

The Fischer-Tropsch synthesis in slurry phase reactors : kinetics and mass transfer

Citation for published version (APA):

Boelee, J. H. (1988). The Fischer-Tropsch synthesis in slurry phase reactors : kinetics and mass transfer. [Phd Thesis 1 (Research TU/e / Graduation TU/e), Chemical Engineering and Chemistry]. Technische Universiteit Eindhoven. https://doi.org/10.6100/IR290777

DOI: 10.6100/IR290777

Document status and date:

Published: 01/01/1988

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.

• The final author version and the galley proof are versions of the publication after peer review.

• The final published version features the final layout of the paper including the volume, issue and page numbers.

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THE FISCHER-TROPSCH SYNTHESIS IN SLURRY PHASE REACTORS

Kinetics and Mass Transfer

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THE FISCHER-TROPSCH SYNTHESIS IN SLURRY PHASE REACTORS

Kinetics and Mass Transfer

proefschrift

Ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, Prof. Ir. M. Tels, voor een commissie aangewezen door het College van Dekanen in het openbaar te verdedigen op vrijdag 14 oktober 1988 te 16.00 uur

door

JOHANNES HERMANUS BOELEE

geboren te Leiden

Dit proefschrift is goedgekeurd door de promotoren:

Prof. Dr. Ir. K. van der Wiele

Prof. Dr. Ir. D. Thoenes

lemand is blij als hij de passende woorden vindt, het juiste woord op het juiste moment is een weldaad.

Spreuken 15 : 23

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SUMMARY

Low olefins such as ethene and propene are important basic chemicals which are generally still obtained from crude oil nowadays, but it may well be that coal could become a major carbon source for the production of these and other hydrocarbons in the future.

With coal as the raw material, there are two main routes, i.e. extraction under simultaneous hydrogenation and gasification, followed by the production of synthesis gas, which, in turn, is converted to hydrocarbons and oxygenated chemicals by Fischer-Tropsch synthesis. This study is concerned with the latter of these routes, i.e. a variation of converting from coal-derived synthesis gas to low olefins.

An important characteristic of synthesis gas, is the H_2/CO ratio. This ratio may vary between 0.4 and 4.0, depending on which gasification process is chosen. In this study the major objective is the ability to convert synthesis gas, having a low H_2/CO ratio (0.46 - 0.68), directly to low olefins in a slurry reactor. Such synthesis gas is produced by modern coal gasifiers, because low H_2/CO ratio's have economic and process advantages.

For the goals set in the objective of this thesis to be fulfilled, it is necessary to apply a suitable catalyst system which not only gives the desired activity and selectivity characteristics for the desired performance in a slurry reactor, but the catalyst system should also be a good water-gas shift catalyst.

In this thesis the selective production of low olefins is investigated at relatively high pressures (e.g. 10 bar) and high measures of conversion from CO rich synthesis gas. Two catalysts are used in this investigation: $RuFe/SiO_2$ and potassium promoted fused iron.

RuFe/SiO₂ has been selected because of its high activity and olefin selectivity observed at low conversions. On the other hand, potassium promoted fused iron is a veteran in the field and therefore served as the best available basis for comparison.

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The slurry bubble column seems promising for the industrial production of low olefins via the Fischer-Tropsch route. Therefore special attention is given to the effect of gas-liquid mass transfer in this type of reactor. The mass transfer of hydrogen is of particular importance because the conversion rate of synthesis gas depends mainly on the hydrogen pressure.

The influence the type of reactor has on olefin selectivity is investigated whereby a bubble column reactor is used which has external recycle of the gaseous reaction products and unconverted CO and H_2 .

The experimental work consist of three parts:

- A kinetic study of Fischer-Tropsch synthesis over RuFe/SiO₂ and fused iron in a stirred autoclave at 1.5 - 17 bar and 200 - 300°C for a maximum measure of conversion of 98%.
- A study of the gas-liquid mass transfer coefficient of H₂ in a 5 cm diameter glass bubble column at atmospheric pressure and 250°C whereby the application of ethene hydrogenation over palladium was applied.
- 3. An investigation of CO and H_2 conversion to low olefins in a 5 cm diameter stainless steel bubble column at 9 bar and 250 270°C over fused iron. Part of the reactor outlet gas is recycled by means of a compressor. The liquid phase in this and the other reactors is squalane ($C_{30}H_{62}$) which can be considered as representive of a Fischer-Tropsch wax.

In the case of fused iron the extent of secondary hydrogenation of ethene and propene mainly determines the olefin selectivity of C_2 and C_3 respectively. The olefin selectivity depends entirely on the olefin/carbon monoxide pressure ratio in the reactor and is independent of the hydrogen pressure. This may be explained by considering carbon monoxide and olefin molecules produced competing for the same catalyst surface sites, whereas the order of hydrogen for secondary hydrogenation and synthesis gas conversion is equal. Thus, an increase of the CO conversion results in a higher olefin/CO pressure ratio and this causes an increase in the hydrogenation of olefins. In the case of ethene it would appear that incorporation also increases with increasing ethene/CO pressure ratio. The latter incorporation of ethene makes it clear why the C_2 -point falls below the Schulz-Flory line at higher conversions.

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The olefin selectivity observed with $RuFe/SiO_2$ is very low in comparison with fused iron, particularly after some time on stream. The olefin selectivity decreases extremely rapidly with increasing CO conversion. Since olefin selectivity appears to be equally low, whether using $RuFe/SiO_2$ or Ru/SiO_2 and the bimetallic phase appears to decompose, it is clear that it is the Ru particle which determines the performance of the $RuFe/SiO_2$ system and therefore the pronounced hydrogenation activity.

There are other properties of the fused iron catalyst which are superior to the $RuFe/SiO_2$ catalyst, such as higher activity and a considerably lower methane selectivity. The latter is even lower than what is predicted by the Schulz-Flory distribution under conditions almost complete CO conversion.

The activities of both fused iron and RuFe/SiO₂ are low to the extent that the mass transfer rate in a bubble column in which a Fischer-Tropsch reaction is operating, is sufficiently large.

The mass transfer coefficient k_{La} reaches exceptionally high values in the squalane liquid medium (>2 m_{L}^3/m_{L+G}^3 s) by using a porous plate as a gas distributor, provided the concentration of the solid particles is low (< 1 wt%).

However, the addition of solids in the diameter range of $3 - 64 \mu m$, which gives a suspension containing 1 -20 wt% of solids, always results in a fall of the k_La. This decline of the k_La with increasing solid concentration is more pronounced for solids with larger particle diameters. The particles added to the system probably cause accelerated coalescence of gas bubbles. The advantage of a porous plate, which is meant to produce small bubbles, gets lost therefore, for a higher concentration of solid particles.

The olefin selectivity was much higher in a bubble column than in a stirred autoclave for equal conversions. This high olefin selectivity is caused by the mean lower olefin/CO pressure ratio and this, in return, is caused by the plug flow characteristic of the gas flow. The effect of "back-mixing" of product gas, investigated by recycling products of reaction and unconverted synthesis gas is less significant than the effect of the conversion taking place.

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1 INTRODUCTION

1.1. Alternatives to crude oil as chemical feedstock

The conversion of a mixture of carbon monoxide and hydrogen (synthesis gas) to aliphatic hydrocarbons, originated by Fischer and Tropsch ¹, enables the chemical industry to replace crude oil as chemical feedstock by coal, natural gas or other carbon containing materials for the production of (synthetic) fuels, light olefins and other important chemicals. As this time coal seems to be the most promising carbon source to substitute oil in the future, since the recoverable resources proven and estimated are by far the largest of fossil fuels in the world 2 . In the past coal was already used for the production of synthetic transport fuels. In 1936 Ruhrchemie installed a Fischer-Tropsch plant with an annual capacity of 200,000 tons of hydrocarbons 3 . During the last year of World War II the installed capacity in Germany was enlarged to 600,000 tons/annual ³. The discovery of large oil desposits in the Middle East in the mid-1950s terminated the use of coal for the production of fuels. Since that period the Fischer-Tropsch process is economically unattractive. The temporary rise of the crude oil price during the seventies caused a revival of interest in the Fischer-Tropsch route which led to a large amount of research at universities and industry. Because the oil price strongly decreased commercialization did not take place.

Political reasons and the availability of large resources of cheap coal resulted in the erection of a Fischer-Tropsch plant in Sasolburg, South Africa which started operation in 1955 4 . This and much larger plants at Secunda, which started operation in the early nineteen-eightees, provide a large percentage of the fuels and chemicals in that country which are derived from crude oil elsewhere.

Energy strategy reasons and the availability of remote natural gas fields may lead to the utilization of natural gas as alternative feedstock for transport fuels ⁵. According to a commercially available process of Shell (Shell Middle Destillate Process), synthesis gas with an H_2/CO ratio of about 2 can be converted into fuel gas (C_1 and C_2), LPG and liquid transport fuels. The synthesis gas is obtained by partial oxidation of natural gas. In this process a high selectivity for heavy paraffins and wax is obtained by the use of a Co catalyst promoted

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with Zr, Ti and/or Cr 6 . The wax fraction is hydroconverted over a noble metal catalyst into liquid fuels.

Instead of the Fischer-Tropsch route, synthesis gas can be converted into methanol as well, from which $C_1 - C_{10}$ hydrocarbons can be produced via the Methanol-To-Gasoline process of Mobil using a ZSM-5 catalyst ⁷. A commercial natural gas to gasoline plant using this technology is running in New Zealand since the end of 1985 ⁸.

1.2. The use of a slurry reactor for the Fischer-Tropsch synthesis

The early Fischer-Tropsch plants installed by Ruhrchemie made use of fixed-bed reactors. The technology of this type of reactor together with that of a high temperature circulating fluidised bed reactor, developed by M.W. Kellogg, were used by SASOL leading to the start of a plant in 1955. These reactors are the only types used commercially. The slurry phase system, developed by Kölbel and Ackermann, has only reached the pilot plant scale at Meerbeck in 1952-1953 9. Although the three phase bubble column operated succesfully, commercialization was not economically attractive due to the enormous supply of crude oil by which almost all activities dealing with synthesis gas were terminated. In the mid-1970s the research concerning the Fischer-Tropsch route revived leading to a renewal of interest in the slurry phase system. Despite several companies having built pilot plants with a slurry reactor, again commercialization did not occur because of the lower oil prices but also due to lack of experience in commercial scale operation resulting in the choice of a down flow fixed-bed reactor in case of the Shell Middle Distillate Process.

Nevertheless, the slurry reactor possesses a number of advantages ⁹: 1. Uniform temperature in the reactor

- 2. High catalyst and reactor productivity
- 3. A catalyst efficiency of about 1

4. Good heat transfer

5. Simple construction and therefore low investment costs

Besides, the H_2/CO inlet ratio may be lower than 1, whereas fixed-bed and circulating fluidised bed reactors usually operate at a ratio of 2 or higher to prevent plugging and agglomeration of catalyst particles by the formation of wax. The formation of heavy hydrocarbons, however, does not

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affect the performance of slurry reactors as long as the liquid viscosity stays low at the reaction conditions. As will be pointed out in Chapter 2 an H_2/CO inlet ratio below 1 is only acceptable if the catalyst itself or a co-catalyst exhibits a high water-gas shift activity. As a consequence of the allowable low H₂/CO inlet ratio, the slurry reactor may use synthesis gas directly from the second generation coal gasifiers. These gasifiers, British Gas/Lurgi Pilot, Koppers/Totzek and Texaco Pilot, operate with a low steam usage by which the thermal efficiency increases to 0.46, 0.56 and 0.68 respectively instead of, for example 2.1 obtained with a conventional Lurgi gasifier 10. Higher thermal efficiency means potentially lower-cost gasification which is important because the predominant costs of a complete Fischer-Tropsch plant is associated with the coal gasification 11. A certain disadvantage of the bubble column reactor is that the residence time behaviour of the liquid phase may approach the behaviour in a stirred tank reactor while that of the gas phase may be deviate substantially from plug flow. This results in a lower synthesis gas conversion and lower selectivities of primary products which can undergo secondary reactions. On the other hand, mixing the liquid phase is essential for catalyst suspension, promotes the uniformity of the liquid phase for which reason the synthesis gas may contain such a high concentration of carbon monoxide.

The use of small catalyst particles in a slurry reactor may cause solid liquid separation problems. According to Farley and Ray 12 the best method investigated on pilot plant scale proved to be that of simple gravity separation. Kölbel 13 , however, reported that centrifugal separation of the hot slurry is a suitable method. In case of iron catalyst particles Kuo 11 showed that the settling of catalyst particles can be accelerated by the use of magnets at 204°C. The settling time decreased from 3 to 1 hour due to the magnetic forces. It can be concluded that the separation of small catalyst particles on a large scale cannot be carried out with filter systems. Separations by settling at a high temperature seems to be a reliable method by which a sufficiently high separation rate is obtained.

1.3. Aim and outline of this investigation

The Fischer-Tropsch synthesis is a suitable way of converting coalderived synthesis gas to hydrocarbons. These are of interest not only for the production of transport fuels but also as a feedstock for the chemical industry. In the latter case, the low olefins are the prefered compounds.

The slurry reactor, especially the bubble column reactor, seems the most promising for the production of low olefins with a high selectivity at a high conversion level.

This study is focussed on the production of low olefins in a slurry reactor, especially at high pressure, a high conversion level and a low H_2/CO inlet ratio. The work is particularly aimed at understanding the factors that determine the selectivity in industrially relevant conditions.

Two types of catalysts are included in this study. From previous research in this laboratory ¹⁴ RuFe/SiO₂ appeared to be a promising catalyst for making low olefins. However, this catalyst has only been investigated at a low conversion level. Therefore, the performance of RuFe/SiO₂ has been studied under industrial conditions in the slurry phase (Chapter 3). The performance of this catalyst has been compared with that of a potassium promoted fused iron catalyst which is similar to the type used commercially (Chapter 2).

The effect of the gas-liquid mass transfer on the overall reaction rate was separately determined in a three-phase bubble column using a rapid hydrogenation reaction under Fischer-Tropsch conditions (Chapter 4). This is justified as the Fischer-Tropsch synthesis over iron catalysts is approximately first order in hydrogen, provided the conversion level is not very high. Special attention has been paid to the influence of the type of the gas distributor, liquid height, concentration and diameter of solid particles. The effect of the reactor type on olefin selectivity has been investigated in a slurry bubble column with external recycle of the gaseous products together with unconverted synthesis gas (Chapter 5).

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2 CATALYTIC PERFORMANCE OF POTASSIUM PROMOTED FUSED IRON IN THE SLURRY PHASE

2.1. Introduction

Promoted iron catalysts have been applied industrially for the Fischer-Tropsch synthesis during many years. These catalysts appear to be stable when synthesis gas with a high H_2/CO ratio is converted in the gas phase. Industrial Fischer-Tropsch catalysts are not commercially available. However, they are closely related to the commercial ammonia catalysts. An ammonia catalyst was therefore selected for this study. As pointed out in the general introduction, the application of a slurry reactor offers a number of advantages including the important benefit of being able to use a low H_2/CO inlet ratio. Hence, special attention is given to the catalyst performance in the slurry reactor at a low H_2/CO ratio and a high conversion level as these are the conditions of industrial importance, especially in a slurry reactor.

Before presenting the catalytic performance of the catalyst in the slurry reactor, the problem of accumulation of hydrocarbons in the reactor will be discussed.

2.2 Materials and catalyst

All the gases (hydrogen, carbon monoxide, nitrogen, helium, argon, ethene and carbon dioxide) were obtained from cylinders supplied by Hoekloos or Air Products. The purity of carbon monoxide and the other gases exceeded 99.5 and 99.9% respectively. Before addition to the reactor, the gases were separately purified by a reduced copper catalyst (BASF R3-11) at 180°C and by a molecular sieve 5A (Union Carbide) at room temperature.

The catalyst was a commercial fused iron ammonia synthesis catalyst, supplied by Süd-Chemie and denoted as C73. On an unreduced weight basis, it contains approximately 1.7% K₂O, 2.7% Al₂O₃, 0.8% CaO, 0.3% MgO and (0.1% SiO₂. The promotors are unevenly distributed over the surface (measured by means of XPS analysis) and the concentration on various particles varies enormously (measured by means of AAS analysis).

The catalyst was reduced with hydrogen for 70 h at 450°C, atmospheric pressure and at a space velocity of at least 30 ml (20° C, 1 bar)/(g

cat.min) in a fixed-bed reactor. After reduction the specific surface area was approximately 15 m^2/g (BET method, nitrogen adsorption).

2.3 Apparatus

A schematic drawing of the experimental apparatus is shown in Figure 2.1. The bold lines indicate the flow path of the main gas stream during continuous operation. The equipment is almost entirely made of stainless steel.



Fig. 2.1 Experimental set-up of the slurry reactor unit;(1) Mass flow controller; (2) Oil supply vessel; (3) Stirrer motor with magnetic transmission (4) Autoclave with electric heating; (5) Cold trap; (6) Pressure regulator valve; (7) Calibration mixture; (8) Washing-bottle; (9) Expansion valve; (10) Soap-film meter; (11) Wet-gas meter

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<u>Reactor.</u> The synthesis was carried out in a 0.5-liter autoclave provided with a variable speed magnetic drive. The reactor contains four baffle bars (6 mm wide) spaced 90°C apart. The agitator is a 38 mm diameter turbine impeller. The impeller has 8 flat-bladed disks, each 156 mm² and is placed 35 mm above the vessel bottom. The autoclave is heated by resistance wire which is wrapped tightly around the reactor wall. The amount of heat is regulated by a PID temperature controller (Eurotherm 070) which controls the liquid temperature within \pm 0.5°C, as measured by a type K thermocouple.

The exact temperature was measured by a second thermocouple connected with a flat-bed recorder (Kipp BD40). The two thermocouples were initially located in a thermowell filled with paraffin oil but the well became covered slowly with carbon. This caused the reliability of the temperature measurement to become unreliable. Therefore, the thermowell was removed and the thermocouples were placed directly in the liquid phase. Gas is sparged by a 0.5 mm bore tube placed in the bottom of the vessel. Studies in a reactor made of glass show that a stirrer speed of about 200 rpm is required to suspend 15 wt% of 45-90 µm unreduced iron particles (hexane, 20°C).

<u>Gas flow.</u> The flow of all gases (four different gases could be connected simultaneously to the reactor system) were regulated by mass flow controllers based on heat conductivity (Hi-Tec F 201). A calibration curve was constructed for each type of gas and controller before the start of a batch. The outlet gas flow rate was measured with a soap-film flowmeter or a wet-test meter. During a run the inlet gas flow could be checked via a bypass.

<u>Product sampling.</u> The composition of the reactor outlet gas flow was measured on-line via a heated sample line which was located ahead of the cold trap. A large amount of volatile products was condensed in this apparatus. The cold trap contained a large quantity of plates which appeared to be necessary for removing very fine liquid droplets in the gas flow. These liquid droplets can plug the orifice of the pressure regulator and this causes large variations of the reactor pressure. A run without catalyst particles at representative temperature and pressure (250°C, 9 bar) showed that no reaction occurred. This proves that the wall of the reactor is effectively inert and cracking of squalane is

negligible.

<u>Liquid carrier.</u> Squalane (2,6,10,15,19,23-hexamethyloctacosane, $C_{30}H_{62}$) was applied as liquid phase. This relative expensive hydrocarbon has a melting point below room temperature which facilitates its handling. Squalane (Fluka AG, purity >95%) contains small amounts of squalene. The boiling point of squalane is 350°C at atmospheric pressure. Below 300°C squalane is thermally stable.

<u>Operating procedure</u>. Continuous experiments lasting more than 800 hours with one catalyst batch have been performed. Operating conditions were changed at intervals of 10 to 24 hours. The reactor system, including the on-line gas analysis, operated 24 h per day without interruption. Possible changes in catalytic activity or selectivity were monitored by periodically repeating a standard experiment.

<u>Analysis.</u> Hydrogen, carbon monoxide and carbon dioxide were separated over a molsieve 13X column (T = 40°C) in a HP5700A gas chromatograph with a TCD. Argon was used as carrier gas. Usually only the hydrogen signal was integrated. Carbon monoxide and carbon dioxide were separated over a porapak Q column (T = 90°C) in a HP5710A gas chromatograph with a TCD. For this analysis helium was used as carrier gas. C_1 to C_3 olefins, paraffins and alcohols were separated over a porapak QS column (T = 95°C) in a Pye 104 gas chromatograph equipped with a FID. C_1 to C_8 hydrocarbons were analysed with a Carlo Erba FID EL480 after separation over a n-octane/poracil C column. This column was attached in the oven of the HP5710A gas chromatograph (T = 90°C).

The signals of the detectors were connected alternately with a HP3392A integrator via a CB4052BM dual 4-channel analog multiplexer which was controlled by a mechanical time switch. A complete analysis could be carried out every 2 hours.

The chromatographs were regularly calibrated for C_1 to C_3 hydrocarbons, H_2 , CO and CO_2 . The response factors of C_4 - C_8 hydrocarbons are based on the report of Dietz ¹. For a flame ionization detector these factors are nearly proportional to the number of carbon atoms in the product.

2.4 Accumulation of hydrocarbons in a stirred laboratory slurry reactor

2.4.1 Introduction

In a stirred slurry reactor the temperature control and uniformity is achieved by the good heat conductivity and homogeneity of the liquid phase. However, the presence of a relatively large liquid volume has its disadvantages when studying rapid changes of the catalytic performance. Hydrocarbons produced accumulate in the liquid phase. This accumulation causes delay in the appearance of the products in the gas phase. A further delay is caused by the gas holdup in and above the liquid phase. The time lag between the head of the reactor and the gas sample valve is negligible.

The reaction conditions affect the accumulation of the products both in the liquid and the gas phase. The accumulation in both phases will be larger at higher pressure because the solubility in the liquid phase and the concentration in the gas phase increases with increasing pressure. The gas flow also influences the accumulation within the reactor.

It is important to note that if the carbon number increases the solubility of the hydrocarbons also increases. This means that the time to attain the steady-state concentration increases with increasing carbon number. Hence, the apparent selectivity will change until the steady-state value of the largest hydrocarbon of interest has been reached.

In this section the length of the time required for hydrocarbons, formed by the Fischer-Tropsch reaction, to reach the steady-state is calculated and compared with the value determined experimentally. In addition, the effect of the reactor pressure on the accumulation within the reactor will be shown.

2.4.2 Theoretical and experimental results

Consider a well-stirred slurry reactor with a perfectly mixed gas, liquid and solid phase. It is assumed that the gas phase in and above the liquid is in equilibrium with the liquid phase. Synthesis gas is supplied to the reactor and gaseous products are removed overhead together with unconverted synthesis gas. The outlet pressure of component i, p_i , follows from a mass balance over the reactor:

$$\frac{P_{i}(t) F_{out}}{RT} = r_{p,i} - V_{L} \frac{d C_{L,i}(t)}{dt} - V_{G} \frac{d C_{G,i}(t)}{dt} \qquad (2.1)$$

Assuming that the concentration in the liquid phase is represented by the Henry's law, Eq.(2.1) can be written as

$$\frac{\mathbf{p}_{i}(t) \mathbf{F}_{out}}{\mathbf{RT}} = \mathbf{r}_{p,i} - \frac{\mathbf{V}_{L}}{\mathbf{m}_{i} \mathbf{RT}} \cdot \frac{\mathbf{d} \mathbf{p}_{i}(t)}{\mathbf{dt}} - \frac{\mathbf{V}_{G}}{\mathbf{RT}} \cdot \frac{\mathbf{d} \mathbf{p}_{i}(t)}{\mathbf{dt}}$$
(2.2)

Integration of Eq.(2.2.) and replacement of the actual gas flow F_{out} by the gas flow F_{out}^* measured at room temperature, T*, and atmospheric pressure, p*, results in

$$p_i(t) = p_i^{\infty} + (p_i^0 - p_i^{\infty}) \exp(-bt)$$
 (2.3)

with

$$b = \frac{F^{*} \text{out } p^{*} T}{(V_{G} + V_{L}/m_{i})p T^{*}}$$

$$p_{i}^{\infty} = \frac{1}{b} \cdot \frac{r_{p,i} RT}{V_{G} + V_{L}/m_{i}}$$
(2.4)
(2.5)

In these equations p_i^{0} and p_i^{∞} represent the pressure of i at t=0 and t= ∞ respectively.From the inspection of Eq.(2.4) follows that the time constant b depends mainly on the gas flow, the pressure, the liquid and gas volume and the solubility. The gas volume is only important for C_1-C_4 hydrocarbons because the value of V_L/m for C_5^+ hydrocarbons is much higher than V_G . Reduction of the time constant can be achieved by increasing the gas flow or decreasing the pressure or liquid volume.

The length of time required to attain the steady-state value of gaseous hydrocarbons in a stirred 0.5-liter autoclave, as used in this study, is illustrated by the theoretical and experimental course of the pressure of various hydrocarbons as a function of time (see Figure 2.2). The course of the pressures is shown after a change of the inlet gas flow.

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This specific change of reaction conditions was chosen because in this manner the effect of the reaction conditions on the intrinsic catalyst activity is less important than in the case where the pressure or the temperature is changed. The theoretical lines in Figure 2.2 are calculated with help of Eq. (2.3) assuming that the production rate of hydrocarbons is constant. Figure 2.2 shows that the time observed experimentally to reach the steady-state is longer than the time predicted. After 4 hours the pressure of C_1 , C_3 and C_5 (with respect to the steady state value) are 2, 5 and 7% higher than the steady state value, respectively. This value is reached after approximately 8 hours for the hydrocarbons shown in Figure 2.2. Taking into account the possibility that the catalyst activity increases slightly in the first hours after a change of the gas flow, the similarity between the time measured and calculated is satisfactory.



Fig. 2.3 Effect of the carbon number on the time required to reach the steady-state value in the gas outlet flow of the stirred autoclave. The lines are calculated according to Eq.(2.3) and the data given in Figure 2.2

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The time required to attain the steady-state value increases with increasing carbon number due to the larger solubility of heavier hydrocarbons. Figure 2.3 illustrates the fraction of the steady-state pressure versus time. Obviously, the C_{10} and C_{13} fraction do not reach the steady-state value within 8 hours after changing the process parameters under the reaction conditions chosen.

As already mentioned, the time constant b in Eq.(2.4) depends on the reactor pressure. Figure 2.4 shows the effect of the reactor pressure on the course of the pressure of C_5 as a function of time. At low pressure the steady-state value of the products is reached rapidly. However, at a higher pressure more time has to elapse before the measured pressure is equal to the "intrinsic pressure". In this study, therefore, the reported performance of the catalyst properties are measured during at least 10 hours. Usually, the reaction conditions were varied after the reaction was monitored 24 h at a particular setting.



Fig. 2.4 Effect of the pressure on the time required to reach the steady-state value in the gas outlet flow of the stirred autoclave. The lines are calculated according to equation (2.3) and the data given in Figure 2.2

2.4.3 Conclusion

At a moderate pressure (10-15 bar) and a low gas flow rate (1 m³ synthesis gas/m³ squalane) a reliable analysis of the concentration of C_1-C_7 hydrocarbons, produced by the Fischer-Tropsch synthesis in a stirred 0.5-liter autoclave, is only possible when at least 8 hours are elapsed after setting the reaction conditions. Catalyst properties, which change much more rapidly and well within the above-mentioned 8-hour period, can only be measured accurately if the gas flow is increased or the total pressure is decreased.

2.5 <u>The importance of the water-gas shift activity for the performance of</u> Fischer-Tropsch catalysts

The H₂/CO outlet ratio in a well-mixed slurry reactor determines the H₂/CO concentration ratio in the liquid which in turn determines the H₂/CO ratio on the catalyst surface, provided mass transfer limitations are absent. The H₂/CO concentration ratio on the catalyst surface is of importance for the deposition of carbon which is the main cause of the deactivation of Fischer-Tropsch catalysts. The H₂/CO outlet ratio is influenced by the usage ratio ¹) which in turn is affected by the water-gas shift activity of the catalyst. This section mainly deals with the relation between the water-gas shift activity of the catalyst and the H₂/CO outlet ratio. In addition, the stoichimetry and the conversion level will be discussed since they affect the H₂/CO outlet ratio as well.

The overall reaction for the production of hydrocarbons from CO and $\rm H_2$ can be written as

 $CO + (1 + \frac{1}{2}x)H_2 \rightarrow CH_x + H_2O$ (2.6)

The product water can be converted to CO_2 by the water-gas shift reaction:

$$zCO + zH_2O \neq zCO_2 + zH_2$$
(2.7)

z being the fraction of the product water which is converted by the water-gas shift reaction.Combining of Eq.(2.6) and (2.7) results in the

1) = net molar ratio in which CO and H_2 are consumed in the reaction

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overall stoichiometry

$$(1 + z)CO + (1 + \frac{1}{2}x - z)H_2 \rightarrow CH_x + zCO_2 + (1 - z)H_2O$$
 (2.8)

As will be pointed out below, the H_2/CO usage ratio, U, plays an important role in determining the required H_2/CO inlet ratio. The overall stoichiometry shows that the H_2/CO usage ratio depends on the H/C atomic ratio in the product (x) and on the fraction of water converted (z):

 $U = (1 + \frac{1}{2}x - z)/(1 + z)$ (2.9)

The H_2/CO usage ratio for some typical products of the Fischer-Tropsch synthesis are presented in Table 2.1.

Table 2.1

The H_2/CO usage ratio (U) for some products of the Fischer-Tropsch synthesis when z = 0 and z = 1 (a low and high watergas shift activity respectively)

	U	
Product	z = 0	z = 1
CH4	3	1
C ₂ H ₆	2.5	0.75
CH2.33	2.2	0.58
C ₂ H ₄	2	0.5

Table 2.1 clearly demonstrates that a high water-gas shift activity is indispensable if the H_2/CO usage ratio has to be lower than the value 1. When the usage ratio is known, the effect of the conversion of CO and H_2 on the H_2/CO outlet ratio, E, can be calculated for a known value of the inlet ratio (I). The value of the outlet ratio follows simply from

$$E = I \frac{1 - X_{H_2}}{1 - X_{CO}}$$
(2.10)

Both the conversion of H_2 and that of CO can be expressed as a function of conversion of CO + H_2 (X_{CO+H_2}):

$$X_{CO} = X_{CO+H_2} \frac{(1+I)}{(1+U)}$$

$$X_{H_2} = X_{CO+H_2} \frac{U(1+I)}{I(1+U)}$$
(2.11)
(2.12)

Substition of Eqs. (2.11) and (2.12) into (2.10) results in

$$E = \frac{I - X_{CO+H_2} \frac{U(1+I)}{(1+U)}}{1 - X_{CO+H_2} \frac{(1+I)}{(1+U)}}$$
(2.13)

By substitution of Eq.(2.9) into (2.13) the H_2/CO outlet ratio can be calculated for each degree of conversion of CO + H_2 when the values of x are known:

$$E = \frac{I(2 + \frac{1}{2}x) - (1+I)(1 + \frac{1}{2}x - z)x_{CO+H_2}}{2 + \frac{1}{2}x - (1+I)(1+z)x_{CO+H_2}}$$
(2.14)

The large effect of the water-gas shift activity on the usage ratio was already illustrated in Table 2.1. As a consequence the value of z strongly effects the outlet ratio as shown in Figure 2.5. Obviously, the H_2/CO outlet ratio decreases as a function of conversion of CO + H_2 if the value of z is lower than 0.6. When the H_2/CO inlet ratio has to be lower than 1.0, the value which was chosen in Figure 2.5, the value of z

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Fig. 2.5 The calculated H_2/CO outlet ratio as a function of the conversion of $CO+H_2$ for various values of z. The inlet ratio (I) is 1.0. The H/C atomic ratio in the product (x) is 2.33

has to be higher than 0.6 to avoid that the H_2/CO outlet ratio decreases with increasing conversion. Note that the value of x, assumed in Figure 2.5. is near the lowest which is possible for Fischer-Tropsch hydrocarbons (see Table 2.1). This means that, to convert synthesis gas with a low H_2/CO ratio, a high water-gas shift activity is absolutely essential.

2.6 The water-gas shift activity of potassium promoted fused iron

2.6.1 Introduction

It is generally accepted that the water-gas shift reaction is a consecutive reaction. Initially water is the principal by-product of the formation of hydrocarbons by the Fischer-Tropsch reaction. Depending on the rate of the water-gas shift reaction, the water formed by the Fischer-Tropsch synthesis will be converted into CO_2 or removed by the outlet gas stream. The water-gas shift reaction is an equilibrium reaction, see Eq.(2.7), of which the equilibrium lies on the CO_2 side for typical Fischer-Tropsch conditions. It can be seen from the equilibrium constant 2

$$K_{\rm S} = \frac{PCO_2 \ PH_2}{P_{\rm H_2O} \ P_{\rm CO}} = 0.0132 \ \exp(4578/T)$$
(2.15)

that only 1% of the water produced is not converted into CO_2 at 250°C and for H_2/CO ratio = 0.85. The question whether the equilibrium is actually reached in practice, in relation to the rate of the water-gas shift reaction, will be answered in this section.

2.6.2 Experimental

About 30 g of crushed (45-90 μ m) fused iron (C73, Sud-Chemie) was reduced in a separate fixed-bed reactor with 0.9 l H₂ (20°C, 1 bar)/ min at 450°C, atmospheric pressure, for 70 hr. It was added into the stirred autoclave without exposure to air and then slurried with 200 g squalane. The stirrer speed (1000 min⁻¹) was high enough to avoid mass transfer limitations and to achieve perfect mixing of the gas and liquid phase. Two batches of fused iron have been used the conditions for which are presented in Table 2.2.

Table 2.2

Experimental conditions

	Condit	cions	
		Batch 1	Batch 2
Temperature	(°C)	250	230, 250, 270
Pressure	(bar)	1.5 - 9	1.5 - 9
(H ₂ /CO)feed	(-)	0.7 - 3	0.67

2.6.3 Results and discussion

In principle, the water-gas shift activity can be determined directly on the basis of the amounts of water and carbon dioxide produced. However, the concentration of water in the outlet gas flow is difficult to measure accurately by means of gas chromatography or aluminium oxide sensors. Therefore, the water-gas shift activity is calculated and expressed by the value of z, which represents the fraction of product water converted to CO_2 . The value of z can be calculated in different ways:

1. Calculation of the value z from the H_2/CO usage ratio and the H/C atomic ratio in the product according to Eq.(2.9) which can be rewritten into

$$z = \frac{1 - U + \frac{1}{2}x}{1 + U}$$
(2.16)

The H_2/CO usage ratio can be calculated from the measured conversion of H_2 and CO

$$U = I \frac{X_{H_2}}{X_{CO}}$$
(2.17)

2. Calculation of z from the production of CO_2 and the conversion of CO. From the overall stoichiometry, Eq.(2.8), it follows that

$$z = \frac{r_{CO_2}}{-r_{CO} - r_{CO_2}}$$
(2.18)

Introducing the CO_2 partial pressure and the conversion of CO gives to rise to the following equation:

$$z = \frac{P_{CO}(1-X_{CO})}{P_{CO} X_{CO} - P_{CO_2}(1-X_{CO})}$$
(2.19)

This equation is prefered for the determination of the value of z because it is sufficient to know the CO_2 partial pressure and CO conversion. It makes it more accurate than Eq.(2.16). Rewriting of Eq.(2.19) shows that the CO conversion divided by 1-X_{CO} increases linearly with the increasing CO₂/CO pressure ratio:

$$\frac{X_{CO}}{1-X_{CO}} = \frac{z+1}{z} \cdot \frac{P_{CO_2}}{P_{CO}}$$
(2.20)

Together with data points, this relation is shown in Figure 2.6 for various values of z. Despite considerable scattering of the data points, the conclusion is justified that the value of z is close to 1 at 250°C. This high value indicates a high rate of the water-gas shift reaction. This means that the water-gas shift equilibrium will be attained at reaction conditions and that application of Eq.(2.15) is allowed for calculation of the water vapour pressure.

As a consequence of the high water-gas shift activity, the H_2/CO usage ratio is very low for the catalyst applied here. Therefore, synthesis gas with a low H_2/CO ratio, such as 0.67, can be converted up to a high degree of conversion. At such a high conversion level the outlet H_2/CO ratio is considerably larger than the inlet ratio as shown in Figure 2.7. The data points in Figure 2.7 can be fit with Eq.(2.13) assuming the H_2/CO usage ratio is 0.55.


Fig. 2.6 Relation between the conversion of CO and the CO_2/CO pressure ratio. The lines represent the theoretical relation (see Eq.(2.16)) for various values of z indicated in the figure. The experimental data are obtained at 250°C (run 1)

2.6.4 Conclusion

The H_2/CO outlet ratio and the usage ratio are strongly dependent on the rate of the water-gas shift reaction. Due to the high water-gas shift activity of potassium promoted fused iron the H_2/CO usage ratio is low (approximately 0.6) and the partial pressure of water is very low even at a high degree of conversion. As a consequence of the high rate of the water-gas shift reaction over this catalyst, synthesis gas with a low H_2/CO ratio can be converted directly to hydrocarbons and carbon dioxide as the main side-product.



Fig. 2.7 The H_2/CO outlet ratio as a function of the conversion of $CO+H_2$. The reaction conditions are reported in Table 2.2 (run 2). The curve is calculated according to Eq.(2.13)

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2.7 Product distribution

2.7.1 Introduction

This paragraph describes experiments in which the product distribution of C_1-C_7 and C_{10}^+ hydrocarbons were investigated over potassium promoted fused iron at various temperatures and pressures. The aim of this experimental work is to obtain a better understanding of the effect of the reaction conditions, especially the degree of CO conversion, on the hydrocarbon product selectivity. At a high degree of CO conversion the concentration of water and carbon dioxide may influence the product selectivity. The effect of a high CO₂ and H₂O pressure on the selectivity was investigated by co-feeding of CO₂.

This section is introduced with some remarks on the Schulz-Flory distribution followed by a review of deviations from this Schulz-Flory distribution.

The product distribution of a variety of Fischer-Tropsch catalysts can be considered as the result of a random chain growth process. It is generally accepted that on iron catalysts the chain growth of hydrocarbons proceeds via insertion of CH_x species ^{3,4}. The experimental product distribution indeed follows the so called Schulz-Flory distribution developed for polymerisation reactions. This Schulz-Flory distribution predicts a linear relationship between log M_n and n, where n is the number of C atoms in the chain and M_n is the mole fraction with chain length C_n :

$$\log M_n = n \log(\alpha) + \log((1-\alpha)/\alpha)$$
(2.21)

with $\alpha = r_p/(r_p+r_t)$ where r_p and r_t are the rates of propagation and termination respectively. In the Schulz-Flory distribution it is a basic concept that the propagation and termination rates are independent of the chain length.

Deviations of the hydrocarbon product distribution from the ideal Schulz-Flory distribution can be categorized as follows: 1. Deviation of $C_1,$ 2. Deviation of $C_2,$ 3. Larger value of α for ${C_{10}}^+,$ 4. Non-Schulz-Flory distribution.

The deviation of C₁

The deviation of C_1 can be positive or negative. Higher methane fractions than predicted by the Schulz-Flory distribution are often reported for Co⁵ and Ru⁶ catalysts.The higher methane fraction is caused by extra mechanisms of methane formation ⁵. The data of Kikuchi⁶, demonstrate that the deviation of the methane fraction depends on the support; Al_2O_3 causes a much higher methane deviation than TiO_2 . As a general trend, the fraction of methane decreases and the product distribution shifts towards higher molecular weights when the reactor pressure increases. However, the difference between the methane fraction observed and predicted did not significantly diminish with increasing pressure for Ru catalysts on Al_2O_3 and TiO_2 ⁶.

Selective suppression of the methane production rate, resulting in values lower than predicted by the Schulz-Flory distribution, can be achieved by the addition of poisons such as sulfur ⁷ to iron catalysts or by the use of carriers which cause strong metal-support interactions e.g. for ruthenium catalysts. The methane reduction for modified catalysts is mostly based on a suppressed chemisorption of hydrogen which often implies a lower overall activity.

Reaction conditions also can affect the methane selectivity, whereby the concentration of water is of particular importance. A high concentration of water, obtained by addition of water vapour, inhibits the methane production rate more strongly than the production rate of higher hydrocarbons. This causes methane formation to be out of line in the Schulz-Flory distribution ⁸. The inhibiting effect of water depends on its concentration and was reversible up to 27 mole% ⁸, while water at higher concentrations or at exposure over a prolonged period caused a permanent loss of activity ^{9,10}. A reversible decrease of the methane selectivity over iron catalysts by the addition of water vapour is also reported by Tramm and Karn ^{9,10}. At a low degree of conversion (< 5%) the addition of only 0.6 vol% H₂O to synthesis gas (H₂/CO = 9) over fused iron leads to a decrease in methane selectivity due to a reduction of the methane production rate of 70% ¹¹. The addition of CO₂ (5 vol%) to synthesis gas also resulted in a reversible decrease of the methane

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selectivity (8 %) ¹¹. According to Dry ¹² the pressure of water did not influence the methane selectivity of fused iron at a high reaction temperature (325°C). On the other hand the CO_2 pressure at the entrance of the reactor appeared to play a major role in the control of the methane selectivity.

Deviation of C₂

Apart from the deviation in respect of methane, there are many reports of the observed C_2 fraction falling below the Schulz-Flory line. A high probability of ethene insertion may explain why the C_2 point of the Fischer-Tropsch products is often lower than that predicted by the Schulz-Flory distribution. According to Sachtler ¹³ the deviation of the fraction of C_2 hydrocarbons for rhodium catalysts is caused by a higher chain growth probability of C_2 intermediates on the catalyst surface. This is not necessarily true. Another explanation is that olefins readsorb on the surface and play a part in consecutive reactions (insertion, chain growth).

Larger value of α for C_{10}^+

There is increasing evidence from a variety of studies that the products from iron catalysts cannot be described with a single value of the chain growth probability, α . A larger α -value for C₁₀⁺ products has been observed for fused iron catalysts 14,15,16,17,18, reduced Fe₂O₃ ¹⁹, FeMn ¹⁷, precipitated iron ^{16,17}, nitrited iron ²⁰ and silica supported iron ²¹. Table 2.3 summarizes nearly all available data regarding the occurrence of two α -values for iron catalysts in slurry reactors.

The occurrence of two values of α is not caused by a particular type of reactor. Eglebor ²¹ reported two values of α over iron catalyst for both slurry and fixed-bed reactor.

Although it is clear that the product distribution of iron catalyst may show a break, it is unclear which compounds are responsible for the discontinuity of the Schulz-Flory distribution. Dictor ¹⁴ reported that the value of α is larger for both C₈⁺ olefins and paraffins while according to Egieborn ²¹ the product distribution of olefins showed no break as opposed to paraffins. Satterfield ¹⁷ demonstrated that only the product distribution of oxygenates showed no discontinuity in the slope of C₁₀⁺. Other authors reported only the sum of olefins and paraffins.

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Ta	b	1	е	2.	3

Summary of values of chain growth probabilities for C_1-C_9 products and C_{10}^+ products over iron catalysts in the slurry phase, reported in literature

Ref.	Catalyst	Temp. [°C]	P [bar]	(H ₂ /CO) _{feed} [mol/mol]	α ₁ (-)	α2 (-)	
71	K/fused iron	248	6.0	2.0	0.63	>0.63	
81	K/fused iron	263	7.9	0.55	0.68	0.93	1 ,0.68 2)
81	Fe/Mn	283	2.4	1.19	0.55	0.75	
72	Fe ₂ 0 ₃	250	8.0	3.0	0.53	0.66	
72	K/Fe ₂ 03	250	8.0	3.0	0.66	0.86	
84	K/Fe/Ti/Zn	325	10.0	1.0	± 0.7 3)	?	
88	K/Fe/Cu	250	9.9	1.4	0.68	0.86	
24	K/Fe/Cu/Si	300	21.3	1.0	0.61	0.78	
83	K/fused iron	260	20.4	1.0	0.70 3)	0.79	3)
78	K/fused iron	251	31.7	0.36	0.70	0.93	
		277	31.4	0.78	0.78	0.78	
		280	33.1	2.0	0.71	0.71	
82	K/Fe/Cu	220	30	1.0	<u>+</u> 0.88 3)	<u>+</u> 0.99	3)
	(nitrided)						
80	K/fused iron	232-263	5-15	0.5-1.8	?	0.90	4)
80	K/Fe/Cu	225-250	11-15	1.0-3.8	?	0.92	4)

1) for linear paraffins

²) for oxygenates

³) calculated from the data reported

4) determined from reactor holdup

An explanation for the break in the product distribution has not been established clearly. Schliebs ²⁴ demonstrated that the addition of K_2CO_3 to iron catalysts caused a break of the Schulz-Flory line at C_{10} without changing the value of α for C_1-C_9 . He proposed that the two branches

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observed with potassium promoted iron are due to synthesis over two groups of active sites: unpromoted and promoted regions. However, this interpretation may not be the only one because unpromoted iron ¹⁹ and iron-magnanese catalysts ¹⁷ also produce Schulz-Flory plots consisting of two branches. The observations of Bauer ¹⁵ (see Table 2.3) suggest that besides properties of the catalyst other effects may be important. The hypothesis of two distinct sites ^{17,24} may be an oversimplification. Stenger ²⁵ has demonstrated that the distributed-site model and the two-site model ^{17,24} are equally capable of fitting the product distribution from potassium promoted iron. The distributed-site model which assumes that potassium is normally distributed is based on a more realistic description of the catalyst surface.

Non-Schulz-Flory distribution

The aim of many investigators was the development of catalysts of which the products would not follow a Schulz-Flory distribution. Until now these studies have not been very successful. Newly developed or modified catalysts invariably show distributions which are close to the Schulz-Flory distribution ¹⁵. For example, the product distribution of Ru catalysts at high pressures (30 bar) showed a suppression of the C_2-C_8 fraction with respect to the Schulz-Flory distribution, but the C_9^+ fraction almost perfectly obeyed the Schulz-Flory distribution ²⁶.

2.7.2 Experimental

The concentration of C_1 - C_7 hydrocarbons, H_2 , CO and CO_2 were analysed on-line. From these data the value of the chain growth probability was determined at various reaction conditions. The chain growth probability for C_{10}^+ hydrocarbons was determined by analysing the reactor holdup after 450 hours on stream with a high-temperature gas chromatography technique. The reactor holdup, 1000 times diluted with hexane, was separated by an empty fused-silica capillary column, applying an initial temperature of 70°C followed by heating to 320°C with a rate of 10°C per minute. The hydrocarbons were detected by a FID (350°C) because of its high sensitivity and identical responce factor for all hydrocarbons of interest. Three batches with fused iron catalyst have been carried out. The catalyst concentration was 2.6, 9.1 and 13.0% respectively. The different catalyst concentrations were necessary to obtain a large range of the degree of CO conversion. The ranges of operating conditions were temperature: 230-270°C; pressure: 1.2-17.0 bar; H_2 /CO inlet ratio: 0.67-3.0; gas flow: 100-300 ml (20°C, 1 bar)/min.

The reaction conditions of the batch from which the value of the chain growth probability for C_{10}^+ hydrocarbons was determined, were 230°C from 0 to 140 H.O.S., 250°C from 140 to 280 H.O.S., 270°C from 280 to 340 H.O.S. and 250°C from 340 to 450 H.O.S.; pressure and gas flow were kept constant at 9 bar and 200 ml (20°C, 1 bar)/min respectively. For each temperature three different values of the H₂/CO inlet ratio were applied: 0.5, 1.0 and 2.0 respectively.

The experimental set-up and catalyst reduction procedure is reported in section 2.3.

2.7.3 Results

The products of the Fischer-Tropsch synthesis over iron catalysts mainly consist of linear olefins and paraffins, methyl-branched olefins, aldehydes and alcohols.

At a low degree of conversion the distribution of hydrocarbons is perfectly described by a Schulz-Flory line. Figure 2.8 shows that all hydrocarbons up to C_7 , C_1 and C_2 included, obey the Schulz-Flory distribution. However, at moderate conversion the C_2 point clearly lies below the Schulz-Flory line as shown in Figure 2.9. When the conversion of CO is very high, not only C_2 but also C_1 fall below the Schulz-Flory line! Figure 2.10 shows the distribution of hydrocarbons at such a high degree of conversion of CO. The deviation of the C_2 fraction appeares to be a function of the CO conversion level. Figure 2.11 demonstrates the decline of the C_2 fraction with respect to the sum of C_3 and C_4 . The values of the chain growth probability were constant in these experiments. However, in contrast with the $p_{\rm C_2}/(p_{\rm C_3}+p_{\rm C_4})$ ratio, the $p_{C_2}/p_{C_1-C_4}$ ratio did not change with increasing conversion of CO. This phenomenon can be explained by the decrease of both the C_1 and the C_2 fraction which apparently compensated each other. In our opinion the parameter $p_{C_2}/(p_{C_3}+p_{C_4})$ gives a better impression of the effect of the CO

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conversion on the C_2 fraction. Figure 2.12 shows that the same trend of the C_2 fraction as function of the CO conversion is also visible at lower conversions of CO.

In the literature it is reported that both CO_2 and H_2O influence the selectivity of the Fischer-Tropsch synthesis. We have studied the effect of the CO_2 and H_2O pressure on the product distribution by co-feeding of CO_2 . The addition of CO_2 provided a high CO_2/CO pressure ratio as shown in Figure 2.22. However, due to the high CO_2 pressure, the conversion of water, produced by the Fischer-Tropsch reaction, was strongly reduced. The reduction of the conversion of H_2O is apparent from the decrease of the $r_{CO_2}/-r_{CO}$ ratio as shown in Figure 2.20. Thus, also the H_2O/CO pressure ratio increased due to the addition of CO_2 .



Fig. 2.8 Schulz-Flory distribution of hydrocarbons at a low conversion
 level. Reaction conditions: temperature = 250°C; pressure =
 l.45 bar; H₂/CO outlet ratio = 1.15; conversion of CO = 10%; a
 = 0.55 (run 4)

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Figure 2.13 demonstrated that even if the CO_2 concentration in the gas feed is as high as 40% the methane selectivity does not change. Although the CO_2/CO ratio corresponded with a CO conversion of 90% (without CO_2 co-feeding) the concentrations of CO_2 and/or H_2O relative to CO probably were not high enough to cause a selectivity change. It should be borne in mind that the maximum H_2O/CO pressure ratio was 0.15 in this study which is considerably lower than for example in the report of Satterfield ⁸. He mentions a decrease of the methane selectivity of 24% with fused iron caused by the presence of 27 mole% H_2O in the gas feed. This addition of water lead to a H_2O/CO pressure ratio of about 4. The H_2O/H_2 pressure ratio does not appear to be a dominant factor.



Fig. 2.9 Schulz-Flory distribution of hydrocarbons at a moderate conversion level. Reaction conditions: temperature = $250^{\circ}C$; pressure = 9 bar; H_2/CO outlet ratio = 0.82; conversion of CO= 47%; α = 0.66 (run 3)

The effect of the reaction conditions on the value of α for C₁-C₇ hydrocarbons is presented in Table 2.4. Obviously, the changes in α are relatively small over a wide range of reaction conditions. Increasing the pressure has only a negligible influence on the value of α . It is probable that the tendency of α to decrease due to increasing H₂ partial pressure and to increase due to increasing CO partial pressure results in a small effect of the total pressure.

Increasing the temperature causes a slight decrease in the value of α . Increasing of the H₂/CO ratio also reduces the value of α , as shown in Table 2.5. It is remarkable that the value of α remains relatively high, even at the extremely high H₂/CO ratio of 63!, that is attained when the conversion of CO is very high. The small influence of pressure, H₂/CO



Fig. 2.10 Schulz-Flory distribution of hydrocarbons at a very high conversion level. Reaction conditions: temperature = $250^{\circ}C$; pressure = 9 bar; H_2/CO outlet ratio = 63; conversion of CO= 97%; $\alpha = 0.47$ (run 2)

Temp	Pressure	H ₂ /CO	α	
[°C]	[bar]	[mol/mol]	[-]	
230	1.2	0.69	0.62	
230	9.0	0.68	0.64	
230	17.0	0.66	0.64	
250	1.2	0.74	0.60	
250	9.0	0.80	0.61	
250	17.0	0.94	0.61	
270	1.2	0.68	0.55	
270	9.0	0.89	0.62	
270	17.0	1.19	0.59	

Table 2.4

Values of the chain growth parameter, α , at three different temperatures and pressures. H_2/CO inlet ratio was ± 0.67

Table 2.5

Variation of α with H_2/CO ratio at 250°C

Pressure [bar]	(%)	H2/CO [mol/mol]	α [-]	
9.0	27	0.41	0.66	-
9.0	69	0.81	0.61	
9.0	57	0.82	0.62	
9.0	52	0.82	0.61	
9.0	58	0.91	0.62	
9.0	75	0.93	0.58	
1.5	18	3.5	0.49	
9.0	97	63	0.47	

ratio and temperature on the value of α of this fused iron catalyst promoted with potassium agree with results of Dictor ¹⁴. The product distribution of *unpromoted* iron catalysts is more dependent on the reaction conditions ¹⁹.Therefore, it may well be that the presence of potassium in this catalyst causes the reaction conditions to have a relatively small effect on the product distribution.

The (possible) existence of a second α -value for C_{10}^+ products was also investigated. Reliable data in literature of the second α -value are scarce because it is difficult to measure the "second" value of α free of experimental errors. The main problem of the analysis of the value of α for the higher products from the gas outlet is due to the low production rate of the heavier products and the transient holdup in the reactor. Therefore, in this part of the study the reactor holdup has been analysed after a long exposure to synthesis gas. The disadvantage of this method



Fig. 2.11 The C₂ fraction as a function of the conversion of CO at a high conversion level range and 250°C

is the lack of knowledge of the influence of reaction conditions on the second value of α . Figure 2.14 shows the concentration of the n-paraffins as a function of carbon number. The variation of reaction conditions during the 450 hours on stream is mentioned in section 2.7.2. The shape of the curve for the C₁₄-C₁₉ paraffins is caused by loss of these hydrocarbons from the liquid phase in the reactor due to their relatively high vapour pressure. The value of α for the heavier hydrocarbons, predominantly paraffins, is obviously larger than for C₁-C₇ hydrocarbons, namely 0.80 and 0.62 respectively. This result is also reported by other investigators as already summarized in Table 2.3.



Fig. 2.12 C₂ fraction as a function of the conversion of CO at a low conversion level range and 250°C

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2.7.4 Discussion

The degree of conversion of CO clearly dominates the product selectivity for fused iron. At low conversion *no* secondary reactions occur which cause the C₂ fraction to fall exactly on the Schulz-Flory line. This agrees with experiments with fused iron by Dictor ¹⁴. The decline of the C₂/C₃ ratio with increasing CO conversion ($\alpha =$ constant) indicates that the C₂ reincorporation into products increases with decreasing CO pressure. As a result of this decreasing CO pressure the ethanol selectivity tends to decrease also (see Figure 2.15). This rules out the proposal that C₂ does fall on the Schulz-Flory line when the fraction ethanol is included in the C₂ fraction, as suggested by Satterfield ²⁷. The importance of C₂ incorporation agrees with other reports ^{5,8,28} but contradicts the conclusion that ethene incorporation plays no role for fused iron in a slurry reactor ²⁹. However, this



Fig. 2.13 Influence of the co-feeding of CO₂ on the methane selectivity at 250°C

conclusion is based on addition experiments of ethene at a too high degree of conversion of CO (>90%). This results in all rates of reactions to reduce, including consecutive reactions. The extent of incorporation of added ethene will be discussed in section 2.12.

It has been reported that water vapour inhibites the rate of the Fischer-Tropsch synthesis 8,9,10,12,30. Therefore, it is likely that when there is a very high degree of conversion of CO the observed inhibition of both primary and secondary reactions is caused by the high pressure of



Fig. 2.14 Schulz-Flory distribution of C_{14}^+ paraffins accumulated in the liquid phase of the slurry reactor. The reaction conditions during the time on stream are reported in section 2.7.2

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water vapour. Apparently, the production rate of methane is much more strongly dependent on the water vapour pressure than is the rate of production of the higher hydrocarbons. This specific suppression of the methane formation probably causes the observed deviation of the methane fraction from the Schulz-Flory line. It depends on the other reaction conditions whether the methane *selectivity* also decreases. When the H_2/CO ratio is very high because of a substantial degree of conversion of CO, the methane selectivity will not decrease, as a reduction of the value of the chain growth probability then compensates for the deviation of the methane fraction from the Schulz-Flory distribution.

The hydrocarbon distribution over fused iron cannot be described with a single value of the chain growth probability, α , at least not for a large range of carbon numbers. The value of α is larger for C_{20}^+ hydrocarbons than for $C_{1}-C_{7}$ hydrocarbons. This value of α is based on the



Fig. 2.15 Ethanol/methane pressure ratio as a function of the pressure of CO at 250°C

analysis of the liquid phase of the reactor after 700 hours on stream at various conditions. Thus it is not possible to exactly determine the carbon number for the point at which the break of the Schulz-Flory line occurs.

2.7.5 Conclusions

The C_1 - C_7 hydrocarbons distribution for fused iron perfectly follows a Schulz-Flory distribution when the conversion of CO is low. At a higher degree of conversion of CO ethene incorporation occurs which causes a deviation of the C_2 fraction from the Schulz-Flory line. The incorporation of ethene increases with the CO conversion. When CO is nearly depleted the methane production rate is more strongly inhibited than the rate of production of higher hydrocarbons. This is probably due to the high water vapour pressure with respect to the CO pressure.

The product distribution of heavier hydrocarbons indicates that the value of the growth probability, α , of C_{20}^+ hydrocarbons is significantly greater than the value of α for C_1-C_7 hydrocarbons.

2.8 Kinetics of the conversion of synthesis gas

2.8.1 Introduction

Kinetic information is indispensible both for reactor design and for the selection of optimal process conditions. In this study special attention is given to the reaction kinetics in a slurry reactor at a low H_2/CO ratio and a high conversion level, as these are the conditions of industrial importance, specifically in a slurry reactor.

This section concerns the overall reaction rate, and hence the effect of the partial pressures of H_2 , CO, CO₂ and H_2O on the conversion of CO and H_2 . Secondary reactions are separately dealt with in section 2.9 - 2.12.

Preceding the experimental work a literature review will be given concerning kinetic models proposed for iron catalysts valid up to high conversion levels, and the effect of co-feeding of H_2O and CO_2 on the reaction rate.

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In spite of the appropriateness of a slurry reactor for the measurement of the kinetics of the Fischer-Tropsch synthesis, most studies are carried out in the vapour phase. Except for the study of Hall et al. 31 , all the kinetic data obtained in the slurry phase with iron catalysts is of recent date. The major kinetic studies concerning the Fischer-Tropsch synthesis over iron catalysts in a slurry reactor are summarized in Table 2.6. The rate determining step (RDS) in the kinetic models proposed can be considered as a hydrogenation of a surface intermediate which exhibits a first order dependency on the hydrogen concentration at low synthesis gas conversion. The zero order rate with respect to CO implies that CO probably occupies completely the available adsorption sites 32. This theory is consistent with the findings of Dry 33 that no measurable amount of H₂ is adsorbed by alkali-free and K₂O promoted iron when CO was presorbed onto the iron catalyst. Two models reported in Table 2.6 will be handled in more detail, namely the model of Ledakowicz ³⁴ and that of Huff and Satterfield ³⁵. Preceding these models the kinetic relation presented by Anderson ³⁶ which is based on vapour phase research will be discussed.

Based on unpublished work at the US Bureau of Mines, Anderson 36 proposed that the conversion of CO and H₂ can be described as:

$$-r_{CO+H_2} = \frac{k p_{H_2}}{1 + a p_{H_2O}/p_{CO}}$$
(2.22)

Dry ³⁰ reported that this equation was found to fit satisfactorily the kinetic data obtained in both fluidized and fixed-bed reactors for K_2O -promoted iron. Eq.(2.22) can be derived from the enol complex theory assuming the following reactions:

co	+	*	÷	CO*	(2.23)
co_2	+	*	4	C0 ₂ *	(2.24)
н ₂ 0	+	*	\$	H ₂ O*	(2.25)
C0*	+	H ₂	RÐS	HCOH*	(2.26)

It is assumed that the hydrogenation of chemisorbed CO is the rate

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Table 2.6.

Summary of kinetic studies for the Fischer-Tropsch synthesis with an iron catalyst suspended in a slurry reactor.

Catalyst	Temp. [°C]	P [bar]	(H ₂ /CO)feed [mol/mol]	Rate expression	Ref
K promoted	250-320	22-24	2.0	kp	31
fused iron					
K promoted	232-263	3-15	0.6-1.8	k pH2/(1 + a pH20/(pC0 PH2)) 35
fused iron					
Precipitated	220-260	10	0.7-0.8	$k p_{H_2}/(1 + a p_{CO_2}/p_{CO})$	34
K promoted iro	m				

determining step in the Fischer-Tropsch synthesis:

 $-r_{CO+H_2} = k p_{H_2} \theta_{CO}$

(2.27)

The adsorption of CO can be described with a Langmuir equation. Neglecting the adsorption of CO_2 (Eq.(2.24)) and assuming that CO and H₂O saturate the catalyst surface leads to Eq.(2.22). This model can be conceived as a competition between product water and CO for available sites. At high conversion, the occupation with CO will reduce by the adsorption of H₂O.

When the adsorption of CO_2 is more important than the adsorption of H_2O and when thus CO_2 + CO saturate the surface, Eq.(2.27) then becomes:

$$-r_{\rm CO+H_2} = \frac{k \, p_{\rm H_2}}{1 + p_{\rm CO_2}/p_{\rm CO}}$$
(2.28)

According to Ledakowicz 34 this equation can be applied when the water concentration is low due to a high water-gas shift activity and a low

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 H_2/CO inlet ratio. Ledakowicz ³⁷ pointed out that a model proposed earlier ³⁴, which comprises both adsorption of CO₂ and H_2O :

$$-r_{CO+H_2} = \frac{k p_{H_2}}{1 + a p_{CO_2}/p_{CO} + b p_{H_2}0/p_{CO}}$$
(2.29)

could not satisfactorily describe the experimental data obtained with different H_2/CO inlet ratios.

When rate inhibition by product water is predominant, the proposed model of Huff 35 turns out to be better than Eqs.(2.28) and (2.29):

$$-r_{CO+H_2} = \frac{k p_{H_2}}{1 + a p_{H_2O}/(p_{H_2}/p_{CO})}$$
(2.30)

This model can be derived from the carbide 38 or the insertion 39 theory by making appropriate assumptions and simplifications. In case of the carbide theory it is postulated that the hydrogenation of adsorbed carbon is the rate determining step:

$$-\mathbf{r}_{\rm CO+H_2} = \mathbf{k} \, \mathbf{p}_{\rm H_2} \, \boldsymbol{\theta}_{\rm C} \tag{2.31}$$

The most important reactions in this model are:

$$CO + 2* \Leftrightarrow C* + O* \tag{2.32}$$

$$0^* + H_2 \Leftrightarrow H_2O + * \tag{2.33}$$

$$C^* + H_2 \xrightarrow{RDS} CH_2^*$$
 (2.34)

If the adsorbed carbon intermediate is assumed to be the most abundant species Eq.(2.31) turns to Eq.(2.30). In this model the rate of reduction by water vapour is explained by the decrease of the surface concentration of the carbon intermediate.

The short and long term effects of the addition of H_2O and CO_2 to synthesis gas over various iron catalysts will now be considered. The inhibition of the conversion of synthesis gas by the addition of water vapour is clearly shown in literature. Karn ⁹ has demonstrated that water is an inhibitor for *nitrided Fe*, but that the rate promptly regaines its previous value when the addition of water was stopped. The conversion of H₂+CO decreased monotonously from 80 to 38% when the concentration of the added water increased from 0 to 30 mole%. Due to the increased conversion of CO by the water-gas shift reaction the conversion of CO did not change.Satterfield ⁸ reports that also *alkali promoted fused iron* exhibits a completely reversible decrease of the catalyst activity when 12 or 27 mole% water is added to synthesis gas. The activity, however, did not recover after removal of the water vapour from synthesis gas that comprised 42 mole% water ⁸. This irreversible reduction of the activity may be caused by a decreased surface area due to recrystallization of iron crystals. This also occurs during the reduction of ammonia catalysts by the water vapour formed from the iron oxide ^{12,37}.

Brötz ⁴⁰ reportes that besides water vapour, CO₂ also inhibits the Fischer-Tropsch synthesis. The addition of 35 mole % CO₂ to CO + H₂ resulted in a reduction of the activity of an iron catalyst from 40%. Tramm ¹⁰ reports that the activity was reduced by half when 52 mole% CO₂ (or 30% H₂O) was added to synthesis gas over iron. According to Dry ¹² the presence of 5-28 mole % CO₂ in synthesis gas had no apparent effect on the activity. However, the addition of water vapour to the feed gas lowered the activity of fused iron. Based on addition of water vapour and carbon dioxide Karn ⁹ concluded that carbon dioxide has only a slight inhibiting effect on the activity of iron catalysts compared with water vapour. It has to be noted that possibly the CO₂ inhibition is not caused by CO₂ itself but by H₂O produced via the water-gas shift reaction from CO₂ added and H₂.

Thus, summarizing this introduction, in all kinetic models presented here a first order H_2 dependency is estimated and a hydrogen occupation which is independent of the CO pressure and that of other gases. The H_2O and CO_2 inhibition is explained by competition between these molecules and CO for the same active sites. Concerning the difference of the activity decrease between H_2O and CO_2 it can concluded that generally water seems to be a stronger inhibitor than CO_2 . Furthermore, it is not certain that the conversion inhibition caused by CO_2 addition is caused exclusively by CO_2 itself.

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Table 2.7 Reaction conditions of run 1 - 4.

Conditions								
		Run 1	Run 2	Run 3	Run 4			
Temperature	[°C] 2	30,250,270	250	250	190-270			
Pressure	[bar]	1.5-17	1.5-9.0	4.0-13	1.1-9.0			
(H ₂ /CO) _{feed}	[-]	0.67	0.67-3.0	0.67-3.0	0.57-1.0			
Flow	[ml/min]	50-300	100-250	150-250	100-360			
Catalyst conc	.[wt%]	13.0	13.0	9.1	2.6			

1) measured at 20°C and 1 bar

2.8.2 Experimental

All measurements were carried out in the stirred autoclave reactor (see section 2.3) using the potassium promoted fused iron catalyst C73 (see section 2.2), and in the absence of mass transfer limitations. Four runs were carried out of which the conditions are presented in Table 2.7.

To investigate the influence of the pressure of H_2O on the synthesis gas conversion rate CO_2 was co-fed. Addition of either CO_2 or H_2O can be applied to attain a certain H_2O concentration in the reactor because the H_2O and CO_2 concentration are practically in equilibrium via the water-gas shift reaction (see section 2.6). The H_2O/CO_2 concentration ratio in the reactor can be adjusted only by changing the H_2/CO ratio.

2.8.3 Results and discussion

The rate of the Fischer-Tropsch synthesis at a low conversion level is considered first. When the conversion of CO was lower than 30%, the rate of the Fischer-Tropsch synthesis approximately obeyed first order H_2 pressure, as shown in Figure 2.16. Figure 2.17 shows that the activity of the iron catalyst increased in the usual way when the temperature rises. It is interesting to note that both data points at $P_{H_2}=0.5$ bar in this figure lie somewhat beyond the curve. Futhermore, the catalyst was not stable at these reaction conditions in contrast with all other experiments. Additional experiments have demonstrated that the height of the hydrogen pressure is important as will be pointed out below. It appears that increasing the hydrogen pressure above a certain value can cause an unexpected increase in the conversion of CO and H₂ as shown in Figure 2.18. This figure indicates that the first order dependency on H₂ is only valid over a small range of hydrogen pressure values . The non-linear increase of the synthesis gas conversion rate was not caused by a decrease in water vapour or CO_2 pressure. This has been shown by the values of the CO conversion in parentheses (since the H₂O pressure increases with increasing CO conversion). In addition, it was also not



Fig. 2.16 Synthesis gas conversion rate as a function of the pressure of hydrogen at 250°C (run 4)

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caused by the sequence in which the experiments were carried out. Fig. 2.19 demonstrates that the sequence of the experiments (shown by the numbers) is not related to the non-linear increase of the conversion of synthesis gas. Thus, two different "regimes" can be distinghuished depending on the value of the absolute H₂ pressure.

The inhibition of the rate of the Fischer-Tropsch synthesis by water or CO_2 does not play a significant role when the CO conversion is kept below 70% and the inlet H₂/CO ratio is lower then 1.0 (see Fig. 2.16). However, at a higher conversion and/or a higher H₂/CO ratio, the increased water vapour and CO_2 pressure can reduce the rate of the Fischer-Tropsch synthesis, as can been seen from model 2 and 3 of Table 2.6.



Fig. 2.17 Rate of hydrocarbon production as a function of the pressure of hydrogen at various temperatures (run 1)

The inhibition by water vapour and CO_2 can be investigated by the addition of CO_2 . As mentioned before, the inhibition by H_2O generally is (much) more important than the inhibition of CO_2 but the influence of the latter cannot be excluded. Due to the high rate of the water-gas shift reaction, the pressure of CO_2 and H_2O are related in this investigation. Therefore, it is not possible to distinguish between the influence of water and CO_2 . Thus, the addition of CO_2 increases both the CO_2 and H_2O concentration, the latter as a result of the water-gas shift reaction. The higher CO_2 concentration causes a decrease of the conversion of H_2O , produced by the Fischer-Tropsh synthesis, into CO_2 . This results in a lower CO_2 production with respect to the CO conversion as shown in Figure 2.20.



Fig. 2.18 Synthesis gas conversion rate as a function of the pressure of hydrogen at 250°C (run 3)

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The co-feeding of CO_2 appeared to have only a moderate effect on the synthesis gas conversion rate. The activity decreases very little, even when the synthesis gas contained 40% CO_2 , as shown in Figure 2.21, despite the high H₂O/CO and CO₂/CO pressure ratio as shown in Figure 2.22.

It follows from literature that two models are available which express the rate of synthesis gas conversion over iron catalysts in the slurry phase. First, the model of Ledakowicz will be discussed. Next, the model of Huff and Satterfield will be compared with the experimental data. Ledakowicz ³⁴ reported that using a precipitated alkali-promoted iron catalyst, CO_2 is one of the most abundantly available components due the high water-gas shift activity of that catalyst. He suspected that the lower synthesis gas consumption rate with respect to the first order rate



Fig. 2.19 Synthesis gas conversion rate versus pressure of hydrogen at 250°C (run 2). The sequence of the experiments is indicated in the figure

in hydrogen could be attributed to competitive adsorption between CO and CO_2 . The argumentation was twofold. First, the water concentration was very small compared with the CO_2 concentration, because of the high rate of the water-gas shift reaction and the low H_2/CO inlet ratio. The water concentration should therefore be neglected. Secondly, there was no correlation between the calculated H_2O concentration and the deviation of the first order rate. Some values of the water concentration calculated even appeared to be negative.



Fig. 2.20 CO_2 production rate with respect to the CO conversion as a function of the percentage of CO_2 in the gas feed (run 3)

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Neither argument, however, is satisfactory. With regard to the first argument: a small H₂O concentration can be significant when the adsorption coefficient is high. With regard to the second one: in case of such low water vapour pressures and a high water-gas shift rate, the water mole fraction can be calculated more accurately via the water-gas shift equilibrium than via the usage ratio (as done by Ledakowicz ³⁴) (see section 2.6.3 Eq.(2.15)). Therefore the water vapour pressure has been recalculated, using the report of Ledakowicz ³⁴ in order ascertain whether his model, Eq.(2.28), gives a better fit than the model of Huff and Satterfield ³⁵, Eq.(2.30). The first step was, therefore, to rewrite Eq.(2.30). Under the assumption that the water-gas shift reaction has reached the equilibrium, the model of Huff, Eq.(2.30), can be written as follows:



Fig. 2.21 Effect of the addition of CO_2 on the hydrocarbon production rate and conversion of synthesis gas (run 3). The pressure of hydrogen is shown in parentheses

$$-r_{\rm CO+H_2} = k p_{\rm H_2} / (1 + a K_{\rm S} p_{\rm CO_2} / p_{\rm CO}^2)$$
(2.35)

After rearrangement of Eqs.(2.35) and (2.28) both models can be written in a comparable form:

 $p_{H_2}/-r_{CO+H_2} = 1/k + (a/k)(p_{CO_2}/p_{CO}) \quad (Ledakowicz) \quad (2.36)$ $p_{H_2}/-r_{CO+H_2} = 1/k + (K_S a/k)(p_{CO_2}/p_{CO}^2) \quad (Huff \& Satterfield) \quad (2.37)$ Figure 2.23 is obtained from the answers from these equations. This
figure shows that, based on this data, it is hardly possible to
discriminate between the two models. With the knowledge that Eq.(2.35) is
only valid at a low water vapour concentration, Eq.(2.37) is preferred



Fig. 2.22 The pressure of CO_2 and H_2O with respect to the CO pressure at various percentages of CO_2 in the gas feed (run 3). The hydrogen pressure is shown in parentheses

for calculating the conversion rate of CO+H₂ over iron catalysts in slurry reactors. Therefore the p_{CO_2}/p_{CO}^2 ratio (see Eq.(2.37)) is chosen as the parameter which might explain the deviation of the first order rate law in the experiments of this study.

A part of the experimental data is shown in Table 2.8. The data is arranged according to a decreasing $-r_{CO+H_2}/p_{H_2}$ ratio. This ratio should be constant if the reaction is first order in hydrogen. Clearly, the decreasing synthesis gas conversion rate per hydrogen pressure unit does not correlate at all with the CO_2/CO^2 pressure ratio which is shown in the last column. Moreover, it turns out to be difficult to find other parameters that can explain the decrease of the activity over such a wide range of reaction conditions as is shown in Table 2.8. Therefore, two series of experiments were carried out wherein the variation of the reaction conditions was limited.



Fig. 2.23 The hydrogen pressure/synthesis gas conversion ratio as a function of both the CO_2/CO and CO_2/CO^2 pressure ratio at 250°C. The data are originated from Ledakowicz ³⁴

P [bar]	-rCO+H2 ^{/PH2} [m/(min.bar]	X _{CO+H2} [%]	PH ₂ [bar]	H ₂ /CO [mol/mol]	PCO2/PCO ² [bar ⁻¹]
9.0	28.1	52.1	2.9	0.78	0.16
9.0	25.9	80.2	2.0	1.43	2.55
9.0	21.7	73.7	2.2	0.99	0.87
9.0	16.0	27.8	2.4	0.42	0.03
4.5	14.5	34.4	1.6	0.71	0.16
3.0	10.0	41.7	2.3	46.3	0.45
1.5	4.6	11.7	1.1	3.3	0.44

Table 2.8

The synthesis conversion rate at various reaction conditions of run 2.

In the first series, the H₂ pressure is increased by increasing the reactor pressure (other variables are kept constant). The water vapour pressure is low in this series which naturally means a low p_{CO_2}/p_{CO}^2 ratio. In the second series the pressure is approximately constant whereas the p_{CO_2}/p_{CO}^2 ratio is increased by co-feeding of CO₂. The results of the first series are presented in Table 2.9. This data clearly shows that the synthesis gas conversion rate is not first order in hydrogen. The nature of this activity increase is not fully understood but it may be considered as a decrease of inactive carbon on the catalyst surface caused by an increase in the hydrogen pressure. This explanation is supported by low pressure measurements which demonstrate that this catalyst loses activity when the H2/CO ratio is lower than about 2 at reactor pressure of 1.5 bar. At even lower reactor pressure, namely 1 bar inclusive 0.4 bar Helium, an H_2/CO ratio of 8 is still not high enough to prevent deactivation (These experiments were carried out in the fixed-bed apparatus as described in Chapter 3.3.8). Thus, the lower the hydrogen pressure, the higher the H_2/CO ratio must be to prevent excessive carbon formation. In this connection it is worth noting that this catalyst does not lose activity when the H_2/CO is as low as 0.4 provided the reactor pressure is 9 bar or higher.

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Table 2.9

Effect of the hydrogen pressure on the relative synthesis gas conversion rate (run 3).

Pressure [bar]	-r _{CO+H2} /PH ₂ [m1/min bar]	^x CO+H ₂ [%]	PCO2/PCO ² [bar ⁻¹]	PH2 [bar]	Flow 1) [m1/min]	H ₂ /CO [mol/mol]
5	27.7	22.3	0.05	2.0	242	0.71
9	33.0	42.5	0.06	3.2 ·	250	0.72
11	36.0	52.2	0.13	3.6	250	0.84
13	40.7	62.5	0.20	3.8	250	0.91

1) measured at 20°C and 1 bar

The results of the second series (high water vapour pressure and approximately constant H₂ pressure) are presented in Table 2.10. In this case the activity decrease with respect to first order H₂ dependency is obviously caused by water vapour as indicated by the correlation between the $-r_{CO+H_2}/p_{H_2}$ and the p_{CO_2}/p_{CO}^2 ratio. Note that the lowest p_{CO_2}/p_{CO}^2 ratio in Table 2.10 is higher than the maximum value in Table 2.9.

Table 2.10 Effect of the p_{CO_2}/p_{CO}^2 ratio on the relative synthesis gas conversion rate (run 3).

Pressure [bar]	^{-r} CO+H ₂ /PH ₂ [m1/min bar]	^х со+н ₂ [%]	<pre>pcO2/pcO² [bar⁻¹]</pre>	PH ₂ [bar]	Flow 1 [ml/min]	F _{CO2}	н ₂ /со [-]
5	40.4	47.4	0.25	1.7	144	0	0.82
7	37.3	43.7	0.96	1.8	157	54	1.05
5	30.0	41.0	3.49	1.9	140	55	2.42
6	26.8	36.8	5.97	2.1	150	100	2.82

1) measured at 20°C and 1 bar

2.8.4 Conclusion

An increasing hydrogen pressure increases the synthesis gas conversion per hydrogen pressure unit. This effect dominates the inhibition by water vapour up to a moderate conversion level of CO. At a high conversion level the inhibition by water dominates as shown by the CO_2 addition experiments.

2.9 Olefin selectivity

2.9.1 Introduction

The production of low olefins from synthesis gas is an interesting potential of the Fischer-Tropsch synthesis. In that context much research has been carried out to develop selective catalysts which specifically produce olefins. Newly developed catalysts are often tested under differential conditions at atmospheric pressure. These reaction conditions obviously are unattractive for industrial application. Therefore, the catalyst performance (including the olefin selectivity) at a high conversion level and high pressure have to be known. In this section the influence of the reaction conditions on the olefin selectivity is investigated. The effects of the conversion level and water vapour is given special attention.

The main products of the Fischer-Tropsch synthesis, CO_2 and H_2O excluded, are olefins and paraffins. Paraffines can be considered as inert under Fischer-Tropsch conditions but olefins formed can undergo consecutive reactions. The experimentally determined olefin selectivity will thus depend on the primary olefin selectivity and the importance of secondary reactions involving olefins, such as hydrogenation, isomerization, cracking and insertion in growing chains. The importance of consecutive reactions depends on the reaction conditions and naturally on the catalyst.

Concerning the reaction conditions the space velocity often is the dominating factor. The magnitude of the effect of the space velocity on the olefin selectivity can be influenced by the temperature (Fe 5,41 , Co 5), the CO pressure (Co 5 , FeMn 42), the H₂ pressure (Fe 43), the H₂/CO

ratio 44 , the alkali content (Fe 41,45), the cystallite size (Mo 46), the iron content of bimetallic catalysts (RuFe 47) and the support (Ru 48).

Apart from the space velocity it is possible that the water vapour and CO_2 pressure also affect the olefin selectivity. Unfortunately, the study of the effect of water and carbon dioxide on the olefin selectivity over potassium promoted iron catalysts is hindered by two problems:

- The dominating effect of the CO conversion level on the olefin selectivity (as will be shown in section 2.9.4 below)
- The high rate of the water-gas shift reaction, causing an interdependence of the water and carbon dioxide concentration. (as shown in section 2.6)

The dominating effect of the CO conversion level requires careful experimentation at a constant conversion. This fact had often been overlooked in literature.

Apart from the space velocity, the water vapour pressure also affects the olefin selectivity according to Dry ¹² and Satterfield ⁸ et al. They report an increase of the olefin selectivity with increasing water vapour pressure. The first author also reports that increasing the CO_2 pressure at the entrance of an integral reactor leads to an increase of the C_2 olefin selectivity using an alkali promoted fused iron catalyst at 593 K. Since the conversion level in both reports was not kept constant, it is uncertain whether the olefin selectivity increase is caused by water and CO_2 . This matter will be clarified with the help of new experimental data.

With regard to the catalyst and to iron catalysts in particular, it is clear from literature that promotors, specially potassium, stongly affect the rate of secondary hydrogenation of olefins and other consecutive reactions 12,46,49,50,51,52,53,54. This rate decreases with higher potassium content on iron catalysts 41,45,53,54. Up to approximately 1 wt% potassium does not affect significantly the synthesis activity of fused iron and precipitated iron catalysts 41,54,55. Higher potassium contents than 1 wt% cause a decrease in activity (unless large amounts of $A1_2O_3$, TiO_2 , or SiO_2 are present 54) but do not result in a further reduction of secondary reactions 45. The presence of potassium on iron does not affect the primary formation of olefins and paraffins 45.

2.9.2 <u>Competition model for the olefin selectivity in a well-mixed slurry</u> reactor

For a quantative description of the experimental results a simple model was developed in this study by which the olefin selectivity in a well-mixed reactor up to a CO conversion level of approximately 90% can be predicted. The model will be explained for the case of C_2 .

In this model three types of reactions, the formation of olefins and paraffins from synthesis gas (primary reactions) and the hydrogenation of olefins into paraffins (secondary reaction) as shown in Figure 2.2.4 are considered.



Fig. 2.24 Simplified model for the formation of olefins and paraffins from synthesis gas and the secondary hydrogenation of olefins, represented for C₂

For ethene + ethane the following mass balances can be written:

$$F_{out} C_{C_2H_4,G} = (r_1 - r_3) V_L$$
 (2.38)

 $F_{out} (C_{C_2H_4,G} + C_{C_2H_6,G}) = (r_1 + r_2) V_L$ (2.39)

Thus, the C₂ olefin selectivity $\frac{{}^{C}C_{2}H_{4},L}{{}^{C}C_{2}H_{4},L + {}^{C}C_{2}H_{6},L}$

is as follows for a perfectly mixed liquid phase reactor

CC2H4,L		r ₁	-	r3	(2.40)
$C_{C_2H_4,L} + C_{C_2H_6,L}$		$r_1 + r_2$		$r_1 + r_2$	

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It was found that the conversion of synthesis gas and the production of hydrocarbons is approximately first order in H_2 , up to a high synthesis gas conversion (about 60%) in agreement with literature 30,35. Therefore, it is assumed that the reaction rates r_1 and r_2 are only dependent on the H₂ pressure. The order in hydrogen of the olefin hydrogenation is not measured but estimated on account of the following reports. Miller 56 reports that the hydrogenation of olefins over evaporated Fe metal films is first order in each reactant at low olefin concentrations and temperatures above 150°C. The hydrogenation of ethene is also reported to be first order in both reactants for a wide variety of forms of nickel above approximately 150°C. In our laboratory the same dependency, using Ni/Al₂O₃, for the hydrogenation of ethene in squalane at 250°C and 1 bar 57 was found. In the knowledge that it is questionable whether hydrogenation should be regarded as hydrogen addition directly to the adsorbed olefin 35 and that the mechanism is not fully understood, the following is assumed: secondary hydrogenation of initially formed olefins during Fischer-Tropsch synthesis is both first order in H₂ pressure and in the fraction of active sites occupied by the olefin (θ olefin).Based on these assumptions, the following equation applies:

$$\frac{C_{C_{2}H_{4},L}}{C_{C_{2}H_{4},L} + C_{C_{2}H_{6},L}} = \frac{k_{1} C_{H_{2},L}}{(k_{1}+k_{2}) C_{H_{2},L}} - \frac{k_{3} C_{H_{2},L} \Theta_{C_{2}H_{4}}}{(k_{1}+k_{2}) C_{H_{2},L}}$$
(2.41)

Replacing the concentration terms which are proportional via Henry's Law to partial pressure gives

$$\frac{PC_{2}H_{4}^{m}C_{2}H_{4}}{PC_{2}H_{4}^{m}C_{2}H_{4}^{m}+PC_{2}H_{6}^{m}C_{2}H_{6}^{m}} = \frac{k_{1}}{k_{1}+k_{2}} - \frac{k_{3}K_{C_{2}H_{4}}PC_{2}H_{4}^{m}C_{2}H_{4}}{(k_{1}+k_{2})(1+K_{COPCO}^{m}CO+K_{H_{2}}PH_{2}^{m}H_{2}^{m}+K_{p}P_{p}^{m})}$$
(2.42)

in which the ethene fraction on the catalyst surface is based on Langmuir adsorption.

Since CO is strongly bound on potassium promoted iron 33,49,52 , it will dominate the adsorption of H₂ and of products at CO conversion

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levels below 90%. Assuming further, that the solubility of ethene and ethane are approximately equal, Eq.(2.42) can be simplified into

$$C_{2} \text{ olefin selectivity} = \frac{PC_{2}H_{4}}{PC_{2}H_{4} + PC_{2}H_{6}} = A - B \frac{PC_{2}H_{4}}{PCO}$$
(2.43)
With $A = \frac{k_{1}}{k_{1} + k_{2}}$ and $B = \frac{k_{3} K_{C_{2}H_{4}} mCO}{(k_{1}+k_{2})K_{CO} mC_{2}H_{4}}$

Note that the olefin selectivity does not depend on the H_2 pressure in this model but on the olefin/CO partial pressure ratio alone.

Thus, the olefin selectivity in a well-mixed slurry reactor is determined by the competition between olefins and CO. With increasing CO conversion, the $p_{C_2H_4}/p_{CO}$ ratio increases, implying a higher probability of olefins to reach the catalyst surface and be hydrogenated.



Fig. 2.25 Influence of the gas flow rate on the olefin selectivity and the conversion of CO and H₂. Reaction conditions: pressure = 9 bar; temperature = $250^{\circ}C$; H₂/CO inlet ratio = 1 (run 1)

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2.9.3 Experimental

The measurements were carried out in the stirred autoclave reactor which is described in section 2.3. The reaction conditions are equal to those presented in Table 2.7 (section 2.8.2).

2.9.4 Results and discussion

A characteristic of a consecutive reaction is the flow dependency. Specially the C_2 olefin selectivity appeared to be strongly dependent on the gas flow as shown in Figure 2.25. This figure indicates that ethene formed during the Fischer-Tropsch synthesis can be subsequently hydrogenated into ethane. The decline of the C_3 olefin selectivity with decreasing gas flow is less pronounced than that of the C_2 olefin selectivity. This can be attributed to the lower reactivity of propene



Fig. 2.26 The olefin selectivity as a function of the conversion of CO at 270°C (run 1)

due to a larger steric hindrance with respect to ethene 58. In consequence of the change of the gas flow, both the CO and H₂ conversion change as well, as is shown in Figure 2.25. It can be seen in this figure that the increase of the olefin selectivity correlates with the decrease of the conversion level. The important role of the CO conversion is shown in Figure 2.26 wherein the decline of the olefin selectivity as a function of CO conversion is demonstrated. The decrease of the CO conversion was achieved by a combination of gas flow and reactor pressure variations.

The validity of the competition model, described in section 2.9.2, is tested by plotting the olefin selectivity versus the olefin/CO pressure ratio. The results for C_2 and C_3 are shown in Figure 2.27 and 2.28 respectively. Obviously, the model describes the experimental data quite



Fig. 2.27 The C₂ olefin selectivity as a function of the ethene/carbon monoxide pressure ratio at $250^{\circ}C$

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satisfactory up to a CO conversion level of 90%. Above this level product concentrations becomes important. This means that it is not generally allowed to simplify Eq.(2.42) in section 2.9.2. This subject will again be dealt later on.

According to the competition model the hydrogen pressure does not affect the olefin selectivity. The results shown in Figure 2.29 and Table 2.11 confirm this independence of the H₂ pressure. Table 2.11 also demonstrates that the CO₂ pressure and the H₂/CO ratio do not correlate with the C₂ olefin selectivity. The results reported in Table 2.11 contradict those of Satterfield ⁴³, who reported that the olefin selectivity over fused iron is entirely dependent on the H₂ pressure. Note that this exclusive H₂ dependency is unlikely since the strong dependency of the CO conversion in this report and by others ⁴¹, 53,59,60,61 cannot be explained by it.



Fig. 2.28 The C₃ olefin selectivity as a function of the propene/carbon monoxide pressure ratio at 250°C (run 2)

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Since it is improbable that the temperature would depend equally on the reaction rate constants in Eq.(2.43), the olefin selectivity will change by changing the temperature, whereas the olefin/CO pressure ratio is kept constant. This means that the slope in Figure 2.28 for example will be a function of temperature. When the temperature decreases to 230°C the C₃ olefin selectivity becomes practically independent of the C₃H₆/CO pressure ratio as shown in Figure 2.30. This indicates a relatively low secondary hydrogenation rate. On the other hand, increasing the temperature to 270°C result in an increase in the slope for both C₂ and C₃, as shown in Figure 2.31. Thus, when the C₂ olefin selectivity at 230, 250 and 270°C with a PC_2H_4/PCO value of 0.02 are compared; the C₂ olefin selectivity then drops from 60% via 50% to 30%. The olefin hydrogenation rate thus strongly increases with increasing temperature.

Table 2.11

The	C2	olefin	selectivity	measured	under	various	process	conditions.
T=25	50°C	;						

CO ₂	H ₂	P	H ₂ /CO	C ₂ olefin sel.
[bar]	[par]	[Dat]	[mor/mor]	101
0.058	0.59	1.5	0.71	89
0.048	1.09	1.5	3.30	71
0.76	1.55	4.5	0.71	80
4.31	2.20	9.0	0.99	40
2.27	2.90	9.0	0.78	76
0.56	3.25	4.5	18	16

It is interesting to note that the olefin selectivity does not approach 100% at zero conversion (olefin/CO pressure ratio = 0). Hence, paraffins are not formed exclusively by secondary hydrogenation of olefins but can also be formed directly from CO and H₂. The initial olefin selectivity, $k_1/(k_1+k_2)$ in Eq.(2.43) is influenced by the

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temperature. The initial paraffin formation increases with decreasing temperature as shown for C_3 in Figure 2.32. Nevertheless, even at 200°C only 10% of the primary C_2 and C_3 hydrocarbons consist of paraffins.

Apart from the investigation of the influence of the temperature, the question whether the H_2/CO ratio affects the initial olefin selectivity has been investigated. The initial olefin selectivity did not appear to be dependent on the H_2/CO ratio over a large range of conditions, as shown in Table 2.12. This confirms the model assumptions in section 2.9.2 which involve that the olefin and paraffin production rate (r_1 and r_2 respectively) are only dependent on the H_2 pressure.



Fig. 2.29 The C_2 olefin selectivity as a function of the ethene/carbon monoxide pressure at 250°C (run 4). The reactor and hydrogen pressure is indicated in the figure

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Table 2.12

The primary C_3 olefin selectivity as function of the H_2/CO ratio.

C3 olefin selectivity			
[%]			
93			
95			
92			
92			

1) carried out in a differential fixed-bed reactor



Fig. 2.30 The olefin selectivity as a function of the olefin/carbon monoxide pressure ratio at 230°C (run 1)

A conversion decrease is usually achieved by an increase of the gas flow or a decrease of either the H_2/CO ratio or the pressure. In the next experiment, however, the conversion decrease is caused by slowing down the stirrer speed. According to the competition model this method should result in a different value of the olefin selectivity with respect to the usual methods at an equal olefin/CO pressure ratio. Obviously, the olefin selectivity increases with decreasing stirrer speed due to the conversion decrease as shown in Table 2.13. However, this increase is significantly lower than with respect to measurements which are kinetically controlled as shown in Figure 2.33. This limited increase of the olefin selectivity is caused by the higher olefin/CO concentration ratio in the liquid phase as a result of the gas-liquid mass transfer limitation.

Table 2.13

Influence of the stirrer speed on the conversion of CO and the olefin selectivity. $T=270^{\circ}C$; P= 9 bar

Experiment	Stirrer	co	Olefin s	electivity
number	speed	conversion	C2	C ₂
	[min ⁻¹]	[%]	[%]	[%]
1	1300	72	34	82
2	900	73	34	81
3	700	72	35	82
4	500	67	33	82
5	250	47	43	85
6	100	35	54	87

At a high CO conversion level the water vapour and CO_2 pressure may additionally affect the olefin selectivity. In a view of the dominating effect of the CO conversion (see Figure 2.26) the influence of H₂O and/or CO_2 on the olefin selectivity was investigated at a constant CO conversion level (H₂O and CO₂ cannot be distinguished in these experiments because H_2O is related to CO_2 , see section 2.6). The water vapour and CO_2 pressure were increased by the addition of CO_2 . The olefin



Fig. 2.31 The olefin selectivity as a function of the olefin/carbon monoxide pressure ratio at 270°C (run 1)

selectivity after addition of 0. 28 and 40% CO_2 is plotted in Figure 2.34. This figure shows that the C_2 olefin selectivity only slightly increases with increasing H_2O and CO_2 pressure (the H_2O/CO and CO_2/CO ratio is shown in Figure 2.22), but this increase of the selectivity can be solely attributed to H_2O and CO_2 because the olefin/CO pressure ratio was kept constant. This small selectivity increase implies that the influence of H_2O and CO_2 can be neglected under normal reaction conditions. Only in case of an almost complete conversion of CO the influence of H_2O and CO_2 will be significant. The latter is indeed shown by the remarkable increase of the C_2 olefin selectivity with increasing

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olefin/CO pressure ratio (and thus with increasing CO conversion), whereby the CO conversion level has passed 90% as shown in Figure 2.35!

Fig. 2.32 Effect of the temperature on the C₃ olefin selectivity (run 4)

Under these extreme circumstances the water vapour pressure will reach high values due to the high H_2/CO ratio as shown by Eq.(2.44)

$$P_{H_2O} = \frac{P_{H_2}}{P_{CO}} \cdot P_{CO_2} K_S$$
 (2.44)

When the water gas shift equilibrium is not reached the water vapour pressure will be even higher than predicted by Eq.(2.44). In this situation the competition model has to be adjusted. Since $pCO<\langle pH_2O + pCO_2 Eq.(2.42) may be written as:$

$$C_{2} \text{ olefin sel.} = A - \frac{k_{3} K_{C_{2}H_{4}}}{(k_{1}+k_{2})m_{C_{2}H_{4}}} \cdot \frac{PC_{2}H_{4}}{1 + \frac{K_{H_{2}O} PH_{2}O}{m_{H_{2}O}} + \frac{K_{CO_{2}} PCO_{2}}{m_{CO_{2}}}$$
(2.45)

The CO_2 pressure does not significantly continue to change above the CO conversion level of 90%. For this reason it is more likely that the high H₂O vapour pressure and not CO_2 prevents the adsorption of olefins on the catalyst surface. This absorption of H₂O decreases both the rate of secondary hydrogenation of olefins and the formation of hydrocarbons as demonstrated by the decrease of the activity shown in Table 2.10.



Fig. 2.33 Effect of the stirrer speed on the C_2 olefin selectivity at 270°C (run 1)

2.9.5 Conclusions

The olefin selectivity observed over potassium promoted fused iron is mainly determined by the degree of secondary hydrogenation. This secondary hydrogenation of olefins is predominantly dependent on the olefin/carbon monoxide pressure ratio indicating that olefins and carbon monoxide compete for the same sites on the catalyst surface. The partial pressure of hydrogen appears to be unimportant.

The effect of water and carbon dioxide on the olefin selectivity of this catalyst is insignificant under normal reaction conditions. Only in case of an almost complete conversion of CO the adsorption of water may become important and cause a decrease of both the olefin hydrogenation and synthesis activity of the catalyst.



Fig. 2.34 The effect of the CO_2 percentage in the gas feed on the C_2 olefin selectivity and the ethene/carbon monoxide pressure ratio (run 3)



Fig. 2.35 The effect of the exhaustion of CO on the relation between the C_2 olefin selectivity and the ethene/carbon monoxide pressure ratio at 250°C (run 2)

2.10 Isomerization

2.10.1 Introduction

In the previous section we have only considered secondary hydrogenation of olefins. Initially formed higher olefins, however, can be hydrogenated as well as isomerized. This section deals with the isomerization of higher olefins and is introduced with a brief literature review. It is widely believed that isomerization and hydrogenation proceed via a common intermediate which is the half-hydrogenated state 42,58,62. A possible reaction scheme is proposed by Schulz 42 (see Figure 2.36). In this model the intermediate is formed by the addition of a hydrogen atom to an adsorbed olefin. Addition of a second hydrogen atom leads to a paraffin. The intermediate may also loose a hydrogen atom, to be converted in an 1-alkene or a 2-alkene molecule. The isomerization and hydrogenation thus proceed on the same catalytic sites 62.



Fig. 2.36 Double bond shift and secondary hydrogenation of olefins according to Schulz 42

On iron Fischer-Tropsch catalysts the formation of 2-alkenes from 1-alkenes is attributed to the presence of SiO_2 , Al_2O_3 or other acid oxides 59,63,64. According to Egiebor and Cooper ⁶⁴ the olefin isomerization increases with an increase of the silica content whereas the total olefin selectivity remained constant. Alkali addition which reduces the acidity of the catalyst, depresses both isomerization and hydrogenation, the latter to a higher degree 59.

Regarding the kinetics the literature is not consistent. Cerveny 62 and Bond 58 report that the slow step in isomerization is the formation of the half-hydrogenated state. However, according to Südheimer 60 the isomerization is independent of the H₂ pressure.

2.10.2 Competition model for both hydrogenation and isomerization

A summary of secondary reactions is presented in Figure 2.37. A value for the H_2 order of the isomerization reaction with respect to hydrogen is omitted as neither the literature data nor our data is conclusive.



Fig. 2.37 Simplified model for the secondary olefin hydrogenation, double bond shift, and the primary formation of alkanes, 1-alkenes and 2-alkenes

Based on the reactions given in Figure 2.37 we can form mass balances for 1-alkenes, 2-alkenes and alkanes:

$$\begin{split} &F_{out}C_{1-alkene,G} = (k_1C_{H_2,L} - k_4C_{H_2,L}{}^x\theta_{1-alkene} - k_3C_{H_2,L}\theta_{1-alkene})v_L \eqref{eq:constraint} (2.46) \\ &F_{out}C_{2-alkene,G} = (k_6C_{H_2,L} + k_4C_{H_2,L}{}^x\theta_{1-alkene} - k_5C_{H_2,L}\theta_{2-alkene})v_L \eqref{eq:constraint} (2.47) \\ &F_{out}C_{alkane,G} = (k_2C_{H_2,L} + k_3C_{H_2,L}\theta_{1-alkene} + k_5C_{H_2,L}\theta_{2-alkene})v_L \eqref{eq:constraint} (2.48) \\ &If the conversion of CO is not too high it can assumed that the occupation of sites by alkenes is dependent on the alkene/CO concentration ratio. The olefin selectivity follows from the sum of Eqs. (2.46) and (2.47) divided by the sum of Eqs. (2.46), (2.47) and (2.48); \end{split}$$

olefin sel. =
$$\frac{k_1+k_6}{k_1+k_2+k_6} - \frac{k_3 C_{1-alkene,L}}{(k_1+k_2+k_6)C_{CO,L}} - \frac{k_5 C_{2-alkene,L}}{(k_1+k_2+k_6)C_{CO,L}}$$
 (2.49)
With $C_{i,L} = \frac{C_{i,G}}{m_i} = \frac{P_i}{RTm_i}$

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Eq.(2.49) can be written as follows:

olefin sel. =
$$\frac{k_1+k_6}{k_1+k_2+k_6} - \frac{k_3 \text{ Pl-alkene mCO}}{(k_1+k_2+k_6)\text{PCO ml-alkene}} - \frac{k_5 \text{ Pl-alkene mCO}}{(k_1+k_2+k_6)\text{PCO ml-alkene}}$$
 (2.50)

If it is assumed that the hydrogenation rates and solubilities are equal for 1-alkenes and 2-alkenes Eq.(2.50) becomes:

olefin sel. =
$$\frac{k_1+k_6}{k_1+k_2+k_6} - \frac{k_3 \text{ mCO Palkenes}}{(k_1+k_2+k_6)\text{malkenes PCO}}$$
(2.51)

With Palkenes = P1-alkene + P2-alkene. If the isomerization rate r_4 and the formation rate of 2-alkenes out of synthesis gas, r_6 , is low with respect to the formation of 1-alkenes, r_1 , the 1-alkene pressure will be much higher than that of 2-alkenes provided the hydrogenation of 1-alkenes is not more rapid than that of 2-alkenes ($r_3 \leq r_5$). When these conditions are satisfied Eq.(2.51) can simplified into:

olefin sel. =
$$\frac{k_1 + k_6}{k_1 + k_2 + k_6} - \frac{k_3 \text{ mCO Pl-alkene}}{(k_1 + k_2 + k_6) \text{ ml-alkene PCO}}$$
 (2.52)

Eq.(2.50) can be also simplified to Eq.(2.52) when the hydrogenation rate of 2-alkenes is much lower than that one of 1-alkenes. Bond ⁵⁸ has reported that the 1-butene/2-butene reactivity ratio is about 4. Cerveny and Ruzicka ⁶² have found that the relative adsorption coefficients of 1-hexene, cis-2-hexene, and trans-2-hexene on platinum catalysts strongly decrease namely: 1.00, 0.15, 0.06 which probably explains the preferential hydrogenation of 1-hexene. Therefore, it is likely that $k_3>>k_5$ by which the olefin selectivity is only dependent on the 1-alkene/CO pressure ratio.

It is obvious that the fraction of 1-alkene with respect to all hydrocarbons of one carbon number depends of the degree of isomerization:

$$\frac{P_{1-alkene}}{P_{1-alkene}+P_{2-alkene}+P_{alkane}} = \frac{k_1}{k_1+k_2+k_6} - \frac{m_{CO}}{m_{1-alkene} (k_1+k_2+k_6)} \cdot (k_3 + \frac{k_4 P_{H_2}^{x-1}}{(m_{H_2}RT)^{x-1}}) \cdot \frac{P_{1-alkene}}{P_{CO}}$$
(2.53)

At a constant H_2 pressure it follows from Eq.(2.53) that the fraction 1-alkene is also only dependent on the 1-alkene/CO pressure ratio. This equation clearly shows that an increasing 1-alkene pressure by increasing the conversion of CO results in a lower 1-alkene fraction. The olefin selectivity decreases naturally with increasing conversion of CO as follows from Eq.(2.52). Finally, from Eq.(2.54) it can be seen that the fraction 2-alkenes increases with increasing $P_{1-alkene}/P_{CO}$ ratio only in case the isomerization is fast with respect to the hydrogenation of 2-alkenes:

$$\frac{P_{2-alkene}}{P_{1-alkene+P_{2}-alkene+P_{alkane}}} = \frac{k_{6}}{k_{1}+k_{2}+k_{6}} + \frac{k_{4} P_{H_{2}}x^{-1} m_{CO} P_{1-alkene}}{(m_{H_{2}}R_{T})x^{-1} m_{1-alkene} P_{CO}}$$
$$- \frac{k_{5} m_{CO} P_{2-alkene}}{(k_{1}+k_{2}+k_{6})m_{2-alkene} P_{CO}}$$
(2.54)

2.10.3. Experimental

All experiments were carried out in the well-mixed stirred autoclave. The reaction conditions were equal to those reported in section 2.8.2.

2.10.4. Results and discussion

The fractions of C₄ hydrocarbons are plotted as function of the 1-butene/CO pressure ratio in Figure 2.38. The 1-C₄H₈ fraction clearly decreases with increasing 1-C₄H₈/CO pressure ratio, in agreement with Eq.(2.52). This decline of the 1-C₄H₈ fraction is caused by both hydrogenation and isomerization. The isomerization rate appears to be higher than the hydrogenation rate as shown by a more pronounced decline of the 1-butene fraction. The latter is more pronounced than that of the total olefin fraction (see Figure 2.38). Conclusions cannot be drawn with regard to the order in hydrogen of the isomerization reaction, x, since the variation of the hydrogen pressure was too small.



Fig. 2.38 Selectivity of various C_4 fractions as a function of the I-butene/carbon monoxide pressure ratio at 270°C (run 1)

The gradual decline of the C₄ olefin selectivity as function of CO conversion (a higher CO conversion also means a higher 1-C₄H8/CO pressure ratio) is comparable with the decrease of both C₃ and C₅ olefin selectivity up to a CO conversion level of 87%, as shown in Table 2.14. The C₃ olefin selectivity is lower than that of C₄ and C₅ only if CO is almost depleted ($X_{CO} = 94$ %). This indicates that the hydrogenation rate of 2-alkenes is lower than that of 1-alkenes and of minor importance for the case of this catalyst. The low C₂ olefin selectivity in comparison with other hydrocarbons shows the high hydrogenation rate of ethene, which is also higher than the isomerization rate of 1-butene and 1-pentene, as shown in Table 2.14.

xco	P	ole	olefin selectivity			1-C4H8	1-C5H10
		C ₂	C3	C4	C5	C_4 , tot	C ₅ , tot
[%]	[bar]	[%]	[%]	[%]	[%]	[%]	[%]
13.2	1.5	89.0	92.7	92.0	89.6	84.7	77.7
36.8	4.5	79.9	90.3	89.3	87.2	79.8	69.8
78.1	9.0	39.9	84.6	83.9	83.5	64.8	60.8
86.5	9.0	28.8	79.4	81.9	79.1	56.6	54.7
94.5	3.0	21.0	64.3	75.8	71.1	31.4	31.5

Table 2.14

Influence of the CO conversion on the C_2-C_5 olefin selectivity, the 1-butene and 1-pentene fraction of C_4 and C_5 hydrocarbons, respectively. $T=250^{\circ}C$, $(H_2/CO)_{in} = 0.67-3.0$

In accordance with the data concerning ethane and propane (see section 2.9.4) n-butane is also a primary product. The initial fraction $k_2/(k_1+k_2+k_6)$ is approximately 9% at 270°C. It is interesting to note that 2-butene also appears to be a primary product. The initial fraction is approximately 10%.

The influence of the temperature on the isomerization and hydrogenation of 1-butene is shown in Table 2.15. Both the rate of isomerization and hydrogenation of butene increase with increasing temperature at approximately equal $p_{1-C_{d}H_{g}}/p_{CO}$ ratio.

2.10.5 Conclusions

The hydrogenation and isomerization of higher olefins depends on the 1-olefin/carbon monoxide pressure ratio indicating competition between 1-olefins and CO for vacant sites on the catalyst surface.

The isomerization rate is more rapid than the hydrogenation rate of 1-olefins and 2-olefins over this potassium promoted iron catalyst. The hydrogenation of 2-olefins is probably of little importance for the case of this catalyst.

Table 2.15

Influence of the temperature on the 1-butene and 2-butene fraction at a constant conversion of CO and approximately equal $p_{1-butene}/p_{CO}$ ratio. P=9 bar, $(H_2/CO)_{in} = 0.67$

Т	x _{CO}	1-C4H8	2-C4H8	P1-C4H8	
		C_4 ,tot	C ₄ ,tot	PCO	
[°C]	[%]	[%]	[%]	[-]	
				•	
230	76.9	74.6	10.2	0.019	
250	74.0	68.6	13.8	0.020	
270	77.0	61.4	17.6	0.025	

2.11 Olefin selectivity as a function of carbon number

The aim of this section is to give a theoretical explanation for the dependency of the olefin selectivity on the chain length. The olefin selectivity of the C_3 fraction is often higher than the olefin selectivity of other fractions. Frequently the olefin selectivity drops gradually for higher hydrocarbons, see for example the review of Schulz ⁴².

The decrease of the olefin selectivity as a function of carbon number is sometimes attributed to the longer residence time for heavier products in the reactor due to the increasing solubility 65,66 . Therefore, higher molucular weight products should have a greater probability of undergoing secondary reactions than lighter products. When the residence time,

$$\tau = \frac{p_n V_L / m_n}{r_n V_L}$$
(2.55)

and the production rate of C_n , $r_n V_L$, for steady-state conditions is

$$r_n V_L = P_n F_{out}/RT$$
(2.56)

the residence time can be simply written as

$$\tau = V_L/(m_i F_{out})$$
(2.57)

Although, is is obvious from Eq.(2.57) that the residence time increases as a function of carbon number due to the decreasing solubility coefficient m_i , the residence time is not a suitable parameter to describe the effect of chain length on the olefin selectivity. As discussed in section 2.10 the olefin selectivity can be described as:

$$C_n$$
 olefin selectivity = A - B' $\frac{P1-alkene}{PCO}$. $\frac{mCO}{m1-alkene}$ (2.58)

If it is assumed that A and B' are proper constants, and not a function of the chain length n, then it is obvious that the effect of the chain length on the olefin selectivity stems from the influence of the carbon number on the solubility coefficient and the partial pressure. The partial pressure, p_n , can be described as a function of the carbon number with the Schulz-Flory distribution:

$$\ln(p_n) = n \ln(\alpha) + \ln((1-\alpha)/\alpha) + \ln(p_{HC})$$
(2.59)

The logarithm of the solubility coefficient of hydrocarbons in paraffin oil and squalane is also a linear function of the carbon number:

$$\ln(\mathfrak{m}_n) = an + b \tag{2.60}$$

Substraction of Eq.(2.60) from (2.59) results in

$$\ln(p_n/m_n) = (\ln(\alpha) - a) n + \ln(p_{HC}) + \ln((1-\alpha)/\alpha) - b$$
 (2.61)

Thus, the concentration of heavier hydrocarbons, p_n/m_n , will increase with n when the value of ln α is larger than a. The value of α is calculated for paraffin oil and squalane. Figure 2.39 shows that the value of a is -0.49 for paraffin oil. The value of a for squalane is calculated by means of data from Donohue et al. ⁶⁷ and Chappelow and Prausnitz ⁶⁸. The authors last mentioned report Henry coefficients (H_{1,2}) only for C₁-C₄ hydrocarbons up to temperatures of 475 K. Therefore, the Henry coefficient of C₂ and C₄ are extrapolated to 523 K, as shown in Fig. 2.40. The solubility coefficient, m, can be calculated from the Henry coefficient H_{1,2} according to

$$m = \frac{(H_{1,2} - 1)}{RT} MW_{squalane} \rho_{squalane}$$
(2.62)

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The value of a, calculated from these data by measuring the slope in a plot of the logarithm of the solubility coefficient as a function of the carbon number turns out to be -0.52 at 250°C for squalane as the liquid phase. This value of a is very close to the value of a in paraffin oil, which means that the increase of the solubility of hydrocarbons as a function of the carbon number is similar in squalane and paraffin oil.



Fig. 2.39 The solubility coefficient of hydrocarbons as a function of the carbon number in paraffin oil for 250°C based on data of De Priester ⁷⁹



Fig. 2.40 The Henry coefficient of C_2 and C_4 in squalane as a function of the temperature based on data of Donohue 67 and Chappelow 68 . The data points for 532 and 543 K are extrapolated

Using the value of a for squalane, the concentration of larger hydrocarbons, p_n/m_n , will increase if the value of α is higher than 0.61. The effect of the value of α on the decline of the olefin selectivity as a function of the carbon number according to Eq.(2.58) and Eq.(2.61) is shown in Fig. 2.41. This figure clearly demonstrates that the decrease of the olefin selectivity with increasing carbon number is more pronounced when the value of α is high. Note, that it is assumed in this figure that <u>1</u>. only the value of α varies, <u>2</u>. the rates of secondary reactions are not affected by the chain length and <u>3</u>. mass transfer limitations do not play a role. Although the assumptions 2 and 3 may be incorrect, the increasing concentration of hydrocarbons with increasing chain length is probably the most important factor in determining the olefin selectivity of heavier hydrocarbons, provided that the value of α is larger than 0.61, which is usually the case for typical Fischer-Tropsch catalysts.

The values of α for potassium promoted iron catalysts vary from 0.6 for C₁-C₈ hydrocarbons to 0.9 for C₁₀⁺ hydrocarbons. (see Table 2.3). This means that for this type of catalysts the ratio p_n/m_n increases as a function of the carbon number. Consequently, it is likely that in consequence of this the olefin selectivity for this type of catalysts will decrease with increasing chain length.



Fig. 2.41 The effect of α on the olefin selectivity calculated with help of Eq.(2.58) and (2.61). The values of A and B are derived from Figure 2.28 where A and B represent the initial fraction of olefins at each carbon number and the rate of secondary hydrogenation of olefins respectively (see section 2.9.2). Data used:

$$A = 90 \%$$
 $m_{CO} = 5.29 \ m^3 L/m^3 G$
 $B = 100 \%$
 $m_{C_3} = 0.77 \ m^3 L/m^3 G$
 $T = 250 \ ^{\circ}C$
 $p_{HC} = 1.0 \ bar$
 $p_{CO} = 3.4 \ bar$
 $(X_{CO} = 80 \%; (H_2/CO)_{feed} = 0.6;$

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2.12 The effect of co-feeding of ethene on the activity and selectivity under various reaction conditions.

2.12.1 Introduction

Alkene addition to the synthesis feed gas has been the subject of many studies concerned with the determination of reaction intermediates, the role of secondary reactions, and the possibility of altering the molecular weight distribution in the Fischer-Tropsch synthesis.

Hall et al. ⁶⁹ investigated the incorporation of radioactive ethene, propanal and propanol in a mechanistic study of the Fischer-Tropsch synthesis. They passed synthesis gas $(H_2/CO = 1)$ containing 1 to 1.25 mole% radioactive ethene over either of two reduced fused iron catalysts in a fixed bed reactor. With an iron catalyst promoted with 0.6% SiO₂, 0.6% Cr₂O₃, 4.6% MgO, and 0.6% K₂O, about 6 mole% of the hydrocarbons formed at 7.5 atm and 249°C stem from the ethene. With an iron catalyst promoted with 0.64% Al₂O₃, and 2.00% ZrO₂, about 12% of the ethene was incorporated into higher hydrocarbons at 1 atm and 224°C. In both experiments the principal reaction of the labeled ethene was hydrogenation to ethane. Only a negligible amount of the labeled ethene was cracked into methane.

Pichler et al. ³⁹ studied the reaction mechanism of Fischer-Tropsch synthesis by adding ¹⁴C labeled ethene to synthesis gas ($H_2/CO = 2$) in a fixed-bed reactor. With an alkalised precipitated iron catalyst they added 0.21 mole% ethene and 0.3 mole% propene to the synthesis gas at 20 atm and 220°C. About 9% of the ethene but only 1% of the propene were converted to higher hydrocarbons. With a fused iron catalyst 0.34 mole% ethene was added to the synthesis gas at 20 atm and 320°C. 11.5% of the ethene was converted to higher hydrocarbons. For both catalysts the major portion of the tagged olefins was hydrogenated to saturated paraffins. Hydrocracking played a negligible role on these catalysts.

Dwyer and Somorjai ⁷⁰ demonstrated that 1-alkene, produced as an initial product, can undergo readsorption in competition with CO and hydrogen, and that such alkene then contributes significantly to the synthesis of high molecular weight hydrocarbons. Under their conditions

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of 6 atm pressure and 573 K, an Fe(111)single-crystal catalyst predominantly produced methane (CO conversion less than 1%). Addition of 0.04 to 2.7 mol% ethene or propene to synthesis gas with an H_2/CO molar ratio of 3 noticeably shifted the selectivity to heavier products. In a representative experiment, after 90 min of reaction, most of the ethene (75.6 mol%) was hydrogenated to ethane; yet 8.2 mol% of the ethene (initial concentration 2.7 mol%) was converted to higher hydrocarbons. Increasing the mole% concentration of ethene caused the amount of higher molecular weight hydrocarbons to increase further while the methanation rate remained practically unchanged. The product distribution became very similar to that obtained over an industrial iron catalyst operated under similar conditions but at substantially higher conversions. This led to the suggestion that the readsorption and incorporation of initially produced alkenes contributed significantly to the synthesis of higher molecular weight hydrocarbons.

Barrault et al. 71 investigated the hydrogenation of carbon monoxide to light olefins on an iron/alumina catalyst. Experiments with ethene (7 mole%) added to synthesis gas ($H_2/CO = 1.5$) at 15 bar and 743 K showed that the olefin significantly enhanced both the formation of C_3-C_4 hydrocarbons and methane, and the hydrogenation to ethane. Barrault and coworkers suggested that chain growth occurred by a carbene olefin mechanism. The only work in the liquid phase was done by Satterfield et al. ²⁹. They studied the addition of ethene and 1-butene in the Fischer-Tropsch synthesis on an iron catalyst. With a reduced fused magnetite catalyst containing 2.0-3.0% Al₂O₃, 0.5-0.8% K₂O, 0.7-1.2% CaO and $\lt 0.4\%$ SiO₂, they added 1.5 mole% C₂H₄ to the synthesis gas (H₂/CO = 1.2) at 248°C (CO conversion more than 90%). At 14.8 bar pressure 32% of the added ethene was hydrogenated to ethane, at 7.9 bar pressure this was 20%. Less than 10% of the added amount of ethene seemed to disappear apart from conversion to ethane. A noticeable effect of ethene addition on the olefin/paraffin ratio or the production of higher hydrocarbons was not observed. Satterfield and coworkers concluded that addition of olefin to the reactant stream is not a viable method of altering the molecular weight distribution over an iron catalyst.

Chang J. Kim ⁷² claimed in US Patent no. 4,547,525 that the methane production in the catalytic Fischer-Tropsch hydrocarbon synthesis reactions is reduced by adding olefins to the H_2 and CO feed mixture. Alpha olefins of ten carbon atoms or less are particularly preferred. For example: with a precipitated iron catalyst containing copper, potassium and silicon, 9.6 mol% ethene was added to the synthesis gas. The CO conversion remained unchanged while the CH_4 selectivity was reduced with 30%.

In a more recent study Snel and Espinoza ⁷³ described the influence of co-feeding small alkenes on the catalytic behaviour of an iron catalyst in the Fischer-Tropsch synthesis. The catalyst used was carbon containing iron calcium oxide prepared via a modified amorphous citrate method.

The oxidic catalyst precursor contained ca. 3 (atomic) % carbon and equiatomic amounts of iron and calcium. Hydrocarbon synthesis was carried out at 2.0 MPa and 543 K with hydrogen-poor synthesis gas $(H_2/CO = 0.5)$ at a volume hourly space velocity of 1000 in a fixed-bed reactor. Alkenes were added to the synthesis gas stream at levels of either 5 or 10 mol%. Co-feeding 10 mole% ethene resulted in a considerable increase in both the olefin selectivity and the activity (increase: 67%). The methane selectivity decreased significantly (decrease: 71%). Sixty percent of the ethene added was hydrogenated. Schulz-Flory statistics were maintained throughout. All changes in catalytic behaviour were reversible. The increasing activity was caused by the rapid incorporation of ethene into the growing chains. The idea is that active, adsorbed ethene scavenges C1* and H* surface species for incorporation and hydrogenation respectively. The resulting decrease in concentration of C1* and H* surface species explains both the drop in methane concentration and the increasing olefin selectivity.

The studies referred to resulted in a better understanding of the Fischer-Tropsch mechanism and the role of secondary reactions of olefins. The relative intensities of the effects of co-feeding ethene (e.g. the percentage of ethene added converted to higher hydrocarbons) described in these studies, differ widely and they probably are strongly dependent on the reaction conditions. This dependence is described and explained in this section.

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2.12.2 Experimental

All experiments were carried out in the well-mixed stirred autoclave. The reaction conditions were equal to those reported in section 2.8.2.

2.12.3 Results

Four series of experiments were carried out to investigate the effect of co-feeding ethene to synthesis gas. A series consists of three experiments: the state before, during and after the addition of ethene. The reaction conditions applied are listed in Table 2.16. Material balances on the C_2 fraction, made by comparing matched experiments with and without added ethene, are listed in Table 2.17.



Fig. 2.42 Effect of the co-feeding of ethene on the olefin selectivity at 250°C (series A)

Series A

The results of this series of experiments are shown in Figure 2.42 to 2.44. Ethene addition causes an increased olefin selectivity, an increased production of C_2^+ hydrocarbons, and a decreased methane selectivity. All these changes in catalytic behaviour are reversible and are presented in Table 2.18. Table 2.17 illustrates that the major part of the ethene converted is hydrogenated to ethane. The competitive adsorption of ethene reduces the availability of CO surface intermediates. This is demonstrated by a drop of the ethanol production, which is too large to be attributed to the reduction of C_1 surface intermediates. Remarkably, the CO conversion itself is not affected by the addition of ethene although the availability of CO surface intermediates decreases. Essentially it means that there is competition between the adsorption of ethene and a particular form of adsorbed CO, which is involved in alcohol formation. It should be noted finally, that there was no change in the chain growth probability.



Fig, 2.43 Effect of the co-feeding of ethene on the production rate of hydrocarbons at 250°C (series A)

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Series B,C,D

The results of these series are qualitatively equal to those of series A, only the magnitude of the resulting effects is different. The results are presented in Table 2.17 and 2.18. The increase of the C_2^+ activity is caused by the incorporation of ethene. This reaction consumes a lot of C_1 surface intermediates and therefore retards the methanation rate. The hydrogenation of ethene consumes hydrogen surface intermediates which may have an inhibiting effect on both the methanation reaction and the hydrogenation of C_2^+ olefins.



Fig. 2.44 Effect of the co-feeding of ethene on the methane selectivity at 250°C (series A)

In summary:

- * The increase of the C_2^+ activity is caused by the incorporation of ethene.
- * The decrease of the methane selectivity is caused mainly by a lower availability of C_1 surface intermediates and a higher concentration of C_2^+ hydrocarbons. The probably lower availability of surface hydrogen may play a minor role.
- The increase of the C₂⁺ olefin selectivity is mainly caused by an enhanced adsorption of very reactive ethene species. Also in this case, the probably lower availability of hydrogen may play a minor role.

Table 2.16.

Summary of the reaction conditions applied during the addition experiments.

Series	Exp.	P	T	F _{H2} 1)	F _{CO} ¹⁾	$F_{C_2H_4}^{(1)}$	CO conv.
	no.	[bar]	[°C]	[ml/min]	[ml/min]	[ml/min]	[%]
Α	1	9.0	250	40	61	0	70
A	2	9.0	250	40	61	6.5	70
A	3	9.0	250	40	61	0	70
в	4	1.5	250	40	61	0	15
в	5	1.5	250	40	61	6.5	15
В	6	1.5	250	40	61	0	15
с	7	1.5	250	73	25	0	25
с	8	1.5	250	74	24	6.5	25
С	9	1.5	250	73	23	0	25
D	10	9.0	250	104	150	0	55
D	11	9.0	250	101	147	6.1	55
D	12	9.0	250	101	145	0	55

1) measured at 20°C and 1 bar

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Table 2.17

Material balances of ethene added.

	Series a	<u>A</u>	Series B		
	[µmol C/s]	[mol%]	[µmol C/s]	[mo1%]	
Ethene added	9.04	100.0	9.04	100.0	
Unconverted	3.41	37.7	8.77	97.0	
Hydrogenated	4.05	44.8	0.21	2.4	
Incorporated	1.58	17.5	0.05	0.6	

	Series C		Series D)
	[µmol C/s]	[mol%]	[µmol C/s]	[mo1%]
Ethene added	9.04	100.0	8.49	100.0
Unconverted	7.07	78.2	7.20	85.6
Hydrogenated	1.56	17.3	1.19	14.0
Incorporated	0.41	4.5	0.03	0.4

Table 2.18

Changes in catalytic behaviour by "co-feeding" of ethene.

Series	Exp. C ₃ no.	olefin s. ³⁾ [%]	^r C ₃ -C ₅ [µg/s]	C1/C3	x _{CO} 4) [%]	PC2H4/PCO [-]
			·····			124
A	1	85	47	1.7	74	0.024
A	2	87	54	1.4	73	0.190
Α	3	86	47	1.8	72	0.021
в	4	93	5	3	15	0.002
в	5	94	7, 4.5 1)	2.5, 3 ²⁾	15	0.118
в	6	93	4.5	3.5	15	0.002
с	7	90	8.5	5.2	25	0.008
С	8	90.5	12	3	25	0.293
С	9	90	8	5.2	25	0.010
n	10	99 E	60	1 5	66	0 012
ט ה	10	00.5	60	1.3	55	0.012
D	11	88.7	60	1.4	55	0.080
D	13	88.5	60	1.3	55	0.012

1) During experiment 5 the production of C_3-C_5 hydrocarbons decreased from 7 to 4.5 μ g/s (deactivation)

2) During experiment 5 the ratio $C_{\rm 1}/C_{\rm 3}$ increased from 2.5 to 3.

- 3) C_3 olefin s. = $PC_3H_6/(PC_3H_6 + PC_3H_8)*100\%$.
- 4) $x_{CO} = (CO_{in} CO_{out})/CO_{in} * 100\%$

Table 2.16, 2.17 and 2.18, illustrate the strong dependence of the reaction conditions applied on the effects of co-feeding ethene. The effects are dependent on:

- * The amount of ethene capable of reaching the catalyst surface. The ratio $PC_{2}H_{4}/P_{CO}$ is the essential parameter to describe this adsorption competition.
- * The amount of ethene converted. This amount depends on the "reactivity" at the reaction conditions applied and can be expressed by the CO conversion rate (µmol CO/s).

This means that the relative magnitude of the effects (e.g. the decrease of methane selectivity (%)) is dependent on the $P_{C_2H_4}/P_{CO}$ ratio, while the absolute magnitude of the effects (e.g. decrease of methanation rate (µg/s) or the increase of the C_3^+ production rate (µg/s)) is dependent on the conversion level. Table 2.18 illustrates the correctness of this statement. It can be seen that the largest decrease of the methane fraction, expressed by the C_1/C_3 ratio, is attained for the series with the highest $P_{C_2H_4}/P_{CO}$ ratio (series C) while the largest increase of the C_3-C_5 production rate is attained in series A of which the CO conversion rate is much higher than that of series C.

Thus, finally, the amount of ethene added to synthesis gas which is hydrogenated and incorporated over a fused iron catalyst can be correlated by the $p_{C_2H_4}/p_{CO}$ ratio in the reactor when the ethene reacted is corrected by the CO conversion rate as shown in Figure 2.45.

2.12.4 Conclusions

The principle conclusion of this study is that the relative magnitude of the effects caused by adding ethene to the reactant stream, is determined by the value of the parameter $p_{C_2H_4}/p_{CO}$ alone. This parameter is related to the CO conversion and represents the reaction conditions applied (pressure, temperature, mole% ethene added, etc.). The effects caused by co-feeding ethene agree completely with the effects of secondary reactions of ethene under normal Fischer-Tropsch conditions.

Although there is more or less complete consensus about the qualitative effects of adding ethene, our study explains why some investigators reported smaller effects than others (or even none). Incorporation of ethene has been

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reported by Hall et al. 69, Pichler et al. 39, Dwyer et al. 70, Barrault et al. 71, and Snel and Espinoza 73. They also showed that the principal reaction of the added ethene was hydrogenation to ethane. Satterfield et al. 29, however, did not find any significant incorporation of ethene added or other effects. This conclusion is based on addition experiments of ethene at too high a degree of conversion of CO (> 90%), causing the reduction of all rates of reactions, including consecutive reactions. Moreover, at these conditions it is very difficult to distinguish the reactions of a very small amount of ethene added.

A decrease in methane selectivity has been reported by Dwyer et al. ⁷⁰, Kim ⁷² and Snel and Espinoza ⁷³. Barrault et al. ⁷¹ however, found an enchanced methanation rate. This is completely due to cracking of ethene on the iron alumina catalyst at the extreme temperature of 745 K. As shown by all the other investigators, hydrocracking plays a negligible role on iron catalysts under normal Fischer-Tropsch conditions.



Fig. 2.45 Hydrogenation and insertion rate with respect to the CO conversion rate as a function of the ethene/carbon monoxide pressure ratio during the co-feeding of ethene at 250°C
An increase in olefin selectivity has only been reported by Snel and Espinoza ⁷³. It is important to notice that their effects reported of co-feeding ethene exceed all the former effects reported. This is due to their very high $p_{C_2H_4}/p_{CO}$ ratio, caused by adding a large amount of ethene under special conditions.

From a commercial point of view, the addition of olefins in Fischer-Tropsch synthesis is only of interest to suppress the methane production. One should realize that adding olefins strongly decreases the olefin production rate.

2.13 Long-term performance of fused iron with 0.55 H_2/CO feed ratio

2.13.1 Introduction

Synthesis gas obtained from advanced coal gasification systems contains a high concentration of CO. This means that synthesis gas with H_2/CO feed ratios as low as 0.5 to 1.0 has to be converted. Due to the unique features of a slurry Fischer-Tropsch reactor, synthesis gas with H_2/CO molar ratios as low as 0.6 to 0.7 can be used directly, provided the Fischer-Tropsch catalyst has a high water-gas shift activity ⁷⁴.

The water-gas shift activity, but also the lifetime of the catalyst is important. In industrial use it is important that the slurry Fischer-Tropsch operation remains stable for prolonged periods. Therefore, in this section, the performance of a fused iron catalyst was investigated in a stirred slurry reactor using a very low H_2/CO feed ratio (0.55) over a period of more than 300 hours on stream. The operating conditions were not changed after the start-up; the performance of the catalyst could thus be examined closely.

2.13.2 Experimental

About 30 g of crushed (45-90 μ m) fused iron (C73, Sud-Chemie) was reduced in a separate fixed-bed reactor with 0.9 l H₂ (20°C, 1 bar) per minute at 450°C, and atmospheric pressure, for 70 hrs. It was added into the stirred autoclave without exposure to air and then slurried with 200 g squalane. The contents were well mixed so the reactor behaved as a continuous stirred tank reactor as far as to the gas phase was concerned. The stirrer speed was high enough to avoid mass transfer limitations. The H_2/CO molar ratio in the synthesis gas was 0.55. The initial temperature was 230°C which was raised once to 250°C after 12 hours on stream. The pressure and feed gas flow were 9 bar and 200 ml (20°C, 1 bar) /min respectively throughout the run.

2.13.3 Results and discussion

Over a period of 300 hours on stream, activity, product selectivity and olefin selectivity data was obtained.

Activity

The activity of the catalyst follows from the pattern of the partial pressures of CO and CO_2 (Fig. 2.46). The small decline of the partial pressure of CO demonstrates that the fused iron catalyst is stable over



Fig. 2.46 The course of the CO and CO_2 pressure versus time on stream. Reaction conditions are reported in section 2.13.2

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the entire run with even a small increase in activity. Due to the high water-gas shift activity almost all product water is converted to CO_2 . This means that the increased conversion of CO (lower p_{CO}) results in a higher production of CO_2 which is demonstrated by the increasing pressure of CO_2 with time in Figure 2.46.

Product selectivity

The increasing conversion of CO results of course in an increasing production of hydrocarbons as shown in Figure 2.47. This figure demonstrates that the pressure of all C_1 - C_5 hydrocarbons increases with time. However, this increase is not the same for each chain length. Figure 2.48 shows the remarkable increase of the C_1 fraction (methane) with respect to the C_3 fraction. Note that the initial value of the C_1/C_3



Fig. 2.47 The course of the pressure of various hydrocarbons versus time on stream. Reaction conditions are reported in section 2.13.2

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ratio, 1.9 , is very low which results in a small deviation of the C₁ point from the Schulz-Flory line. This initial low C₁/C₃ ratio corresponds with a lower value of the chain growth probability ($\alpha = 0.73$) than the value of α measured (0.62). However, the C₁/C₃ ratio increases in time, while the chain growth probability, α , is practically constant (see Table 2.19), by which the C₁ fraction obeys the Schulz-Flory distribution after 205 hours on stream. After this period of time the C₁/C₃ ratio attains a steady-state value which agrees with an α -value of 0.62.

Table 2.19

Values of the chain growth probability, α , at various hours on stream (H.O.S.). T= 250°C; p = 9 bar; (H₂/CO) feed = 0.55; X_{CO}= 51-67%

H.O.S.	12	60	134	205	250	301	
α	0.62	0.62	0.64	0.62	0.62	0.61	

Olefin selectivity

The olefin selectivity of the C₄ fraction is constant over the entire run which is shown in Table 2.20. Also the C₃ olefin selectivity does not significantly vary during the run. However, the C₂ olefin selectivity decreases continuously as a function of time as shown in Fig. 2.49. A small decrease of the C₂ olefin selectivity is conceivable because the $P_{C_2H_4}/P_{CO}$ ratio increases with time due to the increasing conversion of C0. However, the decrease of the C₂ olefin selectivity is larger than expected. Fig. 2.50 shows that the C₂ olefin selectivity/ $(P_{C_2H_4}/P_{CO})$ ratio increases continuously, indicating that the hydrogenation activity increases during the entire run.

Another explanation for the decrease of the olefin selectivity may be an increased incorporation of ethene. In that case, however, the C_2/C_3 ratio should have fallen considerably, but this was not the case (see Figure 2.47).

It is known that ethene is the most reactive olefin and therefore, the C_2 olefin selectivity can be used as parameter for the reactivity of the catalyst for secondary hydrogenation. Thus, the decrease of the C_2 olefin selectivity means that the hydrogenation activity of iron increases over the entire run. The hydrogenation activity correlates with the methane selectivity (C_1/C_3 ratio) for up to 200 hours on stream. After that point of time the C_1/C_3 ratio does not vary anymore. This is in contrast with the hydrogenation activity which then starts to increase again as shown in Figure 2.50.

The increase of the hydrogenation activity and the initial increase of the methane selectivity may be caused by a decrease of the potassium content of the catalyst. The opposite phenomenon has been reported by Kuo 73 : addition of an amount of potassium salt to a slurry reactor with a suspended iron catalyst resulted in a drop of the methane selectivity. This indicates that iron is enable to take up potassium from the liquid phase. Therefore it is probable that the potassium percentage of this iron catalyst decreases during the run. This results in a continious change of the catalyst and its performance.



Fig. 2.48 The course of the C_1/C_3 pressure ratio versus time on stream. Reaction conditions are reported in section 2.13.2

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2.13.4 Conclusions

The activity of fused iron increases slowly over a period of many hours on stream. The activity increase involves an increase of the hydrogenation activity and a preferential increase of the methane production rate. The activity and product selectivity are constant after 200 hours on stream. Only, the olefin hydrogenation activity continues to rise over the entire run.

The behaviour of fused iron as a function of time indicates that a real steady state with respect to all properties of the catalyst may never be attained. This means that experiments with iron catalysts in which process parameters are varied have to be carried out with great care. Therefore, in this study, the behaviour of the catalyst was checked by means of a reference point. The experiments taken in between measuring the reference were considered as reliable only if it was proved that the properties were not significantly changed.



Fig. 2.49 The course of the olefin selectivity of C_2 and C_3 versus time on stream. Reaction conditions are reported in section 2.13.2

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Table 2.20

 C_4 fractions as a function of hours on stream. T= 250°C; p = 9 bar; (H_2/CO)_{feed} = 0.55; X_{CO} = 51-67%

		Hou	cs on s	stream						
		39	86	115 1	61 21	.8 23	3 279	9 303	33	0
$i-C_4H_{10}$	[%]	0.8	3 0.3	7 0.6	0.6	0.7	0.6	0.7	0.6	0.7
n-C4H10	[%]	14.3	3 13.0	5 13.5	13.5	14.2	13.8	13.9	14.0	14.1
2-C4H8	[%]	10.0	5 10.9	9 11.5	11.5	11.7	11.7	12.3	12.6	12.5
1-C4H8	[%]	74.3	3 74.8	8 74.4	74.4	73.4	73.9	73.1	72.8	72.8



Fig. 2.50 The course of the hydrogenation activity versus time on stream. The parameter B is proportional to the rate constant of the ethene hydrogenation (see Eq.(2.43) in section 2.9.2)

2.14 Discussion

The marked influence of the CO conversion level on the olefin selectivity and isomerization indicates that secondary reactions occur after readsorption of olefins on the catalyst surface. Experiments carried out during this study and investigations reported in literature 5,41,65 indicate that these secondary reactions take place on separate sites as will be discussed below.

As reported in this study, the hydrogenation of olefins depends entirely on the olefin/carbon monoxide pressure ratio which suggests competition of olefins and CO for the same sites (see section 2.9 and 2.12). The olefin/carbon monoxide pressure ratio also plays an important role in the isomerization of olefins and the incorporation of ethene as pointed out in section 2.10 and 2.12 respectively. The occurrence of secondary reactions does not affect the CO conversion rate, since the synthesis gas consumption depends only of the hydrogen pressure in the reactor up to a high CO conversion level (see section 2.8). The independency of the CO conversion of the secondary hydrogenation is confirmed by the ethene addition experiments. These experiments show that ethene hydrogenation at various reaction conditions occurs simultaneously with the synthesis gas conversion because the CO conversion level was not affected by the ethene/carbon monoxide pressure ratio in the reactor. In contrast to the CO consumption rate, the production rate of methanol and ethanol drops sharply by ethene addition (up to 30%), indicating that the form of adsorbed CO, which is involved in the formation of oxygenates, is scavenged from the surface. Apparently, this decreased CO coverage does not result in a significant decrease of carbon species, which are involved in the hydrocarbon formation, probably as a consequence of the high CO dissociation rate on this catalyst. Therefore, molecular adsorption of CO and CO dissociation may take place on different sites 4,75

According to Zhang ¹², two types of sites are distinguishable on alkali promoted fused iron under reaction conditions, namely Fe[°] sites, associated with CO dissociation and the production of hydrocarbons, and Fe^{n+} sites on which CO is hydrogenated to methanol and alkyl groups which may be converted into oxygenated products. For CO dissociation, Araki and Ponec ⁷⁵ have reported that this requires sites consisting of several metal atoms, whereas this cooperation of several adjacent metal atoms is not necessary for hydrogenation to take place 4,35,46. Therefore, it is conceivable that CO dissociation and chain growth take place on different sites ("sites 1") from secondary hydrogenation and isomerization ("sites 2"). The existence of different sites may explain why the CO conversion kept constant during the co-feeding of ethene. Adsorption of ethene on "sites 1" may result in olefin insertion in growing hydrocarbon chains.

Thus, in summary the main reactions which will probably occur on the surface of promoted fused iron during the Fischer-Tropsch synthesis are:

"sites 1"

- * CO dissociation
- * Hydrocarbon formation
- insertion of olefins into hydrocarbon chains

"sites 2"

- * molecular CO adsorption without dissociation
- * oxygenate formation
- * hydrogenation and isomerization of olefins readsorbed
- * water gas shift ?

When CO is dissociated on "sites 1", water will be formed there as well. Since the water-gas shift is clearly a secondary reaction 76 and non-dissociated CO is required 2,77,78, it is more conceivable that this reaction will occur on "sites 2" than on "sites 1". A high water vapour pressure may lead to considerable adsorption of water on both sites. This results in a decrease of the carbon intermediates which are involved in chain growth 35 on one type of sites as well as a decrease of secondaire reactions on the other type of sites.

Symbols		
А, В	constants	-
ъ	constant	s ⁻¹
c	constant	bar/s
ci	concentration of component i	mol/m ³
E	H ₂ /CO outlet ratio	mol/mol
F*	gas flow at reference conditions (20°C, 1 bar)	m ³ G/s
F	gas flow, actual temperature and pressure (ATP)	m ³ G∕s
m	solubility coefficient	^{m³L/m³G}
H _{1,2}	Henry's constant for solute	atm
	l in solvent 2 (fugacityl/liquid	
	phase mole fraction of solute 1)	
I	H ₂ /CO inlet ratio	mol/mol
k	reaction rate constant	s ⁻¹
k	reaction rate constant (mol/kg cat s bar H_2)	
Кs	watergas shift equilibrium constant	-
P°i	pressure of a hydrocarbon with i C atoms at $t=0$	bar
Pi	pressure of a hydrocarbon with i C atoms	bar
P	total or reactor pressure	bar
P*	reference pressure (1 bar)	bar
-rCO+H2	synthesis gas conversion rate	mol/kg cat s
r _n	reaction rate	mol/m ³ L s
r _{p,i}	production rate of component i	mol/s
R	gas constant	bar m ³ G/K mol
t	time	s
Т	reactor temperature	K or °C
т*	reference temperature (20°C)	K or °C
U	H ₂ /CO usage ratio	mol/mol
v	volume	m ³
x	H/C atomic ratio in the product	-
х	conversion	%
z	water fraction converted by the	mol/mol
	shift reaction	

Subscripts

- G gas phase
- L liquid phase
- i component i
- in inlet
- out outlet

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3 THE PERFORMANCE OF Rufe/SiO₂ AND Ru/SiO₂ AT HIGH PRESSURE DURING AN EXTENDED RUN

3.1 Introduction

The application of bimetallic systems is an interesting possibility to improve the selectivity and activity of Fischer-Tropsch catalysts. Reports in literature by Vannice et al 1.2. and investigations in our laboratory 3.4 show that bimetallic RuFe catalysts supported on silica have an excellent selectivity for low molecular olefins produced from synthesis gas. However, these investigations have been carried out chiefly at atmospheric pressure in so-called differential fixed-bed reactors, and only during short runs. Therefore, little is known about the performance of RuFe catalysts at elevated pressure and at higher synthesis gas conversion levels.

In this study the performance of RuFe catalysts on silica is investigated at a higher pressure during a long run. The properties of the bimetallic catalyst are compared with that of Ru/SiO_2 and fused iron. The latter was extensively discussed in the previous chapter.

Silica is chosen as support because it appears to be more resistant to carbon build-up 5 and exhibits a higher olefin selectivity than TiO₂ or carbon carriers 3 . In general, silica is known to interact much less with small particles than is the case for other materials. Based on the research of Stoop 3 , a bimetallic RuFe/SiO₂ catalyst with a Ru/Fe ratio of 1/3 is chosen. The olefin selectivity reaches a maximum value for this Ru/Fe ratio, according to Stoop 3 .

This introduction is concluded by a brief literature review, mainly concerning the catalytic performance of unsupported and silica supported RuFe catalysts. This review starts with the characterization of bimetallic RuFe catalysts after reduction with H_2 , followed by the characterization of spent catalysts. It ends with a discussion on the performance of RuFe catalysts.

Studies of silica supported RuFe catalysts with 5^{7} Fe Mössbauer spectroscopy have shown that Ru and Fe are alloyed in this supported form after reduction with hydrogen 1,6,7. A moderate or high metal loading is required to form bimetallic particles if one starts with organic Ru and Fe salts 1,3. When the metal loading is strongly decreased, the formation of bimetallic clusters can only be achieved using the proper substance

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for metal deposition, such as $Fe_3(CO)_{12}$ and $Ru(CO)_{12}$ ⁸. It is important to know of course, whether the catalyst is really bimetallic after preparation and reduction but from the users point of view it is more important to know if the bimetallic state continues to exist under reaction conditions.

Unfortunately, it is not clear from literature under which reaction conditions $RuFe/SiO_2$ catalysts are stable for a particular Ru/Fe ratio. At a temperature level of 570 K, Lazar et al.^{7,9} report the absence of carbides (indicating no catalyst decomposition) but they show the presence of a small amount of carbides apart from the main component metallic component. Higher temperatures appear to accellerate the decomposition of bimetallic clusters ⁹. A higher Fe content reduces the stability of $RuFe/SiO_2$ catalysts ¹⁴. To the knowledge of the author, data on the effect of the pressure of CO, H₂ and H₂O on the stability of $RuFe/SiO_2$ catalysts is not available. In contrast to this uncertainty about the stability of $RuFe/SiO_2$ catalysts is much clearer.

The catalytic performance of RuFe catalysts is markedly different from that of pure Ru catalysts even when only 3% Fe is added. Ott et al.¹⁰ show that the methane mole fraction decreases from 85% to 55% by the addition of 3% Fe to unsupported ruthenium. The tremendous change of the selectivity by this small amount of Fe must be due to iron enrichment of the catalyst surface 10. Probably, the surface hydrogen concentration is reduced on the 93:3 RuFe catalyst compared to that on pure ruthenium. This reduction of the hydrogen concentration causes a decrease of the activity with 40%, an increase of the olefin selectivity and the decrease of the methane selectivity already mentioned. The decrease of the activity and methane selectivity by the addition of Fe to Ru is also reported for RuFe/SiO₂ catalysts 1,2,3,4,11. The difference of iron rich RuFe catalysts with respect to pure Fe catalyst, however, is less clear. Vannice et al.¹, Stoop et al.⁴ and Ott et al.¹⁰ report that going from pure Ru to pure Fe, the methane selectivity goes through a minimum and the olefin selectivity through a maximum. However, Guczi et al. 11 demonstrate that the methane selectivity decreases proportionally with increasing Fe content. Anyhow, it is clear that the difference in selectivity between RuFe and Fe catalyst is less pronounced than between

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RuFe and pure Ru catalysts 1,9,10.

It is important to note that the role played by the conversion cannot be fully ignored in some of the published papers. Notwithstanding the conversion of CO being lower than 3%, Ott et al. 10 report that the value of the olefin selectivity of a pure Fe catalyst was effected by the level of the conversion. Also Stoop ³ reports that the level of CO conversion affected the performance of various RuFe catalysts, although the degree of CO conversion was kept below 5%. A decrease of the conversion by increasing the gas flow results in an increase of both the activity and olefin selectivity for Ru, RuFe and Fe catalysts supported on silica. Thus, the occurrence of secondary reactions and the influence of products is likely for Ruthenium-containing catalysts at a CO conversion level below 5%. In this connection it may be noted that there is very little on this subject concerning this type of catalyst in literature.

The influence of other reaction conditions on the performance of RuFe catalysts has also hardly been investigated. One experiment with RuFe(1:2,6)/SiO₂ at 20 bar shows that the methane selectivity is dramatically decreased while the formation of high molecular weight products is increased with respect to experiments at one bar ¹¹. Unfortunately, no information was thereby provided about the olefin selectivity at this pressure. The activity was only 5 times higher with respect to the atmospheric experiment although the hydrogen pressure was raised from 0.75 to 13 bar. In addition, Berry ¹² reports that the activity of RuFe/SiO₂ is higher at higher pressure and that it tends to form high-molecular weight hydrocarbons.

3.2 Experimental

3.2.1 Catalyst preparation and apparatus

The RuFe and the Ru catalysts were both prepared by incipient wetness impregnation of silica. The procedure is as follows: weighted fractions of RuCl₃ (Merck) and FeCl₃.6H₂O (Merck) are dissolved in an accurately determined quantity of 1N HCl which is just enough to fill the pores of the silica. The silica carrier (AKZO F5), sieved to a fraction with a particle diameter between 45 and 90 μ m, is added to the acidified salt solution under continuous stirring. When the mixture is homogeneous, and the solution absorbed by the particles, the resulting pre-catalyst is dried in a vacuum descicator filled with silica-gel at room temperature until a dry powder is obtained. This powder undergoes thermal treatment at 125°C in air for 16 hours. The pre-catalyst is reduced in a separate fixed-bed reactor with 40 ml (20°C, 1 bar) H_2/g unreduced cat.min. The temperature is raised from 20°C to 350°C at a rate of 3°C/min, from 350-390°C at a rate of 2°C/min and the last 10°C at 1°C per minute. After 2 hours at 400°C, the catalyst is cooled down slowly and transferred to the slurry reactor under exclusion of air.

The catalytic properties were investigated in the same equipment as was used for fused iron (see section 2.3)

3.2.2 Experiments

Three runs with RuFe/SiO₂ and one run with Ru/SiO₂ have been carried out. A run represents a series of experiments performed with a single batch of the catalyst at varying reaction conditions. Therefore, the history of the catalyst in the reactor can influence catalytic behaviour. The outline of the experiments will be briefly discussed in this section.

<u>Run 1</u>

The aim of this run is the investigation of $RuFe(1:3)/SiO_2$ at a high pressure at various temperatures and H_2/CO inlet ratios. An amount of 9.3 g¹⁾ 5.0 wt%²⁾ was suspended in 200 g squalane. The pressure and synthesis gas flow were kept constant at 9.0 bar and 200 ml (20°C, 1 bar)/min. respectively. The reaction conditions are summarized in Table 3.1

Run 2

The second run was carried out with 20 g 5.0 wt% RuFe(1:3)/SiO₂ suspended in 200 g squalane. The main objective of this run was the confirmation of the results of the first run but at a higher degree of CO conversion. In addition to this, the properties of the catalyst were investigated at a low temperature and after pretreatment at a high temperature. The temperature was varied between 230 and 270°C. The

weight of dried unreduced catalyst
 metal weight with respect to the unsupported carrier

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reactor pressure was again 9.0 bar and kept constant. The other reaction conditions are summarized in Table 3.2

Table 3.1

Reaction conditions of the experiments of run 1 carried out with 9.3 g 5.0 wt% RuFe/SiO₂. The reactor pressure was 9.0 bar. The inlet gas flow was 200 ml $(20^{\circ}C, 1 \text{ bar})/\text{min}$.

Exp.	Start	Analysis	Temp.	H ₂ /CO
No.	after	after		feed
	[h]	[h]	[°C]	[-]
1	0	_ 1)	230	1.0
2	88	21	230	2.0
3	113	20	230	0.5
4	137	21	230	1.0
5	159	20	250	2.0
6.1	184	23	250	1.0
6.2	217	11	250	1.0
7	231	. 21	250	0.5
8	255	22	270	2.0
9	280	20	270	1.0
10	304	15	270	0.5
11	329	21	280	1.0
12.1	353	21	280	2.0
12.2		32	280	2.0
12.3		44	280	2.0
13	400	26	280	0.5
14	427	17	270	0.5
15	448	22	250	0.5

1) No analysis data available

Reaction conditions of the experiments of run 2 carried out with 20 g 5.0 wt% $RuFe/SiO_2$. The reactor pressure was 9.0 bar

Exp.	Start	Analysis	Temp.	H2/CO	Flow
No.	after	after		feed	in 1)
	[h]	[h]	[°C]	[-]	[ml/min]
1	0	46	230	2.00	200
2	49	12	230	1.00	200
3	65	17	230	0.50	200
4	89	21	250	2.41	228
5	115	42	250	1.00	200
б	162	16	250	0.50	200
7	184	8	270	2.41	228
8	194	10	270	1.00	200
9	210	26	270	0.50	200
10	238	10	250	2.41	228
11	266	3	230	2.41	228
12	282	3	230	2.41	100
13	332	19	250	2.41	100
14	352	9	230	2.41	100
15	362	17	270	2.41	100
16	382	14	250	2.41	228
17	404	16	250	2.41	228
18	430	15	250	2.41	228
19	506	11	250	2.41	228

1) measured at 20°C and 1 bar

Run 3

The third run was carried out with 20 g 5.5 wt% RuFe(1:3)/SiO₂ suspended in 200 g squalane. The main objective of run 3 was the investigation of the influence of the partial pressures of CO and H₂ on the activity and selectivity. For that purpose first the pressure of H₂ and afterwards the pressure of CO was kept constant during a series of experiments. An activity pattern was established for operation at a low temperature during more than 70 hours on stream, after which the temperature was raised to 280°C and kept there until the activity reached the steady-state. Afterwards the temperature was reduced to 250°C and kept constant during all further experiments. Between experiment number 26 and 27 a reduced commercial water-gas shift catalyst, containing 24% Cu, 23% Zn and 15% Al, was added to the reactor.

The reaction conditions of this run are summarized in Table 3.3 <u>Run 4</u>

The main objective of this run was the investigation of the performance of Ru/SiO_2 which contains an equal amount of Ru as the $RuFe/SiO_2$ catalyst used in run 3, prepared with the same precursor and carrier, reduced and tested in the same equipment as the $RuFe/SiO_2$ catalyst. The data of this run has been used for comparison of the performance of Ru and RuFe on silica catalysts. All experiments were carried out at 250°C and at a high pressure. The reaction conditions are summarized in Table 3.4

3.3 Results

3.3.1 The activity of RuFe/SiO2 and Ru/SiO2

The activity of a fresh RuFe/SiO₂ catalyst decreases dramatically as a function of time on stream as shown in Figure 3.1. The temperature and pressure were 230°C and 9.0 bar respectively. The decrease of the activity significantly slows down after 15 hours on stream but continues even after more than 60 hours on stream at these reaction conditions. When the temperature is raised from 230 to 250°C after 170 hours on stream, the decrease of the activity follows a course similar to that in Figure 3.1. At this temperature the activity also decreases continuously

Table 3.3

Reaction conditions of the experiments of run 3 carried out with 20 g 5.5 wt% RuFe/SiO2

Exp.	Start	Analysis	PH2	PCO	PH ₂ O	Flow	React	or
No.	after	after		feed		in	press	ure
	[h]	[h]	[bar]	[bar]	[bar]	[ml/min]	57 [bar	.]
1	0	7.5	5.79	2.89	0.232	204	9.0	1)
-	-	14.1	5.79	2.87	0.113	204	9.0	
4		40.6	5.77	2.87	0.095	204	9.0	
		57.4	5.77	2.87	0.082	204	9.0	
2	75	38	4.20	4.42	0.283	204	9.0	2)
́З	116	19	5.80	2.55	0.139	214	9.0	3)
4	142	23	4.93	4.76	0.128	191	10.0	
5								4)
6	235	21	5.78	2.65	0.139	209	9.0	
7	261	20	5.69	1.13	0.124	246	7.5	
8	284	18	5.72	3.88	0.121	216	10.0	
9	307	19	5.33	6.39	0.139	184	12.0	
10	333	20	5.61	10.01	0.156	209	16.0	
11	406	17	10.78	5.03	0.305	207	17.0	
12	427	20	7.46	4.93	0.178	209	13.0	
13	451	22	2.85	4.88	0.063	201	7.9	
14	475	21	5.14	4.89	0.152	202	10.5	
15	501	30	1.76	4.98	0.059	198	6.8	
16	574	18	3.78	5.05	0.148	206	9.0	
17	601	15	3.25	4.99	0.133	192	8.5	
18	650	13	5.71	0.57	0.126	249	7.1	
19	672	64	5.63	1.69	0.133	232	8.0	
20	744	16	5.75	4.78	0.162	207	11.0	
21	770	14	0.92	0.39	0.011	235	1.4	
22	789	4	0.93	0.39	0.011	269	1.4	
23	794	12	0.92	0.39	0.010	332	1.4	
24	812	20	0.90	0.39	0.044	52	1.4	
25	839	17	0.92	0.39	0.012	235	1.4	
		40	0.97	0.39	0.013	235	1.4	
		66	0.98	0.39	0.014	235	1.4	
		86	0.98	0.40	0.014	235	1.4	
26	932	22	6.28	2.49	0.125	235	9.0	
276) 958	20	6.21	1.79	0.018	235	9.0	

2) temperature of the reactor: 280°C
3) temperature of the reactor was lowered to 250°C

and kept at this level for the entire run 4) no analysis data available

5) measured at 20°C and 1 bar

6) 20 g of a reduced commercial shift catalyst added

Table 3.4

Reaction conditions of the experiments of run 4 carried out with 21.7 g 2.1 wt% $\rm Ru/SiO_2$

Exp. No. [-]	Start after [h]	Analysis after [h]	PH2 [bar]	PCO feed [bar]	PH ₂ O ¹⁾ [bar]	Flow in [ml/min] ²)	Reactor pressure [bar]
 1.1	0	2.3	2.75	2.00	4.15	208	9.0
1.2		4.0	4.77	2.61	1.13	208	9.0
1.3		5.8	5.34	2.70	0.77	208	9.0
1.4		13.6	5.47	2.81	0.36	208	9.0
1.5		14.3	5.48	2.82	0.40	208	9.0
1.6		39.4	5.67	2.97	0.31	208	9.0
1.7		82.1	5.94	2.84	0.18	208	9.0
2	159	46.8	5.67	3.20	0.10	208	9.0
3	215	41.1	3.57	5.07	0.06	147	8.7
4 3)	258					248	11.0
5	284	23.3	5.48	4.97	0.07	227	10.6
6	312	12.1	2.40	5.95	0.05	128	8.6
7	333	15.8	3.82	5.23	0.06	188	9.6
8	354	16.3	3.44	4.98	0.05	160	8.5
9	374	21.5	1.87	4.75	0.04	123	7.0

1) calculated from hydrocarbons produced

2) measured at 20°C and 1 bar

3) power fail off

as shown by experiment 6.1 and 6.2 in Figure 3.2. When the temperature is further raised to 270°C and later on to 280°C, the process of an initial strong decrease followed by a slow decline of the activity reoccurs and it can be seen that the activity still decreases after 100 hours on stream at a temperature of 280°C (see exp. 12.3 in Figure 3.2). When the temperature is reduced to 270°C, after 430 hours on stream, the activity has been reduced sharply with respect to the value which was measured first at this temperature as can be seen by comparison of the activity of experiment 10 and 14 in Figure 3.2. A further reduction of the temperature to 250°C shows that the activity is much lower after the catalyst has been exposed to a higher temperature (compare exp. 7 and 15 in Figure 3.2).

It is important to know what the course of the activity takes after treatment at such a high temperature. This has been investigated in run 2



Fig. 3.1 The activity of a fresh RuFe/SiO₂ catalyst as a function of time on stream

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Fig. 3.2 Summary of the activity of RuFe/SiO₂ as a function of time on stream for all experiments of run 1. The temperature is reported on the upper side

of which the values of the activity as a function of time on stream are shown in Figure 3.3. The experiments 10,13,16-18 show that once the catalyst has been used at an elevated temperature (270°C), the decline of the activity at 250°C stops and the activity remains practically constant over a period of 300 hours on stream. Note that the level of the activity at 250°C is strongly decreased by the (first) treatment at 270°C (see experiment 4 and 10). This loss of activity is also visible at 230°C (experiment 1 and 14).

It thus appears, that a stable catalyst is obtained by treatment at a high temperature during which an accellerated deactivation takes place. This method of stabilizing the catalyst was applied in run 3, in which the temperature was raised to 280°C and held at this value until the

decrease of the activity became negligeable. This resulted in a very stable catalyst used for kinetic investigations at 250°C. A constant catalyst activity was observed over more than 800 hours on stream.

It is interesting to compare the activity of RuFe/SiO₂ measured in this study with literature data. Comparison of the activity of various catalysts is hindered because authors often do not report after which time on stream the activity was determined. Besides, it is frequently unclear if the catalyst was stable at that point in time. Therefore, the data which is summarized in Table 3.5, may only be used for comparison of the order of magnitude of the activity of RuFe catalysts which contain approximately 25 mole% Ru. It can be seen from this table that three catalysts show activities of the same order of magnitude as the steady



Fig. 3.3 Summary of the activity of $RuFe/SiO_2$ as a function of time on stream for all experiments of run 2. The temperature is reported on the upper side

state value reached in experiment 25.1 of run 3 (note 1), namely 1) 0.5 wt% RuFe (1:2.6)/SiO₂ at its final activity (ref. 11), 2) unsupported RuFe (1:2) and 3) 5.0 wt% RuFe(1:3)/SiO₂. Thus, it appears that the value of the activity after the pretreatment at 280°C as carried out in run 3, does not result in an extremely low activity when compared with literature data. The somewhat lower value can be attributed to the long time on stream before the activity is measured, the lower Ru content of the catalyst and the lower temperature applied in this study.

Table 3.5

A summary of the activity of RuFe catalysts which contain approximately 25 mole % Ru

Cat	alys	t	Т	H ₂ /CO	P	xco	Activity		Ref	•
			[°C] [-]	[bar]	[%]	initial	final		
0.5	wt%	RuFe(1:2.6)/SiO ₂	303	3.0	1.0	< 1	73.0 4)	3.2 4)	11	
		RuFe(1:2.0)	300	3.3	1.0	< 3	1.4 3)	-	10	
5.0	wt%	RuFe(1:3.0)/SiO ₂	277	2.0	1.0	<10	6.2 ³⁾	-	3	
2.0	wt%	RuFe(1:1.9)/SiO ₂	275	3.0	1.0	< 2	14.0 3)	5) _	2	
5.5	wt%	RuFe(1:3.0)/SiO ₂	250	2.5	1.4	3	-	0.9 4)	-	1)
0.5	wt%	RuFe(1:2.6)/SiO ₂	303	2.0	20.0	?		16.0 ⁴⁾	11	
2.0	wt%	RuFe(1:1.9)/SiO ₂	235	2.0	26.0	?	247.0 5)	-	15	
5.0	wt%	RuFe(1:3.0)/SiO ₂	270	2.4	9.0	17	-	123.0 5) 7.9 3)	-	2)

- 1) This study: run 3 experiment 25.1
- 2) This study: run 2 experiment 7
- 3) µmol CO converted in products/g.metal.s
- 4) µmol products/g.metal.s
- 5) mg products/g.metal.s
- 6) calculated from the TON estimating that the adsorption of CO is only caused by Ru atoms

3.3.2. Comparison of RuFe/SiO2 and Ru/SiO2

Run 4 has been carried out with Ru/SiO_2 which contained as much ruthenium as the 5.5 wt% $RuFe(1:3)/SiO_2$ catalyst that was used in run 3. The aim of this run was to investigate the effect of the addition of iron to ruthenium supported on silica on the activity and selectivity.

A fresh Ru/SiO_2 catalyst deactivates rapidly and similarly as $RuFe/SiO_2$, as shown in Figure 3.4. It is interesting to note that initially the catalyst is very active while it produces a great deal of water, resulting in a high water vapour pressure. This is shown by the first data point in Table 3.4 (experiment 1.1). As will demonstrated later, water strongly inhibits the reaction which means that even higher activities should be expected if measurements were made at a lower conversion level.



Fig. 3.4 The activity of a fresh Ru/SiO_2 catalyst as a function of time on stream (see experiments 1-4 of Table 4)

It appears that the activity of Ru/SiO₂, after the steady-state is reached, is hardly different from the activity of RuFe/SiO₂ as demonstrated in Table 3.6. It can thus be concluded that the addition of iron to Ru supported on silica hardly influences the steady-state activity reached after a moderate time on stream.

Table 3.6

The activity of 2.1 wt% Ru/SiO2 and 5 wt% RuFe/SiO2 at 9 bar and 250°C.

Catalyst	Run no.	H.O.S.	PH ₂ [bar]	PCO [bar]	F _{in} [ml/min]	Activity 2) 1)
5.0 wt%(1:3)RuFe/SiO2	2	238	5.96	2.62	228	1.4
5.5 wt%(1:3)RuFe/SiO2	3	116	5.80	2.55	214	1.6
2.1 wt%Ru/SiO ₂	4	215	5.67	3.20	208	1.1

1) measured at 20°C and 1 bar

2) [mg C₁-C₇/kg cat.s]

3.3.3 Comparison of RuFe/SiO2, Ru/SiO2 and fused iron

Comparison of Ru(Fe)/SiO₂ and fused iron catalysts promoted with potassium (see 2.2) shows remarkable differences. The activity of fused iron is not only much higher at comparable reaction conditions but the increase of the activity versus the temperature is also larger for fused iron as is clearly shown in Figure 3.5. It has to be noted that the activities in Figure 3.5 are related to the total weight of the catalyst (including support material). This means that the activity differences are less pronounced when only considering the weight of the metals. No reliable data is available to compare the catalyst on the basis of the metal surface exposed.

3.3.4 Kinetic model for RuFe/SiO2

The influence of the total pressure, the H_2 pressure, the CO pressure and the water vapour pressure on the activity and conversion of synthesis gas over RuFe/SiO₂ resulting in an emperical kinetic relation will be presented in this section. The results are based on the experiments carried out during run 3.

Regarding the performance of $RuFe/SiO_2$ at higher pressures, the influence of the total pressure on the conversion of CO over fused iron was investigated first. As demonstrated in Chapter 2, the conversion of synthesis gas over fused iron is linearly proportional to the hydrogen pressure up to a high conversion. Increasing the total pressure therefore, results in an increase of the conversion of CO as shown in





Table 3.7. Surprisingly, the pressure does not significantly affect the conversion of CO over RuFe/SiO₂ despite an increase of the H₂ pressure with a factor 10 as shown in Table 3.8. Apparently, the conversion of synthesis gas is strongly hampered. The effect of the H₂ pressure has been investigated by keeping the pressure of CO constant. As expected, the pressure of H₂ has a positive effect on the activity of RuFe/SiO₂ as shown in Table 9. However, the precise relation between the pressure of H₂ and the activity is not very clear and complicated by the fact that the increasing water vapour pressure interferes (see below).

Table 3.7

The effect of the pressure on the conversion of CO over fused iron (C73) at 250°C. The H_2/CO inlet ratio was 0.67

Flow [ml/min] 1)	H ₂ /CO [-]	PH2 [bar]	P [bar]	^x co [%]	
287	0.70	0.5	1.2	5	
291	0.80	3.2	9.0	44	
298	0.94	5.7	17.0	64	

1) measured at 20°C and 1 bar

Table 3.8

The effect of the pressure on the conversion of CO over $RuFe/SiO_2$ at 250°C. The H_2/CO ratio was approximately constant (run 3)

Experiment number	Flow [ml/min] 1)	H ₂ /CO [-]	x _{CO} [%]	P [bar]	PH2 [bar]
21	235	2.4	11	1.4	0.9
б	209	2.2	16	9.0	5.8
11	207	2.1	14	17.0	10.8

1) measured at 20°C and 1 bar

Contrary to this effect of H_2 , CO inhibits the conversion of synthesis gas. The activity obviously decreases with increasing pressure of CO as shown in Figure 3.6.

The effect of the water vapour pressure has been investigated by the addition of a water-gas shift catalyst which provides for the conversion of product water into CO_2 until the watergas-shift equilibrium is reached. Both the conversion of CO and H₂ as well as the activity increase, and a rather large portion is converted to CO_2 , as shown in Table 3.10. The increase of the activity can be attributed almost completely to the decrease of the water vapour pressure because the pressure of H₂ does not change while the decrease of the CO pressure has but a small effect as shown in Figure 3.6. This experimental proof of the inhibition by water can be used to explain the moderate effect of the



Fig. 3.6 The influence of the CO pressure on the activity of RuFe/SiO₂ (run 3, experiment 3-10). The H₂ pressure was approximately 5.7 bar

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increase of H_2 on the activity as shown in Table 3.9. It is clear that the increase of the H_2 pressure results in a higher H_2O pressure due to a higher conversion level. This increased water vapour pressure causes a decrease of the activity which is only slightly smaller than the increase by H_2 , resulting in an irregular activity pattern with increasing H_2 pressure as shown in Table 3.9.

Table 3.9

The influence of the H_2 pressure on the activity of $RuFe/SiO_2$ (run 3). Other reaction conditions are reported in Table 3.3

Exp. no.	PH2 [bar]	PCO [bar]	PH20 [bar]	Activity [mg/kg.cat.s]
15	1.8	5.0	0.059	0.84
13	2.9	4.9	0.063	0.78
17	3.3	5.0	0.13	1.46
16	3.8	5.1	0.15	1.62
14	5.1	4.9	0.15	1.40
12	7.5	4.9	0.18	1.36
11	10.8	5.0	0.31	1.79

Before attempting to express the effect of the partial pressure of H_2 , CO and H_2O in a kinetic model, some relations proposed in literature will be discussed.

A prerequisite for the model to be selected is a negative influence of both the pressure of CO and H_2O on the conversion rate of synthesis gas. Keeping this in mind, the relation proposed by Huff and Satterfield 16 must be rejected. Although this relation does account for the decrease of the reaction rate at a higher degree of conversion over a fused iron catalyst, it does not describe inhibition at increasing CO pressure:

$$-\mathbf{r}_{\rm CO+H_2} = \frac{a \ PH_2 \ PCO \ PH_2/PH_2O}{1 + b \ PCO \ PH_2/PH_2O}$$
(3.1)

The kinetic relation of Anderson 1^7 and Dry 1^8 based on the CO insertion theory can also be ruled out because this relation assumes that CO and H₂O compete for the same active sites:

$$-r_{\rm CO+H_2} = \frac{a \, p_{\rm H_2}}{1 + b \, p_{\rm H_2O}/p_{\rm CO}}$$
(3.2)

The pressure of CO actually has a positive effect on the rate in this relation which is certainly not the case for this catalyst as earlier shown in Figure 3.6.

Table 3.10

The effect of a decrease of the water vapour pressure on the activity of $RuFe/SiO_2$. The water vapour pressure was lowered by the addition of a water-gas shift catalyst (run 3)

Exp.	PH20	PCO2	PH2	PCO	× _{C0} ³) x _{H2}	Activity
no.	[bar]	[bar]	[bar]	[Dar]	[%]	[%]	[mg/kg.Cat.s]
26	0.13 1)	<0.005	6.3	2.5	8.6	13.3	3.19
27	0.02 2)	0.48	6.2	1.8	15.1	18.6	5.48

1) calculated from hydrocarbons produced

2) calculated by means of the water-gas shift equilibrium

3) based on the conversion to hydrocarbons

Dixit and Taviarides ¹⁹ proposed a model based on kinetic data obtained on 0.5% Ru/Al_2O_3 at a high degree of conversion and pressures up to 10 bar, at steady state conditions (which are hardly available for supported ruthenium catalysts):

$$-r_{\rm CO} = \frac{a \, P_{\rm CO} \, P_{\rm H_2}}{(1 + b \, P_{\rm CO})^2}$$
(3.3)

This model is based on the assumption that the rate determining step is the hydrogenation of adsorbed CH_x species. This fits in with the kinetic data moderately well, because in this model inhibition by CO is accounted for. However, the data can be described better with a model that accounts for the adsorption of H₂O also.

As such model has not been presented in literature for RuFe catalysts, two models were developed in this study based on the reaction network proposed for supported Ruthenium by Kellner and Bell ²⁰. The latter has been adjusted because also Kellner and Bell do not account for water inhibition (see appendix 1)either. In the models developed the assumption is made that the rate determining step is the hydrogenation of adsorbed CH_x species. In model I the assumption is that surface oxygen reacts with hydrogen irreversibly in contrast with model II, wherein this reaction is assumed reversible. The best fit is obtained with model I, thereby assuming further that

* the rate determining step is the hydrogenation of θ_{CH}

* carbon and water saturate the active sites: This results in the following simplified expression:

$$-r_{CO} = \frac{a P_{CO}^{1/2} P_{H_2}}{(P_{CO}^{1/2} + b P_{H_2O})^2}$$
(3.4)

with a is 1.14 and b is 4.3.

The experimental data and the predicted rate of conversion of CO are shown in Figure 3.6 and 3.7. Eq.(3.4) shows the strong inhibition of CO and H₂O. It is clear that the activity of RuFe decreases sharply with decreasing space velocity due to the decrease of the H₂ pressure and the replacement of CO by H₂O which supresses the activity even more than CO, as demonstrated in Eq.(3.4).



Fig. 3.7 Comparison of experimental and predicted rate of CO conversion for RuFe/SiO₂ (run 3, experiment 3-20). The closed symbols are the same experiments as shown in Figure 3.6

3.3.5. Kinetic model for Ru/SiO2

A single run with Ru/SiO_2 has been carried out to compare the kinetics over Ru/SiO_2 and $RuFe/SiO_2$. A reliable critical assessment of models for the kinetics over Ru/SiO_2 is not possible in view of the limited number of experiments. However, the data can be used to obtain an indication of the similarity between the kinetics of both catalysts. The experimental data is well described by Eq.(3.4) which has been derived for $RuFe/SiO_2$; only the parameters a and b are somewhat different:

$$-r_{\rm CO} = \frac{0.58 \ p_{\rm H_2} \ p_{\rm CO}^{\frac{1}{2}}}{(p_{\rm CO}^{\frac{1}{2}} + 10p_{\rm H_2O})^2}$$
(3.5)
It is interesting to note that the rather close correspondence between the kinetics for $RuFe/SiO_2$ and Ru/SiO_2 indicates that the presence of Ru dominates the performance of these catalysts.

3.3.6 Product distribution over RuFe/SiO2

This section starts with the description of the product distribution of a fresh catalyst, followed by that of a used catalyst at various temperatures and pressures and ends with some remarks on the Schulz-Flory distribution.

During the first hours on stream, traces of CO_2 were observed but the CO_2 production fell sharply to such low level that it was not measurable during all other experiments. This indicates that the rate of the water-gas shift reaction is rather low with respect to the production and removal of water from the reactor.



Fig. 3.8 The C_1/C_3 mole ratio as a function of time on stream for both RuFe/SiO₂ and Ru/SiO₂ (run 3 and 4, respectively)

During this initial period the product distribution changes in spite of the low reactor temperature. Figure 3.8 shows that the C_1/C_3 ratio increases gradually during the first 60 hours on stream at 230°C, indicating that the value of α decreases during this period.

During run 1 and run 2 the temperature was increased with increasing time on stream which caused a decrease of the value of α (see Figure 3.9 and 3.10). This decline of α is irreversible. Figure 3.9 shows that when the temperature is reduced from 280 to 250°C, α does not significantly change. After the temperature reduction to 250°C, the value of α versus time on stream is constant also, as shown in Figure 3.10 (see experiment number 10 and 13). When, however, the temperature is increased again to a higher level, the value of α at 250°C is lower than before this rise of temperature took place (compare no. 13 and 16 in Figure 3.10). This means that a second temporary temperature increase may again result in a lower α . Summarizing, the value of α decreases irreversibly and slowly at a low



Fig. 3.9 Summary of the values of α of RuFe/SiO₂ for all experiments of run 1. The temperature is reported on the upper side

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Fig. 3.10 Summary of the values of α of RuFe/SiO₂ for all experiments of run 2. The temperature is reported on the upper side

constant temperature to a steady-state value (as shown for a fresh catalyst in Figure 3.8). This decline is enhanced by a higher temperature.

This knowledge is applied to run 3. The temperature at the beginning of this run was kept constant at a relatively high temperature level (280°C) until the steady-state was reached (this steady-state was desired for kinetic experiments). Figure 3.11 demonstrates that α stayed almost constant after this "high temperature treatment" during the experiments 2-20, which cover a time period of 700 hours on stream. It is noteworthy that the behaviour of α versus time on stream corresponds with that of the activity. Thus, if the value of α is constant or decreases, the activity keeps constant or decreases as well.

The influence of the pressure on α is shown in Figure 3.11. The mean value of α is obviously lower for low pressure experiments (no. 21-25.4)

than for experiments at higher pressure (no. 2-20). Although the value of α increases with increasing pressure, it appears that the C₁/C₃ ratio hardly depends on the pressure as shown in Table 3.11. In fact, the methane fraction exceeds the value predicted by the Schulz-Flory distribution at high pressures (see Figure 3.12).

In contrast to the C_1/C_3 ratio, the C_1/C_2 ratio increases with increasing pressure due to the decrease of the C_2 fraction, probably caused by insertion of ethene (see Table 3.11). This ethene insertion may thus be responsible for the dip in the Schulz-Flory distribution at carbon number 2, as clearly shown in Figure 3.12.

Table 3.11

The influence of the pressure on the product distribution of $RuFe/SiO_2$ at an approximately constant H_2/CO ratio (run 3)

Experiment number	н.о.s. [h]	H ₂ /CO [mol/mol]	Pressure [bar]	C1/C1-C4 [mol/mol]	C ₁ /C ₂ [mol/mol]	C ₁ /C ₃ [mol/mol]
25	904	2.5	1.4	73	5	8
21	784	2.4	1.4	73	5	8
22	793	2.4	1.4	74	5	8
6	256	2.2	9.0	76	9	7
3	135	2.3	9.0	79	9	9
11	423	2.1	17.0	79	11	9

3.3.7 Product distribution over Ru/SiO2 and comparison with RuFe/SiO2

The outlet gas of the reactor freshly charged with Ru/SiO_2 and running for two hours at 250°C and 9 bar, consists almost exclusively of methane. The C_1/C_3 ratio decreases sharply with increasing time on stream as shown in Figure 3.11. This is due to the strong decrease of the methane production rate which is expressed by the activity decrease (Figure 3.4). However, the methane fraction and the C_1/C_3 ratio reach a minimum and start to increase again after approximately 10 hours on stream. This increase is similar to that of $RuFe/SiO_2$. The increase of

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the C_1/C_3 ratio flattens after 60 hours on stream. After this point of time the C_1/C_3 ratio remained practically constant.

The product distribution for Ru/SiO_2 has been investigated for various H_2/CO ratios. Both the methane and the C_1/C_3 ratio decrease with increasing H_2/CO ratio, as generally reported. More important is the remarkable similarity of the methane fraction and the C_1/C_3 ratio for $RuFe/SiO_2$ and Ru/SiO_2 , as shown in Table 3.12. Thus, the product distributions of both catalysts appear to resemble each other closely.

In accordance with $RuFe/SiO_2$, the C_2 fraction for Ru/SiO_2 also shows a considerable dip in the Schulz-Flory distribution as shown in Figure 3.13. The C_2 fraction was even lower than the C_3 fraction for all experiments. Assuming that the deviation of the C_2 fraction is caused by



Fig. 3.11 Summary of the values of α of RuFe/SiO₂ for all experiments of run 3. Open symbols: high pressure; filled symbols: low pressure

the insertion of ethene in the chain growth this indicates that this secondary reaction of ethene occurs very rapidly over both catalysts despite the very low CO conversion and ethene concentration.



Fig. 3.12 Schulz-Flory distribution for RuFe/SiO₂ (run 3) at a low pressure (experiment 25.1) and a high pressure (experiment 13). The reaction conditions are reported in Table 3.3





0.0

-0.2

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Fig. 3.13 Schulz-Flory distribution for Ru/SiO2 (run 4) at a low and high H₂/CO ratio (experiment 5 and 6 respectively). The reaction conditions are reported in Table 3.3

Table 3.12

The effect of the H_2/CO ratio on the product distribution for both $RuFe/SiO_2$ (run 3) and Ru/SiO_2 (run 4) at 250°C

Exper	riment nber	н.с).S.	H ₂ /CO [mol/mol]	Pres [ba	sure r]	C ₁ /C ₃ ratio [mol/mol]		C ₁ fraction [mol %]	
RuFe	Ru	RuFe	Ru	-+ *	RuFe	Ru	RuFe	Ru	RuFe	Ru
11		423		2.1	17		8.6		76.7	
12	-	447	-	1.5	13	-	8.8	-	76.4	-
14	5	496	307	1.1	10.5	10.6	7.9	7.8	74.8	74.4
16	-	592	-	0.8	9.0	-	6.4	_	70.5	
17	8	616	370	0.7	8.5	8.5	5.9	6.2	68.0	69.5
15	-	531	395	0.4	6.8	7.0	5.5	4.6	66.5	62.5

3.3.8 Olefin selectivity for RuFe/SiO2

In this section the dependence of the olefin selectivity on the reaction conditions and the time on stream of $RuFe/SiO_2$ is considered.

After some notes on the olefin selectivity of a fresh catalyst, the influence of the process conditions on the olefin selectivity will be discussed. The course of the C_2 and C_3 olefin selectivity as a function of time on stream for a fresh RuFe/SiO₂ catalyst (the start of run 2) is shown in Figure 3.14. The magnitude of the olefin selectivity is surprisingly low in view of results at low pressure ³, the low conversion of CO (< 10%) and the low temperature (230°C). The increase of the olefin selectivity with increasing time on stream is mainly caused by the decline of CO conversion which is also shown in Figure 3.14. The low olefin selectivity after only a few hours on stream shows that the hydrogenation of olefins occurs very rapidly over fresh RuFe/SiO₂ at a high pressure (9 bar) and under conditions which are certainly not differential.





Fig. 3.14 The C₂ and C₃ olefin selectivity and CO conversion as a function of time on stream for a fresh RuFe/SiO₂ catalyst (run 2) The CO conversion shown is based on CO converted in C_1-C_3 hydrocarbons. The reaction conditions are reported in Table 3.2

The effect of changing of reaction temperature on the olefin selectivity has been investigated for three H_2/CO ratios. At the highest H_2/CO ratio the olefin selectivity of C_2 , C_3 and C_4 apparently decreases with increasing temperature as shown in Figure 3.15. At a lower H_2/CO ratio, however, the C_3 and C_4 olefin selectivity increase with increasing temperature despite the increase of both the conversion of CO and the pressure of olefins. This increase of the olefin selectivity may be caused by a decrease of the formation of paraffins directly from synthesis gas. A decrease of the secondary hydrogenation rate with respect to the Fischer-Tropsch synthesis rate, which would also explain the olefin selectivity increase, is unlikely in view of the small temperature dependence of the Fischer-Tropsch synthesis (see Figure 3.5). The effect of the H_2/CO ratio is shown in Figure 3.15. This figure demonstrates that the olefin selectivity increases when the H_2/CO ratio is lowered. It has to be noted that this increase of the olefin selectivity can be caused both by the lower H_2/CO ratio as such and by the decreased CO conversion level. The effect of the pressure of H_2 and CO on the olefin selectivity will be shown later.

As pointed out in section 2.11, the olefin selectivity will increase with increasing carbon number when the value of α is lower than 0.6. This is due to the fact that at α below 0.6 the concentration of hydrocarbons decreases with increasing carbon number, in spite of a decreasing volatility. In accordance with this prediction, the C₄ olefin selectivity is indeed always higher than the C₃ olefin selectivity (see Figure 3.15).

The influence of the pressure of both CO and H_2 has been investigated by varying the CO pressure at a constant H_2 pressure and reverse, in order to verify the competition model, presented in section 2.9 for fused iron, for the results of RuFe/SiO₂. The effect of the CO pressure will



Fig. 3.15 The olefin selectivity for $RuFe/SiO_2$ as a function of the temperature at various H_2/CO ratios (run 1)

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first be considered, followed by that of the H2 pressure.

When the pressure of H_2 is kept constant, the C_2 and C_3 olefin selectivity increases with increasing CO pressure as shown in Figure 3.16. This increase of the olefin selectivity correlates with a decline of the olefin/CO pressure ratio alone, as shown by the data reported in Figure 3.16.

Unfortunately, this correlation is no longer valid when the H_2 pressure is varied over a large range. The decline of the olefin selectivity cannot be explained by a change of the olefin/CO pressure ratio alone as shown in Figure 3.17. Although the olefin/CO pressure ratio for the first two data points increases, this ratio does not significantly change further in respect of the other data points whereas the olefin selectivity continues to decrease. Apparently, the increase of the H_2 pressure promotes the formation of paraffins. It is not clear from



Fig. 3.16 The C₂ and C₃ olefin selectivity for RuFe/SiO₂ as a function of the CO pressure (run 3). The H₂ pressure is approximately 5.7 bar. The numbers reported are the values of the olefin/CO pressure ratio



Fig. 3.17 The C₂ and C₃ olefin selectivity for RuFe/SiO₂ as a function of the H₂ pressure (run 3). The pressure of CO is approximately 5.0 bar. The numbers reported are the values of the olefin/CO pressure ratio

these experiments whether promotion of the primary formation of paraffins or enhancement of the secondary hydrogenation of olefins to paraffins is the main cause of the hydrogen influence. Note that when the secondary hydrogenation advances by a high H₂ pressure this may indicate that the overall order in hydrogen for this hydrogenation reaction is higher than that of the Fischer-Tropsch reaction. The influence of the H₂ pressure on the olefin selectivity implies that the parameter $p_{\text{olefin}}/p_{\text{CO}}$ has to be modified to obtain a suitable parameter which correlates all experiments. The best fit is obtained when the data are correlated with the parameter $p_{\text{olefin}}P_{\text{H}_2}/p_{\text{CO}}^{1.4}$. This empirical parameter satisfactory describes the experimental data of both the C₂ and C₃ olefin selectivity in view of the large range of reaction conditions (1-17 bar, H₂/CO = 0.4-10) as shown in Figure 3.18 and 3.19.

CZ OLEFIN SELECTIVITY (x)

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Fig. 3.18 and 3.19 The course of the olefin selectivity as a function of $POlefinPH_2/PCO^{1.4}$ for both RuFe/SiO₂ (run 3) and Ru/SiO₂ (run 4)

3.3.9 Olefin selectivity for Ru/SiO2

In this section the olefin selectivity of Ru/SiO_2 will be handled. Firstly, the olefin selectivity of a fresh catalyst will be discussed. Secondly, the steady-state olefin selectivity will be considered and compared with that of $RuFe/SiO_2$.

The secondary hydrogenation as well as the Fischer-Tropsch activity of a fresh Ru/SiO_2 catalyst is very high. These properties of a fresh catalyst result in an extremely low olefin selectivity and in a high conversion of CO shortly after the start of the exposure to synthesis gas as shown in Figure 3.20. The olefin selectivity increases sharply with increasing time on stream whereas the conversion of CO decreases strongly. It is important to note that this increase of the olefin



Fig. 3.20 The course of the olefin selectivity and CO conversion as a function of time on stream for a fresh Ru/SiO_2 catalyst (run 4). The CO conversion is based on CO converted to C_1-C_7 hydrocarbons

selectivity is not caused by the lower degree of CO conversion but is due to a strong decrease of the secondary hydrogenation. This is demontrated by the results in Table 3.13. It can be seen in this table that the partial pressures of the olefins increase initially and decline slowly later on, in contrast with the partial pressures of the C_2 and C_3 fractions which decrease sharply with increasing time on stream. Apparently, the decreased hydrogenation of olefins and a reduced formation of hydrocarbons by the Fischer-Tropsch reaction largely balance out.

Table 3.13

The olefin selectivity and the pressure of the C_2 , C_3 , C_2H_4 and C_2H_6 fractions as a function of time on stream for a fresh Ru/SiO₂ catalyst (run 4)

Exp.	H.O.S.	PC2H4	PC3H6	PC2	PC3	Olefin se	lectivity (%)
no.	[h]	[mbar]	[mbar]	[mbar]	[mbar]	c ₂	C3
1.1	2.3	3.80	26.7	228.9	193.3	1.2	13.8
1.2	4.0	6.30	39.0	93.8	105.4	6.7	37.0
1.3	5.8	5.52	40.6	48.6	72.1	11.4	56.3
1.4	13.6	4.90	28,4	21.6	37.5	22.7	75.7
1.5	14.3	5.18	29.3	22.1	38.6	23.4	75.6
1.6	39.4	3.23	13.6	11.3	17.5	28.7	77.8
1.7	82.1	2.04	7.6	6.5	10.1	31.6	75.6

Another indication for the strong initial secondary hydrogenation is the C_2/C_3 mole ratio. The relatively high C_2 fraction which forms initially, as compared to the C_3 fraction indicates that the insertion of ethene does not occur due to the much more rapid hydrogenation to ethane. When the hydrogenation rate of ethene and other olefins (naturally also the Fischer-Tropsch activity) decreases with increasing time on stream, the insertion of ethene does occur, resulting in a decrease of the C_2 fraction with respect to the fraction of C_3 .

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The C₂ and C₃ olefin selectivity do not rise beyond 32 and 76% respectively after 40 hours on stream. The CO conversion declines to approximately 3% at the same time. These low values of the olefin selectivity at such a low conversion level means that the rate of the secondary hydrogenation of olefins over Ru/SiO₂ stays high with respect to the rate of the Fischer-Tropsch reaction.

The olefin selectivity of Ru/SiO_2 has been investigated at various reaction conditions after the steady-state activity was attained. The experimental data can be correlated with the same parameter as used for $RuFe/SiO_2$. Although it is not possible to conclude that this parameter is the optimum one to describe the dependence of the olefin selectivity on the reaction conditions, it fits the data points satisfactorily and gives an indication of the order of magnitude. Besides, the olefin selectivity can be compared in this way with the data obtained for $RuFe/SiO_2$. The Figures 3.18 and 3.19 clearly demonstrate that the C_2 and C_3 olefin selectivity for Ru/SiO_2 hardly differ from that of $RuFe/SiO_2$. Thus, not only activity and product distribution but also the magnitude of the olefin selectivity of $RuFe/SiO_2$ and Ru/SiO_2 are similar.

3.3.10 Comparison of the olefin selectivity over RuFe/SiO2 and fused iron

In contrast with the small difference between the olefin selectivity of RuFe/SiO2 and Ru/SiO2, the degree of secondary hydrogenation of olefins between RuFe/SiO2 and potassium promoted fused iron differ enormously. The C_3 olefin selectivity for both catalysts as a function of the optimum parameter for RuFe/SiO2 is shown in Figure 3.21. As pointed out in Chapter 2 the p_{olefin}/p_{CO} ratio is the right parameter to describe the effect of the reaction conditions on the olefin selectivity for fused iron. Nevertheless for the purpose of merely giving an idea of the difference between the olefin selectivity of these two types of catalysts, the parameter $p_{C_3H_6}p_{H_2}/p_{CO}^{1.4}$ can be used also for fused iron if the pressures of ${\rm H}_2$ and CO do not vary much. Obviously, the decline of the olefin selectivity is very severe for RuFe/SiO2, with respect to the hardly noticable decrease of the C3 olefin selectivity for fused iron over the range shown in Figure 3.21. The olefin selectivity of other hydrocarbon fractions demonstrates a similar pattern. A survey of the C_2 olefin selectivity for both catalysts at various reaction conditions is

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Fig. 3.21 Comparison of the C₃ olefin selectivity between RuFe/SiO₂ and potassium promoted fused iron at 250°C

presented in Table 3.14. This data clearly shows that the C_2 olefin selectivity for RuFe/SiO₂ is always lower than that of fused iron even at a low pressure and a low degree of CO conversion. The differences are extremely large at high pressure; particularly regarding the mole fraction of ethene with respect to the C_1 - C_4 mole fraction (last column of Table 3.14). The final conclusion therefore is that the yield of olefins over RuFe/SiO₂ is much lower than that over potassium promoted fused iron because of a higher hydrogenation rate as well as a larger incorporation.

Table 3.14

Survey of the C_2 olefin selectivity and the ethene mole fraction for both $FeRu/SiO_2$ and potassium promoted fused iron (C73) at 250°C and various pressures.

Catalyst	Exp. 1	H.O.S.	Flow	xco	PH2	PCO	P	PC2H4	C ₂	PC2H4
	no.		in 1)	[%]	[bar]	[bar]	[bar]	[bar]	01.sel. [%]	PC1-C4 [-]
RuFe/SiO ₂	14.25	839	235	12.6	0.92	0.39	1.4	3.2E-4	31.4	0.041
Fe	16.08	242	98	28.1	1.09	0.33	1.5	25.OE-4	71.4	0.136
RuFe/SiO ₂	14.16	574	206	9.1	3.78	5.05	9.0	2.8E-3	31.0	0.031
Fe	16.24	692	205	26.8	2.40	5.78	9.0	16.3E-3	84.8	0.221
RuFe/SiO ₂	14.11	406	207	13.5	10.78	5.03	17.0	2.7E-3	19.9	0.014
Fe	13.17	240	318	64.0	5.65	6.02	17.0	100.6E-3	61.1	0.150

1) ml(20°C and 1 bar)/min

3.3.11 The olefin selectivity observed with other bimetallic catalysts

Besides RuFe other combinations with iron has been developed as well. Below the performance of a few catalysts in respect of the olefin selectivity is compared with that of RuFe and promoted fused iron

The properties of the catalysts are summarized in Table 3.15. Considering PdFe/ZnO and $CoFe/SiO_2$ it can be concluded that Pd and Co addition lowers the olefin selectivity despite the very low conversion. The value of the olefin selectivity is of the same order of magnitude as that obtained for RuFe/SiO₂ but much lower than that for fused iron as shown in Table 3.15. At a higher conversion iron promoted with copper produces predominantly paraffins

The addition of manganese differs from that of ruthenium, copper, cobalt and palladium because manganese lowers the activity 21 . Diffenbach et al. 22 , Lehmann et al. 23 , and Kölbel and Tillmetz 24 report that MnFe catalysts with a high manganese content produce hydrocarbons with a high

 C_2-C_4 fraction which predominantly contains olefins. However, when the performance of these MnFe catalysts (results of other investigators 21,25,26,27 included) are compared with that of the iron catalyst used in this study, it can be concluded that the latter produces low hydrocarbons with a higher olefin content. Secondary hydrogenation appear to be more significant with MnFe catalysts 21,25,26,28 which may be attributed to the higher reactor temperature used with MnFe (see Table 3.15). This higher temperature is necessary to achieve a sufficiently high activity.

Finally, it may be concluded that the addition of potassium to iron is much more succesful to obtain a catalyst which produces hydrocarbons with a high olefin content than the addition of Co, Cu, Pd, Ru or Mn.

Table 3.15

Comparison of the olefin selectivity obtained with various catalysts

Catalyst	T	P	(H ₂ /CO) _{in}	x _{CO}	Olefin s.	Ref.
	[°C]	[bar]	[mol/mol]	[%]	[%]	
3.5 wt%PdFe(1:4.8)/ZnO	300	6.8	1.0	<5	45 (C ₂)	29
2.5 wt%Fe/ZnO	300	6.8	1.0	<5	67 (C ₂)	29
4.9 wt%CoFe(1:4.0)/SiO ₂	250	13.6	3.7	9	18 (C ₂)	30
4.9 wt%Fe/SiO ₂	250	13.6	3.7	6	28 (C ₂)	30
5.0 wt%RuFe/SiO ₂	230	9.0	1.0	14	29 (C ₂)	31
CuFe(1:19)	250	_	-	71 1)	28 (C ₂ -C ₄) 21
Fused iron	250	9.0	0.7	74 1)	71 (C ₂ -C ₄) 32
MnFe(9.6:1)	275	13.6	1.0	18	60 (C ₂ -C ₄) 26
Fused iron	250	13.6	1.0	17	81 (C ₂ -C ₄) 26

1) Conversion of H₂+CO

3.3.12 Mössbauer analysis

3.3.12.1 Introduction

From the Fischer-Tropsch synthesis experiments carried out with both RuFe/SiO₂ and Ru/SiO₂, it has become clear that the catalytic performance of RuFe/SiO2 does not differ significantly from the performance of Ru/SiO2. Therefore it is likely that the active surface of these catalysts is similar. This would indicate that the bimetallic character has disappeared under the reaction conditions used in this study. This bimetallic character of RuFe/SiO₂ is responsible for the different activity and selectivity of RuFe catalysts according to various reports 1,2,3,4,8 with respect to monometallic Ru and Fe catalysts. However, these reports are mostly based on measurements at atmospheric pressure and only after a short time on stream. Therefore, the existence of the bimetallic phase of a used RuFe/SiO2 was analyzed by means of Mossbauer measurements after the catalyst had been exposed to a high pressure during a few days on stream. This Mössbauer analysis was compared with that of a fresh RuFe/SiO₂ catalyst and a sample which had been exposed to synthesis gas for only 3 hours at atmospheric pressure.

3.3.12.2 Experimental

Three samples 5.0 wt% RuFe $(1:3)/SiO_2$ were prepared and reduced with hydrogen in accordance with the procedure described in section 3.2.1. The first sample was reduced without any further treatment; it is used as reference. The second sample (0.5 g) was exposed to synthesis gas in a conventional down flow fixed-bed reactor for a short time, as described by Sommen et al.¹².

The reaction conditions are reported in Table 3.16. The third sample was pretreated with $CO_{+}H_{2}$ in a high pressure down flow fixed-bed reactor as described by Stoop ³. The reaction conditions are also reported in Table 3.16. From these three samples Mössbauer spectra were recorded. These experiments were performed and interpreted by A.M. van der Kraan and E. Gerkema at the "Interuniversitair Reactor Instituut" in Delft.

Table 3.16

Reaction conditions of the pretreatment of sample 2 and 3

Sample	Temperature [°C]	Pressure [bar]	Flow [ml/min] ¹⁾	H ₂ /CO [mol/mol]
2	275	1	180	2
3	275	31 (1 day)	180	2
		21 (3 days)		
		11 (1 day)		
		1 (1 day)		

1) measured at 20°C and 1 bar

3.3.12.3 Results and discussion

The spectra of the samples mentioned are shown in Figure 3.22. The spectra of sample 1 and 2 are similar. These spectra suggest the absence of iron carbides. This should mean that the catalyst is still completely bimetallic after 3 hours on stream. However, the spectrum of sample 3 significantly differs from that of the other two samples. The Mössbauer spectrum of sample 3 indicates that RuFe(1:3)/SiO₂ is carburized completely after 144 hours on stream. The carbides have been characterized as χ -Fe₅C₂ and an iron carbide phase which consists of small particles with supermagnetic performance 13. The complete carburization of the iron implies that Ru and Fe completely segregated either before or during to the carburization process. Thus, these results clearly show that bimetallic RuFe(1:3)/SiO2 is not stable during the Fischer-Tropsch synthesis at a moderate temperature and high pressure. The presence of a small amount of iron carbide together with the metallic component for RuFe(4.8:1)/SiO2 after having been kept in a 2H2/CO mixture at 570 K and atmospheric pressure for only 38 hours 14 , suggests the instability of bimetallic RuFe on a silica carrier even at atmospheric pressure. Therefore, it is likely, that the decomposition of the bimetallic particles starts immediately after contact with CO and H₂. The extent of decomposition depends on the time on stream and the rate of





DOPPLER VELOCITY (MM.S⁻¹)

Fig. 3.22 Mössbauer spectra of 5 wt% RuFe(1:3)/SiO2.

Sample 1: only reduced

2: after 3 hours on stream at atmospheric pressure

3: after 6 days on stream at high pressure

decomposition which, in turn, depends on the reaction conditions.As could be expected, this rate increases with increasing temperature, pressure, synthesis gas conversion level (water vapour pressure!) and iron to ruthenium ratio.

Unfortunately, these conditions prevent the commercial application of this type of catalyst for the synthesis gas conversion via the Fischer-Tropsch route.

3.4 Discussion

During the first hours on stream, the production of a Ru/SiO_2 catalyst, freshly reduced with hydrogen, mainly consists of methane. This is probably due to a high surface coverage by hydrogen as is indicated by the high value of the H₂ chemisorption ³. The product distribution and the course of the activity is noticeably influenced by the addition of Fe to Ru. In contrast with Ru/SiO₂, the methane selectivity over fresh RuFe(1:3)/SiO₂ is relatively low but it increases rapidly as time goes on, along with the deactivation of the catalyst. The initial activity of RuFe/SiO₂ is much lower than that of Ru/SiO₂. This can also be explained by the lower H₂ coverage of an iron containing metal surface with respect to pure ruthenium ³.

Nevertheless, the very low olefin selectivity obtained with fresh $RuFe/SiO_2$ at a high pressure and a low CO conversion level indicates that the hydrogenation activity is still much too high to prevent secondary hydrogenation of olefins.

The results reported here have shown that the olefin selectivity drops extremely rapidly as the conversion increases. Secondary hydrogenation is already important at a 0.1% conversion level! This explains why such low selectivities are found at elevated pressure, relative to satisfying values at atmospheric pressure. It may also explain the selectivity difference between the Ru/SiO₂ catalyst and the much less active FeRu/SiO₂ catalyst.

Contrary to the initial period, the performance of $RuFe/SiO_2$ is similar to that of Ru/SiO_2 after only one day on stream. The activity, the product distribution and the olefin selectivity are hardly distinguishable. It appears that the properties of $RuFe/SiO_2$ are eventually determined by the Ru atoms alone, unaffected by the presence of Fe. The absence of a close contact between the Ru and Fe atoms is supported by Mössbauer analysis which indicates that Ru and Fe are segregated after a few days on stream at a high pressure. The segregation is probably accellerated by the carburization of Fe, which is thermodynamically favoured by higher CO pressures.

The olefin selectivity of $RuFe/SiO_2$ is very low relative to that of fused iron, particularly when the comparison is made after sometime on stream. The selectivity decreases extremely rapidly with increasing olefin/CO pressure ratio. Moreover, it appears that the hydrogen pressure strongly influences this selectivity, indicating that a simple competition model as described in Chapter 2 does not apply here. Apparently, the pressure of H₂ promotes the formation of paraffins either by an increase of the secondary hydrogenation or by an increase of the formation of paraffins directly from synthesis gas.

The low steady-state activity of $RuFe/SiO_2$ and Ru/SiO_2 is partly caused by the very strong inhibition by water. The CO conversion has to be below 1% for it to prevent the inhibition of the hydrocarbon synthesis by water. The product distribution is not significantly influenced by the water pressure, indicating that water does not occupy specific reaction sites.

Summarizing, it can be concluded that the addition of Fe to Ru supported on silica is only effective during the first hours on stream. The instability of the bimetallic RuFe particles under Fischer-Tropsch conditions results in the formation of a mixture of active Ru particles with inactive iron carbides with properties similar to a normal Ru/SiO₂ catalyst.

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Appendix 1

<u>Model I</u>

According to Kellner and Bell 20 the kinetics of hydrocarbon synthesis over Ruthenium catalysts can be derived from the following reactions:

1.	CO	+ *	k <u>]</u> k_1	CO*	θ _{CO}	= $K_1 p_{CO} \theta_v$
2.	C0*	+ *	k <u>2</u> k_2	C* + O*	$\Theta_C \Theta_0$	= $\kappa_2 \theta_{CO} \theta_v$
3.	H ₂	+ 2*	k3 ≄ k_3	2H*	θ _H	$= (K_3 p_{H_2})^{\frac{1}{2}}$
4.	0*	+ H ₂	k4	H ₂ O + *	r _{H2} 0	$= \kappa_4 \Theta_0 p_{H_2}$
5.	C*	+ H*	k <u>5</u> k_5	CH* + *	$\theta_{CH} \; \theta_v$	$= \kappa_5 \Theta_C \Theta_H$
б.	CH*	+ H*	k <u>6</u> k_6	CH ₂ * + *	$\theta_{CH_2} \theta_V$	$= \kappa_6 \Theta_{CH} \Theta_H$
7	CH2*	+ H*	k <u>7</u> k_7	CH3*+ *	$\theta_{CH_3} \theta_V$	$= \kappa_7 \Theta_{CH_2} \Theta_H$
8.	сн ₃ *	+ H*	k₿	CH ₄ + 2*	^r CH ₄	= $\kappa_8 \Theta_{CH_3} \Theta_H$
9.	сн ₃ *	+ CH2	* ^{k9}	C ₂ H ₅ * + *	$r_{C_2H_5}$	$= \kappa_9 \Theta_{CH_3} \Theta_{CH_2}$
10.	C2H5*	÷ *	kļ0	$C_2H_4 + H^* + *$	^r C₂H₄	= $\kappa_{10} \Theta_{C_2H_5} \Theta_v$
11.	с ₂ н ₅ *	+ H*	kļ1	C ₂ H ₆ + 2*	^r C₂ ^H 6	= $\kappa_{11}\Theta_{C_2H_5}$ Θ_{H}
12.	C ₂ H ₅ *	+ CH ₂	* ^k]2	C ₃ H ₇ * + *	rC ₃ H7	= $\kappa_{12} \Theta_{C_2H_5} \Theta_{CH_2}$
(0 _v	is the	fract	ion	of active sites which	h is not o	ccupied)

They suppose that the catalyst surface is saturated by CO at a low conversion level. However, it is clear from the experiments presented in Table 3.10 that the influence of water will have to be considered. Therefore it is supposed that water can absorb on the active sites and inhibites the rate of synthesis gas conversion: -168-

$$H_2O + * \Rightarrow H_2O*$$

It is supposed further that the rate determing step (RDS) is the hydrogenation of a $\mbox{CH}_{\rm X}$ intermediate:

$$CH_{x}^{*} + H^{*} \stackrel{RDS}{\rightarrow} CH_{x+1} + *$$
(14)

The formation of water via a sequence of Langmuir-Hinshelwood steps is more likely than a Rideal-Eley step. Therefore equation (4) is replaced by

$$Q^* + H^* \to OH^* + *$$
 (4.1)

$$OH^* + H^* \rightarrow H_2O + 2^*$$
 (4.2)

The rate determining step can be written as:

$$r_{\rm CO+H_2} = k \,\theta_{\rm CH_y} \,\theta_{\rm H} \tag{15}$$

which can be expressed as

$$r_{CO+H_2} = k' p_{CO} p_{H_2} k'(x+1) \theta_v^2$$
 (16)

whereby it is estimated that $k_6 \gg k_{-6}$ and $k_{41} \gg k_{-41}$ If CO, C* and H₂O* are the most abundant surface species equation (16) can be written as

$$r_{CO+H_2} = \frac{k' p_{CO} p_{H_2} k(x+1) k_1 k_2 k_{4.1} / k_5 k_3^{k}(x+1)}{\left[1 + k_1 p_{CO} + \frac{k_{4.1} k_1 k_2 p_{CO} k_3}{k_5} + \frac{p_{H_2O}}{k_1}\right]^2}$$
(17)

with $k' = k_5$, k_5k_6 , $k_5k_6k_7$ for x = 0,1,2 respectively.

Model II

This model is similar to model I but the reactions 4.1 and 4.2, the hydrogenation of surface oxygen and surface hydroxide, are estimated to be equilibrium reactions. This results in:

$$\mathbf{r}_{\text{CO+H}_{2}} = \frac{\mathbf{k}' (K_{1}K_{2}K_{3}K_{4.1}K_{4.2} K_{3}^{\prime\prime} (\mathbf{x}+1)/K_{13}) (\mathbf{p}_{\text{COPH}_{2}}/\mathbf{p}_{\text{H}_{2}O})\mathbf{p}_{\text{H}_{2}}^{\prime\prime} (\mathbf{x}+1)}{\left[1 + K_{1}\mathbf{p}_{\text{CO}} + \frac{K_{1}K_{2}K_{3}K_{4.1}K_{4.2}}{K_{13}} \cdot \frac{\mathbf{p}_{\text{COPH}_{2}}}{\mathbf{p}_{\text{H}_{2}O}} + K_{13}\mathbf{p}_{\text{H}_{2}O}\right]^{2}$$
(18)

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4. GAS-LIQUID MASS TRANSFER IN A SLURRY BUBBLE COLUMN REACTOR AT FISCHER-TROPSCH CONDITIONS

4.1 Introduction

The catalytic performance of Fe and FeRu/SiO₂ was investigated in a vigorously stirred autoclave in order to eliminate physical transport limitations. However, for the industrial application of the Fischer-Tropsch synthesis in the liquid phase a bubble column type reactor is preferred. Therefore, special attention is given to mass transfer in such a reactor.

The most important transport resistance in bubble column slurry reactors is the mass transfer from gas bubbles to liquid. The rate of the conversion of synthesis gas is first order with respect to the hydrogen pressure, provided the CO conversion level and the H_2/CO inlet ratio are lower than 90% and 1 respectively. Thus particular attention has to be given to the mass transfer of hydrogen.

Before explaining the aim of the experiments presented in this chapter, the scarce amount of literature concerning gas-liquid mass transfer in a Fischer-Tropsch bubble column reactor will be briefly discussed. The extent to which the performance of a Fischer-Tropsch bubble column reactor is limited by this hydrogen transport has been the subject of some discussions recently 1,3,4,5,6,7. The main subject of this discussion is the length of the mean gas bubble diameter. The calculation of this is hindered by a lack of consistent relations predicting the bubble diameter and specific contact area as function of observable parameters such as power consumption, specific gas load and gas, liquid and solids properties ¹⁸.

Furthermore reliable experimental data are scarce. Only Zaidi 9,12 and Hammer 13 have determined values of k_{La} in a bubble column containing catalyst particles suspended in molten wax. These k_{La} -values are related to CO. From this data the value of k_{La} for H_2 can be calculated, although the $k_{L,H_2}/k_{L,CO}$ ratio is also unclear 2,3,4,10,11 .

The gas-liquid surface has been measured by Calderbank et al.¹⁴ using a light-transmission method ¹⁵ in molten wax, but in the absence of suspended particles. From this report it follows that the mean bubble diameter in a Fischer-Tropsch bubble column is 2.1 mm in the bubble flow regime. The correlation of Deckwer ¹⁶ for calculation of the gas-liquid surface, which is frequently used, reads:

 $a = 4.5 U_{G,O}^{1.1}$

This correlation is based on values of the gas holdup and photographically determined bubble diameters, which are approximately 0.7 mm in the bubble flow regime 5,8,9. These bubble diameter measurements were also carried out without the presence of solids.

In view of this lack of experimental data for the value of $k_{La} H_2$ under Fischer-Tropsch conditions and especially the effect of solids on the value of k_{La} , it was decided to carry out our own experiments, particulary regarding the influence of catalyst particles and also that of the gas distributor and liquid column height on the value of $k_{La} H_2$.

Because of the low reaction rate, and the complicated behaviour of the catalyst, a catalytic model reaction for the determination of k_{La} was selected, rather than the Fischer-Tropsch reaction itself.

The results obtained in this study will be used in the last section to predict the importance of gas-liquid mass transfer to the rate of the Fischer-Tropsch synthesis in a slurry bubble column.

4.2 The resistance in series model

For the determination of the volumetric liquid-side mass transfer coefficient (k_La) one can apply the principle of the "resistance in series" model. In this section the suitability of the graphical determination of k_La is described by plotting the inverse of the reaction rate versus the inverse of the catalyst concentration.

According to this graphical method the $k_{L}a$ -value can be obtained from conversion measurements if the catalyst concentration, and hence the reaction rate, is varied over a sufficiently wide range. Under steady-state conditions and assuming the liquid phase is not mixed, the rate of transport from gas bubbles to liquid is given by

$$r = k_{La}(C*_{L} - C_{L})$$
 (4.1)

This rate is equal to the rate of transport from the bulk of liquid phase to the catalyst surface

$$r = k_{SaS}(C_L - C_S)(1 - \varepsilon_G)$$
(4.2)

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and the rate of reaction

$$r = k_{\rm fl} C_{\rm cat} C_{\rm S}(1 - \epsilon_{\rm G}) \tag{4.3}$$

Combining the Eqs.(4.1) - (4.3), in order to eliminate C_L and C_S , the following equation emerges:

$$\frac{C_{L}^{*}}{r} = \frac{1}{k_{L}a} + \frac{1}{k_{S} a_{S}(1-\epsilon_{G})} + \frac{1}{k \eta C_{cat}(1-\epsilon_{G})}$$
(4.4)

The right hand side of this equation consists of the sum of the gas-liquid mass transfer resistance, the liquid-solid mass transfer resistance and the "chemical" resistance, including pore diffusion limitation.

If catalyst particles are spheres of diameter d_p , than

$$a_{\rm S} = \frac{6 C_{\rm cat}}{\rho_{\rm S} d_{\rm p}}$$
(4.5)

Subsituting of Eq.(4.5) into (4.4) gives:

$$\frac{C_{L}^{*}}{r} = \frac{1}{k_{L}a} + \frac{1}{k_{0}(1-\epsilon_{G})} \cdot \frac{1}{C_{cat}}$$
(4.6)

wherein

$$\frac{1}{k_0} = \frac{1}{k_S} \cdot \frac{\rho_S d_p}{6} + \frac{1}{k_\eta}$$
(4.7)

Furthermore, if it is assumed that gas bubbles behave as spheres, an assumption which is justified in the homogeneous regime and for non-viscous liquids, the gas bubble interfacial area, a_S, can be calculated as follows:

$$a_{\rm S} = \frac{6 \epsilon_{\rm G}}{d_{\rm b}} \tag{4.8}$$

Combining Eq.(4.8) and (4.6) we obtain

$$\frac{C_{L}^{\star}}{r} = \frac{d_{b}}{6 k_{L} \epsilon_{G}} + \frac{1}{k_{o} (1-\epsilon_{G})} \cdot \frac{1}{C_{cat}}$$
(4.9)

A plot of CL*/r versus 1/Ccat should yield a straight line with the

ordinate intercept representing the gas-liquid mass transfer resistance $(1/k_{L}a)^{-9,17}$. However, this implies that both d_p , ϵ_G and k_L are not affected by the catalyst loading. Later on it will be demonstrated that this assumption is only justified at very low catalyst concentrations. It is interesting to note that the value of the slope in Eq.(4.9) depends on the gas holdup. This means that the slope decreases with increasing gas velocity due to an increase of the gas holdup. Naturally the slope will flatten also with an increase of the temperature due to a faster reaction rate.

When one or more parameters on the right hand side of Eq.(4.9) change due to the addition of catalyst particles, a plot of C_L*/r versus $1/C_{Cat}$ will not yield a straight line. The effects of possible changes of ϵ_G , d_b and k_L on the value of k_La and the shape of the curve will be discussed briefly. We start with the estimation that the value of the gas holdup decreases due to the addition of catalyst particles. At higher catalyst loadings this decrease of the gas holdup can cause an increase of the total resistance instead of the usual, gradual decline as shown in Figure 4.1. In order to construct this figure, it is assumed that the gas holdup decreases linearly with increasing catalyst concentration (which is found experimentally). Thus, at higher catalyst concentration the increase of the $1/k_La$ -value is much higher than the decrease of the "chemical resistance". This decrease of the k_La -value may remain unnoticed due to the usual experimental scattering, if the value of k_La is determined on basis of a relatively small range of catalyst concentrations.

In case the mean gas bubble diameter increases due to the addition of solids, naturally this also causes a decrease of the k_La -value. Since a linear increase of the bubble diameter is not likely, it is assumed that the bubble diameter quickly reaches an equilibrium value. When the increase of the bubble diameter depends exponentially on the catalyst concentration a curve as shown in Figure 4.2 will be found. Again it may be noted that this deviation of the normal straight line might not be visible by scattering of the data points.

Finally, catalyst addition may influence the k_L -value and thus k_La as well. In this connection it may be said that this effect on the k_La -value cannot be distinguished from that due to the increase of the bubble diameter if both k_L and d_b change by the addition of catalyst particles.

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Assumptions:

 $k_{L}a = 1.0 \quad (C_{cat} = 0)$ $e_{G} = 0.322(1-0.00298C_{cat})$ $k_{o}n = 0.074$

 $m^{3}L/m^{3}L+G s$ $m^{3}G/m^{3}L+G$ $m^{3}L/kg_{cat} s$

Deviations from the straight line, obtained according to the graphical method (Eq.(4.9)), also emerge when the gas absorption rate is enhanced by the addition of catalyst particles. Two possibilities can be distinguished. The first one is enhancement by an increase of k_L 19,20,21,22,23. This "shuttle" mechanism or "grazing" model has been proved nearly exclusively for active carbon particles ²³, i.e. particles with extremely high specific surface areas. Thus, this type of enhancement is of no importance for other, more common, catalyst materials.







The second possibility is enhancement of the gas absorption rate by reaction on catalyst particles in the liquid film around gas bubbles. In that case two conditions must be fulfilled. Firstly, the catalyst particle diameter, d_p , has to be sufficiently small compared to the liquid film thickness, δ , for instance $d_p = 0.1\delta^{-23}$. Secondly, the concentration of the gas in the bulk liquid must be approximately zero 24 . It is clear that the second condition is not fulfilled when applying

the graphical method ($C_{H_2,L}>0$). It may be noted that in case the concentration of the gas in the liquid is indeed approximately zero (high catalyst concentration) the catalyst must be extremely active in order to cause a substantial conversion in the liquid film. It can thus be concluded that enhancement of gas absorption will not play a role in this study, in which a common catalyst is used.

Finally, the value of k_{La} may depend on the concentration of the catalyst particles. In that case, no linear curve is obtained if C_L*/r is plotted versus 1/m. Nevertheless, this figure can be used for the determination of the order of magnitude of the k_{La} -value. The influence of the catalyst concentration on the k_{La} -value cannot be determined by this method.

Therefore, in this study, two procedures have been applied. The first procedure, the graphical method (variation of the catalyst loading), was applied for the determination of the k_La -value at low catalyst concentrations. The second procedure was applied for the determination of k_La at higher solid concentrations. The initial amount of catalyst was high enough to provide that the conversion of H_2 was only determined by the gas-liquid mass transfer resistance. Therefore, a change of the conversion by the addition of catalyst or inert particles could be directly attributed to a change of the k_La -value.

4.3 Calculation of kLa from conversion data

The volumetric mass transfer coefficient $k_{L}a$ of H_2 can be determined applying the graphical method or directly from the conversion of H_2 as pointed out in the previous section. In both cases the behaviour of the gas and liquid phase has to be known. This section describes the relation between the hydrogen conversion, the value of the gas-liquid mass transfer resistance and the chemical resistance for various reactor models. All models are based on the following assumptions:

- * the reaction equation is $A + H_2 \rightarrow P$
- * the production rate of P,r, is first order in H_2 and independent of the concentration of A : $r = k_0 C_{H_2,L}$
- * the catalyst concentration in the liquid phase is uniform
- * the temperatures of the gas, liquid and solid phase are uniform and equal

Model 1. Gas phase behaves as plug flow; liquid phase is not mixed

The combination of a tall reactor with respect to the diameter and a rapid reaction results in a concentration profile of hydrogen in the liquid phase over the height of the reactor. The liquid phase can be considered as non-mixed if the reciprocal first order reaction constant is much smaller than the mixing time. Especially for a reactor which is relatively high the mixing may not be sufficiently rapid to prevent a concentration profile in the liquid phase. In that case the mixing of the gas phase occurs probably slowly as well because the mixing of both phases are related. When the gas mixing time is so large that this time is much larger than the gas residence time, the gas phase can be regarded as plug flow. The mass balance of hydrogen over a differential element in this bubble column is then:

$$\frac{-d(U_G C_{H_2,G})}{dz} = k_L a(C^*_{H_2,L} - C_{H_2,L})$$
(4.10)

The reaction rate, r, follows from Eq.(4.4) and is equal to

$$r = k_{ov} C_{H_2,L}^* = k_{L^a} (C_{H_2,L}^* - C_{H_2,L})$$
(4.11)

In this equation $1/k_{OV}$ is the overall resistance, i.e. the sum of the resistances mentioned in Eq.(4.4) Combination of the Eqs. (4.10) and (4.11) gives:

$$\frac{-d(U_G C_{H_2,G})}{dz} = k_{OV} \frac{C_{H_2,G}}{m}$$
(4.12)

where m is the solubility coefficient

$$m = \frac{C_{H_2,G}}{C_{H_2,L}}$$
(4.13)

Both gas velocity and hydrogen concentration depend on the conversion of $\rm H_2$

$$U_{\rm G} = U_{\rm G}^{\rm in}(1-f X_{\rm H_2})$$
 (4.14)

$$C_{\rm G} = C_{\rm H_2}^{\rm in}, G \frac{(1-X_{\rm H_2})}{(1-f X_{\rm H_2})}$$
 (4.15)
where f is the H_2 fraction in the inlet gas flow.Finally, after substituting Eqs.(4.15) and (4.16) in Eq.(4.12) and integrating over the height L, the relation between the overall resistance and the conversion of H_2 is obtained:

$$\frac{1}{k_{ov}} = \frac{L_{L+G}}{U_{G}^{in} m_{H_2}(f-1)\ln(1-X_2) + fX_{H_2}}$$
(4.16)

The value of $k_{\rm OV}$ is determined experimentally; the value of $k_{\rm L}a$ can be calculated.

Model 2. Gas phase behaves as plug flow; liquid phase is perfectly mixed

A perfectly mixed liquid phase is approached in bubble columns if the chemical reaction is slow compared to the mixing time of the liquid phase. Nevertheless, the mixing time of gas phase can be large relative to the gas residence time, resulting in a plug flow behaviour of the gas phase. The mass balance of H_2 for the gas phase is given by:

$$\frac{-d(U_G C_{H_2,G})}{dz} = k_L a(C_{H_2,L} - C_{H_2,L})$$
(4.17)

Replacing Eqs.(4.13), (4.14) and (4.15) in (4.17) gives

$$U_{G}^{in} C_{G}^{in} \frac{d X_{H_{2}}}{dz} = k_{L}a \left[\frac{C_{G}^{in}}{m_{H_{2}}} \cdot \frac{1 - X_{H_{2}}}{1 - f X_{H_{2}}} - C_{H_{2},L} \right]$$
(4.18)

This equation can be integrated without replacement of $C_{\rm L}$ because this concentration is constant over the height. Thus, we obtain

$$\int_{0}^{XH_{2}} \frac{1 - f X_{H_{2}}}{1 - X_{H_{2}} - \frac{C_{H_{2},L} m_{H_{2}}(1 - f X_{H_{2}})}{C^{in}_{H_{2},G}} = \int_{0}^{L_{L}+G} \frac{k_{L}a}{U^{in}_{G} m_{H_{2}}}$$
(4.19)

or

$$\frac{f-1}{\left[1-\frac{f C_{H_2,L} m_{H_2}}{C^{in}_{H_2,G}}\right]^2} \ln \left[1-\frac{\frac{1-f C_{H_2,L} m_{H_2}}{C^{in}_{H_2,G}}}{1-\frac{C_{H_2,L} m_{H_2}}{C^{in}_{H_2,G}}}\right] + \frac{f}{1-\frac{f C_{H_2,L} m_{H_2}}{C^{in}_{H_2,G}}} X = \frac{k_L a L_{L+G}}{U_G^{in} m_{H_2}}$$

$$(4.20)$$

The unknown C_L in Eq.(4.20) can be written in terms of conversion with the help of the following mass balances:

$$r = k_S a_S (C_{H_2,L} - C_{H_2,S})(1-\epsilon_G)$$
 (4.21)

$$\mathbf{r} = \mathbf{k} \, \eta \, C_{\text{cat}} \, C_{\text{H}_2, \text{S}} \, (1 - \epsilon_{\text{G}}) \tag{4.22}$$

$$r = U_{G}^{in} \wedge C^{in}_{H_2,G} X_{H_2} / V_{L+G}$$
(4.23)

After combining Eqs. (4.21), (4.22), (4.23), and (4.7), the following equation is obtained:

$$C_{L} = \frac{U_{G}^{in}C_{G}^{in} X_{H_{2}}}{k_{o} C_{cat} L_{L+G}(1-\varepsilon_{G})}$$
(4.24)

Finally, on replacing Eq.(4.24) in Eq.(4.20) and introducing the dimensionless parameters

$$N_{\rm m} = k_{\rm L} a \frac{L_{\rm L+G}}{m U_{\rm G} in}$$
(4.25)

and

$$N_{r} = k_{o} C_{cat}(1-\varepsilon_{G}) \frac{L_{L+G}}{m U_{G}^{in}}$$
(4.26)

the following equation is obtained:

$$\frac{f-1}{\left[1-\frac{f X_{H_2}}{N_r}\right]^2} \ln \left[1-\frac{1-\frac{f X_{H_2}}{N_r}}{1-\frac{X_{H_2}}{N_r}} . X_{H_2}\right] + \frac{f X_{H_2}}{1-\frac{f X_{H_2}}{N_r}} = N_m \quad (4.27)$$

Clearly, the value of $k_{L}a$ cannot be determined by way of the method indicated in Eq.(4.9). This is only possible for the special case where the contraction of the gas phase is neglible (low value of f), in which case Eq.(4.27) can be simplified and written as follows:

$$\frac{1}{X_{H_2}} = \frac{1}{1 - \exp\left[-k_L a \frac{L_{L+G}}{m_{H_2} U_G^{in}}\right]} + \frac{U_G^{in} m}{k_O L_{L+G}(1-\epsilon_G)} \cdot \frac{1}{C_{cat}}$$
(4.28)

The value of k_{La} can be found via a similar method as given in section 4.2. Thus, when 1/X is plotted versus $1/C_{cat}$, a straight line should arise, provided the conditions reported in section 4.2 are fulfilled. The value of k_{La} and the reaction rate constant can be determined from the intersection on the ordinate and slope respectively.

Model 3 Gas and liquid phase behave as two mixed reactors in series

The last model is based on the assumption that the reactor can be described as two mixed reactors in series (see Figure 4.3). The mass balances for the first mixed reactor are

$$U_{G}^{0} C^{0}_{H_{2},G} - U_{G}^{1} C^{1}_{H_{2},G} = k_{L} a (C^{1}_{H_{2},G}/m - C^{1}_{H_{2},L}) k_{L+G}$$
(4.29)

$$k_{La}(C^{1}_{H_{2},G}/m - C^{1}_{H_{2},L}) \& V_{L+G} = k_{SaS}(C^{1}_{H_{2},L} - C^{1}_{H_{2},S}) \& V_{L+G}(1-\varepsilon_{G}) \quad (4.30)$$

$$k_{SaS}(C^{1}_{H_{2},L}-C^{1}_{H_{2},S})^{k}V_{L+G}(1-\varepsilon_{G}) = k \eta C_{cat} C^{1}_{H_{2},S}^{k}V_{L+G}(1-\varepsilon_{G}) \quad (4.31)$$

By combining Eqs. (4.29), (4.30), and (4.31) Eq.(4.32) is obtained

$$U_{G}^{0} C_{H_{2},G}^{0} - U_{G}^{1} C_{H_{2},G}^{1} = k_{ov} C_{H_{2},G}^{1} L_{L+G}^{1} m$$
 (4.32)

For the second mixed reactor Eq.(4.33) is obtained similarly

$$U_{G}^{1}C_{H_{2},G}^{1} - U_{G}^{2}C_{H_{2},G}^{2} = k_{ov} C_{H_{2},G}^{2} \% L_{L+G}^{1} m$$
 (4.33)

Replacing Eq.(4.32) in (4.33), then rearranging, Eq.(4.34) is obtained in which the conversion is expressed:

$$1 - X_{H_2} = \frac{U^1_G + U^2_G}{(U^1_G + k_{ov} / L_{L+G}/m) (U^2_G + k_{ov} / L_{L+G}/m)}$$
(4.34)



Fig. 4.3 Diagram of model 3

The gas velocities U_G^1 and U_G^2 in this equation are dependent on the conversion. Therefore, k_{ov} cannot be written as a function of X. In the case the gas contraction is negligible ($U_G^1 = U_G^2 = U_G$), Eq.(4.34) can be reduced to:

$$\frac{1}{k_{ov}} = \frac{\frac{\chi_{L_{L+G}}}{m_{H_2} U_G} \cdot \frac{(1-\chi_H)^{\frac{1}{2}}}{1-(1-\chi_{H_2})^{\frac{1}{2}}}$$
(4.35)

Knowing the values of $k_{\rm OV}$ from measured conversion data, the value of $k_{\rm L}a$ can be calculated.

4.4 Choice of the reactor models

The models which have been used for calculating the overall resistance from the conversion are chosen on account of calculated values of the mixing time of the liquid, t_m , the number of mixing cells for the gas phase and experimental determined values of the reaction time t_r .

The mixing time of the liquid is calculated according to 43:

$$t_{m} = 3.75 \ \varepsilon_{G} \ \frac{D_{r}^{2/3}}{U_{G}} \left[1 - 0.174 \left[\frac{L_{L+G}}{D_{r}} - 1 \right] + 0.17 \left[\frac{L_{L+G}}{D_{r}} - 1 \right]^{2} \right] \quad (4.36)$$

The characteristic reaction time, t_r , simply follows from the experiments

$$t_r = \frac{1}{k_0 m}$$
(4.37)

The number of mixing cells for the gas phase are calculated from the Bodenstein number $^{\rm 44}$

$$\frac{1}{n} = \frac{2 [Bo - 1 + exp (-Bo)]}{Bo^2}$$
(4.38)

wherein Bo = $\frac{U_G^0 L_{L+G}}{D_G \epsilon_G}$

For the calculation of the Bo-number the dispersion coefficient of the gas phase must be known. This dispersion coefficient has been calculated according to the correlation of Mangartz and Pilhofer 42

$$D_{\rm G} = 5 \times 10^{-4} \frac{U_{\rm G}^3}{\epsilon_{\rm G}^3} D_{\rm r}^{1.5}$$
(4.39)

With help of the relations mentioned above, the behaviour of the gas and liquid phase are estimated for the bubble column used, having an inner diameter of 5 cm. The reactor models chosen for four experimental situations are shown in Table 4.1. The choice has been made on the base of reaction time, number of mixing cells and mixing time. The models 2

Table 4.1

Calculated liquid mixing times, numbers of mixing cells of the gas phase and reaction times for four experimental situations. The superficial gas velocity varies from 2-5 cm/s.

Distributor	L/D _r		tm	nG	tr	Chosen			
	[-]		[s]	I	[-]	[s]	liquid	gas	no.
perforated	2%		1-2	13	4-2%	2-4	2 mixing cells	2 mixing the state of the state	3
perforated	20	>	160	>	10	4-20	non-mixed	plug flow	1
porous	2½		4-6	>	6	1-20	mixed	plug flow	2
porous	20	>	240	>	40	2-40	non-mixed	plug flow	1

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and 3 have been chosen at low L/D_r ratio (2%). When this ratio exceeded the value of 5, model 1 was used. Using the porous plate at a low L/D_r ratio (2%), the reaction time was longer than the mixing time when the catalyst loading was low. Although the opposite was the case for a higher loading, model 2 was used because the situation at lower catalyst concentrations is the most important as than the graphical method was applied. It should be borne in mind that the degree of mixing at high catalyst concentrations is less important because the hydrogen concentration then approaches zero. The gas flow for this case (second line from the bottom in Table 4.1) is supposed to be plug flow. It should be noted that the difference of the degree of mixing between the perforated and porous plate is caused by the difference in gas holdup as will be shown later.

4.5 Choice of the model reaction

A simple reaction for measuring the gas-liquid mass transfer resistance of hydrogen is more appropriate than the Fischer-Tropsch synthesis itself since the latter reaction is very complex and perhaps too slow for accurate determination of the volumetric mass transfer coefficient. Such a catalytic model reaction must comply with a number of conditions. The main ones are:

- * (pseudo) first order in hydrogen
- * high reaction rate
- * applicable at 300°C

The requirements concerning the catalyst are:

- * stable up to 300°C
- * selective
- * non-coagulating

A suitable reaction appeared to be the hydrogenation of ethene catalysed by palladium on alumina. This system complies with the conditions mentioned above provided that the inlet ethene and hence is at least 97%. The liquid phase can then be regarded as saturated with ethene and the reaction rate then depends on the hydrogen pressure only. The activity of the catalyst is so high that a few weight percent is enough to reduce the hydrogen concentration in the liquid phase to practically zero. The only drawback of this catalyst is the formation of foam in case of low concentrations of very small catalyst particles (d_p <10 µm). The foam dissapears when the catalyst concentration is increased to approximately 3 wt% or higher. With larger particles the production of foam is not significant, irrespective of the concentration.

4.6 Experimental

4.6.1 Materials and catalyst

All the gases used (ethene, helium, hydrogen and nitrogen) were obtained from cylinders (purity>99.5%). The cylinder with ethene (polymer grade) contained a maximum of 0.05% ethane, which was experimentally veryfied. Nitrogen, used as carrier gas, was dried with molsieves. The reactant gases were not purified. The catalyst, a prereduced hydogenation catalyst, was supplied by Degussa Nederland B.V. It consists of 5 wt% $Pd/\gamma-Al_2O_3$ and was designated as E 207 R/D. The specific surface area was $400m^2/g$. Fractions with a mean diameter of 35 and 45 µm were obtained after sieving. A 7 µm mean diameter fraction was obtained by crushing a sieve fraction with a diameter smaller than 25 µm. Fresh catalyst particles were added to the reactor without further treatment. Used catalyst particles were washed and reduced with hydrogen at 250°C.

The liquid phase, squalane, was equal to that used for the kinetic investigation (see Chapter 2). Squalane was recycled by separation of catalyst particles and vacuum destillation at 70°C.

4.6.2 Apparatus

A schematic diagram of the apparatus is shown in Fig. 4.4. The reactor consists of a glass tube, (height 1.6 m and diameter 0.050 m) which is heated externally by electric wire. The amount of heat is regulated by a PID temperature controller (Eurotherm 070) which holds the reactor temperature constant at 250°C within 0.5°C. The temperature is measured by a thermocouple type K which is inserted in the liquid phase. The gas distributor is a porous plate with a pore diameter range of 16-40 μ m or a perforated plate with 19 300 μ m diameter holes. Only for holdup experiments porous plates with different pore size ranges were used.



Fig. 4.4 Experimental setup:

(1) calibration mixture; (2) molsieves; (3) cooling; (4)
electric heat wire; (5) cyclones for entrained squalane; (6)
oil filter; (7) magnetic valve; (8) relais; (9) time switch;
(10) sample valve; (11) water saturator

Ethane and ethene were analysed on-line by a Pye 104 gas chromotograph equipped with a flame ionization detector. The GLC signal was integrated by a HP 3392A integrator. Initially, the concentration of hydrogen was also measured for the sake of controlling. Since both analyses agreed closely, only ethane and ethene were measured during most of the experiments. The traces of ethane present in the ethene feed were measured before the start of each experiment. The fraction of ethane in the reactor outlet gas originating from the ethene cylinder was usually below 10 vol%.

4.7 Results and discussion

4.7.1 Effect of the gas distributor

Production of small bubbles by a porous plate distributor with small pore diameters makes sense only, if the diameter of bubbles remains small during a considerable part of their residence time. In that case gas holdup and gas-liquid mass transfer will be noticeably larger than in case initally larger bubbles are formed. The influence of the gas distributor type thus provides information on the tendency of bubbles to coalesce. This section deals with the influence of the type of the gas distributor on the gas holdup followed by the effect on the gas-liquid mass transfer.



Fig. 4.5 The gas holdup as a function of the gas velocity in the absence of solids for various gas distributors. The liquid column height is 0.80 m

The gas holdup observed in a bubble column filled with squalane only is considerably larger with a porous plate than with a perforated plate as gas distributor as shown in Figure 4.5. The larger gas holdup observed with a porous plate can be attributed to the visibly smaller gas bubbles. The pore diameter of the porous plate hardly affects the gas holdup in the bubble flow regime (up to 4-5 cm/s). In the transition range, however, the porous plate with the smallest pore diameter produces the largest gas holdup as shown in Figure 4.5. Especially at higher gas velocities (>4cm/s) relatively large bubbles are formed which have a low contribution to the gas holdup due to their high rising velocity. These (large) bubbles are formed more easily at a distributor with larger pore or orifice diameter. Consequently, the maximum gas holdup and the change



Fig. 4.6 The gas holdup as a function of the gas velocity in the presence of solids. The liquid level is 0.13 m. The particle diameter and catalyst concentration are 45 μ m and 120 kg/m³_L (15.4 wt%) respectively

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from bubble to heterogeneous flow is reached at a lower gas velocity when the perforated plate is used as shown in Figure 4.5. The large difference between the gas holdup obtained with a porous plate and that with a perforated plate as gas distributor indicates that small bubbles coalesce slowly in a bubble column with squalane as liquid.

The addition of solids does not significantly reduce the large difference in gas holdup between a porous and perforated plate as shown in Figure 4.6, in which the gas holdup is depicted versus the gas velocity for a suspension with 15.4 wt% solids. Generally, the addition of solids leads to a gas holdup decrease as will be shown in section 4.7.3. An exception is the gas holdup at gas velocities above 4 cm/s with a perforated plate as gas distributor as shown in Figure 4.7. The higher



Fig. 4.7 The gas holdup as a function of the gas velocity in the absence and presence of solids. The liquid level is 0.60 m. The gas distributor is the perforated plate

gas holdup with 11.7 wt% solids in this figure indicates that the change from bubbling to heterogeneous flow may occur at higher gas velocities by the presence of solids. Probably, the solids inhibit the formation of large bubbles specially bubbles with the dimension of the column diameter.



Fig. 4.8 The value of $k_L a$ as a function of the gas velocity. The suspension level is 0.13 m. The catalyst concentration is 80 kg/m^3_L (10.8 wt%).

In consequence of the higher gas holdup and the smaller gas bubbles, the gas-liquid mass transfer is considerably larger when a porous plate is used instead of a perforated plate as shown in Figure 4.8. The k_{La} porous/ k_{La} perforated ratio (\approx 2), however, is smaller than the gas holdup ratio (\approx 3). This may be attributed to an (average) lower k_{L} value with the porous plate due to the presence of a large amount of small bubbles with a rigid surface. The diameter of these small bubbles is approximately 0.7 mm as this value is reported by Zaidi et al.¹² for gas bubbles in a Fischer-Tropsch wax without solids. Although visible observation in the three phase bubble column indicates that bubbles grow rapidly as a function of the height, the bubble diameter close to the porous plate will be of the order of 0.7 mm. The k_L value of such small bubbles is significantly lower (\simeq 50%) than that of bubbles with a diameter larger than 2.5 mm, according to the well-known correlation of Calderbank and Moo-Young ²⁶. This lower k_L value decreases the effect of both the larger gas holdup and (initially) smaller bubbles formed by the porous plate.



Fig. 4.9 The gas holdup as a function of the gas velocity for various pore sizes of a porous plate distributor in the absence of solids

4.7.2 Effect of the liquid/suspension level

The degree of coalescence determines the influence of the liquid/ suspension level on the mass transfer in a bubble column. In this section the influence of this level on the gas holdup will be considered first and thereafter on the volumetric mass transfer, for various catalyst concentrations.

In the two phase system squalane/nitrogen or squalane/ethene, the liquid level does not affect the gas holdup in the bubble flow regime for both types of gas distributors as shown in Figure 4.9. This indicates that coalescence is rather unimportant in this flow regime. Increasing the gas velocity up to 9 cm/s does not change this situation with a sieve plate. With a porous plate, however, the liquid level does reduce the gas holdup when the gas velocity is larger than 4 cm/s as shown in Figure 4.9. In this case thus coalescence cannot be neglected . Nevertheless, squalane without solids can be considered as a "non-coalescending medium".



Fig. 4.10 Effect of the suspension level on the gas holdup. The gas distributor is the porous plate. The diameter of the catalyst particles is 45 μm

Due to the addition of catalyst particles the influence of the suspension level on the gas holdup is considerably different compared with the situation in the absence of solids. Contrary to the two phase system the gas holdup now decreases considerably with increasing suspension column height. This decrease already occurs at low gas velocities as shown in Figure 4.10. The effect of the height of the suspension column is more pronounced at a higher particle concentration (see Figure 4.8). This concentration effect will be discussed further in the following section. The lower gas holdup at a higher liquid level can be attributed to a larger mean bubble diameter, and hence a higher bubble rising velocity 25 . It can be expected that the volumetric mass transfer decreases with increasing suspension column height as a consequence of both a lower gas holdup and a larger mean bubble diameter.

The value of k_{La} decreases indeed as a function of the suspension column height in the three phase system as shown in Figure 4.11. If the



Fig. 4.11 The value of $k_L a$ as a function of the suspension level. The catalyst concentration is 73 kg/m³_L (10 wt%)

assumption is made that the k_L value does not vary significantly, the parameter $k_L a / \epsilon_G$ is inversely proportional to the mean bubble diameter. This $k_L a / \epsilon_G$ ratio appears to decrease sharply as shown in Figure 4.12, indicating that the mean bubble diameter increases. After comparing Figures 4.9 and 4.10 the conclusion is that the bubble diameter is the dominating factor with respect to the dependence of the volumetric mass transfer coefficient on the suspension level for 45 µm catalyst particles.



Fig. 4.12 The $k_L a/e_G$ ratio as a function of the suspension level. The catalyst concentration is 73 kg/m³_L (10 wt%)

4.7.3 The effect of solids on the gas holdup and volumetric mass transfer

This section deals with the influence of solid particles on the gas holdup and the volumetric gas/liquid mass transfer in a 5 cm bubble column at 250°C with squalane as the liquid phase.

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The addition of 45 μ m particles results in a decrease of the gas holdup in all circumstances. The conditions only determine the degree of the gas holdup decline. These conclusions can be drawn from Figure 4.13 which demonstrates the gas holdup as a function of the solid concentration at various conditions. The largest gas holdup decrease is obtained with the porous plate, a low liquid level and a high gas velocity. This means that in the presence of small particles (45 μ m mean), in contrast to the two phase system, small bubbles coalesce easily, causing a lower gas holdup. Relatively large bubbles produced by a perforated plate do not coalesce significantly as is indicated by the small decline of the gas holdup compared with that observed with a porous plate (see Figure 4.13).

Addition of 45 µm catalyst particles, thus, results in a lower gas holdup. Consequently, the volumetric mass transfer will decrease as well. The effect of the solid concentration together with that of the type of the gas distributor and the suspension column height are shown in Figure 4.14 and 4.15. The value of $k_{L}a$ is very high when the catalyst concentration is lower than 1 wt% and the initial bubbles are small which can be achieved by using a porous plate. However, the value of k_{La} observed with this gas distributor drops sharply with increasing solid concentration. When also the suspension level is increased to 1 m the value of $k_{f,a}$ obtained is even lower with a porous plate than that with the perforated plate in a bubble column with an equal concentration of solids but with a lower suspension level. Thus the influence of the suspension column height dominates the influence of the gas distributor for moderate solid concentrations. This indicates that the mean bubble diameter at a high suspension level is lower than the initial bubble diameter formed by the perforated plate. Obviously, the lowest mass transfer is obtained in the column equipped with the perforated plate at a 1 m suspension column height. It is interesting to note that this $k_{f,a}$ value is about 10 times lower than that observed with a porous plate at a low suspension level and a low solid concentration.

It is important to know whether an equilibrium bubble diameter is reached or not by the addition of solids. In any case the $k_{L}a$ value, which is an average value over the whole suspension volume, will decrease with increasing suspension column height. Only the course of the $k_{L}a$ decline



Fig. 4.13 The effect of the solid concentration on the gas holdup. Legends: open symbols, perforated plate; filled symbols, porous plate



Fig. 4.14 The value of k_{La} as a function of the gas velocity under various conditions. Legends: open symbols, perforated plate; filled symbols, porous plate



Fig. 4.15 The effect of the solid concentration on the value of $k_{\rm L}a$

differs. In case an equilibrium bubble diameter is reached rapidly (just above the gas distributor) $k_{L}a$ will approach rapidly a minimum value with increasing suspension column height. If bubbles even at the top of the column have not reached an equilibrium diameter, the $k_{L}a$ value will continue to decline with increasing suspension column height. The influence of the suspension column height on the hydrogen conversion for two different particle sizes is shown in Figure 4.16. The conversion with



Fig. 4.16 The conversion of hydrogen as a function of the suspension level for the perforated plate. The catalyst concentration is 73 kg/m³_I (10 wt%). The gas velocity is 3 cm/s

7 μ m diameter particles increases continuously but surprisingly the conversion with 45 μ m particles reach a maximum value at approximately 0.7 m and appears even to decrease slightly with increasing suspension column height. This can only be explained by a decrease of the k_La-value in the lower part of the column. As k_La decreases with increasing solid concentration (see Figure 4.14), apparently the increase of the

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suspension column height leads to an increase of the solid concentration in the lower part of the column. In order to verify the presence of a concentration profile, the solid concentration was measured at the top of the column for 3 and 45 μ m diameter particles (suspension level and superficial gas velocity were 1.12 m and 3 cm/s respectively). It appeared that 3 μ m particles were completely homogeneously suspended (5 wt % suspension) whereas with 45 μ m particles the solid concentration at the top was only 35% of the mean concentration (10wt%).

In order to confirm that the influence exerted by the solid concentration on k_{La} depends strongly on the particle diameter, the following experiments were carried out. The column was filled with 10 wt% 7 μ m diameter catalyst particles. After that carrier particles (these



Fig. 4.17 The effect of the addition of 35 and 45 μ m diameter carrier particles to a 10 wt% suspension of 7 μ m diameter catalyst particles on the value k_La. The gas velocity is 3 cm/s. The gas distributor is the perforated plate

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particles are indentical to the catalyst particles only palladium is lacking) with a diameter of 35 or 45 µm were added to the column. The effect of these carrier particles is shown in Figure 4.17. This figure shows that the presence of just a few percent of carrier particles causes a strong decrease of the $k_{L}a$ value. This decline of $k_{L}a$ depends both on the suspension level and the particle diameter. As these factors affect especially the concentration profile in the column 27, it may be concluded that this profile is a main cause of the strong $k_{\rm f}$ a decline observed with 45 µm solids in Figure 4.17 and the conversion decrease in Figure 4.16. This points to a sharp decrease of k_f as well, as shown in Figure 4.11. Thus both as a result of the suspension column height increase (Figure 4.16) and carrier addition (Figure 4.17), the solid concentration in the vicinity of the distributor increases, resulting in a lower specific area in this region. The decrease of the gas-liquid area is caused by an increased coalescence resulting both in a lower gas holdup and in a larger mean bubble diameter as indicated by Figure 4.18. Here the $k_{\Gamma,a}/\epsilon_{C}$ decline represents the increase of the mean bubble diameter, provided the k_L value is not significantly changed.

It is interesting to note that the k_r a value reaches a constant value when 4 wt% 45 µm carrier particles are added for the case of the suspension level being 0.88 m (see Figure 4.17). This indicates that the suspension level at which bubbles reach their equilibrium diameter is not affected anymore by further increasing the carrier particle concentration. In contrast to a high suspension level, at 0.33 m the k_{La} value continues to decline with increasing carrier concentration to a value of 0.35 $m_{T,f}^{3}$, $m_{T,fc}^{3}$, at 10 wt% carrier particles. This value is much lower than with 10 wt% 45 μ m catalyst particles alone (0.52 m³_L/m³_{L+G}.s). Apparently, the 7 µm carrier particles strengthen the affect of the 45 µm particles on the coalesence. This implies that the level at which the equilibrium bubble diameter is reached in the 0,33 m column is lower when both 7 and 45 µm particles are present. This situation, however, is different at a high suspension level. The $k_{L}a$ value with 10 wt% 45 μ m alone and with the combination of 10 wt% 7 µm and 4-8 wt% 45 µm carrier particles are 0.24 and 0.22 $m_{I,fm_{L+G}}^{3}$ s respectively at 0.88 m suspension column height. As these values are so close together it can be concluded that the k_{L} avalue is not affected by the coexistence of 7 and 45 μ m

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Fig. 4.18 The effect of the addition of 35 and 45 μ m diameter carrier particles to 10 wt% suspension of 7 μ m diameter catalyst particles on the k_La/e_G ratio. The gas velocity is 3 cm/s. The gas distributor is the perforated plate

particles compared with 45 μ m particles alone. Probably, the mass transfer coefficient has already reached the minimum value when exclusively 45 μ m particles are present. Therefore, it is likely that the equilibrium bubble diameter with these particles is already reached at a small distance from the gas distributor.

It may be noted that the viscosity of the suspension plays no role as the viscosity hardly changes by the small addition of 45 μ m diameter particles. Thus, the influence of particles on the volumetric mass transfer differs considerably from that in a stirred reactor with kerosine as the liquid phase, since the k_La decline in this type of reactor correlated with the apparent viscosity ²⁸.

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The strong influence of only a few percent of 45 μ m particles and the higher k_La value observed when 35 μ m particles are used, denotes that the promotion of coalescence by particles decreases with decreasing particle diameter. This may result in an increase of the suspension level at which bubbles reach the equilibrium diameter. This equilibrium diameter is of the order of 2-3 mm which is much larger than that reported by Quicker and Deckwer ⁵, Zaidi et al.⁹ and Deckwer et al. ¹⁶.

Finally, it can be concluded from the results of section 4.7.1-4.7.3 that in a gassed two phase bubble column with squalane as the liquid, coalescence is of little importance allowing a high gas holdup and a high volumetric gas-liquid mass transfer coefficient to be obtained by the application of a gas distributor with small pores. However, in the presence of 7-45 µm diameter solids, bubbles coalesce rapidly to the equilibrium diameter. Hence, the formation of initially small bubbles hardly increases the gas-liquid mass transfer in this three phase system. The promotion of coalescence by solids appears to increase with the diameter of the solids.

4.8 <u>The relevance of gas-liquid mass transfer limitations to the</u> Fischer-Tropsch slurry process

As written in the introduction of this chapter it is uncertain whether gas-liquid mass transfer exerts an influence on the conversion of synthesis gas in a bubble column. Although in many models 1-4, 14, 33 the Fischer-Tropsch reaction is assumed to be first order in hydrogen, no experimental data of the volumetric gas-liquid mass transfer coefficient is available. Therefore, this data is calculated and used for the prediction of the importance of gas-liquid mass transfer of hydrogen. In this section, these calculated k_La values are compared with the experimental results obtained in this study and the first order reaction rate constants of various iron catalysts.

The calculation of k_La is divided into two or three parts: k_L and a or k_L , ε_G and d_b . The value of k_L is often calculated by means of the correlation of Calderbank and Moo-Young ²⁶, although this correlation is derived for a two phase system.

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$$k_{\rm L} = 0.31 \left(\frac{D^2_{\rm L} \rho_{\rm L} g}{\mu_{\rm L}} \right)^{1/3} d_{\rm b} < 2.5 \, \rm{mm}$$
 (4.40)

$$k_{\rm L} = 0.42 \left(\frac{D^3_{\rm L} \rho_{\rm L} g^2}{\mu_{\rm L}} \right) 1/6 \qquad d_b > 2.5 \, \rm{mm} \qquad (4.41)$$

Table 4.2

Experimental and calculated values of the diffusion and mass transfer coefficient in "Fischer-Tropsch liquids" at 250°C.

^D L,H ₂ [m ⁴ L/m ² L+G s]	6) ^k L,H2 [m ³ L/m ² G-L s]	Ref.
10.0×10^{-8} 1)	$15.0 - 28.9 \times 10^{-4}$	30
7.0×10^{-8} 2)	$13.0 - 24.0 \times 10^{-4}$	31
2.3×10^{-8} 3)	$5.5 - 14.1 \times 10^{-4}$	-
0.9×10^{-8} 4)	$3.0 - 8.8 \times 10^{-4}$	3
0.9×10^{-8} 5)	$2.9 - 8.6 \times 10^{-4}$	-

1) measured in Krupp wax

2) measured in squalane

 $^{3)}$ calculated for squalane according to the relation of Wilke-Chang 42 :

 $D_{L,H_2} = 7.4 \times 10^{-8} \frac{T (X MW)^{0.5}}{\mu_L V_b^{0.6}}$

wherein the association parameter X is equal to 1, the molecular weight MW=422.83 g/mol and the molar volume of H_2 , V_b = 14.3 cm³/mol.

4) calculated for n-triacontane CH_3 (CH_2)₂₈ CH_3 according to Wilke-Chang

5) calculated for squalane according to the correlation of Sovova 32 :

 $D_{L,H_2} = \frac{3.374 \times 10^{-4}}{\mu_{L,H_2}^{0.5} V_{B,H_2}^{0.6}}$

wherein D is in $cm^2/s,\;\mu_L$ in cP, and V_{B,H_2} is the molar volume of hydrogen (14,3 $cm^3/mol)$

6) calculated according to Calderbank and Moo-Young ²⁶:

 $\begin{aligned} \mathbf{k}_{L,H_2} &= 0.31 \ (\mathbf{D}_{L,H_2}^2 \ \rho_L \ g/\mu_L)^{0.33} & \mathbf{d}_b < 2.5 \ \text{mm} \text{ and} \\ \mathbf{k}_{L,H_2} &= 0.42 \ (\mathbf{D}_{L,H_2}^3 \ \rho_L \ g^2/\mu_L)^{0.17} & \mathbf{d}_b > 2.5 \ \text{mm} \end{aligned}$

In these correlations the value of the diffusion coefficient is a matter of dispute and the predicted values vary considerably (a few examples are given in Table 4.2). Therefore, the diffusion of hydrogen in squalane is measured experimentally. This value agrees well with the diffusion of hydrogen in Krupp wax as shown in Table 4.2. It is interesting to note that both experimental values are much larger than values predicted according to Wilke-Chang or Sovova. Furthermore the reported values of the viscosity of wax (paraffin) differ substantially. The values reported in literature for the density of wax (paraffin) agree closely (see Table 4.3). In view of the foregoing it can be concluded that an accurate

Table 4.3

Type of wax	μ <u>r</u> [Ns/m ²]	ρ _L [kg/m ³]	Ref.
	2.80×10^{-3}	675	1
Krupp	1.80×10^{-3}	680	14
Squalane	0.61×10^{-3}	660	_ 1)
Paraffin	0.33×10^{-3}	-	29 ²⁾

Viscosity and density of various "Fischer-Tropsch liquids"

1) this work

²⁾ used by Stern et al. ²

prediction of k_L is difficult. As the specific area (gas holdup and bubble diameter) is in dispute as well (see section 4.1) the predicted values of k_La vary appreciably as shown in Figure 4.19, in which values determined experimentally in this study are shown as well. As a result of the high diffusion coefficient observed in Krupp wax Calderbank ¹⁴ predicts a high k_La value (0.53 m^3_L/m^3_{L+G} s) despite the low specific area in comparison with Deckwer. The k_La value predicted by the latter agrees well with that of this study, although the values of k_L and a seem to be too low and too high respectively, with respect to the results obtained in squalane. The k_La value reported by Satterfield ³ seems to be





	k _L [m ³ _L /m _{G-L} s]	a [m ² G-L/m ³ L+G]	d _b [mm]
Calderbank 14	15×10-4	350	2.1
Deckwer 16	2×10 ⁻⁴	1500	0.7
Zaidi ^{g 1)}	1x10 ⁻⁴	1500	0.7
Satterfield ³	3x10 ⁻⁴	350	2.1

1) data obtained for CO

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too low as this value is even lower than the k_{La} observed for CO by Zaidi et al. ¹². From Figure 4.19 it may be concluded that the value of k_{La} for hydrogen in a Fischer-Tropsch bubble column under industrial conditions will be at least 0.2 m_{L}^3/m_{L+G}^3 s at a superficial gas velocity of 3 cm/s or higher. It is assumed that the influence of the pressure can be neglected ⁴¹.

Table 4.4

First order reaction rate constants of hydrogen for various iron catalysts. The rate constant is based on a 20 wt% suspension and calculated with help of the data reported by Deckwer 4 .

Authors	Catalyst	Temperature [°C]	k _H [1/s]
Kölbel, Ackerman ³⁴	Pptd. Fe	268	0.15
Kölbel, Ralek ³⁵	Pptd. Fe	266	0.18
Schlesinger et al. ³⁶	Fused Fe	258	0.032
Mitra, Roy ³⁷	Pptd. Fe	260	0.077
Kunugi et al. ³⁸	Pptd. Fe	260	0.37
Mohammed ³⁹	Red mud	280	0.36
Mohammed ³⁹	Pptd. MnFe	327	0.054
Schmidt et al. ⁴⁰	^p ptd. MnFe	303	0.29

Pptd. Fe = precipitated Fe

Finally, when this $k_{L}a$ value is compared with the first order reaction rate constants of the hydrogen conversion over iron catalysts, based on a 20 wt% suspension (see Table 4.4), it can be concluded that the gas-liquid mass transfer will certainly limit the conversion of synthesis gas over active iron catalysts in a Fischer-Tropsch bubble column. Consequently, the olefin selectivity will be lower than obtained in the kinetic regime (see Chapter 2, section 2.9.4) due to an increased olefin/carbon monoxide concentration ratio in the liquid phase.

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Symbols

a	gas bubble interfacial area	^{m²G-L/m³L+G}
as	external catalyst surface area	
	per liquid or suspension volume	^{m²L-S^{/m³L}}
C _{cat}	catalyst concentration	kg cat/m ³ L
CL	concentration of hydrogen in the liquid phase	mol/m ³ L
c*L	hydrogen concentration in the liquid phase at	
	equilibrium with the gas phase	mol/m ³ L
C _S	hydrogen concentration at the catalyst surface	mol/m ³ L
db	bubble diaméter	mG
DL	diffusion coefficient in the liquid phase	m ⁴ L/m ² L+G s
D_{G}	dispersion coefficient in the gas phase	m ² G/s
dp	particle diameter	m or µm
Dr	reactor diameter	m _L or m _{L+G}
£	fraction hydrogen in the feed gas	-
F	gas flow	m ³ G/s
g	gravity	m/s ²
н	Henry coefficient	dm ³ atm/mol
k	reaction rate constant	m ³ L/kg cat.s
k _L	liquid film mass transfer coefficient	m ³ L∕m ² G−L s
k _L a	volumetric gas-liquid mass transfer coefficient	m ³ L/m ³ L+G s
ko	apparent reaction rate constant	m ³ L/kg cat s
kov	reciproke of the overall resistance	m ³ L∕m ³ L+G s
k _S	liquid-particle mass transfer coefficient	^{m³L/m²L-S s}
L	liquid or suspension column height without gas	mL
	bubbles	
L _{L+G}	expanded liquid or suspension column height	^m L+G
m	solubility coefficient (H/RT)	^{m³L∕m³G}
nG	number of mixed cells	
r	reaction rate	mol/m ³ L+G ^S
tm	mixing time of the liquid phase	S
tr	charateristic reaction time (k _o m)	s
UG	superficial gas velocity	m ³ g∕m ² L+g s
vL	volume of expanded liquid or suspension	m ³ L
v_{L+G}	liquid or suspension	^{m³L+G}
х	conversion of hydrogen	vol %

z	vertical coordinate	mL or mL+G
δ	liquid film thickness	т
εG	gas fraction	^{m³G^{∕m³L+G}}
η	effectiveness factor	~
u	dynamic viscosity	Ns/m ² L
ρL	density of the liquid phase	kg∕m ³ L

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5 THE EFFECT OF THE CONVERSION AND THE RECYCLE OF PRODUCT GAS ON THE OLEFIN SELECTIVITY OVER POTASSIUM PROMOTED FUSED IRON IN A BUBBLE COLUMN

5.1 Introduction

At industrial scale a bubble column type of reactor is more suitable than a stirred reactor. Using the kinetic data obtained in the stirred autoclave and the mass transfer data obtained from ethene hydrogenation experiments, the performance of such a reactor can be predicted.

To verify this, a bubble column reactor was built and operated with the fused iron catalyst. Unfortunately, this catalyst is not sufficiently active to demonstrate severe effects of mass transfer limitations. It is very interesting however to compare selectivities obtained in the bubble column reactor, which behaves more like a plug flow system, as one would expect, with those from the stirred reactor.

As the reactor was equipped with a gas recycle compressor direct evidence was obtained of the effect of "backmixing" of product gas on selectivity at various conversion levels. At high recycle ratio this column should closely resemble the stirred system.

A simple reactor model for the bubble column was designed based on results obtained in the stirred autoclave. The model was derived as support to experimental data and may be used to explain trends observed rather than to predict absolute values of conversion and selectivity of the Fischer-Tropsch synthesis in a bubble column.

5.2 Modelling a bubble column with recycling of product gas

In this section a simple model is presented which predicts the conversion of synthesis gas in a bubble column for which part of the product gas is recycled. The objectives of the model are to predict the olefin selectivity and support experimental results.

A schematic drawing of the reactor system is given in Figure 5.1. Fresh synthesis gas is fed together with recycle gas to the bubble column. Products and unconverted synthesis gas are cooled in a cold trap in which water and higher hydrocarbons condense. A part of the gas, consisting of low boiling products and unconverted CO and H_2 is recycled by means of a compressor. The remainder leaves the system.



fresh_synthesis_gas

Fig. 5.1 Schematic diagram of the reactor system

The mass balances of the gas phase are derived on the grounds that both the concentration of water in the outlet stream of the condensor and the concentration of hydrocarbons in the water phase of the condensor are equal to zero. The gas flows of reactor inlet and outlet and the condensor outlet are equal to:

- $\mathbf{F}_0 = \mathbf{F}_r + \mathbf{F}_f \tag{5.1}$
- $F_1 = F_w + F_r + F_p$ (5.2)
- $\mathbf{F}_2 = \mathbf{F}_r + \mathbf{F}_p \tag{5.3}$

For the concentration of various components in these streams, the following equations apply:

$$C_{i,0} = \frac{F_{f} C_{i,f} + F_{r} C_{i,r}}{F_{f} + F_{r}}$$
(5.4)

$$C_{i,1} = \frac{F_{p} C_{i,p} + F_{r} C_{i,r}}{F_{p} + F_{r} + F_{w}}$$
(5.5)

$$C_{i,2} = C_{i,p} = C_{i,r}$$
 (5.6)

The conversion of CO or H_2 per pass is:

$$X_{i,ps} = \frac{F_0 C_{i,0} - F_1 C_{i,1}}{F_0 C_{i,0}}$$
(5.7)

The (total) conversion $X_{i,t}$

$$X_{i,t} = \frac{F_{f} C_{i,f} - F_{p} C_{i,p}}{F_{f} C_{i,f}}$$
(5.8)

can be related to the conversion per pass as follows:

$$X_{i,ps} = \frac{X_{i,t}}{1 + (1 - X_{i,t})F_r/F_p}$$
(5.9)

or, after introduction of the recycle ratio R, which is defined as the recycle flow/fresh synthesis gas flow ratio (F_r/F_f) , and rearrangement

$$X_{i,t} = \frac{X_{i,ps}(1 + R F_{f}/F_{p})}{1 + X_{i,ps} R F_{f}/F_{p}}$$
(5.10)

The assumptions made to develop the model are:

a) The synthesis gas conversion rate is first order in H_2 and zero order in CO and products

b) The rate of the secondary hydrogenation is equal to

 $r = k C_{ole,L} C_{H_2,L}/C_{CO,L}$

c) The water-gas shift reaction completely reaches equilibrium

d) The usage ratio and chain growth probability are constant

- e) Equilibrium is achieved between gas and liquid according to Henry's Law
- f) The gas phase behaves as plug flow
- g) The liquid phase is non-mixed
- h) The catalyst particles are uniformly suspended
- i) Steady-state isothermal and isobaric operation
- j) The overall reaction rate is dependent on the chemical reaction rates only and not on mass transfer rates
- k) Gases behave as ideal

In this model the formation of hydrocarbons and the water-gas shift reaction are defined in a slightly different way to facilitate the computation:

$$2 \operatorname{CO} + \frac{1}{2} \operatorname{K} \operatorname{H}_{2} \rightarrow \operatorname{CH}_{x} + \operatorname{CO}_{2}$$
(5.11)

$$(1-z)CO_2 + (1-z)H_2 \neq (1-z)H_2O + (1-z)CO$$
 (5.12)

The material balance equations for hydrogen with regards to Eq.(5.11) are: <u>Gas phase</u>:

$$d((F_{G} C_{H_{2},G})/dz = k_{L,H_{2}} a(C_{H_{2},L} - C_{H_{2},G}/m_{H_{2}})A$$
(5.13)

Liquid phase:

$$k_{L,H_2} a(C_{H_2,L} - C_{H_2,G}/m_{H_2}) = -k(1-\epsilon_G)C_{Fe} C_{H_2,L}$$
 (5.14)

By substitution of Eq.(5.14) into Eq.(5.13) follows:

$$-d(F_{G} p_{H_2})/dz = k C_{Fe}(1-\varepsilon_G)p_{H_2} A/m_{H_2}$$
(5.15)

The value of the holdup is calculated according to the relation below which follows from experiments presented in Chapter 3:

$$\varepsilon_{\rm C} = 0.942 (F_{\rm C}/{\rm A})^{0.7} \tag{5.16}$$

It is assumed in Eq.(5.11) that only CO_2 is formed. This means that the concentration of H₂ must be adjusted for the water-gas shift reaction. The correction of H₂ (-dpH₂) is equal to the increase of H₂O (dpH₂O) by which Eq.(5.15) changes into:

$$-\frac{d(F_{G} P_{H_{2}})}{dz} = k C_{Fe}(1-\epsilon_{G}) p_{2}^{H} A/m_{H_{2}} + \frac{d(F_{G} P_{H_{2}}O)}{dz}$$
(5.17)

The decline of the CO pressure and the increase of both the pressure of the CO_2 and hydrocarbons are:

$$-\frac{d(F_{G} P_{CO})}{dz} = \frac{k C_{Fe}(1-\epsilon_{G})P_{H2} A}{m_{H2} U} - \frac{d(F_{G} P_{H2})}{dz}$$
(5.18)

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$$\frac{d(F_{G} P_{CO_2})}{dz} = \frac{k C_{Fe}(1-\varepsilon_G) p_{H_2} A}{m_{H_2} 2U} - \frac{d(F_G p_{H_2}O)}{dz}$$
(5.19)

$$\frac{d(F_G p_{prod})}{dz} = \frac{k C_{Fe}(1-\varepsilon_G)p_{H_2} A}{m_{H_2} 2U \Sigma C_n}$$
(5.20)

where ΣC_n represents the number of moles of CO which is required to produce 1 mole of hydrocarbons. The value of ΣC_n can be calculated by means of the Schulz-Flory distribution:

$$\Sigma C_n = \sum_{i=1}^n \left[(i \alpha)^{i-1} (1-\alpha) \right] = 2.5 \quad \text{for } \alpha = 0.6 \quad (5.21)$$

The pressure of water is calculated by means of the water-gas shift equilibrium:

$$p_{H_2O} = \frac{p_{H_2} p_{CO_2}}{K_s p_{CO}}$$
 (5.22)

The value of the gasflow, F_G , in the reactor varies along the height due to the contraction which is calculated with the help of the Schulz-Flory distribution.

The calculation of the olefin selectivity is based on the model developed in section 2.9. According to this model the increase of the pressure of ethene, for example, can be written as:

$$\frac{d(F_G C_{2H_4,G})}{dz} = (r_1 - r_3)A$$
(5.23)

and for the increase of ethene + ethane:

$$\frac{d(F_G C_{C_2,G})}{dz} = (r_1 + r_2)A$$
(5.24)

in which the production rates of ethene and ethane directly from $CO+H_2$ are represented by r_1 , and r_2 , respectively. The secondary hydrogenation of ethene is represented by r_3 . Following the assumptions on the kinetics of these reactions (see section 2.9.2) Eq.(5.23) can be written as:

¹⁾ The value of K_s is reported in section 2.6

$$\frac{d(F_G PC_2H_4)}{dz} = \frac{r_1 \alpha(1-\alpha)}{r_1 + r_2} \cdot \frac{d(F_G P_{prod})}{dz} - k_3' \frac{PH_2 PC_2H_4}{P_{CO}}$$
(5.25)

The olefin selectivity follows from the outlet pressure of ethene and ethane, obtained by integration of Eq.(5.24) and (5.25).

The differential equations were solved by numerical integration using Euler's method. The concentration changes due to the Fischer-Tropsch and water-gas shift reaction were accounted for. To start the integration initial values are given for:

- * the extent and composition of the fresh synthesis gas supply
- * the recycle ratio
- * the recycle gas composition

The latter is an estimate, which should match the composition of the recycle gas that follows from calculations over the column. Hence the solution is reached by iteration.

5.3 Experimental

5.3.1 Materials and catalyst

The gases, the liquid phase, the catalyst and the method of catalyst reduction are identical to those used for experiments in the stirred autoclave. Only the catalyst particle diameter, approximately 3 μ m, was considerably smaller in order to prevent settling of catalyst particles in the bubble column.

5.3.2 Apparatus

A schematic diagram of the apparatus is shown in Figure 5.2. The equipment is principally made of stainless steel. The flows of oxygen and water-free CO and H_2 are regulated by thermal mass flow controllers, mixed by a static mixer and fed to the bubble column together with recycle gas. The inlet gas of the reactor is distributed by a perforated plate which contains 19 0.3 mm diameter holes (equal to the perforated plate used for the experiments presented in Chapter 4). The head of the



Fig. 5.2 Schematic diagram of the apparatus

reactor is enlarged and provided with baffles for decreasing liquid entrainment. The outlet gas flow is cooled in two steps; the high boiling products are condensed first at 90°C and the lower ones thereafter at 4°C. The recycle gas is slightly pressurized (a pressure increase of 0.3-1 bar) and fed to the column. The gas rate of the recycle flow is measured by means of a turbine meter and is independent of the gas viscosity, density and composition. The composition of the fresh synthesis gas, the reactor outlet and the recycle gas are analyzed by means of on-line gas chromatography. The flow rate of the product gas is measured by a wet or dry gas meter.

5.4 Results and discussion

The reaction conditions of the experiments carried out in the bubble column are shown chronologically in Table 5.1. All the experiments are carried out at 9 bar. The experiments are divided into four series of which three are discussed. The reliability of the last series (no.4) proved insuffucient to be included.

In series 1 the recycle ratio R is changed while the fresh synthesis gas flow is kept constant. The conversion per pass decreases continuously with increasing recycle ratio, as shown in Figure 5.3, due to the higher space velocity in the reactor. The (total) conversion decreases as well, because the plug flow character of the gas phase changes into that of ideally mixed. The deviation of the first data point from the calculated curve is caused by a higher catalyst activity in comparison with other experiments. The last data point (R=14), shown in Figure 5.3, deviates for unknown reason. It is interesting to note that the first order rate constant used for calculating the conversion of hydrogen in the simulation agrees well with the experimental value observed in the stirred autoclave.

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Table 5.1

Reaction conditions of the experiments carried out with 260 g fused iron at 9 bar in the bubble column reactor. The initial amount of squalane is 1.54 kg.

Exp.	Series	Start	Temp.	н ₂ /со	Flow	Recycle
No.	No.	after			in 1)	ratio
[-]	[-]	[h]	[°C]	[-]	[1/min]	[-]
1	1	0	250 2)	0.65	2.04	3.2
2	1	86	250	0.66	1.94	10.2
3	4	119	250	0.74	8.06	0
4	1	134	250	0.66	1.93	14.5
5	-	161	250 3)	0.66	1.94	6.7
6		174	250	_ 4)	1.94	0
7			250	0.66	1.94	11.8
8	1	246	250	0.66	1.94	13.8
9	1	278	250	0.66	1.98	9.6
10	2	306	250	0.72	12.2	0
11 · ,	2	316	250	0.62	5.64	1.3
12	2	331	250 5)	0.69	0.81	14.00
13	2	381	250	0.71	1.34	6.7
14	• • 4 . • •	404	270	0.71	1.34	9.5
15	4	424	270	0.69	0.8	9.0
16	. 4	482	270	0.67	6.25	0
17	3	501	270	4.00	6.25	0
18	3	529	270	3.88	8.52	0
19	· 3 · ·	553	270	4.12	16.6	0
20	3	599	270	3.76	10.2	0

1) measured at 20°C and 1 bar

 2) the centre heat element of the reactor failed

3) too high wall temperature above the suspension level

4) only H_2 gas flow

5) the lowest heat element of the reactor failed

The pattern of the olefin selectivity and olefin/CO pressure ratio are shown in Figure 5.4. The experimental data shows that increasing the recycle ratio above R=9 does not significantly affect the olefin selectivity, in accordance with the simulation. The experimentally observed low olefin selectivity at R=3 is caused by the high olefin/CO pressure ratio. This ratio is higher than predicted due to the high activity of the catalyst during this experiment (see above). The PC_2H_4/PCO ratios of the other points are much lower than that predicted from the model. This difference is partly caused by insertion of ethene as the deviation for propene (not shown) is substantially smaller.





Fig. 5.3

The conversion of CO+H₂, overall and per pass, versus the recycle ratio at a constant fresh synthesisgas supply (series 1)

Fig. 5.4

The C_2 and C_3 olefin selectivity and the C_2H_4/CO pressure ratio versus the recycle ratio at a constant fresh synthesis gas supply (series 1) The poor minimum of the olefin selectivity predicted from the model at R=3 is caused by the change from plug flow to ideally mixed flow. From the fact that the olefin selectivities at R=0 and R= ∞ are equal, it can be concluded that the conversion decrease compensates the higher mean olefin/CO pressure ratio due to mixing of the gas phase at a high recycle ratio. The poor minimum and the course of the experimental data took, show that mixing of the gas phase at a moderate conversion level (\pm 60%) is of little importance to the olefin selectivity of this catalyst.

At high recycle ratio the experimental olefin selectivity observed should match the values obtained in the stirred autoclave at an equal olefin/CO partial pressure ratio. The values of the olefin selectivity for the stirred autoclave follow from Figure 2.27 and 2.28. The values of the C₃ olefin selectivity are close together: 88 and 90% for the bubble column and stirred autoclave, respectively. The olefin selectivity of the C₂ fraction observed in the bubble column at high recycle ratio, however, is higher than in the stirred autoclave, namely 76% in the column compared with 65% in the autoclave.

In contrast to series 1, in series 2 the gas flow at the entrance of the reactor is stays constant. This means that the conversion per pass stays constant with increasing recycle ratio if the reaction rate is first order. The experimental data are in accordance with this theory as shown in Figure 5.5. A constant conversion per pass means that the total conversion increases with increasing recycle ratio. The experimental conversion follows the trend of the simulation but the absolute values are lower (see Figure 5.5).

As a result of the increasing conversion the olefin/CO pressure ratio increases with increasing recycle ratio as shown in Figure 5.6. The experimental values are considerably lower than those obtained in the simulation. This was also observed in series 1. From Chapter 2 we know that the olefin selectivity decreases with increasing olefin/CO pressure ratio. Hence, the olefin selectivity decreases with increasing recycle ratio as shown in Figure 5.6. The experimental values are lower than the simulated values, indicating that the hydrogenation activity is higher than was estimated in the model.

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At a high recycle ratio the olefin selectivity should match comparable experiments in the stirred autoclave. The similarity is reasonable as shown in Table 5.2. The last series, number 3, is carried out without recycling product gas. The inlet H_2/CO ratio was 4 (instead of 0.67) and the temperature 270°C (instead of 250°C) in order to obtain a high CO conversion. This high CO conversion level was chosen because it is particularly interesting to measure the olefin selectivity reached in a bubble column at a high CO conversion level.

The experimental conversion of CO (Figure 5.7) clearly deviates from the simulation at lower gas velocities, probably due to mass transfer limitation of CO and inhibition by H_2O . Both factors are caused by the high H_2/CO ratio which varies from 4 (inlet) to ≥ 10 (outlet). Table 5.2 Comparison of the C_2 and C_3 olefin selectivity observed in the bubble column at high recycle ratio (series 2) with those in the stirred autoclave. The latter originate from Figure 2.27 and 2.28 at equal olefin/CO pressure ratio.

	Olefin selectivity [%]		
	C2	C3	
		<u> </u>	
Bubble column	51	76	
Stirred autoclave	~ 40	85	

The olefin selectivity appears to be independent of the gas flow and is 77 and 84% for C_2 and C_3 respectively as shown in Figure 5.8.

The simulated olefin selectivity on the contrary increases sharply with increasing gas velocity as a result of the strong decline of the CO conversion. As the experimental conversion is less dependent on the gas velocity, so the olefin/CO pressure ratio will change less than what would be expected according to the model. Thus the olefin selectivity will also vary less than expected. When the olefin selectivity observed in the bubble column at the lowest gas velocity is compared with results obtained in the stirred autoclave it can be concluded that the olefin selectivity is very high relative to the olefin/CO pressure ratio at the exit of the reactor. The olefin selectivity in the stirred autoclave was only $\pm 20\%$ and 70% for C₂ and C₃ respectively at these high olefin/CO pressure ratios (see Figure 2.30) The large difference of the olefin selectivity observed in the bubble column and the stirred autoclave supports the model of secondary hydrogenation of primary olefins as developed in Chapter 2. According to this model the olefin selectivity depends on the (local!) olefin/CO pressure ratio. The average value of this ratio will be lower in a bubble column, resulting in a higher olefin selectivity as shown in this section.





Fig. 5.7 The conversion of CO versus the superficial gas velocity (series 3, R=O)

The olefin selectivity and p_{olefin}/p_{CO} ratio of C_2 and C_3 versus the superficial gas velocity (series 3, R=0)

5.5 Conclusions

The olefin selectivity observed in a bubble column with product gas recycling depends mainly on the conversion of CO and to minor a degree on the recycling of product gas. If the gas flow at the entrance of the reactor is kept constant, (series 2) the olefin selectivity strongly decreases with increasing recycle ratio because of the combined effect of increased conversion and olefin recycling. However, if the fresh synthesis gas supply is kept constant (series 1) the olefin selectivity increases slightly or stays constant with increasing recycle ratio due to the CO conversion decrease which dominates the effect of olefin recycling.

Without recycling product gas, the value of the olefin selectivity is high even at high CO conversions. The much higher olefin selectivity obtained in the bubble column, when compared with results observed in the stirred autoclave is caused by a lower average olefin/carbon monoxide pressure ratio in the former.

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St	mbols		
	a	gas bubble interfacial area	m ² G-L/m ³ L+G
	A	area of the column	m ² L+G
	Ccat	catalyst concentration	kg cat/m ³ L
	C	concentration	mol/m ³
	C _{Fe}	catalyst concentration	kg cat/m ³ L
	F	gas flow	m ³ G/s
•	k	reaction rate constant	m ³ L/kg cat s
	kL	liquid film mass transfer coefficient	m ³ L/m ² G−L s
	kLa	volumetric gas-liquid mass transfer coefficient	m ³ L/m ³ L+G s
	КS	equilibrium constant of the water-gas shift	-
	m	solubility coefficient	m ³ L∕m ³ G
	ni	mol fraction with carbon number i	-
	p	pressure	bar
	r	reaction rate	mol/m ³ L+G ^s
	R	recycle ratio (F_r/F_f)	-
	T	temperature	°C
	U	usage ratio	mol/mol
	x	conversion	-
	z	vertical coordinate	^m L+G
	εG	gas fraction	^{m³G^{/m³L+G}}
	PL	density of the liquid phase	kg∕m ³ L
	α	chain growth probability	-

Subscripts

0	entrance of the column
1	outlet of the column
2	outlet of the condensor
£	fresh
G	gas
i	component
L	liquid
P	product
ps	per pass
r	recycle
t	total
w	water

SAMENVATTING

Kleine olefinen zoals etheen en propeen zijn belangrijke basischemicaliën, die in het algemeen op dit moment uit ruwe olie worden verkregen, maar in de toekomst kan steenkool een belangrijke koolstofbron worden voor de productie hiervan en die van andere koolwaterstoffen.

Uitgaande van steenkool als grondstof zijn twee routes van belang: extractie met gelijktijdige hydrogenering en vergassing tot synthesegas dat vervolgens tot koolwaterstoffen en zuurstofhoudende componenten wordt omgezet door de Fischer-Tropsch synthese. Deze studie betreft de laatst genoemde route, d.w.z. de omzetting van synthesegas, geproduceerd uit steenkool, tot kleine olefinen.

De verhouding van H₂ en CO in het synthesegas is van groot belang en kan tussen 0,4 en 4 variëren, afhankelijk van het gekozen vergassingsproces. De doelstelling van deze studie is synthesegas met een lage H₂/CO verhouding (0.46 - 0.68) in één stap in een slurry reactor om te zetten tot kleine olefinen. Dit synthesegas wordt door moderne kolenvergassers geproduceerd, omdat een lage H₂/CO verhouding economischeen procesvoordelen biedt.

Voor het bereiken van de doelstelling van dit proefschrift is het noodzakelijk uit te gaan van een geschikt katalysatorsysteem, dat niet alleen de gewenste eigenschappen bezit ten aanzien van aktiviteit en selectiviteit, maar dit systeem dient ook een goede water-gas shift katalysator te zijn voor toepassing in een slurry reactor.

In dit proefschrift is de selectieve produktie van kleine olefinen onderzocht bij relatief hoge druk (10 bar) en een hoge conversie van CO rijk synthesegas. Er zijn twee katalysatoren gebruikt: RuFe/SiO₂ en met kalium gepromoteerd "fused iron".

De RuFe/SiO₂ katalysator is gekozen vanwege de hoge activiteit en olefineselectiviteit (waargenomen bij een laag conversieniveau). Ter vergelijking is de bekende met kalium gepromoteerde "fused iron" katalysator gekozen. De slurry bellenkolom lijkt veelbelovend voor de industriële productie van kleine olefinen via de Fischer-Tropsch route. Derhalve is de invloed van het gas-vloeistof massatransport in dit type reactor onderzocht. Vooral het massatransport van waterstof is van belang omdat de omzettingssnelheid van synthesegas voornamelijk door de waterstofdruk bepaald wordt.

De invloed van het reactortype op de olefineselectiviteit is onderzocht in een bellenkolomreactor waarvan gasvormige reactieproducten en niet omgezet CO en H_2 extern gerecirculeerd werden.

Het experimentele werk bestaat uit drie gedeelten:

- Een kinetische studie van de Fischer-Tropsch synthese over RuFe/SiO₂ en "fused iron" in een geroerde autoclaaf bij 1,5-17 bar, 200 - 300°C en een conversieniveau tot 98%.
- Een studie van de gas-vloeistof massatransport coëfficiënt van H₂ in een glazen bellenkolom met een diameter van 5 cm bij atmosferische druk en 250°C, waarbij de hydrogenering van etheen over palladium is toegepast.
- 3. De omzetting van CO en H_2 tot kleine olefinen in een roestvrij stalen bellenkolomreactor met een diameter van 5 cm bij 9 bar, 250 - 270°C en met "fused iron" als katalysator. Een gedeelte van het gas uit de reaktor wordt met behulp van een compressor gerecirculeerd. De vloeistoffase in deze en in de andere reaktoren is squalane ($C_{30}H_{62}$), dat beschouwd kan worden als een kunstmatige Fischer-Tropsch was.

In het geval van "fused iron" wordt de C_2 en C_3 olefineselektiviteit voornamelijk bepaald door de mate waarin secundaire hydrogenering van respectievelijk etheen en propeen plaatsvindt. De olefineselectiviteit hangt geheel af van de olefine/koolmonoxide drukverhouding in de reaktor en is onafhankelijk van de waterstofdruk. Dit kan worden verklaard door competitie te veronderstellen tussen koolmonoxide en de gevormde olefinen voor dezelfde plaatsen op het katalysatoroppervlak, waarbij de orde in waterstof van zowel de secundaire hydrogenering, als die van de conversie van synthesegas, gelijk is. Een toename van de CO conversie resulteert dus in een hogere olefinen/CO drukverhouding, wat een toename van de hydrogenering van olefinen veroorzaakt. Een hogere etheen/CO drukverhouding blijkt voor etheen ook tot een grotere inbouw te leiden. Met deze inbouw wordt het duidelijk waarom bij hogere conversies het C_2 punt onder de Schulz-Flory lijn valt.

De olefineselectiviteit voor RuFe/SiO₂ is zeer laag in vergelijking met "fused iron", vooral enige tijd na start van de reaktie. De olefineselectiviteit daalt bijzonder snel met toenemende CO conversie. Aangezien de olefineselectiviteit voor zowel RuFe/SiO₂ als Ru/SiO₂ even laag blijkt te zijn en bimetallische RuFe deeltjes uit elkaar blijken te vallen, is het duidelijk dat de werking van het RuFe/SiO₂ systeem bepaald wordt door Ru deeltjes. Deze Ru deeltjes zijn verantwoordelijk voor de grote hydrogeneringsactiviteit.

Ook andere eigenschappen van de "fused iron" katalysator zijn superieur aan die van RuFe/SiO₂ zoals een hogere activiteit en een aanzienlijk lagere methaanselectiviteit. De laatst genoemde blijkt zelfs lager te zijn dan berekend volgens de Schulz-Flory verdeling indien CO nagenoeg geheel is omgezet.

De activiteit van zowel "fused iron" als RuFe/SiO₂ is zo laag dat de snelheid van massatransport in een bellenkolom waarin de Fischer-Tropsch reaktie wordt uitgevoerd, voldoende groot is.

De gas-vloeistof massatransportcoëfficiënt k_{La} bereikt in squalane uitzonderlijk hoge waarden (>2 $m^{3}L/m^{3}L+G$ s) bij gebruik van een poreuze plaat als gasverdeler, mits de concentratie van vaste stof laag is (< 1 gew. %).

De toevoeging van deeltjes, met een diameter van 3-64 µm, resulterend in een suspensie van 1-20 gew.%, leidt altijd tot een daling van $k_{L}a$. Deze daling is sterker voor deeltjes met een grotere diameter. De toegevoegde deeltjes veroorzaken waarschijnlijk een toename van coalescentie van gasbellen. Het voordeel van een poreuze plaat, die als doel heeft kleine gasbellen te produceren, gaat dus verloren bij hogere concentraties vaste stof.

Bij gelijke conversie is de olefineselectiviteit in een bellenkolom aanzienlijk hoger dan in een geroerde autoclaaf. Deze hogere olefineselectiviteit wordt veroorzaakt door een gemiddeld lagere olefine/CO drukverhouding als gevolg van het plug flow karakter van de gasstroom. Het effect van "terugmenging" van produktgas, onderzocht door recirculatie van reactieprodukten en niet omgezet synthesegas, is minder belangrijk dan het effect van de conversie. Dankwoord

Het in deze dissertatie beschreven onderzoek is mogelijk geweest dank zij de inspanningen van velen. Een woord van dank aan hen, die hetzij direct, hetzij indirect, betrokken zijn geweest, is dan ook op zijn plaats.

Het onderzoek is mede mogelijk gemaakt door de financiële steun van de stichting Scheikundig Onderzoek Nederland (SON).

Voor de bouw van de geroerde slurry reactor en de hoge drukbellenkolomreactor gaat mijn dank uit naar Dick Francois en Rinus v.d. Heijden. De technische ondersteuning was van groot belang in dit onderzoek. Hiervoor gaat mijn dank uit naar de Technische Dienst van de TUE, vooral die van de vakgroep TCC en met name Rein van der Weij.

Ook de andere leden van de vakgroep waarvan ik Paul Dijkgraaf speciaal wil vermelden, wil ik bedanken voor hun hulpvaardigheid en belangstelling voor het onderzoek. De prettige herinnering die ik aan de "Eindhovense periode" heb is voor een belangrijk gedeelte te danken aan de prettige sfeer in de vakgroep TCC.

Het experimentele werk is grotendeels door studenten verricht. Cees Hovingh en Leo Kaland hebben de inleidende experimenten met fused iron uitgevoerd. René de Schutter en Reinoud Biesbroek hebben respectievelijk de performance van fused iron en RuFe/SiO₂ in een geroerde slurry reactor onderzocht. De etheenadditie experimenten en de afsluitende experimenten met fused iron zijn door Hans Cüsters uitgevoerd. Het stofoverdrachtsonderzoek is verricht door Maarten Jansen, Nico Steijaert, Roel Hoff, Adrie Teurlings en Han Lemmens. Frank Groenen en Robert Kint hebben de experimenten in en de simulaties van de Fischer-Tropsch bellenkolom uitgevoerd. Voor het vele werk maar vooral voor de plezierige en leerzame samenwerking wil ik bovengenoemden hartelijk danken.

A.M. van der Kraan en Edo Gerkema van het "Interuniversitair Reactor Instituut" te Delft ben ik erkentelijk voor de Mössbauer experimenten.

Een bijzonder woord van dank gaat uit naar Kees van der Wiele die als promoter niet alleen het onderzoek heeft begeleid maar die het concept proefschrift zeer zorgvuldig heeft gelezen en op vele plaatsen voorzien van kritische opmerkingen en suggesties.

Mijn speciale dank gaat uit naar dhr T. v.d. Zeyde die in korte tijd van het Engels "Engels" heeft gemaakt.

Als laatsten maar niet als minsten wil ik Marquerite de Faber en Tanja Beerden danken voor het typen van het proefschrift dat toch veel meer werk bleek te zijn dan voorzien.

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Curriculum vitae

De schrijver van dit proefschrift werd op 16 september 1957 te Leiden geboren. Hij behaalde het HAVO diploma in 1974 en het atheneum diploma in 1976 beide aan de "Christelijke Scholengemeenschap Leiden-Zuidwest" te Leiden. Aansluitend begon hij zijn studie Scheikundige Technologie aan de Technische Universiteit Delft te Delft. Het kandidaatsexamen werd afgelegd in maart 1981. Het ingenieursexamen, met als hoofdvak Bioproces Technologie bij prof. N.W.F. Kossen, werd in juni 1983 behaald.

Van 15 augustus 1983 tot 15 augustus 1987 was hij in dienst van de Technische Universiteit Eindhoven bij de vakgroep Chemische Technologie. Hier werd, onder leiding van prof. dr. ir. K. van der Wiele, het onderzoek uitgevoerd waarvan de resultaten in dit proefschrift zijn beschreven.

Sinds 15 september 1987 is hij werkzaam bij AKZO Chemicals B.V. te Deventer.

Stellingen

 Bimetallische katalysatoren gebaseerd op ijzer en een edelmetaal, bezitten in verse toestand zeer interessante eigenschappen voor de Fischer-Tropsch synthese. Industrieël zijn deze katalysatoren evenwel oninteressant door de instabiliteit van het bimetallische systeem onder technische synthese condities.

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 Ledakowicz e.a. sluiten op verkeerde gronden water uit als inhibitor voor de Fischer-Tropsch synthese over geprecipiteerd ijzer.

Ledakowicz, S.; Nettelhof, H.; Kokuun, R.; Deckwer, W-D., I.E.C. Proc. Des. Dev., 24 (1985), 1043-1049

3) Het effect van de toevoeging van palladium en ruthenium aan ijzer op de olefineselektiviteit, gemeten bij een (te) laag conversieniveau van CO, levert een sterk vertekend beeld op van de werking van deze metalen.

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4) Aan de lage (schijnbare) activeringsenergie en de hoge katalysatoractiviteit, gemeten voor de Fischer-Tropsch synthese in een bellenkolomreaktor, verzuimen Sakai en Kunugi de conclusie te verbinden dat de synthesegasconversie gelimiteerd wordt door het transport van CO en H₂ van gas naar vloeistof.

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5) De beldiameter in een "Fischer-Tropsch" bellenkolomreaktor is aanzienlijk groter dan de door Deckwer c.s. aangeduide waarde van ca. 0,7 mm.

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- 6) De snelheid en de toegankelijkheid van printers en copieermachines heeft op veel plaatsen in onze maatschappij reeds geleid tot dusdanig massale papierstromen dat de beoogde verspreiding van informatie wordt belemmerd in plaats van vergroot.
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- 9) Waar de Bijbel wet wordt, wordt de wetgever een tiran.
- 10) Aan diegenen die hun gewicht willen verminderen dient het starten van sportaktiviteiten te worden ontraden.

Eindhoven, augustus 1988

J.H. Boelee

THE FISCHER-TROPSCH SYNTHESIS IN SLURRY PHASE REACTORS

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