CHAPTER 5

Formation of Carbonaceous Species

5.1. INTRODUCTION

In the previous chapter we concluded that the deactivation of the catalysts is caused by the formation of some carbonaceous species on the catalyst surface. These deactivating species can be: i) adsorbed products, ii) reaction intermediates or iii) "carbon". Conclusions about the nature of these carbonaceous species could not be drawn from the experiments in chapter 4. Therefore we decided to investigate the reaction between the catalysts and carbon monoxide more closely in the thermobalance. Furthermore we performed experiments in the flow reactor in which after a period of a standard run of the Fischer-Tropsch synthesis the products were flushed from the catalyst surface by helium and hydrogen.

Various reactions are possible between carbon monoxide and cobalt, the occurrence of which depends very strongly on the temperature and the condition of the metal surface:

i) Adsorption of carbon monoxide (associative or dissociative).
At lower temperatures up to room temperature carbon monoxide is adsorbed on cobalt in a molecular form. This can be concluded from several adsorption studies in which the surface of cobalt has been investigated with various spectroscopic methods like infra-red /110-113/, ultra-violet photo-electron and X-ray photo-electron spectroscopy /29/. These conclusions have recently been supported by LEED and Auger electron spectroscopy /106,107/.

When the cobalt surface on which carbon monoxide is adsorbed under high vacuum conditions is heated above 400 K a new surface structure appears, which is interpreted as surface carbide /107,114/.

ii) Formation of carbonyls.
A volatile dicobalt octacarbonyl $\left[Co(CO)_4\right]_2$ is stable only at low temperatures, decomposing already at 325 K under atmospheric pressure

/9/. Thermodynamically low temperatures and high pressures favour the formation of carbonyls.

iii) Formation of carbon, which is converted into bulk carbide, amorphous carbon or graphite layers, according to the following reactions:

$$2\ Co + 2\ CO \rightarrow Co_2C + CO_2 \qquad (5.1a)$$

$$3\ Co + 2\ CO \rightarrow Co_3C + CO_2 \qquad (5.1b)$$

$$2\ CO \rightarrow C + CO_2 \qquad (5.2)$$

$$Co_2C \rightarrow 2\ Co + C \qquad (5.3)$$

The old studies of the carbonization of the cobalt catalysts can be summarized as follows /14/: below 480 K cobalt carbide is formed when carbon monoxide is allowed to react with cobalt powder, above 570 K free carbon is formed and between 480 K and 570 K both carbide and carbon are present. Thermodynamically carbon formation (5.2) is slightly more favourable than carbide formation (5.1a); the change of free energy for reaction (5.1a) is -60 kJ mol^{-1} and for reaction (5.2) -50 kJ mol^{-1}.

Above 570 K cobalt carbide decomposes to α-cobalt and free carbon. At 680 K Kehrer and Leidheiser /115/ only observed reaction (5.2) and not the formation of carbides or oxides as it was found with iron. But Renshaw et al. /116/ have shown that at temperatures between 670 K and 1070 K carbide (Co_3C) is an intermediate in the formation of graphite on cobalt single crystals.

5.2. CARBONIZATION FOLLOWED IN THE THERMOBALANCE

5.2.1. EXPERIMENTAL

The experiments with the Co/Al_2O_3 catalyst are carried out in the following way (unless otherwise stated):

i) the sample is heated under nitrogen to 673 K and kept at this temperature until a constant weight is reached;

ii) the oxides are reduced by hydrogen (x_{H_2} = 0.90) at 673 K for 58 ks, followed by

iii) cooling to the carbonization temperature and flushing with nitrogen for 7 ks at that temperature. Thereafter

iv) a reaction mixture is admitted;

v) after the carbonization the catalyst is treated with nitrogen at the reaction temperature and then with hydrogen (x_{H_2} = 0.44). Each of the two treatments is continued until a constant weight is reached.

First, however, the weight changes of the hydrogen reduced catalysts are followed as a function of the temperature, when a carbon monoxide mixture (x_{CO} = 0.20, x_{N_2} = 0.80) is passed over the catalysts.

The quantity of the catalyst is in most experiments 50-60 mg and in every stage the total gas flow is 4.2 $cm^3\ s^{-1}$.

The unsupported oxide is heated to 523 K and reduced at that temperature by hydrogen (x_{H_2} = 0.44) for 5.5 ks; otherwise the procedure is the same as for the Co/Al_2O_3 catalyst.

To compare the supported and the unsupported catalysts on an equal basis, the rate of weight gain is calculated either per m^2 of cobalt surface, as calculated from monolayer coverage by carbon monoxide, or per gram cobalt. The surface structure of the catalysts changes very likely during the experiments, so that relations of the kinetic behaviour to the initial monolayer coverage become less useful as the experiment proceeds.

5.2.2. CARBONIZATION BY CARBON MONOXIDE

The influence of the temperature on the formation of carbonaceous species is studied in experiments in which the samples are heated under carbon monoxide (x_{CO} = 0.20, x_{N_2} = 0.80) from room temperature to 675 K at a rate of 0.03 K s^{-1}. In figure 5.1 the weight gain is plotted as a function of the temperature for both catalysts. The reaction starts at a somewhat lower temperature on the unsupported catalyst than on the supported

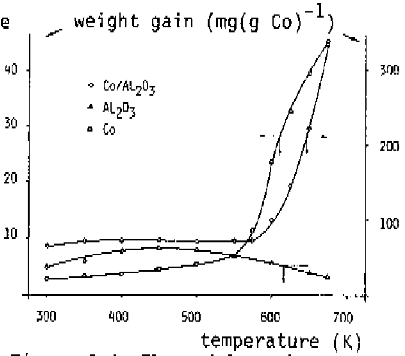


Figure 5.1. The weight gain as a function of the temperature. x_{CO} = 0.20. Heating rate: 0.03 K s^{-1}.

catalyst, but below 550 K both reactions proceed at a low rate. On the unsupported catalyst the maximum rate is reached at around 600 K. On the supported catalyst the rate increases up to 675 K. The weight gain is 340 mg (g Co)$^{-1}$ for the supported catalyst and 45 mg (g Co)$^{-1}$ for the unsupported catalyst between room temperature and 675 K. The rate of weight gain (calculated per gram cobalt) is much higher for the supported catalyst than for the unsupported one. Above 550 K the rates of weight gain per gram catalyst tend to become equal, indicating that on both catalysts a comparable mechanism becomes operative. Based on the results reviewed by Anderson /16/ we ascribe the second stage to the decomposition of carbon monoxide to coke.

Most of our experiments described in chapter 4 were carried out at temperatures below 550 K. Therefore on the following pages attention is paid only to the formation of carbonaceous species at the lower temperature range (i.e. below 550 K).

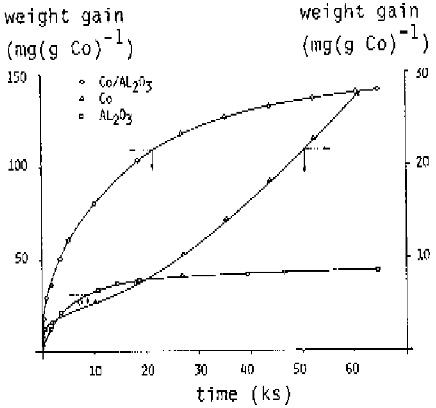


Figure 5.2. The weight gain as a function of time. x_{CO} *= 0.20. T = 524 K. (*Al_2O_3 *is calculated on the scale as* Co/Al_2O_3*).*

The weight gain per gram cobalt is plotted as a function of time in figure 5.2 for the Co/Al_2O_3, Al_2O_3 and unsupported catalyst. The mole fraction of carbon monoxide is 0.20 in nitrogen and the temperature is 524 K. In the beginning a fast increase of the weight is observed on both catalysts. This increase we call below a "step". But thereafter the behaviour of the catalysts is different: the rate of weight gain on the Co/Al_2O_3 catalyst slowly decreases and an almost constant weight is obtained in 65 ks. On the unsupported catalyst after the fast decrease the rate reduces considerably and thereafter starts to increase again. The maximum rate is reached after 55 ks. The weight gain based on the cobalt content of the catalysts is 13.9% for the Co/Al_2O_3 catalyst and 3.1% for the unsupported catalyst after 65 ks. The maximum rate of weight gain is 3.1 μg (s g cat)$^{-1}$ for the supported catalyst and 0.55 μg (s g cat)$^{-1}$ for the unsupported catalyst. Per monolayer of adsorbed carbon monoxide the values are 4.1 ks^{-1} and 0.3 ks^{-1} respectively. Thus the rate on the former catalyst is in all respects higher than on the latter one.

In order to find out what is the ratio between adsorbed carbon monoxide and carbon during the experiments we flush the catalysts with nitrogen and hydrogen at 524 K, after carbon monoxide (x_{CO} = 0.20, x_{N_2} = 0.80) has been passed over the catalyst at that temperature for 3.6 ks and for 65 ks. Three types of species can be found: 1) products which are removable by nitrogen, 2) products which are removable by hydrogen but not by nitrogen and 3) products which cannot be removed by hydrogen at 524 K in 30 ks. The quantities of these species are given in table 5.1 for both catalysts.

From table 5.1 one can notice that the product distributions for the supported and the unsupported catalyst are different and that the fraction which can be removed by nitrogen decreases with time for both catalysts.

Table 5.1. Quantity of various species on the catalysts after CO treatment at 524 K. x_{CO} = 0.20, x_{N_2} = 0.80.

	removable by N_2 mg (g Co)$^{-1}$ (%)	removable by H_2 mg (g Co)$^{-1}$ (%)	not removable mg (g Co)$^{-1}$ (%)
Co/Al_2O_3			
3.6 ks	24 (59)	– 1)	– 1)
65 ks	38 (27)	73 (52)	30 (21)
Co			
3.6 ks	2.4 (77)	– 1)	– 1)
65 ks	3.8 (13)	3.8 (13)	22 (75)
Al_2O_3			
65 ks	19 (44)	0 (0)	24 (56)

1) not measured.

We compare also the amounts which cannot be flushed off by nitrogen and hydrogen after a carbon monoxide exposure of 65 ks for various mole fractions of carbon monoxide. These data are collected in table 5.2.

Table 5.2. Irremovable quantity formed (mg (g Co)$^{-1}$) as a function of the mole fraction of carbon monoxide. T = 524 K. Exposure time: 65 ks.

x_{CO}	Co/Al_2O_3 mg (g Co)$^{-1}$	Co mg (g Co)$^{-1}$
0.10	32	15
0.20	30	22
0.44	40	23

The amount which cannot be removed by nitrogen and hydrogen at 523 K slightly increases with an increasing mole fraction of carbon monoxide. But no essential difference in the behaviour of the two catalysts is noticed as a function of the mole fraction of carbon monoxide. Further it should be mentioned that heating of the catalysts to 673 K under hydrogen restores the original weight.

The relation between the irremovable quantity and the temperature is totally different for the two catalysts, as shown in table 5.3.

Table 5.3. Irremovable quantity (mg (g Co)$^{-1}$) as a function of the temperature. x_{CO} = 0.20. Exposure time: 65 ks.

T (K)	Co/Al_2O_3 mg (g Co)$^{-1}$	Co mg (g Co)$^{-1}$
503	32	2
524	30	22
543	43	76

Presumably on the supported catalyst some final stage has been approached in all cases whereas on the unsupported catalyst steady-state levels are not yet reached. On the supported catalyst the rate of formation of inactive species increases much faster as a function of the temperature than on the supported catalyst.

Models for weight gain

The weight gain as a function of time for various mole fractions of carbon monoxide is shown for the supported catalyst in figure 5.3

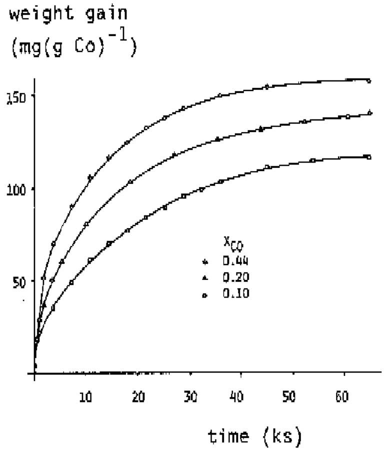


Figure 5.3. The weight gain as a function of time for various mole fractions of carbon monoxide. Catalyst: Co/Al_2O_3. T = 524 K.

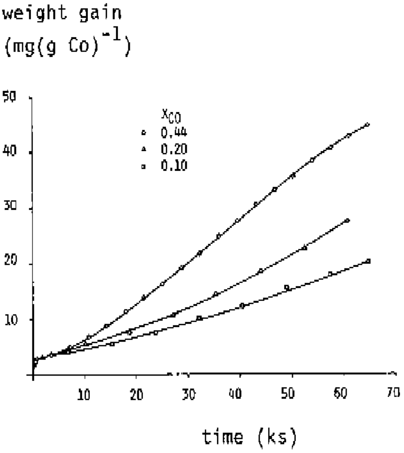


Figure 5.4. The weight gain as a function of time for various mole fractions of carbon monoxide. Catalyst: Co. T = 524 K.

and for the unsupported catalyst in figure 5.4. On the supported catalyst the rate continuously decreases and after 65 ks a fairly constant weight is reached which depends only marginally on the carbon monoxide mole fraction.

The rate of weight gain $\frac{dw}{dt}$ can be described by a semi-empirical equation:

$$\frac{dw}{dt} = k\, p_{CO}^{\gamma} \left(1 - \frac{w}{w_m}\right) \qquad (5.4)$$

i.e. the rate has a first order dependence on the fraction which is not yet occupied $1 - \frac{w}{w_m}$. w is the weight gain, w_m is the equilibrium weight, k and Y are constants. In an integrated form equation (5.4) reads:

$$\ln (w_m - w) = - k \, p_{CO}{}^{Y} \, t + C_1 \, . \qquad (5.5)$$

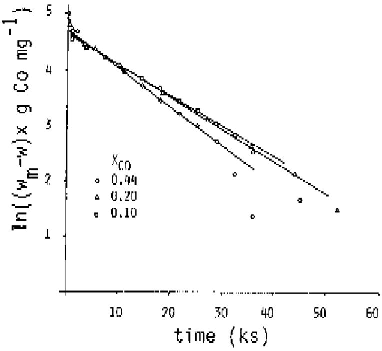


Figure 5.5. ln $(w_m - w)$ as a function of time for various mole fractions of CO.
Catalyst: Co/Al_2O_3. T = 524 K.

In figure 5.5 the left-hand side of equation (5.5) is plotted as a function of time for various mole fractions of carbon monoxide. A linear relation is obtained up to a value of (w/w_m) of about 0.9. The dependence of the rate on the mole fraction is calculated from the slopes of the lines in figure 5.5. The order, Y, is 0.2.

On the unsupported catalyst the rate of weight gain increases as a function of time and thus as a function of the quantity deposited. Apparently a certain induction period is needed before the reaction can proceed. This is typical for an autocatalytic reaction. This further means that in the beginning of the experiment the reaction rate is proportional to the quantity of carbonaceous species deposited on the catalyst and also to the fraction which is not yet occupied $(1 - w/w_m)$. In analogy with the reaction model used for the reduction of cobalt oxides in chapter 3 the overall rate can be described by equation (5.6):

$$- \frac{dw}{dt} = k' \, p_{CO}{}^{Y} \left(a' + \frac{w}{w_m}\right) \left(1 - \frac{w}{w_m}\right) \qquad (5.6)$$

where w_m is the maximum weight gain and a' is a constant.

It is assumed that the equilibrium adsorption of carbon monoxide is reached fast and that an increase in the amount of reversibly adsorbed carbon monoxide is only a fraction of the total weight gain.

Then the rate of weight gain reflects the rate at which carbonaceous species move away from the sites active for the adsorption of carbon monoxide and thus allow further adsorption.

In an integrated form equation (5.6) is

$$\log \frac{a + w}{w_m - w} = k\, p_{CO}{}^{\gamma}\, t + C \quad . \tag{5.7}$$

With the values a = 18 and w_m = 68 mg (g Co)$^{-1}$ a good fit of the experimental values to equation (5.7) is obtained. In figure 5.6 the left-hand side of equation (5.7) is plotted as a function of time for various mole fractions of carbon monoxide at 524 K. The slopes of the lines slightly depend on the mole fraction of carbon monoxide. The order calculated from these slopes is 0.6. Equation (5.7) indicates that the weight gain should reach a maximum value of 68 mg (g Co)$^{-1}$. However, we carried out also an experiment lasting 260 ks. The weight gain after that period was 82 mg (g Co)$^{-1}$, and the weight was not yet constant. If we nevertheless calculate the weight increase

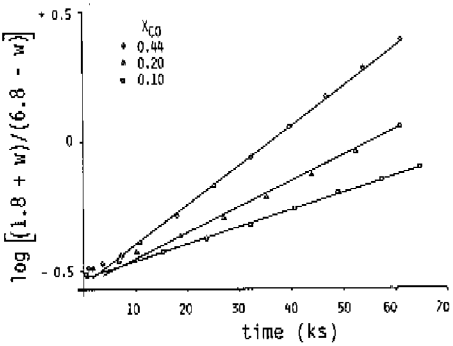


Figure 5.6. log $\left[(1.8 + w)\,(6.8 - w)^{-1}\right]$ *as a function of time for various mole fractions of CO.*
Catalyst: Co. $T = 524$ *K.*

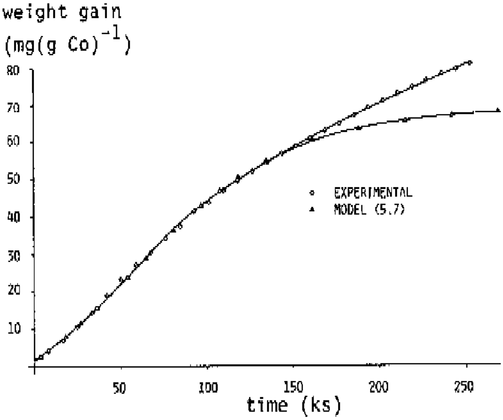


Figure 5.7. The weight gain as a function of time. Catalyst: Co. $x_{CO} = 0.20$, $T = 524$ *K.*

from equation (5.7) with w_m = 68 mg (g Co)$^{-1}$, we see (figure 5.7) that the model predicts the weight increase accurately for the period up to 160 ks. It would indicate that the formation of carbonaceous species takes place in two stages. The first stage seems to proceed to a maximum value as predicted by equation (5.7). After 160 ks a second stage becomes operative. In this stage the weight increases almost at a constant rate of 0.2 µg (s g Co)$^{-1}$. This could be a decomposition of carbon monoxide on inactive carbon laid down on the surface, and might be related to the carbon formation at higher temperatures (compare with figure 5.1).

Reactivity of bulk carbide

The reactivity of bulk carbide, Co_2C, towards hydrogen has been tested as well in the thermobalance. At 523 K carbide can be hydrogenated to cobalt metal. But if Co_2C is heated to 673 K under nitrogen before the hydrogen treatment, a weight loss of less than 1 wt % is obtained at 523 K. This shows that carbide can be transformed into some inactive form of carbon.

5.2.3. CARBONIZATION BY SYNTHESIS GAS

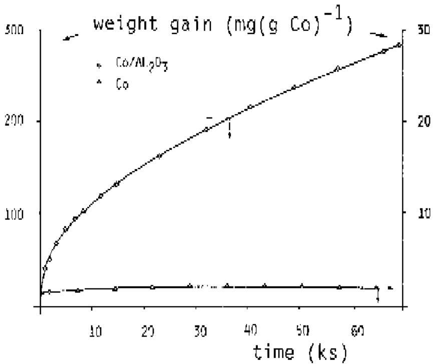


Figure 5.8. The weight gain as a function of time for the supported and the unsupported catalyst. $x_{H_2} = x_{CO} = 0.20$. $T = 524$ K.

The weight gain as a function of time is shown for the supported and unsupported catalyst in figure 5.8, when the synthesis gas (x_{CO} = 0.20, x_{H_2} = 0.20 and x_{N_2} = 0.60) is passed over the catalysts at 524 K. When these curves are compared with the curves in figure 5.2 (the feed without hydrogen), one notices that on the supported catalysts the rate of weight gain is further increased but it is remarkably decreased on the unsupported catalyst. After 65 ks the weight is not yet constant at all on the supported catalyst just as when using only carbon monoxide; even after 238 ks the weight still increases. However, the weight of the unsupported catalyst is practically constant after the first step just in the beginning of the experiment.

The higher weight increase of the alumina supported catalyst is likely caused by the fact that the alumina can adsorb both hydrocarbons and water formed from the synthesis gas. From the observations of the unsupported catalyst one would conclude that hydrogen effectively prevents the formation of unreactive carbonaceous species.

In table 5.4 the weight gain is given after 65 ks at two temperatures, 524 K and 543 K for the unsupported catalyst; the amount left after the flushing with nitrogen is also included.

Table 5.4. The weight changes (mg (g Co)$^{-1}$) under the synthesis gas of $x_{H_2} = x_{CO} = 0.20$ and under nitrogen. Catalyst: Co. Exposure time: 65 ks.

T (K)	weight gain under the synthesis gas mg (g Co)$^{-1}$	left after N_2 treatment mg (g Co)$^{-1}$
524	2.3	0.4
543	2.9	0.9

For the Co/Al_2O_3 catalyst the weight gain is 280 mg (g Co)$^{-1}$ after 65 ks.

At the two temperatures the amounts which can be taken off with nitrogen from the unsupported catalyst are almost the same and are about 90% of the monolayer coverage. This suggests that the main part of the catalyst surface is covered by desorbable species which are either adsorbed carbon monoxide or reaction intermediates and products.

5.2.4. DISCUSSION

Three types of carbonaceous species are formed on the cobalt catalysts, when they are treated by carbon monoxide between 503 K and 543 K:

1) species which can be flushed off with nitrogen, i.e. reversibly adsorbed carbon monoxide or carbon dioxide;
2) species which cannot be flushed off with nitrogen, but can be flushed off with hydrogen, i.e. species that can be hydrogenated at temperatures between 503-543 K. These can be the surface carbon, from dissociatively adsorbed carbon monoxide or bulk carbide, as for both compounds it is known that they can be hydrogenated to methane at the temperatures used /14,33/;
3) species which cannot be hydrogenated at temperatures between 503-543 K. This inactive carbon is possibly present in the form of amorphous carbon clusters or graphite or strongly adsorbed carbon monoxide on the alumina.

The reactions just mentioned can be summarized as follows:

$$\begin{array}{lcll} & \nearrow\!\!\!\swarrow & CO(ads) & (a) \\ CO(g) & \longrightarrow & C_{active} & (b) \\ & \searrow & C_{inactive} & (c) \end{array} \qquad (5.8)$$

Carbonaceous species which can be hydrogenated are defined as active carbon (5.8 b) and carbonaceous species which cannot be hydrogenated are defined as inactive carbon (5.8 c). The amount of carbon that is deposited in or on cobalt is greater than the solubility of carbon in cobalt /117/. This could mean that carbides, the carbon content of which is much higher (6.4 wt % for Co_3C and 9.2 wt % for Co_2C), are intermediates in the formation of inactive carbon. The experiments with cobalt carbide, Co_2C, showed that carbide can be converted into an inactive form of carbon. Thus reaction (5.8) can be written as

$$CO(g) \rightleftharpoons CO(ads) \rightarrow C_{active} \rightarrow C_{inactive}, \qquad (5.9)$$

i.e. the inactive carbon is formed from carbon monoxide via an active carbon intermediate.

Further support for this idea is the observation that after short exposure times (for carbonization or for the Fischer-Tropsch synthesis) most carbon is still active but that in the course of time inactive carbon is formed, evidently by a consecutive reaction. If these reactions were parallel both types of carbonaceous species would be formed at some more or less constant ratio.

In the following we are going to deal in more detail with the various carbonaceous species.

Reversible adsorption of carbon monoxide

On the unsupported cobalt initially there is room for about 2.1 mg CO per gram cobalt. This increases slowly with time and becomes almost a double after 65 ks. On the supported catalyst the quantity of the reversibly adsorbed carbon monoxide increases also with time (table 5.1). After the substraction of the quantity that can be flushed off from a corresponding quantity of alumina an increase of about 60% is obtained, which is somewhat smaller than in the case of the unsupported catalyst. On both catalysts that extra adsorbed quantity can be ascribed to the enlargement of the cobalt surface caused by lattice distortion by carbon.

Active carbon

On the unsupported catalyst only 13 wt % of the total adsorbable material is recovered by hydrogen. This is in strong contrast to the supported catalyst where the active carbon is about 50 wt %. Also the absolute quantities differ, being about twenty times higher on the supported catalyst. The suggestion, also based on the results of the next section, is that on the supported catalyst a part of the active carbon is situated on the support.

Inactive carbon

The first observation is that at 524 K the differences between the two catalysts are less than a factor two, with more inactive carbon per gram cobalt on the unsupported catalyst.

The small temperature dependence of the formation of inactive carbon on the supported catalyst can be explained by the fact that in all cases steady-state quantities of carbonaceous species have more or less been reached uninfluenced by the kinetics.

Conclusions

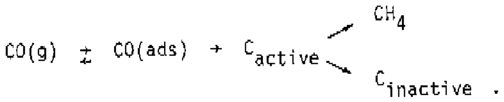
On the supported catalyst there is more reversibly adsorbed carbon monoxide and more active carbon per gram cobalt than on the unsupported catalyst, but no essential difference is found in the quantity of inactive carbon. These observations suggest - if our explanation is correct - that the mobility of the carbonaceous species is at least on the supported catalyst rather high. We expect that the mobility of hydrogen containing surface species, C_nH_m, is higher than the mobility of species without hydrogen.

Reaction rates

An essential difference in the rates of weight gain on the supported and the unsupported catalysts is found. On the unsupported catalyst the rate starts to increase slowly after the first step, reaching a maximum value at a weight gain of around 25 mg (g Co)$^{-1}$. It seems that some induction period is needed before carbonaceous species can be formed. After the first step the surface is for a great part full of carbonaceous materials corresponding to an equilibrium adsorption. Further adsorption is then only possible by the formation of more empty sites on which, as the "step" shows, adsorption is fast. The model derived in section 5.2.2 indicates an interaction between an occupied site and an empty site or between an occupied site and the not yet occupied neighbourhood to create a new empty site, an interaction that pervades the complete crystal lattice. As a result of carbide formation the exposed cobalt surface seems to be increased. This could also explain the increase in the quantity of reversibly adsorbed carbon monoxide. This process then leads to the formation of cobalt carbide, Co_2C. This is verified by X-ray diffraction analysis after the carbon monoxide treatment during 260 ks.

On the supported catalyst no induction period is found and the rate remains high after the first step. However, it is slowly decreasing. The high initial rate indicates that at the beginning of the reaction already an abundance of reactive sites where carbon can be deposited is available for carbon monoxide decomposition. These sites could be the open high index crystallographic planes, places of contact with the carrier or various defects.

By adding hydrogen to carbon monoxide the formation of carbon on the unsupported catalyst clearly decreases. It is not to be expected that hydrogen would decrease the rate of decomposition of carbon monoxide /34/. This then means that in the presence of hydrogen the carbonaceous species from the carbon monoxide dissociation are mainly hydrogenated to methane and thus the deposition of carbon is avoided. Hence two conclusions can be drawn: i) there is an intermediate which is active both in hydrogenation and in carbon formation; ii) the hydrogenation of that intermediate is a faster reaction than the formation of inactive carbon. Thus we arrive at the following scheme:



$$CO(g) \rightleftarrows CO(ads) \rightarrow C_{active} \begin{array}{l} \nearrow CH_4 \\ \searrow C_{inactive} \ . \end{array} \tag{5.10}$$

5.3. FLUSHING OF THE CATALYSTS AFTER THE FISCHER-TROPSCH SYNTHESIS

5.3.1. INTRODUCTION

In the thermobalance experiments it was noticed that when synthesis gas was passed over the Co/Al_2O_3 catalyst at 524 K the weight of the catalyst increased up to a value of 280 mg $(g\ Co)^{-1}$ in 65 ks. It was a challenge to try to identify the species which cause that increase. There are several possibilities:

i) adsorbed carbon monoxide;

ii) reaction intermediates;

iii) adsorbed products;

iv) inactive carbon or high molecular weight hydrocarbons.

The most simple way to determine the total quantity of carbon on the catalyst would be to treat the catalyst with oxygen. From water and carbon dioxide formed the quantities of carbon and hydrogen can then be calculated. But because our analysis of water is not accurate enough and because we are also interested in the nature of the various species we use helium and hydrogen for flushing the species away from the surface of the catalyst. Using hydrogen instead of oxygen in flushing is not without difficulties, either. Under hydrogen reactions like hydrocracking can take place and change the product distribution. Therefore we also flush the catalyst with helium. By combining these experiments information about the nature and the quantity of the surface species can be obtained.

5.3.2. EXPERIMENTAL

After the synthesis with various concentrations of hydrogen and carbon monoxide at 523 K the following flushing procedures are applied:

i) with hydrogen (x_{H_2} = 0.20, x_{He} = 0.80) for 58 ks at 523 K;

ii) with helium for 3.6 ks at 523 K, then with hydrogen for 58 ks at 523 K and thereafter heating (0.06 K s^{-1}) under hydrogen to 673 K; helium flushing is used in this case before hydrogen in order to remove gas phase carbon monoxide, which otherwise could react to hydrocarbons;

iii) with helium for 3.6 ks at 523 K and thereafter heating (0.06 K s^{-1}) under helium to 673 K.

An experiment using procedure (ii) was also carried out in the thermobalance and showed that within the experimental error the original weight (after the hydrogen reduction) can be restored by that treatment. This means that the temperature of 673 K is high enough for the desorption and hydrogenation of all adsorbed species. Therefore this procedure is used in the determination of the total quantity of carbonaceous species on the catalyst.

5.3.3. FLUSHING WITH HYDROGEN

Procedure (i)

When the synthesis gas (x_{H_2} = 0.20, x_{CO} = 0.20, x_{He} = 0.60) is changed after 18 ks to hydrogen (x_{H_2} = 0.20, x_{He} = 0.80) at 523 K, the rates of formation of all hydrocarbon fractions increase. The rates after 60 s and after 1.2 ks under hydrogen are compared with the rates during the Fischer-Tropsch synthesis in table 5.5.

It can be seen that the absence of carbon monoxide enhances the rates of formation of all fractions. A few things are worth mentioning: after 60 s i) the rate of methane formation has increased more than the rates of the other products; ii) from C_3 to C_7 the relative increase is more or less constant, i.e. the product distribution stays constant; iii) during flushing the C_2/C_3 ratio is 2, i.e. more C_2-products than C_3-products are formed. During synthesis the ratio C_2/C_3 is 0.8; iv) no ethylene or propylene are formed. The formation

Table 5.5. The ratio of the formation rate of various hydrocarbon fractions during the initial period of hydrogen flushing and during the Fischer-Tropsch synthesis. Catalyst: Co/Al$_2$O$_3$. T = 523 K.

t (ks)	$\frac{c_{f,1}}{c_1}$	$\frac{c_{f,2}}{c_2}$	$\frac{c_{f,3}}{c_3}$	$\frac{c_{f,4}}{c_4}$	$\frac{c_{f,5}}{c_5}$	$\frac{c_{f,6}}{c_6}$	$\frac{c_{f,7}}{c_7}$
0.06	6.7	3.2	1.4	1.3	1.3	1.2	1.4
1.2	2.3	0.1	0.07	0.04	0.06	0.1	0.2

of higher hydrocarbons decreases very fast and after 1.2 ks the rates are only one tenth of the rates during the synthesis. Because of the low concentrations of the various products these measurements are not too accurate, but they show anyhow that no shift in the product distribution towards lower products, excluding methane, has taken place. After 7 ks only methane can be detected and still after 85 ks at 523 K some traces of methane are found. The total amount which can be flushed off is 4.5 mmol (g Co)$^{-1}$.

When procedure (i) is applied to the unsupported cobalt catalyst at 523 K, only the formation of methane increases there with a factor of 1.6. Only traces of ethane and propane but no higher products are found. Also with this catalyst some traces of methane can be detected after 85 ks of hydrogen flushing.

Procedure (ii)

During the thermobalance experiments it was noticed that the weight of the Co/Al$_2$O$_3$ catalyst increased continuously as a function of time when the synthesis gas mixture was passed over the catalyst at 523 K. Thus we would expect that the longer the reaction time, the more hydrocarbons can be flushed off. Therefore a series of experiments is carried out in which the synthesis is stopped after 7.2, 18 and 58 ks under the mixture of hydrogen and carbon monoxide, x_{H_2} = 0.20, x_{CO} = 0.20 at 523 K. Thereafter the flushing with helium and subsequently with hydrogen is performed. The results are presented in table 5.6.

Table 5.6. The quantity of hydrocarbons flushed off after the Fischer-Tropsch synthesis during increasing period at 523 K with $x_{H_2} = x_{CO} = 0.20$*. Catalyst:* Co/Al_2O_3*.*

t (ks)	total quantity flushed off; procedure (ii)		C_1	quantity flushed off at 523 K	
	$\frac{\mu mol}{g\ cat}$	$\frac{\mu mol\ C}{g\ cat}$	mole %	$\frac{\mu mol}{g\ cat}$	$\frac{\mu mol\ C}{g\ cat}$
7.2	86	93	97	35	42
18	171	197	93	93	114
58	217	293	91	117	139

It can be seen that i) the amount flushed off indeed increases with the duration of the synthesis, and ii) the amount of higher hydrocarbons increases as well.

The amount flushed off at 523 K is already higher than the monolayer coverage of carbon monoxide, being 1.3, 3.5 and 4.5 times higher after 7.2, 18 and 58 ks, respectively. The results suggest that during the Fischer-Tropsch synthesis higher hydrocarbons (or their intermediates) are built on the surface and thus the average molecular weight increases as a function of time.

The dependence of the surface coverage of carbonaceous species on the mole fractions of hydrogen and carbon monoxide is shown in table 5.7. Procedure (ii) is applied after an 18 ks synthesis with various mole fractions of the reactants at 523 K.

Table 5.7. The quantity of hydrocarbons flushed off using the procedure (ii) after the Fischer-Tropsch synthesis performed with various mole fractions of H_2 *and CO at 523 K for 18 ks. Catalyst:* Co/Al_2O_3*.*

x_{H_2}	x_{CO}	total quantity flushed off; procedure (ii)		C_1	quantity flushed off at 523 K	
		$\frac{\mu mol}{g\ cat}$	$\frac{\mu mol\ C}{g\ cat}$	mole %	$\frac{\mu mol}{g\ cat}$	$\frac{\mu mol\ C}{g\ cat}$
0.6	0.2	103	110	96	36	43
0.2	0.2	171	197	93	93	114
0.2	0.6	199	236	94	163	200

An increasing mole fraction of hydrogen diminishes the quantity of carbonaceous species and an increasing mole fraction of carbon monoxide increases it. More than 90 mole % of the total amount flushed off under hydrogen is again methane. A little amount of water and carbon monoxide is detected just after the change to hydrogen but they disappear fast.

Unsupported cobalt

On the unsupported catalyst the amounts flushed off after the Fischer-Tropsch synthesis at 483 K with various mole fractions do not essentially differ, being 76, 66 and 72 μmol (g Co)$^{-1}$ respectively with feeds of x_{H_2} = 0.80 and x_{CO} = 0.20, x_{H_2} = 0.20 and x_{CO} = 0.20, x_{H_2} = 0.20 and x_{CO} = 0.80. No formation of water but some traces of carbon dioxide are detected during the flushing.

5.3.4. FLUSHING WITH HELIUM

Procedure (iii)

When the synthesis gas mixture (x_{H_2} = 0.20, x_{CO} = 0.20) is replaced by helium at 523 K, after the Fischer-Tropsch synthesis has been running for 18 ks, the rate of formation of every product decreases. The ratios of the rates of various hydrocarbons after 60 s in the helium stream to the rates during the synthesis are given in table 5.8.

Table 5.8. Ratio of the formation rates for three hydrocarbon fractions under He and under synthesis gas. Catalyst: Co/Al$_2$O$_3$.

fraction	C_1	C_2	C_3
$\frac{C_i\text{, flushed}}{C_i\text{, synthesis}}$	0.7	0.6	0.6

The concentrations decrease steadily and after 600 s only some methane is found.

By heating to 673 K under helium traces of hydrocarbons from C_1 to C_5 are released, but around 650 K 1 µmol (g cat)$^{-1}$ of C_6-products desorbs, which consists for 94 mole % of benzene. Also 35 µmol (g cat)$^{-1}$ of carbon dioxide is formed during this heating, coming either from adsorbed carbon monoxide or from adsorbed carbon dioxide. After 3,6 ks at 673 K under helium hydrogen is admitted; a further quantity of 47 µmol (g cat)$^{-1}$ is flushed off. The total quantity desorbed with this sequence (helium and hydrogen) is smaller than when the whole treatment is performed under hydrogen. This shows that during the heating under helium a part of the carbonaceous species on the surface is transformed into a form which cannot be hydrogenated any more at 673 K.

5.3.5. DISCUSSION

The formation of hydrocarbons under the hydrogen flow (procedure (i)) can occur via several reactions:

i) carbon monoxide present in the gas phase can react further according to the Fischer-Tropsch route;
ii) adsorbed intermediates can be hydrogenated and desorbed;
iii) surface intermediates and products can be cracked to lighter hydrocarbons.

Both the first and the third possibility are expected to shift the product distribution towards smaller hydrocarbons. But as seen in table 5.5 no such shift was observed. Therefore we conclude that at least during the first 1,2 ks of hydrogen flushing we mainly deal with the reactions (ii), i.e. termination reactions.

When the ratios of the products in hydrogen flushing and in helium flushing just after the synthesis are compared, some conclusions about the termination can be drawn. There are two possibilities for the termination: 1) desorption and 2) interaction with hydrogen followed by desorption. If the termination consisted of a desorption step only, we would expect that flushing with hydrogen and flushing with helium should have the same effect. Since on several metals the heat of adsorption for hydrocarbons like e.g. ethylene is higher than the heat of adsorption for hydrogen /118/, hydrogen is not expected to displace olefins from the surface by a purely "thermodynamic" mechanism.

The importance of hydrogen for termination would also explain the relation between the quantities flushed off and the duration of the Fischer-Tropsch synthesis and with the mole fractions of hydrogen and carbon monoxide used in the synthesis. Hydrogen increases the overall conversion and thus increases the concentrations of the products in the gas phase. Thus if for all products the adsorption equilibrium would be reached, more of each product should remain on the catalyst surface when a higher hydrogen mole fraction is used. But an opposite effect is observed: a smaller quantity of the various products is on the surface with a higher hydrogen mole fraction than with a lower one.

In the beginning of the hydrogen flushing (procedure (i)) the rate of formation of C_1- and C_2-hydrocarbons is more enhanced than the rate of formation of the other products when compared with normal Fischer-Tropsch conditions (table 5.5). That indicates that the influence of hydrogen on the termination of the fractions having carbon number 3 and higher is the same but that that influence for the terminations of C_1- and C_2-fractions is different. We ascribe the higher methane formation to the fact that this compound has a higher order in hydrogen than all the other products (chapter 6) and possibly to the slow conversion of rather inactive carbon into methane.

The ratio of the C_2-fraction to the C_3-fraction alters clearly, when the synthesis gas mixture is replaced by hydrogen. According to the Flory- Schulz distribution the mole ratio of C_2/C_3 should be 1.9 for $\alpha = 0.51$ ($x_{H_2} = 0.60$, $x_{CO} = 0.20$, chapter 4) and 1.5 for $\alpha = 0.65$ ($x_{H_2} = 0.20$, $x_{CO} = 0.20$). Under the hydrogen flushing the C_2/C_3 ratio is of the order of two, which is higher than predicted by the Flory model. These results suggest that the reason for the C_2-fraction to be below the Flory-line is a small rate constant for C_2 termination or, what amounts to the same, a low rate constant for the desorption of the C_2-fraction under the Fischer-Tropsch conditions used.