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.

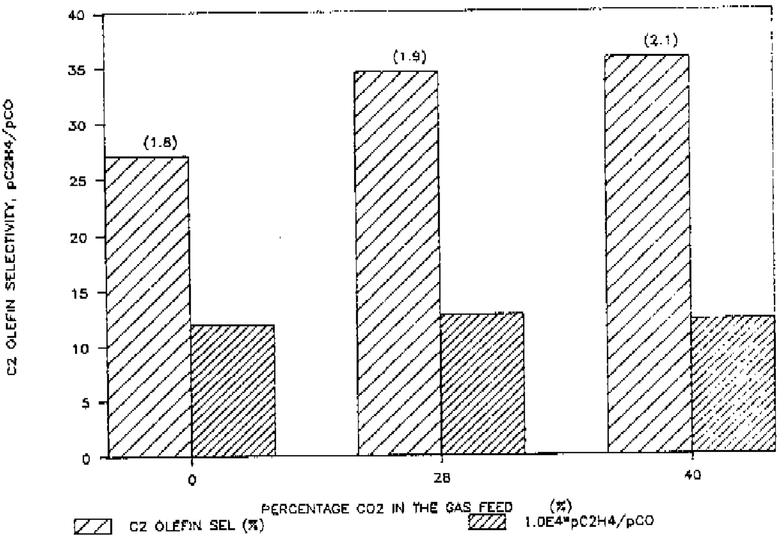


Fig. 2.34 The effect of the CO_2 percentage in the gas feed on the C_2 olefin selectivity and the ethene/carbon monoxide pressure ratio (run 3)

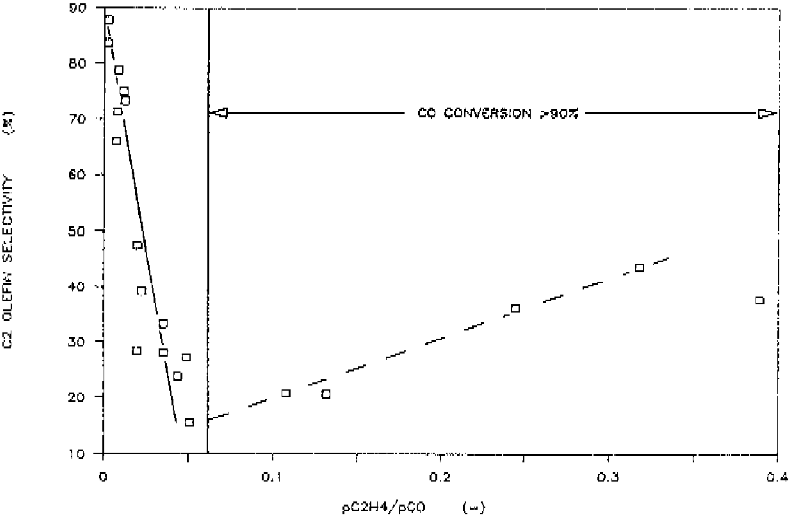


Fig. 2.35 The effect of the exhaustion of CO on the relation between the C_2 olefin selectivity and the ethene/carbon monoxide pressure ratio at 250°C (run 2)

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].

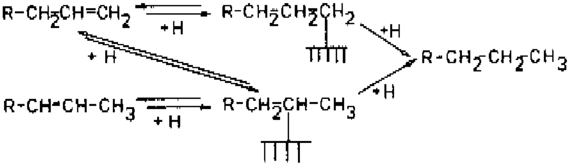


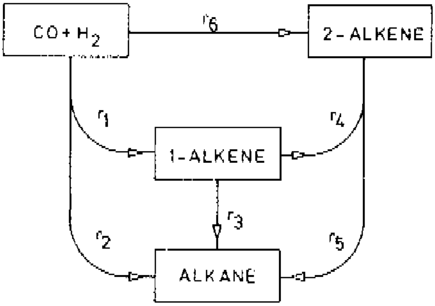
Fig. 2.36 Double bond shift and secondary hydrogenation of olefins according to Schulz [42]

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 H_2 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.



$r_1 = k_1 C_{H_2}$

$r_2 = k_2 C_{H_2}$

$r_3 = k_3 C_{H_2} \theta_{1\text{-Alkene}}$

$r_4 = k_4 (C_{H_2})^x \theta_{1\text{-Alkene}}$

$r_5 = k_5 C_{H_2} \theta_{2\text{-Alkene}}$

$r_6 = k_6 C_{H_2}$

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:

$$F_{out}C_{1\text{-alkene},G} = (k_1 C_{H_2,L} - k_4 C_{H_2,L}^{\;x} \theta_{1\text{-alkene}} - k_3 C_{H_2,L} \theta_{1\text{-alkene}}) V_L \quad (2.46)$$

$$F_{out}C_{2\text{-alkene},G} = (k_6 C_{H_2,L} + k_4 C_{H_2,L}^{\;x} \theta_{1\text{-alkene}} - k_5 C_{H_2,L} \theta_{2\text{-alkene}}) V_L \quad (2.47)$$

$$F_{out}C_{alkane,G} = (k_2 C_{H_2,L} + k_3 C_{H_2,L} \theta_{1\text{-alkene}} + k_5 C_{H_2,L} \theta_{2\text{-alkene}}) V_L \quad (2.48)$$

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):

$$\text{olefin sel.} = \frac{k_1+k_6}{k_1+k_2+k_6} - \frac{k_3\ C_{1\text{-alkene},L}}{(k_1+k_2+k_6)C_{CO,L}} - \frac{k_5\ C_{2\text{-alkene},L}}{(k_1+k_2+k_6)C_{CO,L}} \quad (2.49)$$

$$\text{With } C_{i,L} = \frac{C_{i,G}}{m_i} = \frac{P_i}{RTm_i}$$

Eq.(2.49) can be written as follows:

$$\text{olefin sel.} = \frac{k_1+k_6}{k_1+k_2+k_6} - \frac{k_3\, P_{1\text{-alkene}}\, m_{CO}}{(k_1+k_2+k_6) P_{CO}\, m_{1\text{-alkene}}} - \frac{k_5\, P_{2\text{-alkene}}\, m_{CO}}{(k_1+k_2+k_6) P_{CO}\, m_{2\text{-alkene}}} \qquad (2.50)$$

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

$$\text{olefin sel.} = \frac{k_1+k_6}{k_1+k_2+k_6} - \frac{k_3\, m_{CO}\, P_{alkenes}}{(k_1+k_2+k_6) m_{alkenes}\, P_{CO}} \qquad (2.51)$$

With $P_{alkenes} = P_{1\text{-alkene}} + P_{2\text{-alkene}}$.

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:

$$\text{olefin sel.} = \frac{k_1+k_6}{k_1+k_2+k_6} - \frac{k_3\, m_{CO}\, P_{1\text{-alkene}}}{(k_1+k_2+k_6)\, m_{1\text{-alkene}}\, P_{CO}} \qquad (2.52)$$

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 $k_3 \gg k_5$ 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:

$$\frac{p_{1\text{-alkene}}}{p_{1\text{-alkene}}+p_{2\text{-alkene}}+p_{\text{alkane}}} = \frac{k_1}{k_1+k_2+k_6} - \frac{m_{CO}}{m_{1\text{-alkene}}\,(k_1+k_2+k_6)} \cdot \left(k_3 + \frac{k_4\,p_{H_2}^{\,x-1}}{(m_{H_2}RT)^{x-1}}\right) \cdot \frac{p_{1\text{-alkene}}}{p_{CO}} \qquad (2.53)$$

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 $p_{1\text{-alkene}}/p_{CO}$ ratio only in case the isomerization is fast with respect to the hydrogenation of 2-alkenes:

$$\frac{p_{2\text{-alkene}}}{p_{1\text{-alkene}}+p_{2\text{-alkene}}+p_{\text{alkane}}} = \frac{k_6}{k_1+k_2+k_6} + \frac{k_4\,p_{H_2}^{\,x-1}\,m_{CO}\,p_{1\text{-alkene}}}{(m_{H_2}RT)^{x-1}\,m_{1\text{-alkene}}\,p_{CO}} - \frac{k_5\,m_{CO}\,p_{2\text{-alkene}}}{(k_1+k_2+k_6)\,m_{2\text{-alkene}}\,p_{CO}} \qquad (2.54)$$

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 C_4 hydrocarbons are plotted as function of the 1-butene/CO pressure ratio in Figure 2.38. The $1\text{-}C_4H_8$ fraction clearly decreases with increasing $1\text{-}C_4H_8$/CO pressure ratio, in agreement with Eq.(2.52). This decline of the $1\text{-}C_4H_8$ 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.

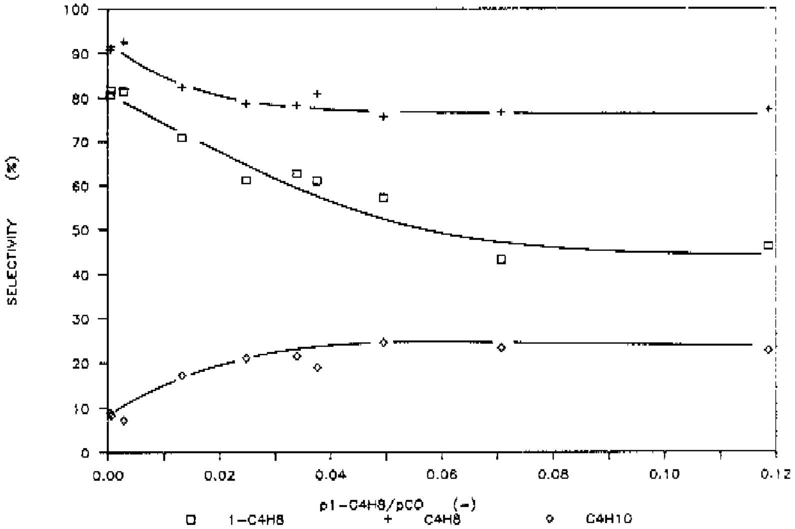


Fig. 2.38 Selectivity of various C_4 fractions as a function of the 1-butene/carbon monoxide pressure ratio at 270°C (run 1)

The gradual decline of the C_4 olefin selectivity as function of CO conversion (a higher CO conversion also means a higher 1-C_4H8/CO pressure ratio) is comparable with the decrease of both C_3 and C_5 olefin selectivity up to a CO conversion level of 87%, as shown in Table 2.14. The C_3 olefin selectivity is lower than that of C_4 and C_5 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 C_2 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.

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. $T=250°C$, $(H_2/CO)_{in} = 0.67-3.0$

x_{CO}	p	olefin selectivity				$1-C_4H_8$ / $C_{4,tot}$	$1-C_5H_{10}$ / $C_{5,tot}$
		C_2	C_3	C_4	C_5		
[%]	[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

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 $p_{1-C_4H_8}/p_{CO}$ 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 $p_{1\text{-butene}}/p_{CO}$ ratio. P=9 bar, $(H_2/CO)_{in} = 0.67$

T [°C]	X_{CO} [%]	$\frac{1\text{-}C_4H_8}{C_{4,tot}}$ [%]	$\frac{2\text{-}C_4H_8}{C_{4,tot}}$ [%]	$\frac{p_{1\text{-}C_4H_8}}{p_{CO}}$ [-]
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,

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

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

$$r_n V_L = p_n F_{out}/RT \qquad (2.56)$$

the residence time can be simply written as

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

Although, is is obvious from Eq.(2.57) that the residence time increases as a function of carbon number due to the decreasing solubility coëfficient 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:

$$C_n \text{ olefin selectivity} = A - B' \frac{p_{1\text{-alkene}}}{p_{CO}} \cdot \frac{m_{CO}}{m_{1\text{-alkene}}} \tag{2.58}$$

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:

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

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

$$\ln(m_n) = a\ n + b \tag{2.60}$$

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

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

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 C_1-C_4 hydrocarbons up to temperatures of 475 K. Therefore, the Henry coefficient of C_2 and C_4 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

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

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.

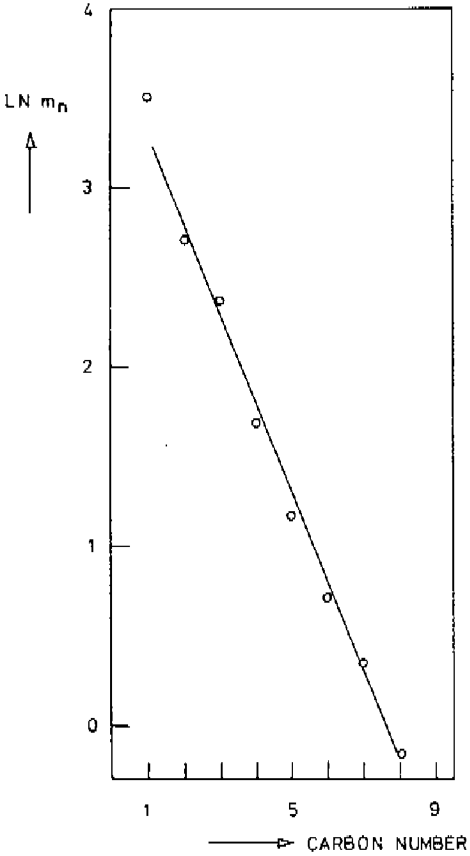


Fig. 2.39 The solubility coefficient of hydrocarbons as a function of the carbon number in paraffin oil for 250°C based on data of De Priester [79]

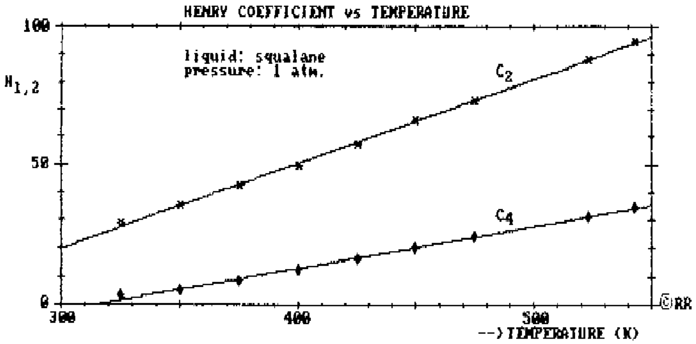


Fig. 2.40 The Henry coefficient of C_2 and C_4 in squalane as a function of the temperature based on data of Donohue [67] and Chappelow [68]. The data points for 532 and 543 K are extrapolated

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 1. only the value of α varies, 2. the rates of secondary reactions are not affected by the chain length and 3. 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 C_1-C_8 hydrocarbons to 0.9 for C_{10}^+ 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.

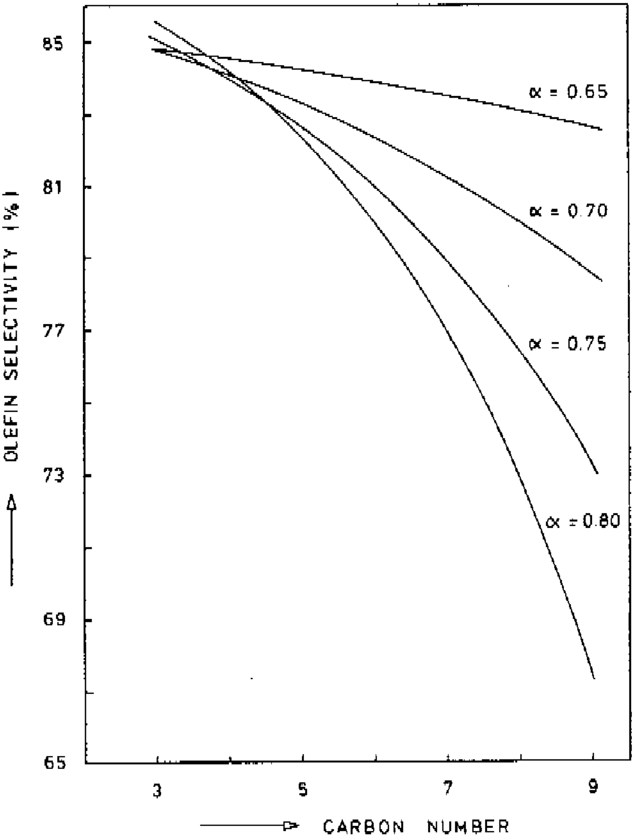


Fig. 2.41 The effect of α on the olefin selectivity calculated with help of Eq.(2.58) and (2.61). The values of A and B are derived from Figure 2.28 where A and B represent the initial fraction of olefins at each carbon number and the rate of secondary hydrogenation of olefins respectively (see section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

$A = 90$ %

$B = 100$ %

$T = 250$ °C

$p_{CO} = 3.4$ bar

$m_{CO} = 5.29\ m^3{}_L/m^3{}_G$

$m_{C_3} = 0.77\ m^3{}_L/m^3{}_G$

$p_{HC} = 1.0$ bar

($X_{CO} = 80$ %: $(H_2/CO)_{feed} = 0.6$:

$P = 9.0$ bar)

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% SiO_2, 0.6% Cr_2O_3, 4.6% MgO, and 0.6% K_2O, 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% Al_2O_3, and 2.00% ZrO_2, 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 ^{14}C 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 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% Al_2O_3, 0.5-0.8% K_2O, 0.7-1.2% CaO and < 0.4% SiO_2, they added 1.5 mole% C_2H_4 to the synthesis gas (H_2/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 C_1* and H* surface species for incorporation and hydrogenation respectively. The resulting decrease in concentration of C_1* 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.

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.

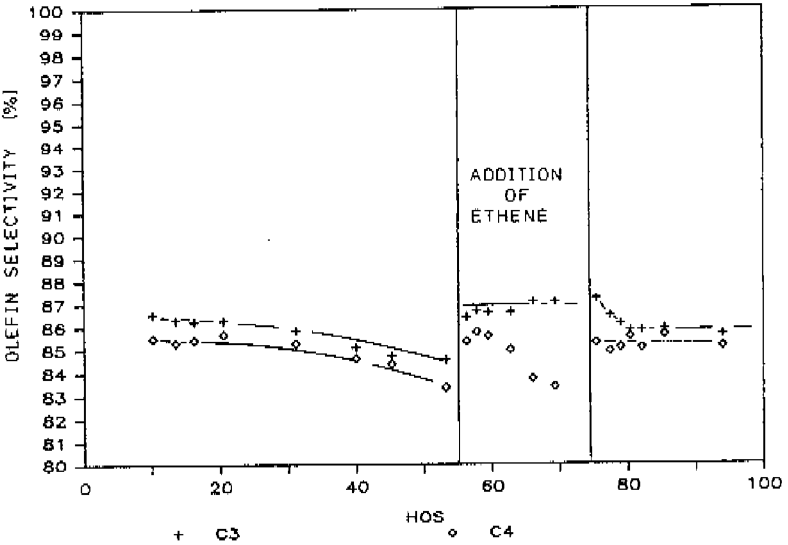


Fig. 2.42 Effect of the co-feeding of ethene on the olefin selectivity at 250°C (series A)

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.

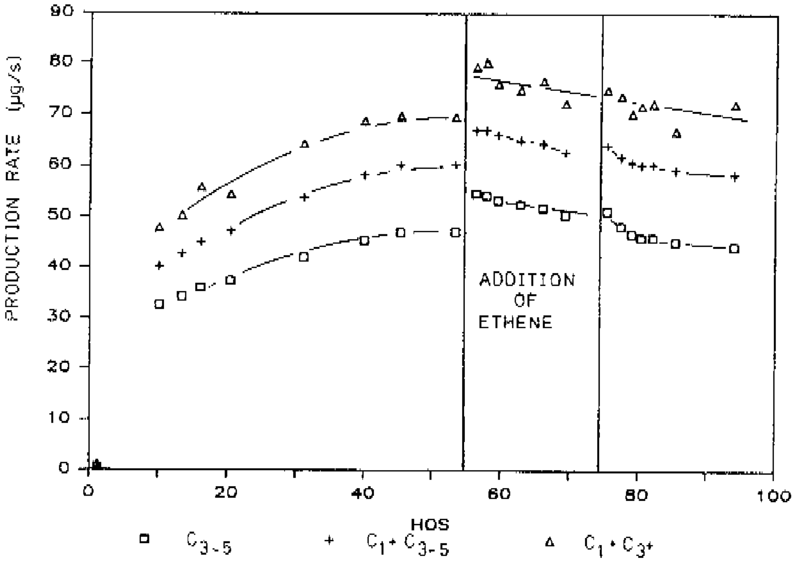


Fig. 2.43 Effect of the co-feeding of ethene on the production rate of hydrocarbons at 250°C (series A)

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.

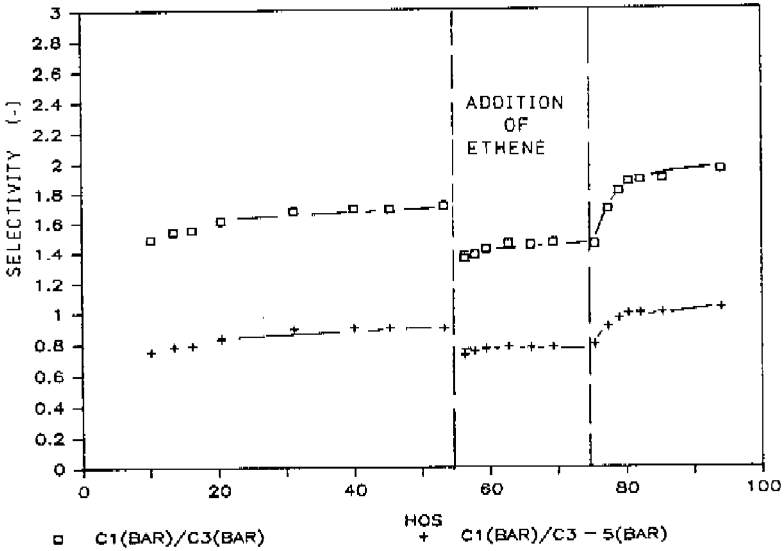


Fig. 2.44 Effect of the co-feeding of ethene on the methane selectivity at 250°C (series A)

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 C_2^+ 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. no.	P [bar]	T [°C]	F_{H_2} 1) [ml/min]	F_{CO} 1) [ml/min]	$F_{C_2H_4}$ 1) [ml/min]	CO conv. [%]
A	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
B	4	1.5	250	40	61	0	15
B	5	1.5	250	40	61	6.5	15
B	6	1.5	250	40	61	0	15
C	7	1.5	250	73	25	0	25
C	8	1.5	250	74	24	6.5	25
C	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

Table 2.17

Material balances of ethene added.

	Series A		Series B	
	[µmol C/s]	[mol%]	[µmol C/s]	[mol%]
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]	[mol%]
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. no.	C_3 olefin s.[3] [%]	$r_{C_3-C_5}$ [µg/s]	C_1/C_3	X_{CO} [4] [%]	$P_{C_2H_4}/P_{CO}$ [-]
A	1	85	47	1.7	74	0.024
A	2	87	54	1.4	73	0.190
A	3	86	47	1.8	72	0.021
B	4	93	5	3	15	0.002
B	5	94	7, 4.5 [1]	2.5, 3 [2]	15	0.118
B	6	93	4.5	3.5	15	0.002
C	7	90	8.5	5.2	25	0.008
C	8	90.5	12	3	25	0.293
C	9	90	8	5.2	25	0.010
D	10	88.5	60	1.3	55	0.012
D	11	88.7	60	1.2	55	0.080
D	13	88.5	60	1.3	55	0.012

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

[2] During experiment 5 the ratio C_1/C_3 increased from 2.5 to 3.

[3] C_3 olefin s. = $P_{C_3H_6}/(P_{C_3H_6} + P_{C_3H_8})* 100\%$.

[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 $p_{C_2H_4}/p_{CO}$ 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 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.

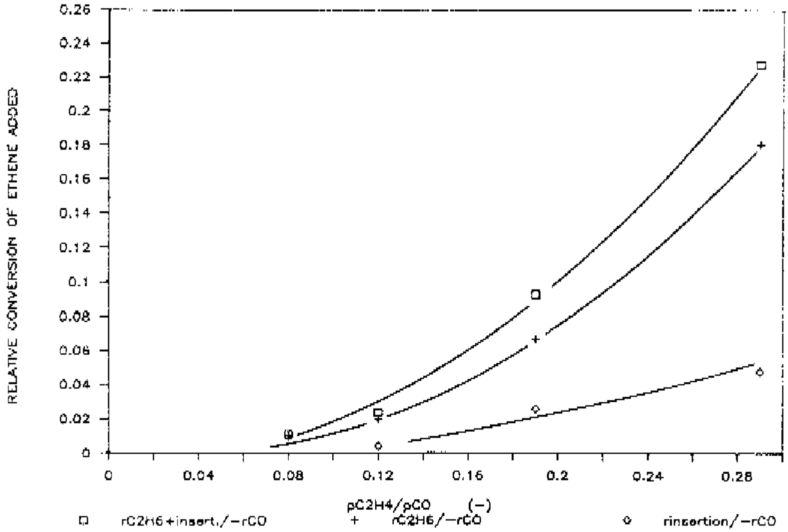

Fig. 2.45 Hydrogenation and insertion rate with respect to the CO conversion rate as a function of the ethene/carbon monoxide pressure ratio during the co-feeding of ethene at 250°C