CHAPTER 3

Preparation and Characterization of the Catalysts

3.1. INTRODUCTION

It is a well-known fact that oxides do not catalyze the Fischer-Tropsch reaction. Because both reactants, hydrogen and carbon monoxide, are reducing agents, at least a part of a catalyst which initially is in an oxide form, is reduced by the reaction mixture. In most cases the reduction is performed by H_2 before a mixture of hydrogen and carbon monoxide is passed over the catalyst. On the other hand by the reaction water and carbon dioxide are formed, which are oxidizing compounds. During synthesis at a steady state the following equilibria are often reached /16/:

$$M_xO_y + y\,H_2 \rightleftarrows x\,M + y\,H_2O \tag{3.1}$$

$$M_xO_y + y\,CO \rightleftarrows x\,M + y\,CO_2 \tag{3.2}$$

M = metal.

Table 3.1. Equilibrium constants for the reduction of cobalt oxides.

	ln K			
reducing agent	hydrogen		carbon monoxide	
T (K)	473	573	473	573
CoO	4.5	4.9	9.9	7.9
Co_3O_4	46	41	68	56

The equilibrium constants for the reduction of cobalt oxides Co_3O_4 and CoO are given in table 3.1 /9/.

These high values show that the equilibria are very much on the right-hand side of the equations and thus oxide formation is not favoured under reaction conditions. However, as all thermodynamic values above are for bulk oxides and bulk metal, the possibility of the presence of surface oxides cannot be excluded on this basis.

The reduction conditions have a strong influence on the properties of catalysts. In the old Fischer-Tropsch processes cobalt catalysts were normally reduced by hydrogen at temperatures up to 573 K. The degree of reduction varied then between 40 and 90%; the maximum activity was observed for 65-70% reduction, and it was noticed that complete reduction was neither necessary nor desirable /14,16/.

In this chapter we pay attention to the activation of the catalysts by hydrogen, carbon monoxide and mixtures of H_2 and CO. The experiments were carried out both in the thermobalance and in the flow reactor. The preparation and some properties of the catalysts are discussed as well.

3.2. PREPARATION OF THE CATALYSTS

Two types of cobalt catalysts are used in this study: supported and unsupported. The former ones are prepared by impregnation and the latter ones by precipitation.

Cobalt oxide on alumina

Alumina (Ketjen 0.06-1.5 E; particle size 0.3-0.5 mm) used as a carrier is stabilized by heating at 873 K for 9 ks. The impregnation is performed by an aqueous solution of cobalt(II) nitrate (1.9 m $Co(NO_3)_2 \cdot 6\ H_2O$; Merck P.A.) at 303 K for 13 ks. The amount of the solution is five times the total pore volume of the carrier. After impregnation the catalyst is filtered off and dried at 393 K for 58 ks. The nitrates are decomposed in air at 573 K for 3.6 ks. The surface area (BET) of the catalyst is 120 $m^2\ g^{-1}$ and the cobalt content measured by atomic absorption is 6.3 wt %.

Cobalt oxides

Cobalt(II,III) oxide is prepared by precipitation from a 0.5 m cobalt(II) nitrate solution by concentrated ammonium hydroxide (25% NH_3, Merck P.A.) /77/. The suspension is heated to 383 K. The blue precipitate is filtered off and washed five times with distilled water. The catalyst is dried at 393 K for 58 ks and calcined at 723 K for 3.6 ks. The catalyst is sieved to three fractions with sieves of 0.3-0.5 mm (this fraction is used in the flow reactor), 0.2-0.3 mm and 0.5-0.6 mm (used in the thermobalance).

Formation of Co_3O_4 is confirmed by X-ray diffraction analysis using Mn-filtered FeK_α-radiation. The peaks agree with the diffraction file card for Co_3O_4 (ASTM 9-418). The average crystallite size is calculated from the broadening of (311), (220) and (440) lines by the Scherrer equation /78/, and found to be 33 nm. It has been shown that the calcination temperature strongly influences the crystallite size of unsupported cobalt oxide. For cobalt oxide calcined at 758 K a crystallite size of 34 nm was found /79/, which agrees well with our results. Cobalt(II) oxide is prepared by decomposing cobalt(II) carbonate ($CoCO_3$, J.T. Baker) /80/. The decomposition is performed under nitrogen at 673 K for 7 ks. Then the catalyst is calcined at 1273 K for 29 ks in air and after that directly dropped into liquid nitrogen. The catalyst is sieved like Co_3O_4. X-ray diffraction analysis confirms the presence of CoO (ASTM 9-402) with an average crystallite size of 77 nm.

3.3. CRYSTAL STRUCTURE OF THE CATALYSTS

The properties of cobalt oxide on alumina catalysts have been investigated intensively mainly because combined with molybdenum oxide they are used in the hydrodesulphurization of petroleum feedstocks /81/.

From magnetic susceptibility measurements a two-phase model for cobalt oxide on Al_2O_3 has been proposed /82/: a β-phase consisting of Co_3O_4 and a δ-phase, well-dispersed Co^{2+} ions on the alumina. The relative proportions of these two phases depend critically on the preparation procedure. Further it has been stated that only the β-phase can be reduced in hydrogen.

Richardson and Vernon /83/ concluded from their magnetic susceptibility and X-ray diffraction measurements that cobalt oxides on Al_2O_3 can be represented by a spinel form $Co^{2+}{}_{xm}\ Al^{3+}{}_{yn}\ (\square_t\ Co^{3+}{}_{(1-x)m}$

$Al^{3+}_{(1-y)n}) O_4$, where x can be calculated from the magnetic moments $\mu^2 = x (4.28)^2 + (1-x)(1.61)^2$, m from the cobalt content, n from the valence requirements and the y and t values follow from the spinel structure. These authors /83/ also showed that at low cobalt concentrations cobalt exists only as Co^{2+} ions in tetrahedral sites of alumina.

Ashley and Mitchell /84/ studied cobalt oxide on Al_2O_3 systems in different stages of the preparation, using magnetic susceptibility and spectroscopic measurements. After drying at room temperature cobalt is in an octahedral oxygen environment and at 403 K it enters tetrahedral sites of alumina. At higher concentrations cobalt(II) is incorporated also in alumina pores and at 403 K remains there in octahedral oxygen coordination. During the calcination in air only the octahedral cobalt is partly oxidized to cobalt(III). By electron spin resonance (ESR) and X-ray photo-electron spectroscopy (ESCA) these results were fully confirmed /85,86/. Cobalt was found as Co^{2+} ions in a monolayer on alumina. When the concentration of cobalt was higher than 3 wt %, Co_3O_4 became noticeable as a separate phase. With 6 wt % Co about 95% of the cobalt was in the form of Co_3O_4. The reduction by hydrogen modified the dispersion of cobalt because metallic cobalt can migrate over the surface of alumina /86/. In cobalt oxide/SiO_2 catalysts cobalt was only found as oxide, Co_3O_4. For the compound formation with silica higher calcination temperatures were required than those used normally /87/.

Co_3O_4 (without carrier) has a cubic spinel structure with eight molecules per unit lattice, a = 8.084 Å. The ionic structure $Co^{2+}\left[Co^{3+}\right]_2O_4$ has been confirmed by magnetic /83/, NMR /88/ and Mössbauer /89/ measurements. Cobalt(II) ions are tetrahedrally surrounded and cobalt(III) ions octahedrally surrounded.

A defect Co_3O_4, containing more oxygen is also known /89/. X-ray diffraction of that compound remains the same as for Co_3O_4 and the composition can be written as $Co_3O_4 \cdot nO_2$.

By reducing Co_3O_4 by hydrogen below 673 K α-cobalt with a hexagonal, close-packed lattice is formed. Above 673 K this transforms into β-cobalt with a face-centred cubic lattice /90/. Above 1023 K Co_3O_4 decomposes to CoO /90/ which has a face-centred cubic lattice with four molecules per unit cell, a = 4.16 Å. The composition of this oxide should in fact be described by the formula $Co_{1-x}O$ showing a deficit in the metallic sublattice /91/. Also this oxide can be reduced by hydrogen to cobalt metal /90/.

3.4. REDUCTION OF THE CATALYSTS

3.4.1. EXPERIMENTAL

Reduction experiments are performed in the thermobalance, where the weight of a catalyst can be followed as a function of time. Some reduction experiments are also carried out in the flow reactor, where a greater amount of a catalyst can be used, and where the outcoming gas can be analyzed more accurately than in the thermobalance. This is especially helpful in the case that the reduction is carried out by carbon monoxide.

Unless otherwise stated the following experimental procedures are followed.

The reduction of cobalt oxide on alumina

The catalyst (50-60 mg) is first flushed by nitrogen (the flow 3.8 $cm^3\ s^{-1}$) at room temperature and atmospheric pressure for at least 3.6 ks. After that it is heated under nitrogen to 673 K and kept at that temperature until the weight is stabilized. About 20 ks are needed for the desorption of water from the alumina and for the decomposition of residual nitrates (the catalyst is calcined at 573 K). The reduction temperature is adjusted and then the gas flow, with a known concentration of the reducing agent, is admitted. The total flow is again 3.8 $cm^3\ s^{-1}$. In order to avoid a rate limitation due to film diffusion a highest possible gas flow is used. As incipient instabilities can be noticed at flows of about 5.4 $cm^3\ s^{-1}$ we have set the flow at 3.8 $cm^3\ s^{-1}$.

The reduction is continued until a constant weight is reached or until a minimum weight is reached. This choice is made because sometimes upon reduction by carbon monoxide the weight starts to increase at the end of the reduction.

The reduction of cobalt oxides (Co_3O_4 and CoO)

These reduction experiments are performed similarly as those with cobalt oxide on alumina except that before reduction the weight is stabilized at 523 K. Within 4 ks the stable level is reached.

Cobalt(II,III) oxide is known to decompose according to the reaction /90/

$$Co_3O_4 \rightarrow 3\ CoO + \tfrac{1}{2}\ O_2\ . \tag{3.3}$$

At 673 K the equilibrium partial pressure of oxygen is as low as 2.6 x 10^{-6} Pa /9/. As it is unrealistic to assume that the concentration of oxygen in the thermobalance approaches such a low value we believe that the reaction (3.3) does not take place during the heating period.

The reduction rate is calculated from the weight loss, assuming that there is no adsorption of products. For the reduction of unsupported cobalt oxides by hydrogen this assumption is justified by the fact that the total weight loss equals indeed the total amount of oxygen in the unreduced sample. However, with the supported catalysts the adsorption of water on alumina disturbs the measurements. This point will be discussed in 3.4.2. The possibility of carbon formation during the reduction by carbon monoxide cannot be excluded. Therefore only the initial reduction rates are dealt with quantitatively for these catalysts.

3.4.2. REDUCTION BY HYDROGEN

In order to be able to deal with the rates of the reduction quantitatively, the experiments should be carried out under such conditions that no diffusion limitations occur. Therefore first the possibility of inter- and intra-particle diffusion limitation was studied. We used cobalt(II,III) oxide, Co_3O_4, in these studies.

The occurrence of film diffusion is checked by carrying out experiments with various quantities of catalyst at a constant concentration of hydrogen (x_{H_2} = 0.44) at 524 K. In figure 3.1 the reduced fraction (f) is plotted as a function of time. In the beginning the quantity of catalyst has no influence but at higher degrees of reduction the rate per gram of catalyst is lower for a higher quantity of catalyst. However, a complete reduction is reached at the same time in all cases. This indicates that with a higher quantity of the catalyst, when the concentration of water during the reduction is higher, the weight loss does not agree anymore with the degree of reduction.

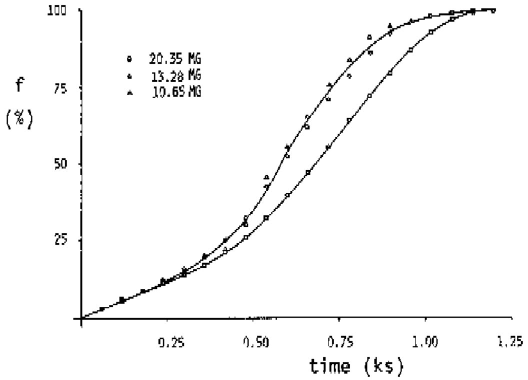

Figure 3.1. The degree of reduction as a function of time for various quantities of catalyst.
Catalyst: Co_3O_4. T = 524 K. x_{H_2} = 0.44.

The occurrence of a pore diffusion limitation is checked by carrying out reduction experiments with different sizes of catalyst particles. The amount of catalyst is 13.1-13.2 mg, the concentration of hydrogen x_{H_2} = 0.44 and the temperature 524 K. The results are in figure 3.2. If the pore diffusion played a role, the rate per gram catalyst should have decreased with increasing particle diameter. But as shown in figure 3.2 that is not the case.

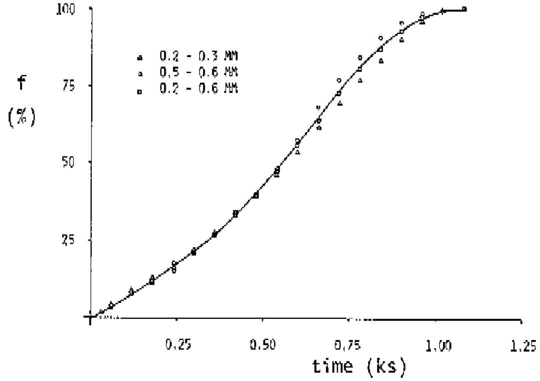

Figure 3.2. The degree of reduction as a function of time for various particle sizes.
Catalyst: Co_3O_4. T = 524 K. x_{H_2} = 0.44.

The maximum reduction rate is obtained at a degree of reduction of about 60%. As it will be shown later in this section, at that stage we deal with the reduction of CoO. Since the enthalpy of that reaction is only 0.8 kJ mol^{-1} /9/ no temperature gradient is expected to be formed.

The reduction experiments have to be performed in the thermobalance under conditions where high rates (i.e. high concentrations of water) are avoided. The following conditions are chosen: 13 mg catalyst with a particle size between 0.2 and 0.3 mm. Under these conditions no inter- and intra-particle diffusion limitation is expected.

Reduction of Co_3O_4

The reduction of Co_3O_4 is carried out with various mole fractions of hydrogen at 524 K and with a constant mole fraction of hydrogen $x_{H_2} = 0.19$, at various temperatures. The rates (calculated as oxygen atoms released per second per gram catalyst) as a function of the degree of reduction are depicted in figures 3.3 and 3.4. At lower temperatures and with various partial pressures at 524 K the reduction seems to proceed in two steps via an intermediate form at 20 to 30% reduction which is first formed from Co_3O_4 and reacts further forming

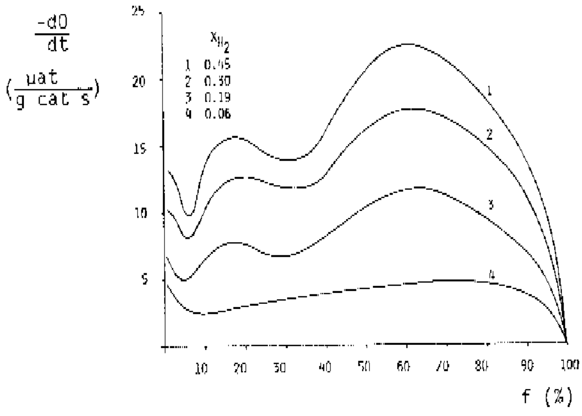

Figure 3.3. The rate of reduction as a function of the degree of reduction for various mole fractions of hydrogen. Catalyst: Co_3O_4. *T = 524 K.*

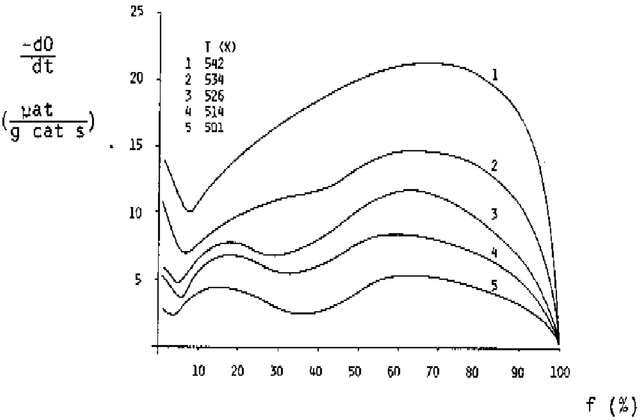

Figure 3.4. The rate of reduction as a function of the degree of reduction at various temperatures.
Catalyst: Co_3O_4. $x_{H_2} = 0.19$.

cobalt metal. As mentioned earlier cobalt(II,III) oxide can decompose to cobalt(II) oxide. If only this reaction occurs the degree of reduction is 25%. That would mean that first CoO is formed from Co_3O_4. We have checked that by stopping the reduction at increasing degrees of reduction and analyzing these samples by X-ray diffraction. With more than 25% reduction only α-cobalt and cobalt(II) oxide are found, which supports the idea of a two-step mechanism.

Reduction of CoO

Because it seemed that the reduction proceeds via CoO we decided to study the reduction of this oxide as well. These experiments are carried out with three different concentrations of hydrogen at 524 K and at three different temperatures with a mole fraction of hydrogen $x_{H_2} = 0.44$. The degree of reduction as a function of time is given in figures 3.5 and 3.6. The curves are clearly sigmoidal which is typical for an autocatalytic reaction. The reaction rates as a function of the degree of reduction are depicted in figures 3.7 and 3.8.

The reduction of nickel oxide and copper oxide have been shown by Pospisil /92/ and Pospisil and Taras /93/ respectively to behave

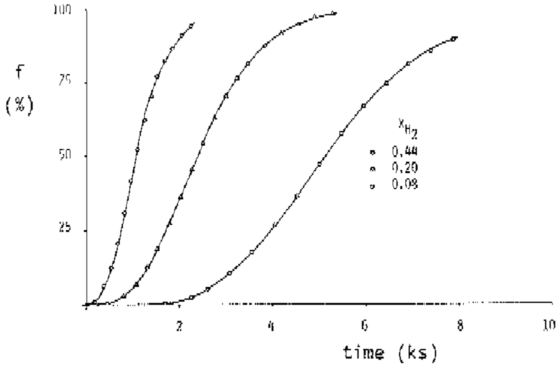

Figure 3.5. The degree of reduction as a function of time for various mole fractions of hydrogen.
Catalyst: CoO. T = 524 K.

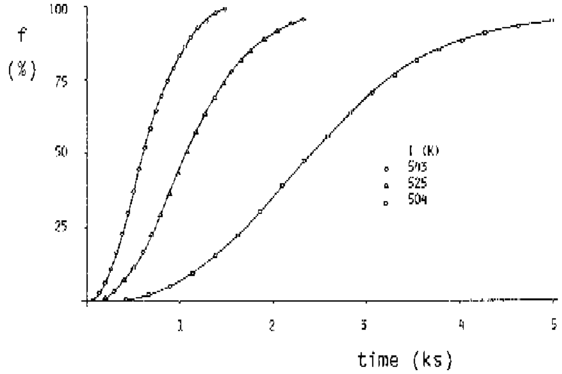

Figure 3.6. The degree of reduction as a function of time at various temperatures.
Catalyst: CoO. $x_{H_2} = 0.44$.

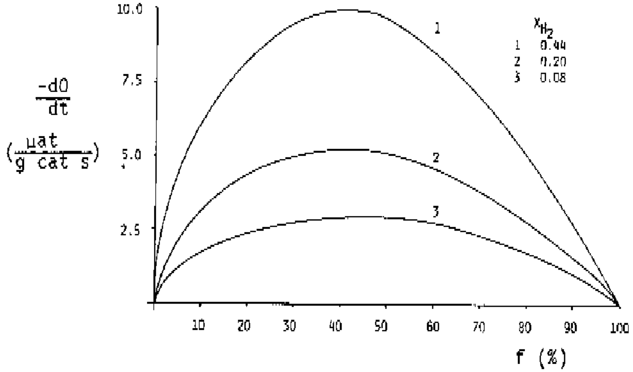

Figure 3.7. The rate of reduction as a function of the degree of reduction for various mole fractions of hydrogen.
Catalyst: CoO. T = 524 K.

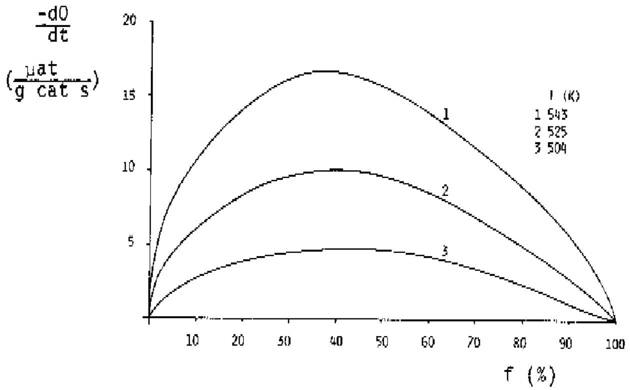

Figure 3.8. The rate of reduction as a function of the degree of reduction at various temperatures.
Catalyst: CoO. $x_{H_2} = 0.44$.

similarly. Reduction kinetics can be described by the modified equation of Prout and Tompkins. This was originally derived from the decomposition of certain compounds /94/ where the rate is observed to increase in the early stage and to decay at the end of the reaction. This behaviour is interpreted as arising from the random formation of nuclei, followed by the growth of these nuclei. The decay of the reaction rate begins when the outgrown nuclei start to overlap, what renders that the interface between oxide and metal decreases.

For cases where the maximum rate is reached before 50% reduction Bond /95/ derived the following equation for the relation between the degree of reduction and the time:

$$\log \frac{1 - 2 f_m + f}{1 - f} = \frac{1 - f_m}{f_m} (k't + c') \qquad (3.4)$$

where f_m is the degree of reduction at maximum rate and c' and k' are constants. In figures 3.7 and 3.8 f_m appears to be 0.4, independent of the mole fraction of hydrogen and the temperature. Thus equation (3.4) reads

$$\log \frac{0.2 + f}{1 - f} = kt + c \ . \qquad (3.5)$$

In figures 3.9 and 3.10 the left-hand side of equation (3.5) is depicted as a function of time. It can be seen that the constant k depends both on the mole fraction of hydrogen and on the temperature.

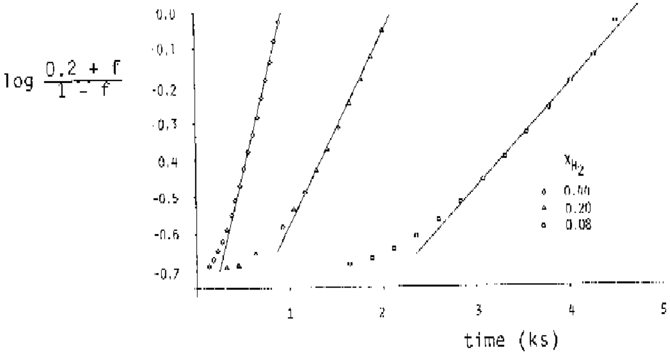

Figure 3.9. $\log \frac{0.2 + f}{1 - f}$ *as a function of time for various mole fractions of hydrogen.*
Catalyst: CoO. T = 584 K.

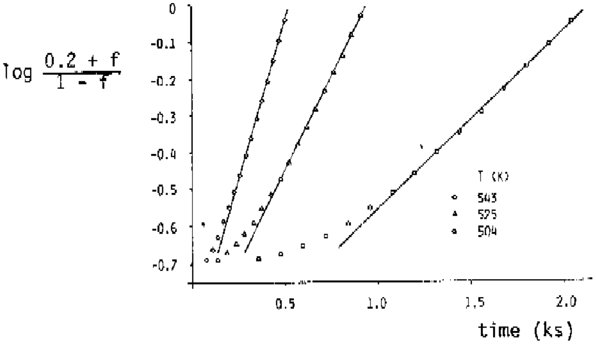

Figure 3.10. log $\frac{0.2 + f}{1 - f}$ *as a function of time at various temperatures. Catalyst: CoO.* $x_{H_2} = 0.44$.

We assume that this dependence can be described in a form

$$k = k_0 \, e^{-E/RT} \, p_{H_2}{}^{X} \quad . \qquad (3.6)$$

From the slopes of the lines in figure 3.9 and 3.10 we calculate the values of X and E; X = 0.7 and E = 74 kJ mol^{-1}. The same results are obtained if the dependences are calculated from the maximum rates.

From figures 3.9 and 3.10 it can be seen that the kinetic equation described above does not fit the results in the beginning of the reduction. Therefore this induction period has to be dealt with separately. A useful equation can be derived as follows. The oxide structure is taken as a system of oxygen layers, where each layer can react independently. The reduction starts from certain lattice points (defects or edges and corners of layers) and spreads with a linear growth. Assuming that the rate is proportional to the border line enclosing the unreacted oxygen, the rate of the reaction can be described as /96/

$$- \frac{dO}{dt} = k \, O_0 \, f(p_{H_2}) \, n \, r \qquad (3.7)$$

where n is the number of nuclei, k is the rate constant and O_0 is the initial concentration of oxygen. The rate is assumed to be also a function of the concentration of hydrogen.

If we further assume that the linear rate of nucleus growth is constant, i.e. that the radius increases linearly as a function of time, we can write for the radius of a nucleus

$$r = c\ k\ f(p_{H_2})\ t \quad . \tag{3.8}$$

By substituting (3.8) in (3.7) we have

$$-\frac{dO}{dt} = c'\ k^2\ f^2(p_{H_2})\ n\ t \tag{3.9}$$

i.e. the rate increases linearly as a function of time. In figures 3.11 and 3.12 the rates determined experimentally are plotted as a function of time, for experiments with various mole fractions of H_2 and at various temperatures, respectively. These curves have been drawn for degrees of reduction lower than about 5%.

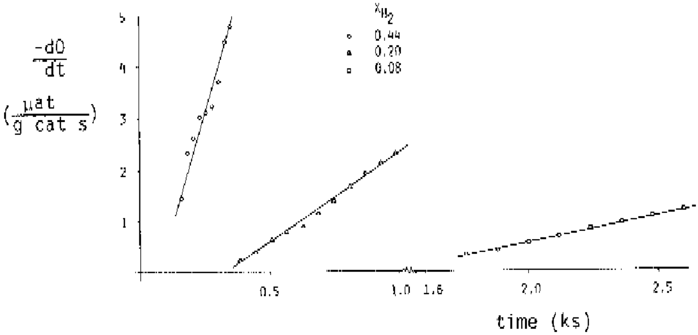

Figure 3.11. The rate of reduction as a function of time for various mole fractions of hydrogen.
Catalyst: CoO. T = 524 K.

If we assume that

$$f^2(p_{H_2}) = c^2\ p_{H_2}^{\ 2x} \tag{3.10}$$

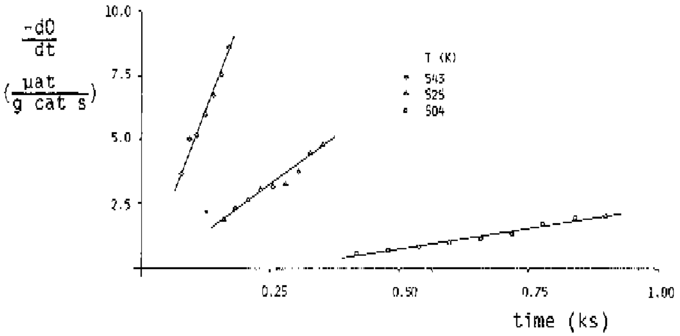

Figure 3.12. The rate of reduction as a function of time at various temperatures.
Catalyst: CoO. $x_{H_2} = 0.44$.

the value X = 0.7 is calculated from the dependence on the partial pressure of hydrogen. The activation energy calculated for k is found to be 80 kJ mol^{-1}. Thus both the induction and the acceleratory period as described by equations (3.9) and (3.5) have the same dependence on the partial pressure of hydrogen and on the temperature.

The reduction can be sometimes described by a "shrinking core model", as e.g. used for the reduction of cobalt(II) oxide /97/. In this model the degree of reduction depends on the time according to the equation

$$1 - (1 - f)^{1/3} = kt \quad . \qquad (3.11)$$

It is clear that an increasing reaction rate as we found experimentally is never obtained with this model.

We now return to the reduction of Co_3O_4. The dependence of the maximum rates on the partial pressure of hydrogen and on the temperature has been calculated for both steps. For the first step the order in hydrogen is 0.8 and the activation energy 52 kJ mol^{-1}, as determined at 15% reduction. For the second step the values are 0.7 and 75 kJ mol^{-1} respectively, at 60% reduction. The latter values are the same as found for the reduction of cobalt(II) oxide, which again confirms our idea that the reduction of Co_3O_4 proceeds via CoO.

One might expect that at a high reduction rate insufficient time is available for the recrystallization of the reduced Co_3O_4 lattice into a CoO lattice. This would mean that a number of the original reduction nuclei or reduction sites would stay available for the further reduction of the compound that is stoichiometrically in the CoO state. This could also explain the changes in reduction rate as a function of the temperature found by Batley et al. /98/. The assumption that changes in kinetics occur is then not necessary.

Reduction of cobalt oxide/Al_2O_3

Reduction of cobalt oxide on alumina has also been studied in the thermobalance. However, no kinetic measurements of the reduction could be performed. Since water is formed during the reduction and it is readsorbed, even at 673 K, the weight changes do not represent the correct degree of reduction. When the reduction is interrupted for some time a subsequent weight decrease is recorded, caused by desorption of water. This difficulty could be avoided by using higher reduction temperatures, but at higher temperature the total degree of reduction decreases most likely as a consequence of spinel formation. Also heating (e.g. to 723 K) before reduction diminishes the obtainable degree of reduction to 80% in the mentioned case. Ratmasamy et al. /99/ reduced a cobalt on alumina catalyst at 763 K and they reached about 75% reduction. Because of these difficulties only the total degree of reduction has been measured in this thesis, at various temperatures, using the mole fraction of hydrogen $x_{H_2} = 0.44$. The results are collected in table 3.2.

Table 3.2. The maximum degree of reduction f (%) obtained at various temperatures. Catalyst: Cobalt oxide/Al_2O_3.

T (K)	f (%)
523	50
573	60
673	93
763	75 *

* /99/

This dependence of the degree of reduction on the temperature has also been found by Dollimore and Rickett /100/. In the case of nickel oxide it has been observed that the reduction of a supported oxide is more difficult than of the unsupported /101/ because of interactions between the oxide and the support. The strongest influence was noticed with an alumina support. The dependence of the degree of reduction on the temperature (table 3.2) indicates an interaction of oxides, which at higher temperature leads to the formation of cobalt aluminates. Under our standard experimental conditions the cobalt oxide on alumina catalyst is reduced by hydrogen at 673 K; this seems to be near the optimum reduction temperature (table 3.2).

3.4.3. REDUCTION BY CARBON MONOXIDE

Co_3O_4

A typical conversion-time curve for the reduction of Co_3O_4 by carbon monoxide is given in figure 3.13. Here the weight loss is

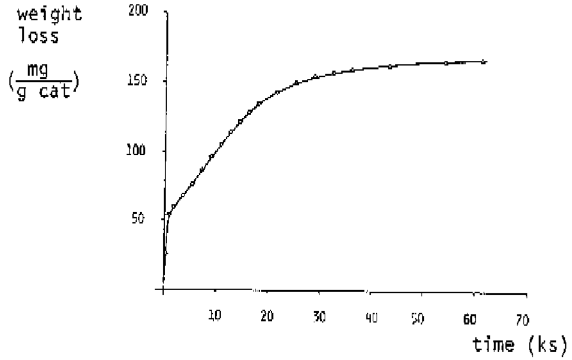

Figure 3.13. The weight loss as a function of time.
Catalyst: Co_3O_4, x_{CO} = 0.44, T = 524 K.

given as a function of time at 524 K. In the beginning there is a fast weight decrease until a degree of reduction of 22-23%. After that period the weight decreases more slowly. This again indicates that the reduction proceeds via the formation of CoO. In this particular case the total weight loss after 65 ks when the weight is already steady is 166 mg (g cat)$^{-1}$. According to X-ray diffraction analysis cobalt carbide, Co_2C, has been formed (ASTM 5-0708). This measurement has been done after 18 ks with synthesis gas because directly after the reduction by carbon monoxide the catalyst is pyrophoric and will be oxidized to cobalt(II) oxide when exposed to air. If it is assumed that the reduction goes to cobalt metal and thereafter cobalt carbide is formed, the total weight loss should be 191 mg (g cat)$^{-1}$, with a carbon content of 9.2%. The carbon content after reduction is found to be 11.9%, which means that some extra carbon has been formed. (The carbon content is calculated from the weight differences). Another possibility is that the catalyst has not totally reacted up to a stoichiometric carbide. In order to check that possibility we carried out some experiments also in the flow reactor with 0.50 g catalyst. In 58 ks 11.5 mmol CO_2 is formed; the total reduction to Co_2C corresponds to 11.7 mmol CO_2. In the CO_2 production rate a minimum is found after about 4 ks. When the total amount of carbon dioxide formed until that point is calculated, we obtain exactly the amount that is needed for the reduction of Co_3O_4 to CoO. When these results are combined with those obtained in the thermobalance we can say that a small part of the catalyst is not in the form of carbide but that some free carbon is formed as well and a small quantity of oxygen is still left. When the mixture of hydrogen and carbon monoxide ($x_{H_2} = 0.2$, $x_{CO} = 0.2$) is passed over the catalyst after a steady weight has been obtained no weight change is observed. Thus no further reduction is obtained with synthesis gas.

We assume that no carbon deposition takes place during the first minutes of the experiments. With this assumption the fraction reduced is depicted as a function of time for that initial period in figure 3.14 and 3.15, for various mole fractions of carbon monoxide and various temperatures, respectively. In all cases the rate is constant during the first minutes. The reduction rate of Co_3O_4 can be expressed in the form of equation (3.12) with a zero order in the oxygen concentration on the surface:

$$-\frac{dO}{dt} = k_o\, e^{-E/RT}\, p_{CO}^{\gamma} \,. \qquad (3.12)$$

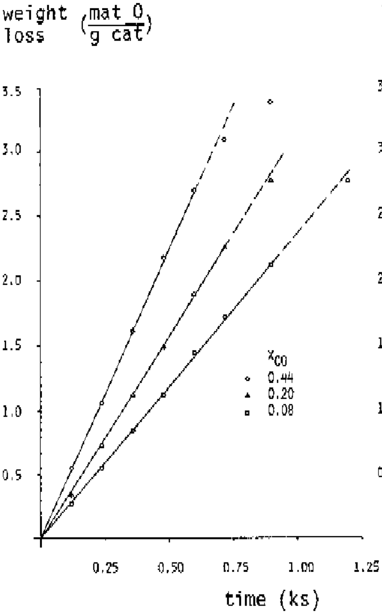

Figure 3.14. The weight loss as a function of time for various mole fractions of carbon monoxide.
Catalyst: Co_3O_4, T = 524 K.

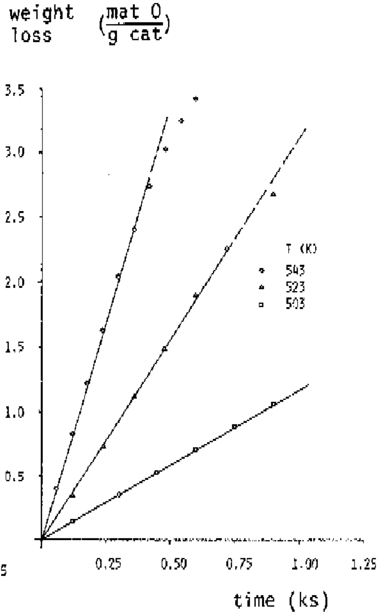

Figure 3.15. The weight loss as a function of time at various temperatures.
Catalyst: Co_3O_4, x_{CO} = 0.20.

The dependence on the partial pressure of carbon monoxide, Y, is 0.4 and the activation energy is 99 kJ mol^{-1}.

The latter part of this reduction process can be best described by an overall reaction

$$2\ CoO + 4\ CO \rightarrow Co_2C + 3\ CO_2 \qquad (3.13)$$

which is a combination of two reactions:

$$CoO + CO \rightarrow Co + CO_2 \qquad (3.14)$$

and

$$2\ Co + 2\ CO \rightarrow Co_2C + CO_2\ . \qquad (3.15)$$

In order to estimate roughly the size of the observed effects we shall use the following equation:

$$\frac{dw}{dt} = - k_1 (1 - f) + k_2 f^2 . \qquad (3.16)$$

For the sake of simplicity the formation of free carbon is neglected and the reduction rate is - for this purpose - taken proportional to the amount of the unreacted CoO. The first term on the right-hand side of equation (3.16) shows the weight loss during the reduction and the second term the weight increase from the formation of carbide. During the experiment at 524 K the weight decreases and no weight increase is observed. From equation (3.16) it can be concluded that if k_1 is much bigger than k_2 the weight increase is observed only at an almost complete reduction ($k_1/k_2 = 100$, $f = 0.99$). This means that in this case the rate constant of bulk carbide formation is much smaller than the reduction rate constant. If the rates of reduction and carbide formation were of the same order of magnitude a weight increase should be observed at earlier stages of reduction.

The rate of weight decrease is practically independent of the partial pressure of carbon monoxide. At higher temperatures the rate of carbon deposition increases which can be seen from the fact that the weight starts to increase (at 573 K already after 1.5 ks).

CoO

Cobalt(II) oxide is reduced very slowly by carbon monoxide at 524 K. In 65 ks the total weight loss is 3.8 mg (g cat)$^{-1}$ which corresponds with a degree of reduction of 1.5% only.

Cobalt oxide on alumina

The reduction of the cobalt oxide on alumina catalyst by carbon monoxide cannot be followed in the thermobalance. There is practically no change in weight. This means that the weight decrease caused by the reduction is compensated by the adsorption of carbon monoxide and the formation of carbonaceous species. For this reason the state of the catalyst after the reduction is determined in the flow reactor, where a bigger quantity of catalyst can be used, and the production of carbon dioxide can be measured. The amount of carbon deposited is obtained subsequently from the methane produced by a hydrogen treatment. The experiment is carried out in the following way:

i) reduction by CO (x_{CO} = 0.25, x_{He} = 0.75) at 523 K for 60 ks
ii) cooling under CO to 373 K
iii) flushing with He at 373 K
iv) heating under H_2 to 523 K

The production of carbon dioxide during the reduction is 0.65 mmol (g cat)$^{-1}$; for the total reduction to cobalt metal 1.47 mmol CO_2 (g cat)$^{-1}$ is required. The formation of methane in the mentioned case is 0.053 mmol (g cat)$^{-1}$. This carbon can be in the form of carbide or of surface carbon and situated on the cobalt and on the support (see sections 3.5 and 5.2).

The obtained results show that only a part (33%) of the supported oxide is reduced. Further there is a possibility that the surface of cobalt is totally covered with carbonaceous species.

3.4.4. REDUCTION OF Co_3O_4 BY MIXTURES OF HYDROGEN AND CARBON MONOXIDE

The reduction of Co_3O_4 is studied at 524 K with mixtures of hydrogen and carbon monoxide containing a constant mole fraction of carbon monoxide (x_{CO} = 0.20) and varying mole fractions of hydrogen (x_{H_2} = 0.1, 0.2, 0.5). In table 3.3 the total degree of reduction is given for these three cases. We assume that the weight loss equals the oxygen loss. The weight gain due to C deposition is neglected.

Table 3.3. Total degree of reduction f (%) as a function of the gas concentration. Catalyst: Co_3O_4. T = 524 K.

x_{H_2}	x_{CO}	f (%)
0.1	0.2	$75^{*)}$
0.2	0.2	82
0.5	0.2	96

*) maximum weight loss; after 43 ks the weight starts to increase.

In none of these cases total reduction is reached. If the catalyst were converted completely to cobalt carbide an apparent degree of reduction of 71.9% would be found. According to X-ray diffraction analysis the catalyst obtained is a mixture of α-cobalt and cobalt(II) oxide; no carbide is detected. Subsequent hydrogen treatment leads to a weight loss which only in the case that the reduction was done by the mixture with $x_{H_2} = 0.5$ corresponds to a reduction of 100%. This proposes that some carbon was deposited as well during the reduction.

In the flow reactor the catalyst is flushed by hydrogen after 54 ks of the synthesis gas ($x_{H_2} = 0.2$ and $x_{CO} = 0.2$). The total amount of methane formed is 0.76 mmol (g cat)$^{-1}$, which corresponds with a carbon content of 0.9%.

3.5. ADSORPTION OF HYDROGEN AND CARBON MONOXIDE

As a measure of the active surface of supported catalysts the amount of adsorbed hydrogen or carbon monoxide at room temperature is often used. The difficulty in using the adsorption of carbon monoxide is that already at room temperature it can dissociate /28/. The adsorption of hydrogen is usually assumed to take place dissociatively.

After the reduction by hydrogen in situ the catalyst is evacuated at the reduction temperature for 7.2 ks. The adsorption measurements are carried out by admitting a hydrogen pressure of 1.8 kPa at the reduction temperature and then cooling to room temperature. The adsorbed amount is calculated from the overall pressure decrease. The results are given in table 3.4.

Table 3.4. The amount of adsorbed hydrogen at room temperature.

catalyst	H_2 μmol (g cat.)$^{-1}$
Co	44
Co/Al_2O_3	20

The dispersion of cobalt on the supported catalyst is 3.4% when we assume dissociative adsorption of hydrogen with one hydrogen atom adsorbed per surface metal atom.

In the case of the Fischer-Tropsch synthesis determination of the amount of carbon monoxide adsorbed is of interest, particularly under the reaction conditions. However, the adsorption measurements cannot be carried out under reaction conditions because at reaction temperature carbon monoxide reacts on cobalt and forms carbon. Therefore we carried out some adsorption experiments in the thermobalance at room temperature with a mole fraction of carbon monoxide of 0.19. At first the oxides are reduced by hydrogen: Co_3O_4 at 523 K and cobalt oxide/ Al_2O_3 at 673 K and then cooled to room temperature under nitrogen. In figure 3.16 the weight increase is plotted as a function of time for Co, for Co/Al_2O_3 and for Al_2O_3. With both catalysts the step in the beginning is taken as a measure for the monolayer coverage of carbon monoxide. This is 26 μmol (g cat)$^{-1}$ for Co/Al_2O_3 (this is the difference between the first steps of Co/Al_2O_3 and Al_2O_3) and 76 μmol (g Co)$^{-1}$ for the unsupported cobalt.

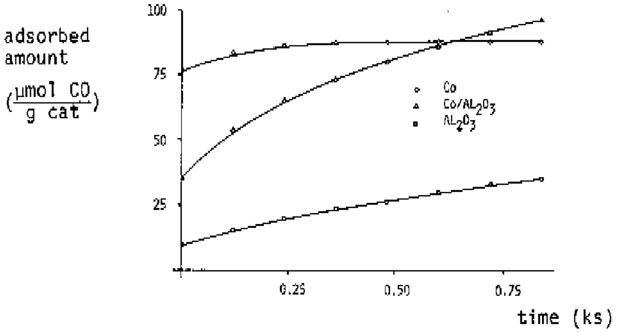

Figure 3.16. The amount of adsorbed carbon monoxide at room temperature as a function of time.