(3) $C^* + x\, H^* \xrightarrow{k_3} CH_x^*$ (RDS)

(4) $O^* + y\, H^* \xrightarrow{k_4} H_yO^* \longrightarrow H_2O$

At the steady state $r_3 = r_4$, so the rate of reaction is

$$r_3 = k_3\, \theta_C\, \theta_H^{\,x} \tag{6.31}$$

$$= k_3 \left(\frac{K_C\, p_{CO}}{k\, p_{H_2}^{\,z}}\right)^{1/2} p_{H_2}^{\,x/2} \left(\frac{1}{1 + (1 + k\, p_{H_2}^{\,z})(K_C\, p_{CO}/k\, p_{H_2}^{\,z})^{1/2}}\right)^{x+1}$$

where $k = k_3/k_4$ and $z = x - y$. As a function of the partial pressure of carbon monoxide the equation reads, with $x = 2$:

$$r_3 = k \frac{\sqrt{p_{CO}}}{(1 + K'\sqrt{p_{CO}})^3} \tag{6.32}$$

which has the same dependence on $p_{CO}$ as equation (6.30).

Thus our experimental results can be explained by the following model:

i) the dissociation of carbon monoxide is rapid (i.e. the surface coverage of molecularly adsorbed CO is small compared to the surface coverage of surface carbon);

ii) the rate determining step is the hydrogenation of surface carbon;

iii) the adsorbed oxygen is removed as water.

These results agree with some recently published data in which it has been shown that at least the formation of methane proceeds via the dissociation of carbon monoxide /30-35/.

### 6.5.3. CHAIN GROWTH

In principle there are two types of mechanisms for chain growth:

i) the unit added in chain growth (building unit) is formed via the same steps as the surface complex which starts to grow;

ii) the building unit is not formed via these steps.
Based on the conclusions in the previous section we say that from the mechanisms discussed in chapter 1 the insertion of a $CH_x$-complex belongs to the first group and the insertion of carbon monoxide and the dehydrocondensation of an alcohol complex to the second group. In the following the two groups are discussed separately.

In chapter 4 the product distribution was shown to follow the Flory distribution model. It was pointed out that the fit of the product distribution to the Flory curve is independent of the detailed mechanism for chain growth. The Flory constant, $\alpha$, is noticed to be a weak function of the partial pressures of hydrogen and carbon monoxide. But the relation between $\alpha$ and the partial pressures will be presumably different for different mechanisms. This allows us to distinguish between chain growth mechanisms via the insertion of carbon monoxide and via the insertion of a $C_1$-complex. The dehydrocondensation is not considered further because no evidence of the existence of an alcohol-type complex was found. Moreover the chain growth mechanism proposed by Anderson /16/ can be described by the same kinetic expressions as the mechanism of the $[C_1{*}]$ insertion.

*Chain growth via CO insertion*

The parameter $\alpha$ for the insertion of carbon monoxide can be represented as

$$\alpha = \frac{k_p\ \theta_{CO}\ \theta_H^{\ x_2}\ [C_i{*}]}{k_p\ \theta_{CO}\ \theta_H^{\ x_2}\ [C_i{*}] + k_t\ \theta_H^{\ x_1}\ [C_i{*}]} \tag{6.33}$$

which can be transformed into

$$\frac{1-\alpha}{\alpha} = \frac{k_t\ \theta_H^{\ x}}{k_p\ \theta_{CO}}\ , \text{ where } x = x_1 - x_2. \tag{6.34}$$

By substituting the surface coverages of hydrogen and carbon monoxide we obtain an equation that gives the dependence of $\alpha$ on the partial pressure of carbon monoxide at a constant pressure of hydrogen. Three cases can be distinguished:

1) $x \geqslant 2$; 2) $x = 1$; 3) $x \leqslant 0$

1) if $x \geqslant 2$ (and assuming a low coverage of $H_2$) equation (6.34) can be written in the form

$$\left(\frac{\alpha}{(1-\alpha)\ p_{CO}}\right)^{\frac{1}{x-1}} = A + B\ p_{CO} + C\sqrt{p_{CO}} \qquad (6.35)$$

$$A,\ B,\ C > 0.$$

$\frac{\alpha}{(1-\alpha)\ p_{CO}}$ calculated from the experimental results is given as a function of the partial pressure of carbon monoxide in table 6.7.

*Table 6.7.* $\frac{\alpha}{(1-\alpha)\ p_{CO}}$ *as a function of* $p_{CO}$.

| $p_{CO}$ (kPa) | 10 | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|---|
| $\frac{\alpha}{(1-\alpha)\ p_{CO}}$ | 12.5 | 5.0 | 3.7 | 3.3 | 2.6 | 2.3 |

This shows that the left-hand side of equation (6.35) decreases when the partial pressure of carbon monoxide increases. As however the right-hand side of equation (6.35) is an increasing function of the partial pressure of carbon monoxide, because all the constants A, B and C are positive, this model is unapplicable.

2) if $x = 1$, the right-hand side of equation (6.35) should be constant. This also does not correspond to the experimental results.

3) if $x = 0$, the equation (6.35) gets a form

$$\frac{(1-\alpha)\ p_{CO}}{\alpha} = A' + B'\ p_{CO} + C'\sqrt{p_{CO}} \qquad (6.36)$$

When $x = 0$ the same amount of hydrogen is used in the rate determining steps of the chain growth and of the termination. This situation is checked by calculating the dependence of $\alpha$ on the partial pressure of carbon monoxide for $x_1 = 0, 1, 2$. These calculations are discussed in the next section, which deals with models. Anyhow, we can mention already here that in all cases the calculated order for $\alpha$ in carbon monoxide is higher (0.3) than found experimentally (0.1-0.2).

*Chain growth via $C_1$ insertion*

The parameter $\alpha$ for the chain growth via the insertion of a $C_1$-complex is

$$\alpha = \frac{k_p \left[C_1^*\right] \left[C_i^*\right]}{k_p \left[C_1^*\right] \left[C_i^*\right] + k_t \theta_H^x \left[C_i^*\right]} \quad . \qquad (6.37)$$

The surface coverage of a $C_1$-complex $\left[C_1^*\right]$ is the real root of the following equation:

$$\left[C_1^*\right]^3 + \frac{k_t}{k_p} \theta_H^x \left[C_1^*\right]^2 + \left(\frac{k_t \theta_H^x}{k_p}\right)^2 \left[C_1^*\right] - \frac{r_{init.} k_t \theta_H^x}{k_p^2} = 0$$

($r_{init.}$ = rate of initiation) (6.38)

which is obtained from the steady-state assumption that $d \left[C_1^*\right]/dt = 0$. Because of the complex dependence of $\alpha$ on surface coverages and through those on partial pressures, this mechanism is also checked with the calculations presented in section 6.5.4.

## 6.5.4. REACTION MODELS

In section 6.5.3 it sometimes appeared impossible to describe $\alpha$ as a function of the partial pressures using simple mathematical equations. Therefore we decided to analyze the whole product distribution instead of $\alpha$. To this end we develop two models: one for chain growth by carbon monoxide insertion and another for chain growth by $C_1$-complex insertion. Both models allow the product distribution to be calculated as a function of the partial pressures. The following assumptions are used:

i) the initiation takes place via the hydrogenation of dissociatively adsorbed carbon monoxide;

ii) all the chain growth steps have the same mechanism and the same reaction rate constant;

iii) the termination mechanism is the same for the $C_2$ and higher hydrocarbons;

iv) there is no product readsorption.

The reaction scheme is:

$$\begin{tikzcd}
C* + x\ H* \arrow[r, "k_o"] & \left[C_1*\right] \arrow[r, "k_p"] \arrow[d, "k_1"] & \left[C_2*\right] \arrow[r, "k_p"] \arrow[d, "k_t"] & \left[C_3*\right] \arrow[r] \arrow[d, "k_t"] & {} \\
 & C_1 & C_2 & C_3 &
\end{tikzcd} \qquad (6.39)$$

*Models with CO insertion*

The following rates are used:

| | |
|---|---|
| initiation | $k_o\ \theta_C\ \theta_H^{x_o}$ |
| chain growth | $k_p\ \left[C_i*\right]\ \theta_{CO}\ \theta_H^{x_2}$ |
| termination of $C_1$ | $k_1\ \left[C_1*\right]\ \theta_H^{z}$ |
| termination of $C_2$ .. $C_{10}$ | $k_t\ \left[C_i*\right]\ \theta_H^{x_1}$ |

where $\left[C_i*\right]$ is the surface coverage of the complex with i carbon atoms.

In the previous section we could reject the mechanisms in which $x_1 > x_2$, i.e. where more hydrogen was involved in the termination than in the chain growth. Therefore we discuss here only the cases $x_1 \leq x_2$, i.e. where the same or a higher amount of hydrogen is involved in the chain growth than in the termination.

In the appendix the detailed equations of the surface coverages are given. The constants in the rate expressions have been adjusted to obtain the best fit of the experimental data for a mole fraction of hydrogen of 0.20 and of carbon monoxide of 0.20. With this set of constants we calculated the product distribution and the reaction orders for other partial pressures. The following values of the $x_i$'s have been used: $x_0 = 2$, $x_1 = x_2 = 0, 1, 2$ and $z = x_1$ or $x_1 + 1$. It was found that the different values of $x_1$ do not change the product distribution. The product distributions are plotted in figure 6.15 for $x_1 = 2$ and $z = 3$. The calculated orders are in the appendix, table 1.

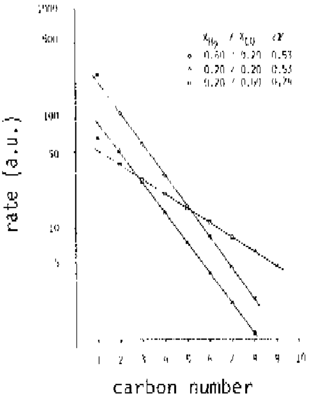


*Figure 6.15. Calculated product distributions. Model: chain growth via CO insertion.*

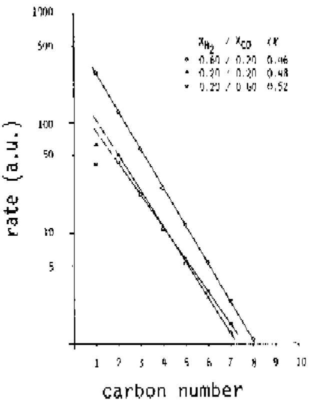


*Figure 6.16. Calculated product distributions. Model: chain growth via $CH_x$ insertion.*

The orders in hydrogen agree reasonably well with those found experimentally for the $Co/Al_2O_3$ catalyst (tables 6.1 and 6.2), also for individual products. To obtain these correct orders for all products we need to assume $z = x_1 + 1$. This model fails however in the prediction of the right orders for carbon monoxide. E.g. the predicted order of α in carbon monoxide is 0.36 while experimentally an order of about 0.1 is found. This can be clearly seen in the difference between the orders in carbon monoxide for two consecutive hydrocarbons.

If $x_2 > x_1$, i.e. more hydrogen is involved in the chain growth than in the termination the orders of α both in hydrogen and in carbon monoxide are positive. This would mean that a higher partial pressure of both reactants increases the formation of higher hydrocarbons. This is in contradiction with the experimental results.

### *Models with $C_1$-complex insertion*

The rates used are:

| | |
|---|---|
| initiation | $k_o \, \theta_C \, \theta_H^{x_o}$ |
| chain growth | $k_p \, [C_i^*] \, [C_1^*]$ |
| termination of $C_1$ | $k_1 \, [C_1^*] \, \theta_H^{z}$ |
| termination of $C_2$ .. $C_{10}$ | $k_t \, [C_i^*] \, \theta_H^{x}$ |

Again the detailed equations for the calculation of the surface coverages are given in the appendix.

The best fit to the experimental data is obtained with values of $x_o = 2$, $x = 1$ and $z = 2$. The results are represented in figure 6.16 and in the appendix, table 2.

Variations in the partial pressures of hydrogen and carbon monoxide change the product distribution slightly, just as found experimentally. The orders, also those calculated on different levels of "constant pressure" change in correspondence with those found experimentally. Also according to this model the termination of methane kinetically needs one hydrogen atom more than the other terminations. Consequently at a high partial pressure of carbon monoxide the amount of methane becomes less than that of the $C_2$-fraction.

### *The unsupported catalyst*

The results of the unsupported catalysts are also fitted into the reaction models described above.

For the model with CO insertion the best correspondence is obtained with the values $x_o = 3$ and $x_1 = x_2 = z = 1$, while the best results for the model with $C_1$-complex insertion are obtained with the values $x_o = x = z = 2$. The calculated orders are given in the appendix.

In both models the same amount of hydrogen has to be used for all the terminations. The orders should be compared with the experimentally found orders (table 6.3). It can be noticed that if the chain growth proceeds via CO insertion, at one "constant level" of the partial pressures the orders agree quite well with the experimental values. But when the "constant level" is varied the changes take place in the wrong directions: the orders both in hydrogen and in carbon monoxide increase with increasing "constant levels" of the partial pressures. If the chain growth goes via a $C_1$-complex, the orders in hydrogen decrease too fast at a "constant level" of the partial pressure of carbon monoxide. Increasing the level of the partial pressure of carbon monoxide decreases the orders in hydrogen as found experimentally. The orders in carbon monoxide first increase and then decrease. Thus none of the models describes the results obtained with the unsupported catalyst completely. One point should be added: in the studies of the hydrogenation of ethylene /133/ it was noticed that on the unsupported catalyst about 60% of ethylene was cracked to methane at a low concentration of ethylene. That means that also other reactions than those included in our models of the Fischer-Tropsch synthesis occur on this catalyst.

The following conclusions can be drawn from the reaction models:

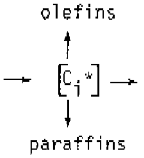
i) it is not likely that chain growth takes place via CO insertion;

ii) on the $Co/Al_2O_3$ catalyst in the termination of methane one hydrogen atom more is involved than in the other terminations.

### 6.5.5. OLEFIN-PARAFFIN RATIO

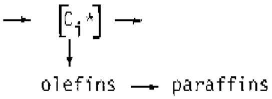
Basically there are two possibilities for the formation of paraffins:

1) parallel with the formation of olefins (i.e. both are formed from the same surface complex):



(6.40)

2) consecutively from olefins:



(6.41)

For the first case the rates of olefin and of paraffin formation can be written in the forms:

$$r_{olef,i} = k_{olef,i} \left[C_i{}^*\right] \theta_H{}^y$$

$$r_{paraf,i} = k_{paraf,i} \left[C_i{}^*\right] \theta_H{}^x, \; y < x$$

The ratio of olefins to paraffins is thus

$$\frac{r_{olef,i}}{r_{paraf,i}} = k_i \; \theta_H{}^{y-x}$$

$$= k' \left( \frac{\sqrt{K_{H_2} p_{H_2}}}{1 + K_{CO}\, p_{CO} + \sqrt{K_{H_2} p_{H_2}}} \right)^{y-x} \qquad (6.42)$$

(i.e. a negative order in hydrogen).

As an example we calculate the orders in hydrogen for the ethylene-ethane ratio at the different levels of carbon monoxide on the Co/$Al_2O_3$ catalyst. The results are in table 6.4 in section 6.2.3.

The orders in hydrogen increase with increasing partial pressure of carbon monoxide. According to formula (6.42) the order should remain constant (if $1 + K_{CO}\, p_{CO} \gg \sqrt{K_{H_2} p_{H_2}}$) or decrease with increasing partial pressure of carbon monoxide but never increase, as observed experimentally.

A stronger argument against the exclusively parallel formation of olefins and paraffins is the fact that experimentally the olefin-paraffin ratio decreases with the residence time whereas with parallel reactions no influence of the residence time would be expected.

For the second case the rates of olefin and paraffin formation can be written as:

$$r_{olef,i} = k_{olef,i} \left[C_i{}^*\right] \theta_H{}^y - k_{paraf,i} \left[c_{olef,i}\right] \theta_H{}^x \qquad (6.43)$$

and

$$r_{paraf,i} = k_{paraf,i} \left[c_{olef,i}\right] \theta_H{}^x \qquad (6.44)$$

At high olefin-paraffin ratios the second term on the right-hand side of equation (6.43) can be neglected. Then the olefin concentration depends linearly on the residence time. That would further mean that the olefin-paraffin rate ratio can be expressed by equation (6.45):

$$\frac{r_{olef,i}}{r_{paraf,i}} = k_i' \cdot \frac{1}{\tau} \qquad (6.45)$$

where τ is the residence time. Equation (6.45) is equal to

$$\frac{r_{paraf,i}}{r_{olef,i}} = k_i \tau \qquad (6.46)$$

i.e. a linear relation between the paraffin-olefin ratio and the residence time.

If paraffins are also formed via a parallel reaction, equation (6.46) becomes

$$\frac{r_{paraf,i}}{r_{olef,i}} = k_i \tau + k_1 \qquad (6.47)$$

where $k_i$ and $k_1$ are constants which depend on the reaction rate constants and the surface coverages of reaction intermediates and of hydrogen. In figure 6.17 the paraffin-olefin ratios for the $C_2$- and the $C_3$-fraction are plotted as a function of the residence time. The model indicates that

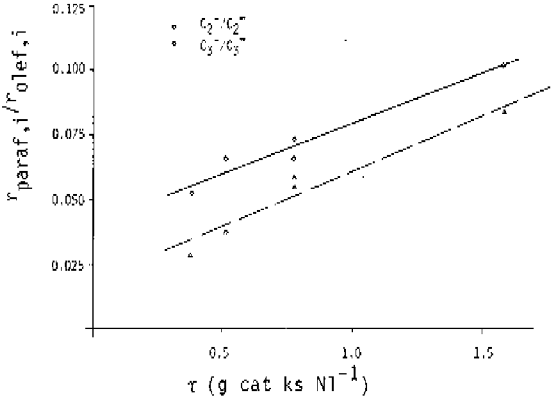


*Figure 6.17. Paraffin-olefin rate ratio as a function of the residence time. Catalyst: $Co/Al_2O_3$. $p_{H_2} = p_{CO} = 20$ kPa. T = 523 K.*

paraffins are mainly formed in a consecutive reaction, but that some formation in a parallel reaction is possible and is somewhat more likely for ethane than for propane.

# CHAPTER 7

## Final Discussion

In this chapter we shall summarize our conclusions on the mechanism of the Fischer-Tropsch synthesis. They will be based on the results described in the preceding chapters and on the relevant literature.

### 7.1. INITIATION

For the low turnover frequencies, also found in this study, various explanations can be suggested:

i) a low intrinsic activity of sites,
ii) a small number of active sites and
iii) side reactions.

The overall rate of the Fischer-Tropsch synthesis is only one hundredth of the rate of the ethylene hydrogenation under the same conditions. This difference cannot be explained by an essential difference in the coverages of ethylene and of carbon monoxide, because of the similarity of the adsorption heats. Since we excluded the dissociation of carbon monoxide as a rate determining step, the difference mentioned above can be explained by a difference in reactivity of the adsorbed intermediates towards hydrogen, i.e. the reactivity of $C_xH_y$-species is much higher than that of carbon from dissociated carbon monoxide. But in chapter 6 we calculated that only a small fraction of the catalyst surface is active during the Fischer-Tropsch synthesis. This indicates that the low turnover frequencies calculated are also caused by a small number of active sites and not only by a low intrinsic activity of the active sites as proposed by Dautzenberg et al. /134/. Their conclusions were based on experiments on a ruthenium catalyst. This further implies that the amounts of adsorbed hydrogen are not a correct measure for the number of active (i.e. working) sites.

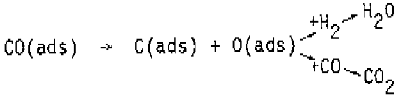
The kinetic results could be described by the model in which the rate determining step is the hydrogenation of carbon from the dissociatively adsorbed carbon monoxide. A first order in hydrogen for the total conversion of carbon monoxide supports this mechanism. In several studies it has been shown that on transition metals the adsorption of carbon monoxide takes place dissociatively at temperatures normally used for the Fischer-Tropsch synthesis /27-29/. Further some recently published results about the reactivity of surface carbon show that surface carbon is an active intermediate in methanation /30-35/ and also in the formation of higher hydrocarbons /36/.

The initiation consists thus of three stages:

1) the adsorption of hydrogen and carbon monoxide;
2) the formation of surface carbon from the adsorbed CO;
3) the hydrogenation of surface carbon.

There are two possibilities for the second stage:

a) $$2\ CO(ads) \rightarrow C(ads) + CO_2 \qquad (7.1)$$

b) 

$$CO(ads) \rightarrow C(ads) + O(ads) \begin{array}{l} \nearrow +H_2 \nearrow H_2O \\ \searrow +CO \searrow CO_2 \end{array} \qquad (7.2)$$

In the first case carbon dioxide is formed as a primary oxygen containing compound. This means that water is then formed via the water-gas shift reaction

$$H_2 + CO_2 \rightleftarrows H_2O + CO \qquad (7.3)$$

The equilibrium constant for reaction (7.3) is of the order of 0.01 at 523 K /16/. This means that with equal concentrations of hydrogen and carbon monoxide the concentration of water should be much less than that of carbon dioxide, if water is formed according (7.3). On the supported cobalt catalyst the quantity of produced carbon dioxide was around 5% of the total conversion of carbon monoxide to hydrocarbons. A low formation of carbon dioxide on cobalt catalysts has been found in several cases /16/. Also on an iron catalyst Dry et al. /119/ found a higher production of water than of carbon dioxide under the conditions in which the Boudouard reaction could be neglected. For none of these catalysts a correlation was found between the formation of methane and that of carbon dioxide. Thus the overall reaction equation given by Sachtler et al. /35/ for cobalt films at low pressures of CO,

$$2\ CO + 2\ H_2 \rightarrow CH_4 + CO_2 \qquad (7.4)$$

is only relevant for the conditions of their experiments.

The removal of oxygen from the surface depends on its reactivity towards hydrogen and carbon monoxide and the pressures of these components. The reduction of cobalt oxides by hydrogen and by carbon monoxide are much faster reactions than the Fischer-Tropsch reaction, which indicates that no oxide formation occurs during the synthesis under our conditions. The situation is totally different for iron catalysts where also the thermodynamics of the reduction of oxides is less favourable than for cobalt oxides. And indeed, during the synthesis on iron catalysts oxide formation is observed /19/.

In chapter 6 we concluded that the Fischer-Tropsch reaction on cobalt catalysts proceeds via an oxygen free complex. During the years several authors have suggested that an oxygen containing complex, especially an alcohol-type complex, is an intermediate in the Fischer-Tropsch synthesis. Blyholder and Neff /135/ studied the coadsorption of hydrogen and carbon monoxide on a silica supported iron catalyst by infra-red spectroscopy at 293 K and at 453 K. The increased intensity of the O-H stretching band at 453 K was interpreted as evidence for an alcoholic surface complex. Later on the authors interpreted the band at 6.4 and 6.96 μ as surface carboxylate /136/. But because of the stability of these compounds they were assumed not to take part in the reaction. The formation of methane was observed as well at 453 K. That would mean that also water was formed. Thus the increase of the O-H band could be caused by an intermediate in water formation instead of by an alcoholic intermediate. On a silica supported nickel catalyst no interaction of hydrogen and carbon monoxide was observed during the adsorption of their mixtures /137/. Further Blyholder et al. /136/ have shown that oxygen containing complexes are formed in the coadsorption of ethylene and carbon monoxide on various transition metals. The species resemble surface carboxylates and are stable up to 423-473 K. But the presence of oxygen containing complexes in their studies need not mean that these also take part in the Fischer-Tropsch synthesis. Moreover Heal et al.

/113/ studied the coadsorption of hydrogen and carbon monoxide on silica supported cobalt, and they did not detect any intermediate complex between 398 K and 488 K. Sastri et al. /138-139/ found the ratio of adsorbed hydrogen to adsorbed carbon monoxide from their mixtures to be 1:1 on cobalt/thorium oxide catalysts between 273 K and 368 K. That was interpreted as an indication for the formation of an alcoholic complex. The same interpretation has been suggested by Kölbel et al. /140/. However such ratio of adsorbed hydrogen to adsorbed carbon monoxide can be also explained by the formation of CH- and OH-groups.

Kölbel and Tillmetz /141-142/ have calculated, using the extended Hückel theory, that on iron and cobalt a stable complex of alcoholic type may be possible, but that on nickel a complex of the methylene type is more likely. On the other hand Goddard et al. /143/ have calculated that on nickel both a chemisorbed formyl radical and a chemisorbed $C_2$-species (without hydrogen) may be catalytically active intermediates. As there is ample evidence that the Fischer-Tropsch reaction pathways are kinetically determined and not thermodynamically, the value of this type of stability calculations is rather doubtful.

From the discussion above we can conclude that the existence of an oxygen containing complex on cobalt and on iron has not been proven convincingly. The situation is more difficult for ruthenium and the dissociation of carbon monoxide has been an open question for a long time. But the results of Singh and Grenga /144/ show that carbon monoxide decomposes on ruthenium at 823 K. Moreover Rabo et al. /33/ did not find any essential difference between nickel, cobalt and ruthenium in the way these metals adsorb carbon monoxide at various temperatures. The reactivity of carbonaceous species formed from the decomposition of carbon monoxide is also similar. The results of Goodman et al. /145/ show that on ruthenium the formation of methane is faster from formaldehyde than from the synthesis gas. They concluded that an active intermediate can be derived from formaldehyde. But whether that intermediate contains oxygen has not been demonstrated.

The mechanism of the Fischer-Tropsch synthesis with carbon as an intermediate has already been proposed by Fischer and Tropsch. Anderson has presented a number of arguments against that model /16/. But as pointed out by Ponec /63/ the evidences were based on experiments with bulk carbides and bulk carbon and the behaviour of surface carbon can be different. In our study it was found that the rate of carbonization is much lower than that of the Fischer-Tropsch reaction. In the presence of hydrogen no carbon formation was found at all on the unsupported catalyst. This shows that bulk carbon or carbide formation need not be related to the Fischer-Tropsch reaction.

Mechanisms where the hydrogenation of surface carbon is the rate determining step can explain the first order in hydrogen and the slightly negative order in carbon monoxide calculated in chapter 6. One would expect that a mechanism with hydrogen involved in the rate determining step would lead to a kinetic isotope effect, i.e. the reaction rate would be influenced by substituting hydrogen with deuterium. But Dalla Betta and Shelef /146/ did not find any rate changes on nickel, ruthenium and platinum catalysts. Therefore they concluded that the rate determining step probably is the dissociation of carbon monoxide without any hydrogen involved in that step. The calculations in chapter 6 showed that with that type of mechanism the observed reaction order in hydrogen cannot be obtained. Biloen et al. /37/ have explained the absence of an isotope effect by assuming that a carbon to metal distance is the transition state featuring in the rate determining step. That would mean that the positive orders are obtained due to a competition between the formation of an active intermediate, $CH_x$, and inactive carbon from surface carbon, and additionally due to a competition between chain growth and termination. We are inclined to ascribe the absence of the kinetic isotope effect to a compensating effect between an increased surface coverage and a decreased rate constant when hydrogen is replaced by deuterium.

## 7.2. CHAIN GROWTH

Our results can be explained quantitatively by a model with chain growth via the insertion of a $CH_x$-complex. The chain growth via an alcoholic complex would lead essentially to the same kinetic equations as via an oxygen free complex. But because we concluded that the initiation proceeds via dissociatively adsorbed carbon monoxide and not via an alcoholic complex we also exclude alcoholic complexes in the chain growth.

The mechanism of the chain growth via polymerization of $CH_2$-groups was proposed already by Fischer and Tropsch /24/. The results of Blyholder and Emmett /147-148/ from experiments in which labelled ketenes were added to synthesis gas showed that the $CH_2$-group of ketene was more reactive than the CO-group of ketene. Both groups could take part in the chain growth. On iron and on cobalt catalysts more $CH_2$-groups were built into the hydrocarbons than CO-groups. Also results of reactions with ketene by Toyoshima /149/ on an iron catalyst indicate that the $CH_2$-group is involved in the chain growth reaction. The elegant experiments of Biloen et al. /37/ on a nickel catalyst prove convincingly that the chain growth can proceed via $CH_x$-groups, probably via $CH_2$-groups. To this we can add our results of the ethylene hydrogenation which showed that chain growth via a $CH_x$-complex is possible. Therefore we state: Chain growth via a $CH_x$-group is possible under the conditions of the Fischer-Tropsch synthesis. And on cobalt catalysts at a pressure of 100 kPa that mechanism is very probable.

When the chain growth proceeds via a $CH_x$-complex the question is still open about the value of x.

One method to investigate the nature of adsorbed intermediates is to carry out exchange reactions in which the exchange of hydrogen atoms with deuterium takes place /150/. Tompson et al. /151/ studied the reaction of deuterium with hydrocarbons over a cobalt/thorium oxide catalyst at 455 K. They concluded that the most stable radicals formed from methane were $CH_3$ and C and from ethane $C_2H_4$ and C. The methyl radical was the most stable group, but it seems unlikely to us that this group acts as a building unit because dehydrogenation reactions would be required, even for the formation of paraffins.

The chain growth via a CH-group would lead to highly unsaturated products and would require substantial subsequent hydrogenation, even for the formation of olefins. Hence a $CH_2$-group is the most likely unit.

In the liquid phase $CH_2$-groups formed by photolysis of ketene can insert into a carbon-hydrogen bond but not into a carbon-carbon bond, forming unsaturated hydrocarbons /152/. Further the results of Yamamoto /153/ and Young and Whitesides /154/ show that the insertion of the carbene into a metal-carbon bond is possible.

Many studies have been carried out to demonstrate that olefins and alcohols can initiate the chain growth. Emmett et al. /155-158/ have shown in series of experiments the influence of the addition of radioactive alcohols, aldehydes and olefins to synthesis gas. All of these compounds can only initiate the chain growth, but especially methanol and formaldehyde, which would be the most relevant species, react more slowly than the higher alcohols. Further it was found that olefin selectivities increase by addition of alcohols /155/. This would mean that a part of olefins is formed directly from alcohols via dehydration. But as mentioned in the previous section there is little evidence that these compounds exist under normal operation in noticeable quantities.

Another mechanism for the chain growth, the insertion of carbon monoxide, has been proposed by Pichler and Schulz /19/. The recent results of van Barneveld and Ponec /36/ have been interpreted by that mechanism. The idea is based mainly on the well-known property of transition metals to form carbonyls, but no real experimental evidence has been offered. The probability of chain growth increases with an increasing concentration of carbon monoxide.

In the absence of carbon monoxide methane is formed from carbonaceous species on the surface (chapter 3). These results can be used to support the chain growth mechanism by the carbon monoxide insertion. But another explanation is equally possible: when carbon monoxide is present, the hydrogen surface coverage is low. Without carbon monoxide a higher hydrogen surface coverage causes the formation of methane, which has a higher order in hydrogen and has a higher rate constant than the other products. So we can say that carbon monoxide is needed to protect the $C_1$-intermediates against the reaction with hydrogen, which would accelerate the termination as $CH_4$ and decrease the probability of chain growth, as less $CH_x$-species would be available for insertion.

To support the mechanism of the insertion of carbon monoxide analogies have been suggested between the mechanism of hydroformylation and of the Fischer-Tropsch synthesis /159/. In both cases carbon monoxide insertion could take place. But in the hydroformylation carbon monoxide insertion leads to the formation of compounds with only one carbon atom more than the original molecule and insertion does not lead to further chain growth. Such a reaction could be operative in the Fischer-Tropsch synthesis, when alcohols are formed.

## 7.3. TERMINATION

The termination reaction has not been studied as much as the other two reaction parts, initiation and propagation. It is generally assumed that the termination is a hydrogenation reaction followed by desorption, or only a desorption step /16,63/.

We came to the same conclusion in chapter 5 with the experiments in which the synthesis gas was changed into hydrogen. But it should be pointed out that then mainly paraffins were formed. The low orders for olefins in hydrogen and in some cases the positive orders in carbon monoxide (chapter 6) suggest that for the termination of olefins no hydrogen is needed i.e. the termination is only the desorption of the intermediates. If the chain growth proceeds via $CH_2$-groups, the polymerized form $(CH_2)_n$ has the same formula as olefins.

Further it was noticed that the terminations for methane and a $C_2$-fraction differ from the other terminations. A high order in hydrogen for methane formation indicates that more hydrogen is involved in that termination than in the other terminations. Our reaction models support that mechanism. The difference in the termination of the $C_2$-fraction can be explained by a strong adsorption of a $C_2$-intermediate which therefore is assisted by hydrogen for the desorption step and thus leads to a lower olefin-paraffin ratio in that fraction than e.g. in the $C_3$-fraction.

The dependence of the olefin-paraffin ratio on the residence time indicates that an important part of the paraffins is formed by a consecutive hydrogenation reaction from primary formed olefins. As the initiation is a hydrogenation step, the combination of low activity and high olefin selectivity can be understood.

For a high production of the low olefins we should have a very active catalyst, so that short residence times can be used. One way to increase the overall conversion is to increase the temperature. But as shown in chapter 5 at higher temperatures the carbon deposition increases considerably, which causes deactivation of the catalysts. Hence the olefin selective catalysts have to be resistant against the formation of carbon at higher temperatures but maintain a high activity. Further the chain growth activity should be low i.e. with a low value of $\alpha$. For the normal Fischer-Tropsch catalysts a low $\alpha$ leads to a high selectivity for methane. But as it has been shown that the termination of the $C_1$-fraction differs from the other termination reactions and that the initiation activity and product distribution need not be correlated (chapter 4), it is feasible to inhibit the methane formation without losing the initiation activity or increasing the probability of chain growth. Some promising results in that direction have already been obtained /160/.