4.2.2 Low temperature / 1 bara total pressure

Some experiments were done at lower temperature and pressure with the intent to achieve kinetically controlled rates. The total pressure was 1 bara and the temperature was 473 K. Figure 4-28 compares the experimental run plots for CO hydrogenation over Co/Al_2O_3B, Co1.0Pt/Al_2O_3B and Co1.0Re/Al_2O_3B. Figure 4-29 shows how the ratio between the rate over the promoted catalysts and the rate over the unpromoted catalyst changes with increasing rate. All the measurements of activity in Figure 4-29 are done after 300 minutes reaction time. In Table 4-14 the rates over different unpromoted and promoted cobalt catalysts are compared after 300 and 1400 minutes reaction time. Table 4-15 shows the corresponding turnover frequencies (TOF) over some of these catalysts based on H_{tot}:Co_{tot} and CO_{tot}:Co_{tot} from the volumetric chemisorption.

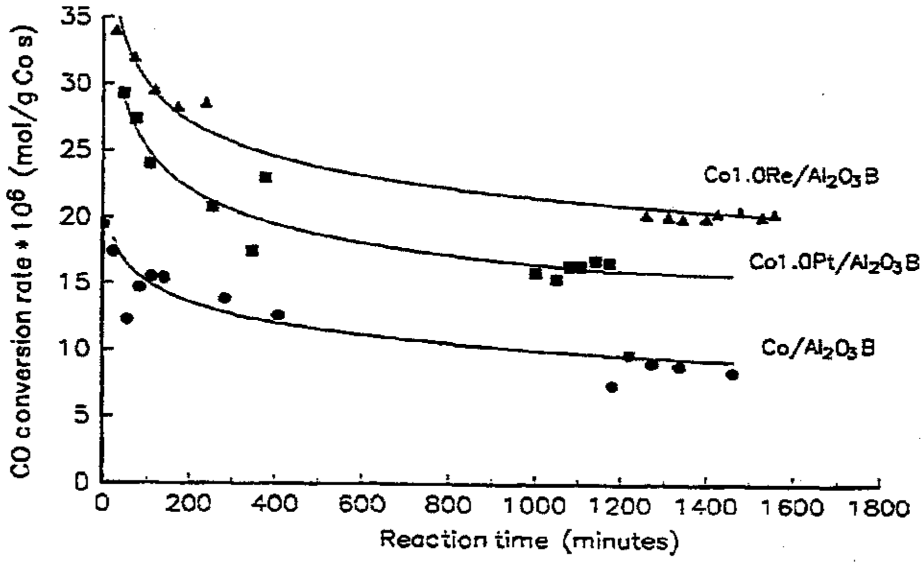

Figure 4-28. CO hydrogenation activity as function of reaction time over Co/Al_2O_3B, Co1.0Pt/Al_2O_3B and Co1.0Re/Al_2O_3B at T=473 K, P=1 bar, H_2/CO=2.

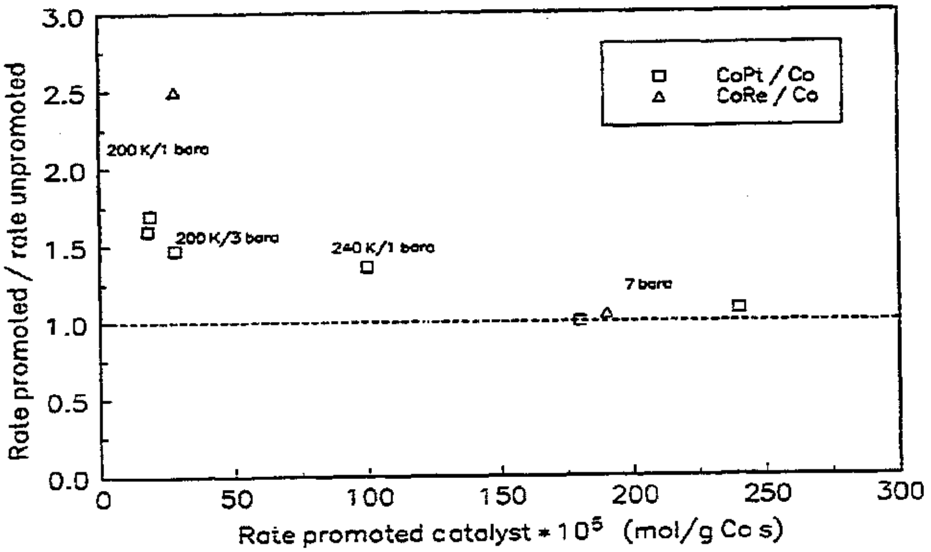

Figure 4-29. The ratio between the activity over Re or Pt promoted catalysts and over unpromoted catalysts, as a function of reaction rate (at varying temperature and pressure).

Table 4-14. Activity at 473 K and 1 bara after 300 and 1400 minutes reaction time, H_2:CO = 2, GHSV = 5000 h^{-1}, CO conversion = 4-10 %.

Catalyst	Rate (μmol CO/g Co·s)		Relative rates (catalysts)[a]		Relative rates (time)[b]
	300 min.	1400 min.	300 min.	1400 min.	
$Co/Al_2O_3A^c$	11		1		
$Co/Al_2O_3B^d$	11	9	1	1	0.82
$Co1.0Pt/Al_2O_3A^c$	18		1.6		
$Co1.0Pt/Al_2O_3B^d$	19	16	1.7	1.8	0.84
$Co1.0Re/Al_2O_3B^d$	28	20	2.5	2.2	0.71

[a] [rate over actual catalyst]/[rate over the corresponding unpromoted catalyst].

[b] [rate at 1400 minutes]/[rate at 300 minutes]

[c] Calcination temperature 673 K.

[d] Calcination temperature 573 K.

Table 4-15. Turnover frequency (TOF) of cobalt catalysts after 5 h reaction time. T = 473 K, P = 1 bara, H_2:CO = 2, GHSV = 5000 h^{-1}, conversion = 4 - 10 %.

Catalyst	H_{tot}:Co_{tot}	CO_{tot}:Co_{tot}	Reduction (%)[a]	Rate[b]	N_{CO}[c]	
					H_2	CO
Co/Al_2O_3A[d]	0.046	0.023	52	11	0.014	0.028
Co/Al_2O_3B[e]	0.054	-	-	11	0.012	-
Co1.0Pt/Al_2O_3A[d]	0.086	0.065	79	18	0.012	0.016
Co1.0Pt/Al_2O_3B[e]	0.082	-	-	19	0.014	-
Co1.0Re/Al_2O_3B[e]	0.067	0.061[f]	78[f]	28	0.025	0.027

[a] Reduction extent from O_2 titration. The amount of oxygen to formation of PtO_2 or Re_2O_7 is subtracted from the total O_2 consumption before calculating the extent of reduction.

[b] Rate as (μmol CO/g Co· s)

[c] Turnover frequency (s^{-1}) based on H_{tot}:Co_{tot} or CO_{tot}:Co_{tot} from volumetric chemisorption data.

[d] Calcination temperature 673 K.

[e] Calcination temperature 573 K.

[f] Measurements are not done for this catalyst, but values from measurements on Co1.0Re/Al_2O_3A is used.

All the figures and tables above show a difference in activity (per gram of cobalt) between the promoted and the unpromoted catalysts. This is different from what was reported at high temperature and pressure in the previous chapter, and the results are more as expected in view of the characterization results.

When comparing the activity curves for CO hydrogenation over Co/Al_2O_3B, Co1.0Pt/Al_2O_3B and Co1.0Re/Al_2O_3B at 473 K and 1 bara in Figure 4-28, with those in Figure 4-27 the same shape of the curves is observed. But in this case there is a difference in activity between the catalysts, which does not disappear during the initial deactivation period.

The difference which appear between the catalysts at conditions giving low rates, support that the lack of difference at high rates was due to reactant (more precisely CO) diffusion control. At 473 K and 1 bara the reaction is from the same reason assumed to be kinetically controlled. Then the shape of the activity curves in this case can not be caused by increasing extent of diffusion limitations with increasing amount of wax in the pores, as suggested as a possible explanation in the last chapter. In the same discussion both reoxidizing and sintering of the reduced cobalt, as well as formation of carbidic and or/graphitic carbon were mentioned as other plausible explanations of the observed decrease in CO conversion rate with increasing time. The coincidence in the shape of the three activity curves support that the cobalt phases present on the surfaces of all three catalysts undergo the same changes leading to the observed decrease in activity. But although the same deactivating processes takes place on the catalyst surfaces, they may take place to different rates.

Table 4-14 shows that after 300 minutes reaction time the platinum promoted catalyst, Co1.0Pt/Al_2O_3B, is 1.7 times more active than the unpromoted catalyst. The rhenium promoted catalyst Co1.0Re/Al_2O_3B, is 2.5 times more active. After 1400 minutes the rates are lower, but the ratio between the rates over unpromoted and platinum promoted catalysts remains almost constant. The ratio between the rate over unpromoted and rhenium promoted catalysts decreases slightly. When the rate at 300 minutes is compared to the rate at 1400 minutes for each catalyst, it is seen that the rhenium promoted catalyst looses activity fastest, while the platinum promoted catalyst is the most stable.

Before discussing these trends in detail it must be mentioned that some uncertainty is bound to the drawing of the curves in Figure 4-28. However, it could nevertheless be speculated in explanations of the apparent differences observed.

Rhenium could be suggested to promote reoxidation of cobalt, giving the observed decrease in reaction rate. But since rhenium is more difficult to reduce than platinum, and is reduced at higher temperatures than the reaction temperature, it is assumed to be relatively fast reoxidized itself. Then a specific rhenium promoting effect seems less probable. Platinum promoted catalysts showed the largest H_2 uptake in the chemisorption experiments, and some of the hydrogen was assumed to be adsorbed on platinum. A higher H_2 concentration on these surfaces could therefore be suggested to slow down the reoxidation rate. This is in agreement with the lowest deactivation rate for the platinum promoted catalyst.

On the other hand, the main reason to the decrease in rate could be deposition of insoluble carbonaceous materials. If a well dispersed cobalt phase was present after the reduction of the promoted catalysts, they could be assumed to be faster deactivated by carbonaceous deposition than the larger cobalt particles from Co_3O_4, present on all catalysts. This can explain why the rhenium promoted catalyst deactivate faster than the unpromoted catalyst. A higher H_2 concentration on the platinum promoted catalyst could be suggested to give a higher extent of hydrogenation of the coke precursors, giving a slower decrease in the reaction rate /49/.

Figure 4-29 could be used to illustrate the increasing degree of diffusion limitations with increasing reaction rate. The ratio between the promoted and the unpromoted catalysts decreases and stabilizes near 1 when the rates increases above a certain level. The limitations is assumed to be caused by the reactant diffusion through the liquid product present in the pores. The reaction ratio measured at 513 K and 1 bara deviates to some extent from the other results, showing higher reaction ratio than could be expected from the general trend. The low rate points in Figure 4-29 are measured at 473 K, and theoretical the diffusion rates (if no other reason) becomes more important with increasing temperature, and that is in disagreement with the result observed. However, at higher temperature the chain growth probability is lower, this means that the CO diffusion rate could be assumed to increase due to a increased viscosity of the lighter liquid. In addition, the solubility of the reactants could also be higher at a higher temperature and in a liquid with other properties. The apparent effective diffusion can be related to both molecular diffusion and to the gas solubility in the liquid /4/.

The calculated turnover frequencies (TOF) shown in Table 4-15 is not the same when the calculations are based on hydrogen and on carbon monoxide chemisorption data. When the total hydrogen uptake is used, the TOF of the rhenium promoted catalyst is almost twice the value of the other two. When the total CO uptake is used in the TOF calculations, the TOF of the unpromoted catalyst equals TOF of the rhenium promoted catalyst, while TOF of the platinum promoted catalyst is lower.

The differences in TOF connected to the choice of adsorbate are due to the differences in chemisorption of the two gases (Figure 4-16 and 4-17) discussed in Chapter 4.1.3.2. It was suggested that the hydrogen uptake on the platinum promoted catalyst partly was on platinum, which is known /31/ to show low activity in CO hydrogenation. The hydrogen uptake on the rhenium promoted catalyst was suggested to be a better measure of the increase in the number of cobalt surface sites, due to reported /126,127/ results concluding with very little hydrogen adsorption on rhenium. If the hydrogen uptake on Co1.0Re/Al_2O_3A is used in calculation of TOF of Co1.0Pt/Al_2O_3A, it will be 0.017 s^{-1}. Then, if the hydrogen uptake is the most correct basis for the calculations of turnover frequencies (as suggested in the literature /35/), these results indicate an increased TOF for both the promoted catalysts, which means increased intrinsic activity of the active cobalt sites on the promoted catalysts. This could be suggested to be due to the large part of cobalt oxide on the unpromoted catalyst. If this phase is active in the reaction, the rates could be expected to be low compared to the rates on reduced cobalt.

If the CO uptake is chosen as the basis for the TOF calculations, the conclusion can be the opposite. There is some uncertainty about CO adsorption taking place on the support or on the promoter, but the main part of the CO adsorption can be assumed to take place on the metallic cobalt. In this case the results indicate that the activity of each cobalt site is unchanged after rhenium addition, and that the increase in rate is due to an increase in the number of active sites. The main effect of this promoter is then the facilitation of the cobalt reduction, giving more available metallic cobalt surface. Further, when using the CO adsorption data, the results indicate a reduction in the activity of the cobalt sites after platinum addition. However, it can also be assumed that e.g. 35 % of the CO adsorption takes place on the support, spilled over from the promoter, or on the promoter, both not active in the Fischer-Tropsch reaction. Then the number of active sites is overestimated, while the turnover frequency becomes underestimated. In this case the result is in agreement with the TOF from hydrogen adsorption data: the same TOF for the platinum promoted catalyst compared to the unpromoted, and increased TOF for the rhenium promoted catalyst. As another complicating factor the degree of H_2 and/or CO spillover from platinum and rhenium can be different.

The discussion above demonstrates the difficulties in interpretation of the chemisorption data for bimetallic cobalt catalysts. As a matter of fact, TOF values for this kind of catalytic systems is to the best of the knowledge of the author not available in the literature.

The increase in activity could also be discussed in view of the increased extent of reduction, found from TPR and O_2 titration. For the platinum promoted catalyst Table 4-14 shows very good agreement between the increase in extent of reduction and the increase in CO conversion rate. For the rhenium promoted catalyst the increase in CO conversion rate is larger than the increase in reduction extent. Even though it can not be concluded anything about the metal dispersion from the reduction extent, this result is in agreement with the tabulated TOF values based on H_2 adsorption.

Lapidus et al. /118/ observed about 50 % increase in conversion in CO hydrogenation over 10% Co/Al_2O_3 after adding 0.1 - 0.5 wt% Pd or Ru to the catalyst. This result is similar to the increase due to platinum promotion in the present study. The increase in CO conversion was attributed to /118/ an observed promoting effect of palladium and ruthenium on the reduction of cobalt.

Both calculation of TOF and comparisons of the increase in reduction extent with the increase in conversion rate, indicate that the reactivity of the active cobalt sites increases with rhenium promotion. Several explanations to the increase in reactivity for the rhenium promoted catalysts could be discussed:

If the promoted catalyst after reduction consist of two different cobalt metal phases, the well dispersed surface cobalt could be sintered to small 3D crystalline particles or be present as smaller cobalt "clusters". The degree of sintering to crystalline particles could be suggested to be promoter dependent. CO is dissociated before reaction with hydrogen, and this is suggested /45/ to demand special density of the cobalt sites. If rhenium increases the extent of sintering of surface cobalt compared to platinum, this will give increased activity, due to a higher number of active sites. A similar explanation was used to explain the faster deactivation of the rhenium promoted catalyst in Chapter 4.2.1. However, this is not in agreement with the increased TOF, indicating an increased intrinsic activity. Further, when Johnson et al. /87/ found CO dissociation on a layer of cobalt on tungsten (W (100)) it was assumed to be a consequence of electronic interaction between cobalt and tungsten, rather than geometric strain of cobalt.

Iglesia et al. /141/ studied cobalt on different supports. They found that the rate of hydrocarbon synthesis from H_2 and CO is proportional to the number of exposed metal atoms. Cobalt-time yields (CO conversion 50 - 60 %) increased linearly with increasing dispersion of Co crystallites supported on SiO_2, Al_2O_3, TiO_2 and ZrO_2/SiO_2, while the site-time yields (TOF) did not depend strongly on support or metal dispersion.

It could therefore be suggested that platinum and rhenium promote the CO hydrogenation on the surface cobalt, but to different extent. The difference could be due to different dispersion of rhenium and platinum, or to different properties of the metals. These effects will appear independent of the cobalt particle size.

If the reduced surface cobalt immediately after the start of the reaction sinters to "large" particles, the difference in activity between the platinum and rhenium promoted catalysts could be caused by a fast platinum promoted deactivation of some of the active sites. But this is not in agreement with the unchanged TOF for the platinum promoted catalyst compared to unpromoted catalysts, unless the same deactivation step is present on the unpromoted catalyst, as well. In the last case rhenium must inhibit the deactivation on the catalyst. It must be taken into mind that TOF is based on chemisorption on reduced catalysts, not used in CO hydrogenation.

Transient kinetic CO hydrogenation experiments on the same catalysts have been done at NTH /119/. They were performed at 493 K and 1 bara with a CO/H_2/inert ratio 0.75/5.5/5, giving mainly methane as the product. Promotion with platinum and rhenium resulted both in a rate 1.9 times the rate over the unpromoted catalyst. The residence time (τ) of CH_X species on surface was the same on all three catalysts. These results indicating an increase in the number of active sites and constant intrinsic activity on the sites.

4.2.3 Summary of the activity measurements

- The kinetical experiments show that 1 wt% platinum or rhenium addition to 9wt%Co/Al_2O_3 increases the reaction rate.

- Rhenium increases the reaction rate [mol CO/g Co·s] more than platinum.

- Calculations of turnover frequencies indicate that in the case of platinum promotion, the increase is due to increased degree of reduction giving a larger amount of cobalt metal sites available for reaction. This is supported from a comparison with the increase in reduction extent, and from transient kinetic experiments. However, if taking account for hydrogen adsorption on platinum, TOF will increase compared to TOF of the unpromoted catalyst.

- Calculations of TOF of the rhenium promoted catalyst indicate that the increase in rate is due to increased number of active sites and to an increased intrinsic activity.

- An increase in TOF for the promoted catalysts compared to the unpromoted catalyst, could be explained by a slow reaction taking place on the oxidic cobalt phase on the unpromoted catalyst or to CO adsorption on cobalt oxide on the unpromoted catalyst (in the chemisorption measurements), giving a too large number of active sites on the unpromoted catalyst.

- At conditions giving high CO conversion rates (> 50 - 100 μmol CO/g Co·s) the reaction is diffusion controlled, due to reactant (CO) diffusion through liquid wax in the catalyst pores.

4.3 Selectivity measurements

4.3.1 High temperature / 7 bara total pressure

During the CO hydrogenation experiments at 7 bara presented in the previous chapter, two to four analyses of the product composition were taken during each run. The results presented below are measured after 200 - 300 minutes on stream.

An example of a Schulz Flory plot is shown in Figure 4-30. The chain growth probability, α, can be found from the slope of the straight line part of a Schulz Flory plot of the products. The variation in α over Co/Al_2O_3A with reaction time at 513 K and 7 bara is seen in Figure 4-31. The product distribution from CO hydrogenation over Co/Al_2O_3A with increasing temperature are in Figure 4-32 shown as α, and in Figure 4-33 expressed as percentages. The influence of H_2:CO ratio is shown in Figure 4-34, while Figure 4-35 shows the percentage distribution of hydrocarbon products over Co/Al_2O_3A, $Co0.1Pt/Al_2O_3A$ and $Co1.0Pt/Al_2O_3A$.

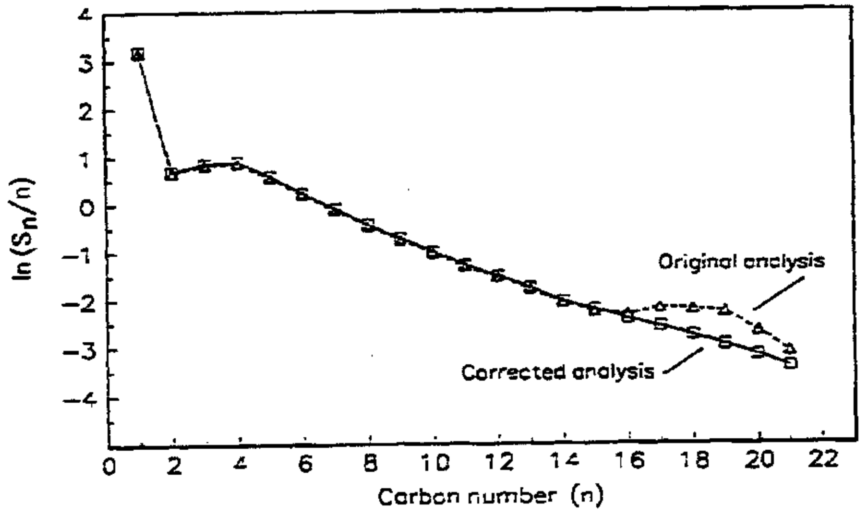

Figure 4-30. Schulz-Flory plot of the hydrocarbons produced over Co/Al_2O_3A at 527 K and 7 bara. H_2:CO ratio = 2 and CO conversion = 4.5 %.

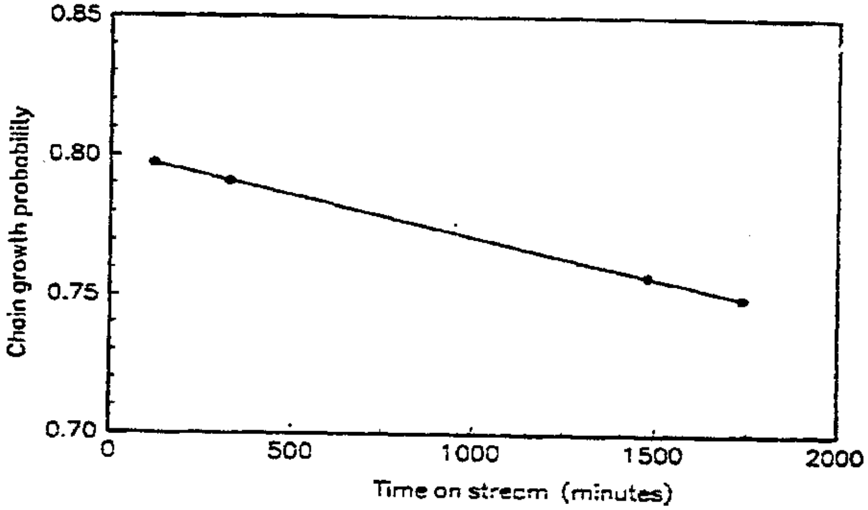

Figure 4-31. Chain growth probability, α, over Co/Al_2O_3A as a function of reaction time. T = 507 K. P = 7 bara. H_2:CO ratio = 2. The CO conversion decreases from 6 to 3.5 % during the period.

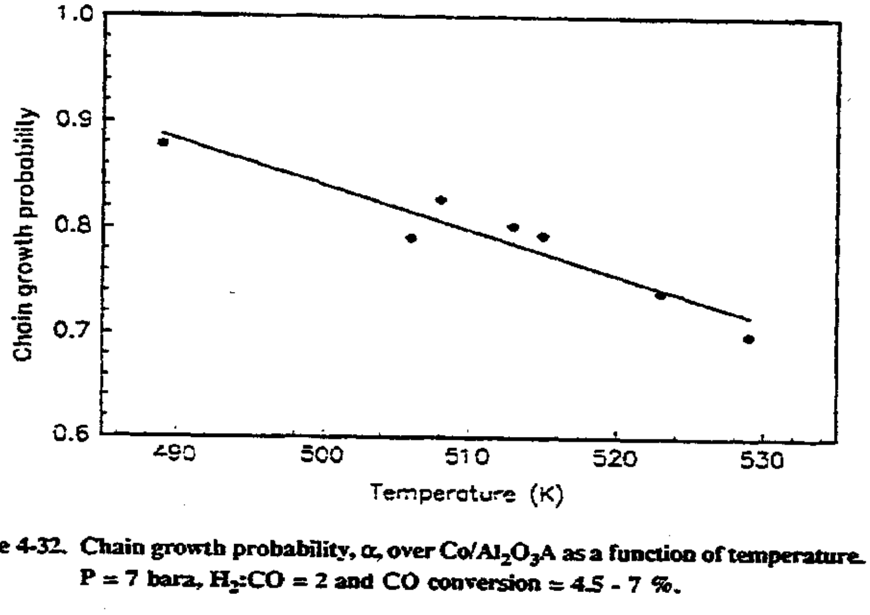

Figure 4-32. Chain growth probability, α, over Co/Al_2O_3A as a function of temperature. P = 7 bara, H_2:CO = 2 and CO conversion ≈ 4.5 - 7 %.

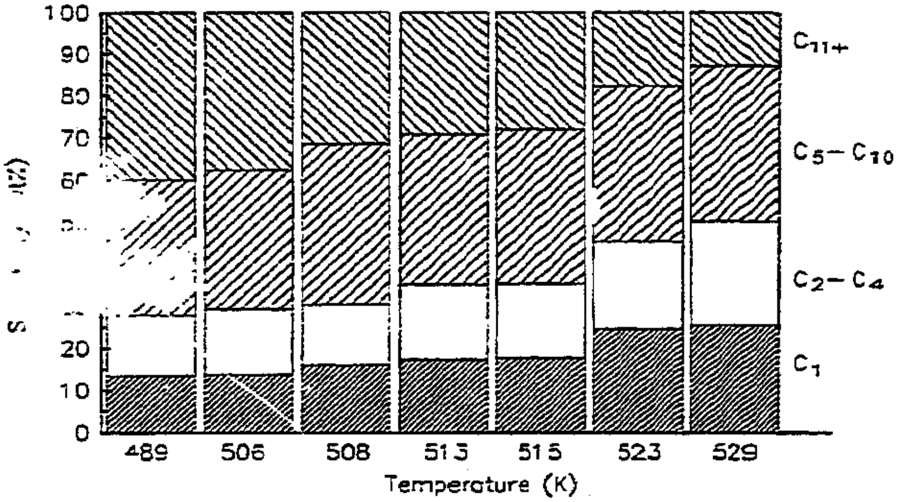

Figure 4-33. Product distribution over Co/Al_2O_3A as a function of temperature. P = 7 bara, H_2:CO ratio = 2 and CO conversion = 4.5 - 7 %.

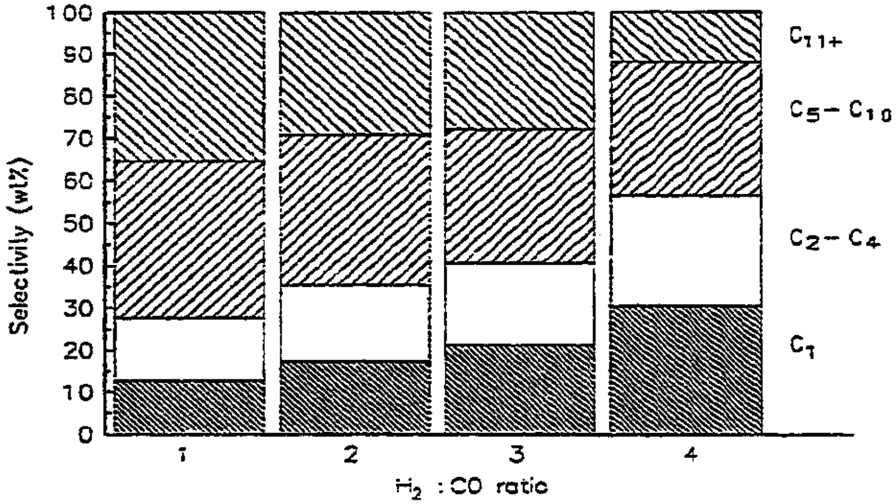

Figure 4-34. Product distribution over Co/Al_2O_3A as a function of H_2:CO ratio. T = 511 ± 3 K, P = 7 - 9 bara and CO conversion = 4.5 - 6.5 %.

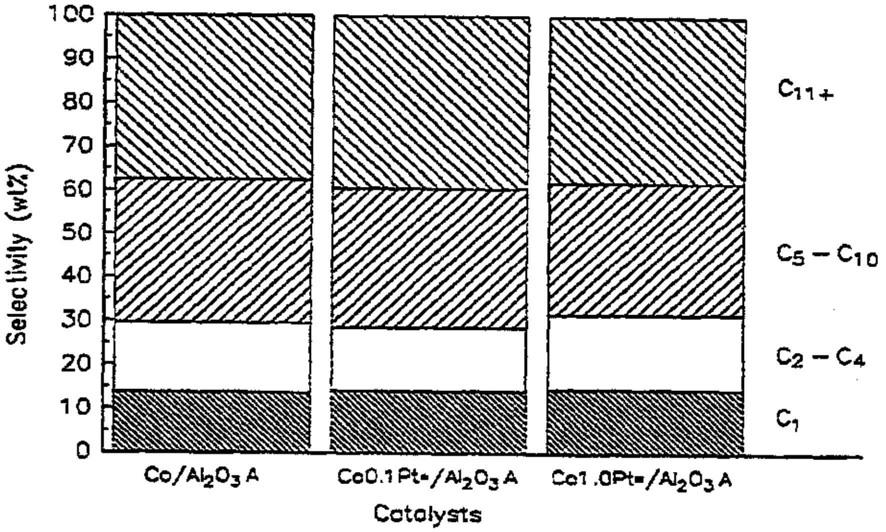

Figure 4-35. **Product distribution over Co/Al_2O_3A, $Co0.1Pt/Al_2O_3A$ and $Co1.0Pt/Al_2O_3A$ at 506 K. P = 7 bara, H_2:CO ratio = 2 and CO conversion = 4.5 - 5 %.**

The carbon dioxide selectivity was found to be below 1 wt% in all the catalyst tests. This low CO_2 content leads to difficulties in determining CO_2 selectivity accurately, and trends in the production of CO_2 are therefore not available. Because of the low CO_2 production and the assumed absence of significant carbonaceous material formation, the hydrocarbon selectivities are almost equal to the overall selectivities.

In Figure 4-30 a disturbance in the straight line part of the Schulz Flory plot is observed at carbon number 16. This break is due to experimental problems caused by condensation/ vaporization of heavy products in the heated sample lines. In the flame ionization detector hydrocarbons up to 21 carbon atoms was detected, but after carbon number 14 - 15 the analysis data becomes unreliable. This condensation problem was more pronounced after some time with catalyst testing, and is sought to be corrected for in the selectivity calculations by extrapolating the straight line part of the Schulz Flory plot to higher carbon numbers.

Figure 4-31 shows that during a run there was a slight decrease in the chain growth probability, α. Simultaneously the methane selectivity increased. Over a period of 27 hours the drop in α was from 0.80 to 0.75. Iglesia et al. /81/ predict a decrease in α as CO arrival becomes diffusion-limited because CO transport limitations lead to high effective hydrogen to carbon monoxide ratios at catalytic sites, which increases the chain termination probability. The observed increase in degree of methane formation during a run could also indicate more hydrogen available on the surface as a result of the higher effective H_2:CO ratio. Dry /55/ has reported a tendency to decreased chain growth with increased H_2:CO ratio. The same is observed in the present study (Figure 4-34). When changing the H_2:CO ratio from 1 to 4 at 513 K and 7 bara, methane selectivity increased from 13 to 30 wt%, while the C_{5+} fraction decreased from 72 to 44 wt%. Even though no further effects of diffusion limitations on CO conversion rate was expected after the initial period in the discussion in Chapter 4.2.1, a higher extent of waxfilling in the pores might influence on the chain growth probability.

Liu /32/ reported a linear increase in α with an increase in the cobalt particle size. If this is the case for the catalysts in the present study as well, α could be expected to increase if sintering of the cobalt particles takes place during the run. Sintering was suggested in Chapter 4.2.1 as an explanation of the decrease in rate with reaction time. Figure 4-31 shows decreased α with time, and this is therefore not in agreement with sintering. However, the assumed diffusion limitations could disguise this effect.

Figure 4-32 shows that over a temperature interval of 40 K (from 489 K to 529 K) α decreases from 0.88 to 0.70. The methane selectivity is nearly doubled, from 13 wt% of the total hydrocarbon selectivity to 25 wt%. The C_2 - C_4 fraction show the same increasing tendency, while the liquid fraction decreases correspondingly. At 529 K the fraction heavier than gasoline (C_{11+}) represents only 12 wt%, while it was approximately 40 wt% at 489 K. The gasoline fraction (C_5 - C_{10}) is nearly unchanged with the temperature increase in this range, and represents around 35 wt% of the hydrocarbon products.

Dry /55/ has also reported these trends for different cobalt and iron catalysts tested at Sasol (with increased reaction temperature the methane production increased while the hydrocarbons became lighter due to higher terminating rates compared to the chain growth rates). α-values reported by Liu /32/ over 10 % Co/Al_2O_3 at 1 bar and the same temperature range is somewhat lower (0.75 - 0.57) than found in the present study. But Liu reported selectivities after 30 hours on stream, and this explains the lower level on the α-values. Higher pressure in the present study can also explain the higher α values obtained. Cobalt catalysts have shown /34,55/ increased average carbon number with increasing pressure. Higher total pressure will give higher CO concentrations on the catalyst surface which favours chain growth.

When comparing the product distribution over Co/Al_2O_3A with the distribution over $Co0.1Pt^*/Al_2O_3A$ and $Co1.0Pt^*/Al_2O_3A$ at 506 K and 7 bara (Figure 4-35), it is seen that neither 0.1 nor 1.0 wt % platinum addition change the hydrocarbon selectivity. This could indicate that platinum is not involved in the chain growth reactions. However, at these conditions the rates are assumed to be limited by the reactant (CO) diffusion through the wax products present in the pores. The limitation will alter the effective H_2:CO ratio at the catalytic sites /81/ and could thereby disguise a possible effect of platinum on selectivity. The diffusivity of hydrocarbons is lower than the diffusivity of CO. This means that also the product desorption from the catalyst surface is limited, and this will also influence on the product distribution /81/.

Variations in the olefin selectivity are shown in Figure 4-36 to 4-39. Figure 4-36 shows how the α-olefin/n-paraffin ratio changes with carbon number in the hydrocarbon products. Figure 4-37 shows the α-olefin/n-paraffin ratio of the C_2 and the C_4 fraction obtained over Co/Al_2O_3A as a function of temperature. The variations in olefin selectivity with variations in the H_2:CO ratio is shown in Figure 4-38. Figure 4-39 shows the α-olefin/n-paraffin ratio of the C_2 and the C_4 fraction obtained over cobalt catalysts with increasing platinum addition.

Four parallel experiments is shown in Figure 4-36, and the differences between the parallels reflects the variation with increasing extent of CO conversion. The values are measured at CO conversion between 5 and 7 %. The olefin selectivity decreases with increasing CO conversion.

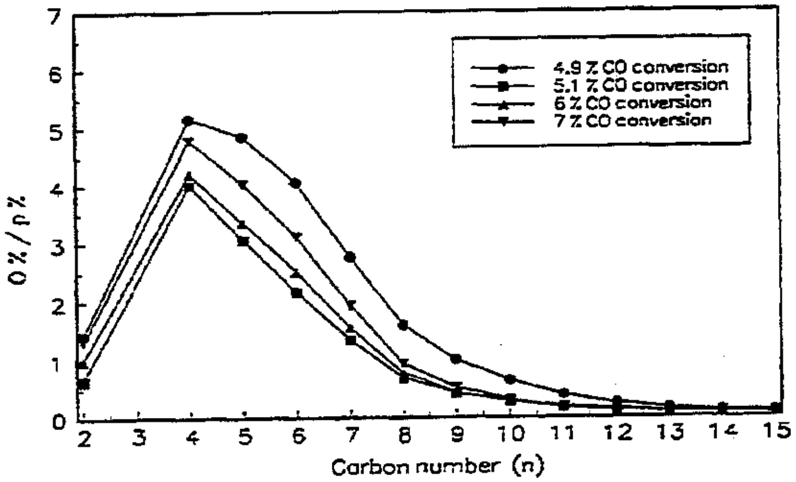

Figure 4-36. The α-olefin/n-paraffin ratio of the hydrocarbons as a function of carbon number. Co/Al_2O_3A, T = 510 ± 3 K, P = 7 bara and H_2:CO = 2.

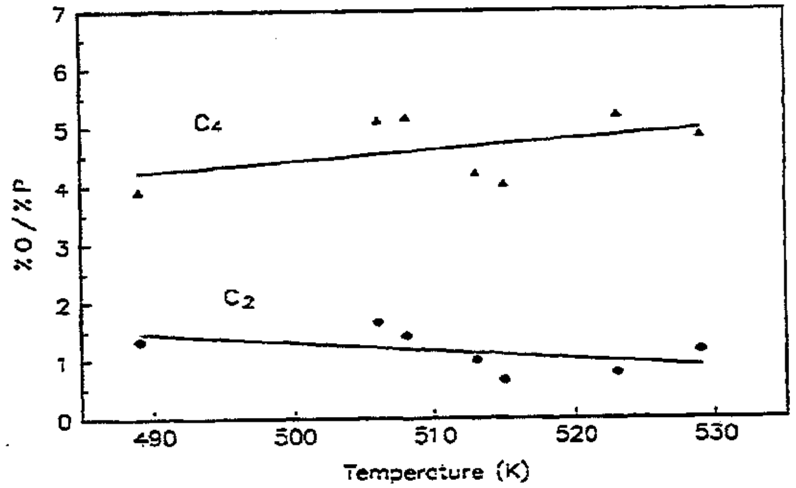

Figure 4-37. α-olefin/n-paraffin ratio of the C_2 and C_4 fraction as a function of temperature. Co/Al_2O_3A, P = 7 bara, H_2:CO = 2 and CO conversion = 4.5 - 7%.

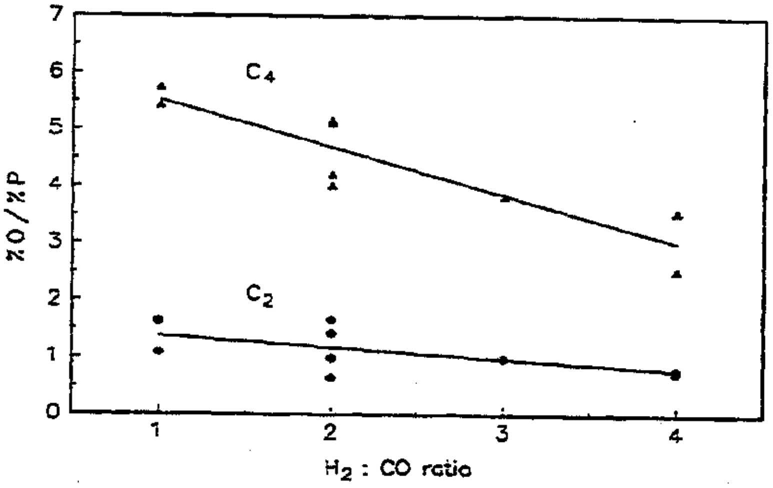

Figure 4-38. The α-olefin/n-paraffin ratio in the C_2 and C_4 fraction as a function of H_2:CO ratio. Co/Al_2O_3A, T = 510 ± 3 K, P = 7 - 9 bara and CO conversion = 5 - 7 %.

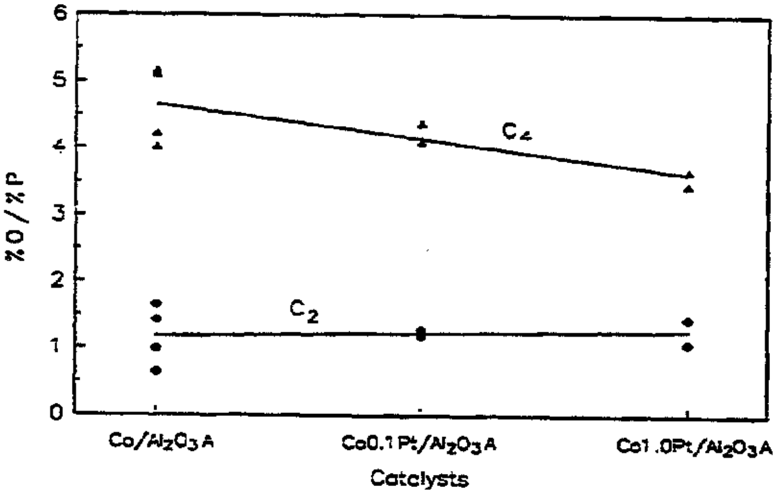

Figure 4-39. The α-olefin/n-paraffin ratio in the C_2 and C_4 fraction over catalysts with increasing platinum addition. T = 510 ± 3 K, P = 7 bara, H_2:CO = 2 and CO conversion 4.5 - 7 %.

Due to separating limitations of the product analyses, the olefin/paraffin ratio for the C_3 fraction was not measured. Among the measured olefin fractions in the product over Co/Al_2O_3A, the highest value is found for the C_4 fraction. At 510 K, 7 bara and with the H_2:CO ratio = 2, the olefin/paraffin ratio is 4 - 5. The α-olefin/n-paraffin ratio decreases down to the C_{12} fraction, and the C_{13+} fraction contains almost only paraffins.

The trends in olefin selectivity as a function of carbon number are in agreement with results reported by Sasol works /55/. It was found that as the carbon number increased from 6 to 17 the olefin selectivity decreased. However, the olefinicety for cobalt catalysts measured at 463 K and 1 bara /76/ at Sasol seems to be somewhat lower than the results in this study show. With a higher degree of CO conversion as there is in the process plant, a higher extent of secondary hydrogenation is expected. At Sasol /76/ it was also found that the cobalt catalyst products are more paraffinic than those of the iron catalysts, due to the higher activity to hydrogenation for the cobalt catalysts. Pannel et al. /34/ suggested that the decreasing olefin content with increasing carbon number indicate rapid hydrogenation, and it may be balanced by slower product desorption as carbon number increases. But Iglesia et al. /81/ conclude that secondary α-olefin hydrogenation is inhibited by the water formed during the CO hydrogenation. They suggest that olefin pore residence time and fugacity increases with carbon number, due to decreasing diffusion rates through the liquid in the pores with increasing carbon number. This leads to enhanced readsorption of olefin, which initiate surface chains, and thus gives higher paraffin content in the higher molecular weight fractions.

CO hydrogenation over Co/Al_2O_3A gives only small changes in the olefin selectivity in the temperature range from 489 to 529 K. The observed variations in Figure 4-37 of the C_2 and the C_4 fraction could indicate a weak increase in C_4 olefin selectivity and constant C_2 olefin selectivity. The measurements are done with CO conversion between 4.5 and 7 %, but the trend is not due to changes in the CO conversion. It is earlier reported /55,77/ that the percentage of olefins in the various carbon number cuts either remained constant or decreased over cobalt catalysts as the temperature was increased.

When changing the H_2:CO ratio from 1 to 4 at 511 K and 7 - 9 bara over Co/Al_2O_3A a significant decrease in olefin production appears for the C_4 fraction, while the decrease is more moderate for the C_2 fraction. These trends shown in Figure 4-38 are in agreement with studies of cobalt catalysts at Rhurchemie /77/ and iron catalysts at US Bureau of Mines /78/.

Figure 4-39 shows that the C_4 olefin fraction is decreasing when increasing amounts of platinum are added to the cobalt catalyst. The C_2 olefin fraction is unaffected of the platinum addition.

The lower olefin content in the products from the platinum containing catalyst is not unexpected, due to the known hydrogenation activity of platinum /65/. The platinum is apparently active in rapid secondary hydrogenation reactions only, while the primary chain growth reactions takes place on cobalt.

4.3.2 Low temperature / 1 bara total pressure

The hydrocarbon product selectivity from Co/Al_2O_3A was measured at 473 K and 1 bar, with a H_2:CO ratio of 2 and 3. The results from these experiments are shown in Figure 4-40. The product distribution from Co/Al_2O_3A and Co1.0Pt/Al_2O_3A at a H_2:CO ratio of 3 are compared in Figure 4-41.

Figure 4-40 shows that when the H_2:CO ratio was increased from 2 to 3 it resulted in more light gaseous hydrocarbons produced, while the amount of liquid hydrocarbons decreased. This is due to higher terminating rates with increased hydrogen concentrations /55/.

From Figure 4-41 it is seen that there are no significant differences in selectivity from the promoted and the unpromoted catalyst. When comparing these selectivities with the trends in selectivities observed with increasing temperature (489 - 529) at 7 bara (Figure 4-33 to 4-35), there is good agreement between the results. The methane selectivity is somewhat

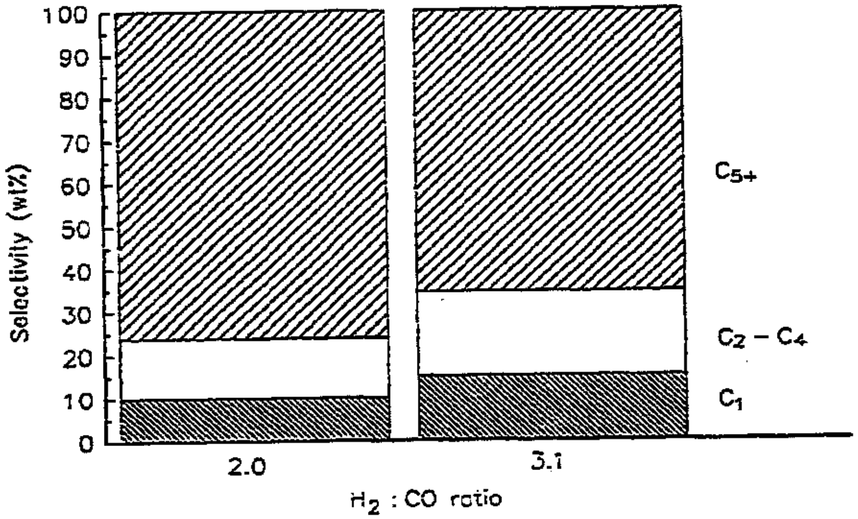

Figure 4-40. Hydrocarbon product selectivity over Co/Al_2O_3A with H_2:CO = 2 and 3.1 at 473 K and 1 bara. GHSV = 5000 and 7000, CO conversion = 3.4 and 5.5, respectively.

lower and the selectivity to longchained hydrocarbons is somewhat higher at 473 K and 1 bara. This result shows that the change in reaction temperature, and not the pressure, is most important for the selectivity. The general trend for increasing pressure is increasing chain length /34,55/.

As shown in previous chapters, the promoted catalysts showed a much higher degree of reduction compared to the unpromoted catalyst. Then the lack of differences in hydrocarbon selectivity from the promoted and the unpromoted catalyst could be discussed in terms of the degree of reduction of the catalysts. The effect of reduction extent on hydrocarbon selectivity is discussed in the literature, and there seems to be some disagreements. Lee et al. /38/ did not find any differences in product distribution with varying degree of reduction over 10 % Co/Al_2O_3 at 523 K and 1 atm., with H_2:CO = 3 and CO conversion = 1.8 % when the calcination temperature was kept constant. This is in agreement with the results found in this investigation.

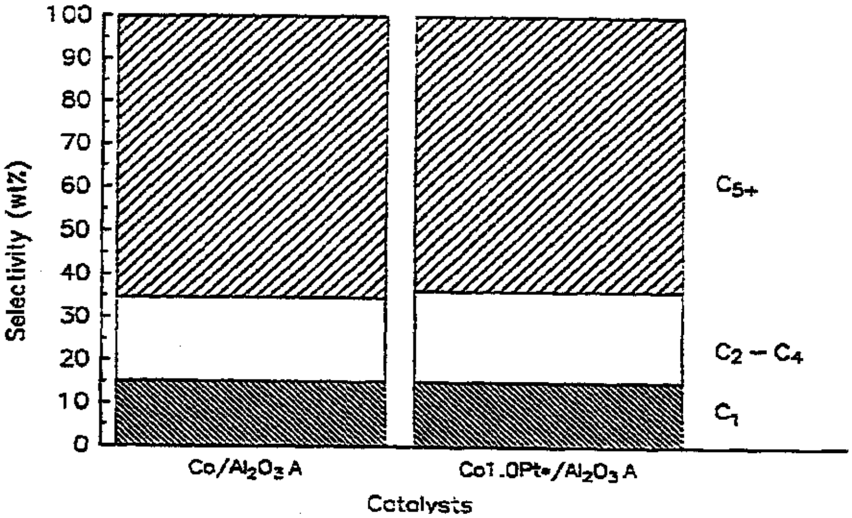

Figure 4-41. Hydrocarbon product selectivity Co/Al_2O_3A and Co1.0Pt/Al_2O_3A with H_2:CO = 3 at 473 K and 1 bara. GHSV = 7000, CO conversion = 5.5 and 7.7 %, respectively.

Lapidus et al. /46/ found a higher total yield and more C_{5+} hydrocarbons with increasing degrees of reduction. But in these investigations the degree of reduction was changing as a result of increased calcination temperature, and thus more dramatical changes in the distribution of the cobalt phases could be expected. The changes in selectivity were explained by changes in the cobalt support interactions and differences in the nature of the oxide phases. IR studies /46/ showed an increasing amount of linearly bound CO when the catalyst was calcined in air. The increased number of weak CO adsorption centers on the cobalt catalyst surface was suggested to be the cause of the observed increase in liquid hydrocarbon yield. Moon and Yoon /36/ found only a small increase in methane selectivity with increasing extent of reduction, while there was a significant decrease in the olefin selectivity at higher extent of reduction. This was measured at conversion degrees less than 1 % with a H_2:CO ratio = 3 at 513 K and 1 bara. Since the extent of paraffin formation depends on availability of reactive hydrogen, the lower olefin selectivity on well reduced catalysts was explained with suppressed H_2 adsorption on poorly reduced catalysts.

Lapidus et al. /118/ report that bimetallic CoRu and CoPd systems result in a higher yield of C_{5+} hydrocarbons in comparison with the unpromoted cobalt catalyst. Ruthenium gives the most pronounced increase in the selectivity to liquid hydrocarbons.

In the promoted catalysts two different phases of cobalt are reduced and active in CO hydrogenation in contrast to unpromoted catalysts where only Co_3O_4 particles are assumed to be reduced. As this does not give significant changes in selectivity it could be used as an evidence for CO hydrogenation as a structure *in*sensitive reaction. Johnson et al. /44/ found that the activity was independent of dispersion, and concluded that the CO hydrogenation is structure insensitive. On the other hand, it could also be used to suggest that the reduced cobalt from the surface layer forms particles much like the particles formed from Co_3O_4.

Unfortunately, complete C_{2+} selectivity measurements were not performed when testing Co/Al_2O_3B, $Co1.0Pt/Al_2O_3B$ and $Co1.0Re/Al_2O_3B$ at low temperature, 1 bara and with H_2/CO ratio = 2. Only the CH_4 selectivities are available. An increase from 11 wt % to 13 wt% methane can be observed when adding 1 wt% Pt or Re to Co/Al_2O_3B. This could indicate that the second metal takes part in the methane forming reactions. When a difference between the unpromoted and the promoted catalysts is observed at these conditions, this support the suggested diffusion limited product distribution at more severe conditions.

5 CONCLUSIONS

5.1 Reduction behavior

TPR studies show that monometallic 9%Co/Al_2O_3 after calcination in the range 573 - 698 K contains two main cobalt phases: Crystalline Co_3O_4 particles which is reduced at temperatures between 600 and 650 K, and a cobalt oxide layer containing cobalt ions interacting with the alumina support surface. The surface cobalt phase is reduced between 700 and 1050 K. Some amounts of very heavily reducible $CoAl_2O_4$ are also present in the catalyst.

Addition of Pt, Ir, Pd, Ru or Re lowers the reduction temperature of the cobalt phases. The temperature shifts are dependent of the second metal loading, but also of the type of second metal and its precursor. Addition of 0.1 and 1.0 wt% Pt from a chloride containing precursor lowers the Co_3O_4 reduction temperature with about 80 K. The reduction temperature of the surface cobalt ions are lowered with 100 - 200 K compared to the monometallic cobalt catalyst: increasing platinum loading gives increasing temperature shift.

Addition of 1 wt% Pt from a chloride free platinum precursor increases the above mentioned shift for the reduction of Co_3O_4 to 140 K, while reduction of the surface cobalt phase is shifted 100 K compared to the monometallic catalyst.

The ability of the different second metals to shift the Co_3O_4 reduction decreases in the order

$$Pt = Pd = Ir > Ru >> Re.$$

This seems to be in the same order as the ease of reduction of the different second metals. The ability of the metals to shift the reduction of the cobalt surface phase decrease in the order

$$Pt = Ru > Ir > Pd > Re.$$

At 623 K reduction temperature it is found that the bimetallic CoPt and CoRe catalysts are reduced to a larger extent compared to the monometallic cobalt catalyst. In the bimetallic catalysts the surface cobalt oxide are reduced, while this is not the case for the monometallic catalyst.

The degree of decomposition of the cobalt precursor, $Co(NO_3)_2$, during the calcination is dependent of the calcination temperature. The decomposition of nitrate ions is incomplete after two hours in flowing air at temperatures below 700 K. The reductive decomposition of the cobalt nitrate left after calcination do not shift to a lower temperature after addition of a second metal. The degree of decomposition of nitrate during the calcination is also unaffected by addition of a metal promoter.

5.2 Chemisorption of H_2 and CO

When measured by volumetric chemisorption at 298 K, both the H_2 and the CO uptake on the 9%Co/Al_2O_3 catalyst increase with increasing amounts of platinum added to the catalyst. The H_2 uptake on the catalyst with 1 wt% Pt added is twice the H_2 uptake on the unpromoted catalyst. The CO uptake on the 9%Co1%Pt-catalyst is nearly three times the CO uptake on the monometallic cobalt catalyst.

Addition of 1 wt% Re also increases the gas uptake on the catalyst, but the increase in the H_2 uptake is lower compared to the increase with 1 wt% Pt addition. The increase in H_2 uptake is 50 % compared to the unpromoted catalyst. The increase in CO adsorption is about the same for the rhenium promoted catalyst as for the platinum promoted catalyst.

The CO:H adsorption ratio for the investigated catalysts increases in the order

9%Co1%Re > 9%Co1%Pt > 9%Co0.5%Pt > 9%Co.

Chemisorption of H_2 on chloride containing, platinum promoted catalysts shows that these catalysts adsorb somewhat less hydrogen compared with the monometallic cobalt catalyst.

Increased calcination temperature of the 9%Co/Al_2O_3 catalyst slightly decreases the H_2 uptake on the catalyst.

5.3 Catalyst activity and selectivity

Activity measurements done with differential conditions at 473 K and 1 bara show that promotion of the cobalt catalyst with platinum or rhenium approximately doubles the rate of CO conversion to hydrocarbons. The increase in CO conversion due to Re addition is larger compared to the increase due to Pt addition. The increase in CO conversion over the platinum promoted catalyst is in agreement with the observed increase in degree of reduction and the increase in H_2 uptake. However, some of the hydrogen uptake is considered to be on platinum. Promotion with platinum as well as rhenium then gives increased turnover frequency on the cobalt sites. The results therefore indicate that the increase in rate for both promoted catalysts is due to increased number of sites, as well as increased intrinsic activity.

When the activity measurements were done at more severe conditions (513 K and 7 bara) giving increased rates, the promoting effect of Pt and Re could not be observed. It is suggested that the reaction rate most probably is controlled by the gas diffusion through liquid product present in the catalyst pores.

Selectivity measurements did not show significant differences in hydrocarbon chain length between the mono- and bimetallic cobalt catalysts. The α-olefin/n-paraffin ratio of the C_4 fraction decreased with increasing platinum addition. On the other hand, the α-olefin/n-paraffin ratio of the C_2 fraction was not dependent of platinum addition.

Over 9%Co/Al_2O_3 the methane selectivity increases from 13 to 25 wt% over the temperature range 489 - 529 K at 7 bara, while the C_{5+} fraction decreases from 72 to 50 wt%. The α-olefin/n-paraffin ratio does not change significantly within this temperature range.

When changing the H_2:CO ratio from 1 to 4 at 513 K and 7 bara, methane selectivity increased from 13 to 30 wt%, while the C_{5+} fraction decreased from 72 to 44 wt%. The α-olefin/n-paraffin ratio of the C_4 fraction at the H_2:CO ratio = 4 was half the value at the H_2:CO ratio = 1. The α-olefin/n-paraffin ratio of the C_2 fraction was also unaffected by the H_2:CO ratio.

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