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 µm) fused iron (C73, Süd-Chemie) was reduced in a separate fixed-bed reactor with 0.9 l H_2 (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

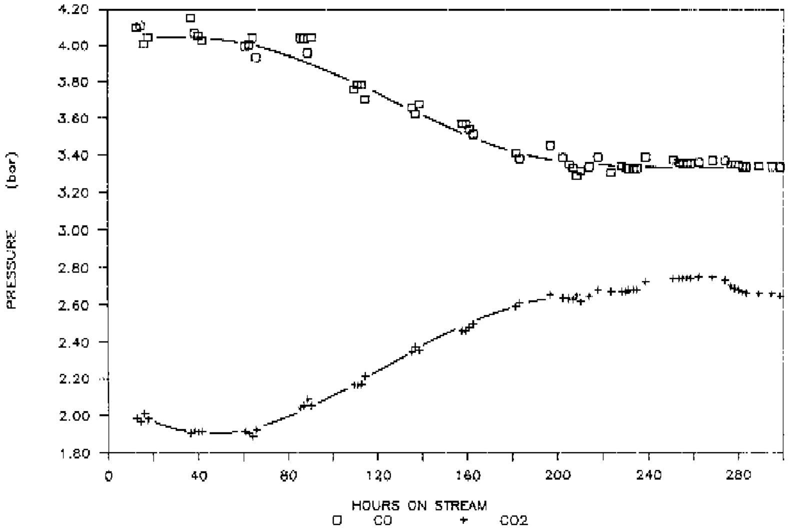

Fig. 2.46 The course of the CO and CO_2 pressure versus time on stream. Reaction conditions are reported in section 2.13.2

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

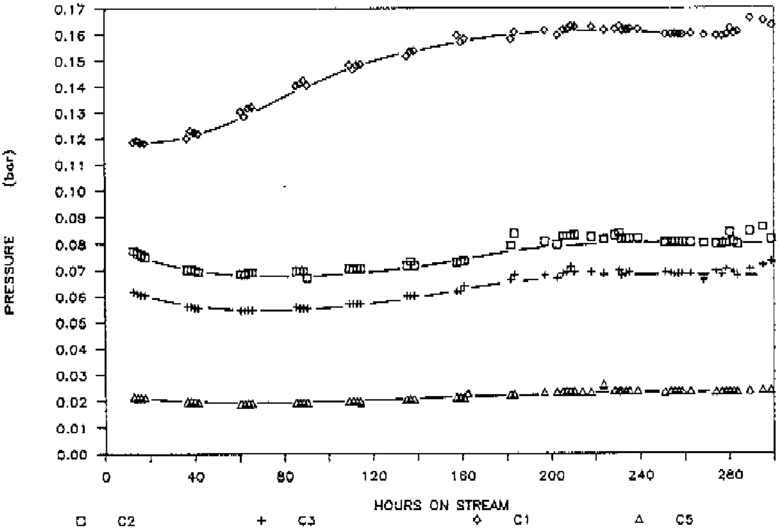

Fig. 2.47 The course of the pressure of various hydrocarbons versus time on stream. Reaction conditions are reported in section 2.13.2

ratio, 1.9 , is very low which results in a small deviation of the C_1 point from the Schulz-Flory line. This initial low C_1/C_3 ratio corresponds with a lower value of the chain growth probability ($\alpha = 0.73$) than the value of α measured (0.62). However, the C_1/C_3 ratio increases in time, while the chain growth probability, α, is practically constant (see Table 2.19), by which the C_1 fraction obeys the Schulz-Flory distribution after 205 hours on stream. After this period of time the C_1/C_3 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; (H_2/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 C_4 fraction is constant over the entire run which is shown in Table 2.20. Also the C_3 olefin selectivity does not significantly vary during the run. However, the C_2 olefin selectivity decreases continuously as a function of time as shown in Fig. 2.49. A small decrease of the C_2 olefin selectivity is conceivable because the $p_{C_2H_4}/p_{CO}$ ratio increases with time due to the increasing conversion of CO. However, the decrease of the C_2 olefin selectivity is larger than expected. Fig. 2.50 shows that the C_2 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.

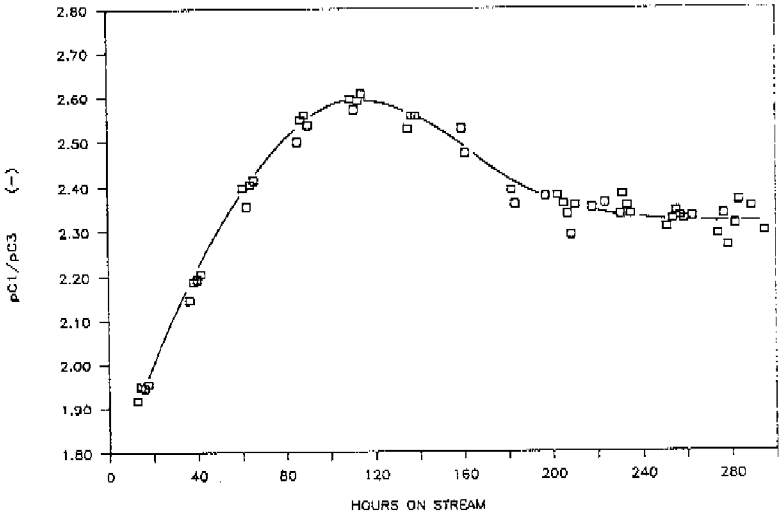

Fig. 2.48 The course of the C_1/C_3 pressure ratio versus time on stream. Reaction conditions are reported in section 2.13.2

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.

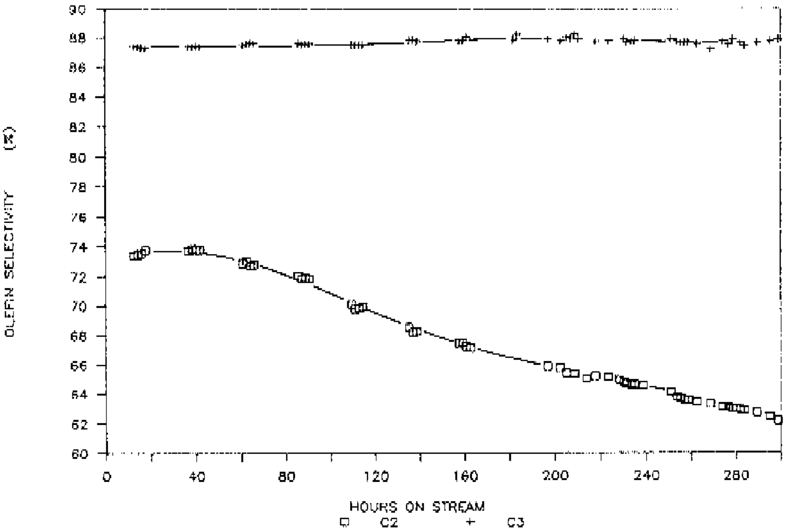

Fig. 2.49 The course of the olefin selectivity of C_2 and C_3 versus time on stream. Reaction conditions are reported in section 2.13.2

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%

	Hours on stream								
	39	86	115	161	218	233	279	303	330
$i\text{-}C_4H_{10}$ [%]	0.8	0.7	0.6	0.6	0.7	0.6	0.7	0.6	0.7
$n\text{-}C_4H_{10}$ [%]	14.3	13.6	13.5	13.5	14.2	13.8	13.9	14.0	14.1
$2\text{-}C_4H_8$ [%]	10.6	10.9	11.5	11.5	11.7	11.7	12.3	12.6	12.5
$1\text{-}C_4H_8$ [%]	74.3	74.8	74.4	74.4	73.4	73.9	73.1	72.8	72.8

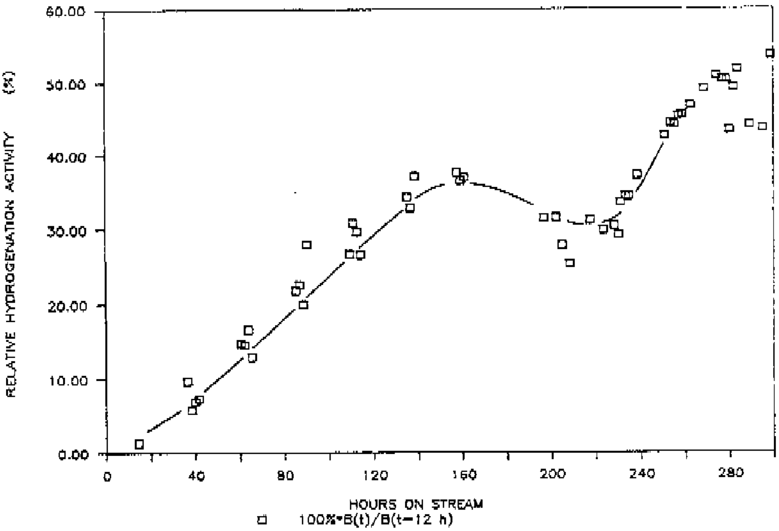

Fig. 2.50 The course of the hydrogenation activity versus time on stream. The parameter B is proportional to the rate constant of the ethene hydrogenation (see Eq.(2.43) in section 2.9.2)

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"	"sites 2"
* CO dissociation * Hydrocarbon formation * insertion of olefins into hydrocarbon chains	* 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

A, B	constants	-
b	constant	s^{-1}
c	constant	bar/s
c_i	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	$m^3{}_L/m^3{}_G$
$H_{1,2}$	Henry's constant for solute 1 in solvent 2 (fugacityl/liquid phase mole fraction of solute 1)	atm
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)	
K_s	watergas shift equilibrium constant	-
$p^\circ{}_i$	pressure of a hydrocarbon with i C atoms at t=o	bar
p_i	pressure of a hydrocarbon with i C atoms	bar
P	total or reactor pressure	bar
p*	reference pressure (1 bar)	bar
$-r_{CO+H_2}$	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
T	reactor temperature	K or °C
T*	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	-
X	conversion	%
z	water fraction converted by the shift reaction	mol/mol

Subscripts

G gas phase

L liquid phase

i component i

in inlet

out outlet

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3 THE PERFORMANCE OF $RuFe/SiO_2$ AND Ru/SiO_2 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 TiO_2 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 $RuFe/SiO_2$ 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 ^{57}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 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, H_2 and H_2O on the stability of $RuFe/SiO_2$ catalysts is not available. In contrast to this uncertainty about the stability of $RuFe/SiO_2$ catalyst, the initial catalytic performance of these 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 $RuFe/SiO_2$ 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

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)/SiO_2 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/SiO_2 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 $RuCl_3$ (Merck) and $FeCl_3.6H_2O$ (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 μm, 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 $RuFe/SiO_2$ and one run with Ru/SiO_2 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.

Run 1

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 g (1) 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% $RuFe(1:3)/SiO_2$ 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

(1) weight of dried unreduced catalyst

(2) metal weight with respect to the unsupported carrier

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/SiO_2. The reactor pressure was 9.0 bar. The inlet gas flow was 200 ml (20°C, 1 bar)/min.

Exp. No.	Start after [h]	Analysis after [h]	Temp. [°C]	H_2/CO feed [-]
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

Table 3.2

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. No.	Start after [h]	Analysis after [h]	Temp. [°C]	H_2/CO feed [-]	Flow in [1] [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
6	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)/SiO_2 suspended in 200 g squalane. The main objective of run 3 was the investigation of the influence of the partial pressures of CO and H_2 on the activity and selectivity. For that purpose first the pressure of H_2 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

Run 4

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/SiO_2 and Ru/SiO_2

The activity of a fresh RuFe/SiO_2 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/SiO_2

Exp. No.	Start after [h]	Analysis after [h]	P_{H_2} [bar]	P_{CO} feed [bar]	P_{H_2O} [bar]	Flow in [ml/min] 5)	Reactor pressure [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	
		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)
3	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	
27 6)	958	20	6.21	1.79	0.018	235	9.0	

1) temperature of the reactor: 230°C
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% Ru/SiO_2

Exp. No. [-]	Start after [h]	Analysis after [h]	P_{H_2} [bar]	PCO feed [bar]	P_{H_2O} 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

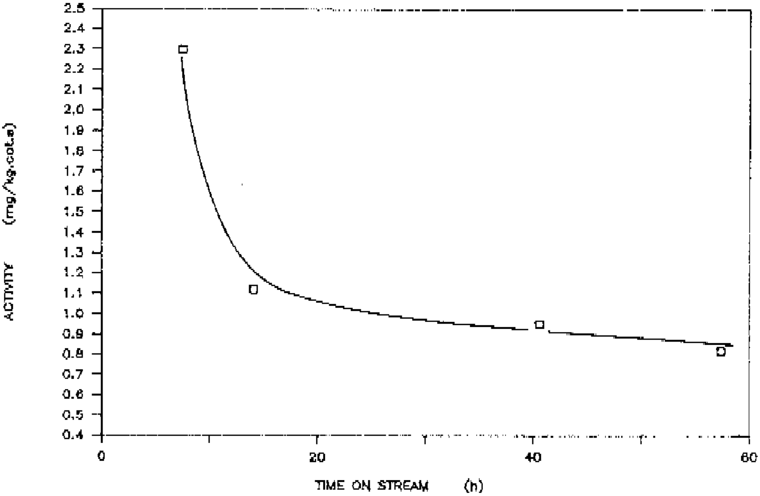

Fig. 3.1 The activity of a fresh RuFe/SiO_2 catalyst as a function of time on stream

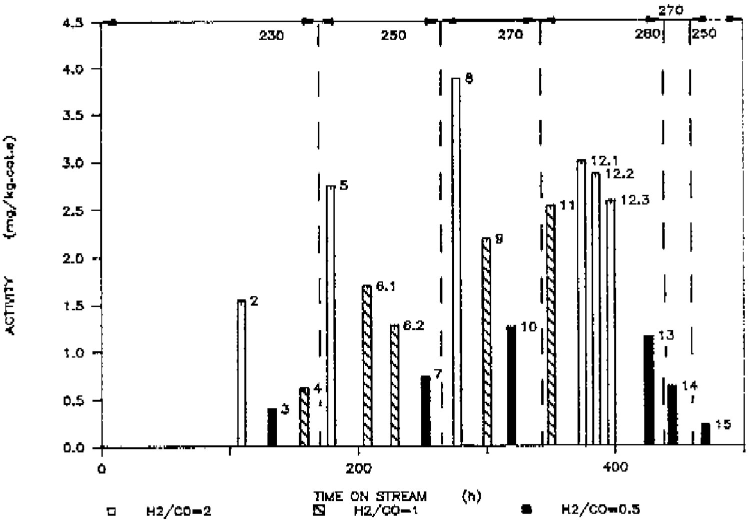

Fig. 3.2 Summary of the activity of RuFe/SiO$_2$ as a function of time on stream for all experiments of run 1. The temperature is reported on the upper side

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/SiO$_2$ 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

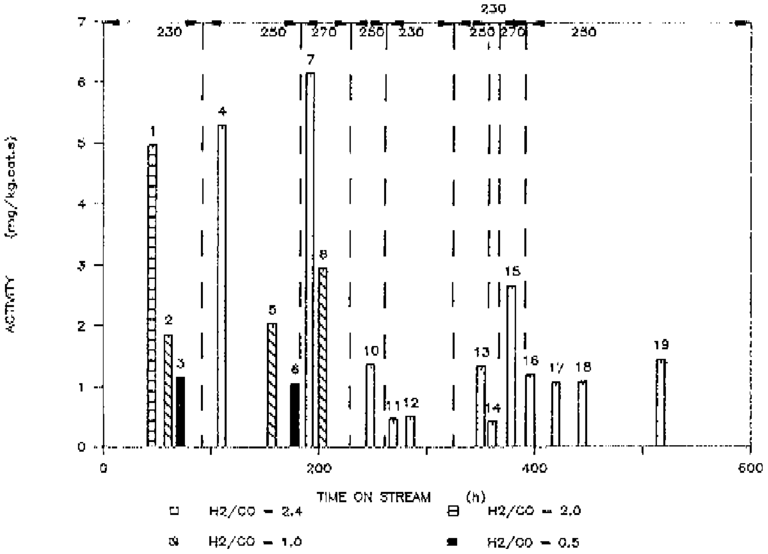

Fig. 3.3 Summary of the activity of RuFe/SiO$_2$ as a function of time on stream for all experiments of run 2. The temperature is reported on the upper side

state value reached in experiment 25.1 of run 3 (note 1), namely 1) 0.5 wt% RuFe (1:2.6)/SiO_2 at its final activity (ref. 11), 2) unsupported RuFe (1:2) and 3) 5.0 wt% RuFe(1:3)/SiO_2. 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

Catalyst	T	H_2/CO	P	X_{CO}	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)6)	-	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