ~106 was obtained at 5.7 (l(n)/gcat/h). At the low space velocity less product was drained relative to the higher space velocities. This may have caused problems since C_{10} (decane which condenses out as oil) is used to determine the flow rates of the products. If errors are made in obtaining the quantity of C_{10} in the oil fraction you may obtain an erroneous mass balance.

The Anderson-Schulz-Flory distributions at the various space velocities are indicated in Figure 3.61. Typical Anderson-Schulz-Flory distributions were obtained. The C_2 fraction was below the curves. This may be attributed to the higher reactivity of the ethene. The
α-values at the various space velocities are very similar (Table 3.18). It may seem that change in the space velocity had no significant influence on chain growth probability of the catalyst. Change in the reactor conditions may lead to change in the partial pressures of the gasses over the reactor, since the conversions were influenced by the change in space velocity. These changes may have an influence on the chain growth probability.

![Graph](image1)

**Figure 3.61** Anderson-Schulz-Flory distribution at various space velocities over JG 9C (3.9 Rh / 100 g Fe). ($T^{\text{red}} = 533$ K, $P^{\text{red}} = 1$ bar, $SV^{\text{red}} = H_2$ (6.36 (l(n)/gcat/h), $T^{\text{xn}} = 533$ K, $P^{\text{xn}} = 20$ bar).

The olefin content in the fraction linear hydrocarbons increased with an increase in space velocity (Figure 3.62).

![Graph](image2)

**Figure 3.62** Olefin content in the fraction linear hydrocarbons at various space velocities over JG 9C (3.9 Rh / 100 g Fe). ($T^{\text{red}} = 533$ K, $P^{\text{red}} = 1$ bar, $SV^{\text{red}} = H_2$ (6.36 (l(n)/gcat/h), $T^{\text{xn}} = 533$ K, $P^{\text{xn}} = 20$ bar).

The increase in olefin content may be ascribed to a decrease in secondary reactions. A decrease in secondary reactions can also be seen in the change in the shape of the
curves. The curves become more horizontal with an increase in space velocity. At the lower space velocity the shape of the curve is indicative of secondary olefin selectivity. The C2 value is low followed by an increase in olefin content. The olefin content then decreased with an increase in carbon number.

The 1-olefin content in the linear olefins increased with an increase in space velocity. The curves approached a horizontal appearance with increased space velocity. It is an indication that secondary 1-olefin isomerisation decreased with an increase in space velocity.

![Graph showing olefin content vs carbon number](image)

**Figure 3.63** 1-Olefin content in the linear olefins at various space velocities over JG 9C (3.9 Rh / 100 g Fe). ($T_{\text{red}} = 533 \, \text{K}$, $P_{\text{red}} = 1 \, \text{bar}$, $SV_{\text{red}} = H_2$ (6.36 (l(gcat/h)), $T_{\text{xn}} = 533 \, \text{K}$, $P_{\text{xn}} = 20 \, \text{bar}$).

The changes in space velocity influenced the trends observed for oxygenates, in the hydrocarbon fraction, in the gas phase (Figure 3.64). There were no obvious trends with an increase in space velocity. At 5.7 (l(gcat/h)) the C2 and C3 fractions are higher than the higher carbon number oxygenates. The trends observed at the higher space velocities seem similar. The C1 levels and the higher carbon numbered oxygenate fractions were low while the C2 fraction was high.
Figure 3.64 Oxygenate content in the hydrocarbons at various space velocity over JG 9C (3.9 Rh / 100 g Fe). (T^\text{red} = 533 K, P^\text{red} = 1 \text{ bar}, SV^\text{red} = H_2 (6.36 \text{ (l/n)/gcat/h}), T^\text{xn} = 533 K, P^\text{xn} = 20 \text{ bar}).

In the oil fraction, the oxygenate content in the hydrocarbons shows a strong decline with increased carbon number at the various space velocities (Figure 3.65). A slight increase in oxygenate content was observed with an increase in space velocity. This may be ascribed to a decrease in secondary reactions at higher space velocities.

Figure 3.65 Oxygenate content in the hydrocarbons, in the oil phase, at various space velocities over JG 9C (3.9 Rh / 100 g Fe). (T^\text{red} = 533 K, P^\text{red} = \text{ atmospheric}, SV^\text{red} = H_2 (6.36 \text{ (l/n)/gcat/h}), T^\text{xn} = 533 K, P^\text{xn} = 20 \text{ bar}).

The alcohol content in the oxygenate was high (Figure 3.66) and it increased with an increase in space velocity. Trends observed for the different space velocities were similar. The increase in oxygenate content may be related to a decrease in secondary reactions with an increase in space velocity. A gradual increase in alcohol content with an
increase in carbon number was observed, while near C_{13} the alcohol content decreased again.

![Graph showing alcohol content in oxygenates as a function of carbon number.]

**Figure 3.66** Alcohol content in oxygenates at various space velocities over JG 9C (3.9 Rh / 100 g Fe). (T^{\text{red}} = 533 K, P^{\text{red}} = 1 bar, SV^{\text{red}} = H_2 (6.36 (l(n)/gcat/h), T^{\text{xn}} = 533 K, P^{\text{xn}} = 20 bar).

The Anderson-Schulz-Flory distribution of oxygenates and hydrocarbons in the oil fraction in the range C_6-C_{15} were obtained at varying space velocity. Linear plots were obtained for the Anderson-Schulz-Flory distributions for the oxygenates (Figure 3.67).

![Graph showing log(formation rate) vs. carbon number.]

**Figure 3.67** Anderson-Schulz-Flory distribution at various space velocities over JG 9C (3.9 Rh / 100 g Fe). (T^{\text{red}} = 533 K, P^{\text{red}} = 1 bar, SV^{\text{red}} = H_2 (6.36 (l(n)/gcat/h), T^{\text{xn}} = 533 K, P^{\text{xn}} = 20 bar).

The curves are near parallel indicating very similar chain growth probabilities. The chain growth probability of the hydrocarbons and oxygenates were determined at the various space velocities and are shown in Table 3.20. The \( \alpha \)-value of the oxygenates were lower compared to that of the hydrocarbons. The chain growth probability of the hydrocarbons
and oxygenates increased slightly with an increase in space velocity. Changes in the reaction conditions may lead to changes in the partial pressures over the reactor, which in-turn may influence chain growth.

Table 3.20 The chain growth probabilities of the oxygenates and hydrocarbons in the oil fraction over JG 9C (3.9 Rh / 100 g Fe). (T_{red} = 533 K, P_{red} = atmospheric, S_{red} = H_{2} (6.36 l/(n)/gcat/h), T_{rxn} = 533 K, P_{rxn} = 20 bar).

<table>
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<th>14.1</th>
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<td>0.60</td>
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<tr>
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<td>0.76</td>
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4 : DISCUSSIONS

4.1 Rh as promoter

4.1.1 Rh as reduction promoter

α-Fe has been found to be more active for FT synthesis compared to iron with higher oxidation states (Bukur et al., 1989). Rh was shown to facilitate the reduction of the less noble metal, Fe (Niemandsverdriet et al., 1984). Niemandsverdriet et al. performed in-situ MES reduction experiments on a co-impregnated RhFe/Si₂O (1.76 mass-% Fe and 3.24 mass-% Rh) catalyst at 725 K. It was concluded that zero-valent iron was alloyed with Rh and no isolated particles of metallic iron were formed. These conclusions were based on the observation that the isomeric shift of Fe⁰ was higher than that of the metallic iron and that no contribution of Fe²⁺ was present. Ichikawa and Fukushima (1985) also concluded from in-situ infrared studies that co-impregnated RhFe/Si₂O catalysts formed RhFe alloys.

The catalysts JG 9 (0 Rh / 100 g Fe), JG 9A (1.3 Rh / 100 g Fe), JG 9B (0 Rh / 100 g Fe) and JG 9 (0 Rh / 100 g Fe) were reduced ex-situ at 533 K and 298 K MES spectra were obtained. The addition of Rh to the base catalyst, marginally influenced the reduction of Fe³⁺ to α-Fe with the exception of JG 9B. MES results of the reduced JG 9B exhibited an enhancement in the reduction of Fe³⁺ to α-Fe. Considering Niemandsverdriet et al. (1984) findings on the isomeric shift differences between Fe⁰ in the metallic and alloyed form it may seem that our catalysts consist of isolated particles of metallic iron and that no FeRh alloy was formed. MES data on the reduced catalyst indicated no difference in isomeric shift (IS) between the Rh promoted and un-promoted catalysts. All the catalysts exhibited Fe²⁺ and Fe₃O₄ species, which are produced during the reduction of Fe-based catalysts.

Niemandsverdriet et al. (1984) collected their spectra at low temperatures (295-44 K), where more detailed information can be obtained. It may be that FeRh particles exist on the catalyst surface but represent a negligible fraction of the total iron atoms and does not appear in the MES spectra obtained at 298 K. In addition Niemandsverdriet et al. (1984), Ichikawa and Fukushima (1985) performed reduction experiments at 725 K and 673 K respectively. Our catalysts were reduced at 533 K, while more severe reaction conditions may be needed for
alloy formation. Platinum-iron catalysts afforded alloy formation at reduction temperatures of up to 773 K (Moss, 1976).

The addition of Rh to the base catalyst JG 9 (0 Rh / 100 g Fe) may not have enhanced the formation of metallic iron via alloy formation as was found by Niemandsverdriet et al. (1984). Instead the MES data indicate that the catalysts consist of isolated particles of metallic iron. It has been reported that for palladium to facilitate the reduction of iron and alloy formation close contact between palladium particles and the iron oxides is required. Hydrogen spill over occurs preferentially over a short range via diffusion across interfacial regions rather than migration over the support (Moss, 1979). It may be that the addition of Rh enhanced the reduction of Fe$^{3+}$ species to metallic iron via a spill over effect. Atomic hydrogen adsorbed on the Rh may have migrated to the iron particles leading to increased $\alpha$-Fe levels. The enhancement of Fe$^0$ formation with the addition of Rh may indicate that the Rh and iron oxide particles may be in close proximity.

The % $\alpha$-Fe in the reduced Rh promoted catalysts exhibited a cone effect (Figure 3.3). It may be that at higher Rh levels, JG 9C, the Fe surface may be blocked too severely thus inhibiting the formation of $\alpha$-Fe or the reaction may be inhibited by the presence of residual Cl ions (Lee and Lee, 1989), which were introduced during the third impregnation step. Rhodium was added as RhCl$_3$ salt and the residual Cl$^-$ may be inhibiting the reduction process. While JG 9A may have contained insufficient Rh to observe any significant reduction enhancement.

4.1.2 Rh as promoter for Fischer-Tropsch synthesis
4.1.2.1 Influence of Rh on the catalyst activity

The behaviour of the catalyst JG 9 (0 Rh / 100 g Fe), JG 9A (1.3 Rh / 100 g Fe), JG 9B (2.4 Rh / 100 g Fe) and JG 9C (3.9 Rh / 100 g Fe) were compared after approximately 97 hours on line. After this time period changes in activity and in the product distribution was minimal.

The activity of the Rh promoted catalyst was lowered significantly (Figure 4.1). The trend observed is that the addition of Rh decreased the FT integral rate. The initial assumption
made, that the addition of small quantities of Rh would not influence the catalysts activities, was erroneous. The integral rates of the reactions after approximately 97 hours on line were compared since different space velocities were applied to obtain approximately similar levels of CO + CO₂ conversions.

![Graph](image)

**Figure 4.1** The integral rate with varying Rh content after ~ 97 hours on line. (\(T^\text{red} = 533 \, \text{K}, P^\text{red} = 1 \, \text{bar}, SV^\text{red} = H_2 \, (l/(n)/gcat/h)), T^\text{rxn} = 533 \, \text{K}, P^\text{rxn} = 20 \, \text{bar}, JG 9, SV^\text{rxn} = 18.21 \, (l/(n)/gcat/h)), JG 9A, SV^\text{rxn} = 13.50 \, (l/(n)/gcat/h)), JG 9B, SV^\text{rxn} = 15.34 \, (l/(n)/gcat/h)), JG 9C, SV^\text{rxn} = 13.93 \, (l/(n)/gcat/h))).

Vannice (1975-a) indicated that Fe based catalysts have higher activities for the synthesis of hydrocarbons from \(H_2/CO\) compared to Rh based catalysts. The Rh was added in a post-impregnation step to the base catalyst, JG 9. This preparation manner may result in the Rh covering the more active FT metal. It must be kept in mind that Rh was added as RhCl₃ salt, since chloride poisoning might also have the same result, i.e. decreasing the catalyst activity. Vannice (1975-b) has however indicated that chloride ions, on the \(Al_2O_3\) surface after impregnation with chloride salts, decrease with time on stream. The \(Cl^-\) reacts to form \(CH_3Cl\) or \(HCl\), due to the water formed during the synthesis reaction. The affect of the \(Cl^-\) ions is only temporary and does not alter the activity of the metal. If it can be assumed that all chloride ions have been removed after reduction and after 97 hours on-line in the Fischer-Tropsch synthesis, the decrease in activity may be ascribed to the coverage of the active iron surface with less active rhodium.
Some researchers consider FeC to be the active phase during FT synthesis (Raupp and Delgass, 1979). Our MES data on the spent catalysts indicated that $\varepsilon'$-Fe$_{2.2}$C was the only carbide formed. Figure 4.2 shows the correlation between the % $\varepsilon'$-Fe$_{2.2}$C in the spent catalysts and the integral rate for the CO conversion to hydrocarbons of the catalysts. The trend observed in Figure 4.2 was not very obvious, since the $\varepsilon'$-Fe$_{2.2}$C in the promoted and un-promoted catalyst did not vary significantly with the exception of JG 9B.

![Figure 4.2](image_url)  

Figure 4.2 % $\varepsilon'$-Fe$_{2.2}$C content as determined by MES. ($T^\text{red} = 533$ K, $P^\text{red} = 1$ bar, $SV^\text{red} = H_2$ (6.36 (l/(n)/gcat/h)), $T^\text{rxn} = 533$ K, $P^\text{rxn} = 20$ bar, JG 9, $SV^\text{rxn} = 18.21$ (l/(n)/gcat/h)), JG 9A, $SV^\text{rxn} = 13.50$ (l/(n)/gcat/h)), JG 9B, $SV^\text{rxn} = 15.34$ (l/(n)/gcat/h)), JG 9C, $SV^\text{rxn} = 13.93$ (l/(n)/gcat/h)).

Lee and Lee (1989) prepared Fe supported catalysts using iron (III) chloride. Temperature programmed decarburization (TPDC) investigations with $H_2$, were performed on their catalysts after FT reactions of 24 hours. The TPDC profiles were correlated with the catalytic properties observed. Lower peak temperatures were associated with higher hydrogenation ability of the catalysts, increased CO conversion and lower molecular weight products since C-H bonds were favoured. Catalysts with higher peak temperatures showed larger C-C chain growth probability. Vacuum dried catalysts showed higher peak temperatures. It was indicated that the vacuum dried catalysts had significant amounts of residual Cl$^-$ and it enhanced the catalyst carburization ability. When supported on the same material the air-dried catalysts contained trace amounts of residual Cl$^-$. It was proposed that when the
catalysts were heated in air the Cl\(^-\) would be released as HCl. Trace amounts of Cl\(^-\) had little effect on carbide formation. The air-dried silica supported catalyst showed that all the metallic iron was converted to ε\(^-\)-Fe\(_{2.2}\)C and it co-existed with unreduce Fe\(^{3+}\) after 24 hours on line. While the vacuum dried silica supported catalyst showed Fe\(^0\), three different \(\chi\)-Fe\(_{5}\)C\(_2\) species and Fe\(^{3+}\).

Lee and Lee (1989) did not mention the quantity of residual Cl\(^-\) that would influence carbide formation. They calcined at 723 K for 3 hours while we calcined at 523 K for 5 hours. We suspect that our catalysts might contain sufficient amounts of residual Cl\(^-\) to influence the carbide formation.

Our spent catalyst showed only ε\(^-\)-Fe\(_{2.2}\)C. ε\(^-\)-Fe\(_{2.2}\)C is a metastable O-type carbide with the C atoms at the octahedral sites (Caër et al., 1982). The stability of the carbides increases with decrease in C content.

\[
\text{Fe}_2\text{C} < \text{Fe}_{2.2-2.4}\text{C} < \chi\text{-Fe}_5\text{C}_2 < \text{θ-Fe}_3\text{C}
\]

Carbides formed during FT synthesis may result from competing effects, the tendency to form high carbon content carbides and the decrease in stability when the carbide content increases. O-carbides may be stabilised by structural defects and the interaction with the support (Caër et al., 1982).

The MES spectrum of the spent JG 9 (0 Rh / 100 g Fe) was obtained after ~150 hours on line while, JG 9A (1.3 Rh / 100g Fe), JG 9B (2.4 Rh / 100 g Fe) and JG 9 (3.9 Rh / 100 g Fe) were obtained after ~ 130 hours on line. Different times on line may influence the Fe phases of the spent catalysts (Motjope, 2000). The activity of the catalysts differed which may indicate that the catalysts were exposed to different gas compositions. These different gas compositions may play a role in the phase transformations of the catalysts during the reaction run.

The water gas shift activity varied with the Rh content in the catalyst. The WGS activity of the catalysts was compared by plotting the RQ\(_{\text{WGS}}\) as a function of Rh content (Figure 4.3).
The $RQ_{\text{WGS}}$ showed a minimum at JG 9B (2.4 Rh / 100 g Fe). Lee (1989) reported that the WGS reaction is inhibited by the presence of residual Cl$^-$ ions. This may explain the decrease in the WGS activity with the exception of JG 9C (3.9 Rh / 100 g Fe). Fe$_3$O$_4$ was shown to be the active component of Fe based WGS catalysts (Jung and Thomson, 1991). The WGS activity as a function of the Fe$_3$O$_4$ content in the spent catalysts is shown in Figure 4.4.
The trend observed in Figure 4.4 was not very obvious while no correlation between the Rh content and the % Fe₃O₄ in the spent catalysts exist. Bartholomew et al. (1999) indicated that the carbides formed during CO pre-treatment for their Fe precipitated catalysts were converted to Fe₃O₄ during FT reaction due to oxidation by water vapour. While for a Fe precipitated catalyst with higher K₂O and SiO₂ content the Fe₃O₄ was converted to carbides since the catalysts exhibited higher resistance to oxidation by water vapour pressure. It was suggested that the resistance to oxidation could be due to the Fe carbide silica interaction. JG 9B (2.4 Rh / 100 g Fe), of the Rh promoted catalysts, exhibited the highest FT integral rate and the lowest WGS activity, thus the ε'-Fe₂₋₂C may have been oxidised during the FT reaction. It may also be that during the preparation of JG 9A (1.3 Rh / 100 g Fe) and JG 9C (3.9 Rh / 100 g Fe) the Fe support interactions may have been influenced resulting in higher resistance of the FeC to oxidation by the water vapour pressure.

The olefin content in the linear hydrocarbon fraction after ca. 97 hours on line for various Rh loading is shown in Figure 4.5.

![Olefin content graph](image)

**Figure 4.5** The olefin content in the linear hydrocarbon fraction at various Rh loading after ~97 hours on line. (*T*¹⁰⁰ = 533 K, *P*¹⁰⁰ = 1 bar, *SV*¹⁰⁰ = H₂ (6.36 (l(n)/gcat/h)), *T*²⁰⁰ = 533 K, *P*²⁰⁰ = 20 bar, JG 9, SV²⁰⁰ = 18.21 (l(n)/gcat/h)), JG 9A, SV²⁰⁰ = 13.50 (l(n)/gcat/h)), JG 9B, SV²⁰⁰ = 15.34 (l(n)/gcat/h)), JG 9C, SV²⁰⁰ = 13.93 (l(n)/gcat/h)).

Bell shaped curves resulting from secondary olefin reactions were obtained. Bukur (1989) has indicated that K suppresses the secondary hydrogenation of olefins. It was proposed
that the presence of K enhanced the CO chemisorption whereas the H₂ chemisorption decreased resulting in a lower hydrogenation activity. From the EDS results of our catalysts it was concluded that the K is also associated with the Al₂O₃ and not only on the surface of the catalytically active material.

JG 9A (1.3 Rh / 100 g Fe) showed the highest olefin content while there seem to be no correlation with the Rh added and the olefin content. The high olefin content exhibited by JG 9A may be due to its low activity relative to the other catalysts. Raupp and Delgass (1979) reported that smaller iron particles form FeC faster and favour less stable carbides. Caër et al., (1982) indicated that C-rich O-carbides might be stabilised by surface defects and metal support interactions. It may be that JG 9A consist of small iron particles in which the ε' Fe₂C formed during FT synthesis may be stabilised by metal support interactions leading to lower FT activity.

The 1-olefin content in the linear olefin fraction exhibited bell shaped curves (Figure 4.6).

![Figure 4.6](image-url)

**Figure 4.6** The 1-olefin content in the linear olefin fraction at various Rh loading after ~97 hours on line. (T^red = 533 K, P^red = 1 bar, SV^red = H₂ (l/(n)/gcat/h)), T^{rxn} = 533 K, P^{rxn} = 20 bar, JG 9, SV^{rxn} = 18.21 (l/(n)/gcat/h)), JG 9A, SV^{rxn} = 13.50 (l/(n)/gcat/h)), JG 9B, SV^{rxn} = 15.34 (l/(n)/gcat/h)), JG 9C, SV^{rxn} = 13.93 (l/(n)/gcat/h)).

The bell shaped curves may be ascribed to secondary olefin isomerisation. Although the alumina has the ability to hydrogenate olefins it is more active for olefin isomerisation (John and Scurrrell, 1976). In addition, K suppresses the isomerisation of 1-alkenes, while the
addition of Cu enhances the isomerisation activity of Fe based catalysts (Bukur et al., 1989). The EDS analysis indicated that the near surface of the catalysts contained higher Cu / Fe ratios relative to the K / Fe ratios (Table 3.2). Thus the higher Cu levels may also enhance the isomerisation activity of the catalysts.

JG 9A (1.3 Rh / 100 g Fe) again exhibited the highest 1-olefin content, which may be related to its low FT activity. A low activity would result in low partial pressures of the primarily formed 1-olefins. Hence, the secondary reaction would be slowed down.

4.1.2.2 Influence of Rh on the oxygenate formation

Alcohols were the predominant oxygenates formed. Figure 4.7 shows the oxygenate content in the fraction hydrocarbons after approximately 97 hours on line. The observed trends were, low C₁ fraction, high C₂ fraction and less of the high carbon number oxygenates. The C₂ fraction was high for all the catalysts and showed no correlation with Rh content.

![Graph showing oxygenate content vs. carbon number](image)

**Figure 4.7** The Oxygenate content with increased Rh loading after ~97 hours on line. (T_{red} = 533 K, P_{red} = 1 bar, SV_{red} = H₂ (6.36 ((l(n)/gcat/h))), T_{xn} = 533 K, P_{xn} = 20 bar, JG 9, SV_{xn} = 18.21 ((l(n)/gcat/h))), JG 9A, SV_{xn} = 13.50 ((l(n)/gcat/h))), JG 9B, SV_{xn} = 15.34 ((l(n)/gcat/h))), JG 9C, SV_{xn} = 13.93 ((l(n)/gcat/h))).

The C₂ oxygenates consisted predominantly of ethanol. Olefins can principally be hydrated to form alcohols if an acid catalyst is present (Hart, 1982). Alumina has acidic properties and
there may exist a possibility that ethanol formation can occur via ethene hydration. The reaction coefficient was obtained as a function of Rh loading (Figure 4.8).

![Graph showing the ethene hydration coefficient with Rh loading after ~97 hours on line.](image)

**Figure 4.8** The ethene hydration coefficient with Rh loading after ~97 hours on line. \( T^{\text{red}} = 533 \text{ K}, P^{\text{red}} = 1 \text{ bar}, S V^{\text{red}} = H_2 \text{ (6.36 (l(n)/g/h))}, T^{\text{xrn}} = 533 \text{ K}, P^{\text{xrn}} = 20 \text{ bar}, JG 9, S V^{\text{xrn}} = 18.21 \text{ (l(n)/gcat/h)), JG 9A, S V^{\text{xrn}} = 13.50 \text{ (l(n)/gcat/h)), JG 9B, S V^{\text{xrn}} = 15.34 \text{ (l(n)/gcat/h))}, JG 9C, S V^{\text{xrn}} = 13.93 \text{ (l(n)/gcat/h)).} \)

The reaction coefficients of ethene hydration were above equilibrium, indicating that if a direct reaction pathway between ethene and ethanol exist, ethanol will be dehydrated to ethene and water. It has been found that Lewis acid sites on the alumina may interact with primary alcohols, such as ethanol, and catalyse alcohol dehydration (John and Scurrrell, 1976). The curve (Figure 4.8) indicates that the possible dehydration over JG 9 (0 Rh / 100 g Fe), JG 9A (1.3 Rh / 100 g Fe) and JG 9B (2.4 Rh / 100 g Fe) may occur to the same extent, while JG 9C (3.9 Rh / 100 g Fe) may exhibit higher activity.

The trend observed for the C₃ oxygenate fraction, with Rh content, seem to be similar to that observed for the C₂ oxygenates (Figure 4.7). The trend in the higher carbon number fraction for the oxygenate content is less obvious. A possible pathway, by which the C₃ oxygenate, n-propanol can be formed, is the hydroformylation of ethene. The ethene hydroformylation coefficient over the various catalysts is shown in Figure 4.9.
Figure 4.9 The ethene hydroformylation coefficient with Rh loading after ~97 hours on line. \((T^{\text{red}} = 533 \, \text{K}, P^{\text{red}} = 1 \, \text{bar}, SV^{\text{red}} = H_2 (6.36 \, (l(n)/g/h)), T^{\text{exit}} = 533 \, \text{K}, P^{\text{exit}} = 20 \, \text{bar}, JG \, 9, SV^{\text{exit}} = 18.21 \, (l(n)/g/h)), JG \, 9A, SV^{\text{exit}} = 13.50 \, (l(n)/g/h)), JG \, 9B, SV^{\text{exit}} = 15.34 \, (l(n)/g/h)), JG \, 9C, SV^{\text{exit}} = 13.93 \, (l(n)/g/h))).

The ethene hydroformylation coefficient is far below the equilibrium concentration. This may be due to the reaction conditions used. Hydroformylation reactions are done at low temperatures of ~ 423 K and up to 200 atm (Pines, 1982). Ethene hydroformylation over the catalysts might be a possible route to form n-propanol. The trend observed in Figure 4.9 is that the Rh addition may enhance the ethene hydroformylation pathway.

The iron carbide in the spent catalysts may explain the trends observed in the oxygenates. Iron carbides have been found to be important in controlling the active surface sites in Fe based catalysts (Raupp and Delgass, 1979), if it can be assumed that iron carbide is the active surface sites for oxygenate formation. Figure 4.10 shows the \(\varepsilon^\prime\)-Fe\(_{22}\)C content in the spent catalysts relative to the C\(_3\) oxygenates over the various catalysts.
Figure 4.10 $C_3$ oxygenates after ~97 hours on line with the $\% \varepsilon' - Fe_{2.2}C$ in the spent catalyst determined by MES. ($T^{red} = 533 K$, $P^{red} = 1$ bar, $SV^{red} = H_2$ (6.36 (l(n)/gcat/h)), $T^{oxn} = 533 K$, $P^{oxn} = 20$ bar, JG 9, $SV^{oxn} = 18.21$ (l(n)/gcat/h)), JG 9A, $SV^{oxn} = 13.50$ (l(n)/gcat/h)), JG 9B, $SV^{oxn} = 15.34$ (l(n)/gcat/h)), JG 9C, $SV^{oxn} = 13.93$ (l(n)/gcat/h))).

The observed trend was not very obvious, since the $\varepsilon' - Fe_{2.2}C$ content in the spent Rh promoted and un-promoted catalyst did not vary significantly with the exception of JG 9B (2.4 Rh / 100 g Fe). No obvious trends could be observed with Rh loading.

It has been shown that the incorporation of Fe into Rh clusters resulted in the enhancement of CO insertion. The MES of the reduced catalyst showed $Fe^0$ and $Fe^{3+}$. The $Fe^{3+}$ was located at the metal support interface. It was suggested that during CO adsorption the C co-ordinates with the Rh while the O co-ordinates with the adjacent $Fe^{3+}$. The enhancement in alcohol formation was related to the bi-site interaction of the C and O, which may promote CO insertion (Ichikawa, 1988, Ichikawa, 1987). Gučzi and Lázár (1991) reported that for alcohol formation from CO/H₂ over iron catalysts the metallic, carbide, oxide and inter-phases might play determining roles.

The oxygenate content in the hydrocarbons in the oil fraction after approximately 97 hours on line increased with the addition of Rh, as seen in Figure 4.11.
Figure 4.11 Oxygenate content in the hydrocarbons in the oil fraction after ~97 hours on line over the various Rh loading. (T_{red} = 533 K, P_{red} = 1 bar, SV_{red} = H_2 (6.36 (l(n)/gcat/h)), T^xn = 533 K, P^xn = 20 bar, JG 9, SV^xn = 18.21 (l(n)/gcat/h)), JG 9A, SV^xn = 13.50 (l(n)/gcat/h)), JG 9B, SV^xn = 15.34 (l(n)/gcat/h)), JG 9C, SV^xn = 13.93 (l(n)/gcat/h)).

Rhodium addition was shown to be associated with a decrease in catalyst activity (Figure 4.2). Xiaoding et al. (1987) has indicated that the addition of K to Co-Cu inhibited catalysts. The addition of K inhibited CO conversion but increased the oxygenate content by influencing the metal ensemble.

The Rh promoted and un-promoted catalysts showed a sharp decrease in alcohol content with an increase in carbon number. It appears that the alcohol content of the promoted catalysts decreased less with carbon number compared to that of the un-promoted catalyst. This may indicate less secondary oxygenate reactions over the Rh promoted catalyst. Rh may have blocked the active Fe surface thus decreasing the CO dissociation (CO to hydrocarbon formation) but the RhFe ensemble may be enhancing oxygenates by suppressing secondary alcohol reactions.

Figure 4.12 shows the alcohol content in the oxygenate fraction in the oil phase after ~97 hours on line.
Figure 4.12 Alcohol content in the oxygenates in the oil fraction after ~97 hours on line over the various Rh loading. ($T_{\text{red}} = 533$ K, $P_{\text{red}} = 1$ bar, $SV_{\text{red}} = H_2$ (6.36 (l(n)/gcat/h)), $T_{\text{xn}} = 533$ K, $P_{\text{xn}} = 20$ bar, JG 9, $SV_{\text{xn}} = 18.21$ (l(n)/gcat/h)), JG 9A, $SV_{\text{xn}} = 13.50$ (l(n)/gcat/h)), JG 9B, $SV_{\text{xn}} = 15.34$ (l(n)/gcat/h)), JG 9C, $SV_{\text{xn}} = 13.93$ (l(n)/gcat/h)).

Initially the alcohol content increased with the promoted as well as the un-promoted catalysts. This may be ascribed to the conversion of some of oxygenates to alcohols, such as the hydrogenation of aldehydes. Near $C_{12}$ the alcohol content decreased. The decrease in the alcohol content for the Rh promoted catalyst occurred to a lesser degree as that observed for the un-promoted catalyst. The decline in alcohol content near $C_{12}$ may be related to the secondary conversion of some of the alcohols. The addition of Rh may be inhibiting the conversion of the higher alcohols. Increased Rh content seem not to influence the alcohol content in the oxygenate fraction.

Rh addition enhanced the chain growth probability for both the higher oxygenates and hydrocarbons (Figure 4.13).
Figure 4.13 Chain growth probability of the oxygenates and hydrocarbons in the oil fraction after ~97 hours on line over the various Rh loading. ($T^{\text{red}} = 533 \text{ K}, \ P^{\text{red}} = 1 \text{ bar}, \ SV^{\text{red}} = H_2$ (6.36 (l(n)/gcat/h)), $T^{\text{run}} = 533 \text{ K}, \ P^{\text{run}} = 20 \text{ bar}, \ JG 9, \ SV^{\text{run}} = 18.21$ (l(n)/gcat/h)), JG 9A, $SV^{\text{run}} = 13.50$ (l(n)/gcat/h)), JG 9B, $SV^{\text{run}} = 15.34$ (l(n)/gcat/h)), JG 9C, $SV^{\text{run}} = 13.93$ (l(n)/gcat/h)).

Lee and Lee (1989) indicated that catalysts with higher chain growth probability favours C-C bond formation while C-H occurs with less ease. Thus catalysts with higher chain growth ability exhibit lower hydrogenation ability. It may seem that Rh addition inhibited the base catalyst hydrogenation ability. This is in agreement with what was suggested earlier that Rh may be enhancing oxygenates by suppressing secondary reactions such as hydrogenation of oxygenates.

The $\alpha$-values of the hydrocarbons are higher than the chain growth probability of the oxygenates. Fujimoto and Oba (1985) observed a similar trend for their Co supported catalyst promoted with molybdenum and potassium. The chain growth probability for the hydrocarbons were higher (0.45-0.55) compared to the oxygenates.

4.2 Factors influencing the oxygenates

4.2.2 Temperature

Increase in reaction temperature is thermodynamically unfavourable for alcohol synthesis (Xiaoding et al., 1987).
Table 1.4 shows that the standard heats of enthalpy increased with an increase in temperature. The low C₁ oxygenate fraction observed might be ascribed to thermodynamically unfavourable conditions.

The C₂ oxygenate fraction was high at the various temperatures while the higher oxygenates were low (Figure 3.54). No obvious trend was observed in the oxygenate content in the gas phase with an increase in temperature.

A possible pathway for the formation of C₂ oxygenates, e.g. ethanol, is the hydration of ethene. The reaction coefficient of ethene hydration to ethanol is above equilibrium (Figure 4.14) indicating that the reverse reaction, i.e. the dehydration of ethanol is more favourable under the reaction conditions used. It may seem that an increase in temperature enhanced the dehydration of ethanol since the reaction coefficient decreased for ethene hydrogenation.

![Graph showing the hydration coefficient over JG 9C at various temperatures.](image)

**Figure 4.14** Ethene hydration coefficient over JG 9C at various temperatures. (T\(\text{red} = 533\) K, P\(\text{red} = 1\) bar, SV\(\text{red} = H_2 (6.36 (l(n)/gcat/h)), P^{\text{xn}} = 20\) bar, JG 9 SV\(^{\text{xn}} = 14\) (l(n)/gcat/h))

The trend that ethanol dehydration increased with an increase in temperature is not reflected in the C₂ oxygenate content since the C₂ oxygenates does not change significantly with an increase in temperature. Although the C₂ oxygenates may be subjected to increased secondary reactions, the rate of ethene transformations may also be enhanced with temperature increases. This may explain why the C₂ oxygenate content does not vary significantly with temperature increases.
The C₃ oxygenate content however shows a slight decrease with temperature. It is expected since increased temperature may enhance the decomposition of the alcohols. However, looking at the possible pathway in the formation of a C₃ oxygenate, ethene hydroformylation to n-propanol, (Figure 4.15) seems that the reaction coefficient for ethene hydroformylation approaches equilibrium and becomes more favourable with an increase in temperature.

![Equilibrium curve](image)

**Figure 4.15** Ethene hydroformylation coefficient over JG 9C at the various temperatures. (T<sup>red</sup> = 533 K, P<sup>red</sup> = 1 bar, SV<sup>red</sup> = H₂ (6.36 (l(n)/gcat/h)), P<sup>xn</sup> = 20 bar, SV<sup>xn</sup> = 14 (l(n)/gcat/h)).

It has been found that at high temperatures oxygenate formation over Rh diminishes. CO insertion is favoured at lower temperatures, ca. 433 K, where the competing CO hydrogenation becomes negligible (Trevino et al., 1997). The increase in temperature may have increased the yield of n-propanol formation while the H₂ and CO partial pressures decreased due to increased conversions.

Our results, that the C₃ oxygenates decreased with an increase in temperature, is in agreement with what Pijolat and Perricon (1985) found. They reported that an increase in temperature increased the alcohol yield but the alcohol selectivity decreased due to higher hydrocarbon yield over their Fe (10 mass %) / Al₂O₃ catalyst.

Our results obtained for the higher oxygenates, are also in agreement with Pijolat and Perricon (1985) findings. The oxygenate content and the alcohol content in the fraction of
oxygenates decreased with an increase in temperature. Stiles et al. (1991) concluded that higher alcohols are formed very efficiently at higher temperatures but the tendency for secondary reactions such as hydrocarbon and methane formation increased.

4.2.2 Space velocity

Change in space velocity did not seem to influence the C₂ oxygenates over JG 9C (3.9 Rh / 100 g Fe) in an obvious manner (Figure 3.63). We inspected the probable reaction of a C₂ oxygenate formation, the hydration of ethene to form ethanol (Figure 4.16) with an increase in space velocity. The reaction coefficients at the various space velocities were above equilibrium, indicating the occurrence of the reverse reaction, the dehydration of ethanol. Increasing the space velocity from 5.7 to 14.7 (l((n)/gcat/h), increased the distance from equilibrium. An increase in space velocity typically increases the yield of primary formed product compounds (Xiaoding et al., 1987). Further increase in space velocity did not to influence the dehydration process of ethanol indicating the primary ratio of $p_{\text{Ethanol}}/p_{\text{Ethene}}$.

![Figure 4.16 Ethene hydration coefficient at various space velocities over JG 9C. ($T_{\text{rad}} = 533$ K, $p_{\text{rad}} = 1$ bar, $SV_{\text{rad}} = H_2$ (6.36 (l((n)/gcat/h)), $T_{\text{xn}} = 533$ K, $p_{\text{xn}} = 20$ bar).](image)

The increase in space velocity from 5.7 to 14.1 (l((n)/gcat/h) resulted in an increase in C₂ oxygenate content due to a decrease in secondary reactions of the C₂ oxygenate. Further increase in space velocity from 14.1 to 26.2 (l((n)/gcat/h) led to a decrease in C₂ oxygenate.
content. Since secondary reactions decreases with an increase in space velocity it may seem the C₂ oxygenates are formed in secondary reactions.

The trend observed in the C₃ oxygenate content with an increase in space velocity was not very obvious. The lowest space velocity exhibited the highest oxygenates content. We investigated a possible pathway in the formation of C₃ oxygenates, ethene hydroformylation to n-propanol with varying space velocity (Figure 4.17). The ethene hydroformylation over JG 9C is possible since the reaction coefficient is far below equilibrium. The increase in space velocity decreased the coefficient even further. The n-propanol was correlated with the C₃ oxygenate content observed over JG 9C. The high C₃ content at the low space velocity (5.7 (l/(n)/gcat/h)) and the decrease in oxygenate content may indicate that the C₃ oxygenate are formed via a secondary reaction pathway, such as ethene hydroformylation.

![Equilibrium](image)

**Figure 4.17** Ethene hydroformylation coefficient at various space velocities over JG 9C. ($T^{\text{red}} = 533 \text{ K, } P^{\text{red}} = 1 \text{ bar, } SV^{\text{red}} = H_2 \text{ (6.36 (l(n)/gcat/h))}, T^{\text{mn}} = 533 \text{ K, } P^{\text{mn}} = 20 \text{ bar}$).

The higher carbon number oxygenate content and alcohol content in the oxygenates increased with an increase in space velocity. This is in agreement with the findings reported by Xiaoding et al. (1987). Xiaoding et al. indicated that an increase in space velocity would be favourable for the synthesis of higher alcohols. An increase in space velocity increases the mass transfer of the reactants to the active sites but hinders secondary reactions due to short contact time. Mass transfer becomes more severe for longer chained alcohols and
hydrocarbons. This may indicate that the higher alcohols are formed via a primary reaction pathway.
5: CONCLUSIONS

Rhodium as catalyst in the homogeneous hydroformylation process and synthesis gas conversion is associated with oxygenate formation. In order to investigate the effect of rhodium as a promoter, a base catalyst 100 Fe / 8.7 Cu / 5.6 K₂O / 372 Al₂O₃ was impregnated with an RhCl₃-solution. The method in which Rh was added to the base catalyst i.e. post-impregnation seem to be an influencing factor in the behaviour of the catalyst. Two instances in which it may influence the catalyst have been proposed. The impregnation of the aqueous RhCl₃ salt may have influenced the Fe to metal ratios as well as the iron particle dispersion. This may have influenced the FeC formed during FT synthesis. The FeC may have been stabilised by support interactions. Rhodium added in a post-impregnation step, might have covered the Fe catalyst resulting in a decrease in the catalyst activity. Residual Cl ions may also have effected the catalysts reduction as well as catalytic performance.

The addition of rhodium slightly enhanced the reduction of Fe³⁺ to Fe⁰. This may indicate that the rhodium and iron oxide particles are in close proximity. Rh might be covering the active Fe particles causing a decrease in the catalyst activity. The olefin and 1-olefin content remained almost unchanged with rhodium addition. The catalyst with the highest olefin and 1-olefin content exhibited the lowest FT activity JG 9A (1.3 Rh / 100 g Fe) and the higher olefin and 1-olefin content can be ascribed to the lower activity and thus also lower activity for secondary reactions.

We have not shown that Rh is actively involved oxygenate formation, since an increase in Rh content did not influence the olefin, 1-olefin and oxygenate content in the lower carbon number fraction. In fact, the influence Rh addition had on the base catalyst is rather obscure. Rh was added as RhCl₃ salt. Cl⁻ may influence the reduction of Fe, the carburisation process and secondary reactions over alumina. The post-impregnation of Rh may have influenced the Fe / metal ratios, which may have influenced the FT activity and secondary reactions. It was however observed for the ethene/n-propanol system that is if a direct reaction pathway between ethene and n-propanol exists, n-propanol will be formed from ethene and synthesis gas.
Rhodium as promoter for our Fe / Cu / K₂O / Al₂O₃ catalyst enhanced the oxygenate formation, the alcohol content in the fraction of oxygenates and the chain growth probability of the higher oxygenates. The higher chain growth probability for both the oxygenates and hydrocarbons with rhodium addition indicate that C-C bond formation was enhanced at the expense of hydrogenation reactions. A decrease in temperature and an increase in space velocity increased the oxygenate content of the higher oxygenates. This may be due to a decrease in secondary oxygenate reactions.

5.1 Further investigations

1. The catalysts were prepared via post-impregnation of rhodium onto the Fe / Cu / K / Al₂O₃ catalyst. Co-impregnating of Rh, Fe, K and Cu onto Al₂O₃ may exhibit different properties.

2. Blocking the active Fe sites upon addition of Rh is speculative. This speculation needs to be confirmed by further investigations, for example in-situ Infrared CO adsorption experiments. It would give an indication what occurs on the surface of the catalyst since CO bonded to Fe give unique absorbance frequencies. Rhodium blocking the Fe surface may be evident by a decrease in CO absorbance associated with Fe or a shift in absorbance due to the formation of Rh-Fe species.

3. Temperature programmed reduction studies are required to correlate with our MES results.

4. It would be interesting to monitor the Fe-phases during reduction and FT synthesis utilizing for example in-situ Mössbauer spectroscopy and correlating the phases with the FT activity. It would be interesting to find out what role Fe oxides play in oxygenate formation.

5. It may seem that the residual chloride ions influenced the catalyst behaviour. It would be interesting to observe the true effect of Rh. Thus catalysts should be prepared using for
example Rh nitrate salts. It would also be interesting to establish if chloride ions influence carbide formation by adding varying amounts of HCl to the base catalyst.

6. It would be interesting to investigate how support interactions influence carbide formation. For example calcine the catalyst at varying temperatures, which will lead to different metal support interactions then correlate this with FeC formed.
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7 : APPENDIX

Appendix A : Calibrations of Mass flow controllers

Mass flow controllers were calibrated at atmospheric pressure using a water flow meter. The flows were standardised to normal pressure (1.013 bar) and temperature (273.15 K). Below are the calibration curves obtained for H₂, APG and Ar.

**Figure 7.1** Reactor H₂ calibrated at atmospheric pressure and standardised to normal temperature, 273.15 K and pressure, 1.013 bar.

**Figure 7.2** Reactor APG calibration at atmospheric pressure and standardised to normal temperature, 273.15 K and pressure, 1.013 bar.
Figure 7.3 Reactor Ar calibrated at pressure and standardised to normal temperature, 273.15 K and pressure, 1.013 bar.

Figure 7.4 Reduction unit H$_2$ calibrated at atmospheric pressure and standardised to normal temperature, 273.15 K and pressure, 1.013 bar.
Appendix B : Data evaluation

1. Gas and oil analyses

Gas samples were obtained using ampoule technique. A gas chromatograph with a TCD (thermal conductivity detector) was employed to determine the permanent gasses. A Gow Mac GC series 580 was used to perform the TCD measurements. The system consisted of two columns in series. The first was a Porapak Q followed by a molecular Sieve 13X. The sample was first analysed using Ar as carrier gas. This allowed measurement of the H₂. The detector switches over to the second system were the other gasses (CO, CO₂, CH₄ and Ar) are measured using He as the carrier gas. The flow rates of the carrier gasses were measured 20 ml/min at 320 K.

The flow rates of the gasses were determined relative to the calibration gas, a gas mixture of known concentration. Ar with known flow rate was used as internal standard. Typical gas chromatograph of the calibration gas and composition is shown below.

![Typical chromatograph of the calibration gas.](image)

Figure 7.5 Typical chromatograph of the calibration gas.

Typical composition of a calibration gas is given in Table 7.1.
Table 7.1 Typical composition of the calibration gas.

<table>
<thead>
<tr>
<th>Calibration gas</th>
<th>Composition, mol-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>40.07</td>
</tr>
<tr>
<td>CO₂</td>
<td>9.99</td>
</tr>
<tr>
<td>Ar</td>
<td>9.91</td>
</tr>
<tr>
<td>N₂</td>
<td>4.95</td>
</tr>
<tr>
<td>CH₄</td>
<td>15.94</td>
</tr>
<tr>
<td>CO</td>
<td>19.59</td>
</tr>
</tbody>
</table>

Typical chromatographs of the inlet and outlet gas streams are shown in Figure 7.6 and Figure 7.7 respectively.

Figure 7.6 Typical chromatograph of the inlet gas.
Figure 7.7 Typical chromatograph of the outlet gas.

The flow rate of a particular component in the sample was determined using the equation 7.1.

\[
\text{Gas}(Z) \text{ flow (mol/s)} = \left( \frac{\% \text{ Z in calibration gas} \times \text{calibration peak area}_Z}{\% \text{Ar in calibration gas} \times \text{calibration peak area}_Z} \right) \times \left( \frac{\text{Ar (mol/s)} \times \text{peak area in sample}_Z}{\text{Ar peak area in sample}} \right)
\]

\[Z = \text{gas under investigation}\]  \hspace{1cm} 7.1

\[\text{H}_2 \text{ and CO conversions were calculated using the equation 7.2.}\]

\[
\text{Conversion} \% (X) = \left( \frac{\text{Flow rate (mol/s)}_\text{in} - \text{Flow rate (mol/s)}_\text{out}}{\text{Flow rate (mol/s)}_\text{in}} \right) \times 100
\]

\[7.2\]

During catalyst testing the CO + CO\textsubscript{2} conversions were used to investigate the CO conversion to organic products, since CO can react with water in the water gas shift reaction to form CO\textsubscript{2} which in-turn can partake in the Fischer-Tropsch synthesis. CO + CO\textsubscript{2} conversion were calculated using the equation 7.3.

\[
X_{\text{CO+CO}_2} = \left( \frac{(\text{CO + CO}_2) \text{(mol/s)}_\text{in} - (\text{CO + CO}_2) \text{(mol/s)}_\text{out}}{(\text{CO + CO}_2) \text{(mol/s)}_\text{in}} \right) \times 100
\]

\[7.3\]
The mass % of the components in the oil fraction, drained over a certain time period, were obtained from gas chromatography with a FID (flame ionisation detector). The components were related to the rate of oil formation per sample draining and were expressed as mol/s. The flow rate of n-decane was used to determine the flow rates of the organic components in the gas samples. This was done on the assumption that all the n-decane detected at the outlet sample point condensed to form oil.

The hydrocarbons, in the gas samples were analysed using gas chromatography with a FID (flame ionisation detector). The FID analyses were performed on a HP5890. A OV-1 column was used and H₂ was used as the carrier gas at 20 ml(n)/min. The sample was introduced at 205 K under N₂. The temperature was increased at 275 K / min to 553 K.

The oil analyses were performed on a Hewlett Packard HP 6890 series consisting of a capillary column, HP-Pona Methyl Siloxane. H₂ was used as the carrier gas. Auto-sampler injected 0.2 μl and analyses started at 323 K. The temperature was increased at 277 K / min to 563 K. The peak areas were normalised with respect to the mass of the sample injected. Peaks were identified from Mass Spectroscopy. Typical FID chromatographs of the gas and oil samples are shown in Figure 7.8 and Figure 7.9.
Figure 7.8 Typical FID of the hydrocarbons in gas samples.
Figure 7.9 Typical FID of the hydrocarbons in oil samples, in the C₇-C₁₆OH range.
The flow rates of the hydrocarbons in the gas samples were determined using equation 7.4.

\[
\text{Flow rate (mol/s)HC} = \frac{\text{Flow rate}_{n-C_{16}} \text{ (mol/s)} \times \text{Peak area}_{n-C_{16}} \times R_{n-C_{16}} \times \text{MW}_{n-C_{16}}}{\text{Peak area}_{n-C_{16}} \times \text{MW}_{\text{HC}}} 
\]

\[R_f = \text{response factor} \quad 7.4\]

The hydrocarbon selectivity was calculated relative to the CO converted excluding CO converted to CO₂.

\[
\text{Selectivity (C - %)} = \left( \frac{\text{Flow rate}_{n-C_{16}} \times N_c}{(\text{Flow rate}_{\text{CO (in)}} - \text{Flow rate}_{\text{CO (out)}}) \times (\text{Flow rate}_{\text{CO₂ (in)}} - \text{Flow rate}_{\text{CO₂ (out)}})} \right) \times 100
\]

\[N_c = \text{the number of carbons in the hydrocarbon molecule} \quad 7.5\]

The yields (C-%) were determined relative to the CO flow rate of the inlet using equation 7.6.

\[
\text{Yield (C - %)} = \left( \frac{\text{Flow rate}_{n-C_{16}} - \text{Flow rate}_{\text{HC (in)}} \times N_c}{\text{Flow rate}_{\text{CO (in)}}} \right) \times 100
\]

\[7.6\]

2. **Carbon balance**

The carbon balance of the reactor runs was calculated using equation 6.7.

\[
\text{Carbon balance} = 100 - (X_{\text{CO}} - Y_{\text{CO₂}} - Y_{\text{CH₄}} - Y_{\text{C}_{2}+})
\]

\[7.7\]

The gas analyses and the wax produced were considered in the carbon balance. Using equation 7.2 the CO conversions were calculated while equation 7.6 was applied to calculate the yields (C %) of the products. The C₂+ yield included wax production. The mass of the wax was converted to equivalent "carbon flow".

3. **Alpha value**

The Anderson-Schulz-Flory distribution is a mathematical model for the Fischer-Tropsch chain growth. It indicates the probability that a growing hydrocarbon (R_{cn-1}) chain would be terminated or propagated.
The distribution implies that the rate of formation of hydrocarbons with \( n-1 \) carbons is independent of the number of carbon atoms in the molecule. This ratio (equation 7.8) is called the growth probability.

\[
\frac{R_{cn}}{R_{cn-1}} = \alpha
\]

7.8

Ideally the product moles in logarithmic representation relative to the carbon number shows a straight line (Schulz, 1999). The Anderson-Schulz-Flory distribution was obtained by plotting the logarithmic sum of the rates of organic product formation in a certain carbon number versus the carbon number. The slope of the plot was used to determine the \( \alpha \)-value.

An example of the data obtained during a reactor run is shown in Table 7.2

<table>
<thead>
<tr>
<th>Time on line, hrs</th>
<th>( X_{\text{CO} + \text{CO}_2} )</th>
<th>( X_{\text{CO}} )</th>
<th>( S_{\text{CH}_4} )</th>
<th>( S_{\text{CO}_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>49</td>
<td>24.23</td>
<td>38.54</td>
<td>21.69</td>
<td>34.93</td>
</tr>
<tr>
<td>72</td>
<td>26.38</td>
<td>40.03</td>
<td>16.72</td>
<td>34.48</td>
</tr>
<tr>
<td>97</td>
<td>26.10</td>
<td>39.40</td>
<td>20.54</td>
<td>31.61</td>
</tr>
<tr>
<td>122</td>
<td>22.26</td>
<td>35.44</td>
<td>19.30</td>
<td>35.09</td>
</tr>
</tbody>
</table>

**Olefin content in linear hydrocarbons**

- \( C_2, \text{ mol-\%} \): 49.05, 45.26, 41.40, 58.54
- \( C_3, \text{ mol-\%} \): 74.55, 74.49, 74.44, 78.93
- \( C_4, \text{ mol-\%} \): 68.62, 70.34, 71.08, 68.91

**1-Olefin content in linear olefins**

- \( C_4, \text{ mol-\%} \): 83.32, 85.35, 83.78, 83.88
- \( C_5, \text{ mol-\%} \): 81.90, 83.42, 83.68, 82.91
- \( C_6, \text{ mol-\%} \): 83.69, 76.65, 75.99, 76.83

**Oxgenate content in hydrocarbons**

- \( C_1, \text{ mol-\%} \): 3.04, 0.84, 0.66, 1.23
- \( C_2, \text{ mol-\%} \): 13.88, 17.73, 21.92, 12.62