CHAPTER 4

Activity and Selectivity of Cobalt Catalysts

4.1. INTRODUCTION

The influence of process variables on the activity and selectivity of the Fischer-Tropsch synthesis has been the subject of many studies during the years /14,16,20-23,102/. The following general conclusions can be drawn from these studies:

i) an increase of the hydrogen-carbon monoxide ratio increases the overall rate, decreases the formation of unsaturated hydrocarbons and decreases the rate of catalyst deactivation;

ii) an increase of the total pressure increases the overall conversion and the formation of higher hydrocarbons (especially on iron catalysts);

iii) at higher temperatures less higher products are formed than at lower temperatures, but the catalyst stability decreases by the formation of inactive carbon (graphite or amorphous carbon);

iv) a high space velocity favours the formation of unsaturated compounds.

For these observations no detailed explanations have been proposed yet. In this chapter the results will be reported of our studies with unsupported and alumina supported cobalt catalysts in which the influence of the concentrations of hydrogen and carbon monoxide and of the temperature on the activity and the selectivity are investigated. The activity of the catalysts is generally expressed per gram catalyst and not as a turnover frequency. The latter is used only in the comparison between the supported and the unsupported catalysts.

First, the standard reaction conditions are described below for experiments with both catalysts. These experiments are used as reference when the influence of changes in the reaction conditions is investigated.

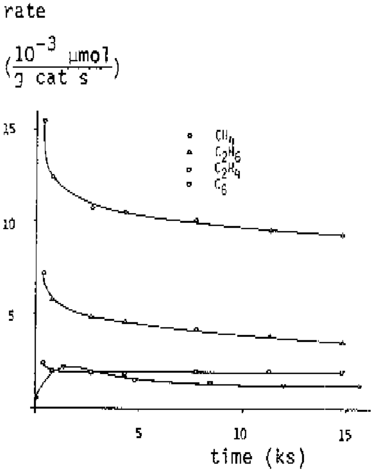
4.2. STANDARD EXPERIMENTS

4.2.1. COBALT ON ALUMINA

The standard experiment is carried out in the apparatus described in section 2.2 under atmospheric pressure in the following way:

i) the catalyst is heated under helium to 673 K followed by
ii) reduction by hydrogen (1.3 cm^3 (s g cat)$^{-1}$) at 673 K for 58 ks and
iii) reaction at 523 K with synthesis gas having the composition: $x_{H_2} = 0.20$, $x_{CO} = 0.20$ and $x_{He} = 0.60$; the total gas flow being 1.3 cm^3 (s g cat)$^{-1}$.

In figure 4.1 the rates of formation of various products are shown for the first few hours of the synthesis. In the beginning the rate of carbon monoxide conversion into hydrocarbons decreases rather fast with time, being 0.20 µmol (g cat s)$^{-1}$ after 60 s and 0.12 µmol (g cat s)$^{-1}$ after 1.2 ks. After 15 ks the rate is 0.074 µmol (g cat s)$^{-1}$, corresponding to a turnover frequency of 2 ks^{-1}.



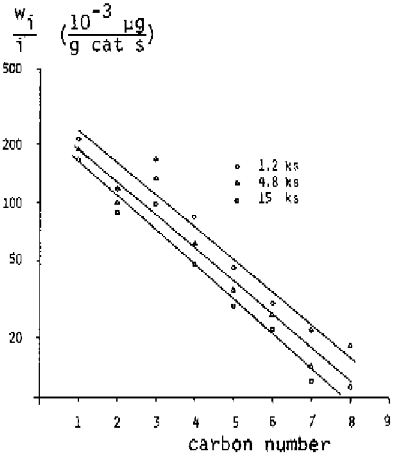


Figure 4.1. The rates of formation of various products as a function of time. Catalyst: Co/Al_2O_3. $x_{H_2} = x_{CO} = 0.20$. $T = 523$ K. Flow: 1.3 cm^3 (s g cat)$^{-1}$.

Figure 4.2. The weight of the product fraction as a function of the carbon number. Catalyst: Co/Al_2O_3. $x_{H_2} = x_{CO} = 0.20$. $T = 523$ K. Flow: 1.3 cm^3 (s g cat)$^{-1}$.

In figure 4.2 the weight fraction divided by the carbon number is plotted as a function of the carbon number according to equation (2.6), for three stages of the same experiment. If straight lines are drawn with methane fitting the Flory-line but with the C_2- and C_3-fractions respectively below and above the line, the values of α are 0.66, 0.68 and 0.67 after 1, 5 and 15 ks. This indicates that in spite of the deactivation the product distribution remains constant.

Some selectivities ($C_2^=/C_2^-$, $C_3^=/C_3^-$ and C_2/C_3) are plotted as a function of time in figure 4.3. In spite of the fact that the overall product distribution is practically constant with time, an increase of both olefin selectivities takes place at the latter stages of the same run. The olefin-paraffin ratio is four times higher in the C_3-fraction than in the C_2-fraction, being 2.2 in the C_3-fraction and 0.55 in the C_2-fraction after 15 ks. The rate of carbon dioxide formation is 4 x 10^{-3} μmol (g cat s)$^{-1}$ after 15 ks.

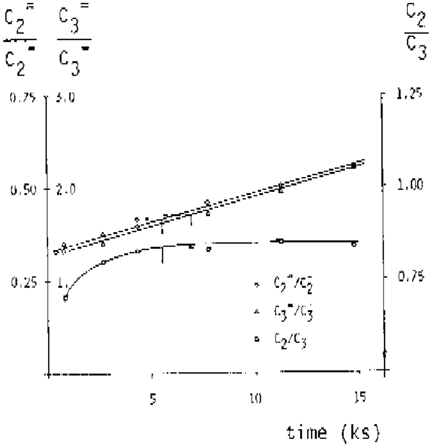


Figure 4.3. Some selectivities as a function of time. Catalyst: Co/Al_2O_3. x_{H_2} = x_{CO} = 0.20. T = 523 K. Flow: 1.3 cm^3 (s g cat)$^{-1}$.

4.2.2. UNSUPPORTED COBALT

The standard experiment is carried out in the following way:

i) the catalyst is heated under hydrogen to 523 K, followed by

ii) reduction by hydrogen (2.6 cm^3 (s g oxide)$^{-1}$) at 523 K for 18 ks and

iii) reaction at 523 K with synthesis gas having the composition: x_{H_2} = 0.20, x_{CO} = 0.20 and x_{He} = 0.60; the total gas flow 3.5 cm^3 (s g oxide)$^{-1}$.

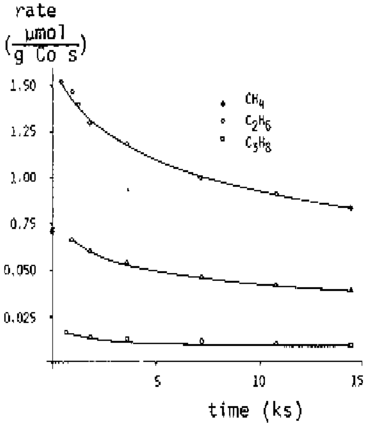


Figure 4.4. The rates of formation of various products as a function of time. Catalyst: Co. $x_{H_2} = x_{CO}$ = 0.20. T = 523 K. Flow: 3.5 cm^3 (s g oxide)$^{-1}$.

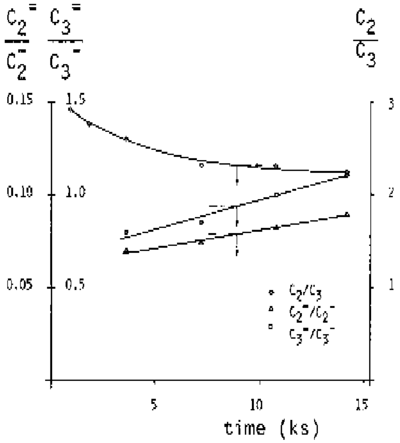


Figure 4.6. Some selectivities as a function of time. Catalyst: Co. $x_{H_2} = x_{CO}$ = 0.20. T = 523 K. Flow: 3.5 cm^3 (s g oxide)$^{-1}$.

In figure 4.4 the rates of formation of various products are depicted as a function of time. During the first hour the rate of carbon monoxide conversion drops to about one half of the value after 60 s; being 1.1 μmol (g cat s)$^{-1}$ after 3.6 ks. After 15 ks the rate is 0.93 μmol (g cat s)$^{-1}$, corresponding to a turnover frequency of 11 ks^{-1}.

The product distribution is given in figure 4.5, where the

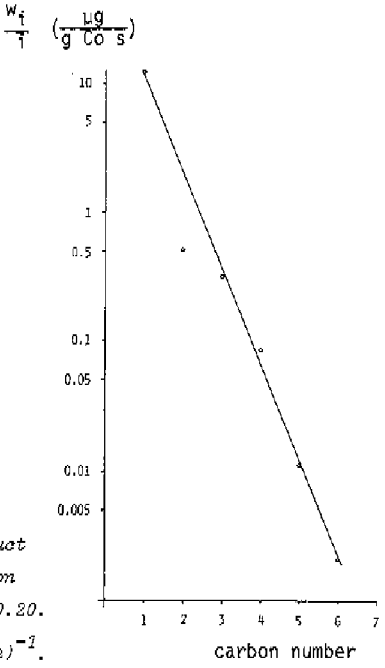


Figure 4.5. The weight of the product fraction as a function of the carbon number. Catalyst: Co. $x_{H_2} = x_{CO}$ = 0.20. T = 523 K. Flow: 3.5 cm^3 (s g oxide)$^{-1}$.

weight fraction is plotted as a function of the carbon number (equation (2.6)). The C_2-fraction is again under the Flory-line, but the other fractions including methane show a good fit. The Flory constant, α, is 0.19 and it stays almost constant during the first hours. The olefin selectivities and the C_2/C_3 ratio are given as a function of time in figure 4.6. The olefin selectivities increase again with time as found with the Co/Al_2O_3 catalyst, but the C_2/C_3 ratio decreases, which was not found with the Co/Al_2O_3 catalyst. The olefin-paraffin ratio is about ten times higher in the C_3-fraction than in the C_2-fraction, being 1.1 in the C_3-fraction and 0.09 in the C_2-fraction after 14 ks. The rate of carbon dioxide formation is 0.075 μmol (s g cat)$^{-1}$ after 15 ks.

4.2.3. DISCUSSION

In the first hours of the experiments both on the supported and on the unsupported catalyst a very fast decrease of the activity takes place. During that period the parameter α for the unsupported catalyst remains constant, being 0.19, whereas for the supported catalyst α increases from 0.34 after 60 s to 0.68 after 1.2 ks. The catalysts are reduced by hydrogen and are thus initially covered by hydrogen. However, the high activity in the beginning cannot be ascribed to this hydrogen, as a catalyst that is flushed first with helium shows the same high initial activity and the same deactivation. This would mean that on reduced catalysts carbonaceous species which are not active in initiation are formed very fast. On the supported catalyst the formation of these species modifies the surface in such a way that the production of higher hydrocarbons becomes more favourable. This change is not observed on the unsupported catalyst indicating that the nature of the carbonaceous species is different on the two catalysts. The experiments further imply that some sites are more liable to deactivation than others, as the deactivation more or less stops after say one third of the sites has been deactivated.

Between 1 and 15 ks the overall product distribution is almost stable, but the olefin-paraffin ratio increases with time on both catalysts. This indicates that the olefinicity and the product distribution are governed by different mechanisms.

A low value for the C_2-fraction is often found on cobalt catalysts /14,103/. In the C_2-fraction ethylene is known to be a very reactive compound that can be built in the hydrocarbon chains or cracked under the conditions used in the Fischer-Tropsch synthesis /104/. Thus a part of the C_2-fraction could disappear via side reactions resulting in a lower yield for that fraction.

4.3. INFLUENCE OF THE HYDROGEN AND CARBON MONOXIDE CONCENTRATIONS

The influence of the concentration of hydrogen and carbon monoxide is first studied in experiments in which after 7 ks the H_2/CO ratio is increased from one (x_{H_2} = 0.20, x_{CO} = 0.20) to three (x_{H_2} = 0.60, x_{CO} = 0.20) and after 14 ks returned again to the initial value. After 18 ks the rates are compared with those of the standard experiment described in section 4.2.1. In table 4.1 the ratios of the rates are given.

Table 4.1. Rates at various times compared to those after 7 ks.

t (ks)	H_2/CO (mol/mol)	$\frac{C_{1,t}}{C_{1,7}}$	$\frac{C_{2,t}}{C_{2,7}}$	$\frac{C_{3,t}}{C_{3,7}}$
7	1	1.0	1.0	1.0
14	3	8.0	3.3	2.8
18 (1)	1	1.3	1.1	1.0
18 (2)	1	0.84	0.87	0.80

(1) between 7 and 14 ks with x_{H_2} - 0.60, x_{CO} - 0.20
(2) the standard experiment

4 ks after the last change has been made the activity of the catalyst is still higher than before the hydrogen concentration is increased. The observations can be explained in two ways:

i) after the change to the higher H_2/CO ratio the surface coverage of hydrogen is maintained at a higher level, higher than initially, also when the H_2/CO ratio is decreased again;

ii) during the period of high hydrogen concentration a part of the deactivating and modifying carbonaceous species is hydrogenated and thus the number of active sites is higher than in the case where H_2/CO is kept low all the time.

The second explanation is more likely because one would expect the coverage of hydrogen to respond to the changes in the gas phase more quickly than carbonaceous species.

We further study the influence of the hydrogen/carbon monoxide ratio after 14 ks, i.e. at a moment when almost a steady state is reached. Some representative product distributions are plotted in figure 4.7 and the Flory constants calculated from the slopes of the lines are given in table 4.2.

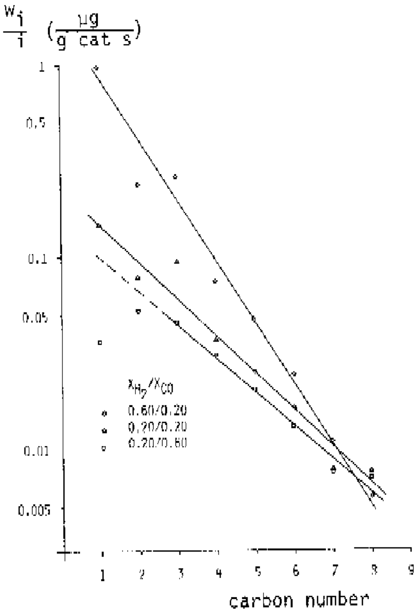


Figure 4.7. The weight of the product fraction as a function of the carbon number for various mole fractions of reactants. Catalyst: Co/Al_2O_3, T = 523 K. Flow: 1.3 cm^3 $(s\ g\ cat)^{-1}$.

Table 4.2. The Flory constant α for various ratios of hydrogen to carbon monoxide. Catalyst: Co/Al_2O_3, T = 523 K. Flow: 1.3 cm^3 $(g\ cat\ s)^{-1}$.

x_{H_2}	x_{CO}	H_2/CO (mol/mol)	$\alpha(C_4-C_8)$
0.6	0.2	3	0.52
0.2	0.2	1	0.65
0.2	0.6	1/3	0.68

The constant α is clearly a function of the reactant concentrations: an increasing mole fraction of hydrogen diminishes the probability for chain growth and to a less extent an increasing mole fraction of carbon monoxide increases that probability. At a high mole fraction of carbon monoxide methane remains below the Flory-line. The results agree in general with the earlier studies on the Fischer-Tropsch synthesis /14/, in which it was found that a high mole fraction of carbon monoxide favoured the formation of higher hydrocarbons. But a product distribution with methane below the Flory-line has - as far as we know - not been reported earlier.

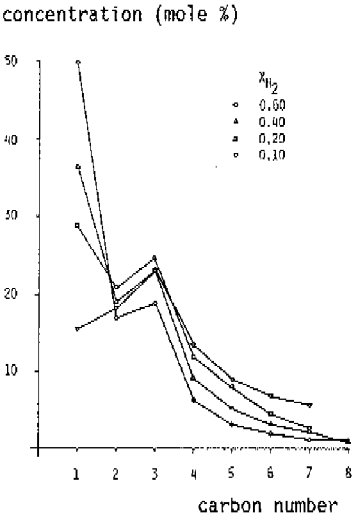


Figure 4.8. The relative mole concentrations as a function of the carbon number. Catalyst: Co/Al_2O_3. x_{CO} = 0.20. T = 523 K. Flow: 1.3 cm^3 (s g cat)$^{-1}$.

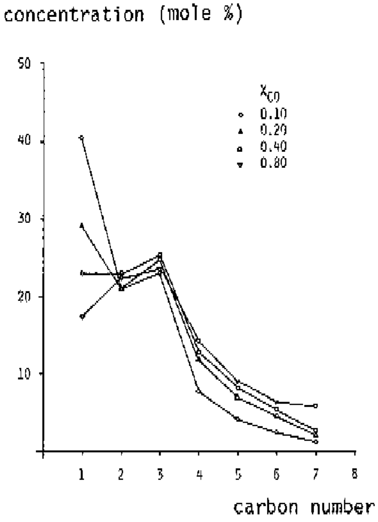


Figure 4.9. The relative mole concentrations as a function of the carbon number. Catalyst: Co/Al_2O_3. x_{H_2} = 0.20. T = 523 K. Flow: 1.3 cm^3 (s g cat)$^{-1}$.

The product distributions as a relative mole concentration as a function of the carbon number with the mole fractions of the reactants as a parameter are also shown in figure 4.8 (constant mole fraction of carbon monoxide, x_{CO} = 0.20) and in figure 4.9 (constant mole fraction of hydrogen, x_{H_2} = 0.20). In both cases the concentration of methane is shown to be very strongly influenced by changes in the reactant concentrations, smaller changes are observed for other products.

The selectivities are collected in table 4.3 for various mole fractions of the reactants.

Table 4.3. The selectivities for various mole fractions of reactants. Catalyst: Co/Al_2O_3. $T = 523$ K. Flow: 1.3 cm^3 $(g\ cat\ s)^{-1}$.

x_{H_2}	x_{CO}	C_2^-/C_2^-	$C_3^=/C_3^-$	C_2/C_3
0.6	0.2	0.08	0.8	0.89
0.2	0.2	0.6	2.3	0.84
0,2	0.6	1.2	14.5	1.1

Reactant concentrations influence the selectivity for olefins very strongly. It seems that the overall conversion and the olefin selectivity are related. Therefore we plotted the olefin selectivities, defined as an olefin percentage in a product fraction with the same carbon number ($C_2^=/C_2$ and $C_3^=/C_3$), as a function of the relative carbon monoxide conversion for several experiments carried out with various concentrations of reactants but with a constant space velocity at 523 K (see figure 4.10). In spite of the scatter a tendency emerges clearly: low conversion levels favour the formation of olefins.

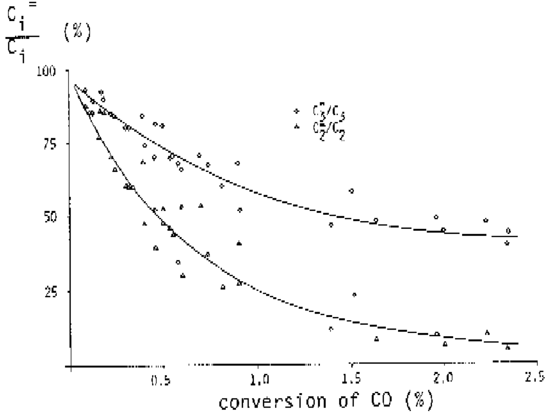


Figure 4.10. Olefin selectivities as a function of the conversion of carbon monoxide. Catalyst: Co/Al_2O_3. $T = 523$ K. Flow: 1.3 cm^3 $(s\ g\ cat)^{-1}$.

The value of the Flory constant α ($r_p/(r_p+r_t)$) depends on the concentration of the reactants. We can formally describe the rates of propagation (r_p) and termination (r_t) as follows:

$$r_{p,i} = k_p \left[C_i^*\right] p_{H_2}^{X_p} p_{CO}^{Y_p} \tag{4.1}$$

$$r_{t,i} = k_t \left[C_i^*\right] p_{H_2}^{X_t} p_{CO}^{Y_t} \tag{4.2}$$

where k_p and k_t are reaction rate constants and X and Y exponents of the partial pressures of hydrogen and carbon monoxide, respectively. Since α changes as a function of these concentrations, the rates of propagation and termination must depend differently on these concentrations, i.e. $X_p \neq X_t$, $Y_p \neq Y_t$. The parameter α decreases with increasing partial pressure of hydrogen, which means that $X_t > X_p$, i.e. more hydrogen is involved in the termination than in the propagation. The deviation of methane from the Flory-line will be discussed in chapter 6.

When the mole fraction of hydrogen is increased the product distribution obtained with the supported catalyst changes in the direction of that of the unsupported cobalt catalyst. With x_{H_2} = 0.60 the selectivity for methane is 0.57. For an experiment, carried out with a mole fraction of hydrogen of 0.90 (x_{CO} = 0.10), the product distribution after 18 ks is shown in

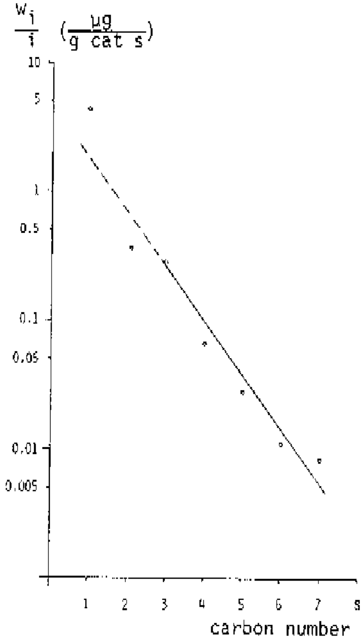


Figure 4.11. The weight of the product fraction as a function of the carbon number. Catalyst: Co/Al$_2$O$_3$. x_{H_2} = 0.90, x_{CO} = 0.10. T = 523 K. Flow: 1.3 cm^3 (s g cat)$^{-1}$.

figure 4.11. The selectivity for methane is 0.83 with a Flory constant 0.3. For the unsupported catalyst in the standard experiment the selectivity for methane is 0.92 with $\alpha = 0.19$.

4.4. INFLUENCE OF THE TEMPERATURE

4.4.1. COBALT ON ALUMINA

During 18 ks in the beginning of the standard experiments (section 4.2) no clear change in the value of α is found in spite of a progressing deactivation. To study the relation between deactivation and product distribution more closely we do some deactivation runs at 573 K with a feed of x_{H_2} = 0.20 and x_{CO} = 0.20. After 21.6 ks the temperature is brought back to 523 K and the product distribution at this temperature is compared with that of the standard experiment (table 4.4; figure 4.12).

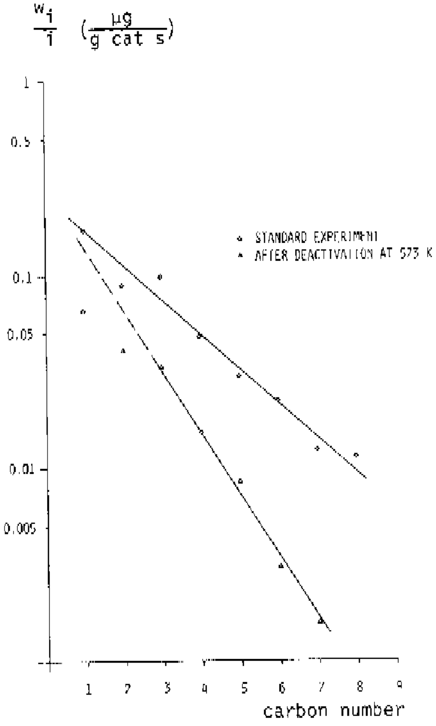


Figure 4.12. The weight of the product fraction as a function of the carbon number. Catalyst: Co/Al_2O_3. $x_{H_2} = x_{CO}$ = 0.20. T = 523 K. Flow: 1.3 cm^3 $(s\ g\ cat)^{-1}$.

The treatment of the catalyst at 573 K influences all selectivities strongly. The Flory constant diminishes, the selectivity for methane increases although the rate of methane formation still falls below the Flory-line. The selectivity for olefins increases and the minimum in the product distribution for the C_2-fraction disappears. If during the deactivation only the number of

Table 4.4. Comparison of the deactivated catalyst with the standard experiment.

Catalyst: Co/Al_2O_3. $x_{H_2} = x_{CO} = 0.20$. $T = 523$ K.

Flow: 1.3 cm^3 $(s\ g\ cat)^{-1}$.

catalyst	ΔCO $\frac{\mu mol}{g\ cat\ s}$	α	ϕ_1	$C_2^=/C_2^-$	C_2/C_3
deactivated cat.	0.019	0.50	0.37	8.6	1.3
standard exp.	0.074	0.67	0.33	0.6	0.8

active aggregates* decreased, no change in the product distribution should take place. Because such a change is observed, we conclude that the nature of active aggregates has changed as well. A lower α means that the probability for chain growth decreases (or the probability for termination increases). This in itself could be ascribed to a higher surface coverage of hydrogen. But as this would also mean a lower olefin selectivity (which is not observed) we exclude this explanation.

A likely reason for the deactivation is that carbonaceous species are deposited on the surface. They do not only decrease the number of active aggregates, but at the same time reduce the size of an aggregate of adjacent metal atoms. That the chance for chain growth diminishes with deactivation then could indicate that a bigger aggregate is needed for chain growth than for termination. This can be understood if the building unit that is inserted into a growing chain is transported from the active centre where it is formed to the centre where the growing chain is attached. If now the mobility of the building units is restricted by inactive species on the surface, the chance of a building unit to meet a growing chain decreases.

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* by aggregates we mean a combination of ensembles; an ensemble is a group of surface atoms necessary to let some reaction step occur.

4.4.2. UNSUPPORTED COBALT

The experiments are performed between 433 and 523 K with mole fractions of hydrogen and carbon monoxide of 0.20 both. In figure 4.13 the product distribution as a relative mole concentration as a function of the carbon number is shown for 433, 463, 483 and 523 K. The low concentration of the C_2-fraction for temperatures below 523 K is striking. In table 4.5 the data are collected; for comparison the results of the standard experiment of the Co/Al_2O_3 catalyst are added.

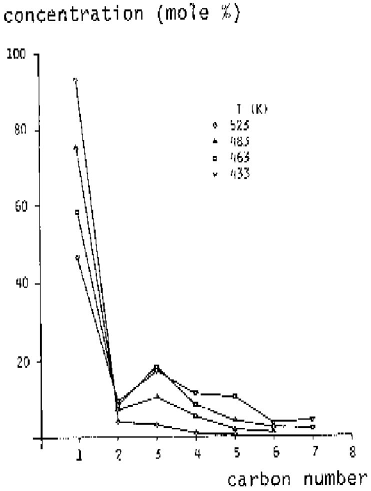


Figure 4.13. The relative mole concentration as a function of the carbon number. Catalyst: Co. $x_{H_2} = x_{CO} = 0.20$. *Flow: 3.5* cm^3 *(s g oxide)*$^{-1}$.

At lower temperatures more higher products are formed, and the selectivity for olefins increases. At temperatures below 463 K the C_2/C_3 ratio is fairly constant but rises at higher temperatures and at 523 K the minimum for the C_2-fraction disappears.

Table 4.5. Influence of the temperature on the product distribution and selectivities.
Catalyst: Co. $x_{H_2} = x_{CO} = 0.20$. Flow: 3.5 cm^3 (s g oxide)$^{-1}$.

T (K)	ACO $\frac{\mu mol}{g\ Co\ s}$	α	ϕ_1	$C_2^=/C_2^-$	C_2/C_3
Co					
433	0.04	0.66	0.46	1.25	0.50
448	0.10	0.58	0.52	0.74	0.43
463	0.22	0.52	0.61	0.40	0.44
483	0.29	0.33	0.76	0.23	0.71
523	0.92	0.19	0.92	0.13	1.61
Co/Al_2O_3					
523	1.2*)	0.67	0.33	0.6	0.84

*) Flow: 1.3 cm^3 (g cat s)$^{-1}$

4.5. INFLUENCE OF VARIOUS CATALYST TREATMENTS

4.5.1. COBALT ON ALUMINA

We apply the following treatments to the cobalt on alumina catalyst:

i) reduction by hydrogen at 673 K for 58 ks (the standard catalyst);
ii) reduction by hydrogen at 673 K for 58 ks, thereafter treatment with carbon monoxide at 523 K for 11 ks;
iii) reduction by hydrogen at 673 K for 58 ks, thereafter treatment with ethylene at 523 K for 18 ks;
iv) reduction by carbon monoxide at 523 K for 58 ks;
v) no prereduction but heating from room temperature to 523 K within 3.6 ks under synthesis gas ($x_{H_2} = x_{CO} = 0.20$).

After the treatment synthesis gas ($x_{H_2} = 0.20$, $x_{CO} = 0.20$) is passed over the catalysts at 523 K.

In figure 4.14 the overall reaction rate is shown as a function of time after hydrogen reduction, (treatment i), after carbon monoxide reduction, (iv), and after heating under the H_2/CO mixture, (v).

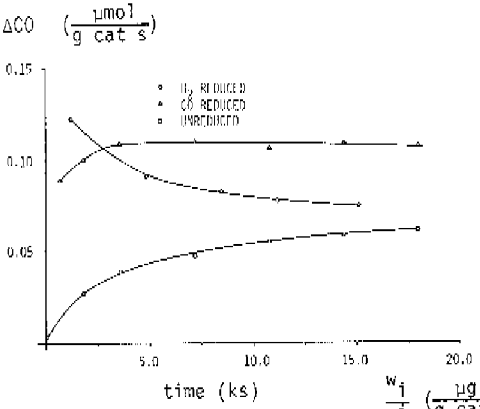


Figure 4.14. The rate of carbon monoxide conversion as a function of time. Catalyst: Co/Al_2O_3. $x_{H_2} = x_{CO} = 0.20$. $T = 523$ K. Flow: 1.3 cm^3 $(s\ g\ cat)^{-1}$.

The stability of the carbon monoxide reduced catalysts is much better than that of the catalyst reduced only by hydrogen. In figure 4.15 the weight of various product fractions is plotted as a function of the carbon number. The treatments with carbon monoxide and with ethylene provide catalysts on which the product distribution deviates more than in the standard experiment from the Flory distribution line. This shows that the assumptions of the Flory model are not more than approximations and that often other effects such as preferential adsorption or cracking and polymerization reactions will also play a role.

The rates and the selectivities are collected in table 4.6.

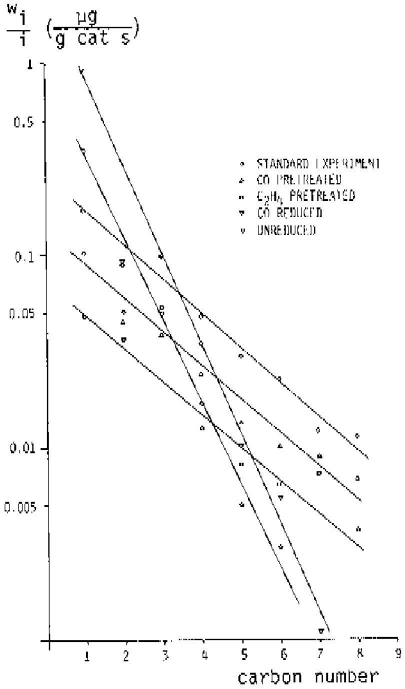


Figure 4.15. The weight of the product fraction as a function of the carbon number. Catalyst: Co/Al_2O_3. $x_{H_2} = x_{CO} = 0.20$. $T = 523$ K. Flow: 1.3 cm^3 $(s\ g\ cat)^{-1}$.

Table 4.8. Influence of the treatments on the product composition.
Catalyst: Co/Al_2O_3, $x_{H_2} = x_{CO} = 0.20$. T = 523 K.
Flow: 1.3 cm^3 $(s\ g\ cat)^{-1}$.

treatment		ΔCO $\frac{\mu mol}{g\ cat\ s}$	α	Φ_1	C_2^-/C_2^-	C_3^-/C_3^-	C_2/C_3
(i)	(H_2)	0.074	0.67	0.33	0.6	2.3	0.8
(ii)	(H_2/CO)	0.044	0.7	0.39	1.0	6.3	1.2
(iii)	(H_2/C_2H_4)	0.033	0.7	0.25	9.8	39	0.7
(iv)	(CO)	0.107	0.36	0.77	0.8	8.8	0.9
(v)	(CO/H_2)	0.052	0.40	0.72	3.7	11	1.0

The values of α can be divided into two groups: one with α around 0.7 and another with α about 0.4. Those belonging to the first one are reduced by hydrogen. That the difference in α is really remarkable is illustrated by the ratio

$$\frac{\text{rate of formation for } C_1}{\text{rate of formation for } C_5}$$

For the treatments (i), (ii) and (iii) this ratio is about 5 and for the two other treatments about 80.

Two points have to be discussed:

(i) the change in the ordinate intercept of the Flory-lines within a group and

(ii) the change in the slope of the Flory-lines.

The fact that a group of parallel Flory-lines is found indicates that, at least to a first approximation, all rates of production can be assumed to change in the same proportion. This suggests that for such a group only the initiation rate changes while the rate constants for the other elementary steps are not influenced.

For the carbon monoxide reduced catalyst it is noticed that compared to the standard catalyst:

(i) the initiation rate is about 30% higher,

(ii) the probability of chain growth is drastically diminished and

(iii) the stability is better.

The rate of formation of methane has increased remarkably, but it still fits the Flory-line quite well. This rate increases slightly during the first hour of the experiment but thereafter stays constant. This means that during the reduction by carbon monoxide a stable surface structure is formed which is active in the initiation, but consequences of this treatment decrease the chance that a growing chain and a building unit meet each other. Instead the growing chains desorb, if necessary after reaction with hydrogen.

If we, however, treat the hydrogen reduced catalyst with carbon monoxide we obtain a catalyst that has a much lower activity (i.e. initiation rate) and a much higher chain growth rate (i.e. higher α) than the carbon monoxide reduced catalyst. Carbonaceous species deposited during the treatment with carbon monoxide performed after hydrogen reduction form inactive carbon areas on the surface. This leads to a decrease in activity, but does not influence the probability of the chain growth.

To study the carbon monoxide reduced catalyst in more details we do some hydrogenation experiments with this catalyst. The catalyst is treated by hydrogen (1.3 cm^3 $(s\ g\ cat)^{-1}$) in the following ways:

i) at 523 K for 7 ks;
ii) at 523 K for 86 ks;
iii) at 523 K for 3.6 ks and at 598 K for 3.6 ks;
iv) at 523 K for 3.6 ks, at 598 K for 5 ks and at 673 K for 6 ks.

The values of α determined after 18 ks under synthesis gas (x_{H_2} = 0.20, x_{CO} = 0.20) at 523 K are given in table 4.7. Only the high temperature treatment brings the catalyst back to the properties of the standard catalyst (hydrogen reduced). It is noticeable that hydrogen treatments at lower temperatures (523 K) increase the activity without changing α much. This enhanced activity is likely to be caused by an increased cobalt surface available for the reaction (see chapter 5).

Table 4.7. Influence of various hydrogen treatments on the activity and the parameter α for the carbon monoxide reduced catalyst.
Catalyst: Co/Al_2O_3, $x_{H_2} = x_{CO} = 0.20$, T = 523 K.
Flow: 1.3 cm^3 $(s\ g\ cat)^{-1}$.

treatment	A_{CO} $\frac{\mu mol}{g\ cat\ s}$	α
untreated	0.11	0.36
(i)	0.13	0.44
(ii)	0.19	0.42
(iii)	0.13	0.45
(iv)	0.06	0.64
hydrogen reduced	0.07	0.67

Hydrogenation of ethylene in absence of CO

To characterize further the hydrogen reduced and the carbon monoxide reduced catalysts their activities for the hydrogenation of ethylene are compared.

The experiments are carried out at 523 K with a gas mixture having the composition $x_{H_2} = 0.20$, $x_{C_2H_4} = 0.20$ and $x_{He} = 0.60$. The conversion of ethylene after 7 ks is 68% for the hydrogen reduced catalyst and 60% for the carbon monoxide reduced catalyst. In table 4.8 the composition of the product after 7 ks is given.

Table 4.8. Product composition in the hydrogenation of ethylene as mole %. Catalyst: Co/Al_2O_3, $x_{H_2} = x_{C_2H_4} = 0.20$, T = 523 K.
Flow: 1.3 cm^3 $(s\ g\ cat)^{-1}$.

catalyst	C_1	$C_{2,par}$	$C_{2,ol}$	C_3	C_4	C_5	C_6	C_7	C_8
	mole %								
H_2 reduced	0.6	63.4	32.4	2.2	1.2	0.2	0.1	0.03	0.02
CO reduced	0.3	58.6	40.2	0.5	0.5	0.02	0.01	0.004	0.003

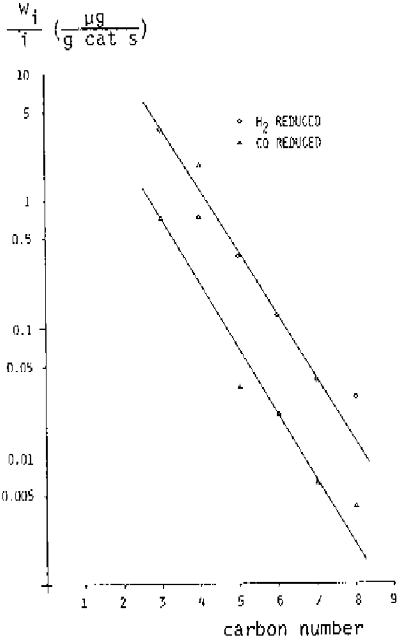
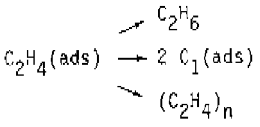


Figure 4.16. The weight of the product fraction as a function of the carbon number in the hydrogenation of ethylene. Catalyst: Co/Al_2O_3. $x_{H_2} = x_{C_2H_4} = 0.20$. $T = 523$ K. Flow: 1,3 cm^3 $(s\ g\ cat)^{-1}$.

Although the conversion of ethylene is about the same for the two catalysts a clear difference is found in the selectivities: on the catalyst reduced by carbon monoxide much less higher products are formed. The product distributions are shown in figure 4.16 for both catalysts. When the product distributions are plotted in the coordinates of the Flory-Schulz equation (2.6), curves of a similar general character are mainly shifted with regard to each other. This could indicate that the number of ensembles for chain growth is diminished with the carbon monoxide reduced catalyst, but that their nature remains the same. The turnover frequency of the hydrogen reduced catalyst for the ethylene hydrogenation is of the order of 0,4 s^{-1}. But the turnover frequency for the Fischer-Tropsch synthesis under the same conditions is 2 x 10^{-3} s^{-1}, which is only one hundredth of the turnover frequency of the ethylene hydrogenation. This shows that it is only for kinetic reasons that ethylene is found in the product during the Fischer-Tropsch synthesis.

The main reaction in the hydrogenation of ethylene is the formation of ethane, but polymerization of C_1 and C_2 units takes place, too.



$$C_2H_4(ads) \rightarrow \begin{cases} C_2H_6 \\ 2\ C_1(ads) \\ (C_2H_4)_n \end{cases} \qquad (4.3)$$

and

$$C_1(\text{ads}) + C_n(\text{ads}) \rightarrow C_{n+1}(\text{ads}) \ . \qquad (4.4)$$

4.5.2. UNSUPPORTED COBALT

The same treatments are performed with the unsupported catalyst as with the supported, except that the reduction by hydrogen is carried out at 523 K for 18 ks. In figure 4.17 the weight of the product fractions is plotted as a function of the carbon number and the relevant data are collected in table 4.9.

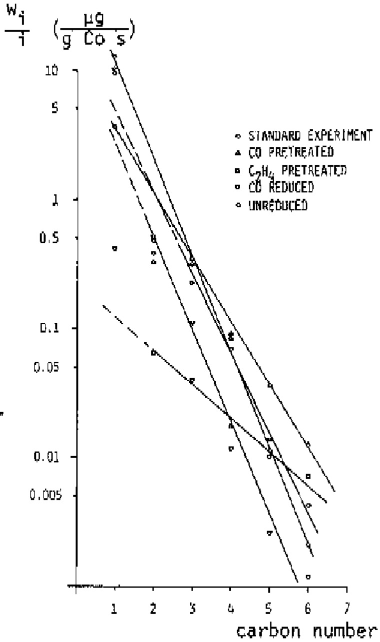


Figure 4.17. The weight of the product fraction as a function of the carbon number. Catalyst: Co. $x_{H_2} = x_{CO} = 0.20$. *T = 523 K. Flow: 3.5* $cm^3\ (s\ g\ cat)^{-1}$.

Table 4.9. Influence of the treatments on the product composition. Catalyst: Co. $x_{H_2} = x_{CO} = 0.20$. *T = 523 K. Flow: 3.5* $cm^3\ (s\ g\ oxide)^{-1}$.

treatment	ΔCO $\frac{\mu mol}{g\ cat\ s}$	α	Φ_1	$C_2^=/C_2^-$	$C_3^=/C_3^-$	C_2/C_3
(i) (H_2)	0.93	0.19	0.92	0.13	1.2	2.2
(ii) (H_2/CO)	0.25	0.41	0.79	2.8	17	1.0
(iii) (H_2/C_2H_4)	0.05	0.56	0.73	6.3	11	1.6
(iv) (CO)	0.74	0.21	0.94	0.02	0.38	4.4
(v) (CO/H_2)	1.2	0.31	0.85	0.28	3.5	1.7

Two groups can be distinguished again: 1) $\alpha < 0.3$ for the treatments (i), (iv) and (v) and 2) $\alpha > 0.4$ for (ii) and (iii). Both hydrogen reduction and carbon monoxide reduction give for this unsupported catalyst a comparable activity and almost the same product distribution. This could indicate that for these two catalysts the surface structure is the same. X-ray diffraction analysis shows that the catalyst prepared by treatment (i) is α-cobalt and that prepared by treatment (iv) is cobalt carbide, Co_2C. Moyes and Roberts have studied the adsorption of carbon monoxide on cobalt films with XPS (X-ray photo-electron spectroscopy) and UPS (ultra-violet photo-electron spectroscopy) /29/. Above 450 K they could not detect any molecularly adsorbed carbon monoxide, but instead a new surface was formed which they interpreted to be a surface carbide. From these data we conclude that the formation of a carbidic structure on the hydrogen reduced cobalt catalyst during the synthesis is probable.

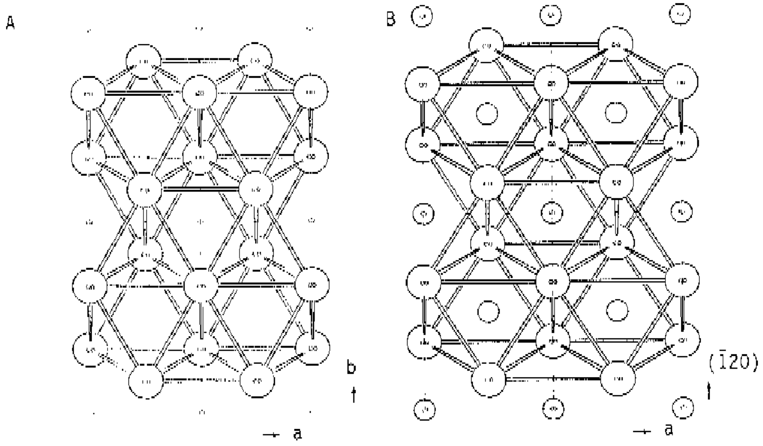


Figure 4.18. Structure of α-cobalt (A) and cobalt carbide, Co_2C *(B).*

In figure 4.18 the structures of α-cobalt and cobalt carbide, Co_2C, are presented. In the carbide the carbon is situated between the cobalt layers, which causes a slight increase in the distances between the cobalt atoms, but the structure of cobalt layers does not change. Thus it is not too surprising that on the α-Co with some surface carbon and on Co_2C the product distribution does not differ much.

The product distributions on the catalyst reduced by carbon monoxide and on the one treated by carbon monoxide after hydrogen reduction are different, as was the case for the supported catalysts. Similar to the supported catalyst also here the carbon monoxide treatment after the hydrogen reduction gives a catalyst with higher α and lower activity than the catalyst that is reduced by carbon monoxide.

4.6. OTHER COBALT CATALYSTS

In order to test how interaction between metal and carrier can influence the product distribution two mechanical mixtures of cobalt oxide (Co_3O_4) and alumina are prepared. The first one (I) is prepared by mixing the powdered components and thereafter subjected to high pressure (5.2 MNm^2). The second one (II) is prepared by grinding the oxide and the support in liquid nitrogen. This is done in order to avoid any heat effects, which could lead to compound formation between cobalt and the support. The cobalt content of both the catalysts is 6 wt %. The reduction by hydrogen is, as normally, performed at 523 K. The catalysts are tested at 523 K with synthesis gas of $x_{H_2} = 0.20$, $x_{CO} = 0.20$ and $x_{He} = 0.60$. The results of these experiments are given in table 4.10.

Table 4.10. Product composition on mechanical mixtures of cobalt oxide and alumina.
$x_{H_2} = x_{CO} = 0.20$. $T = 523$ K. Flow: 1.3 cm^3 $(s\ g\ cat)^{-1}$.

catalyst	ΔCO $\frac{\mu mol}{g\ Co\ s}$	α	ϕ_1	$C_2^=/C_2^-$	C_2/C_3
I	1.07	0.21	0.86	0.49	2.0
II	1.08	0.28	0.80	0.86	1.2
unsupported catalyst *	0.92	0.19	0.92	0.09	2.2

* Flow: 3.5 cm^3 $(s\ g\ cat)^{-1}$

In both cases the rate of carbon monoxide conversion is 1.1 μmol (g Co s)$^{-1}$. Compared with the standard experiment for the unsupported catalyst the probability of chain growth has somewhat increased for catalyst (II). This would indicate that the interaction between cobalt and alumina increases the probability of chain growth. A higher value of α requires a higher mobility of intermediates, which also could go via the alumina support.

A high olefin-paraffin ratio for the mechanical mixtures might mean that the intermediates are more loosely bound on these catalysts than on the unsupported catalyst, presumably because they can desorb in two steps of which the first one then would be a transfer to the alumina.

4.7. DISCUSSION

On the basis of the results described in previous sections the following two points are discussed:

i) the product distribution and the influence of various catalyst treatments on that and

ii) the differences between the supported and the unsupported catalyst.

Ad i). The product distribution obeys in general the Flory model; except the C_2-fraction and in some cases the C_1- or the C_3-fractions.

The fact that the product distribution can be described by the Flory-Schulz equation means that the chain growth proceeds via a repeated stepwise addition to the growing chain of a complex with only one carbon atom. Moreover, it means that for each surface species, independent of the number of carbon atoms that it contains, the ratio of termination (i.e. desorption) rate to propagation (i.e. chain growth) rate is constant. In other words, the product distribution obtained with one particular catalyst can be described by one constant α according to equation (2.6). In figure 4.19 the fraction of various products in mole percent is shown as a function of α. From this figure the maximum selectivity for C_2 is found to be 26 mole % (at $\alpha = 0.5$), which is thus the maximum for catalysts that follow the Flory model. The maximum selectivity in weight percent is found to be 30% at $\alpha = 0.33$.

In a number of cases (during the deactivation between 1 and 15 ks and after a carbon monoxide and an ethylene pretreatment of the hydrogen reduced supported catalyst) it was noticed that the Flory-line can change its ordinate intercept without altering its slope. This indicates that certain changes of the catalyst do not alter the ratio between the termination and propagation rates, but they only alter the rate of one of the initiation steps, i.e. one of the steps that leads from gaseous carbon monoxide and hydrogen to an adsorbed reactive intermediate. This further shows that the initiation rate need not be correlated to the rates of propagation and termination.

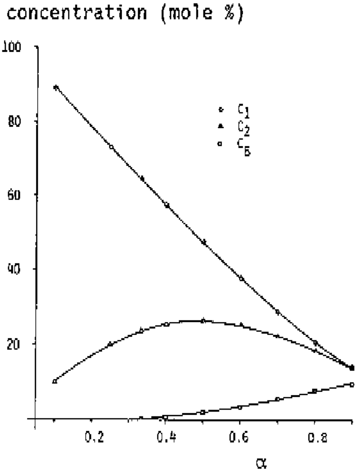


Figure 4.19. The relative mole concentration as a function of α calculated from the Flory distribution.

To explain our observations we will use the concept that the total activity is related to the number of active ensembles but that the chain growth requires an aggregate of several active ensembles that must be in touch when the building blocks manufactured at the ensembles are put into growing chains. If the Flory-line is lowered but does not change its slope it means then that only the number of surface aggregates is reduced, but not the properties of the individual active aggregates. This further suggests that a reduction in activity, which is accompanied by a constant product distribution, is not caused by a random deactivation of active sites, but by a formation of whole continuous areas that consist mainly or completely of deactivated sites. On the other hand if the slope is increased but the total activity is not much impaired (e.g. the supported catalyst after hydrogen reduction and after carbon monoxide reduction), one would expect the aggregates themselves to be affected, e.g. by a random appearance of deactivated sites on the surface. Such deactivation hinders the interaction between the various active ensembles of a surface aggregate and diminishes the chance of chain growth and hence reduces α. This would mean that the deactivation as a result of self-poisoning and deactivation by carbon monoxide or ethylene pretreatments, must be ascribed to the formation of continuous areas of deactivated sites. This may be understood if one assumes that on a hydrogen reduced catalyst the formation of carbon is enhanced by the presence of carbon on neighbouring sites. On the other hand the reduction by carbon monoxide (with or without hydrogen) would result in the formation of randomly distributed inactive sites. The rather high activity of these catalysts indicates that the number of active ensembles in itself is rather high. But the low value of α suggests that the interaction between these active ensembles is impaired. It could be that the average size of aggregates has become too small to provide for an optimal possibility of chain growth.

The methane production is generally in agreement with the Flory equation. But on the deactivated catalyst or with low H_2/CO ratios it remains below the Flory-line. In both cases the olefin-paraffin ratio is increased compared to that of the standard experiment. This indicates that the methane formation is related to the hydrogenation activity of the catalyst, and would further mean that the termination of the C_1-fraction differs from the other terminations, i.e. that more hydrogen is involved in that termination than in the others. The instances where the methane production is higher than the Flory model predicts are restricted to the unsupported catalyst and are gathered in table 4.11.

Table 4.11. Catalyst pretreatments leading to methane concentration above that of the Flory model.
Catalyst: Co. $x_{H_2} = x_{CO} = 0.20$. $T = 523$ K. Flow: 3.5 cm^3 $(s\ g\ oxide)^{-1}$.

treatment	α	$C_2^=/C_2^-$	$C_3^=/C_3^-$
C_2H_4 pretreatment	0.56	6.3	11
CO reduced	0.21	0.023	0.38
CO/H_2 reduced	0.31	0.38	3.5

From table 4.11 one can conclude that the methane formation is not exclusively related to the hydrogenation ability, but that it is also influenced by the structure of the catalyst. This further supports our idea that the chain growth needs an aggregate of active ensembles. By the above mentioned treatments the methane production is favoured.

Another aspect of the product distribution is the olefin-paraffin ratio. The unsupported catalyst generally shows a lower olefinicity, although the carbon monoxide treated catalyst is in this respect an exception. Some relation is observed between the chance of chain growth and the olefin-paraffin ratio: the higher α is, the more olefins are formed. But no simple relation is found between the olefinicity and the probability of chain growth. In other words, there is an antipathetic relation between the olefin formation and the rate of termination. The olefin-paraffin ratio is thus controlled by another step than that of propagation.

Ad ii). The difference in reactivity and selectivity between the supported and the unsupported catalysts could be caused either by the crystallite size effect or by an interaction between the metal and the support.

On the average the crystallite size of supported catalysts is smaller than that of unsupported catalysts. In small crystals the coordination of metal atoms on the surface can be essentially different from the ideal faces of large crystals. According to Boudart /105/ effects of the crystallite size on the catalytic properties can be noticed when the diameter of crystals does not exceed 5 nm and is within a narrow size range for all crystals.

The preparation of well-dispersed catalysts could lead to orientations of crystal faces which possess different activities. Various crystal faces of cobalt have been observed to behave indeed differently with regard to the adsorption of carbon monoxide /106,107/. Cobalt $(10\bar{1}2)$ plane dissociates carbon monoxide at higher temperatures and leads to the formation of a well-ordered carbon structure. This structure is interpreted to be a plane of Co_3C. However, the plane Co (0001) does not apparently decompose carbon monoxide. In our case the average crystallite size of the supported catalyst is of the order of 25 nm. Thus the differences noticed between the supported and the unsupported catalyst cannot be explained in crystallite size.

During the reduction of the Co/Al_2O_3 catalyst by hydrogen a strong influence of the support was noticed (chapter 3); higher temperatures were required and only a part of the cobalt could be reduced. Another possibility to explain the phenomena observed is by the presence of Co^{2+} ions. A part of cobalt on the supported catalyst is situated in the lattice of alumina and this can change - in principle - the intrinsic behaviour of the cobalt metal atoms at the upper surface of the supported metal. However, the mechanical mixture, for which such a direct influence is not to be expected behaves already somewhat as a supported catalyst. Therefore we incline to suggest the following explanation: a "spill-over" of growing chains (C_1-C_i) from cobalt to alumina is possible and by this "storage effect" alumina can increase the probability of chain growth and at the same time decrease the probability of termination. The same type of difference in the product distribution of an unsupported and a supported catalyst has been found /108,109/; e.g. nickel supported on alumina produced more higher hydrocarbons than bulk nickel /108/. Our explanation could cover also these observations.