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Interpretation and kinetic modeling of product distributions of cobalt catalyzed Fischer–Tropsch synthesis

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Abstract

Carbon number distributions of Fischer–Tropsch products on iron and cobalt catalysts show deviations from the ideal Anderson–Schulz–Flory (ASF) distribution. For products obtained on cobalt catalysts these deviations are traced back by many authors to re-adsorption and incorporation of 1-alkenes followed by subsequent chain growth. In the present work, it could be shown by means of model calculations and based on experiments with co-feeding of ethene and 1-alkenes that such subsequent chain growth cannot be regarded as the main reason of observed deviations of the carbon number distribution from the ideal ASF distribution. The co-feeding experiments suggest that these deviations are the consequence of two different mechanisms of chain growth causing a superposition of two ASF distributions.

Consequently, the carbon number distributions are represented by this superposition. In order to describe distributions as a function of reaction conditions the model parameter, the growth probabilities α_1 and α_2 as well as μ_1, the fraction of distribution (α_1) are presented as function of the partial pressures of hydrogen and carbon monoxide. Finally, the typical model parameters of products formed on cobalt and iron are compared. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fischer–Tropsch synthesis; Secondary olefin reactions; Co-feeding of olefins; Chain length dependencies

1. Introduction

If the hydrocarbon chain is formed stepwise by insertion or addition of C_1 intermediates with constant growth probability then the chain length distribution is given by the Anderson–Schulz–Flory (ASF) distribution [1,2]. However, for all Fischer–Tropsch catalysts deviations from this ideal distribution are observed [3–7]. Therefore, many studies were focussed on these deviations from the ideal ASF distribution. It has been shown for iron catalysts [8–11] and later for cobalt catalysts [12] that product distributions can be represented by superposition of two ASF distributions. Madon and Taylor [4] interpreted this bimodal distribution by differently structured sites causing different growth probabilities. This and similar interpretations have been given for products obtained on various catalysts in particular on iron catalysts. For the synthesis on ruthenium, Iglesia et al. [7] interpreted deviations from the simple ASF distribution by readsorption of 1-alkenes and secondary chain propagation. They developed a model of diffusion-enhanced readsorption of 1-alkenes. Diffusion limitation within liquid filled pores slows down the removal of 1-alkenes which causes an increase of their residence time within the catalyst pores. Therefore, the probability of readsorption and, consequently, of subsequent chain initiation is enhanced with increasing chain length of 1-alkenes. The conclusion has been drawn that in the absence of any mass transfer limitation, an ideal ASF distribution characterized by a constant growth probability should be expected. For ruthenium catalysts

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this theory is reasonably founded on experiments with co-feeding of 1-alkenes.

For the synthesis on cobalt deviations from the simple ASF distribution have been interpreted by Madon et al. [13] on the same line based on experiments varying the bed residence time. This theory of readsorption and secondary chain initiation has been applied by several authors [14,15]. However, experiments with co-feeding of 1-alkenes in order to evaluate secondary reactions are still rare.

Recently, Schulz and Claeys [16,17] presented co-feeding experiments of Fischer–Tropsch synthesis on cobalt catalysts carried out in a continuously operated well-mixed slurry reactor. They evaluated the rate of incorporated 1-alkenes leading to start secondary chain growth via the mass balance of co-fed 1-alkenes and the products of secondary reactions. For co-feeding experiments with ethene and 1-octene also product distributions are given. These experiments are in best agreement with ethene and 1-hexene co-feeding experiments presented in this work.

Schulz and Claeys [15,17] developed a kinetic model of Fischer–Tropsch synthesis that allows the calculation of the product distribution of linear and also the selectivity of 1-alkenes. In this model, deviations from the ideal ASF distributions are exclusively traced back to secondary chain growth of readsorbed 1-alkenes. However, the authors did not explicitly present the selectivity of 1-alkene incorporation, although the agreement of calculated selectivity of incorporation with that from the co-feeding experiments is indispensable for the conclusion that secondary chain growth is the exclusive reason for deviations from the ideal ASF distribution.

In a preceding study, Patzlaff et al. [18] concluded that for iron and cobalt catalysts the deviation from the ASF distribution is the result of superposition of two ASF distributions caused by different mechanisms of chain growth. This conclusion is based on the experimental result that in case of iron catalyst the fraction of 1-alkene incorporation and secondary chain growth is negligible and is relatively low for cobalt catalysts. Furthermore, the shapes of the product distributions of co-feeding experiments (ethene, 1-hexene) have led to the conclusion that secondary chain growth of readsorbed 1-alkenes is characterized by a lower growth probability than that observed for the range of carbon numbers >10.

The goal of the present work was to check once more the consistency of both contradictive theories in view of all experimental data of ethene/1-alkene co-feeding studies and to propose an appropriate model to represent the product distributions as a function of reaction conditions.

2. Experimental and data reduction

For theoretical considerations of this work, the experimental data of Schulz and Claeys [16] obtained in a continuously operated slurry reactor and of this study obtained in a fixed bed reactor are used. Both experimental units and the procedure of the synthesis runs are described in detail by both groups of authors in [16,17] and [18]. The advantages and disadvantages of the slurry reactor, a CST-reactor without mass transfer resistances, and the fixed bed reactor, and integral reactor with mass transfer resistances in the liquid filled pores of the catalyst pellets, have been discussed by Patzlaff et al. [18]. The carbon number distributions presented in this work as functions of the hydrogen and the carbon monoxide pressure were obtained by the synthesis in the fixed bed integral reactor.

The following catalysts were employed:

- 100% Co/15% ZrO_2/100% SiO_2/0.66% Ru in the experiments presented by Schulz and Claeys [16];
- pure precipitated catalyst [18] and 15% Co/9% ZrO_2/100% SiO_2 [19] in the experiments presented in this study.

The data reduction for the representation of the chain length distribution by superposition of two ASF distributions followed the method proposed by Satterfield and co-workers [9]. The modification of this method is described in detail by Patzlaff et al. [18]. The characteristic parameters are the two growth probabilities α_1 and α_2 and the molar fraction m_1 of the distribution (α_1).

3. The kinetic model

In order to elucidate the role of 1-alkene incorporation, the model presented in the doctoral thesis of Claeys [17] has been modified. However, all assumptions with regard to readsorption of 1-alkenes and subsequent chain initiation are identical with those of the original version and also with those of the model presented by Iglesia [20]. Instead of the calculation of 1-alkene selectivities experimentally obtained 1-alkene selectivities are taken as input of the modified model. It is obvious that this modification does not at all affect the role of secondary chain growth. Therefore, the new model is set free from any assumptions concerning the transfer of 1-alkenes into the gas phase.

The comparison of the reaction schemes of the original model of Claeys [17] and of the modified model, Fig. 1a and b shows two further modifications.

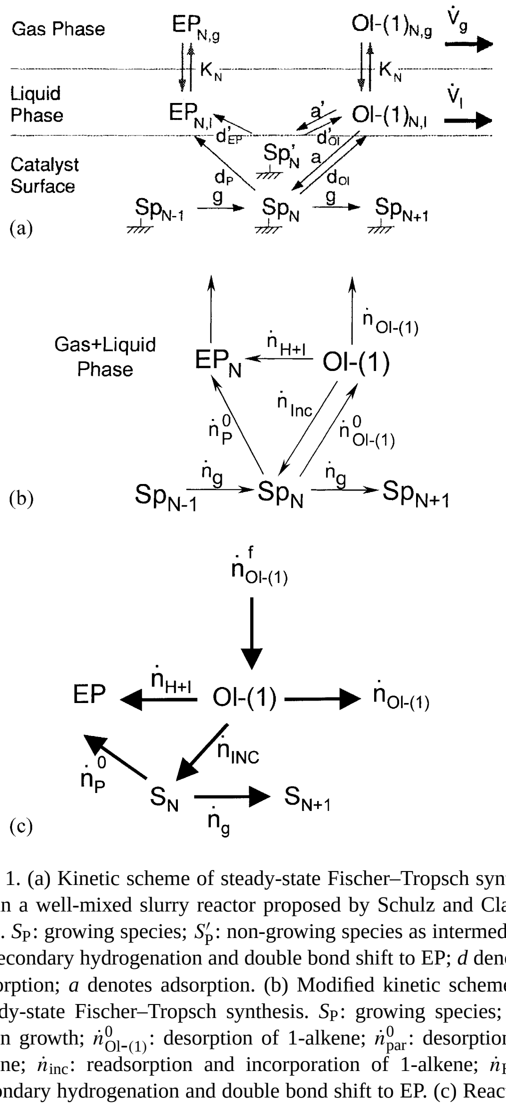


Fig. 1. (a) Kinetic scheme of steady-state Fischer–Tropsch synthesis in a well-mixed slurry reactor proposed by Schulz and Claeys [15]. S_P: growing species; S'_P: non-growing species as intermediate of secondary hydrogenation and double bond shift to EP; d denotes desorption; a denotes adsorption. (b) Modified kinetic scheme of steady-state Fischer–Tropsch synthesis. S_P: growing species; $\dot{n}_g$: chain growth; $\dot{n}^0_{\text{Ol-(1)}}$: desorption of 1-alkene; $\dot{n}^0_{\text{par}}$: desorption of alkane; $\dot{n}_{\text{inc}}$: readsorption and incorporation of 1-alkene; $\dot{n}_{\text{H+I}}$: secondary hydrogenation and double bond shift to EP. (c) Reaction scheme of co-feeding experiments.

1. The surface species S'_P formed by reversible 1-alkene adsorption is omitted because it is not capable to grow and can only desorb to end products, EP, alkanes and alkenes with internal double bond. The formal introduction of the desorption term d'_{Ol} as done in the original model requires an additional model parameter. Since no experimental information about this desorption is available it is not useful to specify an adsorption and desorption term. It is sufficient to define subsequent reaction steps of hydrogenation and double bond shift which may be regarded to occur on specific sites of the catalysts. These reaction steps are assumed of first order with regard to the olefin concentration also in accordance with the original model.
2. Since the experimentally obtained selectivities of 1-alkenes are taken as an input of the modified model, it is no longer necessary to calculate the 1-alkene concentration in the liquid phase. In thermodynamic equilibrium, the concentration in the liquid phase is proportional to the vapor phase concentration.

4. The modified kinetic model

The model is based on the mass balances of 1-alkenes:

$$\dot{n}_{\text{Ol-(1)}} + \dot{n}_{\text{H+I}} + \dot{n}_{\text{inc}} = \dot{n}^0_{\text{Ol-(1)}} \tag{1}$$

The other equations of the model are the definition of the 1-alkene selectivity

$$S_{\text{Ol-(1)}} = \frac{\dot{n}_{\text{Ol-(1)}}}{\dot{n}_{\text{Ol-(1)}} + \dot{n}^0_{\text{P}} + \dot{n}_{\text{H+I}}} \tag{2}$$

and the definition of the selectivity of incorporation with regard to all subsequent reactions of 1-alkene

$$S_{\text{inc}} = \frac{\dot{n}_{\text{inc}}}{\dot{n}_{\text{inc}} + \dot{n}_{\text{H+I}}} \tag{3}$$

Furthermore, the assumption is made that the ratio $\dot{n}^0_{\text{P}}/\dot{n}^0_{\text{Ol-(1)}} = a$ is independent of the carbon number. For the calculation of the effective growth probability, we need the ratio $\dot{n}_{\text{inc}}/\dot{n}^0_{\text{Ol-(1)}}$ which is calculated from the set of Eqs. (1)–(3) as

$$\frac{\dot{n}_{\text{inc}}}{\dot{n}^0_{\text{Ol-(1)}}} = \frac{S_{\text{inc}}(1 - S_{\text{Ol-(1)}}(1 + \alpha))}{1 - S_{\text{inc}}S_{\text{Ol-(1)}}} \tag{4}$$

Schulz and Claeys [15] introduced the parameter α_0, the primary chain growth probability, defined as

$$\alpha_0 = \frac{\dot{n}_{\mathrm{g}}}{\dot{n}_{\mathrm{g}} + \dot{n}^0_{\mathrm{Ol\text{-}(1)}} + \dot{n}^0_{\mathrm{P}}} \tag{5}$$

The effective growth probability α_{eff} taking into account the incorporation of 1-alkenes is given by

$$\alpha_{\mathrm{eff}} = \frac{\alpha_0/(1-\alpha_0)}{(\alpha_0/(1-\alpha_0)) + 1 - [S_{\mathrm{inc}}(1 - S_{\mathrm{Ol\text{-}(1)}}(1+a))/(1 - S_{\mathrm{inc}}S_{\mathrm{Ol\text{-}(1)}})(1+a)]} \tag{6}$$

This equation contains only three parameters a_0, a and S_{inc} which are assumed as independent of the carbon number. The input $S_{\mathrm{Ol\text{-}(1)}}$ depends on the carbon number so that the calculated value α_{eff} are the individual growth probabilities depending on the carbon number. α_0 and a are identical with the corresponding parameters of the model presented by Claeys. The assumption that the ratio $\dot{n}^0_{\mathrm{P}}/\dot{n}^0_{\mathrm{Ol\text{-}(1)}} = a$ and the selectivity S_{inc} are independent of the carbon number is founded by the detailed kinetic studies of Schulz and Claeys [16]. The constancy of S_{inc} implies implicitly a formal first order with regard to 1-alkenes of all secondary reactions, hydrogenation, isomerization and incorporation of 1-alkene.

For cobalt catalysts, it could be shown by both groups [16,18] that in the case of ethene co-feeding the degree of ethene conversion and the selectivities of hydrogenation and incorporation are independent of the ethene partial pressure, an indication of first-order reactions (Table 1).

Unfortunately, studies on the secondary conversion of 1-alkenes which could prove the first-order reactions also for these components are not available for cobalt at present. However, the assumption of first-order kinetics also for 1-alkenes is justified because of less strongly adsorbed 1-alkenes compared to that of ethene.

This very simple equation (6) reflects the interrelation of 1-alkene readsorption and subsequent chain initiation and the selectivity of 1-alkenes expressing the part of formed 1-alkenes that could escape from readsorption and subsequent reactions. The higher the 1-alkene selectivity, the lower the effective growth probability.

However, it must be considered that the evaluation of co-feeding experiments gives the selectivity of secondary chain growth $S_{\mathrm{g,s}}$

$$S_{\mathrm{g,s}} = \frac{\dot{n}_{\mathrm{g}}}{\dot{n}_{\mathrm{g}} + \dot{n}_{\mathrm{H+I}} + \dot{n}^0_{\mathrm{P}}}$$

According to the scheme in Fig. 1c, we obtain

$$\dot{n}_{\mathrm{g}} = \alpha_0 \dot{n}_{\mathrm{inc}}, \qquad \dot{n}_{\mathrm{H+I}} = \frac{1 - S_{\mathrm{inc}}}{S_{\mathrm{inc}}}\dot{n}_{\mathrm{inc}},$$

$$\dot{n}^0_{\mathrm{P}} = \frac{1-\alpha_0}{1+1/a}\dot{n}_{\mathrm{inc}}$$

and finally

$$S_{\mathrm{g,s}} = \frac{\alpha_0}{\alpha_0 + [(1 - S_{\mathrm{inc}})/S_{\mathrm{inc}}] + [(1-\alpha_0)/(1+1/a)]}$$

5. Model calculations

Calculations were carried out for the experiment given by Schulz and Claeys [15]: Co/ZrO$_2$/SiO$_2$/Ru

Table 1
Fischer–Tropsch synthesis with the addition of ethene. Degree of ethene conversion and selectivity of hydrogenation and incorporation

	$P_{\mathrm{C_2H_4}}$ (mbar)	$X_{\mathrm{C_2H_4}}$	S_{Hyd}	S_{inc}
Co/Ru catalyst ($P_{\mathrm{H_2}} = 5.5$ bar, $P_{\mathrm{CO}} = 2.2$ bar, $P_{\mathrm{H_2O}} = 1.1$ bar, $T = 190\,^\circ$C) [16]	10	0.89	0.82	0.18
	18	0.88	0.74	0.26
	46	0.85	0.80	0.20
	56	0.88	0.86	0.14
Co-catalyst ($P_{\mathrm{H_2}} = 1$ bar, $P_{\mathrm{CO}} = 1$ bar, $T = 220\,^\circ$C)	7	0.99	0.74	0.26
	14	0.99	0.74	0.26
	28	0.98	0.75	0.25
	70	0.95	0.75	0.25
	150	0.93	0.74	0.26

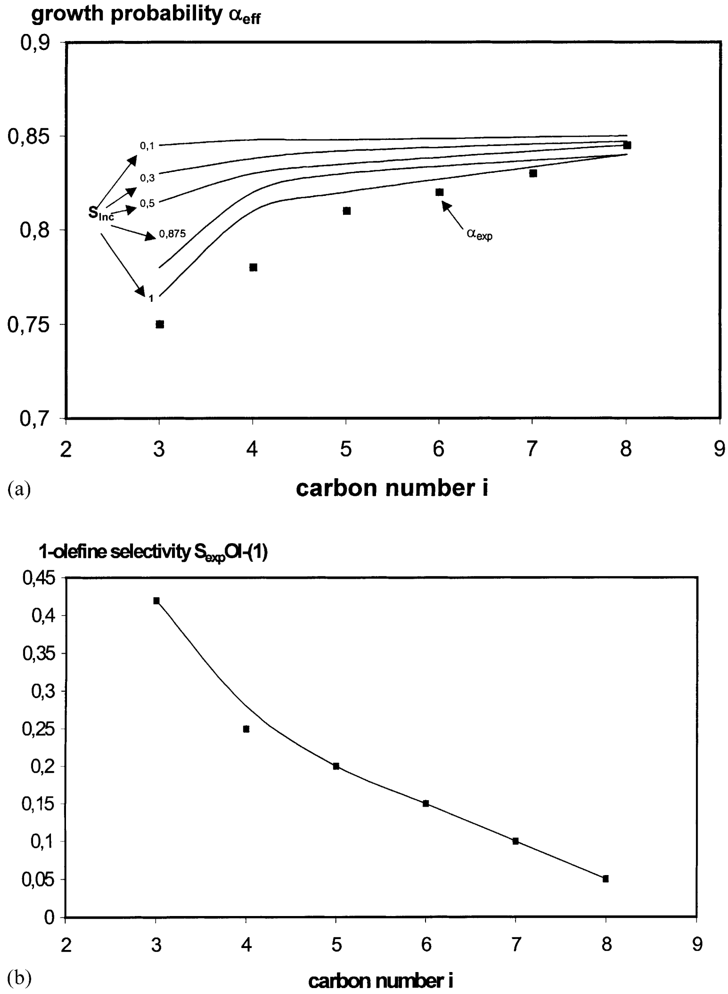


Fig. 2. (a) α_{eff} calculated by means of the modified model: $\alpha_0 = 0.63$, $a = 0.25$. Reaction conditions for α_{exp} [15]: Co/Ru catalyst, $P_{H_2} = 5.5\,\mathrm{bar}$, $P_{CO} = 2.2\,\mathrm{bar}$, $T = 190\,^{\circ}\mathrm{C}$. (b) Experimental 1-olefin selectivities. Reaction conditions are the same as in (a).

catalyst; $P_{H_2} = 5.5\,\mathrm{bar}$; $P_{CO} = 2.2\,\mathrm{bar}$; $P_{H_2O} \approx 1.1\,\mathrm{bar}$; $T = 190\,^{\circ}\mathrm{C}$, with the parameters $\alpha_0 = 0.63$ and $a = 0.25$ as used by these authors and the data of 1-alkene selectivity, Fig. 2b, the limiting value $\alpha_{\mathrm{eff}} = 0.85$ for carbon numbers >10 and the lowest effective growth probability for C_3 as calculated by Claeys can only be obtained with the parameter $S_{\mathrm{inc}} = 0.875$. The latter parameter corresponds to the ratio of parameters $k_a/k_{a'} = 14$ of the original model, see Fig. 1a, also indicating a very high selectivity of incorporation [15].

Fig. 2 shows the effective growth probabilities for varied selectivities of S_{inc}. For all curves $a = 0.25$ and the 1-alkene selectivities are set as given in Fig. 2b.

The primary growth probability a_0 is chosen that the limiting value of $\alpha_{\mathrm{eff}} = 0.85$ is reached at the carbon number 10. The corresponding value of S_{inc}, α_0 and $S_{g,s}$ are listed in Table 2. These calculations reveal that the experimentally observed values of α_{eff} can only be calculated assuming a very high selectivity of incorporation. The best approximation of the data points is obtained with the limiting value of $S_{\mathrm{inc}} = 1$.

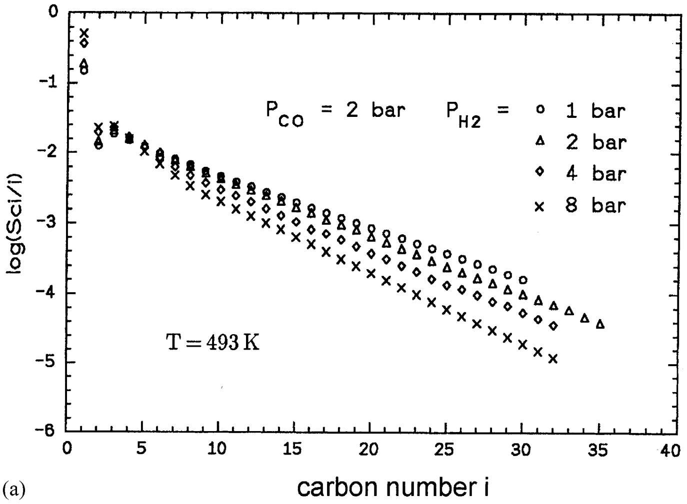
However, these calculations are strongly contradictory to the experimental results of co-feeding

Table 2
Corresponding values to Fig. 2a

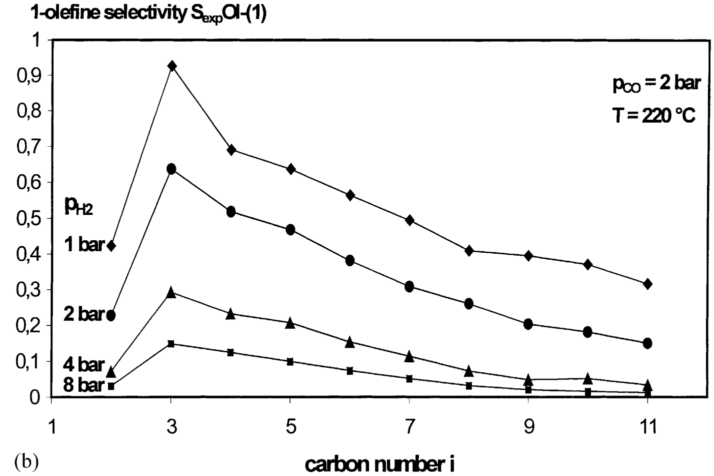
S_{inc}	α_0	$S_{g,s}$
0.1	0.84	0.084
0.2	0.83	0.17
0.3	0.81	0.26
0.5	0.77	0.42
0.875	0.63	0.74
1	0.53	0.85

experiments. The experiments of Schulz and Claeys [16] show for the reaction conditions given above a selectivity of secondary chain growth of $S_{g,s} \approx 0.1$ in accordance with the data of 1-hexene co-feeding experiments of Patzlaff et al. [18]. As shown in Fig. 2a, it is impossible to describe the course of growth probabilities when the incorporation selectivity is set $S_{g,s} = 0.1$ or even 0.5.

The growth probabilities reported by Iglesia [20] for the experiment: catalyst Co/TiO$_2$, 11.7%; fixed bed integral reactor, 9.5% CO conversion, $T = 200\,°C$,



(a)



(b)

Fig. 3. (a) Carbon number distribution of products obtained on Co–ZrO$_2$–SiO$_2$ catalyst at constant P_{CO} and varied P_{H_2}; (b) 1-alkene selectivity at constant P_{CO} and varied P_{H_2}.

$P = 20$ bar, $H_2/CO = 2.1$, can be represented with the model parameter $\alpha_0 = 0.6$, $a = 0.06$ and $S_{g,s} = 0.9$. This calculation is in accordance with the statement of Iglesia [20] that subsequent hydrogenation and double bond shift are negligible. However, a detailed consideration of the experimental results of this study shows for the C_4 fraction a selectivity of secondary chain growth of $S_{g,s} = 0.8$ and for ethene co-feeding experiments also values of $S_{g,s}$ around 0.8. Although, this value is relatively high it is not possible to calculate with this parameter the limiting growth probability of $\alpha_{eff} = 0.94$ and the value for C_3. Therefore, the conclusion must be drawn that the dependency of the growth probabilities on the carbon number cannot be calculated with the parameter $S_{g,s}$ obtained from aforementioned co-feeding experiments.

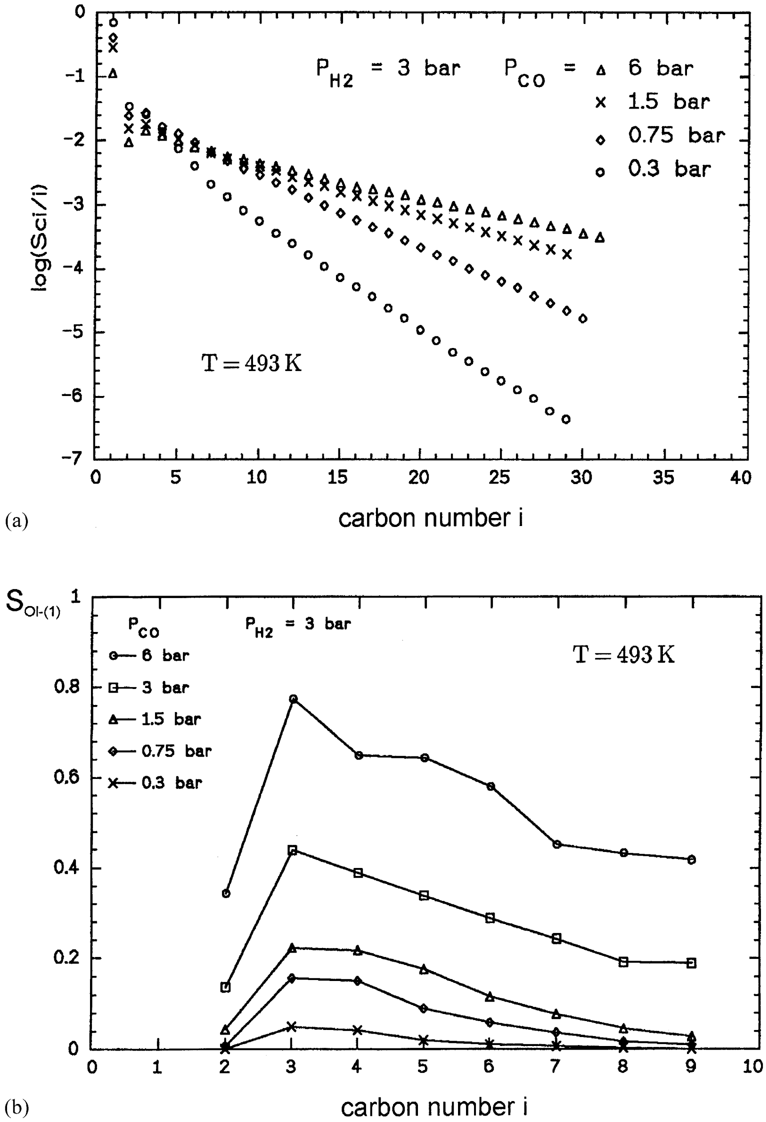


Fig. 4. (a) Carbon number distribution of products obtained on Co–ZrO$_2$–SiO$_2$ catalyst at constant P_{H_2} and varied P_{CO}; (b) 1-alkene selectivity at constant P_{H_2} and varied P_{CO}.

Nevertheless, it is remarkable that under the elevated pressure (total and CO) of the experiment reported by Iglesia [20], a much higher incorporation selectivity is obtained than under the relatively low pressure of carbon monoxide of the considered experiment of Schulz and Claeys [16]. But these authors have also found a considerably increased incorporation selectivity of $S_{g,s} = 0.45$ under the increased carbon monoxide pressure of $P_{CO} = 4.8\,\text{bar}$. With the reservation that different catalysts were used these results of both authors suggest that with increasing P_{CO} the subsequent hydrogenation decreases strongly, while the incorporation of 1-alkenes is less or even not affected.

Furthermore, it is of interest to discuss the dependency of the carbon number distribution on the partial pressure of hydrogen with regard to the role of 1-alkene incorporation. Fig. 3a shows that the deviation from the ideal ASF distribution decreases with decreasing hydrogen pressure. Supposing that the deviation is caused by readsorption and incorporation of 1-alkenes, we expect the opposite effect as Eq. (6) predicts an increasing deviation with increasing 1-alkene selectivity. Therefore, using this model, we expect a straight line in the ASF plot for high hydrogen pressures because of very low 1-alkene selectivities, Fig. 3b. However, we still have to discuss possible effects of the hydrogen pressure on the crucial parameter S_{inc}. If we suppose that both incorporation and hydrogenation are of the same order with regard to hydrogen S_{inc} is independent of the hydrogen pressure. If the incorporation is of a lower order than the hydrogenation S_{inc} would decrease with increasing hydrogen partial pressure. In both cases, we would expect the lowest deviation at the highest hydrogen pressure, while the experiments show the opposite effect, Fig. 3a.

As shown in Fig. 4a and b, the deviation from the ideal distribution increases as well with decreasing 1-alkene selectivity when the partial pressure of carbon monoxide is varied. Under the highest pressure of carbon monoxide ($P_{CO} = 6\,\text{bar}$), the lowest deviation from the ideal ASF distribution is obtained although the 1-alkene selectivities are rather high.

The comparison of model calculations and experimental results in particular with that of co-feeding experiments shows without doubt that incorporation of 1-alkenes cannot be regarded as the main reason for the marked deviation from the ideal ASF distribution. In a preceding study, Patzlaff et al. [18] came to the conclusion that these deviations can be interpreted by the superposition of two ASF distributions. Co-feeding experiments with ethene and 1-hexene have shown that only the ASF distribution characterized by the lower chain growth probability is affected by secondary incorporation of 1-alkenes. This has led to the conclusion that the superposition of two ASF distributions is due to different mechanisms of chain growth as already suggested by Dictor and Bell [21]. Since the new experimental results of Schulz and Claeys [16] are very useful to discuss the reason for the deviation of ASF distribution, the following sections are dedicated to an extended discussion of these controversially discussed questions.

6. Effects of ethene incorporation

As already shown in Table 1, the selectivity of ethene incorporation is independent of the ethene concentration and about $S_{inc}(C_2H_4) \approx 0.2$. The carbon number distributions with and without addition of ethene determined by Schulz and Claeys [16] and Patzlaff et al. [18] are in best agreement as demonstrated in Fig. 5a and b. It turned out that the slope and, consequently, the growth probability in the range of higher carbon numbers is not affected by the addition of ethene. Both experiments show in the case of ethene co-feeding an increased fraction of hydrocarbons in the range of low carbon numbers. Similar results are reported by Kibby et al. [22].

Former studies have shown that ethene can act as a chain starter and as an intermediate that can be inserted into growing chains [23]. The latter effect would probably cause an increased growth probability. Since in the range of high carbon numbers the growth probability is not affected by ethene additions the effect of insertion into a growing chain can be regarded as negligible at least in this range.

If ethene acts as a chain starter an increased synthesis activity but no change of the growth probability would be expected. However, a decreased formal chain growth probability in the range of low carbon numbers is observed. It is obvious that chains started with adsorbed ethene grow with a lower probability than chains started in the absence of ethene. Therefore, also these experiments support the theory of superposition

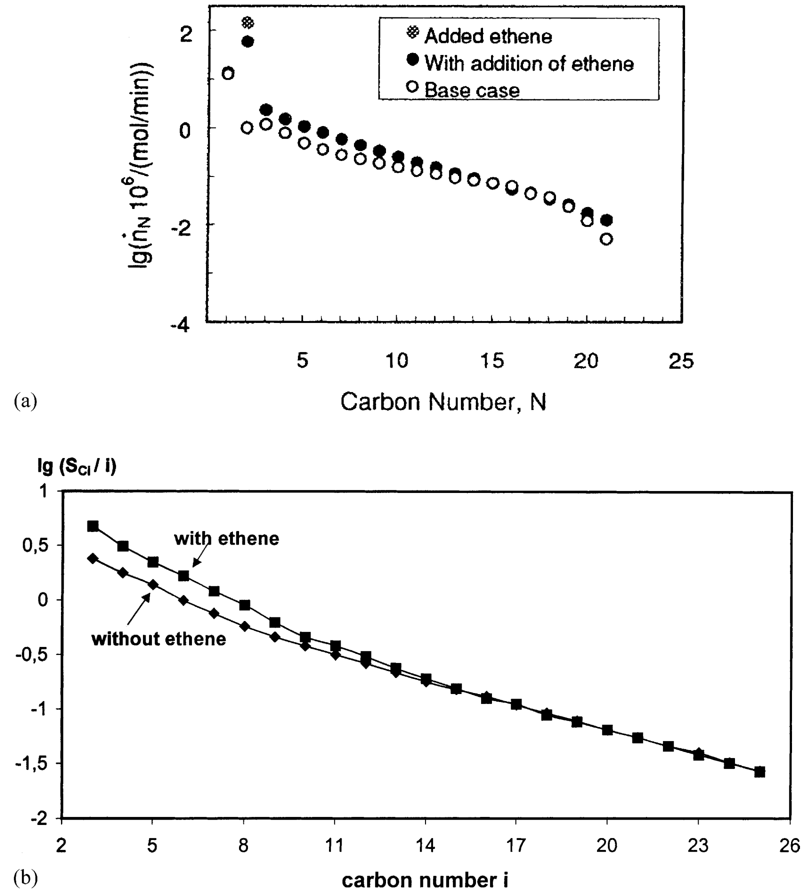


Fig. 5. (a) Molar formation rates of linear hydrocarbons with and without additions of ethene during Fischer–Tropsch synthesis given by Schulz and Claeys [16]. The diagram is equivalent to non-normalized carbon number distributions. Reaction conditions: Co/Ru catalyst, $P_{H_2} = 5.1\,\text{bar}$, $P_{CO} = 2.2\,\text{bar}$, $P_{C_2H_4} = 0.046\,\text{bar}$. (b) Carbon number distributions of linear hydrocarbons with and without additions of ethene during Fischer–Tropsch synthesis [18] normalized for comparison with (a). Reaction conditions: Co catalyst, $P_{H_2} = 1\,\text{bar}$, $P_{CO} = 1\,\text{bar}$, $P_{C_2H_4} = 0.07\,\text{bar}$.

of two ASF distributions caused by different chain growth mechanism.

All product distributions can be well represented by the model of superposition [18]. The parameters of this model, both growth probabilities and the fraction of the distribution μ_1 characterized by the lower growth probability α_1, are shown in Fig. 6 as a function of the partial pressure of ethene. The growth probability α_2 is not affected by ethene addition, while α_1 shows a slight increase as the ethene concentration is raised. The latter effect is interpreted by the action of ethene as an intermediate capable of some insertion into growing chain characterized by α_1. The main effect is a drastic increase of the fraction μ_1 of hydrocarbons that grow with the lower growth probability α_1 caused by ethene as chain starter.

7. Effects of 1-alkene incorporation

In the case of the simple kinetic model, it is expected that a co-fed 1-alkene additionally starts new growing chains with the same constant growth probability. Therefore, in the usual plot of the ASF distribution, a

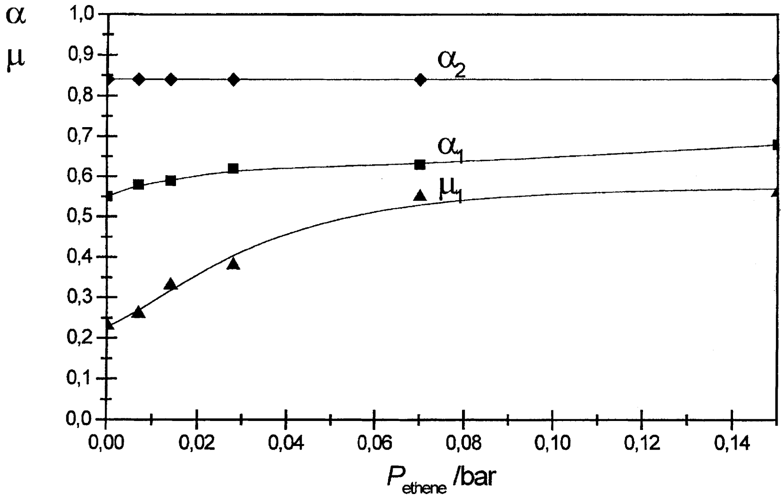


Fig. 6. Effect of ethene addition on chain length distribution: Co catalyst, $T = 220\,^{\circ}\mathrm{C}$, $P_{H_2} = 1\,\mathrm{bar}$, $P_{CO} = 1\,\mathrm{bar}$.

step and a parallel upward shift of the straight line is expected.

The product distributions of the synthesis runs with co-fed 1-hexene [18] and co-fed 1-octene [16] show indeed an increased selectivity of the C_7-, respectively, C_9-fraction. However, the increase of the following fractions strongly declines with increasing carbon number, so that the distribution approaches that one obtained without co-feeding of the 1-alkenes within a few carbon numbers. This result suggests that readsorbed 1-alkenes initiate chains growing with a lower probability than that of chains formed directly in the Fischer–Tropsch syntheses. The interpretation on the basis of the theory of superposition of two ASF distributions is finally that readsorbed and incorporated 1-alkenes grow according the mechanism characterized by the lower growth probability α_1.

As discussed in detail by Patzlaff et al. [18], the step of incorporation is assumed as semi-hydrogenation of readsorbed 1-alkenes forming alkyl species as the growing intermediate of the CH_2-insertion mechanism. Since the growing intermediate of the other chain growth mechanism (a_2) is suggested as different to alkyl species an incorporation of readsorbed 1-alkenes is impossible. 1-Alkenes are only compatible with the CH_2-insertion mechanism.

8. Dependence of product distributions on hydrogen and carbon monoxide pressure

The hypothesis of two different mechanisms suggests to represent the distribution by superposition of two ASF distributions. As shown in Figs. 7 and 8, the distribution is well described by this procedure. Chain length distributions given in Fig. 4a for constant hydrogen pressure and varied P_{CO} and in Fig. 5a for constant carbon monoxide pressure and varied P_{H_2} show that the average growth probability indicated by the slope of the curves is raised with increasing carbon monoxide pressure and is reduced with increasing hydrogen pressure.

At low carbon monoxide pressure both growth probabilities increase with increasing P_{CO} approaching a nearly constant value, Figs. 9 and 10. The fraction μ_1 decreases as P_{CO} is raised and increases with increasing P_{H_2}.

The countercurrent dependency of the fraction m on P_{H_2} and P_{CO} has been interpreted by the preference for the mechanism with the intermediate of the highest degree of hydrogenation at high hydrogen and low carbon monoxide pressures [18]. However, an interpretation of the relatively moderate dependencies of the growth probabilities on the partial pressures would be rather speculative because α is the ratio of the rates of chain growth and termination.

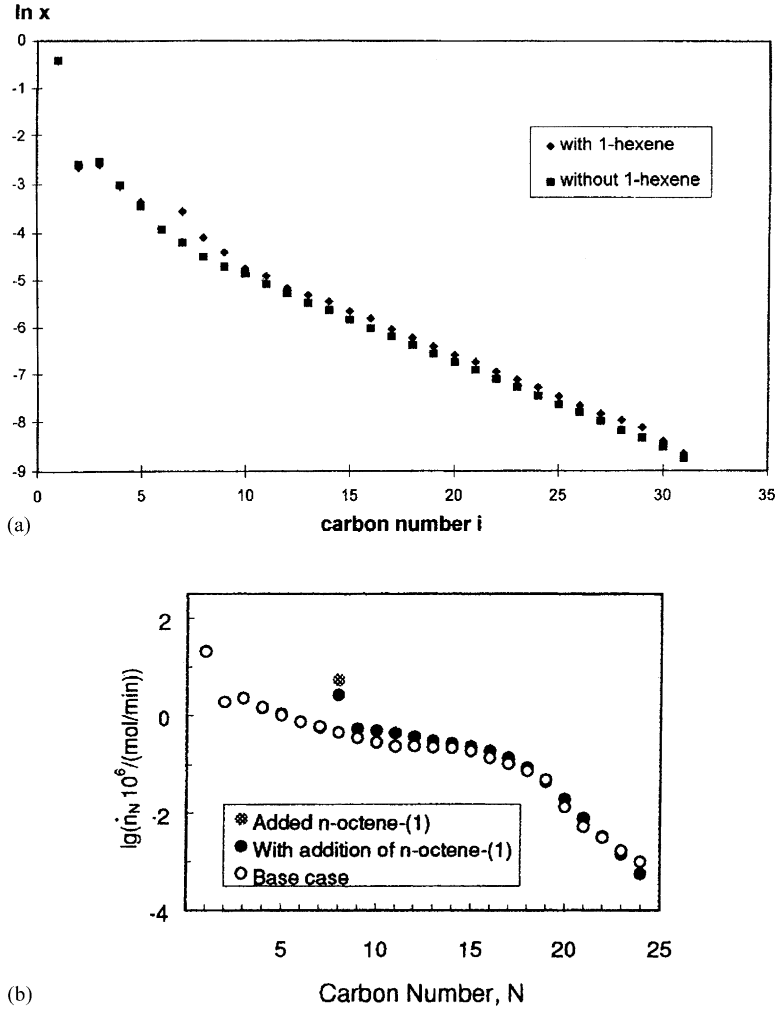


Fig. 7. (a) Effect of 1-hexene addition on chain length distribution: Co catalyst, $T = 220\,^{\circ}\mathrm{C}$, $P_{H_2} = 1\,\mathrm{bar}$, $P_{CO} = 1\,\mathrm{bar}$, $P_{1\text{-hex}}/P_{1\text{-hex(base case)}} = 60$. (b) Molar formation rates of linear hydrocarbons with and without the addition of 1-octene during Fischer–Tropsch synthesis given by Schulz and Claeys [16]. The diagram is equivalent to non-normalized carbon number distributions. Reaction conditions: Co/Ru catalyst, $P_{H_2} = 5.5\,\mathrm{bar}$, $P_{CO} = 2.2\,\mathrm{bar}$, $P_{1\text{-oct}}/P_{1\text{-oct(base case)}} = 25$.

Nevertheless, the representation of distributions by means of superposition of two ASF distributions is a rough approximation because the incorporation of 1-alkenes which concerns the distributions (α_1) is not explicitly taken into account and hydrogenolysis of alkenes is neglected. With respect to hydrogenolysis there are only few informations available from ^{14}C tracer experiments given by Schulz et al. [23]. However, it is still impossible to take into account this effect by a correction term. We suppose that all alkenes formed suffers hydrogenolysis to a small extent. Thus, hydrogenolysis takes formal effect by a slight reduction of the growth probability.

The experiments with co-feeding of 1-hexene at low P_{CO} have revealed a low selectivity of 1-alkene incorporation of about 0.1. Since, we have concluded that incorporation of 1-alkenes occurs exclusively via the mechanism characterized by the growth probability α_1 consequently the incorporation has to be related to this

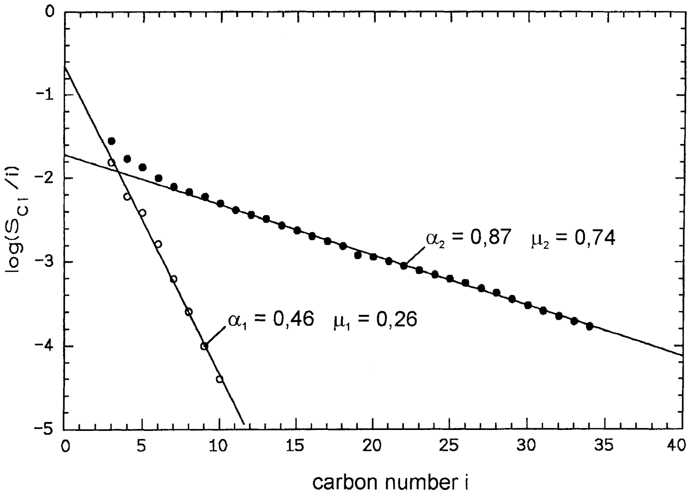


Fig. 8. Representation of carbon number distribution by means of superposition of two ASF distributions. Reaction conditions: Co catalyst, $P_{H_2} = 3\,\text{bar}$, $P_{CO} = 1.5\,\text{bar}$, $T = 220\,^{\circ}C$.

distribution. At elevated P_{CO} the incorporation selectivity reaches relatively high values up to 0.8 [20]. In this case, it is expected that $a_{1,\text{eff}}$ and also μ_1 increases markedly with increasing bed residence time, respectively, with decreasing degree of synthesis gas conversion. Therefore, also the experiments of Iglesia [20] can be interpreted on the basis of the proposed hypothesis.

9. Comparison of cobalt and iron catalysts

In a preceding study, it could be shown that the carbon number distribution of Fischer–Tropsch products obtained over iron catalysts is best represented by superposition of two ASF distributions [18]. Readsorption and incorporation of 1-alkenes is negligible as found by means of co-feeding of 1-alkenes.

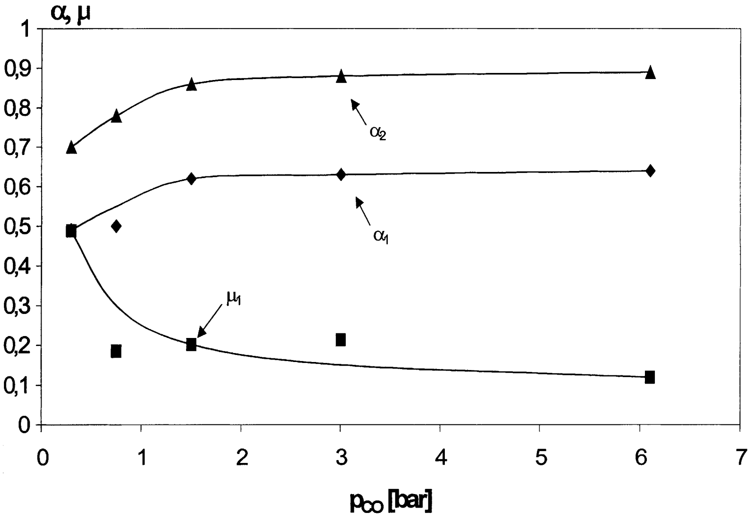


Fig. 9. Growth probabilities α_1, α_2 and fraction μ_1 versus P_{CO}. Reaction conditions: Co–ZrO$_2$ catalyst, $P_{H_2} = 3\,\text{bar}$, $T = 220\,^{\circ}C$.

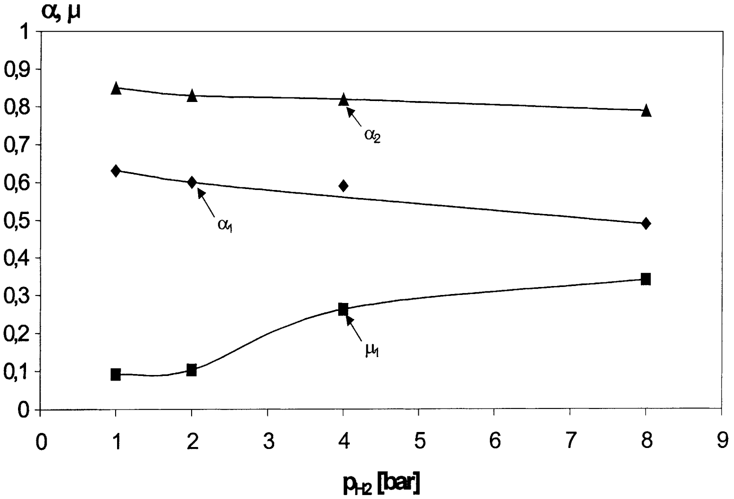


Fig. 10. Growth probabilities α_1, α_2 and fraction μ_1 versus P_{H_2}. Reaction conditions: Co–ZrO$_2$ catalyst, $P_{CO} = 2$ bar, $T = 220\,°C$.

In Fig. 11, the distribution of products obtained on pure iron and cobalt catalysts, unpromoted and unsupported, are compared. The difference is mainly manifested in the fraction μ_1, which is low for cobalt and high for iron and in the growth probability α_2 which is lower in the case of iron. Addition of K$_2$O/K$_2$CO$_3$ to iron leads to an increase in α_2 and also to a decrease of μ_1, so that the distribution of products obtained on alkalized iron becomes similar to that obtained on cobalt.

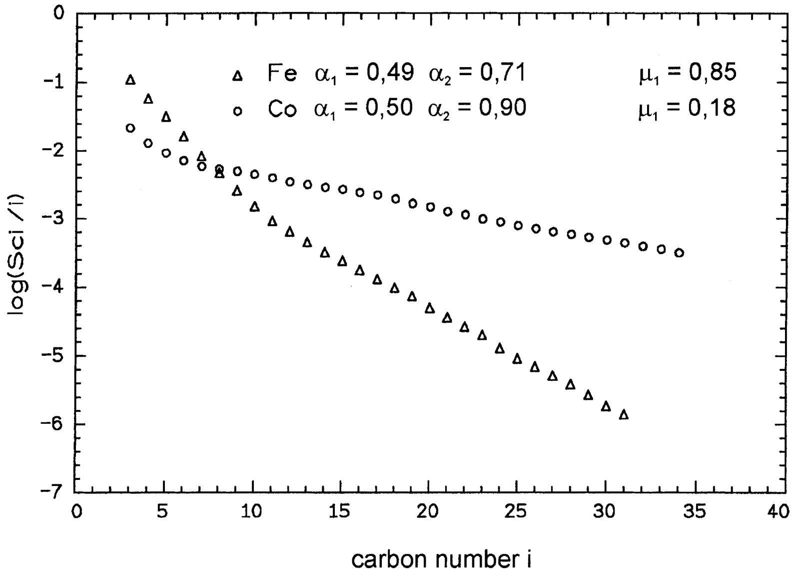


Fig. 11. Carbon number distributions of products obtained on unsupported and unpromoted cobalt and iron catalysts. Reaction conditions: $P_{H_2} \approx 5$ bar, $P_{CO} \approx 2$ bar, $T = 220\,°C$.

10. Conclusion

In this study, the widespread hypothesis of readsorption and incorporation as the main reason of deviations from the ideal ASF distribution of Fischer–Tropsch products has been thoroughly discussed in view of co-feeding experiments with ethene and 1-alkenes. Based on the kinetic model of chain growth it could be shown that in the case of cobalt catalysts incorporation of 1-alkenes cannot be the main reason of these deviations. All experiments suggest the superposition of two ASF distributions caused by different mechanisms of chain growth as the reason for deviations from the ideal ASF distribution. Consequently, carbon number distributions are described by this superposition. The characterizing parameters α_1, α_2 and the molar fraction of the distribution (μ_1) are presented as a function of the partial pressures of hydrogen and carbon monoxide.

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