CHAPTER 6

Kinetics

6.1. INTRODUCTION

The kinetics of the Fischer-Tropsch synthesis has been the subject of a number of experimental studies during last years /23,119,123/. The results are usually described by "power laws" and no attempts have been made to correlate the kinetic data with possible mechanisms. Only in the case of methanation such an attempt has been made, but here no generally accepted conclusions have been reached either.

To draw conclusions about the mechanism only from the kinetic results is difficult for several reasons:

1) simplifications of full equations are often needed in order to avoid too complex mathematical expressions;
2) the kinetic behaviour is often governed by one rate determining step, rendering that only that part of the overall mechanism is reflected by the kinetic data;
3) various mechanisms (models) can be described by the same kinetic equation.

In spite of these shortcomings kinetic data can be used either to disprove models or to support them, although they seldom will prove a model.

In this chapter we try to draw conclusions concerning the mechanism of the Fischer-Tropsch reaction from our kinetic data.

The two catalysts, Co/Al_2O_3 and Co, are studied. As described in chapter 4 the product distributions of these catalysts were totally different at 523 K. Thus the first question we try to answer is whether the reaction goes via a similar mechanism on both catalysts. The results of both Co/Al_2O_3 and unsupported cobalt catalysts are used in the discussion below on the initiation step. However, on the unsupported cobalt catalyst the formation of higher products is too small at 483 K to be used for kinetic studies of the mechanism of the chain growth; only the results from the supported catalyst are valuable in this respect.

As a first step the overall reaction rate and the rates of various products are described in the form of power laws. We realize that by discussing the rates in the form of power laws inaccuracies are introduced. However we take this risk because the power law equations are unambiguous and have an immediate experimental basis. Moreover the various orders obtained can be compared with each other and with the values found in literature.

Based on the calculations in section 2.2.3 we concluded that our experiments were carried out under conditions where neither mass nor heat transfer limitations are expected. But it must be mentioned that those calculations were based on the assumption that the concentration of the products is negligible. However, in the flushing experiments (section 5.3) we found that on the surface of the supported catalyst there are hydrocarbons retained in amounts sufficient for more than five times the monolayer coverage. This in principle could hinder the diffusion of the reactants. The activation energies calculated in section 6.4 are of the order of 100 kJ mol^{-1}, which indicates that there is little influence of film diffusion. The activation energies of reactions with film diffusion as rate controlling step are generally smaller than 10 kJ mol^{-1}.

6.2. REACTION ORDERS

6.2.1. EXPERIMENTAL

The relations between the reaction rates and the partial pressures of hydrogen and carbon monoxide were obtained from the series of experiments in which the partial pressure of one component was kept constant at one of the three levels 10, 20 or 40 kPa, while that of the other was varied between 10 and 80 kPa. The total flow of the synthesis gas was 1.3 cm^3 (s g cat)$^{-1}$ for the Co/Al_2O_3 catalyst and 3.5 cm^3 (s g cat)$^{-1}$ for the Co catalyst. When we later on discuss the influence of this level on the order in the other component we will indicate this as the influence of a variation of the "constant level". In order to avoid changes in the state of the catalysts in the course of the experiments the catalysts were at first stabilized in the following way:

Co/Al_2O_3: after reduction at 673 K the synthesis gas (x_{H_2} = 0.20, x_{CO} = 0.20) was passed over the catalyst for 18 ks at 573 K and thereafter for 72 ks at 523 K;

Co : after reduction at 523 K the synthesis gas was passed over the catalyst for 58 ks at 483 K.

To be sure that indeed no changes occurred the points measured first were always repeated at the end of a series. Within the experimental error no difference could be noticed between these two sets of data. The measurements were performed with the Co/Al_2O_3 catalyst at 523 K and with the unsupported cobalt catalyst at 483 K. The stability of these catalysts is always better at lower temperatures. Therefore it is favourable to carry out experiments at as low a temperature as possible for a measurable conversion. Another reason to use low temperatures is that under those conditions conversion is low, and thus the reactor works like a pseudodifferential reactor. But on the other hand lower temperatures favour the formation of higher hydrocarbons which could form a layer on the surface of the catalyst and thus cause diffusion limitations. For the cobalt on alumina catalyst the temperature was therefore chosen in such a way that a sensible compromise between these two requirements is reached. This appeared to be 523 K. The unsupported cobalt catalyst was studied at a lower temperature (483 K) because at 523 K no steady-state operation appeared to be possible. As the product stream contained here mainly methane no hindrance by higher products was expected with the catalyst.

6.2.2. OVERALL ORDERS

The total reaction rate, r_T, is represented in the form

$$r_T = k_T \, p_{H_2}^{X_T} \, p_{CO}^{Y_T} \qquad (6.1)$$

where k_T is the rate constant and X_T and Y_T are the orders in hydrogen and in carbon monoxide respectively. When the partial pressure of carbon monoxide is constant, formula (6.1) can be transformed into the form:

$$\log r_T = \log k_T' + X_T \log p_{H_2} \tag{6.2}$$

and similarly for a constant partial pressure of hydrogen

$$\log r_T = \log k_T'' + Y_T \log p_{CO} \ . \tag{6.3}$$

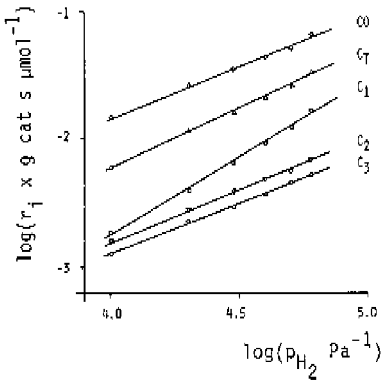

Figure 6.1. Reaction rate as a function of the partial pressure of H_2. Catalyst: Co/Al_2O_3. p_{CO} = 20 kPa. T = 523 K.

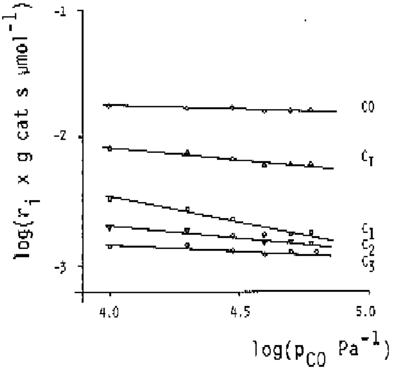

Figure 6.2. Reaction rate as a function of the partial pressure of CO. Catalyst: Co/Al_2O_3. p_{H_2} = 20 kPa. T = 523 K.

In figures 6.1 and 6.3 the rates are drawn as a function of the partial pressure of hydrogen and in figures 6.2 and 6.4 as a function of the partial pressure of carbon monoxide. In these figures the "constant level" (i.e. the pressure of the other component) is 20 kPa. In table 6.1 the calculated orders are presented for each of the three "constant levels" for the Co/Al_2O_3 and the Co catalyst. The rates are calculated both as carbon monoxide converted into hydrocarbons (ΔCO) and as moles hydrocarbons formed (C_T).

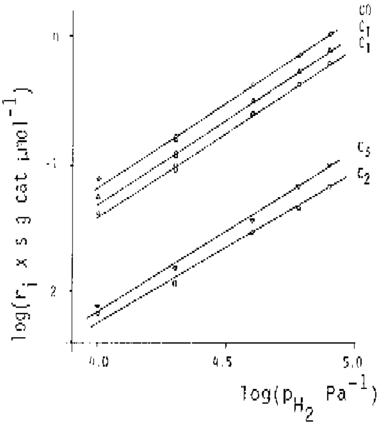

Figure 6.3. Reaction rate as a function of the partial pressure of H_2. Catalyst: Co. p_{CO} = 20 kPa. T = 483 K.

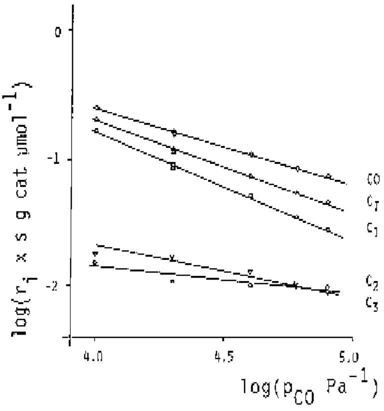

Figure 6.4. Reaction rate as a function of the partial pressure of CO. Catalyst: Co. p_{H_2} = 20 kPa. T = 483 K.

Table 6.1. Overall reaction orders.

	order in hydrogen				order in carbon monoxide		
	Co/Al_2O_3						
p_{CO} (kPa)	10	20	40	p_{H_2} (kPa)	10	20	40
ACO	0.8	0.8	0.8	ACO	-0.2	-0.1	-0.1
C_T	1.0	0.9	0.9	C_T	-0.4	-0.2	-0.3
	Co						
p_{CO} (kPa)	10	20	40	p_{H_2} (kPa)	10	20	40
ACO	1.4	1.3	1.0	ACO	-0.4	-0.7	-0.8
C_T	1.4	1.3	1.1	C_T	-0.5	-0.7	-1.0

The orders in hydrogen are positive and the orders in carbon monoxide negative in all cases. Further one can notice that there are no great differences between the orders calculated for the two rates (moles CO converted and moles hydrocarbons formed).

The influence of the value of the "constant level" on the order in the other component is very small for the cobalt on alumina catalyst. For the cobalt catalyst the influence is noticeable: all orders decrease with increasing "constant level".

In figure 6.5 the total rate is plotted as a function of the partial pressures of hydrogen and carbon monoxide for the hydrogen reduced catalyst without any deactivation. Also in this case a first order in hydrogen and a slightly negative order in carbon monoxide are found.

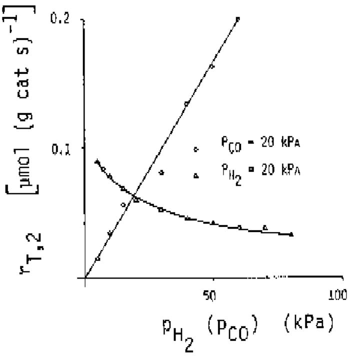

Figure 6.5. The total reaction rate as a function of the partial pressures of H_2 and CO. Catalyst: Co/Al_2O_3. T = 523 K.

The orders found are generally in agreement with the results reported in literature on the Fischer-Tropsch synthesis: a first order in hydrogen and a slightly negative or zero order in carbon monoxide /23,119/. Only at low concentrations of carbon monoxide (< 1%) a positive order in carbon monoxide has been obtained /120,121/. Yang et al. /103/ found the reaction order to be 1 in H_2 and -0.5 in CO with a Co-Cu/Al_2O_3 catalyst at 523 K.

6.2.3. ORDERS OF VARIOUS PRODUCTS

We have calculated also the orders for the various hydrocarbons, CO_2 and water according to the equations (6.2) and (6.3). The results are represented graphically in figures 6.1-6.4 and tabulated in table 6.2 for the Co/Al_2O_3 catalyst and in table 6.3 for the Co catalyst.

Table 6.2. Reaction orders. Catalyst: Co/Al_2O_3. T = 523 K.

	order in hydrogen				order in carbon monoxide		
P_{CO} (kPa)	10	20	40	P_{H_2} (kPa)	10	20	40
C_1	1.5	1.2	1.5	C_1	-0.8	-0.4	-0.7
C_{2-}	0.7	0.8	0.8	C_{2-}	-0.4	-0.2	-0.2
$C_{2=}$	1.9	1.6	1.1	$C_{2=}$	-0.9	-0.6	-1.0
C_2	0.4	0.7	0.8	C_2	-0.4	-0.1	+0.2
C_{3-}	0.4	0.8	0.6	C_{3-}	-0.3	-0.1	0
$C_{3=}$	0.9	1.2	0.6	$C_{3=}$	-0.3	-0.3	-0.7
C_3	0.4	0.7	0.6	C_3	-0.3	-0.1	+0.2
C_4	0.5	0.7	0.7	C_4	-0.1	-0.02	+0.2
C_5	0.3	0.7	0.8	C_5	+0.25	-0.01	+0.3
C_6	0.05	0.4	0.5	C_6	+0.15	-0.1	+0.1
H_2O	0.3	1.4	0.8	H_2O	-0.4	-	+0.1
CO_2	0.5	0.1	0.2	CO_2	+0.1	+0.2	+0.1

Table 6.3. Reaction orders. Catalyst: Co, T = 483 K.

	order in hydrogen				order in carbon monoxide		
P_{CO} (kPa)	10	20	40	P_{H_2} (kPa)	10	20	40
C_1	1.3	1.3	1.1	C_1	-0.7	-0.9	-1.1
C_{2-}	1.3	1.2	1.1	C_{2-}	-0.05	-0.5	-0.8
$C_{2=}$	1.5	1.3	1.6	$C_{2=}$	-1.0	-1.0	-1.0
C_2	0.1	0.1	0	C_2	+0.9	+0.7	+1.5
C_{3-}	1.4	1.3	1.0	C_{3-}	~ 0	~ 0	-0.4
$C_{3=}$	1.7	1.9	2.4	$C_{3=}$	-1.6	-1.4	-1.3
C_3	1.1	1.0	0.8	C_3	+0.5	+0.4	+0.4
CO_2	0.3	-	-	CO_2	~ 0	-	-

Again clearly positive orders in hydrogen and slightly negative or positive or zero orders in carbon monoxide are found for the different fractions of hydrocarbons. The accuracy of the orders given in tables 6.2 and 6.3 is on the average 0.1. Some tendencies can be noticed when the orders at different "constant levels", or as a function of the number of carbon atoms are compared. On the Co/Al_2O_3

catalyst the increasing "constant level" of the partial pressures increases the orders both in H_2 and in CO. On the Co catalyst all the orders decrease by increasing the "constant level" of both partial pressures.

The orders of carbon dioxide are positive both in hydrogen and in carbon monoxide. The orders of water are not reliable; on Co/Al_2O_3 because of the adsorption of water on the support, and on the unsupported catalyst the production of water was too low to be measured accurately.

When we compare our results with those found in literature we see that the orders of methane agree quite well with the orders reported by Vannice /122/ for a Co/Al_2O_3 catalyst at 548 K: $X = 1.2$ and $Y = -0.5$. (That is actually somewhat surprising because in his experiments the samples were taken after 20 minutes which according to our experiments falls still in the period of fast deactivation). The orders in carbon monoxide for the different hydrocarbons have also been calculated by Zein el Deen et al. /123/. The comparison with our results is difficult, because they assumed that the rates of all the products are proportional to the partial pressure of hydrogen, i.e. a first order in hydrogen. But this is not the case according to our results. Their assumption could also explain a positive order of ethane and a negative order of ethylene in carbon monoxide, which they found, but which contradicts the generally quoted observation that increasing the partial pressure of carbon monoxide increases the selectivity for olefins.

The relation between the olefin-paraffin ratios and the partial pressures are also described formally by power laws. The results are collected in table 6.4.

The partial pressures have a stronger influence on the ethylene-ethane ratio than on the propylene-propane ratio. Increasing "constant level" increases both the orders in hydrogen and in carbon monoxide. The orders obtained with the unsupported catalyst are not very accurate, but they are presented to show that the results are qualitatively the same with both catalysts.

Table 6.4. Orders of olefin-paraffin ratios.

order in hydrogen				order in carbon monoxide			
	Co/Al_2O_3						
P_{CO} (kPa)	10	20	40	P_{H_2} (kPa)	10	20	40
$C_2^=/C_2^-$	-1.4	-1.0	-0.7	$C_2^=/C_2^-$	~0	0.5	1.3
$C_3^=/C_3^-$	-1.0	-0.4	-0.3	$C_3^=/C_3^-$	~0	0.3	0.9
	Co						
P_{CO} (kPa)	10	20	40	P_{H_2} (kPa)	10	20	40
$C_2^=/C_2^-$	-1.5	-1.3	-1.6	$C_2^=/C_2^-$	1.4	2.0	2.6

6.3. INFLUENCE OF THE RESIDENCE TIME

Experiments with the residence time as parameter were carried out at 523 K with 1 gram of the stabilized Co/Al_2O_3 catalyst. The synthesis gas flow was varied between 0.7 and 2.8 $cm^3\ s^{-1}$. The partial pressures of hydrogen and carbon monoxide were both 20 kPa in the first series and 60 kPa and 20 kPa respectively in the second series.

The concentrations of the products as a function of the residence time are given in figure 6.6. A linear relation is obtained as could be expected for our differential reaction conditions. In figure 6.7 the olefin-paraffin ratio and the Flory constant α are given as a function of the residence time. For both H_2/CO ratios the olefin-paraffin ratio decreases with increasing residence time.

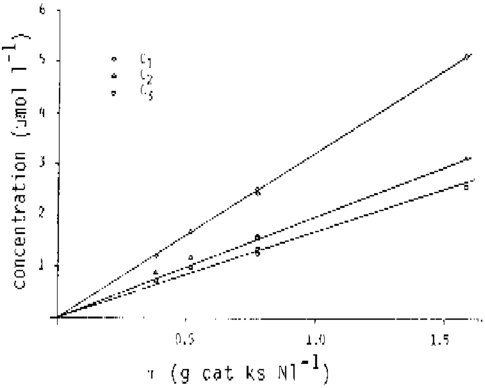

Figure 6.6. Concentrations as a function of the residence time. Catalyst: Co/Al_2O_3. p_{H_2} = p_{CO} = 20 kPa. T = 523 K.

These results will be discussed in connection with the discussion on the termination, section 6.5.5.

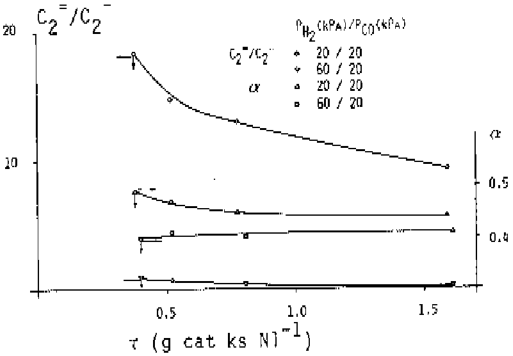

Figure 6.7. $C_2^=/C_2^-$ *and* α *as a function of the residence time. Catalyst:* Co/Al_2O_3*.* $T = 523$ *K.*

The Flory constant α decreases with the residence time for the low H_2/CO ratio (1:1), but is constant for the higher H_2/CO ratio (3:1). Some correlation between the olefin selectivity and α is found. This might suggest that under the conditions for which a higher selectivity for olefins is obtained, also higher products are formed.

6.4. APPARENT ACTIVATION ENERGIES

The influence of the temperature on the formation of various products was investigated for the stabilized supported and the unsupported catalysts. With the supported catalyst experiments were performed at 493 K, 508 K and 523 K and with the unsupported catalyst at 433 K, 448 K and 463 K. The H_2/CO ratio was either 1:1 (p_{H_2} = 20 kPa, p_{CO} = 20 kPa) or 3:1 (p_{H_2} = 60 kPa, p_{CO} = 20 kPa). The Arrhenius plots are shown in figures 6.8 and 6.9 respectively for the supported and the unsupported catalysts with a H_2/CO ratio of 1:1. From these graphs it follows that the Arrhenius relation is better followed for the unsupported catalyst than for the cobalt on alumina catalyst. The apparent activation energies calculated from the slopes of the lines are collected in table 6.5. The accuracy in the activation energies is between 5 and 10 kJ mol^{-1} for the supported catalyst and between 2 and 5 kJ mol^{-1} for the unsupported catalyst.

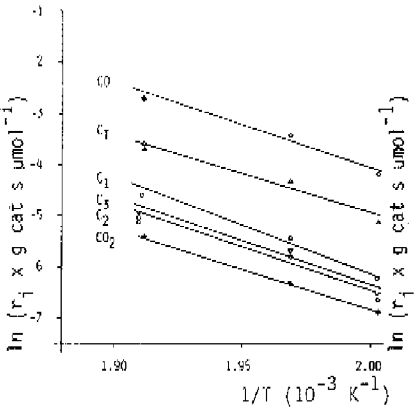

Figure 6.8. Reaction rate as a function of 1/T. Catalyst: Co/Al$_2$O$_3$. $p_{H_2} = p_{CO} = 20$ kPa.

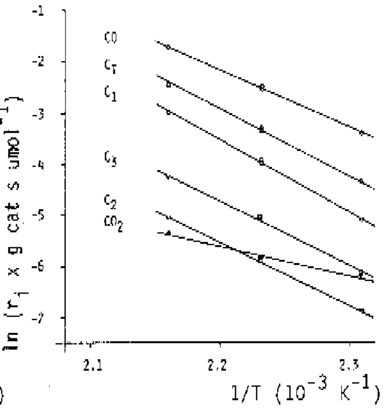

Figure 6.9. Reaction rate as a function of 1/T. Catalyst: Co. $p_{H_2} = p_{CO} = 20$ kPa.

Table 6.5. Apparent activation energies.

catalyst	Co/Al$_2$O$_3$		Co	
H_2/CO	1/1	3/1	1/1	3/1
product	E (kJ(mol)$^{-1}$)			
ACO	106	108	96	116
C_T	111	121	110	125
C_1	119	132	125	130
C_2	112	118	103	126
$C_2^{=}$	142	143	129	156
C_2^{-}	100	55	65	23
C_3	111	99	110	128
$C_3^{=}$	160	130	166	210
C_3^{-}	105	78	104	114
C_4	105	95	92	130
C_5	112	82	58	114
C_6	100	49	74	118
C_7	70	44	51	86
CO_2	111	118	46	74

At higher temperatures the apparent activation energies on the unsupported catalysts are clearly lower, being between 483 K and 503 K 77 kJ mol^{-1} for the overall conversion, 91 kJ mol^{-1} for methane and 55 kJ mol^{-1} for ethane.

A reasonable agreement of the results is obtained for the two conditions and the two catalysts. The main features of the data are that the apparent energies of activation slowly decrease with increasing chain length. The apparent energies of activation for total C_2 and total C_3 are lower than those for C_2 and C_3 paraffins and higher than those for the corresponding olefins. This is in agreement with the model that all or a great part of the paraffins are produced in a consecutive reaction from olefins.

The activation energies for supported cobalt catalysts reported in literature vary between 40 kJ mol^{-1} /25/ and 120 kJ mol^{-1} /124/. The most recent results on Co/Al_2O_3 catalysts are 100 kJ mol^{-1} for the overall reaction /103/ and 113 kJ mol^{-1} for methane /122/. The difference between the activation energy of the overall reaction and of the formation of methane has been observed also on a ruthenium catalyst by Dalla Betta et al. /125/. For the formation of methane on a cobalt foil Palmer and Vroom /126/ calculated an activation energy of 71 kJ mol^{-1}.

6.5. DISCUSSION

6.5.1. THE OVERALL ORDERS OF REACTION

The negative orders in carbon monoxide for the Fischer-Tropsch synthesis are often explained by the strong adsorption of carbon monoxide competing with hydrogen for the same sites.

It is assumed usually that the surface is almost totally covered by carbon monoxide /119,126,127/. The fact that the heat of adsorption of carbon monoxide is higher than that of hydrogen is used as an argument. However, it can be shown (see below) that a negative order in carbon monoxide can be obtained already at not too high a coverage of carbon monoxide; the only condition is that the surface coverage of hydrogen is smaller than that of carbon monoxide. We will illustrate this for the formation of methane on the unsupported catalyst.

According to recently published results /30-34/ the formation of methane can be best described by the reactions

$$C^* + x\,H^* \longrightarrow CH_x \xrightarrow{(4-x)\,H^*} CH_4 \qquad (6.5)$$

i.e. a reaction between a surface carbon atom, from dissociatively adsorbed carbon monoxide, and adsorbed hydrogen. The rate of the methane formation is thus

$$r_1 = k_1\,\theta_C^*\,\theta_H^{*x} \qquad (6.6)$$

where θ_C^* and θ_H^* are the fractions of the *active* surface covered by carbon and hydrogen respectively.

We assume that the surface fraction of hydrogen is small compared to the fraction of empty sites. The surface coverage of hydrogen is then

$$\theta_H^* = \sqrt{K_{H_2}\,p_{H_2}}\,(1 - \theta_{carbon}^*) \qquad (6.7)$$

where $\theta_{carbon}^* = \theta_{CO}^* + \theta_C^*$, i.e. the sum of the surface coverages by molecularly and dissociatively adsorbed carbon monoxide. Further the quantity of dissociatively adsorbed carbon monoxide (θ_C^*) can be shown to be linearly proportional to the surface coverage of molecularly adsorbed carbon monoxide (θ_{CO}^*). The presence of adsorbed oxygen is of no importance, provided that the rate of hydrogenation of the oxygen is higher than that given in equation (6.6). The rate equation (6.6) can therefore be transformed into

$$r_1 = k_1'\,\theta_{carbon}^*\,(1 - \theta_{carbon}^*)^x . \qquad (6.8)$$

In figure 6.10 this rate is given as a function of the surface coverage of carbonaceous species, θ_{carbon}^*, for different values of x. It can be seen that the coverage needed for a decreasing rate depends on x (a possible interpretation is that x is the number of hydrogen atoms in a rate determining step). The required surface fractions for a zero order in carbon monoxide are 0.5, 0.33 and 0.25 for x = 1, 2 and 3 respectively. These values are far from an "almost total" coverage. It should be noted that these *fractions* remain the same irrespective of the total number of sites available for reaction (i.e. sites for the precursors of the rate determining step plus the active empty sites).

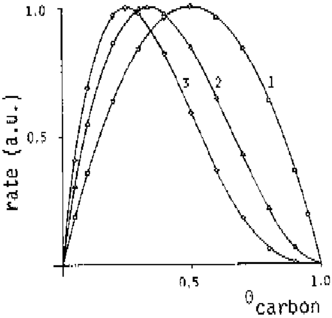

Figure 6.10. The reaction rate as a function of the surface coverage of carbonaceous species. 1. $x = 1$. 2. $x = 2$. 3. $x = 3$.

In section 5.3 we observed that the amount of surface species which was in total flushed off by hydrogen from the unsupported catalyst after synthesis, corresponded to more than 95% of the monolayer coverage. These species are a) the precursors of the rate determining step i.e. adsorbed carbon monoxide and surface carbon and b) all other (in the synthesis inactive) carbon containing surface intermediates. The fraction of the *total* surface covered by the former species is denoted as θ_a and that by the latter as θ_b. If we assume that all the carbonaceous species are distributed as a monolayer (compare with figure 5.8) we can write

$$\theta_a + \theta_b = 0.95 \tag{6.9}$$

Based on the calculations above the surface coverage θ_a for a zero order reaction for x = 2 at a first approximation is

$$\theta_a = 0.33\ (1 - \theta_b) \tag{6.10}$$

By solving equations (6.9) and (6.10) for θ_a we arrive at the value of $\theta_a = 0.02$. This would mean that during the reaction only a small fraction of the catalyst surface is active. It further suggests that the low turnover frequencies found for the Fischer-Tropsch synthesis could be caused by a low number of sites active for the rate determining step.

Orders of individual products

In chapter 4 it was noticed that the product distribution is a function of the partial pressures of hydrogen and carbon monoxide. That was explained by the fact that α, the probability of chain growth, is related to the propagation and termination rates. When α is expressed in the form:

$$\alpha = \alpha_0 \, p_{H_2}^{X_\alpha} \, p_{CO}^{Y_\alpha}, \tag{6.11}$$

it can be shown that the values X_α and Y_α equal the differences of the orders for the various products. The rate of termination can be written as

$$r_{t,i} = k_t \left[C_i^*\right] p_{H_2}^{X_t} \, p_{CO}^{Y_t}. \tag{6.12}$$

We also assume that the surface coverage of the C_1 -complex can be expressed in a form

$$\left[C_1^*\right] = k_1 \, p_{H_2}^{X_1} \, p_{CO}^{Y_1}. \tag{6.13}$$

Because

$$\left[C_i^*\right] = \alpha^{i-1} \left[C_1^*\right] \tag{6.14}$$

the rate of termination becomes

$$r_{t,i} = k_t' \, p_{H_2}^{X_1+(i-1)X_\alpha+X_t} \, p_{CO}^{Y_1+(i-1)Y_\alpha+Y_t} \tag{6.15}$$

or

$$X_i = X_1 + (i - 1) X_\alpha + X_t \tag{6.16}$$

$$Y_i = Y_1 + (i - 1)\, Y_\alpha + Y_t \qquad (6.17)$$

which can be written as

$$\Delta X_i = X_\alpha \quad \text{and} \quad \Delta Y_i = Y_\alpha$$

Table 6.6. The dependence of α on the partial pressures.
Catalyst: Co/Al_2O_3. $T = 523$ K.

p_{CO} (kPa)	10	20	40
X_α	-0.09	-0.04	-0.01
p_{H_2} (kPa)	10	20	40
Y_α	0.2	0.1	0.2

In table 6.6 the values of X_α and Y_α are given for the Co/Al_2O_3 catalyst on the various levels of the partial pressures. A slightly negative X_α and a positive Y_α are obtained. It must be noted that if α were independent of the partial pressures, the rate determining steps of propagation and of termination would both be proportional to the same function of the partial pressures. Further it would mean that the orders of all the product fractions would be equal. For the Co/Al_2O_3 catalyst the orders for methane are an exception in the series of orders, being higher in hydrogen and lower in carbon monoxide than for the others. This indicates that more hydrogen is involved in the formation of methane than in the formation of other products. This can be understood since methane can terminate only as paraffin. We will come back to this point in section 6.5.4.

6.5.2. INITIATION

The Fischer-Tropsch reaction proceeds via the adsorption of hydrogen and carbon monoxide. Under the conditions used for the synthesis hydrogen is adsorbed dissociatively /118/. For the adsorption of carbon monoxide there are two possibilities: molecular adsorption and dissociative adsorption. Using the kinetic data it is possible to distinguish between these two forms of carbon monoxide adsorption.

First we simplify the process by the following assumptions:

- the total reaction rate is determined by one rate determining step. All the steps (if any) before that rate determining step are in equilibrium;
- the surface fraction available for the reaction remains constant, i.e. there is no continuing deactivation;
- the surface coverage of hydrogen is considerably smaller than that of carbon monoxide.

There are several possibilities for the rate determining step (RDS), some of which have already been mentioned in the literature:

(i) the adsorption of hydrogen /128/

$H_2 + 2^* \rightarrow 2\ H^*$

(ii) the adsorption of carbon monoxide

$CO + {}^* \rightarrow CO^*$ or $CO + 2^* \rightarrow CO^{**}$

(iii) the formation of an oxygen containing complex /129/

$CO^* + n\ H^* \rightarrow COH_n{}^* + n^*$

(iv) the hydrogenation of a surface complex /64,130,131/

$COH_n{}^* + x\ H^* \rightarrow C_1{}^* + H_2O + x^*$

(v) the dissociation of carbon monoxide /126/

a) $CO^* + {}^* \rightarrow C^* + O^*$

b) $2\ CO^* \rightarrow C^* + {}^* + CO_2$

c) $CO^* + 2\ H^* \rightarrow C^* + 2^* + H_2O$

(vi) the hydrogenation of surface carbon

$C^* + x\ H^* \rightarrow CH_x{}^* + x^*$

Ad (i). The adsorption of hydrogen as RDS.

The rate of the reaction with the adsorption of hydrogen as the rate determining step can be expressed by the equation

$$r = k\ p_{H_2}\ \theta_e{}^2 \qquad (6.18)$$

where θ_e is the surface fraction of empty sites. Equation (6.18) can be rewritten, assuming Langmuir adsorption equilibrium and a surface coverage of hydrogen that is small compared to the fraction of empty sites:

$$r = k\ p_{H_2} \left(\frac{1}{1 + f(p_{CO})}\right)^2 . \tag{6.19}$$

$f(p_{CO})$ is a function of the partial pressure of carbon monoxide which depends on the form of the adsorbed carbon monoxide. According to the Langmuir adsorption isotherms $f(p_{CO})$ is $K_{CO}p_{CO}$ for the molecularly adsorbed carbon monoxide and $2\sqrt{K_{CO}p_{CO}}$ for the dissociatively adsorbed carbon monoxide; K_{CO} is the equilibrium constant for the CO adsorption. With these functions it is impossible to obtain a positive order in carbon monoxide from equation (6.19). However at low concentrations of carbon monoxide a positive order in carbon monoxide has been found /120/. Thus equation (6.19), i.e. the adsorption of hydrogen as the rate determining step, does not explain all the available results.

Ad (ii). The adsorption of carbon monoxide as RDS.

In analogy to the previous case the rate of reaction is

$$r = k\ p_{CO}\ \theta_e{}^x = \left(\frac{1}{1 + \sqrt{K_{H_2}p_{H_2}}}\right)^x . \tag{6.20}$$

It is assumed that the surface coverage of CO is small. K_{H_2} is the equilibrium constant for the hydrogen adsorption. x is either 1 or 2 depending on whether carbon monoxide is adsorbed on one or two sites. In both cases the rate is of first order in carbon monoxide. This contradicts the negative orders often found for carbon monoxide. Thus we can conclude that to obtain the orders in hydrogen and carbon monoxide found experimentally, a competitive adsorption of these reactants has to be considered.

Ad (iii) and (iv). The formation and the hydrogenation of an oxygen containing complex as RDS.

In these cases we have to deal separately with the adsorption of carbon monoxide on one site and on two sites.

The one site adsorption of CO.

From the third and fourth model we arrive at the same mathematical expression as a function of the partial pressure of carbon monoxide, if in the fourth model the surface complex from adsorbed hydrogen and carbon monoxide is the most abundant surface species /132/.

By using the Langmuir model for the surface coverage of CO and assuming that $\theta_H \sim 0$ we have for case (iii):

$$r = k' \, \theta_{CO} \, \theta_H{}^n = k \, \frac{p_{H_2}{}^{n/2} \, p_{CO}}{(1 + K \, p_{CO})^{n+1}} \qquad (6.21)$$

The overall order in H_2 was found to be around 1 (table 6.1), so the most likely value for n (and for x) is 2. With this value equation (6.21) can be linearized as

$$A + B \, p_{CO} = \left(\frac{p_{CO}}{r}\right)^{1/3} \qquad (6.22)$$

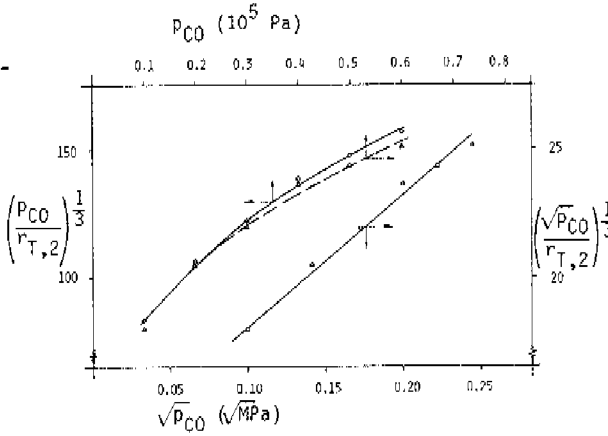

Figure 6.11. Checking of the models for initiation. Catalyst: Co/Al$_2$O$_3$. p_{H_2} = 20 kPa. T = 523 K.

$\left(\frac{p_{CO}}{r}\right)^{1/3}$ as a function of the partial pressure of carbon monoxide is shown in figures 6.11 and 6.12, in 6.11 for the Co/Al$_2$O$_3$ catalyst, the rate calculated as total CO conversion ($r_{T,2}$) and in 6.12 for the unsupported cobalt catalyst, the rate as a number of molecules hydrocarbons formed ($r_{T,1}$).
It can be seen that the linear relation predicted by equation (6.22) is not obtained. Further we observed no essential difference in the behaviour of the two catalysts.

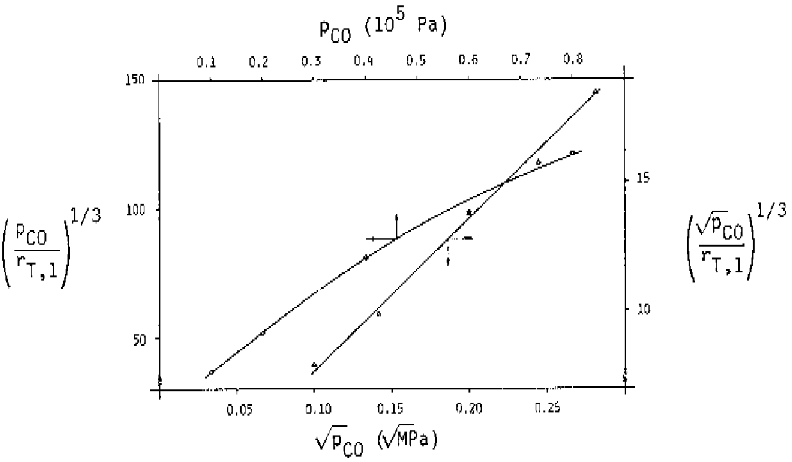

Figure 6.12. Checking of the models for initiation.
Catalyst: Co. p_{H_2} = 20 kPa. T = 483 K.

The two site adsorption of CO.

The surface coverage of carbon monoxide can be obtained from the equilibrium $K_{CO}\, p_{CO}\, \theta_e^2 = \theta_{CO}$ and has the form

$$\theta_{CO} = \frac{2\, K_{CO}\, p_{CO} + 1 - \sqrt{4 K_{CO} p_{CO} + 1}}{2\, K_{CO}\, p_{CO}} \qquad (6.23)$$

Again the surface coverage of H_2 is neglected.

The rate of reaction, if the complex formation is the rate determining step, is

$$r = k'\, \theta_{CO}\, \theta_H^n = k\, \theta_{CO}\, (1 - \theta_{CO})^n \qquad (6.24)$$

at a constant partial pressure of hydrogen. Using the value n = 2 the dependence of the rate on $\theta_{CO}\,(1 - \theta_{CO})^2$ should then be a straight line going through the origin, if the model is correct. $\theta_{CO}\,(1 - \theta_{CO})^2$ is calculated for different values of K_{CO} and the rate is drawn as a function of $\theta_{CO}\,(1 - \theta_{CO})^2$ in figure 6.13 for the Co/Al_2O_3 catalyst and in figure 6.14 for the unsupported catalyst. In both cases the rates are calculated as total CO conversion. A linear relation is not obtained with the Co/Al_2O_3 catalyst, because experimentally almost a zero order in carbon monoxide is found. The fit is much better with the other catalyst. We assume that the same mechanism is functioning on both catalysts and therefore we reject this possibility.

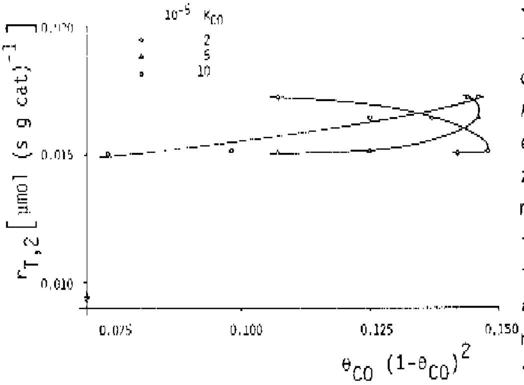

Figure 6.13. A model of two site adsorption of CO. Catalyst: Co/Al_2O_3. p_{H_2} = 80 kPa. T = 523 K.

Also in this case the models (iii) and (iv) have the same dependence on the partial pressure of carbon monoxide at a constant partial pressure of hydrogen, if the surface complex is the most abundant surface species. Thus they can be rejected on the same base as above.

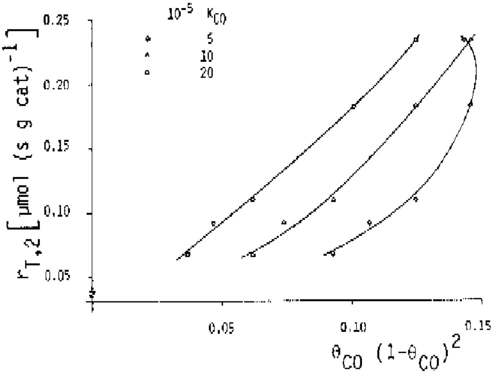

Figure 6.14. A model of two site adsorption of CO. Catalyst: Co. p_{H_2} = 80 kPa. T = 483 K.

Ad (v). The dissociation of carbon monoxide as RDS.

For the dissociation of carbon monoxide as the rate determining step the following scheme can be written:

$CO + * \rightarrow CO*$
a) $CO* + * \rightarrow C* + O*$
b) $2\ CO* \rightarrow C* + * + CO_2$
c) $CO* + 2\ H* \rightarrow C* + 2* + H_2O$

The corresponding rate equations are (when the Langmuir adsorption equilibrium is assumed for the surface coverage of CO and the surface coverage of H_2 is neglected):

$$r_a = k\ \theta_{CO}\ \theta_e = k\ \frac{K_{CO}\ p_{CO}}{(1 + K_{CO}\ p_{CO})^2} \tag{6.25}$$

$$r_b = k\ \theta_{CO}{}^2 = k\left(\frac{K_{CO}\ p_{CO}}{1 + K_{CO}\ p_{CO}}\right)^2 \tag{6.26}$$

and

$$r_c = k\ \theta_{CO}\ \theta_H{}^2 = k\ \frac{K_{H_2}\ p_{H_2}\ K_{CO}\ p_{CO}}{(1 + K_{CO}\ p_{CO})^3}\ . \tag{6.27}$$

According to equation (6.25) the order in carbon monoxide is between -1 and +1 and according to (6.26) between 0 and +2. The experimental values are within the first range. But it can easily be noticed that no positive order in hydrogen can be obtained. Only when the concentration of hydrogen is much higher than that of carbon monoxide a zero order in hydrogen would follow /130/. Equation (6.27) results in a positive order in H_2 and a negative order in CO as found experimentally. But this possibility can be neglected on the same basis as equation (6.21) which in fact is equal to (6.27) for n = 2.

Ad (vi). The hydrogenation of surface carbon as RDS.

The rate equation for the case when the hydrogenation of surface carbon is the rate determining step is

$$r = k\ \theta_C\ \theta_H{}^x = k\ \frac{p_{H_2}{}^{x/2}\sqrt{p_{CO}}}{(1 + K_{CO}\ p_{CO} + K\sqrt{p_{CO}})^{1+x}}\ . \tag{6.28}$$

The surface coverages are calculated by assuming Langmuir adsorption isotherms and neglecting θ_H. x is the number of hydrogen atoms which take part in the RDS. If x = 2 (first order in H_2 is then obtained) and the dissociatively adsorbed carbon monoxide is the most abundant surface species, the rate equation is

$$r = k \frac{p_{H_2}\sqrt{p_{CO}}}{(1 + K\sqrt{p_{CO}})^3} \qquad (6.29)$$

which in a linear form is

$$A + B\sqrt{p_{CO}} = \left(\frac{\sqrt{p_{CO}}}{r}\right)^{1/3} . \qquad (6.30)$$

The right-hand side of equation (6.30) is depicted as a function of $\sqrt{p_{CO}}$ in figures 6.11 and 6.12 for the two catalysts. From the figures 6.11 and 6.12 it can be seen that in all cases a better fit is obtained with equation (6.30) (dissociatively adsorbed carbon monoxide) than with equation (6.22) (molecularly adsorbed carbon monoxide). To check also the possibility that the molecularly adsorbed carbon monoxide is the most abundant surface species we plotted $\left(\frac{\sqrt{p_{CO}}}{r}\right)^{1/3}$ as a function of p_{CO}, figure 6.11. This does not lead to a linear relation either.

Because of the good fit of equation (6.30) a more detailed study of that will be made. At a first approximation we arrived at equation (6.30) by assuming that the surface coverages of carbon and oxygen from dissociatively adsorbed carbon monoxide are equal. The constant K equals then to $2\sqrt{K_{CO}K_C}$. But as seen in chapter 3 the reduction rate of cobalt oxides by hydrogen is several orders of magnitude higher than the rate of the Fischer-Tropsch synthesis (chapter 4). Hence the removal of adsorbed oxygen is expected to be fast. So the following scheme is written down:

(1) $H_2(g) + 2* \rightleftarrows 2\ H*$

(2) $CO(g) + 2* \rightleftarrows C* + O*$